



Oxidation of organics in water by active chlorine performed in microfluidic electrochemical reactors: a new way to improve the performances of the process

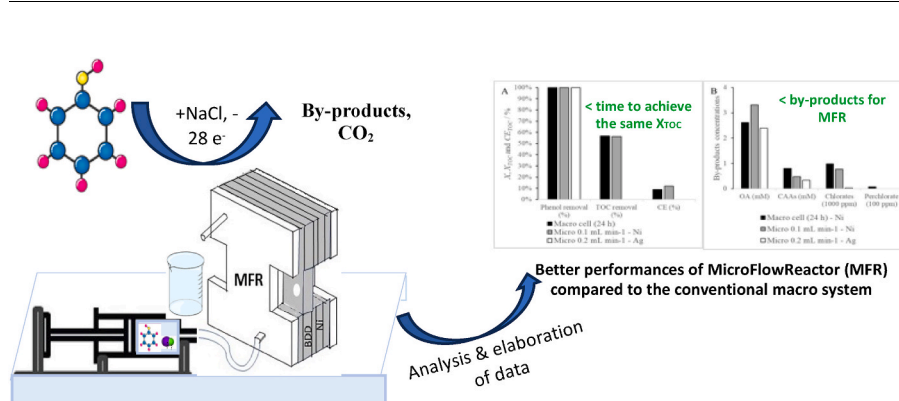
Serena Randazzo, Ange Geagea, Federica Proietto, Alessandro Galia, Onofrio Scialdone*

Università Degli Studi di Palermo, Dipartimento di Ingegneria, Viale Delle Scienze, Palermo, Italy

HIGHLIGHTS

- Electrochemical wastewater treatment by active chlorine was done in microfluidic cells.
- Higher current efficiencies and lower generation of ClO_3^- and ClO_4^- were achieved.
- The performance of the process improved using an Ag cathode.

GRAPHICAL ABSTRACT



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ABSTRACT

Wastewater polluted by organics can be treated by using electro-generated active chlorine, even if this promising route presents some important drawbacks such as the production of chlorinated by-products. Here, for the first time, this process was studied in a microfluidic electrochemical reactor with a very small inter-electrode distance (145 μm) using a water solution of NaCl and phenol and a BDD anode. The potential production of chloroacetic acids, chlorophenols, carboxylic acids, chlorate and perchlorate was carefully evaluated. It was shown, for the first time, up to our knowledge, that the use of the microfluidic device allows to perform the treatment under a continuous mode and to achieve higher current efficiencies and a lower generation of some important by-products such as chlorate and perchlorate. As an example, the use of the microfluidic apparatus equipped with an Ag cathode allowed to achieve a high removal of total organic carbon (about 76%) coupled with a current efficiency of 17% and the production of a small amount of chlorate (about 30 ppm) and no perchlorate. The effect of many parameters (namely, flow rate, current density and nature of cathode) was also investigated.

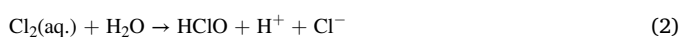
* Corresponding author.

E-mail address: onofrio.scialdone@unipa.it (O. Scialdone).

1. Introduction

Recently, an increasing number of researchers have investigated the development of new technologies or the innovation of existing ones to restore polluted water. This is due, on one hand, to the dramatic problem of scarcity and deterioration of the quality of water in many countries, and, on the other hand, to the occurrence of highly resistant pollutants often generated by industrial sources.

It was highlighted that many kinds of waters are effectively treated by chlorinated oxidants, as Cl_2 , HClO or ClO^- . These oxidants, able to remove organic pollutants resistant to conventional routes and/or pathogen microorganisms, can be produced at suitable anodes by oxidation of chlorides and, in particular, of NaCl . This compound is often present in liquid effluents [Ganiyu and Martínez-Huitle, 2019; Martínez-Huitle and Brillas, 2008; Martínez-Huitle et al., 2015, 2023; Scialdone et al., 2021] and the generation of active chlorine occurs by reactions (1)–(3).



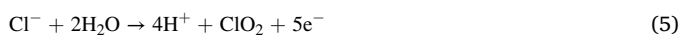
ClO^- prevails at high pH, Cl_2 at low pH and HClO at pH moderately acid [Scialdone et al., 2021]. Moreover, at low pH chlorine bubbles can be present. This process generates also other oxidants.

(i) adsorbed chloro and oxychloro radicals;

(ii) other reactive oxygen species (ROS), produced by water anodic oxidation such as $\text{HO}\bullet$ (Eq. (4)), H_2O_2 and $\bullet\text{O}_2^-$, [Jeong et al., 2009; Martínez-Huitle et al., 2023];



(iii) Cl_2O and ClO_2 formed by anodic (Eqns. (5) and (6)) or homogeneous oxidation [Chianca de Moura et al., 2014; Martínez-Huitle et al., 2015, 2023; Mostafa et al., 2018; Powell, 2010; Scialdone et al., 2021].



It was shown in the last years that the electrochemical removal of organics or pathogen microorganisms in water by active chlorine can result in the generation of toxic chlorinated species [Bagastyo et al., 2012; Scialdone et al., 2021; Spahr et al., 2017], such as chlorinated phenols, chlorinated amines, chloroacetic acids (CAAs), chlorinated oligomers, trihalomethanes, ClO_3^- and ClO_4^- [Bergmann and Rollin, 2017; Jasper et al., 2016; Richardson, 2005]. Hence, in order to develop the electrochemical removal of organics or pathogen microorganisms in water by active chlorine on an applicative scale it is mandatory to develop an experimental set-up that can allow to effectively treat the wastewater and, at the same time, to minimize/avoid the production of chlorinated toxic by-products. Driven by this aim, many researchers have investigated the effect of many operative conditions and they found that the performances of the electrolyses can be improved by a proper selection of various operative conditions such as: (i) anode nature, (ii) current density, (iii) flow dynamic regime, (iv) concentration of pollutants and Cl^- and (v) the nature of the cathode [Martínez-Huitle et al., 2015, 2023; Scialdone et al., 2021]. As an example, the use of boron doped diamond (BDD) anodes allows to improve the removal of organics and microorganisms but gives rise to significant concentrations of chlorate and perchlorate that can be in part reduced using low current densities [Martínez-Huitle et al., 2023]. In addition, the adoption of carbon felt and silver cathodes reduces, respectively, the production of ClO_3^- and ClO_4^- and of CAAs [Cotillas et al., 2015; Hao et al., 2022a]. Moreover, at carbon felt cathodes, higher removals of TOC and lower productions of ClO_3^- and ClO_4^- are obtained using pressurized air [Hao et al., 2022b].

However, it is still necessary to further improve the performances of conventional processes and to determine a suitable apparatus and proper operative conditions that allow to effectively treat wastewaters minimizing the formation of toxic chlorinated substances [Martínez-Huitle et al., 2023; Scialdone et al., 2021]. Driven by this aim we report here for the first time the use of an electrochemical cell characterized by a very small inter-electrode distance for the electrochemical treatment of wastewater by active chlorine and we demonstrated that the use of such device allows to improve the performances of the process.

