

Electrochemical treatment of a simple azodye and analysis of the degradation products using high performance liquid chromatography-diode array detection-tandem mass spectrometry

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Abstract

The simple, low molecular weight, azodye acid yellow 9 (AY9) is electrochemically treated in a suitable electrolytic cell using NaCl as a supporting electrolyte, carbon fleece as cathode and platinated titanium as anode. Samples from certain time periods of treatment are analysed. HPLC–UV chromatograms demonstrate the degradation of the initial azodye, while diode array detector (DAD) spectra give evidence concerning the aromaticity of the degradation products and tandem mass spectrometry (MS²) offer structural information on some final products. In order to distinguish cathodic and anodic processes, separated cells connected with electrolytic junction are used, clarifying the oxidative and reductive decomposition pathways of the studied azodye. Several intermediate products are identified in very low concentrations such as hydrazo-derivatives, chlorinated aromatic and aliphatic compounds as well as amino- and hydroxyl-products. Experiments in separated electrolytic cells show that azodye degradation proceeds mainly oxidatively, since cathodic action is extremely limited, while treatment in common cells results in complete decoloration and presence of degradation products in very low concentration. Finally, simple degradation mechanisms are suggested based on tandem mass spectrometric identification of several degradation products.

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1. Introduction

The safe disposal of industrial wastewater requires complete and satisfactory treatment, in order to fulfil the international quality standards (Cooper, 1995; Leon et al., 2006; Yuan and Weng, 2006). Azodyes are nowadays the main category of dyestuffs; thus treatment of such waste-

waters is of crucial importance (Hao et al., 2000; Liu et al., 2005; Zhang et al., 2005). Electrochemical degradation (Hao et al., 2000; Xiong et al., 2001; Bechtold et al., 2002; Wang et al., 2004) appears as an alternative procedure in addition to the traditional methods such as biological, physicochemical, photocatalytic and ozonation treatment (Cisneros et al., 2002; Zhao et al., 2004; Deo-Mall et al., 2005; Eichlerova et al., 2005; Hsueh et al., 2005). Furthermore, electrochemical treatments offer low operation costs together with the fast and almost complete decoloration (Sakalis et al., 2005, 2006). However, decoloration must be followed by wastewaters free of any organic residues. At the same time, environmental parameters such

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as color absorbance, biological oxygen demand (BOD₅), chemical oxygen demand (COD), total organic carbon (TOC), total suspended solids (TSS) and toxicity tests, should be followed by a detailed research of the wastewater composition giving information concerning the presence and the degradation pathways of potentially harmful colorless final products.

The degradation mechanisms of azodyes during the electrochemical treatment using NaCl as supporting electrolyte are not fully described so far. However, it is known that azobond can be reduced on a cathode giving hydrazo-intermediates and aromatic amines. At the same time, free chlorine (Cl₂) or hypochlorite anions (OCl⁻) produced by oxidation of NaCl on the anode can oxidize azodye indirectly in the bulk giving other chloro-substituted aromatic products. Many products have been identified at very low levels using hyphenated techniques such as high-performance liquid chromatography with mass spectrometry (HPLC/MS) (Baiocchi et al., 2002; Sakalis et al., 2004; Vaněrková et al., 2006). Ion-pairing HPLC is already used for azodye chemical degradation products separation, while mass spectrometry is used for identification of final products (Holčapek et al., 2001; Ansorgová et al., 2003). The presence of aromatic compounds such as amines (Chung et al., 1997; Benigni and Passerini, 2002) in significant concentrations can cause harmful properties of the final wastewaters. Many authors (Manning et al., 1996; Schnell et al., 2000; Ramos et al., 2002) report that various aromatic amines, chloro-substituents of them and free chlorine as hypochlorite anions exhibit toxicity on several bacterial and microbial respirations (*Escherichia coli*, *Ceriodaphnia dubia*, *Raphidocellus subcabitata*, etc.) in a range of concentrations between µM and mM.

In this work, a simple azodye of low M_r is electrochemically treated using specially treated glassy carbon as a cathode and platinated-titanium (Pt/Ti) as an anode under similar experimental conditions to earlier publications (Sakalis et al., 2005, 2006). Furthermore, a special arrangement with separate cells containing individually the anode and the cathode is used in order to distinguish cathodic and anodic reactions. The electrochemically treated samples are analyzed with ion-pairing HPLC/DAD and HPLC/MS/MS techniques. HPLC/DAD experiments resulted in fast and easy display of aromaticity, based on UV-Vis spectra of separated final products, while HPLC/MS/MS analyses gave structural data such as chlorination and azobond cleavage. Simple degradation mechanisms are suggested based on the identification of several degradation products and the final treated solutions are described.

