Towards a more realistic heterogeneous electro-Fenton

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ABSTRACT

With the aim of bringing the heterogeneous electro-Fenton (EF) treatment one step closer to a more realistic operation, the scaling-up of that technology was evaluated. Assays were performed firstly at lab scale in a stirred-tank reactor and then at bench scale in a flow setup including a jet aerator and a microfluidic flow-through electrochemical cell. A fluidized-bed reactor was added to the bench-scale installation in order to retain the solid catalyst, iron-containing alginate beads. To the best of the authors' knowledge, there are no precedent studies reporting a heterogeneous EF treatment in a similar bench scale-configuration. Hydrogen peroxide generation and clofibric acid removal were assessed at both scales at current intensities of 0.12 and 0.25 A. Results showed that the scaled-up treatment was more efficient and cost-effective: at bench scale 18 times more volume was treated, the mass production of hydrogen peroxide was 28 higher and the specific cost for the removal of clofibric acid was cut by more than half. The most efficient treatment turned out to be the EF performed at 0.12 A at bench scale. Those results highlighted the importance of the reactor design in the scaling-up process. Additionally, aromatic intermediates were detected by liquid chromatography-mass spectrometry (LC-MS) and a degradation route was suggested. Carboxylic acids were also measured by HPLC confirming that the pollutant is mineralizing.

1. Introduction

Electro-Fenton (EF) is an electrochemical advanced oxidation process that stands out as a suitable alternative to treat highly persistent pollutants that are refractory to conventional water treatments. It is an environmentally friendly technique in which hydrogen peroxide is firstly generated at the cathode via the two-electron reduction of O2, and then decomposed under the catalytic effect of iron to generate the hydroxyl radical, a powerful oxidant that allows the degradation in aqueous media of virtually any organic compound [1,2].

Despite being a promising technology, research on EF has been performed mostly at a lab scale, and less attention has been paid to aspects such as equipment, scale-up or economic issues, which should be tackled in order to treat real wastewater at industrial scale [3]. Investigations at lab scale have been extensively performed in mixed-tank cells with electrodes arranged in a parallel-plate configuration, where compressed air or oxygen is bubbled into the solution so as to provide the oxygen required for the in situ generation of hydrogen peroxide [4,5]. However, this layout presents several bottlenecks preventing the full-scale application of EF, such as energy consumption issues, mass transfer limitations and low solubility of oxygen [5,6]. Therefore, if the EF treatment is to be applied industrially at some point, it is necessary to increase its technology readiness level (TRL), which at the moment is at an intermediate level [7]. In this sense, the scaling-up of the process should not merely deal with increasing the size of the reactor or the volume treated; conversely, a more comprehensive approach should be taken, focusing on addressing the abovementioned limitations as well, with the perspective of bringing the EF process closer to a future actual implementation.

With this in view, flow cells are the most common alternative found in literature to mixed-tank cells, and have been extensively applied in bench-scale studies. Their main advantage is the enhanced mass transport properties. In most investigations, a single-pass flow cell is connected to a reservoir auxiliary tank through a recirculation pump in order to increase the number of times wastewater flows through the cell. Even if that "flow cell-tank" setup presents a different flow
pattern, from a macroscopic point of view that configuration can be modeled as a mixed-tank reactor, but with the benefit of presenting much greater efficiencies than a conventional stirred tank and the possibility of further scaling-up the process by stacking the cells [5].

In this regard, some investigations have been conducted towards the development of a novel flow electrochemical reaction system at bench scale that deals with several of the limitations stirred-tank reactors present [8]. One of the main strengths of that system is the use of a microfluidic flow-through (MF-FT) electrochemical cell. Firstly, the microfluidic design, with an inter-electrode gap in the order of micrometers, contributes to minimize Ohmic drops, thus reducing the energy consumption associated with the electrochemical cell [9]. Additionally, the flow-through configuration of the reactor maximizes the mass-transfer coefficient thanks to the special hydrodynamics conditions established when forcing the liquid to circulate across the flow-through electrodes. Moreover, the use of three-dimensional electrodes allows benefiting from a high specific surface area [9,10]. When compared to a commercial flow-by reactor, the MF-FT cell proved to reduce the specific charge required and specific energy consumption by almost 5 and 6 times, respectively [11]. Another fascinating feature of the bench-scale reaction system is the jet aerator. This device, based on the Venturi effect, supplies air to the system without the need of an external compressor. When liquid flows through the constricted section of the jet, fluid pressure is reduced, creating a driving force that aspirates gas into the solution. The bubbles formed during this process create a biphasic mixture that supersaturates the solution in oxygen, increasing its transfer to the cathode and promoting the hydrogen peroxide formation [6,12].

To the best of the authors’ knowledge, there are only two previous studies that report the use of a MF-FT reactor combined with a jet aerator for an EF treatment at bench scale [10,13]. However, in both cases the EF assays were performed with homogeneous catalysts. Therefore, the application of the MF-FT reactor with the jet aerator technology to a heterogeneous EF treatment still remains to be explored.

