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Electrochemical degradation of RB-5 dye by anodic oxidation, electro-Fenton and by combining anodic oxidation-electro-Fenton in a filter-press flow cell

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Abstract

This paper reports the removal of a recalcitrant and toxic dye, Reactive Black 5 (RB-5) by three methods; 1) anodic oxidation (AO) on Boron-Doped Diamond (BDD), 2) by electro-Fenton (EF) process where hydrogen peroxide was produced by oxygen reduction on reticulated vitreous carbon (RVC) electrodes and 3) by the combination of AO-EF. The BDD and RVC electrodes were fitted in a filter-press flow cell in recycle batch mode of operation. The experimental set up for the AO and EF processes consisted on two electrolyte compartments separated by a Nafion membrane with the dye contained in the anolyte and the catholyte, respectively. The combined AO-EF process used only one electrolyte compartment. The color and total organic carbon (TOC) removal were more efficient when the AO and EF processes were used separately than the combined process, AO-EF. The influence of current density and initial concentration of ferrous ions were examined. The lowest energy efficiency (208 kWh kg⁻¹) with the EF process was found when -0.4 V vs Ag/AgCl was applied to a RVC electrode and the concentration of Fe²⁺ was 1.0 × 10⁻⁴ mol dm⁻³ achieving total color and 74% of TOC removals in less than 90 min electrolysis. All proposed processes were able to promote high percentages of TOC removal following a pseudo first order kinetic oxidation. The BDD electrode was the most effective material to remove RB-5 dye within 7.5 min and presented the highest apparent rate constant (0.835 min⁻¹) with 82% TOC removal within 30 min at an energy consumption of 291 kWh kg⁻¹ and 41.1 mA cm⁻² current density. In the case of the combined process AO-EF the electrodegradation rate of RB-5 was at least three times lower, apparent rate constant (0.269 min⁻¹), and 32% of TOC was removed with a high EC (682 kWh kg⁻¹). Therefore oxidation process applied separately was more efficient.

Keywords: boron-doped diamond; electrochemical oxidation; electro-Fenton process; filter-press flow cell; reactive black 5 dye; reticulated vitreous carbon.

1 Introduction

Worldwide environmental problems have been intensified by the continuous increase of population and the misuse of natural resources. In the semiarid region of the northeast of Brazil water resources in the communities are limited for human consumption [1] and nowadays this problem also begins to appear in the southeast of the country. Therefore it is increasingly important to maintain the quality of underground and surface water resources that supply these communities. One way to do this is to adopt preventive methods and to avoid discharging untreated wastewater containing dissolved heavy metals ions and organic material in the environment. In the case of the textile industry large volumes of water are consumed and nearly 90% of the input is discharged as wastewater generating enormous volumes that contain dyes and organic material [2]. Billions of cubic meters of wastewater with synthetic organic dyes are produced daily around the world [3]. More than 80,000 t of reactive dyes are produced and consumed each year [4].

Reactive Black 5 (RB-5) is a recalcitrant compound classified as reactive dye because it forms covalent bonds with the textile material becoming part of the fibers. It is an azo-dye with chromophoric groups (-N=N-) [5] and is considered a moderate toxic substance by Ramsay and Nguyen [6] with $25 < EC_{20} < 50$ %. EC₂₀ refers to the concentration substances that decrease the luminescence of *Vibrio fischeri* by 20 %. The EC₅₀_{30min} levels of the hydrolyzed and no-hydrolyzed forms of RB-5 dye determined by Gottlieb *et. al* [7] are 11.49 ± 3.68 mg dm⁻³ and 27.59 ± 4.01 mg dm⁻³, respectively, against *Vibrio fischeri* bioluminescent bacteria. These concentrations are low and the hydrolyzed form of RB-5 is still a weak genotoxic; even low concentrations of dyes into wastewater are highly visible [8] and can cause many environmental problems because

they are toxic and interfere in photosynthetic processes by consuming the oxygen needed for living species. The toxicity of the dye substances has forced the textile industries to meet tight environmental legislations. In Brazil, the regulation of standards for wastewater discharge into water bodies is the responsibility of the Federal Government by Conselho Nacional do Meio Ambiente (CONAMA), by CONAMA resolution N° 430 of 13 of May of 2011, the following standards are mandate for all wastewater, including the textile effluents: pH between 5 and 9; temperature < 40 °C; minimal removal of 60% in biological oxygen demand and others [9].

It is clear that there is a need to develop new technologies that are able to treat textile wastewaters effectively and at low cost. This is not only important due to the environmental issues mentioned above but also from the financial aspect inasmuch as the textile industry uses large volumes of water. By an efficient treatment process of these wastewaters, they can be recycled and consequently reduce production costs [10]. Advanced Oxidation Processes (AOP) are known for their powerful ability to degrade persistent organic pollutants through the reaction with hydroxyl radicals [11]. Hydroxyl radicals have one of the highest oxidizing potential ($E^0 = 2.80 \text{ V vs. SHE}$), consequently they are extremely reactive and the reaction rates with most organic compounds are close to the diffusion control values, i.e. the reaction time is less than a millisecond with rate constants in the range of 10^7 - $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [12]. Among the AOP, the Electro-Fenton (EF) process is able to promote total mineralization of organic material in short periods of time; the method needs oxygen in solution and Fe^{2+} ions to produce the hydroxyl radical and is suitable to treat wastewater since most of them normally contain certain amount of Fe^{2+} and/or Cu^{2+} ions and air bubbles can be supplied from compressed air to provide oxygen [13]. The main advantages of this process are: H_2O_2

is produced *in situ*, avoiding risk and cost associated with storage, transport and handling of this material; in optimized experimental condition, total mineralization at low cost is possible; Fe^{2+} is continuously regenerated at the cathode avoiding the production of sludge and promoting higher degradation rate reactions; through this method it is possible to control the rate of the degradation which has led to mechanistic studies [14-16]. Another important AOP process includes the use of Boron-Doped Diamond (BDD) films on the anode electrode [17] that also produces highly oxidant hydroxyl radicals via the oxidation of water furthermore other weaker oxidizing species such as sulfate radical anions ($E^0 = 2.01 \text{ V vs. SHE}$), peroxodisulfate ion ($E^0 = 2.60 \text{ V vs. SHE}$) can be produced by the oxidation of the ion sulfate on these electrodes [18-20]. BDD electrodes have high mechanical strength and excellent chemical and electrochemical stability and unusual offset potentials for the evolution of hydrogen and oxygen in aqueous media providing very wide electrochemical potential window [21]. They also exhibit low double-layer capacitance, low adsorption, low background and high oxidation efficiencies [22]. One of the disadvantages of these electrodes is the high cost and the erosion of the thin BDD layer over time due to friction with the electrolyte flow however; there have been reports of life time up to 240 hours operation at 50 mA cm^{-2} of these electrodes [23].

Electrochemical methods have been used to study wastewater containing dyes by many research groups [24, 25]. However, the combination of AO using BDD anode and EF using RVC cathode for the generation of hydrogen peroxide in order to degrade RB-5 dye using a filter-press electrochemical reactor has not been reported. BDD electrodes alone have been used to treat RB-5 dye by Ceron-Rivera *et al.* [26] at a 3 cm^2 area cathode electrode and four different anode materials achieving 95% color removal and

65-67 % COD removal; Yavuz and Shahbazi [27] studied the oxidation of RB-5 using BDD Raschig rings of 176 cm² geometric area as working and counter electrodes. EF processes have been used to degrade RB-5 using anode and cathode graphite electrodes of 84.16 cm² area [28]. Glassy carbon electrodes also have been used [29] as well as graphite (area 15 cm²) and Fe alginate gel beads and iron-loaded sepiolite [30, 31]. Bocos *et al.* [28] used two graphite sheets electrodes of 15 cm² area and an iron supported in polyacrylamide hydrogel [32].

The aim of this paper is to compare the electrochemical degradation of Reactive Black 5 dye in a divided flow cell by AO using Boron-Doped Diamond anode and EF using RVC as cathode to produce H₂O₂. The degradation will also be studied by the combination of AO-EF processes in an undivided flow electrolyser. The degradation efficiency was monitored by UV-VIS spectrophotometer (200-800 nm) and by the determination of the Total Organic Carbon (TOC). The performance of the degradation of the dye in terms of energy composition of electrolysis was also examined.

2 Experimental details

The study of hydrogen peroxide production and the degradation of RB-5 dye were carried out using a filter-press flow reactor with two compartments separated by a 115 Nafion[®] membrane. The membrane was conditioned by boiling it in water for 30 min and kept in 1 mol dm⁻³ H₂SO₄ during 24 h. The filter-press flow reactor [33] was composed by five acrylic flat plates of 15.0 × 9.0 × 0.66 cm held together with a series of bolts and silicone rubber gasket in between in order to avoid leaks of the electrolyte. Each compartment contained an inlet and outlet and the electrolyte was circulated from the reservoirs using magnetically driven centrifugal pumps TE-3K-MD (March May).

The volumetric flow rate can vary between 20 and 100 dm³ h⁻¹ and was controlled by two variable flowmeter in each compartment, in line with the electrolyte. The reason that a two-compartment reactor was used was to avoid the oxidation of H₂O₂ [13] and to study the degradations process separately. The cathode and anode compartments had a thickness of 17 and 9 mm, respectively; the cathode compartment was larger in order to accommodate a Reticulated Vitreous Carbon (RVC) electrode with 60 pores per inch (ppi) with dimensions of 9 × 4 × 1.2 cm which represents a surface area around 1,540 cm² if the volumetric area of 35.5 cm³ cm⁻² is considered [34]. The anode compartment was fitted with a Boron-Doped Diamond (BDD) electrode of ≈ 27 cm² projected area with a boron level between 1,000 and 5,000 ppm. A commercial reference electrode of Ag/AgCl in a saturated KCl solution was fitted to the system using a 3 mm diameter plastic tube as Luggin capillary inserted in one of the outlet pipes of reactor. The system was connected to a computer controlled Autolab potentiostat (PGSTAT 302 N) fitted with a general purpose electrochemical system (GPES) software to carry out the electrochemical experiments.

