Research Article

Treatment of aqueous solutions of oxytetracycline by different electrochemical approaches: anodic oxidation, pressurized electro-Fenton and oxidation by electrogenerated active chlorine

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Abstract

The tetracycline group (TCs) includes the most common antibiotics for treatment of both human and animal infections. TCs are resistant to biological degradation; hence, conventional wastewater treatments are unable to remove these contaminants. Here, the utilization of different electrochemical processes, such as electro-Fenton (EF), direct anodic oxidation (AO) and indirect oxidation by electrogenerated active chlorine (EAC), for the treatment of aqueous solutions of oxytetracycline (OTC), which is one of the TCs, was studied. The effect of various operating conditions was evaluated to optimize the selected processes. EAC gave the fastest abatement of OTC, but the lowest removal of TOC and formation of chlorate. However, the utilization of carbon felt cathodes allowed the formation of chlorate to be reduced. AO gave the highest TOC removals, but it required the use of an expensive anode, as BDD, and high cell potentials. EF performed with pressurized-air (5–10 bar) presented intermediate removals of OTC and TOC with respect to AO and EAC and consumed the least energy.
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INTRODUCTION

In the last decade, it has been demonstrated that wastewater contaminated by organic pollutants resistant to conventional biological processes can be effectively treated by different electrochemical approaches including anodic oxidation (AO), electro-Fenton (EF) and oxidation by electrogenerated active chlorine (EAC). Moreover, these processes can be performed under mild operative conditions, such as room temperature (RT) and low pressures, and do not require the transport and storage of chemical oxidants. AO gives in most cases the highest abatements of organics and total organic carbon (TOC), but it often requires the use of an expensive anode, such as boron doped diamond (BDD).[1,2] In particular, at nonactive anodes, such as BDD (denoted as M in the following equations), the oxidation of organics takes place mainly by physisorbed hydroxyl radicals (M($^{\bullet}$OH)) [Eqn (2)] formed at the anode surface by the oxidation of water [Eqn (1)].[1]

$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^- \qquad (1)$$

$$a\,M(^{\bullet}OH) + R \rightarrow M + mCO_2 + nH_2O + xH^+ + e^- \qquad (2)$$
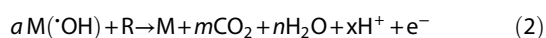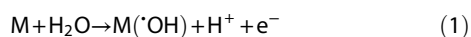
EF uses the oxidant ability of hydroxyl radicals produced, in the presence of catalytic amounts of Fe(II), by hydrogen peroxide (H_2O_2) [Eqn (4)] generated by cathodic conversion of oxygen (O_2) [Eqn (3)].[3,4] EF is usually performed with cheap carbon cathodes, but its performance can be limited by a slow production of H_2O_2 due to the low solubility of oxygen in water contacted with air at atmospheric pressure.

$$O_{2(g)} + 2\,H^+ + 2\,e^- \rightarrow H_2O_2 \qquad (3)$$
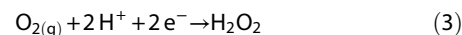
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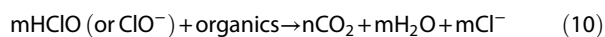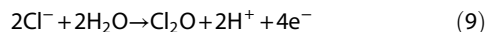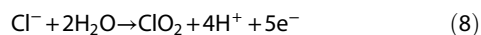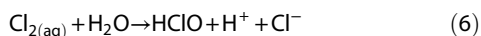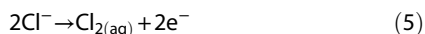
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$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^- \tag{4}$$
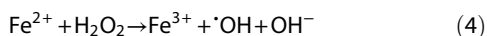
Another effective electrochemical route is oxidation by EAC. In this case, organic pollutants are oxidized by chlorinated oxidants produced by the anodic oxidation of chlorides, usually in the form of sodium chloride (NaCl, which is a cheap reagent present in many kinds of wastewater).[1,5,6] Indeed, the anodic oxidation of chlorides leads to the formation of dissolved chlorine [Eqn (5)] which is converted mainly into hypochlorous acid (HClO) [Eqn (6)] in moderate acidic conditions and hypochlorite (ClO$^-$) in basic ones [Eqn (7)]. Moreover, Cl_2O and ClO_2 can be formed by both chemical and electrochemical paths [Eqns (8) and (9)].[3,11] Equation (10) reports, as an example, the oxidation reaction by HClO or ClO$^-$.

$$2Cl^- \rightarrow Cl_{2(aq)} + 2e^- \tag{5}$$

$$Cl_{2(aq)} + H_2O \rightarrow HClO + H^+ + Cl^- \tag{6}$$

$$HClO \leftrightarrows H^+ + ClO^- \tag{7}$$

$$Cl^- + 2H_2O \rightarrow ClO_2 + 4H^+ + 5e^- \tag{8}$$

$$2Cl^- + 2H_2O \rightarrow Cl_2O + 2H^+ + 4e^- \tag{9}$$

$$mHClO\ (\text{or } ClO^-) + \text{organics} \rightarrow nCO_2 + mH_2O + mCl^- \tag{10}$$

However, this process can give rise to the formation of chlorinated toxic compounds, such as chlorinated aromatic substances, haloacetic acids (HAAs), chlorate and perchlorate, that can drastically enhance the toxicity of treated waters.[5]

Antibiotics are very important organic pollutants fed into the soil, surface waters and, therefore, in ground and drinking water from pharmaceutical factories, hospital discharge, and urine and excrement of humans and animals. The tetracycline group (TCs) includes the most common antibiotics for the treatment of both human and animal infections, such as oxytetracycline (OTC). TCs are resistant to biological degradation; hence, conventional wastewater treatment methods are unable to remove these contaminants. Moreover, the presence of tetracyclines in several environmental matrices has been reported because of their resistance to biodegradation.[7]

It recently has been shown that various electrochemical processes can treat wastewater contaminated by TCs and, in particular, OTC.[8-15] Its anodic oxidation was evaluated at various anodes including Ti/Ta$_2$O$_5$-IrO$_2$,[7] RuO$_2$,[8] platinized titanium,[9] SS316, SS316/β-PbO$_2$,[10] and BDD anodes.[11-13] All of these anodes allowed a very high removal of OTC. Unfortunately, for platinized titanium anodes and RuO$_2$, no data on the removal of the TOC were provided, whereas in the case of Ti/Ta$_2$O$_5$-IrO$_2$, an abatement of TOC close to 34% was obtained.[7] Conversely, in the case of BDD, a mineralization value higher than 70% was reported.[11] Sun *et al.* have shown that OTC also can be effectively removed using Ti-Sn-Sb/γ-Al$_2$O$_3$ particle electrodes.[14] However, lower removals of TOC were reported in comparison to that achieved using BDD.

