Effect of operational parameters on the decolorization of C.I. Reactive Blue 19 in aqueous solution by ozone-enhanced electrocoagulation

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Abstract

The aim of this paper was to investigate the efficiency of the ozone-enhanced electrocoagulation (EC) process in the decolorization of C.I. Reactive Blue 19 in water using iron electrodes. We determined the effects of various operating parameters such as initial pH, initial dye concentration, current density, salt concentration, temperature, ozone flow rate, and distance between electrodes on decolorization efficiency in a laboratory-scale reactor. Increasing the initial dye concentration decreased the decolorization efficiency, whereas increasing the distance between electrodes increased it. The other operating factors had both positive and negative effects. With an initial pH of 10.0, an initial dye concentration of 100 mg/L, current density of 10 mA/cm^2, salt concentration of 3000 mg/L, temperature of 30 °C, ozone flow rate of 20 mL/min, and distance between electrodes of 3 cm, over 96% of the color was removed after 10 min. As a consequence, removal of total organic carbon (TOC) was over 80%.
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1. Introduction

The textile industry usually produces vast quantities of wastewater that are characterized by strong color, high chemical oxygen demand (COD), and highly fluctuating pH. An estimated 1–15% of the dye is lost during dyeing and finishing processes and is released into wastewater [1]. Accordingly, dye effluent may contain chemicals that are toxic, carcinogenic, mutagenic, or teratogenic to various fish species [2]. Reactive dyes, which have good water solubility and are easily hydrolyzed into insoluble forms, are extensively used in dyeing processes, and about 20–40% of these dyes remain in the effluent [3]. Thus, an effective and economical technique for removing reactive dyes from textile wastewaters is needed.
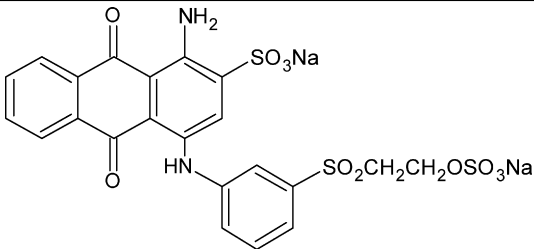
Traditional methods of dye removal include biodegradation, precipitation, adsorption, chemical degradation, photodegradation, and chemical coagulation. Although biodegradation is less inexpensive than other measures, it is often ineffective because the toxicity of the dyes inhibits the activity of the microorganisms [4,5]. Precipitation and adsorption methods are time consuming and costly and are not very efficient. Chemical degradation by oxidative agents such as chlorine is one of the important and effective means of dye removal, but it produces some very toxic products, such as organochlorine compounds. [6]. Photoreactions operate most efficiently with UV rather than visible light which reducing efficiency and increasing operating costs. Besides, nanoparticle morphologies can be challenging to handle and recovery for reuse is difficult.

Electrocoagulation (EC) is an attractive alternative for the treatment of textile dyes. It has a high removal efficiency and provides a reliable, simple, and economical way to treat wastewater without any need for additional chemicals and subsequent secondary pollution. It also reduces the amount of sludge that would require disposal [5,7,8]. Ozonation, which is effective, versatile, and environmentally sound, decolorizes the color of the dye in wastewater by oxidation. However, the industrial application of ozonation has been limited by the high production and operational costs of ozone and by the poor mass transfer rate of ozone [9]. When ozone is injected into wastewater treated by the EC process, active species of free radicals are produced that can react with target pollutants. To the best of our knowledge,

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Table 1
General characteristics of RB19

Chemical structure	
Commercial name	Remazol Brilliant Blue R
C.I. number	61,200
λ_{max} (nm)	592
Molecular mass (g/mol)	626.55
IC_{50} (mg/L)	55

decolorization of reactive dyes using a combination of EC and ozonation technology has received little attention.

The purpose of this study was to investigate the decolorization of a representative reactive dye, C.I. Reactive Blue 19 (RB19), by an ozone-enhanced EC process. The effects of several parameters, including initial pH, initial dye concentration, current density, salt concentration, temperature, ozone flow rate, and the distance between electrodes, on decolorization efficiency were investigated.

2. Methods

2.1. Materials and apparatus

We used an RB19-bearing solution as simulated wastewater in the ozone-enhanced EC process. RB19 (Zhejiang Runtu Co. Ltd., Shaoxing, China) is a blue reactive dye with special dye strength and fastness characteristics. It is a vinyl sulfone-based dye and is used in the form of sulfate ethyl sulfone [10]. Table 1 summarizes the general characteristics of RB19.

