

# Electrochemical degradation of 4-chloroguaiacol for wastewater treatment using $\text{PbO}_2$ anodes

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## Abstract

Electrochemical oxidation of 4-chloroguaiacol (4-CG) at Nb/ $\text{PbO}_2$  anodes was studied under different experimental conditions such as initial concentration of substrate, electrolysis time, temperature and pH. We measured the concentrations of 4-chlorocatechol (4-CC), 2-methoxyhydroquinone (2-MHQ), maleic acid (MA) and carbon dioxide as the main products. Black solid particles consisting mainly of polymers were formed during electrolysis. A mechanism of electrochemical oxidation of 4-CG was investigated. The oxidation of 4-CG can generally be described by simple pseudo first-order kinetics. The degradation of 4-CG was favoured at high temperature and lower initial concentration of 4-CG and low solution pH. However, the increase of temperature has not a significant effect on the mineralization of carboxylic acids. Moreover, these products required long electrolysis time.

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## 1. Introduction

Chloroguaiacols (CGs) are widespread pollutants in pulp and paper effluents [1]. Due to their environmental impact, these effluents require treatment before being released. The conventional biological detoxification of these effluents has always been a difficult and limited process because of its strong resistance to microbial degradation [2–5]. Gonzalez et al. (1993) have reported the metabolism of CGs by a bacterial strain (*Acinetobacter junii*) that is able to use guaiacol as the sole carbon and energy source. These authors found that chlorocatechols which is the primary substrates formed, inhibited the degradation of CGs.

The wet oxidation process catalysed by Pt/alumina, manganese/cerium and cobalt/bismuth composite oxide for the degradation of 4-CG has been reported by Hamoudi et al. [6]. The self-inhibition of parent pollutant, the recalcitrance of oxidation intermediate by-products and catalyst deactivation were

the main causes that prevented full mineralization of wastewater organic load.

Recently, there has been an increasing interest in the application of electrochemical methods for the treatment of recalcitrant toxic wastes [7–12]. The electrochemical treatment consists of either a simple transformation of the toxic compounds to biodegradable products or a complete combustion of the organic materials to  $\text{CO}_2$ . Electrochemical treatment of wastewater containing 4-CG has been reported in our previous papers [11]. We have studied the electrochemical oxidation of 4-CG aqueous solution by cyclic voltametry at treated gold electrodes. 4-CC, 2-MHQ and 5-chloro-3-methoxycatechol are the main products. However, it is difficult to completely oxidize aromatic compounds on metals such as gold. Thus, to oxidize an organic compound in a water solution, anode material should have a high overvoltage for oxygen evolution and low cost. Among the materials which meet this criteria are  $\text{SnO}_2$  and  $\text{PbO}_2$  [7,8,13–19]. In this context, preliminary study showed that 4-CG is quantitatively oxidized by electrolysis at Nb/ $\text{PbO}_2$  anode [11]. Therefore, it is necessary to fine-tune the process by examining the reaction kinetics at different concentrations of 4-CG, temperature and initial pH of the electrolyte.

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## 2. Experimental

### 2.1. Chemicals

4-CG, 4-CC, 2-MHQ and MA (analytical grade) were purchased from Aldrich and were used as received. Lactic acid, used as standard in liquid chromatography, was analytical grade from sigma. Methanol was HPLC grade from Fisher Chemicals. All solutions were prepared with double-distilled water.

### 2.2. Preparation of Nb/PbO<sub>2</sub> electrodes

A deposit of lead dioxide was made by electrochemical oxidation of an aqueous solution of lead dioxide at a rectangular plate of massive niobium (50 mm × 10 mm × 1 mm). The niobium surface was chemically stripped for 30 s in 40% hydrofluoric acid at room temperature.

The lead dioxide was galvanostatically deposited using a two-compartment Pyrex glass cell of 500 ml volume thermoregulated at 65 °C. The anolyte was an aqueous solution containing only lead nitrate at a concentration of 1 mol l<sup>-1</sup>; the cathodic compartment containing a solution of 1 mol l<sup>-1</sup> sulfuric acid. The use of a porous ceramic separator (Norton, RA 84) between the two compartments avoids the formation of lead dendrites at the cathode. The deposition of PbO<sub>2</sub> was carried out for 2.5 h using an anodic current density of 20 mA/cm<sup>2</sup>. The average mass of PbO<sub>2</sub> was 0.22 g/cm<sup>2</sup>. The obtained deposit was mat grey, adherent, regular and uniform.

