

# SIMULTANEOUS ELECTROCHEMICAL OXIDATION AND REDUCTION OF REPRESENTATIVE ORGANIC POLLUTANTS

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## ABSTRACT

In the present work we present a proof-of-concept for the simultaneous treatment of representative organic pollutants at the anode and cathode of an electrolytic cell. The experimental procedure entails the separate study of the anodic and cathodic processes, followed by that of the simultaneous process. Analysis of the products on both sides of the cell proves the validity of the proposed concept.

**KEYWORDS:** simultaneous electrochemical processes, electrochemical treatment of pollutants, hazardous materials treatment, phenol, dichlorophenol.

## INTRODUCTION

Typical methods for the treatment/removal of organic pollutants from industrial aqueous effluents include incineration, biological treatment, adsorption, chemical treatment, and electrochemical oxidation. Incineration is an expensive process because it implies physical transportation, fuel consumption, secondary pollutant generation, as well as direct and indirect losses due to the corrosivity of some chemical compounds [1]. Biological treatments are more commonly used; nonetheless, the degree of biodegradability of a given substance strongly depends on its chemical nature and there are many substances not amenable to undergo these treatments [1, 2].

According to the list of priority pollutants of the European Community, halogenated organic compounds (of which chlorinated aromatics are on the top of the list) are considered among the most abundant and dangerous to the environment [3]. An increase in toxicity and decrease in biodegradability are directly related to the number of chlorine substituents in the molecule [3]. Non-halogenated organics like phenols and other organics are important pollutants as well.

The electrochemical route has gained importance as an alternative final treatment method or else as an intermediate stage, depending on the specific problem. There are numerous studies involving for example halogenated and non-

halogenated organics [1-13]. Advantages include the utilization of ambient pressures and temperatures, environmental compatibility, versatility, cost efficiency, and amenability to automation and control [14, 15]. Previous works have typically focused either on the reduction or the oxidation reactions, allowing the concomitant decomposition of the solvent at the counter electrode. We hereby propose that the energy used at the counter electrode can also be used for the treatment of pollutants in a simultaneous fashion at both electrodes [16]. This increases the energetic yield, and decreases operation times and costs.

The present work is intended to demonstrate as a proof-of-concept the possibility of performing the simultaneous electrochemical treatment of dichlorophenol and phenol as representative, non biocompatible pollutants in aqueous media. Analogous processes have been proposed for the simultaneous removal of a metal ion (e.g., Cd(II) or Cu(II)) and the destruction of CN<sup>-</sup> [17, 18], and for the combined electroprecipitation and Fenton oxidation of organics [19]. However - to the best of our knowledge - this is the first time that a direct electrolytic approach is proposed for the simultaneous treatment of organic compounds.

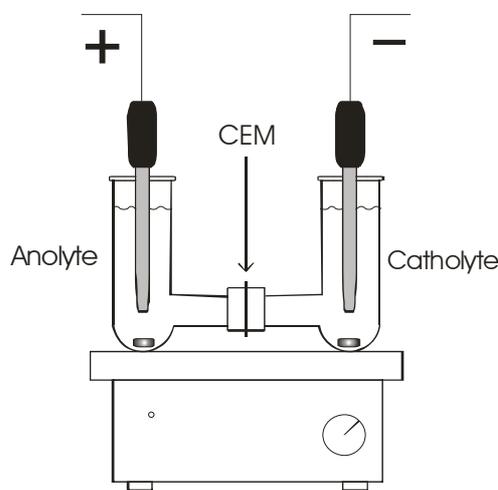
## MATERIALS AND METHODS

All the experiments were performed in a small-scale glass cell divided in two compartments (each one with an approximate volume of 10 mL), and equipped with a cationic exchange membrane, CEM sandwiched between them (membrane R1010, The Electrosynthesis Co.). The two cell compartments and the membrane were kept together by several layers of parafilm that also prevented liquid leakage (see Figure 1). Magnetic stirring bars were inserted in the anodic and cathodic compartments, and constant stirring was provided during the experiments. The potential source was an AMEL Instruments potentiostat (Model 2051), and an Ag/AgCl electrode (Bioanalytical Systems) was the reference electrode. The working and counter electrodes are described in each experiment below.

