Journal of Applied Electrochemistry **32**: 1241–1246, 2002.

Combined electrooxidation and assisted electrochemical coagulation of aqueous phenol wastes

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Received 13 May 2002; accepted in revised form 23 July 2002

Key words: assisted electrochemical coagulation, electrochemical oxidation, wastewater treatment

Abstract

The electrochemical treatment of basic (pH 12) aqueous phenol wastes using stainless steel electrodes is described. Two different processes have been identified in the removal of the phenol from aqueous wastes: electrooxidation, which leads to the formation of carboxylic acids and carbon dioxide, and solids-forming assisted electrochemical processes (including complexation, precipitation and/or coagulation) produced by the generation of Fe^{3+} ions in the waste during treatment. The effect of the initial carbon concentration, temperature and current density has also been investigated. It was determined that increases in the initial carbon concentration and temperature lead to increases in the reaction rates of the treatment processes and that increased current density leads to a decrease in the rate of electrooxidation and an increase in the rate of the solid-forming processes.

1. Introduction

Electrochemical technologies have undergone rapid development in recent decades [1–6] in terms of the treatment of aqueous wastes. Among the methods described, two are of particular interest in the treatment of wastewaters polluted with organic compounds: electrooxidation and electrochemically assisted coagulation. Both techniques have a significant advantage over other commonly used techniques (e.g., ozonization): namely, their ease of use on several types of wastes [7].

Electrooxidation involves the destruction of the organic matter contained in the wastewater by either direct anodic oxidation or by mediated oxidation performed by indirect electroreagents generated at the electrode surface. This technique depends mainly on the type of anode used [8–10] but also on the properties of the wastewater [11–16] and on the operating conditions [17–19]. This technique has been applied in recent years on bench and pilot-plant scale. Indeed, there are several commercial processes in use today. The main problem associated with this type of electrochemical treatment is its high operating cost. Recently, a great deal of research has been undertaken aimed at gaining a better understanding of the process and, consequently, obtaining a less expensive procedure.

In addition to electrooxidation, there are several other electrochemical technologies available for wastewater treatment although our understanding of these processes is less advanced. One of these technologies is assisted electrochemical coagulation. This technique can be applied to wastes that contain particulate matter as the contaminants and is based on the continuous production of a reagent (generated by the dissolution of the anode) that causes coagulation of the particles. The electrochemically generated coagulant destabilizes the particles and allows them to link and form flocs (flocculation process). The gas-forming side reactions that occur at the electrodes (evolution of oxygen and hydrogen) provide turbulence that improves the flocculation process and the subsequent solid/liquid separation by flotation. Clearly, the nature of the anode material, the waste characteristics and the operating conditions are the main factors that influence the efficiency of the process.

In the work described here, a stainless steel (SS) anode was used for the treatment of aqueous phenol wastes. This electrode acts as a source of Fe^{3+} ions (the most typically used precipitant and coagulant reagent) and can simultaneously electrooxidize organic matter directly (on its surface) or by mediated reagents (electrogenerated on its surface). The influence of the initial phenol concentration, temperature and current density were studied for the two simultaneously occurring processes. Two studies were carried out in order to characterize the processes: voltammetric and galvanostatic electrolysis experiments.

2. Experimental details

2.1. *Analytical procedure*

Carbon concentrations were monitored using a Shimadzu TOC-5050 analyser. Organic compounds were identified and quantified by liquid chromatography (HPLC). The separation and analysis of carboxylic acids was performed on a Supelcogel H column, with a mobile phase of 0.15% phosphoric acid solution at a flow rate of 0.15 $cm^3\ min^{-1}$. The u.v. detector was set at 210 nm. Aromatics were monitored using a Nucleosil C_{18} column, with a mobile phase of 40% methanol/60% water at a flow rate of 0.50 $cm^3\ min^{-1}$. In this case the u.v. detector was set to 270 nm. To quantify the total amount of iron in solution, atomic absorption measurements were performed using a SpectrAA 220FS spectrophotometer. Prior to measurement, samples containing insoluble compounds were dissolved in sulfuric acid and diluted to the measurement range.

