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Electrochemical incineration of benzoquinone in aqueous media using a quaternary metal oxide electrode in the absence of a soluble supporting electrolyte

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Electrochemical incineration of *p*-benzoquinone was evaluated as a model for the mineralization of carbon in toxic aromatic compounds. A Ti or Pt anode was coated with a film of the oxides of Ti, Ru, Sn and Sb. This quaternary metal oxide film was stable; elemental analysis of the electrolysed solution indicated the concentration of these metal ions to be 3 μg L^{-1} or less. The anode showed good reactivity for the electrochemical incineration of benzoquinone. The use of a dissolved salt matrix as the so-called 'supporting electrolyte' was eliminated in favor of a solid-state electrolyte sandwiched between the anode and cathode. This substitution permitted the electrolysis solution to be analysed by electrospray mass spectrometry (ESMS); however, as a consequence, electrolysis periods were excessively long. Total organic carbon (TOC) and chemical oxygen demand (COD) decreased to 1–2 mg L^{-1} after 64 h of electrolysis. The solution pH changed from 5 to 4. Phenolic and carboxylic acid intermediate products such as hydroquinone, maleic acid, fumaric acid, succinic acid, malonic acid, acetic acid and formic acids were identified and quantified using solid phase microextraction with gas chromatography with mass spectrometric detection (GCMS) or liquid chromatography (LC) with conductivity detection, absorbance detection, or electrosprary mass spectrometry (ESMS). Less than 1% of the carbon in benzoquinone was converted to acetone and acetaldehyde.

1. Introduction

Public awareness of the discharge of industrial wastes has resulted in governmental and private development of efficient, economical and safe procedures for the destruction of toxic organic waste. Alternatives to the traditional use of thermal incineration include supercritical water oxidation, photochemical degradation, sonochemical oxidation and electrochemical incineration.

Supercritical water oxidation is performed above the critical point of water (374 °C, 218 atm) in the presence of O_2 or H_2O_2 [1]. Organic species only slightly soluble in water are miscible with supercritical water [2]. The literature contains descriptions of reaction mechanisms, kinetics and engineering aspects of supercritical water oxidation applied to numerous organic pollutants including: phenol [3–6], 1,3-dichlorobenzene and benzene [6], pyridine [2, 7], acetic acid [2, 8], 1,4-dichlorobenzene [9], chlorophenols [2], pulp and paper mill sludge [1], and explosives [10]. Major reaction products are water, carbon dioxide and inorganic salts. Supercritical water oxidation is well suited for destruction of large volumes of toxic organic waste; however, for disposal of small quantities of toxic organic waste, supercritical water oxidation is not considered feasible economically. Therefore, evaluation of less costly methods is appropriate.

Recently, interest in photochemical degradation of toxic organic waste in aqueous media has expanded rapidly. The primary oxidant is the photogenerated hydroxyl radical formed on semiconductor metal oxide surfaces [11]. Typically, TiO_2 powder is the semiconductor used because it is inexpensive, insoluble under conditions used in photochemical degradation, stable and nontoxic [12]. The literature of photochemical degradation describes applications to chlorophenols, dichloroacetate and oxalate [13], 4-chlorophenol [14–17], humic acids [11], dichlorophenols [18], benzene [19], phenol [20], dimethoxybenzene [21] and toluene [22]. Applications of photochemical degradation appear most suitable for solutions having low turbidity [23].

Sonochemical oxidation has been used for degradation of phenol [23] and humic acids [24]; and of 4-chlorophenol, 3,4-dichloroaniline and 2,4,6-trinitrotoluene [25]. The primary reaction in sonochemical oxidation is the pyrolysis of solute present in bubbles generated by acoustical cavitation. Secondary reactions also occur as a result of interactions of solute with hydroxyl radicals and hydrogen atoms produced by the sonication of water [23].

Electrochemical incineration is an alternative to the degradation methods just described. This is a waste remediation process whereby oxygen atoms are transferred from H_2O in the solvent phase to the oxidation product(s) by direct or indirect reactions on the anode surface. This procedure is attractive for low-volume applications such as confined living spaces (e.g., spacecraft, and research laboratories). Kaba *et al.* described successful electrochemical incineration of waste biomass using Pt and PbO_2 electrodes [26]. They reported the major advantages of electrochemical incineration over thermal incineration include: absence of CO and NO_x generation, and low operating temperatures. Because of the high cost of Pt and the toxicity of lead salts, Kotz *et al.* [27] and Comninellis and Pulgarin [28] compared PbO_2 and Pt electrodes to SnO_2-film electrodes doped with Sb(v) ('Sb–SnO_2'). Both Swiss groups demonstrated that phenol is removed from aqueous solution more efficiently with Sb–SnO_2 anodes than with Pt and PbO_2 anodes. Their work also indicated that for Pt anodes, oxidation stops with the formation of small carboxylic acids, for example, maleic, fumaric and oxalic. More recently, Comninellis and Battisti [29] compared Pt, IrO_2/Ti and Sb–SnO_2/Ti anodes and proposed a mechanism for the electrolysis of organic compounds. These and other descriptions of electrochemical incineration literature are reviewed by Rajeshwar *et al.* [30]. Advantages of electrochemical incineration discussed by Rajeshwar *et al.* include: versatility, energy efficiency, amenability to automation, environmental compatibility and low cost.

The major challenge for future development of electrochemical incineration is the discovery of nontoxic anode materials and electrolysis conditions that can achieve conversion of toxic organic waste to innocuous products with high current efficiencies. Other desirable electrode properties include low cost, lack of toxicity, high stability and high activity. The matter of current efficiency is especially pertinent because the desired O-transfer reactions require the anodic discharge of H_2O to produce adsorbed hydroxyl radicals (OH_{ads}). However, a high surface access of the OH_{ads} species leads to evolution of O_2, an undesired product. Previous work in this laboratory has demonstrated that electrodes comprised of Fe(III)-doped β-PbO_2 films on Ti substrates ('Fe–PbO_2/Ti') are quite stable in acetate buffered media (pH 5) and offer significantly improved catalytic activity over pure β-PbO_2 film electrodes for conversion of CN^- to CNO^- under potentiostatic conditions [31] as well as the anodic degradation of *p*-benzoquinone under galvanostatic conditions [32].

