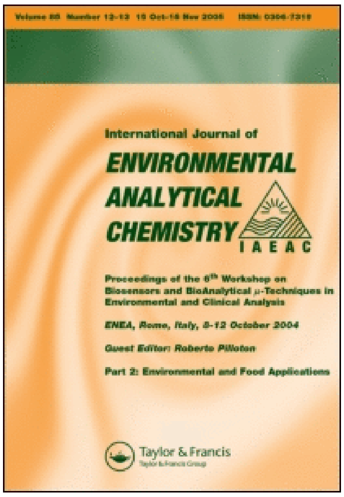

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ANALYSIS OF SULPHONATED AZODYES AND THEIR DEGRADATION PRODUCTS IN AQUEOUS SOLUTIONS TREATED WITH A NEW ELECTROCHEMICAL METHOD

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Aqueous solutions of four sulphonated azodyes, Reactive Orange 91, Reactive Red 184, Reactive Blue 182 and Reactive Black 5, containing 0.2 mol/L of electrolyte were treated in a laboratory scale electrolytic cell with a new electrochemical method intended for the textile wastewater treatment. The electrochemical process was monitored by means of absorbance of UV-Vis light and chemical oxygen demand values. Carbon fleece was used as a cathode, and platinated titanium was used as an anode. Reversed-phase high-performance liquid chromatography coupled with photodiode array and mass spectrometric detectors was applied for the analysis of dyes, their impurities and degradation products after the electrochemical treatment. Dihexylammonium and triethylammonium acetate as ion-pairing reagents, or alternatively ammonium acetate as an ion-exclusion suppressing reagent, were used to improve the separation.

Keywords: Azodyes; Electrochemical treatment; Liquid chromatography; Mass spectrometry; Degradation

INTRODUCTION

Azodyes are used as the main category of dyestuffs in the textile industry [1]. These compounds are decomposed in wastewater with extreme difficulty, since they are very resistant to biodegradation, mainly due to stereochemical interferences. Regardless of their incomplete biodegradation, the biological treatment is still the most widely applied method [2–4]. Other conventional methods, such as photochemical/chemical degradation and ozonation, are rather expensive with possible generation of harmful intermediates, whereas the application of synthetic polyelectrolytes as adsorptive materials produces solid waste material that is difficult to treat further [5–9].

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The electrochemical treatment is a relatively new trend in the azodyes wastewater management, giving very promising results [10–12]. Concerning the quality of the treated wastewater, only bulk properties are usually monitored, such as pH value, temperature, chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC) and total suspended solids (TSS). These parameters can only generally characterize the treated wastewater, but they do not provide any information about the composition and concentration of final degradation products, even though many of them may exhibit highly toxic and carcinogenic properties. No systematic research has been performed on the final degradation products in treated textile wastewater, except for some recent applications of mass spectrometry [13–20].

In this work, a novel electrochemical method for textile wastewater treatment is described, and the decoloration process in synthetic wastewater samples is discussed. Further, the conditions for the separation of the initial dyes from impurities by ion-pairing high-performance liquid chromatography (HPLC) are optimized, and coupling of HPLC with mass spectrometry (HPLC/MS) is used to determine the molecular mass and characterize the degradation products in the final wastewater. Based on the results of the HPLC/MS experiments, the aromatic character and presence and number of chlorine atoms in the products of electrochemical degradation can be determined. The proposed methods can be useful for further elucidation of the structures of the degradation products and subsequent recognition of the degradation mechanisms of polysulphonated azodyes.

EXPERIMENTAL

Materials and Reagents

The Sigatherm PR201-16 carbon fleece was obtained from SGL Carbon Group (Germany). The platinated titanium ($50\,\mathrm{g\,Pt/m^2}$) anode was obtained from Metakem GmbH (Germany). The plexiglas laboratory scale electrolytic cell was obtained from the Institute of Physical Chemistry, University of Erlangen-Nuremberg (Germany). All dyes used were of commercial purity grade. Reactive Orange 91(trade name Cibacron Yellow F-3R), Reactive Red 184 (Cibacron Red FB) and Reactive Blue 182 (Cibacron Blue FR) were obtained from Ciba Co. (Switzerland). Reactive Black 5 (Remazol Black B 133X) was obtained from DyStar Textilfarben GmbH & Co. (Germany KG). All salts used as electrolytes were of analytical purity grade and were obtained from Merck (Darmstadt, Germany). Methanol for HPLC was purchased from Merck. Water was doubly distilled in glass in the presence of potassium permanganate. The solvents were filtered through a 0.45-μm Millipore filter prior use and degassed in an ultrasonic bath before use in HPLC with UV detection or by continuous stripping by a stream of helium in the HPLC/MS experiments. The ion-pairing reagents triethylamine and dihexylamine of the best available purity (> 99%) were obtained from Aldrich (Milwaukee, WI, USA) and acetic acid (99%) from Sigma (St. Louis, MO, USA). Ammonium acetate (> 99%) was obtained from LaChema (Brno, Czech Republic).

