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# Solar photoelectro-Fenton: A very effective and cost-efficient electrochemical advanced oxidation process for the removal of organic pollutants from synthetic and real wastewaters<sup> $\star$ </sup>

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# HIGHLIGHTS

# G R A P H I C A L A B S T R A C T

- Advances in solar photoelectro-Fenton (SPEF) process in the period 2007–2022 are summarized.
- Similar degradation of organic pollutants with homo-EF, homo-PEF, and homo-SPEF at pH 3.0
- Larger mineralization by homo-SPEF than homo-PEF: more potent UV intensity from sunlight.
- $\bullet$  Good performance of hetero-SPEF with  $Fe_3O_4$  or sodium vermiculite as heterocatalyst at pH 3.0
- Combined processes with solar photoelectrocatalysis, anaerobic digestion, and nanofiltration.

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# ABSTRACT

Recalcitrant and toxic organic pollutants from wastewaters are scarcely removed in conventional wastewater treatment plants. To preserve the water quality, organics need to be removed by developing powerful oxidation technologies. Our laboratory proposed in 2007 a potent electrochemical advanced oxidation process (EAOP) for wastewater remediation, so-called solar photoelectro-Fenton (SPEF). This review summarizes the advances of this emerging technology up to 2022, making evident its effectiveness and cost-efficiency for the destruction of usual organic pollutants. The simultaneous action of generated hydroxyl radicals and the photolysis by sunlight explains the high oxidation power of SPEF respect to other EAOPs. The review is initiated by describing the fundamentals of the process to remark the role of the produced oxidants and the benefits of using solar irradiation in its performance. The photoelectrochemical systems used (bench tank reactor and solar pre-pilot flow plant) and the assessment of the operating variables are discussed. The characteristics of the most common homogeneous SPEF for the degradation and mineralization of several synthetic solutions of industrial chemicals, herbicides, pharmaceuticals, and synthetic organic dyes, as well as of some real wastewaters, are further described. The influence of the photoelectrochemical cell, electrodes, solution pH, electrolyte composition, Fe<sup>2+</sup> and pollutant concentration, and current density is analyzed. The performance of a homogeneous SPEF-like process with active chlorine and heterogeneous SPEF processes with solid catalysts such as  $Fe_3O_4$  and sodium

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vermiculite is also discussed. Finally, the advances of homogeneous SPEF combined with other techniques like solar photocatalysis, solar photoelectrocatalysis, anaerobic digestion, and nanofiltration are reported.

Symbols and acronyms		FTO I	Fluorine-doped tin oxide Current (mA or A)
Α	Absorbance	i	Current density (mA $cm^{-2}$ )
ACE	Average current efficiency	$k_1$	Pseudo-first-order rate constant for the target compound
ACF	Activated carbon fiber		decay (min <sup>-1</sup> )
BDD	Boron-doped diamond	$k_{\rm dis}$	Pseudo-first-order rate constant for discoloration (min <sup>-1</sup> )
COD	Chemical oxygen demand (mg $O_2 L^{-1}$ )	λ	Wavelength (nm)
CPC	Compound parabolic collector	MCE	Mineralization current efficiency (%)
DSA	Dimensionally stable anode	PEF	Photoelectro-Fenton (with UV light)
GDE	Gas-diffusion electrode, usually of carbon-	ROS	Reactive oxygen species
	polytetrafluoroethylene (PTFE) (for $H_2O_2$ generation)	SPC	Solar photocatalysis
EC	Energy consumption per unit volume (kWh m <sup><math>-3</math></sup> )	SPEC	Solar photoelectrocatalysis
$E_{\rm cat}$	Cathodic potential (V)	SPEF	Solar photoelectro-Fenton
EC <sub>COD</sub>	Energy consumption per unit COD mass (kWh (kg COD) $^{-1}$ )	SPF	Solar photo-Fenton
EC <sub>TOC</sub>	Energy consumption per unit TOC mass (kWh (kg TOC) $^{-1}$ )	TOC	Total organic carbon (mg C $L^{-1}$ )
EF	Electro-Fenton	UVA	Ultraviolet A (315–400 nm)
EO	Electrochemical oxidation	UVB	Ultraviolet B (280–315 nm)
EO-H <sub>2</sub> O <sub>2</sub>	Electrochemical oxidation with electrogenerated $\mathrm{H_2O_2}$	UVC	Ultraviolet C (100–280 nm)

## 1. Introduction

A good quality of water is essential for the life and subsistence of living beings. However, this quality is lost by the continuous discharge of toxic and non-biodegradable organic pollutants in the aquatic environment from human activities. High amounts of many industrial chemicals, herbicides, pharmaceuticals, and synthetic organic dyes are continuously released to rivers, lakes, and oceans (Moreira et al., 2017; Brillas, 2020). This causes a pervasive threat worldwide because most of them become persistent in the environment due to their stability to sunlight and temperature, as well as their inefficient destruction by conventional biological and physicochemical processes used in wastewater treatment plants (WWTPs). For this reason, a large variety of these pollutants are detected not only in natural waters at contents from µg  $L^{-1}$  to ng  $L^{-1}$ , but also at lower concentration even in drinking water (Brillas and Martínez-Huitle, 2015; Martínez-Huitle and Panizza, 2018). The presence of such toxic organics in the aquatic environment represents a serious health risk for living beings, making necessary their removal in their origin. To do this, safe, effective, and simple to use oxidation technologies for the remediation of wastewater effluents are being developed.

Over the past three decades, powerful advanced oxidation processes (AOPs) have been proposed to remove organics from wastewaters (Yu et al., 2014; Martínez-Huitle and Panizza, 2018; Brillas, 2021; Martínez-Huitle et al., 2023). AOPs include a large variety of environment-friendly chemical, photochemical, electrochemical, and photoelectrochemical methods where organics are removed by the attack of reactive oxygen species (ROS) generated on site, mainly the hydroxyl radical (°OH). This radical is the second strongest oxidant know with a so high standard redox potential ( $E^\circ$  = 2.80 V/SHE) that destroys most organic pollutants (Cornejo et al., 2020; Mousset and Dionysiou, 2020).

Fenton and Fenton-based treatments are among the most ubiquitous AOPs. The so-called Fenton's reagent  $(H_2O_2/Fe^{2+} mixture)$  acting in these methods produces homogeneous •OH from the classical Fenton's reaction (Moreira et al., 2017). However, the mineralization process of organics is largely inhibited by the formation of hardly oxidizable Fe (III)-carboxylate complexes with such oxidant. This drawback of the

Fenton method can be largely improved by exposing the treated solution to UV light or sunlight using the photo-Fenton (PF) or solar PF (SPF) techniques, respectively. The irradiated light generates more •OH and photolyzes the Fe(III)- complexes, with the consequent enhancement of the mineralization process of organics (Brillas and Sirés, 2015).

Several interesting properties have been specified for the EAOPs to remark their environmental compatibility. They include high efficiency, safety by operating at ambient conditions, versatility, and amenability of automation. Electro-Fenton (EF) is the simplest Fenton-based EAOP, which has been developed in the laboratory of the author of this review since 1995. Our approach outperformed the chemical Fenton method due to the continuous generation of both reagents (Fe $^{2+}$  and H<sub>2</sub>O<sub>2</sub>) at a gas-diffusion electrode (GDE) cathode fed with O<sub>2</sub> or air of an undivided electrolytic cell giving rise to the main removal of organics by homogeneous 'OH formed from Fenton's reaction. In this EF method, the anode also played an important role in the removal process because it can directly oxidize the organics and/or produce heterogeneous 'OH from water discharge than can react with organics by mediated oxidation. When only the latter oxidative actions of the anode are applied, the electrochemical oxidation (EO) process takes place, showing much lower oxidation power than EF. If EO is performed in an undivided cell with a GDE cathode generating H<sub>2</sub>O<sub>2</sub>, the process is so-called EO-H<sub>2</sub>O<sub>2</sub> where additional destruction of organics with this weak oxidant can occur as well. In our pioneer work over EF in 1995, it was already found that the mineralization process was decelerated due to the persistence of some by-products such as final Fe(III)-carboxylate complexes, in the same way as in the chemical Fenton method. To solve this situation, we propose the application of the so-called photoelectro-Fenton (PEF) process, already in 1995, consisting of the illumination of the solution treated by EF with UVA light. Excellent mineralization results were obtained due to the faster formation of homogeneous <sup>•</sup>OH from photo-Fenton reaction and the quicker photolysis of the Fe(III) species. However, the PEF process was not useful in practice because of the excessive cost of the artificial UVA lamp applied. For this reason, in 2007, we proposed a practical method so-called solar PEF (SPEF) in which inexpensive, free, and renewable sunlight was used as energy source, thus avoiding the expensive electricity required for the artificial UVA lamp. Since then, many works performed in our laboratory and others have studied the good performance of this emerging method to remediate

wastewaters polluted with organics.

This paper presents a comprehensive review on the advances achieved by SPEF from 2007 to 2022. Once a brief description of its fundamentals is made, the review summarizes and analyzes the most common homogeneous SPEF (homo-SPEF) process of organic pollutants including industrial chemicals, herbicides, pharmaceuticals, and synthetic organic acids. The treatment of real wastewaters with a complex composition by homo-SPEF is further examined. Later, the performance of a homo-SPEF-like process with active chlorine and that of some heterogeneous SPEF (hetero-SPEF) treatments with solid catalysts are described. Finally, combined processes of homo-SPEF with other techniques such as solar photocatalysis (SPC), solar photoelectrocatalysis (SPEC), anaerobic digestion, and nanofiltration among others for real wastewater treatment are analyzed.

