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On the performance of Ti/SnO$_2$ and Ti/PbO$_2$ anodes in electrochemical degradation of 2-chlorophenol for wastewater treatment

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Electrochemical oxidation of 2-chlorophenol was studied at Ti/PbO$_2$ and Ti/SnO$_2$ anodes. The performance of the electrodes was evaluated in terms of faradaic yield and fraction of toxic intermediates removed during the electrolysis. Results showed that, although similar average faradaic yields were obtained using Ti/PbO$_2$ or Ti/SnO$_2$ anodes, the latter material is preferred because of its better ability to oxidise toxic compounds. An effective electrochemical treatment ($\eta_F \cong 50\%$) may be accomplished, in which electrolysis at Ti/SnO$_2$ can be stopped when, in spite of a relatively high COD, only a small amount of easily biodegradable oxalic acid is present in the effluent.

Keywords: *2-chlorophenol, Ti/PbO$_2$, Ti/SnO$_2$, electrochemical oxidation*

List of symbols

A_e	electrode surface area (cm^2)
F	Faraday's constant (96487 C mol^{-1})
i	current density (mA cm^{-2})
k	true kinetic constant (cm s^{-1})
K	apparent rate constant (s^{-1})
r	reaction rate (mol s^{-1} dm^{-3})
R	concentration of reactant (mol dm^{-3})
t	time (s)
V_{sol}	volume of the solution (cm^3)
ε	fraction of cyclic compounds removed during electrolysis
θ_{OH}	fractional surface coverage of OH radicals
η_F	faradaic yield
COD	Chemical Oxygen Demand (mg dm^{-3})

1. Introduction

Improper discharge of industrial wastewater and chlorination of naturally occurring aromatic material during water purification are major sources of halogenated aromatic compounds. The presence of these hazardous compounds in water represents a major threat to the environment. In particular, chlorophenols cause severe problems, because of their carcinogenicity. Among the different technologies for wastewater treatment, biological oxidation is frequently used. However, when wastewater contains organo-chlorinated compounds biological treatment may become ineffective. In such cases, slow rates of degradation or lack of suitable organisms may require alternative techniques to be employed, such as wet air oxidation (WAO) and UV oxidation.

Recently, electrochemical oxidation has also been proposed as an alternative method for the removal of organic pollutants [1–3], especially for dilute solutions of biorefractory organics. The economic feasibility of this type of process is associated with its ability to limit side reactions and good faradaic efficiency. The choice of anodic material plays an important role: it should be stable over a wide range of anodic potentials and should present high overpotential for oxygen evolution, which constitutes the main side reaction in anodic oxidation.

Metallic dioxide electrodes such as PbO$_2$ and SnO$_2$ are used. The former has a high oxygen overpotential, the latter is a promising material, due to its catalytic properties in organic oxidation.

Both types of electrode have recently been the subject of studies concerning oxidation of organic compounds [4–10]. Electrochemical oxidation of phenol has been widely studied, but little attention has been paid to electro-oxidation of chlorophenols. In this laboratory electrochemical oxidation of chlorophenols was previously investigated at porous carbon electrodes [11]. In the present work the study is extended to metal oxide electrodes (Ti/PbO$_2$ and Ti/SnO$_2$) at which electrochemical oxidation of 2-chlorophenol was studied.

2. Experimental

Figure 1 shows a schematic view of the apparatus. It consisted of a stirred reservoir (300 ml), a peristaltic pump and a three-electrode electrochemical cell. A

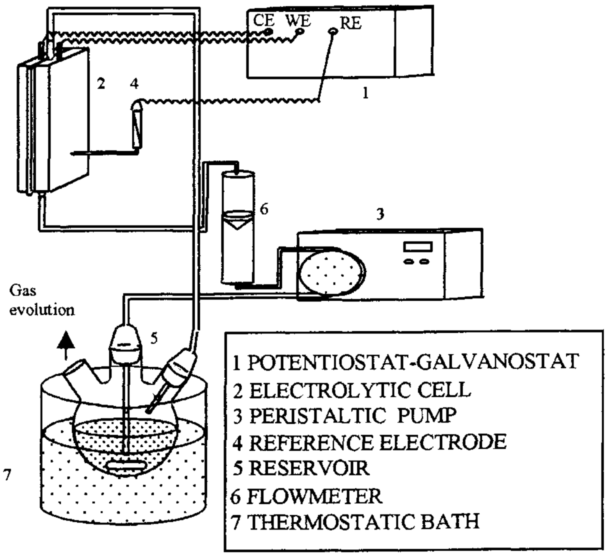

Fig. 1. Experimental apparatus.

