On the design of a jet-aerated microfluidic flow-through reactor for wastewater treatment by electro-Fenton

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Abstract

The design of cost-effective reactors for wastewater treatment by electrochemical advanced oxidation processes is still a challenge. In this work, a novel electro-Fenton reactor concept is presented. The combination of a jet aerator and a microfluidic flow-through cell configures a reactor with low ohmic drop, improved mass transfer which is, in addition, aerated by a compressor-free system. The production of H_2O_2 was assessed, obtaining an instantaneous production rate of $12.4 \text{ mg H}_2\text{O}_2 \text{ cm}^{-3} \text{ electrode h}^{-1}$ at an instantaneous current efficiency of 98.6 % with a low electrical energy consumption of $7.8 \text{ kWh kg H}_2\text{O}_2^{-1}$ in 0.05 M Na_2SO_4 using a RVC with a deposition of CB/PTFE as the cathode. The performance of two mesh anodes (covered with mixed mineral oxides and boron doped diamond) and two cathodes (Duocel® RVC and Aluminium foams) was evaluated for the degradation of 0.75 dm^3 with 100 mg dm^{-3} of clopyralid as model bio-refractory organic pollutant. The combination of BDD + CB/PTFE – Al was found to be synergistic due to the production of oxidizing radicals from water oxidation and electro-generated Fenton reagent. It was selected as the optimum configuration allowing a fast and efficient degradation of clopyralid after the application of approximately 0.44 Ah dm^{-3} (less than 1 h) resulting in an energy consumption of 0.02 kWh g^{-1} clopyralid at 20 mA cm^{-3} in a medium with only $7 \text{ mM Na}_2\text{SO}_4$ of supporting electrolyte.

26   **Keywords:** jet aerator, microfluidic, ohmic resistance, flow-through, 3D electrodes, mass
27   transport, EAOP, electro-Fenton, wastewater treatment

1. Introduction

Electro-Fenton (EF) is an efficient electrochemical advanced oxidation process (EAOP) which consists, essentially, in the reduction of oxygen to produce hydrogen peroxide (Eq. 1) and Fe^{3+} to yield Fe^{2+} (Eq. 2) on the cathode of an electrolytic cell, with the final aim of promoting Fenton's reaction (Eq. 3) [1]:

This technology was firstly applied to wastewater treatment by Sudoh et al. [2] and popularized by Oturan's and Brilla's groups since the 90's using carbon felt (CF) and gas diffusion electrodes (GDEs), respectively [1, 3, 4]. EF and related technologies have shown a great efficiency in the remediation of those effluents that are not efficiently treated using biological technologies [1, 5, 6]. Comparatively, most of the studies have been focused on the influence of the electrode material and operating conditions and less attention has been paid to other aspects of cell design [7, 8]. Traditionally, EF has been extensively applied in either simple stirred tank reactors or in parallel-plate flow-by cells [1, 9]. Despite the positive results achieved by conventional EF reactors so far, there is still work to be done to speed up and reduce costs of this technology in order to make it a reliable and competitive alternative on an industrial scale [10].

A key aspect in the design of EF reactors is a fast and efficient H_2O_2 electro-generation. Carbon-based materials gather adequate characteristics for their industrial implementation [11-13] and different types have been extensively used for H_2O_2 electro-generation including graphite [14, 15], carbon felt [15, 16], carbon cloth [11], carbon sponge [17, 18], graphene [19, 20] or reticulated vitreous carbon (RVC) [15, 21]. Oxygen transfer to above-said electrodes often limits the working current density, and therefore

the production of H_2O_2 , because of the low solubility of oxygen in water (around 8 mg dm^{-3} under room conditions) [15]. Different approaches have been studied such as direct bubbling in the solution [22, 23], indirect through gas diffusion electrodes [24, 25] or the use of pressurized systems [14, 16]. However, all the options described so far require the use of a compressor which entails costs that are usually neglected from the economic estimations required for the treatment. In previous works, the use of the jet aerator was studied to supply oxygen and produce H_2O_2 in the absence of a compressor [26, 27]. It is important to highlight that the jet aerator not only saturate in oxygen the solution but also increases the oxygen flow that is carried by the stream thanks to the generation of air bubbles and, therefore, allows the production of H_2O_2 at higher current densities [27].

