The degradation of reactive red dye from wastewaters by advanced electrochemical oxidation

S. Moţoc, F. Manea, A. Pop, A. Baciu, G. Burtică & R. Pode
"Politehnica" University of Timisoara, Timisoara, Romania

Abstract

In the present study, electrochemical degradation experiments were conducted to degrade a textile dye namely Reactive Red 147 (RR) from water. The process performance was assessed in terms of the electrochemical decolourisation and mineralization of aqueous RR solutions. Electrolyses were carried out under galvanostatic conditions using boron-doped diamond (BDD) electrodes in 0.1 M Na_2SO_4 supporting electrolyte using undivided electrolytic cell. Also, the effect of in-situ electrolytic generation of chlorine/hypochlorite at BDD electrode from a mixture of 0.05 M Na_2SO_4 and 0.05 M NaCl supporting electrolyte on the electrochemical degradation process of RR has been studied. Prior to electrolysis application, the electrochemical behaviour of RR dye on BDD electrode was characterized in both supporting electrolytes without/with chloride presence by cyclic voltammetry in order to establish the working potential-current conditions. The influence of operating variables on the electrochemical process efficiency was studied as a function of the supporting electrolyte type, current density, and the initial pH. Under all applied conditions, the complete decolourisation of dye synthetic solution was achieved after several minutes of electrolysis. Acidic medium and the chlorine/hypochlorite generation favored the decolorization and mineralization process of RR. The complete mineralization of dye synthetic solution was not achieved, and the maximum mineralization efficiency of 35% was reached under the working conditions of hypochlorite presence, which informs about the intermediates generation during the application of electrochemical process based on BDD electrodes.
Keywords: advanced wastewater treatment, electrochemical degradation, Reactive Red 147 dye, boron-doped diamond electrode.

1   Introduction

The rapid increase in population and increased demand for industrial systems to meet human necessities have created problems such as overexploitation of available resources, leading to pollution of land, air and water surroundings.

With the increased demand for textile products, the wastewater of textile industry is increasing proportionally, making it one of the main sources of worldwide severe pollution problems. In particular, the release of textile wastewater to the natural water courses is the main dispersion path of a wide variety of dyestuff in the environment [1].

Many dyes and their breakdown products are toxic and/or mutagenic to aquatic life. Azo dyes are among the most widely used synthetic dyes and usually considered as major pollutants in textile wastewater [2].

At the moment, several biological, physical and chemical processes are used to treat dye effluents [2–6]. However, conventional sewage plant treatments are usually ineffective for dye removal because of their high biochemical stability, their relatively high molecular weight and the presence of aromatic rings.

In recent years, there has been an increasing interest in the use of electrochemical methods for the destruction of toxic and biorefractory organic pollutants.

These methods use the electron as the main reagent, but also require the presence of supporting electrolytes. In general, the supporting electrolytes exist in the dye-containing wastewaters to be treated, but not always in sufficient concentrations. These processes can operate at ambient temperature without a need of temperature control [2, 7].

It is well-known that the electrode material is the most important parameter in the electrochemical oxidation of organics, constituting the key for process performance. Boron-doped diamond (BDD) electrode exhibits a great potential for electrochemical applications, especially for the treatment of wastewater and drinking water because of the extraordinary chemical inertness offering the opportunity to use such electrodes (anodes as well as cathodes) in very aggressive media [8–10].

The aim of the work is to assess the performance of boron-doped diamond (BDD) electrodes in 0.05 M Na_2SO_4 and 0.05M NaCl supporting electrolyte for Reactive Red 147 (RR) dye electrooxidation based on the electrochemical decolourisation and mineralization degrees. The electrochemical behaviour of RR dye on BDD electrode was studied cyclic voltametry (CV) technique to select the operating variables in relation with the current density. The effect of the current density and pH was studied to determine the optimum working conditions for bulk electrolysis under galvanostatic regime.