steel sheet was used as cathode, while the anode was a sheet of titanium (4 × 3 cm) coated with SnO_2 or PbO_2. A Luggin capillary was used to connect a saturated calomel reference electrode (SCE) with the anode. The electrolyte was pumped through the cell and then returned to the reservoir for recycle.

2.1. *Preparation of electrodes*

Pre-treatment of the titanium surface was carried out following the procedures suggested by Feng [4]. The sheet of titanium was polished on 320-grit paper strips, using water as lubricant, followed by 1 μm siliceous paste blasting. The sheet was then degreased in 40% NaOH, cleaned in a hot 1:1 mixture of HNO_3 and H_2SO_4 and finally washed in water. The treated surface was immersed in a boiling aqueous solution of oxalic acid (15%) until the TiO_2 dissolved. Coating by active metal oxide was carried out immediately to minimise formation of TiO_2.

The thermal deposition of SnO_2 on titanium sheet was carried out according to the procedure of Lipp and Pletcher [12]. The pre-treated titanium sheet was immersed for some minutes in a solution of 20% wt $SnCl_4\ 5H_2O$ and 0.2% wt $SbCl_3$ in 2-propanol. The excess of alcohol was allowed to evaporate by heating in air at 363 K for 10 min. This stage was then repeated. After two applications, the oxide layer was formed thermally by heating at 773 K for 20 min in a muffle furnace, with a low and continuous flow of oxygen. These stages were repeated until the SnO_2 coating reached a loading of about 0.8 mg cm^{-2}: it was normal to employ five applications. Finally, the coating was annealed at 773 K for 60 minutes.

The electrodeposition of PbO_2 was performed at constant anodic current (100 mA, 30 min) from 0.1 M HNO_3 solution containing 0.5 M $Pb(NO_3)_2$ and 0.04 M NaF. During electrolyses the potential ranged from 1.5 to 1.8 V. Electrodeposition was carried out for 30 min, achieving a PbO_2 loading of about 14 mg cm^{-2}.

In order to verify the reproducibility of the electrode preparation, experimental runs were repeated with three different electrodes prepared according to the procedure described above. Results showed a fair reproducibility: current efficiencies measured on the three electrodes (when the same operative conditions were adopted) differed by about 5%. Electrodes were also sufficiently stable to allow their use in consecutive runs: the analyses of solutions revealed that no metal dissolution occurred during electrolyses.

2.2. *Experimental procedures*

Galvanostatic electrolyses were carried out at both kinds of electrode with current density ranging from 8 to 16 mA cm^{-2}. All runs were performed at 25 °C. Solutions of 400 to 600 mg dm^{-3} (3.1 and 4.7 m mol dm^{-3}) of 2-chlorophenol were used. Phosphoric solutions buffered at pH 7 (0.05 M Na_2HPO_4 + 0.05 M NaH_2PO_4) and 3 (0.05 M NaH_2PO_4 + 0.05 M H_3PO_4) were used as supporting electrolyte. Some runs were also performed in which 1000 mg dm^{-3} of chlorides were added to the solution.

During the electrolysis samples were withdrawn at regular intervals. For each sample, the chemical oxygen demand (COD) was measured by a closed reflux, titrimetric method [13]. The concentrations of 2-chlorophenol and of its oxidation products were determined by HPLC (UV detector; column Chrompack Chromsphere 5 C8 ODS; mobile phase, CH_3OH + 0.1% H_3PO_4 and 0.05 M KH_2PO_4 + 0.1% H_3PO_4; flow rate, 1.7 cm^3 min^{-1}; column temperature, 25 °C).