Catalyst recovery and reuse is another challenge of the EF treatment [14]. The use of heterogeneous catalysts in EF presents several advantages with a view to scaling up the process, such as reducing the formation of iron hydroxide sludge, allowing the easy recovery from the solution and the reuse of the catalyst or permitting the operation in continuous mode [3,14]. Several investigations have focused on the preparation of efficient catalysts for EF using natural polymeric matrices [15]. As an example, iron-containing alginate beads, gels obtained by cross-linking iron into an alginate structure, have demonstrated high catalytic activity for the degradation of various pollutants, like pesticides [16], ionic liquids [17] and dyes [18], showing reusability after several cycles [18,19]. Although heterogeneous EF suffers from slow kinetics (limited by the mass transfer of hydrogen peroxide to the catalyst surface) and the formation of catalyst agglomerations, those drawbacks could be overcome by the use of fluidized-bed Fenton reactors [20]. Therefore, the incorporation of a fluidized-bed to the abovementioned bench-scale setup is explored in this investigation.

With all this in mind, this research is focused on approaching the heterogeneous EF treatment one step closer to a more realistic operation. In order to do so, the treatment was performed firstly at lab scale in a stirred-tank reactor and then tested at bench scale in the combined MF-FT jet aerator installation, so as to assess the differences observed in the scaling up of the heterogeneous EF process. Clofibric acid was selected as a model pollutant for the tests. It is a pharmaceutical metabolite of blood lipid regulation pharmaceuticals [21] and a growth control pesticide [22] reportedly present in aquatic environments [23,24], which has demonstrated to pose acute toxicity to invertebrates and has been associated with endocrine disruption and other harmful issues on aquatic environments [25–27].

2. Materials and methods

2.1. Reagents

Clofibric acid (2-(p-Chlorophenoxy)-2-methylpropionic acid, 97%), sodium sulfate and titanium(IV) oxysulfate solution (1.9–2.1%) were supplied by Sigma-Aldrich. For the electrode preparation, carbon black (Vulcan® XC72) was purchased to Cabot Corporation, polytetrafluoroethylene (a 60% wt. Teflon® emulsion solution in H2O) was provided by Sigma-Aldrich and isopropanol, hydrochloric acid and oxalic acid were provided by VWR Chemicals, Scharlab and Panreac, respectively. For the catalyst elaboration, sodium alginate and iron (III) sulfate hydrate were supplied by Sigma-Aldrich, respectively. Methanol, formic acid and sulfuric acid used for preparing HPLC mobile phases were provided by Sigma-Aldrich.

2.2. Electrode materials and catalyst

In the experiments at lab scale, a boron-doped diamond (BDD) plate provided by Condias GmbH was used as the anode (5 × 2.5 × 0.1 cm) and a carbon felt from Carbon-Lorrain was used as the cathode (5 × 2.5 × 0.5 cm).

In the experiments performed at bench scale, the anode was a thin-film BDD electrode supported on a niobium mesh (Diachem®) provided by Condias GmbH. The cathode was fabricated by depositing a mixture of carbon black (CB) and polytetrafluoroethylene (PTFE) on a titanium mesh (CB/PTFE/Ti). The mesh was purchased to Xian Howah Technology Co., Ltd. (China) and the electrode was obtained as follows: 1) Ti mesh pretreatment: the mesh was submerged two times in a 20% HCl solution and two times in a 10% oxalic acid solution, heating the liquid at 100 °C until it boiled, keeping it boiling for 15 min and rinsing the mesh with Milli-Q water after each immersion; 2) Ink preparation: 1 mg mL−1 of CB and 5 mg mL−1 of PTFE were dispersed into isopropanol and sonicated for 2 h; 3) Deposition of ink on the electrode: the mesh was placed on a hot plate at 130 °C and painted dispensing 100 mL of ink on each side of the mesh using a spray gun; 4) Electrode annealing: the electrode was introduced in a muffle furnace, with a heating rate of 12 °C min−1 until it reached 360 °C, and kept at that temperature for 1 h, and 5) Second coat: the electrode was painted a second time repeating steps 2, 3 and 4. All the electrodes used at bench scale were 8 × 9.5 cm, with 33 cm2 corresponding to the wet area (the electrochemical cell’s inlet pipe has a diameter of 6.5 cm). The surface area of the BDD anode and the CB/PTFE/Ti cathode were calculated to be of 49.5 cm2, by determining the surface/geometric area ratio as described elsewhere [9]. The holes of the meshes are diamond-shaped, with a height and width of 1 × 2 mm.

As for the catalyst, iron-containing alginate beads were prepared following a similar procedure to that found elsewhere [16]. Drops of a sodium alginate solution (2% w/v) were added into a 0.05 M Fe3+ hardening solution prepared from iron(III) sulfate hydrate, keeping them in the iron solution for 1 h. After, they were filtered, washed repeatedly with distilled water and stored at 4 °C [17]. The iron content of the catalyst obtained in this manner, which was determined to be of 4 mg Fe per gram of alginate beads, was obtained by performing an acid digestion of the alginate beads and measuring the iron concentration afterwards by ICP-OES.

