Effect of the pressure on the cathodic production of H_2O_2 and on electro-Fenton in undivided and divided cells

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ABSTRACT

The key step for both the electrochemical H_2O_2 production and the electro-Fenton (EF) process is the cathodic reduction of O_2 which is adversely affected by the low oxygen solubility in water contacted at atmospheric pressure of air. In this work, we studied the effect of current density and air pressure on the H_2O_2 production and on the EF process using both a divided and an undivided cell. It was shown that the use of pressures between 5 and 15 bar allows to enhance drastically the H_2O_2 production in both undivided and divided cells and that the best results were achieved in the presence of the separator. Moreover, the coupled use of pressurized air and divided cells made it possible to accelerate the organics removal achieved by the EF process. Eventually, the advantages given by the utilization of divided and undivided cells and of pressurized air were analyzed from both technical and economic points of view.

1. Introduction

Different research groups have demonstrated that the cathodic reduction of oxygen using carbonaceous cathodes (Eq. (1)) in aqueous solutions can be effectively used for the H_2O_2 production [1]. Moreover, the H_2O_2 can be used for the electro-Fenton (EF) process by the addition of catalytic amounts of iron catalysts (Eq. (2)), thus allowing to generate hydroxyl radicals able to oxidize organic pollutants (Eq. (3)) [2–5].
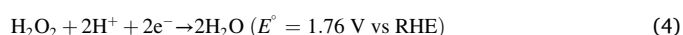
$$O_2 + 2H^+ + 2\,e^- \rightarrow H_2O_2 \ (E^0 = 0.67 \text{ V vs RHE}) \tag{1}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \overset{\cdot}{O}H + OH^- \tag{2}$$

Indeed, the reaction between H_2O_2 and Fe^{2+} (Eq. (2)) produces the strong oxidant •OH that reacts with organics causing the generation of bio-degradable carboxylic acids or even the complete mineralization (Eq. (3)). Moreover, Fe^{2+} is regenerated by the cathodic reduction of Fe^{3+}.

$$\text{Organics} + p\,\text{OH} \rightarrow m\text{CO}_2 + n\text{H}_2\text{O} \tag{3}$$

The cathodic reduction of O_2 in aqueous solution is strongly limited by its low solubility in water at atmospheric pressure, thus giving rise to slow H_2O_2 productions. Moreover, the H_2O_2 can be converted in other

compounds such as water and/or O_2 (Eqs. (4)–(6)) by cathodic reduction (Eq. (4)), anodic oxidation (Eq. (5)) and homogenous decomposition (Eq. (6)) [3]:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \ (E^\circ = 1.76 \text{ V vs RHE}) \tag{4}$$

$$H_2O_2 = O_2 + 2H^+ + 2\,e^- \ (E^\circ = 0.67 \text{ V vs RHE}) \tag{5}$$

$$2\,H_2O_2 = 2H_2O + O_2 \tag{6}$$

The EF process suffers of the same disadvantages; moreover, the EF process conducted with conventional homogeneous iron catalysts suffers from the disadvantage of requiring low pH values to avoid iron precipitation. [2–5], and iron catalysts and carboxylic acids form rather resistant complexes [3]. Different approaches were proposed to deal with these problems. In particular, numerous heterogeneous catalysts were proposed to increase the working pH [6–10], while modified carbon felts (MCF), other innovative cathodes [11–14], or gas diffusion electrodes (GDEs) [2–5] were used to accelerate the cathodic process even in the presence of low O_2 concentrations in water. The process was improved also using innovative electrochemical cells, such as microfluidic [15,16], jet [17] and pressurized ones [18–20].

The hurdle of the low solubility of gaseous reagents in water can be

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reduced using pressurized systems. Indeed, pressurized systems were successfully used for the cathodic conversion of CO_2 [21,22], the production of H_2O_2 [17,18,23–26], ozone and peroxone [26], pressurized electro-Fenton (PrEF) process [9,17,18,25], photo electro-Fenton [27] and oxidation of organics by electro-generated active chlorine [28]. The pressure's effect on both the H_2O_2 production and on electro-Fenton process was studied in undivided cells. It was reported that at 80 mA the increase of the pressure from 1 to 11 bar allowed, using compact graphite cathodes, to increase the final concentration of H_2O_2 after 2 h from 1.3 to 12.3 mM [18]. The effect of the pressure was even more remarkable using carbon felt based cathodes [20]. Similarly, it was shown that the increase of the pressure allows to strongly increase the removal of organics by EF for the treatment of water contaminated by dyes [18] antibiotics [26], caffeic acid, 3-chlorophenol [9], etc. In particular, the utilization of PrEF resulted in quite high removals of some organics comparable or even higher than that achieved by the direct oxidation at BDD [12,25]. However, the use of undivided cells allows the anodic oxidation of H_2O_2 to O_2 (Eq. (5)), thus potentially reducing the final H_2O_2 concentrations in the cell. Hence, in this study, we have studied for the first time the possibility to perform the H_2O_2 electrochemical production and the electro-Fenton process in divided cells. Moreover, we used also undivided cells for the sake of comparisons. The effect of various operative conditions, including the current density (*j*), the nature of the cell, the pressure and the nature of the cathode, was studied. PrEF was studied using an aqueous solution of Acid Orange 7 (AO7), an azoic dye very resistant to biological processes.