2   Experimental

2.1   Electrochemical characterization of BDD electrode

The electrochemical behaviour of the disc BDD electrode with the surface areas of 0.07068 cm^2 (Windsor Scientific Ltd, UK) in the presence of RR dye was

studied by cyclic voltammetry (CV). Subsequently, an electrochemical pretreatment by three repetitive cycling between -0.5 V to 2 V vs. SCE in 0.1M Na_2SO_4, and 0.05 M Na_2SO_4 and 0.05M NaCl supporting electrolytes was performed. All measurements were carried out using an Autolab potentiostat/galvanostat PGSTAT 302 (Eco Chemie, The Netherlands) controlled with GPES 4.9 software and a three-electrode cell, with a saturated calomel electrode as reference electrode, a platinum counter electrode and BDD working electrode.

2.2 Bulk electrolysis experiments and analytical procedures

The electrochemical experiments were carried out at room temperature (22–25°C) by batch process using an undivided cell of 0.7 dm^3 volume in 0.05 M Na_2SO_4 and 0.05M NaCl supporting electrolyte. The solution pH was initially adjusted to 3 and 5 with small volumes of H_2SO_4, and respectively to 9 with NaOH solution. The BDD/Nb electrodes (100 mm x 50 mm x 1 mm) with 280 cm^3 geometric area provided by CONDIAS, Germany were used as anodes, and stainless steel plates (100 mm x 50 mm x 1 mm) were employed as cathodes under vertical arrangement. A regulated DC power supply (HY3003, MASTECH) was used under galvanostatic regime at current densities of 10 and 30 mA cm^{-2}.

After each minute, samples were drawn from the cell and RR dye degradation was followed by UV-VIS spectroscopy using a Varian Cary UV-VIS spectrophotometer. RR mineralization was checked by TOC parameter which was analyzed using a Shimadzu TOC analyzer. An Inolab WTW pH meter was used to measure the solution pH. General parameters for the assessment of the performance of the applied processes were used.

Thus, the decolourisation of RR dye was followed based on absorbance recorded at 525 nm (A_{525}). The percentage of colour removal was determined using the expression (1):

$$Colour\,removal\,(\%) = \frac{\left(A_{525,0} - A_{525}\right)}{A_{525,0}} x100 \quad (\%) \tag{1}$$

The electrochemical efficiency for RR dye oxidation was determined based on eqn. (2):

$$E_{DBR} = \frac{\left(RR_0 - RR\right)}{Q * S} \times V \quad (mgC \cdot cm^{-2}) \tag{2}$$

where RR_0-RR represent the change in the RR dye concentration determined by A_{525}, during experiments for a charge consumption of Q corresponding to various electrolysis time, V is the sample volume (700 cm^3) and S is the area of the electrode surface (cm^2).

The electrochemical efficiency for RR dye mineralization defined as an overall efficiency for complete oxidation to CO_2 was determined based on

eqn. (2) modified as (2') taking into consideration the change in TOC measurements during experiments, determining ($TOC_0 - TOC$):

$$E_{TOC} = \frac{(TOC_0 - TOC)}{Q * S} \times V \qquad \text{(mgC·cm}^{-2}\text{)} \qquad (2')$$

The mineralization current efficiency (MCE, %), defined also as current output for direct faradayc complete oxidation, for each electrolyzed solution was calculated based on eqn. (3):

$$MCE = \frac{nFV_s \Delta(TOC)_{exp}}{4.32 \times 10^7 \, mIt} \times 100 \qquad \text{(%)} \qquad (3)$$

where n is the number of electrons consumed in the mineralization process of RR dye, F is the Faraday constant (=96 487 C mol^{-1}), V_s is the solution volume (dm^3), $\Delta(TOC)_{exp}$ is the experimental TOC decay (mg dm^{-3}), 4.32×10^7 is a conversion factor for units homogenization (=3 600 s h^{-1} x 12 000 mg of carbon mol^{-1}), m is the number of carbon atoms in RR dye, I is the applied current (A), and t is time (h). The number of electrons consumed is determined based on the overall mineralization reaction of RR dye to CO$_2$ ($C_{31}H_{14}N_6S_4O_{14}Na_{14}F_2Cl$ + 33H$_2$O + 33HOCl → 31CO$_2$ + 14Na$^+$ + 2F$^-$ + 34Cl$^-$ +4SO$_4^{2-}$ +6NH$_4^+$ + 89H$^+$ + 55e$^-$).