2.3. Experimental setup at lab scale

Experiments at lab scale were carried out in an open undivided cylindrical glass reactor operated in discontinuous mode, introducing 0.15 L of a solution containing 0.05 M Na2SO4 and, in the case of AO and EF treatments, 10 mg L−1 of clofibric acid too. The reactor
had a mixed-tank flow pattern, obtained by continuously stirring the solution with a magnetic bar to avoid concentration gradients. A constant current was applied by connecting the two electrodes, which were placed at the center of the cell and at a distance of 1 cm from each other, to a direct power supply (Siglent SPD3303C). A continuous bubbling of 0.5 L min$^{-1}$ of air at atmospheric pressure was kept near the cathode in EF and $\text{H}_2\text{O}_2$ production assays, in order to trigger $\text{H}_2\text{O}_2$ in situ electrogeneration. For EF experiments, the solution pH was adjusted to 3.0 using sulfuric acid and 1 g of iron-containing alginate beads were added to the reactor as the catalyst.

### 2.4. Experimental setup at bench scale

At bench scale, experiments were performed in a flow system, a closed-circuit configuration operated in discontinuous mode. The installation was filled with 2.7 L of a solution containing 0.05 M $\text{Na}_2\text{SO}_4$ and, in the case of EF treatments, 10 mg L$^{-1}$ of clofibrac acid too. The system setup is represented in Fig. 1. The solution was pumped from the bottom of the biphasic tank through a jet aerator at a flow rate of 140 L h$^{-1}$. The pressure difference at the jet led to the entrance of air from the top of the biphasic tank. The obtained solution-air biphasic mixture flowed through a peephole, which allowed to observe the formed bubbles, and then was introduced in the MF-FT cell, passing firstly through the anode and then through the cathode, which were separated by a thin PTFE insulating layer (150 μm). A power supply was connected to the electrodes, using platinum wire as the current collector. Just before the solution was returned into the biphasic reservoir tank, it passed through a heat exchanger, in order to keep the temperature of the system at 22 °C. More information about the installation can be found in [8].

For EF experiments, the solution pH was adjusted to 3.0 using sulfuric acid. Additionally, a self-elaborated fluidized-bed reactor was connected to the outlet of the electrochemical cell to contain the solid catalyst (6 g of iron-containing alginate beads). It was built using a transparent pipe made of crystal PVC with an internal diameter of 5.1 cm and an effective height of 7.7 cm, values that were empirically determined to allow an adequate fluidization of the catalyst. A perforated acrylate plate was placed on the bottom of the bed. Moreover, a thin sponge was placed on the lower and upper part of the bed, allowing the solution to pass through but preventing the alginate beads to leave the reactor.

### 2.5. Analytical methods

Hydrogen peroxide production was measured by following the concentration of the complex formed between $\text{H}_2\text{O}_2$ and $\text{Ti}^{4+}$, using a titanium (IV) oxysulfate solution as the reagent, and measuring the complex absorbance at 410 nm in a UV-1700 Spectrophotometer (Shimadzu) [28].

Clofibrac acid decay was followed by high performance liquid chromatography (HPLC) using an Agilent 1200 series equipment with a DAD detector. The mobile phase, 60:40 MeOH: $\text{H}_2\text{O}$ with 0.1% of formic acid, was pumped through a ZORBAX Eclipse Plus C18 column at a flow rate of 1 mL min$^{-1}$. Temperature was kept at 25 °C and measurements were performed at a wavelength of 225 nm.

Carboxylic acids were detected by ion-exclusion HPLC by means of an Agilent 1100 equipment with a DAD detector connected to a Zorbax Eclipse Plus C18 column at a flow rate of 1 mL min$^{-1}$. Temperature was kept at 60 °C and measurements were done at 206 nm.

Total organic carbon (TOC) was measured with a Multi N/C 3100 Analytik Jena analyzer at CACTI (Universidade de Vigo).

Intermediates were identified by liquid chromatography–mass spectrometry (LC-MS), on a TIGER-TOF mass spectrometer (Buerker Daltonics, Bremen, Germany). Measurements were carried out at CACTI (Universidade de Vigo). Ionization was achieved by electrospray, using a voltage of 3500 V applied to the needle, an end plate offset of 500 V and a dry gas flow of 8 L min$^{-1}$ at a temperature of 220 °C. Mobile phase, composed by a gradient of H$_2$O and acetonitrile both with 0.1% of formic acid, flowed at 0.4 mL min$^{-1}$ through a Zorbax Eclipse XB-C18 Rapid Resolution High Definition column.

Iron lixiviation was determined by ICP-OES using a Perking Elmer Optima 4300 DV. The same procedure was followed to determine the iron content of the alginate beads after an acid digestion of the catalyst.

