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Electrochemical treatment of bisphenol-A containing wastewaters

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The effectiveness of electrochemical methods in purification of synthetic wastewaters containing bisphenol-A has been tested. The role of electrode material and electrolysis parameters have been considered. The kinetics of bisphenol oxidation have been followed using different analytical techniques and a degradation mechanism has been proposed.

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1. Introduction

Purification of wastewaters containing phenols has long been a problem owing to their low biodegradability and high toxicity. In particular, 2,2-bis(4′-hydroxyphenyl)propane (BPA) is an important raw material which finds wide application in the polymer industry [1]. Different processes have been applied for its removal from wastewater, either chemical or biological or a combination of the two [2, 3]. With biological treatment, problems arise when waters of high chloride content are discharged, so pretreatment becomes mandatory. On the other hand, treatment with chemicals leads to the problem of excess reagent removal and to the possible generation of side-products even more dangerous than the original pollutants.

Electrochemical methods for detoxification of wastewaters containing heavy metals are well known, while their application to removal of organic pollutants is little used industrially. Electrochemical decontamination is an attractive idea [4–7] because of the simultaneous oxidation–reduction process taking place at the electrodes without the need to add chemicals. Furthermore, when direct oxidation of organic pollutants is not feasible, it is still possible to attempt an oxidation mediated by some electrogenerated strong oxidizing species, like ozone and chlorine, reacting at the electrode surface with the electrosorbed organic species.

In this paper the results of the electrochemical treatment of a synthetic effluent in concentration ranging from 20 to 2000 mg dm^{-3} and NaCl 2.8% at pH > 10.5 are reported. High solubility of BPA was obtained by NaOH addition with increasing pH of solution and formation of bisphenate species [8]. The influence of some parameters like current density, electrode material and electrolysis cell geometry has been tested. Some explanations regarding the oxidation path have been attempted.

2. Experimental details

The electrochemical oxidation kinetics of bisphenol-A was monitored both by thin layer chromatography and u.v. spectrometry to detect the disappearance of aromatic rings. The electrochemical degradation products obtained at different times and conditions were recovered from the aqueous solution, before and after mineral acid treatment down to pH $\leqslant 2$, by means of $CHCl_3$ extraction. The different fractions were obtained by silica column separation and analysed by FTIR, NMR and GC-MS spectrometry. Chemical oxygen demand (COD) determination on synthetic wastewaters was carried out as reported in [9].

2.1. *Electrochemical apparatus*

Electrochemical tests were conducted galvanostatically using, an AMEL model 553 potentiostat, both in a two compartments, two electrode, and in a single compartment, two electrode assembly, with a titanium mesh as cathode and a platinum mesh or a titanium supported lead dioxide film as anode. All solutions were prepared using analytical grade reagents and milli-Q water.

2.2. *Gas chromatography/mass spectrometry*

Mass spectra were collected using a Hewlett-Packard model 5988A quadrupole mass analyser interfaced to an Hewlett-Packard model 5890 gas chromatograph. The following parameters were used for the analyses: source temperature 200° C, electron impact energy 70 eV, emission current 300 μA, source pressure 2×10^{-6} Torr. Chemical ionization was performed utilizing CH_4 reacting gas at pressure 0.75 Torr and electron impact energy 200 eV. Mass calibrations were performed by means of PFTBA. SPB-1 Supelco chromatographic column of 60 m × 0.32 mm i.d. with a film 1 μm thick was directly connected with the mass spectrometer. The helium carrier gas flow varied from 0.9 to 1.2 ml min^{-1}. The gas chromatograph oven was heated from 80° C up to 300° C at a heating rate of 10° C min^{-1} and maintained at this temperature for 28 min. In directly connected GC–MS, the injector and the transfer line were held at 300° C. The samples were analysed in the mass range between 20 and 500 a.m.u. To show the presence of acidic and other hydrogen reactive species the samples were silylated with bis(trimethylsilyl)-trifluoroacetamide, BSTFA [10].