2.2. *Electrochemical cell*

The oxidation of phenol was carried out in a single compartment electrochemical flow cell (Figure 1). Stainless steel (AISI 304) was used as the anode and cathode. Both electrodes were square in shape (100 mm side) with a geometric area of 100 cm^2 each and with an electrode gap of 9 mm. The electrolyte was stored in a 500 ml glass tank and circulated through the electrolytic cell by a centrifugal pump. A heat exchanger was used to maintain the temperature at the desired set point.

2.3. *Preparation of the stainless steel electrode*

Commercial AISI 304 stainless steel sheets were used as the electrode material in this work. The stainless steel was sanded and degreased with 2-propanol in an ultrasound bath and then cleaned with deionized water.

2.4. *Voltammetric studies*

Voltammetric studies were carried out in a conventional three-electrode cell using a computer-controlled potentiostat/galvanostat (model PGP 201, Voltalab 21, Radiometer-Copenhagen). Stainless steel was used for the working and counter electrodes, and $Hg/Hg_2Cl_2 \cdot KCl$ as the reference electrode. The electrodes used in the voltammetric studies were cathodically polarized at a potential of -0.5 V for 5 min in a solution containing sodium sulfate (5000 ppm) and sodium hydroxide (pH 12) to remove surface oxides. Voltammetry experiments were performed in unstirred solutions.

2.5. *Experimental procedures*

Galvanostatic electrolyses were carried out to determine the influence of the main parameters in the process. The average composition of the wastewater used (synthetic wastewater) in the experiments was 1050 mg C (phenol) dm^{-3}, 5000 mg Na_2SO_4 dm^{-3} and NaOH in suitable amounts to give a pH of 12. The pH was kept constant at 12.0 ± 0.1 during electrolysis by the continuous introduction of sulfuric acid (or sodium hydroxide) to the electrolyte reservoir. To establish the influence of the initial concentration of organic compound (C^0) as well as the temperature and current density, several experiments were performed with the ranges used being 610–1670 mg of C (phenol) dm^{-3} for the initial carbon concentration, 25–60 °C for temperature and 15–60 mA cm^{-2} for current density. Table 1 summarizes the conditions applied in each experimental run. The electrolyte flow rate through the cell was 1250 $cm^3\ min^{-1}$.

Voltammetric studies were carried out in order to study the mechanisms involved in the process. The voltages ranged from 0 to 2000 mV vs SCE at different scan rates (25 and 50 mV s^{-1}) and with different concentrations of phenol (0, 500 and 1000 mg dm^{-3}).

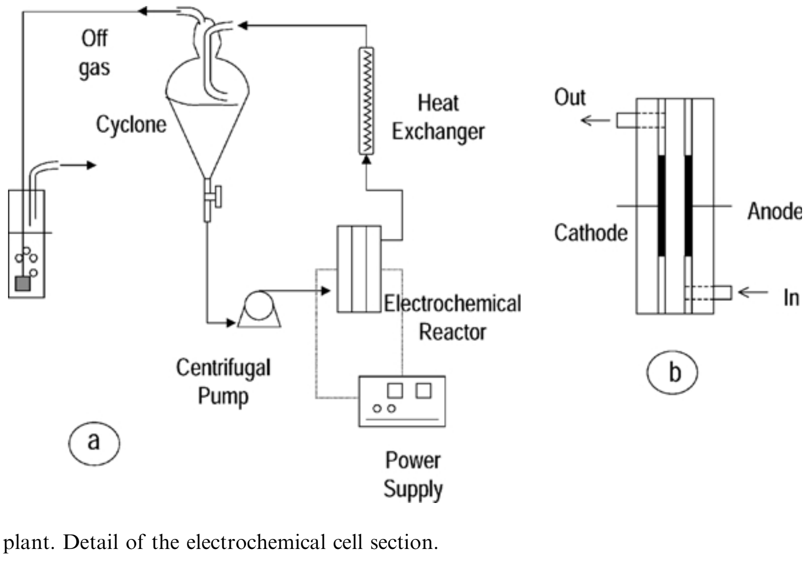

Fig. 1. Layout of the pilot plant. Detail of the electrochemical cell section.