Lai *et al.* have shown that OTC can be effectively removed also by the EF process using sodium hydroxide (NaOH)-activated carbon felt.[15] Likewise, Hasani *et al.* have reported that EF can be used to remove OTC.[10] However, few data on mineralization were reported in these studies. Moreover, the possibility of coupling EF and anodic oxidation was studied using an iron oxychloride-integrated graphite felt cathode and a sub-stoichiometric titanium oxide (Ti$_4$O$_7$)-based porous reactive electrochemical membrane (REM) anode.[16] Conversely, fewer studies have reported on the treatment of OTC by EAC. However, it was shown that the addition of chlorides at different anodes enhanced the removal of OTC, even if a low removal of TOC was observed.[7,9]

In this work, the removal of OTC in aqueous electrolyte was investigated by a large series of experiments to compare the performances of three different electrochemical processes: AO, EF and oxidation by EAC. Moreover, the performances of EF were boosted using pressurized air (5–10 bar) whereas that of EAC using proper cathodes was able to enhance the effectivity of such a process.

EXPERIMENTAL SECTION

Electrolyses

Most of electrolyses were performed in an undivided glass cell with magnetic stirring equipped with a BDD (Condias, Itzehoe, Germany) or Ti/IrO$_2$-Ta$_2$O$_5$ (commercial DSA®; De Nora SpA, Milan, Italy) anode with a wet surface close to 3.5 cm^2 and stainless steel, silver (Ag; Carlo Erba Reagents, Emmendingen, Germany) or carbon felt (*CF*; Carbon Lorraine/CL Brakes, Gennevilliers, France) cathodes. The volume of solution was 75 mL. The stirring rate was set at 400 rpm. Some EF experiments were performed with an undivided high-pressure cell composed of AISI 316 stainless steel with a coaxial cylindrical geometry.[17,18] A borosilicate-glass beaker was sited inside the reactor storing electrolyte. The upper part of the cell was equipped with a gas inlet, a vent, two electrical connections for the electrodes and a dip tube that allows extraction of liquid samples during the experiment. A manometer was used to control the operating pressure. Air (Alphagaz™ 1, purity 99.999%; Air Liquide, Paris, France) was used to fill the reactor until it reached the desired operative pressure. Pressure effect was studied at 1, 5 and 10 bar. Under pressurized conditions, the volume of solution was 50 mL and the electrodes were immersed in the electrolyte inside the beaker with an inter-electrode gap of 1 cm. The anode was Ti/IrO$_2$-Ta$_2$O$_5$ (commercial DSA®; De Nora SpA) with a total front wet area of 3.5 cm^2, whereas the cathode was *CF* (Carbon Lorraine) with a total wet area of 3.5 cm^2. Electrolyses were performed in amperostatic conditions (2053 potentiostat/galvanostat; Amel S.r.l., Milan, Italy) at RT. All of the experiments were repeated at least twice, giving rise to a good reproducibility of results (±4%).

Reagents and analyses

Bi-distilled water was used as solvent. OTC (Fig. 1) from Sigma Aldrich (Waltham, MA, USA) was used as a model compound of the TCs group. The initial OTC concentration was 100 mg L^{-1}, which corresponds to an initial TOC value of 50 mg$_{carbon}$ L^{-1}.

Sodium sulfate (Na$_2$SO$_4$) 0.100 mol L^{-1} (Janssen, Beerse, Belgium) or NaCl 1 mol L^{-1} (Sigma Aldrich) was used as supporting electrolyte. Sulfuric acid (H$_2$SO$_4$; Sigma Aldrich) and sodium
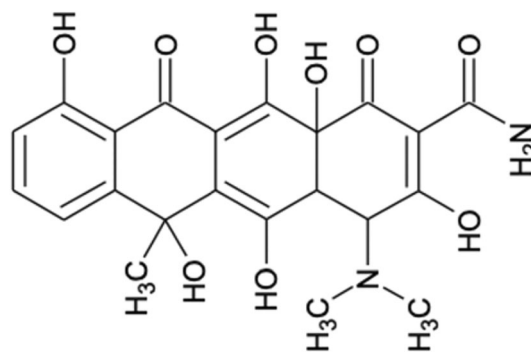

Figure 1. OTC chemical structure.

hydroxide (NaOH; Sigma Aldrich) were used to adjust the pH and ferrous sulfate (FeSO$_4$; AnalaR NORMAPUR; VWR International, Radnor, PA, USA) 0.27 mmol L^{-1} as catalyst at pH 3. The TOC was analyzed by a TOC-L CSH/CSN analyzer (Shimadzu, Kyoto, Japan). The concentration of OTC was evaluated from the decay of the absorbance at $\lambda = 354$ nm using Cary 60 UV-visible spectrophotometer (Agilent Technologies, Santa Clara, CA, USA. The concentration of chlorate was evaluated by ion chromatography (IC) analysis. A 882 compact IC (Metrohm, Herisau, Switzerland) was equipped with a Metrosep A Supp 5–250/4.0. Solutions of 1 mmol L^{-1} sodium bicarbonate (NaHCO$_3$) and 3.2 mmol L^{-1} sodium carbonate (Na$_2$CO$_3$)were used as standard eluent and flowed at 0.7 mL min^{-1}. Concentration of chloroacetic acids (HAAs) was evaluated by high-performance liquid chromatography (HPLC) using an Agilent 1260 fitted with a Kinetex 5 u C18 column (Phenomenex, Macclesfield, UK) at 25 °C and coupled with a UV detector working at 210 nm. A 25 mmol L^{-1} KH$_2$PO$_4$ (Sigma Aldrich) aqueous solution at pH 2.5 (H$_3$PO$_4$) was eluted at 0.5 mL min^{-1} as the mobile phase. The solution pH was measured with a Checker® pH Tester (HI98103) supplied by HANNA® instruments (Woonsocket, RI, USA). The abatement (e.g. the conversion) of the OTC, TOC, the current efficiency for the removal of the TOC (CE) and the energetic consumption (EC) were defined by Eqns (11)–(14), respectively.

