

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.

Yongyong Hao^{a, b}, Hongrui Ma^a, Federica Proietto^b, Alessandro Galia^b, Onofrio Scialdone^{b,*}

^a School of Environmental Science and Engineering, Shaanxi University of Science & Technology,

Xi'an 710021, P.R. China

^b Dipartimento di Ingegneria, Università degli Studi di Palermo, Palermo 90128, Italy.

*onofrio.scialdone@unipa.it

Abstract

In the last years, large attention has been devoted to the electrochemical treatment of wastewater polluted by recalcitrant organics and containing chlorides. However, the utilization on an applicative scale of this route is limited by the fact that usually it is not possible to achieve high removals of organics without the generation of significant amounts of chlorinated by-products. Here, the role of several operative parameters on the performances of the process was systematically evaluated using phenol as a model organic pollutant. It was shown that the removal of phenol and TOC and the generation of many by-products including chlorophenols, chloroacetic acids, chlorate and perchlorate dramatically depend on the adopted operative conditions (i.e., nature of anode and cathode, current density and concentration of chlorides). The use of boron doped diamond (BDD) anode gave the highest removal of TOC but also the highest final concentrations of chlorate and perchlorate and the lowest concentrations of chloroacetic acids. Conversely, the use of Ti/IrO₂-Ta₂O₅ gave the lowest generation of chlorate and no perchlorate. The use of lower current densities allowed as well to reduce the concentrations of these compounds. It is worth to mention that lower amounts of chlorinated by-products were achieved using suitable cathodes. Carbon felt cathodes, as previously reported for the water disinfection, allowed to reduce the generation of chlorate. Moreover, it was shown, for the first time, that the use of silver cathodes minimized the concentrations of chloroacetic acids. In addition,

it was found that the use of a system equipped with both silver and carbon felt cathodes and proper current densities allowed to increase remarkably the removals of TOC and the current efficiency and to achieve very low concentrations of chlorinated by-products.

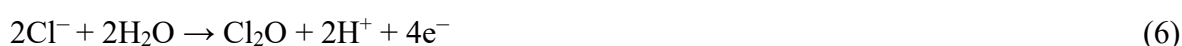
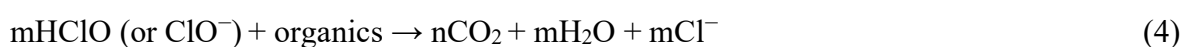
Keywords: electrochlorination, active chlorine species, wastewater treatment, toxic chlorinated compounds; silver cathodes; carbon felt cathodes.

1. Introduction

One of the relevant emerging topics is the development of new technologies to restore the quality of contaminated water due to water scarcity which is one of the main concerns of this century. In this context, many kinds of wastewaters, contaminated by organic pollutants resistant to conventional biological processes and/or by pathogen microorganisms, can be treated by chlorinated oxidants, such as chlorine or hypochlorous acid. In the last years, a large number of scientific studies have shown that these oxidants can be effectively produced by anodic oxidation of chlorides, such as sodium chloride, which is a rather cheap reagent often present in liquid effluents [1-5] by reactions reported in eq. (1) – (3). In particular, dissolved chlorine generated by chlorides oxidation (eq. (1)) may be involved in a disproportionation reaction (eq. (2)) with the formation of hypochlorous acid, a weak acid (pKa 7.5), that is in equilibrium with ClO^- (eq. (3)). The concentrations of Cl_2 , HClO and ClO^- depend on the pH: indeed, Cl_2 prevails at very low pH, HClO in more moderate acidic conditions and ClO^- in basic ones. Moreover, chlorine bubbles can be formed at low pH.



It is worth to mention that the removal of organics is particularly effective when carried out in the same electrochemical cell where these oxidants are generated [1-2]. Indeed, in this case, organics can be oxidised by many concomitant routes [2,4-5] involving: *i*) homogeneous oxidation by active chlorine (eq. (4)) or *ii*) by Cl_2O and ClO_2 that can be formed by both chemical and electrochemical paths (eqs. (5) - (6)); *iii*) the oxidation at the anode surface by adsorbed chloro and oxychloro radicals and *iv*) the oxidation by various other reactive oxygen species (ROS), including $\text{HO}\cdot$, H_2O_2 and $\cdot\text{O}_2^-$, produced by water anodic oxidation [6-13].



However, these methods present some relevant disadvantages, such as a difficult selection of most suitable operative conditions and, in particular, of the nature of the anode and, above all, 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 [1-2,13]. In particular, in the last years, some interesting results were obtained in this frame, mainly for the case of electrochemical water disinfection, but additional efforts are necessary to enhance the applicative perspectives of this tool for the treatment of wastewater contaminated by organics [2]. Hence, in this paper, a wide and systematic study was devoted to evaluate the effect on the electrochemical treatment of water containing organic pollutants and chlorides in terms of both removal of TOC and minimization of chlorinated by-products of numerous operative parameters, such as the nature of anode and cathode, concentration of chlorides and current density. Phenol was used as a model organic compound for its high resistance to many conventional processes and the potential formation of many toxic by-products. The formation of many intermediates and by-products including chlorophenols, HAAs, chlorate and perchlorate, chloroform and carboxylic acids was evaluated. The

operative conditions suitable to achieve high removals of phenol and TOC and to minimize the formation of toxic chlorinated compounds were found.

2. Experimental

2.1. Electrolyses

Electrolyses were performed in a conventional glass undivided cell with magnetic stirring. The anodes were Ti/RuO₂ (ElectroCell AB), Ti/IrO₂-Ta₂O₅ (commercial DSA®, De Nora SpA) and boron doped diamond (BDD) (Condias) with a total front wet area of 3 cm² whereas the cathode were Ni (Carlo Erba Reagents), carbon felt (Carbon Lorraine, France) or Ag plate (Carlo Erba Reagents) with a total wet area of 3 cm². For some experiments the system was equipped with one anode and two cathodes (both areas of 3 cm²). The volume of solution was 75 mL. The electrolyses were performed with amperostatic alimentation (Amel 2053 potentiostat/galvanostat) at room temperature. Most of experiments were repeated at least twice, giving rise to a good reproducibility of results.

2.2. Reagents and analyses

Bi-distilled water and phenol 2 mM (purity > 99%, Merck) were used as received as solvent and model pollutant, respectively, while NaCl (Sigma Aldrich, 0.5 M) was used as supporting electrolyte. The total organic carbon (TOC) was analyzed by a TOC-L CSH/CSN analyzer Shimadzu. The concentration of chlorate, perchlorate and carboxylic acids 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 mL min⁻¹. 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 mL min⁻¹ as the mobile phase. It was used a gradient type elution. In

particular, the gradient profile was: *i*) time = 0 min 20/80%_{vol/vol} acetonitrile/water ; *ii*) time = 5 minutes 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 mL min⁻¹ as the mobile phase. To detect the presence of chloroform and dichloroethane, gas chromatographic analyses were performed using an Autosystem XL Perkin Elmer GC equipped with a ZB-FFAP capillary column (30m*0.250mm*0.25µm) or a HP-5 capillary column (30m*0.320mm*0.25µm) and a FID detector. Helium (99.999%, Air Liquide, Italy) was used as carrier gas (15 psi). In the case of ZB-FFAP column, the following temperature profile was adopted: oven holding at 50°C for 4 min followed by a heating ramp at 20°C/min up to 150°C with a holding time of 0 min. In the case of DB-5 column, the following temperature profile was adopted: oven holding at 50°C for 0 min followed by a heating ramp at 3°C/min up to 150°C with a holding time of 0 min. Injector and detector were heated at 250°C. Adopted injection volume was 0.2 µL with 15/1 split ratio.