The specific energy consumption, W_{sp}, was calculated with the relation (4):

$$W_{sp} = \frac{(Q * V^{-1})U}{1000} \quad \text{(kWhdm}^{-3}\text{)} \qquad (4)$$

where Q represents the specific charge consumption, U is the cell voltage (V), V is the solution volume (dm^3).

Sodium sulphate and sodium chloride solutions were analytical grade from Merck, and RR dye solutions were freshly prepared with double-distilled water.

3   Results and discussions

3.1 Preliminary studies regarding electrochemical behaviour of DBR dye in aqueous solutions

The electrochemical behaviour of the BDD electrode in 0.05 M Na$_2$SO$_4$ and 0.05M NaCl supporting electrolyte in comparison with 0.1 M Na$_2$SO$_4$ was studied by cyclic voltammetry (CV) to identify the electrochemical characteristics of RR dye in relation with its oxidation process on the electrode surface to set the experimental variables for degradation experiments performing. No significant differences regarding RR dye oxidation on BDD electrode in both

supporting electrolytes were noticed (the results are not shown here). However, it is observed an important difference regarding the potential value for which a high increase of the current occurred, which can be explained by O_2 evolution only in 0.1 M Na_2SO_4 and by chlorine and hypochlorite generation that overlapped O_2 evolution in 0.05 M Na_2SO_4 and 0.05M NaCl supporting electrolyte (Figure 1). The application of a large overpotential on the BDD electrode led to an indirect oxidation of dye through hydroxyl radicals (OH·) in the absence of chloride and through Cl_2/HOCl(ClO^-) in the presence of chloride.
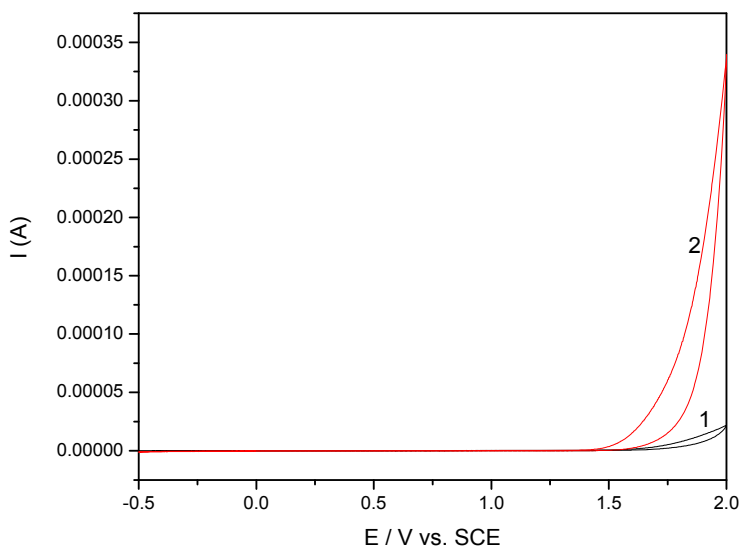

Figure 1:   Cyclic voltammograms recorded at BDD electrode in: 1-0.1 M Na_2SO_4supporting electrolyte; 2- 0.05 M Na_2SO_4 and 0.05M NaCl supporting electrolyte; potential scan rate 0.05Vs^{-1}; potential range: -0.5 to +1.5V/ SCE.