2.3. *Nuclear magnetic resonance*

All NMR experiments were performed on a Bruker AMX 300 Fourier Transform spectrometer equipped with a 5 mm dual probe-head (^{1}H/^{13}C) operating at an observation frequency of 300.13 and 75.47 MHz for ^{1}H and ^{13}C, respectively. The measurements were carried out at room temperature (about 300 K) using $CDCl_3$ as solvent. Chemical Shifts, δ, are relative to internal tetramethylsilane (TMS). Proton NMR spectra were obtained with 2890 Hz spectral width, 2.834 s acquisition time, 10.6 μs 90° pulse, and 1 s relaxation delay and the number of transients was 64. The ^{13}C NMR spectra were recorded in the power-gated proton decoupling mode, using Waltz modulation, 30° flip angle and 16 666 Hz spectral width, 1.966 s acquisition time, 4.5 μs 90° pulse, 6 s relaxation delay. The number of transients varied with samples: 6000 for F1 and 10 000 for F2. The proton coupled ^{13}C NMR spectra were measured

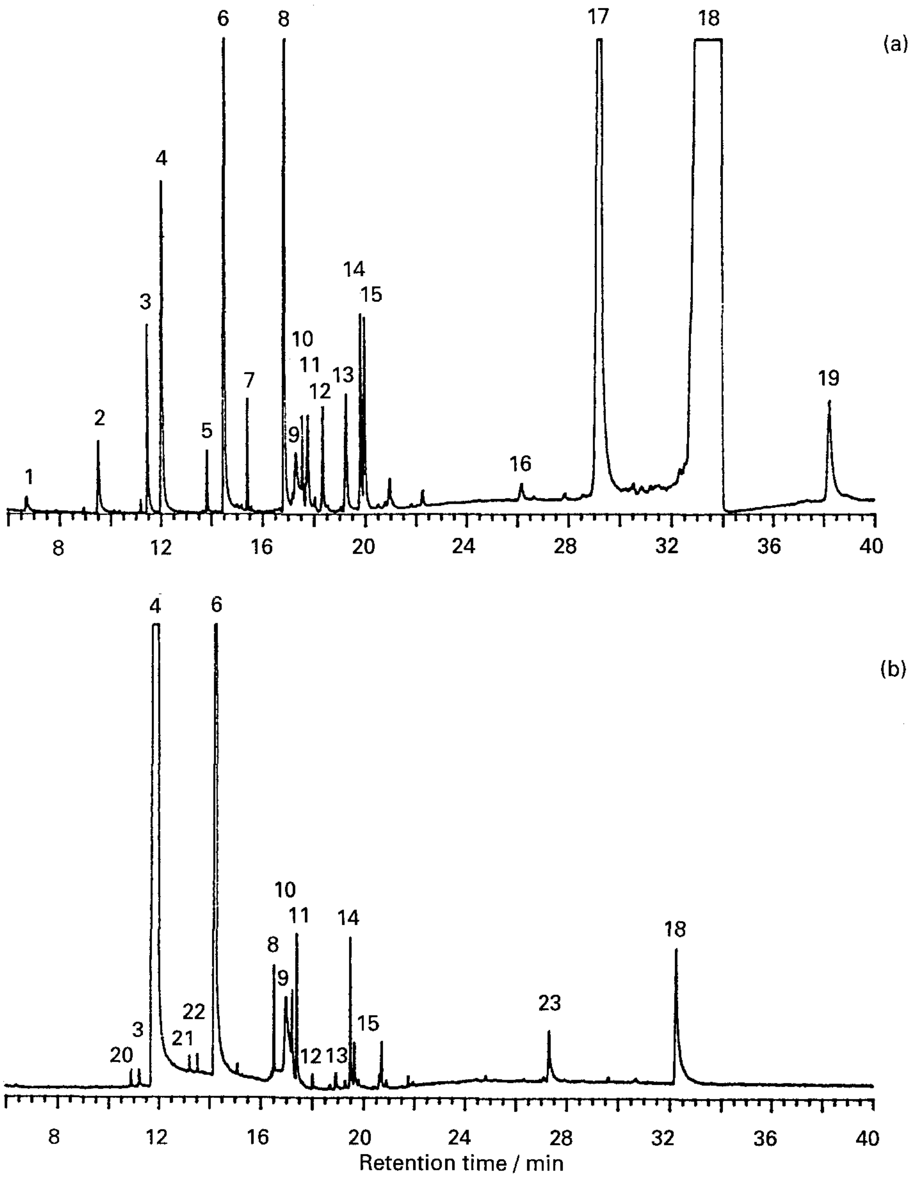


Fig. 1. TIC chromatograms of two fractions of the solution extracted after electrolysis for 2 h. Current density $j = 100\ \mathrm{A\,m^{-2}}$. (a) Fraction F1, (b) fraction F2.

in the gated decoupling mode with 30° flip angle. DEPT spectra were obtained with ^{1}H flip angles of 45°, 90° and 135° for the differentiation of the CH, CH_2 and CH_3 carbon atoms.

2.4. *Fourier transform infrared spectrometry*

The FTIR spectra were collected at room temperature by means of a Nicolet 740 spectrophotometer equipped with a CsI beamsplitter and DTGS detector, in the wavenumber range between 5000 and 250 cm^{-1}. Each spectrum was the average of 32 scans at 8 cm^{-1} resolution. The samples were analyzed on KBr wafer and in $CHCl_3$ and $CDCl_3$ solvents by means of a KBr cell having 0.025 mm optical path.

3. Results and discussion