Triethylammonium acetate (TEAA) was prepared by mixing equimolar amounts of triethylamine and acetic acid. Dihexylammonium acetate (DHAA) was prepared by mixing equimolar amounts of dihexylamine and acetic acid. The mobile phases were prepared by dissolving appropriate amounts of ion-pairing reagents in water or in aqueous methanol. All mobile phases containing ammonium acetate (AA) were filtered again through a 0.45-μm Millipore filter prior the use.

All samples were filtrated through a PTFE 0.45-μm filter before HPLC injection (Titan, Czech Republic).

A LiChrospher C18 column (125 × 4 mm I.D., 5 μm particle size) was used for the isocratic elution, and a LiChrospher C18 column (250 × 4 mm I.D., 5 μm particle size) was used for the gradient elution, both purchased from Merck.

Instrumentation

The capacity of the laboratory-scale electrolytic cell was 0.5 L. The aeration was normally provided by a central aeration system or alternatively by compact air pumps initially manufactured for aquariums.

The carbon fleece plate was a specially treated and modified carbon with dimensions 120 × 70 × 3 mm with a high porosity and large active surface area, low density and low weight, because of its loosely woven low-density structure. This type of electrode shows a great stability, shows acid, base and redox resistance, and is not easily deactivated. Platinum is a material with rather good characteristics, such as a wide potential range of stabilities, good conductivity and resistance to redox, acidic and basic media, but it is very expensive for use as an electrode. Instead, much cheaper platinated titanium (Pt/Ti, offering similar properties) was used. This electrode consisted of titanium as a substrate, covered with a thin film of platinum, and had three parallel wires of platinated titanium settled on a plastic frame, providing a high current density and good mixing of the solution in the electrochemical cell. The diameter and length of the wires were 1.2 and 115 mm, respectively.

A home-made power supply was used to apply the potential in the range 0–30 V on to the cell. The temperature and pH values were measured using a Hanna Instruments pH-meter equipped with a temperature sensor, while the current was measured by an amperometer connected to the power supply. A Jasco model V-530 (Japan) spectrophotometer was used together with a cell with a 1-cm optical path length to measure the UV spectra.

A chromatographic system consisting of an isocratic pump, model LCP 4020 from Ecom (Czech Republic), a column oven model LCO 101 from Ecom and a single-wavelength UV detector model 440 (Waters, Milford, MA, USA) was used to separate the original dyes from impurities and to optimize the ion-pairing mobile phases on electrochemically treated samples. An Esquire 3000 ion trap mass analyser from Bruker Daltonics (Bremen, Germany) was used to analyse direct infusion of the initial dyes. The gradient elution HPLC/MS instrumentation used for the analysis of electrochemically treated samples consisted of a Model 616 Pump, a Model 996 diode-array UV detector (PDA), a Model 717+ autosampler (Waters, Milford, MA, USA) and a Platform single quadrupole mass spectrometer equipped with electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) probes (Micromass, Manchester, UK). The in-source collision-induced dissociation (CID) mass spectra of the quasi-molecular ions were measured by increasing a positive or negative voltage of the cone electrode, as specified in the Methods section.

Methods

Electrochemical Treatment

The procedure was based on batch operation, and the aeration of the solution proceeded from the bottom of the electrolytic cell, thus ensuring a better and quicker transport of the dye molecules to the electrode surface. Two different electrode arrangements were used. In the first arrangement, two electrodes, one cathode and one anode, were accommodated in the electrolytic cell. The distance between them could be varied from 2 to 6 cm. In the second arrangement, five electrodes, three cathodes and two anodes were accommodated in the electrolytic cell in alternating order, with a distance of 2 cm between electrodes.

Synthetic samples containing 5×10^{-4} mol/L of individual azodyes and a suitable concentration of electrolyte (0.2 mol/L NaCl) were used in all experiments. This concentration represented the salt concentration of a typical textile wastewater and was adequate for satisfactory conductivity. Furthermore, it was an optimal value combining the least possible production of unwanted ClO^- anions, together with an adequate decoloration rate and well-controlled electrochemical conditions, such as current, potential and temperature. All dyes and electrolytes were diluted in tap water. A suitable potential ranging from 10 to 18 V was applied between anode and cathode, and the treated solution from the electrolytic cell was sampled every 5 or 10 min, depending on the progress of the experimental process, indicated by the online measured values of pH, temperature and current, as well as by the rate of decoloration observed. For each sample, the UV-Vis spectrum was recorded as well as the COD, and the concentrations of chlorides and hypochlorites were measured according to standard methods [21].