$$\text{Abatement of OTC} = (C°_{OTC} - C_{OTC,t})/C°_{OTC} \qquad (11)$$

$$\text{Abatement of TOC} = (\Delta TOC)_t/TOC° \qquad (12)$$

$$CE_{TOC} = n\,F\,V\,C°_{OTC}\,X_{TOC}/It \qquad (13)$$

$$EC = I^* \Delta V\, t/mg_{TOC} \qquad (14)$$

where $C°_{OTC}$ and C_{OTC} are the OTC concentration (mol L^{-1}) at the time zero and at time t, respectively, $(\Delta TOC)_t$ is the decay of the TOC (mg$_{carbon}$ L^{-1}), TOC° is the initial concentration of the TOC (mg$_{carbon}$ L^{-1}) inside the electrochemical cell, n is the number of electrons exchanged for the oxidation of the organic pollutant to CO$_2$ ($n = 104$ for OTC), F is the Faraday constant (96 487 C mol^{-1}), I is the applied current intensity, ΔV is the cell potential, t is the electrolysis time and V is the volume of the cell.

RESULTS AND DISCUSSION

Removal of OTC by anodic oxidation (AO)

First experiments were performed in order to evaluate the utilization of AO for the remediation of water solutions of OTC. An aqueous solution of OTC (100 mg L^{-1}) and Na$_2$SO$_4$ (0.100 mol L^{-1}) was electrolyzed using Ti/Ta$_2$O$_5$-IrO$_2$ or BDD as anodes, under amperostatic conditions (60 mA cm^{-2}) with magnetic stirring (400 rpm) for 3 h (194 °C). Ti/Ta$_2$O$_5$-IrO$_2$ was chosen as an example of an inexpensive and stable anode, whereas BDD was used as according to the literature it is the most effective material for AO of organic pollutants. Stainless steel was chosen as cathode to favor the water reduction to hydrogen. As shown in Fig. 2(A), both anodes allowed a reduction in the concentration of OTC. However, at the Ir-based anode, after 3 h the removal of OTC was slightly lower than 50%. Conversely, at BDD the abatement of OTC was higher than 96% after 1.5 h. Figure 2(A) also reports the abatement of TOC. In the case of Ti/Ta$_2$O$_5$-IrO$_2$ a quite slow removal of TOC was observed ($\approx$10% after 3 h). Indeed, according to the literature, the anodic oxidation at Ti/Ta$_2$O$_5$-IrO$_2$ proceeds with the formation of many intermediates with a rather high

molecular weight.[7] Conversely, at BDD the electrolysis resulted in a very high abatement of TOC ($\approx$80% after 3 h).

Consequently, BDD gave a higher CE if compared to that achieved at Ti/Ta$_2$O$_5$-IrO$_2$ [Fig. 2(B)]. The oxidation process at BDD results, according to the literature, in the formation of quite short carboxylic acids as main byproducts (maleic, oxalic, fumaric and acetic acids), thus showing the ability of this anode to convert large molecules, such as OTC, into small molecules and CO$_2$. The large difference in the mineralization data achieved at these two anodes can be explained, according to the literature, considering that anodes can be grouped in active and inactive ones. According to the literature, the water discharge produced adsorbed hydroxyl radicals [Eqn (1)] that can, for active electrodes, give rise to the formation of the so-called higher oxide MO$_{x+1}$, due to a possible transition of oxygen from the radical to the oxide lattice [Eqn (15)].

$$MO_x(•OH) \rightarrow MO_{x+1} + H^+ + e- \qquad (15)$$
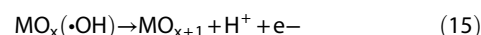
According to the literature, physically adsorbed •OH and higher oxide MO$_{x+1}$ are likely to favor different routes in the presence of oxidizable organic compounds.[1] The first should promote the complete combustion of organics in association with O$_2$ evolution, whereas the second is likely to give rise to selective oxidation of organics instead of mineralization. Active anodes, such as Ir ones, present higher oxide MO$_{x+1}$, thus favoring selective oxidation, whereas inactive anodes, such as BDD, are characterized by physisorbed •OH, thus favoring the mineralization pathway.

Moreover, according to the literature, in the presence of Na$_2$SO$_4$, the formation of other stronger oxidants, such as persulfate (S$_2$O$_8^{2-}$), can occur from the electro-oxidation of sulfate species, by both direct [Eqn (16)] or indirect [Eqn (17)] mechanisms considering that SO$_4^{•-}$ can be generated via reaction with heterogeneous free •OH, which is formed via water discharge [Eqn (1)].[20] These species also can aid the organic's mineralization. The formation of these species has been confirmed using BDD electrodes, whereas no such demonstration was achieved for the Ti/Ta$_2$O$_5$-IrO$_2$ anode.

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \qquad (16)$$

$$SO_4^{2-} + •OH \rightarrow 2SO_4^{2-} \rightarrow S_2O_8^{2-} \qquad (17)$$
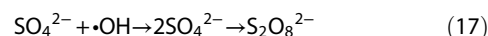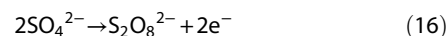
According to the literature, the AO of OTC can be favored by low pH.[7] Hence, some electrolyses were repeated with BDD at pH 3. However, just a slight increase in the removal of TOC was achieved with respect to the electrolyses performed without alteration of pH (from 81% to 84% after 3 h).

