Testing and Scaling-up of a novel Ti/Ru_{0.7}Ti_{0.3}O₂ mesh anode in a microfluidic flow-through reactor

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Graphical abstract

Abstract

This work investigates the scale-up of the electrolysis and photo-electrolysis of water polluted with clopyralid using a novel $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ mesh anode produced by CO_2 laser. Two different cells were used: a mixed tank cell (MT) and a microfluidic flow-through reactor (MF-FT). The main advantages of the MF-FT reactor are the simultaneous reduction of the ohmic resistance and mass transfer limitations, which are two critical factors in electrochemical oxidation. Thus, the goal is the scale-up evaluation and the study of the effects of the kind of water matrix towards practical application of the laser-made anode in water treatment. Aqueous solutions of clopyralid and groundwater intensified with this pollutant were studied in the context of the scale-up evaluation to clarify the effects of the water matrix. Single photolysis was also studied for comparison purposes. It was demonstrated that photo-electrolysis results in a faster clopyralid and TOC removal in both the MF-FT reactor and mixed tank cells as compared to single electrolysis. This work also focuses on the synergy coefficient to evaluate the effect of the coupling of different processes on system performance. Higher synergistic effects occur on clopyralid removal in the MF-FT reactor (110% and 358%, for natural groundwater and synthetic water, respectively) and TOC (233.3% and 15396% for natural groundwater and synthetic water, respectively). The best performance was obtained in the MF-FT reactor, which was attributed to the more uniform potential/current distribution associated with the reduced interelectrode gap (few microns) in comparison

with the MT cell (gap of one centimeter), which also results in reduced energy consumption.

Keywords: Electrolysis; scale-up; anode material; UV irradiation; clopyralid.

Highlights

- Highest efficiencies in photo-electrolysis with Ti/Ru_{0.3}Ti_{0.7}O₂ mesh anode in MF-FT
- Synergism associated with the activation of hydroxyl, chlorine and sulfate radicals
- Reduced interelectrode gap results in improved efficiencies and energy consumptions
- Neither chlorate nor perchlorate was found in the final treated water

1. Introduction

The contamination of water with bio-refractory anthropogenic organic pollutants is an issue of great concern, with a significant negative impact on ecosystems and human health. Because of that, the development of treatment technologies capable of removing this type of pollutants from water and wastewater is becoming an important topic worthy of research.

Electrochemical technologies are a promising alternative, widely investigated in recent years [1–6]. Many of the contributions have focused on the anode materials and the mechanical cell design [7]. Regarding the anode materials, it is worth to highlight electrodes based on mixed metal oxide (MMO) coatings, which are particularly attractive due to their low cost and good electrocatalytic properties [8]. Thus, according to the literature, besides direct oxidation occurring on the MMO anode surface through chemisorbed hydroxyl radicals, the mediated oxidation by other oxidants electrogenerated from the salts contained in the electrolyte plays an essential role in increasing the global efficiency of the electrolysis [9].

Regarding the cell type, the conventional mixed-tank cell (MT) is the most widely used configuration in lab-scale studies [1]. These reactors can be easily scaled-up, but mass transport is a significant issue that cannot be solved only by increasing the stirring rate. For larger scales, flow cells are typically applied, being these systems appropriate even for treating wastes in continuous mode [10–12]. The main advantage exhibited by flow cells is the enhanced mass transport properties, which make them more suitable for treating much lower concentrations than MT cells. These are the two main models of electrochemical reactors commonly reported in the scientific literature for the removal of organic pollutants from wastewater. However, very few studies are carried out focused on the scale-up of these cells in environmental applications [13]: the studies facing the scale-up of novel anode materials from mixed-tank to flow cells are almost null, which is

a significant lack in the literature and a drawback for the full application of the electrolytic technology.

