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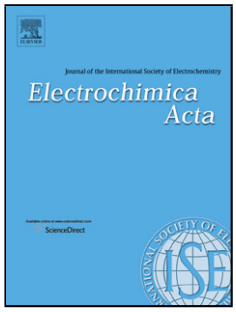

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Author: Onofrio Scialdone Alessandro Galia Carolina Gattuso Simona Sabatino Benedetto Schiavo

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Effect of air pressure on the electro-generation of H_2O_2 and the abatement of organic pollutants in water by electro-Fenton process

Onofrio Scialdone*, Alessandro Galia, Carolina Gattuso, Simona Sabatino, Benedetto Schiavo

Dipartimento di Ingegneria Chimica, Gestionale, Informatica, Meccanica, Università degli Studi di Palermo, Viale delle Scienze, 90128 Palermo, Italy. Tel: 0039 09123863754; Fax: 0039 09123860841; e-mail: Onofrio.scialdone@unipa.it

Abstract

The electro-generation of H_2O_2 and the abatement of the model organic pollutant Acid Orange 7 (AO7) in water by an electro-Fenton process were performed under moderate air pressures (up to 11 bar) for the first time to our knowledge. An increase of the pressure gave rise to a drastic enhancement of the concentration of hydrogen peroxide. In systems pressurized with air at 11 bar, the electro reduction of oxygen at a graphite cathode gave rise to a concentration of H_2O_2 of about 12 mM, about one order of magnitude higher than that achieved at atmospheric pressure. This result is attributed to the mass transfer intensification induced by the higher local concentration of molecular oxygen dissolved in the aqueous phase. Similarly, for electro-Fenton, a drastic increase of the TOC abatement was achieved upon increasing the air pressure. The effect of the current was also investigated in detail.

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Keywords

Wastewater treatment; Air pressure; AOPs; Electro-Fenton; Acid orange 7; Hydrogen peroxide; Compact graphite.

1. Introduction

The environmental protection requires advanced processes for the treatment of wastewater contaminated by organic pollutants which are resistant to conventional biological processes. Within this context, great progress has been made in the electrochemical technologies. The main electrochemical procedures utilized for the remediation of wastewater are electroreduction, electrochemical oxidation and indirect electro-oxidation with active oxidants [1]. The most important advantages of electrochemical methods for the treatment of wastewater are their high efficacy, mild operation conditions, ease of automation, versatility and low costs, especially when they are powered by renewable energy from wind and solar sources [1-4]. Recently, the treatment by emerging technologies such as electro-Fenton (EF) has received a great deal of attention [4]. EF process is a very promising tool for the treatment of wastewater contaminated by a wide series of organic pollutants resistant to conventional biological processes [4]. It is based on the electro-generation of hydrogen peroxide in aqueous solution by two-electron reduction of dissolved oxygen (eq. (1)), directly injected as pure gas or bubbled air, on a cathode such as mercury pool [5] or carbonaceous materials, such as compact graphite [4,6-7], carbon felt [4,8-9], reticulated vitreous carbon [4,10] and carbon-polytetrafluoroethylene (carbon-PTFE) gas diffusion electrodes (GDE) [4,11]. The utilization of air is usually preferred for its low cost with respect to oxygen. The oxidizing power of H_2O_2 is enhanced in the presence of Fe^{2+} via classical Fenton's reaction (Eq. (2)) which leads to the production of hydroxyl radicals.

$$O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2 \qquad (1)$$

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$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^{\bullet} + OH^- \quad (2)$$

Reaction (2) is propagated through the continuous electro-generation of Fe^{2+} by cathodic reduction of Fe^{3+} (Eq. (3)).

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

H_2O_2 is consumed by cathodic reduction (eq. (4)), disproportionation (eq. (5)) and in undivided cells, often used to avoid the voltage penalty of the separator, anodic oxidation (eq. (6)) [4,11].

$$H_2O_2 + 2\ H^+ + 2\ e^- \rightarrow 2\ H_2O \quad (4)$$

$$2\ H_2O_2 \rightarrow O_2 + 2\ H_2O \quad (5)$$

$$H_2O_2 \rightarrow O_2 + 2\ H^+ + 2e^- \quad (6)$$

Consequently, the rate of H_2O_2 accumulation is lower than its rate of electro-generation. Due to the poor solubility of O_2 in aqueous solutions at 1 atm and 25 °C (about 40 or 8 mg L^{-1} in contact with pure oxygen or air, respectively) [12] two dimensional cheap graphite electrodes give quite slow generation of H_2O_2, thus resulting in low H_2O_2 bulk concentrations especially in undivided cells [4,7]. The generation of H_2O_2 is usually accompanied by the parasitic cathodic evolution of hydrogen (eq. (7)) while at the anode the oxygen evolution reaction is expected (eq. (8)).

