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Journal of Hazardous Materials B75 (2000) 99–113

**Journal of  
Hazardous  
Materials**

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## Anodic destruction of 4-chlorophenol solution

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Received 31 October 1999; received in revised form 22 February 2000; accepted 24 February 2000

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### Abstract

The electrochemical oxidation of 4-chlorophenol solutions was studied using a dimensional stable anode (DSA), made of pure titanium sheet mesh coated with Ti/TiO<sub>2</sub> and RuO<sub>2</sub> film. An electrochemical cell with one working electrode and two counter-electrodes was designed. A gas collecting system to collect the electrolysis gaseous products was also designed.

The influence of current density (6.51–21.58 mA/cm<sup>2</sup>), pH (2.0–12.6) and initial 4-chlorophenol concentration (25–100 mg/l) on the destruction was investigated. Complete elimination was successfully achieved within 2 h for most investigated conditions. Highest rates of elimination were achieved at a pH of 12.6.

A new approach to calculate the current efficiency (CE) of the cell was proposed. The volumes of the gases produced at the anode and at the cathode were the basis for the new CE calculations.

It was observed that the worst CE was approximately 20% and the best CE was approximately 89%. The most efficient pH was at 12.6 and the most efficient current density was at 11.39 mA/cm<sup>2</sup>. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* 4-Chlorophenol; Anodic oxidation; Electrochemical destruction; Wastewater

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### 1. Introduction

Phenolic wastes in wastewater arise in many segments of the process industry including oil refineries, coke plants, chemical and plastic plants. Phenols have been classified as one of the 65 priority pollutants. Present guidelines (according to the Jordanian Ministry of Water and Irrigation) limit phenols concentration in wastewater to

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less than 0.1 mg/l, where phenols here refer to aromatic derivatives that contain one or more hydroxyl groups. When phenols contain halide compounds, the acceptable concentration limit in wastewater falls to 0.02 mg/l (20 ppb).

The most common process for treating phenol-laden industrial wastes are biological treatment (often using an acclimated population of microorganisms due to phenol toxicity), adsorption using proper adsorbent such as activated carbon, and advanced oxidation processes, such as UV/O<sub>3</sub> or H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>. The choice of treatment method depends on the economics of the method as well as ease of control, reliability and treatment efficiency.

Electrochemical methods for wastewater treatment, which could be considered as one of the advanced oxidation processes, have recently attracted a great deal of attention. This is mainly because of their ease of control and the increased efficiency provided by the use of compact bipolar electrochemical reactors and by the large surface area of three-dimensional electrodes [1].

Anodic oxidation of organic compounds has been extensively studied for synthesis of compounds, reaction mechanism studies, fuel cell development and wastewater treatment [2,3].

DeSucre and Watkinson [4] studied the anodic oxidation of phenol for wastewater treatment on lead dioxide packed bed anode cell which was operated in both batch and continuous modes with feed stream concentrations up to 1100 mg/l of phenol dissolved in aqueous solutions of Na<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> or NaOH. All the phenol in solution, which they used, could be readily oxidized. They found that the percent of oxidized phenol increased with increased current, and decreased as the initial phenol concentration, electrolyte flow rate, pH and anode particle size were increased.

Franklin et al. [5] investigated the destruction of organic compounds in the presence of barium peroxide as a mediator in aqueous sodium chloride containing cationic surfactants. A reactive intermediate was formed, which destroyed chloroform, 1,2,4-trichlorobenzene, hexachlorobenzene and hexafluorobenzene. They carried out the electrolysis both potentiostatically (0.9 V vs. saturated calomel electrode (SCE)) and galvanostatically (16.6 mA/cm<sup>2</sup>) using graphite anode. They failed to destroy ethylene diamine and aromatic nitrobenzenes by this technique.

Cominellis and Pulgarin [6] studied the electrochemical oxidation of phenol at a platinum anode. The analysis of their reaction intermediates and carbon balance showed that the reaction occurs by two parallel pathways, namely chemical oxidation with electrogenerated hydroxyl radicals and direct combustion of adsorbed phenol and/or its aromatic intermediates to CO<sub>2</sub>.

Farmer et al. [7] studied mediated electrochemical oxidation methods for hazardous waste treatment and for the conversion of mixed waste to low-level radioactive waste. They used a rotating cylinder anode that operated under the limiting current of Ag(II) generation. They measured the generation rate of CO<sub>2</sub> and used it to calculate the destruction of the waste and the current efficiency (CE) of the process.

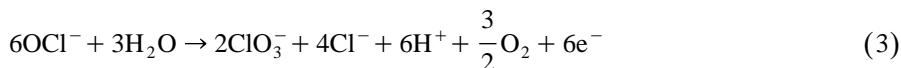
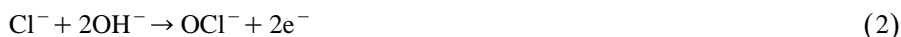
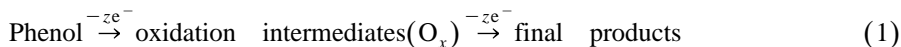
Feng et al. [8] studied the electrochemical destruction of benzoquinone. They tested several anode materials. They determined the chemical oxygen demand (COD) for benzoquinone. Their objective was to find the optimal electrochemical conditions for the conversion of benzoquinone in acetate buffer to CO<sub>2</sub>.

