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Comparative mineralization of textile dye indigo by photo-Fenton process and anodic oxidation using boron-doped diamond anode

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ABSTRACT

In the present study, we applied two advanced oxidation processes (AOPs); photo-Fenton and anodic oxidation (using a boron doped diamond (BDD) anode) processes, to oxidative degradation and mineralization of the textile dye Indigo in sodium dithionite aqueous media. The effect of key parameters, such as H_2O_2 dosage for photo-Fenton process and initial pH for anodic oxidation, on the degradation and mineralization kinetics of dye Indigo was investigated. The highest mineralization rates were observed at pH 3.0 for anodic oxidation process, and for a ratio R: $[H_2O_2]/[Fe^{2+}] = 40$ for photo-Fenton process. Under optimal operating conditions a complete mineralization of Indigo dye was achieved after 7 h treatment by anodic oxidation whereas only 63% of TOC removal was obtained after 10 h treatment by photo-Fenton process. The carboxylic acids (glyoxylic, malonic, oxalic, acetic and formic) formed as oxidation by-products were identified and their evolution was followed by ion-exclusion chromatography. The evolution of NO_3^- and NH_4^+ ions released to the solution during the treatment was followed by ion chromatography. These results show that anodic oxidation using a BDD anode is an efficient environmentally friendly technology for the remediation of wastewaters containing textile dye Indigo.

Keywords: Indigo; Hydroxyl radical; Anodic oxidation; Photo-Fenton; Water treatment

1. Introduction

The dye Indigo is extensively used in textile industries and is considered as a recalcitrant pollutant to classical water treatment processes. Its major industrial application is the dyeing of clothes (blue jeans) and other blue denim products. However, it is practically insoluble in water (2 ppm) and has no affinity for cellulose fibres in such a state. Thus, it has to be reduced before dyeing in order to be converted into the water-soluble form using a powerful reducing agent such as sodium dithionite ($Na_2S_2O_4$).

The extensive use of this dye contributes to pollution problems associated with disposal of a considerable amount of coloured wastewater containing residual dispersed particles of Indigo and amounts of sodium sulphate. Consequently, various techniques have been proposed for the treatment of coloured wastewater such

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as adsorption [1], membrane filtration, coagulation/floculation/filtration [2]. Nevertheless, these methods are non-destructive since they lead to the removal of the dye from wastewater and its relocation elsewhere [3,4]. As for biological processes, they remain ineffective in the case of toxic and/or non-biodegradable pollutants [5,6].

Recently, more attention has been paid to use of advanced oxidation processes (AOPs) for destruction of persistent organic pollutants [7–15]. These processes focus on the production of hydroxyl radicals, highly reactive species, which promote oxidation of persistent organic compounds until their complete mineralization that is their transformation into CO_2, water and inorganic ions. In this paper we are extending our work by looking at the comparative study of Indigo degradation by two AOPs, namely anodic oxidation and photo-Fenton processes.

The photo-Fenton process is based on the photo reduction of $Fe(OH)^{2+}$, the predominant form of Fe(III) at optimal pH value, that is pH 3 for Fenton related processes, to Fe(II) producing $^{\bullet}OH$ on the one hand (Eq. (1)) and catalyzing the Fenton's reaction (Eq. (2)) to generate additional $^{\bullet}OH$ on the other hand [16–19]:

$$Fe\left(OH\right)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \tag{1}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe\left(OH\right)^{2+} + {}^{\bullet}OH \tag{2}$$

Additional sources of $^{\bullet}OH$ through photolysis of H_2O_2 should be considered [20]:

$$H_2O_2 + h\nu \rightarrow 2\ {}^{\bullet}OH \tag{3}$$

The amount of $^{\bullet}OH$ produced by Eq. (3) is generally negligible compared to that formed by Eqs. (1) and (2) due to its very low adsorption coefficient of H_2O_2. On the other side, the $^{\bullet}OH$ production rate is significantly higher in photo-Fenton process than that of Fenton's reaction or H_2O_2 photolysis methods alone because additional $^{\bullet}OH$ generating from Eq. (1) and then catalyzing the Fenton's reaction (Eq. (2)).

Electrochemical methods, such as electro-Fenton and anodic oxidation, which are effective for the direct production of hydroxyl radicals, are used for water remediation. In this method organic pollutants are destroyed [21–24] by reaction with hydroxyl radicals generated electrochemically in bulk solution through Fenton's reagent (electro-Fenton) [21] or at the surface of a high O_2-overvoltage anode from water oxidation in acid and neutral media (anodic oxidation) [22–24]:

$$M + H_2O \rightarrow M({}^{\bullet}OH)_{ads} + H^+ + e^- \tag{4}$$

or hydroxide ion at pH ≥10:

$$M + OH^- \rightarrow M({}^{\bullet}OH)_{ads} + e^- \tag{5}$$

where M denotes the anode. It is recently demonstrated that the boron-doped diamond (BDD) thin film anode shows very good properties in electrochemical treatment of wastewaters contaminated with organic pollutants [25,26]. In addition this electrode has great chemical and electrochemical stability with a very large hydroxyl radical generation ability compared to the conventional anodes such as PbO_2, SnO_2, IrO_2 and Pt [27,28] producing then larger amounts of $^{\bullet}OH_{ads}$ by reaction (4) to yield a quicker oxidation of aromatic pollutants. The use of BDD anode in anodic oxidation process allows the almost complete mineralization of the organics pollutants in the wastes with very high current efficiencies [29–32].

