Photoelectro-Fenton treatment of pesticide triclopyr at neutral pH using Fe(III)–EDDS under UVA light or sunlight

Izabelle C. Da Costa Soares1,2 · Roger Oriol1 · Zhihong Ye1,3 · Carlos A. Martínez-Huitle2 · Pere L. Cabot1 · Enric Brillas1 · Ignasi Sirés1

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Abstract
One of the main challenges of electrochemical Fenton-based processes is the treatment of organic pollutants at near-neutral pH. As a potential approach to this problem, this work addresses the use of a low content of soluble chelated metal catalyst, formed between Fe(III) and ethylenediamine-\(N,N'\)-disuccinic (EDDS) acid (1:1), to degrade the herbicide triclopyr in 0.050 M \(\text{Na}_2\text{SO}_4\) solutions at pH 7.0 by photoelectro-Fenton with UVA light or sunlight (PEF and SPEF, respectively). Comparison with electro-Fenton treatments revealed the crucial role of the photo-Fenton-like reaction, since this promoted the production of soluble Fe(II) that enhanced the pesticide removal. Hydroxyl radicals formed at the anode surface and in the bulk were the main oxidants. A boron-doped diamond (BDD) anode yielded a greater mineralization than an \(\text{IrO}_2\)-based one, at the expense of reduced cost-effectiveness. The effect of catalyst concentration and current density on the performance of PEF with BDD was examined. The PEF trials in 0.25 mM \(\text{Na}_2\text{SO}_4 + 0.35\text{ mM NaCl}\) medium showed a large influence of generated active chlorine as oxidant, being \(\text{IrO}_2\) more suitable than \(\text{RuO}_2\) and BDD. In SPEF with BDD, the higher light intensity from solar photons accelerated the removal of the catalyst and triclopyr, with small effect on mineralization. A plausible route for the herbicide degradation by Fe(III)–EDDS-catalyzed PEF and SPEF is finally proposed based on detected byproducts: three heteroaromatic and four linear \(N\)-aliphatic compounds, formamide, and tartronic and oxamic acids.

Keywords Ethylenediamine-\(N,N'\)-disuccinic (EDDS) acid · Hydroxyl radical · Pesticide · Photoelectro-Fenton · Sunlight · Triclopyr · Water treatment

Introduction
In recent years, the treatment of biorecalcitrant organic pollutants dissolved in water by electrochemical advanced oxidation processes (EAOPs) such as electrochemical oxidation (EO), electro-Fenton (EF), and photoelectro-Fenton (PEF) has received substantial attention (Brillas and Martínez-Huitle 2015; Ganiyu et al. 2018; Martínez-Huitle and Panizza 2018). PEF is the most complex process, since it combines the oxidation ability of EO and EF with the photolytic action of UVA photons (Martínez-Huitle et al. 2015). Artificial UVA light can be replaced by natural sunlight to increase the sustainability of the technology, giving rise to the so-called solar PEF (SPEF) process (Brillas 2014; Pérez et al. 2017). The common feature of EF, PEF, and SPEF processes is the continuous electrochemical generation of Fenton’s reagent \(\text{Fe}^{2+}\)
plus $\text{H}_2\text{O}_2$, a mixture that ensures the in situ production of hydroxyl radical (‘OH) in the bulk. This strong oxidant can react non-selectively and very quickly with most organics, thanks to its high standard reduction potential ($E^0$) of 2.73 V/SHE. Usually, pure $\text{O}_2$ or air is pumped into the system to allow the reduction reaction (1) at a suitable carbonaceous cathode. Carbon felt is a cheap cathode to do this (El-Ghenemy et al. 2014; Ganzenko et al. 2018), but air-diffusion cathodes may be preferred because of the larger $\text{H}_2\text{O}_2$ production (Galia et al. 2016; El-Ghenemy et al. 2015; Roth et al. 2016; Lanzalaco et al. 2017; Ye et al. 2019b).

$$\text{O}_2(\text{g}) + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2 \quad (1)$$

The application of EO process, which requires relatively simple setups, induces the destruction of organics by adsorbed hydroxyl radical (M(‘OH)) that is formed as $\text{O}_2$ evolves during water oxidation at the anode $M$, as represented in reaction (2) (Martinez-Huitle et al. 2015). Non-active anodes like boron-doped diamond (BDD) are optimum to generate very reactive and oxidizing M(‘OH) because of their higher $\text{O}_2$-evolution overpotential as compared to active anode materials like Pt and dimensionally stable anodes (DSA) (Steter et al. 2016; Clematis et al. 2017; Lanzalaco et al. 2018; Ridruejo et al. 2018). When EO is performed in a one-compartment cell and the cathode produces $\text{H}_2\text{O}_2$ via reaction (1), it is so-called EO with electrogenerated $\text{H}_2\text{O}_2$ (EO-$\text{H}_2\text{O}_2$). The mild oxidation caused by $\text{H}_2\text{O}_2$ becomes powerful in the presence of dissolved $\text{Fe}^{2+}$, originating the EF process, in which the oxidant ‘OH is formed in the bulk from Fenton’s reaction (3) at optimum pH~3.0 (Vasudevan and Oturan 2014; Ganiyu et al. 2018). Although the electrodeposition of $\text{Fe}^{3+}$ to $\text{Fe}^{2+}$ via reaction (4) is feasible at some cathodes (Yahya et al. 2014; Yang et al. 2019), the regeneration of ferrous ion is more effective using UVA radiation ($\lambda = 320–400$ nm) in PEF or sunlight ($\lambda > 300$ nm) in SPEF. In such systems, the UV photons cause the photolysis of hydrated $\text{Fe}^{3+}$ species, which are photoactive at pH near 3.0, via photo-Fenton reaction (5), having a positive impact on the rate of destruction of the target pollutant (Brillas 2014; Pérez et al. 2017). In addition, the formation of short-linear carboxylic acids upgrades the mineralization because their $\text{Fe}^{3+}$ complexes are photodecomposed via reaction (6) (Brillas 2014; Martínez-Huitle et al. 2015). In the PEF and SPEF processes, the anode composition usually has low significance due to the predominant role of photoreduction reactions.

$$\text{M} + \text{H}_2\text{O} \rightarrow \text{M(‘OH)} + \text{H}^+ + e^- \quad (2)$$
$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{‘OH} + \text{OH}^- \quad (3)$$
$$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \quad (4)$$
$$[\text{Fe(OH)}]^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \text{‘OH} \quad (5)$$