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%, ACROS), trichloroacetic acid (purity > 99%, Sigma-Aldrich). The solution pH was measured with a Checker® pH Tester (HI98103) supplied by HANNA® instruments. 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 Eqs. (7) and (8), respectively.

$$\text{Abatement of TOC} = X_{TOC} = (\Delta TOC)_t / TOC^{\circ} \quad (7)$$

$$CE_{TOC} = nFV C^{\circ} X_{TOC} / It \quad (8)$$

where $(\Delta\text{TOC})_t$ is the decay of the TOC ($\text{mg}_{\text{carbon}} \text{L}^{-1}$), TOC° and C° the initial concentrations of the TOC ($\text{mg}_{\text{carbon}} \text{L}^{-1}$) 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.

3. Results and discussion

3.1 First experiments at Ti/RuO₂ anode

A first series of electrolyses was performed in an undivided cell using Ti/RuO₂ anode, Ni cathode, a current density (j) of 10 mA cm^{-2} and magnetic stirring (400 rpm). Ti/RuO₂ was chosen as anode material because it was largely used in the literature for the treatment of water contaminated by organics and containing chlorides. This anode strongly catalyzes the chlorides oxidation, thus allowing to minimize the water oxidation to oxygen at least under very acidic conditions [4] and to generate high concentrations of active chlorine [2,13]. A synthetic aqueous solution of phenol (2 mM) and NaCl (0.5 M) was used. As shown in Figure 1, the use of Ti/RuO₂ anode allowed a fast removal of phenol, but a quite slow abatement of TOC (fig. 1A), because of the formation of many organic by-products and intermediates. In particular, after 100 C, when almost all the phenol was removed, a negligible abatement of TOC (~2%) with a current efficiency for the mineralization process (CE_{TOC}) close to zero was obtained, as a result of the conversion of phenol to by-products which are mineralized at longer times. According to the literature, the formation of chlorinated by-products is expected, due to the chlorination of phenol and its oxidation products. It has been reported that the chemical oxidation of phenol with NaClO (10 mM) gives rise to the formation of 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol [15]. Various authors have shown that the electrolysis of water solutions of phenol and NaCl using different anodes (including carbon and Ti/PbO₂) gives rise to the formation of *p*-chlorophenol, *o*-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol, but also to their removal at high electrolysis time [16,17]. According to the

literature, we have detected the formation of many chlorophenols and, in particular, 2-chlorophenol, 4-chlorophenol, 2,4 dichlorophenol, 2,6 dichlorophenol and 2,4,6 trichlorophenol. Indeed, as reported by Deborde and von Gunten [18], due to the activating ortho/para directing hydroxyl group, the chlorination of phenol proceeds by a stepwise substitution of the 2, 4 and 6 positions. Moreover, the formation of chloroacetic acids (HAAs) and chlorate was observed. The generation of these compounds was not previously described, up to our knowledge, for the electrochemical oxidation of phenol. However, their formation was reported for many different cases, and, in particular, for the electrochemical treatment of latrine wastewater, reverse osmosis retentate, urine, etc. [2,19-26]. Some authors have found also the formation of carboxylic acids, chloroform and dichloroethane for the treatment of aqueous solutions containing chlorides and organics [2,15]. However, no presence of chloroform and dichloroethane was found at the end of the electrolyses. Conversely, the presence of some carboxylic acids (namely, acetic and oxalic acid) was detected.

As shown in fig. 1B, chlorophenols were formed very quickly in the first stages of the electrolyses. After 25 C, the conversion of phenol in the detected chlorophenols was higher than 75%, thus showing that most of the moles of phenol were chlorinated. In particular, 2- and 4-chlorophenols presented the highest concentrations (fig. 1B), according to the literature [18]. However, the plot concentration vs. charge passed presented a maximum for all the chlorophenols that were totally removed after 120 C, thus showing that the adopted process is able to remove completely these compounds (fig. 1B). A very different picture is observed for HAAs. The generation of mono, di- and tri-chloroacetic acids was detected after about 100 C (fig. 1C). Moreover, the presence of both dichloroacetic and trichloroacetic acids was observed also at the end of the electrolysis while monochloroacetic acid was completely removed after about 700 C. On overall, the total concentration of HAAs reached a value close to 0.9 mM after about 700 C and remained almost constant up to the end of the electrolysis (fig. 1C), as a result of the high resistance of these compounds to the oxidation by means of active chlorine [28]. Indeed, when NaClO was added to a synthetic solution of the three

HAAs no significant abatement of their concentrations was observed after 4 days of treatment. Similar results were found for the chemical chlorination of waters containing various organic molecules, such as resorcinol, phloro-glucinol, p-hydroxybenzoic acid and m-hydroxybenzoic acid. In these cases, it was reported that the total concentrations of HAAs increased in the first part of the experiments up to a plateau value (time of the experiments more than 160 hours) [27]. As above mentioned, also the presence of chlorate was detected at the end of the electrolysis that, according to the literature, is formed by a multi-step oxidation of chlorides or by reaction between hypochlorite ions and hydroxyl radicals formed by water oxidation [2].

As shown in fig. 2B, the plot CE_{TOC} vs. charge passed presented a maximum close to 25% for a charge passed close to 400 C due to the fact that in the first part of the electrolysis most of active chlorine produced at the anode is spent for the chlorination of phenol to chlorophenols, while in the last part of the experiment the mineralization is made difficult by the permanence in the solution of very resistant organics, such as HAAs.

A water solution of phenol (2 mM) was treated with NaClO (10 mM) in order to compare the performance of the chemical chlorination with that of the electrochemical process. According to the literature, it was found that phenol was converted to 2-chlorophenol, 4-chlorophenol, 2,4 dichlorophenol, 2,6 dichlorophenol and 2,4,6 trichlorophenol that remained in the solutions for longer times. Indeed, after 48 h a total concentration of chlorophenols close to 1.4 mM was still detected and the removal of TOC was lower than 6 %, thus showing that the chemical process is significantly slower than the electrochemical one. After 8 days, the removal of TOC was still very low and the total concentrations of phenol was 1.2 mM. Moreover, a slight formation of chlorate, perchlorate and HAAs was found.

3.2 Effect of the nature of the anode

It was previously shown that the nature of the anode affects drastically the performances of the electrochemical treatment of organics in water containing chlorides in terms of generation of active chlorine and removal of TOC [1-3]. Hence, the electrolyses described in the section 3.1 and performed with Ti/RuO₂ were repeated using two very different and promising anodes:

- boron doped diamond (BDD) which is the most effective anode for the oxidation of organics by hydroxyl radicals generated by water oxidation (eq. (9));



- Ti/IrO₂-Ta₂O₅ that is, on one hand, less effective for organics oxidation by hydroxyl radicals, but, on the other hand, characterized by a quite fast generation of active chlorine [21]; moreover, it was reported that, for the treatment of some waters including reverse osmosis concentrate, this anode gives a lower generation of some chlorinated by-products [21].