The electrolysis of a concentrated solution of BPA (2 g dm^{-3}) conducted on a platinum mesh with a total current $I = 250\,\mathrm{mA}$ ($j \approx 100\,\mathrm{A\,m^{-2}}$) in a two-compartment cell, initially showed the formation of a yellow–orange film on the working electrode. This inhibited further oxidation of the bisphenol present in solution and disappeared only very slowly. As is well known, severe filming of electrode surfaces occurs during the anodic oxidation of aromatic hydroxy compounds, which complicates mechanistic studies [11]. The lowering of the local pH near the anode surface, due to oxygen evolution, shifts the bisphenol/bisphenate equilibrium toward the acid form, which is water insoluble and causes a phase separation. This phenomenon is enhanced, by the increase in bisphenol concentration.

After 2 h of electrolysis two fractions of the solution (named F1 and F2) were separated on a silica column and analysed by GC–MS. The TIC chromatograms shown in Fig. 1 indicate the presence of various species. The most intense peaks are those labelled 4, 6, 8, 17 and 18 in fraction F1 (Fig. 1(a)), and those labelled 4 and 6 in fraction F2 (Fig. 1(b)). The compounds identified on the basis of the fragmentation patterns are reported in Table 1 along with the peak number and the chemical formula. The number of chlorine atoms present in each compound was determined on the basis of the isotopic relative abundances. The fragmentation pattern of compound 18 is in agreement with that of the non-substituted BPA [12].

To further confirm the assignment done for the chromatographic peaks, ^{1}H and ^{13}C NMR spectroscopy was used. The number of protons bonded to each carbon atom was determined by means of proton coupled ^{13}C NMR spectra and of DEPT (*d*istortion less *e*nhancement by *p*olarization *t*ransfer) experiments. Furthermore, the ^{13}C chemical shift assignment is in good agreement with that calculated from the benzene and BPA resonances, taking into account the substituent effect due to the presence of chlorine atoms in the aromatic ring.