In the last years, it was shown that the use of microfluidic electrochemical cells (e.g., reactors that present an inter-electrode distance h of tens or few hundreds of micrometres) can positively affect the performances of various electrochemical routes including the restoration of wastewaters [Dong et al., 2022; Khongthong et al., 2016; Perez et al., 2018, 2019] and the synthesis of various chemicals [Lu et al., 2017; Paddon et al., 2006; Scialdone et al., 2014; Watts et al., 2014]. The utilization of these devices presents many interesting features such as (a) enhancement of mass transport of reagents to the electrode surfaces; (b) use of low concentrations of supporting electrolytes; (c) good control of the temperature; (d) simple scale-up by parallelization of several units, (e) fast optimization procedures because each experiment requires a very small amount of time; (f) operations carried out under continuous mode with high conversions of the reagents for passage [Watts et al., 2014; Ziogas et al., 2009].

In particular, the utilization of microfluidic reactors can drastically improve the treatment of wastewater performed by direct electrochemical oxidation of organics [Ma et al., 2018; Scialdone et al., 2012], cathodic reduction of halogenated pollutants [Scialdone et al., 2010b, 2012] and electro-Fenton [Scialdone et al., 2013]. However, only a small number of studies is related to water treatment [Dong et al., 2022]. Moreover, in spite of the good results achieved with these processes, the use of microfluidic cells was not used, up to our knowledge, for the purification of water in the presence of chlorides.

Hence, in this work the treatment of a synthetic water solution containing phenol and NaCl was realized in a microfluidic cell with a very small distance inter-electrodes gap, a Boron Doped Diamond (BDD) anode and a Ni or Ag cathode. Phenol was selected as a model pollutant for its stability and since its oxidation by electrochemical methods was largely investigated in conventional reactors. Moreover, experiments were performed also in conventional lab cells to compare the performances of microfluidic reactors with that of macro ones. It was found for the first time, up to our knowledge, that the use of microfluidic cells for the electrochemical treatment of wastewater contaminated by organics by active chlorine allows to both increase the removal of organics and to achieve lower concentrations of chlorate and, in most of cases, to avoid the formation of perchlorate.

2. Materials and methods

2.1. Electrochemical set-up

For the electrolyses, undivided cells were used. In particular, (i) a standard glass lab (macrocell) and (ii) a commercial filter press flow devices (ElectroCell AB) were utilized. For microcell, polytetrafluoroethylene (PTFE) micrometric spacers (see references [Scialdone et al., 2012, 2014] for details) were used to achieve a nominal distance h between cathode and anode of 145 μm (two adjacent spacers of 120 and 25 μm , respectively) and with plate electrodes (surface 4.15 cm^2). An anode of BDD/Nb from Condias (Germany) and Ni or Ag (both from Carlo Erba reagents) as cathode were used. Solutions were fed into the system by using a syringe pump from New Era Pump Systems, Inc.

The conventional bench-scale glass undivided cell was equipped with the same type of electrodes used in the microfluidic cell with an active surface of 3 cm^2 , a Saturated Calomel Electrode (SCE) as reference electrode and magnetic stirring at 400 rpm.

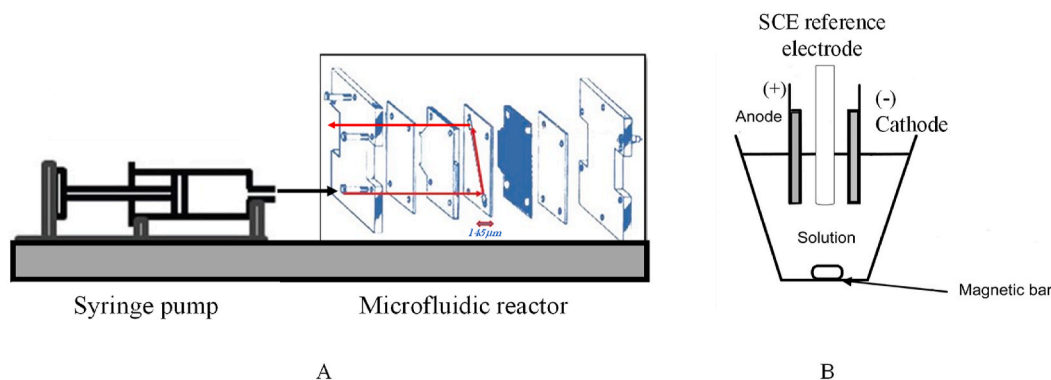


Fig. 1. Scheme of adopted reactors. A) Microfluidic reactor B) Conventional bench-scale glass undivided cell.

The schemes of both the apparatuses are reported in Fig. 1.

2.2. Electrolyses and analyses

Electrolyses were driven by an Amel instruments potentiostat/galvanostat model 2053 under galvanostatic condition. Concerning the macrocell, the electrolyses were performed at 10 and 20 mA cm⁻², while for the microfluidic system current densities (*j*) from 5 to 30 mA cm⁻² were set.

Experiments in the macrocell were carried out under batch mode by using a volume of 0.075 L, while those in the microfluidic system were carried out under continuous mode (the wastewater passed in the cell only one time). All experiments were performed at room temperature. For each experiment, at least 3 data were achieved every 10 min after reaching the steady state conditions. In most of cases, data were reproducible with an error lower than 15%. Moreover, each experiment was replicated at least two times. Average data were provided in the manuscript.

In both the apparatuses an aqueous solution prepared with phenol with a concentration of 2 mM (purity >99%, Merck) and 0.5 M NaCl (Sigma-Aldrich) was used. A Shimadzu VCSN ASI TOC-5000 TOC analyzer was used to analyze the total organic carbon (TOC), whereas the abatement of phenol and the presence of chlorophenols was detected by High-Performance Liquid Chromatography (HPLC) adopting an Agilent 1260 system, including a UV-vis detector, and using a Kinetex 5u C18 column from Phenomenex, at 20 °C. The injection volume was of 5 μL. The eluent was a solution of acetonitrile (HPLC grade, Carlo Erba Reagents) and water (HPLC grade, VWR) fluxing at 1 mL min⁻¹ by

performing an elution gradient-type with a profile as follows: i) 80/20/%vol/vol water/acetonitrile at 0 min; ii) 95/5/%vol/vol water/acetonitrile at 5 min; ii) back to 80/20/%vol/vol water/acetonitrile at 10 min. Detection was performed at 214 nm. Also chloroacetic acids (CAAs), namely monochloroacetic, dichloroacetic and trichloroacetic acids, concentrations were measured using the same system by using a solution of KH₂PO₄ (Sigma Aldrich) 25 mM at pH 2.5 (H₃PO₄) with a flow rate of 0.5 mL min⁻¹. A wavelength of 210 nm was used for detection and 10 μL of the samples were injected. For carboxylic acids, the same system equipped with a Rezex ROA-Organic Acid H⁺ (8%) column (Phenomenex) with a solution of H₂SO₄ acid 5 mN as mobile phase was used. The detection was performed at 210 nm with a flow rate of 0.5 mL min⁻¹ and the injected volume was of 10 μL. The presence of perchlorate and chlorate anions was monitored by Ionic Chromatography (IC) using a Metrohm 882 Compact IC where the anion-exchange column was a Metrosep® A Supp 5. A solution of Na₂CO₃ 3.2 mM and NaHCO₃ 1 mM was fluxed at 0.7 mL min⁻¹ as mobile phase.

