Available online at www.sciencedirect.com

Dyes and Pigments 73 (2007) 86–89

www.elsevier.com/locate/dyepig

Electrochemical degradation of anthraquinone dye Alizarin Red S by anodic oxidation on boron-doped diamond

Ahmadi Mohamed Faouzi [a], Bensalah Nasr [b,*], Gadri Abdellatif [a]

[a] *Ecole Nationale d'Ingénieurs de Gabès, 6029 Zrig Gabès, Tunisia*

[b] *Institut Supérieur des Sciences Appliquées et Technologie de Gabès, 6072 Gabès, Tunisia*

Received 28 February 2005; received in revised form 11 June 2005; accepted 20 October 2005

Abstract

The electrochemical oxidation of Anthraquinone dye (Alizarin Red S) has been studied on boron-doped diamond (BDD) electrodes on acid medium by cyclic voltammetry and bulk electrolysis. Galvanostatic electrolyses cause complex oxidation reactions that lead to the incineration of Alizarin Red S. The analyses of the chemical oxygen demand (COD) and the total organic carbon (TOC) during the galvanostatic electrolyses at BDD anodes confirm that the electro-oxidation of Alizarin Red S leads to CO_2. The complete removal of organic compounds contained in the waste has been obtained at low and high current densities.

Keywords: Electrochemical oxidation; Anthraquinone dye; Boron-doped diamond; Current density

---

1. Introduction

Removing dyes from textile wastewaters is a difficult and expensive process [1]. Anthraquinone dyes belong to the group of most durable dyes, so they are often used in products that must satisfy strict requirements concerning resistance to solar radiation and ambient conditions [2,3]. This useful feature of dyes is naturally a problem in their neutralisation. The classical processes of physico-chemical and biological oxidation used in their degradation are not always sufficient, and so it becomes necessary to introduce new, more efficient oxidants [4–7]. The most advantageous method of dyes wastewaters decolouration seems to be chemical and/or photochemical oxidation, and then (if necessary) elimination of decomposition products by biological methods. Chemical treatment processes often yield insufficient results if the water contains high amounts of non-biodegradable (refractory) organic substances.

Oxidative electrochemical processes are among new technologies for the treatment of wastewaters particularly when they are charged with toxic and bioresistant organics. Anodic oxidation is an advanced oxidation process with many advantages compared to other known chemical and photochemical ones. This process aims for the mineralization of organics to CO_2 or for its conversion to biocompatible compounds. In this context, the electrochemical oxidation of modal substrates has been investigated at several anodic materials, generally metal oxides [8–11] like IrO_2, PbO_2, SnO_2 and SnO_2–Sb_2O_5. These electrodes may be either inefficient in treating wastewaters or chemically unstable especially in an acidic medium. Recently, boron-doped diamond (BDD), which are the boundaries of the new electrode materials technology, have been used for oxidation of organics. In fact, the wide potential window and the high anodic stability of the BDD films allow their applications in various fields like electroanalysis, synthesis of powerful oxidants and wastewaters treatment. Diamond anode surfaces allow to produce large quantities of hydroxyl radicals from water electrolysis [12–14]. The diamond surface does not interact with these radicals (exhibits a non-active behavior) and as a consequence, these radicals

---

[*] Corresponding author. Tel.: +21 67 5392404; fax: +21 67 5392390.
E-mail address: nasr.bensalah@issatgb.rnu.tn (B. Nasr).

0143-7208/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2005.10.013

can only couple to form oxygen or oxidize the organic matter present in the waste. This anodic material has shown high performance levels for the conversion and/or the combustion of different compounds such as phenol, carboxylic acids, 4-chlorophenol, 3-methylpyridine, benzoic acid, 2-naphtol, polyacrylates, 4-chlorophenoxyacetic acid, amaranth dyestuff, chlorophenols, nitrophenols and polyhydroxybenzenes by electrochemical oxidation [15–30]. The results of these works show that the electrochemical oxidation with diamond anodes achieves a very high current efficiency as compared with other electrochemical treatments, and very high conversions of the organic carbon into carbon dioxide.

The goal of the work described here was to use the electrochemical oxidation on boron-doped diamond anodes for the treatment of wastewaters containing an anthraquinone dye (see Fig. 1): Alizarin Red S (C.I. Mordant Red 3). The removal of the dye from the solution was followed by chemical oxygen demand (COD), total organic carbon (TOC) analyses and UV–visible spectrophotometry.

