Chemical Engineering Journal 153 (2009) 138–144

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Electrochemical treatment of Remazol Brilliant Blue on a boron-doped diamond electrode

Daniele Montanaro, Elisabetta Petrucci*

Department of Chemical Engineering Materials & Environment, Sapienza - University of Rome, Via Eudossiana 18, 00184 Rome, Italy

ARTICLE INFO

Article history:
Received 11 March 2009
Received in revised form 12 June 2009
Accepted 22 June 2009

Keywords:
Remazol Brilliant Blue Reactive
Chloride effect
Discolouration
Mineralisation
Boron-doped diamond electrode

ABSTRACT

A detailed study on the electrochemical oxidation of aqueous solutions of Remazol Brilliant Blue Reactive on a boron-doped diamond electrode is presented. Electrolyses, conducted under galvanostatic conditions, were monitored evaluating the removal of colour, chemical oxygen demand and total organic carbon.

The influence of the supporting electrolyte, current density, initial dye concentration, temperature and pH is discussed.

Colour removal was found to be dependent mostly on the chloride concentration suggesting the involvement of electrogenerated active chlorine in the reaction of discolouration. Rate constants calculated from colour decay versus time revealed a zero order reaction up to 150 mg L^{-1} in dye.

The degradation efficiency was directly related to the dye concentration thus indicating that oxidation and mineralisation occurred under mass transfer control.

Using 0.01 M chloride, under mild operating conditions of pH, temperature and current density, the treatment proposed enabled to achieve complete discolouration and total mineralisation of Remazol Brilliant Blue solution in a range from 50 to 150 mg L^{-1}.

1. Introduction

Although no precise data are available in literature on total world production of synthetic dyes and pigments, it can be reasonably estimated around several Mtonnes per year [1]. Dyes are commonly classified according to the chemical structure of the colour-bearing group (chromophore). After azo dyes, characterised by nitrogen double bonds, the most important class of these products is the anthraquinone dyes, widely used in the textile manufacture because, besides their brilliant appearance, they meet the demand for products with dye durability and high resistance to ambient conditions [1]. A second classification based on the dye–substrate interaction in the fixing process is also used. In this case, a particular class, accounting for around 25% of the global market, is represented by reactive dyes containing a functional group that is able to form covalent bonds with fibres. The advantages of using reactive dyes are the improved colour fastness and the simplification of the dyeing process, since no reactions of oxidation/reduction are required. The main drawback associated with reactive dyes is the competition between the colouring reaction and the hydrolisation of reactive group resulting in a consistent loss of unfixed dye (20–25%) during the process [2]. The presence of dyes in effluents of textile industries represents a relevant problem not only for the aesthetic condition of the receiving water body, but also because their presence interferes with the oxygen solubility and the photosynthetic activity of the aquatic flora. Moreover, some dyes can exhibit characteristics of toxicity and recalcitrance. Due to the deep impact on the environment, the treatment of wastewaters from textile industries constitutes an issue of major economical and environmental concern [3]. Different treatments are still known ranging from adsorption, coagulation and flocculation to chemical or biological oxidation [1,4].

Remazol Brilliant Blue Reactive (RBBR), also known as Reactive Blue 19, is an industrially important anthracene derivative dye containing an alkyle sulphonate group responsible for the binding with cellulosic fibres under alkaline conditions [2]. RBBR colour removal has been extensively studied. Great attention has been mainly focused on treatments catalysed by different enzymes such as laccase [5,6], oxygenase [7] and peroxidase [8]. A wide variety of microorganisms and biomasses have been also used for the development of biological processes for discolouration [9–12] even if, in anaerobic systems, a toxic effect on methanogenic bacteria was observed [13]. The recent development of advanced oxidation processes (AOP) has produced further investigations on RBBR colour removal using strong oxidants such as ozone, hydrogen peroxide and persulfate catalysed by ultrasound and/or UV-light [14–19].

---

* Corresponding author. Tel.: +39 06 44585569; fax: +39 06 44585622.
E-mail address: elisabetta.petrucci@uniroma1.it (E. Petrucci).

1385-8947/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.06.031

The increasing interest in the electrochemical applications, due to their ease in controlling a "clean" process of oxidation/reduction where the main reagent is the electron, is testified by numerous papers concerning the treatment of textile effluents [20–24]. In particular, electrochemical treatment of RBBR using different electrodes such as TiO_2, DSA, Ti–Ru, Ti–Pt/PbO have been so far investigated [25–28]. One of the most appealing electrode materials is the boron-doped diamond (BDD), due to its outstanding properties such as high electrochemical stability, low background current, chemical inertness and hardness. The high efficiency of BDD in anodic oxidation processes is to be attributed to the capability to produce a large amount of hydroxyl radicals by water discharge (Eq. (1)), in a wide potential windows:

$$\mathrm{BDD} + \mathrm{H_2O} \rightarrow \mathrm{BDD(HO\cdot)} + \mathrm{H^+} + \mathrm{e^-} \tag{1}$$

Due to its versatility and efficiency, a variety of application are still known [29–32] also in the field of dyes treatment [33–38].

In this paper a detailed study on the electrochemical oxidation on a boron-doped diamond electrode of aqueous solutions of RBBR has been carried out. The influence of supporting electrolyte, temperature, pH, current density and dye concentration on the process performance has been investigated. The efficiency of the treatment has been evaluated in terms of colour, chemical oxygen demand (COD) and total organic carbon (TOC) removal.

2. Experimental

The Remazol Brilliant Blue dye (Fig. 1) ~50% (1-amino-4-[4-(1-sulfonyl-ethyl-2-sulfoxy)]-2-(9,10-anthraquinone)-sulfonic acid disodium salt) was obtained from Sigma–Aldrich. Sodium chloride and anhydrous sodium sulphate used as supporting electrolytes were analytical grade.

Unless otherwise indicated, tests were conducted on solutions of distilled water containing 50 mg L^{-1} RBBR, 0.05 M Na_2SO_4 and 0.01 M NaCl with an initial pH of 5.8 and conductivity 8.5 mS cm^{-1}. To evaluate the effect of the pH, the solution's pH was adjusted initially by adding 0.01N NaOH or 0.01N H_2SO_4, otherwise the experiments were carried out at the original pH of the solution.