As shown in fig. 2A, phenol was removed in a very fast and similar way using BDD and Ti/RuO₂ anodes and its concentration reached a value close to zero after about 300 C. For Ti/IrO₂-Ta₂O₅ anode, a slower abatement of phenol was observed; however, also in this case, after about 500 C, phenol was completely removed. Quite interestingly, for both BDD and RuO₂ anodes, the abatement of TOC started only when the removal of phenol was almost completed. This indicated that, at these electrodes, the fastest process is the chlorination of phenol to chlorophenols as confirmed by data reported in fig. 2C and that the mineralization process involves these compounds and not directly the phenol. For Ti/IrO₂-Ta₂O₅ anode, a slightly different picture was observed. In this case, in the first stages of the electrolysis a slower removal of phenol (fig. 2A) and a slower formation of chlorophenols (fig. 2B) occurred coupled with a faster TOC removal (fig. 2A). However, a similar and quite slow removal of TOC was achieved in the second part of the electrolyses for the two adopted metal oxide anodes. Conversely, in the case of BDD, a faster and higher abatement of TOC was achieved after 300 C, thus showing that the BDD anode is more effective for the degradation of some

resistant intermediates (fig. 2A). This is probably due to the fact that, using BDD, the oxidation by active chlorine is coupled with the mineralization achieved by very reactive hydroxyl radicals.

A quite interesting example is reported in fig. 2D that reports the trend of the total concentration of HAAs vs. the charge passed. For Ti/IrO₂-Ta₂O₅ anode, a very slow formation of HAAs was observed according to the results achieved by Bagastyo et al. for the treatment of reverse osmosis concentrate [21]. Hence, the utilization of Ti/IrO₂-Ta₂O₅ anode can allow to minimize the formation of these compounds for short electrolyses. However, for long times and large charge passed, the formation of HAAs increased significantly and was closer to that achieved using Ti/RuO₂. Conversely, for BDD, a faster formation of HAAs was observed but they were partially removed at longer times (fig. 2D). As a consequence, at the end of the electrolyses the lowest concentrations of HAAs were obtained using the BDD anode. This demonstrated the ability of BDD anode to remove some very resistant organic intermediates. In particular, the final total concentration of HAAs was close to 0.95-1 mM for the two metal oxide anodes and close to 0.25 mM for BDD. Similar results were previously found for the electrochemical treatment of latrine [19-20]. Fig. 2E reports the concentrations of chlorate formed in the electrolyses. According to the literature [2,13,33-34], it was found that the concentration of chlorate strongly depended on the nature of anode. In fact, at the end of experiment, it was close to 40, 260 and 6200 ppm for Ti/RuO₂, Ti/IrO₂-Ta₂O₅ and BDD anodes, respectively. It is worth to mention that a very low formation of chlorate was observed using Ti/IrO₂-Ta₂O₅ anode. Using this electrode, it would be possible to achieve a total removal of phenol (fig. 2A) with a small formation of HAAs (fig. 2D) and chlorate (fig. 2E) with a proper setting of the charge passed. However, only a partial removal of TOC could be obtained in these conditions (fig. 2A). Conversely, a very fast and high formation of chlorate was obtained using BDD. Also, using this anode the formation of perchlorate was observed according to the literature (fig. 2E).

Fig. 2B reports the trend of CE_{TOC} vs. charge passed for the three adopted anodes. In all cases, a curve with a maximum was obtained for a charge passed close to 400 C due to the fact that, in the first part of the electrolysis, most of active chlorine is used for the chlorination of phenol to chlorophenols and,

in the second part, the mineralization is made difficult by the permanence in the solution of very resistant organics such as HAAs. It is worth to mention that however BDD presented highest maximum and final values of CE_{TOC} , due to its higher ability to mineralize the organics formed during the electrolysis.

3.3 Effect of concentration of NaCl

It was previously shown that the concentration of NaCl can drastically affect the performances of the electrochemical treatment of liquid effluents contaminated by organic pollutants [1,2]. The effect of NaCl concentration was investigated here using Ti/RuO₂ and BDD anodes and different NaCl concentrations in the range 0.5-5 M. In all the cases, a quite fast removal of phenol and chlorophenols was achieved. However, as shown in fig. 3, the concentration of NaCl affected remarkably the performances of the process. In particular, a slight enhancement of the final abatement of TOC from 43 to 50 % was observed using Ti/RuO₂ anode by increasing the concentration of NaCl from 0.5 to 5 M (fig. 3A), due to the higher generation of active chlorine at high concentrations of NaCl [1]. Conversely, in the case of BDD, the higher was the concentration of NaCl the lower was the final removal of TOC (74, 54 and 39 % at 0.5, 3 and 5 M, respectively). Indeed, at higher NaCl concentrations, the oxidation of chlorides is expected to predominate and to drastically reduce the water oxidation to hydroxyl radicals which are particularly important for the performances of BDD anode and for the oxidation of more resistant intermediates such as HAAs. Indeed, the final concentrations of HAAs using the BDD anode were 0.2 and 0.4 mM for a concentration of NaCl of 0.5 and 5 M, respectively.

It is worth to mention that at 0.5 and 5 M a very different effect of the nature of the anode was observed; indeed, at low concentration of chlorides, where the hydroxyl radicals generation is expected to be more important, a higher removal of TOC was achieved using BDD (74 vs. 43% using BDD and Ti/RuO₂ anodes, respectively), which produces very reactive hydroxyl radicals. Conversely, at high concentrations of NaCl, where the active chlorine generation is expected to

prevail, a higher abatement of TOC was achieved using the DSA anode (50 vs. 39 %) which is more effective for the production of active chlorine [14]. It is worth to mention that similar results were previously reported for the treatment of water solutions of oxalic acid and methylene blue dye using BDD and DSA anodes [3,36].

In addition, a remarkable effect of NaCl on the final concentrations of chlorate was observed using BDD anode. Indeed, the increase of the concentration of NaCl up to 5 M allowed to reduce significantly the final concentration of chlorate. This result is probably due to the fact that the generation of chlorate is favored by the presence of hydroxyl radicals [2] whose formation is hampered at high NaCl concentrations. Moreover, in the case of BDD, no formation of perchlorate was detected when the electrolysis was performed at 5 M. Indeed, the formation of perchlorate requires very strong oxidants such as hydroxyl radicals generated at BDD [2].

3.4 Effect of the nature of the cathode

Very few studies were devoted in the past to the study of the effect of the cathode on the electrochemical treatment of water contaminated by organics and containing chlorides. However, in the last years, some research have shown that the nature of the cathode can affect the concentration of chlorinated by-products generated during electrochemical disinfection. In particular, some scientists have reported that it is possible to reduce the formation of chlorates and perchlorates using carbon felt cathodes [22]. Furthermore, silver cathodes are known for their ability to dehalogenate various organic chlorinated compounds, including chloroacetic acids [28,30-31]. For this reason, we have performed some experiments with carbon felt or silver as cathode with both Ti/RuO₂ and BDD anodes with a concentration of NaCl of 0.5 M and a j of 10 mA cm⁻². It was found that the nature of the cathode did not change significantly the abatement of phenol (data not shown). Conversely, it strongly affected the removal of TOC (fig. 4A). Indeed, the abatement of TOC increased using both silver or carbon felt cathodes. In the case of Ti/RuO₂ anode, the final abatement of TOC was 43, 52

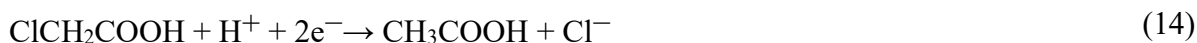
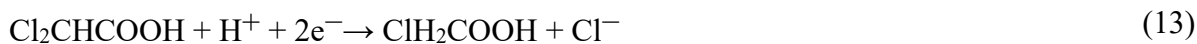
and 57% using Ni, Ag and carbon felt, respectively. For BDD, the final abatement of TOC was 74, 81 and 92 % using Ni, Ag and carbon felt, respectively. Fig. 4B (for Ti/RuO₂ anode) and 4C (for BDD anode) report the trend CE_{TOC} vs. charge passed at the three adopted cathodes. It can be seen that experiments performed with carbon felt cathode gave the highest final CE_{TOC} at both metal oxide and diamond anodes. These results can be due in part to the ability of carbon felt to convert O₂ to H₂O₂, a weak oxidant that can contribute to the oxidation of organics. Moreover, as recently reported by the group of Rodrigo in the frame of the electrochemical reclamation of urban treated wastewaters, H₂O₂ may react with hypochlorite, causing its reduction to chloride (eq. (10)), and with chlorate to give ClO₂ (eq. (11)) [32], an effective oxidant which, unlike chlorine, is reported not to lead to the formation of chlorinated byproducts [29].