2. Experimental

2.1. Reagents

C.I. acid yellow 9 of chemical purity grade (95%) is obtained from Sigma (St. Louis, MO, USA). NaCl used as the supporting electrolyte is of analytical grade and

methanol is of HPLC grade, both from Merck (Darmstadt, Germany). Ultra-pure water is provided by a milli-Q system from Millipore (Jaffrey, New Hampshire, USA). The solvents are filtered through a 0.45 µm Millipore filter and degassed in an ultrasonic bath before use in HPLC. Triethylamine of the best available purity (>99%) is obtained from Aldrich (Milwaukee, WI, USA) and acetic acid (99%) from Sigma (St. Louis, MO, USA). Triethylammonium acetate (TEAA) ion-pairing reagent is prepared by mixing equimolar amounts of triethylamine and acetic acid.

2.2. Electrochemical degradation process

A 0.5 l laboratory scale Plexiglas electrolytic cell (Sakalis et al., 2006) is obtained from Institute of Physical Chemistry, University of Erlangen-Nuremberg (Germany). Batch operation is supported by compact air pumps for aeration to enhance the migration of dye molecules to the electrodes. Carbon fleece used as a cathode is Sigatherm PR201-16 model obtained from SGL Carbon Group (Germany). The carbon fleece electrode shows high porosity and large active surface area, low density and low weight, because of its loosely woven low-density structure, great stability, acid-base and redox resistance, and is not easily deactivated. The anode made of platinated titanium (Pt/Ti, 50 g Pt/m²) is obtained from Metakem GmbH (Germany) and shows stability in a wide potential range, good conductivity and resistance to redox, acidic and basic media.

Water solutions containing 5×10^{-4} mol/l acid yellow 9 and 0.2 mol/l NaCl as the supporting electrolyte are used and 12 V potential is applied between anode and cathode using a suitable homemade power supply with potential range 0–30 V and current range 0–10 A. In case of separate electrolytic cells, an appropriate electrolytic junction containing 0.2 mol/l NaCl is used, while 30 V potential is applied between the separate cells and 70 min of treatment is chosen. Sampling of the treated solution is performed regularly depending on the progress of the process as this was controlled in previous studies (Sakalis et al., 2004, 2006), using the following codes: DORIG: original azodye, D5 and D30: 5 and 30 min electrochemical degradation of the dye in common electrolytic cell, D10C and D70C: 10 and 70 min electrochemical degradation of the dye in cathodic cell, D10A and D70A: 10 and 70 min electrochemical degradation of the dye in anodic cell. The specific time of treatment is studied in previous research (Sakalis et al., 2004, 2006) and is chosen as an acceptable time of treatment for an environmentally applicable method, since it is proposed in several previous studies (Xiong et al., 2001).

2.3. HPLC/DAD/MS conditions

HPLC/UV/MS analysis is applied with the system consisted of an HP 1090 liquid chromatograph with ternary

solvent gradient pump and a UV detector (Hewlett Packard, Palo Alto, USA) coupled with a platform single quadrupole mass spectrometer equipped with ESI probe (Micromass, Manchester, UK). Negative-ion electrospray ionisation is used within 35–600 m/z range. The ESI ion source temperature is set at 100 °C and a cone voltage of 30 V is used in all experiments. The detection wavelength of 254 nm is used in all runs.

The HPLC/MS/MS system consisted of a Waters (Milford, MA, USA) liquid chromatograph assembled from a Model 616 Pump, a Model 996 diode-array UV detector, a Model 717+ autosampler and an Esquire 3000 ion trap mass spectrometer (Bruker Daltonics, Bremen, Germany). A nitrogen flow-rate of 12 l/min, temperature of 365 °C, nebulizer pressure of 48.25×10^4 Pa (70 psi), m/z range of 50–1000 in the negative-ion ESI mode, automatic measurement of MS/MS spectra with the isolation width of $\Delta m/z = 4$ and the collision amplitude of 1 V are used.

A LiChrospher C18 column (125 × 4 mm I.D., 5 μ m particle size) purchased from Merck (Darmstadt, Germany) is used for the gradient elution from 0% to 20% B in A in 20 min, with 2.5 mM TEAA in water as the solvent A and 2.5 mM TEAA in methanol as the solvent B. The column temperature is 40 °C, the flow-rate 0.8 ml/min and the injection volume 20 μ l in case of initial dyes and 80 μ l in case of samples after treatment. Finally, the column effluent was diverted to waste for the first 5 min to prevent salts contaminate the ion source of the mass spectrometer.

3. Results and Discussion

3.1. Analysis of the initial azodye

The chromatographic analysis of the untreated azodye solution (DORIG) shows a clear peak with $t_r = 12.0$ min corresponding to acid yellow 9 (Fig. 1a). The molecular weight ($M_r = 357$) is confirmed by ions observed in the first-order mass spectrum (Fig. 1b), $[M-H]^-$ at m/z 356, $[M-2H+Na]^-$ at m/z 378 and $[2M-H]^-$ at m/z 713. The dye structure is proved by the fragmentation in the ion trap analyser, as can be seen from MS² spectrum of deprotonated molecule (Fig. 1c), where the neutral losses of SO₂, SO₃, N₂ and aromatic ring are observed. Two impurities with higher retention times are identified in the sample, monosulphonated aminoazobenzene (one sulphonic acid group is missing in comparison to the original dye, $M_r = 277$) and disulphonated azobenzene (aminogroup is missing in comparison to the original dye, $M_r = 342$). (see Fig. 3, Section 3.3).

