Electrochemical Treatment of synthetic and Actual Dyeing Wastewaters Using BDD Anodes

Authors: Bensalah, Nasr, and Abdel-Wahab, Ahmed

Source: Air, Soil and Water Research, 3(1)

Published By: SAGE Publishing

URL: https://doi.org/10.1177/ASWR.S3639

Air, Soil and Water Research

ORIGINAL RESEARCH

Electrochemical Treatment of Synthetic and Actual Dyeing Wastewaters Using BDD Anodes

Nasr Bensalah[1,2] and Ahmed Abdel-Wahab[2]

[1]Faculty of Sciences of Gabes, 6072 Zrig, Gabes, Tunisia. [2]Chemical Engineering Program, Texas A&M University at Qatar, PO Box 23874, Doha, Qatar. Email: nasr.bensalah@issatgb.rnu.tn

---

Abstract: In this work, the treatment of synthetic wastewaters containing methylene blue (MB) and rhodamine B (RB) and actual textile wastewaters (ATW) using boron doped diamond (BDD) anodic oxidation was investigated. Voltammetric study has shown that both MB and RB can be oxidized directly at the anode surface in the potential region where the electrolyte salt is stable. Galvanostatic electrolyses of synthetic and actual industrial wastewaters have led to total abatement of COD and TOC at different operating conditions (electrolyte salt and initial pollutant concentration and current density) and the efficiency of the electrochemical process was governed only by mass-transfer limitations. The nature of the supporting electrolyte has a great influence on the rate and the efficiency of the electrochemical oxidation of dyes. The treatment in the presence of NaCl appears to be more efficient in the COD removal, while in the presence of Na_2SO_4 improves the TOC removal. From the experimental results it seems that the primary mechanisms in the oxidation of dyes are the mediated electro-oxidation by hydroxyl radicals and other oxidants electro-generated from supporting electrolyte oxidation.

Keywords: BDD-anodic oxidation, methylene blue and rhodamine B, actual industrial wastewaters, COD and TOC abetments, hydroxyl radicals and electrolyte salt, direct and mediated oxidation

---

Air, Soil and Water Research 2010:3 45–56

Introduction

The treatment with advanced oxidation processes (AOP) appears as one of the most promising methods for the treatment of wastewater containing hazardous organic pollutants produced in many industrial processes. The facts have been associated with the generation of radical species mainly hydroxyl radicals ($OH^{\bullet}$). Hydroxyl radical is a strong oxidizing agent able to react with organics and causing their conversion to CO_2, H_2O and inorganic ions or at least to other organics that can be treated by biological degradation.

Residual colors and dyes in wastewaters are difficult to be entirely removed by biological and/or chemical treatment processes.[1–5] Because of this difficulty of removing dye residues from wastewaters by traditional treatment methods, advanced oxidation processes (AOPs) have became the most capable procedures to treat textile wastewaters in terms of effective decolourization and mineralization of the refractory pollutants.[6–13]

Recently BDD-anodic oxidation was considered as an advanced oxidation process. This is related to the production of large amounts of hydroxyl radicals from water electrolysis.[14,15] Moreover, diamond surface does not interact with hydroxyl radicals and consequently these radicals can only couple to form oxygen or oxidize the organics. In addition to the electro-generation of hydroxyl radicals, this emergent material has important characteristics including high resistance to corrosion, good electrical conductivity, great chemical and electrochemical stability, which enhance the lifetime of the electrode.[16] Compared to other overvoltage anodes the electrochemical oxidation with BDD anode appears clearly more efficient in the mineralization of organic compounds.[17–20] Numerous studies were performed using BDD-anodic oxidation for the treatment of both real and synthetic industrial wastewaters in lab and bench-scale plants.[21–36] From the results of these studies, it could be concluded that BDD-anodic oxidation achieves the almost total removal of chemical oxygen demand contained in the wastes with very good current efficiencies. Conversely, it is noticed that the waste characteristics and operating conditions play an important role in the electrochemical oxidation of organic wastewaters and have a marked influence on the rate and efficiency of the electrochemical process because the organic compounds contained in the wastewater may have different degrees of oxidability. It is also reported that both direct oxidation at the BDD surface and mediated oxidation by hydroxyl radicals and other oxidants electro-generated on the surface from the electrolyte salts are involved in the mechanism of the electrochemical process. Unfortunately, only few studies have engaged on the BDD-anodic oxidation of dyes and actual industrial waste from textile and they have mainly focused in the treatment of small molecules and colorless wastes.[7,10,25,30,33]

The goal of the work described here is (i) to study the treatment of synthetic wastewaters containing methylene blue (MB), rhodamine B (RB) and actual industrial wastewaters from textile (AWT) with BDD-anodic oxidation regarding the effect of various experimental parameters and operating conditions; (ii) to give more comprehensive understanding of the oxidative mechanisms in the electrochemical oxidation of organics with conductive diamond electrodes. The main characteristics of the dyes and the actual industrial waste are shown in Figure 1 and Table 1, respectively. The removal of the organics from the effluent was followed by chemical oxygen demand (COD), total organic carbon (TOC), and UV-visible spectrophotometry.

Experimental Section

Chemicals

MB and RB were of analytical grade and purchased from Fluka. The other chemicals such as Na_2SO_4, NaCl, Na_3PO_4, $K_2Cr_2O_7$, H_2SO_4, NaOH, $HgSO_4$ and Ag_2SO_4 are of analytical grade and purchased from Fluka or Merck. All solutions were prepared with deionized water having 18 $m\Omega^{-1}cm^{-1}$ resistivity from a Mill-Q™ system.

Analytical procedure

The carbon concentration was monitored using a Shimadzu TOC-5050 analyzer. Chemical Oxygen Demand (COD) was determined using a HACH DR200 analyzer. UV-visible spectra were obtained using a Shimadzu 1603 spectrophotometer and quartz cells.

Voltammetry experiments

Electrochemical measurements were obtained using a conventional three-electrode cell in conjunction with a computer-controlled potentiostat/galvanostat (Autolab Model PGSTAT 30, Eco Chemie B.V.,