The present focus of our research related to electrochemical incineration is directed away from the use of a PbO_2 film electrode to a quaternary metal oxide consisting of a SnO_2 film doped with varying amounts of the oxides of antimony, titanium and ruthenium. The cathode is a porous stainless steel cylinder. In this study, a Nafion® membrane is used as a solid-state electrolyte sandwiched between the anode and cathode. Use of Nafion®, a perfluorinated membrane, precludes the need for addition of soluble inorganic salts to function as supporting electrolytes. A dramatic increase in lifetime of anodes has been observed to result from omission of added electrolytes. Furthermore, the low ionic strength of the electrolysis solution facilitates the use of ESMS for determination of ionic products and there is little or no electrolyte to remove from the remediated solution.

2. Experimental details

2.1. *Reagents*

All chemicals were reagent grade (Fisher Scientific) and water was purified in a Nanopure-II system (Barnstead, Newton, MA). Quaternary metal oxide films were prepared from a solution comprised of 0.4 M $SnCl_2 . 2H_2O$, 0.03 M $SbCl_3$, 0.08 M $RuCl_3$ and 0.02 M $TiCl_4$ in a 1:1 mixture of 12 M HCl and *i*-propanol. This composition was chosen on the basis of patents claiming high stability for TiO_2–RuO_2–SnO_2 [33] and RuO_2–Sb_2O_3–SnO_2 [34] films on Ti substrates in saline solutions. *p*-Benzoquinone (Fisher Scientific) was purified by sublimation and used for preparation of 100 mg L^{-1} stock solutions in water. Carboxylic acids (Aldrich) were dissolved in water to prepare 1000 mg L^{-1} standard stock solutions, which were then frozen until needed to prevent microbial degradation.

2.2. *Electrolysis apparatus*

Quaternary metal oxide films were prepared by a thermal procedure in which Ti or Pt substrates were alternately painted with the solution of the four metal salts followed by heating above the flame of a Bunsen burner for about 15 s. After ten wetting–heating cycles, the electrode was annealed in a muffle furnace for 1 h at 600 °C. The resulting quaternary metal oxide films on Ti and Pt substrates are designated here as 'Ru–Ti–Sb–SnO_2/Ti' and 'Ru–Ti–SnO_2/Pt', respectively. Preliminary work made use of a Ti substrate (10 cm^2 working area), in the form of a rectangular plate, and a Pt cathode. Subsequently, a Pt wire (0.62 mm o.d. × 24 cm length, 4.7 cm^2 working area) was used as the substrate for quaternary metal oxide films. In the latter case, a rectangular piece of Nafion® 117 membrane (2 cm × 4 cm) was placed around the cathode and wrapped tightly with the quaternary metal oxide-coated wire anode, as shown in Fig. 1. The cathode was prepared from a rod of type-360 stainless steel (6.4 mm o.d. × 3.5 cm length) drilled with 20 holes (3 mm dia.) positioned normal to the axis of the rod. Other anodes include those described by Feng *et al.* [31, 32].

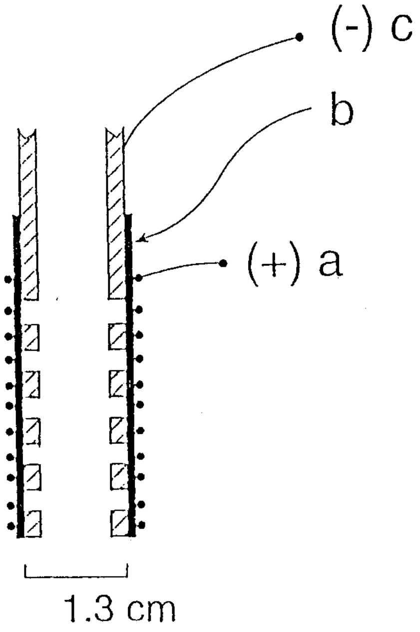

Fig. 1. Two dimensional view of electrode assembly: (a) quaternary metal oxide film on coiled Pt anode (0.62 mm thick); (b) solid state electrolyte (0.2 mm thick); and (c) stainless steel cathode (1 mm wall).

The electrolysis cell was assembled from a 50 mL three-necked pyrex flask. Teflon stoppers were machined to fit the outer two ports of the cell. One stopper allowed entry of the electrode assembly. The other stopper allowed passage of a hypodermic needle to add water or introduce a solid phase microextraction fibre for headspace analysis. A tapwater-cooled condenser was inserted in the center neck of the cell to decrease evaporative water loss during long electrolysis periods. All glassware was washed in 1 M KOH in a 1:1 mixture of ethanol and water, then in 2 M H_2SO_4, then rinsed with water and then dried overnight at 100 °C.

The power supply was a potentiostat/galvanostat (model 363, EG&G) Princeton Applied Research, Princeton, NJ) operated in the galvanostatic mode.

2.3. *Electrolyses*

Electrolyses were performed under galvanostatic control at 1.0 A ($\sim$0.2 A cm^{-2}) on 50 mL aliquots of benzoquinone stock solution. At the conclusion of each electrolysis, deionized water was added to bring the volume in the cell back to 50 mL (i.e., the starting volume).

2.4. *Surface characterization*

Micrographs and elemental analyses of the electrodes were obtained using a Hitachi S-246N scanning electron microscope (SEM, Mountain View, CA) equipped with a Link Isis energy dispersive X-ray spectrometer (EDS, Oxford). The response for the analyte elements was calibrated by the ZAF procedure with matrix effects corrections, as provided by the manufacturer.

2.5. *Chemical analyses*

The elemental content of the initial benzoquinone solution and one that had been electrolyzed for 64 h was determined by inductively coupled plasma mass spectrometry (ICPMS). The apparatus and typical operating conditions have been described by Hu *et al.* [35]. A semiquantitative analysis mode was used for calibration. Spectral scans were measured in separate m/z windows typically 50 Da wide. Analyte signals were adjusted for blank signal, isotopic abundance and approximate degree of ionization [36] and then compared to those for known concentrations of Co, La or Tl, whichever was in the particular m/z window of interest. Scans of the full m/z range showed that matrix effects were negligible.

