



## Electrochemical degradation of aromatic amines on BDD electrodes

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### ABSTRACT

The electrochemical oxidation of four aromatic amines, with different substituent groups, 3-amino-4-hydroxy-5-nitrobenzenesulfonic acid (A1), 5-amino-2-methoxybenzenesulfonic acid (A2), 2,4-dihydroxyaniline hydrochloride (A3) and benzene-1,4-diamine (A4), was performed using as anode a boron-doped diamond electrode, commercially available at Adamant Technologies. Tests were run at room temperature with model solutions of the different amines, with concentrations of 200 ppm, using as electrolyte 0.035 M Na<sub>2</sub>SO<sub>4</sub> aqueous solutions, in a batch cell with recirculation, at different current densities (200 and 300 A m<sup>-2</sup>). The following analyses were performed with the samples collected during the assays: UV–Vis spectrophotometry, chemical oxygen demand (COD), total organic carbon (TOC), total Kjeldahl nitrogen, ammonia nitrogen, nitrates and HPLC. Results have shown a good electrodegradation of all the amines tested, with COD removals, after 6 h assays, higher than 90% and TOC removals between 60 and 80%. Combustion efficiency ( $\eta_C$ ), which measures the tendency to convert organic carbon to CO<sub>2</sub>, was also determined for all the amines, being  $\eta_{CA1} < \eta_{CA2} < \eta_{CA3} < \eta_{CA4} = 0.99$ .

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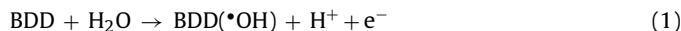
### 1. Introduction

Aromatic amines are widely applied in many industrial processes, including various steps of industrial textile processing [1,2] and as an intermediate in the production of dyes and various other chemicals [3]. Their monitorization in the environment is gaining importance due to their toxic nature and potential carcinogenic properties [4], especially the aromatic sulfonated amines, since they are very soluble in water and many of them are resistant to microbial degradation [5]. In fact, many aromatic amines produced as a result of the anaerobic azo bond reduction of dyes are known to resist to further degradation under these conditions [4,6]. Examples are aniline and sulfanilic acid that appear in liquid effluents as a consequence of biological reduction of azo dyes [7]. Consequently, aromatic sulfonated amines have been found in wastewater as well as in surface waters [4].

It is known that simple aromatic amines can be mineralized under methanogenic conditions [2,7]. However, aromatic sulfonated amines are difficult to degrade even under aerobic conditions [2]. In this context, biological treatments do not give all the answers relative to the degradation of these compounds, being necessary to find alternatives. Consequently, combining electrochemical advanced oxidation processes (EAOPs) with biological processes may be a solution to achieve the required degree of

treatment of amines-containing wastewaters, so that regulatory standards can be met [2].

EAOP based on the in situ electrogeneration of the highly reactive hydroxyl radical ( $\bullet\text{OH}$ ) are a promising environmental friendly technique and, in the last few years, anodic oxidation using high O<sub>2</sub>-overvoltage anodes such as boron doped diamond (BDD) electrodes has received much attention [3]. During the electrolysis, in the potential region of water discharge, BDD anodes enable the production of weakly adsorbed hydroxyl radicals, from water oxidation according to Eq. (1) [8]:



In fact, this hydroxyl radical being the most oxidizing species after fluorine ( $E^\circ = 2.8 \text{ V vs. SHE}$ ) is capable of promoting unselectively the mineralization of different classes of organic compounds. However, it is well known that other strong oxidizing species can also be electrogenerated in the BDD surface, such as the peroxy-derivatives coming from the oxidation of the anion of the supporting electrolyte. For instance, the peroxydisulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) results from the sulfate oxidation [9,10]. These oxidizing agents can participate in the oxidation of organic compounds in the region close to the anode surface and/or in the bulk of the solution. These electrochemical processes using BDD are able to perform chemical conversion/combustion with high current efficiency, without the additional use of reactants and, consequently, in most cases without the formation of by-products. This electrode material presents many advantages, namely, chemical inertness and extended lifetime [11]. Recent literature presents several successful applications

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of anodic oxidation using BDD on the degradation of a wide range of organic persistent pollutants. These studies in the last two decades have been compiled in numerous review papers [10,12–15].

The anodic oxidation of few aromatic amines have been studied on different anode materials and under different conditions: Pt anode was used in the electrodegradation study of aniline [16], chloroanilines [17] and 5-amino-6-methyl-2-benzimidazolone [18]; 4-amino-dimethyl-aniline hydrochloride was electrodegraded with a Ti/Ru–Ti–Sn ternary oxide coated anode [19]; Pt and Ti–TiO<sub>2</sub>/RuO<sub>2</sub> were used to degrade 1-aminonaphthalene-3,6-disulfonic acid [20]. BDD anodes were also used in the anodic oxidation of aromatic amines, like aniline [21,22], sulfanilic acid and 1-amino-2-naphthol [23], ortanilic, metanilic and sulfanilic acids [22], p-aminophenol [24] and naphthalenesulfonates [25].

This work continues a previous one [22] and its objective is to study the electrodegradation of four aromatic amines, with different substituent groups, 3-amino-4-hydroxy-5-nitrobenzenesulfonic acid, 5-amino-2-methoxybenzenesulfonic acid, 2,4-dihydroxyaniline hydrochloride and benzene-1,4-diamine, using a BDD anode, in order to understand the influence of the different groups in the structure of the aniline.

## 2. Materials and methods

3-Amino-4-hydroxy-5-nitrobenzenesulfonic acid (A1) (Aldrich, 97%), 5-amino-2-methoxybenzenesulfonic acid (A2) (Aldrich, 97%), 2,4-dihydroxyaniline hydrochloride (A3) (Aldrich, 97%) and benzene-1,4-diamine (A4) (Fluka, 97%) were used without further purification. As supporting electrolyte, 0.035 M sodium sulfate (Merck, 99.5%) aqueous solutions were used in all the degradation tests.