The goal of this study is to investigate the comparative oxidation kinetics of the textile dye Indigo and the mineralization efficiency of its aqueous solution through TOC abatement yield, evolution of short-chain carboxylic acids and release to the solution of nitrate and ammonium ions concentration compared to theoretical amount present initially on the Indigo molecule.

2. Materials and methods

2.1. Chemicals

Indigo (C.I 73000, Vat Blue 1), of chemical formulae $C_{16}H_{10}N_2O_2$ was provided by Aldrich. $Fe_2(SO_4)_3.5H_2O$ used as catalyst source was from Acros and have a purity of 99.9%. Sodium dithionite (>80%) and hydrogen peroxide (30%) were from Fluka. Carboxylic acids and all other chemicals used for chromatographic analysis were purchased from Acros, Sigma, Fluka and were analytical grade. All solutions were prepared with high purity water obtained from Millipore simplicity 185 System (conductivity $<6.10^{-8}$ S cm^{-1}) at room temperature (23 ± 2°C). The initial solution pH was adjusted with sulphuric acid or sodium hydroxide, both of analytical grades, purchased from Acros and Fluka, respectively.

2.2. Electrochemical apparatus and procedures

Electrolytic experiments were carried in an open, cylindrical, one-compartment electrochemical cell of 10-cm diameter and 500-ml capacity, and equipped with two electrodes, in which the dye aqueous solutions were placed. The electrolyses were performed with a Hameg HM8040 triple power supply at constant current. A 25-cm^2 boron-doped diamond electrode (BDD thin-film deposited on a niobium substrate from CONDIAS, Germany) was used as the anode, the cathode being a Pt mesh of 5.5 cm high. Indigo aqueous solutions were prepared at 0.1 mM Indigo concentration dissolved in 30 mM sodium dithionite to ensure its solubility. All solutions were vigorously stirred in a rate of 900 rpm with a magnetic bar during treatment and submitted to electrolysis at room temperature (23 ± 2°C) at 500 mA constant current for all experiments. The initial pH of solutions was in the range of 3.0–12.0, adjusted by adding small volumes of H_2SO_4 or NaOH.

2.3. Photoreactor

All photochemical experiments were carried out at room temperature in a laboratory-made batch Pyrex annular photoreactor with a total volume of 1.3 l, equipped with a hollow cylindrical quartz tube and a 40 W low-pressure mercury lamp from Heraeus Noblelight GmbH, Germany (NNI 40/20) of a nominal electric power output of 40 W and of a nominal UV power output of 12 W, emitting at 253.7 nm with a photonic flow (P_0) of 11.12×10^{-6} Einstein s^{-1} as described previously [33]. The lamp that was positioned vertically within the inner part of the photoreactor is protected from the solution by an annular quartz sheath of 3.5 cm thickness. Cooling water was circulated through a Pyrex jacket surrounding the tube. The reaction mixture which set initially to pH 3 was continuously pumped through the photoreactor with a peristaltic pump (Heidolph, type 523.030) by means of PTFE tubing at a flow rate of 3 l min^{-1}. Two top orifices in the reactor allowed the introduction of reagents as well as the sampling at selected times. Zero time corresponded to the moment when the lamp was switched on. In all experiments, solutions were prepared at 0.1 mM Indigo concentration dissolved in 30 mM sodium dithionite and were acidified to pH = 3.0 with sulphuric acid.

2.4. High performance liquid chromatography (HPLC)

The dye concentration decay of Indigo was monitored by a Merck-Hitachi Lachrom High Perfomance Liquid Chromatography (HPLC) equipped with a diode array UV-Visible detector (model L-7455) and a L-7100 pump fitted with a reverse phase Purospher RP-18, 5 µm, 4.6 mm (i.d.) × 250 mm column. The column was eluted at isocratic mode for kinetic experiments with a mobile phase composed of methanol/water/acetic acid (69/29/2 v/v) at a flow rate of 0.5 ml min^{-1}. The column was placed in an oven (Merck L-7350) thermostated at 40°C. Detection was performed at 580 nm. The standard solutions used to establish the external calibration curves of dye were prepared in a methanol/water medium.

Carboxylic acids generated as end-products during oxidation of Indigo by hydroxyl radicals were identified and quantified by ion-exclusion chromatography using the above HPLC system fitted with a Supelcogel H, 9 µm, 250 mm × 4.6 mm (i.d.), column at 40°C. Detection was carried out using a diode array detector selected at $\lambda = 210$ nm. A 0.1% H_3PO_4 solution was used as the mobile phase at a flow rate of 0.5 ml min^{-1}. 20-µl samples were used to monitor the short-chain aliphatic carboxylic acids, the measurements being controlled through EZChrom Elite 3.1 software.