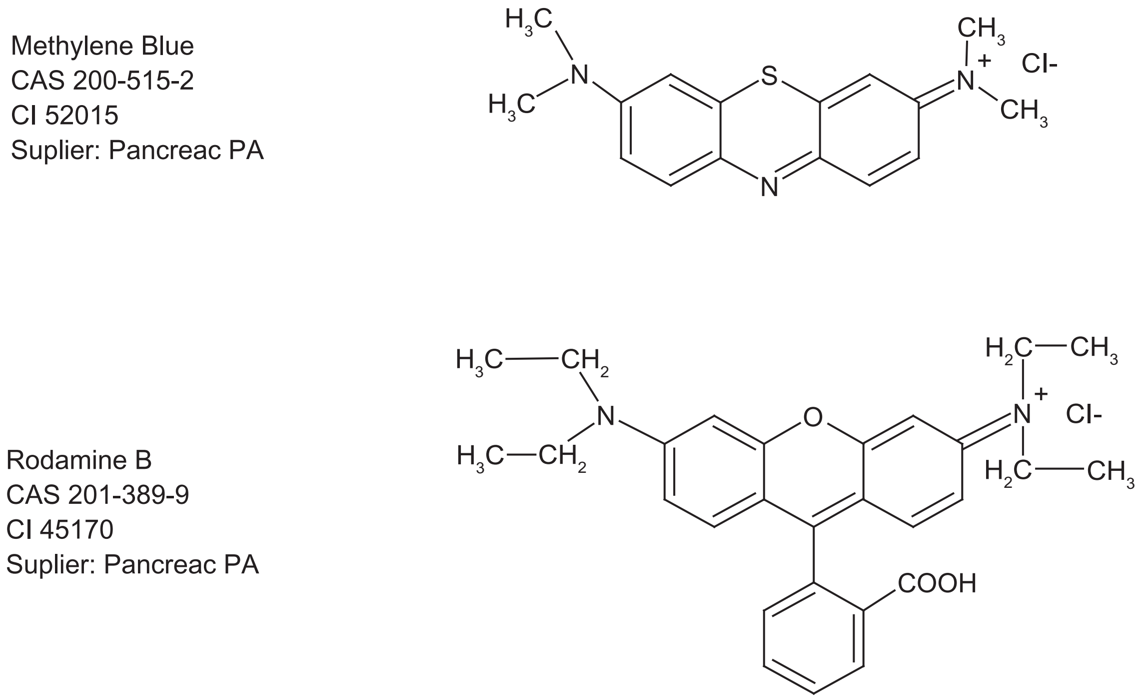

Figure 1. Chemical structures of Methylene Blue (MB) and Rhodamine B (RB).

Utrecht, Netherlands). Diamond was used as the working electrode, $Hg/Hg_2Cl_2{\cdot}KCl$ (sat) as a reference and platinum as a counter electrode. The BDD electrode was circular (25 mm diameter) with a geometric area of 1 cm^2. Voltammetry experiments were performed in unstirred solutions (100 ml). Anode was anodically polarized during 5 minutes with a 1 M H_3PO_4 solution at 0.1 A prior to each experiment.

BDD-anodic oxidation

The galvanostatic electrolyses were carried out in a single-compartment electrochemical flow cell. Diamond-based material (Adamant Technologies, Switzerland) was used as anode and stainless steel (AISI 304) as the cathode. Both electrodes were circular (100 mm diameter) with a geometric area of 78 cm^2 each and an electrode gap of 9 mm. The electrolyte was stored in a glass tank (500 ml) and circulated through the electrolytic cell by means of a centrifugal pump. The electrolyte flow rate through the cell was 2500 $cm^3 \cdot min^{-1}$. The mass transport coefficient of the electrolytic system was calculated using the system ferro/ferri cyanide and it was equal to 2.10^{-5} $m \cdot s^{-1}$. A heat exchanger was used to maintain the temperature at the desired set point. The experimental setup also contained a cyclone for gas–liquid separation, and a gas absorber to collect the carbon dioxide contained in the gases evolved from the reactor into sodium hydroxide. During the experiments the pH was monitored but not controlled.

Table 1. Main characteristics of actual textile wastewaters.

	AW1	AW2	AW3
pH	8.7	7.5	6.8
COD (mg $O_2 \cdot L^{-1}$)	1332	624	494
TOC (mg C $\cdot L^{-1}$)	351.1	211.6	190.8
Chlorides (mg $\cdot L^{-1}$)	2433	3567	2746
Sulfates (mg $\cdot L^{-1}$)	1545	1442	1261
Conductivity (mS $\cdot cm^{-1}$)	10.11	3.69	3.63

Determination of instantaneous current efficiency (ICE)

The chemical oxygen method was used for the determination of the current efficiency during the BDD anodic oxidation of organics. In this method, the COD was measured during electrolysis and the instantaneous current efficiency (ICE) was calculated using the relation.[37,38]

$$ICE = \frac{[COD_t - COD_{t+\Delta t}]\,F\,V}{8\,I\,\Delta t}$$

where COD^0, COD_t and $COD_{t+\Delta t}$ are the initial chemical oxygen demand (in g O_2 dm^{-3}) and the chemical oxygen demand at times t and t + Δt (in seconds), respectively, I is the current intensity (A), F is the Faraday constant (96487 C mol^{-1}), t is the time (in seconds), V is the volume of the electrolyte (dm^3) and 8 is a dimensional factor for unit consistence

$$\left(\frac{32\ g\ O_2 \cdot mol^{-1}\ O_2}{4\ mol\ e^- \cdot mol^{-1}\ O_2}\right)$$

Results and Discussion

Cyclic voltammetry

Figure 2 shows cyclic voltammograms of aqueous solutions containing 1 mM MB and 1 mM RB in 0.1 M of Na_2SO_4 at BDD anodes with a scan rate of 100 mV s^{-1} and under natural pH. A cyclic voltammogram without organic matter is also plotted in the same graphs for the sake of comparison. As it can be observed, the presence of MB leads to the appearance of three anodic peaks around 1.35 and 1.7 V and 1.95 V (vs. SCE) but when RB is added to the aqueous solution only two peaks are observed; the first peak is clearly marked at 1.0 V (vs. SCE) but the second peak is overlapped with the sulphate oxidation. In the two cases the oxygen evolution reaction seems to be shifted towards lower oxidation potentials. The anodic oxidation on BDD anodes of the two dyes is carried out in the same potential region as those of several aromatic compounds.[21–34]

In every case, as the number of cycles increases the voltammograms decrease in size. This deactivation of the anode surface can probably be due to the adsorption of organic molecule (or some of its oxidation products) and/or the deposition of a polymer film on the electrode surface.[23,32] However, the anode can restore its initial activity by an anodic polarization at 300 mA · cm^{-2} current density during 3 min before scanning other voltammograms. To explain this, it has to be taken in mind that at high anodic current densities, the oxidation of water leads to the formation of significant amounts of hydroxyl radicals. These radicals react rapidly with the organics at the surface of the anode leading to their total mineralization and activating the surface once again.

Thus, it looks clear that both MB and RB can be oxidized directly on the surface of the BDD in the potential region of electrolyte stability. The oxidation products of the direct oxidation of the two dyes lead to a deactivation of the anodic surface (probably fouling) being this problem solved working in the potential region of water oxidation.