Removal of OTC by EF

In order to evaluate the EF process, some preliminary electrolyses were performed with a water solution of OTC (100 mg L^{-1}) and Na$_2$SO$_4$, at pH 3, a CF cathode and a Ti/Ta$_2$O$_5$-IrO$_2$ anode, under amperostatic conditions (60 mA cm^{-2}) and magnetic stirring (400 rpm) for 3 h (194 °C) both in the absence and in the presence of FeSO$_4$ catalyst at 1 bar [Fig. 3(A)].

As mentioned above, carbonaceous cathodes, such as CF, allow the reduce of oxygen to H$_2$O$_2$ [Eqn (3)], an oxidant that can contribute to the oxidation of organic pollutants. However, in the absence of iron, quite similar abatements of OTC (43% and 44%) and TOC ($\approx$10%) were obtained with stainless-steel and CF cathode. Indeed, OTC was reported to present a rather high chemical resistance. Hence, oxidants more powerful than H$_2$O$_2$ are
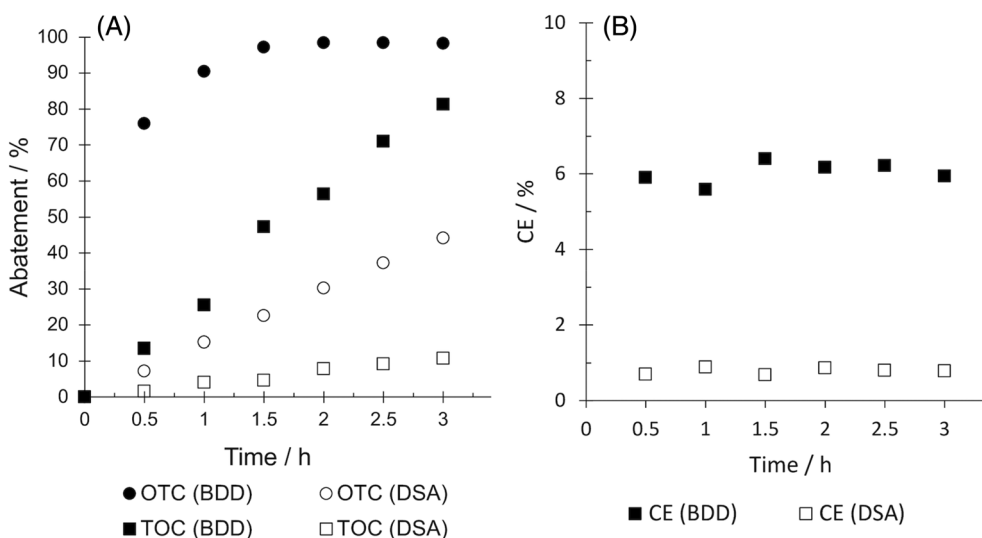
Figure 2. Abatement of OTC and TOC (A) and CE (B) achieved after 3 h by amperostatic electrolysis (60 mA cm^{-2}) of an aqueous solution of OTC and Na$_2$SO$_4$ with Ti/Ta$_2$O$_5$-IrO$_2$ or BDD anode, and stainless-steel cathode. Stirring rate = 400 rpm.
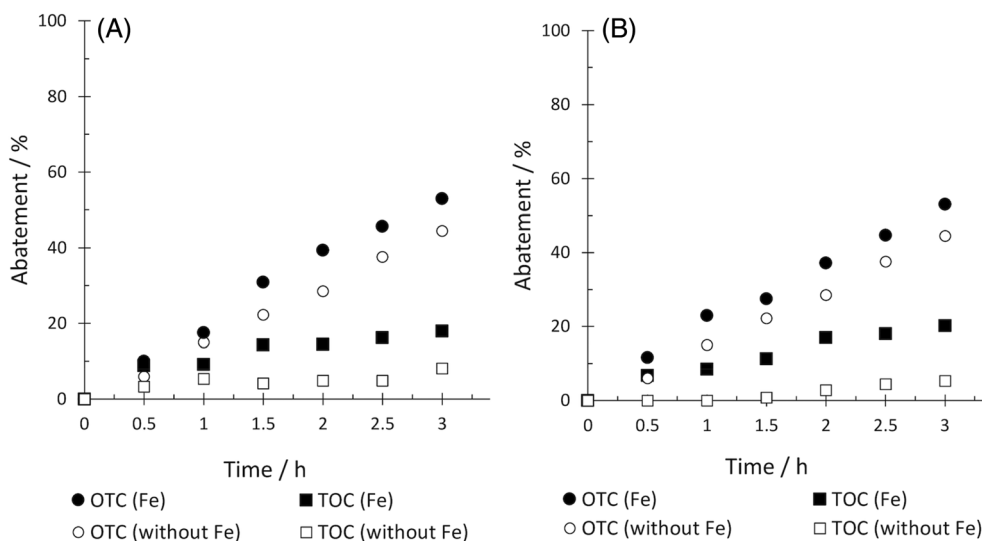

Figure 3. Abatement of OTC and TOC achieved after 3 h by EF by amperostatic electrolyses at (A) 60 mA cm^{-2} and (B) 10 mA cm^{-2} of an aqueous solution of OTC, Na$_2$SO$_4$ with Ti/Ta$_2$O$_5$-IrO$_2$ anode and carbon felt cathode in the absence and in the presence of FeSO$_4$. Stirring rate = 400 rpm.

required. When FeSO$_4$ was added to the solution, a significant enhancement of both OTC and TOC abatement was achieved, as a result of the formation of the more powerful oxidant hydroxyl radical [Eqn (4)]. Indeed, as shown in Fig. 3(A), after 3 h the removal of OTC was close to 45% and 51% in the absence and in the presence of iron, respectively. A more relevant effect of the iron catalyst on the removal of TOC was observed. Indeed, it was close to 10% and 17% in the absence and in the presence of iron, respectively.