Indeed, according to this hypothesis, the use of carbon felt allowed to decrease significantly the final concentration of chlorate as shown in fig. 4F. In particular, in the case of Ti/RuO₂ and BDD anodes, using carbon felt as cathode, the final concentration of chlorate was just about 8 and 16 %, respectively, of that detected with Ni cathode. Furthermore, a lower concentration of perchlorate was also obtained using carbon felt (190 vs. 255 ppm) and BDD as anode. However, the replacement of Ni with carbon felt did not result in a significant change of the final concentrations of HAAs for experiments performed with Ti/RuO₂ anode (fig. 4E).

As shown in fig. 4A-4C, Ag cathode gave for all the duration of the electrolyses higher abatement of TOC and CE_{TOC} with respect to that obtained with Ni. These results are probably due to the ability of Ag to reduce chlorinated by-products into the corresponding dehalogenated organics that are more easily oxidizable. Indeed, as shown in figure 4E, the utilization of Ag cathode allowed to reduce the final concentrations of HAAs to negligible values using both BDD and Ti/RuO₂ anodes. Indeed,

according to the literature, Ag cathode is able to reduce, even if with slow kinetics, HAAs to acetic acid by reactions (12) – (14) [28].



As an example, the total concentration of HAAs at the end of the electrolysis was 0.94 and 0.26 mM using Ni cathode and RuO₂ and BDD anodes, respectively, and it became 0 and 0.04 mM using Ag cathodes. Moreover, as shown in fig. 4D and 4F, the utilization of Ag cathode allowed to reduce the concentrations of chlorophenols, remove them in a shorter time and reduce slightly the production of chlorate. Hence, it can be concluded that the selection of the cathode is a key parameter to enhance the removal of TOC and limit the final concentrations of chlorinated by-products.

3.5 Effect of current density

The effect of j on the treatment of wastewater by electro-generated active chlorine was widely investigated in the last years [1-3]. It was shown that if adopted j are lower than the limiting current density for the mass transfer of chlorides to the electrode surface (j_{lim}), an increase of j favors the generation of active chlorine and, usually, accelerates the removal of organic pollutants at least at metal oxide anodes [1]. Conversely, according to various studies mainly focused on electrochemical disinfection, an enhanced formation of chlorate and/or perchlorate with j was reported using both BDD [13,33-38] and IrO₂-Ta₂O₅ anodes [31,39]. In particular, Schaefer and co-authors have shown, for the electrochemical treatment of surface waters using Ti/IrO₂-Ta₂O₅ anode, that the concentration of chlorate and perchlorate can be limited under regulatory levels working with low current densities (0.25 - 8 mA cm⁻²) [39].

Here the effect of j was studied using both Ti/RuO₂ and BDD anodes by performing a series of electrolyses in the range 5.7 – 14.5 mA cm⁻² with a concentration of NaCl of 0.5 M and a Ni cathode. As shown in fig. 5A, which plots the abatement of TOC vs. time passed, higher j gave higher abatements, but the differences were very slight for Ti/RuO₂. As an example, using Ti/RuO₂ after 24 hours, the abatement of TOC was close to 33, 35 and 40% at 5.7, 10.3 and 15.4 mA cm⁻². Similarly, after 48 h quite similar values (41 and 43%) were achieved at 5.7 and 10.3 mA cm⁻². For BDD, higher differences were observed; after 24 hours, the removal of TOC was of ~55 and 68 % at 5.7 and 10.3 mA cm⁻², respectively. Fig. 5B reports the total concentration of HAAs vs. time. In the case of Ti/RuO₂ at the beginning of the electrolyses, a higher concentration of HAAs was observed for the experiments performed at higher j because of the higher charge passed. However, in all these electrolyses, the total concentration of HAAs tends to a very similar plateau value. In the case of BDD, a quite similar trend was achieved at the two adopted j for the plot total concentration of HAAs vs. charge passed (data not shown). Hence, as shown in fig. 5B, at the end of the electrolysis for the same time passed a higher total concentration of HAAs was found for the experiment performed at the lower j because of the lower amount of charge passed.

A strong effect of j on the formation of chlorate was observed as previously shown for the electrochemical disinfection of water. Indeed, the higher was j the higher was the concentration of chlorate detected for the same amount of time passed. As an example, using Ti/RuO₂ after 24 hours the concentration of chlorate was 14, 178 and 424 ppm at 5.7, 10.3 and 15.4 mA cm⁻², respectively (fig. 5C). In the case of BDD, after 24 hours the concentrations of chlorate and perchlorate were 4800 and 63 at 5.7 mA cm⁻², respectively, and 6200 and 255 ppm at 10.3 mA cm⁻², respectively. Moreover, in the case of Ti/RuO₂, the concentration of chlorate decreased for lower values of j also for the same amount of charge passed. Indeed, after 2600 C, it was 31, 178 and 468 ppm at 5.7, 10.3 and 15.4 mA cm⁻², respectively (fig. 5C).

3.6 Experiments with two cathodes.

According to the results reported in the section 3.4, the use of both carbon felt and Ag cathodes allow to improve the performances of the process in terms of higher removal of TOC and lower generation of HAAs (for Ag) and chlorate and perchlorate (for carbon felt). For this reason, we decided to explore the possibility to use a system equipped with two cathodes (carbon felt and Ag), in the following namely Ag-CF, and one anode. First experiments were performed with both BDD, selected for the high removal of TOC, and Ti/IrO₂-Ta₂O₅ anode, chosen for the low generation of chlorate, with a concentration of 0.5 M NaCl and a j of 10 mA cm⁻². As shown in fig. 6A and in Table 1, the use of the system equipped with two cathodes allowed to strongly increase the removal of TOC achieved using both Ti/IrO₂-Ta₂O₅ and BDD anodes. In particular, for the experiment performed with the metal oxide anode, the final abatement of TOC increase from 44 to 67 % replacing the Ni cathode with Ag-CF cathodes. Similarly, using BDD anode, the final removal of TOC was close to 74 and 86 % using Ni and Ag-CF cathodes, respectively. It is worth to mention that the system with two cathodes gave a significant improvement of the removal of TOC (fig. 6A) and of CE_{TOC} (fig. 6B) mainly in the second part of the electrolyses. Hence, the role of Ag and carbon felt cathodes is probably related to their ability to convert organics that are formed during the electrolyses, such as HAAs, that are particularly resistant to the oxidation by means of active chlorine. Indeed, using Ti/IrO₂-Ta₂O₅ anode, the total concentration of HAAs reached a plateau value of 1 M when the Ni cathode is used ,while it decreased to about 0.55 M in the last part of the electrolysis in the system equipped with the Ag-CF cathodes (fig. 6C). Similarly, for BDD anode, the final value of the total concentration of HAAs was close to 0.26 and 0.04 mM using Ni and Ag-CF cathodes, respectively (Table 1 and fig. 6C). Moreover, as shown in Table 1, the use of carbon felt cathode allowed to reduce the concentration of chlorate and perchlorate. In the case of BDD, the final concentrations of chlorate and perchlorate were reduced from 6200 and 255 to 1027 and 157 ppm, respectively. Moreover, the even low concentration of chlorate achieved with Ti/IrO₂-Ta₂O₅ and Ni electrodes was further reduced using the Ag-CF cathodes from 40 to 20 ppm. Hence, it can be concluded that the use of the system equipped with Ag and carbon felt cathodes allowed to achieve both *i*) higher removals of TOC and

CE_{TOC} and *ii*) lower concentrations of HAAs, chlorate and perchlorate. Moreover, as shown in Table 1 for BDD, the use of two cathodes gave a higher removal of TOC also with respect to the experiments performed with a single Ag or carbon felt cathode.