One of the main points in the design of electrochemical cells is the interelectrode distance because the space between two electrodes (gap) affects the total resistance of the cell. Thus, the lower is the electrode gap, the lower is the cell potential and, in turn, the operation costs of this technology [14]. With this focus, Pérez *et al.* [15] have reported the excellent performance of microfluidic reactors with a gap in the order of some tens of microns for the treatment of a low-conductive soil-washing effluent polluted with clopyralid. Further studies have demonstrated high abatement of pollutants under continuous mode by using microfluidic flow-through (MF-FT) electrochemical reactors [16, 17]. This good performance is also attributed to the improvement of mass transport phenomena (that typically limits electrochemical processes). Additionally, the considerable reduction of the ohmic resistance (due to the micro interelectrode gap) leads to the reduction of the operational costs [17].

Moreover, another interesting case in terms of reactor design is the activation of oxidants by coupling UV irradiation to the electrolytic reactor [18–20], in order to increase the efficiency of these systems by the activation of oxidants in the bulk solution, transforming them into radical species. The most common approach consists of the use of UV lamps inside the electrochemical cell [21].

As has been pointed out, the scale-up of the anode material and the electrochemical cell is a topic of major importance. However, it is not less important the application of environmental remediation technologies to treat real wastes instead of synthetic solutions of pollutants. Thus, studies on the low TRL (technology readiness level) in electrochemical technology are mainly focused on the degradation of pollutants contained in synthetic solutions. These studies are essential, but the evaluation of the differences observed in real matrixes gives important details that must be faced in the scale-up. In

this frame, in this work, the degradation of pollutants in both matrixes is going to be compared. Regarding real matrixes, the relevance of the treatment of groundwater contaminated by pesticides of high solubilities, such as clopyralid, has a significant health concern, due to high toxicity and poor biodegradability of these compounds [22–25]. The herbicide clopyralid has been used to control grasses as well as broadleaved weeds, is highly soluble in water (solubility $> 1 \text{ g L}^{-1}$ at 20°C), and mobile under both laboratory and field conditions [22]. Thus, it may leach into groundwater if the herbicide is applied to areas where soils are very permeable, and the water table is shallow [26]. Clopyralid has recently been reported to occur in drinking water at concentrations above the permitted value for an individual pesticide (EU directive 98/83/EC) [27–29].

In this work, the primary purpose has been to scale-up a promising anode material (a $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ mesh prepared by CO_2 laser heating) using it in conventional mixed tank (MT) cells and microfluidic flow-through (MF-FT) reactors. The performance of the anode was assessed by evaluating the removal and mineralization of clopyralid (model pollutant) from contaminated groundwater, and the feasibility of combined with UVC irradiation. The current density and volume/irradiated area were kept fixed for both configurations in order to have a better understanding of the scale-up procedure.

2. Experimental section

2.1 Chemicals and groundwater

Clopyralid (3,6-dichloro-2-pyridine-carboxylic acid) (99,9 %) was purchased from Sigma Aldrich®. Methanol ($\geq 99.0 \%$) and formic acid ($\geq 95.0 \%$), used for the mobile phase of high-performance liquid chromatography (HPLC), were also purchased from Sigma Aldrich®. Oxalic, maleic, and oxamic acid (99.5 %) from Panreac®. All reactants were used as received. Characteristics of the natural groundwater used in this study are

provided in Table 1. Sodium chloride used as supporting electrolyte, for the synthetic water was purchased from Panreac.

Table 1. Characteristics of natural groundwater used in this study.

Parameter	Value ^a
Chloride (mg L ⁻¹)	84.0
Sulfate (mg L ⁻¹)	449.8
Nitrate (mg L ⁻¹)	8.5
Ammonium (mg L ⁻¹)	0.035
Calcium (mg L ⁻¹)	188.3
Potassium (mg L ⁻¹)	4.72
Magnesium (mg L ⁻¹)	66.5
Sodium (mg L ⁻¹)	81.7
Conductivity (μS cm ⁻¹)	2.42
pH	7.83

^aThe natural groundwater was collected and stored to perform all experiments in order to avoid an experimental error.

