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Effect of quenchers on the electrochemical oxidation of phenol in presence of electro-generated active chlorine

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ABSTRACT

According to the literature, the treatment of water and wastewater by electro-generated active chlorine is a very promising method from an applicative point of view. However, the production of toxic organic and inorganic chlorinated by-products, occurring during the oxidation of organic compounds by electro-generated active chlorine, must be carefully minimized to accomplish law constraints. If organic species could be oxidized, inorganic ones are persistent and difficult to be removed. Thus, it is necessary to avoid or minimize their production. Here, the use of quenchers able to react with active chlorine was investigated in the frame of the electrolysis of solutions of phenol and chlorides at BDD anodes in order to systematically evaluate the effect of various operative conditions (nature and concentration of the quencher, addition at different times, production in-situ) both on the degradation of organics and on the formation of by-products. In particular, for the first time, the analysis of several by-products was provided (both organic, such as chloroacetic acids, chlorophenols and carboxylic acids, and inorganic, as active chlorine, ClO_2, chlorate and perchlorate) in the presence of quenchers. It was found that the use of a quencher under suitable operative conditions results in a relevant reduction of the concentration of various by-products, including chlorate, without reducing the removal of TOC.

1. Introduction

Electrochemical oxidation process can be successfully used for chlorination and disinfection of water by removing recalcitrant pollutants and pathogen microorganisms with the help of electro-generated active chlorine. Indeed, due to the widespread presence of chloride ions in wastewaters, active chlorine can be generated during an electrochemical oxidation treatment, with the advantage of reducing the reliance on transportation and storage of chemicals and contributing to the sustainability of the process [1].

However, it has been demonstrated that electrochemical chlorination leads also to achieve significant concentrations of toxic organic and inorganic by-products [2–5]. Among them, chlorate and perchlorate are suspected to be carcinogens and mutagens [5]. In particular, perchlorate is an endocrine disruptor posing an adverse impact on thyroid gland function [6]. For this reason, a maximum value of 56 μg/L was provided for perchlorate in drinking water by US Environmental Protection Agency (EPA) [6,7]. For what concerns chlorates, a limit of 30 mg/L was established for ambient water in water guideline of British Columbia, Canada, while, for drinking water, stricter values of 0.21 mg/L and 0.7 mg/L were provided by EPA [3] and by the World Health Organization (WHO) [7,8]. Moreover, these anions are highly soluble in water and quite stable; thus they are difficult to be degraded, even by electrochemical treatment [4].

Thus, to better exploit the advantages of electrochemical oxidation process for the abatement of organic compounds, it is mandatory to avoid generating high concentrations of these toxic by-products in treated waters.

It was studied that the rate determining step in ClO_4^- production is the oxidation of ClO_3^- to ClO_4^- as shown in the following equations, where the oxidation pathway from chloride ion to perchlorate is reported [7,9–11]:

$$2Cl^- \rightarrow Cl_{2(aq)} + 2e^- \quad (1)$$

$$Cl_{2(aq)} + H_2O \rightarrow HClO + H^+ + Cl^- \quad (2)$$

$$HClO \leftrightarrows H^+ + ClO^- \quad (3)$$

$$ClO^- + H_2O \rightarrow ClO_2{}^- + 2H^+ + 2e^- \quad (4)$$

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$$ClO_2^- + H_2O \rightarrow ClO_3^- + 2H^+ + 2\,e^- \tag{5}$$

$$ClO_3^- + H_2O \leftrightarrows ClO_4^- + 2H^+ + 2e^- \tag{6}$$

$$ClO^- + \dot{O}H \rightarrow ClO_2^- + H^+ + e^- \tag{7}$$

$$ClO_2^- + \dot{O}H \rightarrow ClO_3^- + H^+ + e^- \tag{8}$$

$$ClO_3^- + \dot{O}H \rightarrow ClO_4^- + H^+ + e^- \tag{9}$$

As shown, the generation of chlorate and perchlorate depends on ClO^- availability in the electrolytic solution and the process could involve both direct anodic oxidation (Eqs. (4)–(6)) and reaction with hydroxyl radicals, that can be formed at suitable anodes (Eqs. (7)–(9)). In turn, ClO^- is formed by oxidation of Cl^- to Cl_2 (Eq. (1)) and successive dissociation in HClO in water (Eqs. (2) and (3)). Thus, the reduction of the concentration of ClO^- could be a main pathway to reduce the production of chlorate and perchlorate.

Moreover, it was reported by many researchers that BDD anode shows very high performances in mineralization of organic compounds mainly due to the ability to generate radicals [12]. However, it was demonstrated that this anode leads to higher production of chlorate and perchlorate [2,4,13–15]. In fact, at BDD, the reaction for active chlorine production via hydroxyl radicals occurs besides direct anodic oxidation [16,17].

Thus, to achieve high TOC abatements and lower chlorinated inorganic by-products production, it could be of paramount importance to control and reduce the presence of active chlorine during the process. This could represent the key to a more sustainable oxidative process also when a BDD anode is used.

Some authors aimed to study the optimum operation conditions to obtain water disinfection without high production of non-desired inorganic by-products by investigating the applied current density. Cano et al. found that chlorine speciation strongly depended on this parameter and the amount of chlorate observed increased as the current density increased from 1.3 to 13 to 130 A/m^2 [15]. Other authors have found that a proper selection of both cathodes and anodes allows to reduce the production of chlorinated by-products [16,18].

In this context, introducing free chlorine quenchers, such as H_2O_2 and bisulphite, could be one of the strategies for controlling the formation of the undesired Oxidation By-Products (OBPs) [6,14]. Indeed, these compounds are able to react with active chlorine according to the following equations related to H_2O_2 (Eqs. (10)–(11)) and $NaHSO_3$ (Eqs. (12)–(13)):

$$H_2O_2 + HOCl \rightarrow H_2O + O_2 + H^+ + Cl^- \tag{10}$$

$$H_2O_2 + OCl^- \rightarrow H^+ + Cl^- + H_2O + O_2 \tag{11}$$

$$NaHSO_3 + HOCl \rightarrow NaHSO_4 + H^+ + Cl^- \tag{12}$$

$$NaHSO_3 + Cl_2 + H_2O \rightarrow NaHSO_4 + 2H^+ + 2Cl^- \tag{13}$$

However, very few studies were focused up to now on this approach. Barisci and Suri studied the effect of some quenchers, such as H_2O_2, bisulphite, methanol and bicarbonate on the electrochemical degradation of PFAS in the presence of 200 mg/L of NaCl by investigating their interaction with free chlorine and hydroxyl radicals, proposing these two possible pathways: scavenging of OH• (Eq. (14)) and free chlorine quenching (Eqs. (10)–(11)) [7]:

$$OH^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \tag{14}$$

In particular, they obtained chlorate inhibitions of 24 % and 87 % with the addition of 50 and 100 mM H_2O_2, respectively, without observing a significant effect on the removal of PFAS [7].

Also Yang et al. studied the effect of using 50 mM H_2O_2 as free chlorine quencher during electrochemical oxidation of PFOS and PFOA using BDD anode. They observed a complete inhibition of perchlorate when the quencher was used. Furthermore, through computational kinetic modeling based on the two stated mechanisms (Eqs. (10)–(12)), they reported that H_2O_2 reacts with free chlorine more slowly than with OH• and that the former contributes the most to perchlorate inhibition [6,13]. Moreover, recently, some groups have shown that the production in situ of H_2O_2 by cathodic reduction of oxygen at suitable carbonaceous cathodes can allow to reduce the production of chlorate [11,18–20].

