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Anodic oxidation of phenol on Ti/IrO_2 electrode: Experimental studies

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ABSTRACT

The electrochemical oxidation of acidic solutions of phenol on a Ti/IrO_2 anode has been investigated by cyclic voltammetry and bulk electrolysis in a single-compartment cell. In the potential region of oxygen evolution, anodic oxidation resulted in electrode passivation (as evidenced by voltammetric measurements) allegedly due to the formation of a polymeric film on its surface. Phenol degradation increased with increasing temperature in the range investigated 30–80 °C and it was affected by the addition of Cl^- and Br^- anions in the supporting electrolyte. Complete conversion of 10 mM phenol was achieved after 37 Ah L^{-1} of charge passed at 80 °C under galvanostatic conditions (50 mA cm^{-2}) in absence of Cl^-. In contrast only 10 Ah L^{-1} were needed in the presence of 35 mM Cl^-. The presence of chloride can induce reactions involving chlorohydroxyl radicals and electrogenerated oxidants such as free chlorine. On the other hand, addition of Br^- slightly inhibited degradation possibly due to bromide scavenging of electrogenerated active species. Phenol degradation proceeded through the formation of three dominant, aromatic intermediates, namely 1,4-benzoquinone, hydroquinone and pyrocatechol, while total oxidation to CO_2 was not significant unless harsh conditions (i.e. high temperatures and charges) were employed.

1. Introduction

Toxic and non-biodegradable organic pollutants, such as phenolic substances, are typically found in various industrial wastewaters including pulp and paper mill industries, petrochemical refineries, plastics and glue manufacturing and coke plants [1]. Such wastewaters usually have to be pre-treated in order to minimize their organic charge which is frequently quite toxic and biorecalcitrant. There are several methods of wastewater treatment including incineration, adsorption, biological treatment and chemical or electrochemical oxidation. The choice of the treatment depends on the economics, as well as the reliability and the treatment efficiency. Electrochemical oxidation processes have proven to be an efficient and versatile technology capable of handling a wide variety of wastewaters [2,3]. Increased efficiencies can be achieved through the use of compact bipolar electrochemical reactors and three dimensional electrodes providing large surface areas. Depending on the anode material and reaction conditions, electrochemical oxidation can either promote total oxidation of the organics to CO_2 (i.e. using "non active" type electrodes) or convert them to intermediate products (i.e. using "active" type electrodes) [4]. In previous studies [5–8], several anode materials have been tested for the electrochemical oxidation of phenol under various experimental conditions. Iniesta et al. [5] studied the oxidation of phenol on boron-doped diamond (BDD) anodes and reported that phenol and its oxidation by-products could readily be converted to CO_2 upon prolonged anodic treatment. Although anodic oxidation on BDD appears to be an efficient mineralization process, it still remains unattractive for industrial applications due to its relatively high cost. Hence, several other traditional anodes have been investigated regarding their efficiency towards phenol electrochemical oxidation. Using a Ti/SnO_2 electrode, only small amounts of aromatic intermediates were formed in contrast to a Pt anode, where such intermediates were deserved at higher concentrations [6]. Moreover, Ti/SnO_2 gave high current efficiencies and also allowed the quasi-complete total organic carbon elimination. On the other hand, electrodes such as Ti/IrO_2 and Ti/RuO_2 gave relatively low current efficiencies [6,7]. In a recently published work concerning phenol oxidation on Ti/IrO_2 in a two-compartment flow cell under pseudo-potentiostatic electrolysis for electroorganic synthesis [8], it was found that phenol was almost completely converted to partial oxidation organic aromatic products (hydroquinone, benzoquinone and pyrocatechol). In general, the distribution of reaction intermediates seems to be significantly dependent of the electrode materials, as well as the working conditions including electrolyte composition and temperature. The main by-products