Johnson et al. [9] studied the electrochemical destruction reaction of 4-chlorophenol. They identified 26 intermediate products. It took them 24 h of electrolysis to bring 108 mg/l 4-chlorophenol solution down to 1 mg/l total organic content (TOC).

This work includes a design of an electrochemical cell to study the effect of different parameters on the anodic destruction of chlorinated phenols. Specifically, the effect of pH, 4-chlorophenol concentration and current density on the destruction of 4-chlorophenol was investigated.

## 2. Theory

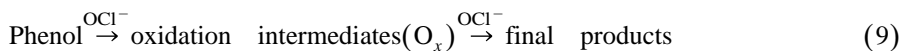
Several main reactions are believed to occur during the oxidation of phenol in the presence of KCl [2,10]. For basic solutions, reactions (1)–(4) take place at the anode, whereas reaction (5) takes place at the cathode.



On the other hand, in acidic solutions, reactions (1), (6) and (7) are believed to occur at the anode, while reaction (8) takes place at the cathode.



In addition to the reactions occurring at the anode and the cathode, reaction (9) takes place in basic solutions away from the surfaces of the electrodes, while reaction (10) takes place in acidic solutions.



Some researchers [6] also believe that the hydroxyl radical formation at the electrode surface is one of the mechanisms of oxidation. It is believed that the hydroxyl radical is formed by the electrochemical oxidation of water according to the following reaction:



The hydroxyl radicals are then adsorbed at the electrode surface and react with the organic molecule (phenol or its oxidation products) according to reaction (12), or can subsequently react giving  $\text{O}_2$  according to reaction (13):



At the same time, organics are adsorbed at the electrode surface and oxidation to carbon dioxide occurs as shown in reaction (14):



Many researchers [2,4,11] believe that the destruction of phenolic compounds is first order with respect to phenol concentration. Thus, increasing the concentration of phenol will cause it to take a longer time to disappear from the solution. On the other hand, decreasing the phenol concentration, under the same current density and other conditions, leads to lower energy consumption, and therefore less time is required for the disappearance of phenol from the solution.

The pH affects the electrochemical cell performance. Increasing the pH decreases the oxygen over potential ( $\eta$ ) as apparent from Eq. (15) shown below. In addition, it will decrease the hydrogen potential ( $\varepsilon_{\text{H}}$ ) and so the cell potential ( $\varepsilon$ ) will decrease (Eq. (16)).

$$\eta = \varepsilon - \varepsilon_{\text{O}} = \varepsilon - 0.961 - 0.059 \text{ pH} \quad (15)$$

$$\varepsilon_{\text{H}} = \frac{RT}{F} \ln(a_{\text{H}^+}) = - \frac{RT}{2.3F} \text{pH} \quad (16)$$

The pH is expected to determine whether the products of the destruction process will adsorb to the anode surface for further oxidation, and therefore blocking some active sites, or they (the products) will dissolve leaving the active sites for other phenolic species to be destroyed [6]. The pH also affects the stability of the oxide film at the anode surface. Camara et al. [12] reported that for Ti/TiO<sub>2</sub> electrode, the most stable oxide film takes place at a pH of 4, otherwise the film will dissociate into the solution if a certain limit of current density is exceeded.

### 3. Current efficiency

There are two methods found in the literature to calculate the CE. The first method is the COD [2]. In this method the COD is measured at different time intervals. The instantaneous current efficiency (ICE) is then calculated as:

$$\text{ICE} = \frac{((\text{COD})_t - (\text{COD})_{t+\Delta t})}{8i\Delta t} FV. \quad (17)$$

The average current efficiency (ACE) is then calculated by:

$$\text{ACE} = \frac{\int_0^\tau \text{ICE} dt}{\tau}. \quad (18)$$

This method could be misleading, since it measures the CE with respect to the final product (carbon dioxide) and not the amount of hydrocarbon that has been destroyed. For example, if the hydrocarbon has been totally destroyed to some intermediate products other than carbon dioxide, the COD method would still give some value for the ICE, while in reality the destruction is complete (in the sense that no amount of the initial compound of interest is found).

The second method used to calculate the CE is the oxygen flow rate [2]. In this method, the sample that has been taken from the solution is exposed to a constant flow rate of oxygen, which oxidizes the organic material in the sample. The ICE is then calculated as follows:

$$\text{ICE} = \frac{V_{\text{O}} - (V_t)_{\text{org}}}{V_{\text{O}}} \quad (19)$$

The choice between the above two methods for measuring the CE depends on the solubility of the electrolysis' products. The oxygen flow rate method can be used for both soluble and insoluble products, while the COD method is not recommended when insoluble products are present.