### 2.6. Energy consumption

The specific energy consumption was determined per unit of clofibrac acid mass ($E_{\text{CA}}$) and per unit of hydrogen peroxide mass ($E_{\text{H}_2\text{O}_2}$) as shown in Eqs. (1) and (2), respectively, where $E_{\text{d}a\text{f}}$ is the average potential difference in the electrochemical cell (V), $I$ the applied current intensity (A), $t$ the time (h), $V$ the solution volume (L), $\Delta C_{\text{CA}}$ the difference in clofibrac acid concentration (mg L$^{-1}$) and $C_{\text{H}_2\text{O}_2}$ the concentration of hydrogen peroxide (mg L$^{-1}$).

$$E_{\text{CA}} = \frac{E_{\text{d}a\text{f}} \cdot I \cdot t}{V \cdot \Delta C_{\text{CA}}}$$

$$E_{\text{H}_2\text{O}_2} = \frac{E_{\text{d}a\text{f}} \cdot I \cdot t}{V \cdot C_{\text{H}_2\text{O}_2}}$$

### 3. Results and discussion

#### 3.1. Experiments at lab scale

#### 3.1.1. Hydrogen peroxide generation at lab scale

The electrogeneration of hydrogen peroxide at the cathode via the two-electron mechanism oxygen reduction reaction is key for the EF process (Eq. (3)) [29]. Therefore, the production of hydrogen peroxide was initially studied. Two different current intensities were analyzed, and the results are plotted in Fig. 2. As it can be observed, the hydrogen peroxide generation rate is almost identical for both current intensities, achieving the maximum concentration at around 30 min (15.8
and 14.7 mg L\(^{-1}\) at 0.12 and 0.25 A, respectively) and slightly decreasing after that time. The fact that a rise in the current intensity does not provide an increase in hydrogen peroxide concentration suggests that the process is working above the limiting current, and thus is being controlled by the oxygen mass transfer to the cathode [30]. Because of the imbalance between current intensity and oxygen, there is an excess of current which has no oxygen available to produce hydrogen peroxide by means of Eq. (3). Therefore, this excess is used in other reactions, such as the parasitic reaction where hydrogen peroxide is reduced to water (Eq. (4)) [31]. The problematic of this situation is two-fold: current intensity is not only not fully exploited to generate the desired product, but also used to destroy it [12]. In view of the aforementioned results, it can be concluded that current efficiency was higher when working at 0.12 A. This fact can also be observed in the inset of Fig. 2, which depicts hydrogen peroxide generation versus the specific charge and shows that, in general, for a same specific charge a higher hydrogen peroxide yield is provided in the assay with lower current intensity.

\[
O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{3}
\]

\[
H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O \tag{4}
\]

### 3.1.2. Electro-Fenton treatment at lab scale

As already mentioned in the introduction, EF treatment relies on the formation of a highly reactive species, the hydroxyl radical, via the Fenton reaction (Eq. (5)), where the hydrogen peroxide previously generated at the cathode (Eq. (3)) is decomposed under the catalytic action of the ferrous ion. Radicals produced by this means are known as homogeneous hydroxyl radicals. However, when non-active anodes with a high O\(_2\)-overpotential are used, such as the BDD anodes used in this investigation, additional hydroxyl radicals are generated from water discharge on the anode surface (Eq. (6)), where they remain physisorbed (M(\text{OH})) [31]. These are referred to as heterogeneous hydroxyl radicals.

\[
H_2O_2 + Fe^{2+} \rightarrow OH^- + HO^- + Fe^{3+} \tag{5}
\]

\[
M + H_2O \rightarrow M(\text{OH}) + H^+ + e^- \tag{6}
\]

As a consequence of the creation of heterogeneous hydroxyl radicals during the EF treatment, AO collaborated in the mineralization of the clofibrac acid in EF assays. Therefore, in order to assess that contribution, AO experiments were carried out separately and the results were compared with those obtained from EF experiments. As depicted in Fig. 3a, clofibrac acid was successfully removed after 1 h of EF treatment at 0.12 and 0.25 A, whereas for obtaining a 95% and 100% elimination with AO treatment alone 2 h were required at 0.12 and 0.25 A, respectively. The inset in Fig. 3a shows how the specific charge applied was more efficiently profitied for removing clofibrac acid in assays at 0.12 A than at 0.25 A for both EF and AO treatments. Additionally, it can be observed that regardless of the current intensity, EF assays always required less charge for attaining the complete degradation when compared with AO. Kinetic pseudo-first order constants (Table 1) of EF experiments, compared with those of AO alone, are 4.5 times higher at 0.12 A and 2.8 times higher at 0.25 A. This seems to indicate that, during the initial minutes of the EF treatment, the contribution of homogeneous hydroxyl radicals obtained from the Fenton reaction was greater than that of the heterogeneous ones. This fact is in accordance with the results reported by Olvera-Vargas et al. [32], which pointed out that homogeneous hydroxyl radicals were dominant during the first stages of EF treatment, whereas hydroxyl radicals physiosorbed on the anode surface prevailed in the last stages.

In terms of the applied current intensities, the increase from 0.12 to 0.25 A provided a moderate improvement in the pollutant elimination in AO assays. However, when it comes to the EF treatment, the lower current intensity showed a slightly faster elimination of clofibrac acid (Fig. 3a). This could be related with the abovementioned fact that the Fenton reaction is having a greater contribution at the beginning of the treatment and, as discussed in section 3.1.1, the generation of hydrogen peroxide at 0.12 A was slightly higher. By contrast, the TOC removal obtained during the EF treatment was considerably boosted when increasing the current intensity from 0.12 to 0.25 A, attaining a 42% and a 61%, respectively, after 2 h.