# 2. Bibliometric search

The keyword "Solar photoelectron-Fenton" was introduced in the Scopus database to retrieve the peer-reviewed literature (reviews and scientific papers) related to the application of this treatment to remove organic pollutants from synthetic and real wastewaters up to January 2023. Once excluded conferences and communications in congresses, as well as book chapters, the selection of the articles summarized in this review was made from their individual analysis based on the title and abstract. Only the articles published in English were considered. A total of 9 reviews referring to this topic and 71 scientific articles dealing with the SPEF application to wastewater remediation were finally selected within the period 2007 to 2022. Apart from the treatment of complex real wastewaters, the removal of several organics including industrial chemicals, herbicides, pharmaceuticals, and synthetic organic dyes by SPEF has been described. These works reported: (i) the effect of the experimental variables, including electrodes, on organic removal, (ii) the clarification of the oxidizing agents generated, (iii) the experimental parameters associated with the mineralization process such as total organic carbon (TOC) and/or chemical oxygen demand (COD) decay, (iv) energetic parameters, and (v) the identification of by-products with the proposal of the corresponding reaction sequences. The treatment of pollutants like industrial chemicals, herbicides, pharmaceuticals, and synthetic organic dyes, as well as real wastewaters, was analyzed. Most studies considered the homo-SPEF treatment, whereas a reduced number of articles used homo-SPEF-like and hetero-SPEF processes. Combined treatments with other methods like SPC, SPEC, anaerobic digestion, and nanofiltration for real wastewaters were developed. Bench tank reactors and solar pre-pilot flow plants were used as photoelectrochemical systems. The present review briefly exposes the fundamentals of SPEF, followed by the analysis of the removal of the different classes of organics, real wastewaters, and combined processes. Special emphasis over the systems used, the operating parameters, and the by-products detected is made. The review includes one table and six figures, along with another table and other nine figures in Supplementary Material, specially designed to remark the advances reported.

Ten reviews have described some results on the SPEF process of organic pollutants. Five of them have been written by the author of this review, alone or as coauthor, corresponding to general electrochemical advanced oxidation treatments for synthetic organic dyes (Brillas and Martínez-Huitle, 2015), pharmaceuticals (Brillas and Sirés, 2015), herbicides (Brillas, 2021), and organic pollutants (Moreira et al., 2017; Brillas, 2020) with some reference to SPEF. On the other hand, 3 reviews considered the removal of organic pollutants by EAOPs (Yu et al., 2014; Martínez-Huitle and Panizza, 2018; Divyapriya et al., 2021) with little mention over SPEF, whereas other 2 reviews tried the characterization of flow reactors (Cornejo et al., 2020) and photoelectrochemical reactors (Mousset and Dionysiou, 2020) for wastewater remediation with some examples on the use of SPEF. However, any previous review has described a comprehensive study detailing the advances of SPEF to destroy organic pollutants such as summarized in the present review

covering up to 2022, i.e., all the time in which this emerging technology has been developed since out proposal in 2007.

The above bibliometric analysis identified 71 scientific articles regarding the destruction of organic pollutants by SPEF. A total of 19 articles were published between 2007 and 2013, 26 articles from 1014 to 2017, and other 26 articles between 2018 and 2022, making evident the interest of the application of this EAOP to organics abatement. Considering the kind of pollutant destroyed, 12 articles have been published with industrial chemicals (16.9%), 9 with herbicides (12.7%), 18 with pharmaceuticals (25.3%), and 22 with synthetic organic dyes (31.0%), whereas 10 articles (14.1%) have treated real wastewaters with a complex mixture of organics. Thus, the removal of synthetic organic dyes followed by that of pharmaceuticals have been the most extensively studied. It can be mentioned that a slightly higher of works has been performed with solar pre-pilot flow plants (37 articles, 52.1%) in front of those made with bench tank reactors (34 articles, 47.9%). This means that the results found for the former systems can be useful as key information for their scaling-up to pilot plants and subsequent feasible building of plants at industrial level.

## 3. Fundamentals of solar photoelectro-Fenton process

As an electrochemical Fenton-based process, homo-SPEF is based on the  $H_2O_2$  production at the cathode of the cell to further react with a small amount of added Fe<sup>2+</sup> to the solution to form Fe<sup>3+</sup> and homogeneous <sup>•</sup>OH from the homogeneous Fenton's reaction (1), optimal at pH  $\approx 3.0$  (Brillas, 2020):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- k_2 = 63 M^{-1} s^{-1}$$
 (1)

H<sub>2</sub>O<sub>2</sub> electrogeneration arises from the 2-electron cathodic reduction of  $O_2$  from reaction (2) ( $E^\circ = +0.68$  V/SHE) as an intermediate of its 4electron reduction to H<sub>2</sub>O ( $E^{\circ} = +1.23$  V/SHE). Reaction (2) is then the key point of this method because it competes with the cathodic reduction of H<sup>+</sup> to H<sub>2</sub> gas ( $E^{\circ} = 0$  V/SHE) (Moreira et al., 2017). Carbonaceous cathodes have shown an excellent and specific electrocatalytic selectivity to favor reaction (2) and so, continuously produce H<sub>2</sub>O<sub>2</sub> from injected O<sub>2</sub> (pumped as pure gas or from air). Carbon felt (CF) and GDE are cathodes typically used for this purpose and their ability to generate H<sub>2</sub>O<sub>2</sub> depends on the experimental conditions tested (Martínez-Huitle and Panizza, 2018). However, in an undivided cell, the accumulated H<sub>2</sub>O<sub>2</sub> is partially removed due to its oxidation at the anode M via reaction (3). In this process, another weak ROS, the physisorbed hydroperoxyl radical  $M(HO_2^{\bullet})$  at the anode surface is formed. Reaction (3) competes with the anodic water discharge to O<sub>2</sub> that evolves through the intermediate generation of the strong physisorbed hydroxyl radical M (\*OH) from reaction (4) (Brillas and Martínez-Huitle, 2015; Cornejo et al., 2020). The nature of the anode to produce M(\*OH) determines its oxidation power, and so, non-active boron-doped diamond (BDD) anodes have been found more powerful to generate reactive BDD(\*OH) than conventional active ones such as Pt or dimensionally stable anodes (DSA) (Boye et al., 2002; Brillas et al., 2008).

$$O_2 + 2H^+ + 2e^- \to H_2O_2$$
 (2)

$$M + H_2O_2 \rightarrow M(HO_2^{\bullet}) + H^+ + e^-$$
 (3)

$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^-$$
(4)

In the EO-H<sub>2</sub>O<sub>2</sub> process, organics are mainly oxidized by the attack of M (<sup>•</sup>OH), limited near/at the anode surface. The oxidation with other weaker ROS like H<sub>2</sub>O<sub>2</sub> and M(HO<sup>•</sup><sub>2</sub>) is also feasible, as well as with the singlet oxygen (<sup>1</sup>O<sub>2</sub>) formed from direct anodic O<sub>2</sub> oxidation and the superoxide radical anion (O<sup>•</sup><sub>2</sub>) initially generated during O<sub>2</sub> reduction (Brillas, 2020). All these species are also generated in the more potent homo-EF process, where the addition of Fe<sup>2+</sup> strongly accelerates the destruction of organics by reaction with homogeneous •OH formed from Fenton's reaction (1) in acid medium. The anode has a notable influence

in this treatment, bur it becomes less significant in homo-PEF and homo-SPEF by the large oxidative power of irradiated light, as will be discussed below. Compared to the chemical Fenton method, the homo-EF process presents the following advantages: (i) the in situ  $H_2O_2$  electrogeneration that avoids the handle of this hazardous product due to its explosive thermal decomposition, (ii) the continuous cathodic regeneration of Fe<sup>2+</sup> from reaction (5) that allows the presence of very small amounts of this ion to maintain the rate of homogeneous Fenton's reaction (1) and •OH production, and (iii) the much smaller Fe(OH)<sub>3</sub> precipitation as sludge (Moreira et al., 2017; Martínez-Huitle and Panizza, 2018).

$$\mathrm{Fe}^{3+} + \mathrm{e}^{-} \to \mathrm{Fe}^{2+} \tag{5}$$

The main drawbacks of homo-EF in the removal of organic pollutants are the limitation to acidic pH, being optimal at pH = 3.0, and the generation of persistent Fe(III) complexes like final Fe(III)-carboxylate species that excessively enlarge the time needed for their mineralization to CO<sub>2</sub>. Fortunately, these complexes can be photolyzed by UV light and this phenomenon is taken advantage in the homo-PEF treatment with the additional illumination of the treated solution with artificial lamps emitting UVC with  $\lambda = 100-280$  nm, UVB with  $\lambda = 280-315$  nm, or UVA with  $\lambda = 315-400$  nm. The latter radiation is energetic enough to accelerate the mineralization process by: (i) the extra production of homogeneous 'OH from the photo-Fenton reaction (6) where the Fe  $(OH)^{2+}$  species formed from Fe<sup>3+</sup> is rapidly photoreduced at pH 2.8–3.5, and (ii) pre-eminently, the photolysis or photodecarboxylation of Fe (III)-carboxylate species, expressed as Fe(OOCR)<sup>2+</sup>, according to the general reaction (7) (Brillas, 2020). Note that the most energetic UVC irradiation can yield the additional photolysis of organics alongside the homolysis of  $H_2O_2$  to •OH by reaction (8).

$$Fe(OH)^{2+} + h\nu \to Fe^{2+} + {}^{\bullet}OH$$
(6)

$$Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^{\bullet}$$
(7)

$$H_2O_2 + h\nu \to 2^{\bullet}OH \tag{8}$$

The homo-PEF process is not useful at industrial scale due to the high electrical cost of the artificial UV lamp. This is overcome in the much more cost-effective homo-SPEF treatment in which the solution is irradiated by sunlight with  $\lambda > 300$  nm. The high UV input of sunlight (about 3% of its maximum intensity) combined with the additional photolysis removal of Fe(III)-carboxylate species at  $\lambda > 400$  nm, make the homo-SPEF process usually more powerful than homo-PEF. However, homo-SPEF can only be applied during the daily hours of sun, which depends on the climatology and geographic site. For this reason, we envisage the combination of homo-PEF with UVA light in the absence of sunlight and homo-SPEF in its presence for the best wastewater remediation at industrial level.