3.2. Electrochemical degradation in separate cells

In Fig. 2, HPLC–UV chromatograms of acid yellow 9 solutions treated for 10 and 70 min in separate cells are presented. Fig. 2a shows the chromatograms after 10 and 70 min of treatment in the cathodic (reductive) cell, while Fig. 2b shows the same treatment in the anodic (oxidative) cell. As shown on HPLC–UV chromatograms, cathodic

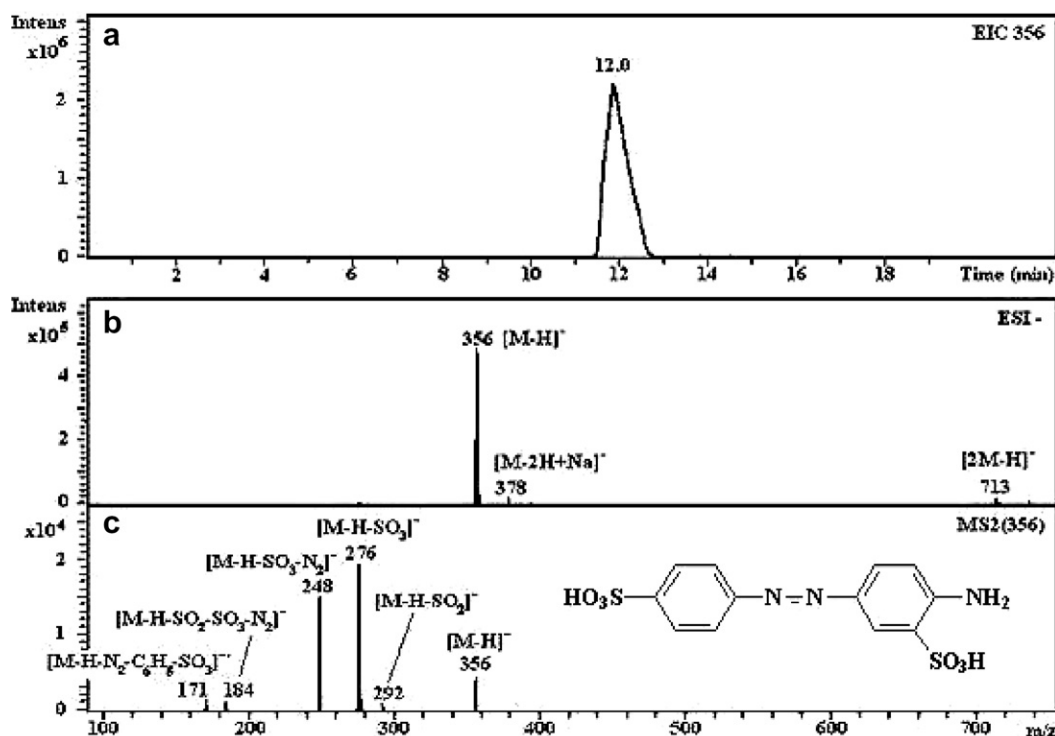


Fig. 1. LC/MS/MS analysis of acid yellow 9 untreated aquatic solution (DORIG). (a) Extracted ion chromatogram of m/z 356, (b) negative-ion ESI mass spectrum of initial azodye, and (c) MS² spectrum of m/z 356.