The electrochemical cell used in this study is composed by a BDD anode, of 8 cm<sup>2</sup> geometric area, and a stainless steel cathode, with identical area. The BDD anode was obtained from CSEM/Adamant Technologies and has a silicon substrate. Assays were performed in a batch with recirculation mode, using a PAN world magnet pump, model NH30PX, with a flow rate of 1.3 L min<sup>-1</sup>. A GW, Lab DC, model GPS-3030D, was used as power supply. All anodic oxidation assays were performed under galvanostatic conditions, with imposed current densities of 20 or 30 mA cm<sup>-2</sup>, using 200 mL of a solution containing 200 mg L<sup>-1</sup> of the respective amine.

The cyclic voltammetric measurements were performed in a potentiostat/galvanostat VoltaLab PGZ 301, in a one compartment cell, with a 1 cm<sup>2</sup> BDD electrode as working electrode, a 1 cm<sup>2</sup> platinum plate as the counter electrode and a commercial Ag/AgCl (KCl sat) as reference electrode. Voltammograms were recorded for different amine concentrations (0.2, 0.5 and 1 g L<sup>-1</sup>), at different scan rates (20, 100, 500 and 1000 mV s<sup>-1</sup>), in 0.035 M sodium sulfate aqueous solutions.

Electrochemical experiments were conducted at room temperature (22–25 °C). Degradation tests were followed by UV–Vis spectrophotometry, with absorbance being measured from 200 to 600 nm using a UNICAM Helios- $\alpha$  UV/VIS spectrophotometer. Chemical oxygen demand (COD) determinations were made using the titrimetric method with closed reflux [26]. The total Kjeldahl nitrogen (TKN), defined as the organic nitrogen plus the ammonia nitrogen, the ammonia nitrogen (AN) and nitrates (NN) were determined according to standard procedures [26]. The decrease in organic carbon content during the assays was monitored by measurements of total organic carbon (TOC), performed in a Shimadzu TOC-V CPH/CPN apparatus.

Aromatic amines and the degradation products were analysed by HPLC in a Spectra-Physics (USA) system equipped with a gradient pump, a reversed-phase column RP-18 (i.d. 4.6 mm,

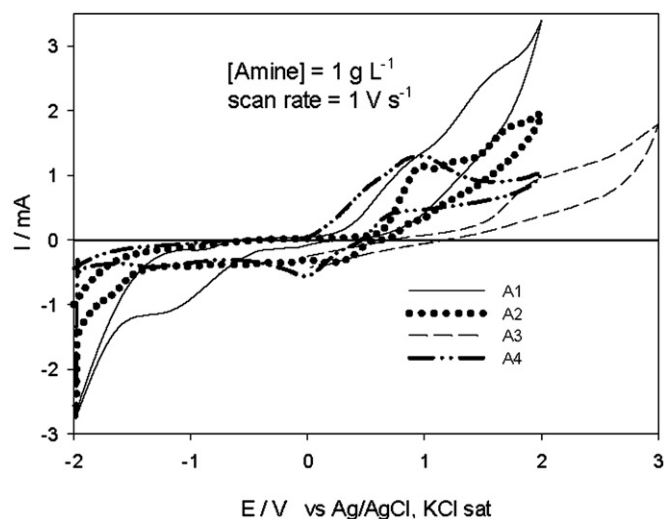


Fig. 1. Cyclic voltammograms obtained from a BDD electrode (1 cm<sup>2</sup>) as working electrode in a 0.035 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution containing 1 g L<sup>-1</sup> of the different amines. Reference electrode Ag/AgCl, KCl sat; counter electrode Pt plate (1 cm<sup>2</sup>); scan rate 0.1 V s<sup>-1</sup>.

length 250 mm, stationary phase particle size 10  $\mu$ m) and an ultraviolet–visible detector. Data were acquired at the specific wavelength of 254 nm and a phosphate buffer solution 0.15 M H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/HPO<sub>4</sub><sup>2-</sup> (70%) and methanol (30%) were used as mobile phase, with a flow rate of 0.5 mL min<sup>-1</sup>, and an injection volume of 20  $\mu$ L. The eluents and the samples were previously filtered. The identification of the compounds was achieved by comparison of the retention times to those of the respective standards. HPLC quantitative analysis was made for all the amines and qualitative for several other compounds, namely: oxalic and maleic acids, benzoquinone, hydroquinone and catechol.