Separation of the Initial Dyes from Impurities and Identification of Their Structures

To separate the original dyes from their impurities, a simple isocratic ion-pairing liquid chromatographic system equipped with a single-wavelength detector set at 254 nm was used, using mobile phase with 2.5 mmol/L DHAA in a suitable percentage of aqueous methanol (optimized to accomplish a good separation of the impurities from the original dyes in acceptable time). The flow rate was 1 mL/min, the column temperature was 40°C, and the injection volume was 10 μL.

The negative-ion ESI mass spectra of initial azodyes were measured for the structure confirmation under the following conditions: mass range m/z 50–1200, fragmentation amplitude 0.6 V, nebulizer pressure 10 psi (69 kPa), drying gas flow 4 L/min and drying gas temperature 300°C. The compounds were dissolved in 80 : 20 (v/v) water/methanol and directly introduced into the mass spectrometer at a flow rate of 5 μL/min.

Separation and Characterization of Final Degradation Products

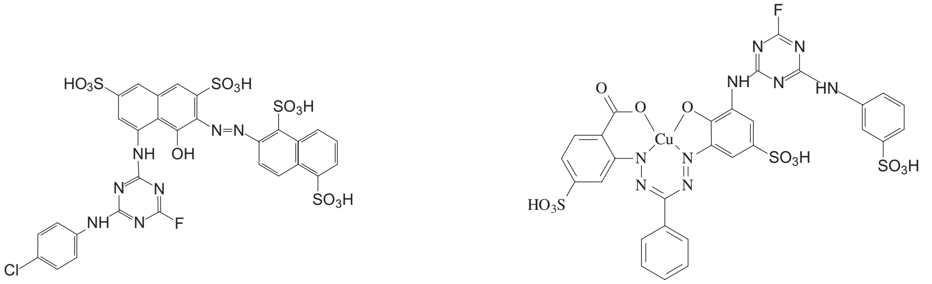
To optimize the separation conditions for the final degradation products occurring in the decomposed dye solutions after 30 min of treatment, DHAA, TEAA ion-pairing reagents and AA ion-exclusion suppressing reagent in methanol/water were used as the mobile phases (1 mL/min flow rate, 40°C column temperature and 10 μL injection volume).

The gradient ion-pairing HPLC method was optimized on the basis of the data obtained from the isocratic experiments of the electrochemically treated samples. The optimized gradient program has a relatively wide percentage range, since highly polar compounds require a very low methanol concentration to achieve a reasonable retention, while non-polar degradation products require the very high concentration of methanol to be eluted. UV spectra recorded with PDA detector were used to evaluate the aromaticity in the electrochemically treated samples. The column temperature was set at 40°C, and the injection volume was 80 µL. The following gradient program was used for the separation: 0 min – 100% A, 8 min – 100% A, 25 min – 100% B and a final 10 min hold-up period with 100% B for a 0.5 mL/min flow rate or alternatively 0 min – 100% A, 15 min – 100% A, 50 min – 100% B and a final 10 min hold-up period with 100% B for a 0.2 mL/min flow rate. The solvent A was 5 mmol/L of AA in water and the solvent B was 5 mmol/L of AA in methanol. The final method is a compromise between the acceptable analysis time and the separation selectivity and can be modified by the steepness of the gradient.

To characterize the final degradation products, the optimized gradient ion-pairing HPLC method was used with a Platform single-quadrupole mass-spectrometric detector with atmospheric pressure chemical ionization (APCI) in both negative- and positive-ion modes. The injection volume was 80 µL, the flow rate was 0.5 mL/min, and the column temperature was 40°C. For both modes, the source temperature was 100°C, the APCI probe temperature was 400°C, and the scan range was *m/z* 12–600. The cone voltage was 10 V for positive-ion mode, 20 V for negative-ion mode and 40 V for in-source CID.

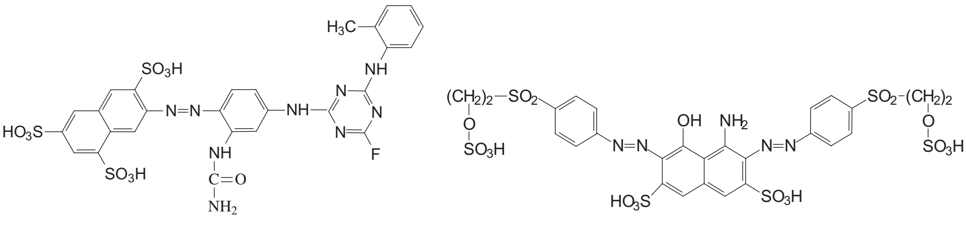
RESULTS AND DISCUSSION

The structures of the azodyes are shown in Fig. 1. All of them are reactive azodyes containing three or four sulphonic acid groups for good water solubility. Reactive Orange 91, Reactive Red 184 and Reactive Blue 182 contain one fluoro-triazine ring,



I. REACTIVE RED 184

II. REACTIVE BLUE 182



III. REACTVE ORANGE 91

IV. REACTIVE BLACK 5

FIGURE 1 Structures of the four azodyes studied.

whereas Reactive Black 5 contains two (–SO_2–$(CH_2)_2$–O–) groups. Both groups provide a strong adherence to the textile substrate.