EF, PEF, and SPEF are very efficient to degrade the organic matter under acidic solutions. However, the progressive precipitation of $\text{Fe(OH)}_3$ as pH increases is highly detrimental, and, hence, these processes are considered quite inefficient at circumneutral pH. Accordingly, unconventional approaches have been developed, including heterogeneous Fenton treatments with solid iron catalysts (Ye et al. 2020b) and homogeneous processes with soluble chelated iron (Clarizia et al. 2017; Ganiyu et al. 2018). In previous work, some of us explored the viability of chelators like oxalate for pentachlorophenol degradation by solar photo-Fenton (Ye et al. 2019c) and ethylenediamine-$N,N'$-disuccinic acid (EDDS) to destroy butylated hydroxyanisole by EF (Ye et al. 2019a) and fluoxetine by PEF (Ye et al. 2020a). EDDS has been found more interesting because of its biodegradability and the high efficiency of $\text{Fe(III)}$–EDDS-catalyzed treatments at neutral pH (Miralles-Cuevas et al. 2019). $\text{Fe(III)}$–EDDS can be reduced via the Fenton-like reaction (7), and then, the produced Fe(II)–EDDS catalyzes the $\text{H}_2\text{O}_2$ decomposition to ‘OH via reaction (8) (Zhang et al. 2016), which predominates over Fenton’s reaction (3) at neutral pH. The ‘OH production is stimulated as Fe(II) is formed under UV light irradiation, via photo-Fenton-like reaction (9), whose quantum yield is much higher than that of classical photo-Fenton reaction (5) (Ye et al. 2020a). Note that the Fe(III)–EDDS-catalyzed EAOPs at neutral pH reported so far have mainly addressed the treatment of aromatic pollutants. Conversely, scarce information is available on the performance regarding the removal of heteroaromatic contaminants, which are very abundant in natural water and urban wastewater.

$$\text{Fe(III)} – \text{EDDS} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(II)} – \text{EDDS} + \text{O}_2^{2-} + 2\text{H}^+ \quad (7)$$
$$\text{Fe(II)} – \text{EDDS} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} – \text{EDDS} + \text{‘OH} + \text{OH}^- \quad (8)$$
$$\text{Fe(III)} – \text{EDDS} + h\nu \rightarrow \text{Fe}^{2+} + \text{EDDS}^{+} \quad (9)$$

Triclopyr (C$_7$H$_4$Cl$_3$NO$_3$, 3,5,6-trichloro-2-pyridyloxyacetic acid, $M = 256.46$ g mol$^{-1}$) is a selective pyridine herbicide widely employed for controlling herbaceous plants. It presents low toxicity in mammals, like rats and rabbits, and birds, but it has been found moderately toxic to sensitive aquatic biota like fish and larval amphibians (Edginton et al. 2003; Sensesman 2007; Li et al. 2018). Triclopyr has been detected in soil and surface water at concentrations up to 3 µg L$^{-1}$ in different countries like the USA (Battaglin et al. 2009) and Australia (Rippy et al. 2017). Despite being recalcitrant to photodegradation and oxidation, this pesticide has been efficiently degraded by several photo-assisted AOPs like...
Photocatalysis with TiO₂/UV (Qamar et al. 2006) and ZnO/SnO₂ (Yadav et al. 2019), photocatalytic ozonation with Au/TiO₂ (Maddila et al. 2015; Solís et al. 2016), and photo-assisted peroxonation (Pérez-Lucas et al. 2020). The herbicide triclopyr yields 3,5,6-trichloro-2-pyridinol as primary intermediate (Janíková-Banduchová et al. 2015), further being converted into acetic acid (Qamar et al. 2006) or oxalic acid (Lei et al. 2018). It is of note that the treatment of triclopyr by Fenton-based EAOPs has never been reported. The development of these processes in the presence of a quite un-explored chelated iron catalyst like Fe(III)–EDDS is necessary for the remediation of natural water and urban wastewater contaminated with this pesticide at neutral pH. This system has a potentially greater viability as compared to conventional Fenton-based treatments that need acidification for optimum operation.

This work reports the removal of the heteroaromatic herbicide triclopyr at neutral pH by EO-H₂O₂, EF, PEF, and SPEF, using Fe(III)–EDDS as soluble chelated iron catalyst in the three latter methods and an air-diffusion cathode in all cases. Comparative treatments were made with an IrO₂-based or BDD anode in sulfate medium, considering the Fe(III)–EDDS concentration and current density (j) in PEF. Selected tests were carried out in a mixed sulfate + chloride medium to clarify the role of generated active chlorine. In this matrix, the performance of SPEF was analyzed with a BDD anode. Primary and final byproducts of triclopyr, the pollutant under study, were detected by high-performance liquid chromatography (HPLC) and gas chromatography-mass spectrometry (GC-MS). The study has been made with 0.12 mM triclopyr, and other chemicals used, including analytical standards of organic carbon (TOC) by catalytic combustion, triclopyr, and Fe(III)–phenylenediamine (1:1) oxalate (99% purity) provided by Acros Organics. Organic solvents of HPLC or analytical grade and other chemicals used, including analytical standards of carboxylic acids, were supplied by Panreac. Ultrapure Milli-Q water (> 18.2 MΩ cm) was employed for the preparation of synthetic and analytical solutions. The combination of Fe(ClO₄)₃ and EDDS, both at a concentration of 0.03, 0.06, or 0.09 mM, gave rise to the corresponding Fe(III)–EDDS (1:1) complexes in solution, following the methodology described in earlier work (Ye et al. 2019a).

**Materials and methods**

**Chemicals**

Triclopyr (98% purity), EDDS trisodium salt solution (~ 35% in H₂O), and analytical grade Fe(ClO₄)₃ were purchased from Sigma-Aldrich. Na₂SO₄ (99.9% purity) was purchased from Merck. Analytical grade H₂SO₄, NaCl, and NaOH were supplied by Panreac. An acidic solution of Ti(IV) oxysulfate (Panreac) was used for H₂O₂ determination. L-ascorbic acid (99% purity) and 1,10-phenanthroline monohydrate (99% purity) employed for the analysis of soluble iron were purchased from Sigma-Aldrich and Alfa-Aesar, respectively. Active chlorine was determined by reaction with N,N-diethyl-p-phenylenediamine (1:1) oxalate (99% purity) provided by Acros Organics. Organic solvents of HPLC or analytical grade and other chemicals used, including analytical standards of carboxylic acids, were supplied by Panreac. Ultrapure Milli-Q water (> 18.2 MΩ cm) was employed for the preparation of synthetic and analytical solutions. The combination of Fe(ClO₄)₃ and EDDS, both at a concentration of 0.03, 0.06, or 0.09 mM, gave rise to the corresponding Fe(III)–EDDS (1:1) complexes in solution, following the methodology described in earlier work (Ye et al. 2019a).