2.2. Experimental setup

Two different experimental cells were used in this work: a typical lab-scale mixed-tank cell (henceforth referred to as the MT cell) and a microfluidic flow-through reactor (henceforth referred to as the MF-FT reactor) (Figure 1).

Figure 1. The schematic diagram of the electrochemical reactors: a) mixed tank cell, b) microfluidic flow-through (MF-FT) reactor, and c) set-up of the MF-FT cell. WE: working electrode and CE: counter electrode.

In both systems, a Ti/Ru_{0.7}Ti_{0.3}O₂ anode prepared using CO₂ laser heating was used as the working electrode. The anode used in the MT cell (geometric area: 4.0 cm²) was produced according to the methodology described in previous work [25, 30]. For the mesh anode (geometric area: 66.0 cm² considering both sides) used in the MF-FT reactor, the methodology was adapted adopting a strategy of scanning (See Supplementary material). As cathode, it was used a home-made perforated plate of stainless steel AISI304. The inter-electrode separator consisted of a thin Teflon foil of 0.1 mm (100 μm) and two thin aluminum foils (50 μm) as of current collectors, producing 200 μm of the inter-electrode

gap. In MF-FT reactor configuration, there are two holes where the anode and cathode are placed, one facing the other, and the solution is forced to flow through them. This configuration makes the process faster and improves the mass transport limitations that are commonly reported for the mixed tank cell (MT). Also, one of the main obstacles of conventional MT cells is the need for a high conductivity electrolyte to reduce the cell potential through the reduction of the ohmic resistance and potential difference between the anode and cathode. Moreover, the fast circulation of the fluid through the cross-sectional area makes that the evolved gases do not be an operational problem for the tiny inter-electrode distance.

In order to compare on equal terms, experiments for the removal of clopyralid (100 mg L⁻¹) were carried at the same current density (30 mA cm⁻²), electrolytic medium (natural groundwater), and electrical charge (6.4 A h L⁻¹). Because of that, experiments conducted in the MF-FT reactor lasted after 7.17 h, while 8h were required for the MT cell for the same applied current charge passed. In the experiments using the MF-FT reactor, the solution pass through the electrodes by using a Micropump[®] (GB-P25 J F5 S, with a head coupled to a DB 380 A 24 V motor with speed control 0-5 V DC supplied by Techma GPM S.l.r.) that fed the solutions at a fixed flow rate of 140 dm³ h⁻¹ and the volume of the solution was 2.2L. For the photoelectrolysis, a UVC lamp ($\lambda = 254$ nm) was used to irradiate 9 W directly to the electrolyte solution.

2.3 Analytical techniques

HPLC was used to identify clopyralid and aromatic intermediates using an Agilent 1100 series with UV detection set at 280 nm, equipped with an Eclipse Plus C-18 column (4.6 mm $\times$ 100 mm; 3.5 μ m). The mobile phase was methanol/water (containing 0.1% formic acid) (30/70, v/v) with a flow rate of 1.0 mL min⁻¹. The column temperature was adjusted to 20 °C, and the volume injected was 20.0 μ L. Acid intermediates were identified by

HPLC using a Zorbax SB-Aq column (4.6 mm × 150 mm). The mobile phase consists of 5 mM H₂SO₄ / water (50/50, v/v) with a flow rate of 0.8 mL min⁻¹. The UV detection was set at 210 nm. Measurements of inorganic ions (nitrite, nitrate, ammonium, chlorate, and perchlorate) were performed by ion chromatography with a coupled conductivity detector (Metrohm 732IC). A Metrosep A Supp 4-250 column was used as the stationary phase and 3.6 mM 85:15 (V /V) Na₂CO₃/acetonitrile as the mobile phase. Total organic carbon concentration (TOC) was monitored using a Multi N/C 3100 Analytik Jena analyzer. Hypochlorite was measured by titration using a solution of As₂O₃ in 2.0 M NaOH (0.001 M). Oxidants were determined by iodometric titration.