Pure standards were used to obtain the calibration curves for the related compounds.

The abatement of phenol (*X*) and of TOC (*X*_{TOC}) were calculated as reported in Eqns. (7) and (8):

$$X = ([\text{Phenol}]^{\circ} - [\text{Phenol}]^{\text{f}}) / [\text{Phenol}]^{\circ} \quad (7)$$

$$X_{\text{TOC}} = ([\text{TOC}]^{\circ} - [\text{TOC}]^{\text{f}}) / [\text{TOC}]^{\circ} \quad (8)$$

where [Phenol][°] and [Phenol]^f and [TOC][°] and [TOC]^f are the values of phenol and TOC concentration before and after the treatment, expressed in mM.

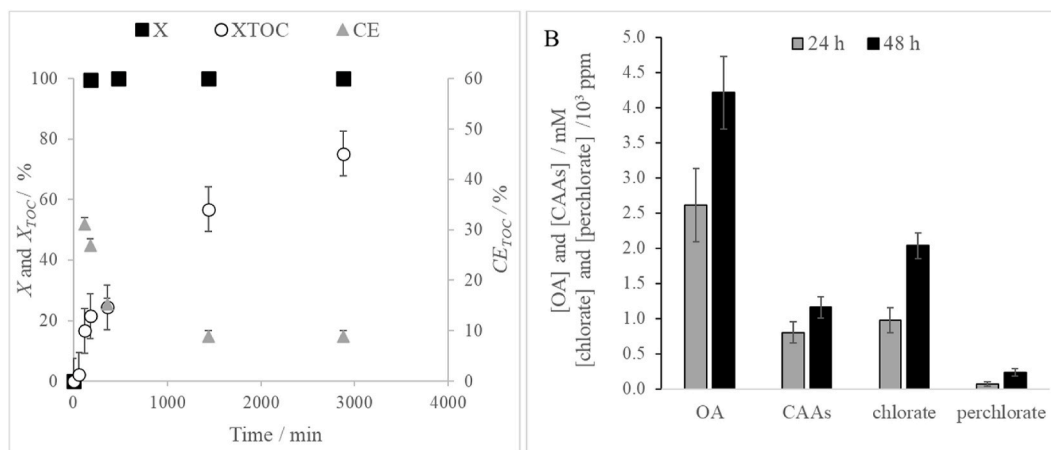


Fig. 2. Removal of phenol *X* and TOC *X*_{TOC} and CE_{TOC} vs. time passed (Fig. 2A) and concentration of oxalic acid (OA), chloroacetic acids (CAAs), chlorate and perchlorate after 24 and 48 h (Fig. 2B). Aqueous solutions contained phenol (2 mM) and NaCl (0.5 M). Experiments performed at 10 mA cm⁻² in a conventional cell using BDD anode, Ni cathode and magnetic stirring (400 rpm). Standard deviations are reported in the form of error bars.

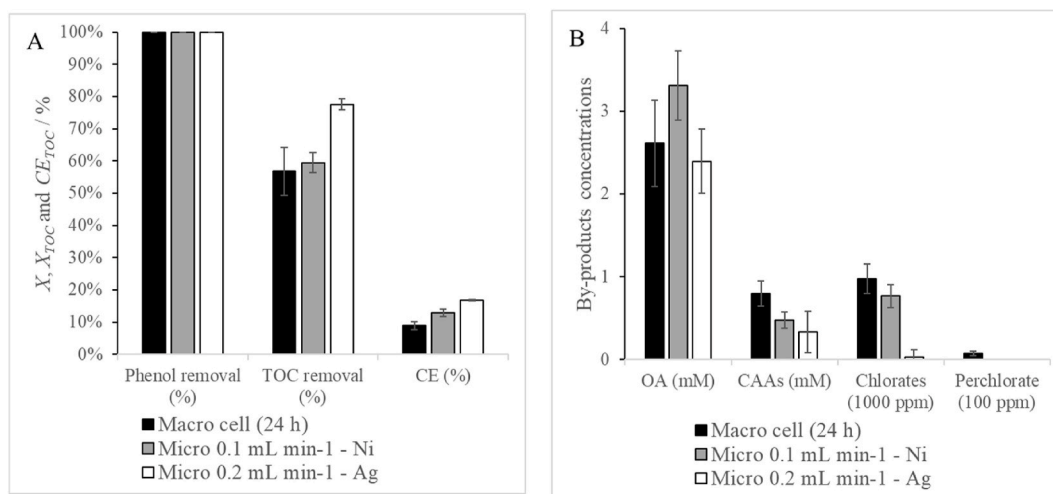


Fig. 3. Comparison between experiments performed in the macro and in the micro devices. Fig. 3A reports the abatements of phenol (X) and TOC (X_{TOC}) and the CE_{TOC} while Fig. 3B the final concentration of CAAs, OA, chlorate and perchlorate. Aqueous solutions contained phenol (2 mM) and NaCl (0.5 M). Experiments in macro cell were performed with 75 mL of electrolyte at 10 mA cm⁻² with a BDD anode and a Ni cathode and magnetic stirring for 24 h (charge passed 2592 C). Experiments in an undivided microfluidic cell were performed at BDD under the following operative conditions: (i) Ni cathode, 0.1 mL min⁻¹, 10 mA cm⁻² (charge passed for 75 mL of solution 1870 C); (ii) Ag cathode, 0.2 mL min⁻¹, 20 mA cm⁻² (charge passed for 75 mL of solution 1870 C). Standard deviations are reported in the form of error bars.

The faradaic efficiency for the removal of TOC (CE_{TOC}) was given for the macro and the microfluidic cells, respectively, by Eqns. (9) and (10):

$$CE_{TOC} = z F V [\text{TOC}]^{\circ} X_{TOC} / (j A t) \quad (9)$$

$$CE_{TOC} = z F Q [\text{TOC}]^{\circ} X_{TOC} / (j A) \quad (10)$$

where $z = 28$ is the number of electrons involved for the mineralization of phenol to CO₂, F the Faraday constant (96,487 C mol⁻¹), V the volume of the solution (dm³) and Q the volumetric flow rate, j the current density (A/m²), A the active surface (m²) and t the time (s).

