Development of an innovative approach for low-impact wastewater treatment: a microfluidic flow-through electrochemical reactor

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Abstract

In this work, a novel approach for the development of fast and low-consuming electrochemical reactors for wastewater treatment is studied. It consists in the use of a microfluid flow-through cell with a very narrow inter-electrode gap (to minimize ohmic drops) and flow-through electrodes (to maximize mass transport towards the electrodes). The ohmic drop was studied for different inter-electrode gap and electrolyte conductivities. A low ohmic drop of $6\ \Omega$ was measured using an inter-electrode gap of $400\ \mu\text{m}$ in a liquid electrolyte with $0.7\ \text{mS cm}^{-1}$ of conductivity. The mass transfer coefficient (k_m) was evaluated at different inlet flow velocities, obtaining $1.45 \cdot 10^{-5}\ \text{m s}^{-1}$ at a velocity of $1.0 \cdot 10^{-2}\ \text{m s}^{-1}$, considerably superior to the data reported for flow-by cells. Finally, the efficiency for wastewater treatment via anodic electro-oxidation with diamond anodes was evaluated. In this work, 100 ppm of clopyralid contained in a synthetic soil washing effluent were completely removed in this system using $2.71 - 8.54\ \text{Ah dm}^{-3}$ and $12.5 - 115.0\ \text{kWh m}^{-3}$ at 10 and $100\ \text{mA cm}^{-2}$, respectively. Comparison with a commercial flow-by (Diacell[®] 101) shows that the novel approach requires between 4 to 10 times less electric charge and from 6 to 15 times less energy consumption.

The microfluidic flow-through configuration stand as a promising approach to reduce the environmental impact of electrochemical wastewater technologies.

Keywords: microfluidic, ohmic resistance, flow-through, 3D electrodes, mass transport, reactor design, wastewater treatment

1. Introduction

One of the reasons that impede the widespread application of electrochemical technologies for wastewater treatment is the high energy consumption (EC) when it comes to treat low-conductive effluents [1, 2]. EC is directly proportional to the cell voltage (E_{cell}) which can be, in turn, subdivided into different contributing terms: reversible cell voltage ($E_e^c - E_e^a$), cathodic/anodic overpotential ($|\eta_c|, |\eta_a|$) and the sum of the different ohmic resistors of the electrical circuit ($\sum I \cdot R$) [3-5].

The E_{cell} depends on the reaction taking place in the reactor while the overpotentials are mainly a function of the electrode materials and the current density. Hence, all the aforementioned parameters are largely independent from the electrode layout. Conversely, the term $\sum I \cdot R$ strongly depends on cell design. Ohmic drops represent an inefficiency and a loss of energy, being always detrimental for the performance of the cell. Therefore, they must be minimized to reduce EC [3, 5].

Among the different ohmic resistors, the contribution of aqueous electrolytes is normally critical due to their low conductivity [3, 5]. Electrolyte concentration can be strongly increased to minimize the ohmic drop in the inter-electrode (IE) gap, such as in chloro-alkali industry or in water electrolyzers [6, 7]. However, the addition of extra supporting electrolyte in the case of wastewater treatment leads to a secondary pollution since the inorganic compounds will persist in the effluent after the treatment [2, 8, 9]. Furthermore, it also increases the operating costs and compromises the viability of the electrochemical processes on an industrial scale.

A different approach to keep the IR drop using aqueous electrolytes low consists in reducing the distance between the electrodes (IE gap), such as in micro-fluidic (MF) reactors [8, 10, 11]. Those devices deal with fluids constrained in environments with internal dimensions in the order of micro-meters [12, 13]. The main feature of MF

electrochemical reactors is the small IE gap (normally $< 1,000\ \mu\text{m}$) [14, 15]. In this context, Scialdone et al. reported the use of microfluidic flow-by (electrolyte passing between the parallel-plate electrodes) reactors for wastewater treatment by means of electroFenton and anodic oxidation with boron-doped diamond (AO-BDD) technologies, obtaining high abatements of organic pollutants and moderate E_{cell} even in the absence of supporting electrolyte [8, 16-20].

Nevertheless, the reduction of the IE gap increases the pressure drop of the fluid passing by the reactor due to the higher surface area-to-volume ratio which implies a higher relative friction. This undesired characteristic of microfluidic flow-by reactors limit the flow rates and, thus, the treatment capacity of those devices, which are normally operated at mL min^{-1} in single-pass mode [17, 19, 21]. These reactors also suffers from partial clogging of the channel when gas-evolving electrodes are used and high current densities are applied, as previously reported by Bouzek et al. [22, 23].

Another important aspect in the design of electro-chemical reactors is the evaluation of mass-transport conditions, since electro-chemical reactions are of a heterogeneous nature and the reactants have to be transported towards the electrode and the products transported away from it [3, 24]. In the particular case of reactors for wastewater treatment, mass-transport is usually considered a bottleneck and its improvement is highly desirable to improve the efficiency and attractiveness of such technologies on an industrial scale [1, 25, 26]. Recently, different authors have proposed the use of three-dimensional (3D) electrodes (including meshes, foams or packed) in different flow-through reactor concepts to increase mass transport rate, achieving interesting results [27-35].

In a previous work [36], a novel microfluidic flow-through (MF-FT) cell was introduced. The objective of this geometry is not only the simultaneous minimization of

ohmic drop and maximization of mass transfer but also avoid the operational problems of conventional MF reactors for wastewater treatment derived from the accumulation of gases within the IE gap. In a microfluidic flow-by geometry, the crossing area for the fluid is narrowed when the IE gap is reduced but, interestingly, this is not the case of the MF-FT configuration [36]. In this manner, the MF-FT proposed allows the electrodes to be placed as close as required while keeping constant the crossing area of the fluid and, thus, high circulation velocities can be used to strip the gases out of the IE gap.