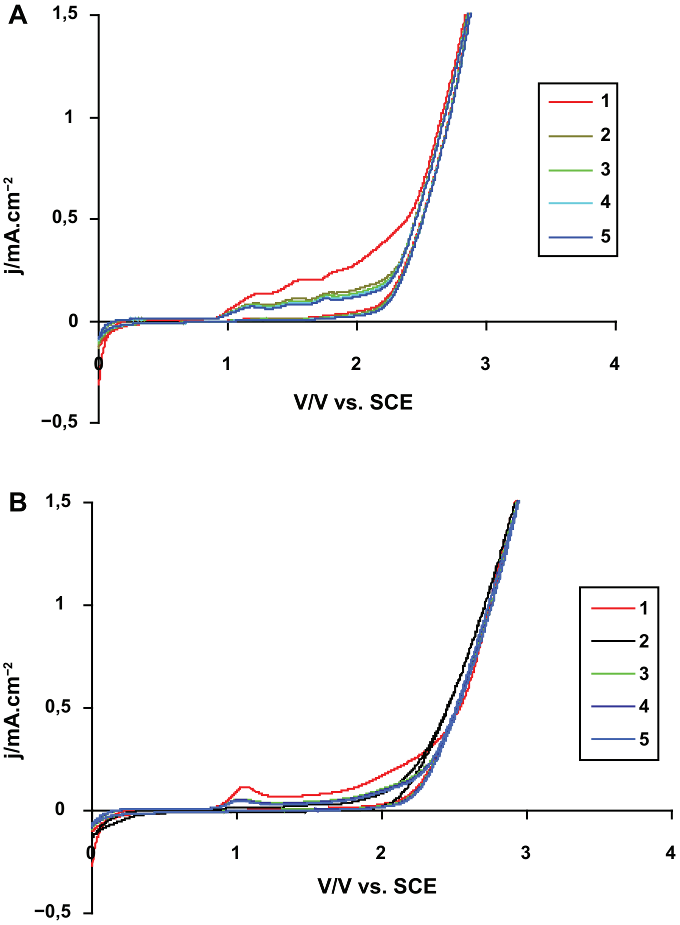

Figure 2. Cyclic voltammograms on BBD anode of **A**) 1 mM MB and **B**) 1 mM RB. Electrolyte: Na_2SO_4 0.1 M, natural pH. Solutions with organic matter: Cycle (1) thinner dashed line; cycles (2) to (5) continuous grey line (all cycles completely overlapped). Solution without organic matter: thicker dashed line (only shown cycle 1). Auxiliary electrode: platinum. Reference electrode: SCE. Scan rate: 100 mV · s^{-1}.

Galvanostic Electrolyses of Synthetic Wastewaters

Figure 3 shows the changes with the specific electrical charge passed of the COD and TOC during the galvanostatic electrolyses of synthetic wastes polluted with MB and RB (T = 25 °C; neutral pH; j = 30 $mAcm^{-2}$; supporting medium, NaCl or Na_2SO_4 5000 ppm). As it can be observed, the electrochemical process can successfully eliminate almost all the COD and TOC contained in the synthetic wastes independently of supporting media but residual refractory carbon is detected only in the presence of NaCl.

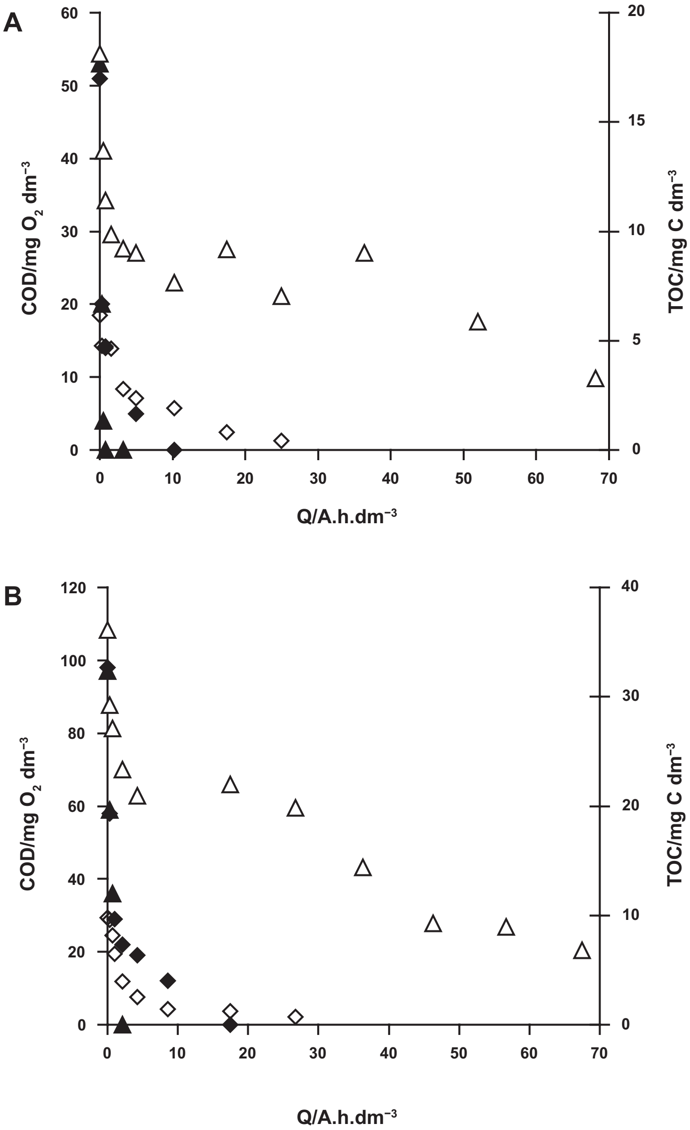

Figure 3. Changes in the COD (◆, ▲) and in the TOC (◇, △) with specific electrical charge passed during galvanostatic electrolyses of **A**) MB (COD_0 = 50 mg · L^{-1}); **B**) RB (COD_0 = 100 mg · L^{-1}). Operation conditions: current density 30 mA.cm^{-2}, T = 25 °C. Waste composition: sodium sulphate 0.1 M (◆, ◇); sodium chloride 0.1 M (▲, △); natural pH.

The oxidation rates and the efficiencies seem to depend on the supporting electrolyte nature. TOC removal in Na_2SO_4 media is more effective than that in NaCl media. On the contrary, the COD removal using NaCl as electrolyte support is more rapid than using Na_2SO_4. Moreover, the changes in the COD are more faster than those in the TOC (especially during the treatment in presence NaCl), as it can be estimated[30–33] taking into account the complex structure of MB and RB (the existence of many functional groups and the large molecular weights of the two molecules) which should favor the formation of a diversity of intermediates (changes in the COD) without carbon dioxide formation (changes in the TOC). In addition, the evolution of UV-visible spectra of MB and RB during galvanostatic electrolyses (T = 25 °C; neutral pH; j = 30 mAcm^{-2}; supporting medium, NaCl or Na_2SO_4 5000 ppm) given in Figure 4, shows that the changes in UV-visible spectra of synthetic solutions containing dyes depend also on the supporting media. As it can be seen, the decolourization (disappearance of bands situated in visible region) is immediately obtained (after 5 min of electrolyses beginning) in the presence of NaCl whereas the solutions are totally decolorized after 2 hours of electrolyses when Na_2SO_4 is used as supporting electrolyte. However, the time required for almost disappearance of the UV bands in presence of NaCl is higher than that in presence of Na_2SO_4. This suggests that the oxidation of dyes should be carried out by both direct electro-oxidation and mediated oxidation by hydroxyl radicals and other strong oxidants electro-generated from the oxidation of the supporting electrolyte. It seems also that the mediated oxidation by the electro-generated reagents from the anodic oxidation of salt plays important role in the efficiency of the electrochemical process. To explain these results, it has to be taken into account that BDD-anodic oxidation of aqueous solutions containing chloride and sulphate anions promotes the formation of hypochlorites and persulphates respectively, and that these chemical species are very powerful oxidant with high standard reduction potentials.[7,39,40] This can be explained assuming that the oxidation with hypochlorites lead to a very effective oxidation of the dyes but not of the intermediates formed (probable accumulation of organo-chlorinated compounds) while the oxidation with peroxodisulphate seems to be more severe in the final stages and it promotes the formation of carbon dioxide.