Preliminary runs were performed with flow rates ranging from 0.3 to 1.5 cm^3 s^{-1}, corresponding to linear velocities of 0.1 and 0.5 cm s^{-1}, respectively. No influence of electrolyte velocity was found so that all the experiments were performed with a flow rate of 1 cm^3 s^{-1}.

3. Results and discussion

Fig. 2 shows some examples of the trend of COD normalised with respect to COD_0, as a function of electrolysis time. Different COD removal rates were observed, depending on the anodic material, current density and solution composition. However, a decrease in normalised COD up to about 0.1 was obtained under all experimental conditions. Faradaic efficiency was calculated as follows:

$$\eta_F = \frac{\Delta \mathrm{COD}\ V_{sol}\ F}{8\ i\ A_e\ \Delta_t} \qquad (1)$$

where 8 is the equivalent weight of oxygen.

In the range investigated, good faradaic efficiencies were achieved at both kinds of electrode. In fact, when COD was removed from initial values of about 1000 mg dm^{-3} up to values acceptable for discharge (ranging around 100–150 mg dm^{-3}), an average faradaic yield of about 50% was calculated for electrolysis at the Ti/PbO_2 anode with a current density of

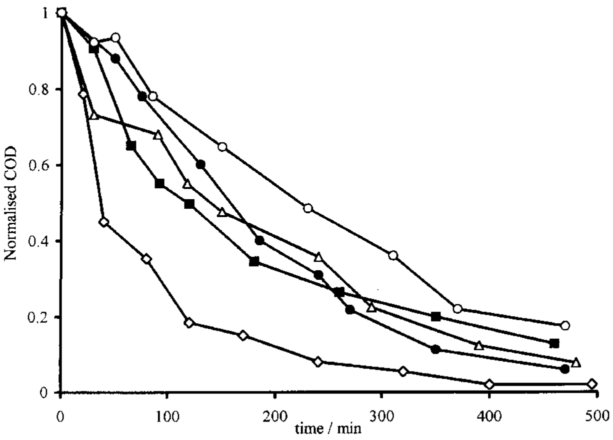

Fig. 2. Trend in time of residual normalized COD (initial value, 1000 mg l^{-1}; working temperature 25 °C) during electrolyses in different experimental conditions. Ti/PbO_2, $[Cl^-] = 0$: $i = 8$ mA cm^{-2} (○); $i = 16$ mA cm^{-2} (△); Ti/PbO_2, $[Cl^-] = 1$ g dm^{-3}: $i = 8$ mA cm^{-2} (●); $i = 16$ mA cm^{-2}, (◇); Ti/SnO_2, $[Cl^-] = 0$, $i = 16$ mA cm^{-2} (■).

8 mA cm^{-2}. Slightly lower efficiencies were obtained when current density was approximately doubled. Faradiac yields of 40% and 35% were achieved at Ti/PbO_2 and Ti/SnO_2 anodes, respectively. In all cases the effect of pH was almost negligible. High faradaic efficiencies (67%) were calculated when the initial solution contained 1000 mg dm^{-3} of chloride ions.

The composition of the solution was also analysed during the electrolyses to identify the intermediate oxidation products. Such compounds might be more toxic than chlorophenol itself: therefore, the purpose of the treatment is not only to achieve a large decrease in the COD, but also a nearly complete removal of all harmful substances initially present in solution or formed during the process. HPLC revealed that cyclic compounds (chloro p-benzoquinone, o-benzoquinone and cathecol) were initially produced, while aliphatic bi-carboxylic acids (mainly oxalic acid with small amounts of maleic and fumaric acids) were detected at longer reaction times.

During oxidation of p-chlorophenol in supercritical water, benzoquinone was found to be the main intermediate [14], whereas benzoquinone and chlorobenzoquinone were detected [15]. Ku *et al.* [16] detected various intermediate products, both chlorinated and non-chlorinated, such as cathecol, hydroquinone and organic acids, during oxidation of 2-chlorophenol by UV irradiation catalysed by TiO_2. In all cases oxalic acid was always found as the main product in the final part of the reaction.