Another definition for the CE, which is based on the change of the concentration of the organic compound, is:

$$\begin{aligned} \text{CE} &= \frac{\text{Experimental change in number of moles of organic material}}{\text{Theoretical change in number of moles of organic material}} \\ &= \frac{-(\Delta n)_{\text{exp}}}{(\Delta n)_{\text{th}}} \end{aligned} \quad (20)$$

where,

$$(\Delta n)_{\text{th}} = \frac{I_{\text{ac}} \Delta t}{ZF} \quad (21)$$

Substituting Eq. (21) into Eq. (20), gives:

$$\text{CE} = \frac{(\Delta n)_{\text{exp}}}{I_{\text{ac}} \Delta t} ZF \quad (22)$$

Assuming constant solution volume leads to:

$$\text{CE} = - \frac{VZF}{I_{\text{ac}}} \frac{(\Delta C)_{\text{exp}}}{\Delta t} \quad (23)$$

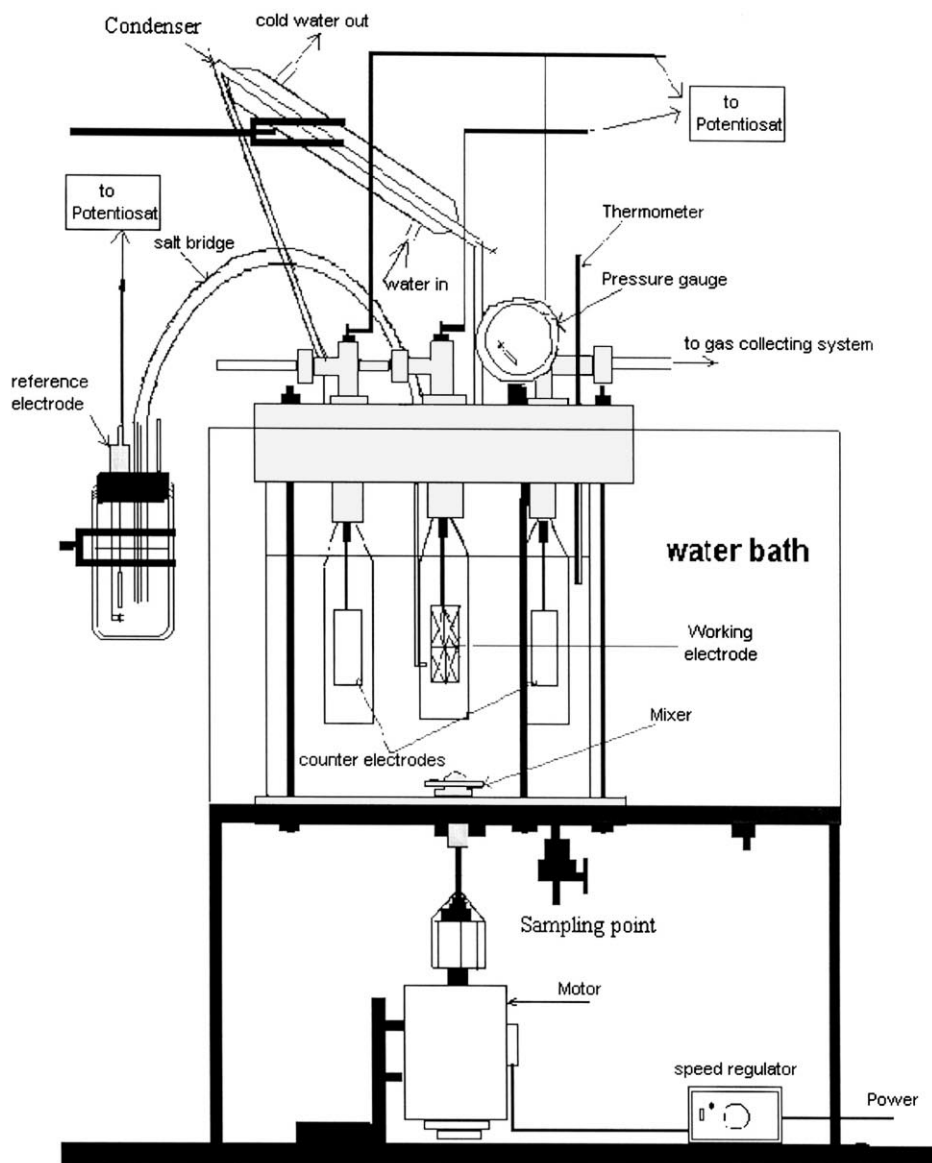
or,

$$\text{ICE} = - \frac{V}{A} \frac{ZF}{i_{\text{ac}}} \left( \frac{dC}{dt} \right)_{\text{exp}} \quad (24)$$

Knowing the actual reaction(s) during the electrochemical destruction of the organic compounds, Eq. (24) could be used to calculate the ICE.