Figure 5 shows the changes in pH and cell potential with the specific charge passed of the COD during the galvanostatic electrolyses of synthetic wastes polluted with MB and RB containing 100 mg · dm^{-3} of COD (T = 25 °C; neutral pH; j = 30 mAcm^{-2}; supporting medium, Na_2SO_4 5000 ppm). As it can be observed, the cell potential is maintained almost constant during the electrolyses, indicating that appreciable deterioration of the electrode or passivation phenomena (formation of non-conductive layers) did not take place. It can be also seen that the pH of the waste obviously increases

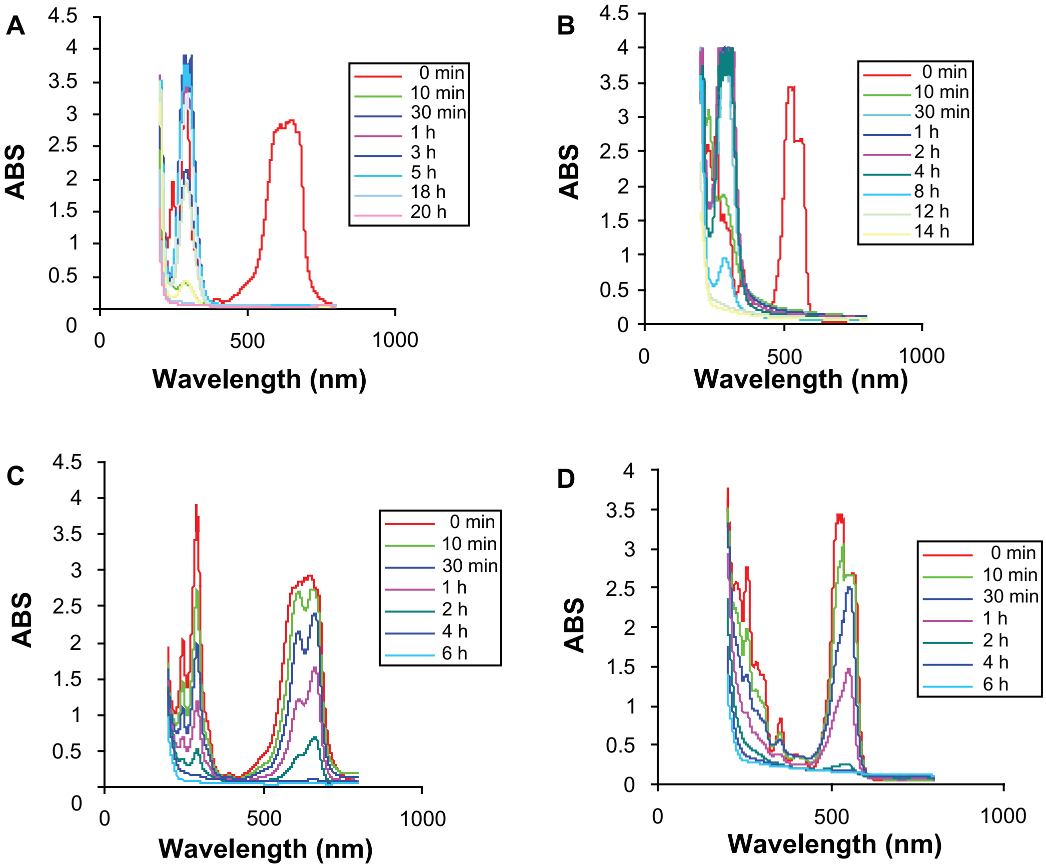

Figure 4. Changes in the UV-Visible spectra with the time passed during galvanostatic electrolyses of synthetic wastes polluted with **A, C**) MB (COD_0 = 50 mg · L^{-1}) and **B, D**) RB (COD_0 = 100 mg · L^{-1}). Operation conditions: current density 30 mA · cm^{-2}, T = 25 °C. Waste composition: sodium chloride 0.1 M **A, B**); sodium sulphate 0.1 M **C, D**); natural pH.

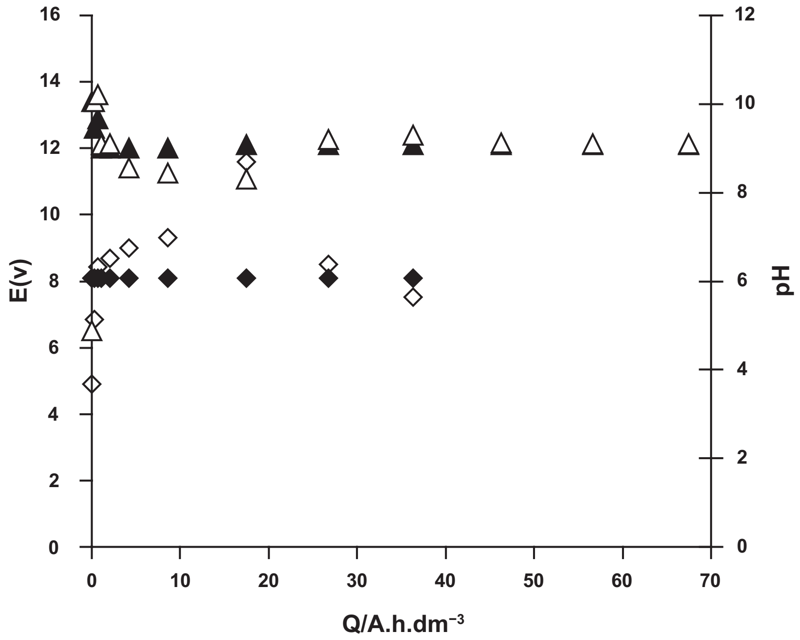

Figure 5. Variation of cell voltage (◆, ▲) and pH (◇, △) with the specific electrical charge passed during galvanostatic electrolyses of synthetic wastes polluted with MB (COD_0 = 50 mg · L^{-1}) (◆, ◇) and RB (COD_0 = 100 mg · L^{-1}) (▲, △). Operation conditions: current density 30 mA · cm^{-2}, T = 25 °C. Waste composition: sodium chloride 0.1 M; natural pH.

at the beginning of the oxidation process of the two molecules. These changes can be explained by the generation of hydroxyl anions on the cathode (from water reduction) which is only partially compensated by the generation of protons from water oxidation on the anode because of its competition with the anodic oxidation of organics (and/or inorganic compounds) and by the formation of amines from the anodic oxidation of dyes (diethylamine in the case of RB and dimethylamine in the case of MB).

Figures 6 and 7 show the influence of the applied current density and dye initial concentration on the evolution with the specific charge passed of the COD during the galvanostatic electrolyses of synthetic wastes polluted with MB and RB containing 100 mg · dm^{-3} of COD (T = 25 °C; neutral pH; supporting medium, NaCl 5000 ppm). As it can be observed the complete removal of COD is obtained, independently of the applied current density and dye initial concentration. As it can be seen, in the BBD-anodic oxidation of the two dyes studied in this work an increase in the current density does not lead to an increase in the efficiency of the oxidation process in terms of COD removal, and similar electrical charges are required to remove the same amount of organic matter (COD removal profiles obtained at different current densities are overlapped). In the range of concentration studied in this work, the COD changes with specific electrical charge passed are in agreement with an exponential law. This behavior is characteristic of mass-transfer-controlled processes in which an increase in the current density can not raise the rate of oxidation of the organics at the electrode and favors anodic side reactions (formation of O_2, O_3 etc.).[38] Moreover, these results suggest that the oxidation of dyes and by products with hypochlorites is not very efficient and hence that the direct oxidation (or the oxidation by hydroxyl radicals) controls the overall oxidation rate.