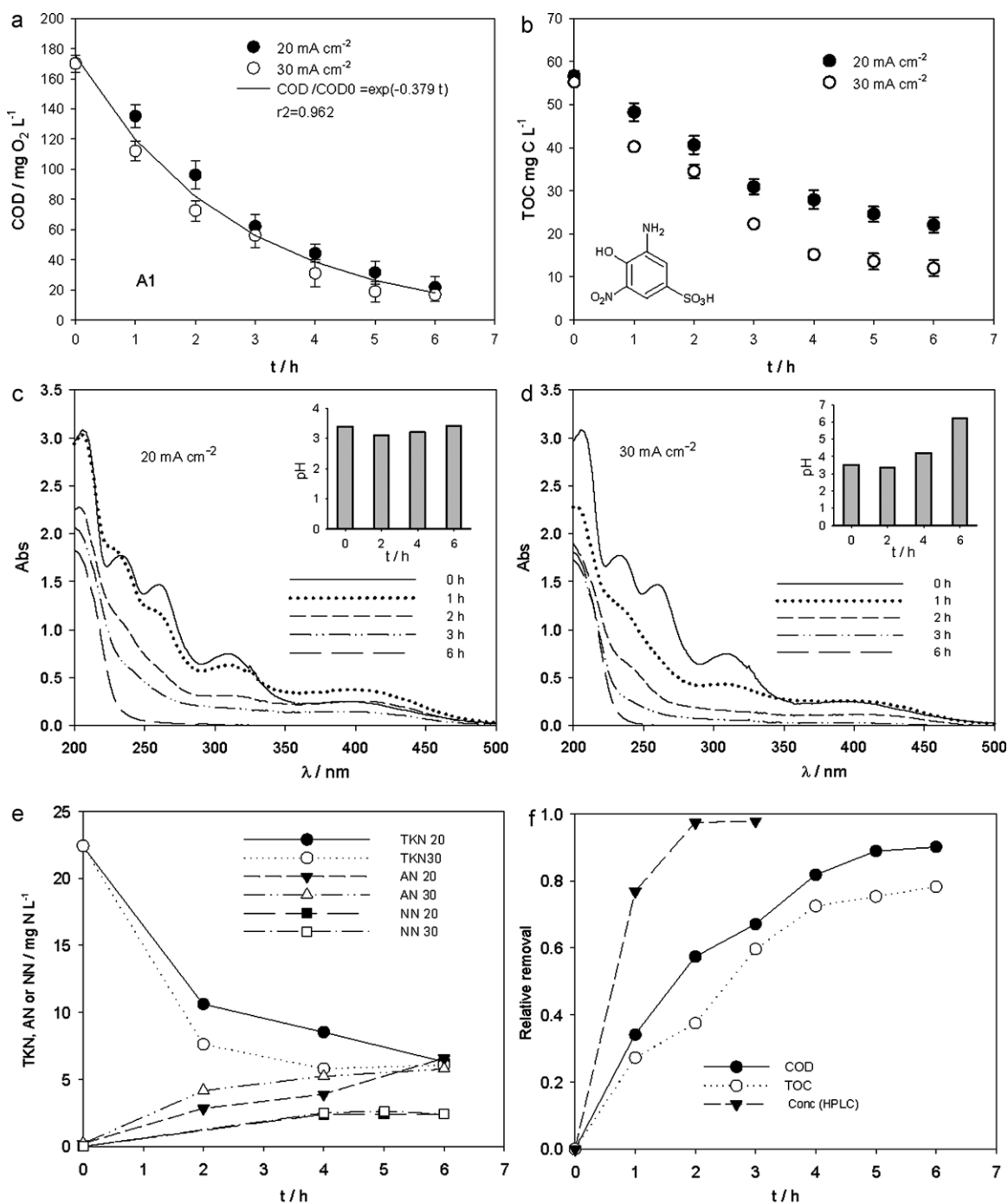
All the assays were repeated at least four times, in order to guarantee the reproducibility of the experimental results.

## 3. Results and discussion

### 3.1. Voltammetric studies

Although voltammograms were run for different amine concentrations and scan rates, the best defined peaks were obtained for the amine concentration of 1 g L<sup>-1</sup>, being the best separation of the peaks obtained for the scan rate of 1 V s<sup>-1</sup> (Fig. 1). During the voltammetric scans, only the solutions containing the amine A1 remained colourless. The solutions containing the amines A2 and A4 became pink and that with amine A3 became brown. In particular, for the amine A3, when voltammetries started at negative potentials, very high cathodic currents were obtained and the solution became almost instantly dark brown, probably due to a cathodic polymerization. This way, after cleaning carefully the working electrode, for the amine A3, the voltammetries were run only for positive potentials and only a less intense brown colour was observed.

For the amine A1 three anodic peaks are visible before oxygen evolution: the two first (at 0.6 and 1.3 V vs. Ag/AgCl, KCl sat) are due to the oxidation of the amine and the other, at 1.7 V vs. Ag/AgCl, KCl sat, corresponds to the oxidation of sulfate to persulfate [27]. Several cathodic peaks are also observed, showing a relative easiness for this amine to undergo reduction. This behavior can be a signal for low combustion efficiency, since the amine seems to be very reactive, thus suffering conversion instead of mineralization. For the amine A2, there are also three different oxidation peaks



**Fig. 2.** Variations of COD (a), TOC (b), absorbance and pH (c,d), TKN, AN and NN (e) and relative removals of COD, TOC and concentration (f) vs. time observed during the degradation assays of the amine A1, with an initial concentration of 200 mg L<sup>-1</sup>, performed with a BDD anode (8 cm<sup>2</sup>). Cathode: stainless steel (8 cm<sup>2</sup>); current density: 20 and 30 mA cm<sup>-2</sup>; electrolyte 0.035 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution.

(0.9V, 1.3V and 1.7V vs. Ag/AgCl, KCl sat), the first two for the amine and the third for the sulfate. However, the first two are closer than those for amine A1, being the first one observed at a potential higher than the one for amine A1. Regarding the negative part of the voltammogram, there is also less evidence for cathodic peaks. Amine A3, due to its tendency to polymerization, shows higher absolute currents at the beginning of the positive scan, being visible a peak at 1.5V vs. Ag/AgCl, KCl sat, besides that due to sulfate oxidation. Finally amine A4 presents an anodic peak at a potential lower than those of the other amines (near 0V vs. Ag/AgCl, KCl sat).