2. Experimental

2.1. Electrochemical apparatus

The electrolyses were performed in a cell with a coaxial cylindrical geometry made with AISI 316 stainless steel cell (Fig. 1A). The cell was previously described in detail in ref. [18]. This cell was equipped with a gas inlet, a $Ti/IrO_2Ta_2O_5$ anode (ElectroCell AB), compact graphite (Carbon Lorraine), carbon felt (The Electrosynthesis Co., thickness 4 mm) or carbon black cathode with an inter-electrode distance of 2 cm and a surface of 2.5 cm^2.

In the case of experiments performed in the divided cell, the AISI 316 SS cell was joined with a nylon liner (Fig. 1B) properly designed to allow to work under pressurized conditions. The selection of Nylon material was based on its enhanced mechanical qualities and chemical resistance. The nylon liner consists of three distinct main components: i.e. two hemispherical units which allow to retain the membrane in the middle and an exterior circular crown that enables to assembly the divided liner to contain cathodic and anionic solutions. After the assembly was done, hydraulic tightness was tested and then the assembled electrochemical device was tested till 50 bar at room temperature. A Nafion® 324 cation exchange membrane was placed into the cell to separate the cathodic and the anodic compartments (Fig. 1). The electrolyte was stirred at a constant stirring rate of 600 rpm using a magnetic stirrer. The cell was equipped with a pressure gauge and a thermocouple for the pressure and temperature measurement, respectively. Compressed air (purity 5.0 supplied by Rivoira) was used to pressurize the cell and a pressure reducer was utilized to select the operative pressure. The Amel 2053 potentiostat/galvanostat was used to perform the experiments in galvanostatic mode at ambient temperature. Experiments were performed for 3 h. To check the reproducibility of the data, all the experiments were
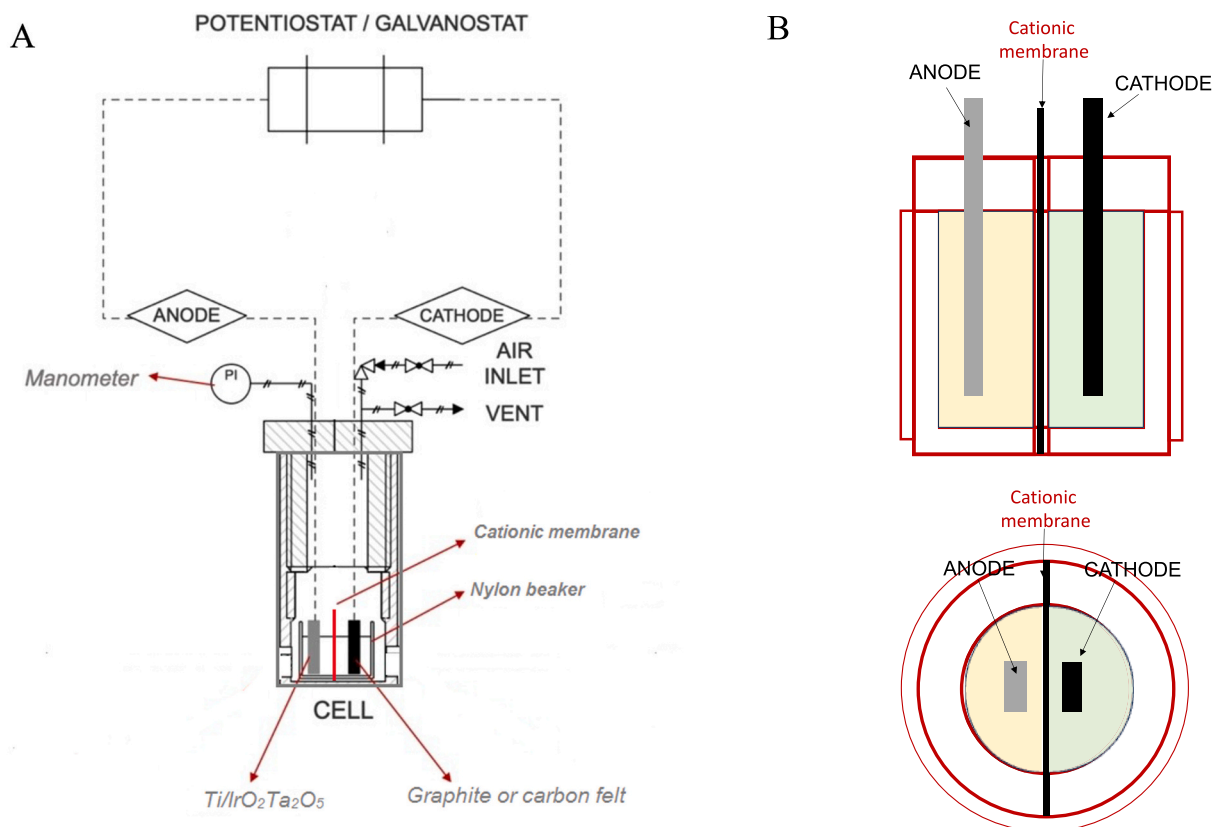

Fig. 1. Scheme of the pressurized electrochemical cell: (A) AISI 316 stainless steel cell; (B) scheme of the divided liner.

repeated at least three times.

