

Removal of Phenol from Water in the Presence of NaCl in Undivided Cells Equipped with Carbon Felt or Ni Cathodes: Effect of Air Pressure

Yongyong Hao,^[a, b] Hongrui Ma,^[a] Federica Proietto,^[b] Claudia Prestigiacomo,^[b] Pengfei Ma,^[a, b] Alessandro Galia,^[b] and Onofrio Scialdone^{*[b]}

Recently, the electrochemical treatment of wastewater polluted by recalcitrant organics and containing chlorides was shown to be significantly improved adopting proper operative conditions such as suitable anodes and cathodes and low current density. In particular, the use of suitable cathodes such as carbon felt or silver could increase the removal of TOC and reduce the formation of chlorinated by-products. In this study, attention was focused on the utilization of carbon felt cathodes with the

Introduction

In the recent years, it has been shown that some electrochemical technologies, such as anodic oxidation, electro-Fenton (EF) and oxidation by electrogenerated active chlorine, can allow to effectively treat wastewaters contaminated by organics very resistant to conventional processes, such as biological ones.^[1–3] In particular, the anodic oxidation process gives the highest removals of organics and of total organic carbon (TOC) but often requires the use of an expensive anode such as Boron Doped Diamond (BDD),^[1,3] even if recently promising results were achieved with other anodes and, in particular, with Ti_4O_7 .^[4,5] The electro-Fenton process is based on the cathodic conversion of oxygen to hydrogen peroxide [Eq. (1)], which is converted in a very good oxidant, the hydroxyl radical, using catalytic amounts of Fe(II) [Eq. (2)].^[1]

$$O_{2(g)} + 2 H^+ + 2 e^- \rightarrow H_2O_2$$
 (1)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$$
(2)

Shaanxi University of Science & Technology Xi'an 710021, P.R. China
[b] Dr. Y. Hao, Dr. F. Proietto, Dr. C. Prestigiacomo, Dr. P. Ma, Prof. A. Galia, Prof. O. Scialdone Dipartimento di Ingegneria Università degli Studi di Palermo Viale delle Scienze, Ed. 6, Palermo 90128, Italy E-mail: onofrio.scialdone@unipa.it
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main aim to evaluate the effect of air pressure on the process using phenol as model organic pollutant. It was shown that, in the presence of carbon felt cathode, the use of pressurized air allows both to increase the removal of TOC and to reduce the formation of chlorate. Moreover, the effect of the nature of the anode and of the presence of FeSO₄, in order to study the involvement of electro-Fenton process, was evaluated.

This process is characterized by the use of cheap carbon cathodes, but its performances are limited by the low solubility of oxygen in water contacted with air at atmospheric pressure which leads to a slow production of hydrogen peroxide. However, this problem can be solved by the use of proper cathodes, such as air gas diffusion ones,^[1] venturi^[6] or microfluidic^[7] cells or by the use of pressurized air.^[8]

Moreover, many kinds of wastewaters, contaminated by both organic pollutants and by pathogen microorganisms, can be treated by chlorinated oxidants produced by the anodic oxidation of chlorides, usually in the form of sodium chloride which is a rather cheap reagent often present in liquid effluents.^[1,2,9–12] This process is characterized by the potential oxidation of organics by means of a plethora of oxidants such as Cl₂, HClO, ClO⁻, Cl₂O and ClO₂, adsorbed chloro and oxychloro radicals and various other reactive oxygen species (ROS), including HO[•], H₂O₂ and $•O_2$.^[2,9–17]

Indeed, the anodic oxidation of chlorides leads to the formation of dissolved chlorine [Eq. (3)] which is converted mainly in hypochlorous acid [Eq. (4)] in moderate acidic conditions and in ClO⁻ in basic ones [Eq. (5)], while Cl₂O and ClO₂ can be formed by both chemical and electrochemical paths [Eq. (6) and (7)]^[2,10] and the ROS by water anodic oxidation.^[1,3] Equation (8) reports, as an example, the oxidation reaction by HClO or ClO⁻.

$$2\mathsf{CI}^- \to \mathsf{CI}_{2(\mathsf{aq})} + 2\mathsf{e}^- \tag{3}$$

$$\mathrm{Cl}_{2(\mathrm{aq})} + \mathrm{H}_2\mathrm{O} \to \mathrm{H}\mathrm{C}\mathrm{I}\mathrm{O} + \mathrm{H}^+ + \mathrm{C}\mathrm{I}^- \tag{4}$$