## 3.2. Degradation assays

### 3.2.1. Amine A1

Fig. 2 presents the results obtained for the amine A1. Although COD decay with time varies slightly with applied current density (ACD) (Fig. 2a) a common exponential equation can be adjusted within the experimental COD standard deviations. The difference in the TOC decays for the two ACDs (Fig. 2b) is enhanced when compared to that of COD, meaning that the increase in current density favor the ratio combustion/conversion, probably due to the increase in hydroxyl radicals that promotes a more intensive indi-

rect oxidation. In Fig. 2c and d the UV–Vis spectra for some of the samples collected during the degradation assays are depicted. For the lowest ACD, there is an increase in absorbance in the region between 350 and 500 nm during the first hour, simultaneously with an increase in the intensity of a yellow colour in the solution. This behavior is less pronounced for the assay at 30 mA cm<sup>-2</sup>, meaning that an increase in current density makes the formation of the intermediate that absorbs in that region more difficult. After the first hour, for both ACDs, there is a regular decay in absorbance with time. The inserts in Fig. 2c and d show the variation of pH with time for the degradation experiments. At 20 mA cm<sup>-2</sup>, the variation of pH is almost negligible, whereas for the highest applied current density an increase in pH can be observed, particularly in the last two hours of the assay. This fact must be related with the final products obtained, which rate of formation increases with current density.

Analyses to some forms of nitrogen in solution were also performed and results are presented in Fig. 2e. A sharp decrease in the TKN happens simultaneously with an increase in AN and NN. This process is enhanced by the increase in the applied current density. After 6 h run, TKN equals AN, meaning that all the organic nitrogen is in the ammonium form.

Finally, Fig. 2f compares the relative removals of COD, TOC and relative amine concentration, determined by HPLC, for the assay run at 30 mA cm<sup>-2</sup>. It is obvious that the degradation promotes a large degree of conversion of the amine into metabolites, since the amine removal rate is much higher than the TOC removal rate. However, at the end of the assay only oxalic acid, among those we have looked for, could be identified by HPLC.

### 3.2.2. Amine A2

In Fig. 3 the results obtained for the degradation of the amine A2 are presented. Within the experimental error, COD decay is independent of the ACD (Fig. 3a). On the other hand, TOC decay (Fig. 3b) shows a decrease with current density, meaning that an increase in ACD, with the consequent increase in the formation of hydroxyl radicals, favors the conversion of the pollutant into metabolites other than CO<sub>2</sub>. An evidence of this fact is also present in Fig. 3c and d, where slightly higher absorbance can be observed in the region between 340 and 400 nm for the assay run at higher ACD, probably the zone where the metabolites formed absorb. Fig. 3c and d have, as inserts, pH variation with time for the assays run at both ACDs and it can be observed that pH does not vary significantly with time or ACD.

Regarding the elimination of the organic nitrogen from the amine group (Fig. 3e), it is removed from the benzenic structure in the form of ammonium, whose rate of elimination from the solution increases with ACD. When NN results for this amine are compared with those for amine A1, a smaller concentration of NN is detected, probably due to the fact that A2 does not contain NO<sub>2</sub> as a substituent group. When the removal of COD, TOC and amine concentration, determined by HPLC, are compared, as in Fig. 3f, we can observe that the different removal rates have the following order of magnitude [A2]<sub>HPLC</sub> > COD > TOC, showing that the degree of mineralization is not complete, although it seems higher than in the case of amine A1. Like in the case of the amine A1, after 6 h assay only oxalic acid was identified as metabolite from the amine degradation.

### 3.2.3. Amine A3

Fig. 4 contains the results obtained for the degradation of the amine A3. Also for this amine, the electrodegradation seems to be controlled by diffusion, since for the ACDs used the same exponential expression can be adjusted (Fig. 4a). Regarding the results obtained for TOC variation with time (Fig. 4b), as it happened with

amine A2, an increase in ACD decreases the TOC removal rate, probably due to the reasons already presented.

The spectra depicted in Fig. 4c and d show a slight increase in absorbance for the region between 320 and 450 nm with ACD. This behavior is usually observed when the solution becomes clouded, due to the formation of dimeric and polymeric substances, with low solubility. The inserts of these figures, where the variations of pH with time are presented, for the two ACDs, show a similar increase in pH during the degradation assay. On the other hand, the removal rate of TKN and AN (Fig. 4e) seems dependent on the ACD, increasing with it. With reference to NN, its amount in solution increases with time, but only very small quantities were detected, even after the 6 h of the assay.

Finally, Fig. 4f presents the relative removals of COD, TOC and amine A3 (determined by HPLC), being the removal of the amine A3 higher than that of COD and much higher than TOC removal. This fact means that, also for this amine, the combustion is not complete after 6 h assay. In fact, for this amine after 6 h degradation, besides small amounts of the amine, hydroquinone and maleic and oxalic acids were also identified.

### 3.2.4. Amine A4

In Fig. 5, the experimental results obtained for the amine A4 are depicted. In this case, COD and TOC (Fig. 5a and b) variations are independent of ACD. However, UV–Vis spectra and pH variation with time (Fig. 4b, c and inserts) show different behaviors for the two ACDs. In fact, increases in absorbance, at wavelengths ranging from 280 to 600 nm, due to the metabolites formed during the electrodegradation, are more pronounced in the case of higher ACD, as it was also observed for the other studied amines. A decrease in pH with the duration of the assay is also observed, being more evident at lower current density. This decrease in pH is most of the times explained with the formation of carboxylic acids, usually the main products at the end of the electrodegradation of organic compounds at BDD electrodes.