2. Experimental

The boron-doped diamond (Si/BDD) electrodes were provided and synthesized by the Swiss Center for Electronics and Microtechnology SA, Neuchatel-Switzerland using the hot filament chemical vapor deposition (HF-CVD) technique on conducting p-Si. The obtained diamond film thickness was about 1 mm. Voltammetric measurements were obtained with a Princeton Applied research Model 174A polarograph equipped by an X-Y type SEFRAM recorder. Working electrodes were Si/BDD plates of 1 cm^2 geometric area. Counter electrode was a platinum wire. Reference electrode was an $Hg/Hg_2Cl_2/KCl$ (sat) (SCE). Linear voltammograms were obtained at a constant sweep rate of 100 $mV\ s^{-1}$.

Bulk anodic oxidation of Alizarin Red S was carried out using an undivided electrochemical cell. The anodes were disks of p-Si/BDD and the cathode was a zirconium plate. The geometric area of both electrodes was 10 cm^2, with an interelectrode gap of 20 mm. The electrolyte was stored in a thermo-regulated glass tank and stirred with a magnetic stirrer at the maximum rate. The electrochemical reactor volume was $V_E = 200\ cm^3$. The electrolyses were performed in galvanostatic mode.

Chemical oxygen demand (COD) was determined by using a bioblock analyzer based on the method of acidic oxidation by bichromate. Total organic carbon (TOC) of the solution was determined by a TOC-5050 Shimadzu apparatus. The electrochemical treatment of Alizarin Red S was followed by means of a HACH-4000 UV–vis spectrophotometer recording the spectra over the 190–900 nm range.

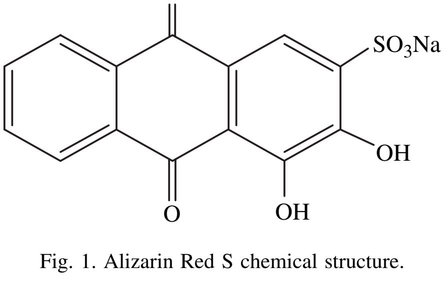

Fig. 1. Alizarin Red S chemical structure.

3. Results and discussion

3.1. Cyclic voltammetry

Fig. 2 shows consecutive linear voltammetric curves recorded with the BDD in the wastewater. The curve obtained under the same conditions but without Alizarin Red S is also shown (curve a, Fig. 1). In the first scan an anodic peak corresponding to the oxidation of Alizarin Red S is observed at about 0.85 V vs. SCE. As the number of cycles increase, the anodic current peak decreases until a steady state after about three cycles (curves c and d, Fig. 1). This decrease in electrode activity appears to be originated by deposition of adhesive products on the electrode surface. Washing with organic solvents (isopropanol) the electrode cannot be reactivated.

However, the electrode surface can restore its initial activity by an anodic polarization in the same electrolyte at high potentials because at this potential BDD involves the production of hydroxyl radicals that oxidize the adhesive products on the surface:

$$2H_2O \rightarrow 2OH^{\bullet} + 2H^+ + 2e^- \quad (1)$$

After an anodic polarization at 100 $mA\ cm^{-2}$ for 2 min, the oxidation peak comes back to its initial position, meaning the complete reactivation of electrode surface. The appearance of a second peak which is partially overlapped by the oxygen evolution can be observed. This voltammetric behavior of Alizarin Red S has also been observed in the anodic oxidation of aromatic compounds on BDD [12–22].