**Electrolytic cells**

Experiments were performed in an open glass tank reactor, with the same solution in contact with the anode and a cathode. In all assays, 150 mL of solution, thermostated at 35 °C, thanks to external water recirculated through a glass jacket and a water bath, were vigorously stirred with a PTFE bar magnet at 800 rpm. Three anodes were tested: (i) an IrO₂-coated Ti plate (DSA-O₂) supplied by NMT Electrodes, (ii) a RuO₂-coated Ti plate (DSA-C₃) supplied by NMT Electrodes, and (iii) a BDD thin film deposited onto Si supplied by NeoCoat. The anode, with a geometric area of 3 cm², was connected to a 3 cm² carbon-PTFE air-diffusion cathode supplied by Sainergy Fuel Cell. This cathode was fitted into a polypropylene tube, used as holder and air chamber, and fed with compressed air at a flow rate of 0.9 L min⁻¹ to electrolysesh H₂O₂. The electrodes were separated by a distance of about 1.0 cm. Galvanostatic experiments (i.e., at constant j) were made with a PAR 273A potentiostat-galvanostat. The instantaneous cell voltage was monitored with a Demestres 601BR digital multimeter. The EO-H₂O₂ and EF trials were run in the dark, whereas the PEF treatments started as a GSC TL2001 T5 6 W fluorescent black light tube lamp (λmax = 360 nm) was switched on. This lamp was placed at about 5 cm over the solution surface, yielding an irradiance of 5 W m⁻². In SPEF, a mirror was placed under the cell to reflect the sunrays back into the solution as much as possible. These tests were made in sunny and clear days of 2019 summer, with an average solar UV irradiance of 28–30 W m⁻².

**Apparatus and analytical methods**

The solution pH was measured with a Crison GLP 22 pH-meter. Samples collected at selected treatment times were microfiltered (0.45 μm) before analysis. The determination of H₂O₂ concentration by the titanate colorimetric method was made with a Shimadzu 1800 UV/Vis spectrophotometer at λ = 408 nm and 25 °C. The spectrophotometric procedure followed to obtain total dissolved Fe concentration has been reported elsewhere (Ye et al. 2019a). Active chlorine content was determined by the N,N-diethyl-p-phenylenediamine colorimetric method using the same spectrophotometer, at λ = 515 nm (APHA, AWWA, WEF 2005).

The systems and procedures needed to quantify the total organic carbon (TOC) by catalytic combustion, triclopyr, and Fe(III)–EDDS concentrations by reversed-phase HPLC,
carboxylic acids content by ion-exclusion HPLC, and the amounts of different ions by ion chromatography (Cl\(^-\), ClO\(_3\), ClO\(_4\), and NO\(_3\)) and colorimetric methods (NH\(_4\)^+), have been detailed in earlier works (Thiam et al. 2015; Steter et al. 2016). For the determination of triclopyr concentration, an acetonitrile volume equal to that of the sample was added to immediately stop the degradation process. A 60:40 (v/v) acetonitrile/water (10 mM KH\(_2\)PO\(_4\), pH 3.0) mixture recirculated as mobile phase at 1.0 mL min\(^{-1}\) allows obtaining a well-defined peak at a retention time (\(t_r\)) of 6.0 min. The identification was made at \(\lambda = 232.3 \text{ nm, revealing limits of detection (LOD) and quantification (LOQ) of } 3.9 \times 10^{-2} \text{ and } 7.8 \times 10^{-2} \text{ mg L}^{-1}, \text{ respectively.}

Duplicate assays were made under each experimental condition, and average values are reported in this work. Figures show the error bar for each data, with 95% confidence interval.

The specific energy consumption per unit TOC mass (EC\(_{TOC}\), in kWh (g TOC\(^{-1}\))) was calculated in each experiment considering the TOC destroyed (\(\Delta\text{TOC}\), in mg L\(^{-1}\)) upon supply of a current \(I\) (in A) over a time \(t\) (in h), as shown in Eq. (10) (Steter et al. 2016):

\[
\text{EC}_{\text{TOC}} = \frac{E_{\text{cell}} I t}{V (\Delta \text{TOC})}
\]

where \(E_{\text{cell}}\) is the average cell voltage (in V) and \(V\) is the solution volume (in L). When \(I\) was varied during the trial, the final EC\(_{TOC}\) was obtained as the sum of the partial values.

The byproducts accumulated after 40 min of PEF treatment of 0.12 mM triclopyr solutions containing 0.05 M Na\(_2\)SO\(_4\) and 0.06 mM Fe(III)–EDDS (1:1) complex, at pH 7.0 and \(j = 16.7 \text{ mA cm}^{-2}\), were identified by GC-MS following the procedure described elsewhere (Ye et al. 2019a) and comparing the spectra with those of the NIST05 MS database. The organic compounds were separated using either a non-polar Teknokroma Sapiens-X5ms or a polar HP INNOWAX column, both of 0.25 μm, 30 m × 0.25 mm.

### Results and discussion

#### Fe(III)–EDDS-catalyzed PEF treatment in sulfate medium

Before starting with the application of the different EAOPs to triclopyr degradation, the stability of the Fe(III)–EDDS complex was assessed under PEF conditions. This study was carried out with 150 mL of solutions containing 0.06 mM Fe(III)–EDDS (at molar ratio of 1:1) and 0.050 M Na\(_2\)SO\(_4\) at pH 7.0 and 35 °C, using an IrO\(_2\)-based or BDD anode and applying \(j = 16.7 \text{ mA cm}^{-2}\). The abatement of the catalyst concentration was fast and very similar with both anodes, attaining its total disappearance after 40–45 min of electrolysis, as can be observed in Fig. 1a. These trends confirm the large effectiveness of Fenton-like reaction (7) and, pre-eminently, photo-Fenton-like reaction (9), to form the most active species for H\(_2\)O\(_2\) decomposition, i.e., Fe(II)–EDDS and Fe\(^{2+}\).

The slightly quicker disappearance occurred with the BDD anode can be ascribed to the larger reactivity of BDD(OH) as compared to IrO\(_2\)(OH), produced via reaction (2) (Steter et al. 2016; Ridruejo et al. 2018). Both radicals might be able to attack the EDDS molecules, thus limiting the regeneration of the Fe(III)–EDDS through reaction (8). In addition, in both cells, the ‘OH produced from reaction (8) can attack the EDDS molecules in a more significant manner. The inset panel of Fig. 1a shows the analogous and good linear profiles obtained from the pseudo-first-order kinetic analysis of the two concentration decays, allowing the determination of an apparent rate constant for the catalyst degradation (\(k_c\)) of 0.11 min\(^{-1}\) in both

![Fig. 1](image-url)
cases, with a squared correlation coefficient \( R^2 > 0.991 \). This behavior suggests the attack of a steady \( ^\cdot \text{OH} \) content on the catalytic complex.