This work introduces a new definition for CE. The new definition comes from the interest of transforming the phenolic compounds into other non-phenolic compounds that are easier to treat. The new CE is calculated by:

$$\text{CE} = \frac{V_{\text{th}} - V_{\text{w}}}{V_{\text{th}}} \quad (25)$$



## Cell system

Fig. 1. Schematic diagram for the cell system.

where  $V_{th}$  is the volume of gases that should be formed at the working electrode if no organic compounds are present in solution. This volume could be calculated by:

$$V_{th} = 2V_{ca} \quad (26)$$

The ACE is then calculated by:

$$ACE = \frac{\sum_0^t CE_i \Delta t_i}{\sum \Delta t_i} \quad (27)$$

Eqs. (25–27) assume that:

1. the cathode produces hydrogen gas only,
2. the only gas produced at the anode is oxygen,
3. the produced gases are ideal.

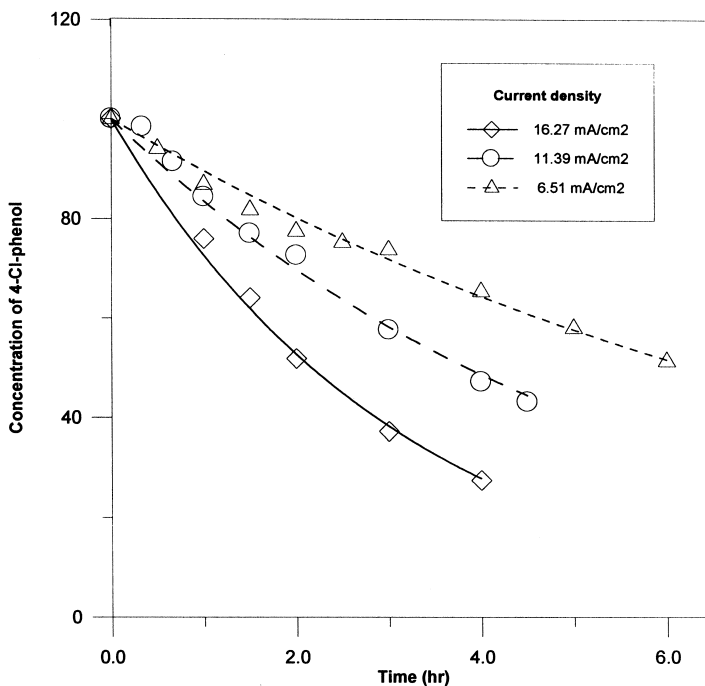


Fig. 2. Influence of current density on the destruction of 4-chlorophenol. Conditions:  $T = 18^\circ\text{C}$ ,  $\text{pH} = 12.6$ , salt concentration = 67.1 mM, initial concentration of 4-chlorophenol = 100 mg/l, working electrode = DSA, counter-electrode = copper.

#### 4. Methodology

The experimental setup is divided into three main parts, namely, potentiostat/galvanostat (AMEL model 553-Potentiostat), the cell system and the gas collecting system.

A cylindrical glass cell (see Fig. 1) was used with an outside diameter of 20 cm, a wall thickness of 0.5 cm and a height of 24 cm. The gases that are produced at each electrode are separately collected. The top cover is made of Teflon. Three electrodes (two counters and one working) are fixed on the top cover in addition to a pressure gauge, salt bridge, mercury thermometer and an inlet/outlet valve for a condenser. The bottom cover is also made of Teflon. A Teflon mixer (connected with a variable speed motor) is fixed at the center of the bottom cover on the cell side, 4 cm below the electrodes. A drain and sampling valve is also fixed at the bottom of the cell. The above cell is immersed in a water bath to allow studying the effect of higher temperatures on electrolysis.

The working electrode is a dimensional stable anode (DSA), manufactured by ELTECH, which is made of pure titanium sheet mesh with Ti/TiO<sub>2</sub> and RuO<sub>2</sub> film and