Table 1. Experimental conditions studied in this work

Experimental run	C^0/mg C dm^{-3}	i/mA cm^{-2}	T /°C	Voltage/V
1	1050	30	25	6.7
2	1220	60	25	11.2
3	1670	30	25	6.9
4	610	30	25	7.6
5	1050	15	25	5.3
6	1060	30	60	5.5

3. Results and discussion

3.1. *Voltammetric study*

Figure 2 shows cyclic voltammograms of SS (first and second cycles) obtained at two different scan rates (25 and 50 mV s^{-1}) on solutions containing 5000 mg dm^{-3} of Na_2SO_4 at pH 12 (NaOH). A single anodic current peak can be seen and this increased in amplitude and moved to more positive potentials upon increasing the scan rate. The corresponding reverse peak cannot been observed, suggesting an EC process. When a solution containing Fe^{2+} was added to the cell the peak size increased, suggesting that it corresponds to the formation of Fe(III).

Figure 3 shows cyclic voltammograms of SS (first cycle) obtained with a scan rate of 25 mV s^{-1} for different phenol concentrations in solutions containing 5000 mg dm^{-3} of Na_2SO_4 at pH 12 (NaOH). A reduction in the peak size is observed as the phenol concentration is increased. This can be interpreted in terms of the formation of a film on the surface of the SS electrode, which then acts as a protective layer against further electrode oxidation. The same behaviour is evident in Figure 4 (voltammogram (two cycles) of a solution containing 5000 mg dm^{-3} of Na_2SO_4 at pH 12 (NaOH) and 500 mg dm^{-3} of phenol) where, in the second scan, the iron oxidation peak is no longer observed.

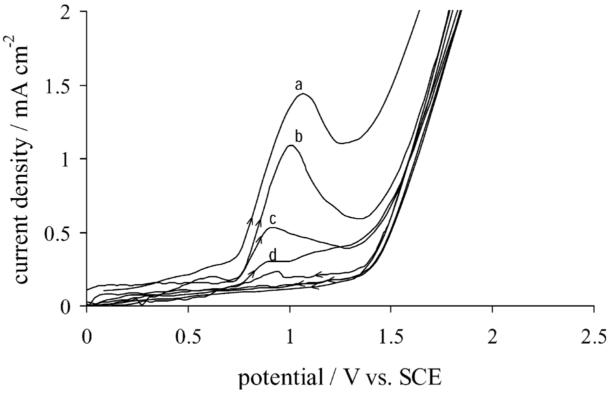

Fig. 2. Voltammetric study of SS anode on sodium hydroxide/sodium sulfate solutions (5000 mg dm^{-3} of Na_2SO_4 at pH 12) not containing organic matter. (a) 50 mV s^{-1}, 1st cycle; (b) 25 mV s^{-1}, 1st cycle; (c) 25 mV s^{-1}, 2nd cycle; (d) 50 mV s^{-1}, 2nd cycle.

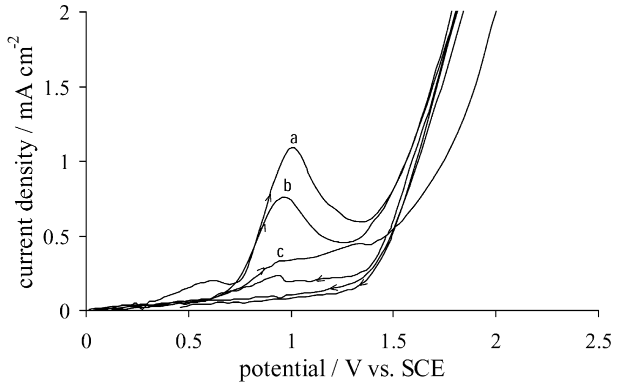

Fig. 3. Voltammetric study of SS anode (50 mV s^{-1}, 1st cycle) on sodium hydroxide/sodium sulfate solutions (5000 mg dm^{-3} of Na_2SO_4 at pH 12) containing different amounts of organic matter. (a) no phenol; (b) 500 mg dm^{-3} phenol; (c) 1000 mg dm^{-3} phenol.