2.5. Ion chromatography

The formation and evolution of ammonium and nitrate ions released from the dye Indigo solution during the treatment were determined by ion chromatography with a Dionex ICS-1000 Basic Ion Chromatography System. To quantify NO_3^- ions, the system was fitted with an IonPac AS4A-SC, 25 cm × 4 mm (i.d.), anion-exchange column linked to an IonPac AG4A-SC, 5 cm × 4 mm (i.d.), column guard and a 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ solution circulating at 2.0 ml min^{-1} was used as the mobile phase. For the determination of the cation NH_4^+, an IonPac CS12A, 25 cm × 4 mm (i.d.), cation-exchange column linked to an IonPac CG12A, 5 cm × 4 mm (i.d.), column guard was used. A 9.0 mM H_2SO_4 solution circulating at 1.0 ml min^{-1} was used as the mobile phase. The system was equipped with a DS6 conductivity detector with a cell heated at 35°C and its sensitivity was improved from electrolyte suppression using an ASRS-ULTRA II or CSRS-ULTRA II self-regenerating suppressor for anions and cations, respectively.

2.6. Total organic carbon (TOC)

The mineralization of aqueous Indigo solutions was monitored from the decay of their total organic carbon (TOC) by catalytic oxidation on a Shimatzu - V analyzer. Samples withdrawn from the treated solution at different electrolysis times were micro-filtered onto a hydrophilic membrane (Millex-GV Millipore, pore size 0.22 µm) before analysis and were acidified with HCl (1% HCl 2 mM) before injection of 50 µl aliquots into TOC analyzer. Calibrations were performed by using standard potassium hydrogen phthalate solutions. Reproducible TOC values were obtained using the non purgeable organic carbon method. TOC measurements were based on the combustion of organics and detection of CO_2 formed by infrared gas analysis method.

3. Results and discussion

The Indigo is the dye very intensively used in the industry of textile for the dyeing of clothing and more precisely for the jeans. However, it is practically insoluble in water and thus does not present any affinity for cellulose fibers. To increase its affinity for fibers, it is reduced by powerful reducing agents, such as the hydrosulphite of sodium (Na_2S_2O4) for obtaining of its water-soluble form. In this work, we tried to degrade a solution of Indigo solubilized with the sodium hydrosulphite by the electro-Fenton process, but this operation was unsuccessfully because of its strong adsorption on the carbon felt cathode. Consequently we tried to study the kinetics of mineralization of the Indigo with two other techniques: anodic oxidation using BDD anode (electrochemical AOP) and photo-Fenton process (photochemical AOP).

3.1. Removal of indigo from water by anodic oxidation: effect of initial pH on mineralization efficiency

We investigated the effect of pH on the mineralization efficiency of Indigo aqueous solution by anodic oxidation. Therefore, the study was performed using a dissolved Indigo solution of 0.1 mM at three different pH values: 3.0, 6.5 and 12.0. The preliminary trials carried out with different current values on the TOC removal efficiency (results not shown) indicated that the value of 500 mA gives better results. Consequently the evolution of solution TOC as mineralization parameter with initial pH was studied at 500 mA constant current and the results obtained are presented in Fig. 1. As can be seen in this figure, the mineralization of Indigo solution is significantly faster for the low pH values. This behaviour can be explained by the higher hydroxyl radical generation rate from reaction (4) than that from reaction (5). On the other hand, the Fig. 1 shows that in all cases, the TOC removal is more than 94% in about 7 h treatment. These results indicate that Indigo and its by-products can be efficiently destroyed at different pH by anodic oxidation using a BDD anode. The residual TOC remaining at the end of the treatment is composed of some short-chain carboxylic acids, in particular, glyoxylic acid that is always present in the solution after 9 h of treatment. The slow TOC removal rate at longer treatment time can be explained by the low reactivity of these carboxylic acids [34] compared to that of aromatics such as Indigo [7].

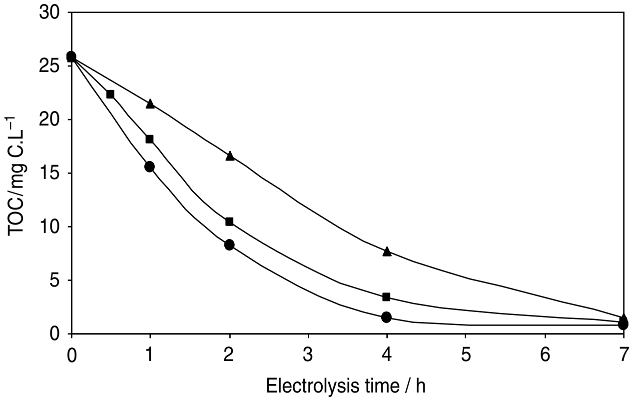

Fig. 1. Effect of initial pH on TOC removal kinetics for the treatment of 500 ml aqueous indigo (C_0 = 0.1 mM) solution in 30 mM $Na_2S_2O_4$ by anodic oxidation with BDD anode at 500 mA constant current. Initial pH: (■) 3.0, (●) 6.5, (▲) 12.0.