The hydrogen peroxide was generated on the RVC electrode by the reduction of dissolved oxygen at different constant potentials (-0.2, -0.4, -0.6 and -0.8 V vs. Ag/AgCl). These potential were selected after a cyclic voltammetry of the oxygen saturated solution was analysed. In order to find the potential with the highest production of hydrogen peroxide samples of 1 cm³ were collected at regular intervals of time during the electrolysis and the concentration quantified by an UV-VIS spectrophotometer from Scinco (NEOSYS-2000); the change on the color of the samples taken during the electrolyses was observed due to the formation of a red-orange color peroxovanadium cation formed by the reaction between hydrogen peroxide and

ammonium metavanadate in acidic medium. The absorbance was monitored at 450 nm [35]. Ammonium metavanadate was Analar grade from Fisher Scientific. The electrolyses were carried out at ambient temperature of 23 °C at a constant flow rate of 100 dm³ h⁻¹ in both the catholyte and the anolyte. The electrolyte in the cathode and anode compartments was 0.5 dm³ of 0.5 mol dm⁻³ Na₂SO₄ adjusted to pH ≈ 3 with H₂SO₄ and measured with a waterproof pH meter from Hanna instruments (HI 98129). Na₂SO₄ anhydrous and H₂SO₄ were Analar grade from Fisher Scientific.

RB-5 (55%) dye from Sigma Aldrich was used to carry out the degradations experiments via three experimental procedures: the first one used the BDD as working electrode at different applied current densities, i.e. 4.1, 8.2, 20.6 and 41.1 mA cm⁻², this procedure was named BDD. In the second procedure an RVC electrode was used as a working electrode in order to generate the Fenton reagent. Different concentrations of Fe²⁺ ions (0, 0.01, 0.05 and 0.10 × 10⁻³ mol dm⁻³) were added to the electrolyte. The source of Fe²⁺ was sulphate of iron (II) Analar grade from Fisher Scientific. The constant potential applied to the RVC electrode was -0.4 V vs. Ag/AgCl and this procedure was named RVC in the discussion section. In these two procedures the electrolyte solutions consisted on 0.6 dm³ of 0.5 mol dm⁻³ Na₂SO₄ + 2 × 10⁻⁵ mol dm⁻³ (20 ppm) of RB-5 at ≈ pH 3 in the working electrode compartment while 0.5 dm³ of 0.5 mol dm⁻³ of Na₂SO₄ at ≈ pH 3 in the anolyte compartment. The third procedure involved the combination of the two procedures described above: an RVC cathode and a BDD anode but only one electrolyte system: the solution was first circulated through the catholyte compartment and then passed to the anolyte compartment through an external pipeline. It was thought that in this way a fraction of the dye will be oxidised by the hydrogen peroxide generated at the RVC electrode and a slightly lower concentrated

dye solution will be feed into the BDD anode compartment. The BDD electrode was used as working electrode and the procedure was named as RVC+BDD. Similar current densities as in the BDD procedure were used, i.e. 4.1, 8.2, 20.6 and 41.1 mA cm⁻². The electrolyte for this procedure consisted on 0.6 dm³ of solution containing 0.5 mol dm⁻³ of Na₂SO₄ + 2 × 10⁻⁵ mol dm⁻³ (20 ppm) of RB-5. This solution as well as that using the EF process were O₂ saturated by bubbling oxygen from a cylinder at all times in the reservoirs during the experiments. Samples were collected at regular intervals of time during the electrolysis and analysed by UV-VIS spectrophotometer (200-800 nm) and TOC. An UV-VIS spectrophotometer was used to monitor the absorbance behaviour and to calculate the color removal through the visible area of the spectrum (400-700 nm) as shown by Equation (1). The energy consumption (*EC*) was calculated considering the TOC removal using equation (2) [36] below:

$$\text{Color removal (\%)} = [(1 - A_t)/A_0] \times 100 \quad (1)$$

A_0 and A_t are the areas of the spectrum from 400 to 700 nm before and after the electrolysis respectively, of the solution with 0.5 mol dm⁻³ of Na₂SO₄ + 2 × 10⁻⁵ mol dm⁻³ (20 ppm) of RB5 dye. The energy consumption, *EC*, (kWh kg⁻¹) was evaluated following the (2) equation bellow where E (V) is the average cell voltage, I (A) is the applied current, Δt (h) the electrolysis time, TOC (kg_c dm⁻³) the total organic carbon and V (dm³) the volume.

$$EC = \frac{E_t I_t \Delta t}{1000(TOC_t - TOC_{t-\Delta t})V_t} \quad (2)$$

3 Results and discussion

3.1 Anodic oxidation of RB-5 on BDD electrode

In the process named BDD, the RB-5 electrodegradation was promoted by the hydroxyl radicals formed at the BDD surface from the water oxidation and other weak oxidizing species formed in the sulphate medium, total mineralization can be achieved in this process, which follows the simplified reactions below [13, 19]:



Figure 1a shows the spectrum of absorbance vs. wavelength of the samples taken during anodic oxidation of RB-5 dye on the BDD electrode at different current densities after 90 minutes of electrolysis. Before any current was applied the initial concentration of RB-5 dye was $2 \times 10^{-5} \text{ mol dm}^{-3}$ (20 ppm). The spectra of the dye at time zero represented by the solid line has two main maximum absorption peaks; one in the UV region ($\lambda_{\text{max}} = 311 \text{ nm}$) and another one in the visible region ($\lambda_{\text{max}} = 600 \text{ nm}$). The absorbance signal in the UV region is related with $\pi\text{-}\pi^*$ transitions in the aromatic groups and the decrease in absorbance in the visible region is associated to the color removal indicated by the linkage chromophore group $\text{N}=\text{N}$ of the azo dye RB-5. The curves in the figure show that at 4.1 and 8.2 mA cm^{-2} current densities there is still some absorption in the UV and visible regions but at 20.6 and 41.1 mA cm^{-2} there is practically no more absorption and the absorption difference between the two current

densities experiments is negligible after 300 nm. Figure 1b shows the development of the absorbance over time when the highest current density of 41.1 mA cm^{-2} was applied during the electrolysis. At this current density only 15 minutes of electrolysis were sufficient to eliminate the highest absorption peak at 600 nm but more time was necessary to remove the absorption at 300 nm. The absorption at 90 minutes of electrolysis is negligible.

3.2 Oxidation of RB-5 by the EF method using RVC electrode to produce H_2O_2

The concentration of hydrogen peroxide at different applied electrode potentials on an RVC electrode of 60 ppi is shown in Figure 2. Concentrations between 0.25 and $0.35 \times 10^{-3} \text{ mol dm}^{-3}$ were achieved within the first 5 minutes of electrolysis at potentials between -0.4 and $-0.8 \text{ V vs. Ag/AgCl}$ with a maximum of $\approx 0.43 \times 10^{-3} \text{ mol dm}^{-3}$ after 30 minutes at $-0.4 \text{ V vs. Ag/AgCl}$ and except at this potential the concentration of hydrogen peroxide decreases gradually over time to $\approx 0.1 \times 10^{-3} \text{ mol dm}^{-3}$ after 45 minutes of electrolysis. The amount of hydrogen peroxide electrogenerated at $-0.4 \text{ V vs. Ag/AgCl}$ was over twelve times higher than applying $-0.2 \text{ V vs. Ag/AgCl}$ at 5 minutes of electrolysis. The electrolysis at $-0.8 \text{ V vs. Ag/AgCl}$ yielded the lowest concentration probably because at this negative potential the production of water from the oxygen reduction, instead of hydrogen peroxide, is favoured. It is also possible that this was due to the uneven potential distribution in the RVC electrode, as it is difficult to ensure the same potential in all the $1,540 \text{ cm}^2$ surface area of this electrode [34]. The amount of hydrogen peroxide electrogenerated at $-0.4 \text{ V vs. Ag/AgCl}$ over the whole electrolysis was the highest. Therefore, this potential was selected to degrade the RB-5 dye using the RVC electrode as working electrode.

In the process named RVC, the electrodegradation of RB-5 was promoted by the hydroxyl radicals formed when the bond of the electrogenerated hydrogen peroxide breaks due to the Fe^{2+} ion catalyst. The Fe^{3+} ion resulted can be regenerated to Fe^{2+} during the electrolysis at the RVC electrode but hydrogen peroxide can also be reduced to O_2 . Hydrogen peroxide production follows the simplified reactions below [13]:

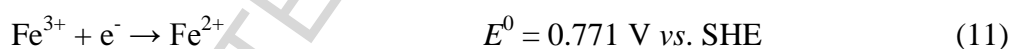
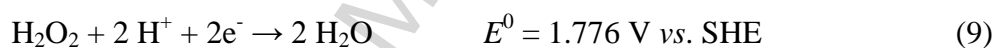


Figure 3a shows the spectrum of absorbance vs. wavelength of the samples after 90 minutes of electrolysis of a solution containing RB-5 dye at the selected potential of -0.4 V vs. Ag/AgCl using different concentrations of Fe^{2+} ions. The curves show that even with no added iron ions the absorption of the major peaks at 311 nm and 600 nm decrease 53% and 90%, respectively. By adding small concentration of Fe^{2+} ions the two absorption peaks almost disappear completely. A concentration of iron ions of $0.1 \times 10^{-3} \text{ mol dm}^{-3}$ was selected to observe the degradation over a period of time. Figure 3b is the development of the absorption of the samples during the electrolysis at -0.4 V vs. Ag/AgCl constant potential and fixed amount of Fe^{2+} . It can be seen that at 1 minute

electrolysis the absorption peaks at 311 nm and 600 nm have already decreased by 25% and 50%, respectively. At longer times the absorption decrease gradually and at 90 minutes the decoloration seems completed. The analysis of figure 3a clearly shows that by adding Fe^{2+} ions the degradation of RB-5 improves due to the homogeneous hydroxyl radicals formed and are responsible for the decolouration and mineralisation of RB-5. The absorbance decay of the peaks at 311 nm and 600 nm in the absence of Fe^{2+} suggests that H_2O_2 helps the decolouration and partial degradation of RB-5.

3.3 Oxidation of RB-5 by combining anodic oxidation and electro-Fenton (AO-EF)

In the process named AO-EF, all the reactions mentioned above are involved and the oxidation of the hydrogen peroxide could be observed by the following reactions [13]:



A series of constant current experiments were carried out with this electrode configuration. Figure 4a presents the absorption results after 90 minutes electrolysis at the different current densities and shows that only at 41.1 mA cm^{-2} the absorbance decreased to zero. Figure 4b shows this absorption at this current density over a period of time. It can be seen that the absorption peaks still are substantial after 5 minutes electrolysis and even at 15 minutes the peak at 310 nm only has decreased by 50%.