In addition to the starting solution, samples representing eight electrolysis periods in the range 0.5–64 h were analysed for TOC, COD, pH and inorganic and organic anions. TOC was determined at the University of Iowa's Hygienic Laboratory, which is EPA approved. Samples were analysed using a DC190 TOC Analyzer (Dohrmann, Santa Clara, CA) using a combustion infrared method. COD was determined by titration with $KMnO_4$ as described by Feng *et al.* [32] or by a Hach DR2000 analyser (Loveland, CO).

Quinone and phenolic compounds were separated with a reverse phase Zorbax SBC18 column (25 cm length × 4.6 mm dia.) developed by Rockland Technologies (Chadds Ford, PA) and detected by absorption at 240 nm using a Kratos Analytical Spectroflow photometer (Ramesy, NJ) or with a Perkin–Elmer SCIEX API/1 ESMS (Thornhill ON, Canada) based on a single quadrupole mass spectrometer. The ESMS was equipped with a Perkin–Elmer SCIEX TurboIonSpray heating probe (Thornhill ON, Canada). The TurboIonSpray employs a heated gas flow near the electrospray needle which increases evaporation of solvent and allows liquid flow rates up to 1 mL min^{-1}. TurboIonSpray eliminates the need to split the eluent stream from the HPLC, eliminates some background peaks improves detection limits where background peaks are eliminated, and allows use of low organic solvent levels. Methanol and water at 1:1 ratio was the eluent used at a flow rate of 0.3 mL min^{-1}. In addition, inorganic and organic anions in the electrolysis solutions were monitored by direct infusion into the ESMS. Carboxylic acids were identified using an ICE-AS6 ion exclusion column from Dionex (Sunnyvale, CA) coupled to ESMS as described by Johnson *et al.* [37].

The inorganic and organic anions were quantified using an AS11 anion exchange column with an ED40 conductivity detector from Dionex. A sodium hydroxide and methanol gradient elution program as described in the literature accompanying the column provided the needed separation of the analytes of interest.

Polyacrylate and carbowax-divinylbenzene coated SPME fibres from Supelco (Bellefonte, PA) were used to extract constituents in the benzoquinone solution and in the headspace. Solid phase microextraction fibres underwent thermal desorption in a Varian 3400 gas chromatograph (Palo Alto, CA) equipped with a DB-1 or DB-5 column from J&W Scientific (Folsom, CA) and coupled to a Finnigan TSQ-700 triple quadrupole mass spectrometer (San Jose, CA).

Aldehydes and ketones were collected with Sep-Pak (DNPH–Silica) cartridges manufactured by Waters Chromatography (Marlborough, MA). The HPLC analysis of the eluent in the Sep-Pak cartridges was performed as described in the manufacturer's instructions accompanying the cartridges.

3. Results and discussion

3.1. *Comparison of electrode materials*

Table 1 presents a comparison of the performance of seven electrode materials applied for anodic degradation of benzoquinone in acetate buffer. Included are values of COD following electrolysis for specified time periods and brief comments pertaining to electrolysis solution or the electrode surfaces. The COD in these solutions was determined by titration with standard $KMnO_4$, a procedure that ignores contribution from the acetate/acetic acid components. The Au anode was least effective, requiring 48 h to decrease the COD to 582 mg mL^{-1}, that is, a 46% decrease from the original value. The Ru/Ti anode was slightly more effective than Au with a COD of 28 mg L^{-1} after 48 h. The PbO_2/Ti anode decreased the COD to 12 mg L^{-1} after 24 h; however, the Fe–PbO_2/Ti anode decreased the COD to 8 mg L^{-1} after only 10 h. The Ru–Ti–Sb–SnO_2/Ti anode was somewhat less efficient than the Fe–PbO_2/Ti anode, producing a COD of 6 mg L^{-1} after 24 h. The glassy carbon anode exhibited significant degradation within 10 h and corrosion of the Ti surface in the Sb–SnO_2/Ti anode was observed after only 0.5 h.

Comments are frequently offered by environmentalists that use of toxic lead-based anodes is not acceptable for electrochemical incineration applied to potable waters. Therefore, even though Ru–Ti–Sb–SnO_2/Ti anodes were slower to oxidize benzoquinone than Fe–PbO_2 anodes, the former was chosen for further evaluation in this project.

Quaternary metal oxide films corroded slowly when operated at large current densities (> 100 mA cm^{-2}) and ambient temperatures (25–35 °C). The U-tube shape of the Ru–Ti–Sb–SnO_2/Ti anode permitted circulation of thermostated water. With this electrode, the quaternary metal oxide films exhibited less corrosion when operated at higher temperature. Typically, corrosive losses were not visible nor detectable by gravimetry following 70 h electrolysis periods when the Ru–Ti–Sb–SnO_2/Ti tubular anode were operated at 200 mA cm^{-2} and 60 °C. The observed benefit from a higher operating temperature is not understood; however, it is known that increased temperature increases the rate of water discharge and, therefore, causes the anode potential to be decreased [38].

3.2. *Morphology and elemental composition of quaternary metal oxide film*

A freshly prepared quaternary metal oxide film on Ti that had not been used for electrolysis was examined by scanning electron microscopy. The micrograph (not shown) indicated a moderately uniform film corresponding to an aggregation of small crystallites with individual diameters $< 2\ \mu m$. The results of energy dispersive spectroscopy for this surface confirmed the presence of Sb, Ru, Ti and Sn. An elemental analysis of two different regions of the electrode surface yielded the following percentage compositions: Sb 7 and 8%, Ru 9 and 9%, Ti 10 and 21% and Sn 34 and 39%. In comparison, the relative concentrations of metallic components of the solution used for thermal preparation of quaternary metal oxide films were: Sb6%, Ru14%, Ti3% and Sn77%.