3.2. Treatment of indigo solution by photo-Fenton process: effect of initial H_2O_2 concentration

The H_2O_2 dose and the ratio $R = [H_2O_2]/[Fe^{3+}]$ are two critical variables in the photo-Fenton process. In order to achieve the maximum mineralization efficiency, two initial H_2O_2 concentrations (10 and 40 mM) were tested with a constant concentration of Fe^{3+} (0.5 mM). Fig. 2 shows the effect of initial hydrogen peroxide concentration on the TOC removal efficiency. The increase in the initial H_2O_2 concentration from 10 mM (R = 20) to 40 mM (R = 80) increases Indigo mineralization ratio in term of TOC removal from 36% to 50% after 3 h of treatment. Indeed, the generation of $^\bullet$OH radicals in photo-Fenton process is carried out through three main mechanisms: photo-reduction of ferric iron ions (reaction (1)), Fenton reaction (reaction (2)) and photolysis of H_2O_2 (reaction (3)). Consequently, the concentration of H_2O_2 in photo-Fenton process is a limiting factor for degradation of organic pollutants in wastewater. It was previously demonstrated that the increase in H_2O_2 concentration leads generally to increase in the amount of hydroxyl radicals formed [14,16,17]. However, after reaching an optimal value, further boost of H_2O_2

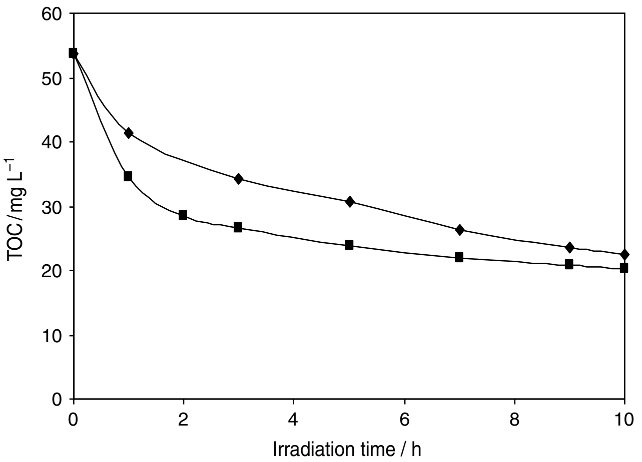

Fig. 2. TOC removal as mineralization efficiency by photo-Fenton process during the treatment of 1.4 l indigo (C_0 = 0.1 mM) aqueous solution in 30 mM $Na_2S_2O_4$, $[Fe^{3+}]$ = 0.5 mM at pH 3 for two different H_2O_2 initial concentrations. R = 20 (◆) and (■) 80.

concentration influence negatively the process efficiency due to the pronounced behaviour of H_2O_2 as a radical scavenger (reactions (6) and (7)) [35,36]. The increase in H_2O_2 concentration results in the increase of the rate of reactions (6) and (7), so that they become competitive for hydroxyl radicals formed in the process. As a consequence, photo-Fenton process efficiency decreases when these waste reactions take importance:

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad (6)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \quad (7)$$

The TOC removal is fast until 2 h treatment; however it becomes slower at longer treatment times. This behaviour can be explained by two reasons: (i) the presence of short-chain carboxylic acids (formed by ring opening reaction of hydroxylated/polyhydroxylated aromatic intermediates) having a weak reactivity versus hydroxyl radicals [34] unlike organics [7] destroyed in the beginning of the treatment, and (ii) the competition of waste reactions (6) and (7) that take relative importance versus reaction by-products, particularly the carboxylic acids.

3.3. Comparison of anodic oxidation and photo–Fenton processes

The degradation kinetics of Indigo with photo-Fenton and anodic oxidation processes was comparatively studied under optimal conditions for each one. The decay of Indigo concentration with time for anodic oxidation and photo-Fenton is represented in Fig. 3 under these conditions. As can be seen, the complete oxidation of Indigo is obtained in less than 5 min with photo-Fenton process whereas it needs 5 h with anodic oxidation. The above concentration decays were well-fitted with a pseudo-first-order reaction kinetics, as can be seen in the inset panel of Fig. 3. From this kinetic analysis, the pseudo-first-order rate constant (k_{app}) values of 0.01 min^{-1} (R^2 = 0.982) and 1.65 min^{-1} (R^2 = 0.968) were found for anodic oxidation and photo-Fenton process, respectively, for the oxidation of Indigo by hydroxyl radicals. The quick oxidation of Indigo dye during photo-Fenton process can be attributed to the greater amount of oxidant $^{\bullet}OH$ formed at the beginning of treatment from reactions (1)–(3).