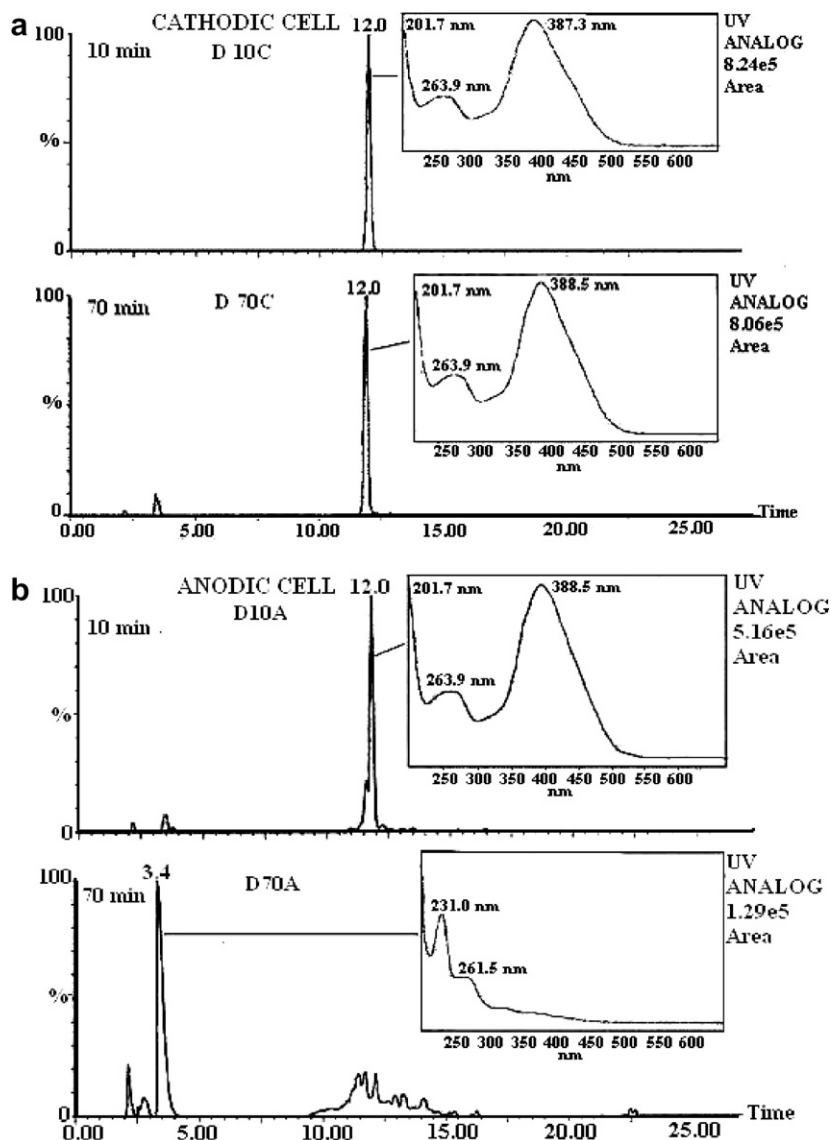


Fig. 2. UV chromatograms of acid yellow 9 treated solution for 10 and 70 min in (a) cathodic cell (D10C–D70C) and (b) anodic cell (D10A–D70A). Inset in every chromatogram is the UV spectrum of the peak noted with the retention time.

process is practically absent, since no differences are observed between 10 and 70 min of treatment. The intensity of the peak is practically constant, while UV spectra are the same supporting the conclusion that even after 70 min of treatment in the cathodic cell, the peak with $t_r = 12.0$ min corresponds exclusively to acid yellow 9 and no other product is formed. On the contrary, the reaction in the anodic cell is rather intensive, since main peak is significantly reduced already after 10 min of treatment. After 70 min of treatment, the main peak of the initial azodye disappears almost completely and new peaks of lower intensity appear that prove the formation of degradation products. The major peak with $t_r = 3.4$ min has some tailing, which indicates possible co-elution of several compounds. The early-eluted compounds are more polar than the original azodye and absorb at 231 and 265 nm, which

gives the evidence for the presence of aromatic compounds. However, the presence of co-eluting aliphatic compounds or of inorganic salts absorbing at the detection wavelength cannot be ruled out since 5 min fraction is driven to waste (see experimental part).

MS and MS² analysis presents a weak reductive process in the cathodic cell. In Fig. 3, mass chromatograms display the three most abundant peaks observed in the 70 min treated sample (D70C). The compounds with retention times 14.9 min ($M_r = 277$, fragment ions: 212-[M-H-SO₂]⁻, 196-[M-H-SO₃]⁻) and 13.5 min ($M_r = 342$, fragment ions: 313-[M-H-N₂]⁻, 277-[M-H-SO₂]⁻, 261-[M-H-SO₃]⁻, 249-[M-H-SO₂-N₂]⁻, 233-[M-H-SO₃-N₂]⁻, 169-[M-H-SO₂-SO₃-N₂]⁻) are impurities ($M_r = 277$ -monosulphonated aminoazobenzene, $M_r = 342$ -disulphonated azobenzene), because they are also detected in the untreated

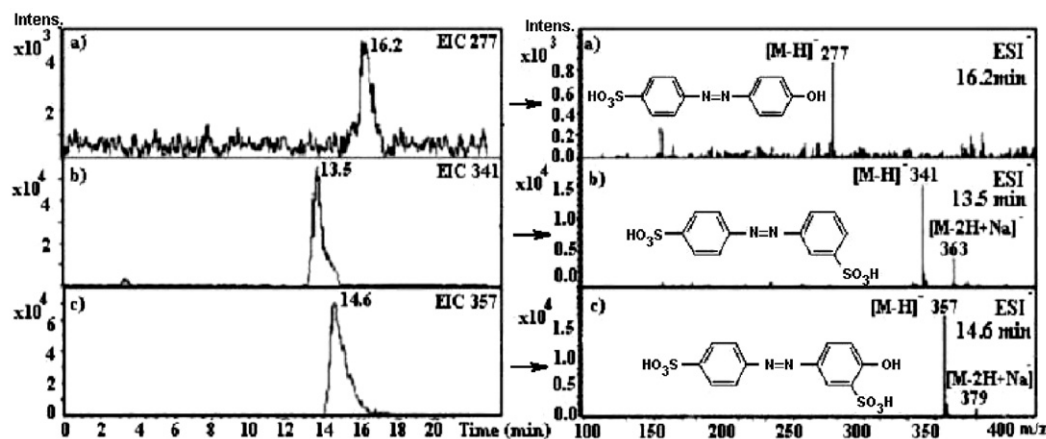


Fig. 3. LC/MS/MS analysis of sample D70C. Extracted ion chromatograms and negative-ion ESI mass spectra of compounds with (a) m/z 277, (b) m/z 341, and (c) m/z 357.