According to the literature, better performance of the EF process is achieved by working at a lower current density than 60 mA cm^{-2}. Hence, electrolyses were carried out at a current density of 10 mA cm^{-2} with a water solution of OTC (100 mg L^{-1}) and Na$_2$SO$_4$, at pH 3, a *CF* cathode and a Ti/Ta$_2$O$_5$-IrO$_2$ anode, with magnetic stirring (400 rpm) for 3 h (194 °C) both in the absence and in the presence of FeSO$_4$ catalyst at 1 bar. As shown in

Fig. 3(B), at the end of the electrolyses, OTC abatement reached 45% and 53% in the absence and in the presence of iron, respectively, coupled with a TOC abatement of approximately 5% and 20%, respectively. It is highly interesting to note that the decrease in current density allows similar values of performance to be reached, but at a low value of charge passed, which consequently results in a significant enhancement of the CE. In detail, a CE of 9% and 1% was observed at 10 and 60 mA cm^{-2} in the presence of iron, respectively, after 3 h. This illustrates how low values of current density favor the EF process due to the formation of a higher amount of hydroxyl radical [Eqn (4)] with respect to the high current density value. However, the abatement of TOC was significantly lower than that achieved at BDD. Indeed, according to the literature, the treatment of OTC by EF proceeds with the formation of many high molecular weight by-products that need time to be oxidized.[15]
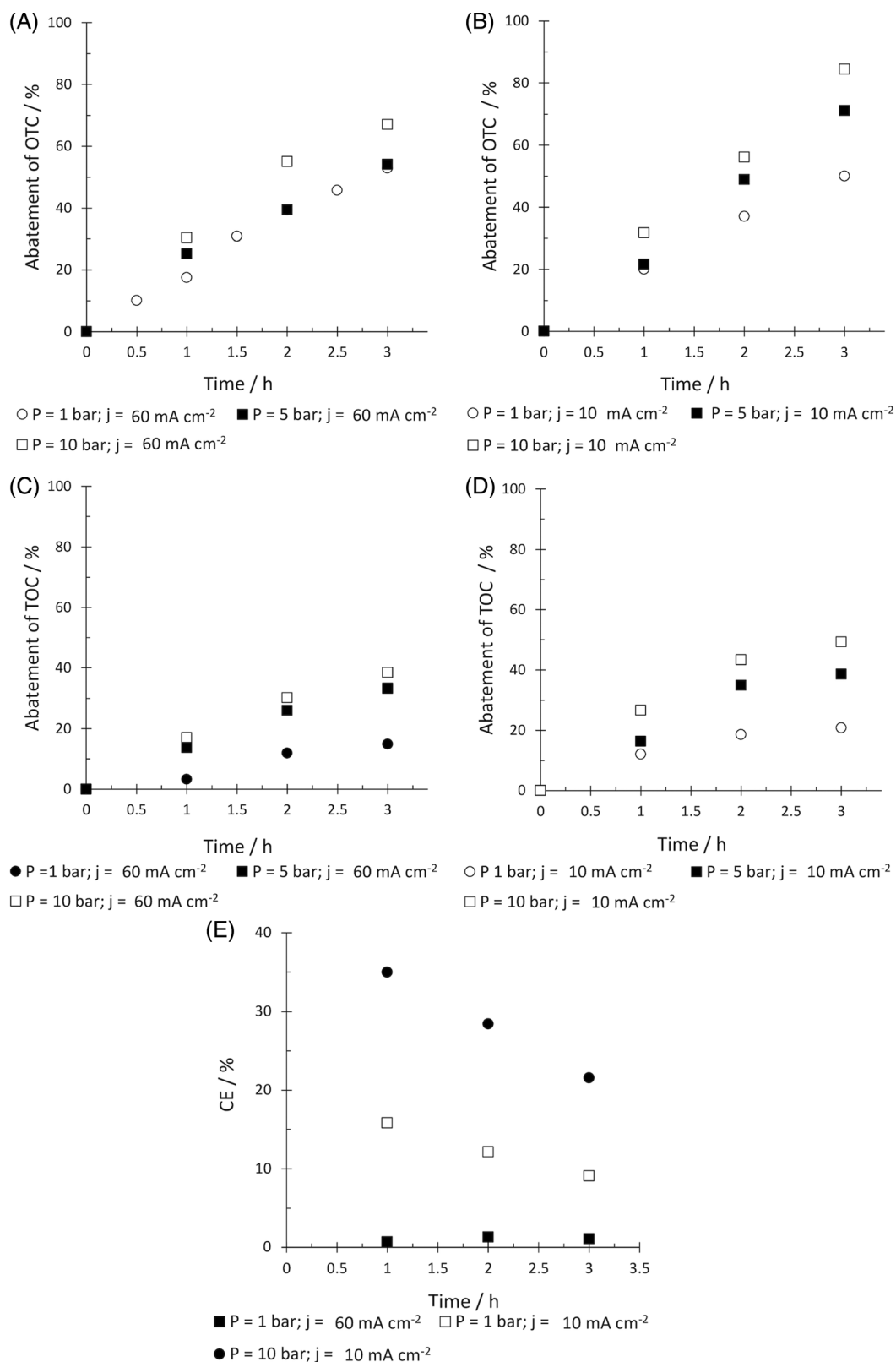
Figure 4. Effect of current density and air pressure (1, 5 and 10 bar) on the abatement of OTC (A and B), TOC (C and D) and CE (E) achieved by EF. Amperostatic electrolysis were carried out at a current density of 60 (A and C) or 10 mA cm^{-2} (B and D) with an aqueous solution of OTC, Na$_2$SO$_4$ and FeSO$_4$ with Ti/Ta$_2$O$_5$-IrO$_2$ anode and carbon felt cathode. Stirring rate = 400 rpm.