However, TOC removal efficiency is significantly higher at longer treatment time for anodic oxidation at pH = 3.0 (97% in 7 h of electrolysis) in comparison to the photo-Fenton process (only 63% TOC removal at 10 h (Figs. 1 and 2). Indeed the highly reactive (BDD($^{\bullet}$OH)) are continuously generated during the electrolysis at the surface of the anode. Indigo molecules reaching to the anode surface are firstly oxidized to aromatic intermediates and then the intermediates formed are subsequently attacked by hydroxyl radicals. Consequently, the mother pollutant and oxidation by-products are simultaneously destroyed by BDD($^{\bullet}$OH) at the anode surface until their mineralization. In contrast, the mineralization process take place step by step during photo-Fenton process which leads, in a first stage, to the formation of aromatic intermediates which will be then transformed into polyhydroxylated products before their oxidative cleavage to form carboxylic acids. It is well known that the mineralization of short-chain carboxylic acids such as oxalic acid is slow by hydroxyl radicals formed in solution by homogeneously chemical (Fenton's reaction) or photochemical (Fe^{3+} or H_2O_2 photolysis) reactions [37–40].

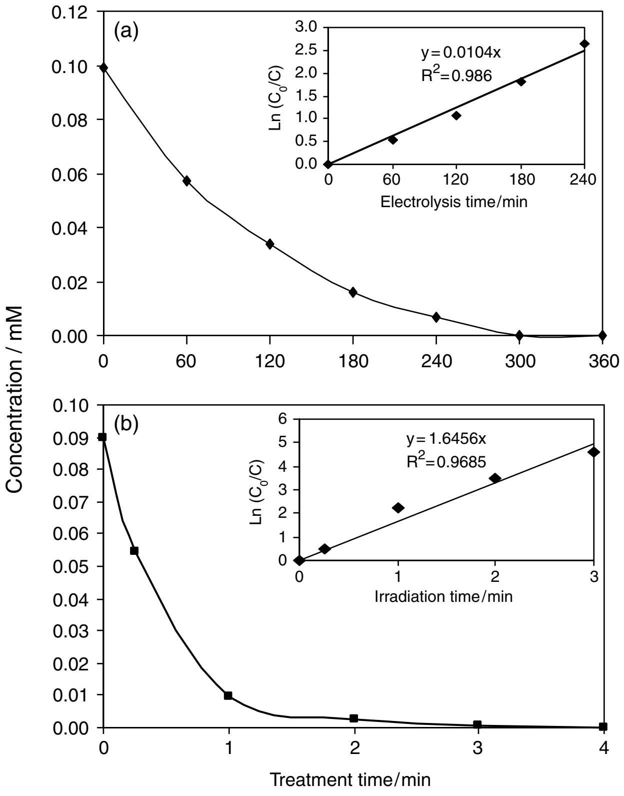

Fig. 3. Time-course of indigo concentration during the degradation by (a) anodic oxidation with BDD anode at pH = 3.0 and (b) photo-Fenton process [Fe^{3+}] = 0.5 mM, [H_2O_2]/[Fe^{3+}] = 80. The insert panels show the corresponding kinetics assuming a pseudo-first-order reaction kinetic for Indigo degradation by hydroxyl radicals.

This is why, despite an apparent rate constant (k_{app}) of Indigo oxidation by anodic oxidation process being significantly smaller compared to that obtained during photo-Fenton process, the solution TOC removal is clearly higher (with an almost mineralization efficiency of 97%) in the case of anodic oxidation. On the other side, a great amount of hydroxyl radicals are produced at the beginning of the process, but a part of this oxidizing agent are consumed by the waste reactions (*see* Section 3.2). In addition, due their high concentration at anode surface and ability (they are physisorbed) to react with organics, the hydroxyl radical generated at the BDD anode, BDD($^{\bullet}$OH), has an oxidizing power clearly higher than that generated in homogeneous medium in the destruction of carboxylic acids and other recalcitrant organics [41,42].

3.4. Identification and evolution of carboxylic acids

The formation of short-chain carboxylic acid as end products before complete mineralization during the oxidation of aromatics with $^{\bullet}$OH is a generally expected situation. In order to identify and follow the evolution of the carboxylic acids generated during advanced oxidation, a 0.1 mM Indigo aqueous solution was treated by anodic oxidation at initial pH of 3.0. Ion exclusion chromatographic analysis permitted to detect oxalic, formic, maleic acids at low concentration, whereas malonic and glyoxylic acids at significant concentration during the anodic oxidation of Indigo. The evolution of the two main carboxylic acids, that is glyoxylic and malonic acids, is presented in Fig. 4. This figure shows both glyoxylic and malonic acids begin to be formed as soon as the process starts. This behaviour evidences that the oxidative degradation and mineralisation occur simultaneously at the surface of the BDD anode. Malonic and glyoxylic acids reach their maximum concentration after 4 h and 6.5 h electrolysis respectively and then their concentration decreases gradually. Malonic acid was completely removed at 6 h treatment, while glyoxylic acid remained in the solution even after 9 h of treatment. The residual TOC present after 7 h of electrolysis can be attributed to these carboxylic acids remained in solution either at the end of treatment. Some carboxylic acids such as acetic, glycolic and fumaric which are identified during photocatalytic degradation of Indigo [43] are not detected in this study during anodic oxidation of BDD anode.