The chemicals used were nitric acid (Baker Analyzed Reagent, 65.3%), dichlorophenol (Baker Analyzed Reagent,

99.5%), potassium nitrate (Baker Analyzed Reagent, 100.01%), calcium hydroxide (Baker Analyzed Reagent, 97.4%), silver nitrate (Baker Analyzed Reagent, 99.9%) and phenol (Baker Analyzed Reagent, 99.8%). All the solutions were prepared with deionized water.

Since electrochemical reduction of halogenated organics produces the rupture of carbon-halogen bonds [4], our cathodic goal was to break C-Cl bonds in 2,4-dichlorophenol. This rupture should free chlorine atoms in the form of the environmentally friendly chloride ions, and thus decrease the toxicity of the solution. On the anodic side, electrochemical oxidation (sometimes also called electrochemical incineration) of organic compounds is targeted to produce  $\text{CO}_2$ .



**FIGURE 1 - Experimental cell.** (Note: The reference electrode, Ag/AgCl – not shown here - was placed either at the anodic or cathodic compartments, according to each experimental requirement. See text).

Accordingly, the experimental sequence firstly involved a study of the electrochemical reduction of 2,4-dichlorophenol; secondly, a study of the electrochemical oxidation of phenol, and lastly a study of the simultaneous electrochemical reduction of 2,4-dichlorophenol plus the electrochemical oxidation of phenol.

#### Part A. Electrochemical reduction of 2,4-dichlorophenol.

A platinum wire (Strem Chemicals, 3N5) was the anode. Due to its large surface area, high permeability, environmental compatibility, high hydrogen overpotential, and adsorption capacity for certain halogenated organics [10], a square piece of graphite felt (2.5 cm x 2.5 cm) was used as the cathode (GC-10, Fine Weave, 0.5 mm, The Electrosynthesis Co.). A 0.005 M dichlorophenol solution in 0.1 M  $\text{KNO}_3$  was used as catholyte, and a 0.1 M  $\text{KNO}_3$  solution in 0.1 M  $\text{HNO}_3$  was used as anolyte. Since reductive halogenations commonly require -1 to -3 V [3], we applied a potential to the system as to obtain -2.4 V vs. Ag/AgCl at the cathode. The catholyte was removed from

the cell at the end of each experiment and stored for subsequent analysis. The experiment was run three consecutive times; the solution and instrumental conditions (other than electrolysis time) did not vary among the runs.

#### Part B. Electrochemical oxidation of phenol

A platinum wire was used as the cathode (Strem Chemicals, 3N5). In order to provide a high overpotential for dioxygen production and to open the possibility for the production of  $\cdot\text{OH}$  radicals, we used a stainless steel anode covered with a layer of  $\text{PbO}_2$ , with an approximate geometrical surface area of  $1.7 \text{ cm}^2$  (The Electrosynthesis Co.). A 0.005 M phenol solution in 0.1 M  $\text{KNO}_3$  and 0.1 M  $\text{HNO}_3$  was used as anolyte, and a 0.1 M  $\text{KNO}_3$  solution was used as catholyte. From previous experience, we applied to the system a potential as to obtain 3.5 V vs. Ag/AgCl at the anode. A glass tube was connected to the anodic compartment of the cell in order to route the electrolysis gases into a saturated and filtered  $\text{Ca}(\text{OH})_2$  solution in a loosely-stoppered beaker to prevent pressure build-up, and at the same time to avoid atmospheric  $\text{CO}_2$  from interfering with the experiment. This was achieved by bubbling high purity nitrogen into both cell compartments as to keep the overall pressure equalized. The experiment was run three consecutive times; the solution and instrumental conditions (other than electrolysis time) did not vary among the runs.