$$2H^+ + 2\ e^- \rightarrow H_2 \quad (7)$$

$$2\ H_2O \rightarrow O_2 + 2\ H^+ + 2\ e^- \quad (8)$$

Various approaches have been described in the literature to increase the local concentration of H_2O_2 [4,7,13-15,27]. Concentrations of H_2O_2 higher than 50 mM in divided cells separated by cationic

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membranes [4,13] were reached by injecting the gas through GDEs which have higher costs and require a more complicated electrochemical cell layout. An increase of the concentration of H_2O_2 of about one order of magnitude was obtained using microfluidic electrochemical devices equipped with cheap compact graphite cathodes at proper operating conditions [7,14]. A significant increase of the concentration of H_2O_2 was also obtained using dual rotating graphite felt disks [15].

A high concentration of hydrogen peroxide could be theoretically also obtained by increasing the solubility of oxygen in water by using pressurized air or oxygen, thus potentially improving the performances of the EF process. In this context, we report here, for the first time to the best of our knowledge, a study on the effect of the air pressure on both the electro-generation of hydrogen peroxide and the abatement of organic pollutants in water by an electro-Fenton process. Moderate air pressures (1-11 bar) easily achievable in applicative scale electrochemical reactors were used. An increase of the concentration of H_2O_2 of about one order of magnitude was obtained by working at proper operating conditions with moderate air pressure (up to 11 bar). Similarly, a drastically higher abatement of the Acid Orange 7 (AO7), an azoic dye selected as a model organic pollutant resistant to conventional biological processes, was obtained by performing the electro-Fenton process upon increasing the air pressures.

Due to their large-scale production and extensive application, synthetic dyes can cause considerable non-aesthetic pollution and are serious health-risk factors [17]. Since dyes usually present high stability under sunlight and resistance to microbial attack and thermal degradation, most of these compounds are not degradable in conventional wastewater treatment plants. Electrochemical methods are considered to be among the more efficient Advanced Oxidation Processes (AOPs) for the removal of dyes [17]. The azo dye Acid Orange 7 (AO7), also called Orange II ($C_{16}H_{11}N_2NaO_4S$), was often chosen as model compound to evaluate promising abatement approaches because, as a simple molecule, it can easily be used to test new methodologies; in addition, it is widely used for coloration in paperboard industries and in wool textile dyeing.

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The electrochemical oxidation of aqueous solutions of AO7 was previously investigated by various authors [18-26]. The anodic oxidation of AO7 was performed both in the absence and in the presence of chlorides [14,18-19]. Peralta-Hernandez et al. compared the performances of hydrogen peroxide based processes (direct photolysis, electro-Fenton process and photoelectro-Fenton process) [21]. In particular, electro-Fenton process (EF) was studied by various authors [14,21-24]. Oturan and co-authors studied in detail the nature of intermediates and by-products [22]. Furthermore, some of the authors have shown that wastewater contaminated by AO7 can be successfully treated by both EF and oxidation by means of electro-generated active chlorine using energy from salinity gradients by reverse electrodialysis processes [25,26].

2. Experimental

2.1 Electrolyses

Electrolyses were performed in an undivided high-pressure AISI 316 stainless steel cell (Fig. 1) with a coaxial cylindrical geometry, previously described in detail [16], equipped with a gas inlet, a $Ti/IrO_2Ta_2O_5$ anode from ElectroCell AB, a graphite cathode from Carbon Lorraine (inter electrode gap 3.7 cm) and a magnetic stir bar. Stirring of the electrolytic solution was performed with a magnetic stirrer centering the autoclave in a fixed position and keeping constant the nominal stirring speed at 600 rpm. Reproducibility of the stirring regime was verified by visual observation of the solution with the open vessel.

In order to increase the generation of hydrogen peroxide by reaction (8) and reducing its consumption by reaction (6), an high ratio between the cathode and anode surfaces was used. The cathode was a hollow cylinder (4.9 cm inner diameter, 0.55 cm thickness, 0.51 cm height, with a lateral wet surface of 40 cm^2) closed at its bottom that was also employed as container of the electrolytic solution. The cathode external diameter was equal to the internal diameter of the steel cell. The anode was a plate (1.6 cm width, 1cm length and 0.2 cm thickness) inserted at the centre of the cell. The cathode was polished with emery paper of decreasing grain size and by ultrasound bath.