Preliminary investigation indicated that the initial organic load influenced the behaviour of the system. As can be seen from figure 3, at high initial chlorophenol concentration (>3000 mg dm^{-3}) a potential value less anodic than that of O_2 evolution was established at the anode; chlorophenol was rapidly removed, and a large amount of quinonic compounds was detected in the solution.

On the other hand, if the initial organic concentration was lower than 1000 mg dm^{-3}, after a short transient, the potential reached the value for oxygen evolution and only a small amount of quinonic compounds was measured in solution.

This behaviour may be explained by considering that two reactions occur at the anode surface, each of which may be dominant depending on the experimental conditions. A direct oxidation of chlorophenol, from which quinonic compounds are produced as first intermediates, may be favoured at high concentration of organic reactant. When dilute solutions are used a second mechanism may prevail in which the oxidising agents are OH radicals produced in water oxidation:

$$H_2O \rightarrow OH^\bullet + H^+ + e^- \tag{2}$$

The OH radicals, absorbed at the electrode surface, react with organic compounds or cause oxygen evolution by a parallel reaction step.

$$\mathrm{Org} + OH^\bullet \rightarrow \mathrm{Product} \tag{3}$$

$$2\,OH^\bullet \rightarrow H_2O + \tfrac{1}{2}O_2 \tag{4}$$

Due to the strong oxidising effect towards most organic compounds, OH radicals are able to attack both chlorophenol and its oxidation products so that they do not accumulate in solution:

Since a particularly interesting area for the application of electrochemical technology is the treatment of solutions with low refractory compound content, the behaviour of dilute solutions was considered in more detail. In order to better quantify the influence of different operating parameters on the electrochemical process, a simplified mathematical model was formulated in which three irreversible consecutive stages were considered:

(1) oxidation of chlorophenol (R1) to quinonic compounds (R2)
(2) a ring opening reaction to form aliphatic acids (oxalic acid (R3) is considered as predominant)
(3) mineralisation to CO_2

Some assumptions were involved. The simultaneous presence of o-benzoquinone and chloro-p-benzoquinone in the reaction mixture indicates that the first step consists of two parallel paths: both the substitution of the chlorine atom with an OH group, to form cathecol, which further oxidises to o-benzoquinone, and the direct formation of chloro-p-benzoquinone. Moreover, due to the undivided electrochemical cell used partial reversibility of the reaction can not be excluded, so that cyclic intermediates may be back reduced at the cathode. However, this should be a secondary effect because, as also highlighted by other authors, when phenol is electrochemically oxidised at both lead and tin oxide anodes, the presence of the membrane does not appreciably modify the trend of the reaction [5, 10].

On the basis of these considerations the overall oxidation process can be represented as:

$$R_1 \xrightarrow[OH^\bullet]{K_1} R_2 \xrightarrow[OH^\bullet]{K_2} 3R_3 \xrightarrow[OH^\bullet]{K_3} CO_2 \tag{5}$$

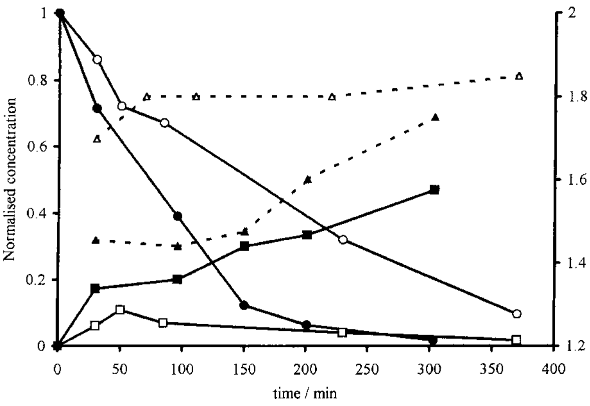

Fig. 3. Trend of anodic potential (△ ▲) and concentration of reactant (○ ●) and cyclic intermediates (■ □) normalised with respect to initial chlorophenol concentration, during electrolysis at Ti/PbO$_2$, i = 8 mA cm^{-2}, with different initial chlorophenol concentration: C_0 = 23.5 mmol dm^{-3} (empty symbols); C_0 = 4.7 mmol dm^{-3} (full symbols).