2.2. Chemicals

The electrogeneration of H_2O_2 was performed in 36 mL of aqueous solutions. In the undivided cell, 0.036 M Na_2SO_4 (supplied by Janssen Chimica) and H_2SO_4 (Sigma Aldrich) were used as the supporting electrolyte and added to achieve a pH of 3, respectively.

In the divided cell, a buffer solution $Na_2SO_4/NaHSO_4$ ($[Na_2SO_4]$ = 0.25 M, $[NaHSO_4]$ = 0.025 M) was used in the cathodic compartment (18 mL) while sodium perchlorate 0.01 M (Fluka) in the anodic compartment (18 mL) as supporting electrolyte [29]. The presence of the buffer solution guaranteed the conductivity, hence no supporting electrolyte was added to the catholyte.

A series of experiments was carried out to compare the efficiency of divided and undivided cells and pressure on the EF process. Acid Orange 7 (Sigma Aldrich) 0.43 mM was used as a model and recalcitrant pollutant and 0.5 mM $FeSO_4$ (Fluka) (in line with the literature [30]) as the catalyst.

2.3. Analytical methods and performances

Cary 60 UV–Vis Agilent Spectrophotometer was used to quantify the H_2O_2 concentration from the light absorption of the colored complex of Ti(IV)–H_2O_2, using $O_5STi·H_2SO_4$ (Sigma Aldrich), at $\lambda = 409$ nm.

The faradaic efficiency FE (Eq. (7)) and the productivity of H_2O_2 (Eq. (8)) were defined as:

$$FE = n\,F\,V\,[\text{H}_2\text{O}_2]/(I_{app}\,t)\,100\,[=]\%\tag{7}$$

$$\text{Productivity of } \text{H}_2\text{O}_2 = FE/100\,j*3600/n\,F\,[=]\,\text{mol h}^{-1}\,\text{m}^{-2}\tag{8}$$

where n is the stoichiometric electrons number ($n = 2$), V (L) the volume of the solution, F the Faraday constant (96,500C mol^{-1}), $[H_2O_2]$ (M) the H_2O_2 concentration, I_{app} (A) the applied current, t (s) the time, 3600 factor to convers seconds in hours and j is the current density (A m^{-2}).

TOC-L CSH/CSN analyzer Shimadzu was utilized to analyze the total organic carbon (TOC). The removal of AO7 (X_{AO7}) and TOC (X_{TOC}) and the TOC current efficiency (CE_{TOC}) were estimated by Eqs. (9), (10) and (11), respectively:

$$X_{AO7} = (\Delta\text{AO7})_t/\text{AO7}^0*100\,[=]\%\tag{9}$$

$$X_{TOC} = (\Delta\text{TOC})_t/\text{TOC}^0*100\,[=]\%\tag{10}$$

$$CE_{TOC} = n\,\text{F}\,\text{V}\,\text{TOC}_0\,\text{X}_{TOC}/(I_{app}\,\text{A}\,t)\tag{11}$$

where $(\Delta\text{AO7})_t$ and $(\Delta\text{TOC})_t$ is the difference between the initial and final concentration of AO7 and TOC (mg L^{-1}), respectively, and $AO7^0$ and TOC^0 is the initial concentration of AO7 and TOC (mg L^{-1}), respectively, and A the electrode surface.

Limiting current density, j_{lim} was estimated as

$$j_{lim} = n\text{F}\left(D_{O_2}/\delta\right)c_{O_2}^b\,[=]\,\text{mA cm}^{-2}\tag{12}$$

where D_{O_2} is the O_2 diffusion coefficient ($D_{O_2} = 2*10^{-5}$ cm^2 s^{-1}), δ is the stagnant layer thickness assumed of 45 μm and $c_{O_2}^b$ (P) is the bulk O_2 concentration at the different pressure value.

Agilent HP 1100 HPLC fitted out with a Rezex ROA-Organic Acid H+ (8 %) column was used to evaluate the carboxylic acids presence. The mobile phase was 0.005 N H_2SO_4 aqueous solution pH = 2 eluted at 0.5 mL min^{-1} and 20 °C.

3. Results and discussion

3.1. Production of H_2O_2

3.1.1. Effect of pressure in undivided cells

First experiments were performed for 3 h with an undivided cell, a carbon felt cathode and a Ti/IrO_2-Ta_2O_5 anode under amperostatic conditions ($j = 2.8$ mA cm^{-2}), magnetic stirring (600 rpm) and different air pressures in the range 1–30 bar. Na_2SO_4 was chosen as supporting electrolyte and H_2SO_4 to have the target pH. As shown in Fig. 2A, an enhancement of the pressure from 1 to 10 bar gave rise to a strong increase in H_2O_2 production of about 4 times. Indeed, the productivity increased from about 0.017 to 0.07 mol h^{-1} m^{-2}. Consequently, the faradic efficiency (FE) increased from 3 to 12 %. To understand the high increase in the H_2O_2 production with the pressure it is important to highlight that the O_2 solubility in water increases with the pressure according to the Henry's law [18]. Indeed, the O_2 solubility enhance from $8\frac{mg}{L_{H_2O}}$ to $80\frac{mg}{L_{H_2O}}$ by increasing the air pressure from 1 to 10 bar [31], thus promoting the electro-generation of H_2O_2 (Eq. (1)).