2.4 Synergy coefficient and energy consumption

The synergy coefficient (%) was used to evaluate the effect of coupling electrolysis and photolysis processes. It was calculated according to Eq. (1) where k is the kinetic constant for clopyralid or TOC removal calculated for the different processes (electrolysis, photolysis, and photo-electrolysis).

$$\text{Synergy coefficient (\%)} = \frac{k_{\text{photoelectro}} - k_{\text{photo}} - k_{\text{electro}}}{k_{\text{photo}} + k_{\text{electro}}} \times 100 \quad (1)$$

The specific energy consumption per unit TOC mass (EC_{TOC}) for the process studied was calculated from Eq (2), where E_{cell} is the average cell potential in V, I is the applied current in A, t is the electrolysis time in h, V_s is the aqueous waste volume in L, $(\Delta\text{TOC})_{\text{exp}}$ is the TOC removal (in g L⁻¹) [31], and P is the nominal power of the UVC lamp (W) [32].

$$EC_{\text{TOC}} (\text{kWh kgTOC}^{-1}) = \left(\frac{E_{\text{cell}} \cdot I \cdot t}{V_s \cdot (\Delta\text{TOC})_{\text{exp}}} \right) \text{ or } \left(\frac{E_{\text{cell}} \cdot I \cdot t + P \cdot t}{V_s \cdot (\Delta\text{TOC})_{\text{exp}}} \right) \quad (2)$$

3. Results and discussion

3.1 Degradation and mineralization of clopyralid by electrolysis and photo-electrolysis

Figure 2 shows the removal of clopyralid and the mineralization attained during photolysis, electrolysis, and photo-electrolysis of the natural groundwater and synthetic water polluted with 100 mg L⁻¹ of clopyralid, in both, the MT cell (Figure 2a,b) and the MF-FT reactor (Figure 2c,d). Electrochemical experiments were carried out galvanostatically at 30 mA cm⁻², and results are plotted in a semilogarithmic scale (for the sake of extracting valuable kinetic information, as trends are linear and this indicates first-order kinetics in the degradation).

For single photolysis, no significant conversion of clopyralid is observed for synthetic water, while in the natural groundwater removals are between 10.3 and 14 %. These results suggest that, individually, this technology is not suitable for the removal of the herbicide. Regarding mineralization, the minimal variation of the TOC concentration may be related to the accuracy of the analytical equipment, more than to a real change, because no trend can be seen. It indicates that only the application of UVC light is not enough to transform the herbicide directly into carbon dioxide, and it can only produce a rather soft transformation of this pollutant.

Changes produced by electrolysis are much important, and they can be explained by the contribution of direct and mediated processes because the natural groundwater contained sulfate and chloride anions. Thus, the production of chlorine (Eq. (3)) and its disproportionation to hypochlorite/hypochlorous acid (Eqs. (4–5)) is expected. Less importantly, because MMO anodes are used, peroxo-sulfates (Eq. (6)) can also be produced in the reaction system [33]. All these oxidants have been found to produce a very efficient depletion of the organics contained in wastewaters.

However, regardless of the system configuration, the integrated photo-electrolysis removes more efficiently the herbicide than the separated electrolysis and photolysis, which may indicate that mediated oxidation can be playing an important role, increasing the efficiency of the process. In this sense, the combination of photolysis with the electrolysis generates an evident positive synergism, reflected by a remarkable improvement in the mineralization, increasing its value up to 4-times. At this point, under UVC (254 nm) irradiation, powerful chlorine and hydroxyl radicals are expected to be formed in the bulk solution by a homolytic homogeneous reaction (Eq. (7)) [34], as well as sulfate radicals (Eq. (8))[35].