3.3. *Performance of the solid state electrolyte*

The Nafion membrane eliminated the need for added soluble salts to serve as supporting electrolytes, which facilitated direct analysis of product solutions using ESMS. These analyses can only be performed on solutions of low ionic strength to prevent build-up of

Table 1. Comparison of values for chemical oxygen demand (COD) and current efficiency achieved with seven electrode materials for the electrochemical incineration of 50 mL *of* 10 mM *benzoquinone in acetate buffer*

Electrode ($10\ cm^2$)	*Current* /mA cm^{-2}	*Time* /h	*COD** /mg L^{-1}	*Observations*
None	n.a.	0	1071	Brown–black solution
Au	10	48	582	Deep yellow solution
Ru/Ti	10	48	28	Yellow solution
Glassy carbon	10	10	–	Carbon particles suspended in solution
PbO_2/Ti	10	24	12	Colourless solution
Fe–PbO_2/Ti	10	10	8	Colourless solution
Sb–SnO_2/Ti	10	0.5	–	Apparent corrosion of Ti substrate
Ru–Ti–Sb–SnO_2/Ti	10	24	6	Colourless solution

* COD determined by titration with $KMnO_4$.

salt deposits that plug the orifice cone in ESMS. The Nafion® 117 membrane also prevented film formation on the anode surfaces during electrochemical incineration of 10 mM benzoquinone solutions over periods of several weeks. Comninellis and Pulgarin reported formation of organic films on Pt electrodes applied for anodic degradation of phenol and stated that film formation was exacerbated by high pH, low current density, high temperature and high phenol concentrations [39]. Similar problems of film formation with loss of electrode activity have been encountered in this laboratory during amperometric detection of phenol at Pt electrodes [40] and electrolysis of benzoquinone at Pt (unpublished).

Construction of electrolysis cells using a solid-state electrolyte required that the membrane be sandwiched tightly between porous anode and cathode materials [41]. Undoubtedly, for applications to solutions having zero ionic strength (i.e., very low conductivity) electrolysis occurred only on those small portions of the electrode surfaces that were in simultaneous contact with solution membrane. The result was a severely attenuated working area of the electrodes with a corresponding increase in the effective current density. We observed cell voltages >10 V as compared to <5 V for the presence of acetate buffer (pH 5).

Whereas this loss of effective electrode area, with a resulting increase in cell voltage, is seen as a disadvantage of this cell design, it is probably the explanation for the absence of organic film build-up on our anode surfaces. The higher effective current density resulted in an elevated rate of H_2O discharge at the working portions of the anode with a corresponding large flux density for OH radicals that are believed to be the source of O-atoms transferred to the product(s) of the electrochemical incineration reaction(s). Therefore, the lifetime of organic radicals was greatly diminished with the beneficial decrease (or elimination) of radical polymerization to form surface films. The smell of $O_3(g)$ also was detected above the electrode assemblies constructed with the Nafion® membranes. This can be expected when high current densities are applied at noble electrodes [42]. It is not known to what extent the evolution of O_3 assists in promoting the desired electrochemical incineration.

A disadvantage of using the solid-state electrolyte in place of added soluble electrolyte was a significant increase in the electrolysis time needed to decrease COD values to specified levels. For example, addition of 0.1 M acetate buffer (pH 5) to our cell resulted in a ~50% decrease in time required to achieve $>90\%$ decrease in COD.

3.4. *COD, TOC and pH results*

Figure 2 contains plots showing the change in COD and pH as a function of electrolysis time during the electrochemical incineration of a solution containing 100 mg L^{-1} benzoquinone. Values for COD, obtained with the Hach DR2000, steadily decreased from an initial value of 190 to 2 mg L^{-1} during a 64 h electrolysis period. Values of TOC (not shown) decreased to 1.2 mg L^{-1} during this same period. The pH of the electrolysis solution decreased sharply to a minimum of about 3 at 2 h followed by a gradual increase to a final value of about 4. Whereas the rate of CO_2 evolution is maximum immediately following the onset of electrolysis, ionization of the resulting H_2CO_3 ($pK_{a,1}$ 6.3) is not sufficiently strong to explain the sharp drop in pH. The most probable explanation is the formation of carboxylic acids by the first steps in benzoquinone degradation. Comninellis and Pulgarin reported the presence of maleic, fumaric and oxalic acids following electrolysis of phenol solutions [28, 39].

3.5. *Dissolved products of benzoquinone solutions*

Benzoquinone is very reactive in water and undergoes condensation reactions. The identity of these condensation products is highly dependent upon starting concentration and pH [43]. Products include dibenzofuran, biphenols, a trimer of molecular weight (MW) 290, plus a higher MW polymer. Condensation occurs rapidly in alkaline media but only slowly in neutral and acidic media. Following addition of benzoquinone to pure water, the colour of the solution changes from light yellow to a tea colour within 72 h and to coffee brown within one week. Because a similar colour transition is observed during the initial phase of the electrochemical incineration of benzoquinone, an attempt was made to look for the compounds named above. None of these compounds was detected using a solid phase microextraction fibre in combination with GCMS for a 10 mM benzoquinone solution.

In the electrolysis solutions (100 mg L^{-1} benzoquinone), only hydroquinone and resorcinol were detected on the solid phase microextraction fibres even though the sensitivity for phenols was increased by derivatization with acetic anhydride. Derivatization was not performed on the 10 mM benzoquinone solution. Results obtained using the polyacrylate fibre during electrolysis were consistent with the presence of hydroquinone and resorcinol following 0.5, 1 and 2 h. At 4 h, hydroquinone was not detected and at 8 h, resorcinol was not detected.

ESMS was also used to look for dibenzofuran, biphenols and other phenolic compounds. Although ESMS could detect these compounds in standard solutions, dibenzofuran and biphenols were not observed before or during the electrolysis of solutions containing 100 mg L^{-1} or 10 mM benzoquinone. However, phenol was detected in a stock solution of week old 10 mM benzoquinone that had not undergone electrolysis.