The simulated wastewater was prepared by dissolving a given amount of RB19 in 1 L distilled water at initial dye concentrations of 100, 300, 400, or 500 mg/L. The conductivity of the experimental solution was adjusted to different values by adding 2000, 3000, 4000, or 5000 mg/L of K_2SO_4 (Zhenxin Reagent Factory, Shanghai, China). pH was measured with a pH meter (Rex Analytical Instrument Co., Ltd., Shanghai, China) and adjusted to 8.0, 10.0, and 12.0 by adding KOH (Shengyu Chemical Co., Ltd., Shanghai, China) solutions or to 2.0 and 4.0 with H_2SO_4 (Juhua Group Co., Ltd., Quzhou, China) solutions. We used iron plates (40 mm × 50 mm × 1 mm) as the cathode and the consumable anode to generate ferric and/or ferrous ions.

As shown in [11], the electrocoagulator was made of plexiglass with a volume of 300 mL, which was coupled with an O_3 supply system (CHYF-3A, rated flow 50 mg/min, Hangzhou Rongxin Electronic Equipment Co., Ltd., Hangzhou, China). The electrodes were connected to a direct current (DC) power supply equipped with current- and voltage-reading meters for the purpose of applying the desired potential or current. The 300 mL electrocoagulator cell that contained the test solution sat in a water bath to maintain the desired temperature, and a magnetic stirrer was used to stir the solution, thereby enhancing the efficiency in the experiments.

2.2. Procedure and analysis

Before every run, the iron electrodes were immersed for 5 min in dilute H_2SO_4 solution to remove oxide and then were rinsed with pure water. Finally, they were polished by sandpaper to further remove oxide. An aqueous solution (300 mL) containing RB19 was placed into the electrolytic cell. In all experiments, we adjusted the initial pH, initial dye concentration, current densities, salt concentration, temperature, ozone flow rate, and distance between electrodes to a desired value before beginning the experiment. At the end of the experiment, the samples were centrifuged at 2000 rpm for 7 min and then analyzed.

We used an ultraviolet-visible spectrophotometer (T6, Beijing Purkinje General Instrument Co., Ltd., Beijing, China) to measure the maximum wavelength (592 nm) of RB19. The decrease of the absorbance peaks was directly proportional to the reduction of the chromophore. The equation used to calculate the color removal efficiency in these experiments was:

$$\eta\% = \frac{abs_0 - abs_t}{abs_0} \times 100\%,$$

where abs_0 and abs_t were the absorbance of the dye in solution at the beginning of the experiment and at the time t, respectively.

To evaluate the feasibility of the application of the technique, the total organic carbon (TOC) in the solution was measured with a TOC-V_{CPH} total organic carbon analyzer (Shimadzu, Kyoto, Japan). The O_3 flow rate was monitored with a rotameter and O_3 concentrations were determined using an iodimetric method [12].

3. Results and discussion

3.1. Comparison of the three processes for the decolorization of RB19 (ozone-enhanced EC, EC, and ozonation)

Fig. 1 presents the decolorization efficiencies of RB19 at an initial concentration of 100 mg/L by treatment with EC alone,
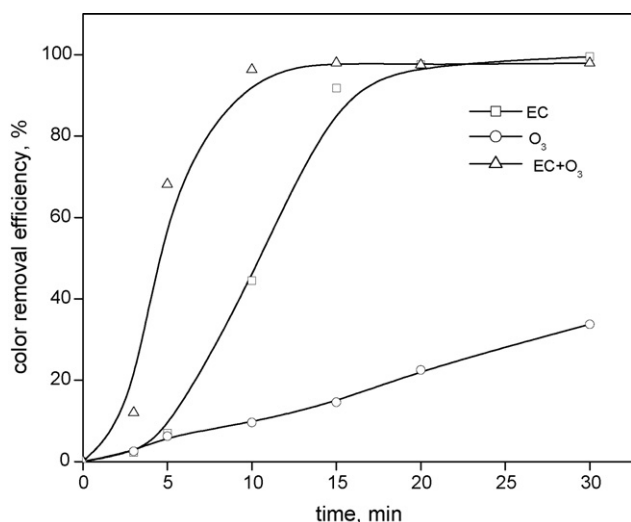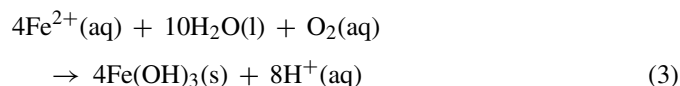
Fig. 1. Comparison of EC, O_3 and EC/O_3 for color removal of RB19: C_0, 100 mg/L; pH 10.0; K_2SO_4 concentration, 3000 mg/L; current density, 10 mA/cm^2; O_3 flow rate, 20 mL/min; electrode distance, 3 cm; temperature, 30 °C.