It recently has been shown that EF can strongly benefit from the utilization of pressurized air[17-19,21-23] and relatively low values of working potential and current density.[18,19] Hence, a series of electrolyses was carried out using a *CF* cathode, Ti/Ta$_2$O$_5$-IrO$_2$ anode, and different air pressures (1, 5 and 10 bar) and current densities (10 and 60 mA cm^{-2}).
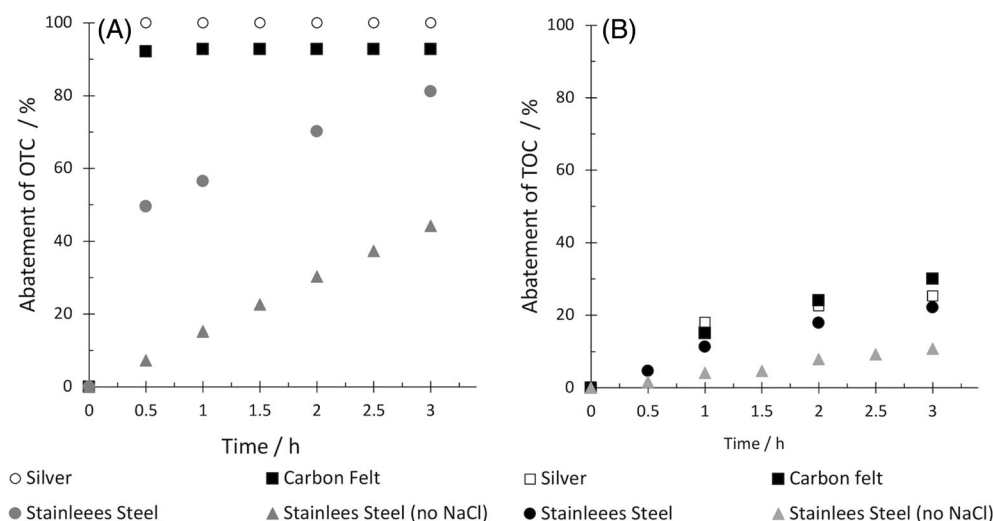
Figure 5. Abatement of OTC (A) and TOC (B) achieved after 3 h by amperostatic electrolyses (60 mA cm^{-2}) of an aqueous solution of OTC, Na$_2$SO$_4$ (0.1 mol L^{-1}) or NaCl (1 mol L^{-1}) with Ti/Ta$_2$O$_5$-IrO$_2$ anode, and stainless-steel, carbon felt or silver cathode. Stirring rate = 400 rpm.
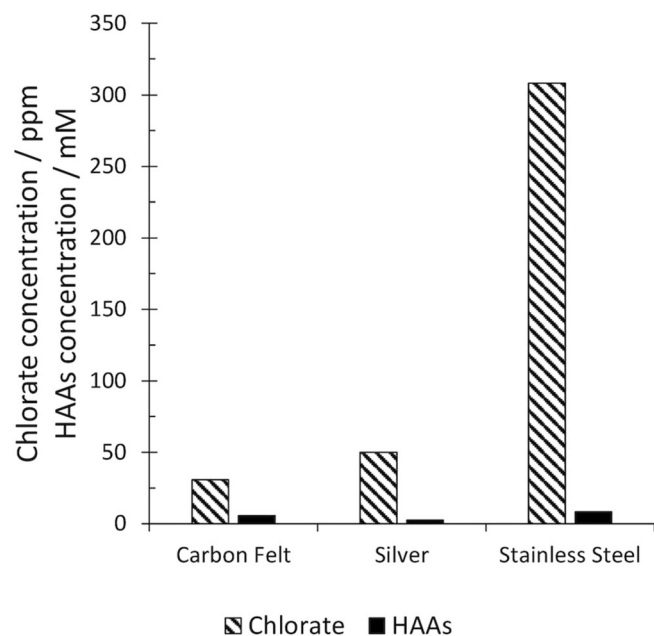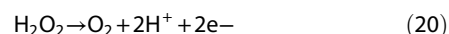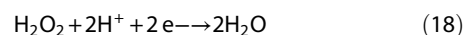

Figure 6. Final concentrations of chlorate and HAAs achieved after 3 h by amperostatic electrolyses (60 mA cm^{-2}) of an aqueous solution of OTC and NaCl (1 mol L^{-1}) with Ti/Ta$_2$O$_5$-IrO$_2$ anode, and stainless-steel, carbon felt or silver cathode. Stirring rate = 400 rpm.

As shown in Fig. 4, the increase of the pressure resulted in a significant enhancement of the abatement of both OTC and TOC. As an example, at 60 mA cm^{-2}, after 3 h a removal of OTC of 51%, 59% and 67% was observed at 1, 5 and 10 bar, respectively. The effect of the pressure on the removal of TOC was even more remarkable. Indeed, the increase of the pressure from 1 to 5 bar, enhanced the TOC removal after 3 h from 17% to 33%. When the electrolysis was repeated with a pressure of 10 bar, a removal of TOC ≈38% was obtained. According to the literature, the remarkable effect of pressure on the performance of EF is due to the fact that a higher air pressure results in higher solubilities of oxygen, thus increasing the generation of H$_2$O$_2$ and consequently that of hydroxyl radicals.[17,19,21-23]

Moreover, as shown in Fig. 4, a significant improvement of the performance of the EF process was obtained working at lower current densities. As an example, at 5 bar, the abatement of OTC and TOC at 60 mA cm^{-2} were 59% and 33%, respectively. When the current density was decreased to 10 mA cm^{-2} the abatement of OTC and TOC increased to 71% and 38%, respectively. To understand the effect of current density on EF, it is important to remember that H$_2$O$_2$ generated at the cathode surface is consumed by cathodic reduction [Eqn (18)], disproportionation [Eqn (19)] and, in undivided cells, anodic oxidation [Eqn (20)].

$$H_2O_2 + 2H^+ + 2e- \rightarrow 2H_2O \qquad (18)$$

$$2H_2O_2 \rightarrow O_2 + 2H_2O \qquad (19)$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e- \qquad (20)$$

High current densities result in more negative working potentials, thus enhancing the cathodic reduction of H$_2$O$_2$ [Eqn (18)] and decreasing its concentration in solution,[19] thus giving rise to a lower production of hydroxyl radicals by reaction (4).[18,19]

As shown in Fig. 4, the utilization of both relatively high pressures (10 bar) and low current density (10 mA cm^{-2}) resulted in a dramatic improvement of the performances of EF process. Indeed, at 1 bar and 60 mA cm^{-2}, the abatement of OTC and TOC were, respectively, 51% and 17%, whereas at 10 bar and 10 mA cm^{-2}, they were close to 85% and 50%, respectively (Fig. 4).