ESMS identified *p*-benzoquinone and hydroquinone in electrolysis solutions at ≤ 4 h. Chromatograms are compared in Fig. 3 for a benzoquinone solution after 1 h of electrolysis (A) and a standard solution (B). In addition to the standards shown in the chromatogram, selected ion monitoring was used to look

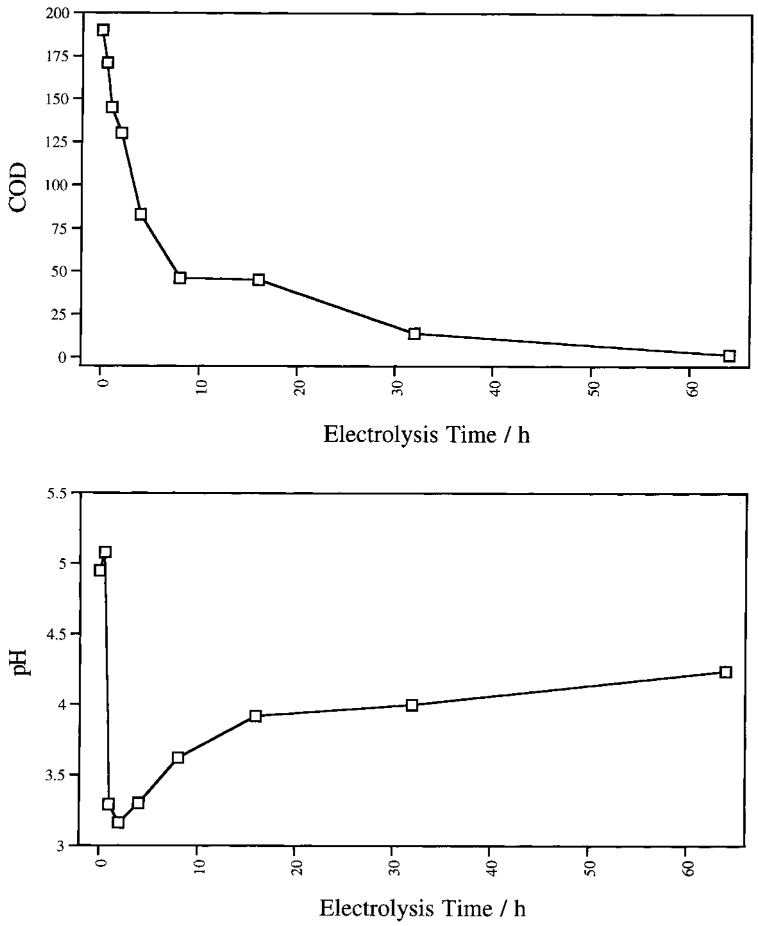

Fig. 2. Plots of COD and pH against time during electrochemical incineration of 100 mg L^{-1} benzoquinone using a Pt anode covered with the quaternary metal oxide film.

for 2-hydroxybenzoquinone. Kurien and Robins [44] reported that benzoquinone in dilute aqueous solution was converted to hydroquinone and 2-hydroxybenzoquinone via a benzene-1,2,4-triol intermediate product. A peak was not seen in the chromatogram for 2-hydroxybenzoquione but a signal was obtained at $m/z = 123$ whenever benzoquinone or hydroquinone were eluted from the column. 2-Hydroxybenzoquinone was not commercially available and was too unstable to be synthesized stored. However, 2,5-dihydroxybenzoquinone was detected by ESMS.

Because resorcinol was detected in the electrolysis sample by the solid phase microextraction method but not when using ESMS, resorcinol might have formed in the sample preparation step of the microextraction method. A high pH was required for the derivatization with acetic anhydride and benzoquinone is very reactive under these conditions. Another possible explanation is that the solid phase microextraction method was more sensitive to resorcinol than LC-ESMS.

The Zorbax SBC18 HPLC column works well for the separation of phenols in conjunction with ESMS. One method of separating phenols is ion suppression chromatography which uses a phosphate buffer (pH 4) to suppress ionization. Phosphate buffers are known to suppress the ESMS signal, as discussed by Johnson *et al.* [37]. Methanol and water are commonly used as a solvent for ESMS analyses; fortunately the SBC18 column retained the phenols with only this eluent. Because detection limits improve as column diameter decreases, the use of a SBC18 column (3 mm i.d.) was tested to improve the sensitivity of the analytical technique. However, resolution between hydroquinone and its isomers was lost unless trifluoroacetic acid was added to the eluent at such a high concentration that signal suppression occurred in the ESMS. Detection limits for HPLC–ESMS of phenols were as follows: hydroquinone and benzoquinone 100 $\mu g\,L^{-1}$, phenol and 2,5-dihydroxybenzoquinone 300 $\mu g\,L^{-1}$ and resorcinol and pyrocatechol 50 $\mu g\,L^{-1}$. When the same chromatographic conditions were coupled to an absorbance detector, the limits of detection for all six compounds were about 20 $\mu g\,L^{-1}$.

Table 2 shows the acidic intermediate products detected during the electrochemical incineration of 100 mg L^{-1} benzoquinone. The major identified intermediate products were formic, acetic, maleic, succinic and malonic acids. Maleic acid concentrations peaked at 2 h and, by 8 h, had decreased to $< 500\,\mu g\,L^{-1}$. The presence of succinic, malonic, acetic and formic acids persisted after 32 h of electrolysis. Fumaric acid was detected in the first 4 h of electrolysis; however, concentrations were always less than 500 $\mu g\,L^{-1}$. The inorganic anions chloride and