To further analyze the current intensity usage, the specific energy consumption per unit of clofibrac acid mass (EC\(_{CA}\)) was determined as shown in Eq. (1). Fig. 3b depicts the values obtained. For both cur-
rent intensities, the specific energy consumption at the end of EF assays is less than half of that at AO assays, due to the shorter treatment times required for completely removing the clofibrate acid. Experiments at 0.12 A had a lower consumption, requiring 0.36 and 0.85 kWh g$^{-1}$ CA at the end of the EF and AO treatments, respectively, whereas at 0.25 A 0.95 and 2.26 kWh g$^{-1}$ CA were consumed, respectively.

Finally, the dissolved iron present at the solution by the end of the heterogeneous electro-Fenton process was determined. Results showed that after 2 h of treatment, 0.082 mM and 0.045 mM of iron was present in assays at 0.12 A and 0.25 A, respectively. Taking into consideration that there is a certain amount of dissolved iron, in addition to the surface-catalyzed process a homogeneously catalyzed Fenton reaction is also probably taking place. A similar behavior, with a mixed contribution of homogeneous and heterogeneous catalytic reactions has been observed in electro-Fenton treatments using different catalysts, such as magnetic [33], iron supported in bentonite [34] and supported in an ion-exchange resin [35].

3.2. Experiments at bench scale

3.2.1. Hydrogen peroxide generation at bench scale

With the aim of scaling up the EF treatment, a bench-scale setup was tested, consisting on a MF-FT electrochemical cell with a jet aerator system. In this configuration, the cathode was changed to a CB/PTFE/Ti electrode. Carbon felt was not selected because it is flexible and the high flow rate used in this setup would bend it, moving it away from the anode and thus increasing the inter-electrode gap.

Firstly, the capacity of the installation for generating hydrogen peroxide was analyzed. Two different current intensities were selected for the assays, taking into account the current densities previously tested at lab scale and the fact that the obtained results showed a more efficient use of the lower value. Since at lab scale 10 and 20 mA cm$^{-2}$ were tested (corresponding to 0.12 and 0.25 A, respectively) were chosen, with the geometrical area of the electrodes), a lower value and one that correspond to 0.25 and 0.50 A, respectively. Calculating with the geometrical area of the electrodes, a lower value and one that correspond to 0.25 and 0.50 A, respectively. Hence, current densities of 7.5 and 15 mA cm$^{-2}$ were chosen for the bench-scale hydrogen peroxide tests, which correspond to 0.25 and 0.50 A, respectively.

The results obtained at bench scale, depicted in Fig. 4, showed that the increase in the current intensity did not promote the hydrogen peroxide generation. On the contrary, the production rate was clearly lower at 0.50 A and, during 5 h of experiment, the maximum concentration of hydrogen peroxide detected was of only 8.5 mg L$^{-1}$, while it was more than doubled (21.5 mg L$^{-1}$) when working at 0.25 A. This fact suggests that at the higher current intensity parasitic reactions such as Eq. (4) are significantly boosted, being detrimental to hydrogen peroxide formation. Consequently, in terms of efficiency, the charge is used more efficiently at 0.25 A when compared to 0.50 A (inset of Fig. 4).

3.2.2. Electro-Fenton treatment at bench scale

Heterogeneous EF assays were performed at bench scale introducing the catalyst in the self-elaborated fluidized-bed reactor. Taking into consideration the electrochemical cell layout (where the flow passes firstly through the anode and then through the cathode), the fluidized-bed reactor was connected at the outlet of the cell, right after the solution has passed through the cathode which is the moment when the concentration of hydrogen peroxide is maximum, and thus the Fenton reaction is favored [10]. Since at 0.50 A the generation of hydrogen peroxide was considerably reduced, this value of current intensity was discarded for the EF experiments. Instead, lower values (the same as in the lab scale assays: 0.12 and 0.25 A) were chosen, which contribute to reduce the energy consumption associated with the electrochemical cell.

Clofibrate acid elimination is shown in Fig. 5a. As it can be observed, almost complete elimination of the pollutant is achieved after 8 h of treatment, being the process very similar at both current intensities, only slightly faster at 0.25 A (see kinetic constants in Table 2). However, in terms of efficiency, the lower current intensity profits better the charge applied since for any given specific charge the decay of clofibrate acid achieved in the assay at 0.12 A is higher, as depicted in the inset of Fig. 5a. This same behavior was observed in the EF tests at lab scale. Also, one of the previous studies using the MF-FT coupled to the jet aerator available in the literature concluded, after testing current densities from 10 to 50 mA cm$^{-2}$ (corresponding with 0.33 to 1.65 A, calculated with the wet cross section of the electrodes specified in the article), that increasing the current density reduced the efficiency of the EF treatment [13].

Additionally, hydrogen peroxide measurements were done over the course of the treatment. A maximum amount of 1.0 mg L$^{-1}$ of hydrogen peroxide was observed in the EF at 0.25 A, which is less than a 5% of the maximum amount obtained in the production assays (section 3.2.1), indicating that most part of the hydrogen peroxide that can be produced is being used to degrade the pollutant or is being decomposed. Dissolved iron at the end of the treatment was measured as well, obtaining after 8 h a concentration of 0.058 mM and 0.045 mM of iron at 0.12 A and 0.25 A, respectively. It is worth mentioning that these concentrations are the same or lower than the ones obtained at the lab-scale configuration. It should be noted, that a previous homogeneous electro-Fenton study, performed at a similar bench-scale installation with a MF-FT electrochemical cell and a jet aerator has determined that the optimal iron concentration in the solution was 0.5 mM [10]. Taking into account that the dissolved iron by the end of the assays in the present study is roughly 10 times lower, although a homogeneous catalytic contribution cannot be discarded,
it seems clear that heterogeneous catalysis is also playing an important role.