 $\mathsf{HCIO} \leftrightarrows \mathsf{H}^+ + \mathsf{CIO}^- \tag{5}$

$$CI^{-} + 2H_2O \rightarrow CIO_2 + 4H^+ + 5e^-$$
 (6)

$$2CI^{-} + 2H_2O \to CI_2O + 2H^+ + 4e^-$$
(7)

[a] Dr. Y. Hao, Prof. H. Ma, Dr. P. Ma

School of Environmental Science and Engineering

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mHClO (or ClO⁻) + organics \rightarrow nCO₂ + mH₂O + mCl⁻ (8)

However, this approach presents some relevant disadvantages, such as a difficult selection of most suitable operative conditions and the formation of chlorinated toxic compounds, such as chlorinated aromatic substances, haloacetic acids (HAAs), chlorate and perchlorate, that can enhance drastically the toxicity of treated waters.^[1,2] However, very recently, quite promising results were obtained in the perspectives to achieve an effective removal of organics coupled with the minimization of chlorinated by-products adopting an innovative set of operative conditions involving (i) low current density (j); (ii) proper anodes and (iii) the use of undivided cells equipped with suitable cathodes, such as silver and carbon felt ones,^[12] as described below.

- (i) Various studies mainly focused on electrochemical disinfection shows a reduced formation of chlorate and/or perchlorate adopting lower values of *j* at both BDD^[18-24] and IrO_2 -Ta₂O₅ anodes.^[25,26]
- (ii) Metal oxide anodes such as IrO_2 -Ta₂O₅ allow to reduce the formation of chlorates and to avoid the occurrence of perchlorate but, conversely, do not inhibit the formation of HAAs.
- (iii) Carbonaceous cathodes, such as carbon felt, convert oxygen to H_2O_2 [Eq. (1)] which can limit the formation of chlorate and perchlorate, as recently shown by the groups of Rodrigo during the electrochemical reclamation of urban treated wastewater^[27] and by that of Scialdone for the treatment of an aqueous solution containing phenol and chlorides.^[12] In particular, H_2O_2 reacts with hypochlorite, causing its reduction to chloride [Eq. (9)], and with chlorate to yield ClO₂ [Eq. (10)],^[28] a strong oxidant, that can be electro-synthetized by anodic oxidation of hypochlorite or cathodic reduction of chlorate.^[29]

 $CIO^{-} + H_2O_2 \rightarrow CI^{-} + 1.5O_2 + 2H^{+} + 2e^{-}$ (9)

$$2H^{+} + 2CIO_{3}^{-} + H_{2}O_{2} \rightarrow 2CIO_{2} + 2H_{2}O + O_{2}$$
(10)

Conversely, silver cathodes allow the reduction of HAAs to acetic acids that can be more effectively removed by oxidation processes.^[12]

It was shown very recently that the adoption of two cathodes (silver and carbon felt) in an undivided cell allows to achieve, during the electrochemical treatment of a water solution of phenol and chlorides, very high removal of TOC minimizing the formation of all halogenated by-products.^[12]

In this study, we focused our attention on the electrochemical treatment of water solutions containing organic pollutants and chlorides in undivided cells equipped with carbon felt cathodes using pressurized air. The main objective was to investigate the effect of air pressure in the presence of chlorides on the removal of organic pollutants and on the generation of chlorinated by-products. Indeed, the use of pressurized air may potentially accelerate the production of hydrogen peroxide [Eq. (1)], as a consequence, the consumption of chlorate [Eq. (10)] and the production of chlorine dioxide [Eq. (9) and (10)]. Moreover, the effect of the nature of the anode and of the addition of FeSO4, in order to study the involvement of electro-Fenton process, was evaluated. The effect of the pressure on the electrochemical treatment of wastewater contaminated by organics was not often investigated in the literature. In particular, Isae and coauthors have shown that the use of pressurized oxygen allows to increase the oxidation of toluene and acetone in water^[30] by favoring the cathodic conversion of oxygen to various oxidants. Moreover, more recently, various groups have shown that the use of pressured air or oxygen can improve drastically the performances of electro-Fenton process.^[8,31] However, the effect of the pressure on the generation of chlorinated by-products during the anodic treatment of aqueous solutions containing both organic pollutants and chlorides was never investigated up to our knowledge.