O_3 alone, and both in combination. EC alone (44% efficiency at 10 min) was more effective than O_3 alone (10% efficiency at 10 min). The efficiency of ozone-enhanced EC (96% efficiency at 10 min), however, exceeded the sum of EC alone and O_3 alone.
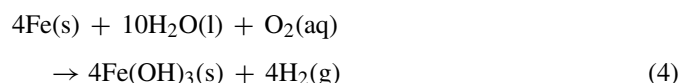
A number of researchers [13–16] have investigated the theory of EC. Metal ion generation takes place at the anode and hydrogen gas is released from the cathode [8]. The reactions are as follows:Cathodic reaction:

$$8H^+(aq) \rightarrow 4H_2(g) - 8e^- \tag{1}$$

Anodic reactions:

$$4Fe(s) \rightarrow 4Fe^{2+}(aq) + 8e^- \tag{2}$$

$$4Fe^{2+}(aq) + 10H_2O(l) + O_2(aq)$$
$$\rightarrow 4Fe(OH)_3(s) + 8H^+(aq) \tag{3}$$

Overall reaction:

$$4Fe(s) + 10H_2O(l) + O_2(aq)$$
$$\rightarrow 4Fe(OH)_3(s) + 4H_2(g) \tag{4}$$

The Fe(OH)$_3$ remains in the aqueous phase as a gelatinous suspension, which can remove pollutants from wastewater either by electrostatic attraction or by complexation followed by coagulation.

Ozone is a strong oxidant that oxidizes organic pollutants via two pathways: (1) direct oxidation with ozone molecules or (2) the generation of free-radical intermediates, such as the $^\bullet$OH radical, which is a powerful, effective, and non-selective oxidizing agent [17].
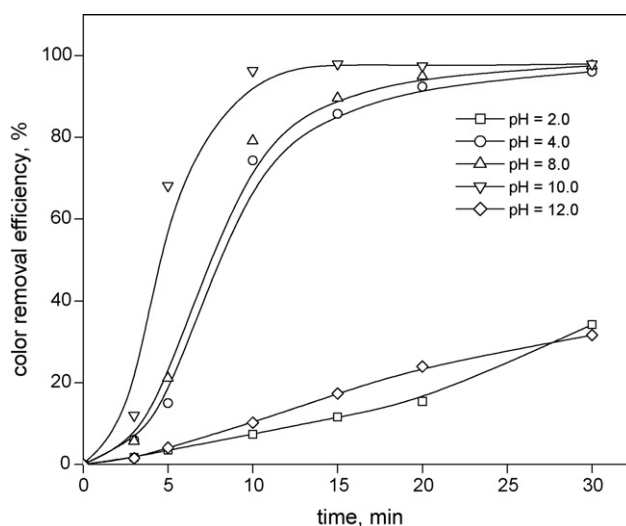
$$O_3 + H_2O \rightarrow 2HO_2^\bullet \tag{5}$$

$$O_3 + HO_2^\bullet \rightarrow HO^\bullet + 2O_2 \tag{6}$$

Fig. 2. Effect of pH on the decolorization of RB19: C_0, 100 mg/L; K_2SO_4 concentration, 3000 mg/L; current density, 10 mA/cm^2; O_3 flow rate, 20 mL/min; electrode distance, 3 cm; temperature, 30 °C.

When ozone is bubbled into an EC system, Fe^{2+} catalyzes ozone decomposition to generate hydroxyl radicals. Therefore, ozone could accelerate the rate of color removal by the EC process. The catalytic O_3/Fe^{2+} system involves direct reaction of Fe^{2+} with ozone to yield the intermediate FeO^{2+}, a species that evolves to $^\bullet$OH [18,19].

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \tag{7}$$

$$FeO^{2+} + H_2O \rightarrow Fe^{3+} + HO^\bullet + OH^- \tag{8}$$
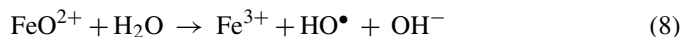
3.2. Effect of initial pH