In particular, the limiting current density for the O_2 reduction for a process under the O_2 mass transport control to the cathode surface (j_{lim}) was evaluated to be close to 0.25 mA cm^{-2} at 1 bar. This value is drastically lower than the applied j of 2.8 mA cm^{-2}. Hence, at 1 bar the cathodic reduction of oxygen to H_2O_2 is under the kinetic control of the mass transport of O_2, thus causing a high impact of the parasitic process of water reduction (Eq. (13)). Conversely, in the case of experiments performed at 10 bar, the j_{lim} was estimated to be 2.5 mA cm^{-2} and very close to the applied j.

$$2\,\text{H}_2\text{O} + 2\,\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2\tag{13}$$

When the pressure was further enhanced from 10 to 15 bar, a slight increase of the H_2O_2 production (from 0.066 to 0.072 mol h^{-1} m^{-2}) and of FE (from 12 to 14 %) was recorded. Indeed, in this case, the j_{lim} is 3.75 higher than the applied j. However, an additional enhance of the pressure to 30 bar led to a strong reduction of the H_2O_2 production (0.038 mol h^{-1} m^{-2}) and of FE (close to 7 %) (Fig. 2). Hence, the optimal value of pressure under adopted operative conditions was 15 bar. The adverse effect of pressure for relatively high-pressure values has not been reported up to now. This effect is probably related to the fact that, under amperostatic regime, a higher O_2 pressure leads to less negative cathode potential, which, in its turn has a drastic effect on the FE of H_2O_2 production [18].

3.1.2. Effect of the pressure in divided cells

The experiments discussed above were repeated in the pressurized divided cell equipped with a membrane described in Section 2. First experiments were performed with the same supporting electrolyte used in the undivided cell (e.g., Na_2SO_4 and H_2SO_4). However, very poor productions of H_2O_2 were achieved due to the very rapid increase of pH in the cathodic compartment that reached 11 at the end of the experiments. The increase in pH is due to the cathodic reduction of both oxygen (Eq. (1)) and water (Eq. (13)) that consumes protons or releases OH^-. In the undivided cell, the pH increase caused by cathodic reactions is compensated by the pH decrease given by anodic processes such as water oxidation (Eq. (14)). Indeed, in the undivided cells, the pH remained almost constant for all the experiments. Conversely, in the divided cell, the presence of the membrane gives rise to different pH in the two compartments (11 and 2 respectively in cathodic and anodic compartments).

$$\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 0.5\,\text{O}_2 + 2\,\text{e}^-\tag{14}$$

Hence, according to the literature [11,29], the experiments in the divided cells were repeated using a buffer solution (see Section 2 for details) in the cathode compartment. As shown in Fig. 2A and B, also in this case both the H_2O_2 production and the FE presented a maximum
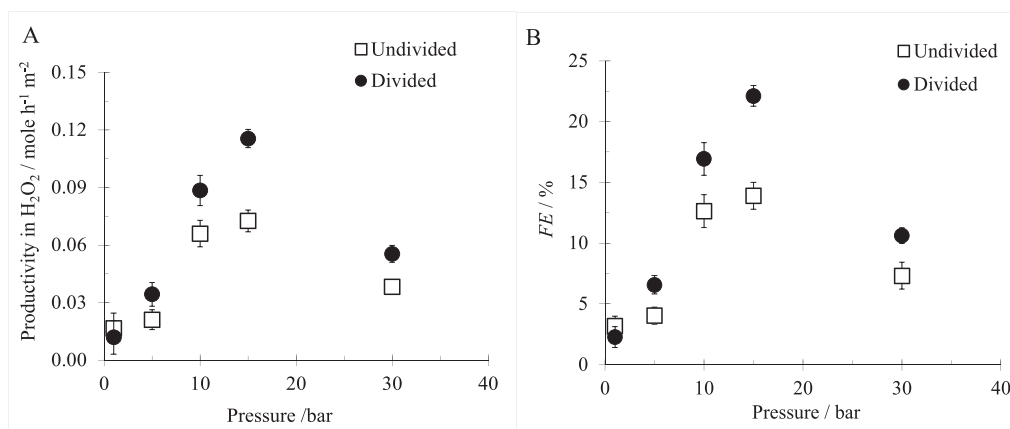
Fig. 2. Effect of pressure on H_2O_2 productivity (A) and *FE* (B) in both undivided and divided cells for amperostatic electrolyses (2.8 mA cm^{-2}).

with the air pressure for a P of 15 bar. In particular, the increase of the pressure from 1 to 15 bar resulted in an enhancement of the productivity of about one order of magnitude from $1.2\ 10^{-2}$ to $1.2\ 10^{-1}$ mol h^{-1} m^{-2} and of *FE* from about 2–3 to 22 %. It is worth mentioning that, for all the experiments performed under pressurized conditions, the use of the divided cell allowed to increase the H_2O_2 production. As an example, at 10 bar the H_2O_2 productivity was 0.066 and 0.084 mol h^{-1} m^{-2} in the undivided and the divided cells, respectively and at 15 bar 0.072 and 0.12 mol h^{-1} m^{-2}, respectively. The better results achieved in the divided cell are likely to be caused by the fact that the membrane avoids the contact of H_2O_2 with the anode and consequently its anodic oxidation to oxygen (Eq. (5)). Moreover, the use of the divided cell can also avoid the reaction of H_2O_2 with scavengers generated at the anode. Indeed, according to the literature H_2O and SO_4^{2-} can be converted at the anode in ozone (Eq. (15)) and peroxymonosulfate (Eq. (16)), respectively, two potential scavengers of H_2O_2 that are expected to reduce its concentration by reactions (17) and (18) [37].