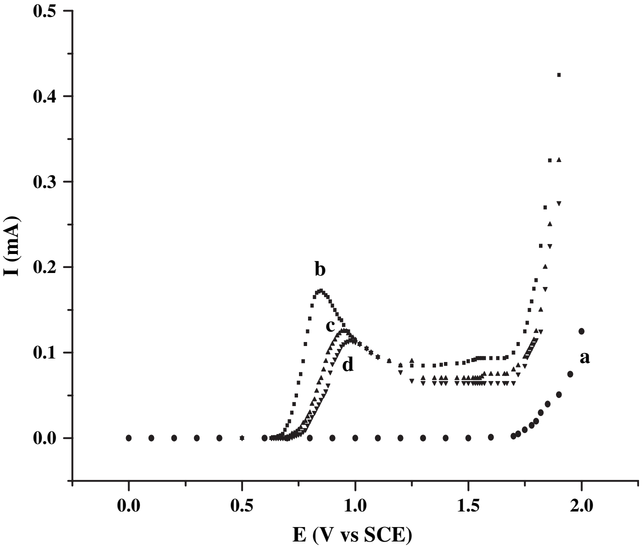

Fig. 2. Linear sweep voltammograms of Alizarin Red S solution. Scan rate: $v = 100\ mV\ s^{-1}$, electrolyte: H_2SO_4 1 M, working electrode: BDD (1 cm^2), reference electrode: SCE, and counter electrode: Pt. (a) H_2SO_4 1 M; (b) Alizarin Red S, $C = 5$ mM, H_2SO_4 1 M, first scan; (c) Alizarin Red S, $C = 5$ mM, H_2SO_4 1 M, second scan; and (d) Alizarin Red S, $C = 5$ mM, H_2SO_4 1 M, third scan.

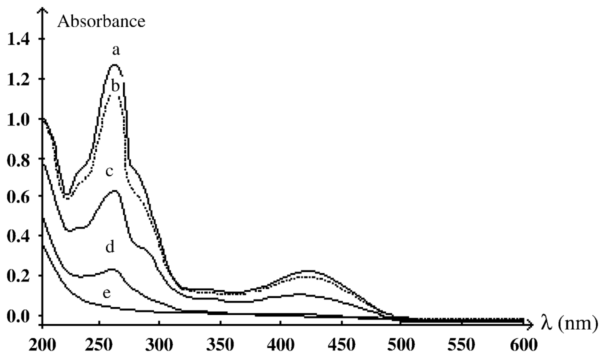

Fig. 3. UV–visible spectral changes of Alizarin Red S solution in aqueous (1 M H_2SO_4) with time during the galvanostatic electrolysis ($j = 30$ mA cm^{-2}) and $T = 25$ °C: (a) 0 min; (b) 30 min; (c) 60 min; (d) 180 min; and (e) 300 min.

3.2. Bulk electrolyses

The anodic oxidation of Alizarin Red S has been performed galvanostatically in sulfuric medium with BDD electrode under different current densities.

The absorption spectral changes during galvanostatic electrolysis ($j = 30$ mA cm^{-2}) in aqueous (1 M H_2SO_4) solution are shown in Fig. 3. It can be observed that the absorption spectrum of Alizarin Red S is characterized by a band in the UV region with its maxima located at 262 nm and by a band in the visible region located at 420 nm. The absorbance peak at 262 nm can be attributed to the benzene ring and the absorbance at 420 nm is probably due to the presence of carbonyl group in the anthraquinone dye. It is observed that the absorption of the bands decreases with time and almost disappears after about 300 min resulting in the complete decolorisation of the solution. The absorbance at 262 nm decreases rather slowly. The slower decrease of this absorbance can be related to the formation of intermediates resulting from the electro-oxidation of the anthraquinone dye which still contains benzene ring.

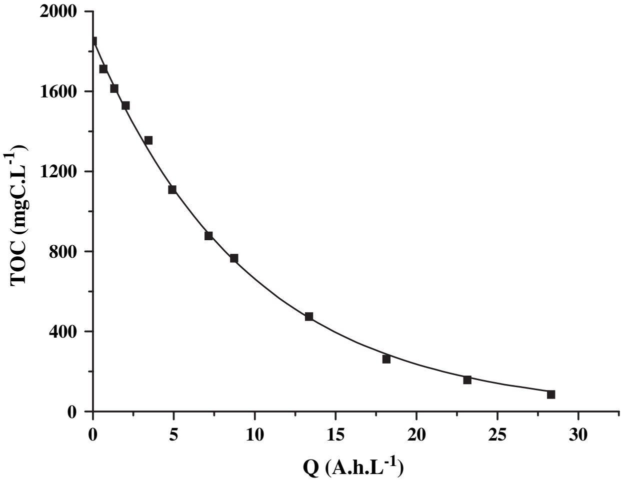

Fig. 4. Variation of the TOC during the galvanostatic electrolysis of Alizarin Red S (10 mM) at BDD electrode (30 mA cm^{-2}) and $T = 25$ °C.