#### Part C. Simultaneous processes: Electrochemical reduction of 2,4-dichlorophenol and electrochemical oxidation of phenol.

We used the same cell system as in Part B, except that a constant-temperature water bath was included to cool down the reaction system. The anode was the same stainless steel electrode as in Part B, and the cathode was the same graphite felt electrode as in Part A. A 0.005 M phenol solution in 0.1 M  $\text{KNO}_3$  and 0.1 M  $\text{HNO}_3$  was used as anolyte. A 0.005 M dichlorophenol solution in 0.1 M  $\text{KNO}_3$  was used as catholyte. From different trials, we found that a potential was required as to obtain 2.7 V vs. Ag/AgCl at the anode. The catholyte was removed from the cell after each experiment and stored for subsequent analysis. The experiment was run three consecutive times; the solution and instrumental conditions (other than electrolysis time) did not vary among the runs.

## RESULTS AND DISCUSSION

#### Part A. Electrochemical reduction of 2,4-dichlorophenol

The use of a graphite felt as cathode has the advantage of a large surface area - a desirable condition for the treatment of pollutants at low concentrations; in addition, graphite has a high overpotential for the production of hydrogen [3, 5, 14]. The use of a cationic exchange membrane is required between anolyte and catholyte as to prevent migration of the cathodically-formed chlorides to the anode. This avoids the anodic production of elemental chlorine that could react with the organics and chlorinate them again [3, 5, 14].

Figure 2 shows the variation of current with time. The observed current increase is mainly due to the use of a relatively high reduction potential that promotes hydrogen formation from water as a parallel reaction at the cathode. This situation is inevitable because – as mentioned earlier – the reduction of halogenated organics requires in general rather negative potentials (ca. -1 to -3 V vs. SCE) [3]. This parallel reaction takes up electrons and at the same time produces OH<sup>-</sup> ions. The concentration difference between these ions and the protons migrating from the anolyte results in pH changes in the catholyte. The presence of more ionic species in solution is beneficial to the process as it diminishes the ohmic drop in the cell. The difference in the obtained currents in each run may be explained by the electrode passivation. In addition, the system's response was found to be partially dependent on the electrode separation, which by virtue of the cell design could not be held constant.

As a qualitative test for the production of chlorides as a result of the dehalogenation, a few drops of 0.1 M of AgNO<sub>3</sub> were added to the catholyte after the electrolysis. A brown precipitate of AgOH was obtained after the first run (the pH at the end of the experiment = 13), whereas a white precipitate of AgCl was obtained from the second run, due to the presence of electrolytically produced chlorides (the pH at the end of the experiment = 4). Chloride ions were probably also produced in the first run, but the high basicity of the solution impeded the observation of the white precipitate. In the second and third runs, the final pH was acidic because the currents obtained were substantially smaller than in the first run; this indicates a lower hydrogen production rate at the cathode and thus fewer OH<sup>-</sup> ions, which most likely were completely neutralized by the pro-

tons that migrated from the anolyte. As a blank test, a few drops of the AgNO<sub>3</sub> solution were added to a non-electrolyzed catholyte sample, and no precipitate was produced.

Lastly, the resulting solution from the third run was titrated argentometrically as to quantify the chlorides produced during the electrolysis. In this way, an 11.7% dehalogenation was calculated. Such a value is considered sufficient for the proof-of-concept objective of the present work, and is susceptible to be enhanced by optimization of the experimental parameters and cell design.