$$3H_2O \rightarrow 6H^+ + 0.5\ O_3 + 6\ e^- \tag{15}$$

$$H_2O + SO_4^{2-} \rightarrow SO_5^{2-} + 2H^+ + 2e^- \tag{16}$$

$$H_2O_2 + O_3 \rightarrow H_2O + 2\ O_2 \tag{17}$$

$$H_2O_2 + SO_5^{2-} \rightarrow H_2SO_4 + 1.5O_2 \tag{18}$$

It is worth mentioning that, as shown in Fig. 2, also in divided cells the enhancement of the pressure from 15 to 30 bar gave rise to a strong

reduction of the *FE* from 22 to 11 %.

3.1.3. Effect of current density and pressure

The effect of *j* was investigated both in undivided and divided cells at 30 bar and 2.8, 4.8 and 7.2 mA cm^{-2}. As reported in Fig. 3, a very strong effect of *j* was observed. A curve with a maximum was observed for both the H_2O_2 production and the *FE*. As an example, for the divided cell, the H_2O_2 productivity was $5.5\ 10^{-2}$, $1.9\ 10^{-1}$ and $1.2\ 10^{-1}$ mol h^{-1} m^{-2} at 2.8, 4.8 and 7.2 mA cm^{-2}. This trend can be due to the fact that higher currents result in a higher amount of charge passed, thus favoring the H_2O_2 production, but also in a complex trend of *FE*. Indeed, when the *j* was increased from 2.8 to 4.8 mA cm^{-2}, both the charge passed and the *FE* increased; however, the further increase of *j* to 7.2 mA cm^{-2} resulted in a strong reduction of *FE* caused by the fact that high working potentials favor the H_2O_2 cathodic reduction (Eq. (4)) [18] and the production of scavengers [37].

Overall, also in this case, the use of the divided cell resulted in higher production of H_2O_2 in most of the adopted operative conditions (Fig. 2). Similar results were achieved only for the highest adopted *j* of 7.2 mA cm^{-2}. Indeed, under these conditions, the removal of H_2O_2 is expected to take place prevalently by its cathodic reduction to water.

Since the increase of the pressure results in an enhancement of the O_2 solubility and, thus, of j_{lim}, the amperostatic electrolyses were repeated using, for each value of the pressure, a *j* close to the corresponding value of j_{lim} even if with a minimum value of 0.8 mA cm^{-2}. As shown in Fig. 4B, for divided cells, the *FE* showed a very slight increase with the pressure and it resulted in 15 and 19 % at 1 and 30 bar, respectively.
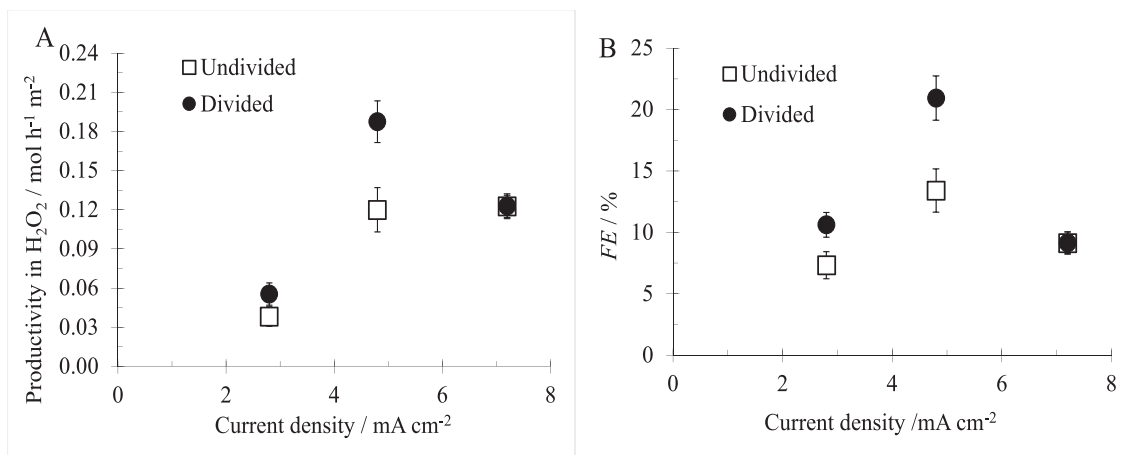