The \( ^\cdot \text{OH} \) generation via reactions (8) and (3) was feasible as long as Fe(III)–EDDS persisted in solution, since it was a continuous source of Fe(II)–EDDS and Fe\(^{2+}\). From Fig. 1a, it can be deduced that at 45 min, the initial complex had been completely converted into Fe(III) and oxidation products of EDDS. This was confirmed by determining the TOC removal from the catalyst solution (initial value of 7.2 mg L\(^{-1}\)) for 300 min. Figure 1b highlights that no mineralization occurred when only 0.06 mM EDDS (without Fe(III)) were treated by EO-H\(_2\)O\(_2\) with an IrO\(_2\)-based anode, informing about the scarce oxidation ability of IrO\(_2\)(OH) and H\(_2\)O\(_2\) towards the chelator. In contrast, the same process with a BDD anode led to 38% TOC decay, in agreement with the greater reactivity of BDD(OH) with organics (Brillas 2014). Figure 1b discloses a TOC reduction of 12% and 57% when the PEF process was applied using the IrO\(_2\)-based and BDD anode, respectively. The enhanced mineralization in PEF can then be attributed to the action of \( ^\cdot \text{OH} \) in the bulk, as explained above, which acted in concomitance with the UV photons on some Fe(III)-carboxylate byproducts (see reaction (6)).

In conclusion, the main oxidizing agents from ~ 45 min of electrolysis were (i) M(\( ^\cdot \text{OH} \)) at the anode surface and (ii) \( ^\cdot \text{OH} \) produced from Fenton’s reaction (3), mainly induced by photo-Fenton reaction (5). The amount of the latter radical was presumably small because the uncomplexed Fe(III) tended to precipitate at pH 7.0, thus being presumably critical the role of UVA light to photodecompose the generated products.

**Comparative removal of triclopyr by EAOPs in sulfate medium**

In a second step, triclopyr solutions at a concentration of 0.12 mM (10 mg L\(^{-1}\) TOC) were prepared in sulfate medium, in the presence of 0.06 mM EDDS to be treated by EO-H\(_2\)O\(_2\) or 0.06 mM Fe(III)–EDDS (1:1) for EF and PEF trials. A very different catalyst content decay can be seen in Fig. 2a during the two latter treatments at pH 7.0 and \( j = 16.7 \text{ mA cm}^{-2} \). In EF, Fe(III)–EDDS needed more than 300 min to disappear using an IrO\(_2\)-based anode, whereas about 240 min were required with BDD. This agrees with the expected superior attack of BDD(OH) on the catalyst. In contrast, a very fast Fe(III)–EDDS removal occurred in PEF, with complete abatement in 80 min regardless of the anode employed (see Fig. 2a). This suggests a high effectiveness of photo-Fenton-like reaction (9) for continuous generation of soluble Fe\(^{2+}\), originating \( ^\cdot \text{OH} \) from Fenton’s reaction (3). From the excellent pseudo-first-order linear plots reported in Fig. 2b for such concentration decays, the \( k_e \) value in EF with the IrO\(_2\)-based anode exhibited a 2.6-fold increase when using BDD, approaching to a tenfold rise when applying PEF with both anodes (see Table 1). However, this rate constant was 0.43-fold lower than that found in the absence of the herbicide (see Fig. 1a). This means that the generated oxidants participated not only in the abatement of Fe(III)–EDDS but also in the simultaneous destruction of triclopyr and its byproducts, as explained below.

Figure 2c shows an increasing herbicide removal in the order: EO-H\(_2\)O\(_2\) with IrO\(_2\) < EF with IrO\(_2\) < EO-H\(_2\)O\(_2\) with BDD < EF with BDD ~ PEF with IrO\(_2\) < PEF with BDD. Table 1 summarizes the percentage of herbicide disappearance after a given electrolysis time in each process. Triclopyr concentration remained unaltered in EO-H\(_2\)O\(_2\) with the IrO\(_2\)-based anode because of the low oxidation power of IrO\(_2\)(OH), whereas the formation of BDD(OH) substantially upgraded the oxidation power of EO-H\(_2\)O\(_2\). In fact, EO-H\(_2\)O\(_2\) with BDD outperformed the EF process with the IrO\(_2\)-based anode, corroborating the key role of BDD(OH) as compared to \( ^\cdot \text{OH} \) originated from reaction (8). Similarly, the oxidation power of EF with BDD was similar to that of PEF with IrO\(_2\), despite the occurrence of photo-Fenton-like reaction (9) that ensured the Fe\(^{2+}\) formation to feed Fenton’s reaction (3). The conjunction of reactions (2), (3), (5), and (7)–(9) yielded sufficient amounts of BDD(OH) and \( ^\cdot \text{OH} \) that made the PEF with BDD the most effective process for triclopyr removal. The relative trends of all these processes agreed with the corresponding apparent rate constants for triclopyr decay (\( k_1 \)), gathered in Table 1, as calculated from the good kinetic analysis of Fig. 2d with \( R^2 > 0.993 \).

Analogous tendencies for the processes tested were also found for the corresponding TOC decays related to the mineralization of both, triclopyr and EDDS, as can be deduced from Fig. 2e and the percentages of TOC removal at 300 min of electrolysis, collected in Table 1. It is noticeable that, once all the Fe(III)–EDDS was consumed, i.e., after 240 min in EF with BDD and 80 min in PEF with IrO\(_2\) or BDD, the organics arisen from triclopyr and EDDS were mainly degraded by M(\( ^\cdot \text{OH} \)), with a small contribution of \( ^\cdot \text{OH} \) produced from a minimal concentration of soluble ferrous ions. In PEF, some final Fe(III)-carboxylate complexes were also photodecomposed via reaction (6). From the residual TOC at 300 min, it is evident that a significant proportion of recalcitrant byproducts were accumulated, impeding the overall mineralization of the solutions. The most favorable conditions were then achieved in PEF with BDD, yielding 35% of accumulated TOC. In contrast, the last column of Table 1 reveals the smaller EC\(_{\text{TOC}}\) obtained in PEF with the IrO\(_2\)-based anode as compared to PEF with BDD (0.88 vs. 1.31 kWh (g TOC)\(^{-1}\)), owing to the smaller \( E_{\text{cell}} \) value (4.0 vs. 8.8 V). This means that the use of the IrO\(_2\)/air-diffusion cell in PEF was more cost-effective despite its lower oxidation ability, thanks to the large contribution of UVA radiation. However, a much higher total EC\(_{\text{TOC}}\) including the electric power needed by the lamp (27.3 vs. 19.2
kWh (g TOC)$^{-1}$ was determined for the IrO$_2$/air-diffusion cell, owing to much smaller mineralization ability. This suggests that the latter cell can be more cost-effective in the SPEF process with free sunlight irradiation.