### 2.3. Electrolysis of 4-CG solutions

The electrolyses of the 4-CG acid aqueous solutions (H<sub>2</sub>SO<sub>4</sub>, pH 2) were carried out in a two-compartment Pyrex glass cell of 150 ml volume. The cathode was a graphite bar (Ø=0.5 cm; L=6 cm), placed in a porous ceramic cylinder (Norton, RA 84) containing a 1 mol l<sup>-1</sup> sulfuric acid solution. The Nb/PbO<sub>2</sub> anode was made up of four identical plates arranged symmetrically around the cathode. The total area of the anode was 20 cm<sup>2</sup>. A DC power supply model ABTP 530 Française d'Instrumentation was used. The acidic solutions of 4-CG were electrolyzed under a constant anodic current density of 10 mA/cm<sup>2</sup> with magnetic stirring.

### 2.4. Analytical methods

The oxidation product formed during the anodic oxidation of 4-CG was monitored by HPLC and TOC techniques. A HPLC system (Hewlett-Packard 1100 HPLC) equipped with a Hamilton PRP X 300 column was used. The mobile phase consisted of methanol/water (50:50, v/v) containing 5 × 10<sup>-2</sup> mol l<sup>-1</sup> sulfuric acid. Samples were monitored with a UV-vis diode array detector (DAD) at a wave length of 254 nm. The mobile flow rate was fixed at 1.3 cm<sup>3</sup>/min. The column temperature was 25 °C. Identification of chromatographic peaks was performed by comparison with pure standards. The total organic carbon (TOC) of the solution was monitored during electrolysis using a Shimadzu TOC analyzer.

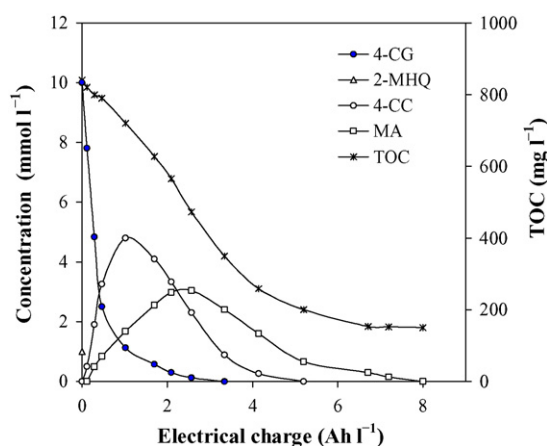


Fig. 1. Variation of 4-CG, 4-CC, 2-MHQ, MA concentration and TOC during the electrolysis of 10 mmol l<sup>-1</sup> 4-CG solution. Anodic current density 10 mA/cm<sup>2</sup>; temperature 30 °C; pH 2.

## 3. Results and discussion

### 3.1. Kinetic study for 4-CG electrooxidation

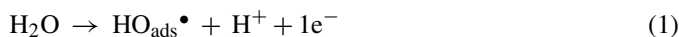
Fig. 1 shows a typical profile of variation of 4-CG, 4-CC, 2-MHQ, MA concentration and TOC with the specific electrical charge (Ah l<sup>-1</sup>) during electrolysis essays of 4-CG. 4-CG was completely eliminated after passing a charge of about 3 Ah l<sup>-1</sup>. Simultaneously, 4-CC, 2-MHQ, MA and even some CO<sub>2</sub> molecules, as shown by the instantaneous drop in the TOC value, were formed. The 4-CC was the main product; its concentration increased over the interval of charge 0–1 Ah l<sup>-1</sup> to reach a maximum of approximately 4.8 mmol l<sup>-1</sup> towards 1 Ah l<sup>-1</sup>. 2-MHQ was less abundant (less than 1 mmol l<sup>-1</sup>). Further destruction of these two stable aromatic products with loss of chloride ions yields maleic, fumaric, formic and oxalic acids which are mineralized by anodic oxidation via CO<sub>2</sub> molecules.