Thus, the homolysis of the *in-situ* electrogenerated active chlorine species employing commercially available Ti/Ru_{0.3}Ti_{0.7}O₂ anodes and low power UVC lamps has been recently reported to improve oxidation and mineralization of refractory pollutants as compared to the electrochemical oxidation or photolysis individually [20, 32, 36, 37]. In a recent paper [25], it was demonstrated in a conventional electrochemical cell that the novel Ti/Ru_{0.3}Ti_{0.7}O₂ anode presents outstanding performance during the photo-electrolysis of clopyralid synthetic wastes, showing significant synergistic effect in the presence of chloride or sulfate anions. It is worthy of mentioning that the position of the lamp is different in both systems. In the mixed tank reactor, the electrode is directly illuminated, while in the MF-FT reactor anode is not directly illuminated due to the specific design of the cell. Thus, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) data were recorded for the Ti/Ru_{0.3}Ti_{0.7}O₂ anode in the

mixed tank cell (Figure S2) to evaluate the effect of the UVC light on the anode surface (i.e., photocatalytic mechanism). The CV profiles unchanged under illumination but are slightly altered due to the effect of the light. Similarly, EIE data shows a slight reduction in the semicircle at the low-frequency range. This behavior indicates the minor effect of the photocatalytic mechanism on the overall anode efficiency in this system.

In the present study, the scale-up of this anode (produced as a mesh) in the MF-FT reactor, interestingly shows a more efficient performance in terms of clopyralid removal from a matrix of low conductivity (i.e., groundwater containing low quantities of salts, mainly chloride and sulfate). It is a fascinating outcome, considering that the same current density and same ratio volume/irradiated volume were employed. The reason behind the better performance of the MF-FT reactor may be attributed to a more uniform potential/current distribution because of the lower interelectrode gap in comparison with the MT cell. Moreover, the mesh anode in the MF-FT reactor favors percolation, increasing the contact area and, in turn, favoring the breakage of organic compounds.

Moreover, the more pronounced improvement observed on the clopyralid and TOC removal in the MF-FT reactor when using the photoelectrolysis can be explained due to the efficient activation of the powerful oxidants in the bulk solution under UVC illumination. It also evidences the stability of the clopyralid molecule and shows that the combined process is suitable for the removal of both clopyralid and its degradation intermediates from polluted water.

Only one slope is seen in the semilogarithmic plots, in the photolysis, with values of kinetic constants very close to zero for clopyralid removal and almost nil for TOC removal. Conversely, it is worth pointing out that not only one, but two slopes are found in all the electrochemically assisted processes. Initially, it was expected only one linear trend that is typically explained in terms of a pseudo-first-order kinetic model (Eq. (9)) associated a rate controlled by mass transfer limitation and/or to mediated

electrochemical processes. However, the existence of two zones indicates a much complex process. The kinetics constants fitted from experimental results are presented in Table 1.

$$\ln \frac{C_0}{C} = k \cdot t \quad (9)$$

In the first zone, the kinetic is slower, and clopyralid is the leading organic present in the solution. In this stage occurs the transformation of the primary pollutants into intermediates (partial oxidation). In the second zone, the kinetic rate increases up to more than double its initial value for clopyralid removal and TOC. In this second zone, between 67.7% and 74.8% of the herbicide is transformed, and 45% and 51% of TOC are removed. In previous works, related to the oxidation of antibiotics and methylparaben, it was also observed this behavior during electrolysis and photoelectrolysis with diamond anodes, and it was explained in terms of unexpected more facile oxidation of short-chain carboxylic acids [35, 38].

Figure 2. Clopyralid and TOC removal in semi-log scale as a function of the applied charge per unit volume of electrolyzed solution (Q) during treatment by different processes in the MT cell (a,b) and the MF-FT electrochemical reactor (MF-FT) (c,d). Conditions: pH: 3.4; current density: 30 mA cm^{-2} ; clopyralid₀: 100 mg L^{-1} . Full symbols: Natural groundwater; Open symbol: Synthetic water.

Although fast kinetics are seen for the irradiated process, it is essential to note that higher kinetic constants were obtained for the coupled process in the MF-FT reactor, regardless of the type of water matrix (i.e., natural groundwater or synthetic water). It is a significant result because it shows that besides the coupled process is promising, the use of the novel enlarged anode in the MF-FT reactor achieves an increase in the kinetics of this herbicide removal in the groundwater matrix.