3. Results and discussion

3.1. Electrolyses performed in conventional macro-cells

The first part of electrolyses was carried out in the undivided macrocell operated under batch mode with a BDD anode, a Nickel cathode, magnetic stirring (400 rpm) and a current density (j) = 10 mA cm⁻². The use of BDD at 10 mA cm⁻² allowed a very fast and complete abatement of phenol and a high removal of TOC even if it required a large amount of time passed (Fig. 2A). A quite high CE_{TOC} was recorded in the initial part of the electrolyses (higher than 30%) that decreased with the time passed up to final values close to 5% (Fig. 2A) because of the reduction of the concentration of oxidizable organics and the increasing impact of the parasitic evolution of oxygen (Eq. (11)).



Indeed, for concentrations of NaCl not too high [Scialdone et al., 2009], BDD anodes catalyze both the water oxidation to HO• (Eq. (4)) and the chlorides oxidation to active chlorine (Eqns. (1)–(3)), thus reducing the impact of water oxidation to O₂ (Eq. (11)) at least at low pH [Scialdone et al., 2009, 2021].

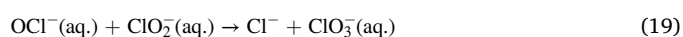
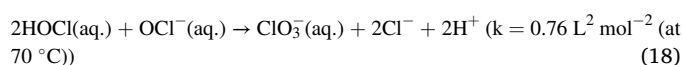
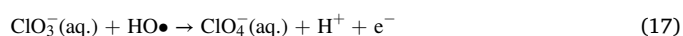
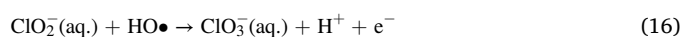
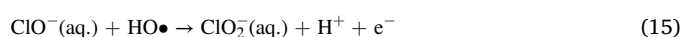
According to the literature [Hao et al., 2022a], the mineralization of phenol was coupled with the formation of many by-products: chlorophenols, chloroacetic acids (CAAs), carboxylic acids, chlorate and, mainly at BDD, perchlorate.

- We have observed the presence of various chlorophenols (2-, 4-, 2,6 di-, 2,4 di- and 2,4,6 trichlorophenols). However, these compounds

were oxidized after a small amount of charge passed and their presence was not detected after 24 or 48 h.

- Concerning the CAAs, both mono and dichloroacetic ones were present after both 24 and 48 h with a similar overall concentration (Fig. 2B). An increasing concentration of oxalic acid was also detected because of its high resistance to electrochemical oxidation processes [Scialdone et al., 2009].
- As shown in Fig. 2B, both chlorate and perchlorate were produced: the concentration of ClO₃⁻ was close to 1000 and 2000 ppm after 24 and 48 h, respectively, while that of perchlorate was lower than 100 and higher than 200 ppm after 24 and 48h, respectively. Indeed, it was reported that BDD anode gives high removals of organic pollutants [Scialdone et al., 2009, 2021], but conversely it gives significant amounts of ClO₃⁻ and ClO₄⁻ [Bergmann and Rollin, 2017; Hao et al., 2022a; Martínez-Huitle et al., 2023; Scialdone et al., 2021].

According to previous studies, chlorate and perchlorate can be formed by various oxidation routes and, in particular, by anodic oxidation of active chlorine (Eqns. (12)–(14)), oxidation by hydroxyl radicals (Eqns. (15)–(17)) or other homogenous reactions such that reported in Eqns. (18) and (19) [Jung et al., 2010; Martínez-Huitle et al., 2015, 2023; Munichandraiah and Sathyanarayana, 1987; Scialdone et al., 2021].



Moreover, the formation of perchlorate is expected to be strongly favored by the presence of hydroxyl radicals [Bergmann and Rollin, 2017; Jung et al., 2010; Martínez-Huitle et al., 2023; Munichandraiah

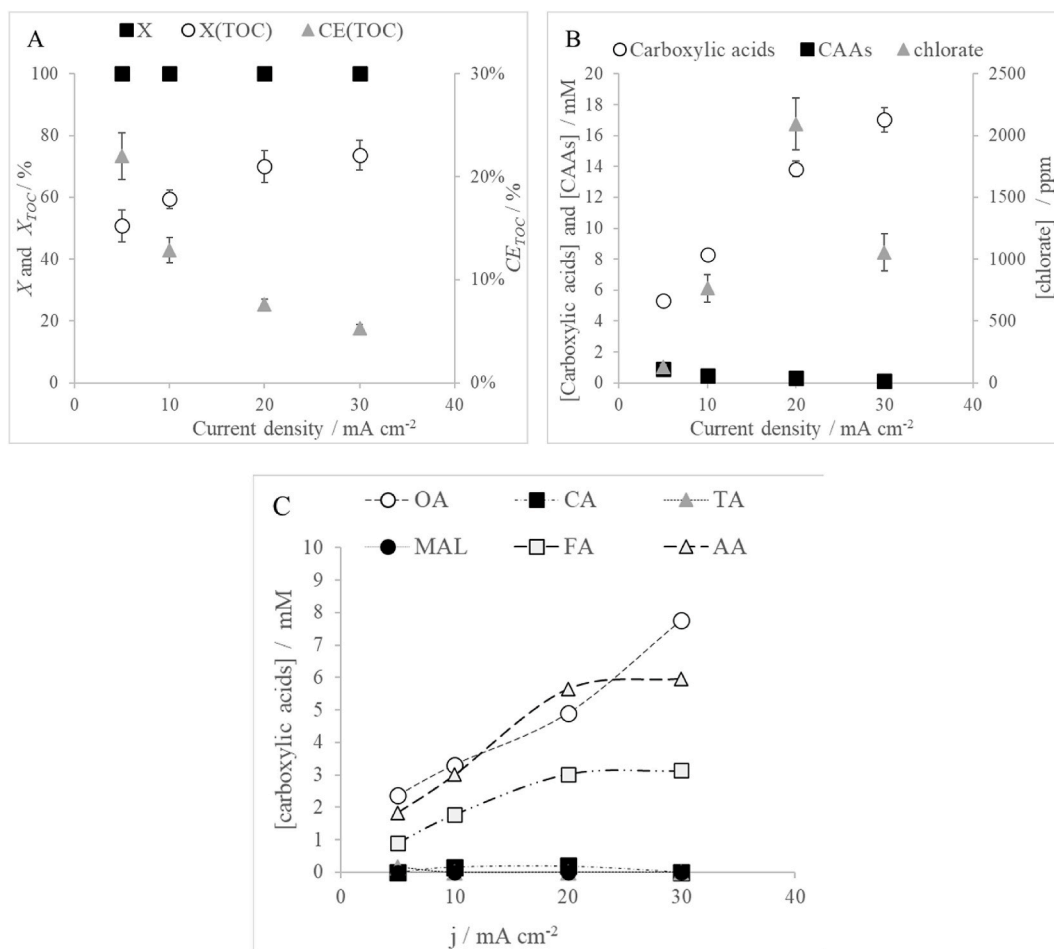


Fig. 4. Effect of j on X , X_{TOC} and CE_{TOC} (Fig. 4A), on the concentration of total carboxylic acids, CAAs and chlorate (Fig. 4B) and on the concentration of the detected carboxylic acids (Fig. 4C) for the electrolyses performed in an undivided microfluidic cell under the following operative conditions: BDD anode, Ni cathode and $Q = 0.1 \text{ mL min}^{-1}$. Standard deviations are reported in the form of error bars.

and Sathyanarayana, 1987] and may involve the adsorption of chlorate radical (Eq. (20)) and its reaction with $\text{HO}\bullet$ [Long et al., 2021]:



In conclusion, the electrolysis performed in the conventional batch cell resulted in very good removals of both phenol and TOC but in a significant generation of chlorinated by-products. Moreover, the process presents the drawback to be performed under batch conditions that could affect the ease of integration with other processes used for the treatment of wastewater which are in most of cases carried out under a continuous mode.