In the last paragraph, it has been shown that the use of low j allows to reduce the concentrations of chlorate and perchlorate. Hence, experiments performed with Ag-CF cathodes were repeated using a j of 5.4 mA cm^{-2} instead of 10.4 mA cm^{-2} . As shown in Table 1, for Ti/IrO₂-Ta₂O₅ similar results were obtained after 48 h (in terms of removal of TOC, generation of chlorate and HAAs) with the two adopted j but with a lower amount of charge passed and, as a consequence, with higher CE_{TOC} (9.1% vs. 5.1% at 5.4 and 10.4 mA cm^{-2} , respectively) and lower energy consumptions. For BDD, the combined use of low j and of a system equipped with two cathodes (Ag and carbon felt) allowed to improve CE_{TOC} and to further decrease the concentrations of chlorate and perchlorate, but, conversely, gave slightly higher concentrations of HAAs (table 1).

Table 1. Electrochemical treatment of water solutions of phenol (2 mM) and NaCl (0.5 M) under amperostatic conditions in an undivided cell at 10.3 (or 5.4 when indicated) mA cm^{-2} for 48 h using an anode (BDD or Ti/IrO₂-Ta₂O₅) and one (Ni or Carbon felt (CF) or Ag) or two cathodes (CF-Ag).

Anode – Cathode →	Ti/IrO ₂ -Ta ₂ O ₅ - Ni	Ti/IrO ₂ -Ta ₂ O ₅ - Ag-CF	Ti/IrO ₂ -Ta ₂ O ₅ - Ag-CF $j = 5.4 \text{ mA cm}^{-2}$	BDD - Ni	BDD - Carbon felt	BDD - Ag	BDD - Ag-CF	BDD - Ag-CF $j = 5.4 \text{ mA cm}^{-2}$
TOC abatement / %	44	67	64	74	92	81	86	82
CE / %	3.3	5.1	9.1	5.6	6.2	7	6.6	12
[ClO ₃]/ ppm	40	20	24	6242	1042	5661	1027	438
[ClO ₄]/ ppm	n.d.	n.d.	n.d.	255	200	259	157	94
[HAAS]/ mM	1	0.55	0.59	0.26	0.05	0	0.04	0.16

4. Conclusions

It was shown that the electrochemical treatment of phenol in the presence of chlorides at Ti/RuO₂, Ti/IrO₂-Ta₂O₅ and BDD anodes gives rise to the formation of many chlorinated products and, in particular, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol, chloroacetic acids and chlorate. Moreover, in the case of BDD also perchlorate was

formed. Chlorophenols were completely removed during the electrolyses while di- and tri-chloroacetic acids, chlorate and perchlorate were found also at the end of the experiments. It was shown that the electrochemical process is dramatically faster than the chemical chlorination and that the performances of the process strongly depended on various operative parameters, including the nature of anode and cathode, the NaCl concentration and the current density, as described below.

- Effect of anode. Ti/IrO₂-Ta₂O₅ gave the slowest formation of HAAs and the lowest final concentrations of chlorate. Conversely, BDD presented the highest abatement of TOC and of HAAs but the highest concentrations of chlorate. Moreover, the formation of perchlorate was found according to the literature only for this anode.
- Effect of NaCl concentration. At relatively low concentrations of NaCl (0.5 M), where the oxidation of water to hydroxyl radicals is expected to be more relevant, BDD gave higher abatements of TOC than Ti/RuO₂. Conversely, for very high concentrations of NaCl (5 M) when water oxidation is expected to be minimized, BDD gave lower abatements with respect to Ru oxide anode. It is worth to mention that at high NaCl concentrations, a lower amount of chlorate and no perchlorate were formed using BDD.
- Effect of cathode. Remarkably higher abatements of TOC were achieved using Ag or carbon felt cathodes instead of Ni. Moreover, carbon felt allowed to decrease drastically the concentrations of chlorate and perchlorate, while Ag gave achieve negligible values of HAAs.
- Effect of current density. According to the literature, the use of lower j gave lower concentrations of chlorate and perchlorate (for BDD).

Moreover, a system equipped with one anode and two cathodes (Ag and carbon felt) was proposed for the first time for the treatment of wastewater contaminated by organics and containing chlorides. This new approach allowed to enhance remarkably the abatement of TOC and to strongly reduce the final concentrations of all detected chlorinated by-products including HAAs, chlorate and perchlorate. Moreover, for BDD the combined use of low current densities and of the system

equipped with two cathodes (Ag and carbon felt) allowed to strongly improve the current efficiency and to further decrease the concentrations of chlorate and perchlorate but gave slightly higher final concentrations of HAAs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figure captions

Figure 1. Plot of the abatement of phenol and TOC (fig. 1A), and of the concentrations of chlorophenols (fig. 1B) and HAAs (fig. 1C) vs. time for the electrolyses 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.

Figure 2. Plot of abatement of phenol and TOC (fig. 2A), CE_{TOC} (fig. 2B) and total concentrations of chlorophenols (fig. 2C) and HAAs (fig. 2D) vs. charge passed for the electrolyses 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, BDD and Ti/IrO₂-Ta₂O₅ anodes and a Ni cathode. Fig. 2E reports the concentrations of chlorate and perchlorate obtained using the three anodes.

Figure 3. Effect of NaCl concentration on the final removal of TOC (fig. 3A) and on the final concentration of by-products (3B). In particular, fig. 3B reports the total concentration of HAAs and the concentrations of chlorate and perchlorate (fig. 3B). Electrolyses of water solutions of phenol (2 mM) and NaCl (0.5 - 5 M) performed under amperostatic conditions (10 mA cm^{-2}) in an undivided cell using Ti/RuO₂ or BDD anodes and a Ni cathode for 48 h.

Figure 4. Effect of the nature of cathode on abatement of TOC (fig. 4A), CE_{TOC} (fig. 4B for Ti/RuO₂ and 4C for BDD), total concentrations of chlorophenols (fig. 4D) and HAAs (fig. 4E) vs. charge passed. Effect of the nature of cathode on concentration of chlorate (fig. 4F). Electrolyses of a water solution of phenol (2 mM) and NaCl (0.5 M) were performed under amperostatic conditions (10 mA cm^{-2}) in an undivided cell using Ti/RuO₂, BDD anodes and Ni, Ag and carbon felt cathodes.

Figure 5. Effect of j on the 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 cathode. Fig. 5A and 5B report the abatement of TOC and the total concentrations of HAAs vs. time passed, respectively, while fig. 5C report the total concentrations of chlorate achieved using Ti/RuO₂.

Figure 6. Electrochemical treatment of water solutions of phenol (2 mM) and NaCl (0.5 M) under amperostatic conditions in an undivided cell equipped with one (Ti/IrO₂-Ta₂O₅ or BDD) anode and two cathodes (Ag and carbon felt) at 10.3 mA cm^{-2} . Fig. 6A and 6B report the plots abatement of TOC and CE_{TOC} vs. charge passed, respectively, while fig. 5C reports the total concentrations of HAAs.