In order to demonstrate the generation of chlorine or hypochlorite and to identify the wavelength at which the dye concentration should be monitored by spectrophotometry during the electrooxidation process applying on 0.05 M Na_2SO_4 and 0.05M NaCl in the absence/presence of RR dye, UV-VIS spectra evolution was recorded (see Figure 2). It can be seen that only decolourisation can be assessed by absorbance recorded at 525 nm and no by absorbance recorded at 286 nm that corresponds to the aromatic ring opening [11] because of the hypochlorite presence at the same absorbance range. These results prove also hypochlorite generation that it is expected to oxidize the RR dye. Based on these preliminary results, the current density applied to operate the further bulk electrolysis under galvanostatic regime should belong to hypochlorite generation and water decomposition range.
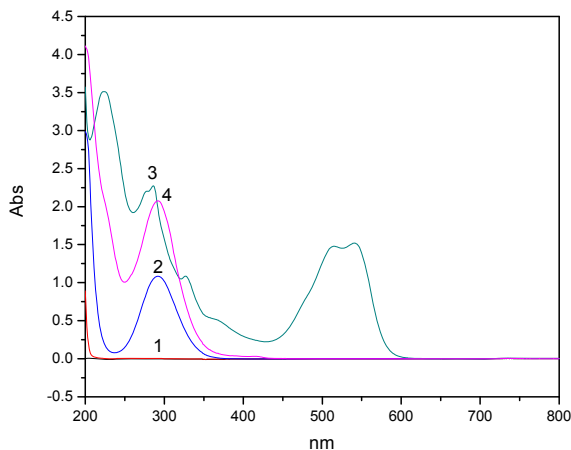
Figure 2:   Evolution of UV-VIS spectra during the electrooxidation process on BDD electrode in: 1- 0.05 M Na_2SO_4 and 0.05M NaCl supporting electrolyte; 2- 0.05 M Na_2SO_4 and 0.05M NaCl supporting electrolyte after 150 min electrolysis time; 3-100 mgL^{-1} RR dye in 0.05 M Na_2SO_4 and 0.05M NaCl supporting electrolyte; 4- 100 mgL^{-1} RR dye in 0.05 M Na_2SO_4 and 0.05M NaCl supporting electrolyte after 150 min electrolysis time; pH 5.

The anodic oxidation of RR dye on BDD/Nb electrodes in 0.05 M Na_2SO_4 and 0.05M NaCl supporting electrolyte has been performed under galvanostatic regime and bulk electrolysis conditions, at two different current densities. The current densities of 10 and 30 mA cm^{-2} were selected to assure the conditions for the formation of hydroxyl radicals and also chlorine/hypochlorite generation at the BDD surface. The influence of operating variables, e.g., the current density, and the initial pH on the electrochemical process efficiency was studied to optimize them for real applications.

3.2 Influence of current density

Two current densities of 10 mA cm^{-2} and 30 mA cm^{-2} were applied for degradation of 100 mg L^{-1} RR dye in 0.05 M Na_2SO_4 and 0.05M NaCl supporting electrolyte at pH 5. In each series, the RR dye degradation efficiency was monitored in terms of decolourisation and TOC parameters. Under both current density conditions applied for the electrooxidation process, the degradation of RR dye occurred under the action of hydroxyl radicals, $S_2O_8^{2-}$, H_2O_2 and O_3 near the BDD surface or in bulk solution. Also, in chloride media, chlorine and hypochlorite are generated in-situ and used immediately. Among the strong oxidants, generation of hypochlorite is cheaper taking into account that its generation occurred at the lower overvoltage (see voltammograms presented in Figure 1) and most of the real effluents contain a certain amount of chloride.