An even more drastic effect on current efficiency was observed: indeed, as shown in Fig. 4(E), at 1 bar and 60 mA cm^{-2}, CE was close to 1% for all of the experiments. The decrease of the current density to 10 mA cm^{-2} resulted in an increase of the final CE to about 9% because of the slight increase of the TOC removal (from 19% to 22%) and, in a more relevant way, of the lower amount of charge passed. Moreover, at 10 mA cm^{-2} and 10 bar, the final CE was higher than 20% because of the drastic increase of the removal of TOC (from 21% to ≈50%).

Removal of OTC by EAC

The oxidation of OTC by EAC was first studied with a water solution of OTC (100 mg L^{-1}) and NaCl (1 mol L^{-1}), at pH 3, a
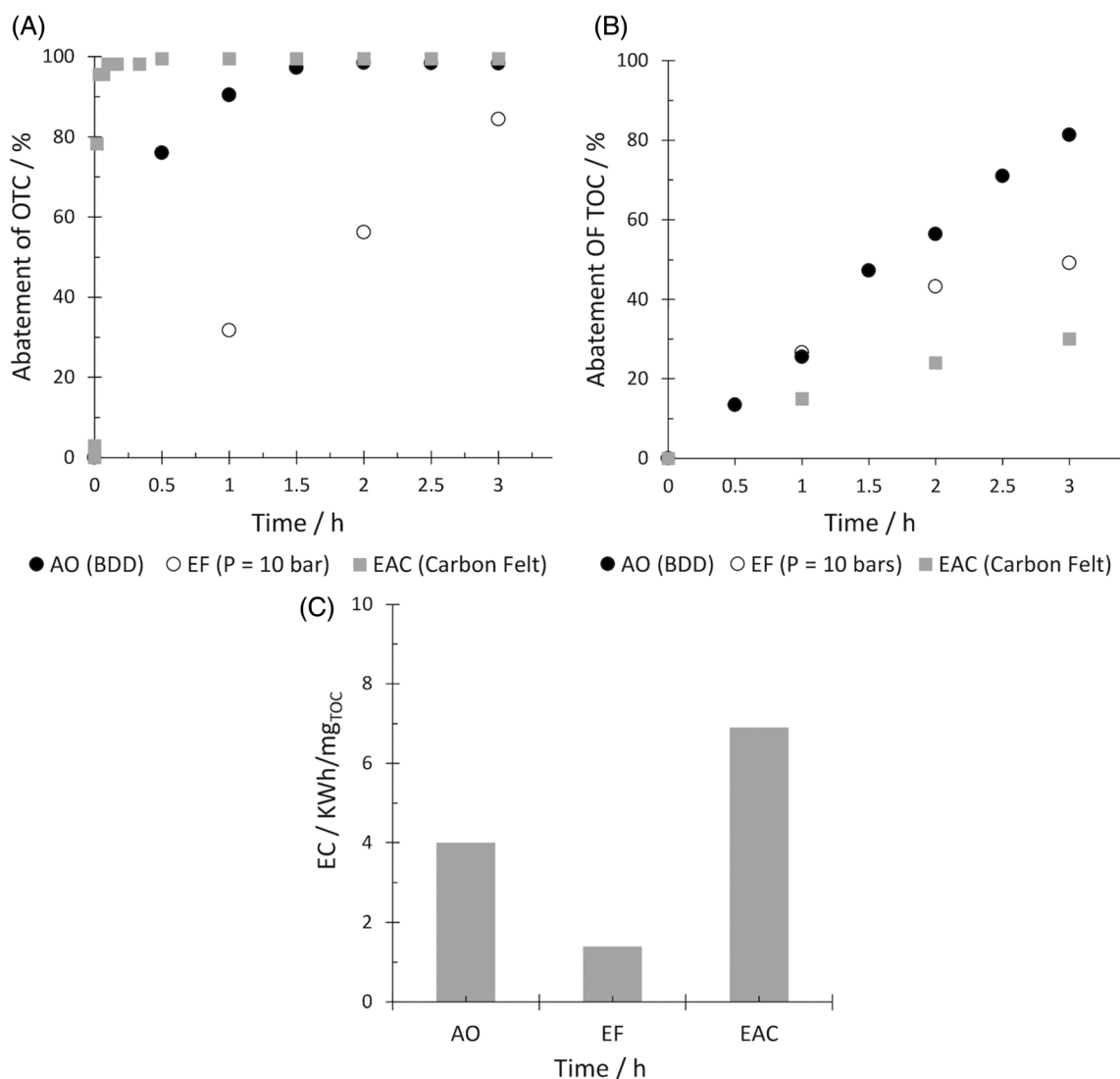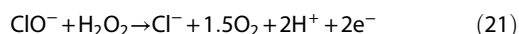
Figure 7. Comparison of AO, EAC and EF in terms of OTC removal (A), TOC abatement (B) and final energy consumption (kWh per mg of removed TOC) (C). AO performed with water solutions of Na_2SO_4 at BDD anode and stainless-steel cathode at 1 bar and 60 mA cm^{-2}; EF performed with water solutions of Na_2SO_4 and $FeSO_4$ at pH 3 with Ti/Ta$_2$O$_5$-IrO$_2$ anode and carbon felt cathode at 10 bar and 10 mA cm^{-2}; EAC performed with water solutions of NaCl with Ti/Ta$_2$O$_5$-IrO$_2$ anode and carbon felt cathode at 1 bar and 60 mA cm^{-2}. Stirring rate = 400 rpm.

stainless-steel cathode and a Ti/Ta$_2$O$_5$-IrO$_2$ anode, under amperostatic condition (60 mA cm^{-2}) with magnetic stirring (400 rpm) for 3 h.