Figure 1

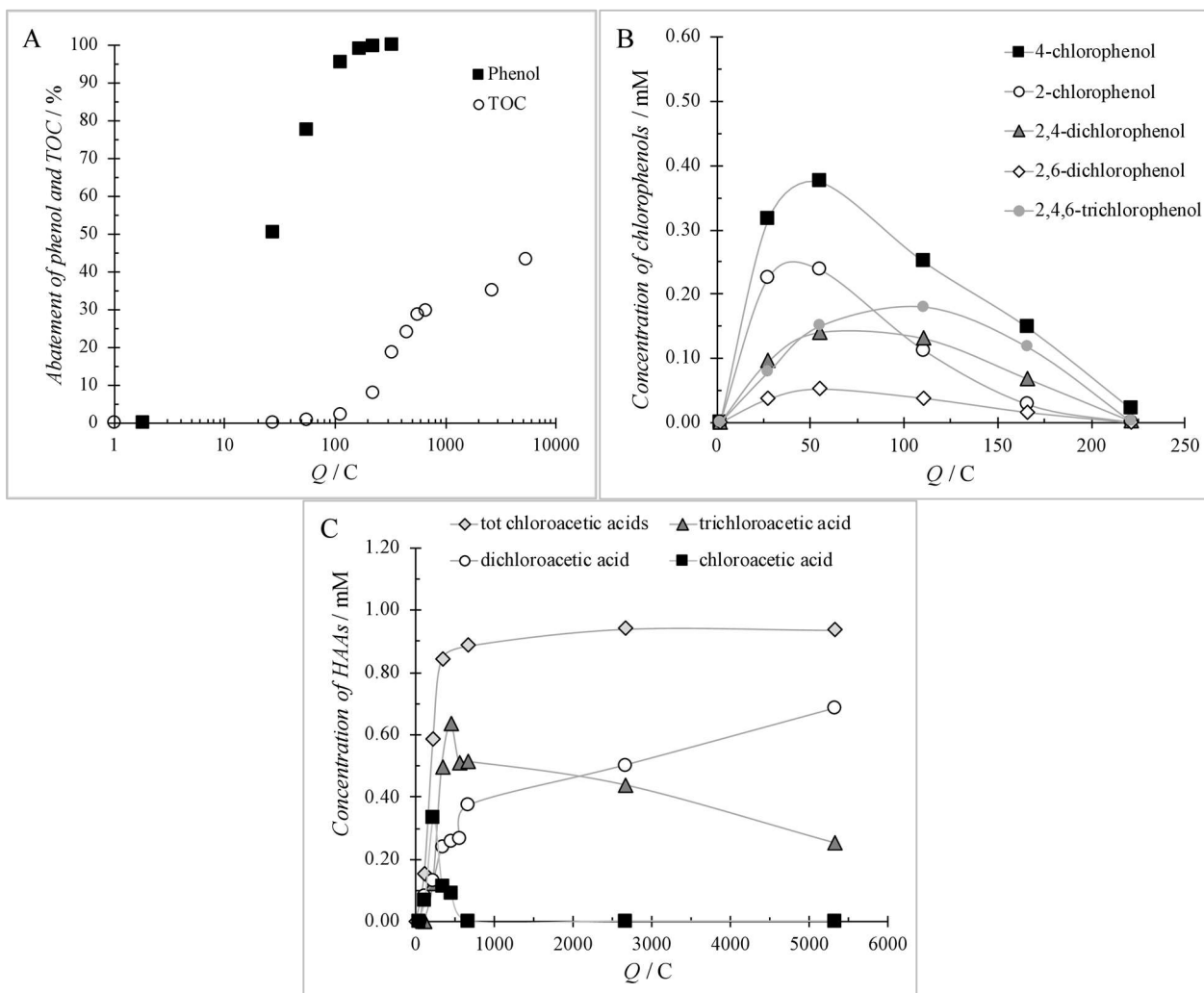


Figure 1. Plot of the abatement of phenol and TOC (fig. 1A), and of the concentrations of chlorophenols (fig. 1B) and HAAs (fig. 1C) vs. time for the electrolyses of water solutions of phenol (2 mM) and NaCl (0.5 M) performed under amperostatic conditions (10 mA cm^{-2}) in an undivided cell at Ti/RuO₂ anode and a Ni cathode.

Figure 2

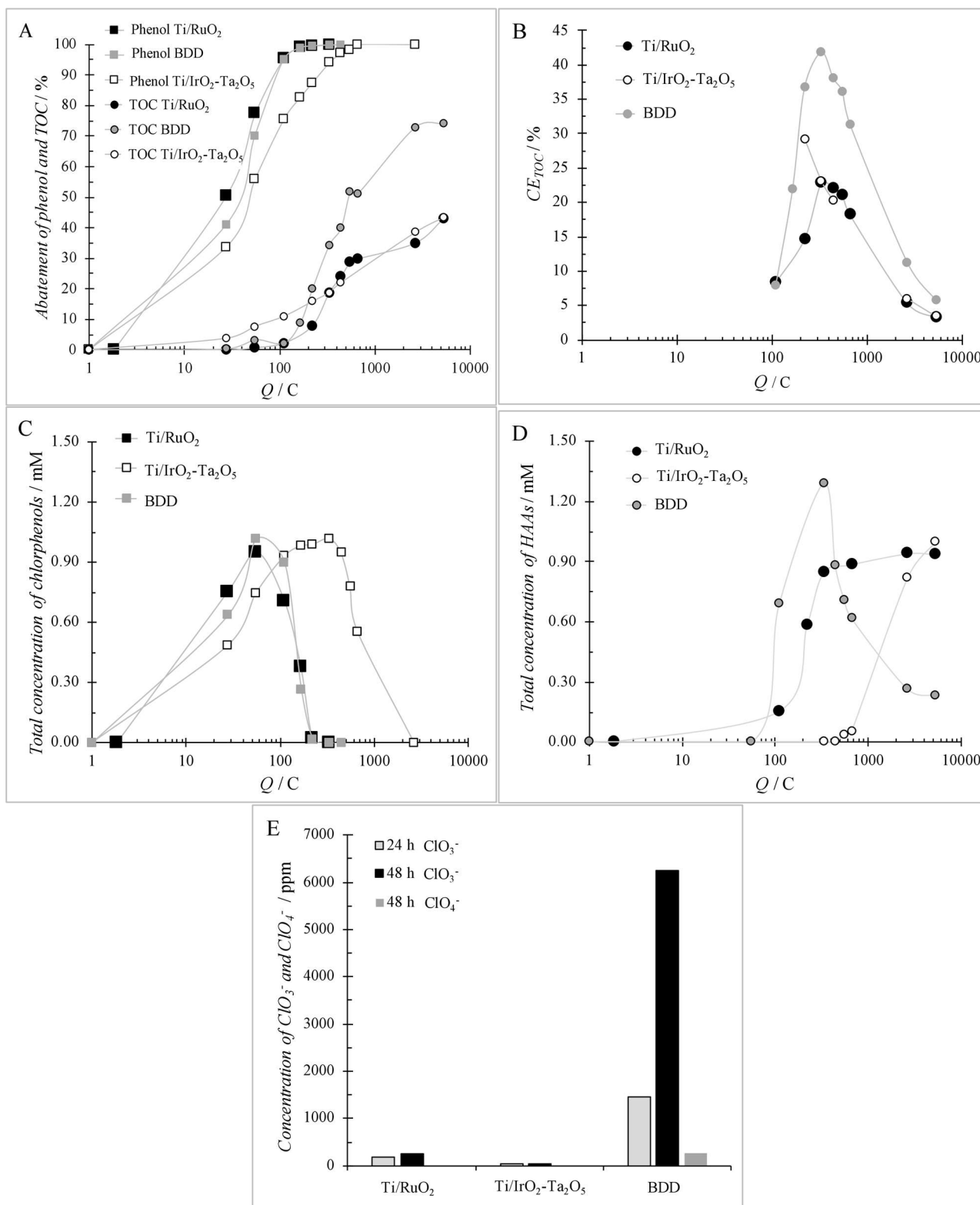


Figure 2. Plot of abatement of phenol and TOC (fig. 2A), CE_{TOC} (fig. 2B) and total concentrations of chlorophenols (fig. 2C) and HAAs (fig. 2D) vs. charge passed for the electrolyses of water

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, BDD and Ti/IrO₂-Ta₂O₅ anodes and a Ni cathode. Fig. 2E reports the concentrations of chlorate and perchlorate obtained using the three anodes.