Another important aspect with important economic relevance is the inter-electrode (IE) gap. It is well known that the IE gap affects the ohmic resistance of the cell and hence the cell voltage [7, 28, 29]. Particularly, EF reactors use the wastewater as electrolyte and given the low conductivities of aqueous electrolytes (several order of magnitude smaller than carbons or metals [30, 31]) small IE gaps are mandatory to achieve reasonable cell voltages and competitive energy consumptions [7, 32]. Scialdone et al. reported the performance of micro-fluidic flow-by EF cells with IE gaps within the order of tens to few hundreds micro-meters to minimize ohmic drops [33-36]. For example, the cell voltage was only reduced by 1% (3.39 vs. 3.35 V) in a reactor with a narrow IE gap (50 μm) upon the addition of 0.035 M Na_2SO_4 as supporting electrolyte in the anodic oxidation of a water solution containing oxalic acid [37]. The main limitation of those reactors are the operational problems derived from the accumulation of bubbles on the electrode surfaces and the IE gap [38, 39], especially at high current densities, as a consequence of the low electrolyte flow (normally mL min^{-1}) permitted in the narrow IE gap [7, 30].

In recent works, our group developed a cell geometry that combines an IE gap in the order of micro-meters with a fast circulation through the IE gap: the microfluidic flow-through (MF-FT) cell [30, 40]. Interestingly, the aforementioned cell design also helps to maximize mass transport, one of the bottlenecks of electrochemical reactors, thanks to *i*) the use of tri-dimensional (3D) electrodes *ii*) fed in flow-through. 3D electrodes allow the design of more efficient and compact reactors than bi-dimensional (2D), mainly thanks to the higher specific surface area [41]. As an example, a RVC (45 pores per inch or ppi) has a surface area per unit volume of $28 \text{ cm}^2 \text{ cm}^{-3}$ [42]. In addition, the local turbulence induced by those electrodes fed in flow-through give rise to higher mass transfer coefficients (k_m) at similar flow velocities [29, 40, 43]. Because of this, a MF-FT required from 4 to 10 times less electric charge and from 6 to 15 less energy consumption to mineralize a diluted solution by anodic oxidation with boron doped diamond (BDD), as compared to a commercial cell [40].

In this work, we describe and test an EF reactor design that combines a compressor-free jet aerator and a MF-FT cell with a low ohmic resistance in the electrolyte, thanks to the narrow IE gap, and an improved mass transfer, due to the use of 3D electrodes in flow-through. The performance of two types of anodes (mixed mineral oxides and BDD) and two cathodes (RVC and Al foams modified with carbon black, CB, and polytetrafluoroethylene, PTFE) for different Fe amount and Na_2SO_4 concentrations for the degradation of clopyralid as model organic pollutant are evaluated.

2. Materials and methods

2.1 Experimental set-up

A picture of the experimental setup is shown in Figure 1. The water to be treated is stored in the reservoir tank and pumped through the system by a centrifugal pump. When the liquid flows through the throat of the jet aerator, atmospheric air is drawn into the system

by means of the Venturi effect, generating a bi-phasic mixture with a concentration in oxygen superior to the equilibrium one, thanks to the formation of air bubbles. The biphasic mixture is fed to the micro-fluidic reactor, placed as shown in Figure 1, passing first through the anode and then, through the cathode (A-C configuration), to make the most of the evolved O_2 by its reduction in the cathode. The electrodes were separated by a solid PTFE (nominal thickness 400 μm). Both sides of the PTFE separator are covered by thin layers of aluminium (20 μm each) which are in contact with the electrodes and act as current feeders.

Figure 1. Representation of the experimental set-up used in this work

2.2 Electrodes

2.2.1 Mixed mineral oxides and boron-doped diamond electrodes

The mixed mineral oxides (MMO) mesh electrodes consisted of a RuO_2/IrO_2 coated titanium-mesh with a total dimension of 9.5 x 8 cm^2 , supplied by Tianode (India). The thin-film BDD electrode, supported on a niobium mesh (Diachem®) also with a size of 9.5 x 8 cm^2 , was supplied by Condias GmbH (Germany). The cross section of the fluid for both electrodes is 33 cm^2 which corresponds to a surface area of 53 and 50 cm^2 for the MMO and the BDD meshes, respectively, estimated in a previous work by using a 3D scanner [40].