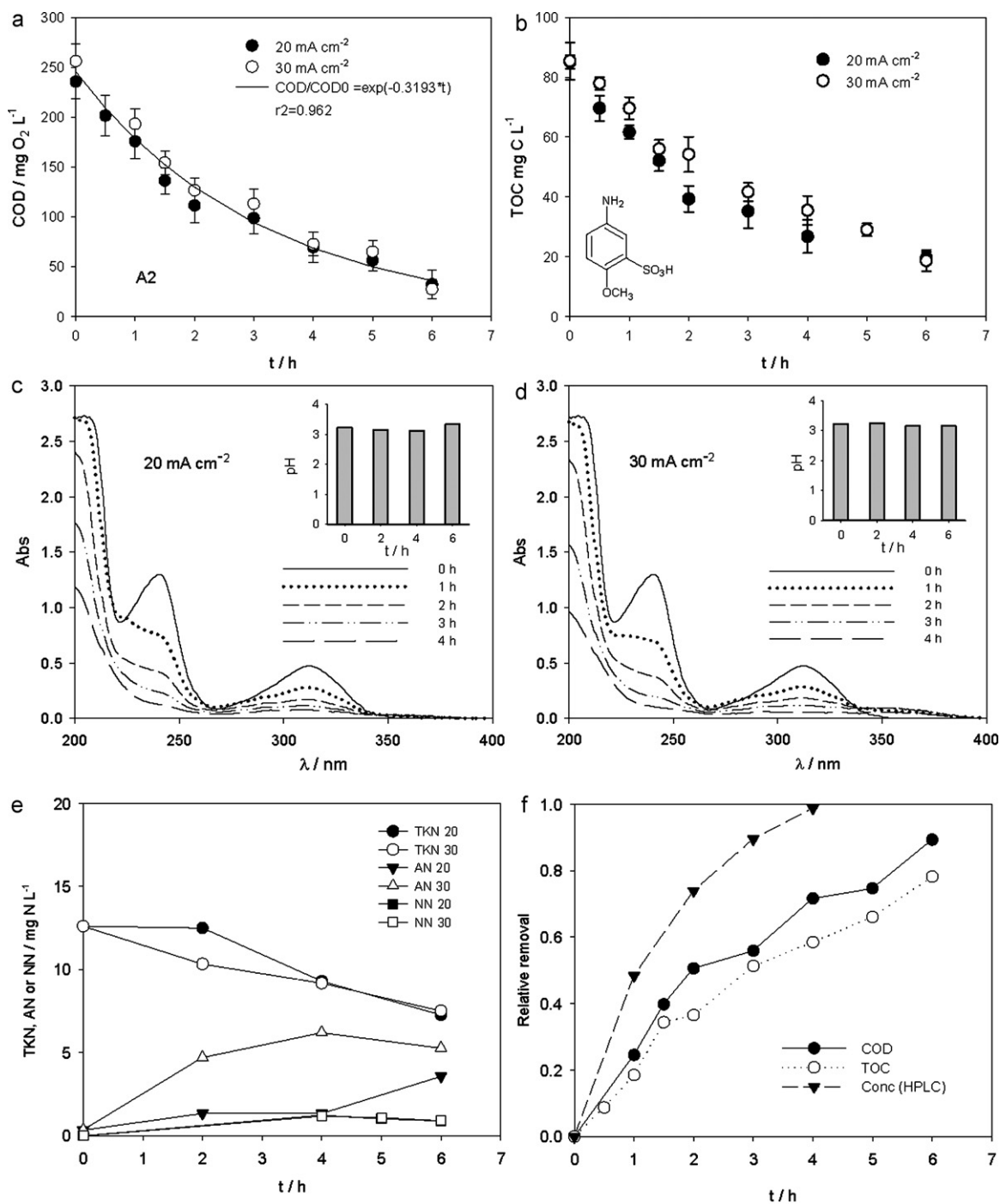
The variation of the different forms of nitrogen during the degradation are depicted in Fig. 5e and we can find a behavior in the elimination of the organic nitrogen similar to that already described for the other amines. In general, after 6 h assays, all the organic nitrogen is in the form of ammonia. In fact, for all the amines studied, there is evidence that the amine group is eliminated from the organic molecule in the form of ammonia.

When the relative removals of COD, TOC and amine concentration, determined by HPLC, are compared, we can observe more similarity among these three parameters than in any other of the former studied amines, i.e., A1, A2 and A3. This fact must be related to a higher ratio combustion/conversion, despite the evidence of new products formed during the degradation shown in the UV–Vis spectra. Although these two conclusions seem inconsistent, they can be explained if the metabolites formed during the degradation have much higher molar absorptivity than the initial pollutant, in the region of the spectrum where they absorb. The formation of metabolites during the degradation, other than those from a complete mineralization, was also identified by HPLC. In fact, at the end of the 6 h assay hydroquinone and maleic and oxalic acids were present, the first two with a bigger expression at 4 h assay.

## 3.3. Average mass transfer coefficient and combustion efficiency

When electrochemical oxidation is controlled by diffusion, average mass transfer coefficients can be calculated by fitting an exponential curve to experimental COD vs. time data, according to the equation proposed by Rodrigo and co-workers [28]:

$$\text{COD} = \text{COD}_0 e^{-(k_d A/V)t} \quad (2)$$



**Fig. 3.** Variations of COD (a), TOC (b), absorbance and pH (c,d), TKN, AN and NN (e) and relative removals of COD, TOC and concentration (f) vs. time observed during the degradation assays of the amine A2, with an initial concentration of 200 mg L<sup>-1</sup>, performed with a BDD anode (8 cm<sup>2</sup>). Cathode: stainless steel (8 cm<sup>2</sup>); current density: 20 and 30 mA cm<sup>-2</sup>; electrolyte 0.035 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution.