Decoloration Process

The experiments under optimal electrolysis conditions resulted in fast and almost complete decoloration for all dyes after 30 min of treatment, as shown in Fig. 2. The percentage removal of the color was 99.9% for Reactive Blue 182, 99.4% for Reactive Black 5, 97.2% for Reactive Orange 91 and only 93.4% for Reactive Red 184. The degree of decoloration was monitored at the wavelength of the maximum absorbance of each dye. The reduced color removal for the red dye can be attributed to the different electrode arrangement, since it was the electrolytic cell with one anode and one cathode. Therefore, the arrangement with two anodes and three cathodes certainly is more efficient than the previous one.

The time profiles of additional parameters such as temperature and pH were measured online and are presented in Table I. Furthermore, in Table I, some crucial environmental parameters such as COD, chloride and hypochlorite concentrations, as well as color removal are presented, concerning the electrochemical treatment of Reactive Orange 91 synthetic wastewater. The value of pH was almost neutral (6.8) after 30 min of treatment. This is a very satisfactory result since the finally treated wastewater should be neutralized prior to the environmental disposal. Temperature shows a small increase during the treatment, but this increase is not harmful for the environment (see Table I). The electric current is initially decreased from 1.82 A to 1.37 A and then becomes constant during the treatment until a final value of 1.46 A, which indicates a good control of the process and gentle electrochemical conditions. The COD is decreased up to 73.7% of the original value after the treatment. The chloride concentration is also decreased, indicating the generation of hypochlorite anions up to 40 mg/L. Hypochlorites are very important for the decoloration process as

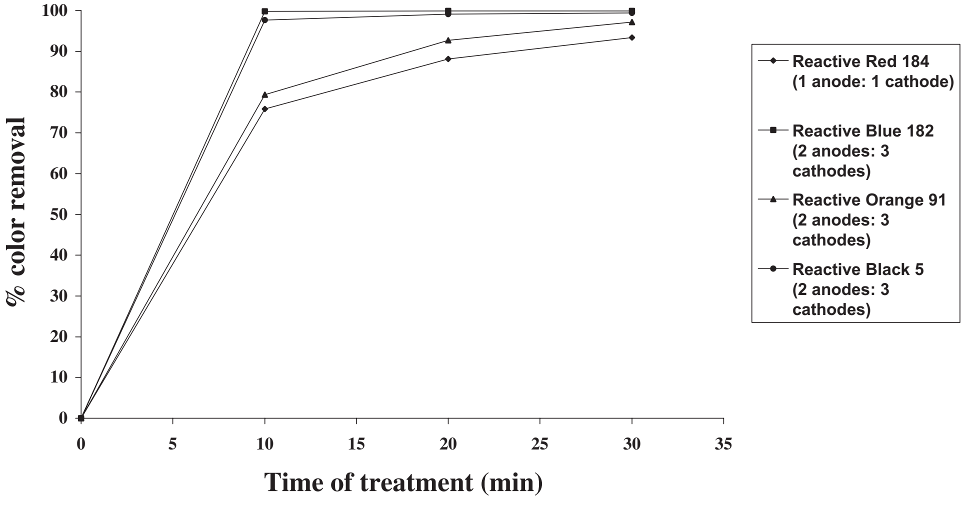


FIGURE 2 Percentage removal of the dyes during the electrochemical treatment. Measured λ_{max}: Reactive Red 184: 550 nm; Reactive Blue 182: 610 nm; Reactive Orange 91: 442 nm; Reactive Black 5: 488 nm. Time of treatment: 30 min.

TABLE I Environmental parameters of the initial and final synthetic wastewater of Reactive Orange 91 (time of treatment: 30 min)

	Initial value	*Final value*
PH	6.2	6.8
Temperature (°C)	19.5	22.0
COD (mg/L)	190	50
Chlorides (mg/L)	7040	6220
Hypochlorites (mg/L)	–	40
Percentage color removal	0	97