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The high pressure vessel was equipped with a thermocouple for temperature measurement and a pressure gauge. Chromatography grade air was used to pressurize the reactor. A pressure reducer was used to control the operative pressure. The volume of the loaded electrolytic solution was 50 mL. The electrolyses were performed with amperostatic alimentation (Amel 2053 potentiostat/galvanostat) at room temperature. Most of the experiments were repeated at least twice, giving rise to a good reproducibility of results. In most of the experiments, the reactor was opened to collect intermediate samples. After each intermediate sampling, the reactor was closed and brought again to the operative pressure, before activate the electrical current flow.

2.2 Reagents and analyses

The concentration of H_2O_2 was determined from the light absorption of the Ti(IV)–H_2O_2 colored complex at = 409 nm, using $O_5STi•H_2SO_4$ from Fluka. The removal of color was monitored from the decay of the absorbance (A) at = 482 nm for AO7 measured by a Cary 60 UV-Vis Agilent Spectrophotometer. The total organic carbon (TOC) was analyzed by a TOC-L CSH/CSN Shimadzu analyzer. The amount of generated hydrogen was evaluated by gas chromatography using an Agilent 7890B GC equipped with a Supelco Carboxen® 60/80 column. The carrier gas for the gas chromatographic analyses, carried out with a thermal conductivity detector (TCD), was Helium 99.999% purity supplied from Air Liquide. Bi-distilled water and AO7 (Sigma Aldrich), added at 0.43 mM concentration, were used as solvent and model pollutant, respectively. 0.036 M Na_2SO_4 (Janssen Chimica) was used as supporting electrolyte. H_2SO_4 (Sigma Aldrich) to achieve a pH of 3 and 0.5 mM $FeSO_4$ (Fluka) as catalyst for electro-Fenton process were used. Air was from Rivoira (99.998% purity).

3. Results and Discussion

3.1 Electro-generation of H_2O_2

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First experiments were performed with air at atmospheric pressure under galvanostatic mode at various current intensities (50, 80 and 110 mA) with a water solution of Na_2SO_4 (35 mM) and H_2SO_4 (pH 3) for 2 h. At 80 mA and atmospheric pressure, the concentration of H_2O_2 increased with time up to a plateau value of 1.2 mM (Fig. 2) as a concomitant result of slow H_2O_2 cathodic formation (due to the low mass transfer kinetics of oxygen to the cathode surface, caused by its low solubility) and its anodic consumption (Fig. 2). When the experiments were repeated at 50 and 110 mA, quite similar H_2O_2 concentrations profiles were obtained (data not shown), resulting in final concentrations of hydrogen peroxide close to 1.2-1.3 mM after 2 h (table 1), as a result of the fact that, under adopted operating conditions, the process was likely to be kinetically controlled by the mass transfer of oxygen to the cathode surface. These final concentrations of H_2O_2 were achieved with low current efficiency (*CE*) ranging from 1.5 to 3.5 % for experiments performed at 110 and 50 mA, respectively (Table 1). Worth mentioning, the profiles of H_2O_2 concentration and of *CE* were fitted by a very simple theoretical model based on the assumption that both the cathodic reduction of oxygen to hydrogen peroxide (eq. (1)) and the anodic oxidation of H_2O_2 (eq. (6)) take place under mass transfer control (see Fig. 2 and Appendix).

In order to enhance the electro-generation of H_2O_2, a set of amperostatic electrolyses was repeated at 80 mA for 2 h, increasing the air pressures from 1 to 6 and 11 bar, corresponding to oxygen partial pressure of about 0.2, 1.2 and 2.2 bar, respectively. As shown in Figure 2A and Table 1, the increase of the pressure gave rise to a drastic enhancement of the concentration of H_2O_2. In particular, upon increasing the air pressure from 1 to 6 bar, the concentration of H_2O_2 reached a value of about 7 mM. A further increase of the air pressure to 11 bar gave rise to a final concentration of H_2O_2 of about 12 mM. Therefore, upon enhancing the air pressure from 1 to 11 bar, the *CE* increased from about 2 to 21 % (Table 1 and Fig. 2B). These drastic enhancements were due to the higher concentration of oxygen molecularly dissolved in water associated, according to the Henry's law, with the higher oxygen partial pressure. Indeed, as shown in Fig. 2, the experimental data achieved at both 6 and 11 bar were well predicted by the above mentioned theoretical model using the same fitting parameters

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obtained at 1 bar, just changing the oxygen concentration according to the Henry's law (Appendix). Worth mentioning, at 11 bar the chromatographic area of the peak of hydrogen (generated by the parasitic cathodic reduction of water) was dramatically reduced with respect to that obtained in the experiment performed at 1 bar.