solution. Furthermore, a product with $t_r = 16.2$ min yields $[M-H]^-$ ion at m/z 277 and the same fragmentation pattern as impurity with molecular mass of 277, thus it is produced by substitution of amino with hydroxyl group. The same reaction leads to a product with $M_r = 358$ (fragment ions: $277-[M-H-SO_3]^-$, $249-[M-H-SO_3-N_2]^-$, $160-[M-H-2-SO_3]^-$, $172-[M-H-N_2-C_6H_5-SO_3]^-$) eluted in 14.6 min. The less abundant product with $M_r = 359$ (fragment ions:

$278-[M-H-SO_3]^-$, $250-[M-H-SO_3-N_2]^-$) and retention time of 12.9 min is hydrazo-compound of the initial azo-dye. Taking into consideration that UV detectors cannot identify the cathodic limited process, the concentrations of the degradation products are regarded to be very low, however complete quantitative analysis for specific compounds is necessary for clear results. Based on identified degradation products, the degradation pathway is pro-

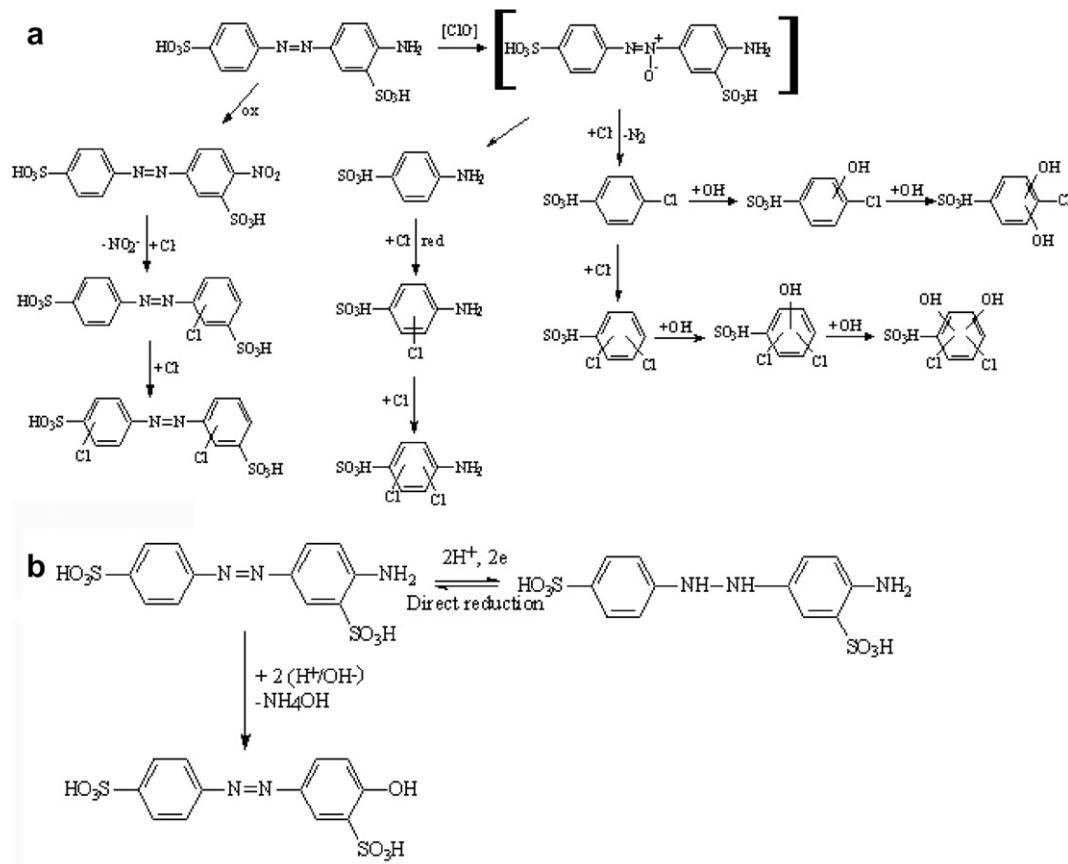
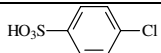
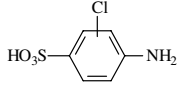
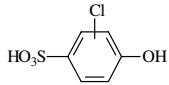
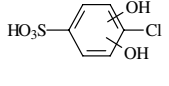
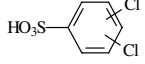
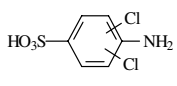
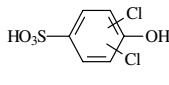
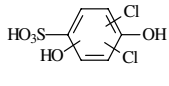
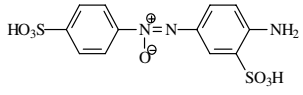
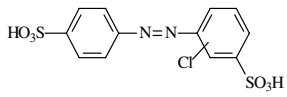
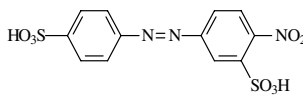
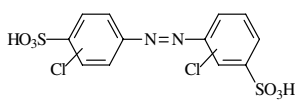