3.4 Comparison of anodic oxidation, Fenton and the combined process

The color removal at the end of the 90 minutes electrolysis was measured by the area of spectrums in the visible region (400-700 nm) and plotted in Figure 5 as a function of concentration of Fe^{2+} for EF process and as a function of current density for the process AO and AO-EF. Color removal > 98% was achieved for process AO and AO-EF when the applied current density was $j \geq 20.6 \text{ mA cm}^{-2}$ or when the concentration of Fe^{2+} was $\geq 0.05 \times 10^{-3} \text{ mol dm}^{-3}$ in the RVC procedure. In general, by increasing the current density (4.1, 8.4, 20.6 and 41.1 mA cm^{-2}) the percentage of color removal improved for AO or AO-EF. At an applied current density of $j = 8.2 \text{ mA cm}^{-2}$ the color removal was higher for the AO process than for AO-EF. This suggests that the oxidation process applied separately was more efficient to remove the color at the current density of 8.2 mA cm^{-2} . Using the AO-EF procedure, the RB-5 was oxidized in the surface of BDD by the heterogeneous BDD($\bullet\text{OH}$) and also by the homogeneous $\bullet\text{OH}$ radical formed by the Fenton reaction from the electrogenerated hydrogen peroxide. However, it is also possible that the RB-5 dye can be reduced at the RVC surface, resulting in a decreased of the color removal efficiency. At current densities different to 8.2 mA cm^{-2} the percentage of color removal was similar for AO and AO-EF processes. High percentage of color removal was noted for the EF process prior to the addition of Fe^{2+} ions, around 87-90%. An increase of Fe^{2+} ions in the range of $0 - 0.10 \times 10^{-3} \text{ mol dm}^{-3}$ the percentage of color removal improved in the EF process where the oxidation of RB-5 dye is due to the homogeneous $\bullet\text{OH}$ formed by linkage of H_2O_2 catalysed by Fe^{2+} ions.

In all the process studied the color removal of the solution containing the RB-5 dye was achieved at high percentages. These results are better than other reported data in the literature for example an Electro-Fenton process applied to RB-5 using graphite

electrode of 84.16 cm^2 geometrical area reported only 52% in color removal, applying a cell potential of 3V [28]; other reports using glassy carbon achieved 95% in color removal at the best condition [29] and also using graphite (geometric area of 15 cm^2) and Fe alginate gel beads a maximum of 90% color removal was observed [30]. 97.2% in color removal was achieved when iron-loaded sepiolite and graphite electrodes (geometric area of 15 cm^2) were used [31]. The electrochemical oxidation of RB-5 dye using BDD Raschig rings (176 cm^2) attained 97% in color removal on the optimized conditions [27].

Promoting total color removal is very important in order to carry out a safety discharge of wastewater containing dye, however it is even more important to promote TOC removal because wastewater, which present high organic load when discharge into environment can interfere in the oxygen transference causing serious environment problems such as the depletion of living organism in rivers and lakes. TOC analysis was carried out during electrolysis of all the process described in and the results are plotted in Figure 6 at 30 and 90 minutes of the electrolysis. The first observation is that the percentage of TOC removal increased with the electrolysis time for all processes. The highest results of TOC removal were achieved for the AO process with BDD with a maximum of 90% TOC removal within 90 min of electrolysis at 41.1 mA cm^{-2} current density. At the same conditions within 30 min, 82% of TOC had been removed; this is a really important finding considering the complexity of RB-5 dye molecule. The TOC removal increased with time and current density for AO and AO-EF processes ($4.1, 8.2, 20.6$ and 41.1 mA cm^{-2}) and with Fe^{2+} ions ($0, 0.01, 0.05$ and $0.10 \times 10^{-3} \text{ mol dm}^{-3}$) for the EF process. The TOC removal using BDD in the AO process were better than the combined AO and EF processes; this finding agrees with Jović *et. al* [37] who achieved

an improved of 22 points percentage in DQO removal of RB-5 dye after added Flemion 0820 membrane between Pt (active area of 25 cm^2) electrodes. Although the EF process without Fe^{2+} promoted high color removal of the solution containing RB-5 dye in this work, the TOC removal was extremely low, under 3% at final of electrolysis (90 min). Using the RVC electrode with $0.10 \times 10^{-3} \text{ mol dm}^{-3} \text{ Fe}^{2+}$ added, the TOC removal improved from 42% to 74% at 30 and 90 minutes of electrolysis, respectively.

Yavuz and Shahbazi [27] studied the oxidation of RB-5 dye using BDD Raschig rings (176 cm^2) as working and counter electrodes. At the optimum conditions they reported only 29.3% of TOC removal. Electro-Fenton processes were studied to degrade RB-5, using glassy carbon, which had only achieved 68% in TOC removal on the best degradation conditions [29]; using graphite (geometric area of 15 cm^2) and Fe alginate gel beads, which observed the maximum of 65% in DQO removal [30]. Results of TOC removal of the RB-5 dye found in this paper were improved comparing with those found in literature, which used similar processes. At 90 min of electrolysis and applying 41.1 mA cm^{-2} , the maximum TOC removal for the AO process with BDD, the EF process with RVC ($0.10 \times 10^{-3} \text{ mol dm}^{-3}$ of Fe^{2+} ions) and the combined processes AO-EF using BDD+RVC was 90%, 74% and 82%, respectively.

3.5 Energy consumption

Color and TOC removal should be achieved at low energy consumption (EC) to propose viable processes to industry in order to be implemented and avoid environment by discharging wastewater containing dyes. Figure 7 shows the EC as a function of concentration of Fe^{2+} for the EF process and as a function of the current density applied for the AO and the AO-EF processes. The highest EC values were found for the EF process using the RVC electrode at zero and $0.01 \times 10^{-3} \text{ mol dm}^{-3}$ concentration of Fe^{2+}

which also corresponds to the lowest TOC removal. However, by increasing the concentration of Fe^{2+} (0.05 and $0.10 \times 10^{-3} \text{ mol dm}^{-3}$) the EC decreased to one of the lowest values (208 kWh kg^{-1}) over 90 minutes. Another good result was found for the AO (291 kWh kg^{-1}) with BDD electrode at 30 minutes of electrolysis. The EC values for this process were lower than those found for the combined process AO-EF using RVC+BDD electrodes. In general, the EC for EF process decreased with the concentration of Fe^{2+} ions (0.01 , 0.05 and $0.10 \times 10^{-3} \text{ mol dm}^{-3}$) since the TOC removal also increased with Fe^{2+} ions concentration. As would expected the EC increased with the applied current density for the AO with BDD electrodes and the combined AO-EF process with RVC+BDD electrodes.

Comparing the energy consumption values for the three processes used to degrade the RB-5 dye, the best results were found for AO using BDD electrodes. The oxidation occurred in short electrolysis time (30 min) resulted in 82% TOC removal and total color removal at low energy consumption of 291 kWh kg^{-1} . The second best results was achieved using the EF process with $0.10 \times 10^{-3} \text{ mol dm}^{-3}$ of Fe^{2+} ions after 90 minutes at constant potential electrolysis achieving 74% of TOC depletion and color removal of > 98% at EC of 208 kWh kg^{-1} . The process using AO-EF combined process resulted in reasonable TOC (82%) and color removal (> 98%) after 90 min of electrolysis, but the EC values (745 kWh kg^{-1}) were slightly higher.

3.6 Kinetics of electrodegradation processes

The concentration decay of RB-5 dye was calculated by the absorbance measured at 600 nm. Figure 8 shows the normalized concentration of RB-5 and theirs inserts show the

semilogarithmic plot of the concentration decay in function of electrolysis time and (a) Fe^{2+} concentration for the EF process using RVC, (b) and (c) current density for process AO with BDD and EF-AO with RVC+BDD, respectively. Figure 8 shows an exponential relationship between the normalized concentration and the time of concentration, and their inserts show that there is a linear correlation between the \ln of normalized concentration and the time of electrolysis. This suggests that the electrodegradation reaction of RB-5 followed a pseudo-first order reaction kinetic in all the cases. Therefore, the velocity of RB-5 electrodegradation reaction depends on the concentration of the dye and is mass transport controlled.

The apparent rate constants reported in Table 1 show that the quickest RB-5 removal was achieved by anodic oxidation with BDD within 7.5 min at 41.1 mA cm^{-2} current density. In this condition the highest apparent rate constant, 0.835 min^{-1} was found. The lowest removal rate was for the combined AO-EF process with nearly four times lower rate than the AO with BDD at $j = 20.6 \text{ mA cm}^{-2}$ current density. For the EF process with RVC the dye was removed quickly and the rate increased with the concentration of Fe^{2+} ($0, 0.01, 0.05$ and $0.10 \times 10^{-3} \text{ mol dm}^{-3}$). The maximum apparent rate constant was 0.572 min^{-1} achieved at the highest concentration of Fe^{2+} ions while TOC removal at low Fe^{2+} ions concentrations were the lowest with the highest EC values. Therefore, the most appropriate process to degrade the RB-5 dye is the AO oxidation with BDD electrode. Applying 41.1 mA cm^{-2} , RB-5 was quickly removed at the highest apparent rate constant (0.835 min^{-1}) at the highest TOC removal (90%) in 90 min of electrolysis.

4 Conclusion

Three processes were studied in order to degrade Reactive Black-5 dye. The first process by anodic oxidation on a BDD electrode resulted in the highest apparent rate constant (0.835 min^{-1}) at 41.1 mA cm^{-2} and the dye was completely removed within 7.5 minutes. In addition, more than 80% of TOC removal was achieved in 30 minutes at low EC (291 kWh kg^{-1}) and reached 90% TOC removal in 90 minutes. This findings are important due to the complexity of RB-5 molecule. In the second method the reduction of oxygen on an RVC electrode generated $> 0.4 \times 10^{-3} \text{ mol dm}^{-3}$ concentration of hydrogen peroxide at constant potential of $-0.4 \text{ V vs Ag/AgCl}$. The percentage of TOC removal was low (5%) and the energy consumption extremely high (3471 kWh kg^{-1}) when Fe^{2+} ions were $\leq 0.01 \times 10^{-3} \text{ mol dm}^{-3}$. However when the concentration of Fe^{2+} ions increased to $0.10 \times 10^{-3} \text{ mol dm}^{-3}$ the TOC removal improved to 74% and the EC was low (208 kWh kg^{-1}) after 90 minutes electrolysis with an apparent rate constant of 0.572 min^{-1} . In the combined process AO-EF using RVC+BDD electrodes reasonable TOC and color removal were achieved but higher EC values were noted. All the proposed methods were able to remove RB-5 dye completely and achieve TOC removal of 90%, 82% and 74% within 90 min for AO (BDD electrode), EF (RVC electrode) and the combined AO-EF (RVC+BDD electrodes), respectively.