To evaluate the effect of the current intensity (*I*) on the electro-generation of H_2O_2 under different air pressure values, the experiments at 6 and 11 bar were repeated at different *I*. Quite interestingly, at both 6 and 11 bar a maximum value of [H_2O_2] was achieved increasing the current value; thus, after a certain current values, the [H_2O_2] started decreasing (Table 1). In the experiments performed at 11 bar, for the lower adopted value of *I* (50 mA), a final concentration of H_2O_2 slightly lower than 7 mM was achieved with a corresponding *CE* close to 20 %. An increase of the current to 80 mA gave higher amounts of H_2O_2 but similar *CE* values, due to the larger passed charge. When *I* was increased up to 200 mA, very similar profiles of H_2O_2 concentration vs. time were achieved (Fig. 3A) as a probable result of the fact that the electro-generation of H_2O_2 at these current densities is limited by the oxygen transfer to the cathode surface (mass transfer-controlled process). Hence, in this range of current intensity (80 – 200 mA), the increase of the current gave rise to a decrease of the *CE* (Fig. 3B). Worth mentioning, a further increase of the current up to 300 mA gave rise to a strong decrease of the concentrations of H_2O_2 (Table 1 and Fig. 3B). This result is probably due to the fact that at high current densities, quite high cathodic potentials are reached and part of the excess of the charge passed is likely to be used for the cathodic reduction of H_2O_2 (eq. (4)). Consequently, the profiles of *CE* vs. time were in good agreement with the theoretical trends expected for the processes occurring under mass transfer kinetics only in the range 80 - 200 mA (Fig. 3B).

3.2 Electro-Fenton

Here, the abatement of AO7 was studied by galvanostatic electrolyses mainly at graphite cathode and iridium based anode with 0.5 mM of $FeSO_4$ as catalyst, Na_2SO_4/H_2SO_4 as supporting electrolyte at pH 3 with an initial concentration of the dye of 0.43 mM. Iridium based anode was chosen since it gives very poor abatement of AO7 by electro-oxidation [14]. Experiments were carried out for seven hours.

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According to the literature, using air at 1 bar as oxygen source and 50 mA current intensity, a very fast abatement of the color was coupled with a slow abatement of TOC (Table 2) as a result of the low concentration of hydrogen peroxide and of the generation of resistant intermediates [14,21-24]. An enhancement of the current to 100 mA did not change substantially the final abatement of the TOC.

In order to enhance the abatement of the TOC, the experiments were repeated at 110 mA and higher air pressures (4, 6 and 11 bar). As shown in Table 2 and Fig. 4, the utilization of higher pressures allowed to achieve drastically higher abatements of TOC after the same passed time, reasonably as a consequence of the enhanced H_2O_2 generation. In particular, an increase of the pressure from 1 to 6 bar allowed to enhance the final abatement of the TOC from 48 to 63%. A further increase of the pressure to 11 bar gave an abatement of the TOC of about 74 %. Hence, it is possible to conclude that the utilization of quite moderate air pressures, that are easily achievable in industrial electrolyzers, can allow to increase substantially the efficacy of EF process. Worth mentioning, this result was not obvious, since previous investigations have shown that, under some operating conditions, an increase of the hydrogen peroxide concentration could not affect the oxidation trend as a result of an over dosage with respect to the concentration of the iron catalyst [27].

At 11 bar the hydrogen concentration (generated by the parasitic cathodic reduction of water) was strongly reduced (giving rise to a current efficiency lower than 1 %) with respect to that obtained in the experiment performed at 1 bar (when the current efficiency in hydrogen was higher than 10 %).

According to the literature, an acceleration of the abatement rate can be achieved in electro-Fenton process by using carbon felt cathodes which present high electrode surfaces. Quite interestingly, when the abatement of AO7 was performed at a carbon felt cathode using air at 1 bar, a lower abatement (about 55 %) was achieved with the same treatment time with respect to that obtained at compact graphite at pressures of 6 or 11 bar. This result clearly highlights that a moderate enhancement of the operating pressure allows the operator to work with compact planar electrodes that are much easier to be modeled in terms of current distribution, mass transfer kinetics and electrochemical performances and that are characterizez by low costs.