Figure 3

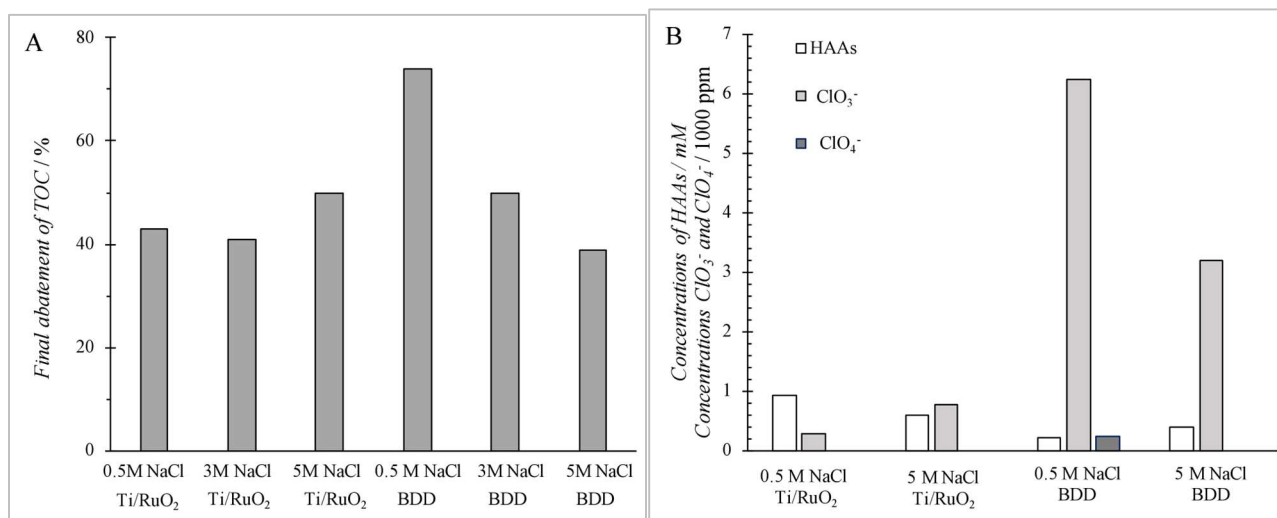


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Figure 4

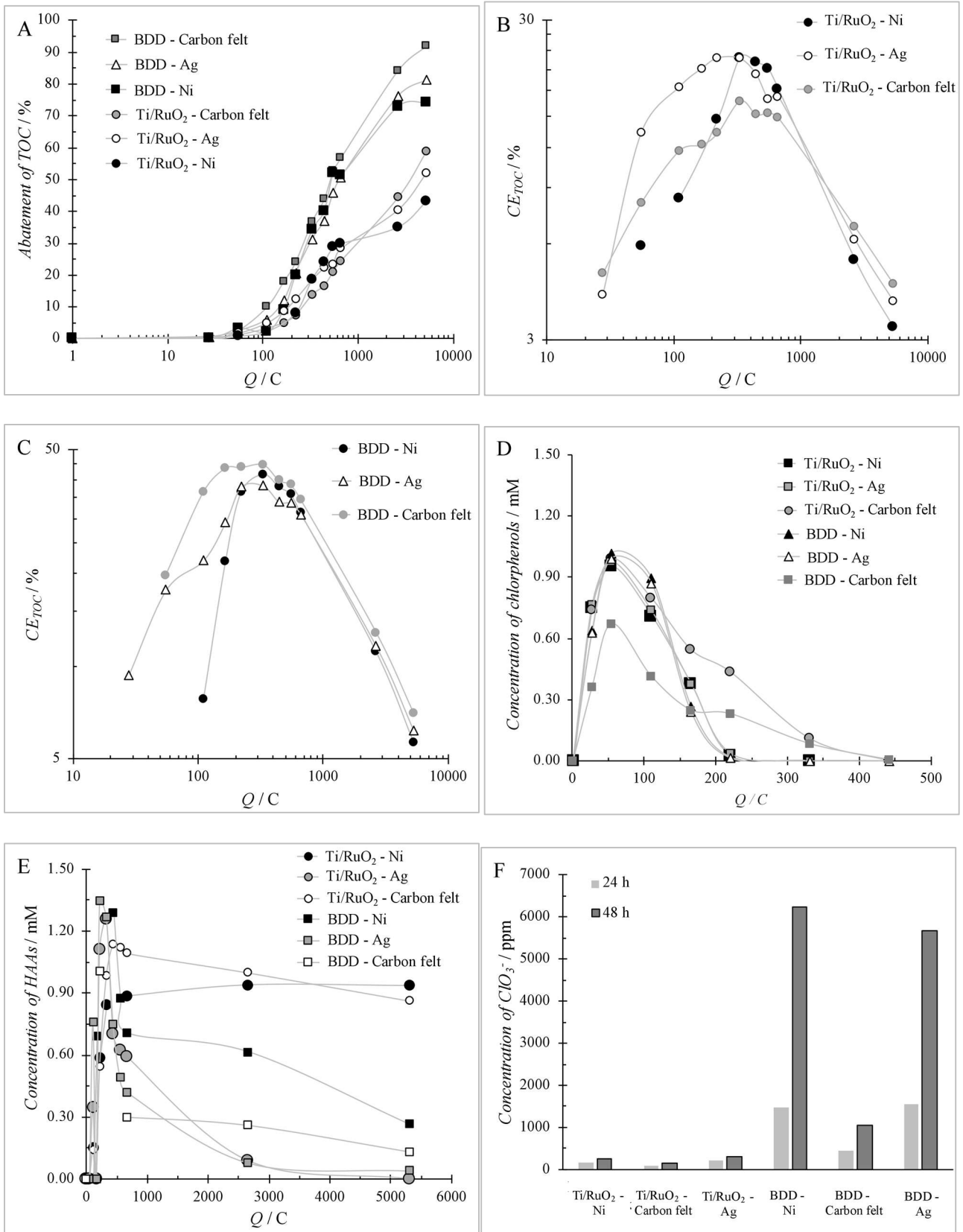


Figure 4. Effect of the nature of cathode on abatement of TOC (fig. 4A), CE_{TOC} (fig. 4B for Ti/RuO₂ and 4C for BDD), total concentrations of chlorophenols (fig. 4D) and HAAs (fig. 4E) vs. charge

passed. Effect of the nature of cathode on concentration of chlorate (fig. 4F). Electrolyses of a water solutions of phenol (2 mM) and NaCl (0.5 M) were performed under amperostatic conditions (10 mA cm^{-2}) in an undivided cell using Ti/RuO₂, BDD anodes and Ni, Ag and carbon felt cathodes.