Several works have described the use of hetero-SPEF treatment with iron solid catalysts with surface  $\equiv$ Fe<sup>2+</sup> sites (dos Santos et al., 2020b; Ganiyu et al., 2018; Pinheiro et al., 2020). The same reactions for generating the oxidants and destroying organics are proposed in this method as in homo-SPEF, with the peculiarity that they take place at the catalyst surface. Thus, the heterogeneous Fenton's reaction can be expressed by reaction (9) yielding heterogeneous <sup>•</sup>OH:

$$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+} + {}^{\bullet}OH + OH^-$$
(9)

Anodes like BDD, Pt, and DSA (metal or mixed metal oxides, usually of RuO<sub>2</sub> and/or IrO<sub>2</sub>) and cathodes like GDE, CF, and activated carbon fiber (ACF) are used in the photoelectrochemical systems. The GDE cathode consists of a carbon fiber filled with polytetrafluoroethylene, PTFE (carbon-PTFE), in contact with a dry face where O<sub>2</sub> or air is directly pumped while the opposite face is in contact with the solution. When a current (*I*) is applied, H<sub>2</sub>O<sub>2</sub> generated by reaction (2) passes to the solution boosted by the gas flow. The selectivity of carbon-PTFE GDE to H<sub>2</sub>O<sub>2</sub> is so high that Fe<sup>2+</sup> regeneration from reaction (5) becomes very slow (Serra et al., 2009). The opposite behavior is found for the CF and ACF cathodes where a smaller quantity of  $Fe^{2+}$  is practically completely regenerated due to the comparative low  $H_2O_2$  production. Surprisingly, the homo-EF process with CF and ACF cathodes yields a faster mineralization of organics as compared with carbon-PTFE GDE ones because persistent Fe(III)-carboxylate complexes are formed at much lesser extent. Consequently, their oxidation power is less enhanced by homo-PEF and homo-SPEF.

The homo- and hetero-SPEF processes have been carried out with bench tank reactors and solar pre-pilot flow plants. Fig. 1 exemplifies the sketch of several photoelectrochemical systems for the homo-SPEF treatment of organic wastewaters. Fig. 1a shows a two-electrode tank reactor with a BDD anode and a carbon-PTFE GDE cathode fed with air (Brillas, 2020), whereas Fig. 1b depicts another two-electrode tank reactor with a Ti|RuO<sub>2</sub> anode and an ACF cathode under O<sub>2</sub> sparging of the solution, powered by a solar photovoltaic cell (Zhang et al., 2016). The solar pre-pilot flow plants with filter-press reactors have similar components, except the solar photoreactor that can be planar (see Fig. 1c, El-Ghenymy et al., 2012) or a compound parabolic collector (CPC) of high light absorption efficiency (see Fig. 1d, Garcia-Segura et al., 2011). The latter figure presents a scheme of the filter-press reactor used as well.

The oxidation power of the homo- and hetero-SPEF processes is experimentally characterized by several operating and energetic parameters that are summarized as Eq. (10) to (25) in Tables SM-1 of Supplementary Material. Several works have determined the accumulation of H<sub>2</sub>O<sub>2</sub> in the electrolyzed solution by measuring the change of its concentration vs. time, e.g., by permanganometry. The percentage of current efficiency (% CE) from Eq. (10) and the energy consumption per unit volume (EC) from Eq. (11) are provided to show the performance of H<sub>2</sub>O<sub>2</sub> electrogeneration. The degradation of a pure pollutant can be followed by reversed-phase high-performance liquid chromatography (HPLC) to assess the abatement of its concentration (c) with time. This parameter is given either as normalized concentration  $(c/c_0)$  by Eq. (12) or percentage of degradation (% Degradation) by Eq. (13). In many cases, the concentration decay obeys a pseudo-first-order kinetics, allowing calculating the pseudo-first-order rate constant for pollutant removal  $(k_1)$  according to Eq. (14). For a synthetic organic dye solution, the evolution of its absorbance (A) measured by UV–Vis spectroscopy at the wavelength of maximum absorption of the dye ( $\lambda_{max}$ ) is determined. In this case, the discoloration of the solution is quantified by the normalized absorbance  $(A/A_0)$  from Eq. (15), the percentage of color removal (% Color removal) from Eq. (16), and the pseudo-first-order rate constant for discoloration  $(k_{dis})$  from Eq. (17). The longer mineralization process related to the overall destruction of the by-products formed is assessed by the variation of the COD and/or TOC of the solution. These parameters are expressed as normalized COD (COD/COD<sub>0</sub>) or TOC (TOC/TOC<sub>0</sub>), and percentage of COD or TOC removals from Eq. (18) to (21), respectively. The percentage of average current efficiency (% ACE) from COD by Eq. (22) or the percentage of mineralization current efficiency (% MCE) from TOC by Eq. (23) can be determined as well. The energetic parameters for the mineralization process are calculated as EC from Eq. (11), energy consumption per unit COD mass (EC<sub>COD</sub>) from Eq. (24), or energy consumption per unit TOC mass (EC<sub>TOC</sub>) from Eq. (25). All these parameters are used to assess the influence of operating variables like the kind of electrodes, solution pH, electrolyte composition, concentration of the catalyst and parent molecule, and current density (j) or cathodic peak potential ( $E_{cat}$ , for three-electrode systems) on the performance of the EAOP tested.

The aromatic, heteroaromatic, and/or cyclic by-products generated during the mineralization of an organic pollutant can be identified by gas chromatography-mass spectrometry (GC-MS) or by LC-MS or LC-MS/MS. This information serves for the proposal of a reaction sequence for its initial degradation. The final short-linear aliphatic carboxylic acids can be easily detected and quantified by ion-exclusion HPLC, which allows proposing a mineralization sequence for the



**Fig. 1.** Schemes of several systems for the solar photoelectro-Fenton (SPEF) treatment of organic pollutants in aqueous matrices. (a) Two-electrode tank reactor with a BDD anode and a carbon-PTFE GDE cathode fed with air (adapted from Brillas (2020)). (b) Two-electrode tank reactor with a Ti|RuO<sub>2</sub> anode and an activated carbon fiber (ACF) cathode under O<sub>2</sub> sparging and powered by a solar photovoltaic cell (adapted from Zhang et al. (2016)). (c) Solar pre-pilot flow plant with a filter-press reactor (adapted from El-Ghenymy et al. (2012)). (d) Solar flow plant (up) with a filter-press reactor (down) and a solar compound parabolic collector (CPC) photoreactor (adapted from Garcia-Segura et al. (2011)).

organic pollutant. This knowledge is key to clarify the superiority of homo-SPEF with respect to homo-PEF, as well as homo-EF and EO-H<sub>2</sub>O<sub>2</sub>. The evolution of some generated oxidants like active chlorine (HClO) and that of released inorganic ions from the heteroatoms by ion chromatography can also be determined, which is interesting to understand the toxicity of the final treated solution. However, there is a lack of techno-economic studies revealing the viability of homo-SPEF in front of other conventional technologies to remediate wastewaters in practice.

## 4. Homogeneous solar photoelectro-Fenton of organics removal

The homo-SPEF process with the addition of  $Fe^{2+}$  as catalyst has been the most studied treatment for organic pollutants, as pointed out above. The removal of several industrial chemicals, herbicides Pharmaceuticals, and synthetic organic dyes in synthetic solutions, as well as the remediation of some real wastewaters, have been assessed. This section analyzes and discusses the characteristics and performance of such processes. Table 1 collects the best results obtained with this EAOP from selected articles, making reference to the pollutant, photoelectrochemical system, and experimental conditions used with tank reactors and solar flow plants.

# 4.1. Industrial chemicals

The treatment of industrial chemicals in synthetic wastewaters with a two-electrode tank reactor like Fig. 1a has been centered in the assessment of  $\alpha$ -methyl-phenylglycine (Serra et al., 2009, 2011), phthalic acid (Garcia-Segura et al., 2013), *trans*-ferulic acid (Flores et al., 2016), oxalic and oxamic acids (Garcia-Segura et al., 2016), and bisphenol A (Burgos-Castillo et al., 2018). A solar pre-pilot flow plant served to assess the removal of *o*-, *m*-, and *p*-cresol (Flox et al., 2007a), sulfanflic acid (El-Ghenymy et al., 2012), methyl-, ethyl, and propyl

# Table 1

Selected results obtained for the solar photoelectro-Fenton (SPEF) process of organic wastewaters using tank reactors and solar flow plants.