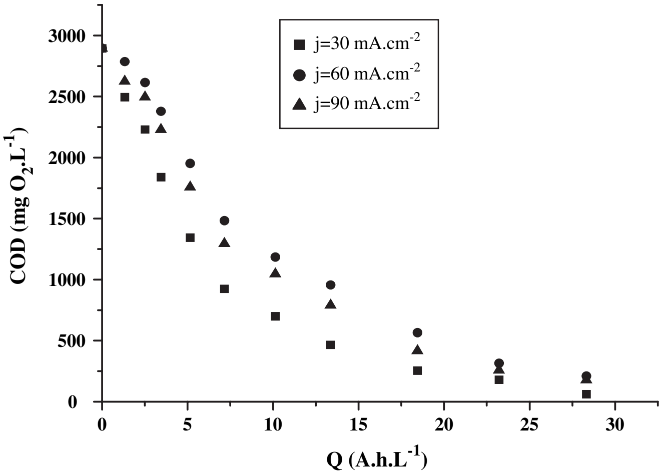

Fig. 5. Variation of the COD during the galvanostatic electrolysis of Alizarin Red S (5 mM) at BDD electrode and $T = 25$ °C.

Fig. 4 shows the evolution with specific electrical charge passed of the total organic carbon (TOC). It can be seen that, the TOC decreased progressively with the specific electrical charge passed leading to the complete mineralization of the Alizarin Red S. After the consumption of 28 A h l^{-1}, the complete removal of the organic compounds contained in the waste is obtained and the electrochemical incineration of Alizarin Red S to CO_2 is achieved. The continuous decrease of the total organic carbon confirms the progressive mineralization of the Alizarin Red S during the galvanostatic electrolyses.

The conversion into carbon dioxide is slower than the disappearance of the substrates, indicating the intermediates are degraded less rapidly than the initial compounds. In particular, the fast removal of TOC observed in the beginning can be attributed to a rapid degradation of the cyclic intermediates while the final slowing down reflects a much slower mineralization of the aliphatic intermediates originated by ring fission [30].

Fig. 5 shows the influence of anodic current density on COD evolution electrolysis with BDD anode of Alizarin Red S. The results show that COD decreases up to zero independently of the applied current due to the oxidation of Alizarin Red S by the electrogenerated hydroxyl radicals (Eq. (1)). However, an increase of the current density resulted in a decrease of the oxidation rate because of the side reactions of oxygen evolution and peroxodisulfates formation [15–24].

The variation of the COD has a typical exponential shape. This behavior was previously explained in literature [14–30] in terms of the controlling mechanisms of the electrochemical process. The exponential zone corresponds to a range of pollutant concentration in which the electrochemical process is mass-transfer controlled.

4. Conclusion

Anthraquinone dye Alizarin Red S was successfully not only decolorized but also totally degraded and mineralized by anodic oxidation at boron-doped diamond in sulfuric medium. The organics were totally converted into CO_2 as measured by the elimination of COD and TOC.

The oxidation process may occur either directly on the electrode surface or can be mediated by hydroxyl radicals and peroxodisulfate electrogenerated at the anode surface [15–30]. The COD variation in the electrochemical oxidation of wastes polluted with Alizarin Red S on BDD anode is limited mainly by mass-transfer process.

This electrochemical technique can be considered as very clean and very suited for treating industrial wastewaters containing anthraquinone dyes.

References

[1] Reife A, Freeman H. Environmental chemistry of dyes and pigments. New York: Wiley/Interscience; 1996.

[2] Lorimer JP, Platees M, Phull SS, Walton DJ. Degradation of dye effluent. Pure Appl Chem 2001;73(12):1957–68.

[3] Brown D. Effects of colorants in the aquatic environment. Chemosphere 1987;12(3):397–404.

[4] Shu H-Y, Huang C-R. Degradation of commercial azo dyes in water using ozonation and UV enhanced ozonation process. Chemosphere 1995;31:3813–25.

[5] Slokar YM, Le Marechal AM. Methods of decolouration of textile wastewaters. Dyes Pigments 1998;37:335–56.

[6] Ledakowicz S, Gonera M. Optimisation of oxidants dose for combined chemical and biological treatment of textile wastewater. Water Res 1999;33:2511–6.

[7] Fernandes A, Morao A, Magrinho M, Lopes A, Gonçales I. Electrochemical degradation of C.I. acid Orande 7. Dyes Pigments 2004;61:287–96.

[8] 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.