Electrochemical Treatment of Actual Industrial Wastewaters

The actual wastewaters used in this work are received from textile industry (Gabes, south of Tunisia). The values of actual textile wastewaters (ATW) conductivities are high enough to directly apply an electrochemical treatment. The results of galvanostatic electrolyses (T = 25 °C; neutral pH; j = 30 mAcm^{-2}) of three types of actual textile wastewaters are shown in Figures 8 and 9. It can be observed that both TOC and COD decrease with specific electrical charge passed down almost to zero independently of the AWT characteristics. The variation of the COD

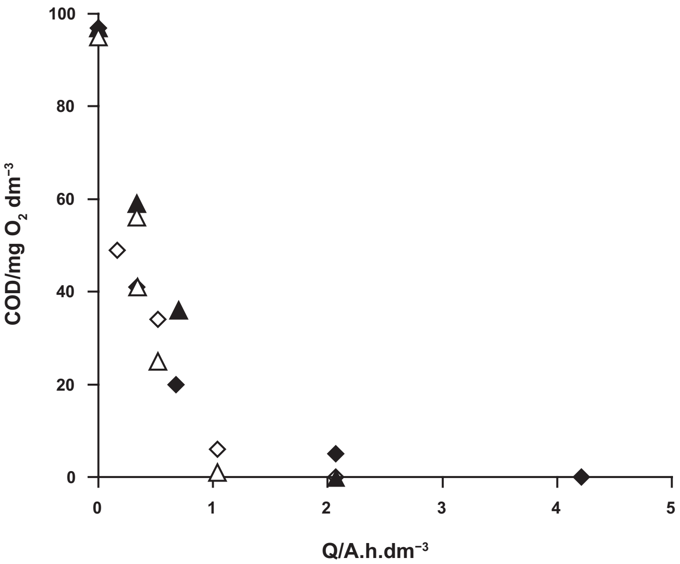

Figure 6. Influence of the current density on the evolution with the specific electrical charge passed of COD during galvanostatic electrolyses of synthetic wastes polluted with MB (◆, ◇) and RB (▲, △). Operation conditions: current density (◇, △) j = 15 mA · cm^{-2}; (◆, ▲) j = 30 mA · cm^{-2}, T = 25 °C. Waste composition: sodium chloride 0.1 M; natural pH; COD$_0$ = 100 mg · L^{-1}.

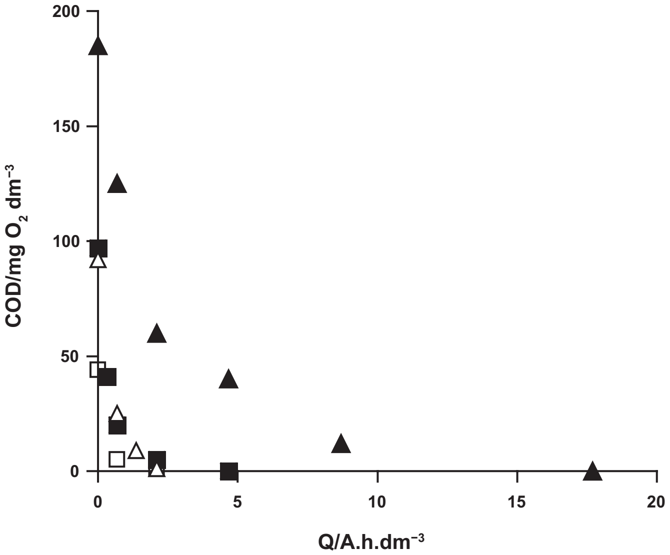

Figure 7. Influence of initial organic load on the evolution with the specific electrical charge passed of COD during galvanostatic electrolyses of synthetic wastes polluted with MB: COD$_0$ = 100 mg · L^{-1} (■), COD$_0$ = 50 mg · L^{-1} (□) and RB: COD$_0$ = 200 mg·L^{-1} (▲), COD$_0$ = 100 mg · L^{-1} (△). Operation conditions: current density 30 mA · cm^{-2}, T = 25 °C. Waste composition: sodium chloride 0.1 M; natural pH.