Pollutant	System (anode/cathode) light irradiation	Experimental remarks	Best results	Ref.
Homo-SPEF Tank reacto α-methyl- phenylglycine	r Chemicals Two-electrode cell (BDD/carbon-PTFE GDE) direct sunlight	250 mL of 500 mg L <sup>-1</sup> of pollutant in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 10 mg L <sup>-1</sup> Fe <sup>2+</sup> , pH = 2.9, cathode fed with 10 L h <sup>1</sup> of O <sub>2</sub> , 25 °C, $I = 100$ –450 mA, 300 min	Faster destruction by homo-SPEF than homo-EF and with raising <i>I</i> . At <i>I</i> = 300 mA in homo-SPEF: total degradation in 30 min and 97% TOC removal in 300 min. Most $Fe^{2+}$ converted into $Fe^{3+}$ . Identification of 15 aromatic by-products by GC-MS and 12 final carboxylic acids by ion-exclusion HPLC, Release of NH <sub>4</sub> <sup>+</sup> > NO <sup>-</sup>	Serra et al. (2009)
<i>trans-</i> Ferulic acid	Two-electrode cell (BDD/carbon-PTFE GDE) 6 W UVA light (for homo-PEF) or direct sunlight (for homo-SPEF)	100 mL of 0.417 and 0.834 mM of pollutant in pure water, 0.10 M Na <sub>2</sub> SO <sub>4</sub> , 0.50 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with 300 mL min <sup>-1</sup> of air, 35 °C, $j = 33.3$ and 100 mA cm <sup>-2</sup> , 120 min	Faster degradation and mineralization by homo-SPEF than homo-EF, and at lower pollutant content and higher <i>j</i> . For homo- SPEF: 93% TOC removal with MCE = 44% for 0.834 mM pollutant at <i>j</i> = 33.3 mA cm <sup>-2</sup> . Identification of 4 aromatic derivatives by GC-MS and 3 final carboxylic acids by ion- exclusion HPLC	Flores et al. (2016)
Oxalic acid Oxamic acid	Two-electrode cell (BDD/carbon-PTFE GDE) direct sunlight	100 mL of 2.08 mM of each pollutant in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.50 mM Fe <sup>3+</sup> and/or 0.50 mM Cu <sup>2+</sup> , pH = 3.0, cathode fed with 300 mL min <sup>-1</sup> of air, 35 °C, <i>j</i> = 8.33–66.6 mA cm <sup>-2</sup> , 120 min	For oxalic acid with 0.50 mM Fe <sup>3+</sup> , degradation: homo-EF < solar photolysis < homo-SPEF. In the latter process at $j =$ 33.3 mA cm <sup>-2</sup> , total removal at 20 min with $k_1 = 4.1 \times 10^{-3} \text{ s}^{-1}$ . For 50:50 Fe <sup>3+</sup> / Cu <sup>2+</sup> , $k_1 = 3.6 \times 10^{-3} \text{ s}^{-1}$ with MCE = 110%. For oxamic acid with 0.50 mM Fe <sup>3+</sup> , degradation: homo-EF < solar photolysis $\approx$ homo-SPEF. In the latter process at $j =$ 33.3 mA cm <sup>-2</sup> , total removal at 100 min with $k_1 = 2.98 \times 10^{-4} \text{ s}^{-1}$ . For 75:25 Fe <sup>3+</sup> / Cu <sup>2+</sup> , $k_1 = 5.02 \times 10^{-4} \text{ s}^{-1}$ with MCE = 60%. Release of NH <sup>4</sup> <sub>4</sub> and NO <sup>3</sup> <sub>3</sub> from oxamic acid	Garcia-Segura et al. (2016)
Bisphenol A	Two-electrode cell (BDD/carbon-PTFE GDE) 6 W UVA light or direct sunlight	150 mL of 0.556 mM of pollutant in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> or 0.008 M NaCl + 0.047 M Na <sub>2</sub> SO <sub>4</sub> , 0.50 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with 1 L min <sup>-1</sup> of air, 35 °C, <i>j</i> = 33.3–100 mA cm <sup>-2</sup> , 240 min	degradation Increasing mineralization in both media: EO-H <sub>2</sub> O <sub>2</sub> < homo-EF < homo-PEF $\leq$ homo- SPEF. For the latter process at <i>j</i> = 100 mA cm <sup>-2</sup> , 98.2% TOC removal with MCE = 13.2% in sulfate medium and 97.4% TOC decay with MCE = 13.1% in mixed matrix. Aromatic intermediates identified by GC- MS: 8 in sulfate medium and 13 in mixed matrix	Burgos-Castillo et al. (2018)
<i>Herbicides</i> Bentazon	Two-electrode cell (BDD, Pt, or Ti  RuO <sub>2</sub> /carbon-PTFE GDE) 6 W UVA light or direct sunlight	130 mL of 0.208 mM of pollutant in pure water or WWTP effluent, 0.050 M Na <sub>2</sub> SO <sub>4</sub> or 0.025 M Na <sub>2</sub> SO <sub>4</sub> + 0.035 M NaCl, 0.25–1.00 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with 1 L min <sup>-1</sup> of air, 30 °C, $j = 3,33$ –100 mA cm <sup>-2</sup> , 240 min	Less performance with homo-PEF than SPEF in all cases. For homo-SPEF, greater mineralization: $Pt < Ti RuO_2 < BDD$ . For the latter anode at 16.6 mA cm <sup>-2</sup> with 0.50 mM Fe <sup>2+</sup> , total degradation, $k_1$ (min <sup>-1</sup> ), TOC removal, and MCE: 20 min, 0.16, 89.2%, and 21% in sulfate medium, 15 min, 0.11, 80.2%, and 19% in mixed matrix, and 45 min, 0.096, and 60.3% in WWTP. Detection of 7 non-chlorinated and 16 chlorinated aromatic by-products and 2 chlorinated aliphatics by GC-MS, and 7 final carboxylic acids by ion-exclusion	Guelfi et al. (2019)
Triclopyr	Two-electrode cell (BDD or Ti IrO <sub>2</sub> / carbon-PTFE GDE) 6 W UVA light or direct sunlight	150 mL of 0.12 mM of pollutant in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.06 mM of Fe (III):EDDS <sup>a</sup> , pH = 7.0, cathode fed with 0.9 L min <sup>-1</sup> of air, 35 °C, $j = 16.7$ mA cm <sup>-2</sup> , 300 min	HPLC Better removal with BDD than Ti IrO <sub>2</sub> . For BDD, TOC removal and $E_{CTOC}$ (kWh (g TOC) <sup>-1</sup> ): 38%, and 2.34 for EO-H <sub>2</sub> O <sub>2</sub> < 47% and 1.81 for homo-EF < 65% and 1.31 <sup>b</sup> for homo-PEF $\approx$ 62% and 1.33 for homo-SPEF. Total degradation in 270, 180, and 80 min for the 3 latter processes, respectively. Detection of 3 aromatic by-products and 4 aliphatic acids by GC-MS and 2 final carboxylic acids by ion-exclusion HPLC	Da Costa Soares et al. (2021)

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# Table 1 (continued)