3.2. Electrolyses performed in microfluidic cells

Some electrolyses were performed in the microfluidic cell ($h = 145 \mu\text{m}$, $j = 10 \text{ mA cm}^{-2}$ and $Q = 0.1 \text{ mL min}^{-1}$). The water solution of phenol and NaCl was fed to the cell for a single passage under continuous mode. For the sake of comparison, experimental conditions very similar to that used in the macro cell (see section 3.1) were selected in terms of j , composition of the solution and electrodes. However, the ratio between the anodic surface and the volume of the solution present in the cell was close to 0.04 and to 70 cm^{-1} in the macro and the microfluidic cells, respectively, and, as a consequence, in the macro device the solution volume required a very long residence time to achieve high TOC removals; conversely in the microfluidic cell, a residence time τ of the

solution close to 35 s took place. Hence, the impact of slow chemical steps is expected to be completely different in the two systems.

Despite the small τ used, an effective treatment of the solution was obtained. Indeed, the experiments performed in the micro cell gave a complete removal of phenol and a X_{TOC} slightly lower than 60% with a CE_{TOC} close to 12%. Carboxylic acids (including oxalic, formic, maleic, citric and acetic acids), CAAs and chlorate were detected. In particular, oxalic acid was the carboxylic acid with the highest concentration. Conversely, no presence of chlorophenols and perchlorate was observed.

Fig. 3 compares the results obtained in the macro and in the micro devices. In order to compare results obtained in these very different devices, the same current density and electrolyte compositions were used. According to the literature, the comparison was performed considering the results obtained in the two devices for the treatment of the same volume of the synthetic wastewater [Scialdone et al., 2014b]. In particular, the results obtained to treat 75 mL of solution with the same value of X_{TOC} ($\sim 58\%$) were first considered. In the micro cell, to obtain this X_{TOC} for 75 mL of solution, a charge passed close to 1870 C and a time close to 17 h is necessary. Conversely, the macro cell requires, to treat the same volume of solution and achieve the same X_{TOC} , a larger time (24 h) and charge passed (2580 C, about 137% of that involved in the microfluidic reactor); hence, the micro cell allowed to achieve a higher CE_{TOC} (12 vs. 9%) (Fig. 3A).

As shown in Fig. 3B, a higher concentration of OA was found in the micro device. Moreover, in the microreactor very low concentrations of formic, maleic, citric and acetic acids were detected that were not found at the end of the tests performed in the macro cell. Conversely, in the

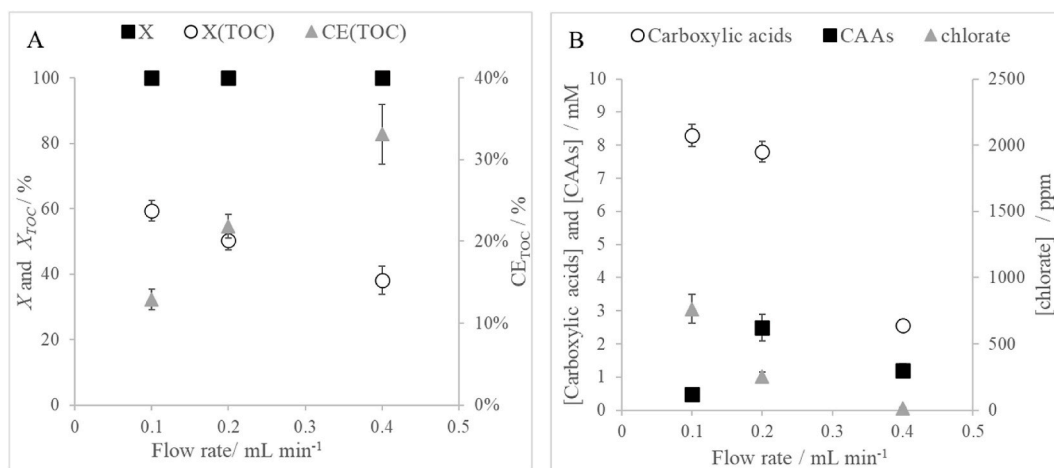


Fig. 5. Effect of Q on X , X_{TOC} and CE_{TOC} (Fig. 5A) and on the final concentration of carboxylic acids, CAAs, and chlorate (Fig. 5B). Electrolyses were operated at 10 mA cm^{-2} in the microfluidic cell with a BDD anode and a Ni cathode. Standard deviations are reported in the form of error bars.

microdevice a smaller concentration of CAAs and chlorate was observed with respect to the macro one. Moreover, while the macro device resulted in a very small but appreciable generation of perchlorate, no presence of this toxic compound was detected in the microfluidic cell. Prompt by these promising results, we decided to evaluate the effect of numerous operative conditions to further improve the performances of the microfluidic reactor.

3.2.1. Effect of current density

The performances of the electrochemical treatment of organics in water solutions of NaCl strongly depends on the current density [Scialdone et al., 2021]. Indeed, at BDD anodes, in conventional macro cells, larger j s are reported to give higher abatements of TOC, CAAs and carboxylic acids, but a larger production of ClO_3^- and ClO_4^- . To evaluate the effect of j in the case of the micro device, a set of electrolyses was operated at 0.1 mL min^{-1} with various j s in the range $5\text{--}30 \text{ mA cm}^{-2}$.

The removal of phenol was complete for any value of j . Conversely, X_{TOC} strongly depended on j (Fig. 4A). The increase of j from 5 to 10, 20 and 30 mA cm^{-2} resulted in an increase of X_{TOC} from 51 to 56, 69 and 75%, because of the larger Q , but in a decrease of CE_{TOC} from 22 to 13, 8 and 5%, due to the higher impact of oxygen evolution that is favored by both the high values of j and the small residual organic content in the final part of the reactor. The value of j had a great impact also on the final concentration of the main by-products. The overall concentration of carboxylic acids increased with j (Fig. 4B) due to the fact that at higher j s the large charge passed (Q_{pass}) allowed a larger conversion of phenol to carboxylic acids. In particular, for the highest values of j (20 and 30 mA cm^{-2}) higher concentrations of small molecules such as oxalic (OA), formic (FA) and acetic (AA) acids (Fig. 4C) were found as a result of the larger charge passed that allowed to convert all large molecules (namely citric (CA), malonic (MAL) and tartaric (TA) acids) in smaller ones. As observed in Fig. 4B, the total concentration of CAAs strongly decreased upon enhancing j presenting a value close to 0.87 and 0.13 mM for 5 and 30 mA cm^{-2} , respectively, because of the ability of BDD to mineralize CAAs for sufficiently large charge passed [Bagastyo et al., 2011; Hao et al., 2022a; Jasper et al., 2016]. It is worth to mention that the plot of the concentration of chlorate vs. j gave a maximum for a j close to 20 mA cm^{-2} . To understand this result, it is useful to remember that the generation of chlorate should increase with Q ; however, chlorate is expected to be partially reduced to chlorides at Ni cathodes. In particular, in microfluidic channels the cathodic reduction of chlorates is likely to be easier due the small inter-electrode distance. Moreover, no formation of perchlorate was detected in all these electrolyses in spite of the relatively large Q_{pass} for the electrolyses performed at the highest adopted j . In particular, the operative conditions used for the