Since several intermediates were detected while measuring clofibrin acid by HPLC, they were used as an approximate indication of the mineralization achieved by adding the area of the peaks of all the intermediates observed at each sample time (see Fig. S1 in the supplementary material). It was observed that at 0.25 A the maximum amount of intermediates was reached between 1 and 2 h and then constantly decreased. At 0.12 A it took more time to reach the maximum concentration of intermediates, around 3 h, and from that time the amount started to be reduced firstly slowly and then sharply in the last 2 h. Whatever the case, it is clear that in both situations the concentration of aromatic intermediates is considerably reduced throughout the treatment, indicating that clofibrin acid is not only being degraded, but also mineralized.

Furthermore, the specific energy consumption at the electrochemical cell for the elimination of clofibrin acid was calculated (Fig. 5b). Energy consumption is remarkably higher at 0.25 A, being 2.6 times higher than at 0.12 A for attaining the same clofibrin acid removal at the end of the treatment. This is directly derived from what observed before: the fact that although the current intensity is doubled the elimination rate of the pollutant is almost the same or, in other words, that the charge applied is more efficiently used at 0.12 A, leads to a significant increase of the specific energy consumption at 0.25 A. Again, a similar outcome was also obtained in the experiments at lab scale.

3.2.3. Degradation pathway

In order to identify some of the intermediates generated during the EF treatment of the clofibrin acid and establish a possible degradation route, LC-MS measurements at negative ionization mode were performed for an EF assay, using 100 mg L\(^{-1}\) of the pollutant, at 0.25 A. Various intermediates were detected, which is typical during an EF treatment. The mainly detected compounds are included in Table S1 in the supplementary material and the proposed route that relates them is presented in Fig. 6. It seems that clofibrin acid \(①\) degradation could occur via three different reaction routes. Firstly, dechlorination of clofibrin acid through the cleavage of \(C_4-Cl\) bond would produce 2-(4-hydroxyphenoxophenyloxy)-2-methylpropanoic acid \(②\). A further attack by hydroxyl radicals to compound \(②\) could break the ether group by separating the \(C_1-O\) bond, which would result in hydroquinone \(③\) and 2-hydroxy-2-methylpropanoic acid \(④\). A second pathway could generate 2-(4-chloro-2-hydroxyphenoxophenyloxy)-2-methylpropanoic acid \(⑤\) after the addition of the OH group to the aromatic ring of clofibrin acid. Subsequently, the cleavage of the \(C_1-O\) bond would generate 4-chlorobenzene-1,2-diol \(⑥\) and intermediate \(④\). The third pathway could occur if the \(C_1-O\) bond is broken directly from the clofibrin acid molecule, which would produce 4-chlorophenol \(⑦\) and intermediate \(⑤\). In turn, 4-chlorophenol could undergo two transformations, namely hydroxylation of the aromatic ring resulting in the creation of \(④\) or the cleavage of its \(C_4-Cl\) bond, forming \(⑤\). Finally, the cleavage of the aromatic ring of \(②\) or \(⑤\) would lead after some oxidation steps to the generation of (E)-2-((2-carboxypropan-2-yloxy)-4-oxobut-2-enio acid \(⑥\), which would be further oxidized to 2-hydroxy-2-methylpropanoic acid \(④\). The successive oxidation of the detected intermediates \(①\), \(③\), \(⑥\) and \(⑦\) would eventually cause the formation of short-chain carboxylic acids, which are the previous steps to the complete mineralization. All the identified compounds had already been reported in literature during the degradation of clofibrin acid by means of different advanced oxidation processes: catalytic ozonation [27,36,37], photocatalysis [21], electro-assisted heterogeneous persulfate process [38] and Fenton-like treatment [27].

### 3.3. Lab scale versus bench scale

#### 3.3.1. Comparison of hydrogen peroxide generation

With the aim of evaluating if experiments at bench scale are as effective as those at lab scale, some comparisons were carried out. Taking into consideration that the volumes treated at each scale are quite different (0.15 L at lab scale and 2.7 L at bench scale), the specific charge is used as the comparison base.

First of all, the hydrogen peroxide generation of both systems was assessed. The comparison of insets in Fig. 2 and 4 shows that the maximum concentration of hydrogen peroxide was obtained at 0.37 A h L\(^{-1}\) in the bench-scale assay at 0.25 A. Only when current intensity was increased to 0.50 A the concentration obtained was lower than at lab scale. However, if the mass production is compared (Fig. 7a), it is clear that, regardless of the current intensity, the bench-scale setup is capable of generating a far greater amount hydrogen peroxide. In fact, comparing the experiments at 0.25 A, at a specific charge of around 0.4 A h L\(^{-1}\) the amount of hydrogen peroxide generated at bench scale is 28 times higher than at lab scale.