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In order to evaluate the effect of the current density on the abatement of TOC, some experiments were performed with air at 11 bar and 50, 110 and 200 mA. As shown in Table 2, an higher abatement was achieved at 110 and 200 mA with respect to that obtained at 50 mA, according to the results obtained from the experiments of electrogeneration of H_2O_2 (see section 3.1).

Worth mentioning, the applicative utilization of electrochemical processes for the treatment of wastewater is up to now often limited by the energetic costs. In this context, EF process presents the advantage to utilize quite low working potentials since the cathodic reduction of oxygen to H_2O_2 requires potential close to 0.5 V vs. SCE. However, EF process usually suffers of lower abatements with respect to other electrochemical processes such as the direct electrochemical oxidation at Boron-doped diamond (BDD) that, on the other hand, requires very high anodic and cell potentials.

In this context, it is important to observe that, according to our experimental results, the utilization of mild air pressures can allow to increasee drastically the abatement of the TOC, while maintaining low energetic costs. Thus according to the data shown in Table 3, the utilization of pressurized air allowed to decrease dramatically the energetic consumptions necessary for the abatement of the pollutant, due mainly to the higher current efficiencies. The energetic costs necessary to provide air at 6 or 11 bar were estimated considering an hypothetic adiabatic compression (polytropic transformation in which the warms up), followed by cooling of the system back to room temperature just via heat exchange with the surrounding environment (without any energy supply). Even assuming an overall compression efficiency of 50%, the energetic costs for compression resulted drastically lower with respect to the energetic gain obtained from the improvement of the energetic efficiency of the electrochemical process.

4. Conclusions

A dramatic increase of the generation of H_2O_2 (up to one order of magnitude) was readily achievable simply through a moderate increase of the air pressure contacted with the electrolytic solution in a pressure range (1 – 11 bar) that can be easily reached in industrial applicative scale electrochemical

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reactors. These drastic enhancements were due to the higher concentration of oxygen molecularly dissolved in water associated, according to the Henry's law, with the higher oxygen partial pressure. Hence, our experimental results quantitatively support the intuitive prediction that increasing the oxygen concentration greatly improves the electro-generation of H_2O_2. We also demonstrated that the increase of the air pressure allowed also to achieve a drastic higher abatement of the TOC of a water solution of AO7 by electro-Fenton process coupled with a decrease of the energy consumption necessary for the abatement of the pollutant, using cheap bulk planar electrodes that are much easier to manage at the industrial scale with respect to carbon felt or GDE.

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Appendix

To rationalize the effect of the air pressure on the electrogeneration of H_2O_2, a simple model was used based on the assumption that both the cathodic reduction of oxygen to hydrogen peroxide (eq. (1)) and the anodic oxidation of H_2O_2 (eq. (2)) take place under mass transfer kinetic control. Other routes involving H_2O_2 were, in a first approximation approach, neglected. As a consequence of above mentioned assumptions, the concentration of H_2O_2 in the bulk of the solution ($c_{(H^2O^2)}^{b}$) is expected to change according to equation (A1), where $k_{m(O^2)}$ and $k_{m(H^2O^2)}$ are the mass transfer coefficients for O_2 and H_2O_2 respectively, $c_{(O^2)}^{b}$ is the bulk concentration of oxygen, A_{cath} and A_{an} are the wet surfaces of cathode and anode, respectively, and V is the solution volume.

$$dC_{H^2O^2}^{b}/dt = k_{m(O^2)}\, c_{(O^2)}^{b}\, A_{cath}/V - k_{m(H^2O^2)}\, c_{(H^2O^2)}^{b}\, A_{an}/V \qquad \text{(A1)}$$

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Let us introduce the terms $a = k_{m(H_2O_2)} A_{an}/V$, $b = k_{m(O_2)} A_{cath}/V$ and $y = b\, c_{(O_2)}^{\ b} - a\, c_{(H_2O_2)}^{\ b}$. Assuming that the concentration of oxygen in the solution is fixed at equilibrium value by the continuous feeding of air during the galvanostatic experiments, $dc_{(H_2O_2)}^{\ b}/dt = -1/a\ dy/dt$ and Eq. (A1) can be written as:

$$dy/dt = -ay \qquad \text{(A2)}$$

As a consequence, $\ln(y/y^{t=0}) = -a\,t$, and the concentration of hydrogen peroxide with the time can be given by the following expression (given that $y^{t=0} = b\, c_{(O_2)}^{\ b}$ as no hydrogen peroxide was present at the beginning of the electrolyses):