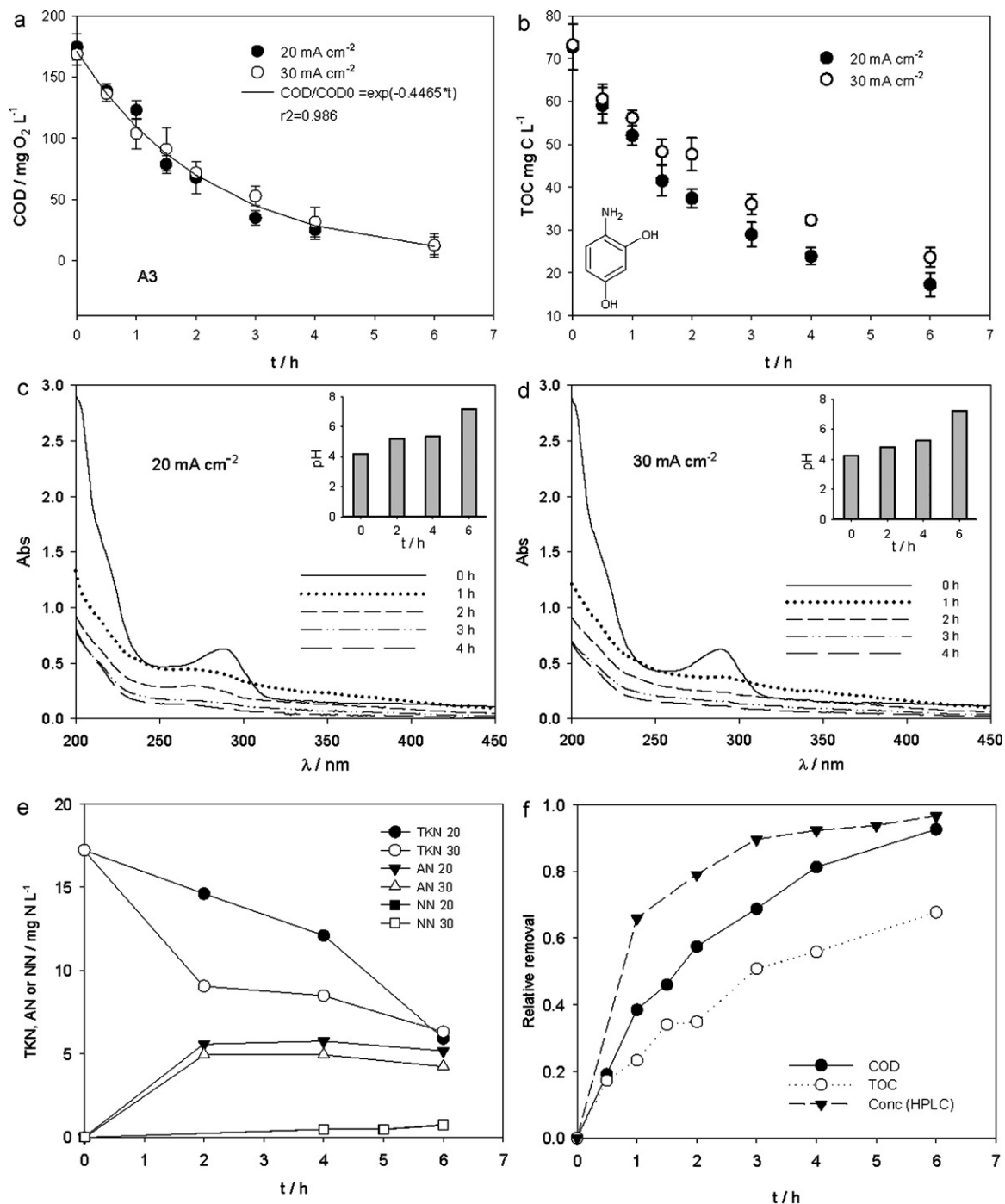
**Table 1**

Values of  $k_d$  and of the parameters for the evaluation of the combustion efficiencies of the studied amines and  $\eta_c$  values, calculated according to Eq. (3).

Amine	$k_d$ (10 <sup>-5</sup> m s <sup>-1</sup> )	$V^a$ (cm <sup>3</sup> )	$D$ (10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )	$n$	$x$	Slope (Fig. 6)	$\eta_c$
A1	2.63	124.7	9.44	18	6	0.1494	0.30
A2	2.22	138.4	8.87	32	7	0.2072	0.63
A3	3.10	88.5	11.6	24	6	0.2586	0.69
A4	3.05	93.9	11.2	26	6	0.3417	0.99

<sup>a</sup> Molar volume, calculated using ChemSketch.





**Fig. 4.** Variations of COD (a), TOC (b), absorbance and pH (c,d), TKN, AN and NN (e) and relative removals of COD, TOC and concentration (f) vs. time observed during the degradation assays of the amine A3, with an initial concentration of 200 mg L<sup>-1</sup>, performed with a BDD anode (8 cm<sup>2</sup>). Cathode: stainless steel (8 cm<sup>2</sup>); current density: 20 and 30 mA cm<sup>-2</sup>; electrolyte 0.035 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution.

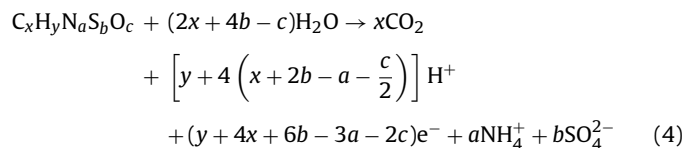
where COD and COD<sub>0</sub> are the chemical oxygen demand, in mg L<sup>-1</sup>, respectively at time  $t$  (s) and  $t=0$ ,  $A$  is the electrode area, in m<sup>2</sup>,  $V$  is the volume of the solution, in m<sup>3</sup>, and  $k_d$  is the average mass transfer coefficient, in m s<sup>-1</sup>. Table 1 includes the values of  $k_d$  calculated with the exponents of that exponential fitting presented in part (a) of Figs. 2–5. The relative magnitude of the  $k_d$  values follow the same order of that of diffusivities,  $D$ , calculated for the different amines using Wilke-Chang equation [29] and also included in Table 1. These relative magnitudes must be mainly due to the volume of the molecules, being the lower values for A1 and A2 due to the groups -OCH<sub>3</sub>, -SO<sub>3</sub>H and -NO<sub>2</sub>.