Galvanostatic electrolyses were conducted in batch mode using a potentiostat AMEL 2051 in a 100-mL single-compartment cell. The cell was thermostated and vigorously stirred with a magnetic bar. A platinum wire counter electrode was used with a boron-doped diamond anode of geometric area 5 cm^2.

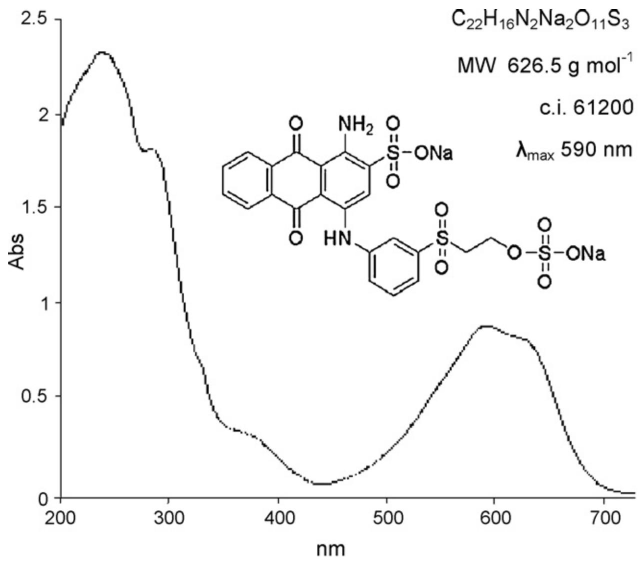

Fig. 1. Chemico-physical properties of Remazol Brilliant Blue R.

pH was measured with a Crison GLP 421 pH meter. Colour removal was monitored as the decrease of absorbance at the maximum wavelength and measured by means of a PG Instruments T80+ UV/vis Spectrophotometer. TOC concentration was measured using a Shimadzu 5000A TOC Analyzer. Chemical oxygen demand (COD) was determined according to standard methods based on acid digestion and reflux [39]. The average current efficiency (ACE) [40] for the oxidation was calculated using the relationship:

$$\mathrm{ACE\%} = 100\frac{(\mathrm{COD}_0 - \mathrm{COD}_t)}{8It}FV$$

where COD_0 (g O_2 L^{-1}) is the initial chemical oxygen demand, COD_t (g O_2 L^{-1}) is the chemical oxygen demands at a given time t (s), F is the Faraday constant (96,487 C mol^{-1}), V is the volume of the treated solution (L), I is the current applied (A), 8 is the oxygen equivalent mass (g eq^{-1}).

3. Results and discussion

3.1. Effect of chloride

To evaluate the feasibility of an anodic oxidation treatment on BDD, a preliminary series of tests was conducted on a 50 mg L^{-1} aqueous solution of RBBR, corresponding to a TOC value of about 40 mg L^{-1}. A conductivity of 8 mS cm^{-1} was assured by adding 0.05 M of sodium sulphate. Electrolyses were carried out at room temperature (24 °C), uncorrected pH and at a current density of 300 A m^{-2}. Under these conditions complete discolouration was observed after 260 min while a residual TOC of about 30% was found after 6 h of treatment.

In further trials conducted under the same conditions, 0.05 M of sodium chloride instead of sodium sulphate was added as an alternative supporting electrolyte. In this case the outstanding result of achieving complete colour removal in less than 2 min was obtained. Therefore, chloride was chosen as the supporting electrolyte and an optimisation of its concentration was investigated in a range from 0.01 to 0.05 M. Since decreasing concentrations of chloride resulted in a drop of conductivity, the addition of 0.05 M sulphate was then supplied in all the tests.

In Fig. 2a the effect of chloride concentration on colour removal as a function of the time is reported. As can be seen, 0.01 M of chloride significantly enhanced the discolouration rate, further improved by increasing concentrations. This can be explained considering that, in the presence of chloride, the electrogeneration of active chlorine took place and indirect oxidation occurred [41] in addition to the oxidation mediated by hydroxyl radicals produced on the BDD anode surface.

Fig. 2b presents the TOC removal as a function of the time with different chloride concentration. Data show that higher TOC removal rates were observed in the presence of chloride and complete mineralisation was obtained in 240 min when 0.01 M chloride was added to the solution. However, a further increase in the concentration of chloride negatively affected the reaction: after 360 min of treatment, total mineralisation of the same amount of RBBR was obtained dosing 0.025 M chloride, while only 90% of TOC depletion was reached when chloride concentration was 0.05 M. Considering the effect on both colour and TOC removal, it can be asserted that active chlorine shows a good selectivity for the break-up of the chromophore group, leading to a rapid discolouration and also promoting a faster mineralisation. However, the longer time required for the treatment with increasing chloride concentration, seems to indicate that it may represent a substrate in competition with RBBR for the oxidation mediated by hydroxyl radicals.

Changes in the UV–vis spectra during the electrolysis were also monitored. RBBR presents two bands at 240 and 288 related to benzene derivative structures and a third band at 590 nm attributed to