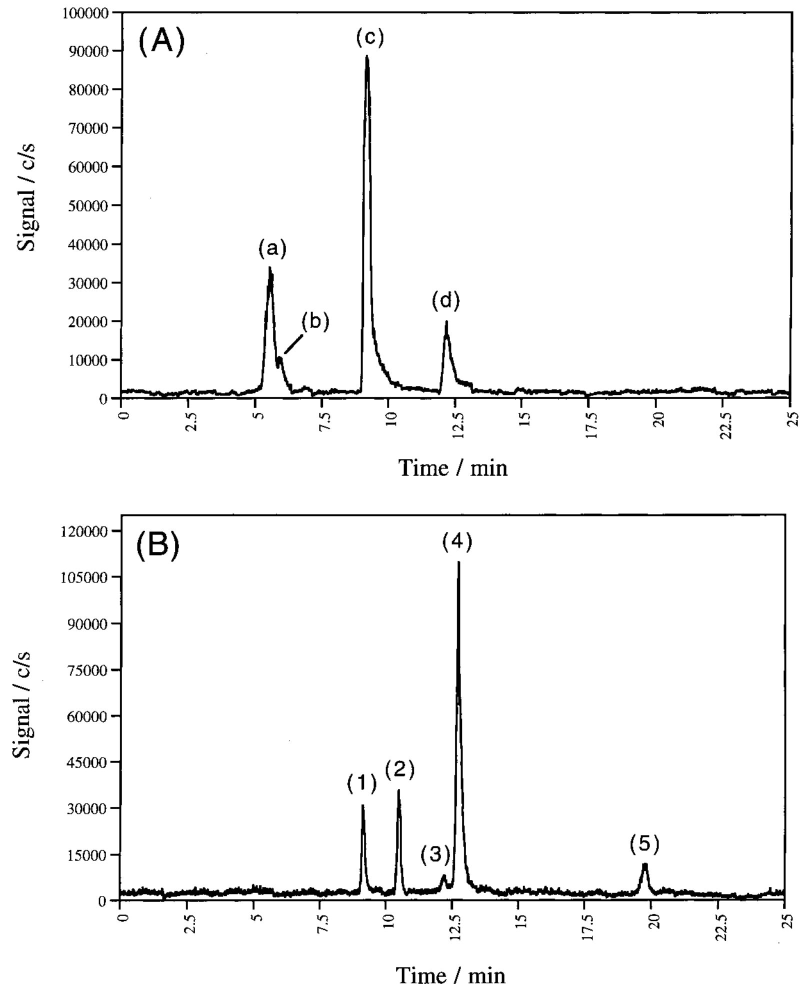

Fig. 3. Total ion signal in LC–ESMS obtained for (A) a 1 h electrolysis solution of 100 ppm benzoquinone and (B) a standard solution. Peaks in A: (a) maleic acid, (b) succinic acid, (c) hydroquinone and (d) benzoquinone. Peaks in B (1 ppm each): (1) *p*-hydroquinone, (2) resorcinol, (3) *p*-benzoquinone, (4) pyrocatechol and (5) phenol.

Table 2. Acidic intermediates identified in the product solution during electrochemical incineration of benzoquinone

Compound	*Peak concentration* /mg L^{-1}	*Electrolysis time* /h
p-Hydroquinone	1	1
Formic acid	5	0.5
Fumaric acid	< 1	0.5
Maleic acid	9	2
Malonic acid	1	8, 16
Succinic acid	10	8
Acetic acid	8	64

sulfate were present as impurities in the starting solution (≤ 1 mg L^{-1}). As a result of the anodic oxidation of chloride, chlorate was found in most electrolysis solutions at low levels ($\sim 500\,\mu g\,L^{-1}$). Because the detection limit for perchlorate was about 5 mg L^{-1} with the anion exchange column, it could not be detected with the conductivity detector. However, perchlorate was detectable by ESMS in all samples after about 4 h at concentrations estimated to be < 5 mg L^{-1}.

It was not possible to identify all the ions detected by direct infusion of the sample into the ESMS. Because of the numerous reactions occurring in the electrolysis process, the interpretation of these data was difficult and necessitated the coupling of the ESMS with LC.

A Dionex AS11 anion exchange column with a conductivity detector was used to quantify the anions listed in Table 2. Fifteen peaks were detected and a typical chromatogram is shown in Fig. 4. Because more peaks could be detected with the anion exchange column than with the ion exclusion column using ESMS detection, the identities of all peaks shown in Fig. 4 have not been established. The anion exchange column could not be coupled with ESMS because the sodium hydroxide eluent was not compatible with ESMS. Using LC–ESMS, acetic acid, formic acid, chloride, succinic acid, malonic acid, maleic acid, fumaric acid and sulfate were identified. Fumaric acid was quantified using LC with absorbance detection.

Figure 5 compares remediation rates for four compounds generated during electrochemical incineration of benzoquinone. Whereas benzoquinone and maleic acid quickly undergo a redox reaction in the electrolysis solution, succinic and acetic acids were only slowly oxidized by electrochemical incineration.

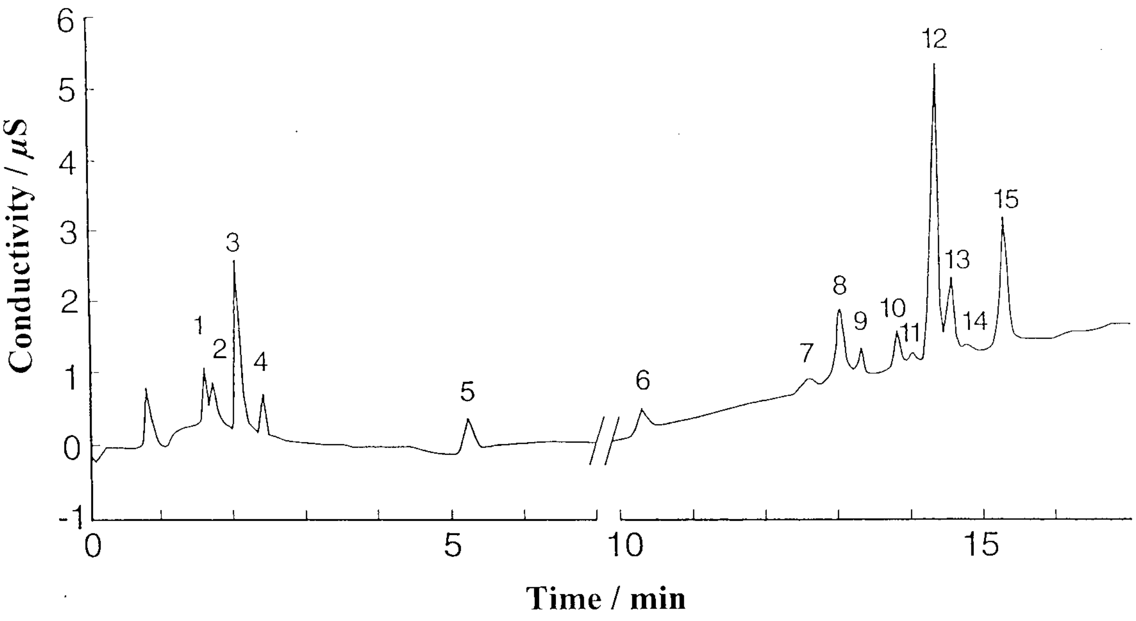

Fig. 4. Chromatogram of 100 mg L^{-1} benzoquinone solution after a 2 h electrolysis period using an anion exchange column with conductivity detection. Peaks: (1) acetic acid, (2) unknown, (3) formic acid, (4) unknown, (5) chloride, (6) chlorate, (7) carbonate, (8) succinic acid, (9) unknown, (10) malonic acid (11) unknown, (12) maleic acid, (13) unknown, (14) fumaric acid and (15) sulfate.