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Nomenclature

ACE	average current efficiency
BQ	1,4-benzoquinone (mmol C L^{-1})
COD	chemical oxygen demand (g O_2 m^{-3})
DSA	dimensionally stable anodes
F	Faraday constant (96,487 C mol^{-1})
HQ	hydroquinone (mmol C L^{-1})
I	applied current (A)
i	applied current density (mA cm^{-2})
ICE	instantaneous current efficiency
PC	pyrocatechol (mmol C L^{-1})
Ph	phenol (mmol C L^{-1})
Q	charge passed (Ah L^{-1})
R	organic matter
S_p	total selectivity
t	time (s)
$(TOC)_{calc}$	calculated total organic carbon (mmol C L^{-1})
TOC	total organic carbon (mmol C L^{-1})
V	solution volume (L)

reported in the literature are various quinones such as hydroquinone, benzoquinone and catechol [5–9], while organic acids (such as maleic, fumaric and oxalic) are also produced on SnO_2 or PbO_2 anodes [6]. Addition of NaCl in the solution results in the formation of organochlorinated compounds such as 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol [7]. In a recent study concerning phenol oxidation over β-PbO_2 in acidic media [10], the dominant degradation pathway proceeded through the formation of organic aliphatic acids rather than quinones.

In this work, the anodic oxidation of phenol on IrO_2 electrodes was studied using a single-compartment cell. Cyclic voltammetry and bulk electrolysis were carried out in 1 M $HClO_4$ to evaluate the activity of Ti/IrO_2, a typical "active" anode, for phenol oxidation and organic transformation under different experimental conditions. Emphasis was given on the effects on degradation of both reaction temperature and the addition of different electroactive anions (Cl^-, Br^-, and SO_4^{2-}) in the electrolyte.

2. Experimental and analytical

The Ti/IrO_2 working electrode was prepared by thermal decomposition of 250 mM H_2IrCl_6 (Acros Organics, 40%) metal precursor dissolved in isopropanol (Fluka, 99.5%), on a disc-shaped titanium support. The titanium substrate was sandblasted to ensure good adhesion of the deposit on its surface. Following sandblasting, the substrate was treated using a 1 M oxalic acid solution to clean its surface from residual sands. The substrate was then dried in an oven at 70 °C and weighed. The precursor solution was spread on the titanium substrate forming a thin film layer on the substrate surface. Afterwards, the sample was heated at 70 °C for 10 min to allow solvent evaporation. Thermal decomposition of the precursor solution was performed at 500 °C in air for 60 min. The final IrO_2 loading was 1.4 mg cm^{-2}.

Cyclic voltammetry was carried out in a conventional three-electrode cell using a computer-controlled Autolab potentiostat (model PGSTAT 30). Ti/IrO_2 was used as the working electrode, $Hg/Hg_2SO_4{\cdot}K_2SO_4$(sat) as the reference electrode and a Pt wire as the counter electrode. The electrolyte was 1 M $HClO_4$ in millipore water. The working phenol solutions were prepared in 1 M $HClO_4$ and always stirred for 20 min before each voltammetric measurement. Voltammetry was performed at room temperature.

Bulk electrolysis was conducted in a single-compartment cell comprising a Ti/IrO_2 anode (loading: 1.4 mg cm^{-2}) with an active working area of 12.5 cm^2 and a zirconium cathode enclosed in a porous porcelain vessel; ideal mixing was achieved using a magnetic stirrer. The temperature remained constant by means of a thermostat. A condenser was used to prevent liquid evaporation at high temperatures. The volume of the reaction mixture was 0.15 L. All experiments were carried out in acidic media, using 1 M $HClO_4$ solution as electrolyte. The electrochemical reactor and procedures are described in detail elsewhere [9].

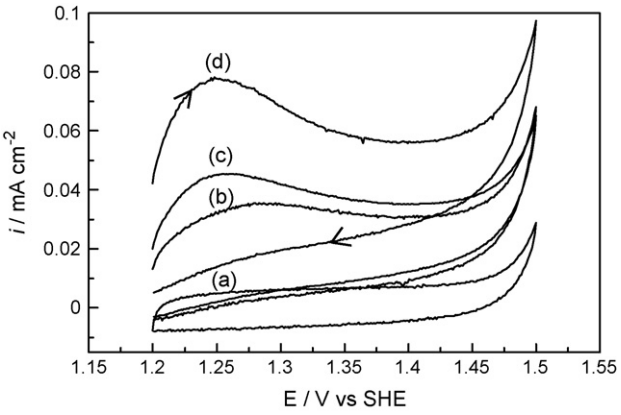

Fig. 1. Cyclic voltammograms (first scan) on Ti/IrO_2 anode at different phenol concentrations in 1 M $HClO_4$. (a) 0; (b) 2; (c) 5; (d) 10 mM. Scan rate 10 mV s^{-1}, T = 25 °C.