In this work, a systematic and detailed evaluation of the effect of quenchers was performed by testing the oxidation of phenol in the presence of electro-generated active chlorine under different operative conditions regarding nature (H_2O_2 and sodium bisulphite), concentration and addition timing of quenchers. For the first time, details on several by-products were provided, both organic, such as chloroacetic acids, chlorophenols and carboxylic acids, and inorganic, namely active chlorine, ClO_2, chlorate and perchlorate. In the case of H_2O_2, both its addition to the cell and its continuous production by cathodic reduction of oxygen was evaluated.

2. Experimental

Experiments were performed out in a glass undivided cell at lab-scale where an anode of Boron doped-diamond (BDD/Nb) from Condias (Germany) and a cathode of Ni (Carlo Erba reagents) or carbon felt (CF) were adopted, setting a 3 cm^2 active surface. A SCE reference electrode was used in the cell and electrolyses were performed at room temperature. The system was mixed by magnetic stirring at 400 rpm and operated under galvanostatic conditions with a current density of 10 mA/cm^2 by adopting an Amel instruments potentiostat/galvanostat (model 2053).

The tested solutions contained phenol at a concentration of 2 mM (purity >99 %, Merck) and 0.5 M NaCl (Sigma-Aldrich). Hydrogen peroxide (30 % by weight, Riedel-de Haën) and sodium bisulphite (Thermo Scientific) were added in the solutions as quenchers with a concentration of 30 mM. In the case of H_2O_2, also a higher concentration value of 150 mM was used.

During all the tests, air was supplied to the solution ($V = 0.075$ L) by using a common aquarium air pump (Jeneca). Electrolyses were replicated to obtain mean data and standard deviations were estimated and reported as error bars.

Several parameters were monitored during the electrochemical oxidation experiments, such as pH, TOC, concentration of phenol and its by-products, concentration of Cl— and its by-products.

The pH was detected by using a Hanna Instrument pH meter (range 0–14 with a resolution of 0.1 pH).

TOC concentrations were detected by adopting a Shimadzu VCSN ASI TOC-5000 TOC analyzer, whereas phenol was monitored by an Agilent 1260 High-Performance Liquid Chromatographer (HPLC) equipped with a UV–vis detector. All the analyses were done in the range of 0–50 mg/L. The detailed procedures were previously described [21].

The electrochemical oxidation of phenol by electro-generated active chlorine is expected to generate many by-products including:

1. chlorophenols;
2. chloroacetic acids;
3. carboxylic acids;
4. chlorate and perchlorate.

The organic by-products produced by the degradation of phenol, i.e. chlorophenols, chloroacetic and carboxylic acids, were characterized by HPLC by using three different methods and columns, as reported in [21]. In these cases, specific calibration curves were performed in the range of 0–10 mM.

Inorganic by-products generated from chloride ions were analyzed as follows: active chlorine and ClO_2 were detected by specific analytical kits containing DPD provided by Merck adopting an Agilent Cary 60 UV–Vis and the anions were detected by adopting a Metrohm 882 Compact Ionic Chromatographer with a Metrosep® A Supp 5 as anion-exchange column. Other details concerning this procedure were previously reported [21].

For the calibration curves, pure compounds were used.

The abatement of TOC (X_{TOC}) and phenol were derived as previously reported by authors [18,21].

The current efficiency for the removal of TOC (CE_{TOC}) and for the generation of active chlorine (CE_{AC}) was given by Eqs. (15) and (16), respectively:

$$CE_{TOC} = z\,F\,V\,[\mathrm{TOC}]^{\circ}\,X_{TOC}/(j\,\mathrm{A}\,t) \tag{15}$$

$$CE_{AC} = z\,F\,V\,\mathrm{C}_{AC}/(j\,\mathrm{A}) \tag{16}$$

where z is the number of electrons involved in the process (28 for the oxidation of phenol to carbon dioxide and 2 for the oxidation of chloride ion to active chlorine, F the Faraday constant (96,487C mol^{-1}), V the volume of the cell, j the applied current density, A the active surface and t the time. $[\mathrm{TOC}]^{\circ}$ is the initial TOC concentration, X_{TOC} is the TOC abatement and C_{AC} is the active chlorine concentration (mM).

The effect of many operative parameters was investigated:

5. nature of the scavenger (hydrogen peroxide or sodium bisulphite);
6. concentration of the scavenger (30 and 150 mM);
7. addition at different times (at the beginning or after 4 h);
8. effect of H_2O_2 produced in-situ by using a carbon felt cathode.

3. Results and discussion

3.1. *Effect of quenchers on the electrochemical production of active chlorine and on the electrochemical oxidation of phenol*

As above mentioned, the electrochemical oxidation of chlorides proceeds at BDD anodes with the production of active chlorine (Eqs. (1)–(3)) which contributes to the oxidation of organics but also to the production of various chlorinated by-products. Indeed, when experiments were performed by adopting BDD as anode and Ni as cathode under galvanostatic conditions at 10 mA cm^{-2} with a solution containing phenol and chloride ions, a significant concentration of active chlorine was produced with a current efficiency close to 60 % for almost all the electrolyses. Here, as previously stated, the effect of the addition of two quenchers, i.e. H_2O_2 and sodium bisulphite, was studied. Different operative conditions were explored. For this purpose, they were added at two initial concentration values in the case of H_2O_2, i.e. 30 and 150 mM, and at different moments of the tests, i.e. at the beginning and after 4th hour. As expected, when the quenchers were added to the solution from the beginning with a concentration of 30 mM, a strong decrease of the active chlorine production was observed (Fig. 1A and B); indeed, maximum current efficiencies of 20 % were observed in the presence of quenchers. In particular, the lowest concentrations of active chlorine were observed in the presence of bisulphite, showing that this quencher reacts in a more effective way with active chlorine with respect to H_2O_2, as reported also in Barisci and Suri [7].

Coherently, when the experiments were repeated adding the quencher to the electrolyte after 4 h of electrolysis, CE_{AC} fell to 0 % at 5 h and then increased at 24 h (Fig. 1A). To evaluate the effect of the concentration of the quencher, experiments with H_2O_2 were repeated with a higher initial concentration of 150 mM. For this high concentration, almost no active chlorine was detected (<1 mM) and current efficiency was close to zero, while at 30 mM current efficiency was about 20 %.

As reported elsewhere by authors [18], in the electrolyses performed in the absence of quenchers, a quite fast removal of TOC occurred in the first hours (about 45 % after 5 h) followed by a slower abatement in the second part of the electrolysis (about 75 % after 24 h), with a final current efficiency close to 13 % (Fig. 2A and B). The remaining TOC is due to the production of some by-products, such as chloroacetic and carboxylic acids, that are more resistant to the anodic oxidation with respect to phenol. The addition of bisulphite strongly affected the process, giving rise to a weak TOC abatement. Indeed, the removal of TOC was close to just 20 % after 24 h due to a very low current efficiency close to 3 % (Fig. 2B).

Conversely, the addition of H_2O_2 gave rise to a significant effect only in the first part of the electrolyses. As an example, if at the 3rd hour the TOC abatement was 33 % in the reference case, a slightly lower value of 26 % was detected in the presence of the quencher, because of a reduction of CE from 41 to 28 %. However, after 24 h no appreciable effects were observed for both TOC abatement (Fig. 2A) and CE (Fig. 2B) in the presence of the H_2O_2 quencher.

When the scavengers were added at the 4th hour, a quite different picture was observed; indeed, their addition did not reduce the removal of TOC abatement also in the case of bisulphite.