Phenol was used as organic pollutant for its high resistance to many conventional processes, the potential formation of many toxic by-products and its large use in literature as a representative model compound.^[32] The formation of many intermediates and by-products including chlorophenols, HAAs, chlorate and perchlorate, chloroform and carboxylic acids was evaluated. The use of pressurized air at Ni cathode did not significantly affect the process. Conversely, it was shown for the first time that higher air pressures at carbon felt cathodes allows both to enhance the removal of TOC and to minimize the concentration of chlorate.

Results and discussion

First experiments at Ti/RuO₂ anode and Ni cathode

A first series of electrolysis was performed in an undivided cell using Ti/RuO₂ anode, a Ni cathode which favors the hydrogen evolution, a *j* of 10 mA cm⁻², magnetic stirring (400 rpm), a water solution of phenol (2 mM) and sodium chloride (0.5 M) contacted with air at 1 and 5 bar, respectively. Ti/RuO₂ was chosen as anode material because it strongly catalyzes the chlorides oxidation, generating relatively high concentrations of active chlorine.^[2,12] As shown in Figure 1, which reports the data achieved using 1 bar, the use of this system allowed a fast removal of phenol (abatement of 99% after 2 h) even if with the formation of many organic by-products and intermediates. Indeed, according to the literature, [12,33,34] p-chlorophenol, ochlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6trichlorophenol were formed, due to the chlorination of phenol, even if they were completely removed after a short time (about 2 h) (Figure 1B).

The formation of all chloroacetic acids (HAAs) was also observed according to the literature^[12] and, after 24 h, a relatively high concentration of both di- and tri-chloroacetic acids was still present (about 0.45 mM each for an overall concentration close to 0.9 mM (Figure 1B)).



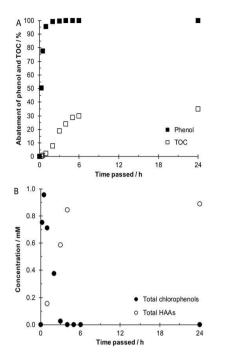


Figure 1. Plot of the abatement of phenol and TOC (A), and of the overall concentrations of chlorophenols and HAAs (B) vs. time for the electrolysis of water solutions of phenol (2 mM) and NaCl (0.5 m) performed under amperostatic conditions (10 mA cm⁻²) in an undivided cell at Ti/RuO₂ anode and a Ni cathode.

As a consequence, just a partial removal of TOC (about 35% after 24 h) was achieved (Figure 1A). Moreover, the presence of chlorate (about 200 ppm) and of some carboxylic acids (namely, acetic and oxalic acid) was detected. As shown in Figure 2, when these experiments were repeated at 5 bar no significant differences were achieved. Indeed, at Ni cathode the formation of hydrogen peroxide is expected to be negligible while the reduction of water to hydrogen prevails.

Effect of the nature of cathode and pressure

In the past, very few studies were devoted to the study of the effect of cathode on the electrochemical treatment of water contaminated by organics and containing chlorides. However, in the last years, some researchers have shown that the nature of the cathode can strongly affect the concentration of chlorinated by-products generated during the electrochemical disinfection or the electrochemical removal of organics. In particular, some scientists have shown that the utilization of undivided cells equipped with carbon felt cathodes can enhance the removal of TOC and reduce the formation of chlorates.^[12,27] Hence, we have performed some experiments using a carbon felt cathode for the treatment of the aqueous solution of phenol with a concentration of NaCl of 0.5 M with a *i* of 10 mA cm⁻² at different pressures (1, 5 and 10 bar). For both Ni and carbon felt, at 1 bar phenol was completely removed and no chlorophenols were present at the end of the electrolysis. Moreover, as shown in Figure 2A and according to

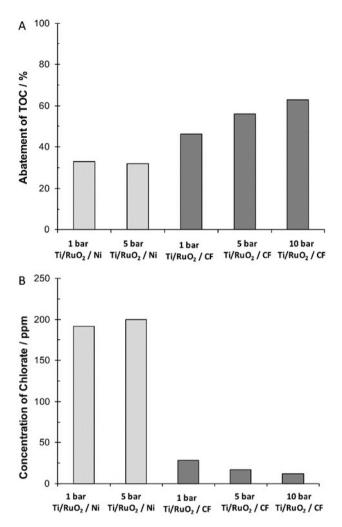


Figure 2. Abatement of TOC (A) and concentrations of chlorate (B) for the electrolysis of water solutions of phenol (2 mM) and NaCl (0.5 M) performed under amperostatic conditions (10 mA cm⁻²) in an undivided cell using Ti/ RuO₂ anodes and Ni or carbon felt as cathode for 24 h.