2.2.2 Reticulated vitreous carbon and Aluminium foams

Duocel® RVC (45 ppi) foams with dimensions of 9.5 x 8 x 0.5 cm³ were supplied by ERG Materials & Aerospace (USA). Duocel® Aluminium foams with the same dimensions, 40 ppi and a relative density 6-8% were also supplied by ERG Materials & Aerospace (USA). Both electrodes have a wet front area inside the reactor of 33 cm² which results in 16.5 cm³ considering the thickness of the pieces (5 mm).

2.2.3 Deposition of CB/PTFE

A mixture of CB (Vulcan XC72, fabricated by Cabot Corporation and distributed by Delta Tecnic, S.A in Spain) and PTFE (Teflon®, 60% liquid emulsion in water supplied by Sigma-Aldrich, USA) henceforth referred to as CB/PTFE was deposited on both supports by spraying an ink following a procedure similar to the one described in a previous work [11]. The inks were prepared by dispersing 1 g dm⁻³ of CB and 5 g dm⁻³ of PTFE into isopropanol for 2 hours at 50 °C in an ultrasound bath. After this, the foams were placed over a home-made plate at 130 °C and 200 cm³ of ink were sprayed (100 cm³ each side). Then, cathodes were annealed at 360 °C for 1 h starting from room temperature at a heating rate of 12 °C min⁻¹.

2.3 Analytical measurements

Hydrogen peroxide was measured by the potassium titanium (IV) oxalate method [44] according to standard DIN 38 409, part 15, DEV-18. Clopyralid was measured by high-pressure liquid chromatography using an Agilent 1200 series coupled a DAD detector and Zorbax Eclipse Plus C18 analytical column. The mobile phase consisted of 30% methanol 70% water with 0.1% of formic acid (flow rate 1 cm³ min⁻¹). The DAD detection wavelength was 280 nm, the temperature was maintained at 25°C and the injection volume was 20 µL. The electrolyses were carried out using a Potentiostat-Galvanostat Autolab 302N controlled with NOVA 2.1 software.

2.4 Wastewater

The herbicide clopyralid ($C_6H_3Cl_2NO_2$) was used as model organic pollutant. The synthetic wastewater was prepared by dissolving 100 mg dm^{-3} of the above-said molecule into Milli-Q water and the corresponding Na_2SO_4 (supporting electrolyte) and $FeSO_4$ (Fenton catalyst) concentrations detailed in each section. Prior to the addition of the iron catalyst, pH was adjusted at 3 with H_2SO_4 and maintained at this value during the whole experimental time.

3. Results and Discussion

3.1 Hydrogen peroxide generation

Prior to EF experiments, the production of H_2O_2 in the MF-FT was studied using a RVC - 40 ppi as the cathode. This material gather some adequate characteristics such as high surface area and low pressure drop [42]. In previous works, it was found that depositing a mixture of carbon black /polytetrafluoroethylene (CB/PTFE) on a carbon cloth [45] or carbon felt [16, 27] boosted the production of H_2O_2 . Thus, CB/PTFE mixture was also used in this work to cover RVC, a 3D carbonaceous material. The concentration curves and the corresponding current efficiency (CE) for different current densities from 20 mA cm^{-3} to 50 mA cm^{-3} are shown in Figure 2.

Figure 2. Hydrogen peroxide generation and current efficiency at different current densities in the MF-FT reactor. ■ 20 mA cm⁻³ ♦ 30 mA cm⁻³ ● 50 mA cm⁻³. Cathode: CB/PTFE-RVC. Anode: MMO. Electrolyte 1 dm³ 0.05 Na₂SO₄. Liquid flow: 70 dm³ h⁻¹. In general terms, H₂O₂ is produced faster at higher current densities but with lower CEs, as seen in Figure 2 within the range 20 - 50 mA cm⁻³. The accumulation reaches a concentration of 134, 156 and 204 mg H₂O₂ dm⁻³ after one hour of electrolysis at 20, 30 and 50 mA cm⁻³. The same tendency is observed for the instantaneous production rates (calculated after 5 minutes of electrolysis), which are 12.4, 16.2 and 23.3 mg H₂O₂ cm⁻³ electrode h⁻¹. It is important to note that the accumulation of H₂O₂ is not linear and tend to a *plateau* due to the occurrence of competing reactions, such as self-decomposition (Eq. 4), anodic oxidation (Eq. 5) or reduction to water on the cathode (Eq. 6), all of them widely discussed in the bibliography [15, 46-49].