Pollutant	System (anode/cathode) light irradiation	Experimental remarks	Best results	Ref.
Ibuprofen	Two-electrode cell (BDD/carbon-PTFE GDE) 6 W UVA light or direct sunlight	100 mL of 41 mg L <sup>-1</sup> of pollutant in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.10–1.0 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with 20 mL min <sup>-1</sup> of O <sub>2</sub> , 25 °C, $j = 3.33$ –66.7 mA cm <sup>-2</sup> , 240 min	At $j = 33.3$ mA cm <sup>-2</sup> with 0.50 mM Fe <sup>2+</sup> , similar overall degradation in 40 min for homo-EF and homo-PEF with Pt and BDD and $k_1$ near 2 × 10 <sup>-3</sup> s <sup>-1</sup> . For homo-SPEF, total degradation in 20 min, and 84% and 88% TOC removal with Pt and BDD, respectively. 4 aromatic derivatives detected by GC-MS and 4 final carboxylic acids quantified by	Skoumal et al. (2009)
Trimethoprim	Two-electrode cell powered by a photovoltaic cell (Ti RuO <sub>2</sub> /ACF <sup>°</sup> ) direct sunlight	125 mL of 200 mg L <sup>-1</sup> of pollutant in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 1.0 mM Fe <sup>2+</sup> , pH = 3.0, 60 mL min <sup>-1</sup> of sparged O <sub>2</sub> , 25 °C, $j$ = 18 mA cm <sup>-2</sup> , 360 min	The product of NLT and the product of the product	Zhang et al. (2016)
Sulfamethoxazole + trimethoprim	Two-electrode cell (BDD, Pt, or Ti IrO <sub>2</sub> / carbon-PTFE GDE) 6 W UVA light or direct sunlight	130 mL of 50.0 mg L <sup>-1</sup> of sulfamethoxazole + 11.1 mg L <sup>-1</sup> of trimethoprim in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> or 0.070 M NaCl, 0.50 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with 1 L min <sup>-1</sup> of O <sub>2</sub> , 35 °C, $j = 33.3$ mA cm <sup>-2</sup> , 240 min	For sulfamethoxazole in 0.050 M Na <sub>2</sub> SO <sub>4</sub> , similar degradation by homo-EF and homo-PEF by BDD, Pt or Ti IrO <sub>2</sub> with $k_1 \approx$ 0.30 min <sup>-1</sup> . Slightly higher by homo-SPEF with BDD, but much greater ( $k_1 = 0.90$ min <sup>-1</sup> ) in 0.070 M NaCl. Similar trends for trimethoprim with higher $k_1$ -values of 0.43–0.64 min <sup>-1</sup> in 0.050 M Na <sub>2</sub> SO <sub>4</sub> , Greater TOC removal of 87.4% with MCE = 7.9% by homo-SPEF with BDD in 0.050 M Na <sub>2</sub> SO <sub>4</sub> , decreasing to 65.8% TOC decay with MCE = 6.0% in 0.70 M NaCl. Final carboxylic acids quantified by ion- exclusion HPLC	Murillo-Sierra et al. (2018)
Dyes Acid Blue 29	Two-electrode cell (BDD, Pt, or Ti  RuO <sub>2</sub> /carbon-PTFE GDE) direct sunlight	130 mL of 118 mg L <sup>-1</sup> of dye in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.50 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with 300 mL min <sup>-1</sup> of air, 35 °C, $j = 33.3$ mA cm <sup>-2</sup> , 360 min	H <sub>2</sub> O <sub>2</sub> accumulated in 180 min with increasing <i>j</i> : 432 mg L <sup>-1</sup> for EO-H <sub>2</sub> O <sub>2</sub> , 152 mg L <sup>-1</sup> for homo-EF, and 85 mg L <sup>-1</sup> for homo-SPEF. Discoloration and COD decay increasing as EO-H <sub>2</sub> O <sub>2</sub> , < homo-EF < homo-SPEF. For the latter, $k_{dis}$ (min <sup>-1</sup> ), COD removal, ACE, and EC <sub>COD</sub> (kwh (g COD) <sup>-1</sup> ): 0.153, 100%, 22.1%, and 0.103 for BDD >0.108, 96%, 18.8%, and 0.115 for Pt > 0.076, 94%, 16.9%, and 0.087 for Ti RuO <sub>2</sub> . Final carboxylic acids quantified by ion- avelusion HPLC	Fajardo et al. (2019)
Acid Orange 7	Two-electrode cell (BDD WO <sub>2'72</sub> /C GDE) UVC (for homo-PEF) or Xe lamp (for simulated homo-SPEF)	350 mL of 0.260 mM of dye in pure water, 0.10 M K <sub>2</sub> SO <sub>4</sub> , 0.50 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with air at 0.2 bar, 20 °C, $j =$ 100–200 mA cm <sup>-2</sup> , 360 min	CE $\approx$ 60% for H <sub>2</sub> O <sub>2</sub> generation at 100 mA cm <sup>-2</sup> for EO-H <sub>2</sub> O <sub>2</sub> . Discoloration, dye content decay, and TOC removal increased with increasing <i>j</i> in the order: EO-H <sub>2</sub> O <sub>2</sub> < homo-EF < homo-PEF $\approx$ homo-SPEF. For the two latter processes at 150 mA cm <sup>-2</sup> , $k_{\rm dis} = 0.041-0.044$ min <sup>-1</sup> , 90% TOC abatement, and MCE = 7.5%. Final carboxylic acids quantified by ionexclusion HPLC	Paz et al. (2020)
Erythrosine B	Two-electrode cell (BDD/CF $^{d}$ ) 25 and 100 W UVA light or direct sunlight	300 mL of 100 mg L <sup>-1</sup> of dye in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.10 mM Fe <sup>2+</sup> , pH = 3.0, air flow rate = 3 L min <sup>-1</sup> , $j = 20$ mA cm <sup>-2</sup> , 120 min	Discoloration, COD removal, ACE, and EC (kWh m <sup><math>-3</math></sup> ): 100% in 50 min, 90%, 10%, and 21 for homo-EF, 100%, 100% 14%, and 516 for homo-PEF with 100 W UVA light, and 100%. 100%, 13%, and 21 for homo-SPEF	Clematis and Panizza (2021)
Wastewaters Washing machine effluent of jeans	Two-electrode cell (BDD/carbon-PTFE GDE) direct sunlight	100 mL of effluent (315 mg L <sup>-1</sup> of TOC), 0.50 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with 300 mL min <sup>-1</sup> of air, 35 °C, $j = 16.6-100$ mA cm <sup>-2</sup> , 240 min	Quicker discoloration with increasing <i>j</i> . Percentage of color removal after 180 min at $j = 66.6$ mA cm <sup>-2</sup> : 95% by homo-EF and 100% by homo-SPEF. TOC decay at 240 min: 68% by homo-EF and 97% by homo- SPEF	dos Santos et al. (2018a)
Solar flow plant Chemica o-, m-, and p-Cresol	Ils Pre-pilot plant with a two-electrode filter-press reactor and a planar photoreactor (BDD/carbon-PTFE GDE) direct sunlight	2.5 L of 128–1024 mg L <sup>-1</sup> of each pollutant in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 1.0 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with O <sub>2</sub> at 1.5 bar, liquid flow rate = 180 L h <sup>-1</sup> , 30 °C, <i>j</i> = 50 mA cm <sup>-2</sup> , 120 min	All cresols undergo similar removal by homo-SPEF. Lower percent of TOC removal with higher MCE at higher pollutant content. For 128 mg $L^{-1}$ of each cresol, total degradation in 70–80 min, 87–90% TOC removal in 120 min with	Flox et al. (2007a)

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# Table 1 (continued)