In this work, the objective is to gain insight in the characteristics of the MF-FT cell. To do this, the ohmic resistance of the MF-FT is systematically evaluated at different IE gap and electrolyte concentrations. The performance is compared with a conventional stirred tank (ST) parallel-plate reactor. On the other hand, mass-transfer is evaluated at different inlet flow velocities and electrode layouts and is compared to previous studies in bibliography. Finally, the performance of the MF-FT reactor as an AO-BDD reactor to abate a model organochlorinated pollutant, clopyralid, is compared both to a state-of-the-art commercial FB reactor and to other previous studies to assess the potentiality of the system.

2. Materials and methods

2.1 Reagents

Sodium sulphate (Na_2SO_4), sodium carbonate (Na_2CO_3), Potassium Hexacyanoferrate (II) 3-hydrate ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$) and Potassium Hexacyanoferrate (III) ($\text{K}_3[\text{Fe}(\text{CN})_6]$) were provided by Panreac (Barcelona, Spain). The simulated soil washing effluent was prepared by dissolving 0.1 g of clopyralid, 0.67 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.13 g of NaCl, 0.13 g of NaNO_3 , 0.025 g of KI and 0.25 g of CaCO_3 per liter of Milli-Q water, according to bibliography [37]. The rest of solutions were also prepared in Milli-Q water.

2.2 Experimental setup

A schematic representation of the experimental setup is shown in Figure 1.

Figure 1. Schematic representation of the experimental setup (a) and the MF-FT cell (b).

The core of the system is the electrochemical cell. It consists in a filter-press cell with electrodes separated by plastic spacers of different thicknesses. The geometric area of the electrodes (which corresponds to the diameter of the inlet/outlet pipe) is 33 cm². The wastewater is fed perpendicularly to the electrodes, flows through them and leaves the system at the opposite end, as can be found in Figure 1.b. More details about the MF-FT reactor and the experimental setup can be found elsewhere [36]. Details about the experimental setup and the commercial electrochemical cell (Diacell[®] 101) used to compare the performance of the MF-FT in Section 3.3 are available in this reference [9]. The ST reactor consisted in a thermostated glass beaker in which the electrodes, arranged

in a parallel-plate configuration, were inserted into the electrolyte, being the latter mixed by means of a magnetic stirrer.

2.3 Electrodes

The mixed mineral oxides (MMO) meshes electrodes (used both as the anode and the cathode) were a RuO₂/IrO₂ coated titanium-mesh supplied by Tianode (India) with a total size of 8 x 9.5 cm. The surface area was calculated by using a Rexcon DS₃ silver 3D scanner equipped with EZScan 8 and the Geomagic Wrap 2015 software. The measured ratio surface / geometric area is 1.60. Therefore, 33 cm² of geometric area produces to a surface area of 52.8 cm² in those 3D mesh electrodes.

The thin-film BDD electrode supported on a niobium mesh (Diachem[®]) was supplied by Condias GmbH (Germany), also with a total size of 8 x 9.5 cm, was used as the anode. The surface area was also calculated by using the 3D scanner (using a negative mesh, due to the optic properties of the diamond film) with a resulting ratio of 1.5 surface / geometric area, which corresponds to 49.5 cm². As the cathode, a home-made stainless steel perforated plate (thickness 3 mm) with holes (ø 2 mm) uniformly distributed along the surface.

2.4 Analytical measurements

2.4.1 Chemical analysis

The concentration of pesticide was measured by reversed-phase chromatography and the total organic carbon (TOC) was monitored using a Multi N/C 3100 Analytik Jena analyzer as described elsewhere [9].

2.4.2 Electrochemical characterization

The electro-analytical techniques were carried out by means of a Potentiostat-Galvanostat Autolab 302N controlled with NOVA 2.1 software. Electrochemical impedance spectroscopy (EIS) was measured using a sinusoidal perturbation with an amplitude of

0.01 V_{RMS} – between $1 \cdot 10^5$ and 0.01 Hz. The ohmic resistance is calculated from the intersection of the X-axis in the Nyquist plot ($-Z''$ vs Z'). Linear sweep voltammetries (LSV) were measured within 0-10 V (cell voltage) at a scan rate of 0.05 V/s. The limiting-current technique for the determination of the mass transport coefficient (k_m) was carried out using the cyanoferrate (II)/(III) as redox pair according to a procedure described previously [38].

3. Results

3.1 Evaluation of the ohmic resistance

The ohmic resistance of the MF-FT reactor was evaluated at different IE gaps (6,000 – 1,000 and 400 μm) using electrolyte concentrations from 0.5 to 50 g L⁻¹ of Na₂SO₄ (0.7 to 40.1 mS cm⁻¹). For comparative purposes, ohmic resistance was also measured in a ST reactor at 25,000 – 6,000 and 1,000 μm using the same electrolyte solutions and electrodes employed in the MF-FT reactor. The results are shown in Figure 2.

Figure 2. Comparison of the ohmic resistance measured in a conventional ST and the MF-FT reactor for different IE gap and electrolyte concentration. Anode (both): MMO mesh; Cathode (both): stainless steel perforated plate; Flow rate (MF): 105 dm³ h⁻¹; Stirring rate (ST): 400 rpm; T = 20 °C.