Steady state conditions can be assumed for hydroxyl radicals produced according to Equation (2) and consumed by organic oxidation (Equation 3) and oxygen evolution (Equation 4), so that the generic reaction may be described by pseudo first order kinetics.

$$r_i = K_i[R_i] \tag{6}$$

The apparent rate constant K_i is related to the true rate constant k_i by

$$K_i = k_i \frac{A_e}{V_{sol}} \theta_{OH} \tag{7}$$

in which θ_{OH} represents the degree of coverage of the electrode by OH radicals in the steady state.

Taking into account the kinetic equations and the stoichiometry of the reaction, the following set of differential equations can be written:

$$\frac{d[R_1]}{dt} = -K_1[R_1] \tag{8}$$

$$\frac{d[R_2]}{dt} = -K_2[R_2] + K_1[R_1] \tag{9}$$

$$\frac{d[R_3]}{dt} = -3K_3[R_3] + K_2[R_2] \tag{10}$$

Integrating Equations 8–10 for the following initial conditions:

$$t = 0 \qquad [R_1] = [R_1]_0 \qquad [R_2] = [R_3] = 0$$

the concentration of reactant and products, normalised with respect to the initial chlorophenol concentration, can be obtained as:

$$\frac{[R_1]}{[R_1]_0} = e^{-K_1 t} \tag{11}$$

$$\frac{[R_2]}{[R_1]_0} = \frac{K_1}{K_2 - K_1}(e^{-K_1 t} - e^{-K_2 t}) \tag{12}$$

$$\frac{1}{3}\frac{[R_3]}{[R_1]_0} = \frac{K_1 K_2}{(K_3 - K_1)(K_2 - K_1)} e^{-K_1 t} + \frac{K_1 K_2}{(K_2 - K_3)(K_2 - K_1)} e^{-K_2 t} + \frac{K_1 K_2}{(K_3 - K_2)(K_2 - K_1)} e^{-K_3 t} \tag{13}$$

Table 1. Estimated values of apparent kinetic constants

	Ti/PbO$_2$			*Ti/SnO$_2$*		
i /mA cm^{-2}	8	16	16	8	16	16
PH	4	4	7	4	4	4
[Cl$^-$] /mg dm^{-3}	0	0	0	1000	1000	0
$K_1 \times 10^3$/s^{-1}	0.08	0.15	0.15	0.16	0.66	0.21
$K_2 \times 10^3$/s^{-1}	0.66	1.16	1.16	0.58	2.5	11.6
$K_3 \times 10^3$/s^{-1}	0.15	0.125	0.125	0.14	0.15	0.05

Table 1 summarises the values of the rate constants obtained for the different experimental conditions, by minimising the sum of the squared residuals between the experimental and calculated values of normalised concentrations.

Fig. 4 shows that the mathematical model can be successfully used to predict the behaviour of the system. As shown in Table 1, at Ti/PbO$_2$, the values of the rate constants increase, but not proportionally, to the applied current density.

Moreover, at both kinds of electrode the second reaction step (ring opening) is faster than the first one in which quinonic compounds originate from chlorophenol oxidation. In particular, higher values of K_1 and K_2, as well as of the K_2/K_1 ratio, are obtained at Ti/SnO$_2$ rather than at Ti/PbO$_2$ anodes, so that a different distribution of cyclic intermediates was observed during electrolysis: a small amount of quinonic compounds was measured at Ti/PbO$_2$ anodes while they were practically absent at Ti/SnO$_2$ anodes. This demonstrates the influence of the electrode material on the kinetics of the different reaction stages. Indeed, a previous study showed that the opening of aromatic rings became the controlling step, when the electrochemical degradation of chlorophenols was performed at carbon electrodes [11]. Analogous results were obtained during oxidation of phenol [1]: quinonic compounds accumulated during electrolysis at Pt anodes, while small amounts of these compounds were found at SnO$_2$ electrodes.