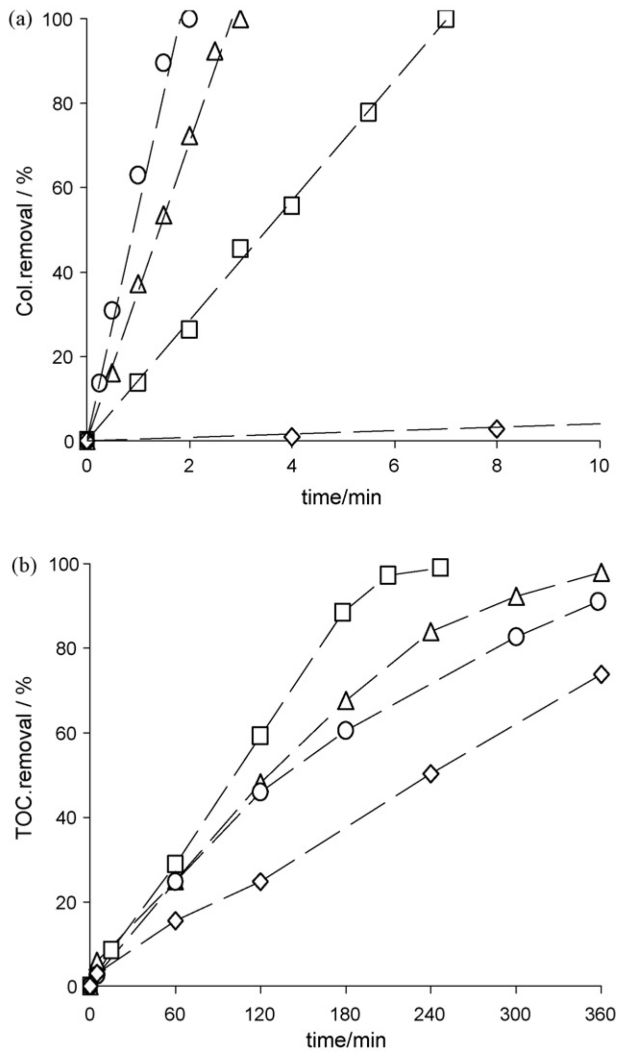

Fig. 2. Effect of chloride concentration on colour removal (a) and TOC removal (b) as a function of time. Operating conditions: RBBR = 50 mg L^{-1}, J = 300 A m^{-2}, T = 24 °C, 0.05 M Na_2SO_4, uncorrected pH. NaCl concentration: (◊) 0 M, (□) 0.01 M, (△) 0.025 M, (○) 0.05 M.

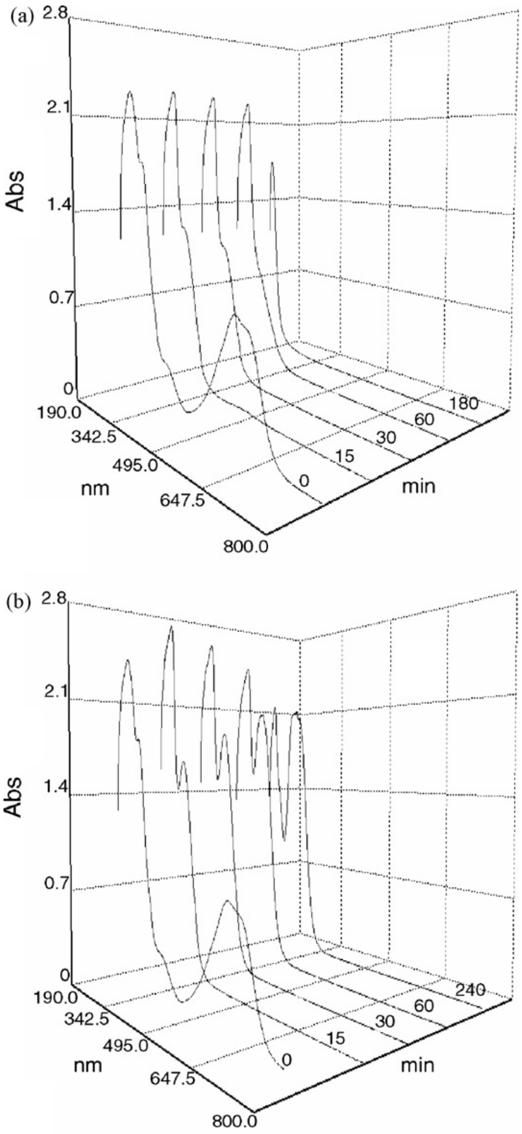

Fig. 3. Evolution of UV–vis absorbance spectra during the electrolysis of 50 mg L^{-1} RBBR. Operating conditions: J = 300 A m^{-2}, T = 24 °C, 0.05 M Na_2SO_4, uncorrected pH. NaCl concentration: (a) 0.01 M and (b) 0.05 M.

the colour. In Fig. 3a, referring to electrolyses conducted with 0.01 M NaCl, the peak in the visible region, underwent a rapid decay and totally disappeared after the first minutes of electrolysis while the intensity of the two other bands exhibited a slower decrease. In the presence of 0.05 M chloride Fig. 3b, a different trend can be observed. In particular, after the rapid colour removal, an increase in the absorbance bands in the UV region of the spectrum proved the generation and accumulation of intermediates that explained the longer treatment required for total mineralisation. The formation of these byproducts was probably due to a different reaction mechanism promoted in the presence of high chloride concentration. To minimise the chloride negative influence an optimum concentration of 0.01 M was adopted in all the following tests.

3.2. Effect of pH

All the experimental tests so far presented have been performed without a pH correction, leaving the pH to naturally vary from the initial value 5.8. Therefore to evaluate the influence of this parameter, a series of tests were carried out adjusting and keeping constant the pH at 3, by addition of H_2SO_4, and 10, by addition of NaOH, and the results were compared with those obtained in electrolyses performed at natural pH.

Data reported in Fig. 4a, suggest that acidic conditions should be adopted to obtain a faster colour removal. In fact, under alkaline conditions 20 min of treatment was required to complete discolouration and only 7 min was needed while working at natural pH. A decrease in the pH from 5.8 to 3, led to a further improvement in the rate of blue colour disappearance. However, under these stronger acidic conditions, the solution showed a persistent reddish colour, with an absorption peak at 500 ± 10 nm and complete visible bleaching was observed only after 20 min.

As for COD removal (Fig. 4b), a similar trend was observed during the electrolysis conducted at acidic and natural condition, while a slower oxidation occurred working at pH 10.

Fig. 4c shows that the decrease in pH resulted in an improvement of the total mineralisation but in this case the effect of this parameter can be considered negligible if compared with the results obtained regarding colour and COD removal.