Phenol and its aromatic oxidation intermediates were quantified by HPLC (Shimadzu, series 6) using a Nucleosil C_{18} column with 45:55 acetonitrile:acetic acid (10%) mixture as the mobile phase at a flow rate of 8×10^{-4} L min^{-1}. Chemical oxygen demand (COD) was measured colorimetrically according to the dichromate micro-digester method using a Hach DR200 spectrophotometer. Total organic carbon (TOC) was measured using a Shimadzu 5050 TOC analyzer.

Based on the measured COD values, the instantaneous current efficiency (ICE) and the average current efficiency (ACE) for the anodic oxidation of phenol can be computed as follows [11]:

$$\mathrm{ICE} = \frac{\left[(\mathrm{COD})_t - (\mathrm{COD})_{t+\Delta t}\right]}{8I\Delta t}FV \quad (1)$$

$$\mathrm{ACE} = \frac{[(\mathrm{COD})_o - (\mathrm{COD})_t]}{8It}FV \quad (2)$$

where $(COD)_o$ is the initial chemical oxygen demand (g O_2 m^{-3}) at time t = 0, $(COD)_t$ and $(COD)_{t+\Delta t}$ are the chemical oxygen demand (g O_2 m^{-3}) at time t and $t + \Delta t$ (s) respectively, I is the applied current (A), F is the Faraday constant (C mol^{-1}) and V is the volume of the electrolyte (m^3).

3. Results and discussion

3.1. Cyclic voltammetry

Fig. 1 shows typical voltammetric curves (first cycle) for different phenol concentrations in 1 M $HClO_4$ recorded at a scan rate of 10 mV s^{-1}. This figure shows clearly that the oxidation peak (current density) increases with increasing phenol concentration for the potential range of concern. This oxidative peak, observed approximately at 1.25 V vs SHE, corresponds to the formation of phenoxy radicals according to previously proposed mechanisms [1].

Consecutive cyclic voltammograms are shown in Fig. 2 for 10 mM phenol in 1 M $HClO_4$ solution and for a scan rate of 10 mV s^{-1}. As the number of cycles increases, the anodic current peak decreases until a steady state is reached (after 5 cycles). In agreement with previous studies [4,9], this decrease in electrode

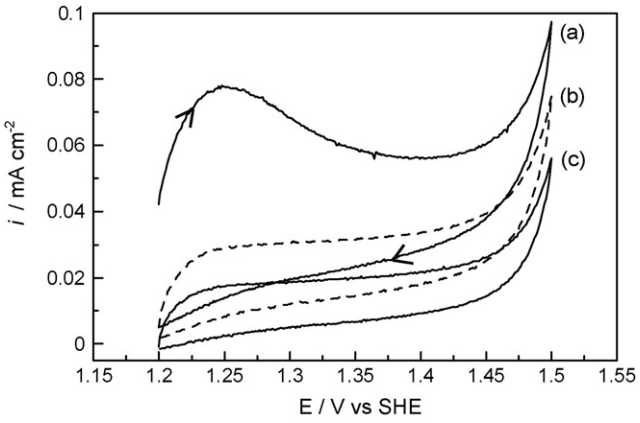

Fig. 2. Cyclic voltammograms on Ti/IrO_2 anode at 10 mM phenol concentration in 1 M $HClO_4$. (a) 1st cycle; (b) 2nd cycle; (c) after five cycles. Scan rate 10 mV s^{-1}, T = 25 °C.

activity is linked with the production and deposition of polymeric adhesive products on the electrode surface (according to Fig. 3).

Recent studies [12,13] have focused their attention on the identification of such polymeric compounds formed during phenol oxidation on DSA® electrodes (such as IrO_2, Pt and β-PbO_2). According to these studies [12,13], polymer formation is thought to occur through a process involving less than two electrons per molecule of phenol, while a decrease in solution pH can lead to polymer precipitation.