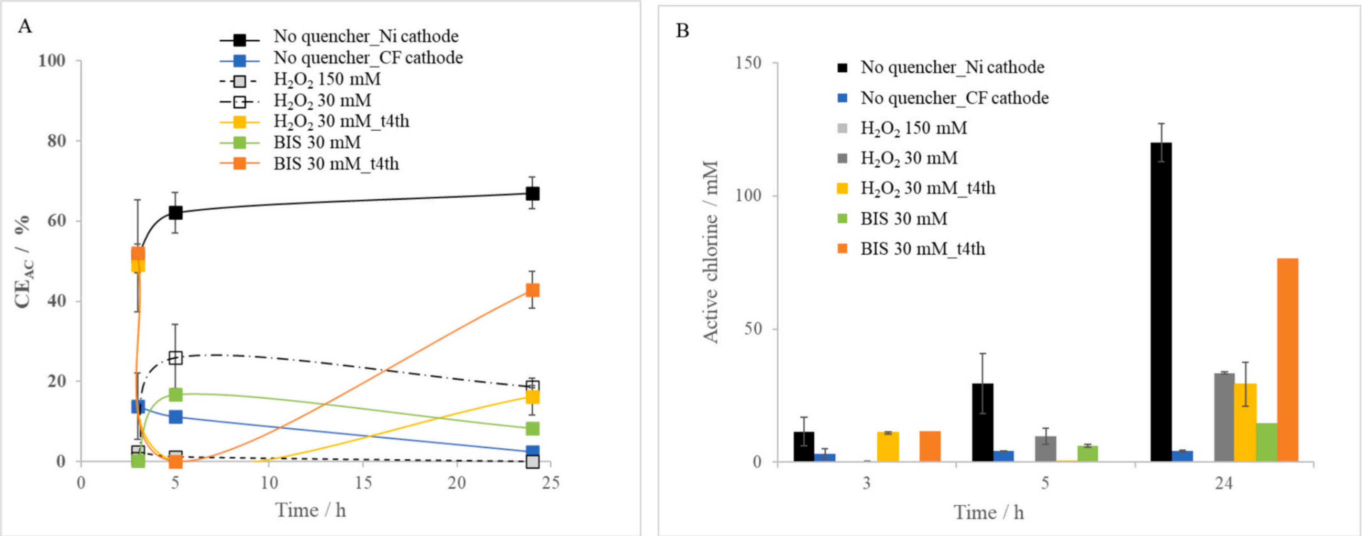

Fig. 1. Current efficiency (A) and concentrations of active chlorine (B) vs. time for the electrolyses carried out in the following operative conditions: C_{in} of phenol 2 mM and NaCl 0.5 M, anode BDD, cathode Ni (except where differently explicated: CF = carbon felt cathode), j = 10 mA/cm^2. Data represent mean values for the replicated results, and the error bars show the standard deviations for each data.

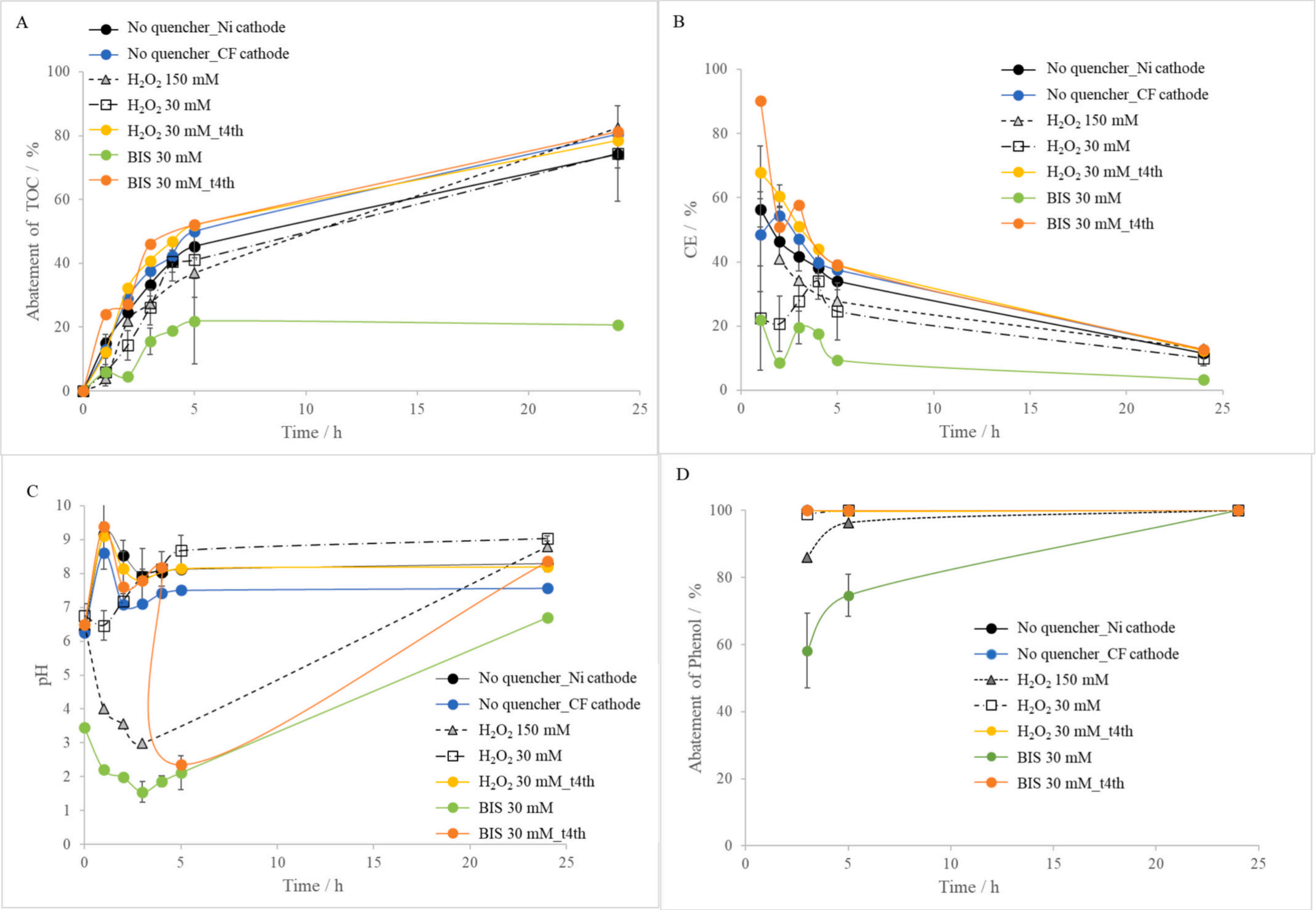

Fig. 2. TOC abatement (A), current efficiency (B), pH (C) and phenol abatement (D) vs. time for the electrolyses carried out in the following operative conditions: C_{in} of phenol 2 mM and NaCl 0.5 M, anode BDD, cathode Ni (except where differently explicated: CF = carbon felt cathode), j = 10 mA/cm^2. Data represent mean values for the replicated results and the error bars show the standard deviations for each data.

The addition of quenchers affected also the pH values of the electrolyte and, as a consequence, the distribution between chlorine, HClO and ClO^- which is pH dependent. The reactions involved in the electrolysis of a water solution of NaCl are expected to have a different effect on pH. Indeed, the oxygen evolution and the production of active chlorine at the anode and the hydrogen evolution at the cathode contribute, respectively, to acidify and basify the solution. In the reference case, the pH values increased from 6.5 until about 9 at 24 h showing a maximum at 1 h with values close to 9.5. Hence, active chlorine was present as a mixture of both HClO and ClO^-. A different trend of pH with time was observed when quenchers were added at the beginning of the experiments. Actually, the operating pH range moved to lower values, especially during the first part of the process, starting from values of 3.5 and 6.5 for bisulphite and H_2O_2, respectively. Hence, active chlorine was 95 % in the HOCl form in both cases [9,22]. As an example, when bisulphite was added since the beginning, strongly acid pHs, down to 1.5, were reached at 3rd hour and, when it was added at 4th hour, the value was close to 2.5 and the presence of chlorine is expected. For what concerns the H_2O_2, higher pH values were obtained respect to the bisulphite and pH decreased as the concentration increased from 30 to 150 mM (pH = 6.4 and 4 after 1 h, respectively). These facts can be ascribed to the high production of H^+ derived from scavenging of free chlorine (Eqs. (10) and (12)), especially in the first 3 h. However, in all cases, values of about 8.5–9 were observed at 24 h, except for bisulphite where a maximum pH of 7 was observed.