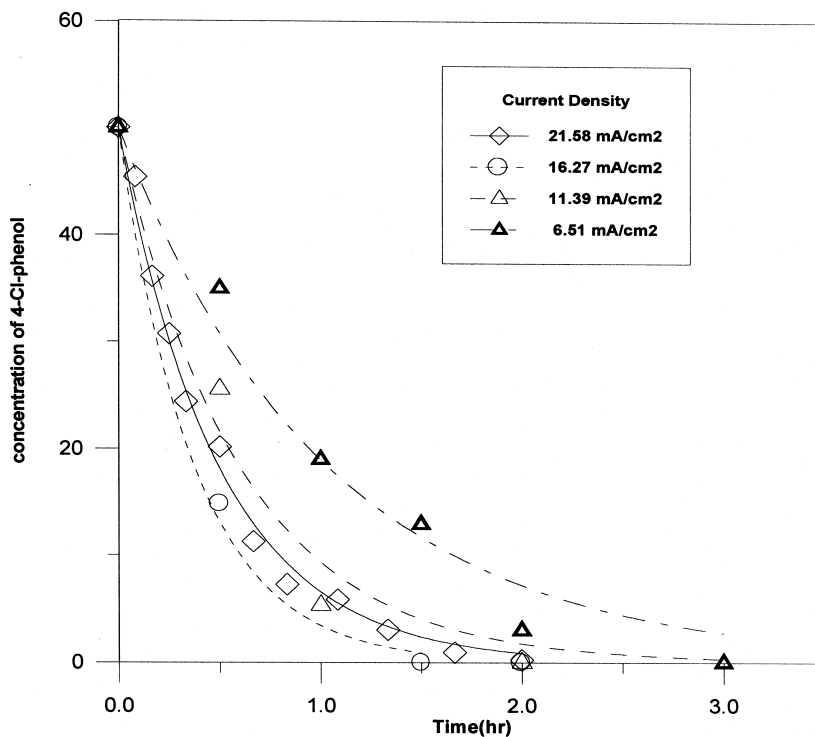


Fig. 3. Influence of current density on the destruction of 4-chlorophenol. Conditions:  $T = 18^{\circ}\text{C}$ ,  $\text{pH} = 12.6$ , salt concentration = 67.1 mM, initial concentration of 4-chlorophenol = 50 mg/l, working electrode = DSA, counter-electrode = copper.



has dimensions of  $3 \times 5$  cm and a thickness of 2 mm. A glass cylinder with a diameter of 4.4 cm surrounds the electrode, and is open from the top, to allow the produced gases to escape to the gas collecting system.

There are also two copper ( $> 99\%$  purity) counter-electrodes, one to the right and another to the left of the working electrode with dimensions of  $3 \times 5$  cm, and 2 mm thick. Each counter-electrode is surrounded with a glass cylinder similar to the one surrounding the working electrode. All glass cylinders are longer than the electrodes by 2 cm in order to prevent gas bubbles, which are formed at the surface of the electrodes, from escaping to the solution. The distance between each counter-electrode and the working electrode is 5 cm. Each counter-electrode is prepared by sanding, then by immersion in concentrated NaOH solution, then by immersion in concentrated HCl solution, and then finally washed by distilled water.

The cell is usually filled with 4 l of electrolyte prepared using deionized double distilled water, 4-chlorophenol (Sigma, C-4914), KCl salt (extra pure by Merck) and NaOH (98% Analar by BDH) or HCl (37% assay by BDH). Solution concentrations of 4-chlorophenol in the range of 25–100 mg/l were used. The pH of these solutions was varied between 2.0 and 12.6. Samples of 10-ml of treated solution were collected from a sampling valve, at the bottom of the cell, at different times during the electrolysis

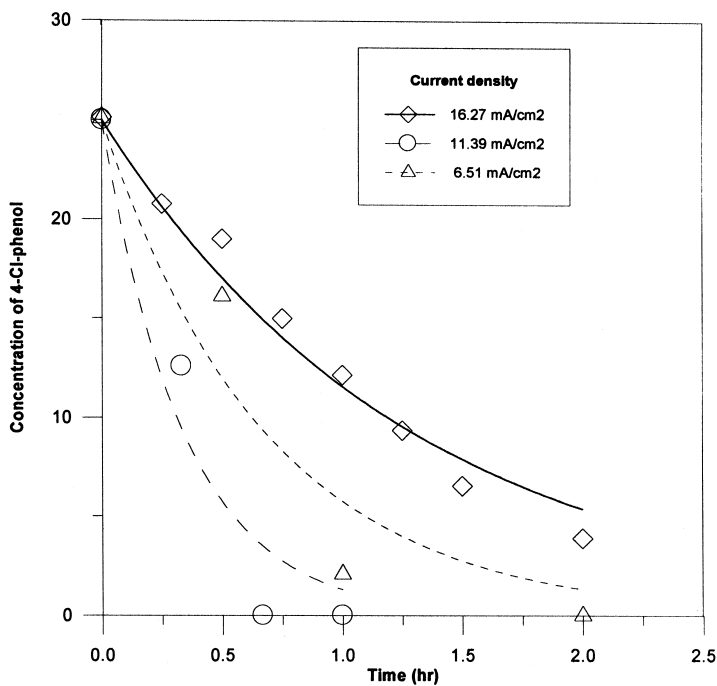


Fig. 4. Influence of current density on the destruction of 4-chlorophenol. Conditions:  $T = 18^\circ\text{C}$ ,  $\text{pH} = 12.6$ , salt concentration = 67.1 mM, initial concentration of 4-chlorophenol = 25 mg/l, working electrode = DSA, counter-electrode = copper.

process for analysis. The pH of the collected samples from the solution was measured using a pH meter (WPA-model CD7400).