With respect CE, Figure 2.b shows that O₂ can be reduced selectively (98.6 %) to H₂O₂ (Eq. 1) at 20 mA cm⁻³ on the CB/PTFE-RVC cathode. However, at higher current densities, charge transfer is faster than the supply of oxygen to the cathodic surface. In other words, the applied current density is above the limiting one. Under those operating conditions, electrons in excess may be used to reduce H₂O₂ to H₂O, (Eq. 6), O₂ directly to water (Eq. 7), or evolve hydrogen (Eq. 8) giving rise to an instantaneous CE below 100% [15, 16, 27, 50]. Because of this, current density and oxygen supply must be balanced for an efficient H₂O₂ production.

These results compare favourably with those shown in the literature obtained with conventional cells. For example, Petrucci et al [15] obtained a better performance of the RCV cathode in comparison to graphite and carbon felt. Thus, in that work, the RVC operated at 10 mA cm^{-3} under oxygen atmosphere (dissolved oxygen $> 20 \text{ mg O}_2 \text{ dm}^{-3}$) in a divided cell reached a maximum instantaneous production rate of $4 \text{ mg H}_2\text{O}_2 \text{ cm}^{-3} \text{ electrode h}^{-1}$ and a maximum CE of 60%. Those values are lower than those provided by the MF-FT (12.4 , 16.2 and $23.3 \text{ mg H}_2\text{O}_2 \text{ cm}^{-3} \text{ electrode h}^{-1}$ at 20 , 30 and 50 mA cm^{-3}), pointing out the relevance of the cell design, even considering that the above-said experiments were conducted in a divided cell fed with pure oxygen and using a denser RVC (100 ppi). It is important to take into consideration that RVC with 100 ppi has approximately 3 times higher surface area per unit of volume [42] than the electrodes used in our work.

With respect to specific energy consumption, it increased with current density both because of the lower CE and the higher cell voltage. Cell voltage reached a value of 4.8 , 5.3 and 7.2 V resulting in an energy consumption of 7.8 , 9.9 and $15.5 \text{ kWh kg H}_2\text{O}_2^{-1}$ at 20 , 30 and 50 mA cm^{-3} , respectively. Unfortunately, specific energy consumption is not widely available in scientific reports. This fact, together with the wide variety of experimental conditions hinder a detailed comparison at this point.

However, the best results are obtained in those electrolyzers designed to produce a bleaching solution for the paper and wood industry in strong ($\cong 1\text{-}2\text{M NaOH/KOH}$) basic medium [51-54]. It is important to mention that H_2O_2 production in alkaline medium present significant advantages, namely *i)* the extremely high conductivity of the electrolytic medium, minimizing ohmic drops *ii)* the lower thermodynamic potential for the reduction of O_2 to H_2O_2 in alkaline medium with respect to neutral-acid medium (0.065 V vs. 0.62 V , both expressed with respect to SHE [51]), which also leads to lower

cell voltages. In alkaline reactors, an electrical energy consumption ranging from 5 to 8 kWh kg H₂O₂⁻¹ is reported [51-54], a similar value to the one obtained in the MF-FT reactor at 20 mA cm⁻³ (7.8 kWh kg H₂O₂). It is particularly interesting because in the MF-FT the electrolyte is 20 times less concentrated and, in addition, the synthesis is performed in neutral-acid medium. Moreover, the aforementioned calculations only consider the energy supplied to the cell but do take into account the costs of aeration by compressors used in conventional systems (investment, maintenance and running expenses) which are expected to be lower using the jet aerator. In this manner, those results do nothing but just confirm the excellent performance of the jet-aerated MF-FT equipped with a CB/PTFE-RVC for the production of H₂O₂.