the literature, the replacement of the Ni with carbon felt allowed to significantly enhance the removal of TOC from 33 to 46% and to reduce drastically the concentration of chlorate from about 200 to 30 ppm while similar concentrations of HAAs were obtained. In order to understand the positive effect of carbon felt, it is useful to remember that this cathode favors the reduction of oxygen to hydrogen peroxide [Eq. (1)] which is expected to (i) act as an oxidant contributing to the mineralization of organics^[1] and (ii) to react with chlorates with the formation of chlorine dioxide [Eq. (10)].^[2] ClO₂ is a strong oxidizing agent used for different applications such as water purification, medical treatment, sanitation, etc. Moreover, it is expected not to deteriorate with increasing pH and to not contribute to the formation of chlorinated organic compounds.

In order to accelerate the formation of hydrogen peroxide, the electrolysis were repeated at the carbon felt cathode using higher pressures of air (5 and 10 bar). In all these electrolysis, phenol was completely removed and no chlorophenols were achieved at the end of the experiments. As shown in Figure 2A,



the increase of pressure leads to a significant enhancement of the mineralization. In particular, the abatement of TOC was 46, 56 and 63% at 1, 5 and 10 bar, respectively. Indeed, as shown by Sabatino et al.,^[8] the increase of pressure enhances the oxygen solubility and as a consequence the generation of H_2O_2 enhancing its contribution to the mineralization. Moreover, as shown in Figure 2B, the increase of the pressure resulted in a decrease of chlorate that presented a concentration close to 30, 17 and 11 ppm at 1, 5 and 10 bar, respectively. In this context, it is quite useful to point out that the energetic costs related to the pressurization of air at relatively low pressures (up to 10– 15 bar) are very low if compared to the energetic costs due to the electrolysis.^[7]

Electrolysis performed with BDD anode

According to the literature, the nature of the anode affects drastically the performances of the electrochemical treatment of organics in water containing chlorides.^[1–3] In particular, boron

doped diamond (BDD) is considered the most powerful anode for the anodic oxidation process due to its ability to generate very reactive hydroxyl radicals.^[1,3] Hence, the electrolysis described in previous sections were repeated using BDD as anode, Ni or carbon felt as cathode at different pressures. As shown in Figure 3A, using BDD as anode and Ni as cathode, a very fast removal of phenol was obtained coupled with a slower but very high removal of TOC (64% after 24 h). Indeed, the use of BDD allowed to achieve at the end of the electrolysis a quite high removal of all organic intermediates.

In particular, according to the literature,^[12] chlorophenols were completely removed after 4 h while the overall concentration of HAAs reached a maximum after 5 h (about 0.8 mM) and after decreased to a value close to 0.17 mM after 24 h (Figure 3B). These very good results are due to the fact that at BDD the oxidation by active chlorine is coupled with the mineralization achieved by very reactive hydroxyl radicals generated by water oxidation [Eq. (11)].

$$H_2 O \rightarrow HO^{\bullet} + H^+ + e^- \tag{11}$$

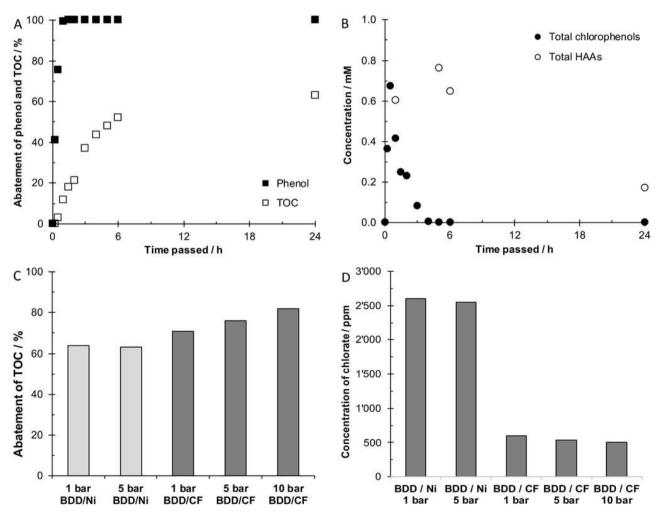


Figure 3. Plot of the abatement of phenol and TOC (A), and of the overall concentrations of chlorophenols and HAAs (B) vs. time for the electrolysis of water solutions of phenol (2 mM) and NaCl (0.5 m) performed under amperostatic conditions (10 mA cm⁻²) in an undivided cell at BDD anode and a Ni cathode. (C, D) The effect of the nature of the cathode and of the pressure for experiments performed at BDD, respectively, on the removal of TOC and on the final concentration of chlorate.