Fig. 4. Degradation mechanism under (a) anodic and (b) cathodic electrochemical treatment.

Table 1
LC/MS/MS data and proposed structures of main compounds found in the samples D10A and D70A treated under anodic conditions

M_r	t_r (min)	Information from first-order MS				Fragment ions in MS/MS (m/z -structure)	Proposed structures	Sample
		$[M-H]^-$ (m/z)	Number of Cl	Number of N	Number of SO_3H			
192	12.5	191	1	Absent or even	1	127- $[M-H-SO_2]^-$ 80- $[SO_3]^-$		D10A D70A
207	11.7	206	1	Odd	1	189- $[M-H-NH_3]^-$ 142- $[M-H-SO_2]^-$ 80- $[SO_3]^-$		D10A D70A
208	13.2	207	1	Absent or even	1	189- $[M-H-H_2O]^-$ 179- $[M-H-CO]^-$ 127- $[M-H-SO_3]^-$		D10A D70A
224	13.5	223	1	Absent or even	1	195- $[M-H-CO]^-$ 143- $[M-H-SO_3]^-$ 123- $[M-H-SO_2-HCl]^-$		D70A
226	15.4	225	2	Absent or even	1	161- $[M-H-SO_2]^-$		D10A D70A
241	14.6	240	2	Odd	1	223- $[M-H-NH_3]^-$ 176- $[M-H-SO_2]^-$ 140- $[M-H-SO_2-HCl]^-$		D10A D70A
242	17.6	241	2	Absent or even	1	223- $[M-H-H_2O]^-$ 161- $[M-H-SO_3]^-$ 141- $[M-H-SO_2-HCl]^-$		D10A D70A
258	18.2	257	2	Absent or even	1	239- $[M-H-H_2O]^-$ 229- $[M-H-CO]^-$ 157- $[M-H-SO_2-HCl]^-$		D70A
373	13.7	372	0	Odd	2	292- $[M-H-SO_3]^-$ 264- $[M-H-SO_3-N_2]^-$ 186- $[M-H-SO_3-C_6H_4NO]^-$		D10A
376	16.2	375	1	Absent or even	2	347- $[M-H-N_2]^-$ 311- $[M-H-SO_2]^-$ 231- $[M-H-SO_3-N_2-HCl]^-$		D10A D70A
387	15.8	386	0	Odd	2	340- $[M-H-NO_2]^-$ 322- $[M-H-SO_2]^-$ 248- $[M-H-SO_3-N_2-NO]^-$		D70A
410	16.8	409	2	Absent or even	2	381- $[M-H-N_2]^-$ 345- $[M-H-SO_2]^-$ 281- $[M-H-SO_2-N_2-HCl]^-$		D10A D70A

posed in Fig. 4b. It is notable that no cleavage of the azo-bond takes place under the specific cathodic conditions despite the high potential applied, probably due to stereo-chemical interferences between azodye and cathode surface. Based on the above results, no significant changes can be observed for time of treatments longer than 70 min.

On the other hand, MS and MS² analysis of samples treated under anodic conditions (D10A–D70A) shows an intensive electrochemical reaction. Table 1 presents HPLC/MS and HPLC/MS/MS data for some of the most

significant degradation products treated in anodic cell. Electrochemical reactions on anode are efficient, produce many degradation products (Table 1) and almost completely remove the original dye. Azobond is oxidatively cleaved under strong oxidative conditions either in the bulk by free chlorine and hypochlorite anions (Appelbaum et al., 2001; Sakalis et al., 2004, 2005, 2006; Szpyrkowicz et al., 2005; Lopez-Grimau and Gutierrez, 2006) or directly via the anodic electron transfer reaction after adsorption of the azodye on the anode surface (Rajkumar and Jong,

2006). It is assumed that both mechanisms proceed via azoxy-intermediate product since the azoxy-intermediate product of AY9 ($M_r = 373$, $[M-H]^-$ at m/z 372) is identified (see Table 1). It is interesting that this intermediate is detected only after 10 min of treatment (D10), because it is further degraded to amino-, nitro and hydroxy-chlorinated products, according to the scheme presented in Fig. 4a. As a result, almost colorless wastewater is produced, either because most of the products do not absorb at the visible spectral region or their final concentrations are very low.