In all the cases, the ohmic resistance strongly decreases with the increase of the electrolyte concentration. The ohmic resistance in the ST at 25,000 μm , a commonly used IE gap in laboratory studies [39, 40], is as high as 346 Ω at 0.5 g L^{-1} . A further increase up to 5 g L^{-1} (35 mM), an electrolyte concentration close to the typical added in laboratory studies [41, 42], reduces the ohmic resistance down to 33 Ω . As it was pointed out previously, the reduction of the IE gap is an effective way of reducing the ohmic losses. In fact, considerably smaller values were measured (145 and 61 Ω) at IE gaps of 6,000 and 1,000 μm , respectively. The addition of 5 g L^{-1} of electrolyte at those IE gaps reduced the ohmic resistance to values of 24 and 9 Ω , respectively.

For comparative purposes, the MF-FT was also configured with IE gaps of 6,000 and 1,000 μm . As shown in Figure 2, the ohmic resistance with 0.5 g L^{-1} is 36 and 11 Ω , respectively, which represents a huge reduction of 300 and 450%. Reducing the IE gap to 400 μm also resulted in a minimization of the ohmic losses. As a way of example, even using the least conductive electrolyte (0.5 g L^{-1}) the ohmic resistance is remarkably low: 6 Ω . This value is even lower than the one (9 Ω) corresponding to 1,000 μm and ten-times higher concentration (5 g L^{-1}) of supporting electrolyte in the ST reactor.

It is worth mentioning that the increase of the concentration up to 50 g L^{-1} resulted in an ohmic resistance of approximately 1 Ω in both systems, which represents approximately the ohmic resistance of the system when the contribution of the electrolyte is minimum (short-circuited conditions). Therefore, according to the experimental data, it can be stated that the performance of the MF-FT is superior to that of the ST in terms of ohmic losses.

Belmont and Girault also studied a microfluidic electro-chemical cell consisting of coplanar interdigitated band electrodes [10]. As expected, the ohmic resistance strongly decreased with the IE gap and the lowest ohmic resistances were measured in the case of

250 μm . Values of 24, 12 and 6 Ω were obtained with 5, 10 and 25 mM of NaCl as electrolyte (which corresponds to 0.29, 0.58 and 1.45 g L^{-1} NaCl). In comparison, 6, 4 and 2 Ω were measured in the flow-through microfluidic reactor for electrolyte concentrations of 3.5, 7.0 and 14.0 mM (which corresponds to 0.5, 1.0 and 2.0 g L^{-1} Na_2SO_4). This comparison confirms the outstanding performance of the MF-FT configuration.

LSV were carried out under the same conditions described in the case of the EIS. It allows one to make sure that the electrodes are not in contact (under short-circuit conditions, the current would flow from very low applied cell voltages) and also double-check the effect of IE gap and electrolyte concentration. The slope of the LSV performed in both reactors under for different IE gap and electrolyte concentrations are shown in Figure 3.

Figure 3. Slope obtained from the LSV analyses. Anode (both): MMO mesh; Cathode (both): stainless steel perforated plate; Flow rate (MF): $105 \text{ dm}^3 \text{ h}^{-1}$; stirring rate (ST): 400 rpm; $T = 20 \text{ }^\circ\text{C}$.

As expected, the tendency of the LSV slope is the opposite to the one of the ohmic resistance. Small IE gaps and high electrolyte concentrations lead to a fast increase of the current with the applied voltage. As an example, at 0.5 g L^{-1} and 1,000 μm , there is an order of magnitude (0.0132 vs 0.1628 A V^{-1}) in the slope for the two reactors under study.

In a broader sense, a difference of two orders of magnitude ($2.89 \cdot 10^{-3}$ vs. $2.38 \cdot 10^{-1} \text{ A V}^{-1}$) are found between the ST (IE gap 25,000 μm) and the MF-FT (IE gap 400 μm) reactors for the lowest electrolyte concentration (0.5 g L^{-1}). This fact highlights the importance of an adequate design of the electrochemical reactor to reduce energy costs, especially when it comes to treat poorly conductive wastewater.

In order to explain the improved performance of the MF-FT reactor, the following deduction may be taken into account. Under the effect of an external electric field, it is well-known that ionic species can move between electrodes as a result of three different driving forces: molecular diffusion, migration and convection [3, 24, 43]. When the latter is present, it is normally the predominant mode of transport [3]. Indeed, important differences are found between both reactors designs in terms of forced convection.

As discussed previously, the closer the electrodes the more constrained is the electrolyte within the IE gap in the ST reactor, limiting the contribution of forced convection. However, in the case of the MF-FT, the circulation of the electrolyte through the cell, and thus the forced convection, is not limited by the narrow IE gap because the hydraulic diameter is several orders of magnitude higher than the IE gap thanks to the geometry of the system. Interestingly, this forced convection contributes to remove the gas bubbles from the electrode surfaces. This contribution may represent a major factor in ohmic drop and should not be neglected. For example, 70% of the energy consumption achieved in chloro-alkali electrolyzers when graphite was substituted by open-mesh DSA[®] electrodes was attributed to the disappearance of the bubble hold-up effect [44].

Considering the previous reasons, the differences found in the performance of both systems may be attributed to the strong forced convection of the electrolyte solution within the IE gap.