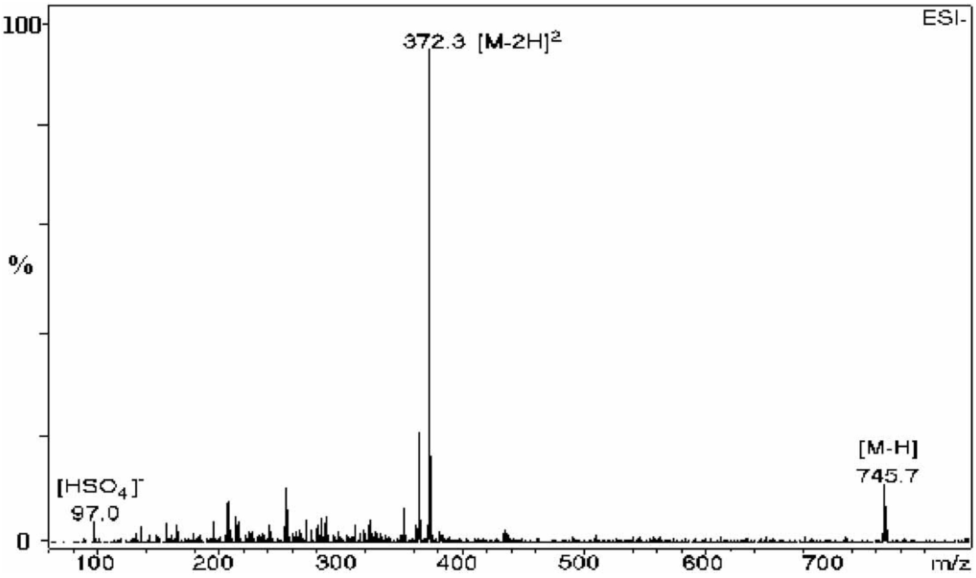


FIGURE 3 Negative-ion electrospray ionization mass spectrum of Reactive Orange 91.

oxidizing agents. However, their concentration should be limited, because they are rather toxic in high concentrations. Finally, there was 97% color removal during the process. Regarding the significant reduction in COD, it can be assumed that the dye degradation proceeds further than the simple reduction or oxidation of original dyes, and wastewater mineralization proceeds to a significant extent.

Separation of the Initial Dyes from their Impurities

As the azodyes tested are commercial samples, their purity was first checked using ion-pairing HPLC and mass spectrometry.

Direct infusion of the initial azodyes into the mass spectrometer (under conditions specified in the experimental section) provided well-developed ESI mass spectra with low noise and intensive signals. The negative-ion ESI mode was chosen as the most suitable for mass spectrometry of polysulphonated aromatic compounds [17]. It provided simple MS spectra with singly and multiply charged deprotonated molecules, such as the $[M-H]^-$ ion (m/z 745.7) and the $[M-2H]^{2-}$ ion (m/z 372.3) in the spectrum of the Reactive Orange 91 (see Fig. 3), in agreement with the structure of the dye in Fig. 1. The ions with lower abundances and lower m/z ratios can be attributed to the impurities in the commercial dye. The MS data for all dyes are presented in Table II. The absence of the quasi-molecular ion of Reactive Black 5 is typical for sulphonic acid esters with an –O–SO_3H group, which show a very strong fragmentation, and the neutral loss of H_2SO_4 may be responsible for the relative abundance or absence of a deprotonated molecule, even under the softest electrospray conditions. For all other dyes, only the peaks of the $[M-H]^-$ and $[M-2H]^{2-}$ ions were observed, together with the peaks of some impurities.

The initial azodyes were separated from the impurities by isocratic ion-pairing chromatography using methanol/water + 2.5 mmol/L DHAA ion-pairing reagent in the mobile phase. The retention times of dyes and impurities for isocratic elution are presented in Table III. A mixture of 57% methanol/water + 2.5 mmol/L DHAA should be used to separate the impurities in the three less retained azodyes (Reactive Blue 182, Reactive Black 5 and Reactive Orange 91). Reactive Red 184 is more strongly retained than Reactive Orange 91, and hence this sample can be separated in 62% methanol/water + 2.5 mmol/L DHAA (see Table III). All peaks of the impurities have lower retention times than the original dyes. The retention times of the sulphonated azodyes generally increase with increasing number of aromatic rings and decreasing number of sulphonic acid groups. To separate more strongly retained impurities that may have existed in the dye samples, the gradient elution should be used.

Separation and Identification of Final Degradation Products

The products of the electrochemical degradation have a range of masses and polarities. Therefore, gradient elution had to be used to separate the products to cover a wide range of retention times. TEAA ion-pairing reagent or AA electrolyte additive suppressing

TABLE II Negative ESI-MS data for the original dyes

Dye	M_r	*m/z*	*Significant ions*
Reactive Black 5	903.0	706.0	$[M-H-2H_2SO_4]^-$
		450.5	$[M-2H]^{2-}$
		412.5	$[M-3H-H_2SO_4+Na]^{2-}$
		401.5	$[M-2H-H_2SO_4]^{2-}$
		363.5	$[M-3H-2H_2SO_4+Na]^{2-}$
		352.5	$[M-2H-2H_2SO_4]^{2-}$
Reactive Red 184	855.0	854.0	$[M-H]^-$
		426.5	$[M-2H]^{2-}$
Reactive Orange 91	747.0	746.0	$[M-H]^-$
		372.5	$[M-2H]^{2-}$
Reactive Blue 182	864.0	863.0	$[M-H]^-$
		431.0	$[M-2H]^{2-}$

TABLE III Isocratic retention times, t_r (min), of the dyes and impurities in ion-pair HPLC with 2.5 mmol/L dihexylammonium acetate as the ion-pairing reagent in various concentrations of methanol–water mobile phases