3.2. Bulk electrolysis

3.2.1. Effect of temperature

Experiments were performed under galvanostatic conditions (50 mA cm^{-2}) using a 10 mM phenol solution and at three different temperatures (30, 60 and 80 °C). The results are shown in Fig. 4

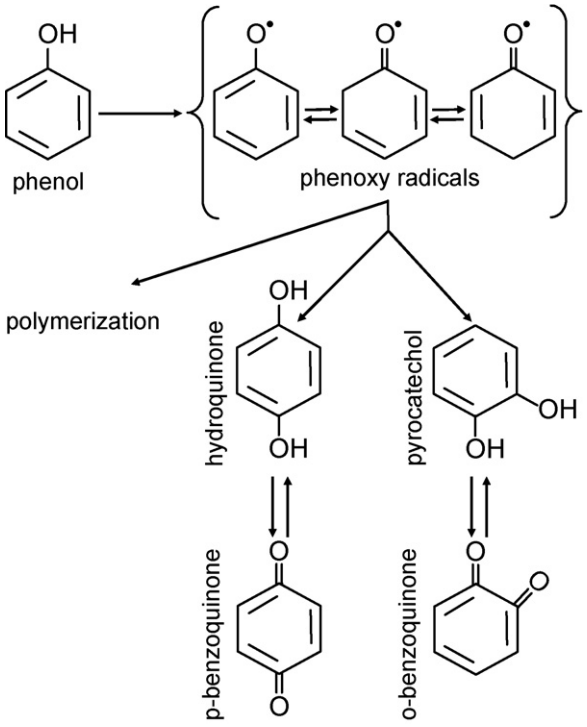

Fig. 3. Reaction pathway of electrochemical phenol oxidation.

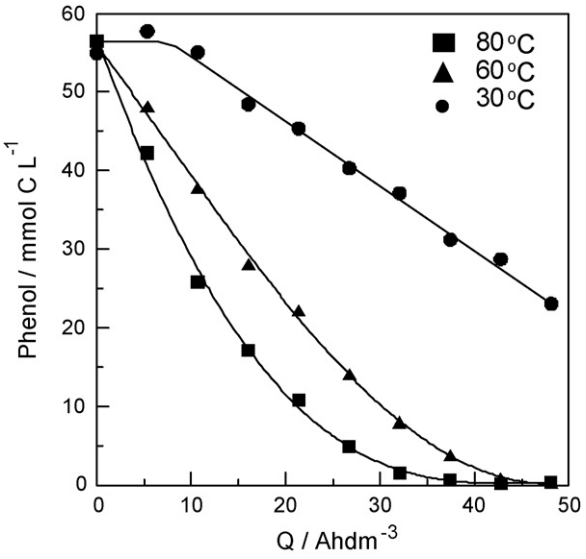

Fig. 4. Evolution of phenol concentration (10 mM) as a function of temperature during electrolysis on Ti/IrO_2 anode in 1 M $HClO_4$ and 50 mA cm^{-2}.

and Table 1. These results show clearly that oxidation of phenol proceeds faster with increasing temperature. After 48 Ah L^{-1} of charge passed quasi-complete conversion of phenol is observed at either 60 °C or 80 °C and this is accompanied by lower levels of TOC reduction (Table 1), thus implying the formation of intermediates as it will be discussed in detail in Section 3.2.3. As a matter of fact, this is more pronounced for the experiment performed at 30 °C where after 48 Ah L^{-1} of charge passed, only 10% of the starting material was mineralized despite a phenol conversion of 60%. This feature is characteristic of "active" type anodes with low oxidation power.

Table 2 shows the average current efficiency after a phenol conversion of 50% and 90%. It is obvious that electrolysis is not favored at low temperature where a low ACE was observed (1.1 for a phenol conversion of 50%). On the other hand, at higher temperatures (60 and 80 °C), the current efficiency is much higher (up to 8.4%). Interestingly, the ACE is quite constant during the process. In fact, even temperature above 60 °C seems to have only a slight effect on the ACE (Table 2). Taking into account that heat is always produced during the electrolytic process, high operation temperatures are recommended. Therefore, all subsequent experiments were performed at 80 °C.

Table 1
Effect of temperature on COD, TOC and phenol reduction (%) after 48 Ah L^{-1} of charge passed and range of ICE (%) values recorded. Initial phenol concentration 10 mM.