The efficiency of the combustion,  $\eta_c$ , can be estimated from the ratio between the rates of TOC and COD decrease [30], according to the equation:

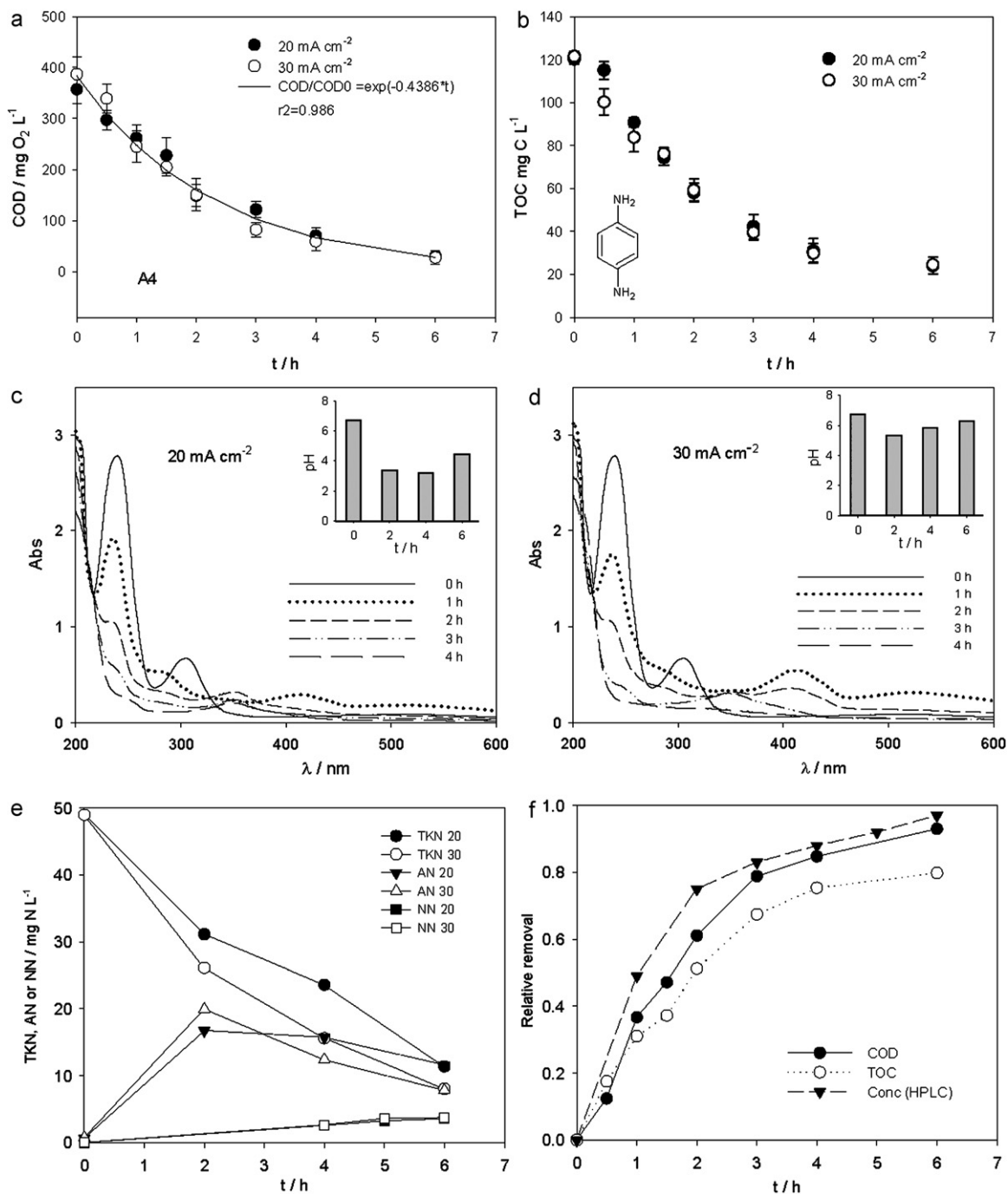
$$\eta_c = \frac{32}{12} \left( \frac{n}{4x} \right) \frac{d\text{TOC}}{d\text{COD}} \quad (3)$$

where TOC is in mg L<sup>-1</sup>, COD in mg L<sup>-1</sup>,  $n$  is the number of electrons transferred to the electrode in the process of the complete combustion of the organic solute and  $x$  is the number of carbon atoms of the organic compound. This parameter corresponds to the ratio between current used for mineralization (complete electro-