At the same time, anodic chlorination of aromatic rings is increased during the treatment time. Mono- and di-chlorinated aromatic products are found either in D10A and D70A samples (Table 1). In a similar way, product with $M_r = 387$, which corresponds to the oxidized initial dye (NH_2^- oxidized to NO_2^-), is detected only after 70 min of treatment (sample D70A). The chlorination generally proceeds via either anodic electrochemical reaction or electrophilic substitution (Rajkumar and Jong, 2006).

Although, most of these compounds have rather low concentrations as seen during the interpretation of the spectra, their presence results in problematic final wastewaters and toxicological investigation for some of these potentially harmful compounds is necessary (Ramos et al., 2002).

3.3. Electrochemical degradation in common cell

The treatment of AY9 in a common electrolytic cell resulted in colorless final solution. It is clear that the initial azodye is significantly reduced in 5 min (Fig. 5a, peak with $t_r = 13.8$ min) of treatment and completely decomposed in 30 min (Fig. 5b). In the same time, several compounds with $t_r < 5$ min are produced, together with some additional products of low concentration with t_r between 10 and 19.5 min. It is notable that the measured signal intensities in normalized chromatograms (intensity %) is reduced from initial 1.47×10^6 (original dye- 5×10^{-4} mol/l, not shown) to 1.05×10^5 in 5 min (Fig. 5a) and to 5.56×10^4 in 30 min (Fig. 5b), resulting in a reduction of 96%. Peak

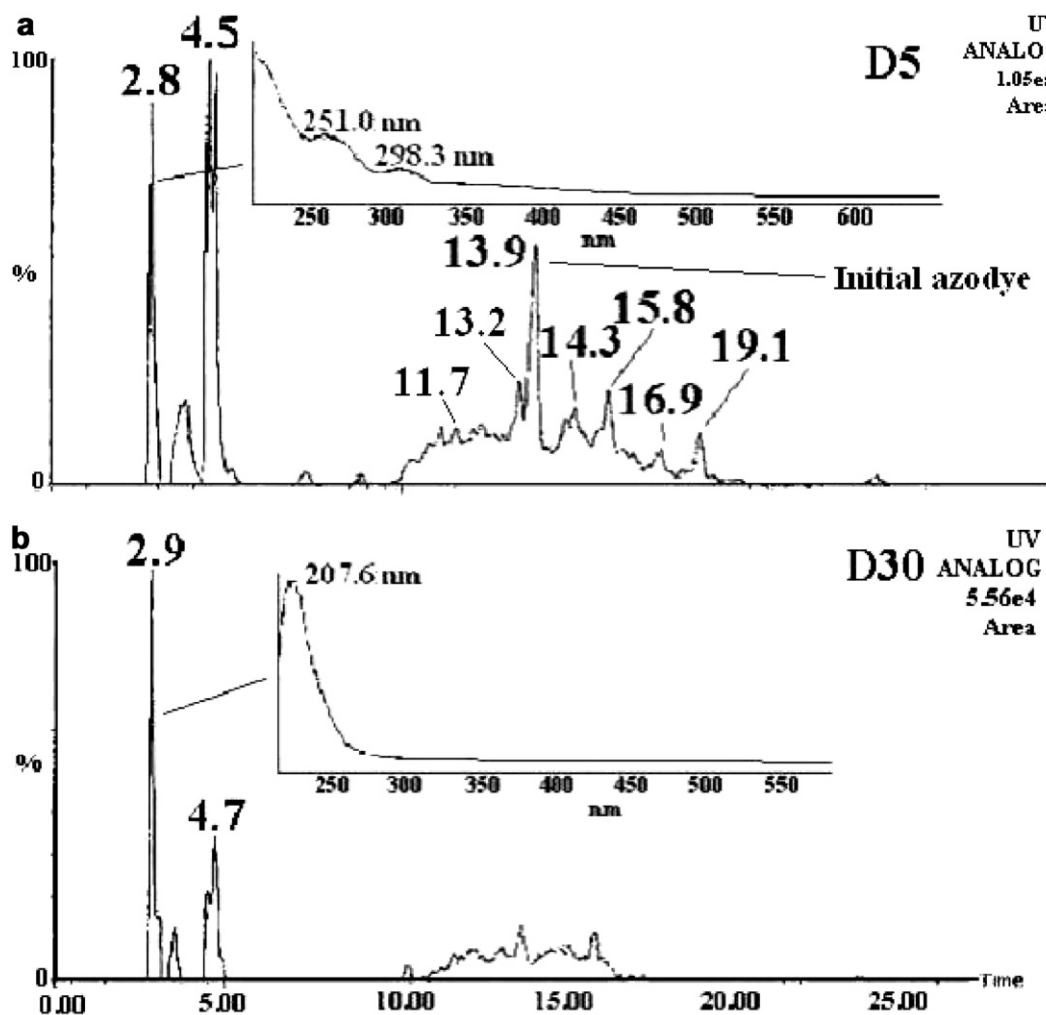


Fig. 5. UV chromatograms of AY9 treated in common electrolytic cell for (a) 5 and (b) 30 min. Inset: UV spectra for peak with $t_r = 2.8$ min and $t_r = 2.9$ min.