pH is a critical parameter in determining the performance of the EC process [20–22]. In our experiments, we used pH values of 2.0, 4.0, 8.0, 10.0, and 12.0 in the coupled EC/O_3 system. Measurements taken before and after the experiments showed that the maximum pH change was less than 4.0. Fig. 2 shows color removal efficiency as a function of pH. Decolorization efficiency clearly increased with the increase of pH from 2.0 to 10.0 and then dropped to 10% at pH 12.0. The maximum decolorization efficiency of 96% was observed at pH 10.0 after 10 min reaction time. Fe^{2+}/Fe^{3+} conversion can explain this result: for the iron electrodes at high pH, some of the hydroxide ions may be oxidized at the anode, reducing the production of iron ions. In addition, $Fe(OH)_6^{3-}$ or $Fe(OH)_4^-$ ions, which lacks the capacity for decolorization [7], may be present at high pH. These factors lead to reduced color removal efficiency at high pH. At lower pH values, the main oxidant remains as molecular ozone rather than hydroxyl radicals formed from ozone decomposition. Molecular ozone have a lower oxidizing potential and are higher selective than hydroxyl radicals, leading to a decolorization decrease [23]. Additionally, the protons in the solution are reduced to H_2 at the cathode, preventing the production of the hydroxide ions. $Fe(OH)^{2+}$ and $Fe(OH)_2^+$, which are disadvantageous for colorant precipitation, and $Fe(OH)_3$ species may also be present under acidic conditions [7].
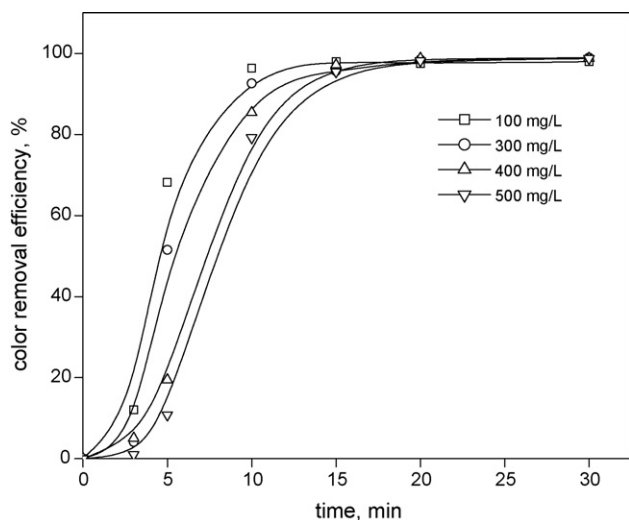
Fig. 3. Effect of initial dye concentration on the decolorization of RB19: pH 10.0; K_2SO_4 concentration, 3000 mg/L; current density, 10 mA/cm^2; O_3 flow rate, 20 mL/min; electrode distance, 3 cm; temperature, 30 °C.

Fig. 4. Effect of current density on the decolorization of RB19: C_0, 100 mg/L; pH 10.0; K_2SO_4 concentration, 3000 mg/L; O_3 flow rate, 20 mL/min; electrode distance, 3 cm; temperature, 30 °C.

3.3. Effect of initial dye concentration

The decolorization of RB19 in the combined EC/O$_3$ system was conducted with initial dye concentrations in the range of 100–500 mg/L. As shown in Fig. 3, the color removal efficiency gradually decreased with an increase in the initial concentration. After 10 min reaction time, the color removal percentage was 96, 93, 85, and 79% at initial dye concentrations of 100, 300, 400, and 500 mg/L, respectively. However, the results in Fig. 3 also show that under the present experimental conditions, the higher the concentration, the more the dye decolorized in 10 min, which indicates that a sufficient number of iron hydroxide complexes were produced by the electrode for a given conductivity and applied cell voltage to coagulate the excessive number of RB19 dye molecules at higher concentrations.

3.4. Effect of current density

Fig. 4 illustrates that the color removal efficiency increased quickly from 8 to 96% by increasing the current density from 2 to 10 mA/cm^2 after 10 min reaction time. As the applied current density was increased from 10 to 15 mA/m^2, the color removal efficiency did not rise significantly. The increase is ascribed to the fact that an increase in current density leads to an increase in the quantity of oxidized irons generated from the electrode, resulting in the growth of flocs and hydroxyl radicals according to Eqs. (7) and (8). Moreover, the bubble generation rate increases and the bubble size decreases with increasing current density; both of these trends are beneficial in terms of a high color removal efficiency by floc flotation, caused by cathodic reduction of H$^+$ to H$_2$ [24].

However, as the current density was increased, the applied potential also increased. Thus, it is advisable to limit the current density to avoid excessive oxygen evolution and to eliminate other adverse effects such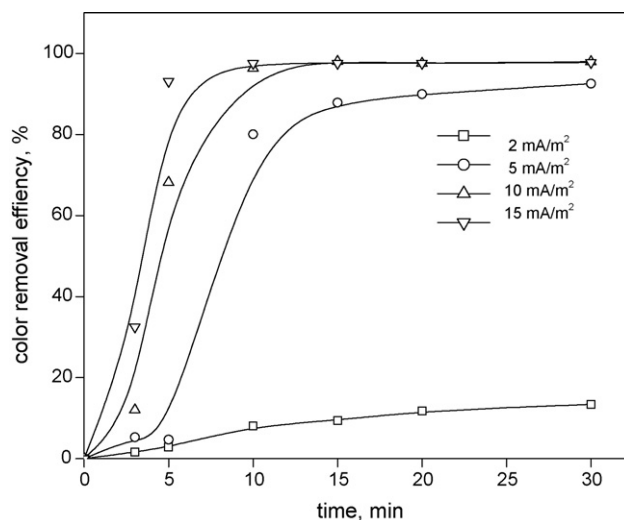 as heat generation [25]. Considering the economic factor here, a reasonable current density in our experiments was 10 mA/cm^2.