Temperature (°C)	COD reduction (%)	TOC reduction (%)	Phenol reduction (%)
30	8.6	10.1	60
60	41.3	19.7	99
80	61.5	59.1	99

Table 2
Effect of temperature on average current efficiency (ACE) for the 50% and 90% phenol elimination.

Temperature (°C)	ACE, % for the 50% Ph elimination	ACE, % for the 90% Ph elimination
30	1.1	–
60	7.0	6.1
80	6.6	8.4

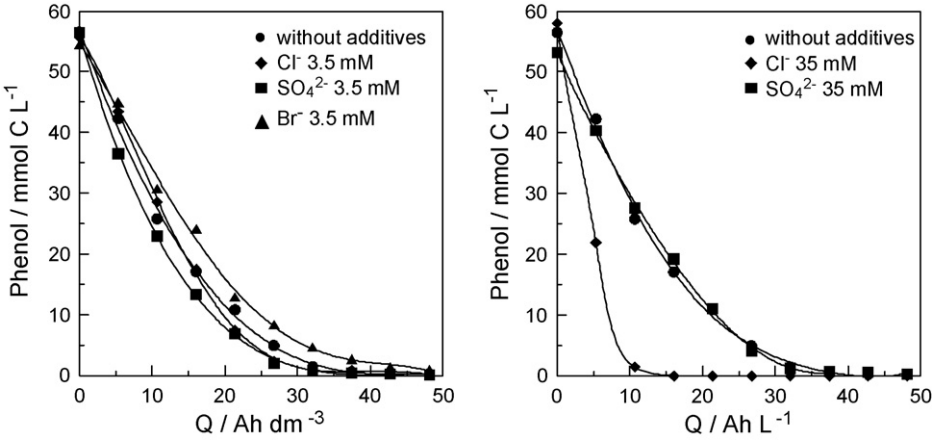

Fig. 5. Evolution of phenol concentration (10 mM) as a function of supporting electrolyte type and concentration during electrolysis on Ti/IrO_2 anode in 1 M $HClO_4$, 80 °C and 50 mA cm^{-2}.

3.2.2. Effect of electroactive anions present in the electrolyte

In order to investigate the effect of the electroactive anions added in the electrolyte on phenol degradation, experiments were conducted at 80 °C in the presence of Cl^-, BR^- and SO_4^{2-} (3.5 mM or 35 mM) using a 10 mM phenol solution in acidic media (1 M $HClO_4$). Fig. 5 shows the effect of these additives on phenol oxidation at 80 °C and 50 mA cm^{-2}. SO_4^{2-} has practically no effect on degradation even for concentrations of 35 mM. The addition of Br^- appears to have a slight effect on degradation and this is possibly due to the fact that bromide acts as scavenger of electrogenerated active species [14]. Conversely, Cl^- has a positive effect, which is pronounced for a concentration of 35 mM; this effect, which is well-documented in the literature [4,7,9] and is pH dependent [15], is associated with the formation of chlorohydroxyl radicals that can also oxidize the organic matter (R) [16]:

$$H_2O + M + Cl^- \rightarrow M[ClOH^\bullet] + H^+ + 2e^- \quad (3)$$

$$R + M[ClOH^\bullet] \rightarrow M + R + H + Cl^- \quad (4)$$

Reactions between water and radicals near the anode (M) in acidic media can yield free chlorine:

$$H_2O + M[ClOH^\bullet] + Cl^- \rightarrow M + O_2 + Cl_2 + 3H^+ + 4e^- \quad (5)$$

Chlorine is quite stable in acidic media and can react in solution with organic matter resulting in further reduction of the organic load (at least for low charges passed, i.e. <30 Ah L^{-1}). The formation of free chlorine during the first few seconds of the reaction was noticeable by its characteristic strong smell and yellowish color. It is worth noting though that large amounts of NaCl could lead to an increase in wastewater toxicity due to the formation of organochlorinated substances [17]. Moreover, as already has been discussed the mechanisms taking place in the presence of chlorine are highly pH dependent [15]. Therefore, the addition of NaCl in electrochemical wastewater treatment should be carefully considered.