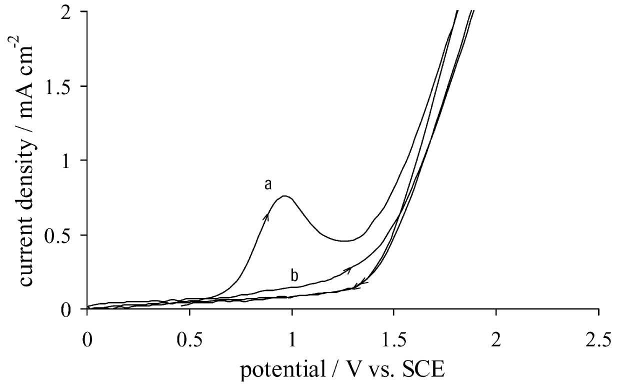

Fig. 4. Voltammetric study of SS anode (50 mV s^{-1}) on sodium hydroxide/sodium sulfate solutions (5000 mg dm^{-3} of Na_2SO_4 at pH 12) containing 500 mg dm^{-3} of phenol. (a) 1st cycle; (b) 2nd cycle.

The voltammograms contain no peaks that could be associated with the direct oxidation of organic compounds. Thus, the oxidation carried out with this electrode can be attributed mainly to the reaction of hydroxyl radicals – generated in the potential region of supporting electrolyte decomposition – and/or by other indirect electroreagents generated by these radicals.

3.2. *Galvanostatic electrolysis study*

Figure 5 shows the typical evolution of the different carbon fractions involved in the process (soluble organic, insoluble organic and inorganic) with the specific current charge passed. These data were obtained using a predetermined set of experimental conditions in order to provide a representative example ($C^0 = 1050$ mg dm^{-3}; $T = 25$ °C; $I = 30$ mA cm^{-2}). The SS electrode transforms the soluble organic matter into carbon dioxide and insoluble carbon compounds (particulate organics). Two different regions can be distinguished. In the first region ($Q < 22$ Ah dm^{-3}) the soluble organic carbon decreases in a linear fashion with the specific current charge and, at the same time, both the carbon dioxide and the insoluble carbon concentrations increase. The

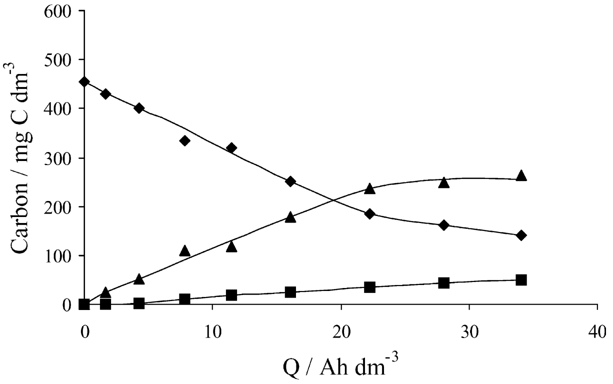

Fig. 5. Evolution of OC (soluble and particulate) and IC for different electrolysis assays. Key: (♦) soluble OC, (▲) insoluble OC, (■) IC.

second region of the graph ($Q > 22$ Ah dm^{-3}) corresponds to stabilization of the concentration of the particulate organics formed. In this region the rate of formation of carbon dioxide is maintained with respect to the first region and its value corresponds to the rate of decrease of the soluble organic carbon concentration.

The insoluble compounds formed in the electrolysis study are yellow/brown in colour, have a bulk aspect and can only be dissolved in strong acid media (pH < 1). GPC shows that the solid materials formed during the process consist of a mixture of various compounds of low molecular weight (ranging from 200 to 500 mg mmol^{-1}). It was determined by incineration that 75% of the solid material was nonvolatile.

Figure 6 shows the influence of the current density, temperature and initial phenol concentration on the concentrations of carbon dioxide and insoluble carbon compounds formed on passing a given specific current charge (25 Ah dm^{-3}), conditions that ensure the behaviour described above for region 2 in every case. It can be observed that particulate compounds are always formed in higher quantities than carbon dioxide, indicating that, in region 1, the rate of combustion is lower than the rate of formation of insoluble carbon compounds. Moreover, in region 1 it can be concluded that the initial carbon concentration and temperature both act to increase the reaction rates, albeit in a different way: a higher temperature favours combustion over solid-forming processes whereas a higher initial carbon concentration favours the evolution of the solid-forming processes. Finally, increased current density leads to a decrease in the rate of combustion and an increase in the rate of the solid-forming processes.