3.2 Electro-Fenton tests

Considering the positive results obtained so far, electro-Fenton tests for the degradation of clopyralid (model organic pollutant) were conducted in the MF-FT reactor. According to the results shown in the previous section, the EF tests were carried out at a fixed current density of 20 mA cm⁻³ (10 mA cm⁻² with respect to the anode), a value at which H₂O₂ is produced with high CE in this system. The influence of different parameters (Fe and Na₂SO₄ concentration, MMO/BDD as the anodes and RVC/Al foams as the cathodes) was evaluated in the following section.

3.2.1 Degradation with MMO/BDD anodes and CB/PTFE-RVC cathode

Firstly, a series of EF experiments were performed with a CB/PTFE-RVC cathode using two different anodic materials: a MMO or a BDD mesh. It has been previously demonstrated that non-active anodes such as BDD acts mainly via generation of quasi-free HO• over the surface [13, 24, 55], so it might be reasonable to think that those radicals could overlap the cathodic area and oxidize H₂O₂/Fe²⁺. In this sense, Kapalka et al. modelled the concentration profile of HO• during oxygen evolution on a BDD

electrode and found that the reaction layer thickness (or reaction cage) at 30 mA cm^{-2} is about $1 \text{ }\mu\text{m}$ in the absence of organics [56, 57]. If organics are present, it drops to tenths of nanometers, a distance several orders of magnitude smaller than the IE gap and therefore the overlapping is not expected.

The first EF runs were conducted in a medium with 100 mg dm^{-3} of clopyralid at $\text{pH} = 3$, and two different values of initial catalyst (0.5 mM and 2 mM of Fe) and supporting electrolyte (7 mM or $50 \text{ mM Na}_2\text{SO}_4$). The decay of clopyralid concentration vs. time and applied charge is shown in Figure 3.

Figure 3. Clopyralid decay vs. time and specific applied electric charge using CB/PTFE-RVC as the cathode and MMO or BDD as the anode: ● MMO, 2 mM Fe , $50 \text{ mM Na}_2\text{SO}_4$; ○ BDD, 2 mM Fe , $50 \text{ mM Na}_2\text{SO}_4$; ■ MMO, 0.5 mM Fe , $7 \text{ mM Na}_2\text{SO}_4$, □ BDD, 0.5 mM Fe , $7 \text{ mM Na}_2\text{SO}_4$. $j = 20 \text{ mA cm}^{-2}$; Volume: 0.75 dm^3 . $[\text{Clopyralid}] = 100 \text{ mg dm}^{-3}$. Temperature: $25 \text{ }^\circ\text{C}$. Liquid flow: $70 \text{ dm}^3 \text{ h}^{-1}$.

It can be seen that BDD anode clearly outperforms MMO, regardless of catalyst dosage and electrolyte concentration. This observation is consistent with previous results found in bibliography where the higher oxidizing power of BDD has been attributed not only to the oxidation of the pollutants on the surface but also to the formation of a mixture of

oxidants in solution [5, 13]. According to Figure 3, faster clopyralid decay is observed when 0.5 mM Fe is added. It has also been established that iron concentration affects the performance of EF process and that it exists an optimum value of catalysts above which the over-dosage leads to poorer degradation results due to scavenging effects or precipitation [58]. In our experience, 0.5 mM performed better than 2.0 mM. The smallest value is, indeed, closer to the optimum Fe concentration found in homogeneous EF in previous works, which is normally within the range 0.1 – 0.5 mM [24, 59, 60]. In addition, in AO processes, inorganics species used as supporting electrolyte may not be inert and, indeed, they may play a role in degradation mechanisms. In particular, it has been previously reported the formation of persulfate ($S_2O_8^{2-}$) in sulphate-containing medium and its participation in the degradation of organics (Eq. 9) [13, 61]:

Apparently, higher concentrations of Na_2SO_4 does not lead to faster removal. This behavior may be explained by considering that such oxidants from inorganic species are kinetically slower than hydroxyl radicals and may play an important $HO^\bullet$ scavenging role at certain concentrations.

Under the best conditions so far, clopyralid is eliminated using BDD as counter-electrode after 120 min of electrolysis which corresponds to 0.88 Ah dm^{-3} . Therefore, BDD was selected for the next experiments in which the influence of the cathodic material is discussed.