Table 1. GC/MS peak assignments

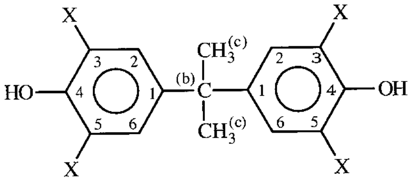
Peak number	*Chemical formula*	*Name*	*Molecular weight*
1	$C_6H_4O_2$	1,4-benzoquinone	108
2	$C_6H_3O_2Cl$	1,4-benzoquinone2-chloro	142
3	$C_6H_2O_2Cl_2$	2,4-dichlorophenol	162
4	$C_6H_2O_2Cl_2$	1,4-benzoquinone2,6dichloro	176
5	C_9H_9OCl	2-(chloro-4-hidroxyphenyl)propene	168
6	$C_6H_3OCl_3$	2,4,6-Trichlorophenol	196
7	$C_6H_3OCl_3$	trichlorophenol	196
8	$C_9H_8OCl_2$	2-(3^1,5^1-dichloro-4-hydroxyphenyl)propene	202
9	$C_6H_4O_2Cl_2$	dichloro1,4-dihydroxybenzene	178
10	$C_6H_2OCl_4$	tetrachlorophenol	230
11	$C_9H_{10}OCl_2$	2-(3^1,5^1-dichloro-4^1-hydroxyphenyl)propano	204
12	$C_9H_7OCl_3$		236
13	$C_9H_7OCl_3$		236
14	$C_9H_7OCl_3$		236
15	$C_9H_7OCl_3$		236
16	$C_{15}H_{14}O_2Cl_2$	2-(chloro-4^1hydroxyphenyl)-2-(chloro-4-hydroxyphenyl)propane	296
17	$C_{15}H_{13}O_2Cl_2$	2-(3^1-chloro-4^1-hydroxyphenyl)2(3,5 dichloro-4-hydroxyphenyl)propane	330
18	$C_{15}H_{12}O_2Cl_4$	2,2-bis(3^1,5^1-dichloro-4-hydroxyphenyl)propane	364
19	$C_{15}H_{11}O_2Cl_5$	2-(trichloro-4^1-hydroxyphenyl)-2-(dichloro-4-hydroxyphenyl)propano	398
20	$C_6H_5OCl_3$	1,4-cyclohexadiene-3-hydroxy-trichloro	198
21	$C_6H_5OCl_3$	1,4-cyclohexadiene-3-hydroxy-trichloro	198
22	$C_7H_6OCl_2$	dichloro-4-metilphenol	176
23	$C_{12}H_5O_2Cl_5$	phenoltrichloro-4-(dichloro-4-hydroxyphenyl)	356
24	$C_6O_2Cl_4$	2,3,6 trichloro-1,4-benzoquinone	210
25	$C_6O_2Cl_4$	2,3,5,6 tetrachloro-1,4-benzoquinone	244
26	$C_6H_5OCl_5$	pentachlorophenol	264
27	$C_6H_2O_2Cl_4$	1,4 dihydroxy-2,3,5,6 tetrachlorobenzene	246
28	$C_7H_6OCl_4$		246

Table 2. ^1H *and* ^{13}C *chemical shift, δ (p.p.m.) for BPA, 18, 4 and 6 compounds*

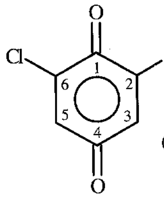
	*BPA**	*18*	*4*	*6*
H_j				
2,6	6.66–6.99	7.07		
3,5			7.03	7.28
a	1.57	1.59	–	–
OH	8.55	5.79	–	5.76
C_j				
1	141.34 (s)	143.06 (s)	172.73 (s)	146.94 (s)
2,6	127.28 (d)	126.59 (d)	143.65 (s)	121.63 (s)
3,5	114.56 (d)	120.86 (s)	133.86 (d)	128.12 (d)
4	154.78 (s)	146.07 (s)	182.48 (s)	125.40 (s)
a	30.96 (q)	30.52 (q)	–	–
b	41.07 (s)	42.09 (s)	–	–