**Effect of experimental variables on PEF performance for triclopyr degradation**

Once demonstrated that the BDD/air-diffusion cell led to the quickest destruction of the target pollutant and TOC using the Fe(III)–EDDS (1:1) complex in PEF, the effect of the concentration of the soluble chelated catalyst on the process performance was assessed. Two reasons justify the low Fe(III)–EDDS contents chosen: (i) the need to avoid an excessive increase of TOC from EDDS, since its presence complicated the mineralization, and (ii) the control of iron precipitation as the soluble complex is destroyed, thus minimizing the sludge production. Based on these considerations, the PEF treatment of 0.12 mM triclopyr solutions within the Fe(III)–EDDS concentration range of 0.03–0.09 mM at pH 7.0 was studied at $j = 16.7$ mA cm$^{-2}$. Figure 3a highlights a quite similar decay of the catalyst content in all cases, always

| Method | Anode | [Fe(III)–EDDS]$^{0}$ (mM) | $j$\textsuperscript{a} \text{n} \text{mA cm}^{-2} \text{ (min)} | Time for complex\textsuperscript{b} \text{ (min)} | $k_{c}$ \textsuperscript{c} \text{(1 0 min$^{-1}$) - 2} | % Triclopyr (1 0 min$^{-1}$) | % TOC removal at 300 min | EC$_{TOC}$ (kWh (g TOC)$^{-1}$) |
|--------|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| EO-H$_2$O$_2^{a}$ | IrO$_2$-based | 0.06 | 16.7 | - | - | 0 | - | 3.0 | - |
| | BDD | 0.06 | 16.7 | - | - | 68 (300) | 0.38 | 38 | 2.34 |
| | EF | IrO$_2$-based | 0.06 | 16.7 | > 300 | 0.49 | 30 (300) | 0.17 | 13 | 3.28 |
| | BDD | 0.06 | 16.7 | 240 | 1.3 | 100 (270) | 1.2 | 47 | 1.81 |
| PEF | IrO$_2$-based | 0.06 | 16.7 | 80 | 4.7 | 100 (270) | 1.2 | 44 | 0.88 (27.3)$^{b}$ |
| | BDD | 0.03 | 16.7 | 80 | 4.8 | 100 (180) | 2.1 | 66 | 1.67 (23.9)$^{b}$ |
| | 0.06 | 16.7 (60) | - | - | 100 (140) | - | 69 | 4.96 (21.8)$^{b}$ |
| | | + 33.3 (240) | | | | | | |
| | 0.06 | 16.7 (60) | - | - | 100 (120) | - | 75 | 10.02 (25.5)$^{b}$ |
| | | + 66.7 (240) | | | | | | |
| | 0.09 | 16.7 | 80 | 4.8 | 100 (180) | 2.4 | 62 | 1.19 (16.7)$^{b}$ |
| SPEF | IrO$_2$-based | 0.06 | 16.7 | - | $^{r}$ | - | $^{r}$ | 44 | 0.88 |
| | BDD | 0.06 | 16.7 | - | $^{r}$ | - | $^{r}$ | 100 (210) | 5.9 | 62 | 1.33 |
| | 0.06 | 16.7 (60) | - | - | - | - | 72 | 4.01 |
| | | + 33.3 (240) | | | | | | |
| | 0.06 | 16.7 (60) | - | - | - | - | 78 | 9.07 |
| | | + 66.7 (240) | | | | | | |

\textsuperscript{a}Current density \textsuperscript{b}Time for total disappearance of the complex \textsuperscript{c}$k_{c}$: apparent rate constant for the Fe(III)–EDDS complex, with $R^{2} > 0.99$ \textsuperscript{d}$k_{1}$: apparent rate constant for triclopyr, $R^{2} > 0.99$ \textsuperscript{e}No Fe(III) in solution \textsuperscript{f}Not determined \textsuperscript{g}No evaluation of pseudo-first-order kinetics \textsuperscript{h}Specific energy consumption per unit TOC mass when the term related to the electric energy supplied to the 6 W UVA lamp (i.e., $6 \varepsilon/\Delta V(\Delta TOC)$), was added to Eq. (10)
disappearing at 80 min. The pseudo-first-order kinetic analysis of these results, presented in the inset of Fig. 3a, yielded good linear correlations with analogous $k_c$-values (see Table 1). Gradually greater Fe(III)–EDDS contents favored the formation of $\cdot$OH from reactions (7)–(9) that could attack the EDDS, but, in turn, the self-destruction reactions between radicals (i.e., parasitic reactions) was also stimulated. As a result, no significant influence of the catalyst content was found within the studied range. Accordingly, Fig. 3b depicts a similar herbicide abatement regardless of the catalyst content. A larger amount of $\cdot$OH was formed at 0.06 and 0.09 mM, but the amount of parasitic reactions increased as well, not being effective in practice those additional radicals. This can also be observed in the analogous TOC decay found at all Fe(III)–EDDS concentrations (see Fig. 3c), close to 62–66% (see Table 1). Since the initial TOC became greater as the catalyst concentration increased, the amount of TOC abated was actually enhanced: 9.0 mg L$^{-1}$ at 0.03 mM vs. 12.9 mg.

Fig. 2 Change of normalized (a) Fe(III)–EDDS (1:1) concentration, (c) triclopyr concentration, and (e) TOC with electrolysis time for the treatment of 150 mL of solutions containing 0.12 mM triclopyr (10.0 mg L$^{-1}$ TOC), 0.050 M Na$_2$SO$_4$, and 0.06 mM (7.2 mg L$^{-1}$ TOC) catalyst at pH 7.0 and 35 °C, using a cell with an IrO$_2$-based or BDD anode and an air-diffusion cathode (3 cm$^2$ electrode area each) at $j =$ 16.7 mA cm$^{-2}$. Method: EO-H$_2$O$_2$ (with EDDS, no Fe(III)) with (blue triangle) IrO$_2$-based or (red circle) BDD, EF with (inverted green circle) IrO$_2$-based or (orange square) BDD, and PEF with (blue-filled triangle) IrO$_2$-based or (red-filled circle) BDD. Plots (b) and (d) depict the pseudo-first-order kinetic analysis of curves shown in (a) and (c), respectively.
This was also reflected in the lower EC TOC value needed at the highest Fe(III)–EDDS content (see Table 1).