The disappearance of 4-chlorophenol during anodic oxidation was measured by Varian VISTA 5500 HPLC system, which consists of a single piston, reciprocating pump driven by stepper motor, a Valco injector equipped with a 100- $\mu$ l loop and UV-200 variable wavelength detector set at 280 nm connected to a Spectraphysics integrator. Operating conditions are programmed through an equipped keyboard. Separation were performed on analytical column (250  $\times$  4.6 mm) using Li-Chrosorb RP-8, 10- $\mu$ m stationary phase (Merck, Darmstadt, Germany). The mobile phase consisted of 1% acetic acid in acetonitrile and water (50:50 v/v), at a flow rate of 2 mm/min. The column temperature was 25°C, while the column pressure was 195–200 atm.

The effluent gases, which are produced due mainly to water electrolysis on the counter- and working electrodes, are collected separately in two cylinders of Plexiglas, which are initially filled with water. The produced gases will displace water in these two cylinders. Both of the above cylinders are placed in a water bath with a controlled temperature.

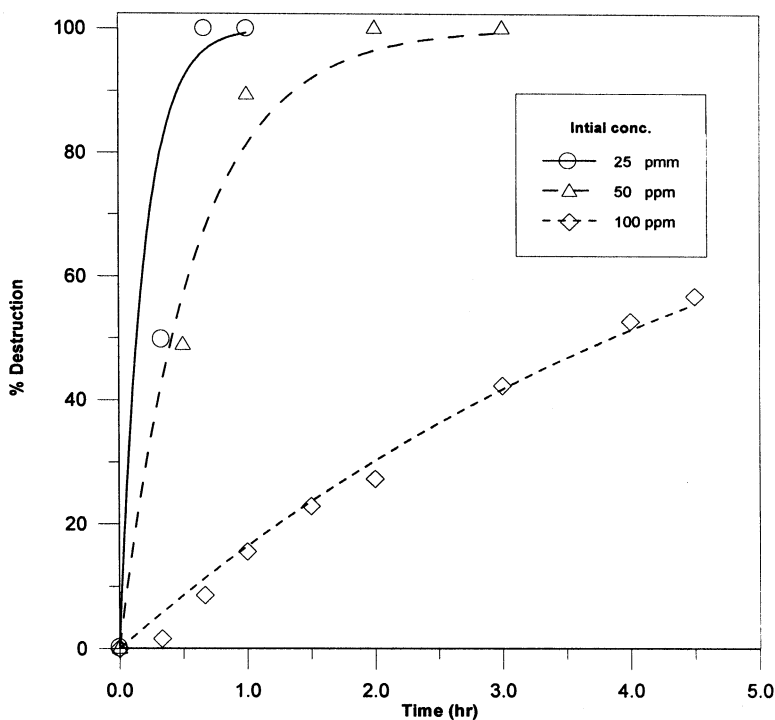


Fig. 5. Influence of initial concentration on the destruction of 4-chlorophenol. Conditions:  $T = 18^\circ\text{C}$ ,  $\text{pH} = 12.6$ , salt concentration = 67.1 mM, set current density = 11.39  $\text{mA}/\text{cm}^2$ , working electrode = DSA, counter-electrode = copper.

## 5. Results and discussion

Experiments on the electrochemical destruction of 4-chlorophenol were carried out. Complete elimination was successfully achieved as would be seen below. The effect of several current densities, pH values and initial 4-chlorophenol concentrations on the destruction process was investigated. The accuracy of the reported concentrations in this work was within 1 mg/l. The experimental data was curve fitted (shown by lines in Figs. 2–7) by a one-parameter fit; of the form shown in Eq. (28); with one constraint:

$$C = C_0 \exp(-bt). \quad (28)$$

The influence of current density on the destruction of 4-chlorophenol, starting with 100 mg/l is shown in Fig. 2. It is noticed that as the current density increases, the rate of destruction increases; which is a natural and expected behavior [13]. The CE at different current densities and different initial concentration of 4-chlorophenol is presented in Table 1.

It is observed from Table 1 that the highest CE, for the 100 mg/l concentration, was not at the highest tested current density, rather it was highest for an intermediate value (11.39 mA/cm<sup>2</sup>). It is expected that the current density affects the selectivity of the