Pollutant	System (anode/cathode) light irradiation	Experimental remarks	Best results	Ref.
			$\label{eq:mce} \begin{array}{l} MCE = 118-122\%, EC_{TOC} = 0.155 \ kWh \ (g \ TOC)^{-1}, \ and \ EC = 15 \ kWh \ m^{-3}. \end{array}$ Detection of 3 aromatic by-products by GC-MS and 7 final carboxylic acids by ion-exclusion HPLC	
Methyl-, ethyl, and propyl paraben	Pre-pilot plant with a two-electrode filter-press reactor and a planar photoreactor (BDD or Ti RuO <sub>2</sub> /carbon- PTFE GDE) direct sunlight	2.5 L of a mixture of 0,30 mM of each pollutant in 0.005 M Na <sub>2</sub> SO <sub>4</sub> , simulated water, or WWTP effluent, 0.20 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with O <sub>2</sub> at 8.6 kPa overpressure, liquid flow rate = $180 \text{ L h}^{-1}$ , $30 \degree$ C, <i>j</i> = 5–30 mA cm <sup>-2</sup> , 240 min	Similar $k_1$ -value for the 3 isomers in the 3 matrices, slightly higher for BDD in WWTP. In this case, total degradation in 150 min and 65% TOC removal with MCE = 200% and EC <sub>TOC</sub> = 0.084 kWh (g TOC) <sup>-1</sup> after 240 min at <i>j</i> = 10 mA cm-2. Higher <i>k</i> -value at higher <i>i</i>	Steter et al. (2018)
Bronopol	Pre-pilot plant with a two-electrode filter-press reactor and a planar photoreactor under direct sunlight for homo-SPEF or an annular photoreactor under a 160 W UVA light for homo-PEF (Ti RuO <sub>2</sub> /CoSxPy MWCNTs <sup>e</sup>  C GDE)	2.5 L of 0.28 mM of pollutant in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.50 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with O <sub>2</sub> at 8.6 kPa overpressure, liquid flow rate = $180 \text{ L h}^{-1}$ , 35 °C, <i>j</i> = 40 mA cm <sup>-2</sup> , 360 min	H <sub>2</sub> O <sub>2</sub> accumulation of 15.9 mM with CE = 53% after 360 min of EO-H <sub>2</sub> O <sub>2</sub> with the modified GDE, superior to 9.5 mM found for raw MWNCTs GDE. Faster degradation and mineralization of pollutant with the modified GDE. For homo-PEF at that time, total degradation with $k_1 = 0.015 \text{ min}^{-1}$ and 79% TOC removal. For homo-SPEF, total degradation at 300 min with $k_1 = 0.016 \text{ min}^{-1}$ and 85% TOC removal with MCE = 5% and EC <sub>TOC</sub> = 2.6 kWh (g TOC) <sup>-1</sup> ) at 360 min. Determination of formic acid by ion-exclusion HPLC and released Br <sup>-</sup> , BrO <sub>3</sub> <sup>-</sup> , and NO <sub>3</sub> <sup>-</sup> ions by ion chromatography	Ye et al. (2019)
Mecoprop	Pre-pilot plant with a two-electrode filter-press reactor and a planar photoreactor under direct sunlight or an annular photoreactor under a 160 W UVA light (BDD/carbon-PTFE GDE)	2.5 L of 100–634 mg L <sup>-1</sup> of pollutant in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.25–5.0 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with O <sub>2</sub> at 8.6 kPa overpressure, liquid flow rate = 180 L h <sup>-1</sup> , 25 °C, $j = 50$ –150 mA cm <sup>-2</sup> , 540 min	At $j = 50 \text{ mA cm}^{-2}$ , total degradation for homo-PEF and homo-SPEF in 16 min ( $k_1 =$ $5.3 \times 10^{-3} \text{ s}^{-1}$ ) for 100 mg L <sup>-1</sup> and 50 min ( $k_1 = 1.4 \times 10^{-3} \text{ s}^{-1}$ ) for 640 mg L <sup>-1</sup> . For the former solution, 97% TOC removal with MCE = 14% for homo-PEF and MCE = 15% for homo-SPEF. Quantification of 3 aromatic derivatives by reversed-phase HPLC, 3 final carboxylic acids by ion-exclusion HPLC, and released Cl <sup>-</sup> by ion chromatography	Flox et al. (2007b)
Tebuthiuron Ametryn	Pre-pilot plant with a two-electrode filter-press reactor and a planar photoreactor (BDD/carbon-PTFE GDE) direct sunlight	2.5 L of 0.04–1.80 mM of each pollutant in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.50 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with O <sub>2</sub> at 8.6 kPa overpressure, liquid flow rate = 200 L h <sup>-1</sup> , 25 °C, $j = 25$ –100 mA cm <sup>-2</sup> , 360 min	For homo-SPEF at $j = 50$ mA cm <sup>-2</sup> , TOC removal, MCE, EC <sub>TOC</sub> (kWh (g TOC) <sup>-1</sup> ): 70%, 11.2%, and 2.23 for 0.18 mM tebuthiuron, 52%, 11.2%, and 2.61 for 0.18 mM ametryn, and 51%, 20.9%, and 1.51 for their mixture. Identification of 4 heteroaromatic byproducts in the mixture by GC-MS	Gozzi et al. (2017)
<i>Pharmaceuticals</i> Paracetamol	Pre-pilot plant with a two-electrode filter-press reactor and a solar CPC <sup>f</sup> photoreactor (Pt/carbon-PTFE GDE) direct sunlight	10 L of 157 mg L <sup>-1</sup> of pollutant in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.33–1.17 mM Fe <sup>2+</sup> , pH = 1.38–4.36, cathode fed with 4.5 L min <sup>-1</sup> of air, liquid flow rate = 180 L h <sup>-1</sup> , 35 °C, $I = 3.5$ –8.5 A, 150 min	Optimized homo-SPEF by response surface methodology: 0.40 mM Fe <sup>2+</sup> . pH = 3.0, and $I = 5.0$ A. Under these conditions, total removal of pollutant in 55 min with $k_1 =$ $1.04 \times 10^{-3}$ s <sup>-1</sup> and 80% TOC removal with MCE = 59%, EC <sub>TOC</sub> = 0.114 kWh (g TOC) <sup>-1</sup> , and EC = 9.1 kWh m <sup>-3</sup> at 150 min. Time-course of 3 aromatic by-products by reversed-phase HPLC, 5 final carboxylic acids by ion-exclusion HPLC, and released Cl <sup>-</sup> by ion chromatography	Almeida et al. (2011)
Sulfanilamide	Pre-pilot plant with a two-electrode filter-press reactor with a planar phtoreactor (Pt/carbon-PTFE GDE) direct sunlight	2.5 L of 239–1195 mg L <sup>-1</sup> of pollutant in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.25–5.0 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with O <sub>2</sub> at 8.6 kPa overpressure, liquid flow rate = 200 L h <sup>-1</sup> , 35 °C, $j = 50$ –150 mA cm <sup>-2</sup> , 300 min	For homo-SPEF of 239 mg L <sup>-1</sup> of pollutant with 0.50 mM Fe <sup>2+</sup> at pH = 3.0: overall degradation in 80 min ( $k_1 = 6.5 \times 10^{-4}$ s <sup>-1</sup> ) and 40 min ( $k_1 = 1.3 \times 10^{-3}$ s <sup>-1</sup> ) at <i>j</i> = 50 and 150 mA cm <sup>-2</sup> , respectively. Under these conditions, TOC removal: 91% and 92%, MCE: 59.9% and 20.4%, EC <sub>TOC</sub> = 0.155 and 0.890 kWh (g TOC) <sup>-1</sup> , respectively. Detection of 3 aromatic derivatives by GC- MS, 5 final carboxylic acids by ion- exclusion HPLC, and released NH <sup>+</sup> <sub>4</sub> > NO <sub>3</sub> by ion chromatography	El-Ghenymy et al. (2013)
Ranitidine	Pre-pilot plant with a two-electrode filter-press reactor and a planar	$2.5~L$ of 33.8–112.6 mg $L^{-1}$ of pollutant in pure water, 0.050 M $\rm Na_2SO_4,$ 0.20–2.0 mM	Better results for 112.6 mg L <sup>-1</sup> of pollutant, 0.50 mM Fe <sup>2+</sup> , and $j = 100$ mA	Olvera-Vargas et al. (2015)

Pollutant	System (anode/cathode) light irradiation	Experimental remarks	Best results	Ref.
	photoreactor (Pt/carbon-PTFE GDE) direct sunlight	Fe <sup>2+</sup> , pH = 3.0, cathode fed with O <sub>2</sub> at 8.6 kPa overpressure, liquid flow rate = 200 L h <sup>-1</sup> , 35 °C, $j = 25$ –100 mA cm <sup>-2</sup> , 300 min	cm <sup>-2</sup> : total degradation in 20 min with $k_1$ = 0.251 min <sup>-1</sup> , 67% TOC removal, MCE = 8.7%, and EC <sub>TOC</sub> = 0.92 kWh (g TOC) <sup>-1</sup> . Detection of 6 final carboxylic acids by ion- exclusion HPLC and released NH <sup>4</sup> <sub>4</sub> , NO <sup>3</sup> <sub>3</sub> , and SO <sup>2</sup> <sub>-</sub> by ion chromatography	
Levofloxacin	Pre-pilot plant with a three-electrode FM01-LC filter-press reactor and a CPC photoreactor (Pt/carbon cloth GF <sup>§</sup> GDE) direct sunlight	6 L of 30–60 mg L <sup>-1</sup> of TOC in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.50 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with air at 0.5 psi, liquid flow rate = 3.0 L min <sup>-1</sup> , 35 °C, $E_{cat} = -0.30$ V/SCE, 360 min	Total mineralization in 180 min for 30 mg $L^{-1}$ of TOC with $EC_{TOC} = 0.015$ kWh (g $TOC$ ) <sup>-1</sup> . Identification of 6 aromatic by-products by GC-MS, 3 final carboxylic acids by ion-exclusion HPLC, and released NH <sub>4</sub> <sup>4</sup> , NO <sub>3</sub> <sup>-</sup> , and F <sup>-</sup> by ion chromatography	Coria et al. (2018)
Dyes Acid Red 88 Acid Yellow 9	Pre-pilot plant with a two-electrode filter-press reactor and a planar photoreactor (BDD/carbon-PTFE GDE) direct sunlight	2.5 L of 50 mg L <sup>-1</sup> TOC of each dye in pure water, 0.050 or 0.100 M Na <sub>2</sub> SO <sub>4</sub> , 0.10–0.80 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with O <sub>2</sub> at 8.6 kPa overpressure, liquid flow rate = 200 L h <sup>-1</sup> , 35 °C, $j = 25$ –150 mA cm <sup>-2</sup> , 360 min	Larger oxidation power for homo-SPEF than homo-EF. Better mineralization with $0.50 \text{ mM Fe}^{2+}$ and higher <i>j</i> . At <i>j</i> = 50 mA cm <sup>-2</sup> , TOC removal, MCE, and EC <sub>TOC</sub> (kWh (g TOC) <sup>-1</sup> ): 98%, 20%, and 0.48 for Acid Red 88 and 98%, 20%, and 0.38 for Acid Yellow 9. Quantification of 5 final carboxylic acids	Ruiz et al. (2011b)
Disperse Blue 3	Pre-pilot plant with a two-electrode filter-press reactor and a planar photoreactor (BDD/carbon-PTFE GDE) direct sunlight	2.5 L of 100–400 mg L <sup>-1</sup> of dye in pure water, 0.100 M Na <sub>2</sub> SO <sub>4</sub> , 0.50 mM Fe <sup>2+</sup> and/or 0.10 mM Cu <sup>2+</sup> , pH = 3.0, cathode fed with O <sub>2</sub> at 8.6 kPa overpressure, liquid flow rate = 200 L h <sup>-1</sup> , 35 °C, $j = 15$ –80 mA cm <sup>-2</sup> , 240 min	by ion-exclusion HPLC, For homo-SPEF, greater amount of TOC decay at higher dye content and <i>j</i> . For 200 mg L <sup>-1</sup> of dye at $j = 50$ mA cm <sup>-2</sup> , total discoloration in 150 min, regardless the catalyst used. After 240 min, TOC removal and EC <sub>TOC</sub> (kWh (g TOC) <sup>-1</sup> ): 96% and 0.18 for 0.50 mM Fe <sup>2+</sup> and 98% and 0.18 for 0.50 mM Fe <sup>2+</sup> + 0.10 mM Cu <sup>2+</sup> . Identification of 15 aromatic derivatives by GC-MS and 4 final carboxylic acids by ion-exclusion HPLC	Salazar et al. (2012)
Allura Red AC	Pre-pilot plant with a two-electrode filter-press reactor and a planar photoreactor (Pt/carbon-PTFE GDE) direct sunlight	2.5 L of 115–460 mg L <sup>-1</sup> of dye in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.50 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with O <sub>2</sub> at 8.6 kPa overpressure, liquid flow rate = 200 L h <sup>-1</sup> , 35 °C, <i>j</i> = 50 and 100 mA cm <sup>-2</sup> , 240 min	For 230 mg L <sup>-1</sup> of dye by homo-SPEF, the solution became colorless in 40 and 30 min at 50 and 100 mA cm <sup>-2</sup> . TOC removal, MCE, and EC <sub>TOC</sub> (kWh (g TOC) <sup>-1</sup> ): 92%, 94%, and 0.12 at 50 mA cm <sup>-2</sup> and 97%, 45%, and 0.31 at 100 mA cm <sup>-2</sup> . At the former <i>j</i> , discoloration at 20 and 80 min for 115 and 460 mg L <sup>-1</sup> of dye, Detection of 16 aromatic derivatives by GC-MS, 11 final carboxylic acids by ion-exclusion HPLC, and released SO <sub>4</sub> <sup>2-</sup> and NO <sup>-</sup> by intercomposite the sector of the sector o	Thiam et al. (2015b)
Congo Red	Pre-pilot plant with a two-electrode filter-press reactor and a planar photoreactor (Pt/carbon-PTFE GDE) direct sunlight	2.5 L of 0.065–0.520 mM of dye in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.50 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with O <sub>2</sub> at 8.6 kPa overpressure, liquid flow rate = 200 L h <sup>-1</sup> , 35 °C, $j = 50$ –150 mA cm <sup>-2</sup> , 240 min	Lower percent of color and TOC removals at higher dye content, but larger performance at greater <i>j</i> . For 0.520 mM of dye at $j = 150$ mA cm <sup>-2</sup> , 94% color removal in 150 min, total removal in 120 min, and 74% TOC decay with MCE = 38.8% and EC <sub>TOC</sub> = 0.110 kWh (g TOC) <sup>-1</sup> at 240 min. Identification of 21 aromatic by-products by LC-MS and 5 final carboxylic acids by ion-exclusion HPLC. Release of SO <sub>4</sub> <sup>2-</sup> , NH <sub>4</sub> <sup>+</sup> and NO <sub>3</sub>	Solano et al. (2015)
Acid Orange 7 Acid Red 151 Disperse Blue 71	Pre-pilot plant with a two-electrode filter-press reactor and a solar CPC photoreactor (Pt/carbon-PTFE GDE) direct sunlight	10 L of 50 mg L <sup>-1</sup> TOC of each azo dye in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.50 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with 4.5 L min <sup>-1</sup> of air, liquid flow rate = 200 L h <sup>-1</sup> , 35 °C, <i>j</i> = 33.2–77.6 mA cm <sup>-2</sup> , 180 min	Discoloration, dye removal, and mineralization decreased in the order: Acid Orange 7 (monoazo) > Acid Red 151 (diazo) > Disperse Blue 71 (triazo). For Acid Orange 7 at $j = 33.2$ mA cm <sup>-2</sup> , 97% discoloration in 60 min, total removal in 30 min ( $k_1 = 2.6 \times 10^{-3} \text{ s}^{-1}$ ), and 96% TOC abatement with MCE = 62.7%, and EC <sub>TOC</sub> = 0.100 kWh (g TOC) <sup>-1</sup> in 180 min. Aromatic and hydroxylated derivatives of each dye identified by LC-MS, as well as their final carboxylic acids by ion- exclusion HPLC.	Garcia-Segura and Brillas (2016)
Acid Blue 29	Pre-pilot plant with a two-electrode filter-press reactor and a solar CPC photoreactor (DSA/carbon-PTFE GDE) direct sunlight	10 L of 233.5 mg $L^{-1}$ of dye in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.50 mM Fe <sup>2+</sup> , pH = 3.0, cathode fed with air, liquid flow rate =	Faster discoloration and mineralization at greater solar irradiation and for 50 mA cm <sup>-2</sup> in the order: EO-H <sub>2</sub> O <sub>2</sub> < homo-EF < homo-SPEF. For the latter process at 1240	Salazar et al. (2019)