The TOC removal rate was high (140 mg/Ah) during the first stages corresponding to the disappearance of the aromatic products (quantity of electricity less than 4 Ah l<sup>-1</sup>) then became low (25 mg/Ah) between 4 and 7 Ah l<sup>-1</sup> and finally tended to stabilize beyond 7 Ah l<sup>-1</sup>. Therefore, after the disappearance of aromatic products (towards approximately 4 Ah l<sup>-1</sup>), the percentage of TOC removal was 70%. It increased to 82% when the electrical charge reached 7 Ah l<sup>-1</sup>. At higher charge, the solution contained aliphatic carboxylic acids (maleic, fumaric formic and oxalic) in small quantities. The oxidation of these acids at PbO<sub>2</sub> anode was relatively difficult; they accumulate in the solution. In these conditions, the principal anodic reaction is the oxygen evolution (parallel reaction with the oxidation of organic compounds). Moreover, as it has been mentioned previously, the oxidation process involved the formation of insoluble product which could be dimers and/or polymers. The oxidation of such products is extremely slow at an Nb/PbO<sub>2</sub> electrode.

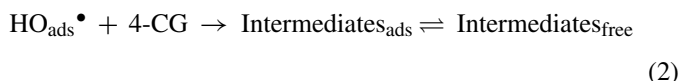
### 3.2. Effect of different operating factors on degradation of 4-CG

In order to study the kinetic of 4-CG degradation, we have tried to determine the order values and the apparent rate constant of the 4-CG oxidation.

It is often assumed that the first step of oxygen transfer is the water molecule discharge at one electron leading to the formation of an adsorbed hydroxyl radical  $\text{HO}_{\text{ads}}^{\bullet}$ :



Hydroxyl radicals generated will attack the organic substrate and form stable and/or mineralized end products:



The parallel reaction is the oxygen evolution:



If we suppose that reaction (2) is of a first-order relating to 4-CG concentration and the hydroxyl radicals concentration is constant during the electrolytic treatment for all temperature used in this investigation, the oxidation rate  $r$  would be governed by the equation:

$$r = \frac{d[4\text{-CG}]}{dt} = K_{(4\text{-CG})}[\text{HO}_{\text{ads}}^{\bullet}]^{\alpha}[4\text{-CG}] = K_{\text{app}(4\text{-CG})}[4\text{-CG}] \quad (5)$$

$\alpha$  is the reaction order relating to the adsorbed hydroxyl radicals concentration,  $K_{(4\text{-CG})}$  the real rate constant and  $K_{\text{app}(4\text{-CG})}$  is the apparent rate constant of the 4-CG oxidation. The above equation can be solved as follows:

$$\ln \frac{[4\text{-CG}]_0}{[4\text{-CG}]} = K_{\text{app}(4\text{-CG})}t = K_m \frac{S}{V}t \quad (6)$$

$[4\text{-CG}]_0$  and  $[4\text{-CG}]$  are respectively the 4-CG concentration at time 0 and  $t$ .  $K_m$  is the apparent mass transfer coefficient,  $V$  the volume of treated solution and  $S$  is the anode area.

#### 3.2.1. Effect of the temperature

The removal of 4-CG (initial concentration  $10 \text{ mmol l}^{-1}$ ) by electrolysis at Nb/PbO<sub>2</sub> anode was carried at three temperatures (30, 50 and 70 °C) controlled continuously with a thermostat. The increase in temperature had a positive effect on kinetic rate. 4-CG disappeared more quickly at 70 °C ( $1.6 \text{ Ah l}^{-1}$ ) than at 30 °C ( $3 \text{ Ah l}^{-1}$ ) (Fig. 2). Using data taken from Figs. 2 and 3 shows plots of Eq. (6) at 30, 50 and 70 °C. The straight lines obtained in these plots were in agreement with a pseudo first-order 4-CG concentration. The values for the apparent rate constant ( $K_{\text{app}}$ ) of the 4-CG oxidation were determined from the slope of the straight line obtained (Table 1). From these values, it can be seen that 4-CG removal rate increased two-fold when temperature was increased from 30 to 70 °C. Furthermore, the values