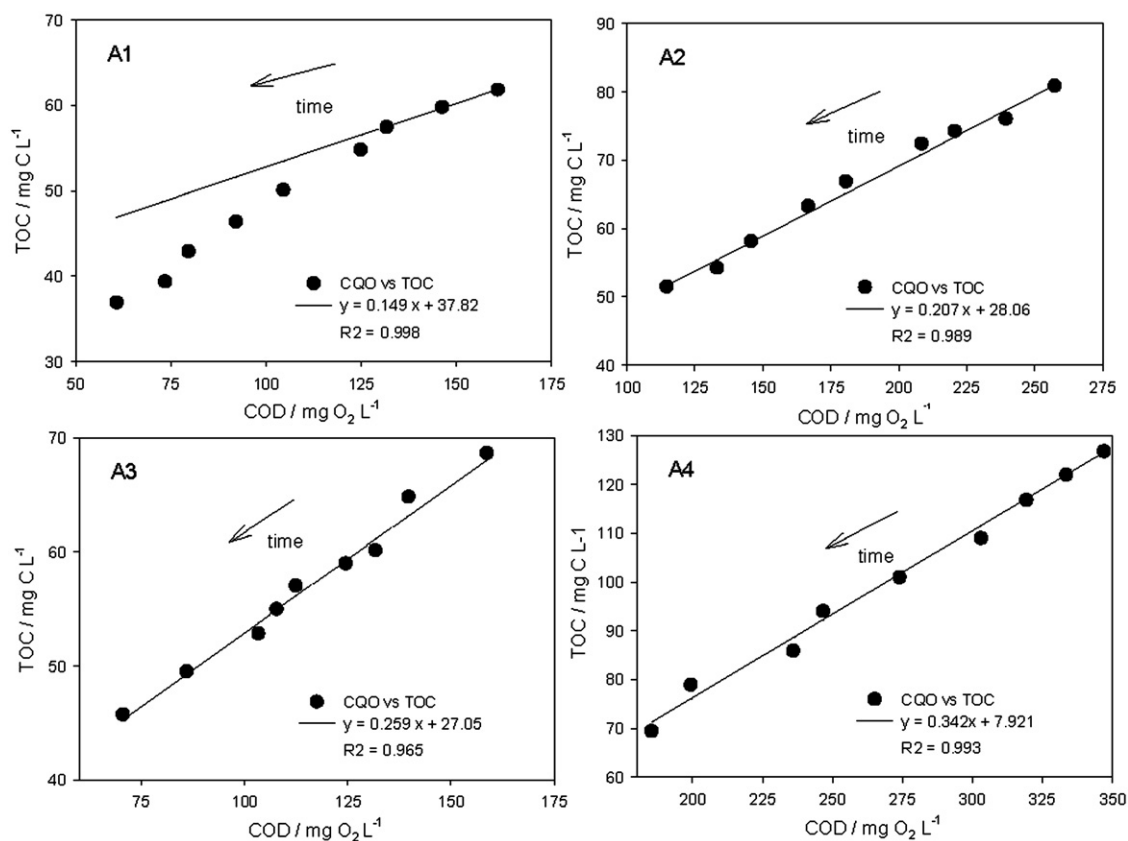
chemical combustion) and current used for oxidation (conversion) of the organic compounds. For the studied amines,  $n$  and  $x$  can be obtained from the following general equation of electrochemical combustion:



The ratio  $dTOC/dCOD$  can be obtained from the slopes of TOC vs. COD plots for the beginning of the assays, where, even when low mineralization is attained, the main organic compound present is the initial amine. This way, short assays were run, at  $30 \text{ mA cm}^{-2}$ , and samples were collected every 15 min, in order to guarantee ideal experimental conditions for the application of the model. Results are depicted in Fig. 6 and the calculated values for the combustion efficiency are presented in Table 1. This table also includes the values of  $n$ ,  $x$  and the slopes of the linear adjustment of TOC and COD data, presented in Fig. 6.



**Fig. 5.** Variations of COD (a), TOC (b), absorbance and pH (c,d), TKN, AN and NN (e) and relative removals of COD, TOC and concentration (f) vs. time observed during the degradation assays of the amine A4, with an initial concentration of  $200 \text{ mg L}^{-1}$ , performed with a BDD anode ( $8 \text{ cm}^2$ ). Cathode: stainless steel ( $8 \text{ cm}^2$ ); current density: 20 and  $30 \text{ mA cm}^{-2}$ ; electrolyte  $0.035 \text{ M Na}_2\text{SO}_4$  aqueous solution.



**Fig. 6.** TOC vs. COD evolution along amines degradation assays performed with a BDD anode ( $8\text{ cm}^2$ ) at an applied current density of  $30\text{ mA cm}^{-2}$ . Initial amine concentration:  $200\text{ mg L}^{-1}$ . Cathode: stainless steel ( $8\text{ cm}^2$ ); electrolyte  $0.035\text{ M Na}_2\text{SO}_4$  aqueous solution.

The values for the combustion efficiency of the studied amines are very different, what was already expected, facing the relative removals of COD, TOC and amine concentration, for the studied amines. Apparently,  $\eta_c$  shows an inverse variation with the number of substituent groups. This behavior was also observed in the degradation study performed with aniline and ortanilic, metanilic and sulfanilic acids [22], being aniline the amine with higher combustion efficiency. However, it was slightly lower than that of the amine A4, performed in the same experimental setup, with similar experimental conditions. This apparent incongruity may be due to the relative easiness with which the  $-\text{NH}_2$  is eliminated, leaving the amine A1 with two reacting positions for the ring opening, instead of one, as in the case of aniline.

#### 4. Conclusions

The anodic oxidation of four aromatic amines, 3-amino-4-hydroxy-5-nitrobenzenesulfonic acid, 5-amino-2-methoxybenzenesulfonic acid, 2,4-dihydroxyaniline hydrochloride and benzene-1,4-diamine was performed, using a BDD anode, with high COD and TOC removals. For the assays run with the first two amines, after 4 h no amine was detected by HPLC. For the tests with the other two amines, small amounts of the amines were still present at the end of the assay and higher combustion efficiencies were observed. Apparently, high initial amine removal rate leads to a lower degree of mineralization.

Average mass transfer coefficients were also determined and they follow the order of the diffusivity calculated for the different amines. Apparently, the substituent has an effect on the rate of degradation mainly due to its contribution to the molar volume, since diffusivity and, consequently,  $k_d$  decrease with its increase. However, the number of substituent groups seems to have a dra-

matic effect on the combustion efficiency, since the amine with only 2 substituent groups presents a  $\eta_c$  that is more than 3 times higher than the corresponding value for the amine with 4 substituent groups.

The anodic oxidation of 2,4-dihydroxyaniline hydrochloride and benzene-1,4-diamine was the only one where hydroquinone and maleic acid were identified as metabolites, after 6 h run, and were also those presenting higher combustion efficiencies. It seems that the early formation of oxalic acid reduces the ability to obtain mineralization. On the other hand, the formation of other intermediates, like hydroquinone, may lead to an easier complete combustion of the organic matter.

Analysis performed to different forms of nitrogen content led to the conclusion that the amino group is mainly eliminated in the form of ammonia, since AN content increases, while TKN decreases during the anodic oxidation.

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