3.2.2 Degradation with BDD anode and CB/PTFE-Al cathode

In the following experiments, the CB/PTFE-RVC is replaced by a Duocel® aluminium foam 40 ppi that is a material with a similar three-dimensional and porous structure. As in the RVC cathode, a CB/PTFE mixture was deposited to act as the active phase for the

generation of H_2O_2 . Figure 4 shows degradation of clopyralid in different media using the BDD anode and CB/PTFE-Al cathode.

Figure 4. Clopyralid removal vs. time and specific applied electric charge using BDD as the anode and CB/PTFE-Al as the cathode. ● 2 mM Fe, 50 mM Na_2SO_4 ; ■ 0.5 mM Fe, 50 mM Na_2SO_4 ▲ 0.5 mM Fe, 7 mM Na_2SO_4 . $j = 20 \text{ mA cm}^{-2}$. Volume: 0.75 dm^3 . Temperature: 25°C . Liquid flow: $70 \text{ dm}^3 \text{ h}^{-1}$.

As in previous experiments, it can also be seen a considerably faster clopyralid removal in the experiments with the lowest dosage of catalysts and Na_2SO_4 concentration. Pignatello pointed out [62] that inorganics compounds may inhibit the degradation of organics as for example via scavenging of $\text{HO}^\bullet$. Scialdone observed lower abatement with higher concentration of Na_2SO_4 using a microfluidic reactor [37]. These results suggest that there might be an optimum concentration of supporting electrolyte above which mediated oxidation does not benefit the degradation of pollutants. Under the best conditions (0.5 mM Fe/7 mM Na_2SO_4) clopyralid is not detected after approximately 1 hour (0.44 Ah dm^{-3}) while for the same time, only 50% and 25% is degraded in those experiments with 0.5 mM Fe/50 mM Na_2SO_4 and 2 mM Fe/50 mM Na_2SO_4 , respectively,

On the other hand, higher supporting electrolyte concentration helps to decrease ohmic resistance and, thus, cell voltage. In those experiments with a concentration of 50 mM Na_2SO_4 , the cell voltage was around 4.3 V and slightly increased up to 5 V in 7 mM Na_2SO_4 using the CB/PTFE-Al cathode. Quite interestingly, the cell voltage was as high as 8.2 V using the CB/PTFE-RVC as the cathode to achieve the same current density in 7 mM Na_2SO_4 medium, which implies a 64% higher energy consumption with the carbonaceous cathode in comparison to the metallic one.

This fact can be readily explained considering that an important part of the total ohmic losses may also be attributed to the circulation of electrical current through the electrodes and the huge difference in electrical conductivity between both materials. According to the manufacturer, there are approximately 4 orders of magnitude of difference ($1.4 \cdot 10^7$ mS cm^{-1} for the Al foam-8% density and $3.1 \cdot 10^3$ mS cm^{-1} for the RVC-45 ppi). Quite importantly, this difference in conductivity may lead to a better voltage/current distribution, a key aspect for an adequate scale-up of electrochemical cells [43]. In addition, RVC is brittle and it poses a problem in the design of filter-press cells in which the components are held together by compression. Compression strength of RVC foams ranges from 0.10 to 0.52 MPa, while it is about 5 times higher in Al foams (2.53 MPa for 8% density alloy 6101-T6 8% nominal density) [63, 64]. Regarding costs, Al foams are around 30% more expensive than RVC (\$0.1 vs \$0.13 per cm^3 , before machining). However, considering the aforementioned advantages exhibited by Al foams both in terms of electrical conductivity and mechanical resistance, it is our opinion that Al foam is the most suitable choice for this application.

3.3 Selection of the best configuration

Figure 5 shows a comparison for clopyralid abatement (Figure 5.a) using different configurations of anode and cathodes in the jet-aerated MF-FT and the corresponding

energy consumed by the power supply to eliminate 1 g of clopyralid (Figure 5.b) in the same medium (0.5 mM Fe – 7 mM Na₂SO₄). For comparative purposes, clopyralid removal by anodic oxidation using the same BDD anode and a stainless steel cathode in the MF-FT are included (data are obtained from this previous work [30]).