* Solvent: $DMSOd_6/CDCl_3$

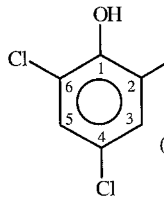
(BPA 18)



X = H
X = Cl



(4)



(6)

Thus, the main compounds giving the NMR spectra of F1 and F2 fraction are the tetrachloro substituted BPA (18), 2,6-dichloro-*p*-benzoquinone (4) and 2,4,6-trichloro-phenol (6). The proton and ^{13}C chemical shifts of these compounds are compared in Table 2 with those measured for BPA. Even if in ^{13}C NMR spectra a great variability in the internal signals ratios is observed, due either to different NOE (nuclear overhauser effect) or to a wide range of relaxation times (T1) for the various carbon atoms present, a semiquantitative approach permitted determination at the relative abundance of the three compounds in the F1 and F2 fractions resulting in

F1: $4/6/18 = 2/2/96$ (wt %)

F2: $4/6/18 = 80/13/7$ (wt %)

The same experiment was repeated using a higher current $I = 700\,\text{mA}$ ($j \approx 280\,\text{A}\,\text{m}^{-2}$) and no film formation at the electrode surface was observed, either in the first stage, or later, in the course of the electrolysis. Furthermore, the decrease of bisphenol disappearance time was greater than that expected solely from the current increase. In this case, for the fraction F3, the main peaks are those labelled 6 and 24, while the tetrachloro-substituted BPA is present in smaller degree with respect to the fractions F1 and F2.

The presence of quinonic moieties was also revealed by FTIR spectroscopy. In Fig. 2, representing the spectrum of the F3 fraction, a strong absorption band in the carbonyl group zone is present, while no signal of chloro substituted BPA is detected, in agreement with the GC–MS data.

Prolonged electrolysis eventually led to complete destruction of BPA and no signal in the u.v.-visible spectrum related to the presence of aromatic rings was detected after 24 h, as reported in Fig. 3.

When a lead dioxide film electrode was used instead of a platinum mesh, the only effect was an increase in the rate of BPA disappearance, at both current densities, while no significant difference was found

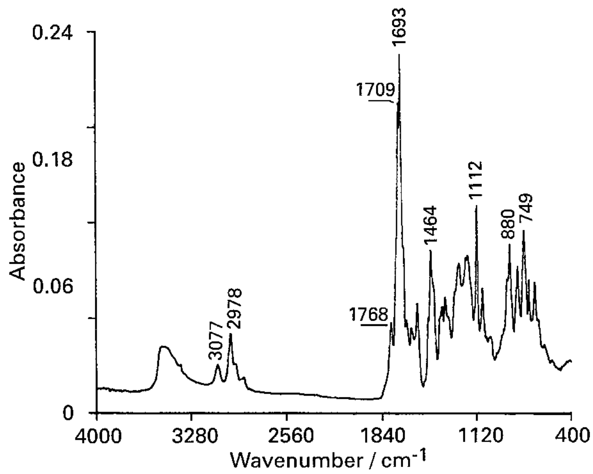


Fig. 2. FTIR spectrum of the fraction F3 of the solution extracted after electrolysis for 2 h. Current density $j = 280\,\text{A}\,\text{m}^{-2}$.