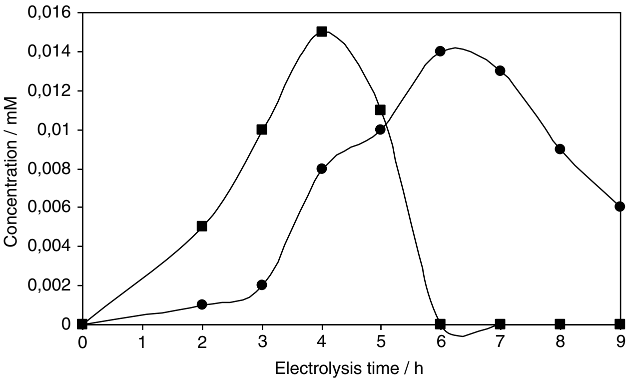

Fig. 4. Time-course of carboxylic acids: malonic (■) and glyoxylic (●) acids, generated during the mineralization of 0.1 mM Indigo aqueous solution in 30 mM $Na_2S_2O_4$ by anodic oxidation with BDD anode at 500 mA constant current.

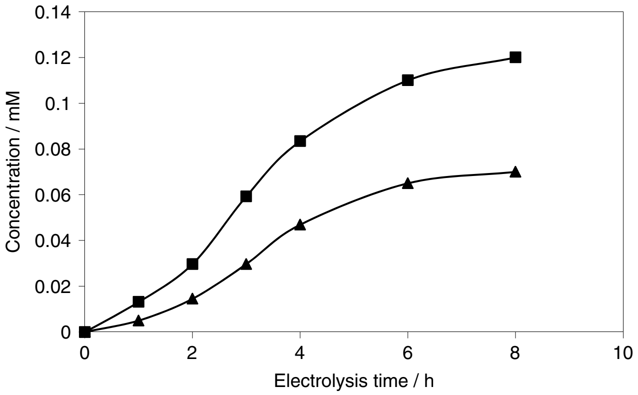

Fig. 5. Evolution of the concentration of ammonium (■) and nitrate (▲) ions released during the mineralization of 0.1 mM Indigo aqueous solution in 30 mM $Na_2S_2O_4$ by anodic oxidation at constant current of 500 mA and pH 3.

3.5. Formation and evolution of nitrate and ammonium ions

During the application of AOPs, the heteroatoms present in the initial organic molecules are transformed into inorganic ions. Nitrogen of N-compounds are converted either nitrate or ammonium ions [44–46]. Therefore it is expected that nitrogen atoms of Indigo oxidize to nitrate and ammonium ions during the mineralization process. Identification of a quantitative amount of these ions may constitute a supplementary evidence for total mineralization of the treated Indigo solution. The ionic chromatography analysis allowed qualitative and quantitative monitoring of inorganic ions released to the solution from the mineralization of Indigo. Thus the evolution of nitrate and ammonium ions during anodic oxidation is presented in Fig. 5. As can be seen in Fig. 5, nitrate and ammonium ions start to be formed from the beginning of the electrolysis, and their concentration increases gradually along the electrolysis to reach, at the end of treatment, to 35% and 60% of the stoichiometric nitrogen present initially in Indigo for nitrate and ammonium respectively. The release of a higher amount of ammonium than that of nitrate ions was also previously reported by Flox et al. [13] in the case of the electro-Fenton treatment of a similar dye, that is, the Indigo carmine. These results highlight again the almost total mineralization of the Indigo aqueous solution by anodic oxidation with BDD anode and confirm its outstanding oxidizing power.

4. Conclusions

The mineralization of a 0.1 mM Indigo dissolved in 30 mM sodium dithionite aqueous solution has been studied by anodic oxidation using BDD anode and photo-Fenton processes. It has been demonstrated that anodic oxidation is able to reach quasi-complete mineralization efficiency higher than 97% in aqueous medium of pH 3.0 at 7 h treatment. In contrast, the photo-Fenton process under conditions $[Fe^{3+}] = 0.5$ mM and $[H_2O_2] = 40$ mM ($R = 80$) yields only 63% of TOC removal after 10 h of UV irradiation. High mineralization rate by anodic oxidation with BDD anode can be attributed to the continuous generation of hydroxyl radicals at the anode surface along the electrolysis and the outstanding oxidizing power of these heterogeneous hydroxyl radicals (BDD ($^{\bullet}OH$)).

Mineralization process generates short-chain carboxylic acids and inorganic ions. Malonic and gloxylic acids are generated at significant amount whereas oxalic, maleic and formic acids are formed at trace level. Ion chromatography analysis of ammonium and nitrate ions during anodic oxidation shows that the nitrogen presented in Indigo is quasi completely released to the solution during the process.

These results highlights that the anodic oxidation using BDD anode presents an outstanding oxidation power compared to the photo-Fenton process for the remediation of wastewaters containing textile dye Indigo.

References

[1] H.M. Pignon, C.F. Brasquet and P.L. Cloirec, Adsorption of dyes onto activated carbon cloths: approach of adsorption mechanisms and coupling of ACC with ultrafiltration to treat coloured wastewaters, Sep. Purif. Technol., 31 (2003) 3–11.

[2] A. Bes-Pia, J.A. Mendoza-Rota, L. Roig-Alcover, A. Iborra-Clar, M.I. Iborra-Clar and M.I. Alcaina-Miranda, Comparison between nanofiltration and ozonation of biologically treated textile wastewater for its reuse in the industry, Desalination, 157 (2003) 81–86.