The better performance observed at acidic pH could be explained considering that under acidic conditions the protona-

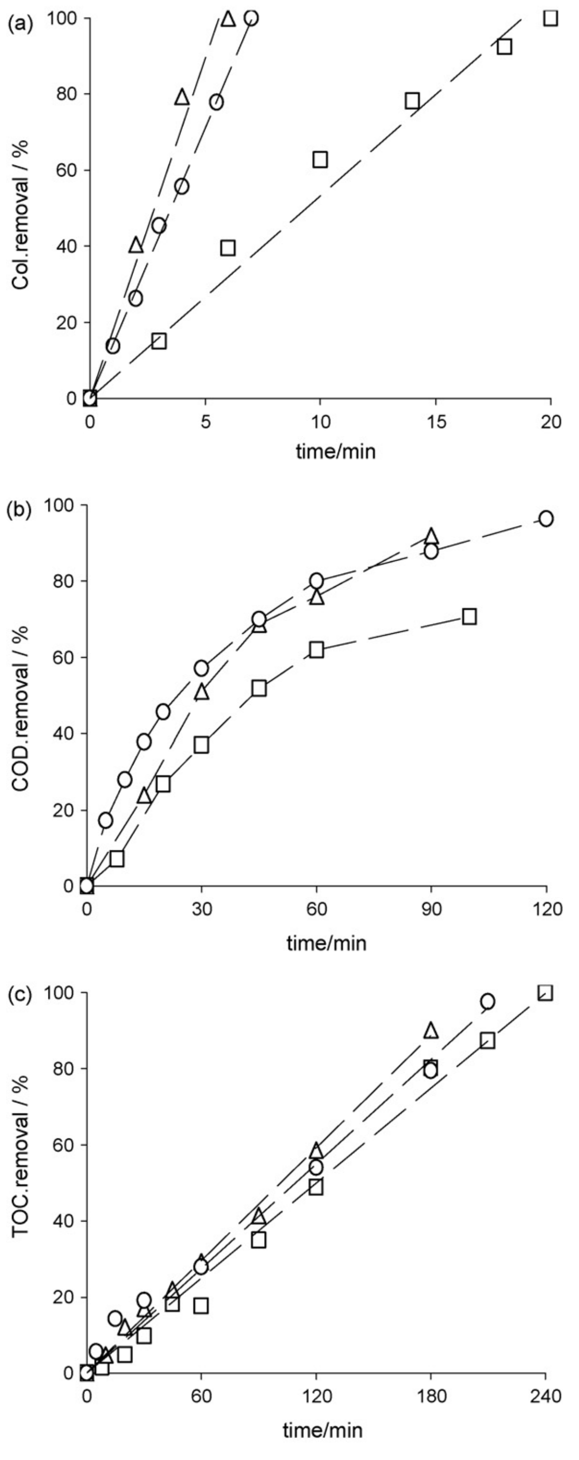

Fig. 4. Effect of pH on colour removal (a), COD removal (b) and TOC removal (c) as a function of time. Operating conditions: RBBR = 50 mg L^{-1}, J = 300 A m^{-2}, T = 24 °C, 0.05 M Na_2SO_4, 0.01 M NaCl. (△) pH 3, (◯) pH 5.8, (□) pH 10.

tion of the amino group occurred resulting in the formation of the cationic form of Remazol [42]. The presence of a positive charge on the NH_3-group probably rendered the dye less stable and more easily oxidisable. But another additional consideration has to be done. Active chlorine is the sum of three different species: chlorine (Cl_2), hypochlorous acid (HClO), and hypochlorite ion (ClO^-) whose relative amounts in solution are determined by a pH-dependent equilibrium. In particular, chlorine is the dominant species under very acidic conditions, where also competing reactions such as chlorate and perchlorate generation are known to occur. At alkaline pH, ClO^- is the main species, while in case of pH values in a range from 3.3 to 7.5 the formation of HOCl is favoured [43]. Among all these species, HClO is the strongest oxidising agent and therefore electrolyses performed at pH 5.8, where its formation should be favoured, was expected to result in faster degradation. The fact that the treatment at pH 3 was more efficient than that conducted at pH 5.8, can be explained considering that in this last case where no pH adjustment was operated a natural increase in pH during the electrolysis (pH 7 after 1 h, pH 10 after 4 h) shifted the equilibrium of active chlorine species towards the formation of ClO^- making the treatment less efficient.

The study of the influence of pH confirmed the important role of the electrogenerated active chlorine in the colour removal and, indirectly, on the COD abatement, while the mineralisation process appeared to be almost pH insensitive since it was mainly dependent on the oxidising action of the hydroxyl radical produced on the BDD surface.

3.3. *Effect of temperature*

The effect of temperature was studied in a range from 24 to 50 °C in electrolyses of RBBR 50 mg L^{-1} conducted at 300 A m^{-2} in the presence of NaCl 0.01 M and Na_2SO_4 0.05 M. Although a no significant effect on the process was observed, some remarks can be made concerning discolouration and TOC removal. Data reported in Fig. 5a

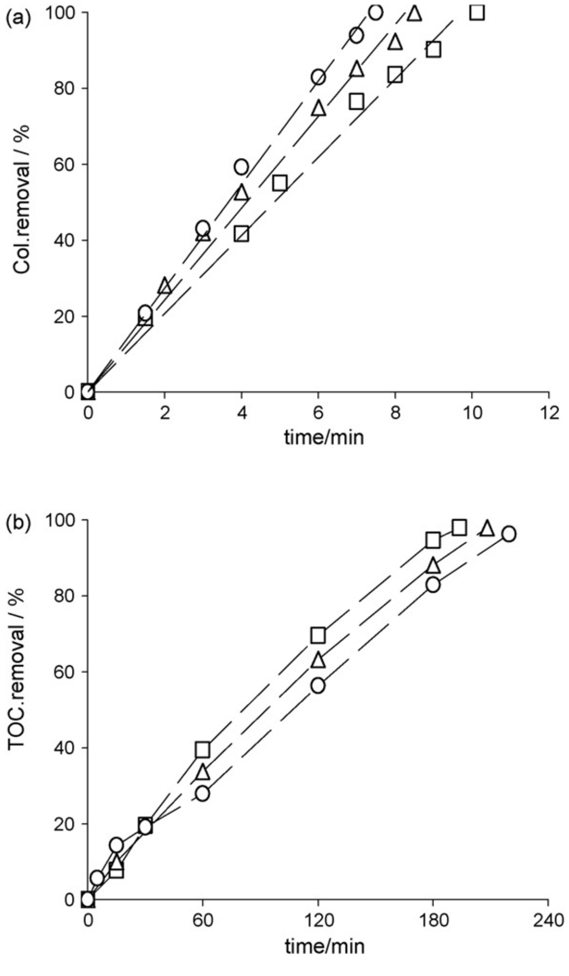

Fig. 5. Effect of temperature on colour removal (a) and TOC removal (b) as a function of time. Operating conditions: RBBR = 50 mg L^{-1}; J = 300 A m^{-2}, 0.05 M Na_2SO_4, 0.01 M NaCl, uncorrected pH. Temperature: (◯) 24 °C, (△) 40 °C, (□) 50 °C.

show that an increase in the temperature led to a slight decrease in colour removal rate. This behaviour is justified considering the negative effect of temperature on gaseous chlorine solubility and therefore on chemical equilibrium of active chlorine that is responsible for the colour removal.