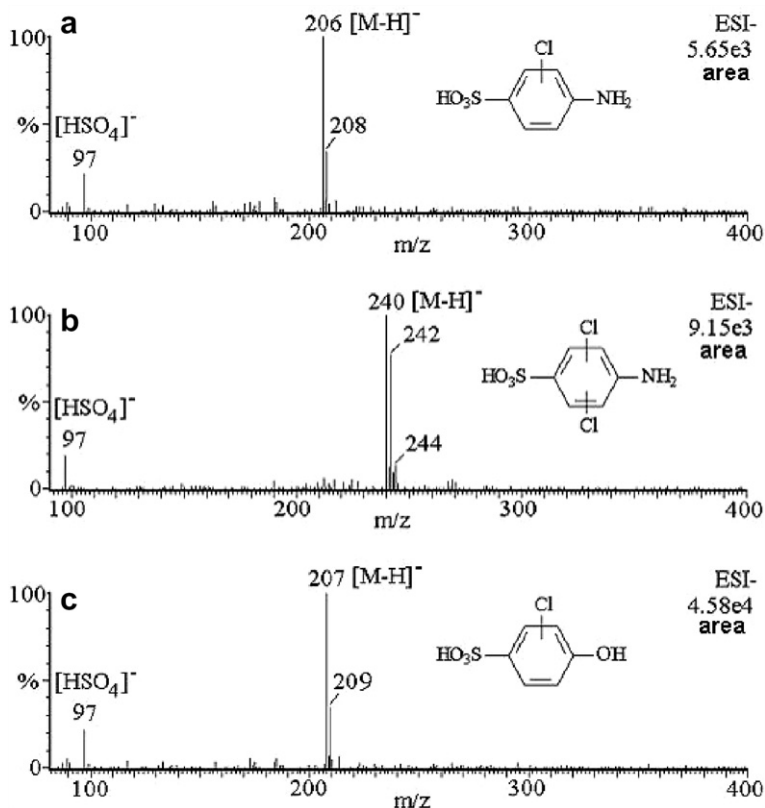


Fig. 6. Normalized negative-ion ESI mass spectra of degradation products with (a) $t_r = 11.7$ min, (b) $t_r = 14.6$ min, and (c) $t_r = 13.2$ min, after 5 min of treatment in common electrolytic cell.

with $t_r = 2.8$ min probably belongs to several compounds which are co-eluted within a very short period of time. These compounds exhibit a very interesting UV-spectrum (251.0 nm, 298.3 nm), indicating the possible presence of aromatic compounds, together with inorganic compounds absorbing the UV-spectra (Fig. 5a, inset diagram). However, these absorptions are not presented after 30 min of treatment (Fig. 5b, inset diagram), indicating both the possible cleavage of aromatic structure and the elimination of UV absorbing inorganic anions. The presence of such inorganic and aliphatic organic compounds has already been reported (Sakalis et al., 2004). The other group of early eluting unresolved co-eluting peaks ($t_r = 4.5$ min) diminishes during the treatment. Overall, the initial azodye is rapidly decomposed mainly through azobond cleavage, chlorination and aromatic ring cleavage, resulting in high concentrations of inorganic and aliphatic organic products with lower retention times, together with lower concentrations of aromatic products with retention times between 10 and 19.5 min. The aromatic character of these products is proved by their MS spectra (Fig. 6) and their chlorination is an expected consequence, since significant amount of NaCl is used as the supporting electrolyte. Other identified products are similar to those found after the treatment in anodic cell only. Thus, after 30 min of treatment in common cell, low concentrations of several degradation products are identified, indicating that probably longer times

of treatment for further reduction of their concentrations should be applied.

4. Conclusions

The electrochemical treatment in separate cells provides the potential to distinguish the electrochemical reactions taking place on the two electrodes. Limited cathodic reactions occur under reductive conditions, resulting in low concentration products of azobond hydrogenation and substitution of amino with hydroxyl substitute. On the contrary, anodic electrochemical processes lead to almost complete azodye decomposition, oxidative azobond cleavage, strong chlorination and oxidation of aminogroups together with the aromatic ring cleavage and aliphatic organic products formation in very low concentrations. Similar reaction is observed during the treatment in common electrolytic cell though with greater intensity and rate of degradation due to the absence of the electrolytic junction resulting in complete decoloration and presence of degradation products in very low concentration. MS² detection provides structural data for the proposal of simple degradation mechanisms. HPLC with DAD detector is useful for a rapid and simple estimation of aromaticity in treated wastewaters. Finally, MS data must be obtained for the early-eluted degradation products, together with suitable toxicological tests and quantitative analysis for the most

efficient and complete characterization of the treated azo-dye solution.

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