3.2.3. Degradation intermediates

Previous studies have shown that electrochemical oxidation of phenol occurs through the formation of various aromatic and aliphatic intermediates including 1,4-benzoquinone, hydroquinone and pyrocatechol (Fig. 3) [4–8,10,18–19]. Fig. 6 shows the concentration–time profiles of the identified intermediates during the electrochemical oxidation of 10 mM phenol at 80 °C, 50 mA cm^{-2} without additives (Fig. 6a) and in the presence of SO_4^{2-} (Fig. 6b), Br^- (Fig. 6c) and Cl^- (Fig. 6d). Furthermore, Fig. 6 shows both the evolution of TOC during electrolysis, as well as the calculated total organic carbon ($(TOC)_{calc}$), which is determined from the carbon balance using the following relation:

$$(TOC)_{calc} = Ph_t + BQ_t + PC_t + HQ_t \quad (6)$$

where Ph_t, BQ_t, PC_t and HQ_t are the concentrations of phenol benzoquinone, pyrocathechol and hydroquinone (in mmol C L^{-1}) at time t, respectively.

Differences between TOC and $(TOC)_{calc}$ are presumably due to unidentified, liquid-phase by-products; interestingly at reaction conditions yielding up to 90% phenol conversion (this is shown by the dashed line in Fig. 6), there is a very good agreement between TOC and $(TOC)_{calc}$ indicating that intermediates other than 1,4-benzoquinone, hydroquinone and pyrocatechol are not formed at appreciable concentrations, i.e. the aromaticity is mostly preserved during the process. Upon prolonged oxidation, the aromatic ring opens and the formation of organic acids was observed [4–8,10,18–19]. Identification of such compounds was not possible with the analytical techniques used in this study as their concentration in the reaction mixture was too low.

Fig. 6 also shows the selectivity (S_p) towards the formation of soluble organic intermediates.

$$S_p = \frac{TOC_t - Ph_t}{Ph_o - Ph_t} \quad (7)$$

where Ph_o and Ph_t are phenol concentrations (in mM of carbon) at the beginning and time t, respectively.

For phenol conversions lower than 90%, the selectivity remains between 70 and 85% indicating that phenol transformation to organic intermediates is the dominant reaction pathway. Upon phenol conversions above 90% the selectivity drops, indicating that total oxidation of aromatic to CO_2 and formation of other intermediates becomes non-negligible. Hydroxylation of phenol to ortho- and para-position yields pyrocatechol and hydroquinone, respectively (Fig. 3). The latter is dominant and this implies that hydroxylation is favored at the para-position of the phenolic ring. It should be noted here that 1,2-benzoquinone was not detected in the reaction mixture since it is highly unstable. As already discussed in Section 3.2.2, the addition of SO_4^{2-} has no influence on phenol degradation and this is also demonstrated in Fig. 6 as the results presented in Fig. 6a and b are similar. The presence of chloride appears to accelerate the degradation of phenol while bromides seem to inhibit the process. In fact, as shown in Fig. 6, the charge needed to achieve 90% phenol conversion in the presence of Br^- is 20% greater than that without BR^-; furthermore, total selectivity remains constant around 70% even after prolonged oxidation in the presence of bromide, suggesting that the mineralization of organic compounds is delayed.