Table 1. Clopyralid and mineralization percentages and observed kinetic constants for clopyralid decay in both the mixed tank cell and the microfluidic flow-through reactor.

	Process	Clop _r / %	TOC _r / %	k _{clop} / min ⁻¹	R ²	K _{2clop} / min ⁻¹	R ²	k _{1TOC} / min ⁻¹	R ²	K _{2TOC} / min ⁻¹	R ²
Natural Groundwater											
MT	EO	28.4	13	0.013	0.95	—	—	0.012	0.80	—	—
	PhEC	67.7	45	0.038	0.95	0.070	0.95	0.017	0.96	0.058	0.90

MF-FT	Photolysis	10.3	0	0.003	0.99	–	–	0	–	–	–
	EO	30.5	27	0.015	0.97	–	–	0.006	0.70	–	–
	PhEC	74.8	51	0.042	0.96	0.124	0.99	0.020	0.86	0.052	0.96
	Photolysis	14	0	0.005	0.88		–	0	–	–	–
Synthetic water											
MT cell	EO	8	4	0.01	0.98	–	–	0.002	0.70	–	–
	PhEC	65.7	51	0.043	0.99	0.167	0.84	0.022	0.98	0.064	0.85
	Photolysis	14.1	0	0.019	0.88	–	–	0	–	–	–
MF-FT	EO	11.1	0	0.008	0.92	–	–	0	–	–	–
	PhEC	72.7	42.3	0.078	0.99	–	–	0.034	0.99	–	–
	Photolysis	13.0	0.9	0.009	0.99	–	–	0	–	–	–

Clopr.: Clopyralid removal; TOC_r: Total organic carbon removal.

In the final stages of the clopyralid degradation, the production of carboxylic acids indicates not only the breakage of the aromatic ring but also further oxidation to shorter-chain carboxylic acids. The residual organic load observed in this work can be explained in terms of these generated short-chain carboxylic acids, being especially important the oxalic acid (shown in Figure 3), which has a lower electrochemical oxidizability than other intermediates and partially accumulates in the system. The maximum accumulation of oxalic acid for the MT cell is observed in photoelectrolysis at 4 h, and its reduction with increased time indicates further oxidation and mineralization to CO₂. This behavior indicates a more effective transformation of clopyralid into acid intermediates for photoelectrolysis.

Figure 3. Acids intermediates detect as a function of electrolysis, photo-electrolysis, and photolysis in the MT cell (a) in the MF-FT reactor (b). Full symbols: Natural groundwater; Open symbol: Synthetic water.

3.2 Ionic species and oxidants in the electrolysis and photo-electrolysis

Regarding inorganic species, the evolution of the formation of the main inorganic ions was monitored. Figure 4 displays the evolution of chlorine species in the electrolysis, photolysis, and photo-electrolysis for the natural groundwater and synthetic water, performed in the microfluidic flow-through reactor, in which the scaling up of the process is being studied. For the synthetic water, which contained a very high initial concentration

of chloride ions (around 2.3 g L^{-1}), the speciation of chloride during the process is quite different. During electrolysis (Figure 4a) the chloride ions decrease to form mainly hypochlorous acid, due to the disproportionation of the electrochemically formed chlorine to hypochlorite/hypochlorous acid; however, under UVC illumination (Figure 4b) chlorine and hydroxyl radicals can be formed by a homolytic homogeneous reaction of HClO (Eq. 7). Note that under photoelectrolysis, the irradiation of UVC light reduced in more than a half the hypochlorite detected, with the consequent increase in chlorates species. Recent reports have also demonstrated this behavior and the successful employment of homolysis of the active chlorine species with UVC lamps of low power [20, 32, 34, 37]. Comparing the amount of oxidants formed in the absence and during the degradation of clopyralid, it can be stated that the oxidants are consumed more significantly in the photo-electrolysis, which agrees with the improved removal of clopyralid in this process.