	% MeOH	*Retention time* (min)	*Retention times of impurities* (min)
Reactive Orange 91	54	7.88	1.32, 1.62, 2.33, 3.59, 4.97
Reactive Red 184	62	5.57	0.82, 1.11, 2.00, 2.41, 3.46
Reactive Blue 182	59	5.05	0.82, 1.39, 2.87
Reactive Black 5	52	3.51	1.21, 1.53, 1.70, 2.00

the ionic exclusion of organic anions from the stationary phase can be used to separate the degradation products with up to two sulphonic acid groups, instead of DHAA, which can cause a significant signal decrease and a strong 'memory effect' in the HPLC/MS system. Therefore, AA acetate was used as the electrolyte additive in gradient-elution chromatography of the degradation products with fewer than (assumed) three sulphonic acid groups, since it shows a similar efficiency to TEAA, together with a lower degree of contamination of the MS system.

Figure 4 shows a gradient elution chromatogram of the degradation products in a 20-μL injection volume of electrochemically treated Reactive Red 184, using a photodiode array detector, flow rate 0.2 mL/min and a gradient elution program consisting of an isocratic step with A (100%) from 0 min to 15 min, followed by a linear gradient to B (100%) in 50 min, with A (water + 2.5 mmol/L ammonium acetate) and B (methanol + 2.5 mmol/L ammonium acetate). The peak of the dye completely disappeared, indicating that all of the initial compound was decomposed to colorlesss products after the electrochemical treatment. Several products were eluted prior to the elution volume of uracil as a non-retained marker. The UV spectra showed that there was no aromaticity for most of these products, which can be either polysulphonated aliphatic products or inorganic ions. These ions can be excluded from the pores of the column packing by repulsive coulombic interactions with negatively charged ionized residual silanol groups of the chemically bonded C18 stationary phase, even in mobile phases with very low concentrations of methanol or in pure aqueous mobile phases at the start of the gradient. The peaks of strongly retained compounds in the last part of the gradient are well separated, and the UV spectra (see Fig. 4) confirm the aromatic character for peaks 1, 3 and 4, where the intensity of the peak 2 is too low to allow the spectrum measurement. Their high retention times are still within the gradient range (the gradient delay is 10 min because the dwell volume is 2 mL) and indicate

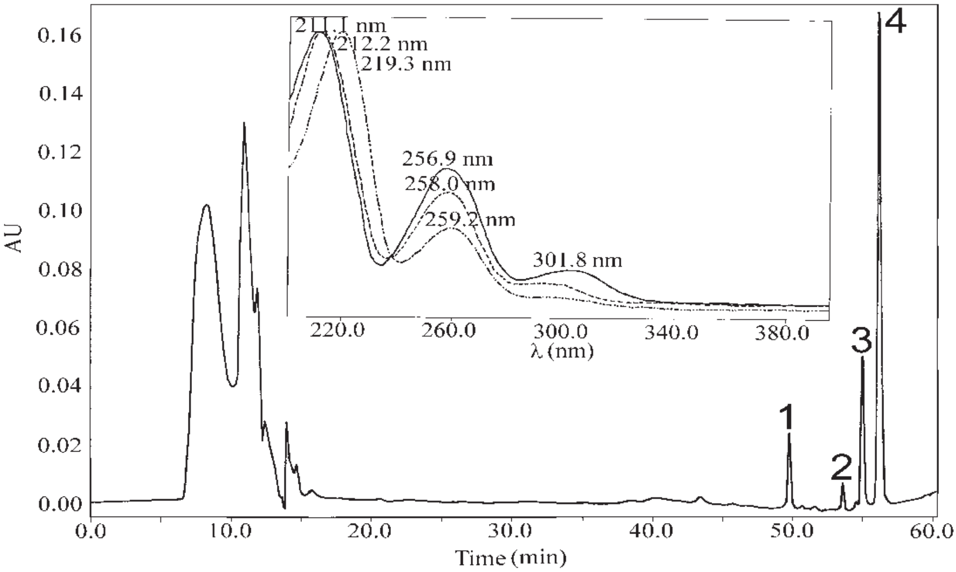


FIGURE 4 HPLC-UV chromatogram of Reactive Red 184 electrochemically treated sample and UV spectra of peaks no. 1 (- - -), No. 3 (——) and No. 4 (· · · · · ·).Time of treatment 30 min (for other conditions, see Experimental).

that they probably do not contain more than one acidic group. Low peak areas of these compounds as compared with the initial dye indicate their low concentrations in the electrochemically treated dye solutions.