experiments performed at 30 mA cm^{-2} would require a charge passed of 5600 C to treat 75 mL of solution, slightly larger than that used to treat 75 mL of the solution in the macro cell under the operative conditions reported in Fig. 1 for a time passed of 48 h. It is interesting to observe that, in the macro cell, this amount of charge passed resulted in a significant generation of perchlorate (about 220 ppm) (Fig. 2B), while in the micro cell no perchlorate was found. The absence of generation of perchlorate in the microdevice at all adopted j s is a quite interesting and novel result that can be due to various reasons such as: (i) the small τ which reduces the impact of both electrochemical and chemical steps involved in its formation and/or the small inter-electrode distance that (ii) can facilitate the cathodic reduction of perchlorate and (iii) increase the local concentration of organics, thus minimizing the concentration of both active chlorine and chlorate and, as a consequence, their oxidation to perchlorate.

3.2.2. Effect of flow rate

The effect of Q on the mineralization of phenol was evaluated by carrying out some experiments with j equal to 10 mA cm^{-2} and Q of 0.1, 0.2 and 0.4 mL min^{-1} . The change in Q results in an important modification of both the τ and the charge passed. In particular, τ was 36, 18 and 9 s for 0.1, 0.2 and 0.4 mL min^{-1} , respectively. The increase of Q gave quite interestingly results (Fig. 5): it resulted in a moderate decrease of the TOC removal and in a strong increase of CE_{TOC} (Fig. 5A); when Q was increased from 0.1 to 0.2 and 0.4 mL min^{-1} , X_{TOC} was 59, 50 and 38% and CE_{TOC} about 13, 22 and 33%. In all the cases, no phenol, chlorophenols and perchlorate were found at the exit of the micro-reactor and a dramatic decrease of chlorate concentration was observed upon increasing Q : indeed, the concentration of chlorate was 760, 250 and 15 ppm for Q of 0.1, 0.2 and 0.4 mL min^{-1} , respectively (Fig. 5B). The experiments performed at 0.4 mL min^{-1} gave also a quite small concentration of OA and of other carboxylic acids (Fig. 5B). For CAAs, a maximum for an intermediate Q of 0.2 mL min^{-1} was found.

To better evaluate the role of Q , numerous experiments were carried out changing both the j (5, 10, 20 and 30 mA cm^{-2}) and the Q (0.1, 0.2 and 0.4 mL min^{-1}), thus giving rise to 12 different combinations of these two key parameters. For all these operative conditions, a complete removal of phenol was achieved coupling with the absence of chlorophenols. Various interesting results are reported in Fig. 6. For 5 mA cm^{-2} , the increase of Q gave a strong reduction of X_{TOC} (Fig. 6A); in particular, at 0.4 mL min^{-1} , X_{TOC} was just close to 20 % probably because the coupling of low j s and high Q s results in a too small amount of charge passed. For all the other adopted j s, the decrease of Q gave just a moderate decrease of X_{TOC} (Fig. 6A) and a marked increase of CE_{TOC} (Fig. 6B). The negative effect of increasing Q on X_{TOC} can be simply