#### Part B. Electrochemical oxidation of phenol.

The electrochemical oxidation of phenol produces intermediate species such as hydroquinone, quinone, maleic, fumaric and oxalic acids as well as CO<sub>2</sub> as the ultimate oxidation product [6, 7, 14]. For the proof-of-concept objective of this work we were only interested in observing the production of CO<sub>2</sub> at the anode as indication of the electrochemical oxidation (incineration) of phenol. Figure 3 shows that in all the experiments the tendency of the current is to decrease with time. This is most likely due to the formation of a polyoxyphenylene film, which is known to strongly adhere to surfaces [14]. This non-conducting polymer results from the oxidation of phenol via phenolate anions and promotes an increase in the anode's electrical resistance. Since this polymerization is favored at high temperatures [7], then the temperature increase obtained in the cell (due to the relatively high currents that passed through the small volume used in the experimentation) facilitates its formation. In addition, the system's response was found to be partially dependent on the electrode separation, which by virtue of the cell design could not be held constant.

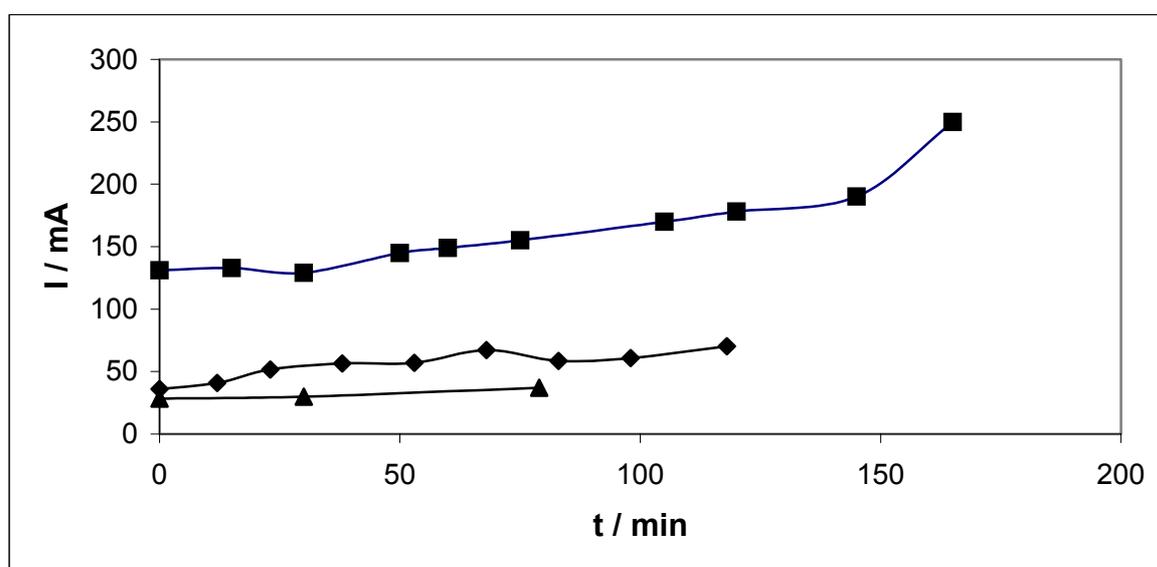


FIGURE 2 - I-t response during the reduction of dichlorophenol at -2.4 V vs. Ag/AgCl. ■ = First experiment, ▲ = second experiment, ◆ = third experiment.