[9] Correa-Lozano B, Comninellis Ch, Battisti AD. Service life of $Ti/SnO_2-Sb_2O_5$ anodes. J Appl Electrochem 1997;27:970–4.

[10] 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.

[11] Kotz R, Stucki S, Carcer B. Electrochemical wastewater treatment using high overvoltage anodes. Part I: physical and electrochemical properties of SnO_2 anodes. J Appl Electrochem 1991;21:14–20.

[12] Marselli B, García-Gómez J, Michaud P-A, Rodrigo MA, Comninellis Ch. Electrogeneration of hydroxyl radicals on boron-doped diamond electrodes. J Electrochem Soc 2003;150:D79.

[13] Michaud P-A, Panizza M, Ouattara L, Diaco T, Foti G, Comninellis Ch. Electrochemical oxidation of water on synthetic boron-doped diamond thin film anodes. J Appl Electrochem 2003;33:151–4.

[14] Cañizares P, García-Gómez J, Lobato J, Rodrigo MA. Modelization of wastewater electro-oxidation processes: part I. General description and application to non-active electrodes. Ind Eng Chem Res 2004; 34:87.

[15] Cañizares P, García-Gómez J, Lobato J, Rodrigo MA. Electrochemical oxidation of aqueous carboxylic acid wastes using diamond thin-film electrodes. Ind Eng Chem Res 2003;42:956.

[16] 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.

[17] Cañizares P, Sáez C, Lobato J, Rodrigo MA. Electrochemical treatment of 4-nitrophenol aqueous wastes using boron-doped diamond anodes. Ind Eng Chem Res 2004;43:1944.

[18] Iniesta J, Michaud P-A, Panizza M, Cerisola G, Aldaz A, Comninellis Ch. Electrochemical oxidation of phenol at boron-doped diamond electrode. Electrochim Acta 2001;46:3573.

[19] Rodrigo MA, Michaud P-A, 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.

[20] Cañizares P, Sáez C, Lobato J, Rodrigo MA. Electrochemical treatment of 2,4-dinitrophenol aqueous wastes using boron-doped diamond anodes. Electrochim Acta 2004;49:4641–50.

[21] Cañizares P, Sáez C, Lobato J, Rodrigo MA. Electrochemical oxidation of polyhydroxybenzenes on boron-doped diamond anodes. Ind Eng Chem Res 2004;43:6629.

[22] Iniesta J, Michaud PA, Panizza M, Comninellis C. Electrochemical oxidation of 3-methylpyridine at a boron-doped diamond electrode: application to electroorganic synthesis and wastewater treatment. Electrochem Commun 2001;3:346.

[23] Montilla F, Michaud P-A, Morallon E, Vazquez JL, Comninellis Ch. Electrochemical oxidation of benzoic acid at boron-doped diamond. Electrochim Acta 2002;47:3509.

[24] Bensalah N, Benamor H, Gadri A, Rodrigo MA. Purification of wet-process phosphoric acid by hydrogen peroxide, activated carbon adsorption and electrooxidation. J Chem Eng Technol 2005;28(2).

[25] Bensalah N, Gadri A. Electrochemical oxidation of 2,4,6-trinitrophenol on boron-doped diamond electrodes. J Electrochem Soc, in press.

[26] Panizza M, Cerisola G. Influence of anode material on the electrochemical oxidation of 2-naphthol: part 1. Cyclic voltammetry and potential step experiments. Electrochim Acta 2003;48:3491.

[27] Panizza M, Cerisola G. Influence of anode material on the electrochemical oxidation of 2-naphthol: part 2. Bulk electrolysis experiments. Electrochim Acta 2004;49:3221.

[28] Boye B, Michaud P-A, Marselli B, Dieng MM, Brillas E, Comninellis C. Anodic oxidation of 4-chlorophenoxyacetic acid on synthetic boron-doped diamond electrodes, new diamond front. Carbon Technol 2002;12:63.

[29] Bellagamba R, Michaud P-A, Comninellis Ch, Vatistas N. Electro-combustion of polyacrylates with boron-doped diamond anodes. Electrochem Commun 2002;4:171.

[30] Hattori S, Doi M, Takahashi E, Kurosu T, Nara M, Nakamatsu S, et al. Electrolytic decomposition of amaranth dyestuff using diamond electrodes. J Appl Electrochem 2003;33:85.