As for TOC removal, results presented in Fig. 5b show a little positive effect of temperature due to a probable enhancement of the mass transport phenomena from the solution bulk to BDD surface, where the oxidation via hydroxyl radicals occurred.

3.4. *Effect of current density*

The effect of current density on the degradation of 50 mg L^{-1} RBBR was investigated in a range from 200 to 400 A m^{-2}.

As shown in Fig. 6a, only a slight effect was observed in the colour removal rate, especially at higher values of current density.

A similar behaviour was observed in the COD trend versus time. As shown in Fig. 6b, only a negligible improvement in the oxidation rate was observed when current density varied from 200 to 300 A m^{-2}, and no effect was evidenced in the experiments conducted at 400 A m^{-2}. In order to obtain further information about the efficiency of the oxidation, the apparent current efficiency was calculated and data reported in the inset of Fig. 6b. Even though the ACE% is usually used to express the current efficiency of a direct oxidation process, in this study, this parameter has been used to indicate a global efficiency due to the concomitant action of direct oxidation by means of hydroxyl radicals and indirect oxidation via electrogenerated active chlorine. As can be observed, an increase in current density caused a decrease in current efficiency.

These results seem to confirm the prevalent role played by active chlorine in discolouration and COD removal. In fact, if the reaction was dependent of hydroxyl radicals concentration, an improvement would be expected with increasing current density. On the other hand, larger amount of $^{\bullet}$OH should allow the generation of higher quantity of active chlorine, by reaction with Cl^{-}. However, the low chloride concentration adopted in these runs represents the limiting factor thus disguising the effect of this parameter.

As for total mineralisation, a considerable effect of the current density was observed in terms of removal rate under the conditions adopted. Fig. 6c shows that in 160 min 45, 70 and 100% of mineralisation was achieved, respectively, when the applied current density was 200, 300 and 400 A m^{-2}. In this case, the TOC removal was strictly dependent on the amount of hydroxyl radicals produced, thus revealing that mineralisation occurs by means of $^{\bullet}$OH. Moreover the almost linear relationship between current density and TOC removal indicates that, in the range investigated, the process was under current control.

It is important to notice that in all the tests, when COD removal was almost completed, the TOC content was still higher, thus confirming the formation of intermediate compounds with low COD but difficult to be transformed into CO$_2$.

3.5. *Effect of RBBR initial concentration*

The influence of the initial dye concentration on the RBBR discolouration and degradation has been investigated in a range from 50 to 150 mg L^{-1}. Tests were conducted maintaining a constant chloride concentration of 0.01 M. RBBR concentration was determined by monitoring the absorbance of the most intense band (λ 590 nm).

Fig. 7 shows that, up to 150 mg L^{-1} of RBBR, there is a linear relationship between the dye concentration and time with the same slope coefficient for all the examined cases thus indicating that discolouration in this range of concentration followed a zero order kinetics with a calculated rate constant k of 5.2 mg L^{-1} s^{-1}. However, a different behaviour was observed when higher concentrations