The results obtained for the abatement of phenol, reported in Fig. 2D, showed a total conversion when quenchers were not added, even at 3 h, and when they were introduced at 4th hour. When H_2O_2 was added in the initial solution, the results changed depending on the initial concentration: a quite lower abatement of phenol was observed by increasing the concentration from 30 to 150 mM, leading to values of 99 and 86 % at 3 h, respectively. In the case of bisulphite, deeply lower abatements of 60 and 75 % were observed at 3 and 5 h, respectively. However, at 24 h, 100 % of phenol was removed in all cases. Furthermore, when bisulphite was added at the 4th hour, negative effects were not observed because the phenol was already quickly converted in the first 3 h of the electrochemical oxidation process.

3.2. *Effect of quenchers on the production of chlorinated organic by-products*

As described in the introduction section, to evaluate the effectiveness of abatement of organics by active chlorine is necessary to evaluate not only the organics and TOC removals, but also the production of chlorinated by-products. Hence, several by-products generated by phenol degradation were identified and monitored. Main results concerning chlorophenols, chloroacetic and carboxylic acids are reported in Fig. 3.

As shown in Fig. 3A, chlorophenols were observed only when quenchers were added, with a concentration of about 0.1 mM at 3 h for both the quenchers. Indeed, a previous work of co-authors shows that chlorophenols are produced also in the absence of quenchers, but they are removed completely before 3 h [18]. As reported in literature, at BDD chlorophenols are quickly destructed into chlorohydrocarbons and successive organic compounds, such as chloroacetic and carboxylic

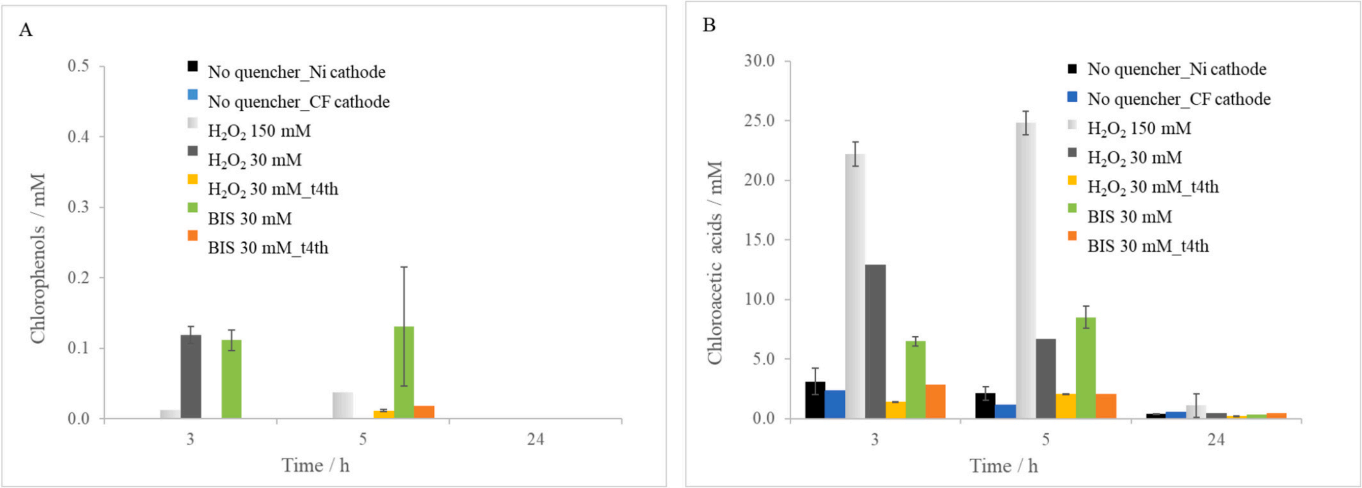

Fig. 3. Concentrations of chlorophenols (A) and chloroacetic acids (B) vs. time for the electrolyses carried out in the following operative conditions: C_{in} of phenol 2 mM and NaCl 0.5 M, anode BDD, cathode Ni (except where differently explicated: CF = carbon felt cathode), j = 10 mA/cm^2. Data represent mean values for the replicated results and the error bars show the standard deviations for each data.

acids [19,23].

As expected, when the quenchers were added at the 4th hour, some chlorophenols were also observed at 5 h, while at 3 h they were not detected as in the reference case.

The detection of chlorophenols in these cases could be ascribed to the fact that free chlorine scavenging entails a decrease of active chlorine, thus giving rise to a slower production and removal of chlorophenols, according to the mechanisms reported in literature [9].

Anyway, at 24 h all the detected chlorophenols, namely 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol, resulted to be oxidized for all the experimental conditions tested.

When the quenchers were added since the beginning, higher concentrations of chloroacetic acids, namely chloroacetic, dichloroacetic