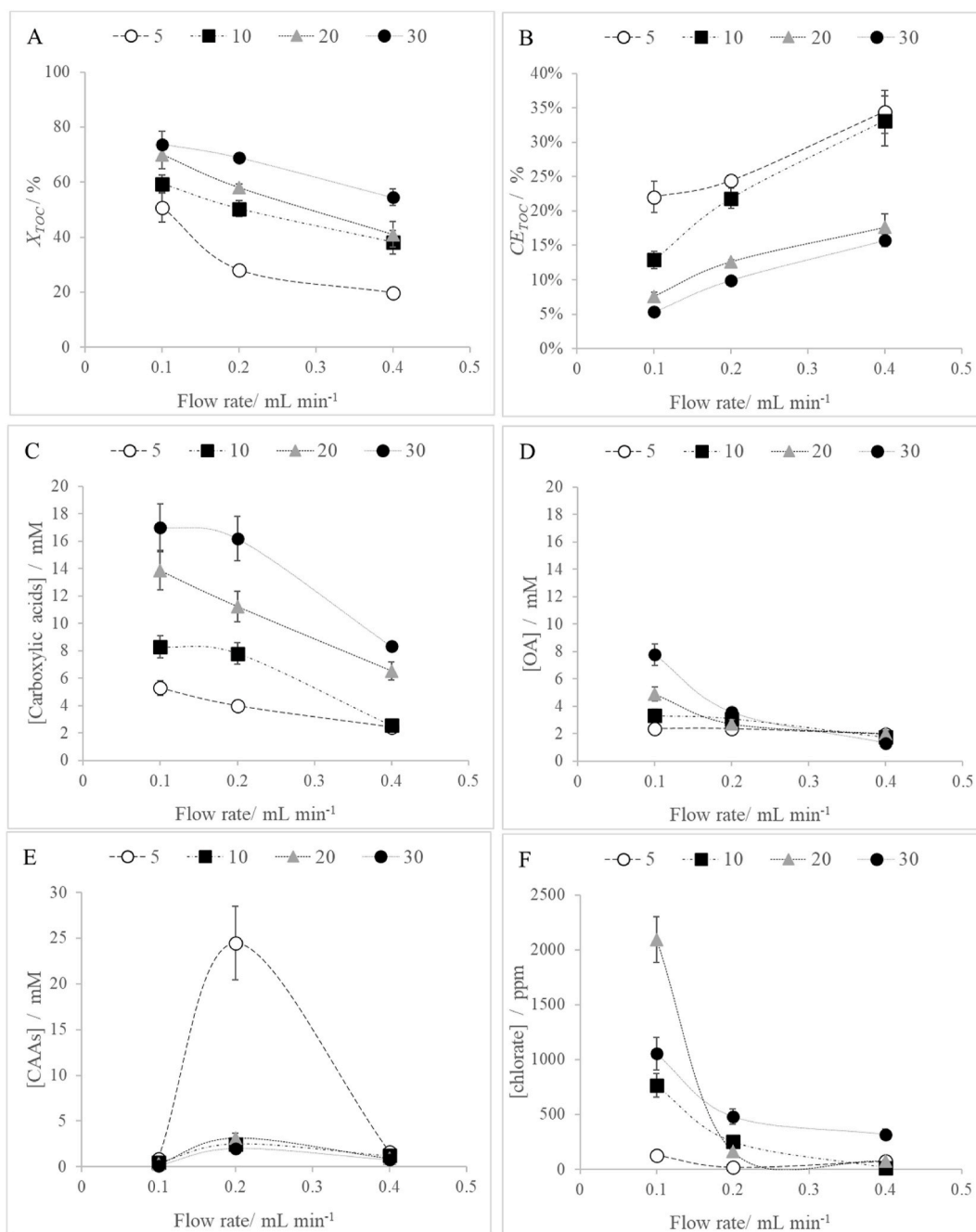


Fig. 6. Effect of Q and j on X_{TOC} (Fig. 6A), CE_{TOC} (Fig. 6B) and on the concentrations of total carboxylic acids (Fig. 6C), OA (Fig. 6D), CAAs (Fig. 6E) and chlorate (Fig. 6F). Electrolyses of aqueous solutions of phenol and NaCl in the microfluidic cell using a BDD anode and a Ni cathode. Standard deviations are reported in the form of error bars.

related to the lower τ (and the lower charge passed) while the positive effect on the current efficiency can be related to many factors: (i) the higher average organic content which favors the mineralization process with respect to the oxygen evolution; (ii) the positive effect of higher Q on the mass transfer of organics to the anode surface; (iii) the easier transport of gas bubbles at high flow rates, thus reducing the coverage of the anode by oxygen and CO_2 bubbles. As shown in Fig. 6C and D, the increase of Q (and consequently the decrease of both τ and charge passed) resulted in a decrease of the concentration of carboxylic acids and, in particular of OA. For all the adopted j , the overall concentration of CAAs vs. Q gave a curve with a maximum for 0.2 mL min^{-1} (Fig. 6E). This result is in part similar to that observed in conventional cells, where it was observed that the overall concentration of CAAs vs. charge (and

time) passed presents a curve with a maximum, as a result of the competition between the formation of these compounds (which prevail in the first part of the electrolyses) and its elimination (which prevails in the final part) [Hao et al., 2022a]. More in detail, in the case of electrolyses performed under a continuous mode in the microfluidic channel, the results shown in Fig. 6E indicate that the Q (and consequently the τ) affects the concentration of CAAs more than the j and the charge passed (except at 0.2 mL min^{-1}). Fig. 6F reports the combined effect of Q and j on the final concentration of chlorate. A smaller effect of j was observed if compared to that of Q . It was observed that:

- for the same value of j , the higher the Q the lower the concentration of chlorate, due to the smaller τ ;

Table 1

Comparison between experiments that involve different j and Q and the same amount of charge passed.

| Operative conditions | X_{TOC} (%) | CE_{TOC} (%) | Carboxylic acids (mM) | CAAs (mM) | Chlorate (ppm) |
|------------------------------------------------------|----------------------|-----------------------|-----------------------|-----------|----------------|
| 5 mA cm ⁻² ; 0.1 mL min ⁻¹ | 51 | 22 | 5.3 | 0.9 | 129 |
| 10 mA cm ⁻² ; 0.2 mL min ⁻¹ | 50 | 22 | 7.8 | 2.5 | 253 |
| 10 mA cm ⁻² ; 0.1 mL min ⁻¹ | 59 | 13 | 8.3 | 0.5 | 764 |
| 20 mA cm ⁻² ; 0.2 mL min ⁻¹ | 58 | 13 | 11.2 | 3.1 | 163 |

- in most of cases, the higher the j the higher the amount of chlorate because the larger time and charge passed; the most relevant exception to this trend was the experiment performed at 0.1 mL min⁻¹ and 30 mA cm⁻² that involved the largest amount of charge passed but gave a lower concentration of chlorate with respect to the tests operated at the same Q at 10 and 20 mA cm⁻².

This result can be attributed to the fact that a part of chlorate is likely to be reduced at the cathode.

It is interesting to mention that similar amounts of charge passed can be achieved using different combinations of Q and j . Two combinations that gives the same amount of charge passed are reported in Table 1.

As shown, the results obtained for the same amount of charge passed using the operative conditions reported in lines 1–2 (set 1) and lines 3–4 (set 2) are compared. The first set resulted in similar abatements of TOC and CE_{TOC} , thus showing that these figures of merit strongly depend on the charge passed. However, different concentrations of various by-products, including carboxylic acids, CAAs and chlorate, were observed, thus showing that the generation of these compounds depends not only on the charge passed but also on the specific values of Q (and of τ) and j . In particular, lower concentrations of carboxylic acids, CAAs and chlorate were obtained decreasing j and Q . Concerning the second set of experiments, where a double value of the charge passed respect to the first one, also in this case, similar removals of TOC and CEs were obtained, but the increase of the Q and j allowed to increase the concentrations of carboxylic acids and CAAs and not of chlorate.

3.3. Electrolyses performed with Ag cathode

Some authors have recently shown that the electrochemical treatment of wastewater contaminated by organics in the presence of NaCl is affected by the nature of the cathode [Cotillas et al., 2015; Hao et al., 2022a]. In particular, the use of Ag cathodes can reduce the CAAs concentration by their cathodic reduction (see Eqns. (22)–(24)).



Hence, some electrolyses were repeated in the presence of Ag cathode at 0.2 mL min⁻¹ and different j in the range 5–30 mA cm⁻². The presence of the Ag cathode allowed to achieve X_{TOC} and CE_{TOC} similar or even higher than that obtained at Ni (Fig. 7A and B). In particular, a maximum value of X_{TOC} close to 76 % was reached at Ag at 20 mA cm⁻² (Fig. 7A). According to the literature [Hao et al., 2022a], Ag cathode favors the de-halogenation of halogenated organics such as CAAs converting them in substances that can be more easily oxidized at BDD anode. Indeed, as shown in Fig. 7C, the use of Ag cathode reduced

drastically the overall concentrations of CAAs. At 5 mA cm⁻², the total concentration of CAAs was about 25 and 1.1 mM at Ni and Ag cathodes, respectively, while, at 20 mA cm⁻², it was about 3.1 and 0.3 mM, confirming the trend of lower concentrations at higher j . Fig. 7D shows the concentrations of mono (CA), di- (DCA) and trichloroacetic (TCA) acids achieved at Ni and Ag cathodes. At Ni, CA prevails at 5 mA cm⁻² while DCA at the other j s. In particular, DCA presented a maximum concentration at 20 mA cm⁻². At Ag cathode, all the 3 CAAs presented lower concentrations with respect to that observed at Ni for each value of j . In particular CA is never present and DCA was present only at 5 mA cm⁻², while TCA presented concentrations close to 0.3 mM at all the adopted values of j . It is worth to mention that the use of Ag allowed to have also smaller concentrations of the carboxylic acids (Fig. 7E) and chlorate (Fig. 7F) with respect to Ni, especially at higher j . However, at the lowest adopted j (5 and 10 mA cm⁻²) at Ag cathode the presence of perchlorate was detected even if in very low concentrations (<10 ppm).