Interestingly, this outstanding increase in the production is not translated into a greater specific energy consumption of the electrochemical cell (see Fig. 7b). Conversely, at around 0.4 A h L\(^{-1}\), which is when the peak of hydrogen peroxide generation is approximately reached in all the assays, the consumption at 0.25 A at bench scale is less than half of that at lab scale. And, even if the consumption at 0.12 A is reduced compared with that at 0.25 A at lab experiments,

<table>
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<th>(I) (A)</th>
<th>(k) (min(^{-1}))</th>
<th>(R^2)</th>
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</table>

### Table 2

Pseudo-first order parameters for the elimination of clofibrin acid by EF at bench scale.
it is still greater than in the bench-scale 0.25 A assay for any given specific charge. Therefore, it is clear that the bench-scale installation outperforms the lab-scale configuration. This fact highlights the importance of the reactor design for the EF treatment, underlining that the scaling-up does not necessarily require a great increase in terms of size, but to bring the process to a more realistic and efficient operation: although the geometrical area of the cathode was only increased by 2.7 times at bench scale, it allowed processing 18 times more volume, increasing 28 times the mass generation of hydrogen peroxide and cutting roughly by half the specific energy consumption. This was achieved thanks to the simple but thoughtful design of the bench-scale setup, with the jet enhancing the aeration and supersaturating the solution and the MF-FT configuration of the electrochemical cell improving mass transfer and reducing the energy consumption. It could be suspected that the difference in the hydrogen peroxide production between lab and bench scale was due to the change from a carbon felt cathode at lab assays to a CB/PTFE/Ti one at bench assays, since there is plenty of evidence in the literature that points out that incorporating the CB/PTFE mixture on the cathode enhances hydrogen peroxide generation [39-41]. However, it should be noted that in a previous investigation of the bench-scale setup, where bare carbon felt was used, it was determined that after 45 mins of experiment (corresponding to a specific charge of 0.75 A h L$^{-1}$), 33 mg L$^{-1}$ of hydrogen peroxide were obtained, equivalent to a mass generation of 33 mg [12]. Taking into consideration that such a mass production is much greater than what achieved at any of the lab scale assays, it is evident that the better performance obtained in the present study when scaling up the process is not due (at least not exclusively) to the modification of the cathode material.

3.3.2. Comparison of the electro-Fenton treatment

A comparative evaluation of the EF treatment at both scales was also carried out. Analyzing the results shown in the insets of Fig. 3a and Fig. 5a, the more efficient assay turned out to be the EF performed at 0.12 A at bench scale. A very similar behavior was observed in the decay of clofibric acid at the 0.12 A lab assay and the 0.25 A bench assay, which have the closer current densities of all the experiments analyzed: 10 mA cm$^{-2}$ (lab) and 7.5 mA cm$^{-2}$ (bench). The efficiency in the use of the charge for the abatement of clofibric acid is improved when scaling up the process to the bench scale, regardless of the current intensity analyzed. This improvement is remarkably higher when working at 0.25 A, since the specific charge required for the complete elimination of the pollutant is reduced by more than half (from 1.67 A h L$^{-1}$ at lab scale to 0.74 A h L$^{-1}$ at bench scale). At 0.12 A the difference between scales is not so remarkable during the last part of the treatment (at around 0.40 A h L$^{-1}$ the removals achieved at lab and bench scale are of 94 and 97%, respectively), but quite important dur-

![Fig. 6. Possible degradation route of clofibric acid during EF treatment.](image)

![Fig. 7. Comparison of hydrogen peroxide production at lab and bench scale evaluating: the mass generated (a) and the specific energy consumption (b).](image)
ing the initial part (at 0.13 A h L$^{-1}$ the removal was of 59% at lab scale whereas it was of 81% at bench scale).

Additionally, the bench-scale setup is advantageous because it allows treating a higher mass of the pollutant: since the concentration used was 10 mg L$^{-1}$ of clofibrate acid in all cases, but the volumetric capacity was greater with the scaled-up installation, the amount of pollutant treated was 18 times higher at bench scale. However, this fact did not entail the need of a greater specific charge to achieve the removal of the pollutant (Fig. 8a). As an example, at a specific charge value of 0.13 A h L$^{-1}$ the mass of clofibrate acid eliminated at 0.12 A at lab scale was of 0.89 mg, while at bench scale it was considerably higher, 21.9 mg.

The energy consumption per gram of clofibrate acid removed, shown in Fig. 8b, also corroborates the benefit of the scaled-up configuration. At 0.25 A, the consumption at lab scale was greater than at bench scale for any given specific charge, being 2.5 times higher by the moment of the complete elimination of clofibrate acid (0.95 kW h g$^{-1}$ CA of consumption at lab scale (data not shown in Fig. 8b) versus 0.38 kW h g$^{-1}$

Fig. 8. Comparison of EF assays at lab and bench scale evaluating: the clofibrate acid mass removal (a) and the specific energy consumption (b).