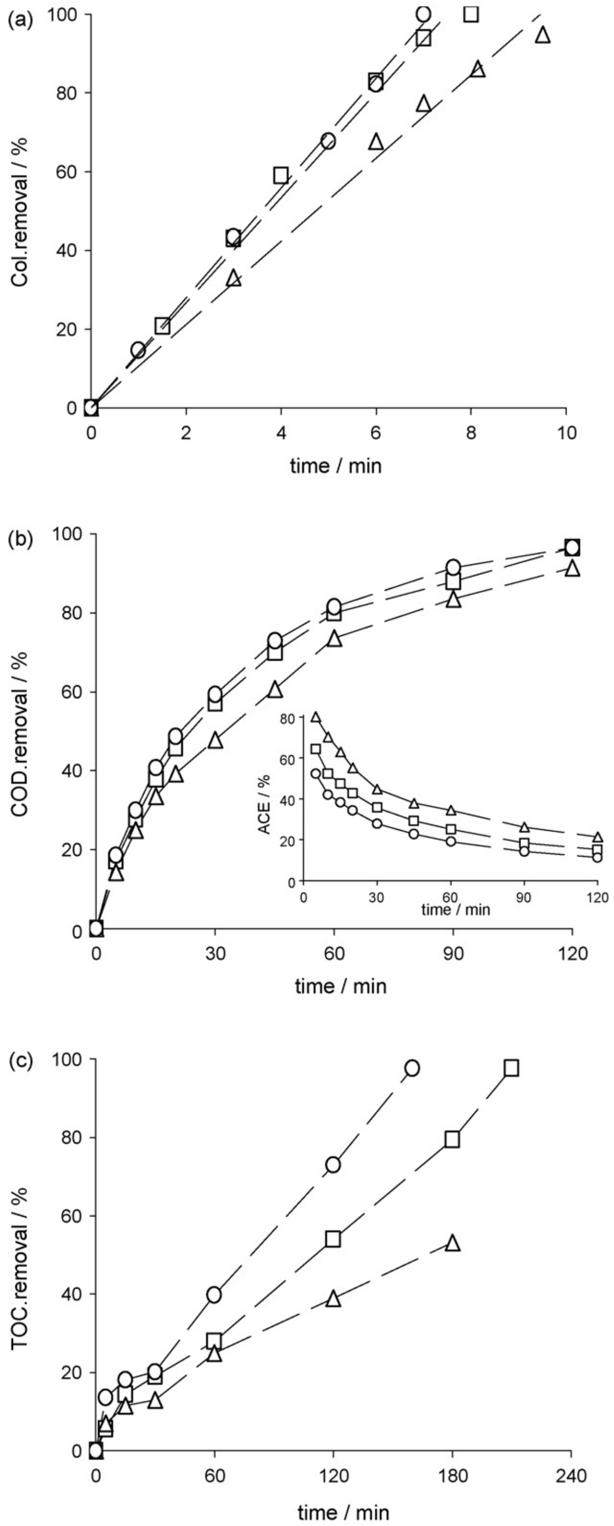

Fig. 6. Effect of current density on colour removal (a), COD removal (b), ACE (inset in (b)) and TOC removal (c) as a function of time. Operating conditions: RBBR = 50 mg L^{-1}, T = 24 °C, 0.05 M Na$_2$SO$_4$, 0.01 M NaCl, uncorrected pH. Current density: (△) J = 200 A m^{-2}, (□) J = 300 A m^{-2}, (○) J = 400 A m^{-2}.

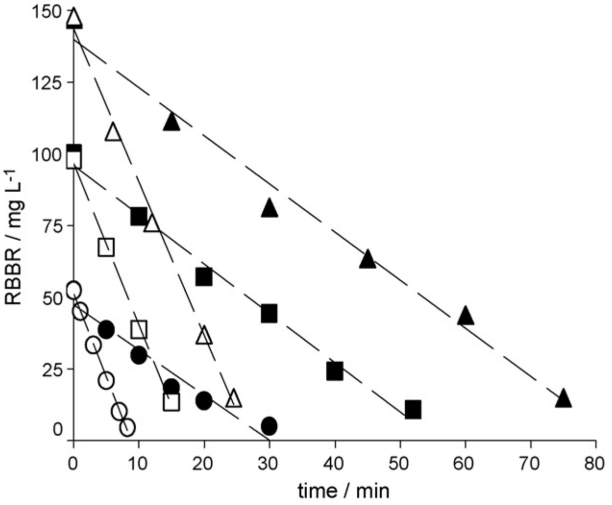

Fig. 7. Effect of dye initial concentration on RBBR removal versus time in electrolyses conducted with 0.01 M NaCl (empty symbols) and 0.005 M NaCl (full symbols). Conditions: $J = 300\,\mathrm{A\,m^{-2}}$, $T = 24\,^{\circ}\mathrm{C}$, 0.05 M Na_2SO_4, uncorrected pH. RBBR concentration: (● ○) 50 mg L^{-1}, (■ □) 100 mg L^{-1}, (▲ △) 150 mg L^{-1}.

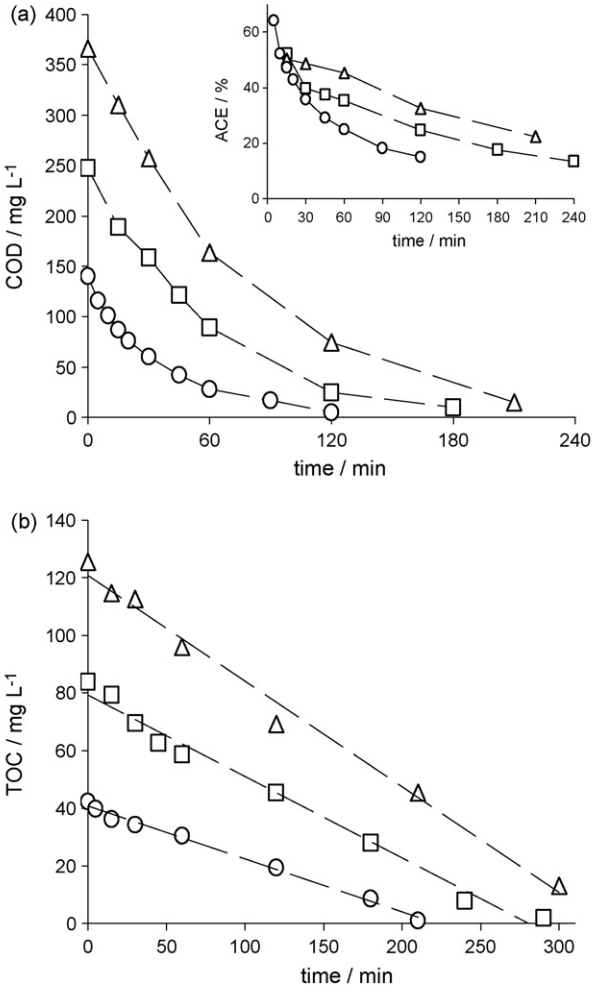

Fig. 8. Effect of RBBR initial concentration on COD (a), ACE (inset in (a)) and TOC (b) versus time. Conditions: $J = 300\,\mathrm{A\,m^{-2}}$, $T = 24\,^{\circ}\mathrm{C}$, 0.05 M Na_2SO_4, 0.01 M NaCl, uncorrected pH. RBBR concentration: (○) 50 mg L^{-1}, (□) 100 mg L^{-1} (△) 150 mg L^{-1}.

of RBBR were treated (data not shown). These results suggest that RBBR disappearance was independent of its concentration, depending only on chloride content in solution. To confirm this assumption a further series of tests were conducted decreasing the concentration of chloride to 0.005 M and varying the RBBR concentration in the same range. As can be seen in the same figure, also in this case, a zero order kinetic was observed but, as expected, the reaction showed a lower coefficient rate ($k = 1.8\,\mathrm{mg\,L^{-1}\,s^{-1}}$).

The effect of the initial RBBR concentration on COD decay is illustrated in Fig. 8a. Data show that total removal of COD was obtained in the whole range of dye concentration investigated and the rate of oxidation increased with concentration. In particular after 1 h of treatment about 80, 160 and 200 mg L^{-1} of COD were removed from the solutions containing respectively 50, 100 and 150 mg L^{-1} of RBBR.

The inset of Fig. 8a where the ACE evolution is illustrated, indicates that the best efficiency was obtained at high concentration of RBBR. This implies that the process was controlled by the mass transfer of RBBR from the bulk to the anode surface where the oxidation occurred via hydroxyl radicals produced on BDD. Such a trend suggests that not only active chlorine but also direct oxidation played an important role in COD removal.