5 Acknowledgements

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	AO (BDD)	AO+EF (RVC+BDD)	EF (RVC)	
Current density / mA cm ⁻²	$k_{app} / \text{min}^{-1}$		Concentration of Fe ²⁺ / × 10 ⁻³ mol dm ⁻³	$k_{app} / \text{min}^{-1}$
4.1	0.007	0.006	0.00	0.148
8.2	0.011	0.008	0.01	0.211
20.6	0.134	0.034	0.05	0.388
41.1	0.835	0.269	0.10	0.572

Table 1 Apparent rate constants of degradation reaction of RB-5 under different methods: anodic oxidation (AO) with BDD electrode, electro Fenton (EF) with an RVC electrode and the combined process AO-EF with BDD+RVC electrodes as a function of the applied current density or the concentration of Fe²⁺. When using the RVC electrode the applied potential was -0.4 V vs Ag/AgCl. The supporting electrolyte was 0.5 mol dm⁻³ of Na₂SO₄ at 23 °C and the flow rate of the electrolyte was 100 dm³ h⁻¹. The initial concentration of RB-5 dye was 2 × 10⁻⁵ mol dm⁻³ (20 ppm).

Figure captions:

- Figure 1a** Spectra of samples after 90 minutes of electrolysis on a BDD electrode at different current densities from a solution containing 2×10^{-5} mol dm⁻³ (20 ppm) of RB-5: (solid line) initial spectrum before the electrolysis and at 4.1 (long dash line) 8.2 (medium dash) 20.6 (short dash line) and 41.1 mA cm⁻² (dotted line). The supporting electrolyte was 0.5 mol dm⁻³ Na₂SO₄ at 23 °C and the flow rate of the electrolyte 100 dm³ h⁻¹.
- Figure 1b** Spectra of samples from solutions containing 2×10^{-5} mol dm⁻³ (20 ppm) of RB-5 during the electrolysis on a BDD electrode at a constant current density of 41.1 mA cm⁻² at different times: (solid line) initial spectrum before the electrolysis and after: 1 min (long dash line), 5 min (medium dash), 15 min (short dash line) and 90 min (dotted line). The supporting electrolyte was 0.5 mol dm⁻³ Na₂SO₄ at 23 °C and the flow rate of the electrolyte 100 dm³ h⁻¹.
- Figure 2** Concentration of electrogenerated H₂O₂ as a function of time during the electrolysis at different potentials on a 60 ppi RVC electrode: (■) -0.2, (●) -0.4, (▲) -0.6 and (◆) -0.8 V vs Ag/AgCl. The electrolyte consisted on 0.5 mol dm⁻³ of Na₂SO₄ at ambient temperature (23 °C) and pH ≈ 3 and the flow rate of the electrolyte 100 dm³ h⁻¹.
- Figure 3a** Spectra of samples taken after 90 minutes of electrolysis at -0.4 V vs Ag/AgCl using an RVC electrode from solutions containing 2×10^{-5} mol dm⁻³ (20 ppm) of RB-5 and different concentrations of Fe²⁺: (solid line) initial spectrum, (long dash line) without Fe²⁺: (medium dash line) 0.01, (short dash line) 0.05 and (dotted line) 0.10×10^{-3} mol dm⁻³. The supporting electrolyte was 0.5 mol dm⁻³ Na₂SO₄ at 23 °C and the flow rate of the electrolyte 100 dm³ h⁻¹.
- Figure 3b** Spectra of samples taken from solutions containing 2×10^{-5} mol dm⁻³ (20 ppm) of RB-5 and 0.10×10^{-3} mol dm⁻³ of Fe²⁺ on an RVC electrode as a function of the electrolysis time: (solid line) initial spectrum before the electrolysis and after: 1 min (long dash line), 5 min (medium dash), 15

min (short dash line) and 90 min (dotted line) of electrolysis. The potential of the RVC electrode was $-0.4 \text{ V vs Ag/AgCl}$ in $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ and electrolyte flow rate of $100 \text{ dm}^3 \text{ h}^{-1}$.

- Figure 4a** Spectra of samples taken after 90 minutes of electrolysis of solutions containing $2 \times 10^{-5} \text{ mol dm}^{-3}$ (20 ppm) of RB-5 using a combined BDD anode RVC cathode (AO-EF) at different current densities: (solid line) initial spectrum before the electrolysis and 4.1 (long dash line), 8.2 (medium dash), 20.6 (short dash line) and 41.1 mA cm^{-2} (dotted line). The electrolyte support was 0.5 mol dm^{-3} of Na_2SO_4 at ambient temperature ($23 \text{ }^\circ\text{C}$) and the flow rate of the electrolyte was $100 \text{ dm}^3 \text{ h}^{-1}$.
- Figure 4b** Spectra of samples taken from solutions containing $2 \times 10^{-5} \text{ mol dm}^{-3}$ (20 ppm) of RB-5 during the electrolysis using a combined BDD anode RVC cathode (AO-EF) at 41.1 mA cm^{-2} over time: (solid line) initial spectrum before the electrolysis, and after: 1 min (long dash line), 5 min (medium dash), 15 min (short dash line) and 90 min (dotted line). The supporting electrolyte consisted on 0.5 mol dm^{-3} of Na_2SO_4 at $23 \text{ }^\circ\text{C}$ and flow rate of the electrolyte at $100 \text{ dm}^3 \text{ h}^{-1}$.
- Figure 5** Color removal after 90 minutes electrolysis using: (■) EF with RVC electrode at applied potential of $-0.4 \text{ V vs Ag/AgCl}$ at different concentrations of Fe^{2+} (○) AO with BDD and (▲) AO-EF with RVC + BDD at different current densities. The electrolyte support was $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ at $23 \text{ }^\circ\text{C}$ and electrolyte flow rate of $100 \text{ dm}^3 \text{ h}^{-1}$. The initial concentration of RB-5 dye was $2 \times 10^{-5} \text{ mol dm}^{-3}$ (20 ppm).
- Figure 6** TOC removal at 30 and 90 minutes of electrolysis. The open symbols show the TOC at 30 minutes: (□) EF with RVC at $-0.4 \text{ V vs Ag/AgCl}$ at different concentration of Fe^{2+} ions, (○) AO with BDD and (△) AO-EF with RVC + BDD varying the applied current density. The black symbols represent the TOC after 90 minutes of electrolysis: (■) EF with RVC at $-0.4 \text{ V vs Ag/AgCl}$ at different concentration of Fe^{2+} , (●) AO with BDD and (▲) AO-EF with RVC + BDD at different current densities. The supporting electrolyte was 0.5 mol dm^{-3} of Na_2SO_4 at $23 \text{ }^\circ\text{C}$ and flow rate of $100 \text{ dm}^3 \text{ h}^{-1}$. The initial concentration of RB-5 dye was $2 \times 10^{-5} \text{ mol dm}^{-3}$ (20 ppm).
- Figure 7** Energy consumption (EC) / kWh kg^{-1} at 30 and 90 minutes electrolysis. The open symbols show the TOC at 30 minutes: (□) EF with RVC at $-0.4 \text{ V vs Ag/AgCl}$ at different concentration of Fe^{2+} ions, (○) AO with BDD and (△) AO-EF with RVC + BDD at different current densities. The black symbols represent the TOC after 90 minutes of electrolysis: (■) EF with RVC at $-0.4 \text{ V vs Ag/AgCl}$ at different concentration of Fe^{2+} , (●) AO with BDD and (▲) AO-EF with RVC + BDD at different current densities. The supporting electrolyte was 0.5 mol dm^{-3} of Na_2SO_4 at $23 \text{ }^\circ\text{C}$ and flow rate of $100 \text{ dm}^3 \text{ h}^{-1}$. Initial concentration of RB-5 dye: $2 \times 10^{-5} \text{ mol dm}^{-3}$ (20 ppm).

Figure 8 Normalized concentration decay of RB-5 against time for: a) EF with RVC electrode applying -0.4 V vs Ag/AgCl and varying concentration of Fe^{2+} : (■) 0.0, (●) 0.01, (▲) 0.05 (◆) $0.10 \times 10^{-3}\text{ mol dm}^{-3}$, b) AO with BDD and c) AO-EF with RVC+BDD at different current densities: (□) 4.1, (○) 8.2, (Δ) 20.6 and (◇) 41.1 mA cm^{-2} . The insets in the figures show the semilogarithmic plot of the concentration decay. The supporting electrolyte was $0.5\text{ mol dm}^{-3}\text{ Na}_2\text{SO}_4$ at 23 °C and $100\text{ dm}^3\text{ h}^{-1}$ flow rate. The initial concentration of RB-5 dye was $2 \times 10^{-5}\text{ mol dm}^{-3}$ (20 ppm).