3.2 Evaluation of mass transport

A series of experiments were carried out to gain further insight in the mass-transport conditions within the MF-FT reactor. It was evaluated in the MF-FT reactor by means of the limiting-current technique using the redox pair ferri/ferrocyanide [38]. It is important to mention that the surface area for the calculation of k_m is that measured by means of the 3D scanner. The results were also compared with the experiments previously reported by our group using a flow-by (FB) cell in which the electrolyte passes between two parallel-plate electrodes [38]. Figure 4 compares the value of mass-transport coefficient (k_m) as a function of inlet velocity (U).

Figure 4. Comparison of mass transport characteristics as a function of flow velocity for the flow-through and flow-by reactors. Anode/cathode (MF): MMO mesh, 400 μm IE gap; $T = 25\text{ }^{\circ}\text{C}$. ● Flow-through ■ Flow-by.

For a given value of U , according to Figure 3 the k_m is considerably higher in the case of the MF-FT reactor. As an example, it is 70% higher at $U = 0.78 \cdot 10^{-2} \text{ m s}^{-1}$ and differences are increasingly important at higher velocities. Interestingly, the higher slope indicates a stronger dependence with velocity. This means that increasing the velocity as a manner to enhance mass transport is clearly more fruitful in the MF-FT configuration. In a previous study found in literature, Dos Santos et al. reported a k_m value of $2.0 \cdot 10^{-5} \text{ m s}^{-1}$

in a FB cell at a flow rate of 151 L h^{-1} which, according to the geometry of the cell, results in a U of $4.6 \cdot 10^{-2} \text{ m s}^{-1}$ [45]. Extrapolating the data of the MF-FT reactor, such value of k_m would be obtained at only $1.6 \cdot 10^{-2} \text{ m s}^{-1}$ approximately, a value of U three times smaller. This is significant, especially for the scale-up and future applicability of the electrochemical reactors, since velocity is closely linked to EC and, thus, the economics of the process [1].

It is important to remark that for a given geometric area, 3D electrodes possess higher surface areas. As described before, in 33 cm^2 of geometric area, the 3D mesh electrode (MMO) used in this work possesses 53 cm^2 of surface area. The high surface / geometric area of 3D electrodes is undoubtedly a great advantage over planar electrodes [5, 28, 29] because it allows the application of a given current density to achieve the required value of electric charge in smaller reactors and, thus, the design of more compact and economic electrochemical installations. Indeed, the size is a critical aspect in the scale-up given that, quite often, electrochemical wastewater treatments require large surface areas for its application on an industrial scale [1]. As a conclusion from this point, it can be stated that the FT configuration allows a higher k_m in electrodes with larger surfaces resulting in an improved mass-transfer conditions.

The limiting-current technique was also applied under different reactor layouts. The cyanoferrate (II)/(III) solution was prepared adding 0.1 M of the compound to be cathodically reduced ($\text{K}_3\text{Fe}(\text{CN})_6$) in excess with respect to $\text{K}_4\text{Fe}(\text{CN})_6$ (0.05 M). In this manner, the value of the limiting current intensity is given by the mass transport towards the anode. The I-V curves were obtained at different velocity flows varying the layout of the reactor in such a way that the flow passes first through the anode and then the cathode, or viceversa (A-C or C-A layouts). The results are shown in Figure 5.

Figure 5. I-V curves obtained for anode-cathode and cathode – anode layouts at different flow rates. ● C- A ○ A – C; Flow rate ($\text{dm}^{-3} \text{ h}^{-1}$): a) 30 b) 45 c) 70 d) 90. Anode/cathode: MMO mesh, 400 μm IE gap; T = 25 °C

As it can be observed in Figure 5, the curves are overlapped at low applied voltages. Under these circumstances, the reaction is expected to be charge transfer controlled and thus independent from mass transport conditions. However, after the plateau and before water electrolysis begins, the reaction is expected to be mass transport controlled. In all the cases, it can be observed that the intensity is slightly higher when the anode (working electrode) is placed after the cathode. This information is useful for optimizing the electrode layout to maximize mass transport to the target electrode, and thus the overall performance of the cell, by simply re-arranging the electrodes with no need of extra investment.

A plausible explanation for the enhancement of mass transport in the flow-through configuration may be found in the local turbulence induced by the 3D electrodes fed in flow-through [5]. In a FT cell with planar electrodes, the turbulent flow occurs at high velocities where the inertial are largely superior to the viscous forces (high Re number),

a classic situation of internal flow [46]. However, when a solid geometry (such as a flow-electrode) is placed in the way of the fluid the problem may be studied from the external flow point of view [3, 47]. The solid geometry induces the rotation of the flow lines and the formation of vortices, reducing the thickness of the boundary layer in the vicinity of the electrodes and, ultimately, favoring mass transport. Fimbres-Weihs and Wiley [48] reviewed 3D computer fluid dynamic (CFD) simulation studies of flow conditions in narrow spacer-filled channels and concluded that vorticity play a primary role in mass-transfer enhancement by promoting mixing of low and high concentrations portions of fluid, increasing wall shear and this way reducing the thickness of the boundary layer [49]. Indeed, it is a common practice to introduce inert geometries such as nets or bars to act as turbulence promoters in advanced electrochemical cells designs [3, 50] or in other such as ultrafiltration systems [51, 52].

3.3 Application to wastewater treatment

The performance of the MF-FT reactor for wastewater treatment is compared with a commercial AO-BDD flow-by reactor (Diacell® 101), a well-known device for environmental applications with a good performance. The wastewater to be treated is a synthetic soil washing effluent containing the pesticide clopyralid as model organic pollutant spiked in a relatively low conductive (1 mS cm^{-1}) aqueous matrix (see this reference for more information [9]). The electrolyses for the abatement of the pollutant were performed at low (10 mA cm^{-2}) and high (100 mA cm^{-2}) current densities. These values cover practically the typical range of variation of this parameters in AO-BDD [53] so the application of this current density permits the assessment of the potential of the system. Figure 6 shows the reduction of clopyralid and TOC in both reactors as a function of the specific applied electric charge.