Further, the influence of applied \( j \) was assessed for the PEF treatment of solutions containing 0.12 mM herbicide, 0.050 M \( \text{Na}_2\text{SO}_4 \), and 0.06 mM Fe(III)–EDDS (1:1) at \( \text{pH} \) 7.0 and 35 °C. These experiments were performed with BDD, at an initial \( j \) of 16.7 mA cm\(^{-2}\) for 60 min, conditions that ensured that 94% of the chelated catalyst had disappeared (see Fig. 3a), and, hence, practically all the iron ions were either hydrated or precipitated. Thereafter, the treatment proceeded at a higher \( j \) of 33.3 or 66.7 mA cm\(^{-2}\) for 240 min. The compared data of Figs. 3b and 4a disclose a progressive enhancement of triclopyr abatement as \( j \) became higher, with time for total removal decreasing from 180 to 120 min when changing from constant \( j \) (16.7 mA cm\(^{-2}\)) to variable \( j_1 \) (16.7)/\( j_2 \) (66.7) (see Table 1). Similarly, Figs. 3c and 4b illustrate a larger mineralization with increasing \( j \), and Table 1 shows that the greatest TOC removal of 75% was reached operating at 16.7 (60 min)/66.7 (240 min) mA cm\(^{-2}\). Moreover, this table also evidences that the latter treatment accounted for a very high EC TOC of 10.02 kWh (g TOC)\(^{-1}\), as result of the high \( E_{\text{cell}} \) of 8.8/17.2 V.

The improved oxidation ability derived from a greater applied \( j \) can be mainly related to the faster production of BDD(\( \cdot \)OH)
from reaction (2), becoming the pre- eminent radical as Fe(III)–EDDS was degraded. A total soluble Fe content close to 0.03 mM was detected in the medium, similar to 0.04 mM permitted in natural water (Moreira et al. 2015). This low amount of soluble iron served to promote the production of ‘OH. Note that the rest of the Fe content initially dissolved was precipitated, deposited as Fe(OH)₃ at the cathode surface due to the strong alkalinity in its vicinity.

The fate of the heteroatoms of the herbicide (0.12 mM N, 0.36 mM Cl) and EDDS (0.12 mM N) was assessed at the end of the PEF treatment with BDD at 16.7 (60 min)/33.3 (240 min) mA cm⁻². Concentrations of 0.260 mM of Cl⁻ (72% if initial Cl) and 0.075 mM of ClO₃⁻ (21% of initial Cl), with traces of ClO₄⁻, as well as 0.043 mM of NO₃⁻ (18% of total N) and 0.125 mM of NH₄⁺ (52% of total N) were determined. These results agree with the complete release of heteroatoms as inorganic ions, which allows discarding the presence of a high amount of toxic chloro-organics in the residual TOC (Fig. 4b). The nitrogenated ions were also measured at the end of the EO-H₂O₂ treatment of 0.06 mM EDDS with BDD at j = 16.7 mA cm⁻², only revealing the formation of 0.053 mM of NO₃⁻ (44% of initial N). It can be inferred that the pyridine group of the herbicide was the source of all the NH₄⁺ ion found.

Treatment of triclopyr solutions by PEF in a mixed sulfate + chloride medium

Natural water and urban wastewater contain high quantities of Cl⁻ ion. To explore the influence of this anion on the PEF treatment of triclopyr with Fe(III)–EDDS, several trials were run in a matrix composed of 0.025 mM Na₂SO₄ + 0.035 mM NaCl. The two salts were mixed in such proportion in order to ensure the same conductivity shown by the 0.050 M Na₂SO₄ solutions (Steter et al. 2016). In these treatments, the formation of Cl₂ from Cl⁻ oxidation at the anode surface via reaction (11), followed by hydrolysis to hypochlorous acid at pH between 3.0 and 8.0 via reaction (12) (Martínez-Huitle et al. 2015), is expected. The occurrence of reaction (11) limits the ability of the anode to generate M(‘OH) by reaction (2), which can be potentially counterbalanced by the contribution of the oxidant HClO. This was assessed under PEF conditions using either active IrO₂- (DSA-O₂) and RuO₂-based (DSA-CI₂) anodes or the non-active BDD one.

\[
2\text{Cl}^- \rightarrow \text{Cl}_2(\text{aq}) + 2e^- \quad (11)
\]

\[
\text{Cl}_2(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{Cl}^- + \text{H}^+ \quad (12)
\]

The progressive accumulation of H₂O₂ during the PEF treatment of 0.12 mM herbicide solutions in the mixed electrolyte with 0.06 mM Fe(III)–EDDS at pH 7.0 and j = 25 mA cm⁻² is depicted in Fig. 5a. Final concentrations of 4.2, 5.1, and 6.4 mM were obtained with the IrO₂-based, RuO₂-based, and BDD anode, respectively. The excess of H₂O₂ detected in solution prevented that Fenton’s reaction (3) and Fenton-like reaction (8) could be limited by a lack of that reagent, thus ensuring the maximum formation of ‘OH. An analogous behavior can be observed in Fig. 5b for active chlorine. The unreacted oxidant was gradually accumulated in the solution, attaining a maximum concentration of 7.2 mg L⁻¹ at 300 min using the RuO₂-based anode that decayed down to 5.5 mg L⁻¹ with BDD. This agrees with the larger ability reported for the DSA-CI₂ to oxidize Cl⁻, as compared to the other two anodes (Brillas and Martínez-Huitle 2015).

Surprisingly, the catalyst and herbicide decays shown in Fig. 5c and d, respectively, did not depend substantially on the anode nature. The Fe(III)–EDDS concentration disappeared at about 120 min, a much longer time than that found in sulfate medium at j = 16.7 mA cm⁻² (80 min, Fig. 2a), whereas triclopyr was removed at 90 min, a quite short time compared to that required in sulfate matrix (180 min, Fig. 2b). These findings, along with the similar k_e and k_l values determined from the kinetic analysis presented in the inset panels of Fig. 5c and d and given in Table 2, suggest that the main oxidant of both organics (the chelator and the herbicide) was the active chlorine, rather than M(‘OH) and ‘OH mentioned in the sulfate one. As compared to those radicals, active chlorine reacted more slowly with Fe(III)–EDDS, but it was more effective to degrade triclopyr. Figure 5e illustrates that the oxidation products were progressively mineralized in this medium, reaching a large TOC abatement close to that found in sulfate medium when using BDD. This result is indicative of the participation of reactive BDD(‘OH), whose oxidation power was greater than that of RuO₂(‘OH) and IrO₂(‘OH).