ACCEPTED MANUSCRIPT

Figures

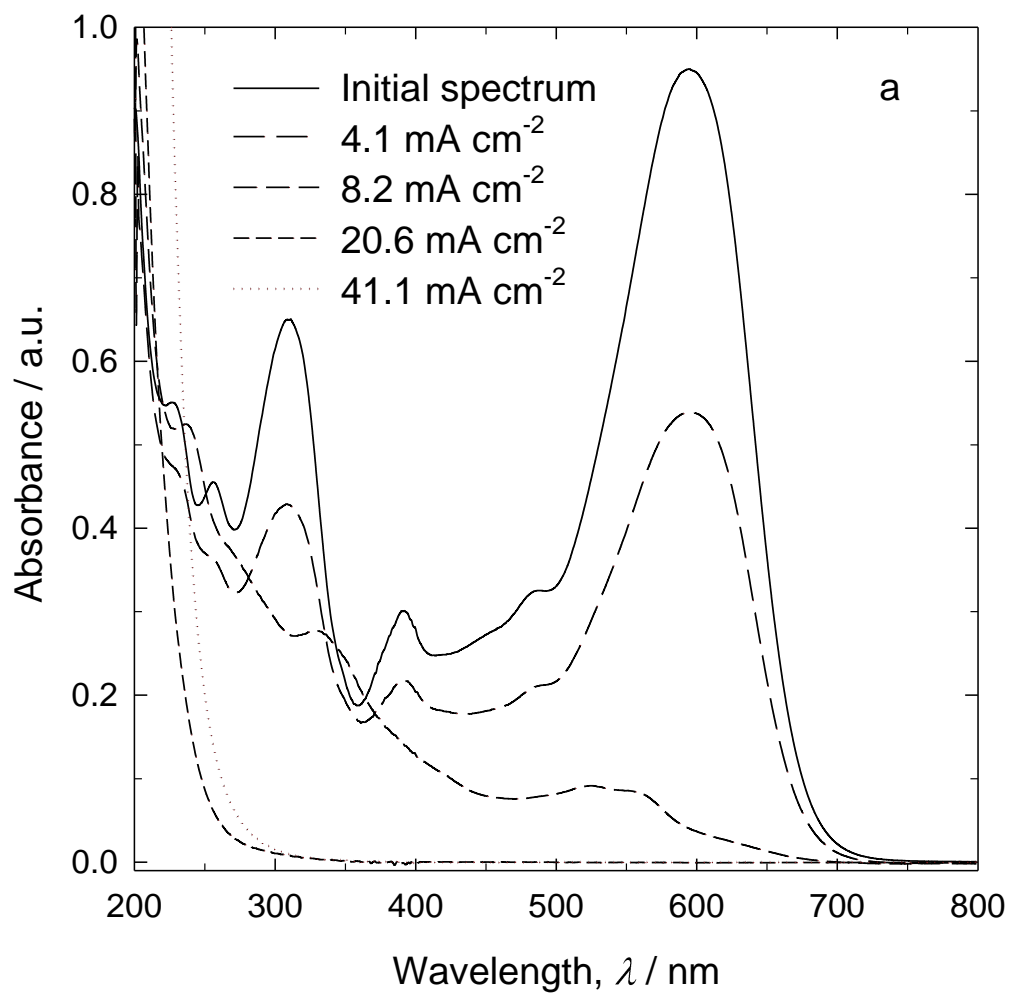


Figure 1a

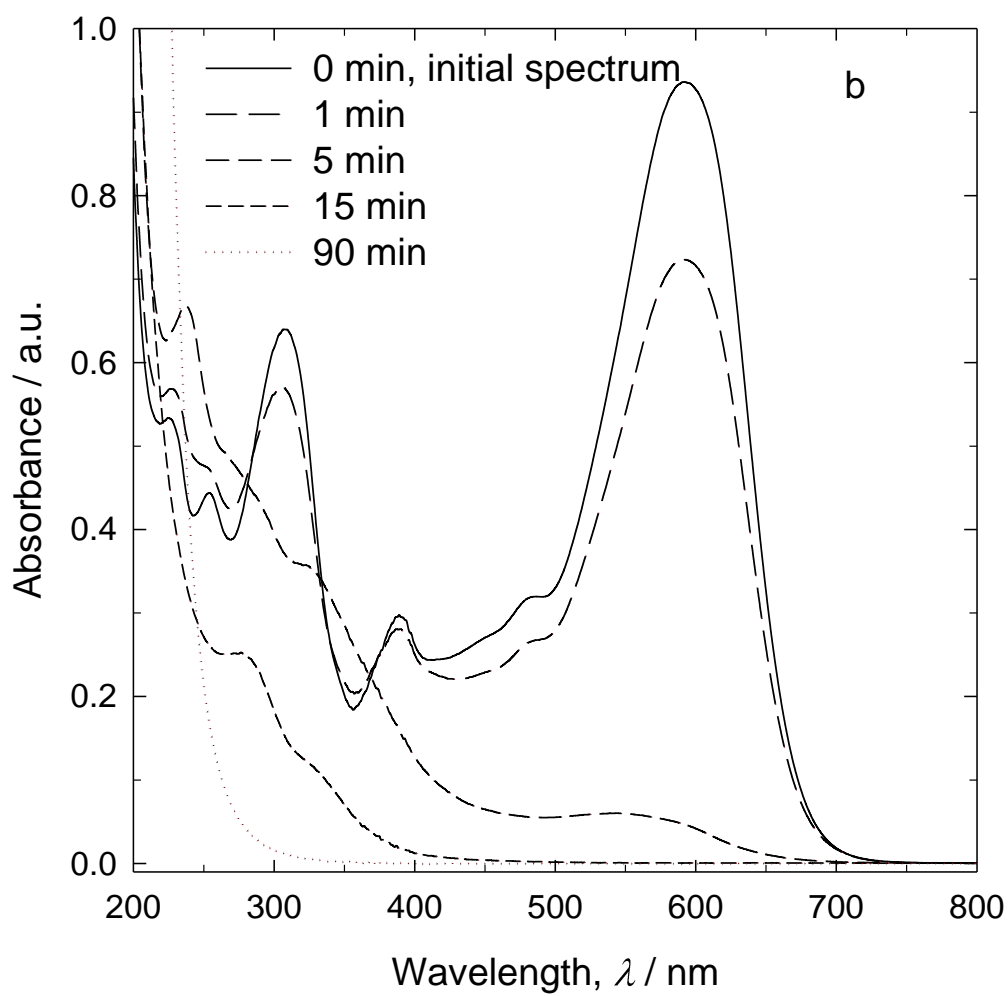


Figure 1b

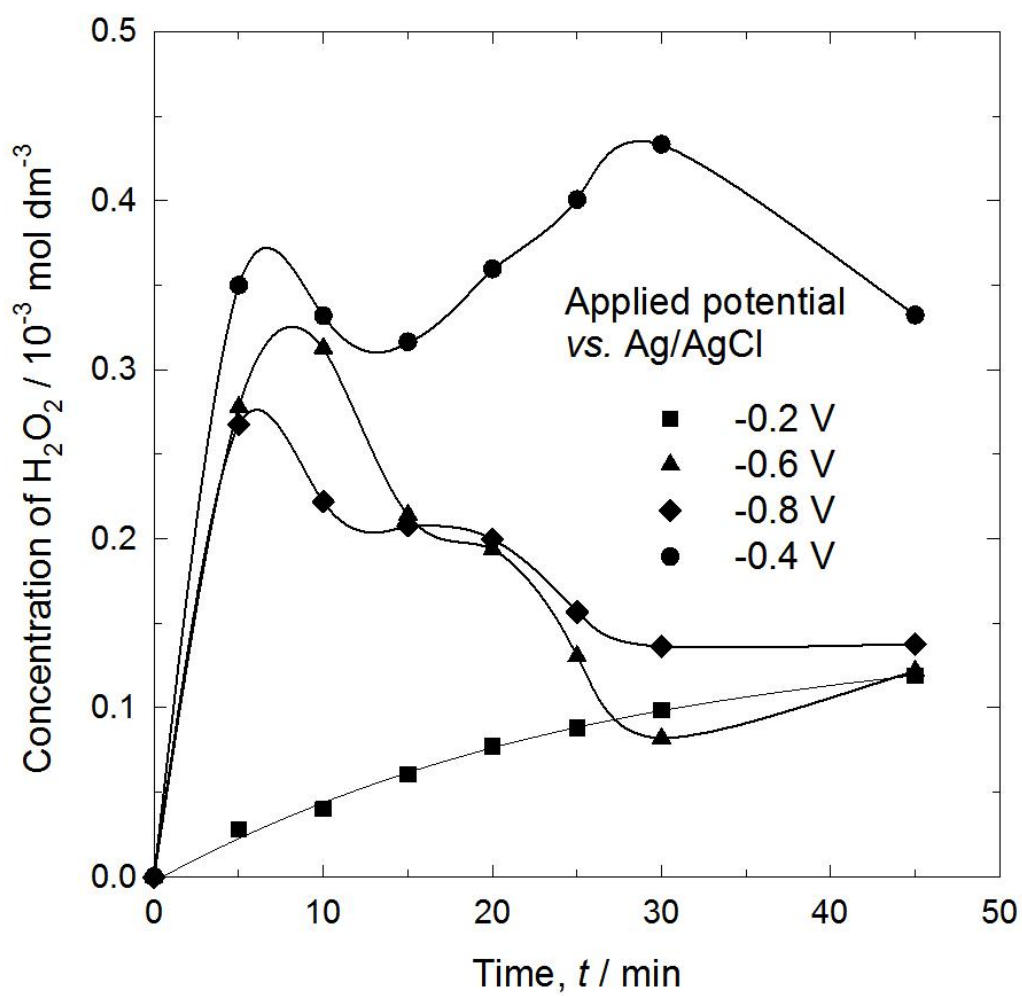


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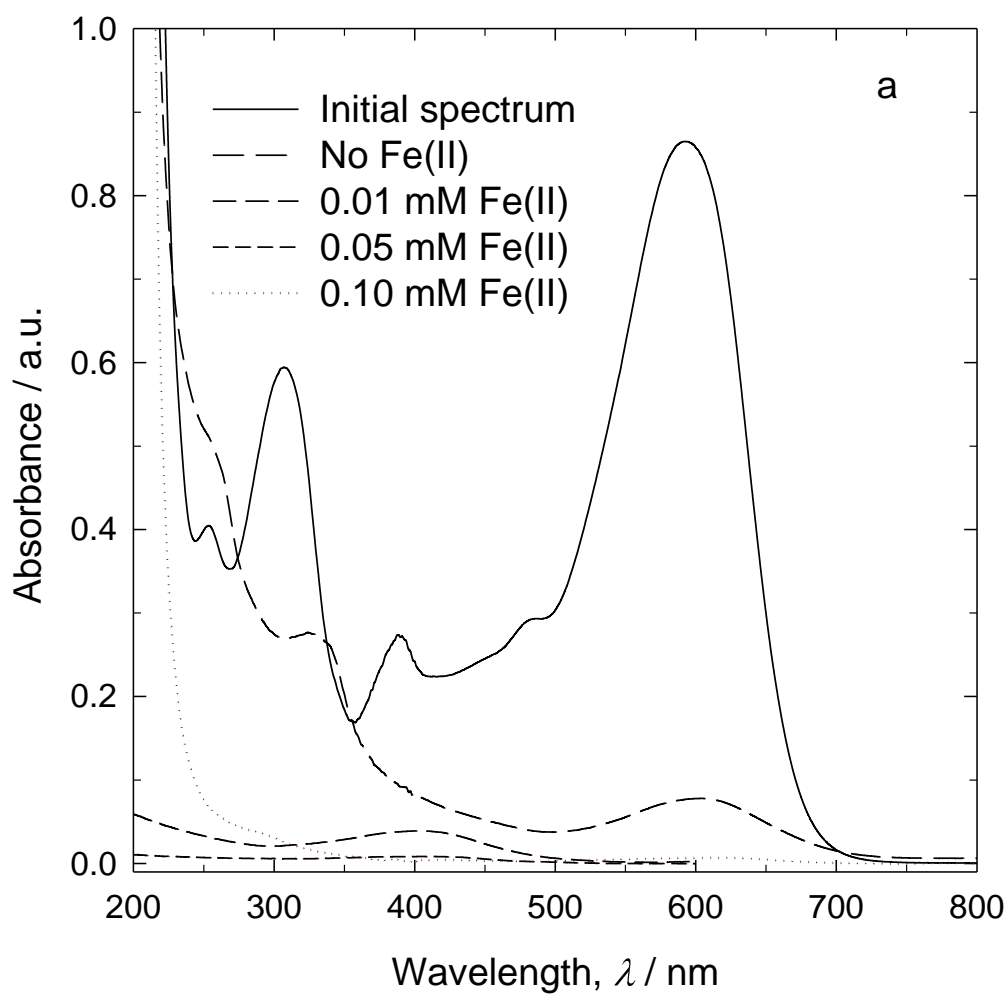