The results obtained with Ag cathode, 0.2 mL min⁻¹ and 20 mA cm⁻² (in the following called “*optimized microcell*”) were compared with that achieved in the macro cell and in the microfluidic reactor equipped with Ni under the operative conditions discussed in section 3.2 and reported in Fig. 3.

The charge passed for the treatment of 75 mL of solution is 2592 C and slightly less than 1900C for the macro and the micro cell, respectively. As shown in Fig. 3A and B, the coupled use of the microfluidic apparatus, of more optimized operative conditions and of an Ag cathode (*optimized microcell*) allowed to significantly improve the results with respect to that achieved in the macro cell operated under usual conditions. Indeed, a drastic higher removal of TOC (about 76 vs 57%) and a higher CE_{TOC} (17 % vs. 9 %) were obtained in the *optimized microcell* with respect to the macro cell operated under conventional operative conditions (Fig. 3A). Moreover, the *optimized microcell* consented to reduce the concentrations of CAAs and chlorate (Fig. 3B).

4. Conclusions and next steps

In this work, the purification of water contaminated by phenol by electrogenerated active chlorine was investigated, for the first time, up to our knowledge, in an undivided microfluidic cell, equipped with very low inter-electrode distance (145 μm). A BDD anode and a Ni or an Ag cathode were utilized. It was shown for the first time, up to our knowledge, that the use of the microfluidic cell allows, under most tested operative conditions, to avoid the production of perchlorate and that the concentration of chlorate can be reduced using higher flow rates (as an example, at 10 mA cm⁻¹, 764 ppm at 0.4 mL min⁻¹ vs. 15 ppm at 0.1 mL min⁻¹), that give rise also to higher current efficiencies (33% at 0.4 mL min⁻¹ vs. 13% at 0.1 mL min⁻¹). Moreover, the use of Ag cathode in the microfluidic cell results in a significant reduction of the concentrations of CAAs (as an example, at 10 mA cm⁻¹, 253 ppm at Ni vs. 88 ppm at Ag) and, in a minor amount, of other by-products. More in general, higher current densities give rise to higher removals of TOC and to lower concentrations of chloroacetic acids, but to lower current efficiencies.

The use of the microfluidic device allowed to perform the process with good results under continuous conditions for a single passage of the solution in the reactor. The adoption of continuous conditions could be, in particular, quite interesting in the frame of a potential integration with other processes used for the treatment of wastewater which are in most of cases carried out under a continuous mode.

These results probably will prompt other investigations aimed to explore more in depth the potentialities of microfluidic cells for the electrochemical generation of active chlorine. In particular, it will be useful to use such devices with other cathodes and inter-electrode distances, as well as to use them for disinfection of water contaminated by microorganisms.

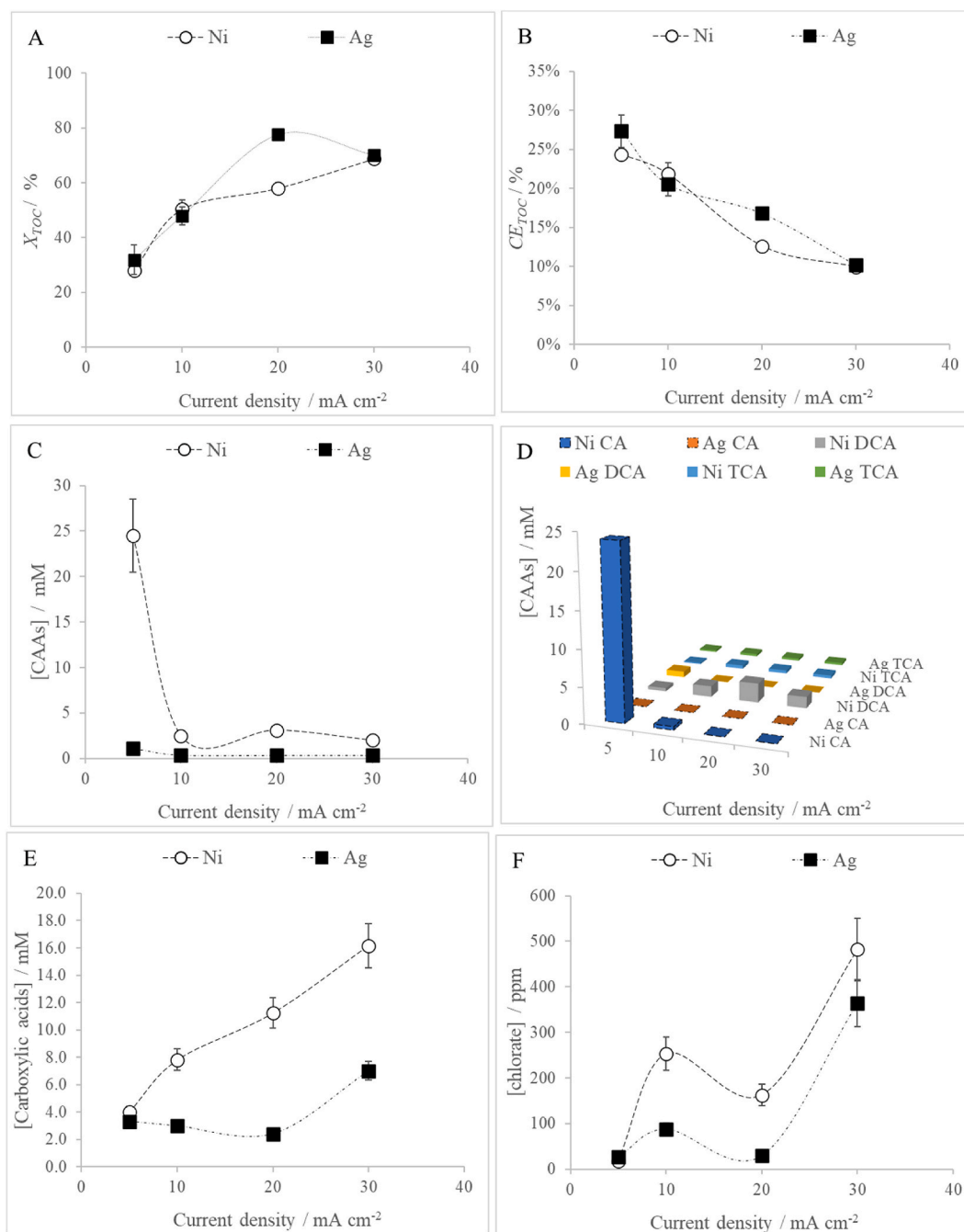


Fig. 7. Comparison between results obtained at Ag and Ni cathode under the same operative conditions. Electrolyses operated in the microfluidic cell at BDD anode, with $Q = 0.2 \text{ mL min}^{-1}$. Standard deviations are reported in the form of error bars.

CRediT authorship contribution statement

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

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.

Data availability

Data will be made available on request.

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