[3] S. Papic, N. Koprivanac and A. Loncaric Bozic, Removal of reactive dyes from wastewater using Fe(III) coagulant, Color. Technol., 116 (2000) 352–358.

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

[5] U. Pagga and D. Brown, The degradation of dyestuffs: Part II behaviour of dyestuffs in aerobic biodegradation tests, Chemosphere, 15 (1986) 479–491.

[6] G. Michaels and D.L. Lewis, Microbial transformation rates of azo and triphenylmethane dyes, Environ. Toxicol. Chem., 5 (1986) 161–166.

[7] E. Brillas, I. Sirés and M.A. Oturan, Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry, Chem. Rev., 109(12) (2009) 6570–6631.

[8] N. Ayten, I. Arslan-Alaton and T. Olmez-Hanci, Application of photo-Fenton-like oxidation for the degradation and detoxification of commercial naphthalene sulfonates a case study with H-acid model pollutant, Desalin. Water Treat., 26 (2011) 139–144.

[9] M. Rodriguez, V. Sarria, S. Esplugas and C. Pulgarin, Photo-Fenton treatment of a biorecalcitrant wastewater generated in textile activities: biodegradability of the photo-treated solution, J. Photochem. Photobiol. A, 151 (2002) 129–35.

[10] M. Neamtu, A. Yediler, I. Siminiceanu, M. Macoveanu and A. Kettrup, Decolorization of disperse red 354 azo dye in water by several oxidation processes—a comparative study, Dyes Pigm., 60 (2004) 61–68.

[11] F. Abdelmalek, S. Gharbi, B. Benstaali, A. Addou and J.L. Brisset, Plasmachemical degradation of azo dyes by humid air plasma: Yellow Supranol 4 GL, Scarlet Red Nylosan F3 GL and industrial waste, Water Res., 38 (2004) 2339–2347.

[12] E. Guivarch, S. Trévin, C. Lahitte and M.A. Oturan, Removal of orgonophosphorus pesticides from water by electrogenerated Fenton's reagent, Environ. Chem. Lett., 1 (2003) 39–44.

[13] C. Flox, S. Ammar, C. Arias, E. Brillas, A.V. Vargas-Zavala and R. Abdelhedi, Electro-Fenton and photoelectro-Fenton degradation of Indigo carmine in acidic aqueous medium, Appl. Catal. B, 67 (2006) 93–104.

[14] S. Hammami, N. Oturan, N. Bellakhal, M. Dachraoui and M.A. Oturan, Oxidative degradation of direct orange 61 by electro-Fenton process using a carbon felt electrode: application of the experimental design methodology, J. Electroanal. Chem., 610 (2007) 75–84.

[15] M.Q. Qiu and C.C. Huang, A comparative study of degradation of the azo dye CI acid blue 9 by Fenton and photo-Fenton oxidation, Desalin. Water Treat., 24 (2010) 273–277.

[16] Y. Sun and J.J. Pignatello, Photochemical reactions involved in the total mineralization of 2,4-D by $Fe^{3+}/H_2O_2/UV$, Environ. Sci. Technol., 27 (1993) 304–310.

[17] G. Kaichouh, N. Oturan, M.A. Oturan, K. El Kacemi and A. El Hourch, Degradation of the herbicide imazapyr by Fenton reactions, Environ. Chem. Lett., 2 (2004) 31–33.

[18] S. Trabelsi-Souissi, N. Oturan, N. Bellakhal and M.A. Oturan, Application of the photo-Fenton process to the mineralization of phthalic anhydride in aqueous medium, Desalin. Water Treat., 25 (2011) 210–215.

[19] M.A. Oturan, N. Oturan, M.C. Edelahi, F.I. Podvorica and K. El Kacemi, Oxidative degradation of herbicide diuron in aqueous medium by Fenton's reaction based advanced oxidation processes, Chem. Eng. J., 171 (2011) 127–135.

[20] F.J. Beltran, Ozone-UV radiation-hydrogen peroxide oxidation technologies, in: M.A. Tarr (Ed.), Chemical Degradation Methods for Wastes and Pollutants—Environmental and Industrial Applications, Marcel Dekker Inc., New York, 2003, pp. 1–77.

[21] E. Brillas, B. Boye, I. Sirés, J.A. Garrido, R.M. Rodríguez, C. Arias, P.L. Cabot and C. Comninellis, Electrochim. Acta, 49 (2004) 4487–4496.

[22] E. Brillas, I. Sirés, C. Arias, P.L. Cabot, F. Centellas, R.M. Rodríguez and J.A. Garrido, Mineralization of paracetamol in aqueous medium by anodic oxidation with a boron-doped diamond electrode, Chemosphere, 58 (2005) 399–406.

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

[24] C. Flox, J.A. Garrido, R.M. Rodríguez, F. Centellas, P.L. Cabot, C. Arias and E. Brillas, Degradation of 4,6-dinitro-o-cresol from water by anodic oxidation with a boron-doped diamond electrode, Electrochim. Acta, 50 (2005) 3685–3692.