However, it is clear from the EC_TOC values of Table 2 that the treatment with the IrO₂-based anode was preferred, despite yielding the lowest mineralization (65%). Without considering the energy consumption for light irradiation, i.e., under SPEF conditions, it was less energy demanding, than to the lower E Cell of 4.0 V as compared to 4.4 V with the RuO₂-based anode and 8.8 V with BDD.

SPEF process in sulfate and mixed sulfate + chloride media

The removal of triclopyr at a concentration of 0.12 mM from solutions containing 0.050 M Na₂SO₄ and 0.06 mM Fe(III)–EDDS (1:1) at pH 7.0 was finally assessed by SPEF as a cheap alternative to PEF. The study was made by comparing the behavior of an IrO₂-based or BDD anode at j = 16.7 mA cm⁻². Figure 6a evidences a clear difference in their performance referred to the herbicide decay, showing a much faster disappearance using BDD. Total removal was achieved at 80 min, a much shorter time than in the case of the active anode (210 min). Note that these abatements were much quicker than those found during the analogous PEF treatments with a 6 W
UVA lamp (180 and 270 min, respectively, see Fig. 2c). The superiority of BDD can be again related to the greater reactivity of BDD(·OH) as compared to IrO₂(·OH), with similar quantities of both radicals being produced in PEF and SPEF. Regarding the process enhancement when sunlight replace UVA light, it can be ascribed to the much greater intensity of the photons of the former light source, thereby increasing the rate of the photolytic reactions (5) and (9) that accelerated the formation of ·OH from Fenton’s reaction (3). The kinetic analysis of the above herbicide decays only allowed describing a pseudo-first-order reaction in the case of BDD, as can be seen in the inset of Fig. 6a. The k₁-value thus obtained in SPEF was 2.7-fold greater than that determined in PEF (see Table 1). However, the TOC decays presented in Fig. 6b in both SPEF systems were analogous to PEF ones shown in Fig. 2e. This means that, at long electrolysis time, once all the Fe(III)–EDDS catalyst has been destroyed and a small amount of uncomplexed iron ions is dissolved in the medium, the

Fig. 5 Effect of the anode on the variation of the concentration of (a) accumulated H₂O₂, (b) active chlorine, (c) normalized Fe(III)–EDDS, (d) triclopyr, and (e) TOC with electrolysis time for the PEF treatment of 150 mL of solutions containing 0.12 mM triclopyr (10.0 mg L⁻¹ TOC), 0.025 M Na₂SO₄ + 0.035 M NaCl, and 0.06 mM (7.2 mg L⁻¹ TOC) Fe(III)–EDDS (1:1) at pH 7.0, 35 °C and j = 25 mA cm⁻². In (c) and (d), the corresponding pseudo-first-order kinetic analysis is shown in the inset panel.
mineralization of byproducts by oxidant OH formed via reactions (3) and (5) or the photodecomposition of their Fe(III) complexes were the main routes using the IrO₂-based anode. In contrast, the contribution of BDD(·OH) to the destruction of such byproducts seems much more relevant. In both types of cells, similar final TOC reductions and EC TOC values were obtained in PEF and SPEF (see Table 1). This is a positive feature for the potential implementation of Fe(III)–EDDS-catalyzed SPEF treatment of pesticides in wastewater at larger scale. It is important to mention that in all the SPEF treatments, the effect of direct solar photolysis on the pesticide degradation can be neglected. Several authors have shown that triclopyr has a long lifetime (as compared to the duration needed for the SPEF trials in natural water under sunlight irradiation [Woodburn et al. 1993]). The effect of on the performance of SPEF process was examined in the same manner described on Fig. 4b for PEF, i.e., by applying a = 16.7 mA cm⁻² for 60 min, when upon reaction.
it was increased to 33.33 or 66.7 mA cm\(^{-2}\) for 240 min. Figure 7 discloses the increase in TOC reduction as \(j\) became higher, reaching final values similar to those of PEF (see Table 1). A maximal of 78% mineralization with an EC\(\text{TOC} = 9.07\ \text{kWh} \text{ (g TOC)}^{-1}\) was found in the treatment at 16.7 (60 min)/66.7 (240 min) mA cm\(^{-2}\). Under these conditions, Fig. 7 and Table 2 also highlight a similar performance in the 0.025 mM Na\(_2\)SO\(_4\) + 0.035 mM NaCl matrix. All these findings suggest that the rise in \(j\) pre-eminently favors the formation of oxidants at the BDD electrode, namely, BDD(\(^{\cdot}\)OH) from reaction (2) and/or HClO from reactions (11) and (12), with minor influence on the photolytic reactions.

One can conclude that the Fe(III)–EDDS-catalyzed PEF and SPEF treatments of triclopyr involve a complex mechanism. On the one hand, M(\(^{\cdot}\)OH) and/or HClO are produced and oxidize both the pesticide and the complex. On the other hand, the Fe(III)–EDDS complex reacts with the electrogenerated \(\text{H}_2\text{O}_2\) to yield \(^{\cdot}\)OH in the bulk from reactions (7) and (8). The role of light irradiation is quite significant, since it ensures the reaction (2) and/or HClO from reactions (11) and (12), with minor influence on the photolytic reactions.

Detection of byproducts

Table 3 collects the chemical name and structure, type of column, retention time, and main fragments for the eight products detected after 40 min of electrolysis of a 0.12 mM triclopyr solution with 0.06 mM Fe(III)–EDDS solution in sulfate medium at pH 7.0 and \(j = 16.7\ \text{mA cm}^{-2}\), under PEF conditions with BDD. All the byproducts identified by GC-MS, which are expected to be the same in SPEF, could only arise from the herbicide structure, i.e., no primary byproducts of EDDS were identified. Note that the possible products formed during the photodegradation of the Fe(III)–EDDS complex have been recently reported by Jaber et al. (2020). Based on our results, one can propose that triclopyr (1) was hydroxylated upon the attack of hydroxyl radicals either over the C(2) and C(3) positions of the pyridine ring to form the compound 2 with loss of Cl\(^{-}\) or over its C(1) atom to yield the derivative 4 with release of the lateral oxacycetic group. It is noteworthy that compound 4 has been reported as the main byproduct of 1 during its oxidation by \(\text{TiO}_2/\text{UV}\) photocatalysis (Qamar et al. 2006) and by EO with BDD (Janíková-Bandžuchová et al. 2015). Further hydroxylation on the C(4) position of the heterocycle ring of the above compounds led to two hydroxylated aliphatic byproducts, the aminobutyric acid 5 and the chloromethylene-propanimidic acid 6. Dechlorination and hydroxylation of 6, alongside the keto-enol tautomerism, yielded the hydroxymethylmalonamic acid 7, whereas the loss of the -CH\(_2\)OH-COOH group upon hydroxylation of 7 yielded the carboxamic acid 8. Finally, decarboxylation of 8 with oxidation of the hydroxymethyl group resulted in formamide 9. From the detected byproducts, a degradation route for 1 by PEF and SPEF is proposed in Fig. 8.