Figure 7 shows, as an example, the main soluble intermediates (identified by HPLC) typically formed during the electrolysis treatment of the waste under the experimental conditions described previously. Only carboxylic acids (maleic, fumaric and oxalic) were detected, indicating that the electrooxidation of phenol leads directly to aromatic ring opening. It has been proposed [20] that oxidation of phenol proceeds through a first stage in which certain aromatic intermediates, such as hydroquinone and benzoquinone, are formed

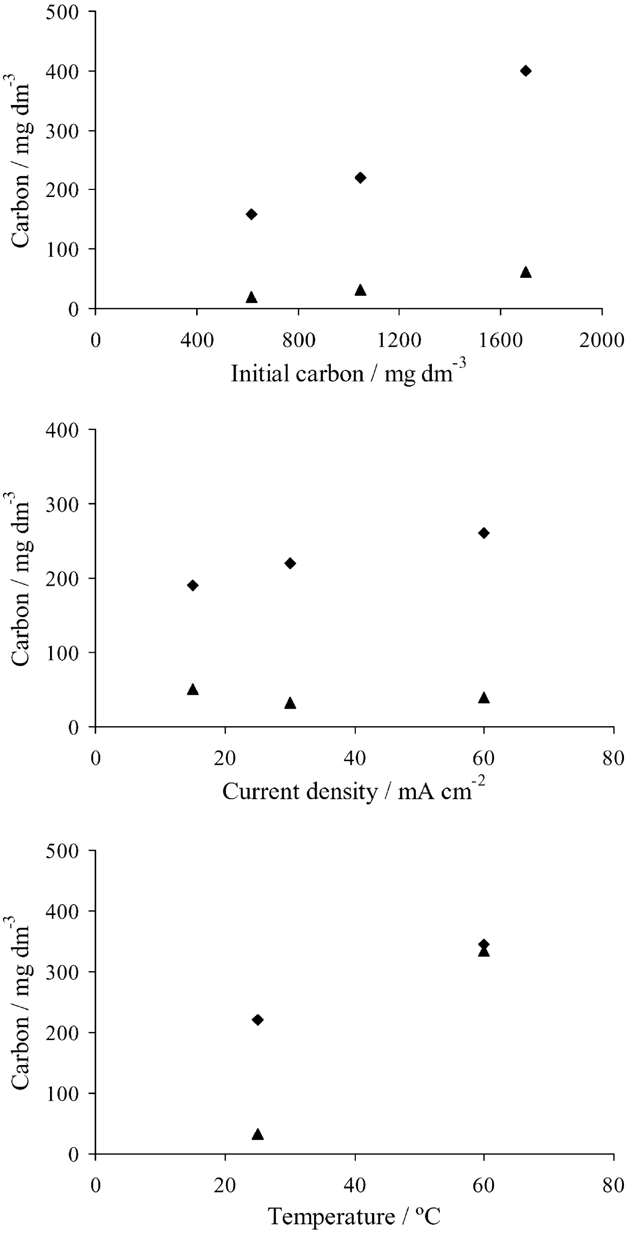

Fig. 6. Inorganic and insoluble compound concentrations corresponding to $Q = 25$ Ah dm^{-3}. Key: (♦) insoluble OC, (▲) IC.