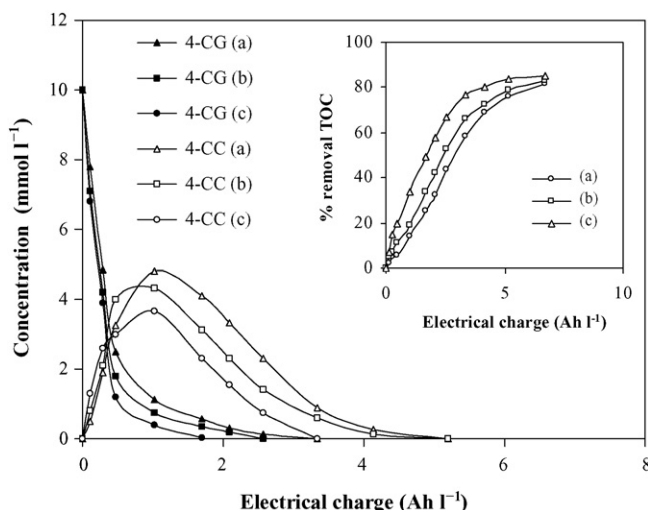


Fig. 2. Effect of temperature on the evolution of 4-CG, 4-CC concentration and % removal TOC during 4-CG electrolysis: (a) 30 °C, (b) 50 °C and (c) 70 °C. Initial concentration of 4-CG  $10 \text{ mmol l}^{-1}$ ; anodic current density  $10 \text{ mA/cm}^2$ ; pH 2.

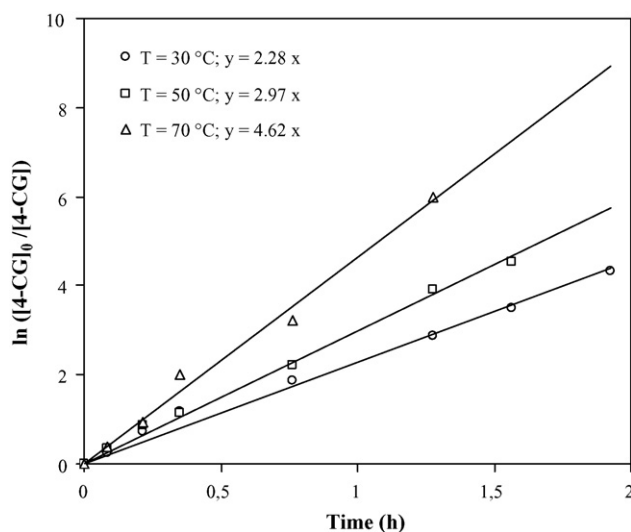


Fig. 3. Linear regression on the disappearance of 4-CG as a function of electrolysis time. Initial concentration of 4-CG  $10 \text{ mmol l}^{-1}$ ; anodic current density  $10 \text{ mA/cm}^2$ ; pH 2.

of apparent rate constants of 4-CC and of MA oxidation were estimated only from the decreasing part of the curves presenting their concentration variation against charge; they increased with temperature (Table 1). The activation energy  $E_a$  values cal-

Table 1  
Kinetic of 4-CG, 4-CC and MA degradation at Nb/PbO<sub>2</sub> anode

Temperature (°C)	$K_{\text{app}} (\text{h}^{-1})$		
	4-CG	4-CC	MA
30	2.28	1.01	0.86
50	2.97	1.41	0.96
70	4.62	1.64	0.99

Anodic current density  $10 \text{ mA/cm}^2$ ; initial concentration of 4-CG  $10 \text{ mmol l}^{-1}$ ; pH 2.

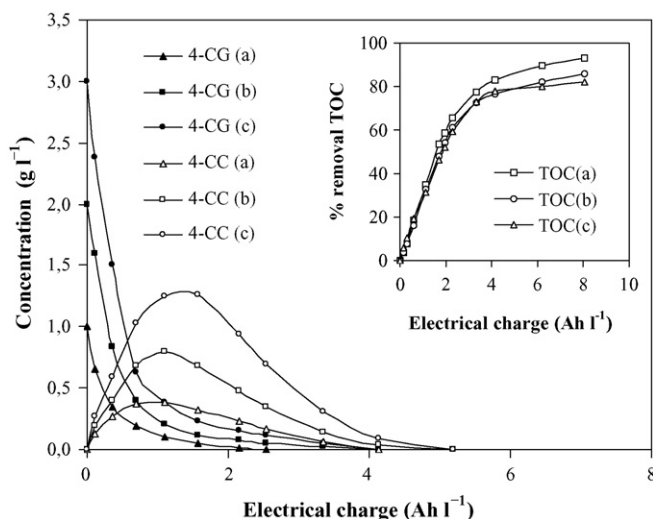


Fig. 4. Degradation kinetics of 4-CG as a function of initial concentration of 4-CG during 4-CG electrolysis. Anodic current density 10 mA/cm<sup>2</sup>; pH 2; initial concentration of 4-CG: (a) 1 g l<sup>-1</sup>, (b) 2 g l<sup>-1</sup> and (c) 3 g l<sup>-1</sup>.