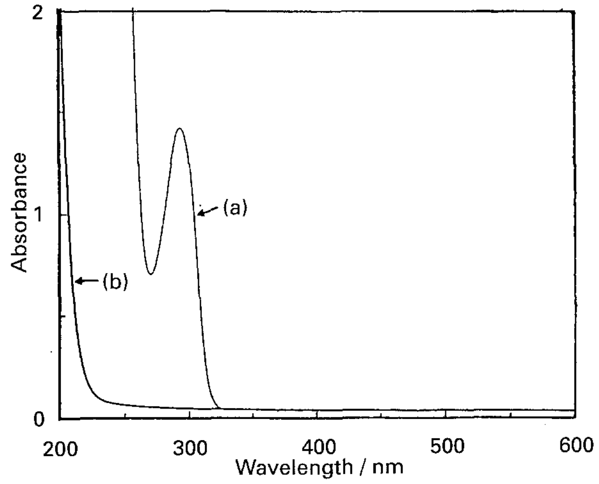
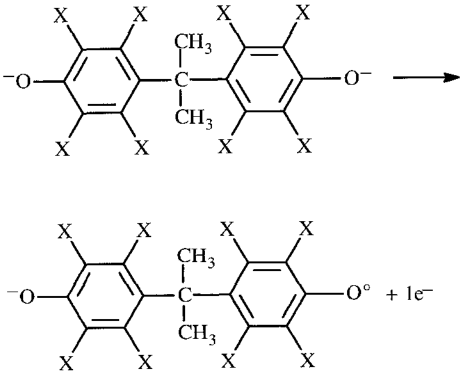


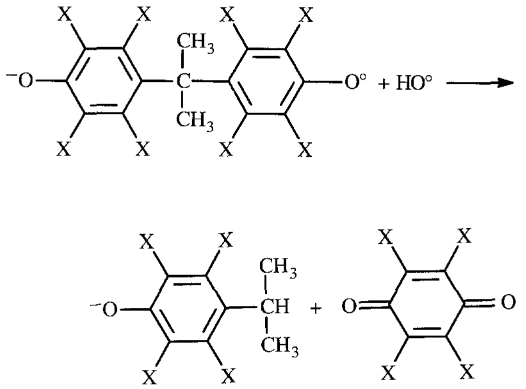
Fig. 3. UV-visible spectra of a BPA solution (a) before and (b) after complete (24 h) electrolysis. Solution contains 10^{-2} M dm^{-3} BPA, 2 g dm^{-3} NaOH and 28 g dm^{-3} NaCl. Electrolysis conditions: $I = 0.84$ A; $j = 0.03$ A cm^{-2}; anode: Pt gauze; cathode: Ti rod.

using a single compartment instead of the two compartment cell. Lower in the bisphenol-A concentration range (20 to 200 mg dm^{-3}) only partial film formation occurred at the electrode and no substantial differences in product formation with varying current density was observed.

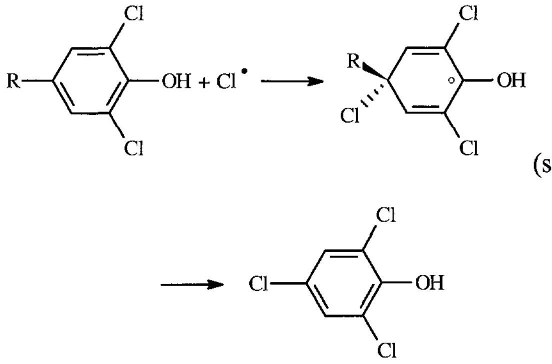
The formation of chlorinated aromatic intermediates is easily understood bearing in mind that the electrolysis of BPA proceeds in a strong chlorinating environment, owing to the presence of NaCl as supporting electrolyte. The simultaneous presence at the anode/solution interface of bisphenate anion and chlorine led to an extended chlorination of the aromatic rings in the activated positions, with formation of polychlorinated bisphenates. Moreover, due to the very strong basic conditions, these species can be oxidized to the corresponding radicals at the anode (step 1) involving 1e$^-$ oxidation path as suggested in previous work [13]. This process leads to the formation of quinones, in accordance with the oxidative process of 3,5 substituted phenols [14], coupled with the elimination of the *p*-hydroxycumyl chloro substituted group (step 2). Furthermore, the presence at the electrode surface of both Cl atoms and substituted phenolic derivatives makes possible the formation of trichloro phenol through an unstable intermediate, with an oxidation mechanism similar to the former (Step 3):



(step 1)