For the analysis of the final degradation products, a single quadrupole analyzer with in-source CID was used to obtain structural information. Attention was focused on the neutral products of the electrochemical degradation and the products with one sulphonic acid group, for which the ESI provides less efficient fragmentation than the APCI. Thus, APCI in both the positive- and negative-ion mode was used, providing a good signal sensitivity for neutral degradation products and for the products with up to two sulphonic acid groups present in the molecule. The positive-ion APCI mass spectrum of the peak No. 3 (see Fig. 4) is shown in Fig. 5. The UV spectra of this compound confirm its aromatic character (Fig. 4). Furthermore, the cluster of the molecular peak isotopic ions at $m/z = 307.0$, 308.9, 310.9 and 312.9 ($M:M+2:M+4:M+6$ intensities $= 27:27:9:1$) clearly confirms the presence of three chlorine atoms in the molecule of the degradation product.

The retention times of the products of the electrochemically treated dyes are listed in Table IV for the negative-ion APCI mode and in Table V for the positive-ion APCI mode. Most degradation products can be ionized in one polarity mode only, some of them in the positive-ion APCI mode, and others in the negative-ion APCI mode. Therefore, both polarity modes yield complementary information (see Tables IV and V). The molecular masses were determined from the $[M-H]^-$ ions in the APCI negative-ion mass spectra and from the $[M+H]^+$ ions in the APCI positive-ion mass spectra, where they were further confirmed by the presence of $[M+NH_4]^+$ and $[M+Na]^+$ ions. In addition to the M_r of the degradation products, more structural information was obtained due to the in-source CID from the fragment peaks corresponding to the neutral losses of CO_2, CO, H_2O or NO_2 fragments (observed with a cone voltage of 40 V) and from the characteristic isotopic peaks of molecular or fragment ions containing one or more chlorine atoms. Further, even or odd molecular masses provide evidence for the presence of even (or none) or odd numbers of nitrogen atoms in the molecules of the degradation products. The UV spectra confirm the aromaticity for many of the degradation products. The carboxylic groups (the neutral losses m/z 44) can be formed by the oxidation (see Tables IV and V). Some products are observed in more than one sample in the molecular mass ranges from m/z 84 to 306. The low intensity of the peaks corresponds to low

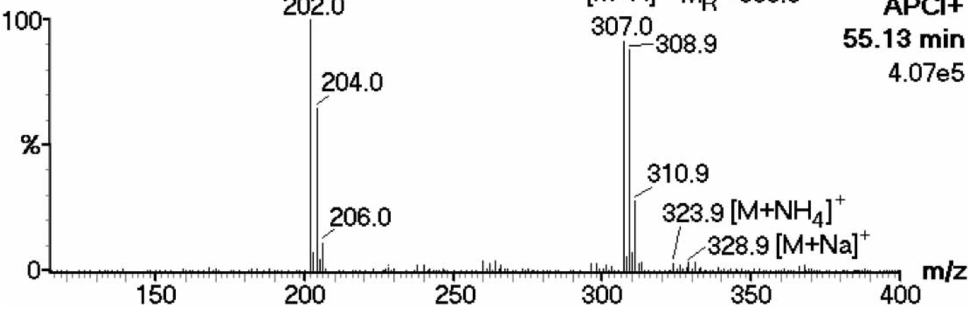


FIGURE 5 Positive-ion atmospheric pressure chemical ionization mass spectrum of the peak No. 3 (Fig. 4).

TABLE IV Retention times, t_r (min), molecular masses, M_r, important fragment ions (m/z) in negative-ion APCI-MS and structural information on the products of electrochemical decomposition of dyes

Dye	M_r	t_r (min)	*Fragment ions* (m/z)	*Presence of*					*Suggestions*
				Cl	*N*	*COOH*	SO_3H	*Neutral losses*	
b, r, bl, o	84	4.5	–	1	[a]	–	–	–	ClO_3^-
b, r, bl, o	98	3.2	–	–	[a]	–	–	–	HSO_4^-
b, r, bl, o	100	4.6	–	1	[a]	–	–	–	ClO_4^-
b, r, b, o	122	5.9	77	–	[a]	1	–	CO_2	Benzoic acid
b, r	129	4.6	111		Odd			NH_3	Aromaticity
b	132	7.0	87	–	[a]	1	–	CO_2	Aromaticity
b, r, bl, o	142	9.1	–	–	[a]	–	–	–	Aromaticity
b, r, bl, o	144	27.3	115	–	[a]	–	–	CO	Aromaticity
b, r, bl, o	152	27.8	–	–	[a]	–	–	–	Aromaticity
b, r	156	3.6	–	1	[a]	–	–	–	Chlorobenzoic acid
b	156	7.0	–	–	[a]	–	–	–	Aromaticity
b, r	164	4.7	–	1	[a]	–	–	–	Non-aromaticity
r	169	29.0	–	1	Odd	–	–	–	Aromaticity
bl	172	22.8	–	1	[a]	–	–	–	Aromaticity
b, r	174	7.0	–	–	[a]	–	–	–	Aromaticity
bl	198	26.1	153	–	[a]	1	–	CO_2	Aromaticity
r	222	4.6	157 141	1	[a]	–	1	SO_2, SO_3	Aromaticity
bl	222	24.7	177 141	–	[a]	1	1	CO_2, SO_3	Aromaticity
bl	232	26.0	–	1	[a]	–	–	–	Aromaticity
bl	242	26.3	213 197	–	[a]	1	–	CO CO_2	Aromaticity
o	252	22.6	146	1	[a]	–	–	Ph–CO	Aromaticity
r	306	24.0	200	3	[a]	–	–	–	Aromaticity

[a] Even number of nitrogen atoms or no nitrogen atom in the molecule. b: Reactive Blue 182; r: Reactive Red 184; bl: Reactive Black 5; o: Reactive Orange 91. Time of treatment: 30 min. For other conditions, see Experimental.

concentrations of the degradation products, thus confirming the high degree of degradation.