Fig. 3. Effect of current density on H_2O_2 productivity (A) and on *FE* (B) in both undivided and divided cells for electrolyses performed under amperostatic conditions at 30 bars for 3 h.
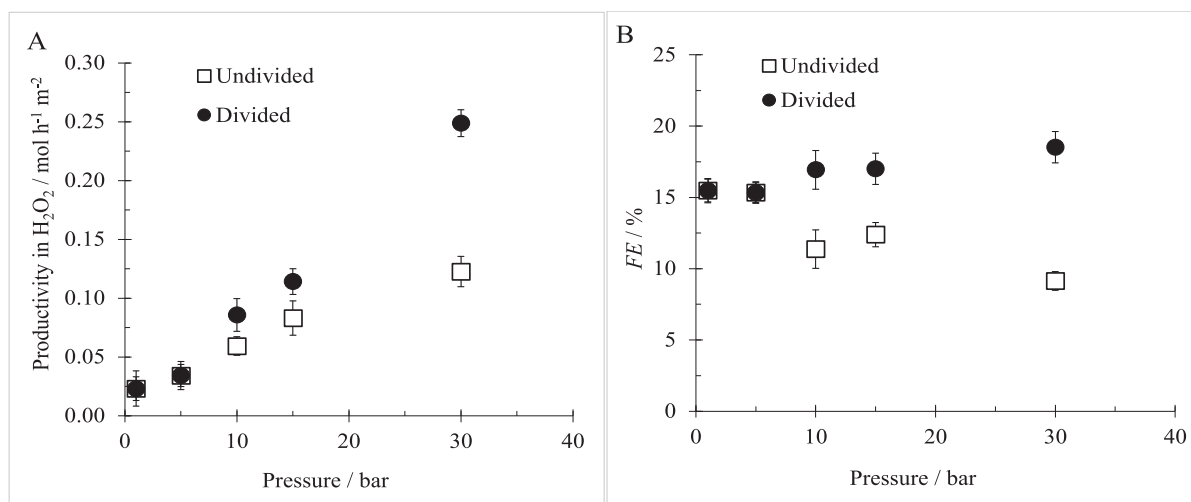
Fig. 4. Effect of pressure on H_2O_2 productivity (A) and *FE* (B) in both undivided and divided cells for electrolyses performed under amperostatic conditions for 3 h. For each value of the pressure, a current density close to j_{lim} was selected with a minimum value of 0.8 mA cm^{-2}.

Hence, the increase of the pressure coupled with the enhancement of j resulted in a strong increase of H_2O_2 productivity (Fig. 4A), which assumed the values of 2.3 10^{-2} and 2.5 10^{-1} mol h^{-1} m^{-2} at 1 and 30 bar, respectively, and of the H_2O_2 final concentration (slightly lower than 1 mM at 1 bar and higher than 10 mM at 30 bar).

In the case of the experiments performed in the undivided cell, the *FE* presented a slight decrease with the pressure. Indeed, the coupled increase of the pressure and j gave a higher concentration of H_2O_2 thus favoring its anodic oxidation (Eq. (5)). Indeed, *FE* was 15 and 9 % for 1 and 15 bar, respectively. However, the coupled increase of the pressure and j resulted in a strong increase of the H_2O_2 productivity (Fig. 4A). It is interesting to observe that divided and undivided cells presented similar results for 1 and 5 bar when the final concentration of H_2O_2 is quite limited, thus making less relevant the impact of its anodic oxidation. Conversely, for higher pressure values, when significant amounts of H_2O_2 are generated, the use of the divided cell allowed a significant enhancement of both *FE* and H_2O_2 production (Fig. 4B).

3.1.4. Effect of cathode nature

The effect of the cathode's nature, including compact graphite, carbon felt and carbon black, was investigated using the undivided cell at both 1 and 15 bar and 7 mA cm^{-2}. As shown in Table 1, at 1 bar the cathode's nature had a strong effect on the H_2O_2 production. Indeed, the *FE* at compact graphite, carbon felt and carbon black were 2.0, 3.2 and 5.6 %, respectively. Indeed, it was previously shown that compact graphite is less effective than carbon felt in producing H_2O_2 [18] and that carbon black presents very interesting results at 1 bar [32]. When the pressure was increased to 15 bar, the *FE* increased at all adopted cathodes. However, also in this case, carbon black presented the best results in terms of both FE and productivity. Thus, at 15 bar, the *FE* at compact graphite, carbon felt and carbon black were 9, 14 and 25 %, respectively. Hence, the productivity at 15 bar was 7.3 10^{-2} and 1.2 10^{-1} mol h^{-1} m^{-2}, at carbon felt and carbon black, respectively

Table 1
Effect of the cathode's nature on the production of H_2O_2.[a]

Entry	Cathode nature	Pressure (bar)	*FE* (%)
1	Compact graphite	1	2.0
2	Carbon felt	1	3.2
3	Carbon black	1	5.6
4	Compact graphite	15	9.1
5	Carbon felt	15	13.9
6	Carbon black	15	25.2

[a] Experiments performed in the undivided cell for 3 h at 2.8 mA cm^{-2}.

(Table 1).