culated using Arrhenius's law were 15, 10 and 3 kJ mol<sup>-1</sup> for 4-CG, 4-CC and MA respectively.  $E_a$  for a diffusion-controlled homogeneous reaction is typically less than 40 kJ mol<sup>-1</sup> [14]. The experimental results were quite inferior to this value and therefore, the limiting step of the 4-CG oxidation is probably of a diffusional nature.

Fig. 2 also shows the TOC abatement. A gradual decrease in pollutant degradation rate with increasing charge (Ah l<sup>-1</sup>) was seen at all temperatures. From the beginning of 4-CG electrolysis until the total disappearance of 4-CG and its aromatic by-products, there were notable differences in TOC removal rates measured at the different temperatures. For instance, after passing a charge of 1.7 Ah l<sup>-1</sup> the TOC removal rate was twice higher at 70 °C than at 30 °C. These differences decreased at longer electrolysis times, suggesting that at the end of the experiments, temperature will not have a sensitive effect on the TOC removal rate. For economic reasons, it is convenient, to work at high temperature only during the removal of aromatic compounds.

### 3.2.2. Effect of the initial concentration of 4-CG

Fig. 4 shows the degradation kinetics of 4-CG as a function of its initial concentration. The electrolysis was carried out for a charge of 6 Ah l<sup>-1</sup>. For all cases, the almost complete elimination of 4-CG was reached after passing about 4 Ah l<sup>-1</sup>; the higher the initial concentration of 4-CG, the faster its oxidation rate. This process can be interpreted in terms of an increase in the mass transport rate ( $K_m[4-CG]$ ) of 4-CG to the anode surface

(Table 2). There was a significant decrease in the value of the 4-CG apparent mass transfer coefficient ( $K_m = K_{app}V/S$ ) relative to its initial concentration (Table 2); this clearly justifies using the term "apparent". The coefficient  $K_m$  was calculated from the variation curve of 4-CG concentration. The decrease in  $K_m$  relative to the initial 4-CG concentration can have two sources:

1. The increase in the flux of 4-CG produces at the electrode surface a higher surface concentration of oxidation intermediates. Under galvanostatic conditions, the production rate of hydroxyl radicals is constant; however, the radicals have non-selective reactivity in relation to the adsorbed intermediates. Consequently, the latter was oxidized to the detriment of new 4-CG molecules.
2. Moreover, it is known that when gas evolution occurs at the electrode surface, the mass transport can be significantly increased. Thus, the decrease in the apparent mass transfer coefficient of 4-CG can be explained by a decrease in the oxygen formation rate when the initial concentration of 4-CG increases.

On the other hand, Fig. 4 shows that the amount of 4-CC, formed during the first period of electrolysis corresponding to the disappearance of 4-CG, increased as a function of the initial 4-CG concentration. The 4-CC concentration reached 1.25 g l<sup>-1</sup> when operating at initial 4-CG concentration of 3 g l<sup>-1</sup>. For a constant charge, the percentage of removal soluble TOC decreased when the initial concentration of 4-CG increased (Fig. 4). Thus, for 1 g l<sup>-1</sup> initial concentration of 4-CG, the

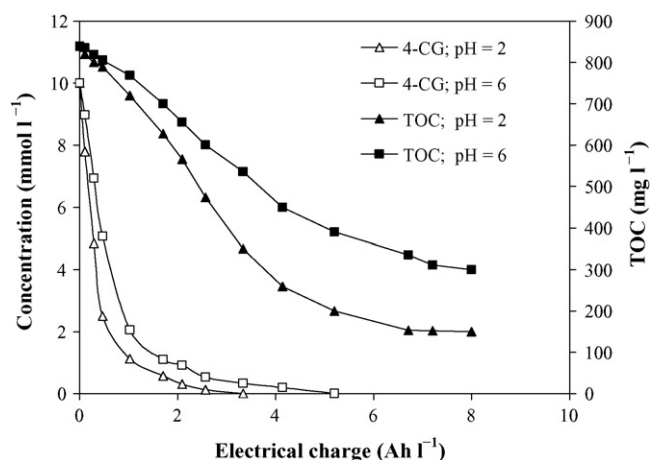


Fig. 5. Effect of solution pH on the variation of 4-CG concentration and TOC as a function of electrical charge passed during 4-CG electrolysis. Initial concentration of 4-CG 10 mmol l<sup>-1</sup>; anodic current density 10 mA/cm<sup>2</sup>; temperature 30 °C.