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# Table 1 (continued)

Pollutant	System (anode/cathode) light irradiation	Experimental remarks	Best results	Ref.
		150 L h <sup>-1</sup> , 35 °C, $j = 25$ and 50 mA cm <sup>-2</sup> , 300 min	mW cm <sup>-2</sup> of solar irradiation and 25 mA cm <sup>-2</sup> , 100% of color removal, 100% of TOC decay, and $EC_{TOC} = 0.057$ kWh (g TOC) <sup>-1</sup> . Thirteen aromatic derivatives detected by LC-MS/MS and seven final carboxylic acids auantified by ion-exclusion HPI C	
Wastewaters			quantified by foll-exclusion fill EC	
Sanitary landfill leachate	Pre-pilot plant with a two-electrode MicroFlowCell reactor and a solar CPC photoreactor (BDD or Pt/carbon-PTFE GDE) direct sunlight	1.19 L of effluent (337–403 mg L <sup>-1</sup> TOC), 20–80 mg L <sup>-1</sup> Fe <sup>2+</sup> or 1:3 Fe(III) complexed with oxalate, pH = 2.8–4.0, cathode fed with air, liquid flow rate = 150 L h <sup>-1</sup> , 15–40 °C, $j = 200$ mA cm <sup>-2</sup> , 300 min	Low effect of temperature between 20 and 40 °C on mineralization, TOC reduction by homo-SPEF with 60 mg $L^{-1}$ Fe <sup>2+</sup> at pH = 2.8: 64% with Pt < 78% with BDD. Using BDD with the same Fe <sup>2+</sup> content as 1:3 [Fe (III)]/[oxalate], TOC removal: 67% at pH 3.0, 83% at pH 3.5, and 75% at pH 4.0.	Moreira et al. (2016)
Elderberry agro- industrial wastewater	Pilot plant with a two-electrode MicroFlowCell reactor and a solar CPC photoreactor (BDD/carbon-PTFE GDE) direct sunlight	75 L of effluent (160–210 mg L <sup>-1</sup> TOC), 20 mg L <sup>-1</sup> Fe <sup>2+</sup> , pH = 3.0, cathode fed with 10 L h <sup>-1</sup> of air, liquid flow rate = 300 L h <sup>-1</sup> , $j = 150$ mA cm <sup>-2</sup> , 240 min	90 mg of H <sub>2</sub> O <sub>2</sub> electrogenerated in 15 min. For homo-SPEF, 25% of TOC abatement with EC = 1.2 kWh m <sup>-3</sup> . Biodegradability enhanced. Detection of released Cl <sup>-</sup> and SO <sub>4</sub> <sup>2</sup> by ion chromatography. Total operation cost ( $\notin$ m <sup>-3</sup> ): 0.40 for homo-SPEF <0.80 for homo-SPF <1.86 for ozonation (0H = 11)	Ferreira et al. (2020)
Greywater	Pre-pilot plant with a filter-press reactor and a solar CPC photoreactor (Pt/ carbon-PTFE GDE) direct sunlight	10 L of effluent (80.8–100.6 mg L <sup>-1</sup> TOC, including 20 mg L <sup>-1</sup> TOC from dodecyl- benzene sulfonic acid), 5 mg L <sup>-1</sup> Fe <sup>2+</sup> , pH = 3.0, cathode fed with air, $j = 77.5$ mA cm <sup>-2</sup> , 240 min	55% TOC removal with $EC_{TOC} = 0.32$ kWh (g TOC) <sup>-1</sup> by homo-SPEF. 60% reduction of the acute toxicity to <i>Artemia salina</i>	dos Santos et al. (2023)
Hetero-SPEF Sunset Yellow	Two-electrode tank reactor (Pt/GDE) UVA light or direct sunlight	350 mL of 100 mg L <sup>-1</sup> of dye in pure water, 0.10 M Na <sub>2</sub> SO <sub>4</sub> or 0.13 M NaCl, 0.25 g Fe <sub>3</sub> O <sub>4</sub> as catalyst, pH = 3.0, O <sub>2</sub> gas bubbled at 0.2 bar, 20 °C, $I = 100$ mA, 90 min	Discoloration in Na <sub>2</sub> SO <sub>4</sub> : 55% by hetero-EF and 78% by hetero-PEF in 90 min. Total color removal in 15 min for both processes with NaCl. TOC removal, MCE. and EC <sub>TOC</sub> (kWh (g TOC) <sup>-1</sup> ) for hetero-SPEF: 49%, 48%, and 1.90 for Na <sub>2</sub> SO <sub>4</sub> , and 50%, 57%, and 1.70 with NaCl. Good reusability of catalyst after 8 consecutive cycles by hetero-PEF with Na SO	Pinheiro et al. (2020)
Ponceau SS	Two-electrode tank reactor (BDD/ carbon-PTFE GDE) 6 W UVA light or direct sunlight	130 mL of 0.075–0.225 mM of dye in pure water, 0.050 M Na <sub>2</sub> SO <sub>4</sub> , 0.018 mM Fe <sup>2+</sup> or 0.25–2.0 g L <sup>-1</sup> sodium vermiculite as catalyst, pH = 3.0, cathode fed with 400 mL min <sup>-1</sup> of air, 25 °C, $j = 16.6-66.6$ mA cm <sup>-2</sup> , 360 min	Discoloration and TOC removal increased as EO-H <sub>2</sub> O <sub>2</sub> < homo-EF (Fe <sup>2+</sup> ) < hetero-EF (sodium vermiculite) < hetero-PEF < hetero-SPEF. For hetero-PEF, higher percentage of color removal with smaller dye concentration and higher sodium vermiculite content and <i>j</i> . For hetero-SPEF with 0.150 mM dye, 1.0 g L <sup>-1</sup> sodium vermiculite, and 33.3 mA cm <sup>-2</sup> : $k_{dis} =$ 0.914 min <sup>-1</sup> , 84.1% TOC decay, and MCE = 6.7%. Final carboxylic acids quantified by ion- exclusion HPLC	dos Santos et al. (2020b)

<sup>a</sup> EDDS: Ethylenediamine-*N*,*N*'-disuccinic acid.