At 64 h, acetic acid was the only significant organic compound remaining in solution. Malonic acid levels were never higher than 1 mg L^{-1} and, therefore, it is apparent that malonate is oxidized more rapidly than either succinate or acetate. Formic acid levels gradually dropped throughout the course of the electrolysis from 5 mg L^{-1} in the solution electrolysed for 0.5 h.

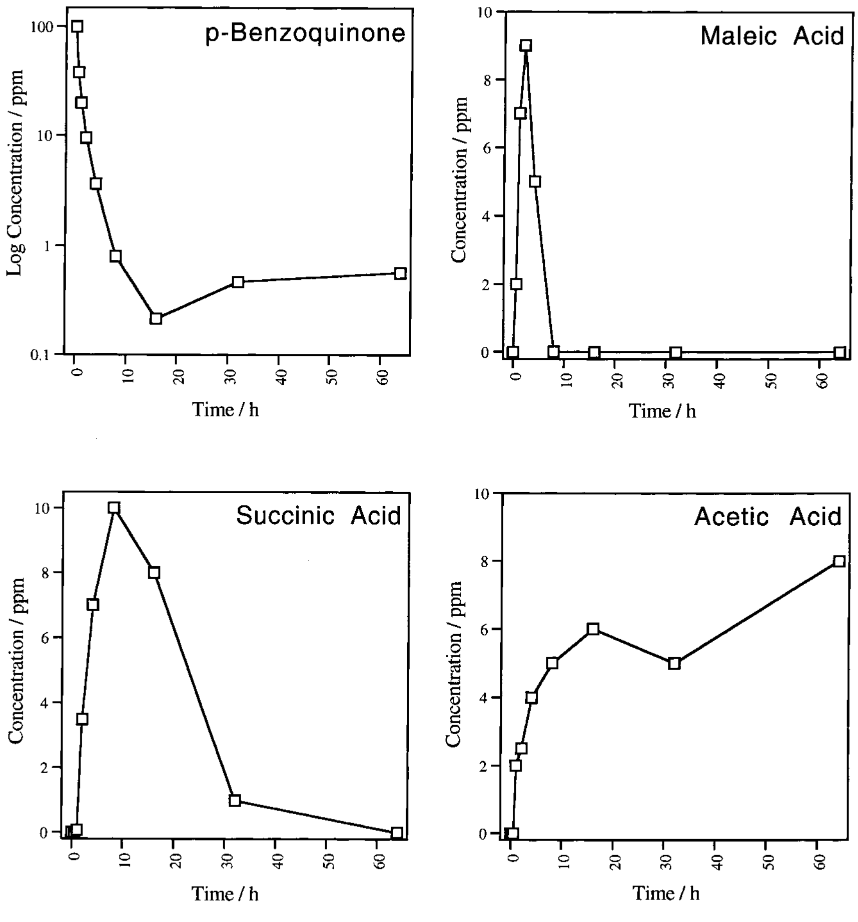

Fig. 5. Change in concentration of selected reaction products against electrolysis time using a Pt anode covered with the quaternary metal oxide film, Nafion membrane, and porous stainless steel cathode.

3.6. *Gas phase products*

The first attempt to analyse the gas phase above the benzoquinone solution during anodic oxidation was to measure the yield of CO_2 using Pt mesh electrodes and compare the CO_2 yields with that from the thermostatically controlled Ru–Ti–Sb–SnO_2/Ti tubular anode. The tubular electrodes were described in Feng *et al.* [32]. Concentrations of CO_2 were determined gravimetrically [45] and yields with Pt mesh electrodes were 63% without use of an antifoam and 72% with an antifoam. Carbon dioxide yields using the quaternary metal oxide tubular electrodes were 74% for electrolysis periods in the range 48–72 h. As stated earlier, there was evidence that some of the organic intermediate products were swept out of the solution by coevolution of CO_2 and O_2 with the result of CO_2 yields $< 100\%$.

Results from analysis of the headspace above the coiled electrode assembly using the solid phase microextraction fibre indicated the presence of acetaldehyde and benzoquinone. Therefore, Sep-Pak cartridges were used to quantify aldehydes and ketones emitted from the electrolysis solution. The Sep-Pak cartridges concentrated aldehydes and ketones from the gas stream. After a 48 h electrolysis period, $< 1\%$ of the carbon in benzoquinone appeared to have been oxidized to acetaldehyde and acetone. No formaldehyde was detected in the gas stream.

Because some of the small carboxylic acids generated by electrolysis are volatile, the condenser above the electrolysis cell was rinsed to see if any acids might adhere to it. Indeed, small peaks for acetic and formic acids were obtained using absorbance detection; however, no attempt was made to quantify these acids.

3.7. *Metal ions in electrolysed solution*

Conceivably, metals from the quaternary metal oxide film, the Pt substrate, or the stainless steel cathode could be dissolved into the product solution. This is an issue of concern in consideration of metal oxide films for remediating organic waste solutions. Therefore, the elemental content of a benzoquinone solution after a 64 h incineration period at a well-used electrode was determined by ICPMS. The estimated concentrations are: Ti 0.5, Cr 0.5, Mn 1, Ni 3, Zn 32, Ru 2.4, Sn 1, Sb 1 and Pt 0.6 $\mu g\,L^{-1}$. The concentrations determined following electrolysis using a newly-prepared electrode ranged from ten to one hundred times larger than those values reported here for a well-used electrode.

Chromium, Sn and Pt are elements of major environmental concern and these were present at very low levels (0.5–1 $\mu g\,L^{-1}$). Unexpectedly, Zn was at 32 $\mu g\,L^{-1}$. To detemine the source of Zn, the solution used for preparation of the quaternary metal oxide film was analysed by ICPMS. Indeed, Zn was present at 260 $\mu g\,L^{-1}$. The source of the Zn is speculated to be the 12 M HCl used to prepare that solution (see Section 2.1); however, that reagent was no longer available and confirmation of this speculation was not possible. The count rates for the Fe peaks at $m/z = 54$ and 56 were approximately the same as for the unremediated blank and, therefore, virtually no Fe dissolved from the stainless steel counter electrode during electrolysis.