Table 2

Apparent rate constants, mass transport rate and apparent mass transfer coefficient of 4-CG as a function of initial concentration of 4-CG

Initial concentration of 4-CG (g l <sup>-1</sup> )	1.00	1.58	2.00	3.00
4-CG apparent mass transfer coefficient, $K_m$ ( $\times 10^5$ m s <sup>-1</sup> )	5.53	4.75	4.16	3.72
4-CG mass transport rate, $K_m[4-CG]$ ( $\times 10^2$ g m <sup>-2</sup> s <sup>-1</sup> )	5.53	7.50	8.32	11.12
4-CG apparent rate constants, $K_{app}$ (h <sup>-1</sup> )	2.62	2.28	1.99	1.78

Anodic current density 10 mA/cm<sup>2</sup>; temperature 30 °C; pH 2.

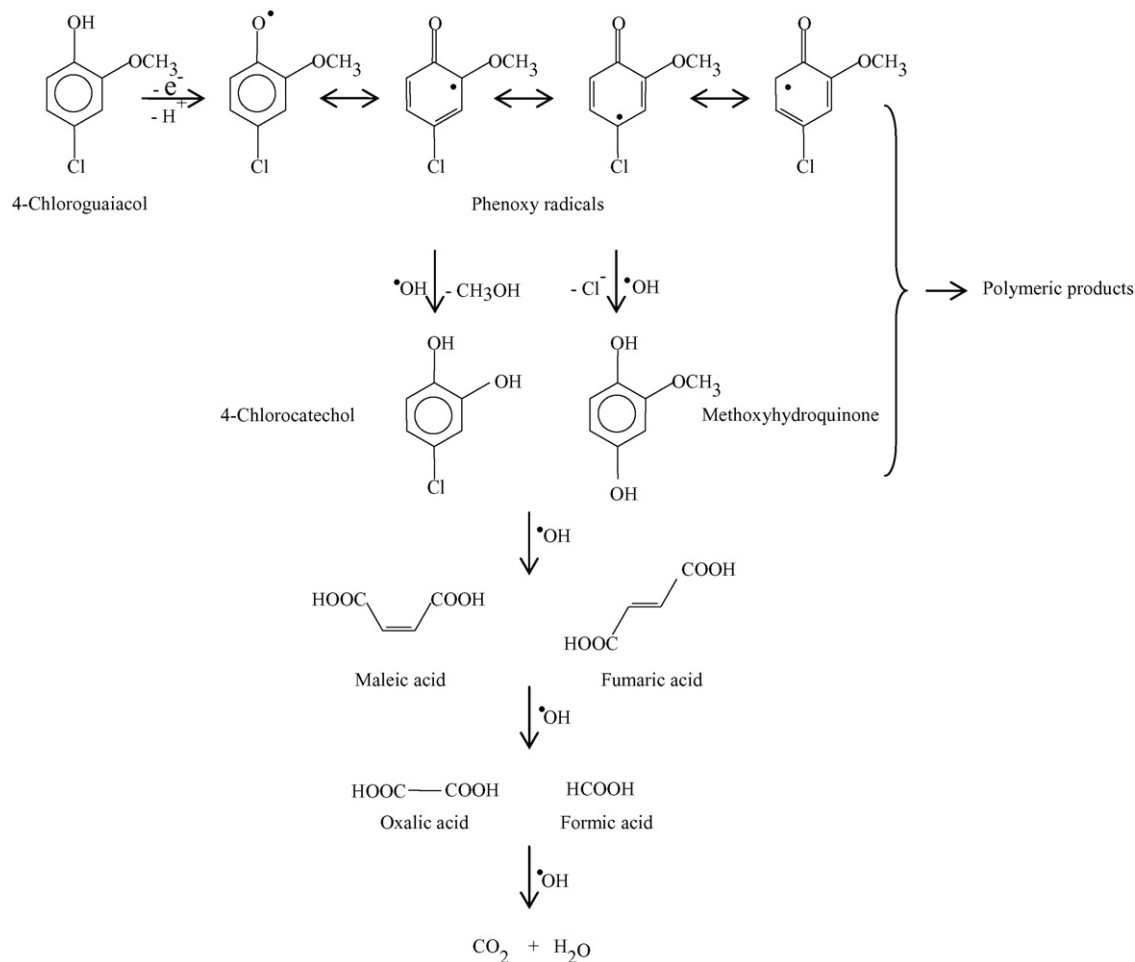


Fig. 6. Proposed reaction pathway of the electrochemical degradation of 4-CG at Nb/PbO<sub>2</sub> anode.

removal TOC can reach 93% for an electric charge of 8 Ah l<sup>-1</sup>. This indicated that the degradation of 4-CG and its by-products was almost complete; the 7% of non oxidized organic carbon could be in the form of polymer previously filtered before TOC measurement. Under the same conditions, only 82% of TOC removal was measured for 4-CG initial concentration of 3 g l<sup>-1</sup>. This can be explained by two reasons: (i) an increase of aliphatic by-products such as MA when operating at higher initial concentration of 4-CG; (ii) an increase of the amount of the precipitated polymer formed during the electrolysis.

### 3.2.3. Effect of solution pH

Several 4-CG solutions at pH between 2 and 6 were tried. Lower initial samples pH value (pH 2) lead to oxidation kinetics higher than those obtained with samples having pH 6 (Fig. 5). The apparent mass transfer coefficient of 4-CG decreased from  $4.7 \times 10^{-5}$  to  $3.2 \times 10^{-5}$  m s<sup>-1</sup> when the pH was increased from 2 to 6. It appears that the increase of the 4-CG solution pH decreased the potential oxygen generation obtained from OH• radicals oxidation and consequently increased the flow rate of oxygen at the electrode surface. As a result, the diffusion flow of 4-CG towards the electrode decreased. Furthermore, it is well

known that the increase of the solution pH favors polymerization reactions; this can be indicated by the decrease of TOC removal measured between pH 2 and 6.