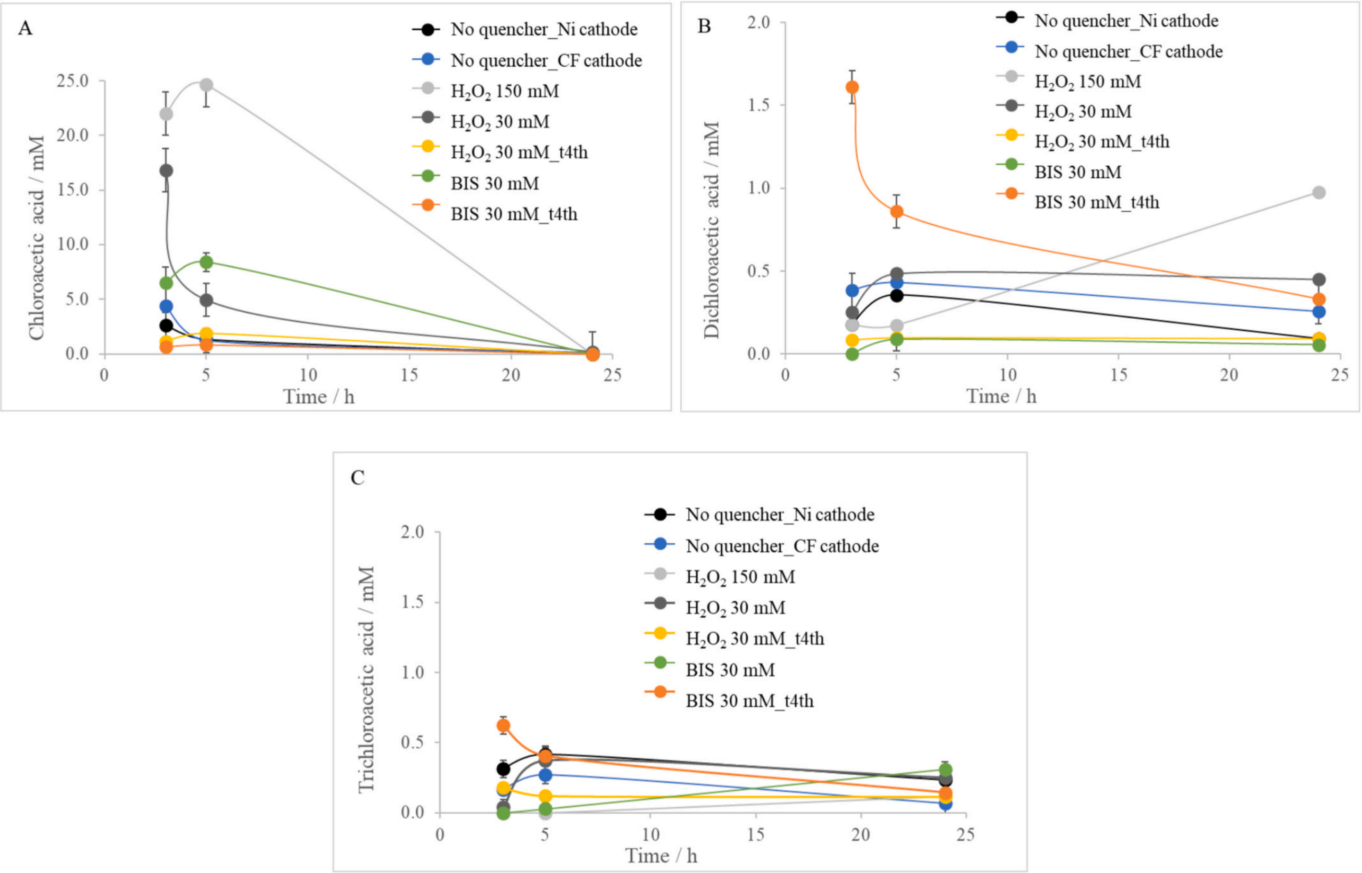

Fig. 4. Concentrations of chloroacetic (A), dichloroacetic (B) and trichloroacetic (C) acids vs. time for the electrolyses carried out in the following operative conditions: C_{in} of phenol 2 mM and NaCl 0.5 M, anode BDD, cathode Ni (except where differently explicated: CF = carbon felt cathode), j = 10 mA/cm^2. Data represent mean values for the replicated results and the error bars show the standard deviations for each data.

and trichloroacetic acids, were observed during the course of the electrolyses with respect to those observed in the reference experiments (see Fig. 3B): as an example, after 5 h, an overall concentration of chloroacetic acids close to 2 mM was detected for the reference experiments and when the quenchers were added at the 4th hour; on the other hand, values close to 6.6 and 8.5 mM were observed when H_2O_2 and bisulphite were added since the beginning with an initial concentration of 30 mM; moreover, still higher values of about 25 mM were detected when H_2O_2 was added with a concentration of 150 mM. However, it is worth to mention that, at the end of the electrolyses, quite low values of the overall concentration of chloroacetic acids were observed for all adopted operative conditions with the exception of experiments performed with the highest concentration of H_2O_2 (Fig. 3B).

More in detail, analysing the speciation of the chloroacetic acids (see Fig. 4), it is possible to observe how the chloroacetic acid, the last in the reduction pathway toward the acetic acid, showed the highest concentration values after about 5 h and these concentrations increased when quenchers are used, going up to about 25 mM for the experiments performed with 150 mM H_2O_2. Interestingly, at 24 h the chloroacetic was completely removed in all cases. Conversely, dichloroacetic acid presented lower peak values but higher final values, particularly in the case of experiments with 150 mM H_2O_2. Moreover, the addition of quenchers after 4 h allowed to minimize also the concentration of trichloroacetic acid.

In Fig. 5 the concentrations of detected carboxylic acids are reported for all the performed electrolyses. In particular, 11 compounds were identified and monitored, i.e. oxalic, tartaric, formic, malic, malonic, α-ketoglutaric, acetic, maleic, citric, succinic and fumaric acids.

In detail, the highest values of the total concentrations of carboxylic acids at 3 and 5 h were observed in the presence of the bisulphite scavenger, with values of about 11 and 6 mM, respectively. Especially at 5 h, the values detected in the presence of quenchers were all higher than that observed for the reference case. However, after 24 h a quite small concentration of carboxylic acids was observed for all experiments and the addition of quenchers did not change significantly the results, except for the case of H_2O_2 150 mM.

Even for carboxylic acids, a deep analysis was done and results are shown in Fig. 5 where the trends of the concentration of some of them, namely oxalic (OA), formic (FA) and acetic (AA) acids, were reported.

Oxalic and formic acids are the smallest carboxylic acids that can be individuated in the pathways toward the oxidation to CO_2; indeed, in the reference tests, their concentrations decreased strongly with the time reaching a total oxidation after 24 as shown in Fig. 5B and C. It is worth to mention that the addition of the quenchers did not result in an increase of the concentration of these two small compounds. Conversely, in most of operative conditions, the presence of quenchers resulted in lower concentrations of both of them during the course of the electrolyses (Fig. 5B and C). As shown in Fig. 5D, the concentrations of acetic acid are almost constant during the electrolyses. This can be due to the continue production and destruction of chloroacetic acid, that gives also to the production of acetic acid. The highest concentrations of acetic acid were observed for the experiments performed with H_2O_2, especially at a concentration of 150 mM, coherently with the highest concentration of chloroacetic acid achieved in the presence of this scavenger (see