Figure 5

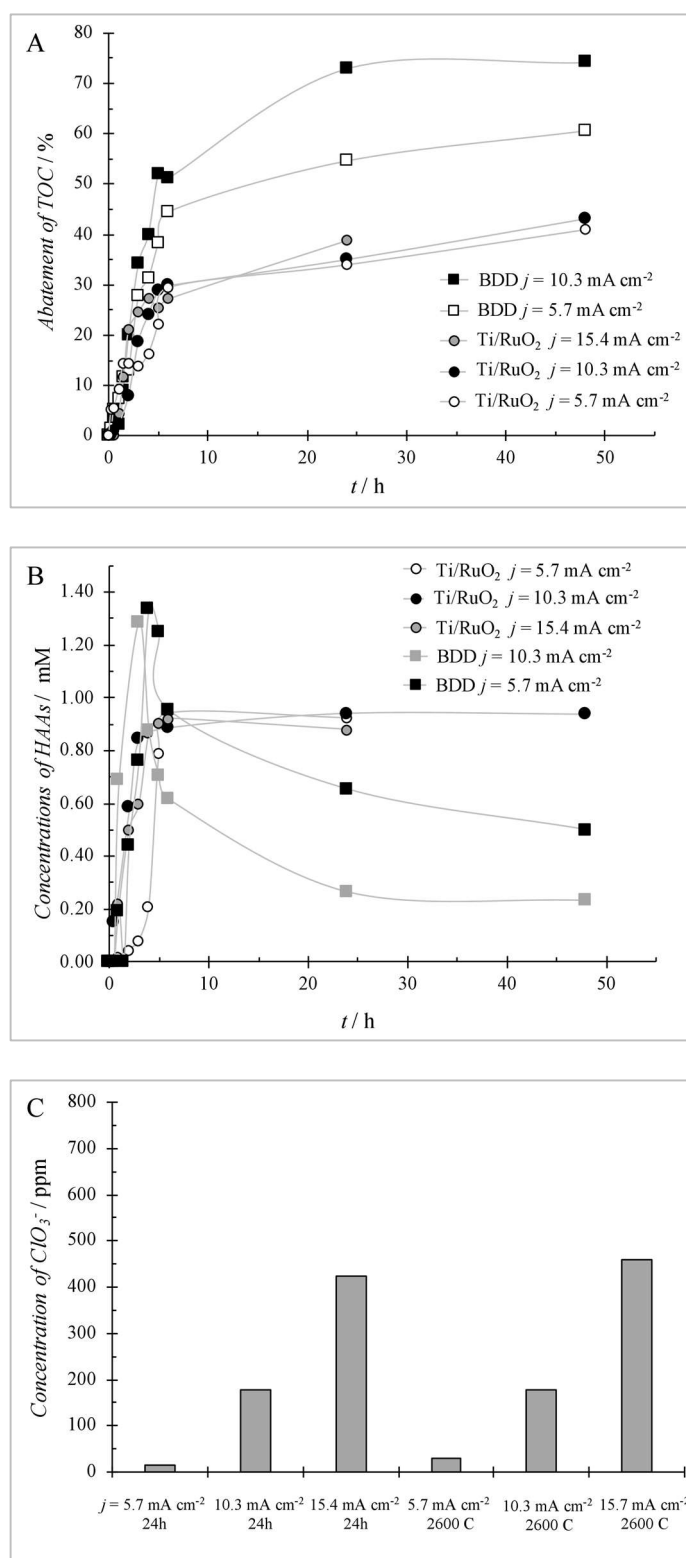


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time passed, respectively, while fig. 5C report the total concentrations of chlorate achieved using Ti/RuO₂.

Figure 6

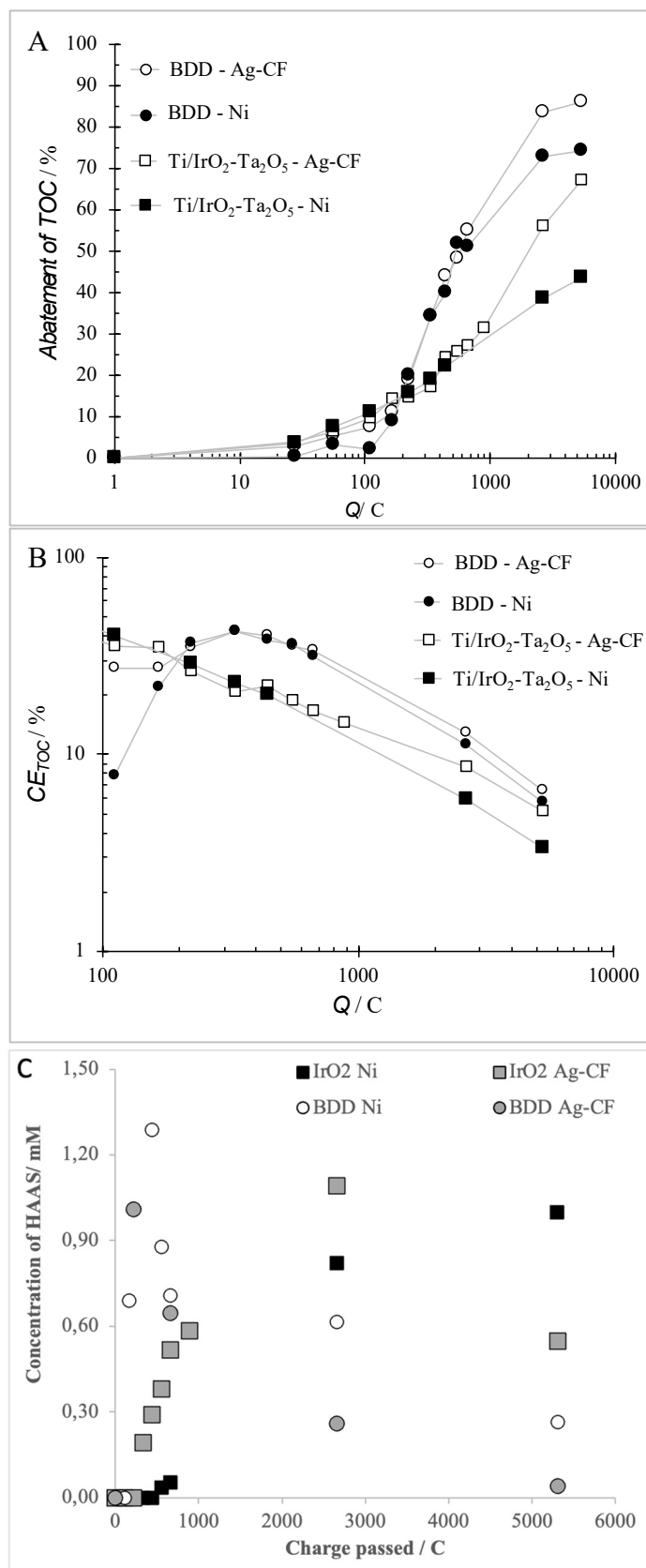


Figure 6. Electrochemical treatment of water solutions of phenol (2 mM) and NaCl (0.5 M) under amperostatic conditions in an undivided cell equipped with one (Ti/IrO₂-Ta₂O₅ or BDD) anode and

two cathodes (Ag and carbon felt) at 10.3 mA cm^{-2} . Fig. 6A and 6B report the plots abatement of TOC and CE_{TOC} vs. charge passed, respectively, while fig. 5C reports the total concentrations of HAAs.