However, according to the literature, the very powerful oxidation activity of BDD anodes resulted also in a very high generation of chlorate (about 2600 ppm) and in the formation of significant amounts of perchlorate (about 300 ppm).

When experiments were repeated at carbon felt at 1 bar, an increase of the removal of TOC was observed coupled with a strong decrease of the concentration of chlorate (Figure 3C and 3D). Indeed, the removal of TOC was 63 and 71% at Ni and carbon felt cathodes, respectively. The effect on the generation of chlorate was still more remarkable: indeed, its final concentration was about 2500 and 600 ppm, respectively, at Ni and carbon felt cathodes. Also in this case, the effect of the pressure was studied by performing a series of electrolysis at both Ni (1 and 5 bar) and carbon felt cathodes (1, 5 and 10 bar). Quite interestingly, for the electrolysis performed with carbon felt cathode, the increase of the pressure allowed a significant increase of the abatement of TOC from 71% at 1 bar to 82% at 10 bar. Moreover, as shown in Figure 3D, the increase of the pressure also gave a decrease of the concentration of chlorate. Conversely, when the pressurized system was used for the undivided cell equipped with the Ni cathode, the removal of TOC did not increase (Figure 3C), thus confirming the key role of the carbon felt material. The coupled use of carbon felt and pressure allowed also to achieve a slight decrease of perchlorate that was close to 300 and 220 ppm using respectively Ni at 1 bar and carbon felt at 10 bar. This result is probably due to the fact that the formation of perchlorate is expected to take place, at least in part, by oxidation of chlorates whose concentration is decreased using carbon felt and pressurized air.

Figure 4 reports the final values of CE_{TOC} for the two adopted anodes and cathodes at various pressures. It can be observed that at both Ru oxide and BDD anodes, the coupled use of carbon felt cathode and high pressure allows to strongly improve the current efficiency, even if the effect seems to be more remarkable for the Ti/RuO₂ anode:

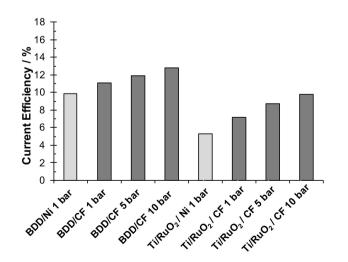


Figure 4. Effect of anode, cathode and pressure on the final current efficiency of the process for a series of electrolysis of a water solutions of phenol (2 mM) and NaCl (0.5 M) performed under amperostatic conditions in an undivided cell using Ti/RuO₂ and BDD anodes and Ni or carbon felt cathodes.

- at BDD, the use of Ni gave a final value of CE_{TOC} close to 10% that increased up to 12.8% using carbon felt and 10 bar;
- at metal oxide anode, the use of Ni gave a final value of CE_{TOC} close to 5.3% that increased up to 9.8% using carbon felt and 10 bar.

It can be also observed that, at the same operative conditions, a higher removal of TOC and a higher value of CE_{TOC} were always achieved at BDD anodes with respect to Ti/RuO₂. However, the differences between the performances of these two anodes were reduced using a carbon felt cathode and pressurized air. Indeed, at Ni cathode the removal of TOC was about 33 ($CE_{TOC} = 5.3\%$) and 64% ($CE_{TOC} = 9.9\%$) at Ru based and BDD anode, respectively; however, at carbon felt cathode and 10 bar the removal of TOC was about 63 ($CE_{TOC} = 9.8\%$) and 82% ($CE_{TOC} = 12.8\%$) at Ru oxide based and BDD anode, respectively. Moreover, the use of Ti/RuO₂ anode, carbon felt cathode and pressurized air gave rise to a very low concentration of chlorate and no perchlorate.