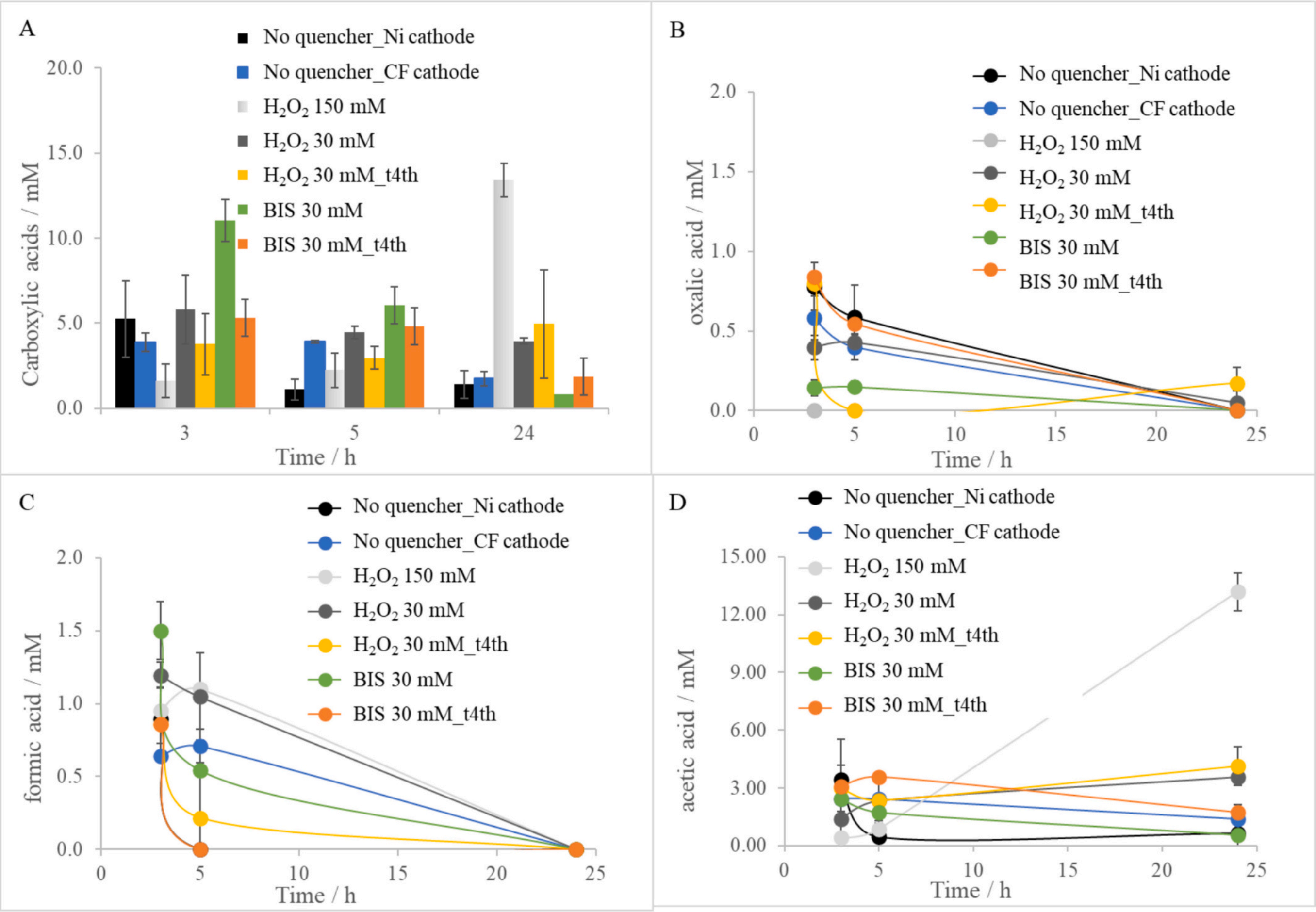

Fig. 5. Concentrations of all carboxylic acids (A), oxalic (B), formic (C) and acetic (D) acids vs. time for the electrolyses carried out in the following operative conditions: C_{in} of phenol 2 mM and NaCl 0.5 M, anode BDD, cathode Ni (except where differently explicated: CF = carbon felt cathode), j = 10 mA/cm^2. Data represent mean values for the replicated results and the error bars show the standard deviations for each data.

Fig. 4).

3.3. Effect of quenchers on the production of inorganic by-products derived from chloride ions

The effect of quenchers on ClO_3^- and ClO_4^- formation was already brought to attention by some authors [6,7,13]. However, here, the inorganic by-products generated by the oxidation of chloride ions, including also ClO_2, were systematically monitored. Indeed, as reported in literature, active chlorine production during the electrochemical process is coupled with the generation in-situ of other oxidants such as ClO_2 according to Eqs. (17) or (18) [11,24]:

$$Cl^- + 2\,H_2O \rightarrow ClO_2 + 4H^+ + 5e^- \tag{17}$$

$$Cl_2 + 4H_2O \rightarrow 2ClO_2 + 8H^+ + 8e^- \tag{18}$$

Fig. 6A reports the effect of the addition of scavengers on ClO_2 production. The addition of 30 mM H_2O_2 reduced the concentration of ClO_2 of about 50 % respect to the reference case at 24 h, whereas the use of 150 mM H_2O_2 gave rise to very low concentrations of ClO_2, under 1 mM. Also in this case, the detected values were lower for bisulphite. When the quenchers were added at 4th hour, the concentrations detected at 5 h were almost zero, and then increased at 24 h up to values similar to the reference case.

Fig. 6B shows the concentrations of ClO_3^-, while perchlorates are not reported as they were not found. As reported also by Cano et al. [15], this could be ascribed to the applied current density which could be not high enough to oxidize chlorates to perchlorates.

As expected, ClO_3^- concentrations were lower in the presence of quenchers in all the studied cases. At 5 h, in the absence of quenchers a concentration of chlorate of 76 ppm was found. Conversely, in the presence of bisulphite, a strong reduction of chlorate was observed; indeed, its concentration was negligible and of 16 ppm when this quencher was added at the beginning and at 4 h, respectively. Similarly, when 30 mM H_2O_2 was used as quencher the concentrations of chlorate after 5 h values were lower than the reference case but higher than bisulphite case.

At 24 h, the use of the quencher gave rise to a reduction of the concentration of chlorate. Very similar results were obtained in the cases of bisulphite and H_2O_2 150 mM, whit a reduction of about 50 % of the final concentration of chlorate, while in the tests performed with the addition of H_2O_2 30 mM a reduction of chlorate close to 20 % was observed. This result implicates that with BDD is possible to achieve high abatements of about 80 % of TOC in the presence of electro-generated active chlorine with a chlorate inhibition of 20–50 %. The reduction of the concentration of chlorate for H_2O_2 scavenger was similar to that found by Barisci and Suri for PFAS oxidation, which was of 24 %, while for bisulphite they found a higher reduction of 86 % [7].

3.4. Effect of H_2O_2 produced in-situ by using a carbon felt cathode

When carbon felt is used as cathode, and air is provided to the electrochemical system, H_2O_2 can be produced in-situ by electrosynthesis based on the two-electron oxygen reduction reaction according to Eq. (19) [6,9,11,25]:

$$O_2 + 2H^+ + 2\,e^- \rightarrow H_2O_2 \tag{19}$$

Hence, it was previously shown that when active chlorine is produced in an undivided cell equipped with carbonaceous cathodes and fed with air, a lower concentration of chlorate and perchlorate is observed with respect to electrolyses performed with other cathodes as Ni [6,17–19].

With these premises, the carbon felt cathode could be ideally coupled with the BDD to achieve good results. Some electrolyses were here performed with these electrodes and the by-products evolution was monitored in order to compare the production in situ of the H_2O_2 quencher with its addition to the solution.

As expected, very low amounts of active chlorine and ClO_2 were observed, compared with that achieved using the Ni cathode, due to the scavenging action of the H_2O_2 electrochemically generated (see Figs. 1 and 6). This fact led to a dramatic decrease of 80 % of ClO_3^- formation, registering a decrease in concentration from about 1600 ppm to about 300 ppm. Interestingly, this value was the lowest obtained, lower than the chlorate concentrations detected when quenchers were added to the solution.

Moreover, quite good general performances of the process were observed when carbon felt was adopted as cathode, obtaining a TOC abatement of 80 %. Even the current efficiency showed very similar results to the reference tests with a value of about 13 % and a total conversion of phenol detected even at the 3rd hour (see Fig. 2). For what concerns the pH, values of about 7–7.5 were observed for most of the electrolyses, lower than those obtained with a Ni cathode, probably due to the presence of gradual formation of H_2O_2 generated in-situ.

For what concerns the chlorinated organic compounds, as shown in Fig. 3, no chlorophenols were detected and the values for chloroacetic acids were lower of 25 % and of about 50 % with respect to the reference

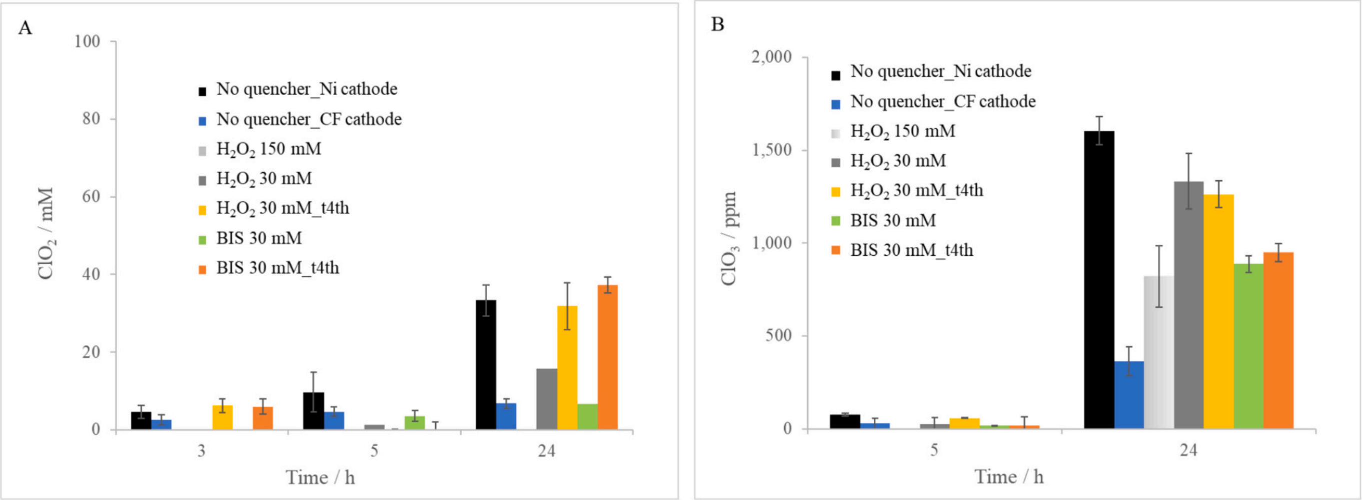

Fig. 6. Concentrations of ClO_2 (A) and ClO_3^- (B) vs. time for the electrolyses carried out in the following operative conditions: C_{in} of phenol 2 mM and NaCl 0.5 M, anode BDD, cathode Ni (except where differently explicated: CF = carbon felt cathode), j = 10 mA/cm^2. Data represent mean values for the replicated results and the error bars show the standard deviations for each data.

case, at 3 and 5 h, respectively. Definitely, using a CF cathode could lead to a higher reduction of chlorate formation keeping high abatements of the organic compound and minimization of other by-products with the advantage of no handling of chemicals [26].