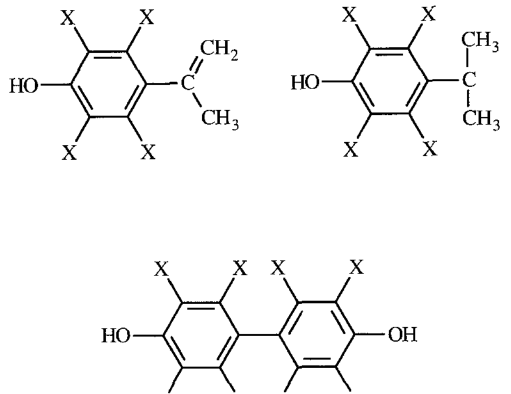
(step 2)



(step 3)

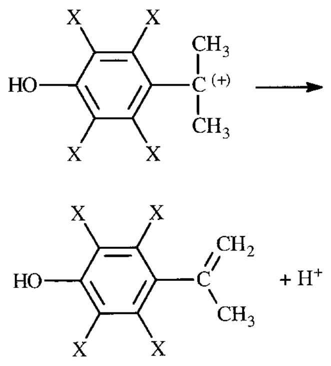
where X = H, Cl and R = CH_3CHCH_3.

This mechanism differs from those proposed by Peltonen and coworkers for the degradation of BPA in the gas phase [15] and by Amadelli and coworkers for the photoassisted degradation of BPA on TiO_2 in solution without the presence of chloride ions [16]. Furthermore, different degradation products were recognized by GC-MS, such as



whose formation can be justified by different degradation paths involving radical intermediates. The formation of a carbonium ion intermediate and the release of a proton is the most probable way to generate chloro substituted hydroxyphenyl-propenes (step 4). These findings suggest an electrochemical substitution process as reported for the case of toluene chlorination [13].

On the other hand, simultaneous oxidation processes occur due to the lower oxygen evolution potential in an alkaline medium as compared to that in acidic medium.



(step 4)

To avoid the formation of a film at the anode, electrolysis was conducted on solutions containing an amount of BPA lower than that reported above, in the following conditions: BPA concentration 570 p.p.m., current intensity 1 A, NaCl content 2.9 g dm^{-3} and pH > 12. This experimental condition, allows higher chlorination yield, with evidence of a concurrently effective oxidation process. In fact, the mass spectroscopy analysis of the silylated fractions recovered after 1 h of electrolysis confirmed the presence of a very small quantity of the previously found polychlorinated species (as 11, 17, and 18 for example), and also indicated the presence of several other degradation species, chlorinated or not, of aldehydic or acidic type, such as 2,6-dichloro, 4-hydroxy benzaldehyde, maleic aldehyde, maleic acid, etc. As an example, Fig. 4(a) and (b) show the mass fragmentation patterns relative to maleic aldehyde and sililated maleic acid derivatives, respectively. It is worth noting the detection of acidic species, in which the cumyl group is still present. The chemical attack on the phenolic or chetonic chlorinated species gives rise to aldehydes and acids, as shown in the literature for anodic oxidation of aromatic compounds [13] and as found for ozonization of phenol in water [17]. Moreover, after 24 h of electrolysis very short chain organic acids were detectable only in traces. This finding was in agreement with COD measurements.

4. Conclusions

These results show the feasibility of bisphenol degradation by means of electrochemical oxidation in