On the other hand, regarding the chlorine speciation and oxidants found during the degradation of clopyralid in natural groundwater, it can be seen that the initial concentration of chlorides is too low (around $0.8 \text{ mg L}^{-1} \text{ Cl}^{-}$) and it is reduced slightly during the electrolysis and photo-electrolysis. An important observation is that oxidants and hypochlorite were not detected during the degradation process, which suggests that these species were consumed immediately, as they were generated. In addition, no chlorates or perchlorates are detected, which is a significant observation because they are typical intermediates when using other anodes such as boron-doped diamond.

Figure 4. Evolution of chlorine species as a function of electrolysis, photo-electrolysis, and photolysis for the natural groundwater (a, b, c) and synthetic water (d, e, f) in the microfluidic flow-through reactor. Full symbols: with clopyralid; Open symbol: without clopyralid.

The evolution of the concentration of the primary nitrogenated ions as a function of applied charge per unit volume during the photolysis, electrolysis, and photo-electrolysis in the MF-FT (Figure 5) indicates significant differences depending on the aqueous

matrix. During the electrolysis and photolysis in the synthetic water is not observed the relevant formation of nitrogenated species. On the contrary, during photo-electrolysis, nitrite can be formed. On the other hand, considering that natural groundwater contains nitrate species, it can be seen as a reduction during photolysis and photo-electrolysis, indicating the formation of gaseous nitrogen. Regarding the ammonium ion, meager concentrations were detected during the different processes employed, confirming the electrochemical denitrification.

Figure 5. Concentration evolution of the main nitrogenated ions as a function of applied charge per unit volume during the photolysis, electrolysis, and photo-electrolysis in the MF-FT.

Figure 6 shows the pH evolution in the different treatments, and the pH changes differently according to the aqueous matrix. In the synthetic water (Figure 6a), the increase in the pH can be explained in terms of the conversion of chloride ions into hypochlorite. This behavior was also observed in the experiments carried in the absence of clopyralid. The explanation of this behavior is based on the chemical reactions taking place during electrolysis of sodium chloride, which is found dissociated into Na^+ and Cl^-

(Eq. (10), in an aqueous solution. During electrolysis, at the cathode the hydrogen evolution reaction occurs (Eq. (11)), and at the anode the chlorine evolution occurs (Eq. (3)), and the formation of active chlorine (Eq. (4)-(5)). It is important to remind that water suffers the autoionization (Eq. (12)). As a result of all reactions occurring, NaOH is accumulated (Eq. (13)), which is responsible for turning the medium alkaline with the time [39].

On the contrary, for the natural groundwater, the pH decrease (Figure 6b), which may be explained in terms of the low concentration of chlorides and the formation of carboxylic acids. Also, it is important to remind that the natural groundwater presents large quantities of mineral salts, such as sulfates and carbonates, that are also responsible for the pH change in the electrolytic system. During electrolysis the generation of hydroxyl ions occurs and this disturbs the equilibrium of the solution [40]. Then, the sulfates and carbonates ions present in their dissociate form are converted into hydrocarbonate (HCO_3^-) and hydrogensulfate (HSO_4^-) ions (Eq. (14)-(15)) that are also responsible for the decrease in the pH with time.

Figure 6. pH evolution as a function of electrolysis, photo-electrolysis, and photolysis in the microfluidic flow-through reactor of the synthetic water (a) and natural groundwater (b).

3.3 Synergistic effect and energy consumption assessment

To better observe the influence of UVC irradiation on the performance of the electrochemical systems, Figure 7 shows the effect of the configuration (i.e., MT cell or MF-FT electrochemical reactor) on the synergy coefficient of coupled technologies. Positive synergistic effects occurred in all cases. However, higher synergisms are seen for the MF-FT reactor with a 110% for clopyralid removal and 233.3% for TOC removal in natural groundwater, whereas in synthetic water, 358% was calculated for clopyralid

removal and 15396.8% for TOC removal. The higher concentrations of salts in synthetic wastewater can help to explain these results. Thus, the amount of oxidant precursors is much higher in those systems as compared to natural groundwater.