Based on the information summarized in Tables IV and V, it was possible to propose the structures of some degradation products, such as simple inorganic anions (ClO_3^-, HSO_4^-, ClO_4^-), naphthalene, benzoic and chlorobenzoic acids. For other peaks, it is

TABLE 5 Retention times, t_r (min), molecular masses, M_r, important fragment ions (m/z) in positive-ion APCI-MS and structural information on the products of electrochemical decomposition of dyes

Dye	M_r	t_r (min)	*Fragment ions* (m/z)	*Presence of*			*Suggestions*
				Cl	*N*	*Neutral losses*	
b, r, bl, o	104	6.6	–	–	[a]	–	Non-aromaticity
r, bl, o	113	24.9	–	–	Odd	–	Non-aromaticity
bl	118	24.8	–	–	[a]	–	Non-aromaticity
bl	128	24.5	–	–	[a]	–	Naphthalene
bl, r, o	134	22.9	–	–	[a]	–	Aromaticity
b, r, bl, o	135	29.1	–	–	Odd	–	Aromaticity
r	169	28.9	–	1	Odd	–	Aromaticity
bl	172	22.8	–	–	[a]	–	Aromaticity
bl	186	24.6	–	–	[a]	–	Aromaticity
b, r, bl, o	194	22.4		–	[a]	–	Aromaticity
bl	198	24.5	171	–	[a]	CO	Aromaticity
b, r, bl, o	204	26.7	187	–	[a]	H_2O	Aromaticity
bl	216	26.5	–	–	[a]	–	Aromaticity
b, r, bl, o	222	30.0	193 177	–	[a]	NO NO_2	Aromaticity
b, r, bl, o	232	27.7	–	–	[a]	–	Aromaticity
bl	236	7.8	–	–	[a]	–	Aromaticity
bl	238	28.6	–	–	[a]	–	Aromaticity
o	252	22.4	148	1	[a]	Ph–CO	Aromaticity
r	276	22.7	–	–	[a]	–	Aromaticity
bl	282	28.6	–	–	[a]	–	Aromaticity
r	306	25.1	202	3	[a]	–	Aromaticity

[a] Even number of nitrogen atoms or none nitrogen atom in the molecule. b: Reactive Blue 182; r: Reactive Red 184; bl: Reactive Black 5; o: Reactive Orange 91. Time of treatment: 30 min. For other conditions, see Experimental.

not possible to derive reliable final structures from a few fragment peaks present in the mass spectra. More information could be obtained from the MS^n spectra of the degradation products and from the comparison with the mass spectra and the retention times of the authentic standard compounds, which will be the topic of our future studies.

CONCLUSIONS

A new electrochemical method has been developed for textile wastewater treatment. Model experiments with synthetic wastewater showed high decoloration rates, color removal up to 99.9%, a neutral final pH value, a small increase in temperature, and a significant decrease in COD and chloride concentration with simultaneous generation of hypochlorites up to 40 mg/L. From the preliminary HPLC and HPLC/MS experiments, it was possible to obtain molecular mass information and to provide structural information for some degradation products. Most products correspond to simple inorganic salts; however, the formation of some aromatic degradation products was detected as well. Further, chlorinated organic compounds are formed due to the presence of NaCl during the electrochemical treatment.

The presence of impurities in the original dyes may cause confusion, since they can be considered as final degradation products, if not decomposed during the electrochemical treatment. These original dye impurities can also be recognized by HPLC/MS experiments.

In future studies, simple dyes of high purity will be used as reference compounds to determine the electrochemical degradation mechanisms. Research is continuing, aimed at improving the separation of the ionic and strongly polar products, using new columns specially designed for highly aqueous mobile phases as well as testing various ion-pairing reagents for optimum separation selectivity and minimum contamination of the ion source and MS signal suppression. Future investigations are aimed at improving the identification of degradation products by the MS^n technique and reference-materials comparison, which is essential for correct identification of degradation products, and at developing a suitable solid-phase extraction procedure for isolation and enrichment of the organic degradation products from aqueous samples with a high salinity. To follow the kinetics of the degradation process, the formation of the decomposition products will be monitored in relation to the time elapsed from the start of the electrochemical treatment.

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