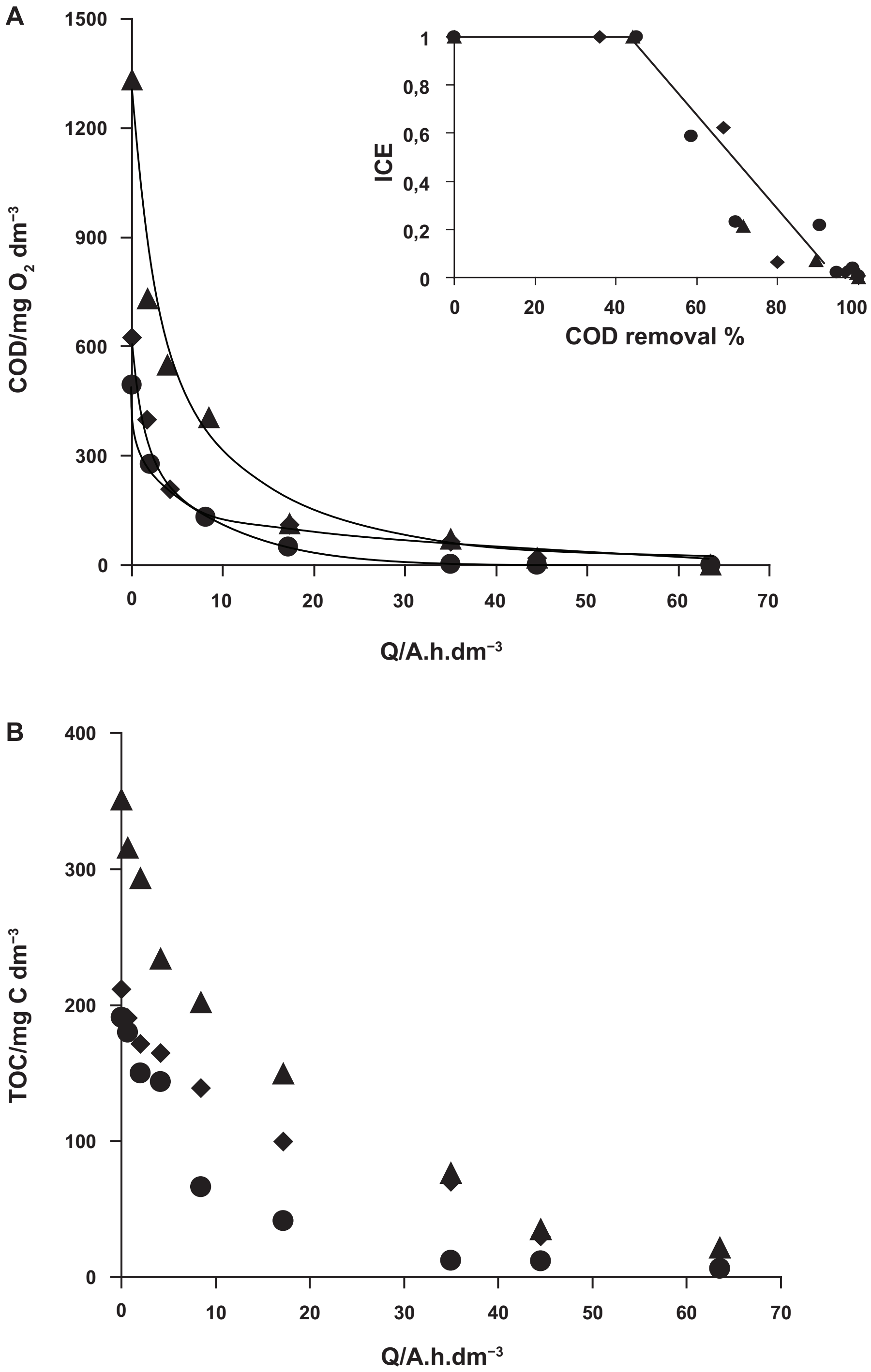

Figure 8. Bulk electrolysis of industrial textile wastewaters ATW: **A**) Changes in the COD; **B**) Changes in the TOC with specific electrical charge passed (inset figure: changes in the instantaneous current efficiency with COD removal percentage). Operation conditions: current density 30 mA · cm^{-2}, T = 25 °C. Waste composition: natural pH; COD$_0$ (mg · L^{-1}): 1332 (▲), 624 (◆) and 494 (●).

has a typical exponential shape in the range of the COD concentration studied. This behavior was previously explained in the literature in terms of the controlling mechanisms of the electrochemical process.[38] The exponential zone corresponds to COD concentrations in which the electrochemical process is mass-transfer controlled. High efficiencies (ICE close to 1) are obtained in the first stages of electrolyses (COD removal <50%) and after removing 50% of COD, linear and continuous decrease of ICE

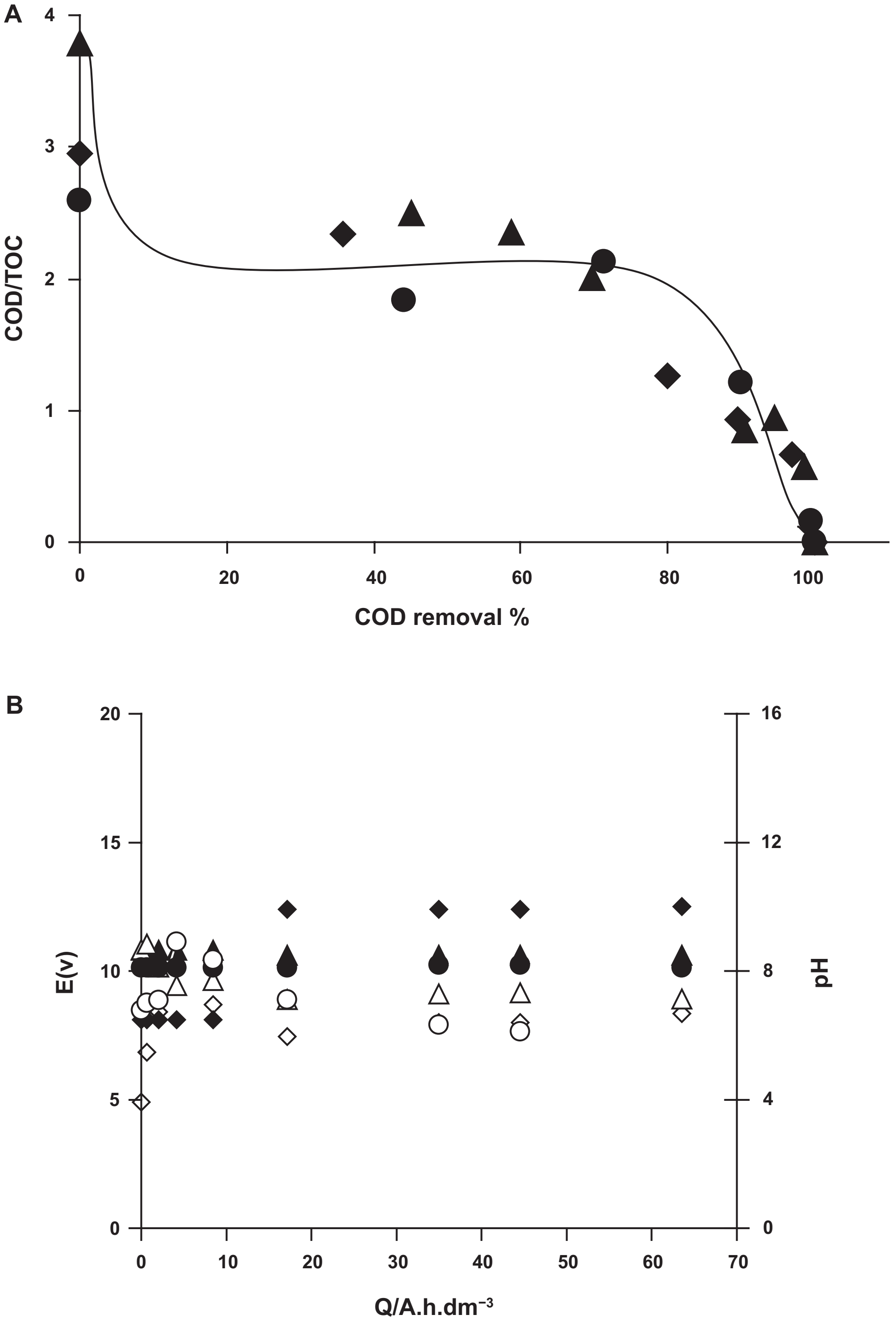

Figure 9. Bulk electrolysis of industrial textile wastewaters ATW: **A**) Changes in the in the COD/TOC ratio; **B**) Changes in cell voltage (▲, ◆, ●) and pH (◇, △, ○) with the specific electrical charge passed. Operation conditions: current density 30 mA · cm^{-2}, T = 25 °C. Waste composition: natural pH; COD$_0$ (mg · L^{-1}): 1332 (▲), 624 (◆) and 494 (●).

with the percentage of COD removal is observed. This decrease is characteristic of electrochemical wastewater treatment processes, and can be justified in terms of a mass transport control of the overall rate of the process.

Changes in the TOC indicate that carbon dioxide is formed from the very early oxidation stages. However, as it can be seen in Figure 9a, the COD/TOC ratio decreases significantly during the first stages (up to 20% of COD removal) and then, it remains constant in a value close to 2 and decreases rapidly at the end of the electrolyses. This means that the oxidation of the organics can be assumed to occur in two main sequential stages: the first is the rapid oxidation of organics to slowly-oxidizable intermediates (average COD/TOC ratio around 2) and the second is the less efficient oxidation of these intermediates to carbon dioxide. In this point it is important to note that the current efficiency (Fig. 8-a inset) decreases rapidly during the treatment being almost negligible in this second stage.