Same considerations can be drawn as for TOC removal. Data collected in Fig. 8b show that an increasing time from 200 to 300 min was necessary to obtain 90% of TOC removal with increasing RBBR initial concentration from 50 to 150 mg L^{-1}. However the slope of the curves clearly proves that at higher concentration a faster mineralisation occurred due to the enhancement of the mass transfer phenomena.

4. Conclusions

The electrochemical treatment of a RBBR solution was studied by means of anodic oxidation on a boron-doped diamond electrode and the influence of operative conditions on discolouration, COD removal and total mineralisation were evaluated.

The following conclusions can be drawn:

- The use of chloride as supporting electrolyte significantly improves the performance of the treatment. This has to be attributed to the concomitant action of indirect oxidation carried out by the electrogenerated active chlorine together with direct oxidation via hydroxyl radicals produced on the BDD surface. In the treatment of 50 mg L^{-1} RBBR an optimum chloride concentration of 0.01 M has been found.
- Colour removal is strongly enhanced by increasing concentration of chloride and it is influenced by temperature and pH since these parameters rule the chemical equilibrium of active chlorine. The discolouration rate is independent of RBBR concentration thus showing a zero order kinetic.
- In the presence of chloride, COD removal occurs rather quickly and a beneficial effect of low pH and high initial dye concentration is observed. The influence of pH suggests that electrogenerated active chlorine, in particular hypochlorous acid, accounts for COD removal, while the influence of concentration and current density shows the typical behaviour of a direct oxidation process, thus indicating that oxidation takes advantage of simultaneous action of active chlorine and hydroxyl radical.
- The longer time required for TOC removal in comparison to that necessary for COD, indicates the formation of recalcitrant intermediates whose amount significantly rises with increasing chloride concentration. Moreover, since chloride behaves like a competitive species with RBBR in the oxidation mediated by hydroxyl radicals, only little amount of chloride is required to achieve total mineralisation in a short electrolysis time. The

positive effect of high temperature and high RBBR concentration, favouring the mass transfer phenomena, corroborates the hypothesis that total mineralisation is carried out by hydroxyl radical produced on BDD.

References

[1] E. Forgacs, T. Cserháti, G. Oros, Removal of synthetic dyes from wastewaters: a review, Environ. Int. 30 (2004) 953–971.

[2] D.M. Lewis, A.H. Renfrew, A.A. Siddique, The synthesis and application of a new reactive dye based on disulfide-bis-ethylsulfone, Dyes Pigments 47 (2000) 151–167.

[3] K.T. Chung, S.E. Stevens, Degradation of azo dyes by environmental microorganism and helminths, Environ. Toxicol. Chem. 12 (1993) 2121–2132.

[4] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresour. Technol. 77 (2001) 247–255.

[5] T. Mechichi, N. Mhiri, S. Sayadi, Remazol Brilliant Blue R decolourization by the laccase from *Trametes trogii*, Chemosphere 64 (2006) 998–1005.

[6] P.P. Champagne, J.A. Ramsay, Reactive blue 19 decolouration by laccase immobilized on silica beads, Appl. Microbiol. Biotechnol. 77 (2007) 819–823.

[7] T. Deveci, A. Unyayar, M.A. Mazmanci, Production of Remazol Brilliant Blue R decolourising oxygenase from the culture filtrate of *Funalia trogii* ATCC 200800, J. Mol. Catal. B: Enzym. 30 (2004) 25–32.

[8] K. Shin, I. Oh, C. Kim, Production and purification of Remazol Brilliant Blue R decolorizing peroxidise from the culture filtrate of *Pleurotus ostreatus*, Appl. Environ. Microbiol. 63 (1997) 1744–1748.

[9] Z. Aksu, G. Dönmez, A comparative study on the biosorption characteristics of some yeasts for Remazol Blue reactive dye, Chemosphere 50 (2003) 1075–1083.

[10] H.D. Özsoy, A. Ünyayar, M.A. Mazmanc, Decolourisation of reactive textile dyes Drimarene Blue X3LR and Remazol Brilliant Blue R by *Funalia trogii* ATCC 200800, Biodegradation 16 (2005) 195–204.

[11] G. Palmieri, G. Cennamo, G. Sannia, Remazol Brilliant Blue R decolourisation by the fungus *Pleurotus ostreatus* and its oxidative enzymatic system, Enzyme Microb. Technol. 36 (2005) 17–24.

[12] I. Eichlerová, L. Homolka, O. Benada, O. Kofronová, T. Hubálek, F. Nerud, Decolorization of Orange G and Remazol Brilliant Blue R by the white rot fungus *Dichomitus squalens*: toxicological evaluation and morphological study, Chemosphere 69 (2007) 795–802.

[13] A.B. Dos Santos, I.A.E. Bisschops, F.J. Cervantes, J.B. van Lier, The transformation and toxicity of anthraquinone dyes during thermophilic (55 °C) and mesophilic (30 °C) anaerobic treatments, J. Biotechnol. 115 (2004) 345–353.

[14] F. Herrera, J. Kiwi, A. Lopez, V. Nadtochenko, Photochemical decoloration of Remazol Brilliant Blue and Uniblue A in the presence of Fe^{3+} and H_2O_2, Sci. Technol. 33 (1999) 3145–3151.

[15] C.A.K. Gouvêa, F. Wypych, S.G. Moraes, N. Durán, N. Nagata, P. Peralta-Zamora, Semiconductor-assisted photocatalytic degradation of reactive dyes in aqueous solution, Chemosphere 40 (2000) 433–440.

[16] Z. Hea, L. Lin, S. Song, M. Xia, L. Xu, H. Ying, J. Chen, Mineralization of C.I. Reactive Blue 19 by ozonation combined with sonolysis: performance optimization and degradation mechanism, Sep. Purif. Technol. 62 (2008) 376–381.

[17] E. Şayan, M.E. Edecan, An optimization study using response surface methods on the decolorization of Reactive Blue 19 from aqueous solution by ultrasound, Ultrason. Sonochem. 15 (2008) 530–538.