3.5. Effect of K_2SO_4 concentration

To evaluate the effect of the salt concentration on decolorization efficiency, we prepared different electrolyte solutions by adding of different amounts of K_2SO_4. Fig. 5 shows that the color removal efficiency increased from 10 to 96% as the K_2SO_4 concentration increased from 2000 to 3000 mg/L after 10 min reaction time. As the K_2SO_4 concentration increased, the conductivity of the electrolyte was enhanced correspondingly. As a consequence, the potential was decreased at a fixed current density to prevent the other reactions, such as the direct oxidation of organic compounds or H_2O [5]. The highest salt concentra-
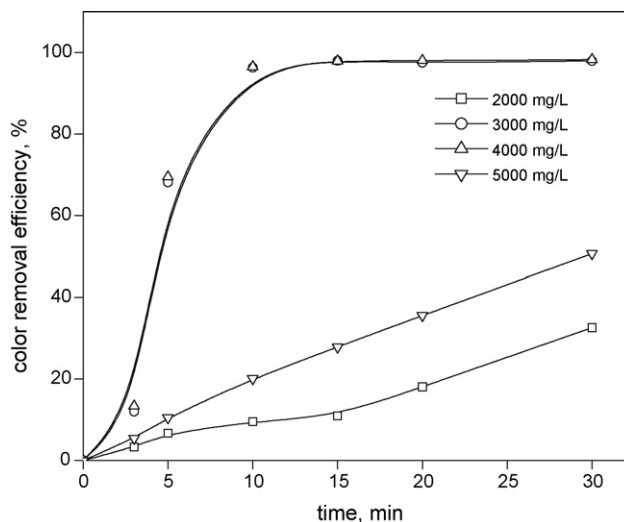

Fig. 5. Effect of K_2SO_4 concentration on the decolorization of RB19: C_0, 100 mg/L; pH 10.0; current density, 10 mA/cm^2; O_3 flow rate, 20 mL/min; electrode distance, 3 cm; temperature, 30 °C.

tion (5000 mg/L) had a negative effect on decolorization (20% at 10 min reaction time). One possible explanation for this finding is that at high salt concentration, the excess SO_4^{2-} ion should react with the hydroxyl radicals to generate $SO_4^{\bullet-}$, which is less reactive than a hydroxyl radical [26]. Another reason may be attributed to the increase of the ionic strength due to adding so much K_2SO_4. Ionic strength affects the kinetics and equilibria of reactions between charged species occurring during the EC process [24,27]. In this study, the optimum K_2SO_4 concentration was 3000 mg/L.

3.6. Effect of temperature

Fig. 6 shows that temperature has a strong effect on color removal. Decolorization efficiency of the RB19 was substantially accelerated by increasing the temperature to 30 °C. The color removal percentages were 6, 90, 96, and 80% at temperatures of 10, 25, 30, and 45 °C, respectively. The temperature increase improved the destruction of the iron oxide film on the electrode surface [8]. Meanwhile, the generation of hydroxyl radicals in the bulk solution was facilitated by increasing the temperature for the higher mass transfer of different species at higher temperatures, which then led to an enhancement of the rate of reaction of the radicals with the pollutant [28]. However, at higher temperatures, the movement of the produced ions increases considerably and as a consequence the ions have little opportunity to aggregate and produce metallic hydroxide flocs. Higher temperature also might cause the formation of unsuitable flocs or an increase in the solubility of the precipitates. As a result, both a positive and negative effect of temperature on EC/O_3 process exist.