Figure 9-b shows that the pH of the waste first decreases slightly and later increases finally to reach a constant value close. These changes can be justified in terms of the anodic and cathodic processes that develop in the cell.[31–36] On the cathode the main reaction is the water reduction which generates hydroxyl ions and moves the pH towards alkaline pH. On the anode several reactions coexist. The main reaction is the oxidation of organic matter. The first stages in this oxidation are the formation of carboxylic acids. These carboxylic acids, together with the protons formed during the oxidation of water, compensate the cathodic hydroxyl ion generation rate. The second step in the oxidation of organic matter is the transformation of carboxylic acids into carbon dioxide. This second process yields a lower global proton generation rate and consequently the pH increases. The cell potential increases slightly during the electrolysis. This fact could be explained in terms of the formation of a layer of carbonates on the surface of the cathode due to the hydroxyl ions generated from water reduction.

Figure 10 shows the energy consumption required to remove the COD as a function of the COD removal percentage. As it can be seen, during the electrolyses of ATW, the energy requirements increase linearly up to 80% of COD removal and then they start to change exponentially. Furthermore, the values obtained are higher than those obtained during the electrolyses for slighter pollutants proposed in the literature (range of 35–50 kW · h · kg^{-1} COD removed) because of the high cell voltage. The use of high concentrations of COD does not affect significantly the energy consumption indicating the important role of mediated oxidation in the electrochemical process.

Conclusion

The main conclusions of this work can be summarized in the following points:

1. BDD-anodic oxidation can be used successfully to remove all the almost COD and TOC of both synthetic wastewaters polluted with MB and RB

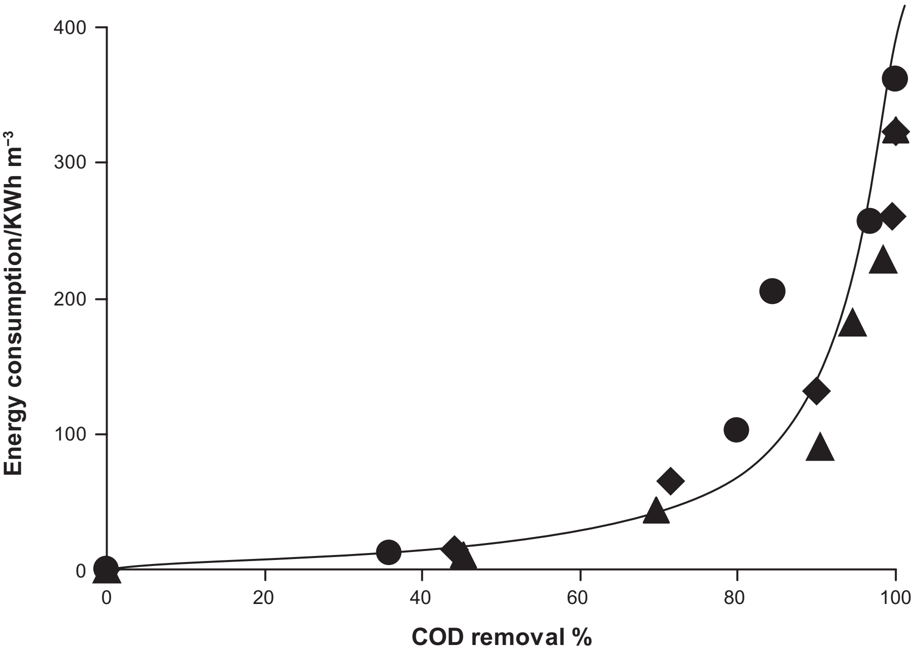

Figure 10. Energy consumption versus the COD removal during the galvanostatic electrolyses of industrial textile wastewaters (ATW). Operation conditions: current density 30 mA · cm^{-2}, T = 25 °C. Waste composition: natural pH; COD$_0$ (mg · L^{-1}): 1332 (▲), 624 (◆) and 494 (●).

and actual textile wastewaters. The oxidation of the organics can be assumed to occur in two main sequential stages: the first is the rapid oxidation of organics to slowly-oxidizable intermediates (average COD/TOC ratio around 2) and the second is the less efficient oxidation of these intermediates to carbon dioxide.

2. The nature of the supporting electrolyte has a great influence on the rate and the efficiency of the electrochemical oxidation of MB and RB. The treatment in the presence of NaCl appears to be more efficient in the COD removal, while in the presence of Na_2SO_4 improves the TOC removal. Accordingly, the mediated oxidation by the electro-generated reagents from the anodic oxidation of supporting electrolyte plays important role in the efficiency of the electrochemical process.
3. High efficiencies (ICE close to 1) are obtained in the first stages of electrolyses, and then linear and continuous decrease of ICE with the percentage of COD removal is observed. This decrease is characteristic of electrochemical wastewater treatment processes, and can be justified in terms of a mass transport control of the overall rate of the process.
4. The specific electrical charges required to complete the treatment are not proportional to the initial organic load of the waste. This can be explained in terms of the oxidation mechanisms that happen inside the electrochemical cell. In this context, from the experimental results it seems that the primary mechanisms in the oxidation of dyes are the mediated electro-oxidation by hydroxyl radicals and other oxidants electro-generated from supporting electrolyte oxidation.

Acknowledgements

The authors would like to acknowledge Professor Manuel A. Rodrigo (University of Castilla-La-Mancha, Spain) for his gracious assistance. Sincere thanks are extended to the Spanish and the Tunisian Governments for financial support (AECI joint project 34/04/P/E).

Disclosures

This manuscript has been read and approved by all authors. This paper is unique and is not under consideration by any other publication and has not been published elsewhere. The authors and peer reviewers of this paper report no conflicts of interest. The authors confirm that they have permission to reproduce any copyrighted material