Figure 6. Clopyralid and total organic carbon reduction in the FB and MF-FT reactors at different current densities. a) 10 mA cm^{-2} b) 100 mA cm^{-2} . ● Clopyralid-FB ○ Clopyralid-MF-FT ■ TOC-FB □ TOC-MF-FT; $[\text{Clopyralid}]_0 = 100 \text{ ppm}$; Conductivity = 1 mS cm^{-1} ; $T = 25 \text{ }^\circ\text{C}$; Volume = 1 dm^3 . FB: flow rate = $50 \text{ dm}^3 \text{ h}^{-1}$ – Electrode area = 78 cm^2 – IE gap: $3000 \text{ }\mu\text{m}$ - $U = 5.80 \cdot 10^{-2} \text{ m s}^{-1}$. MF-FT: flow rate = $100 \text{ dm}^3 \text{ h}^{-1}$ – Electrode geometric area = 33 cm^2 - IE gap: $400 \text{ }\mu\text{m}$ - $U = 0.88 \cdot 10^{-2} \text{ m s}^{-1}$. Anode: BDD mesh; Cathode: stainless steel perforated plate.

In general terms, it can be seen that the MF-FT performs better than the FB reactor both in terms of efficiency (lower applied electric charge) and EC. As expected, the degradation is more efficient at low current densities given that the process is less mass-transfer controlled and, thus, an smaller fraction of the electrical charge is wasted in parasitic reactions [54-56].

Working at 10 mA cm^{-2} , the complete removal of clopyralid and TOC needs 10.1 and 11.38 Ah dm^{-3} , respectively, in the FB reactor. On the other hand, only 2.37 and 2.71 Ah dm^{-3} are required when the MF-FT is used which is traduced in a reduction of more than 4 times in specific electric charge. It implies four times higher current efficiency and four time less treatment time for mineralization below the detection limit.

Similarly, at 100 mA cm^{-2} a reduction of more than ten times for total removal of clopyralid and TOC (78.50 and 93.04 vs. 6.83 and 8.54 Ah dm^{-3} , respectively) is obtained

thanks to use of the MF-FT reactor. Interestingly, the performance of FB reactor only seems to be slightly superior to the MF-FT in the moments at 100 mA cm^{-2} , probably as a consequence of a better current distribution in the commercial reactor [1]. This is a point that should be considered to improve the performance of the MF-FT in the future. At this current density the decay of clopyralid and TOC are more similar than in the case of 10 mA cm^{-2} . It suggests that at higher current densities, the oxidation is stronger and it leads to a more direct mineralization of the parent molecule and less formation of intermediates.

It is important to highlight that the MF-FT did not suffer from operational problems derived from the accumulation of gases (H_2/O_2 evolution) in the IE gap, even working at high current densities, one of the objectives of the design. This is an important advantage versus microfluidic flow-by reactors, which suffers partial clogging of the channel when gas-evolving electrodes are used and high current densities are applied [22, 23].

Interestingly, the MF-FT reactor is more efficient at 100 mA cm^{-2} than the FB at 10 mA cm^{-2} given that it needs 25% less specific electric charge for the complete mineralization of clopyralid (8.54 vs 11.38 Ah dm^{-3}). Also, it can be seen in Figure 6.a and b that FB reactor is considerably inefficient at low concentration of pollutant, in contrast to the MF-FT. This behavior is attributed to the improved mass transfer conditions in the MF-FT reactor as discussed previously.

Regarding EC, Figure 7.a and b shows the EC for different selected mineralization percentages (estimated according to stoichiometric reaction, eq 1) at 10 and 100 mA cm^{-2} , respectively.

Figure 7. Comparison of the energy consumption for different mineralization percentages in the FB and MF-FT reactor. ■ FB □ MF-FT a) 10 mA cm⁻² b) 100 mA cm⁻²

As expected, it increases with the mineralization degree and current density, as widely discussed in bibliography [26, 57]. Under all the conditions the EC is lower in the case of the MF-FT reactor, but not only due to the improved mass transfer and the smaller specific charge required, but also due to the lower E_{cell} . In particular, an average E_{cell} of 8.0 V in the FB vs 5.2 V in the MF-FT (10 mA cm⁻²) and 20.3 vs. 13.9 V (100 mA cm⁻²), respectively, which represents a reduction of around 30-35% thanks to the minimization of the ohmic losses in the MF-FT.

For high mineralization percentages and current densities, the differences between both reactors is even more marked. At 99%, EC is 60.9 vs 12.1 kWh m⁻³ (at 10 mA cm⁻²) and 1,500 vs. 92.3 (at 100 mA cm⁻²). It is worth mentioning that the FB reactor requires an important extra quantity of energy to attain 100% mineralization (75 and 1,786 kWh m⁻³ at 10 and 100 mA cm⁻², respectively) which is not the case of the MF-FT (15.5 and 115 kWh m⁻³ at 10 and 100 mA cm⁻², respectively). As a general conclusion, it can be stated that MF-FT needs within 6 and 15 time less energy at 10 and 100 mA cm⁻², respectively, to attain the complete mineralization of 100 ppm of clopyralid, which represents a huge cut in EC with respect to the conventional FB reactor.