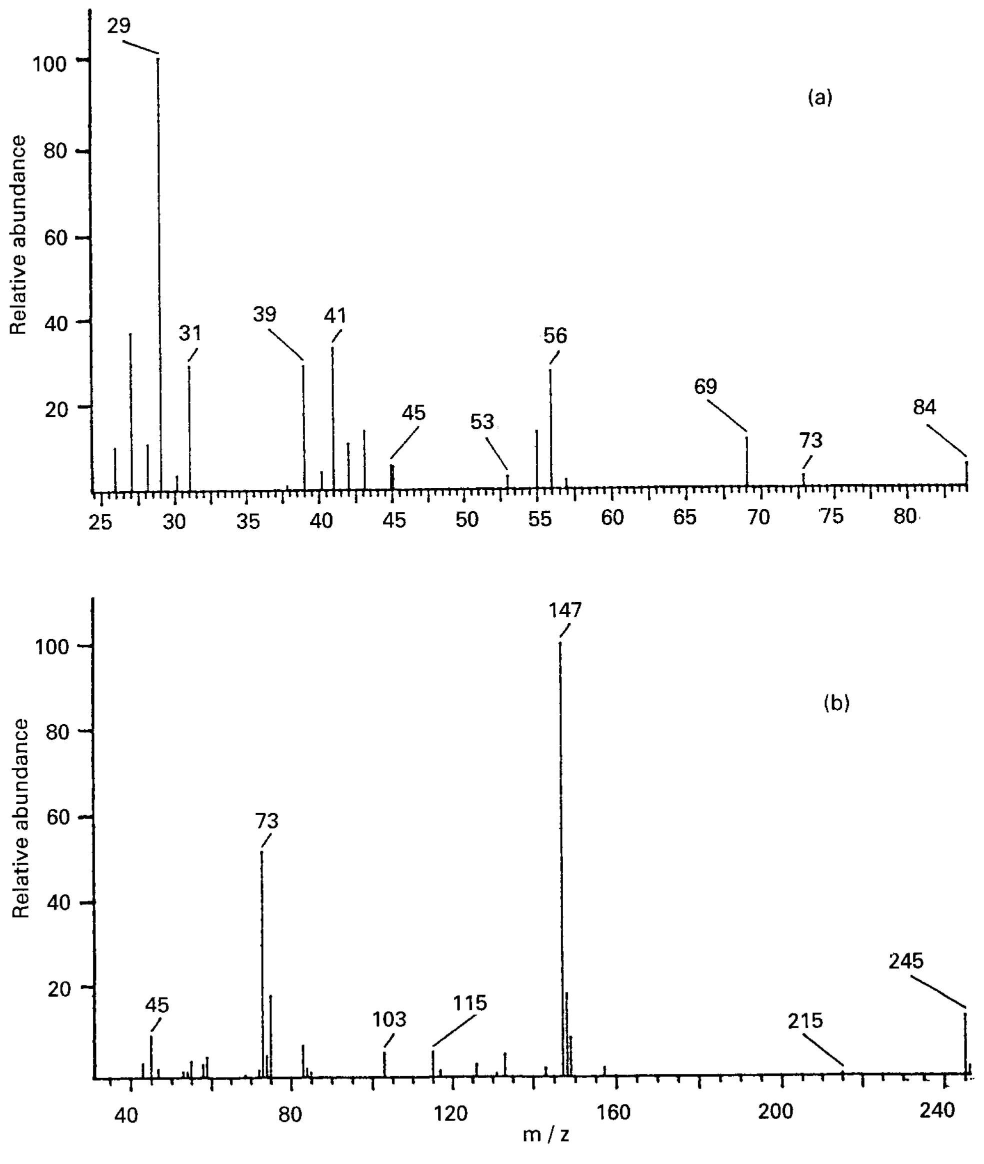


Fig. 4. Mass fragmentation patterns of (a) maleic aldehyde and (b) silylated maleic acid (maleic acid, bis (trimethylsilyl)ester).

aqueous solutions. Although in some less favourable conditions evidence was found for the formation of polychlorinated intermediates, at the end of electrolysis no such compounds were found, the final products consisting of simple short chain aliphatic acids.

Further investigations are necessary to better elucidate the role played by the electrode material, extending the analysis to DSA type anodes, as well as to tin dioxide anodes. To find the optimal electrolysis conditions leading to a reaction path free of dangerous products and therefore to a 'clean' depollution technique, more investigation is also needed of the electrooxidation mechanism.

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