A comparison of main results reported in literature for the electrochemical oxidation of phenol in water in the presence of electrogenerated active chlorine is reported in Table 1. Several parameters are reported such as the nature of the electrodes, the current density j, the presence of quencher and main results obtained after 24 h, i.e. TOC abatement, CE and concentration of chlorate when available. Even some notes on costs are provided.

In the past, various authors such as Iniesta et al. [27] (Table 1, entry 1) reported that the electrolysis of water solutions of phenol and NaCl at BDD anodes gave a total removal of phenol and a high TOC abatement, but the production of chlorate and of other chlorinated by-products was often not analyzed in detail. Later, it was shown that this process gives significant production of chlorate and other by-products (Table 1, entry 2). Recently, it was reported that the production of chlorate can be strongly reduced using CF cathodes (Table 1, entry 3). The concentration of chlorate can be further reduced coupling the use of CF cathode with that of pressurized air. In this case, a reduction of the chlorate concentration of 91 and 95 % was achieved at 5 and 10 bar, respectively. However, the addition of quenchers was not studied up to now for the treatment of water solutions of phenolic compounds. Our results show that the use of quenchers, under adopted operative conditions, allows to reduce the chlorate concentration of 20–50 % for H_2O_2 (Table 1, entry 5) and $NaHSO_3$ (Table 1, entry 6), respectively. It is worth to mention that the use of H_2O_2 allows to maintain high TOC removals, while that of $NaHSO_3$ results in a rather low TOC removal. However, a higher reduction of chlorate concentration coupled with a higher TOC removal is achieved when H_2O_2 is continuously produced at CF cathode (Table 1, entry 7). Moreover, as shown in Table 1, the use of CF is rather interesting also from the economic point of view (Table 1, entry 7).

4. Conclusions

The effect of the addition of quenchers to the electrochemical oxidation of organics at BDD anode was systematically studied, in the frame of the electrolysis of solutions of phenol and chlorides at BDD anodes at various operative conditions (nature and concentration of the quencher, addition at different times, production in-situ), by evaluation of the removal of organics and of the generation of several by-products.

When 30 mM H_2O_2 was used as quencher, lower values of at least 20 % of ClO_3^- were obtained, not affecting in a significant way the general performances of the process in terms of TOC abatement, phenol conversion, current efficiency and final concentrations of other by-products such as chloroacetic and carboxylic acids and chlorophenols. Conversely, the use of the bisulphite scavenger allowed to reduce to a more extent the production of chlorate but strongly affected the oxidation process of the organic compound leading to a very low TOC abatement of 20 % and to a lower conversions of phenol.

It was also found that:

- the addition of the quenchers after 4 h gave better results with respect to that achieved when quenchers were added to the solution from the beginning;
- lower abatements of TOC and phenol were observed in the first hours by increasing the H_2O_2 concentration, along with higher concentrations of chloroacetic acids.

The most effective results, i.e. obtaining a higher reduction of organic by-products and ClO_3^- production and high TOC and phenol abatements, were reached by coupling the BDD anode with a carbon felt cathode that allowed an in situ continuous production of H_2O_2. In fact, a reduction of ClO_3^- production of 80 % was obtained, with the advantage of no managing and handling H_2O_2 as it is generated in-situ by electrochemical reduction of oxygen at the cathode.

In conclusion, free chlorine scavenging resulted to be effective in reducing the chlorate generation without affecting the main performances of the electrolyses and practical and economic advantages could be pursued if a quencher such as H_2O_2 is used and especially if it is produced in-situ during the electrochemical oxidation process as occurs by using a carbon felt cathode.

CRediT authorship contribution statement

Serena Randazzo: Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Alessandro Galia:** Writing – review & editing, Resources, Project administration, Conceptualization. **Onofrio Scialdone:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial

Table 1

Comparison of selected results obtained in the field of the electrochemical treatment at BDD anodes of water solutions of phenol and NaCl after 24 h.

Entry	Anode	Cathode	j (mA/cm^2)	Quencher	TOC Abatement (%)	CE (%)	Notes on ClO_3^-	Notes on additional costs per m^3 of treated solution
1 [27]	BDD	Pt	60	–	71	–	Not available	
2 [18]	BDD	Ni	10	–	73	11	Concentration of 1470 ppm	
3 [20]	BDD	CF	10	–	62	10	The use of CF reduced the chlorate concentration of 85 % with respect to Ni	Cost for CF cathode 14 €/m^3 vs 300€/m^3 for Ni[a,b]
4 [20]	BDD	CF at 5 and 10 bar	10		71	11	The coupled use of pressure and CF reduced chlorate concentration of 91 and 95 % at 5 and 10 bar, respectively.	Costs for pressurization very low compared to the energetic costs of electrolysis
5 (this work)	BDD	Ni	10	H_2O_2 30 mM	74	10	The use of H_2O_2 reduced the chlorate concentration of 20 %	Cost for addition of H_2O_2 1.5 €/m^3[c]
6 (this work)	BDD	Ni	10	$NaHSO_3$ 30 mM	21	3	The use of $NaHSO_3$ reduced the chlorate concentration of 50 %	Cost for addition of $NaHSO_3$ 0.15 cents€/m^3[d]
7 (this work)	BDD	CF	10	–	80	13	The use of $NaHSO_3$ reduced the chlorate concentration of 80 %	Cost for CF cathode 14 €/m^3 vs 300€/m^3 for Ni[a,b]

[a] Estimation based on price of Ni of 8.45 €/kg (http://www.leonland.de/elements_by_price/it/list).

[b] Estimation based on price of CF of 14 €/kg Minke et al., 2017 [28].

[c] Estimation of cost based on price of H_2O_2 of 500 €/ton (https://www.europages.it/it/company/sivex-chemicals-22303643/products/hydrogen-peroxide-36064715).

[d] Estimation of cost based on price of $NaHSO_3$ of 500 €/ton (https://www.europages.it/it/company/van-diemen-chemicals-bv-22213332/products/sodium-metabisulfite-eu-manufacturer-supplier-36289549).

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

References

[1] I. García-López, L.F. Arenas, J. Hereijgers, V.I. Águeda, A. Garrido-Escudero, Drinking water electrochlorination in a single-pass biomimetic flow cell with zero salt dosing, ACS Sustain. Chem. Eng. 12 (2024) 3130–3141, https://doi.org/10.1021/acssuschemeng.3c07066.

[2] M.E.H. Bergmann, J. Rollin, T. Iourtchouk, The occurrence of perchlorate during drinking water electrolysis using BDD anodes, Electrochim. Acta 54 (2009) 2102–2107, https://doi.org/10.1016/j.electacta.2008.09.040.