In a recent and interesting work [57], Lanza-Lopes et al. suggested the use of electrical energy per order (E_{EO} , kWh m⁻³ order⁻¹) as a figure of merit to compare the performance

of EO experiments. This parameter represents the energy per unit of volume required to reduce one order of magnitude (i.e. 90%) the initial TOC at a given current density. They reported an E_{EO} value of $331.8 \text{ kWh m}^{-3} \text{ order}^{-1}$ in the degradation of a solution containing 142 ppm p-chlorobenzoic acid ($n = 29$) and 0.05 M Na_2SO_4 at $j = 100 \text{ mA cm}^{-2}$ in an stirred-tank reactor with 1 cm of IE gap. As can be seen in Figure 7.b, the E_{EO} for degradation of clopyralid ($n = 26$) is as low as $73 \text{ kWh m}^{-3} \text{ order}^{-1}$ which implies a reduction in EC of 450%, even considering that the conductivity of the electrolyte is about 7 times lower in the MF-FT.

Considering all the aforementioned reasons, it can be concluded that the MF-FT design is an interesting approach for the development of electrochemical environmental technologies, not only anodic oxidation but also others such as electroFenton, to reduce the pollution from wastewaters by means of low carbon-footprint processes, especially in a future energetic scenario in which the electricity is mainly produced by CO_2 -free sources.

4 Conclusions

From this work, the following conclusions can be drawn:

- Lower cell voltages can be attained with the microfluidic flow-through reactor with 3D mesh electrodes as compared to conventional electrochemical cells. An ohmic resistance of just 6Ω at $400 \mu\text{m}$ of inter-electrode gap using an electrolyte with low conductivity (0.7 mS cm^{-1}). The ohmic resistance not only depends on inter-electrode gap but also in the fluid-dynamics inside it.
- Higher k_m and surface area in comparison with a flow-by parallel plate cell can be obtained in the microfluidic flow-through reactor with 3D mesh electrodes as compared to conventional cells. At an inlet velocity of $0.78 \cdot 10^{-2} \text{ m s}^{-1}$, the k_m is 70% higher and different are increasingly important with inlet velocity.

- In comparison with a commercial flow-by cell, the microfluidic flow-through requires from 4 to 10 times less electric charge and from 6 to 15 times less energy for the mineralization of 100 ppm of clopyralid.
- The proposed microfluidic flow-through configuration is an interesting approach for the development of low environmental impact electrochemical wastewater technologies.

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References

- [1] C.A. Martinez-Huitle, M.A. Rodrigo, I. Sires, O. Scialdone, Single and Coupled Electrochemical Processes and Reactors for the Abatement of Organic Water Pollutants: A Critical Review, *Chemical Reviews* (Washington, D. C.) 115 (2015) 13362-13407.
- [2] O. Scialdone, C. Guarisco, A. Galia, Oxidation of organics in water in microfluidic electrochemical reactors: Theoretical model and experiments, *Electrochimica Acta* 58 (2011) 463-473.
- [3] D. Pletcher, F.C. Walsh, *Industrial Electrochemistry*, Springer Netherlands 1990.
- [4] H. Wendt, H. Vogt, G. Kreysa, D. M. Kolb, G. E. Engelmann, J.C. Ziegler, H. Goldacker, K. Jüttner, U. Galla, H. Schmieder, E. Steckhan, *Electrochemistry*,

Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co.

KGaA2000.

[5] D. Pletcher, Z.Q. Tian, D.E. Williams, *Developments in Electrochemistry: Science Inspired by Martin Fleischmann*, 2014.

[6] R.K.B. Karlsson, A. Cornell, Selectivity between Oxygen and Chlorine Evolution in the Chlor-Alkali and Chlorate Processes, *Chemical Reviews* 116 (2016) 2982-3028.

[7] M. Wang, Z. Wang, X. Gong, Z. Guo, The intensification technologies to water electrolysis for hydrogen production – A review, *Renewable and Sustainable Energy Reviews* 29 (2014) 573-588.

[8] O. Scialdone, C. Guarisco, A. Galia, G. Filardo, G. Silvestri, C. Amatore, C. Sella, L. Thouin, Anodic abatement of organic pollutants in water in micro reactors, *Journal of Electroanalytical Chemistry* 638 (2010) 293-296.

[9] S. Cotillas, L. Cañizares, M. Muñoz, C. Sáez, P. Cañizares, M.A. Rodrigo, Is it really important the addition of salts for the electrolysis of soil washing effluents?, *Electrochimica Acta* 246 (2017) 372-379.

[10] C. Belmont, H.H. Girault, Coplanar interdigitated band electrodes for synthesis Part I: Ohmic loss evaluation, *Journal of Applied Electrochemistry* 24 (1994) 475-480.

[11] B. Sun, J. Jiang, N. Shi, W. Xu, Application of microfluidics technology in chemical engineering for enhanced safety, *Process Safety Progress* 35 (2016) 365-373.

[12] K.S. Elvira, X.C. i Solvas, R.C.R. Wootton, A.J. deMello, The past, present and potential for microfluidic reactor technology in chemical synthesis, *Nat Chem* 5 (2013) 905-915.

[13] A. Ziogas, G. Kolb, M. O'Connell, A. Attour, F. Lapicque, M. Matlosz, S. Rode, Electrochemical microstructured reactors: design and application in organic synthesis, *Journal of Applied Electrochemistry* 39 (2009) 2297.