3.7. Effect of ozone flow rate

We investigated the effect of the ozone flow rate on color removal efficiency in a series of experiments using flow rates of
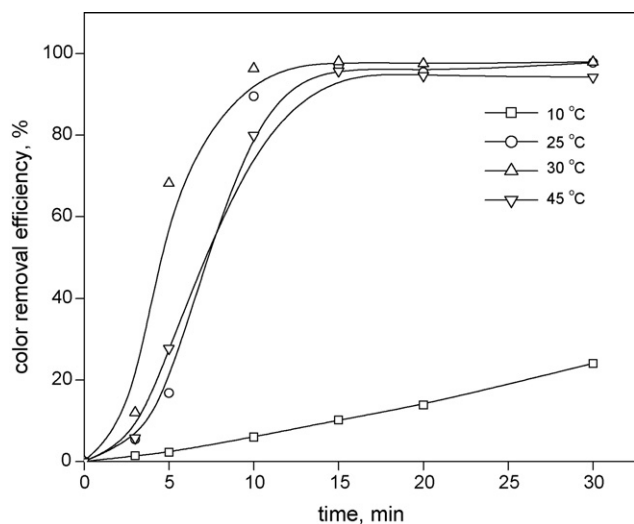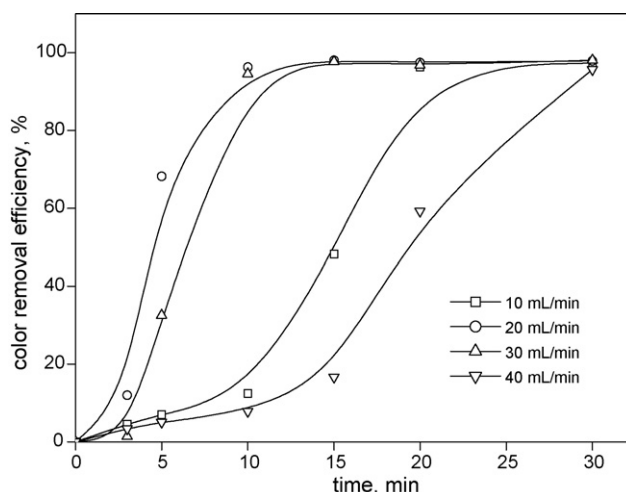

Fig. 7. Effect of ozone flow rate on the decolorization of RB19: C_0, 100 mg/L; pH 10.0; K_2SO_4 concentration, 3000 mg/L; current density, 10 mA/cm^2; electrode distance, 3 cm; temperature, 30 °C.

10, 20, 30, and 40 mL/min (Fig. 7). Enhancing the applied ozone flow rate from 10 to 20 mL/min resulted in an increase in the color removal efficiency from 12 to 96% (after 10 min reaction time). As the applied ozone flow rate increases, the generation of hydroxyl radicals simultaneously rises. In addition, a high ozone flow rate results in the increase of the mass transfer rate of ozone from gas phase to liquid phase [9]. However, at an ozone flow rate greater than 20 mL/min, the color removal efficiency decreased markedly from 96 to 8% (40 mL/min) after 10 min reaction time. Possibly, too high a flow rate of the gas through the solution could cause the flocs to stretch and break-up [29], resulting in a decrease in the color removal efficiency.

3.8. Effect of distance between the electrodes

Fig. 8 depicts the color removal efficiency at different operating interelectrode distances (1, 2, and 3 cm). As the distance
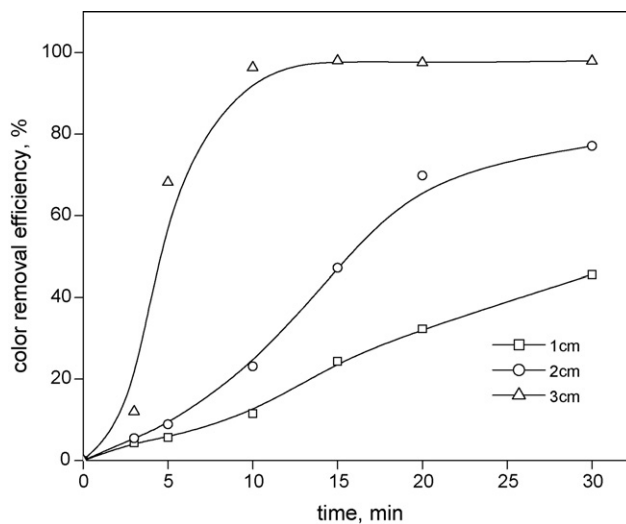

Fig. 6. Effect of temperature on the decolorization of RB19: C_0, 100 mg/L; pH 10.0; K_2SO_4 concentration, 3000 mg/L; current density, 10 mA/cm^2; O_3 flow rate, 20 mL/min; electrode distance, 3 cm.