[3] H. Feng, X. Liao, Y. Ruili, S. Chen, Z. Zhang, J. Tong, J. Liu, X. Wang, Generation, toxicity, and reduction of chlorinated byproducts: overcome bottlenecks of electrochemical advanced oxidation technology to treat high chloride wastewater, Water Res. 230 (2023) 119531–119542, https://doi.org/10.1016/j.watres.2022.119531.

[4] Y. Long, H. Li, H. Jin, J. Ni, Interpretation of high perchlorate generated during electrochemical disinfection in presence of chloride at BDD anodes, Chemosphere 284 (2021) 131418–131426, https://doi.org/10.1016/j.chemosphere.2021.131418.

[5] J. Radjenovic, D.L. Sedlak, Challenges and opportunities for electrochemical processes as next generation technologies for the treatment of contaminated water, Environ. Sci. Technol. 49 (2015) 11292–11302, https://doi.org/10.1021/acs.est.5b02414.

[6] Y. Yang, Recent advances in the electrochemical oxidation water treatment: spotlight on byproduct control, Front. Environ. Sci. Eng. 14 (5) (2020) 85–97, https://doi.org/10.1007/s11783-020-1264-7.

[7] S. Barisci, R. Suri, Evaluation of chlorate/perchlorate formation during electrochemical oxidation of PFAS: the roles of free chlorine and hydroxyl radical, J Water Process Eng 50 (2022) 103341–103351, https://doi.org/10.1016/j.jwpe.2022.103341.

[8] A. Atrashkevich, A. Alum, R. Stirling, M. Abbaszadegan, S.G. Segura, Approaching easy water disinfection for all: can in situ electrochlorination outperform conventional chlorination under realistic conditions? Water Res. 250 (2024) 121014–121024, https://doi.org/10.1016/j.watres.2023.121014.

[9] M. Deborde, U. von Gunten, Reactions of chlorine with inorganic and organic compounds during water treatment—kinetics and mechanisms: a critical review, Water Res. 42 (2008) 13–51, https://doi.org/10.1016/j.watres.2007.07.025.

[10] Y.J. Jung, K.W. Baek, B.S. Oh, J.-W. Kang, An investigation of the formation of chlorate and perchlorate during electrolysis using Pt/Ti electrodes: the effects of pH and reactive oxygen species and the results of kinetic studies, Water Res. 44 (2010) 5345–5355, https://doi.org/10.1016/j.watres.2010.06.029.

[11] C.A. Martínez-Huitle, M.A. Rodrigo, I. Sirés, O. Scialdone, A critical review on latest innovations and future challenges of electrochemical technology for the abatement of organics in water, Appl. Catal. B 328 (2023) 122430–122490, https://doi.org/10.1016/j.apcatb.2023.122430.

[12] O.D. Ogundele, D.A. Oyegoke, T.E. Anaun, Exploring the potential and challenges of electrochemical processes for sustainable waste water remediation and treatment, Acadlore Trans. Geosci. 2 (2) (2023) 80–93, https://doi.org/10.56578/atg020203.

[13] S. Yang, S. Fernando, T.M. Holsen, Y. Yang, Inhibition of perchlorate formation during the electrochemical oxidation of perfluoroalkyl acid in groundwater, Environ. Sci. Technol. Lett. 6 (2019) 775–780, https://doi.org/10.1021/acs.estlett.9b00653.

[14] K. Yang, Z. He, Formation and control of oxidation byproducts in electrochemical wastewater treatment: a review, J. Chem. Eng. 499 (2024) 156160–156173, https://doi.org/10.1016/j.cej.2024.156160.

[15] A. Cano, P. Cañizares, C. Barrera, C. Sáez, M.A. Rodrigo, Use of low current densities in electrolyses with conductive-diamond electrochemical oxidation to disinfect treated wastewaters for reuse, Electrochem. Commun. 13 (2011) 1268–1270, https://doi.org/10.1016/j.elecom.2011.08.027.

[16] O. Scialdone, F. Proietto, A. Galia, Electrochemical production and use of chlorinated oxidants for the treatment of wastewater contaminated by organic pollutants and disinfection, Curr. Opin. Electrochem. 27 (2021) 100682–100689, https://doi.org/10.1016/j.coelec.2020.100682.

[17] S.O. Ganiyu, C.A. Martínez-Huitle, Nature, mechanisms and reactivity of electrogenerated reactive species at thin-film Boron-Doped Diamond (BDD) electrodes during electrochemical wastewater treatment, ChemElectroChem 6 (2019) 2379–2393.

[18] Y. Hao, H. Ma, F. Proietto, A. Galia, O. Scialdone, Electrochemical treatment of wastewater contaminated by organics and containing chlorides: Effect of operative parameters on the abatement of organics and the generation of chlorinated by-products, Electrochim. Acta 402 (2022) 139480–139491.

[19] S. Cotillas, J. Llanos, M.A. Rodrigo, P. Canizares, Use of carbon felt cathodes for the electrochemical reclamation of urban treated wastewaters, Appl Catal B 162 (2015) 252–259, https://doi.org/10.1016/j.apcatb.2014.07.004.

[20] Y. Hao, H. Ma, F. Proietto, C. Prestigiacomo, P. Ma, A. Galia, O. Scialdone, Removal of phenol from water in the presence of NaCl in undivided cells equipped with carbon felt or Ni cathodes: effect of air pressure, ChemElectroChem 9 (2022) e202200091-e202200098, https://doi.org/10.1002/celc.202200091.

[21] S. Randazzo, A. Geagea, F. Proietto, A. Galia, O. Scialdone, Oxidation of organics in water by active chlorine performed in microfluidic electrochemical reactors: a new way to improve the performances of the process, Chemosphere 355 (2024) 141855–141865, https://doi.org/10.1016/j.chemosphere.2024.141855.

[22] J.F. Rodríguez, J.L. Nava, Active chlorine electrosynthesis from dilute chloride solutions in a flow cell equipped with a Ti|Ti-Ru-Ir-oxides anode, Chem. Eng. Process. Process Intensif. 196 (2024) 109634–109642.

[23] T. Đuričić, H. Prosen, A. Kravos, S. Mićin, G. Kalčíková, B.N. Malinović, Electrooxidation of phenol on Boron-doped diamond and Mixedmetal oxide anodes: process evaluation, transformation byproducts, and ecotoxicity, J. Electrochem. Soc. 170 (2023) 023503–023511, https://doi.org/10.1149/1945-7111/acb84b.

[24] E. Mostafa, P. Reinsberg, S. Garcia-Segura, H. Baltruschat, Chlorine species evolution during electrochlorination on boron-doped diamond anodes: in-situ electrogeneration of Cl_2, Cl_2O and ClO_2, Electrochim. Acta 281 (2018) 831–840.

[25] C.A. Martínez-Huitle, M.A. Rodrigo, I. Sirés, O. Scialdone, Single and coupled electrochemical processes and reactors for the abatement of organic water pollutants: a critical review, Chem. Rev. 115 (2015) 13362–13407, https://doi.org/10.1021/acs.chemrev.5b00361.

[26] G. Busca, S. Berardinelli, C. Resini, L. Arrighi, Technologies for the removal of phenol from fluid streams: a short review of recent developments, J. Hazard. Mater. 160 (2008) 265–288, https://doi.org/10.1016/j.jhazmat.2008.03.045.

[27] J. Iniesta, P.A. Michaud, M. Panizza, G. Cerisola, A. Aldaz, Ch. Comninellis, Electrochemical oxidation of phenol at boron-doped diamond electrode, Electrochim. Acta 46 (2001) 3573–3578, https://doi.org/10.1016/S0013-4686(01)00630-2.

[28] C. Minke, U. Kunz, T. Turek, Carbon felt and carbon fiber- a techno-economic assessment of felt electrodes for redox flow battery applications, J. Power Sources 342 (2017) 116–124, https://doi.org/10.1016/j.jpowsour.2016.12.039.