- [14] K. Watts, A. Baker, T. Wirth, Electrochemical synthesis in microreactors, *Journal of Flow Chemistry* 4 (2014) 2-11.
- [15] J. Kristal, R. Kodym, K. Bouzek, V. Jiricny, J. Hanika, Electrochemical Microreactor Design for Alkoxylation Reactions—Experiments and Simulations, *Industrial & Engineering Chemistry Research* 51 (2012) 1515-1524.
- [16] O. Scialdone, A. Galia, S. Sabatino, Electro-generation of H₂O₂ and abatement of organic pollutant in water by an electro-Fenton process in a microfluidic reactor, *Electrochemistry Communications* 26 (2013) 45-47.
- [17] O. Scialdone, E. Corrado, A. Galia, I. Sirés, Electrochemical processes in macro and microfluidic cells for the abatement of chloroacetic acid from water, *Electrochimica Acta* 132 (2014) 15-24.
- [18] O. Scialdone, A. Galia, S. Sabatino, Abatement of Acid Orange 7 in macro and micro reactors. Effect of the electrocatalytic route, *Applied Catalysis B: Environmental* 148–149 (2014) 473-483.
- [19] S. Sabatino, A. Galia, O. Scialdone, Electrochemical Abatement of Organic Pollutants in Continuous-Reaction Systems through the Assembly of Microfluidic Cells in Series, *ChemElectroChem* 3 (2016) 83-90.
- [20] O. Scialdone, A. Galia, S. Sabatino, G.M. Vaiana, D. Agro, A. Busacca, C. Amatore, Electrochemical Conversion of Dichloroacetic Acid to Chloroacetic Acid in Conventional Cell and in Two Microfluidic Reactors, *ChemElectroChem* 1 (2014) 116-124.
- [21] R. Green, R. Brown, D. Pletcher, Understanding the performance of a microfluidic electrolysis cell for routine organic electrosynthesis, *Journal of Flow Chemistry* 5 (2015) 31-36.

- [22] K. Bouzek, V. Jiříčný, R. Kodým, J. Křišťál, T. Bystroň, Microstructured reactor for electroorganic synthesis, *Electrochimica Acta* 55 (2010) 8172-8181.
- [23] J. Křišťál, R. Kodým, K. Bouzek, V. Jiříčný, Electrochemical microreactor and gas-evolving reactions, *Electrochemistry Communications* 10 (2008) 204-207.
- [24] E. Heitz, G. Kreysa, Principles of Electrochemical Engineering: Extended Version of a DECHEMA Experimental Course, VCH1986.
- [25] M. De Francesco, P. Costamagna, On the design of electrochemical reactors for the treatment of polluted water, *Journal of Cleaner Production* 12 (2004) 159-163.
- [26] M. Panizza, G. Cerisola, Direct and mediated anodic oxidation of organic pollutants, *Chemical Reviews* 109 (2009) 6541-6569.
- [27] C. Zhang, Y. Jiang, Y. Li, Z. Hu, L. Zhou, M. Zhou, Three-dimensional electrochemical process for wastewater treatment: A general review, *Chemical Engineering Journal* 228 (2013) 455-467.
- [28] L.F. Arenas, C. Ponce de León, F.C. Walsh, 3D-printed porous electrodes for advanced electrochemical flow reactors: A Ni/stainless steel electrode and its mass transport characteristics, *Electrochemistry Communications* 77 (2017) 133-137.
- [29] F.C. Walsh, L.F. Arenas, C. Ponce de León, G.W. Reade, I. Whyte, B.G. Mellor, The continued development of reticulated vitreous carbon as a versatile electrode material: Structure, properties and applications, *Electrochimica Acta* 215 (2016) 566-591.
- [30] L. Wang, Y. Zhao, Q. Gao, C. Qian, Y. Hu, A new strategy for determination of current efficiency during electro-oxidation of aromatic compounds in a packed-bed system, *Water Science and Technology* 63 (2011) 2685-2691.

- [31] J.L. Nava, A. Recendiz, J.C. Acosta, I. Gonzalez, Electrochemical incineration of vinasse in filter-press-type FM01-LC reactor using 3D BDD electrode, *Water Science and Technology* 58 (2008) 2413-2419.
- [32] G. Ren, M. Zhou, M. Liu, L. Ma, H. Yang, A novel vertical-flow electro-Fenton reactor for organic wastewater treatment, *Chemical Engineering Journal* 298 (2016) 55-67.
- [33] H. Liu, A. Vajpayee, C.D. Vecitis, Bismuth-Doped Tin Oxide-Coated Carbon Nanotube Network: Improved Anode Stability and Efficiency for Flow-Through Organic Electrooxidation, *ACS Applied Materials & Interfaces* 5 (2013) 10054-10066.
- [34] G. Gao, Q. Zhang, Z. Hao, C.D. Vecitis, Carbon nanotube membrane stack for flow-through sequential regenerative electro-Fenton, *Environmental Science and Technology* 49 (2015) 2375-2383.
- [35] L. Ma, M. Zhou, G. Ren, W. Yang, L. Liang, A highly energy-efficient flow-through electro-Fenton process for organic pollutants degradation, *Electrochimica Acta* 200 (2016) 222-230.
- [36] J.F. Pérez, J. Llanos, C. Sáez, C. López, P. Cañizares, M.A. Rodrigo, A microfluidic flow-through electrochemical reactor for wastewater treatment: A proof-of-concept, *Electrochemistry Communications* 82 (2017) 85-88.
- [37] K. Chair, A. Bedoui, N. Bensalah, F.J. Fernández-Morales, C. Sáez, P. Cañizares, M.A. Rodrigo, Combining bioadsorption and photoelectrochemical oxidation for the treatment of soil-washing effluents polluted with herbicide 2,4-D, *Journal of Chemical Technology & Biotechnology* 92 (2017) 83-89.
- [38] P. Cañizares, J. García-Gómez, I. Fernández de Marcos, M.A. Rodrigo, J. Lobato, Measurement of Mass-Transfer Coefficients by an Electrochemical Technique, *Journal of Chemical Education* 83 (2006) 1204.