Fig. 8. Effect of electrodes distance on the decolorization of RB19: C_0, 100 mg/L; pH 10.0; K_2SO_4 concentration, 3000 mg/L; current density, 10 mA/cm^2; O_3 flow rate, 20 mL/min; temperature, 30 °C.
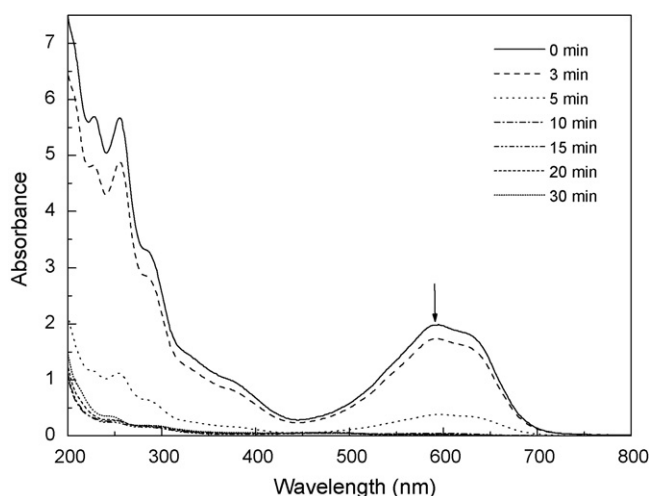
Fig. 9. Absorbance spectra of RB19, recorded before and after ozone-enhanced EC at different electrolysis times (C_0, 100 mg/L; pH 10.0; K_2SO_4 concentration, 3000 mg/L; current density, 10 mA/cm^2; O_3 flow rate, 20 mL/min; electrode distance, 3 cm; temperature, 30 °C).

between the anode and the cathode was increased, the efficiency of decolorization increased (12, 23, and 96% after 10 min reaction time, respectively) because the increase in the electrode gap decreased the electrostatic effects so that the movement of the produced ions would be slower and they would have more opportunity to aggregate and produce flocs. Consequently, these flocs were able to adsorb more dye molecules [30].

3.9. Absorbance spectra and TOC removal

Fig. 9 presents the UV–vis spectra of the initial and various stages of the ozone-assisted EC process. The peak observed in the UV region at 592 nm was due to the blue color of the chromophore. It is clear that a near-complete removal of color was achieved. However, the diminution of color does not necessarily imply the complete removal of a dye. If TOC is reduced, then dye is removed. In our experiments, we attained over 80% TOC removal in the treated solutions under the following conditions: initial pH of 10.0, initial dye concentration of 100 mg/L, current density of 10 mA/cm^2, salt concentration of 3000 mg/L, temperature of 30 °C, ozone flow rate of 20 mL/min, electrode distance of 3 cm, and electrolysis time of 10 min.

4. Conclusions

Our results indicate that the efficiency of the EC process can be improved by applying a simultaneous ozonation process. The EC/O_3 process reported herein is a promising alternative for treatment of wastewater with a high content of recalcitrant reactive dyes. Further investigation is required to elucidate the detailed mechanisms for improved performance and to determine if this process will be effective for a variety of other dye compounds.

References

[1] N. Daneshvar, M. Rabbani, N. Modirshahla, M.A. Behnajady, Photooxidative degradation of Acid Red 27 in a tubularcontinuous-flow photoreactor: influence of operational parameters and mineralization products, J. Hazard. Mater. B 118 (1–3) (2005) 155–160.
[2] N. Daneshvar, H. Ashassi-Sorkhabi, A. Tizpar, Decolorization of orange II by electrocoagulation method, Sep. Purif. Technol. 31 (2) (2003) 153–162.
[3] B. Armagan, O. Ozdemir, M. Turan, M.S. Çelik, Adsorption of negatively charged azo dyes onto surfactant-modified sepiolite, J. Environ. Eng. 129 (8) (2003) 709–715.
[4] N. Daneshvar, D. Salari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water: investigation of the effect of operational parameters, J. Photochem. Photobiol. A 157 (1) (2003) 111–116.
[5] N. Daneshvar, A. Oladegaragoze, N. Djafarzadeh, Decolorization of basic dye solutions by electrocoagulation: an investigation of the effect of operational parameters, J. Hazard. Mater. B 129 (1–3) (2006) 116–122.
[6] N. Daneshvar, A.R. Khataee, N. Djafarzadeh, The use of artificial neural networks (ANN) for modeling of decolorization of textile dye solution containing C.I. Basic Yellow 28 by electrocoagulation process, J. Hazard. Mater. B 137 (3) (2006) 1788–1795.
[7] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC)—science and applications, J. Hazard. Mater. B 84 (1) (2001) 29–41.
[8] G.H. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (1) (2004) 11–41.
[9] H. Zhang, L.J. Duan, D.B. Zhang, Decolorization of methyl orange by ozonation in combination with ultrasonic irradiation, J. Hazard. Mater. 138 (1) (2006) 53–59.
[10] R. Pelegrini, P. Peralta-Zamora, A.R. de Andrade, J. Reyes, N. Durán, Electrochemically assisted photocatalytic degradation of reactive dyes, Appl. Catal. B 22 (2) (1999) 83–90.
[11] S. Song, Z.Q. He, J.P. Qiu, L.J. Xu, J.M. Chen, Ozone assisted electrocoagulation for decolorization of C.I. Reactive Black 5 in aqueous solution: an investigation of the effect of operational parameters, Sep. Purif. Technol. 55 (2) (2007) 238–245.
[12] IOA Standardisation Committee Europe, 001/87 (F), Iodometric method for the determination of ozone in a process gas, Brussels, 1987.
[13] Z. Zaroual, M. Azzi, N. Saib, E. Chainet, Contribution to the study of electrocoagulation mechanism in basic textile effluent, J. Hazard. Mater. B 131 (1–3) (2006) 73–78.
[14] A.F. Martins, M.L. Wilde, T.G. Vasconcelos, D.M. Henriques, Nonylphenol polyethoxylate degradation by means of electrocoagulation and electrochemical Fenton, Sep. Purif. Technol. 50 (2) (2006) 249–255.
[15] Y.Ş. Yildiz, A.S. Koparal, Ş. İrdemez, B. Keskinler, Electrocoagulation of synthetically prepared waters containing high concentration of NOM using iron cast electrodes, J. Hazard. Mater. B 139 (2) (2007) 373–380.
[16] A.K. Golder, N. Hridaya, A.N. Samanta, S. Ray, Electrocoagulation of methylene blue and eosin yellowish using mild steel electrodes, J. Hazard. Mater. B 127 (1–3) (2005) 134–140.
[17] I. Arslan, I.A. Balcioglu, Effect of common reactive dye auxiliaries on the ozonation of dyehouse effluents containing vinylsulphone and aminochlorotriazine dyes, Desalination 130 (1) (2000) 61–71.
[18] J. Sarasa, S. Cortés, P. Ormad, R. Gracia, J.L. Ovelleiro, Study of the aromatic by-products formed from ozonation of anilines in aqueous solution, Water Res. 36 (12) (2002) 3035–3044.
[19] R. Sauleda, E. Brillas, Mineralization of aniline and 4-chlorophenol in acidic solution by ozonation catalyzed with Fe^{2+} and UVA light, Appl. Catal. B-Environ. 29 (2) (2001) 135–145.