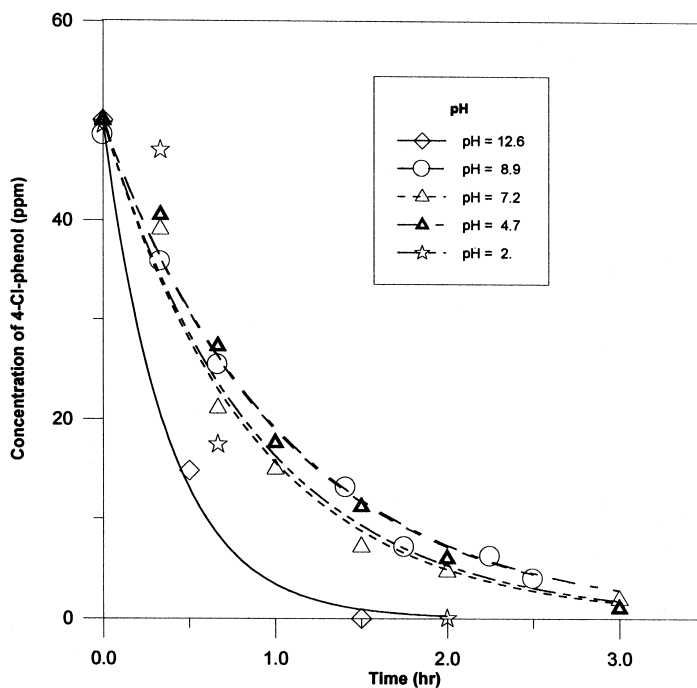


Fig. 6. Influence of pH on the destruction of 4-chlorophenol. Conditions:  $T = 18^\circ\text{C}$ , salt concentration = 67.1 mM, initial concentration of 4-chlorophenol = 50 mg/l, set current density = 16.27 mA/cm<sup>2</sup>, working electrode = DSA, counter-electrode = copper.

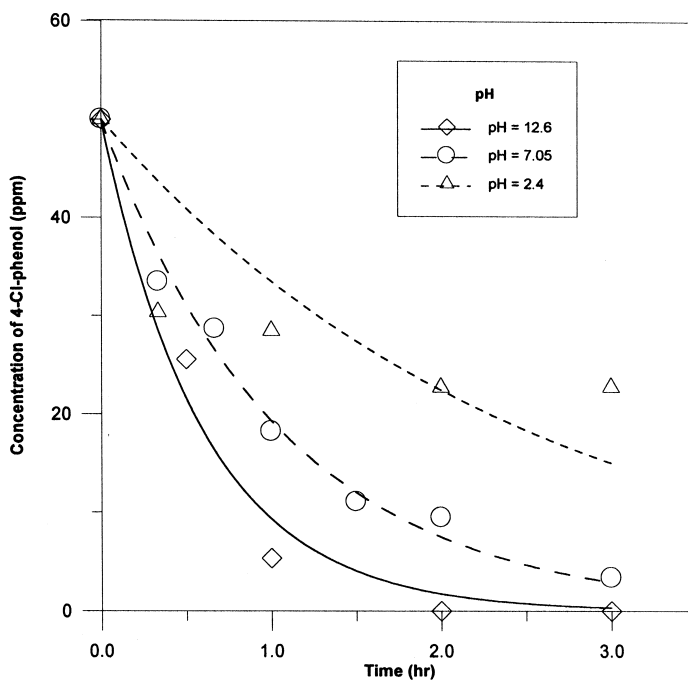


Fig. 7. Influence of pH on the destruction of 4-chlorophenol. Conditions:  $T = 18^{\circ}\text{C}$ , salt concentration = 67.1 mM, initial concentration of 4-chlorophenol = 50 mg/l, set current density = 11.39 mA/cm<sup>2</sup>, working electrode = DSA, counter-electrode = copper.

anode, which could explain the drop in the efficiency from 89% to 33% with increasing current density for the case of 100 mg/l of 4-chlorophenol solution. The same behavior and explanation could be said about the 50 mg/l case (Fig. 3).

It is also observed from Table 1 that the CE increases with increasing initial concentration of 4-chlorophenol for 11.39 mA/cm<sup>2</sup>, which is in agreement with the general observed behavior by Comminellis and Pulgarin [6]. On the other hand, the above behavior is reversed for 6.51 and 16.27 mA/cm<sup>2</sup>. In addition, changing the initial concentration of 4-chlorophenol is expected to affect the intermediates of the destruction process, and therefore, affects the selectivity of the anode. The above reversed behavior means that the selectivity of the anode has changed.

Fig. 4 shows the effect of current density on the destruction of 4-chlorophenol with an initial concentration of 25 mg/l and the same conditions specified in Fig. 2. The rate of destruction is observed to be highest for 11.39 mA/cm<sup>2</sup>, which is neither the highest nor the lowest tested current densities, which means that the selectivity of the anode has a non-linear relation with the current density.

Polymerized intermediate compounds were noticed by HPLC analysis when the current density was at 11.39 mA/cm<sup>2</sup>, but these compounds disappeared after 1.5 h of electrolysis. The lower CE for the 11.39 mA/cm<sup>2</sup> could be due to the blocking of the active sites at the working electrode by the intermediate polymerized compounds.

Table 1

CE at different current densities and different initial concentrations of 4-chlorophenol

Current density (mA/cm <sup>2</sup> )	Initial 4-chlorophenol concentration (mg/l)		
	100	50	25
6.51	20	39	45
11.39	89	49	30
16.27	33	37	45

Fig. 5 shows the effect of initial concentration of 4-chlorophenol on its rate of destruction. It is obvious that increasing the initial concentration decreased the rate of destruction (a similar behavior for anodic oxidation of phenol was reported by De Sucre and Watkinson [4]). This could be due to the presence of intermediate products produced during the electrolysis process at higher concentrations, which then could compete with 4-chlorophenol and water for the active sites on the working electrode, or these intermediate products may be insoluble in water and would block the working electrode active sites. It is worth noting that it was difficult to see any film formation on the surface of the electrode, due to the large size of the cell, however when the cell is opened for cleaning purposes, a thin film was usually observed on parts of the surface of the electrode.