- [39] F. Yu, M. Zhou, X. Yu, Cost-effective electro-Fenton using modified graphite felt that dramatically enhanced on H₂O₂ electro-generation without external aeration, *Electrochimica Acta* 163 (2015) 182-189.
- [40] J.F. Pérez, A. Galia, M.A. Rodrigo, J. Llanos, S. Sabatino, C. Sáez, B. Schiavo, O. Scialdone, Effect of pressure on the electrochemical generation of hydrogen peroxide in undivided cells on carbon felt electrodes, *Electrochimica Acta* 248 (2017) 169-177.
- [41] O. Scialdone, A. Galia, C. Gattuso, S. Sabatino, B. Schiavo, Effect of air pressure on the electro-generation of H₂O₂ and the abatement of organic pollutants in water by electro-Fenton process, *Electrochimica Acta* 182 (2015) 775-780.
- [42] F.C. Moreira, R.A.R. Boaventura, E. Brillas, V.J.P. Vilar, Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters, *Applied Catalysis B: Environmental* 202 (2017) 217-261.
- [43] R. López-Vizcaíno, C. Risco, J. Isidro, S. Rodrigo, C. Saez, P. Cañizares, V. Navarro, M.A. Rodrigo, Scale-up of the electrokinetic fence technology for the removal of pesticides. Part I: Some notes about the transport of inorganic species, *Chemosphere* 166 (2017) 540-548.
- [44] S. Trasatti, Electrocatalysis: understanding the success of DSA®, *Electrochimica Acta* 45 (2000) 2377-2385.
- [45] E.V. dos Santos, S.F. Sena, D.R. da Silva, S. Ferro, A. De Battisti, C.A. Martinez-Huitle, Scale-up of electrochemical oxidation system for treatment of produced water generated by Brazilian petrochemical industry, *Environ Sci Pollut Res Int* 21 (2014) 8466-8475.
- [46] F. White, *Fluid Mechanics*, McGraw-Hill Education 2015.

- [47] G.G. Calleja, F.; Iglesias, J.; de Lucas, A.; Rodríguez, J.M., Introducción a la ingeniería química: fundamentos generales, mecánica de fluidos y transmisión de calor, Síntesis 1999.
- [48] G.A. Fimbres-Weihs, D.E. Wiley, Review of 3D CFD modeling of flow and mass transfer in narrow spacer-filled channels in membrane modules, Chemical Engineering and Processing: Process Intensification 49 (2010) 759-781.
- [49] U.M. López-García, P.E. Hidalgo, J.C. Olvera, F. Castañeda, H. Ruiz, G. Orozco, The hydrodynamic behavior of a parallel-plate electrochemical reactor, Fuel 110 (2013) 162-170.
- [50] E.P. Rivero, F.F. Rivera, M.R. Cruz-Díaz, E. Mayen, I. González, Numerical simulation of mass transport in a filter press type electrochemical reactor FM01-LC: Comparison of predicted and experimental mass transfer coefficient, Chemical Engineering Research and Design 90 (2012) 1969-1978.
- [51] J. Llanos, Á. Pérez, P. Cañizares, Copper recovery by polymer enhanced ultrafiltration (PEUF) and electrochemical regeneration, Journal of Membrane Science 323 (2008) 28-36.
- [52] J. Llanos, R. Camarillo, Á. Pérez, P. Cañizares, Polymer supported ultrafiltration as a technique for selective heavy metal separation and complex formation constants prediction, Separation and Purification Technology 73 (2010) 126-134.
- [53] X. Yu, M. Zhou, Y. Hu, K. Groenen Serrano, F. Yu, Recent updates on electrochemical degradation of bio-refractory organic pollutants using BDD anode: A mini review, Environmental Science and Pollution Research 21 (2014) 8417-8431.
- [54] M. Skoumal, C. Arias, P.L. Cabot, F. Centellas, J.A. Garrido, R.M. Rodríguez, E. Brillas, Mineralization of the biocide chloroxylenol by electrochemical advanced oxidation processes, Chemosphere 71 (2008) 1718-1729.

- [55] A.H. Ltaïef, A. D'Angelo, S. Ammar, A. Gadri, A. Galia, O. Scialdone, Electrochemical treatment of aqueous solutions of catechol by various electrochemical advanced oxidation processes: Effect of the process and of operating parameters, *Journal of Electroanalytical Chemistry* 796 (2017) 1-8.
- [56] C. Flox, P.L. Cabot, F. Centellas, J.A. Garrido, R.M. Rodríguez, C. Arias, E. Brillas, Electrochemical combustion of herbicide mecoprop in aqueous medium using a flow reactor with a boron-doped diamond anode, *Chemosphere* 64 (2006) 892-902.
- [57] M. Lanzañini-Lopes, S. Garcia-Segura, K. Hristovski, P. Westerhoff, Electrical energy per order and current efficiency for electrochemical oxidation of p-chlorobenzoic acid with boron-doped diamond anode, *Chemosphere* 188 (2017) 304-311.