$$c_{H2O2}^{b} = b c_{O2}^{b} \frac{[1-\exp(-at)]}{a} \qquad \text{(A3)}$$

Since we are interested only to evaluate the effect of the pressure on the system, which results mainly on the variation of $c_{(O_2)}^{\ b}$, and we performed experiments in such a way to fix the flow-dynamic regime, a and b are substantially the same for all experiments and they can be simply obtained as fitting parameters for the electrolyses carried out at atmospheric pressure. As shown in figure 2, a good fitting was obtained for $a = 2.6\ 10^{-3}\ s^{-1}$ and $b = 3.1\ 10^{-4}\ s^{-1}$ using 8 mg/L for $c_{(O_2)}^{\ b}$. Please consider that the ratio $b/a = k_{m(O_2)} A_{cath}/(k_{m(H_2O_2)} A_{an})$ assumed a value of 8.6 in agreement to the fact that a drastically higher area of the cathode was used with respect to that of the anode ($A_{cath}/A_{an} > 10$).

Worth mentioning, when the experiments were repeated at 6 and 11 bar the theoretical predictions based on eq. (11) well predict the experimental data (Fig. 2) using the same values of a and b obtained at 1 bar and changing the $C_{O_2}^{\ b}$ according to the Henry law thus offering confirmation that modification of the flow-dynamic regime can be neglected with adopted experimental set-up.

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Table 1. Effect of air pressure and current density on cathodic electro-generation of H_2O_2[a]

Pressure (bar)	Current (mA)	$[H_2O_2]$ (mM)	Current efficiency (%)
1	50	1.3	3.4
1	80	1.2	1.9
1	110	1.2	1.5
6	50	6.5	17
6	80	6.9	12
6	110	6.2	8
6	200	5.0	3
11	50	7.0	19
11	80	12.3	21
11	110	12.2	15
11	200	12.2	8
11	300	4.7	2

[a] Electrolysis of 50 mL of 35 mM Na_2SO_4 solutions (pH 3.0) at 22 °C at compact graphite cathode.

Time: 2 h. Value indicate as 1 bar stays for atmospheric pressure (1.013 bar).

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Table 2. Effect of air pressure and current density on abatement of AO7 by electro-Fenton[a]

Pressure (bar)	Current (mA)	Abatement of color (%)	Abatement of TOC (%)	Current efficiency (%)
1	50	> 99	50	7.3
1	110	> 99	48	2.9
4	110	> 99	54	3.2
6	110	> 99	63	3.7
11	110	> 99	74	4.7
11	50	> 99	65	9.2
11	200	> 99	75	2.4

[a] Electrolysis of 50 mL of 35 mM Na_2SO_4, 0.5 mM $Fe(SO_4)$ and 0.43 mM AO7 aqueous solutions (pH 3.0 by H_2SO_4 addition) at 18 °C on compact graphite cathode. Reaction time: 7 h. Anode: Ti/IrO_2-Ta_2O_5.

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Table 3. Effect of air pressure on energy consumption related to the abatement of AO7 by electro-Fenton[a]

Pressure [bar]	**Cell potential [V]**	**Abatement of TOC [%]**	**Energy Consumption [kWh/g_{TOC}]**
1	9.4	48	3.8
4	7.6	54	2.7
7	8.0	73	2.1
11	7.4	74	1.9

[a] Electrolyses of Table 2.

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FIGURE CAPTIONS

Fig. 1. Schematic diagram of the experimental cell.

Fig 2. Evolution of the concentration of H_2O_2 (2A) and of *CE* (2B) during the electrolysis of 50 mL of 35 mM Na_2SO_4 solutions (pH 3.0 by addition of H_2SO_4) at 25 °C and 80 mA and various air pressures: 1 (●), 6 (o) and 11 (■) bar. Theoretical curves (-) are the predictions under the hypothesis that both the cathodic reduction of oxygen to hydrogen peroxide and the anodic oxidation of hydrogen peroxide take place under kinetic mass transfer control with fitting parameters obtained for the experiments performed at 1 bar (see the Appendix).

Fig 3. Evolution of the concentration of H_2O_2 (3A) and of *CE* (3B) during the electrolysis of 50 mL of 35 mM Na_2SO_4 solutions (pH 3.0 by addition of H_2SO_4) at 25 °C and 11 bar (of air) at various currents: 50 (●), 80 (o), 110 (■), 200 (Δ) and 300 (□) mA. Theoretical curves are the predictions under the hypothesis that both the cathodic reduction of oxygen to hydrogen peroxide and the anodic oxidation of hydrogen peroxide take place under mass transfer control with fitting parameters obtained for the experiments performed at 1 bar (see the Appendix). For the concentration of H_2O_2 (3A), the theoretical predictions (–) do not depend on the adopted current density. For the *CE* (3B), the theoretical predictions change with the current density: 50 (...), 80, 110 and 200 (–) and 300 (--) mA.