As shown in Fig. 5, the addition of NaCl resulted in a very high enhancement of the OTC abatement. Indeed, the final abatement of OTC in the absence and in the presence of NaCl was 44% and 84%, respectively. Moreover, the addition of NaCl resulted in a significant increase of the TOC removal from ≈ 11% to 22%. According to the literature, the positive effect of NaCl is due to the fact that in the EAC process, organic pollutants are oxidized by numerous oxidants, either chlorinated or nonchlorinated, such as active chlorine, adsorbed chloro and oxychloro radicals, Cl$_2$O and ClO$_2$ and hydroxyl radicals.[1,5,24–26] However, the final TOC removal was not very high.

Moreover, according to the literature this process can lead to the formation of toxic organochlorinated derivatives and oxychlorine anions, such as ClO$_3^-$ and ClO$_4^-$, which potentially present negative effects on human health.[1,5] It has been shown that the formation of chlorate and perchlorate during the electrolysis of aqueous solutions containing chlorides can occur by various routes, and it can be favored by the occurrence of relatively high amounts of reactive hydroxyl radicals and limited by the use of Ir based anodes, such as Ti/Ta$_2$O$_5$-IrO$_2$.[3,27,28] Other important byproducts are HAAs.[3,13] During our electrolysis, chlorate, mono-, di- and tri-chloroacetic acids were detected as lateral byproducts. Recently, it has been shown that the use of CF or Ag cathodes can the mineralization of organic pollutants and o decrease the generation of some byproducts. Carbon felt converts oxygen to H$_2$O$_2$ [Eqn (3)] which can limit the formation of chlorate and perchlorate, as recently shown by the work of Rodrigo for the electrochemical treatment of urban treated wastewater[29] and by that of Scialdone for the remediation of an aqueous solution containing phenol.[13,17] Indeed, H$_2$O$_2$ reacts with hypochlorite to give chloride [Eqn (21)], and with chlorate to yield the strong oxidant ClO$_2$ [Eqn (22)].[30]

$$ClO^- + H_2O_2 \rightarrow Cl^- + 1.5O_2 + 2H^+ + 2e^- \qquad (21)$$

$$2H^+ + 2ClO_3^- + H_2O_2 \rightarrow 2ClO_2 + 2H_2O + O_2 \qquad (22)$$

Conversely, Ag cathodes allow the reduction of HAAs to acetic acids that can be more effectively removed by oxidation processes.[13] Hence, the electrolyses were repeated replacing the stainless-steel cathode with both *CF* and Ag. The replacement of the stainless-steel cathode with Ag and *CF* resulted in a very slight enhancement of TOC removal (from 22% to 30% replacing stainless steel with *CF*). More important the utilization of Ag and *CF* allowed a drastic reduction of the concentration of chlorate and a slight decrease of the final concentration of HAAs (Fig. 6).

Comparison of different routes

Figure 7 reports a comparison between the results obtained with the three tested routes: AO, EF and EAC. The data obtained under the best adopted operative conditions found for each route were reported:

- AO performed with water solutions of Na_2SO_4 with BDD anode and stainless-steel cathode at 1 bar and 60 mA cm^{-2};
- EF performed with water solutions of Na_2SO_4 and $FeSO_4$ at pH 3 with Ti/Ta_2O_5-IrO_2 anode and *CF* cathode at 10 bar and 10 mA cm^{-2};
- EAC performed with water solutions of NaCl with Ti/Ta_2O_5-IrO_2 anode and *CF* cathode at 1 bar and 60 mA cm^{-2}.

As shown in Fig. 7(A), the fastest abatement of OTC was obtained by EAC. Indeed, in this case, very high removal of OTC close to 100% was obtained after less than 0.5 h. The slowest removal of OTC was obtained with EF and intermediate results with AO. However, all adopted methods allowed a very high removal of OTC after 3 h. A very different picture was obtained for the TOC removal [Fig. 7(B)]. Indeed, as shown in Fig. 7(B), in this case, the fastest abatement was obtained with BDD as a result of the very mineralization ability shown by this anode,[1] the slowest with EAC and intermediate results with EF. In order to evaluate an electrochemical process for the treatment of wastewater, ECs also have to be evaluated. As shown in Fig. 7(C), EAC presents the highest consumption of energy for mg of TOC removed, due to the low TOC abatement achieved with this process. Conversely, EF presents the lowest EC due to the adoption of small current densities and the relatively high TOC removals. BDD presented higher energetic costs, in spite of the fact that this process gave the highest TOC removal, due to the high cell potentials required for BDD that presents a very high overpotential for water oxidation.[1]

It is worth mentioning that the AO process is expected to present significant higher capital costs with respect to the other processes because BDD has up to now been significantly more expensive than the other electrodes used in the study that are relatively cheap. EF at 10 bar also presents costs resulting from the pressurizations; however, these were estimated to be significantly lower than that related to the electrolysis.[19]

CONCLUSION

The treatment of aqueous solutions of OTC was performed by various electrochemical routes: EF, AO and indirect oxidation by EAC. It was found that the performances of each route could be improved by a proper choice of operative conditions: in particular, the removal of OTC and TOC improved for AO at BDD anodes and

low pH, and for EF using pressurized air (5 or 10 bar). In the case of EAC, the formation of the toxic byproduct chlorate can be reduced using *CF* cathodes. More important, each adopted route presented some advantages and disadvantages:

- EAC gave the fastest abatements of OTC, but the lowest mineralization and the highest energetic consumption;
- AO gave the highest TOC removal, but requires the use of an expensive BDD anode and high cell potentials;
- EF performed with pressurized air presents a slower removal of TOC with respect to AO but the lowest energy consumptions.

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