Figure 3a

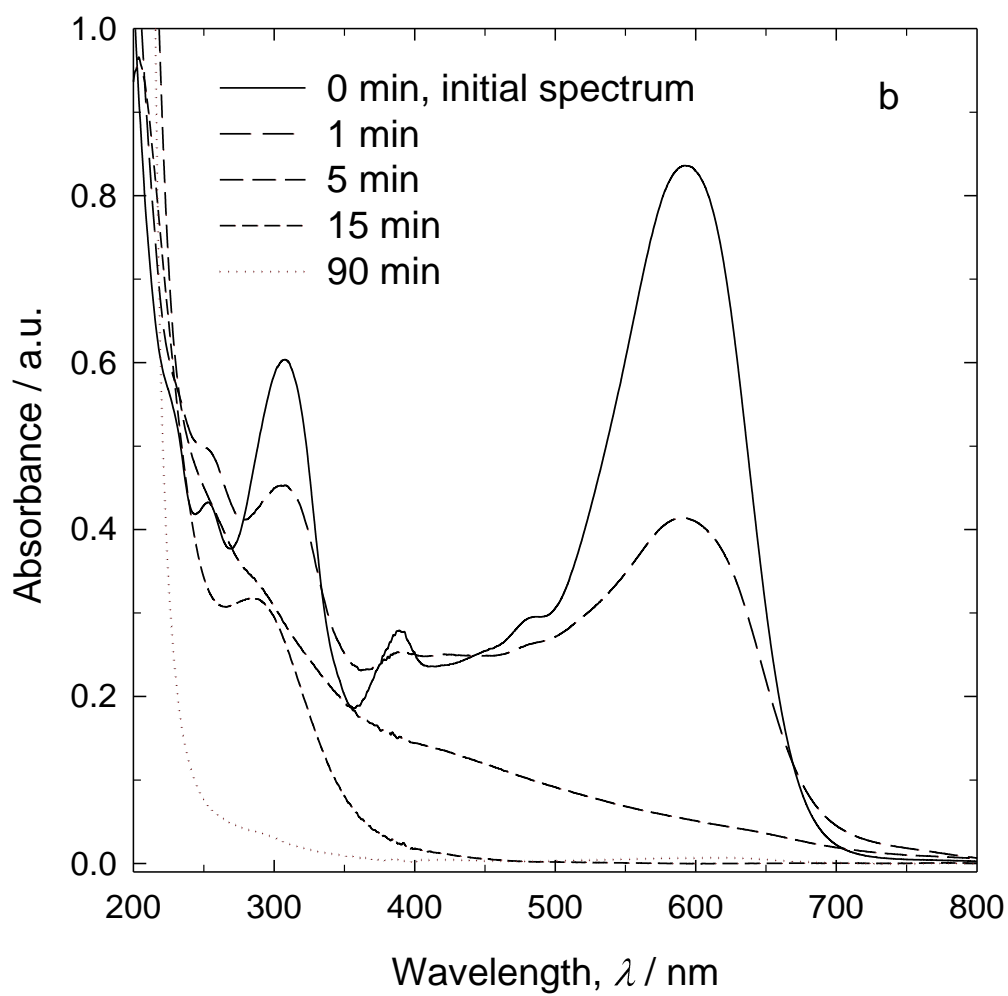


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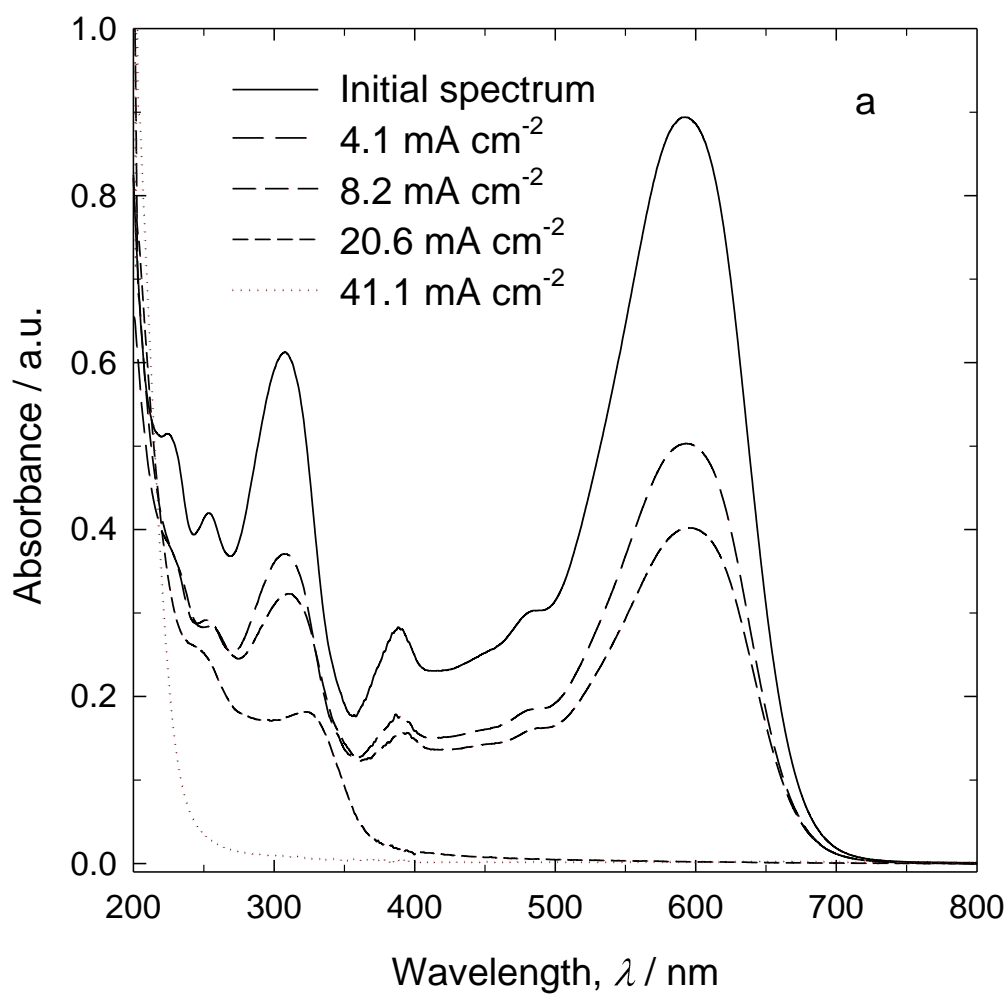