Fig. 4. Electrolysis of 50 mL of 35 mM Na_2SO_4, 0.5 mM $Fe(SO_4)$ and 0.43 mM AO7 aqueous solutions (pH 3.0) at 18 °C nd 100 mA at compact graphite cathode at various air pressures (1, 4, 6 and 11 bar). Anode: Ti/IrO_2-Ta_2O_5.

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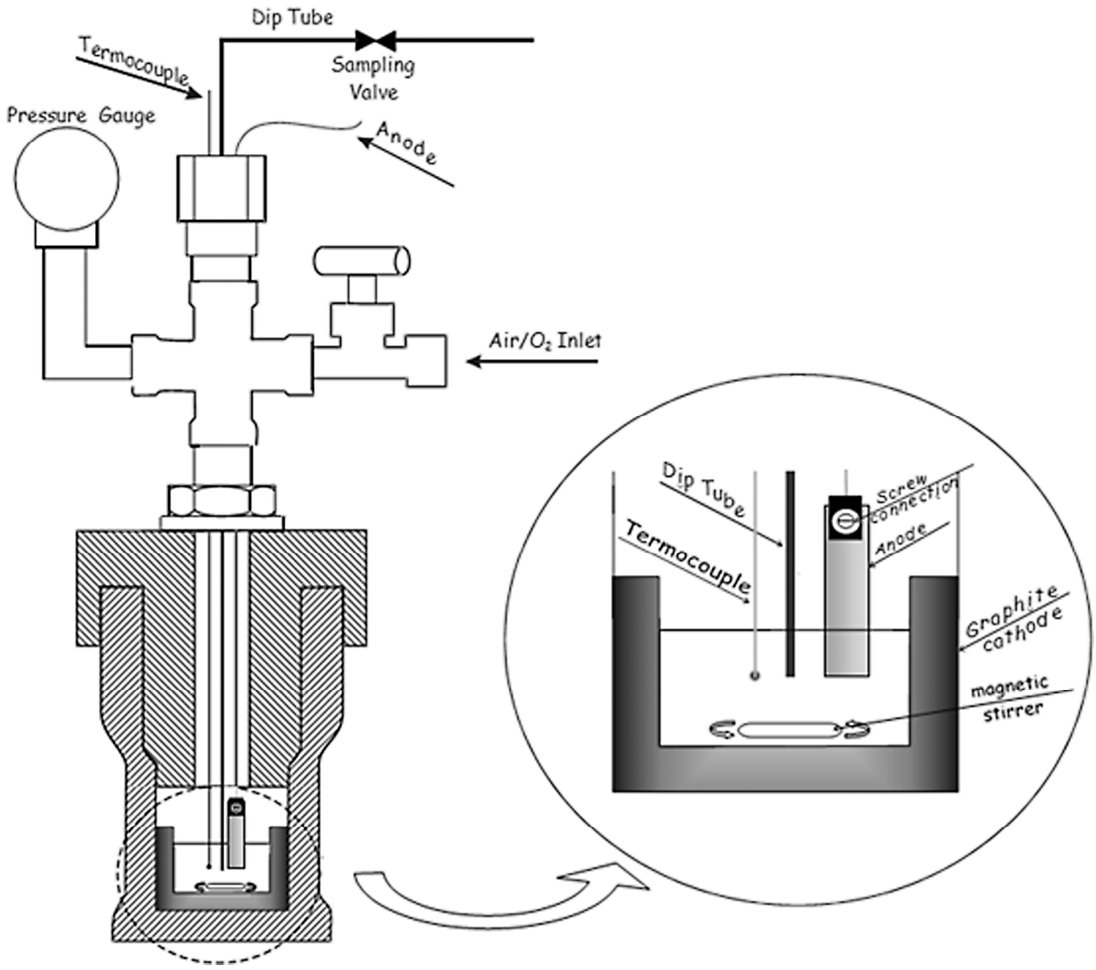