The production of short-chain carboxylic acids before total mineralization of aromatic and heteroaromatic pollutants is expected in Fenton-based processes. These compounds tend to form Fe(III) complexes (Martínez-Huitle et al. 2015). To confirm this, solutions with 0.12 mM triclopyr and 0.06 mM Fe(III)–EDDS in 0.050 M Na\(_2\)SO\(_4\) at pH 7.0 were treated by PEF and SPEF using the BDD/air-diffusion cell at \(j = 16.7\ \text{mA cm}^{-2}\) and analyzed for 300 min by ion-exclusion HPLC. Tartronic acid (10) coming from longer aliphatic carboxylic acids and oxamic acid (11) proceeding from N-derivatives were detected. In PEF, only traces of 10 were found, whereas 11 was accumulated up to 4.0 mg L\(^{-1}\) (1.1 mg L\(^{-1}\) TOC), as shown in Fig. 9a. In the case of SPEF, Fig. 9b discloses a maximum accumulation of 3.5 mg L\(^{-1}\) for 10, disappearing at 300 min, and of 5.7 mg L\(^{-1}\) for 11, dropping.
down up to 1.6 mg L\(^{-1}\) (0.4 mg L\(^{-1}\) TOC). The small quantity of the two byproducts, as compared to 6.0–6.5 mg L\(^{-1}\) TOC found in the final solutions treated by PEF (see Fig. 2e) and SPEF (see Fig. 6b) suggests the generation of recalcitrant undetected byproducts. Figure 9a and b demonstrate a remarkable influence of the light source on the profile of the concentrations of the acids. The illumination with sunlight in SPEF accelerated the production and destruction of the Fe(III) complexes of 10 and 11. Hence, the action of photons is denoted in the final step of the route of Fig. 8, aiming to explain better the mineralization of 1 by both PEF and SPEF treatments.

| No. | Chemical name | Molecular structure | Column | \(t_r^a\) (min) | \(m/z^b\) | Fragments (leaving groups) |
|-----|---------------|---------------------|--------|----------------|---------|---------------------------|
| 1   | Triclopyr     | ![Molecular structure](attachment) | P      | 58.59          | 210 (-COOH) | 197 (-CH\(_2\)-COOH) 180 (-O-CH\(_2\)-COOH) 146 (182,-Cl) 110 (146,-Cl) |
| 2   | (5,6-Dichloro-3,4-dihydroxyxypiridin-2-yloxy)-acetic acid | ![Molecular structure](attachment) | P      | 54.97          | 219 (-Cl) | 209 (-COOH) 179 (-O-CH\(_2\)-COOH) 143 (181, -Cl) |
| 3   | 2-Chloro-6-hydroxymethoxy-pyridine-3,4,5-triol  | ![Molecular structure](attachment) | P      | 23.74          | 207 171 (-Cl) |
| 4   | 3,5,6-Trichloro-2-pyridinol | ![Molecular structure](attachment) | P      | 42.56          | 169 (-CO) | 133 (-CO, -Cl) 107 (-COH, -C(Cl), -CH) 98 (-CO, -2Cl) |
| 5   | 2,3,4-Trihydroxy-4-hydroxyaminobutyric acid | ![Molecular structure](attachment) | P      | 44.87          | 197 169 (-CO) | 133 (-CO, -Cl) 107 (-COH, -C(Cl), -CH) 98 (-CO, -2Cl) |
| 6   | N-Chloromethylene-2,3-dihydroxypropenimidic acid | ![Molecular structure](attachment) | P      | 22.69          | 151 133 (-OH,-H) |
| 7   | 2,N-Dihydroxy-N-hydroxymethyl-malonamic acid | ![Molecular structure](attachment) | P      | 13.52          | 165 135 (-CH\(_2\)OH) | 119 (-COOH, -H) 75 (-CO-N(OH)-CH\(_2\)OH) 61 (-CO-CHOH-COOH, -H) |
| 8   | Hydroxymethyl-carbamic acid | ![Molecular structure](attachment) | P      | 10.31          | 91 61 (-CH\(_2\)OH) | 45 (-COOH, -H) |
| 9   | Formamide    | ![Molecular structure](attachment) | P      | 11.65          | 45 30 (-NH\(_2\), +H) |

\(a\) Non-polar, \(b\) Retention time, \(c\) Chloro-derivatives determined considering \(^{35}\)Cl and \(^{37}\)Cl
Conclusions

The Fe(III)–EDDS (1:1) complex was proven an efficient iron catalyst for treating the herbicide triclopyr at pH 7.0 by PEF process. A catalyst content as low as 0.06 mM performed quite well, although it was gradually destroyed under the action of OH, OH, and, pre-eminently, UV photons, yielding some soluble uncomplexed iron ions that originated from conventional Fenton’s reaction. Triclopyr degradation and TOC decay were enhanced using BDD anode, although the treatment was less expensive with the IrO 2-based one. Similar catalyst, herbicide, and TOC removals were obtained within the range 0.03–0.09 mM Fe(III)–EDDS. The increasing production of BDD(OH) as j became higher enhanced the TOC abatement once all the chelated catalyst had disappeared. The PEF experiments performed in 0.25 mM Na2SO4 + 0.35 mM NaCl revealed a large influence of active chlorine as oxidant. The SPEF process with BDD yielded better results than PEF for triclopyr removal due to the larger photon intensity from sunlight, but the TOC abatement was similar in both systems, attaining a maximal of 78% at j = 66.7 mA cm\(^{-2}\).

Fig. 8 Proposed mineralization route for triclopyr by PEF and SPEF treatments under the action of hydroxyl radical and light. The name of byproducts is given in Table 3

Fig. 9 Evolution of the concentration of (orange-filled triangle) tartronic (10) and (blue-filled squared) oxamic (11) acids detected during the (a) PEF and (b) SPEF treatments of 150 mL of solutions with 0.12 mM triclopyr, 0.050 M Na2SO4, and 0.06 mM (7.2 mg L\(^{-1}\) TOC) Fe(III)–EDDS (1:1) at pH 7.0 and 35 °C, using a BDD/air-diffusion cell at j = 16.7 mA cm\(^{-2}\) for 60 min, followed by 66.7 mA cm\(^{-2}\).
Data availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Compliance with ethical standards

Competing interests The authors declare that they have no competing interests.

Ethical approval Not applicable.

Consent to participate Not applicable.

Consent to publish Not applicable.

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