Fig. 9. Carboxylic acids: mass production and concentration of carboxylic acids at 0.12 A lab scale assay (a) and at 0.25 A bench scale assay (c); calculated TOC represented by carboxylic acids and clofibrate acid at 0.12 A lab scale assay (b) and at 0.25 A bench scale assay (d).
CA at bench scale). At 0.12 A the specific energy consumption was, in general, similar at both scales for each specific charge. However, since the complete removal of the pollutant required a higher specific charge at lab scale, the specific consumption was 2.4 higher than at bench scale (0.36 kW h g⁻¹ CA of consumption at lab scale versus 0.15 kW h g⁻¹ CA at bench scale).

The differences in the cell voltage are partially responsible for the specific energy consumptions obtained, given that those parameters are directly proportional. Irrespective of the current intensity, cell voltages were lower at bench scale (an average of 4.0 V at 0.12 A and 5.0 V at 0.25 A) than at lab scale (an average of 4.4 V at 0.12 A and 5.6 V at 0.25 A), yet another plus point of the scaled-up installation. Another aspect that surely determined this outcome is the inter-electrode gap: working with a micro-fluidic cell at bench scale allowed reducing the space between electrodes to 150 μm (compared to a separation of 1 cm at lab scale), thus minimizing the Ohmic drops. However, it is worth mentioning that Ohmic resistance was found to be dependent on the fluid dynamics too: a previous study determined that a MF-FT cell achieved a 300% reduction in Ohmic resistance over a stirred-tank cell with electrodes arranged in a parallel-plate configuration when using the same electrodes placed at the same distance [9].

Finally, the formation of carboxylic acids during the EF treatment was evaluated for both scales. Since the behavior of the assays at 0.12 A at lab scale and at 0.25 A at bench scale was very similar in terms of carboxylic acid decay and specific energy consumption (see Fig. 8a and Fig. 8c), those experiments were selected for comparison. The profiles of succinic, oxalic and formic acids are represented versus the specific charge for lab and bench assays in Fig. 9a and Fig. 9c, respectively. In both cases, the peak amount of succinic and formic acids was achieved at a specific charge around 0.2-0.4 A h L⁻¹, and then the concentration decreased. In the case of the oxalic acid, it tended to accumulate throughout the treatment. This is typical of the EF process and could be due to the formation of an iron complex with oxalic acid. In any case, the outcome is analogous at both scales, with the lab assay reaching the maximum amount of oxalic acid at 0.80 A h L⁻¹, and then slightly decreasing, and the bench experiment concentration increasing until 0.74 A h L⁻¹, which is the end of the assay.

Additionally, taking into consideration the amount of carboxylic acids and clofibric acid detected, the theoretical amount of TOC that they represent was calculated for the above-mentioned lab (Fig. 9b) and bench assays (Fig. 9d). It can be observed that the portion of the total calculated TOC corresponding to the carboxylic acids increased with the specific charge, but the total TOC decreased as the EF proceeded, which indicates that mineralization was taking place. Comparing the experiments, the calculated TOC that remained at bench scale at a charge of 0.74 A h L⁻¹ is 1.96 mg C L⁻¹, whereas at lab scale at a slightly higher charge, 0.80 A h L⁻¹, 0.99 mg C L⁻¹ persisted. The reason behind this worse performance at the bench scale assay could be due to the lower current density used (7.5 mA cm⁻² compared to 10 mA cm⁻² at lab scale), which did not seem to be detrimental for the hydrogen peroxide generation but could be reducing the anodic oxidation contribution at the bench experiment. However, it should be noted that the TOC calculation only takes into consideration the three measured aliphatic acids and the pollutant, but other intermediates could be present and with a different pattern at each scale.

4. Conclusions
This investigation leads to the following conclusions:

- Both lab- and bench-scale configurations generated hydrogen peroxide and were able to degrade clofibric acid by means of an EF treatment using iron-containing alginate beads as the catalyst.
- A fluidized-bed reactor was successfully installed in the bench-scale setup to contain the solid catalyst.
- Heterogeneous catalysis seems to be complemented by homogeneous catalysis at both scales, due to a certain amount of iron liberated from the alginate beads.
- The scaling-up process was successful: although the geometrical area of the electrodes was only 2.7 times higher, the bench-scale installation allowed treating 18 times more volume, increasing by 28 times the mass of hydrogen peroxide generated, reducing the specific cost of clofibric acid elimination by more than half.
- The most efficient treatment was the EF performed at bench scale at 0.12 A.
- Those outstanding results were obtained thanks to the reactor design, which demonstrated to be key in the scaling-up of the EF process.
- Aromatic intermediates were detected, and a degradation route was suggested.

CRediT authorship contribution statement

Verónica Pozo-Nogueiras: Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Visualization. Ángela Moratalla: Methodology, Validation, Formal analysis, Investigation, Writing - review & editing. Marta Pazos: Conceptualization, Writing - review & editing, Supervision. Ángeles Sanromán: Conceptualization, Resources, Writing - review & editing, Supervision, Funding acquisition. Cristina Sáez: Conceptualization, Writing - review & editing, Supervision, Funding acquisition. Manuel A. Rodrigo: Conceptualization, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

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

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Appendix A. Supplementary data
Supplementary data to this article can be found online at [https://doi.org/10.1016/j.jelechem.2021.115475](https://doi.org/10.1016/j.jelechem.2021.115475).

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