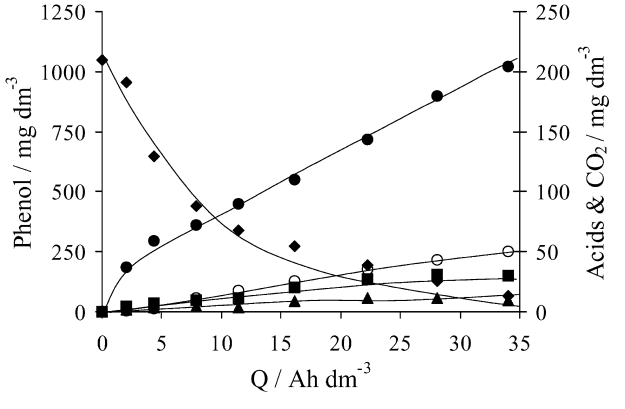

Fig. 7. Evolution of the soluble carbon species in an electrolysis assay ($C^0 = 1050$ mg dm^{-3}; $T = 25$ °C; $I = 30$ mA cm^{-2}). Key: (♦) phenol, (▲) fumaric acid, (■) maleic acid, (●) oxalic acid, (○) carbon dioxide.

and then a second stage during which these acids are oxidized to carbon dioxide. However, in this study the two types of aromatic intermediates were not detected. This can be explained [21] by the high pH of the wastewater in that both compounds are unstable under these conditions.

Figure 8 shows the evolution of the soluble and total iron concentrations during the electrolysis treatment of the wastewater previously used as an example (assay *a*). Figure 8 also shows the evolution of both parameters obtained from a solution (at pH 12) containing only Na_2SO_4 (5000 mg dm^{-3}) under the same electrolysis conditions (assay *b*). The total iron concentration increases in a linear manner with the current charge passed through the system and the rate of iron generation is higher when organic matter is not present in the waste. The current efficiency of SS corrosion (calculated from the total ion concentration) is 6.2% when no organic matter is present in the electrolyte and 3.0% when organic matter is present. This trend can be explained by assuming that current can be used to oxidize both the anode and the organic matter. In both cases the soluble iron concentration was almost negligible, indicating that all measured iron is contained in the solid as a consequence of the high pH values of the waste.

Given the fact that some Fe^{3+} ions are dissolved from the anode surface and that the solids contained iron, and also taking into account the characteristics of the solids, it seems reasonable that these compounds were formed by electrochemically assisted processes involving the organic compounds present in the waste (phenol and organic intermediates) upon treatment with ferric ion. It has been reported that phenol [22, 23] and organic acids [24, 25] can interact chemically with trivalent cations to form insoluble species by combined complexation, precipitation and/or coagulation processes.

In an attempt to confirm the chemical nature of the formation of the insoluble compounds, several simple batch experiments were carried out. In these assays iron(III) chloride was added to solutions containing only one organic component (phenol or intermediates) at pH 12 and containing 5000 mg dm^{-3} of Na_2SO_4. In all cases the formation of insoluble compounds, with similar characteristics to those obtained in the electrolysis assays, were detected. Figure 9 shows the evolution of the steady state concentration of phenol and the organic intermediates monitored with increasing concentration of iron in the waste. In all cases there is a typical evolution of a coagulation process with a maximum in the removal of organics for an intermediate iron concentration.

Due to the high pH of the waste (pH 12), Fe^{3+} ions that are dissolved from the anode precipitate to form iron(III) hydroxide. The organic complexes formed by the interaction of phenol and carboxylic acids with iron (iron phenolates, iron oxalate complexes *etc.*) can be adsorbed onto the surface of this precipitate. These solids can be simultaneously trapped within the forming hydroxides (coagulation process) and the resulting particulate compounds can interact physically to form flocs (flocculation process). These complex processes explain the shape of the organic matter against Fe^{3+} evolution graph since in the case where only adsorption of organics into iron hydroxide occurs, there would not be a decrease in the removal of organic matter with added iron.

The high flow turbulence and the gas evolved from the electrodes in the cell (electrolysis assays) may favour the flocculation process. Moreover, the gas evolving favours flotation of the solids and their removal from the system.