[20] İ.A. Şengil, M. özacar, Treatment of dairy wastewaters by electrocoagulation using mild steel electrodes, J. Hazard. Mater. B 137 (2) (2006) 1197–1205.

[21] M. Kobya, O.T. Can, M. Bayramoglu, Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes, J. Hazard. Mater. B 100 (1–3) (2006) 163–178.

[22] X.M. Chen, G.H. Chen, P.L. Yue, Investigation on the electrolysis voltage of electrocoagulation, Chem. Eng. Sci. 57 (13) (2002) 2449–2455.

[23] O.S.G.P. Soares, J.J.M. Órfão, D. Portela, A. Vieira, M.F.R. Pereira, Ozonation of textile effluents and dye solutions under continuous operation: influence of operating parameters, J. Hazard. Mater. B 137 (3) (2006) 1664–1673.

[24] M. Kobya, E. Demirbas, O.T. Can, M. Bayramoglu, Treatment of levafix orange textile dye solution by electrocoagulation, J. Hazard. Mater. B 132 (2–3) (2006) 183–188.

[25] M.Y.A. Mollah, S.R. Pathak, P.K. Patil, M. Vayuvegula, T.S. Agrawal, J.A.G. Gomes, M. Kesmez, D.L. Cocke, Treatment of orange II azo-dye by electrocoagulation (EC) technique in a continuous flow cell using sacrificial iron electrodes, J. Hazard. Mater. B 109 (1–3) (2004) 165–171.

[26] M. Muruganandham, M. Swaminathan, Photocatalytic decolourisation and degradation of Reactive Orange 4 by TiO_2-UV process, Dyes Pigments 68 (2–3) (2006) 133–142.

[27] M. Bayramoglu, M. Kobya, O.T. Can, M. Sozbir, Operating cost analysis of electrocoagulation of textile dye wastewater, Sep. Purif. Technol. 37 (2) (2004) 117–125.

[28] M.H. Entezari, A. Heshmati, A. Sarafraz-yazdi, A combination of ultrasound and inorganic catalyst: removal of 2-chlorophenol from aqueous solution, Ultrason. Sonochem. 12 (1–2) (2005) 137–141.

[29] R.C. Navarrete, L.E. Scriven, C.W. Macosko, Rheology and structure of flocculated iron oxide suspensions, J. Colloid. Interf. Sci. 380 (1) (1996) 200–211.

[30] N. Daneshvar, H.A. Sorkhabi, M.B. Kasiri, Decolorization of dye solution containing Acid Red 14 by electrocoagulation with a comparative investigation of different electrode connections, J. Hazard. Mater. B 112 (1–2) (2004) 55–62.