### 3.3. Proposed reaction sequence

A general pathway involving all detected products for the mineralization of 4-CG in acidic media is presented in Fig. 6. It is generally believed that organic compounds in aqueous solutions can be oxidized on an anode by direct electron transfer and indirect oxygen atom transfer [8,20]. In the direct electron transfer process, organics are adsorbed on the anode surface and give up electrons to the anode. With the indirect oxygen atom transfer, it is generally considered that oxygen radicals, especially the hydroxyl radicals generated from water electrolysis, readily react with the organic molecules adsorbed on the anode. 4-CG oxidation begins with an electron transfer that leads to phenoxy radicals which exist under four mesomeric forms. Two possible reaction pathways related to these phenoxy radicals include the formation of intermediate aromatic compounds, such as 4-CC and 2-MHQ and the formation of polymeric products by radical–radical, radical–4-CG, radical–intermediate aromatic compounds coupling. Further degradation of 4-CC and 2-MHQ

leads to a mixture of maleic and fumaric acids. With continuous electrolysis, maleic and fumaric acids would be oxidized to oxalic and formic acids, which are directly converted into CO<sub>2</sub>.

#### 4. Conclusion

In this work, the electrochemical oxidation of 4-CG in aqueous solutions at Nb/PbO<sub>2</sub> anode has been studied under different experimental conditions, i.e., different initial concentration of 4-CG, temperature, pH and time of electrolysis. The results of this study revealed the following:

- During the 4-CG oxidation, an increase in temperature significantly improved the percentage of 4-CG elimination: from 25% at 30 °C to 50% at 70 °C, after passing a charge of 1.7 Ah l<sup>-1</sup>.
- The 4-CG degradation was favored when operating at low initial concentration and pH (1 g l<sup>-1</sup>, pH 2).
- The electrochemical oxidation of 4-CG in acidic media produces a wide distribution of oxidation products, 4-CC being the main product before the ring-opening step, which takes place to form aliphatic acids. A pathway of electrochemical degradation of 4-CG was suggested.

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