Coupling with electro-Fenton

Some authors have proposed the coupled utilization of electrogenerated active chlorine and electro-Fenton (EF) for the treatment of wastewater containing both organic pollutants and chlorides.⁽¹⁾ Here, this coupled approach was evaluated at different pressures (1 and 10 bar) using a Ti/RuO₂ anode, a carbon felt cathode and FeSO₄ as catalyst. Figure 5 reports the removal of TOC achieved by electro-Fenton. The data obtained at Ni and carbon felt in the absence of FeSO₄ were also reported for the sake of comparison. As shown in Figure 5, the utilization of carbon felt and FeSO₄ gave better results with respect to that achieved at Ni cathode, thus showing that the presence of hydroxyl radicals generated by EF process [Eq. (2)] can assist the

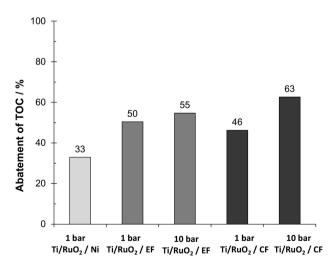


Figure 5. Removal of TOC by electro-generated active chlorine and electro-Fenton under amperostatic conditions in an undivided cell equipped with Ti/RuO_2 anode and carbon felt cathode at 10 mA cm⁻² for water solutions of phenol (2 mM) and NaCl (0.5 m) by addition to the solution of FeSO₄ (0.5 mM) at 1 and 10 bars for 24 h. The performances of the process were compared with that achieved in the absence of FeSO₄ at Ni and carbon felt cathodes.



mineralization process. Indeed, the removal of TOC increased from 33 to 50% by using the electro-Fenton process. Moreover, the utilization of pressurized air for EF gave a small increase of TOC removal (from 50 to 55%). However, it is worth to mention that at 10 bar the highest removal was achieved with carbon felt cathode in the absence of iron catalyst. This is probably due to the fact that for high generations of H₂O₂ the generation of chlorine dioxide is more beneficial for the mineralization process with respect to the generation of hydroxyl radicals. Also, for EF processes, the generation of chlorate was evaluated, and it presented intermediate values (about 70 ppm) with respect to the experiments performed with Ni (about 200 ppm) and that carried out with carbon felt in the absence of iron catalyst (<30 ppm). This is probably due to the fact that the presence of Fe(II) reduces the concentration of H_2O_2 by reaction (2), and, as a consequence, its reaction with chlorate by reaction (10). On overall, the data reported in Figure 5 shows that, both in the absence or in the presence of Fe(II), the replacement of Ni with carbon felt and the use of pressurized air improve the process, even if the best results were obtained in the absence of iron.

Conclusions

The electrochemical treatment of phenol in the presence of chlorides was evaluated using Ti/RuO_2 and BDD anodes, Ni and carbon felt cathodes at different air pressures and in the absence and in the presence of $FeSO_4$. From this work, the following conclusions can be drawn:

- the utilization of carbon felt cathodes allows to increase the mineralization of phenol and to reduce the concentration of chlorate;
- at carbon felt cathodes, the utilization of pressurized air increases the removal of TOC and reduces the concentration of chlorate; at Ni cathode and Ti/RuO₂ anode the final removal of TOC was 33% and the concentration of chlorate was close to 200 ppm; using carbon felt and 10 bar the final removal of TOC was 63% and the concentration of chlorate was close to 10 ppm;
- the electro-Fenton process gave intermediate results with respect to the process performed with Ni cathode and that performed with carbon felt cathode and pressurized air in the absence of iron.

Experimental Section

Electrolysis

Electrolysis were performed in an undivided high-pressure cell composed by AISI 316 stainless steel with a coaxial cylindrical geometry.^[8] A borosilicate-glass beaker was sited inside the reactor to storing electrolyte. The upper of the cell was equipped with a gas inlet, a vent, two electrical connections for the electrodes and a dip tube that allows to extract liquid samples during the experiment. A manometer was used to control the operating pressure. Air (AlphagazTM 1, Air Liquide purity 99.999%) was used to fill the

reactor till the desired operative pressure. The volume of solution was 50 mL, and the electrodes were immersed in the electrolyte inside the beaker with an inter-electrode gap of 2.5 cm. The anodes were Ti/RuO₂ (ElectroCell AB) with a total front wet area of 3 cm² whereas the cathodes were Ni (Carlo Erba Reagents), carbon felt (Carbon Lorraine, France) with a total wet area of 3 cm². The electrolysis were performed with constant current in the 10 mA cm⁻² (Amel 2053 potentiostat/galvanostat) at room temperature. Most of experiments were repeated at least twice, giving rise to a good reproducibility of results.