As also observed from Table 1, the presence of NaCl in the electrolyte causes an increase in K_1, but it does not influence K_3. The specific catalytic action of

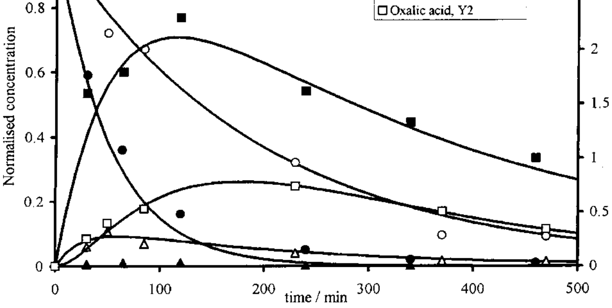

Fig. 4. Model prediction (lines) and experimental data from electrolysis with i = 8 mA cm^{-2} at Ti/PbO$_2$ (empty symbols), and with i = 16 mA cm^{-2} at Ti/SnO$_2$ (full symbols).

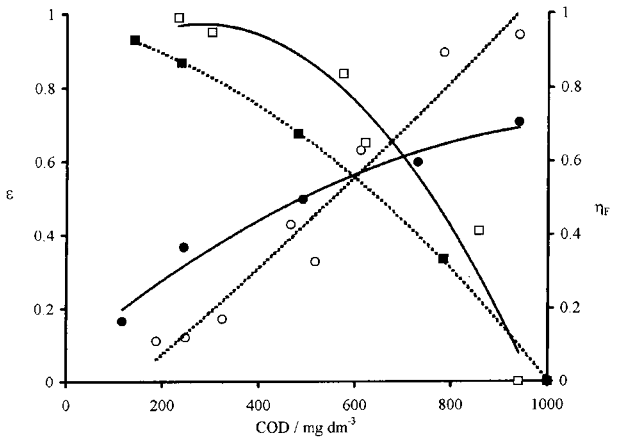

Fig. 5. Faradaic efficiency (● ○) and fraction of cyclic intermediates (■ □) removed during electrolysis with $i = 16$ mA cm^{-2} at Ti/PbO_2 (full symbols) and Ti/SnO_2 (empty symbols).

NaCl has already been reported during phenol oxidation at Ti/IrO_2 [8]. Electrogenerated ClO^- may oxidise cyclic organic compounds in the vicinity of the anode: this parallel reaction path might explain the more rapid decrease observed in chlorophenol concentration during the electrolysis at Ti/PbO_2. Carboxylic acids are stable towards ClO^- oxidation, so that the value of the constant K_3, related to the mineralisation of aliphatic acids to CO_2, does not change. It has also been suggested that non-volatile organochlorinated compounds are generated by phenol oxidation, but they are further oxidised to volatile organochlorinated compounds ($CHCl_3$) [8]. Under the conditions adopted in this work, the presence of organochlorinated compounds cannot be excluded, but their concentration was always low, since no new peaks were revealed by HPLC during electrolysis.

Finally, in order to compare the performance of the two electrode materials, the trends in instantaneous faradaic yield and of the fraction of cyclic compounds removed (ε), as solution COD is progressively reduced, must be considered (Fig. 5). Higher η_F values were obtained at Ti/SnO_2 than at Ti/PbO_2, when the COD of the solution remained high. A reduction in the efficiency was observed only when the removal of cyclic compounds was almost complete. It may be concluded that, even if similar average faradaic yields were obtained using Ti/PbO_2 or Ti/SnO_2 anodes, the latter is preferred because of its better ability to oxidise toxic compounds. Indeed, using Ti/SnO_2 anodes an effective electrochemical treatment ($\eta_F \cong 50\%$) may be accomplished, in which electrolysis is stopped when the COD of the solution is still 300 mg dm^{-3}, since only a small amount of easily biodegradable oxalic acid is present in the effluent ($\varepsilon > 0.95$).

The results obtained are promising and an extension of the study to a wider range of pH and current density is required in order to better match the operating parameters in real applications for waste water treatment.

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