References

1. Ledakowicz S, Gonera M. Optimization of oxidants dose for combined chemical and biological treatment of textile wastewater. *Water Res*. 1999;33:2511–6.
2. Georgiou D, Metallinou C, Aivasidis A, Voudrias E, Gimouhopoulos K. Decolorization of azo-reactive dyes and cotton-textile wastewater using anaerobic digestion and acetate-consuming bacteria. *Biochem Eng J*. 2004;19:75–9.
3. Coughlin MF, Kinkle BK, Bishop PL. High performance degradation of azo dye Acid Orange 7 and sulfanilic acid in a laboratory scale reactor after seeding with cultured bacterial strains. *Water Res*. 2003;37;2757–63.
4. Slokar YM, LeMarechal AM. Methods of decolourization of textile wastewaters. *Dyes Pigments*. 1998;37:335–56.
5. Forgacs E, Cserhati T, Oros G. Removal of synthetic dyes from wastewaters: a review. *Environ Int*. 2004;30:953–71.
6. Shu HY, Huang CR. Degradation of commercial azo dyes in water using ozonation and UV enhanced ozonation process. *Chemosphere*. 1995;31:3813–25.
7. Fernandes A, Morao A, Magrinho M, Lopes A, Goncales I. Electrochemical degradation of C.I. acid Orange 7. *Dyes Pigments*. 2004;61:287–96.
8. Kabita D, Subrata M, Sekhar B, Basab Ch. Chemical oxidation of methylene blue using a Fenton-like reaction. *Haz Mater*. 2001;B84:57–71.
9. Pereza M, Torrades F, Domenech X, Peral J. Fenton and photo-Fenton oxidation of textile effluents. *Water Res*. 2002;36:2703–10.
10. Lin SH, Peng CF. Treatment of textile wastewater by electrochemical method. *Water Res*. 1994;28:277–82.
11. Tzitzi M, Vayenas DV, Lyberatos G. Pretreatment of textile industry wastewaters with ozone. *Water Sci Technol*. 1994;29:151–60.
12. Arslan-Alaton I, Bacioglu IA, Bahnemann DW. Advanced oxidation of a reactive dyebath effluent: comparison of O_3, H_2O_2/UV-C and TiO_2/UV-A processes. *Water Res*. 2002;36:1143–54.
13. Carriere J, Jones P, Broadbent A. Decolorization of textile dye solutions. *Ozone:SciEng*. 1993;15:189–200.
14. Marselli B, García-Gómez J, Michaud PA, Rodrigo MA, Comninellis Ch. Electrogeneration of Hydroxyl Radicals on Boron-Doped Diamond Electrodes. *Electrochem Soc*. 2003;150:D79.
15. Michaud PA, Panizza M, Ouattara L, Diaco T, Foti G, Comninellis Ch. Electrochemical oxidation of water on synthetic boron-doped diamond thin film anodes. *App Electrochem*. 2003;33:151–4.
16. Fujio O, Yukio K, Hidekazu T, et al. Osamu, Preparation of boron-doped semi-conducting diamond films using BF_3 and the electrochemical behavior of the semi-conducting diamond electrodes. *Fluorine Chem*. 2004;125:1715–22.
17. Chen XM, Chen GH, Yue PL. Stable Ti/IrO_x-Sb_2O_5-SnO_2 anode for O_2 evolution with low Ir content. *J Phys Chem B*. 2001;105:4623–8.
18. Correa-Lozano B, Comninellis Ch, Battisti AD. Service life of Ti/SnO_2-Sb_2O_5 anodes. *J Appl Electrochem*. 1997;27:970–4.
19. Feng J, Johnson DC. Electrocatalysis of anodic oxygen-transfer reactions: titanium substrates for pure and doped lead dioxide films. *J Electrochem Soc*. 1991;138:3328–37.
20. Kotz R, Stucki S, Carcer B. Electrochemical wastewater treatment using high over voltage anodes. Part I: physical and electrochemical properties of SnO_2 anodes. *J Appl Electrochem*. 1991;21:14–20.
21. Gandini D, Mahe E, Michaud PA, Haenni W, Perret A, Comninellis Ch. Oxidation of carboxylic acid at boron-doped diamond electrodes. *J Appl Electrochem*. 2000;30:1345–50.
22. Kong W, Wang B, Ma H, Gu L. Electrochemical Treatment of Anionic Surfactants in synthetic wastewater with three-dimensional electrodes. *Haz Mat*. 2006;55–68.
23. Cañizares P, Sáez C, Lobato J, Rodrigo MA. Electrochemical oxidation of polyhydroxybenzenes on boron-doped diamond anodes. *Ind Eng Chem Res*. 2004;43:6629–36.

24. Rodrigo MA, Michaud PA, Duo I, Panizza M, Cerisola G, Comninellis Ch. Oxidation of 4-chlorophenol at boron-doped diamond electrodes for wastewater treatment. *J Electrochem Soc*. 2001;148:D60–3.
25. Ahmadi MF, Bensalah N, Gadri A. Electrochemical degradation of anthraquinone dye Alizarin Red S by anodic oxidation on boron-doped diamond. *Dyes and Pigments*. 2007;73:86–9.
26. Sirés I, Cabot PL, Centellas F, et al. Electrochemical degradation of clofibric acid in water by anodic oxidation. Comparative study with platinum and boron-doped diamond electrodes. *Electrochimica Acta*. 2006;52:75–85.
27. Quiroz Alfaro MA, Ferro S, Martinez-Huitle CA, Vong YM. Boron doped diamond electrode for the wastewater treatment. *J Brazil Chem Soc*. 2006; 17(2):227–36.
28. Martinez-Huitle CA, Ferro S. Electrochemical oxidation of organic pollutants for the wastewater treatment: Direct and indirect processes. *Chem Soc Rev*. 2006;35(12):1324–40.
29. Bensalah N, Gadri A. Electrochemical oxidation of 2,4,6-trinitrophenol on boron-doped diamond electrodes. *J Electrochem Soc*. 2005;152:D113–6.
30. Cañizares P, Gadri A, Lobato J, Bensalah N, Rodrigo MA, Sáez C. Electrochemical oxidation of Azoic Dyes with Conductive-Diamond Anodes. *Ind Eng Chem Res*. 2006;45:3468–73.
31. Cañizares P, Martínez L, Paz R, Sáez C, Lobato J, Rodrigo MA. Treatment of Fenton-refractory olive-oil-mills wastes by electrochemical oxidation with Boron Doped Diamond Anodes. *J Chem Technol and Biotechnol*. 2006;81:352–8.
32. Cañizares P, Lobato J, Paz R, Rodrigo MA, Sáez C. Electrochemical oxidation of phenolic wastes with boron-doped diamond anodes. *Water Res*. 2005;39:2687–703.
33. Faouzi M, Cañizares P, Gadri A, et al. Advanced oxidation processes for the treatment of wastes polluted with azoic dyes. *Electrochimica Acta*. 2006; 52:325–31.
34. Nasr B, Abdellatif G, Cañizares P, Sáez C, Lobato J, Rodrigo MA. Electrochemical oxidation of hydroquinone, resorcinol, and cathecol on boron-doped diamond anodes. *Environ Sci Techol*. 2005;39:7234–9.
35. Cañizares P, Martinez L, Paz R, Sáez C, Lobato J, Rodrigo MA. Treatment of Fenton-refractory olive oil mill wastes by electrochemical oxidation with boron-doped diamond anodes. *J Chem Technol Biotechnol*. 2006;81: 1331–7.
36. Cañizares P, Paz R, Sáez C, Rodrigo MA. Electrochemical Oxidation of Wastewaters Polluted with Aromatic and Heterocyclic Compounds. *J Electrochem Soc*. 2007;154:E165–71.
37. Comninellis Ch, Plattner E. Electrochemical wastewater treatment. *Chimia*. 1988;42:250–2.
38. Martinez-Huitle CA, Ferro S. Electrochemical Oxidation of Organic Pollutants for the Wastewater Treatment: Direct and Indirect Processes. *Chem Soc Rev*. 2006;35:1324–40.
39. Michaud PA, Mahé E, Haenni W, Perret A, Comninellis Ch. Preparation of Peroxodisulfuric Acid Using Boron-Doped Diamond Thin-Film Electrodes. Electrochem. *Solid State Lett*. 2000;3:77.
40. Cañizares P, Larrondo F, Lobato J, Rodrigo MA, Sáez C. Electrochemical Synthesis of Peroxodiphosphate using Boron-Doped Diamond Anodes. *J Electrochem Soc*. 2005;152:D191–6.