Reagents and analyses

Bi-distilled water was used as a solvent. Phenol 2 mM (purity > 99%, Merck) was selected as a model pollutant, while NaCl (Sigma Aldrich, 0.5 M) was used as supporting electrolyte. In some experiment, H₂SO₄ (Sigma-Aldrich) was used to achieve a pH of 3 and FeSO, (AnalaR NORMAPUR, VWR chemicals) 0.5 mM as catalyst. Similar concentrations to that reported in literature^[12] were used for the sake of comparison. The solution pH was measured with a Checker® pH Tester (HI98103) supplied by HANNA® instruments. The degradation of phenol was evaluated by the total organic carbon (TOC) and the HPLC, in addition, we also focused on the produced chlorophenol, chloroacetic acid, and chlorate and perchlorate. The TOC value was assessed by a TOC-L CSH/CSN analyzer Shimadzu. The concentration of phenol and chlorophenols was evaluated by HPLC using an Agilent 1260 fitted with a Kinetex 5u C18 column (Phenomenex) at 25°C and coupled with a UV detector working at 214 nm. A solution of water (Honeywell, HPLC grade) and acetonitrile (Merck, HPLC grade) was eluted at 1 mLmin⁻¹ as the mobile phase. It was used a gradient type of elution. In particular, the gradient profile was: i) time = 0 min $20/80 \%_{vol/vol}$ acetonitrile/water; *ii*) time = 5 mins $95/5 \%_{vol/vol}$ acetonitrile/water. Concentration of chloroacetic acids (HAAs) was evaluated by HPLC using an Agilent 1260 fitted with a Kinetex 5u C18 column (Phenomenex) at 25 °C and coupled with a UV detector working at 210 nm. A 25 mM KH₂PO₄ (Sigma Aldrich) aqueous solution at pH 2.5 (H₃PO₄) was eluted at 1 mLmin⁻¹ as the mobile phase. The concentration of carboxylic acids was evaluated by HPLC using an Agilent 1260 fitted with a Rezex ROA-Organic Acid column (Phenomenex) at 25 °C and coupled with a UV detector working at 210 nm. A water solution 0.005 N of H₂SO₄ (Sigma Aldrich) was eluted at 0.5 mLmin⁻¹ as the mobile phase. The concentration of chlorate and perchlorate was evaluated by ion chromatography (IC) analysis. Metrohm 882 compact IC was equipped with a Metrosep A Supp 5-250/4.0. A solution of 1 mM sodium bicarbonate and 3.2 mM sodium carbonate was used as standard eluent and flowed at 0.7 mLmin⁻¹.

Calibration curves were obtained by using the pure standards of phenol (purity > 99%, Merck), 2-chlorophenol (purity > 99%, Sigma-Aldrich), 4-chlorophenol (purity > 99%, Sigma-Aldrich), 2,4-dichlorophenol (purity > 99%, Sigma-Aldrich), 2,6-dichlorophenol (purity > 99%, Sigma-Aldrich), 2,4,6-trichlorophenol (purity > 99%, Alfa-Easer), chloroacetic acid (purity > 99%, Alfa-Easer), dichloroacetic acid (purity > 99%, Alfa-Easer), dichloroacetic acid (purity > 99%, Sigma-Aldrich). The abatement (e.g., the conversion) of the total organic carbon and the current efficiency for the removal of the TOC (CE_{TOC}) were defined by Equations (12) and (13), respectively.

| Abatement of TOC = $X_{TOC} = (A$ | $\Delta TOC)_{t/} TOC^{\circ}$ | (12) |
|-----------------------------------|--------------------------------|------|
| | | |

$$CE_{TOC} = n F V^{\circ}C X_{TOC/} I t$$
(13)

where (Δ TOC)t is the decay of the TOC (mg_{carbon}L⁻¹), TOC^o and ^oC the initial concentrations of the TOC (mg_{carbon}L⁻¹) and of the organic



pollutant (mol L⁻¹) inside the electrochemical cell, respectively, *n* is the number of electrons exchanged for the oxidation of the organic pollutant to carbon dioxide (28 for the phenol), *F* the Faraday constant (96487 C mol⁻¹), I the applied current intensity, *t* the electrolysis time and V the volume of the cell.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords: active chlorine species · air pressure · electrochlorination · electro-Fenton · toxic chlorinated compounds

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