The proposed mechanism is also consistent with the characteristics of the solids formed in the electrochem-

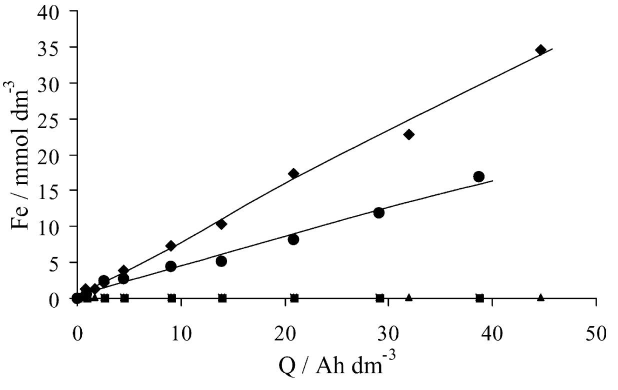

Fig. 8. Evolution of total and soluble iron concentrations. Assay a: (●) total iron, (▲) soluble iron; assay b: (◆) total iron, (■) soluble iron.

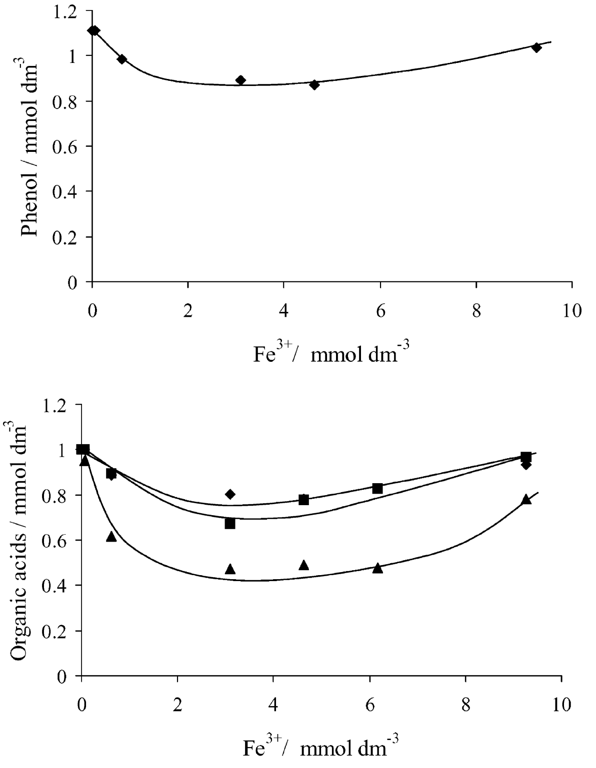

Fig. 9. Evolution of the steady state concentration of phenol and organic acids for different concentrations of added $FeCl_3$. Key: (◆) oxalic acid, (■) maleic acid, (▲) fumaric acid.

ical process, including colour and percentage of non-volatile compounds [mainly due to the high content of iron(III) hydroxide], molecular weight range measured by GPC (due to the organics adsorbed) and solubility of the solid in strong acid media (at $pH < 1$ iron hydroxide is not stable).

The stainless steel used in this work contains nickel and chromium, besides iron, as metallic elements. To test the presence of compounds of these toxic elements in the treated waste, both elements were measured by atomic absorption. No nickel was detected and only low concentrations of chromium were dissolved from the anode (maximum measured concentration in the experiments exposed in this work was $0.09\ \mathrm{mg\ dm^{-3}}$). In previous work [23], similar treatment with acid wastes was carried out. In this case the presence of both toxic metals was detected in higher concentrations. Both facts indicate that this electrode material can be used only for the electrocoagulation of basic phenolic wastes without significant chromium or nickel dissolution.

4. Conclusions

(i) Electrochemical technologies using stainless steel electrodes can be used for treating basic phenolic aqueous wastes. Final products of the electrochemical treatment are carbon dioxide and insoluble organic compounds. Particulate compounds are always formed in higher quantities than carbon dioxide.

(ii) Two different processes have been identified in the removal of phenol from aqueous wastes: electro-oxidation, which leads to the formation of carboxylic acids and carbon dioxide, and assisted electrochemical processes (including complexation, precipitation and/or coagulation), produced by the generation of Fe^{3+} ions in the waste undergoing treatment.

(iii) Increases in initial carbon concentration and temperature increase the reaction rates of the treatment processes, albeit in a different way: high temperature favours combustion over solid-forming processes and a higher initial carbon concentration favours the evolution of the solid forming processes.

(iv) An increase in current density causes a decrease in the rate of combustion and an increase in the rate of the solid forming processes.

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