3.2. EF and PrEF in undivided and divided cells

It was previously shown, in the case of undivided cells, that the use of pressurized air [18–20] or oxygen [9] gives rise to a more effective EF process. However, until now, the use of PrEF has only been investigated, to our knowledge, in undivided cells. Hence, we have evaluated here the use of PrEF in both divided and undivided cells. An aqueous solution of Acid Orange 7 (AO7) was selected as a model recalcitrant organic pollutant. AO7 is largely used as azoic dye and is very resistant to conventional biological processes. Experiments were performed using FeSO$_4$ as a homogeneous catalyst under amperostatic mode. As shown in Fig. 5A, the removal of the azo dye was very high under all adopted operative conditions. Indeed, also at 1 bar, the electrolysis performed in the undivided cell resulted in a removal of AO7 (X_{AO7}) close to 94 % for a charge passed (Q) lower than the theoretical one expected for its complete mineralization (Q^{th}) ($Q/Q^{th} = 0.8$). Indeed, according to the literature, the EF process results in a partial oxidation of AO7 to more resistant intermediate products that need larger amounts of charge passed to be mineralized. Hence, as shown in Fig. 5B, for $Q/Q^{th} = 0.8$, the removal of TOC (X_{TOC}), for the electrolyses carried out at 1 bar in the undivided cell, was quite low and close to 15 %. When the charge was doubled ($Q/Q^{th} = 1.6$), a slight increase of X_{AO7} was achieved (from 93 to 95 %) coupled with a significant increase of X_{TOC} to 27 % for a *FE* for TOC removal (CE_{TOC}) close to 17 %. A significant concentration of carboxylic acids was found. In particular, quite large carboxylic acids such as acetic and malonic acids were detected coupled with the presence of formic acid.

When the experiment in the undivided cell was repeated at 15 bar, a significant improvement in results was obtained:

- as shown in Fig. 5A, a further increase of X_{AO7} up to 97 % was achieved;
- as shown in Fig. 5B, for $Q/Q^{th} = 0.8$, X_{TOC} increased from 15 to 27 % using PrEF instead of simple EF; moreover, when Q/Q^{th} was 1.6, X_{TOC} was 27 and 42 % for EF and PrEf, respectively;
- CE_{TOC}, for $Q/Q^{th} = 1.6$, was 17 and 26 % for EF and PrEF, respectively;
- while EF resulted in the presence of quite large carboxylic acids, PrEF gave mainly small carboxylic ones; indeed, formic and oxalic acids coupled with minor amounts of acetic acid were detected at the end of the electrolyses, due to the more effective oxidation process.
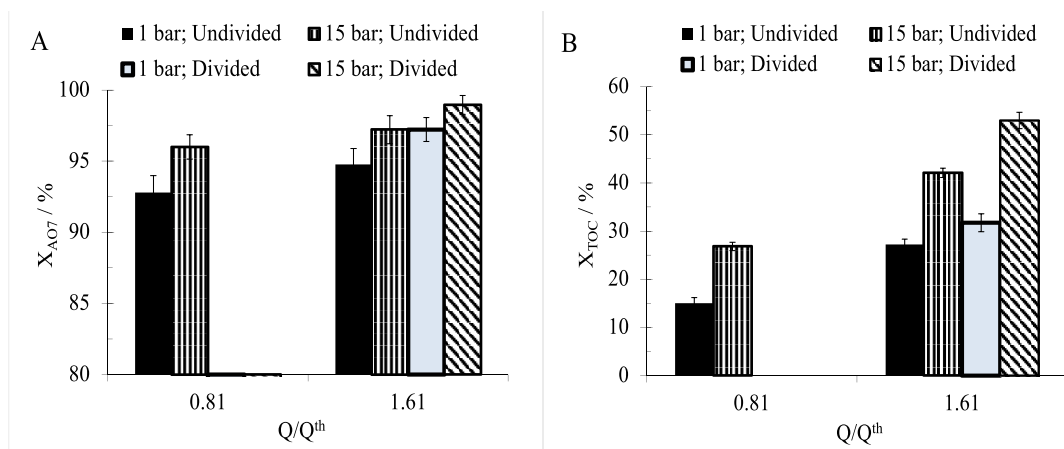
Fig. 5. Effect of pressure and cell on AO7 (A) and on TOC removal (B) for electrolyses performed under amperostatic conditions for 3 h.

The positive effect of the pressure on the TOC removal can be explained remembering that in EF the most important oxidizing agents are the hydroxyl radicals generated by the reaction between Fe^{2+} and H_2O_2 (Eq. (2)). Hence, the increase of the pressure enhances the solubility of oxygen and, as a consequence and as shown in previous section, gives rise to a strong increase of H_2O_2 by reaction (1), thus causing a faster generation of hydroxyl radicals by reaction (2) and a more effective degradation of organics by reaction (3).

The experiments were repeated in a divided cell at both 1 and 15 bar. As shown in Fig. 5A and B, also in this case, PrEF gave better results than EF in terms of X_{AO7} (from 97 to 99 % for $Q/Q^{th} = 1.6$), X_{TOC} (from 32 to 53 % for $Q/Q^{th} = 1.6$) and CE_{TOC} (from 20 to 33 %).

The use of the divided cell allowed to improve the performances of the process both for EF and PrEF processes. In particular, at 1 bar the divided cell gave slightly higher X_{AO7} (from 93 to 97 %), X_{TOC} (from 27 to 32 %) and CE_{TOC} (from 17 to 20 %), due to the higher concentrations of H_2O_2 caused by the fact that the separator prevents its anodic oxidation. Overall, as shown in Fig. 5, the coupled use of the divided cell and pressure gave the highest removals of both AO7 and TOC.