[25] B. Marselli, J. Garcıa-Gomez, P.A. Michaud, M.A. Rodrigo and Ch. Comninellis, Electrogeneration of hydroxyl radicals on boron-doped diamond electrodes, J. Electrochem. Soc., 150 (2003) 79–83.

[26] P. Canizares, L. Martınez, R. Paz, C. Saez, J. Lobato and M.A. Rodrigo, Treatment of Fenton-refractory olive oil mill wastes by electrochemical oxidation with boron-doped diamond anodes, J. Chem. Technol. Biotechnol., 81 (2006) 1331–1337.

[27] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol., 38 (2004) 11–41.

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

[29] M. Panizza and G. Cerisola, Direct and mediated anodic oxidation of organic pollutants, Chem. Rev., 109 (2009) 6541–6569.

[30] P. Canizares, R. Paz, C. Saez and M.A. Rodrigo, Electrochemical oxidation of alcohols and carboxylic acids with diamond anodes. A comparison with other advanced oxidation processes, Electrochim. Acta, 53 (2008) 2144–2153.

[31] M. Skoumal, C. Arias, P.L. Cabot, F. Centellas, J.A. Garrido, R.M. Rodrıguez and E. Brillas, Mineralization of the biocide chloroxylenol by electrochemical advanced oxidation processes, Chemosphere, 71 (2008) 1718–1729.

[32] I. Sirés, P.L. Cabot, F. Centellas, J.A. Garrido, R.M. Rodríguez, C. Arias and E. Brillas, Electrochemical degradation of clofibric

acid in water by anodic oxidation comparative study with platinum and boron-doped diamond electrodes, Electrochim. Acta, 52 (2006) 75–85.

[33] M. Diagne, N. Oturan, M.A. Oturan and I. Sirés, UV-C light-enhanced photo-Fenton oxidation of methyl parathion, Environ. Chem. Lett., 7 (2009) 261–265.

[34] M.A. Oturan, M. Pimentel, N. Oturan and I. Sirés, Reaction sequence for the mineralization of the short-chain carboxylic acids usually formed upon cleavage of aromatics during electrochemical Fenton treatment, Electrochim. Acta, 54 (2008) 173–182.

[35] H. Kusic, N. Koprivanac, A. Loncaric Bozic and I. Selanec, Photo-assisted Fenton type processes for the degradation of phenol: a kinetic study, J. Hazard. Mater., 136 (2006) 632–644.

[36. S. Boufia-Chergui, N. Oturan, H. Khalaf and M.A. Oturan, Parametric study on the effect of the ratio $[H_2O_2]/[Fe^{3+}]$ on the photo-Fenton degradation of basic blue 41 cationic azo dye, J. Environ. Sci. Health. A, 45 (2010) 622–629.

[37] M.A. Oturan, An ecologically effective water treatment technique using electrochemically generated hydroxyl radicals for in situ destruction of organic pollutants. Application to herbicide 2,4-D, J. Appl. Electrochem., 30 (2000) 475–482.

[38] I. Sirés, C. Arias, P.L. Cabot, F. Centellas, J.A. Garrido, R.M. Rodríguez and E. Brillas, Degradation of clofibric acid in acidic aqueous medium by electro-Fenton and photoelectro-Fenton, Chemosphere, 66 (2007) 1660–1669.

[39] M. Diagne, N. Oturan and M.A. Oturan, Removal of methyl parathion from water by electrochemically generated Fenton's reagent, Chemosphere, 66 (2007) 841–848.

[40] I. Sirés, J.A. Garrido, R.M. Rodríguez, E. Brillas, N. Oturan and M.A. Oturan, Catalytic behavior of the Fe^{3+}/Fe^{2+} system in the electro-Fenton degradation of the antimicrobial chlorophene, Appl. Catal. B, 72 (2007) 382–394.

[41] N. Oturan, E. Brillas and M.A. Oturan, Mineralization of atrazine and cyanuric acid by anodic oxidation and electro-Fenton with a boron-doped diamond anode, Environ. Chem. Lett., DOI: 10.1007/s10311-011-0337-z (in press).

[42] N. Oturan, M. Hamza, S. Ammar, R. Abdelhédi and M.A. Oturan, Oxidation/mineralization of 2-nitrophenol in aqueous medium by electrochemical advanced oxidation processes using BDD/carbon-felt cell, J. Electroanal. Chem., 661 (2011) 66–71.

[43] M. Vautier, C. Guillard and J.M. Herrmann, Photocatalytic degradation of dyes in water: case study of Indigo and of indigo carmine, J. Catal., 201 (2001) 46–59.

[44] A. Özcan, Y. Şahin, A.S. Koparal and M.A. Oturan, Degradation of picloram by the electro-Fenton process, J. Hazard. Mater., 153 (2008) 718–727.

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

[46] A. Özcan, Y. Şahin, A.S. Koparal and M.A. Oturan, Electro-Fenton removal of the cationic dye basic blue 3 by using carbon felt cathode, J. Environ. Eng. Manage., 19(5) (2009) 267–275.