In addition, it is known that increasing the bulk solution concentration should increase the rate of mass transfer. Therefore, the rate of destruction of 4-chlorophenol should increase by increasing its bulk solution concentration if the destruction is mass transfer controlled. Fig. 5 shows that the rate of destruction of 4-chlorophenol is decreased with increasing bulk solution concentration, which means that its rate of destruction is not mass transfer controlled.

The influence of the pH on the destruction of 4-chlorophenol at a current density of 16.27 mA/cm<sup>2</sup> was investigated (see Fig. 6). It is observed that there was no appreciable difference in the destruction at pH values between 2 and 8.9, while an appreciable difference was observed when the pH was increased to 12.6, at which the rate of destruction was highest. This may be due to the fact that the 4-chlorophenol at this pH will be in the anionic form, which enhances its oxidation. In addition, the formed chlorine will be in the form of hypochlorite, a known oxidizing agent, which involves further oxidation of either 4-chlorophenol and/or the intermediates [2].

It has been observed that when starting with a pH of 7 or 8.9, a decreased in the pH was noticed during the electrolysis. It is has also been observed that when starting with a pH of 4.7, the pH increased to reach 6.5 during the electrolysis process. This phenomenon was not observed for higher pH values (where the pH was constant throughout the experiment). The main reason for this change in the pH is that the produced intermediates are thought to have weak acid–base properties. These properties are not significant to produce a change in the pH at 2.4 or 12.6.

The HPLC analysis showed a formation of polymerized compounds only at a pH of 2.4 during the electrolysis. The main reason for this formation of such compounds is the protonation of 4-chlorophenol at low pH values. These compounds were destroyed by

Table 2  
Percent CE at different current densities and pH values

Current density (mA/cm <sup>2</sup> )	pH				
	2.4	4.7	7.2	8.9	12.6
11.39	48	–	22	–	31
16.27	48	48	19	19	37

further electrolysis as time passed. The potential of the working electrode was almost constant for all the pH experiments.

Fig. 7 shows the effect of pH on the destruction of 4-chlorophenol using a current density of 11.39 mA/cm<sup>2</sup>. The same general behavior is noticed as that of Fig. 6. The CE at different current densities and different pH values is presented in Table 2. It is noticed from this table that the highest CE (48%) was at a pH of 2.4 for both tested current densities.

## 6. Conclusions

It is concluded from the data presented in this work that 4-chlorophenol could be eliminated completely by electrochemical techniques within 2 h for most investigated cases. In addition, the current density and the pH affect the rate of the above destruction and the CE. The functionality of this dependency is not yet well established. At low 4-chlorophenol concentration, the rate of destruction did not increase with increasing current density. A CE as high as 89% was achieved.

## Nomenclature

$A$	area of the anode (m <sup>2</sup> )
ACE	average current efficiency
$a_{\text{H}^+}$	activity of the hydrogen ions (M)
$b$	fitting parameter
$C$	concentration of 4-chlorophenol at any time (mg/l)
$C_0$	initial concentration of 4-chlorophenol (mg/l)
CE	current efficiency
COD	chemical oxygen demand (mg/ml)
DSA	dimensional stable anode
$F$	Faraday constant
HPLC	high performance liquid chromatography
$i_{\text{ac}}$	current (A)
$I_{\text{ac}}$	actual current used by the cell (A/cm <sup>2</sup> )
ICE	instantaneous current efficiency
$n$	moles of organic material

$P$	pressure of the cell (Pa)
$R$	universal gas constant (Pa/mol K)
$r$	rate of reaction
$T$	temperature (K)
$t$	time (s)
$V$	volume of cell ( $\text{m}^3$ )
$V_{\text{ca}}$	volume of gas collected at the cathode ( $\text{m}^3$ )
$\dot{V}_{\text{O}}$	oxygen flow rate in the absence of phenol in the electrolyte ( $\text{m}^3/\text{s}$ )
$(\dot{V}V_t)_{\text{org}}$	oxygen flow rate at a given time $t$ in the presence of phenol in the electrolyte ( $\text{m}^3/\text{s}$ )
$V_{\text{th}}$	volume collected at the anode in the absence of phenol ( $\text{m}^3$ )
$V_{\text{w}}$	volume of gas collected at the anode ( $\text{m}^3$ )
$z$	valence

### Greek symbols

$\varepsilon$	cell potential (V)
$\varepsilon_{\text{H}}$	hydrogen reversible potential (V)
$\varepsilon_{\text{O}}$	reversible oxygen potential (V)
$\eta$	applied over potential, which is defined for $\text{O}_2$ production (V)
$\tau$	time when ICE is almost zero

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