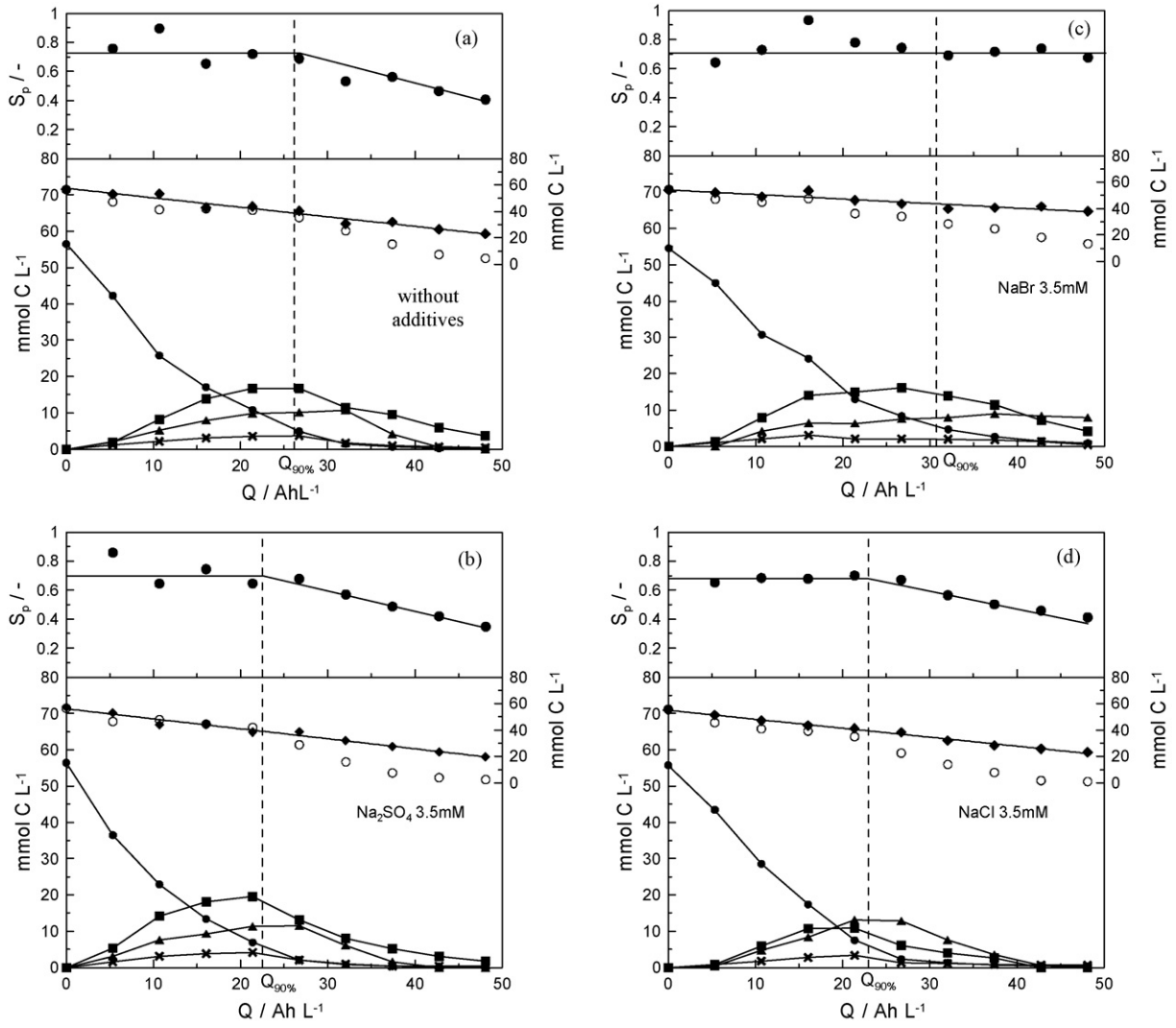

Fig. 6. Lower part shows evolution of (●) phenol; (▲) 1,4-benzoquinone; (■) hydroquinone; (×) pyrocatechol; (♦) TOC (secondary axis); (○) TCOC (secondary axis) during electrolysis of 10 mM phenol solution in 1 M $HClO_4$ at 80 °C and 50 mA cm^{-2} with and without supporting electrolyte. Upper part shows selectivity (●) as defined in Eq. (7).

4. Conclusions

In this work, the electrochemical oxidation of phenol in $HClO_4$ on Ti/IrO_2 anode has been studied through cyclic voltammetry and electrolysis experiments. The main conclusions are as follows:

(1) The electrode surface suffers passivation possibly due to the formation of a polymeric film during cyclic voltammetry measurements.
(2) Reaction temperature and the presence of electroactive anions both affect the oxidation process. Oxidation is favored at increased temperatures and in the presence of chloride ions; the latter induce the formation of additional oxidants that can facilitate degradation in the liquid back and/or near the anode. However, bromide ions behave as scavengers inhibiting degradation.
(3) Anodic oxidation of phenol appears to proceed through the hydroxylation/oxidation of phenol to yield intermediates such as hydroquinone, pyrocatechol and 1,4-benzoquinone with low current efficiency.

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