Figure 4a

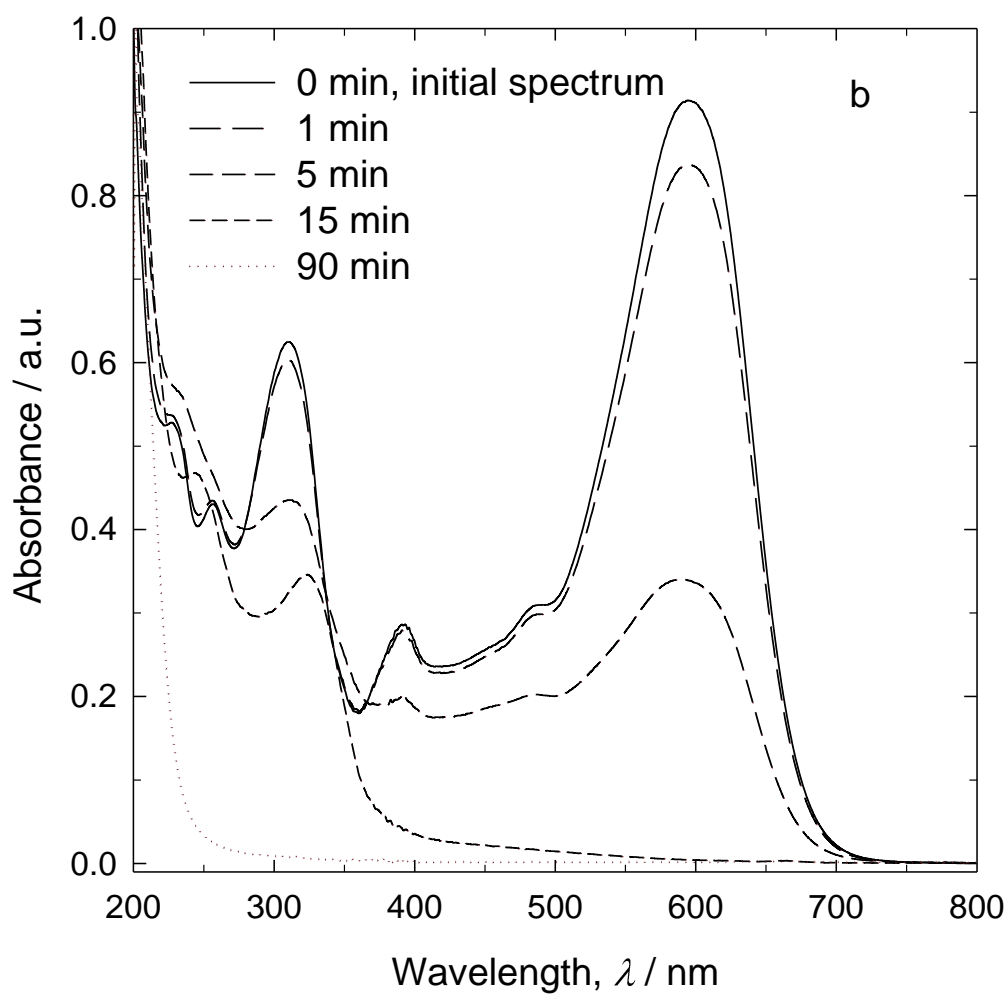


Figure 4b

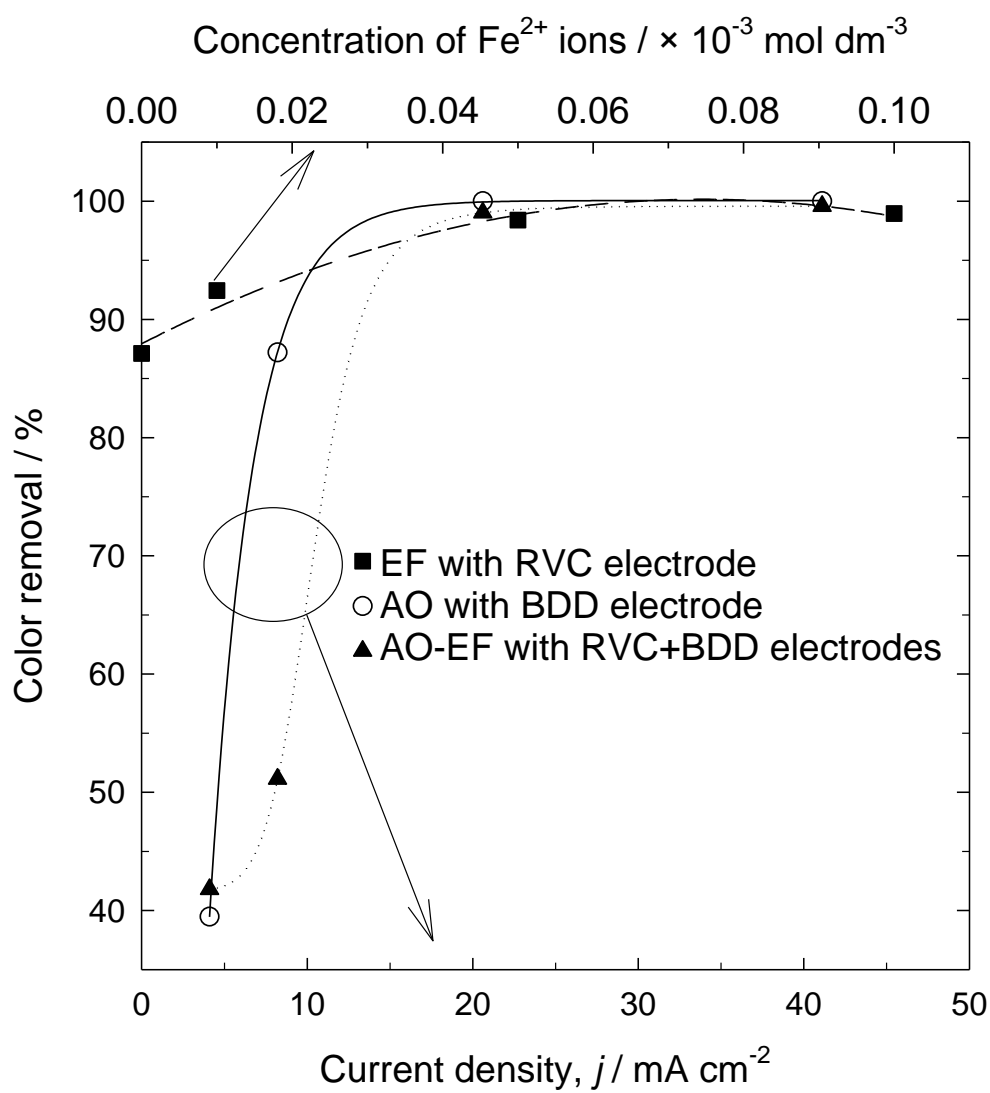


Figure 5

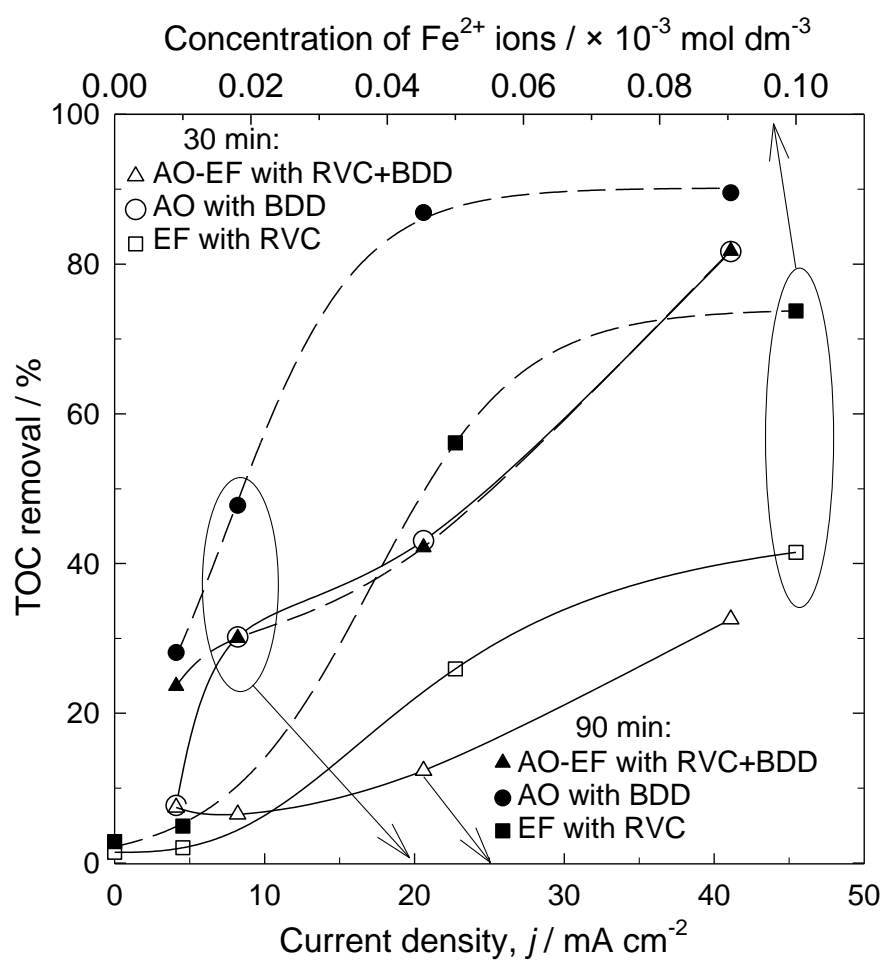


Figure 6

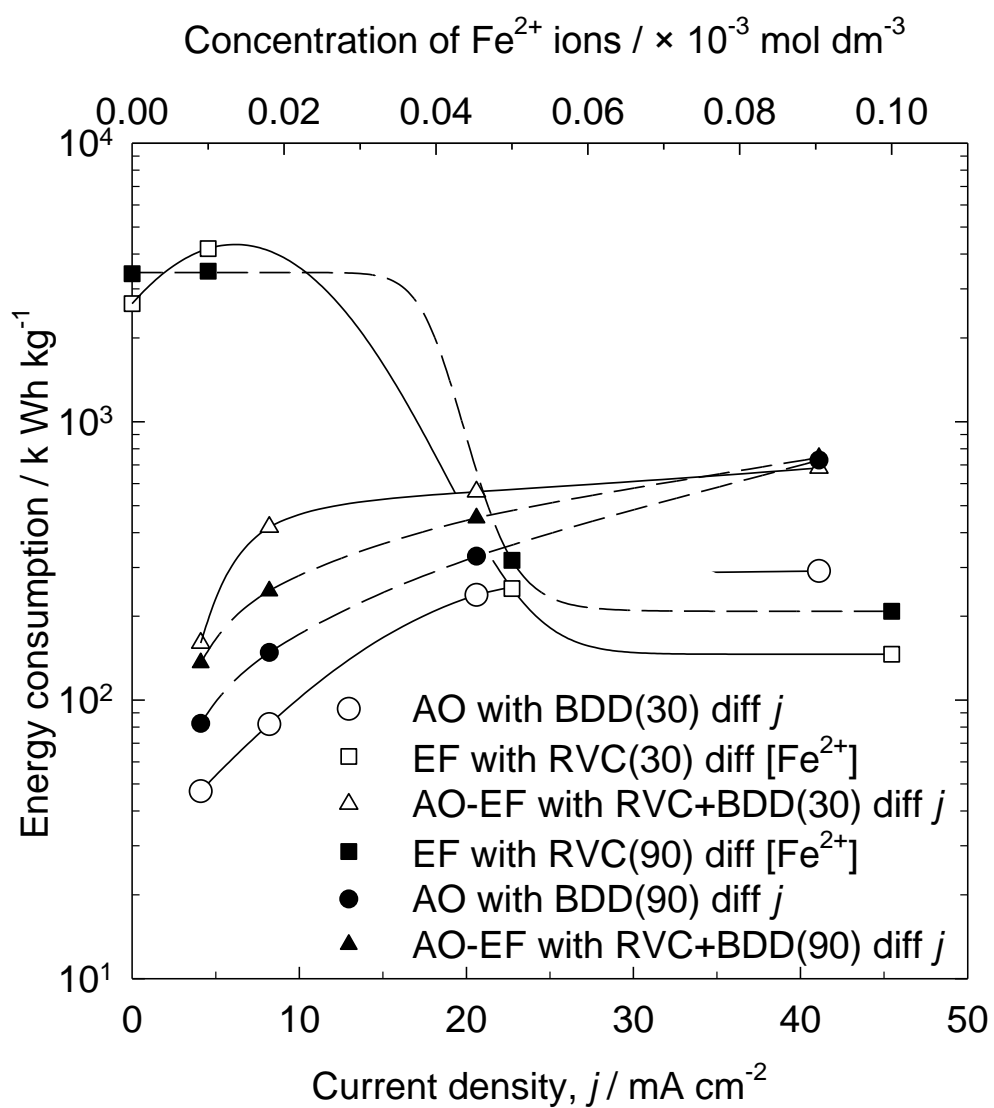


Figure 7

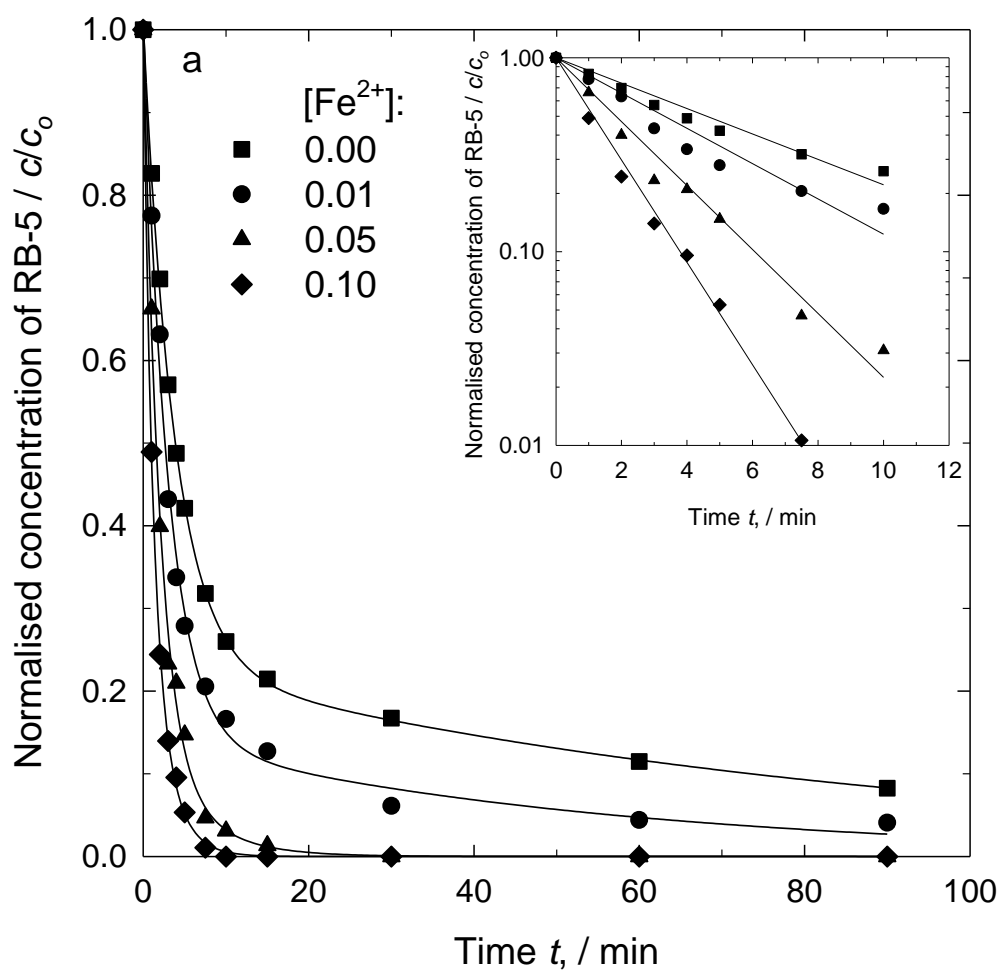


Figure 8a

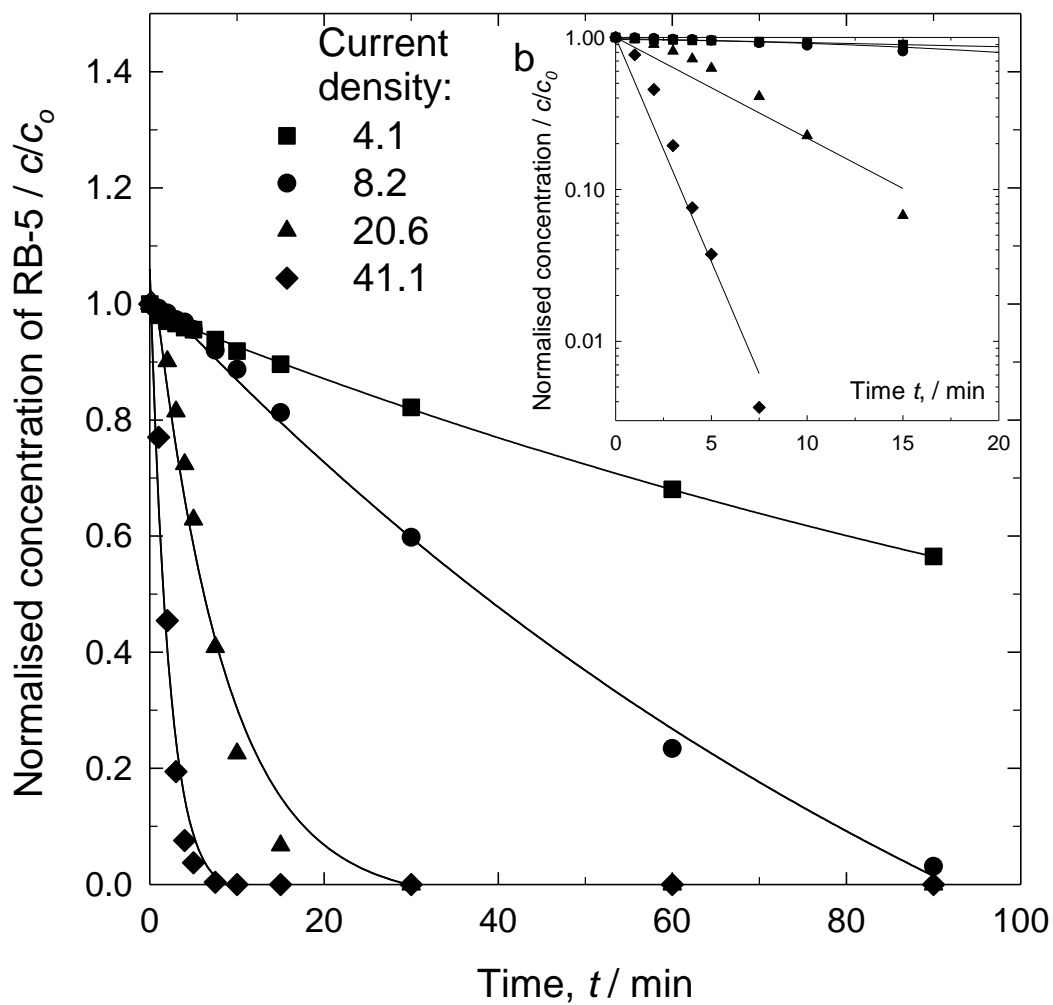


Figure 8b

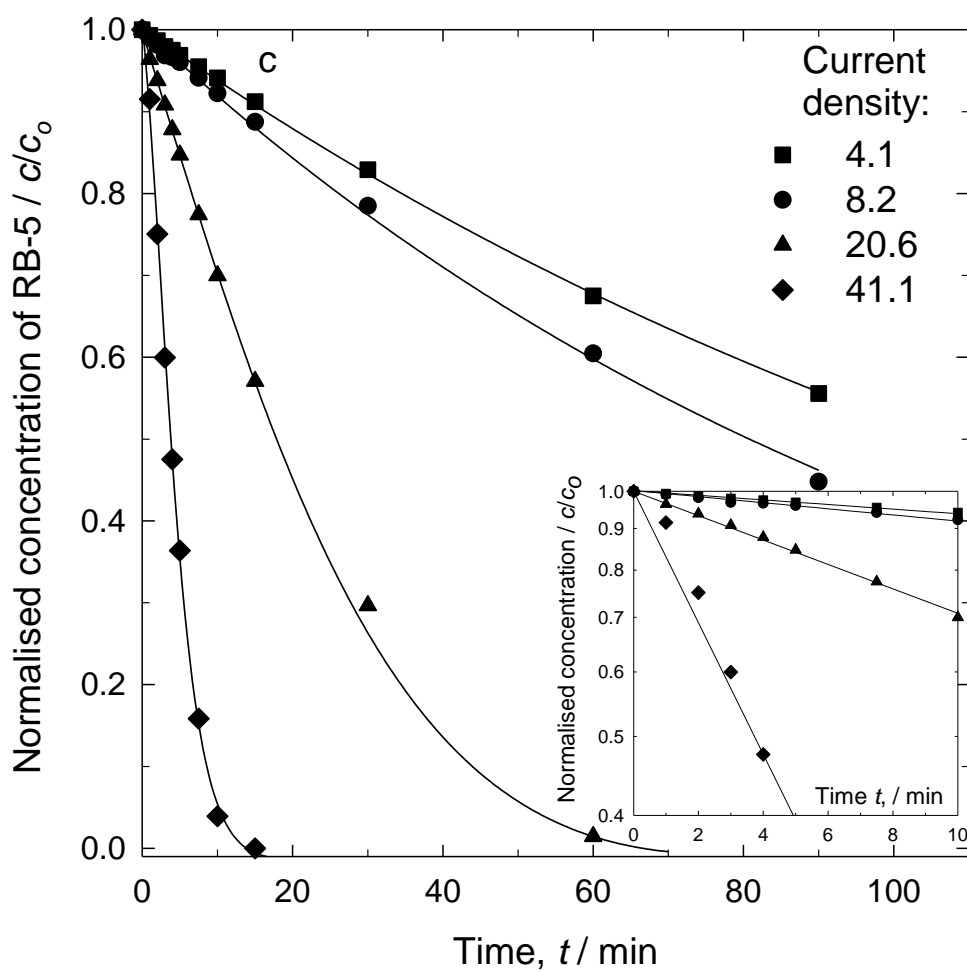
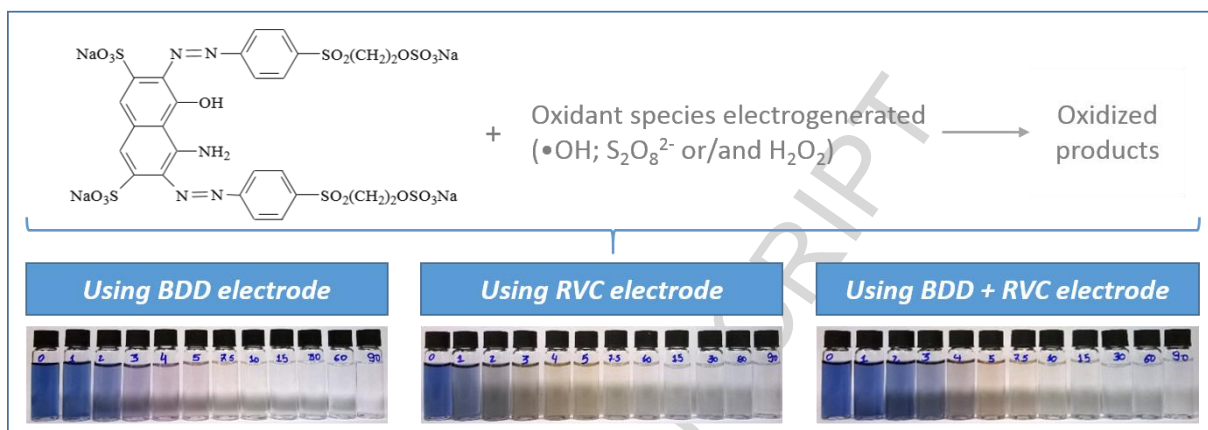


Figure 8c

Graphical abstract

RB-5 ELECTROCHEMICAL/CHEMICAL OXIDATION



Highlights

- Reactive Black-5 removed with BDD and RVC electrodes and their combination.
- BDD electrode removes RB-5 in 7.5 min at high apparent rate constant of 0.835 min^{-1} .
- 82% TOC removal in 30 min with BDD at Energy Consumption (EC) 291 kWh kg^{-1} .
- 74% TOC removal in 90 min by Electro-Fenton at the lowest EC, 208 kWh kg^{-1} .
- All 3 processes promote high TOC removal and follow pseudo first order kinetic.