3.8. *Electrochemical incineration mechanism*

Figure 6 presents a suggested mechanism for the oxidation of benzoquinone to maleic acid. If benzoquinone is absorbed onto the electrode surface and gives up an electron, a neighbouring adsorbed OH radical then attacks the benzoquinone. If this process repeats itself at the para position, the ring could open to form maleic acid and ethene. No ethene was detected in the headspace analysis; however, Tomilov *et al.* reported that ethene is oxidized to CO_2 at Pt but oxidized to acetaldehyde, acetone and propionaldehyde on Au or Pd electrodes [46].

The mechanism in Fig. 6 suggests that maleic acid is reduced to succinic acid at the cathode followed by oxidation to malonic and acetic acid at the anode. Kanakum *et al.* reported on the electroreduction of maleic and fumaric acids to succinic acid at a lead cathode [47]. In our laboratory, an electrolysis of succinic acid resulted in the appearance of malonic acid followed by acetic acid. Tomilov *et al.* reported that alcohols can be oxidized to the corresponding carboxylic acids if the reactants are not reduced at the cathode [46]. It is possible that use of divided cells to prevent access of maleic acid to the cathode might decrease the time for total electrochemical incineration.

4. Conclusions

Quaternàry metal oxide films applied to Ti or Pt substrates exhibited high and persistent activity as anode materials for the electrochemical incineration of benzoquinone. Use of Nafion® membrane, sandwiched between the anode and cathode, eliminated the need for addition of soluble salts and, thereby, permitted product solutions to be analysed by ESMS. However, the low ionic strength of the solutions resulted in a substantial decrease in the working area of the electrodes with a corresponding increase in the electrolysis period needed to bring the COD effectively to a zero value.

Numerous ionic intermediate products formed during the electrochemical incineration of benzoquinone were identified and quantified. The major intermediate products identified were *p*-hydroquinone, formic acid, fumaric acid, maleic acid, malonic acid, succinic acid and acetic acid.

In future work, a cation suppressor with the anion exchange column and ESMS is expected to permit the confirmation of all anions in the electrolysis solution.

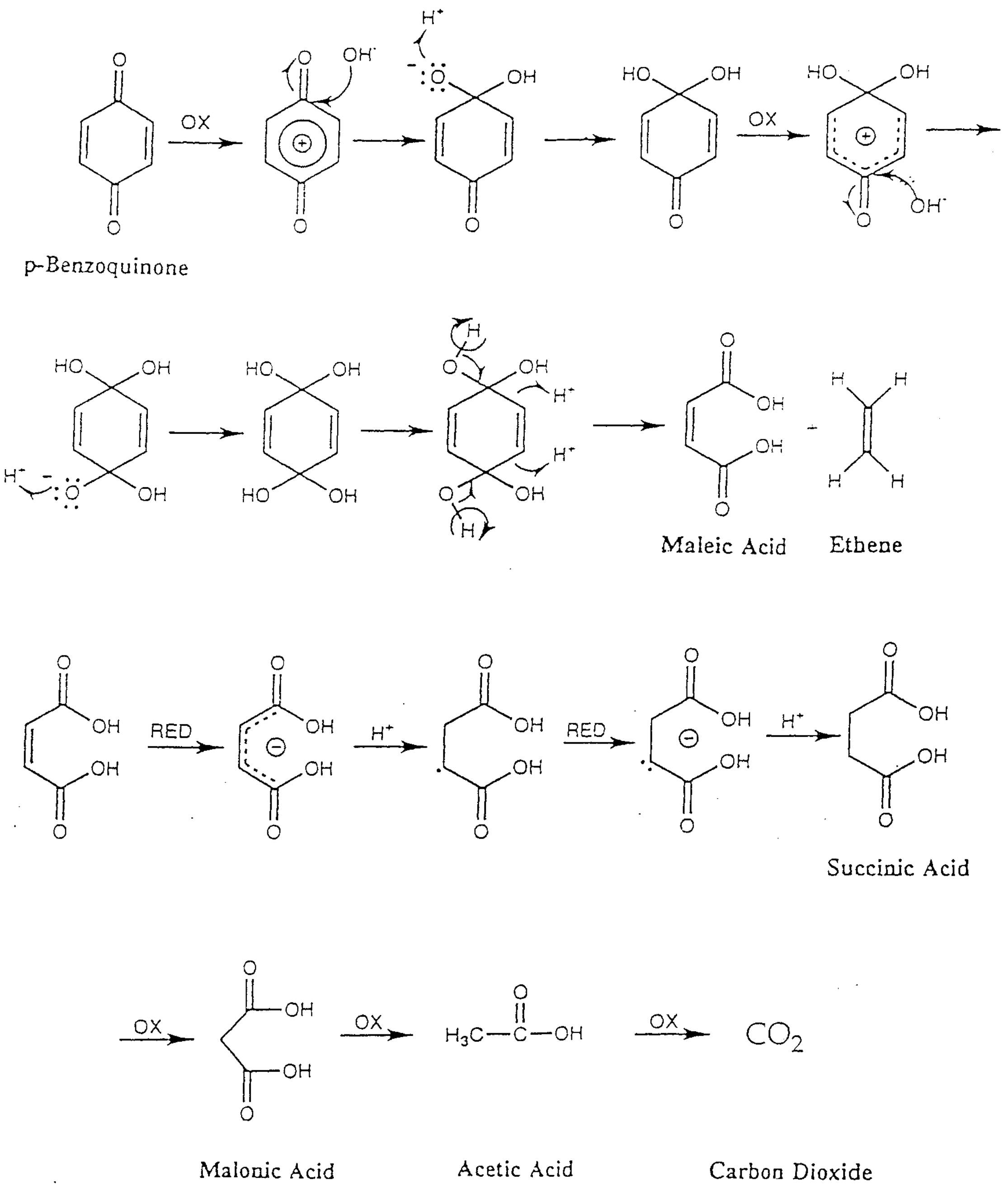

Fig. 6. Suggested reaction pathway for the electrochemical incineration of benzoquinone at a Pt anode covered with the quaternary metal oxide film.

Future work also will seek to shorten the electrolysis time by attempting to find a cathode that does not reduce maleic acid so the pathway can be avoided that results in generation of succinic and acetic acids that are degraded slowly.

A distinct advantage of using the solid-state electrolyte in large-scale applications of electrochemical incineration is the production of a final product which is essentially pure water that can be disposed into sanitary sewage systems without the need for desalting or pH adjustment.

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