The decolourisation degree was slightly influenced by the current density. When current density of 30 mA cm^{-2} was applied, the decolourisation efficiency of 100% was reached after 5 minutes of the electrolysis time, while for current density of 10 mA cm^{-2} the complete decolourisation occurred after 6 minutes (see Figure 3). However, an important influence of the current density was manifested for the mineralization degree. It can be seen that after 10 minutes of the electrolysis time the dye mineralization degree reached 20% for the current density of 10 mA cm^{-2} and 48% for current efficiency 30 mA cm^{-2}.
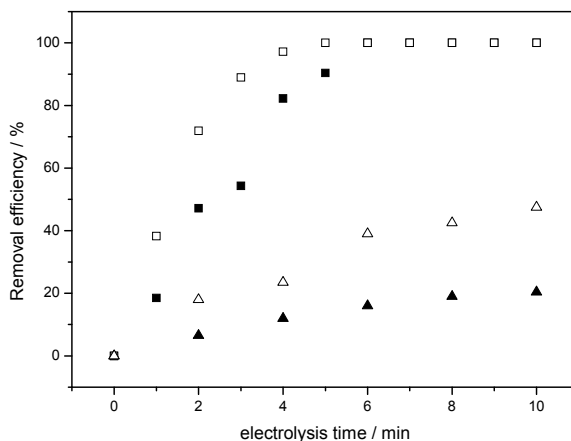

Figure 3: Evolution of dye removal efficiency versus electrolysis time; operating conditions: 0.05 M Na$_2$SO$_4$ and 0.05M NaCl supporting electrolyte, 100 mg L^{-1} RR, pH 5. Removal efficiency: decolourisation (■) j=10mA cm^{-2}, (□) j=30 mA cm^{-2}; TOC removal (▲) j=10 mA cm^{-2}, (Δ) j=30mA cm^{-2}.

The assessment of the electrooxidation performance for RR dye decolourisation and mineralization was performed based on the electrochemical efficiency determination, which takes into account the charge consumed during the electrooxidation process and also, by mineralization current efficiency (Figure 4). No important influence of the current density was noticed for the electrochemical efficiency of the mineralization process and also, for the mineralization current efficiency but a great importance was found for the electrochemical efficiency of decolourisation process, which proposes to select as optimum the current density of 10 mA cm^{-2}. The relationship between specific energy consumption and electrolysis time for each current density is shown in Figure 5, and as we expected a larger increase of the specific energy consumption at current density of 30 mA cm^{-2} was found, which impose a limitation from the economical considerations. Based on these above-presented results, the current density value of 10 mA cm^{-2} is considered as optimum from technical-economical point of view for both decolourisation and the degradation of RR dye from water in the presence of chloride.
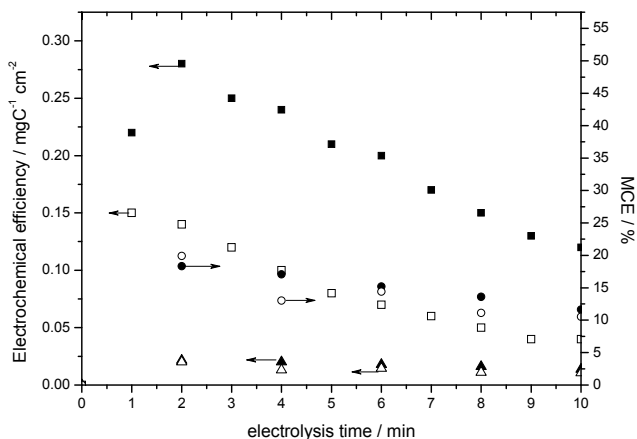
Figure 4: Correlation between electrochemical efficiency, mineralization current efficiency and electrolysis time; operating conditions: 100mgL^{-1} RR, pH 5, 0.05 M Na$_2$SO4 and 0.05M NaCl supporting electrolyte.Electrochemical efficiency: decolourisation (■) j=10 mA cm^{-2}, (□) j=30mA cm^{-2}; TOC removal (▲) j=10 mA cm^{-2}, (Δ) j=30 mA cm^{-2}. Mineralization current efficiency: (●) j=10 mA cm^{-2}, (○) j=30 mA cm^{-2}.
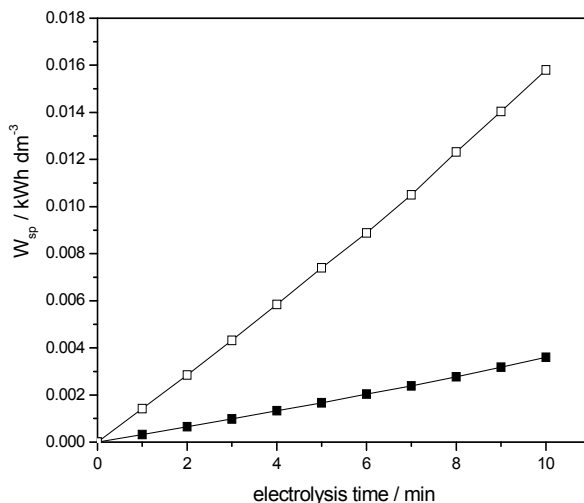