Fig. 1

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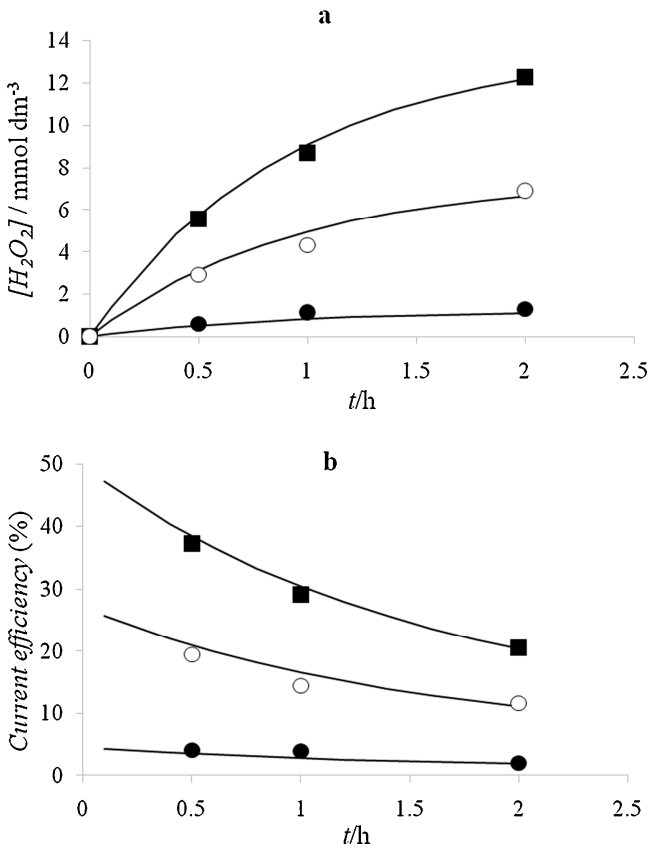

Fig .2

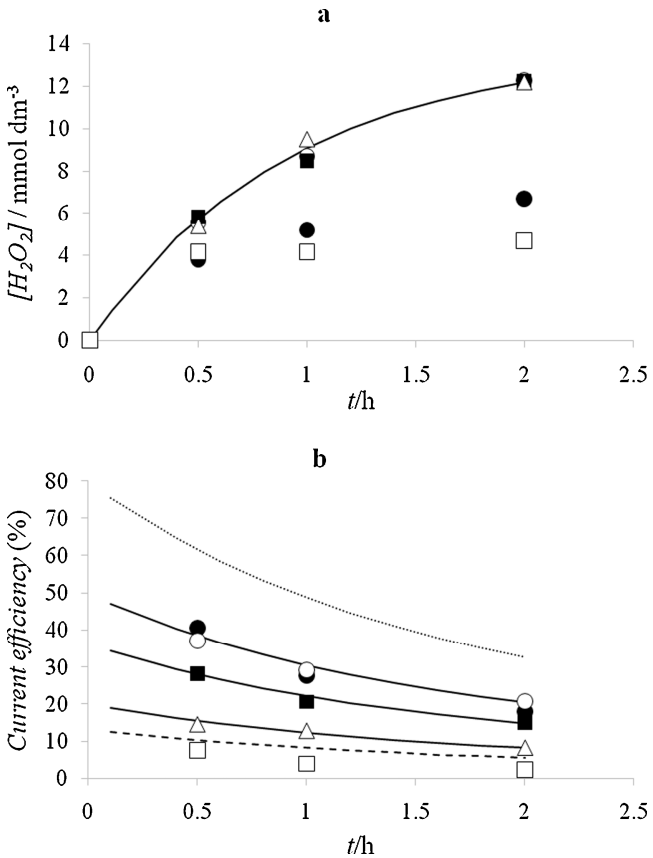

Fig .3

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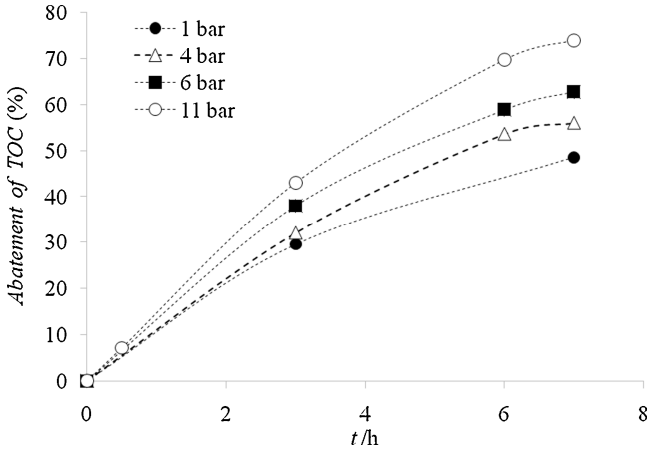

Fig. 4