[18] S. Song, J. Yao, Z. He, J. Qiu, J. Chen, Effect of operational parameters on the decolorization of C.I. Reactive Blue 19 in aqueous solution by ozone-enhanced electrocoagulation, J. Hazard. Mater. 152 (2008) 204–210.

[19] A. Rezaee, M.T. Ghaneian, A. Khavanin, S.J. Hashemian, Gh. Moussavi, Gh. Ghanizadeh, E. Hajizadeh, Photochemical oxidation of Reactive Blue 19 dye (RB19) in textile wastewater by $UV/K_2S_2O_8$ process, Iran. J. Environ. Health. Sci. Eng. 5 (2008) 95–100.

[20] A. Roessler, X. Jin, State of the art technologies and new electrochemical methods for the reduction of vat dyes, Dyes Pigments 59 (2003) 223–235.

[21] M.A. Sanromán, M. Pazos, M.T. Ricart, C. Caemeselle, Electrochemical decolourisation of structurally different dyes, Chemosphere 57 (2004) 233–239.

[22] A. Wang, J. Qu, H. Liu, J. Ge, Degradation of azo dye Acid Red 14 in aqueous solution by electrokinetic and electrooxidation process, Chemosphere 55 (2004) 1189–1196.

[23] E. Chatzisymeon, N.P. Xekoukoulotakis, A. Coz, N. Kalogerakis, D. Mantzavinos, Electrochemical treatment of textile dyes and dyehouse effluents, J. Hazard. Mater. 137 (2006) 998–1007.

[24] G.R.P. Malpass, D.W. Miwa, D.A. Mortari, S.A.S. Machado, A.J. Motheo, Decolorisation of real textile waste using electrochemical techniques: effect of the chloride concentration, Water Res. 41 (2007) 2969–2977.

[25] R. Pelegrini, P. Peralta-Zamora, A.R. de Andrade, J. Reyes, N. Durán, Electrochemically assisted photocatalytic degradation of reactive dyes, Appl. Catal. B: Environ. 22 (1999) 83–90.

[26] D. Rajkumar, J.G. Kim, Oxidation of various reactive dyes with in situ electrogenerated active chlorine for textile dyeing industry wastewater treatment, J. Hazard. Mater. 136 (2006) 203–212.

[27] D. Rajkumar, B.J. Song, J.G. Kim, Electrochemical degradation of Reactive Blue 19 in chloride medium for the treatment of textile dyeing wastewater with identification of intermediate compounds, Dyes Pigments 72 (2007) 1–7.

[28] L.S. Andrade, L.A.M. Ruotolo, R.C. Rocha-Filho, N. Bocchi, S.R. Biaggio, J. Iniesta, V. García-Garcia, V. Montiel, On the performance of Fe and Fe,F doped $Ti–Pt/PbO_2$ electrodes in the electrooxidation of the Blue Reactive 19 dye in simulated textile wastewater, Chemosphere 66 (2007) 2035–2043.

[29] P. Cañizares, F. Larrondo, J. Lobato, M.A. Rodrigo, C. Sáez, Electrochemical synthesis of peroxodiphosphate using boron-doped diamond anodes, J. Electrochem. Soc. 152 (2005) 191–196.

[30] M. Panizza, G. Cerisola, Application of diamond electrodes to electrochemical processes, Electrochim. Acta 51 (2005) 191–199.

[31] S. Palmas, A.M. Polcaro, A. Vacca, M. Mascia, F. Ferrara, Influence of the operating conditions on the electrochemical disinfection process of natural waters at BDD electrodes, J. Appl. Electrochem. 37 (2007) 1357–1365.

[32] D. Montanaro, E. Petrucci, C. Merli, Anodic, cathodic and combined treatments for the electrochemical oxidation of an effluent from the flame retardant industry, J. Appl. Electrochem. 38 (2008) 947–954.

[33] X. Chen, G. Chen, P.L. Yue, Anodic oxidation of dyes at novel Ti/B-diamond electrodes, Chem. Eng. Sci. 58 (2003) 995–1001.

[34] S. Hattori, M. Doi, E. Takahashi, T. Kurosu, M. Nara, S. Nakamatsu, Y. Nishiki, T. Furuta, M. Iida, Electrolytic decomposition of amaranth dyestuff using diamond electrodes, J. Appl. Electrochem. 33 (2003) 85–91.

[35] S. Amma, R. Abdelhedi, C. Flox, C. Arias, E. Brillas, Electrochemical degradation of dye indigo carmine at boron-doped diamond anode for wastewaters remediation, Environ. Chem. 4 (2006) 229–233.

[36] M. Panizza, A. Barbucci, R. Ricotti, G. Cerisola, Electrochemical degradation of methylene blue, Sep. Purif. Technol. 54 (2007) 382–387.

[37] M. Panizza, G. Cerisola, Removal of colour and COD from wastewater containing acid blue 22 by electrochemical oxidation, J. Hazard. Mater. 153 (2008) 83–88.

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

[39] APHA-AWA-WPCF, Standard Methods for the Examination of Water and Wastewater, 17th ed., American Public Health Association, Washington, DC, 1989.

[40] Ch. Comninellis, C. Pulgarin, Anodic oxidation of phenol for waste water treatment, J. Appl. Electrochem. 21 (1991) 703–708.

[41] A.M. Polcaro, A. Vacca, M. Mascia, F. Ferrara, Product and by-product formation in electrolysis of dilute chloride solutions, J. Appl. Electrochem. 38 (2008) 979–984.

[42] P.A. Carneiro, M.E. Osugi, C.S. Fugivara, N. Boralle, M. Furlan, M.V.B. Zanoni, Evaluation of different electrochemical methods on the oxidation and degradation of Reactive Blue 4 in aqueous solution, Chemosphere 59 (2005) 431–439.

[43] F.H. Oliveira, M.E. Osugi, F.M.M. Paschoal, D. Profeti, P. Olivi, M.V.B. Zanoni, Electrochemical oxidation of an acid dye by active chlorine generated using $Ti/Sn_{(1-x)}Ir_xO_2$ electrodes, J. Appl. Electrochem. 37 (2007) 583–592.