Figure 5: Evolution of specific energy consumption versus electrolysis time; operating conditions: 0.05 M Na$_2$SO$_4$ and 0.05M NaCl supporting electrolyte, 100 mgL^{-1} RR, pH 5: (■) j=10 mA cm^{-2}, (□) j=30 mA cm^{-2}.

3.3 pH influence

The initial pH is one of the most important parameter in the electrolysis process. The electroxidation performance was assessed at initial pH of 3, 5 and 9 before electrolysis, under an applied current density of 10 mA cm^{-2} for 100 mg L^{-1} RR dye initial concentration. The results related to the dye decolourisation and mineralization efficiencies are shown in Figure 6.
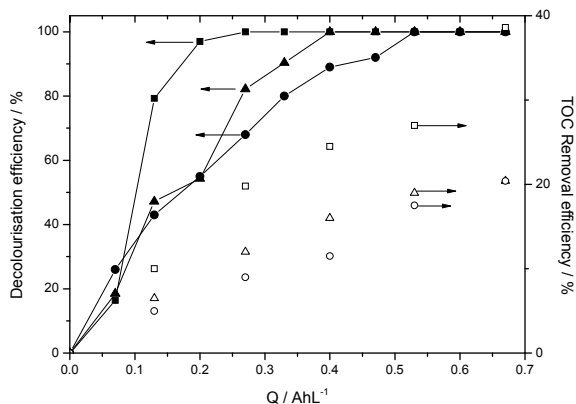

Figure 6:   Correlation between decolourisation efficiency, TOC removal efficiency and charge consumption; operating conditions: 100 mgL^{-1} RR; 0.05M Na$_2$SO$_4$ and 0.05M NaCl supporting electrolyte; j=10mA cm^{-1}; Removal efficiency: decolourisation (■) pH 3, (▲) pH5, (●) pH 9; TOC removal: (□) pH 3, (Δ) pH 5, (○) pH 9.

The performance of the dye removal process by electrooxidation was improved under more acidic versus alkaline conditions for more evidenced for mineralization in comparison with decolourisation. The influence of the pH mainly acts on the level of the oxidation mechanism via the action of hydroxyl radicals and chlorine/hypochlorite oxidants generated in-situ on BDD electrode surface. A possible explanation of the better results under acidic medium should be the predominant presence of hypochlorous acid that is a more effective oxidant in comparison with hypochlorite ions. In addition, acidic conditions favoured the protonation of the azo and amino groups resulting in the formation of the cationic form of RR dye that is less stable and more easily oxidisable [12].