Figure 5. Comparison of different anode/cathode configurations for the elimination of clopyralid in terms of a) applied electric charge ■ BDD + stainless steel (SS) cathode from ref. [30]; ● MMO + CB/PTFE-RVC; ◆ BDD + CB/PTFE-RVC; ▲ BDD + CB/PTFE-Al; Electrolyte: 0.5 mM Fe, 7 mM Na₂SO₄ at pH = 3. Volume: 0.75 dm³. Temperature: 25 °C. Liquid flow: 70 dm³ h⁻¹. b) energy consumption. ■ Energy consumption ● Cell Voltage

In general terms, it is clear that the EF process is faster than AO regardless the medium and that the coupling of both systems is synergistic, due to the production of •OH from both sources. Degradation kinetics varies in the order AO + SS < MMO + RVC < BDD + RVC < BDD + Al. Interestingly, the use of a CB/PTFE-Al as the cathode not only decreases cell voltage but also seems to be more efficient generating the Fenton reagent. It is not an obvious result given that, for the same volume of electrode, RVC has higher surface area than Al foams (28 vs. cm² cm⁻³, respectively) [42, 65]. The reason behind the

good performance may be found in a more uniform potential/current distribution as a consequence of the higher conductivity of the electrode in comparison with RVC. The same tendency is observed in specific energy consumption (Figure 5.b). Cell voltage is considerably lower when metallic cathodes are used (stainless steel or Al support). While AO consumes around 0.13 kWh g⁻¹ clopyralid, EF configurations consume 0.1 kWh g⁻¹ clopyralid (MMO + CB/PTFE-RVC), 0.06 kWh g⁻¹ clopyralid (BDD + CB/PTFE-RVC) and the best combination (BDD + CB/PTFE-Al) reduces this value by an order of magnitude, requiring only 0.02 kWh g⁻¹ clopyralid. Because of the faster clopyralid removal and the lower energy consumption in comparison to the other configurations, BDD-CB/PTFE-Al is selected as the optimum to continue the development of the reactor.

The excellent performance of the jet-aerated MF-FT reactor may also be attributed to the minimization of parasitic reactions, mainly anodic oxidation of H₂O₂ and Fe²⁺, thanks to a curious consequence of the A-C layout. As shown in Figure 6, H₂O₂ and Fe²⁺ may react and, thus, be consumed in the recirculation laze/tank in such a way that in the next pass through the cell their concentration is low (see Figure 6). If the concentration of H₂O₂ and Fe²⁺ is low, their oxidation kinetics may be tightly controlled by mass transport. In this manner, compartments may be virtually separated not by a physical separator but by a chemical reaction. This sort of *membrane-like* effect opens the possibility of constructing an efficient undivided cell for EF, that are normally preferred mainly to avoid ohmic penalty through the separator, by means of an elegant and simple design which is normally the key to make it attractive to users [29]

Figure 6. Schematic representation of the membrane-like effect

Giving the promising characteristics of the jet-aerated MF-FT, further studies will be devoted to the treatment of pollutants contained in different aqueous matrix, study and quantify the membrane-like in more detail, optimize the operational conditions and perform a detailed comparative economic analysis with current technologies.

Conclusions

From this work, the following conclusions can be drawn:

- The jet aerator can be coupled to a MF-FT to configure a compressor-less EF reactor with low ohmic resistance and improved mass transfer.
- Hydrogen peroxide is produced efficiently at 20 mA cm^{-3} using a CB/PTFE-RVC at $12.4 \text{ mg H}_2\text{O}_2 \text{ cm}^{-3} \text{ electrode h}^{-1}$ (CE 98.6%) with a low energy consumption of $7.8 \text{ kWh kg H}_2\text{O}_2^{-1}$ in $0.05 \text{ Na}_2\text{SO}_4$. Higher current densities (up to 50 mA cm^{-3}) implies faster production but higher energy consumption and lower CE.
- The best electrode pair is BDD and CB/PTFE-Al. The cell voltage is a 64% lower at the same current density using an aluminium foam instead of a RVC. 100 mg dm^{-3} of clopyralid were eliminated with only 0.44 Ah dm^{-3} 0.02 kWh g^{-1}

clopyralid in a medium containing 0.5 mM Fe and only 7 mM Na₂SO₄ at pH 3 in this reactor.

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