3.3. Technical and economic considerations

The pressure and the cell configuration (e.g., divided vs. undivided) affect various economic aspects. Indeed, the use of pressure enhances both the capital and the energetic costs. However, according to the literature [18,33], even considering a compression efficiency equal to 50 %, as shown in Table 2 for pressures lower than 20 bar, the energetic costs for compression are drastically lower than the overall electric consumption. Moreover, the utilization of the pressurized air gives rise

both to a decrease of cell potentials, due to the lower concentration polarizations, and to higher TOC removals, thus determining a relevant energetic gain that is drastically higher than the energy demand requested for compression. Conversely, PrEF presents significantly higher capital costs with respect to EF due mainly, for pressures lower than 20 bar, to the cost of pumps [34].

Divided cells present three main disadvantages with respect to undivided cells for EF and PrEF processes:

- higher capital costs due to the presence of membrane;
- higher energetic consumptions due to the ohmic drops given by the separator;
- the presence of a more complex electrolyte in the cathodic compartment due to the necessity to buffer the pH to avoid the precipitation of the iron homogeneous catalyst.

Table 2 reports a comparison between the four routes tested for the treatment of the synthetic water contaminated by AO7 in terms of X_{TOC}, cell potential, energy consumption (kWh/g_{TOC}) and impact of capital costs ($€/g_{TOC}$). It is shown that the use of PrEF allows improving the process in terms of lower energy consumptions and impacts of capital costs for both undivided and divided cells, due from one hand to the higher removals of TOC and from the other hand to the lower cell potentials. Indeed, the use of pressurized air makes it possible to achieve the target *j* with lower cell potentials due to lower concentration polarizations. A more complex comparison is given in the case of divided and undivided cells. Indeed, the use of divided cells results in slightly higher abatements but also in higher cell potentials, due to the ohmic drops given by the presence of the membrane, and higher capital costs.

Table 2
Comparison between the tested routes.[a]

Entry	Route	Cell potential (V)	TOC abatement (%)	Energy consumption (kWh/g_{TOC})	Impact of capital costs ($€/g_{TOC}$)	Energy consumption due to compression (kWh/g_{TOC})	Impact of energy costs for compression ($€/g_{TOC}$)
1	Undivided EF	1.8	27	0.12	0.26	–	–
2	Divided EF	2.5	32	0.14	0.27	–	–
3	Undivided PrEF	1.5	42	0.07	0.20	0.02	0.002
4	Divided PrEF	1.8	53	0.06	0.19	0.04	0.005

[a] Electrolyses of Fig. 4. Capital costs estimated for an electrolyzer of $1 m^2$, 20 years plant lifetime and 8000 h/y of operation. Depreciation, maintenance, taxes and interest were not considered in a first approximation. A replacement factor for electrodes and membranes of 7 and 5.2 years, respectively, was used. The replacement factor was estimated as the ratio plant lifetime/membrane or electrode lifetime; the electrode operation time and the membrane lifetime were assumed of 65,000 and 30,000 h, respectively. The price of the membrane was assumed $1000 € m^{-2}$, which refers to an average price between the fluorinated membrane price ($\sim 1100 € m^{-2}$) and the bipolar membrane price ($\sim 900 € m^{-2}$) [33]. The electrode price was $600 € m^{-2}$. The price of the electrochemical reactor was estimated according to Cañizares et al. [35] of an undivided electrochemical cell operation at atmospheric pressure. For PrEF the additional cost of pumps (close to 20 % of the electrolyzer cost) was considered. The electricity price was $0.11 €/kWh$ according to the average Italy electricity price in December 2023 [36].

In the case of EF, the use of the divided cell gave a very slight increase in both energy consumption (kWh/g_{TOC}) and the impact of capital costs (€/g_{TOC}). Conversely, in the case of PrEF a very slight decrease of these figures is observed for divided cells. However, the use of divided cells imposes also to use a buffer electrolyte, at least for conventional homogeneous iron catalysts. Hence, PrEF in undivided cells is likely to be the most interesting option.

4. Conclusions

In this work, we studied the effect of air pressure and cell typology (divided vs undivided cells) on the cathodic production of H_2O_2 and on the EF process. For the production of H_2O_2, it was found that:

- for a constant value of the current density, the plot production of H_2O_2 vs. air pressure presents a maximum in both divided and undivided cells and a proper choice of the pressure can strongly increase the generation of H_2O_2;
- for a constant pressure, the plot production of H_2O_2 vs. current density presents a maximum in both divided and undivided cells;
- in most of the adopted operative conditions, divided cells gave higher production of H_2O_2 with respect to undivided ones;
- best results were achieved using carbon black instead of carbon felt or compact graphite.

It was also found that, in both undivided and divided cells, the EF process benefits from the use of the pressure. The use of the divided cell slightly improves the TOC removal. Eventually, for undivided and divided cells, similar energetic consumptions and similar impacts of capital costs on the TOC removal were estimated. However, a divided cell presents a more complex operation given by the necessity to buffer the pH.

CRediT authorship contribution statement

Simona Sabatino: Methodology, Investigation, Data curation. **Claudia Prestigiacomo:** Methodology, Investigation. **Federica Proietto:** Supervision, Data curation. **Alessandro Galia:** Writing – review & editing, Supervision, Methodology. **Elisabetta Petrucci:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Onofrio Scialdone:** Writing – original draft, Supervision, Data curation, Conceptualization.

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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