Figure 7. Synergy coefficient of combined electroirradiated process (using 9 W UV-C lamp) in terms of clopyralid and TOC removal.

Finally, an economic comparison was carried out in order to determine the most satisfactory cost-efficiency relationship in the different processes and approaches evaluated. In Figure 8, the energy consumption (kWh (kg TOC)^{-1}), is presented for both the single electrolysis and combined with UVC.

Figure 8. Energy consumption $\text{kWh}(\text{gTOC})^{-1}$ for the electrolysis and photo-electrolysis in the MT cell (a) and MF-FT reactor (b).

The lower energy consumption observed in the synthetic water is an expected result since, in this medium, the conductivity is about three-times higher as compared to the natural groundwater. Also, note that the energy consumption is substantially lower for the photo-electrolysis in the MF-FT reactor (0.0095 and $0.0038 \text{ kWh} (\text{kg TOC})^{-1}$ in the natural groundwater and synthetic water, respectively). This evidences that the scaled-up not only resulted in a reduction of energy consumption but better efficiency in the clopyralid removal and mineralization from the natural groundwater matrix. It is important to take in mind that not only the type of cell changes in this scale-up study but also the size of the anode, which is enlarged up from 4 to 66 cm^2 . It means that the negative effect (which initially could be expected because of the less uniform coating with the enlargement in the electrode from the typical lab-size to a pilot-scale) is not observed with this novel method of preparing the anodes. Besides, the optimized design

of the cell has led to an improved behavior associated with a better fluid-dynamics, as it was stated in previous works using this novel type of cells [39].

Moreover, changes in the cell voltage directly reflect the stability of the anode, i.e., constant values of voltage are a clear indication that the anode is not corroded during the electrolysis or photoelectrolysis. This behavior was seen in all cases (data not shown). Regardless of the anode size and the system configuration, the cell potential observed at the beginning, and the end of the processes (electrolysis and photoelectrolysis with and without clopyralid) are very close and unchanged for the reproducibility experiments. It means that although fabricated in a larger size, the stability properties of the anodes are maintained at a large scale. A recent report showed the successful application of another lab-manufactured MMO (8×8 cm mesh with a composition of Ti/TiO₂-NT/SnO₂-Sb-Bi) inside an electrochemical reactor, and similarly, promising results are observed towards the application of this type of materials in water treatment [42]. Besides, it is worthwhile to consider that the use of laser heating is responsible to almost double the service life of a RuO₂-based anode due to its more compact surface and better adhesion due to the rapid cooling and instantaneous heating [30]. This fact is expected to have a positive impact on the device service life since laser-made anodes with enhanced durability will reduce the need for anodes replacement and, as a consequence reducing the costs of the technology with time.

4 Conclusions

From this work, the following conclusions can be drawn:

- The composition of the matrix (in which clopyralid is contained) influences on the efficiency of the degradation process for the three technologies studied. Single photolysis is not efficient in removing the herbicide, regardless of the matrix, but

important positive synergisms are seen with the irradiation of UVC in both the mixed tank cell and the microfluidic flow-through reactor.

- Similar results are obtained when using the mixed tank cell, and the MF-FT, which indicates that scale-up has been carried out successfully using the same operation parameters in both cells, regardless of increasing the anode size from 4 to 66 cm² and changing the fluid-dynamic conditions of the cell importantly.
- The better performance for photo-electrolysis with the new laser-prepared Ti/Ru_{0.3}Ti_{0.7}O₂ may be attributed to the homolysis of a large number of chlorine species generated at the surface of these anodes.
- The higher synergistic effects at the MF-FT reactor compared with the electrochemical cell (batch system) were attributed to the lower interelectrode gap and percolation of solution through the anode, increasing the contact area and favoring the breakage of organic compounds.
- Notable findings in the scale-up of the new anode material described here are crucial in the context of application in full-scale electrochemical technology for the treatment of refractory contaminants of polluted water.

Conflicts of interest

There are no conflicts to declare.

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