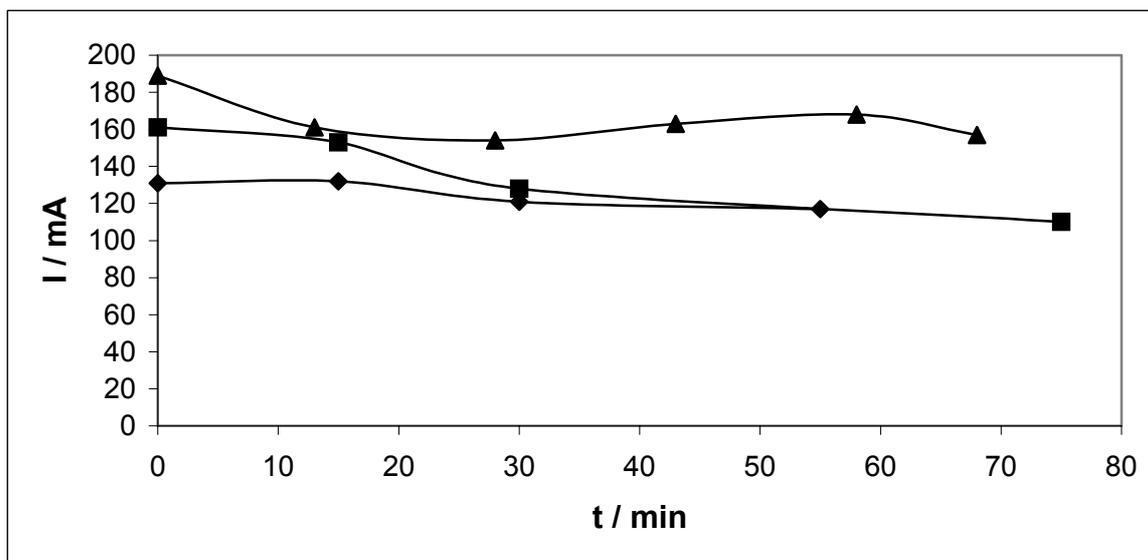


FIGURE 3 - I-t response during the oxidation of phenol at  $-2.4$  V vs. Ag/AgCl.  
 ■ = First experiment, ▲ = second experiment, ◆ = third experiment.

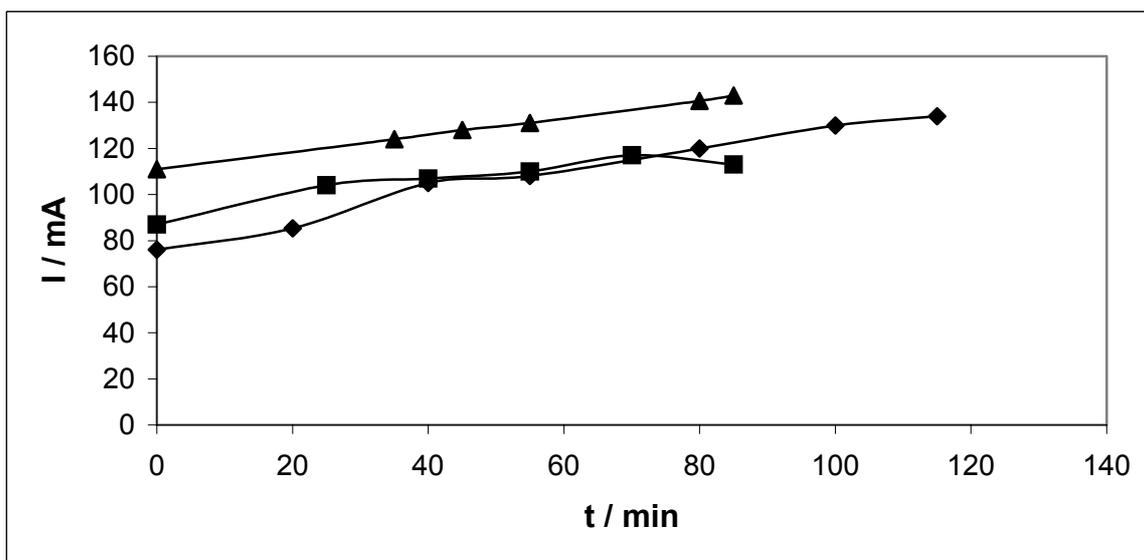


FIGURE 4 - I-t response during the simultaneous oxidation of phenol and the reduction of 2,4-dichlorophenol at  $2.7$  V vs. Ag/AgCl.  
 ■ = First experiment, ▲ = second experiment, ◆ = third experiment.