4   Conclusions

The assessment of the performances of BDD electrodes in Reactive Red 147 dye electrooxidation process was accomplished based on the dye removal and electrochemical efficiencies, mineralization current efficiency and energy consumption. The dye removal and electrochemical efficiencies were assessed

by monitoring decolourisation and mineralization degrees. The electrochemical behavior of BDD electrode in the presence of RR dye in chloride medium studied by cyclic voltammetry indicated the chlorine/hypochlorite occurring before hydroxyl radicals generation. The presence of hypochlorite was also proved by UV-VIS spectra evolution. This study demonstrated good performance of BDD electrode to degrade and mineralize RR dye from aqueous solution by indirect oxidation. No significant influence of the current density was noticed for the electrochemical efficiency of the mineralization process and also, for the mineralization current efficiency but a great influence was found for the electrochemical efficiency of decolourisation process, the current density of 10 mA cm^{-2} being proposed as optimum. Also, this current density value was supported by the specific energy consumption that is in direct relation with the current density for the same electrolysis time. An improvement of the electrooxidation performance using BDD electrode was reached at acidic pH in comparison with alkaline media. Under the studied conditions in the presence of chloride medium, the best performance of BDD electrode for RR mineralization taking into account the technical-economical aspect was achieved at 10 mA cm^{-2} under acidic conditions.

Acknowledgements

References

[1] Malpass, G.R.P., Miwa, D.W., Mortari, D.A., Machado, S.A.S. and Motheo, A.J., Decolorisation of real textile waste using electrochemical techniques: Effect of the chloride concentration. *Water research*, **41**, pp. 2969– 2977, 2007.

[2] Martinez-Huitle, C.A. and Brillas, E., Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review. *Applied Catalysis B: Environmental*, **87**, pp. 105–145, 2009.

[3] Riera-Torres, M. and Gutierrez, M.-C., Colour removal of three reactive dyes electrochemical treatment. *Chemical Engineering Journal*, **156**, pp. 114–120, 2010.

[4] Gupta, V.K. and Suhas, Application of low-cost adsorbents for dye removal – A review. *Journal of Environmental Management,* **90**, pp. 2313–2342, 2009.

[5] Kodam, K.M. and Gawai, K.R., Decolorisation of reactive red 11 and 152 azo dyes under aerobic conditions. *Indian Journal of Biotechnology*, **5**, pp. 422-424, 2006.

[6] Orozco, S., Bandala, E.R., Arancibia, C., Serrano, B., Suarez, R. and Hernandez, I., Effect of iron salt on the color removal of water containing the azo reactive blue 69 using photo-assisted Fe(II)/H_2O_2 and Fe(III)/H_2O_2 systems. *Journal of Photochemistry and Photobiology A: Chemistry*, **198,** pp. 144–149, 2008.

[7] Shen, Z.M., Wu, D., Yang, J., Yuan, T., Wang, W.H. and Jia, J.P., Methods to improve electrochemical treatment effect of dye wastewater. *Journal of Hazardous Materials B*, **131**, pp. 90–97, 2006.

[8] Panizza, M. and Cerisola G., Application of diamond electrodes to electrochemical processes. *Electrochimica Acta,* **51**, pp. 191–199, 2005.

[9] Savas Koparal, A., Yavuz, Y., Gurel, C. and Bakır Ogutveren U., Electrochemical degradation and toxicity reduction of C.I. Basic Red 29 solution and textile wastewater by using diamond anode. *Journal of Hazardous Materials,* **145**, pp. 100–108, 2007.

[10] Faouzi, A.M., Nasr, B. and Abdellatif, G., .Electrochemical degradation of anthraquinone dye Alizarin Red S by anodic oxidation on boron-doped diamond. *Dyes and Pigments*, **73**, pp. 86-89, 2007.

[11] Motoc, S., Manea F., Pop A., Baciu A., Burtica G. and Pode, R., Electrochemical mineralization of Reactive Red 147 dye on boron-doped diamond electrodes. Accepted for publication in *Environmental Engineering and Management Journal.*

[12] Montanaro D. and Petrucci E., Electrochemical treatment of Remazol Brilliant Blue on a boron-doped diamond electrode. *Chemical Engineering Journal*, **153**, pp. 138–144, 2009.