The three runs yielded a  $\text{CaCO}_3$  precipitate in the  $\text{Ca}(\text{OH})_2$  solution where the anodic gases were bubbled. To ensure that this was not formed by the dissolution of atmospheric  $\text{CO}_2$ , a glass vessel containing a representative volume of the solution of  $\text{Ca}(\text{OH})_2$  was held semi-open as a blank test during each run as described earlier. No precipitate was produced here, which means that the precipitates observed in the test solutions are due to the electrolytic generation of  $\text{CO}_2$ .

The use of a commercial anode coated with  $\text{PbO}_2$  is an advantage for the present process since this layer offers

a high overpotential for the production of oxygen [8]. Although  $\text{SnO}_2$  anodes are superior in this regard [1], home-made  $\text{PbO}_2$  electrodes can be produced simply by anodizing Pb in an  $\text{H}_2\text{SO}_4$  medium.

#### Part C. Simultaneous processes: The electrochemical reduction of 2,4-dichlorophenol and the electrochemical oxidation of phenol.

As shown in Figure 4, the current tends to increase with time, contrary to the results obtained in Part B. We ascribe this observation to the fact that the temperature in the cell was held close to room temperature by the use of

a cooling bath; this inhibits – at least partially - the formation of the phenolic polymer. In addition, the system's response was found to be partially dependent on the electrode separation, which by virtue of the cell design could not be held constant. During these three runs the appearance of a  $\text{CaCO}_3$  precipitate was observed in the vessel containing the saturated  $\text{Ca(OH)}_2$  solution through which the anodic gases were bubbled; this evidences the formation of  $\text{CO}_2$  at the anolyte due to the electrochemical incineration of phenol. During the first two runs, the presence of chlorides in the catholyte was demonstrated by the appearance of a white precipitate of  $\text{AgCl}$  when adding a few drops of 0.1 M  $\text{AgNO}_3$  to the catholyte (whose pH was previously neutralized).

In the third run, the production of chlorides was quantified by argentometric titration to determine a dehalogenation percentage of 36.8%. In order to estimate the percentage of phenol converted to  $\text{CO}_2$ , the  $\text{Ca(OH)}_2$  solution from the third run was titrated with acid. In this way, an estimated 11.8% of the initial phenol underwent complete incineration.

The pairing of both processes for field applications can be conceived in at least two different ways:

- a) The simultaneous treatment of effluents containing pollutants of different chemical nature (e.g., halogenated and non-halogenated organics), or
- b) The cathodic treatment of effluents containing a halogenated pollutant in the catholyte followed by recirculation into the anolyte to achieve the electrochemical incineration (i.e., oxidation) of the resulting reduced (dehalogenated) species. This procedure should in principle eliminate totally the pollutant from the aqueous stream. Care needs to be exercised in this last option to prevent a possible re-halogenation of the product at the anode.

## CONCLUSIONS

We have shown that the simultaneous anodic and cathodic treatment of selected organic pollutants is possible. During the cathodic dehalogenation of dichlorophenol and the anodic oxidation of phenol, we were able to dehalogenate ca. 37% of the former and oxidize 12% of the latter. These yields can undoubtedly be increased by optimization of cell parameters (e.g., applied potential, geometry, electrolyte flow type), solution parameters (e.g., pH, temperature, concentration, mass-transfer conditions), and electrode parameters (e.g., geometry, composition, location).

The proposed dehalogenation process is - in all likelihood - more widely applicable since we selected a harsh chemical structure in the sense that an aliphatic organic tends to be more easily dehalogenated than an aromatic (as the one used here); also, rupture of the carbon-halogen link is easier for bromine or iodine than for the chlorine compound selected here.

Lastly, even if the complete dehalogenation or incineration of organic compounds were not achieved in a given process, the obtained toxicity decreases may be enough so as to render the waste amenable to biological treatment. The results obtained herein merit a more thorough determination of the degree of dehalogenation and of electrochemical combustion of target compounds under optimized conditions.

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