<sup>b</sup> Without considering the power of the UVA lamp.

<sup>c</sup> ACF: Activated carbon fiber.

<sup>d</sup> CF: Carbon felt.

<sup>e</sup> MWCNTs: Multi-walled carbon nanotubes.

 $^{\rm f}\,$  CPC: Compound parabolic collector.

<sup>g</sup> GF: Graphite felt.

# paraben (Steter et al., 2018), and bronopol (Ye et al., 2019).

Table 1 shows that the homo-SPEF 'process of these compounds in synthetic sulfate solutions was carried out tat pH = 3.0, i.e., the optimum conditions of Fenton's reaction (1) as well as of photo-Fenton reaction (6) that provide the main oxidant <sup>•</sup>OH. Fig. 2 presents the behavior of this process exemplified for the case of 100 mL of *trans*-ferulic acid solutions in pure water with 0.10 M Na<sub>2</sub>SO<sub>4</sub> at pH = 3.0 and 35 °C using a BDD/carbon-PTFE cell (Flores et al., 2016). For 0.834 mM of pollutant at j = 33.3 mA cm<sup>-2</sup>, Fig. 2a depicts the gradual pollutant decay found by EO-H<sub>2</sub>O<sub>2</sub> with almost total degradation at 360 min, following a pseudo-first-order decay with  $k_1 = 7.2 \times 10^{-3}$  min<sup>-1</sup>, as can

be seen in the inset. This means that *trans*-ferulic acid is very slowly destroyed pre-eminently by BDD(•OH) formed from reaction (4) and other weaker ROS (H<sub>2</sub>O<sub>2</sub>, HO<sub>2</sub><sup>-</sup>). In contrast, Fig. 2b highlights a much faster and similar removal by homo-EF with 0.50 mM Fe<sup>2+</sup> and homo-PEF with additional 6 W UVA light, achieving total abatement in only 15 min with  $k_1$  close to 0.32–0.34 min<sup>-1</sup> (see inset panel). This enhancement can be explained by the large production of homogeneous •OH from Fenton's reaction (1), with little participation of photoelectro-Fenton reaction (6). The predominance of the former reaction also occurred in the homo-SPEF process. Fig. 2c displays that the percentage of TOC removal grew in the order: EO-H<sub>2</sub>O<sub>2</sub> < homo-EF <



**Fig. 2.** Time course of (a,b) *trans*-ferulic acid with the corresponding pseudo-first-order kinetic analysis in the inset panels, (c) TOC removal and (d) the percentage of MCE for the treatment of 100 mL of pollutant solutions in pure water with 0.10 M Na<sub>2</sub>SO<sub>4</sub> at pH = 3.0 and 35 °C using a two-electrode tank reactor like of Fig. 1a with a BDD anode and a carbon-PTFE GDE cathode. Process: (•) EO-H<sub>2</sub>O<sub>2</sub>, (•) homo-EF, (•) homo-PEF (with 6 W UVA lamp), and (•) homo-SPEF of 0.834 mM of pollutant at j = 33.3 mA cm<sup>-2</sup>, and homo-SPEF of (•) 0.834 mM of pollutant at j = 100 mA cm<sup>-2</sup> and (•) 0.417 mM of pollutant at j = 33.3 mA cm<sup>-2</sup>. The Fenton-based processes ran with 0.50 mM Fe<sup>2+</sup>. Evolution of the intermediates (e) vanillin and (f) oxalic acid in the above treatments. Adapted from Flores et al. (2016).

homo-PEF < homo-SPEF, according to the increasing oxidation power of the process. The corresponding enhancement of % MCE is presented in Fig. 2d. For the most potent homo-SPEF, an excellent 93% TOC reduction with a high MCE = 44% can be observed (see also Table 1). This is feasible by the photolysis of the final Fe(III)-carboxylate species formed, which is quicker in homo-SPEF than homo-PÊF due to the higher UV intensity (direct and diffuse) provided by sunlight as compared to that of UVA light in homo-PEF. Fig. 2c and d shows that the rise of *j* from 33.3 to 100 mA cm<sup>-2</sup> for 0.834 mM pollutant caused a faster TOC removal by the generation of more °OH oxidant by the acceleration of reaction (2) but with smaller MCE. This phenomenon can be ascribed to the great increase in rate of the parasitic reactions of this radical that decelerate its oxidation over organics. They can be the dimerization of homogeneous °OH to H<sub>2</sub>O<sub>2</sub> by reaction (26), and its attack over this species by reaction (27) or  $Fe^{2+}$  by reaction (28) (Brillas, 2020):

$$2^{\bullet}OH \rightarrow H_2O_2$$
 (26)

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O$$
<sup>(27)</sup>

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^{-}$$
(28)

Fig. 2c and d also show that when the pollutant content decreased from 0.834 to 0.417 mM at the same j = 33.3 mA cm<sup>-2</sup>, TOC was reduced more rapidly due to the presence of less organic matter with lower % MCE, which can be related to the faster organic oxidation with similar quantity of produced homogeneous •OH. The authors found a rapid generation and destruction of aromatic by-products during the same time as the parent molecule is destroyed, as can be seen in Fig. 2e for the intermediate vanillin. Fig. 2f makes evident the large persistence of the final oxalic acid, which is accumulated in EO-H<sub>2</sub>O<sub>2</sub> and more largely in the more powerful homo-EF because it is slowly destroyed by  $M(^{\circ}OH)$  and homogeneous  $^{\circ}OH$ . In contrast, oxalic acid is completely removed in homo-PEF by the quick photolysis of its Fe(III) complexes via reaction (7). This explains the large mineralization achieved upon homo-SPEF treatment.

The same trend of homo-SPEF with *i* and pollutant concentration as operating variables has been described for other industrial chemicals in sulfate matrices with tank reactors and solar pre-pilot flow plants, always with high TOC abatement demonstrating its very effectiveness (see Table 1). Oxalic and oxamic acids are the ultimate carboxylic acids formed in the destruction of heteroaromatics that are directly transformed into CO2. Garcia-Segura et al. (2016) studied their homo-SPEF treatment using  $\mathrm{Fe}^{3+}$  and/or  $\mathrm{Cu}^{2+}$  as catalysts, since the last ion can also produce homogeneous 'OH from a Fenton-like reaction of the  $Cu^{2+}/Cu^{+}$  pair similar to (1). The trials were made with a BDD/carbon-PTFE GDE tank reactor filled with 100 mL of 2.08 mM of each carboxylic acid with 0.050 M  $Na_2SO_4$  and 0.50 mM  $Fe^{3+}$  and/or 0.50 mM Cu<sup>2+</sup> at pH = 3.0, 35 °C, and j = 8.33-66.6 mA cm<sup>-2</sup>. The degradation of oxalic acid with  $0.50 \text{ mM Fe}^{3+}$  increased in the sequence: homo-EF < solar photolysis < homo-SPEF, showing a synergy between homogeneous 'OH as oxidant and sunlight that photolyzes the Fe (III)-oxalate complexes from reaction (7). At j = 33.3 mA cm<sup>-2</sup>, homo-SPEF yielded a fast and total removal in 20 min with  $k_1 = 4.1 \times$  $10^{-3}$  s<sup>-1</sup> (see Table 1). When a mixture of 50:50 Fe<sup>3+</sup>/Cu<sup>2+</sup>was used,  $k_1$ dropped down to  $3.6 \times 10^{-3} \text{ s}^{-1}$  because less photoactive Fe(III) complexes are formed, although a high MCE = 110% at 120 min was still obtained. Note that the % MCE calculated from Eq. (23) only accounts for the electricity provided to the system, without considering the synergistic effect of sunlight, and then, its value can be >100%. The opposite trend was obtained with oxamic acid that was more slowly destroyed in homo-SPEF yielding CO<sub>2</sub>, NH<sup>+</sup><sub>4</sub>, and NO<sup>-</sup><sub>3</sub>. Total degradation was attained at a longer time of 100 min for j = 33.3 mA cm<sup>-2</sup> with 0.50 mM Fe<sup>3+</sup>, analogously to solar photolysis, indicating that Fe (III)-oxamate complexes were photolyzed but not oxidized with homogeneous  $^{\circ}$ OH. However, the presence of a low proportion of Cu<sup>2+</sup> (75:25 Fe<sup>3+</sup>/Cu<sup>2+</sup>) accelerated the homo-SPEF process up to  $k_1 = 5.02 \times 10^{-4}$  $s^{-1}$  with MCE = 60% (see Table 1). This is explained by the rapid destruction of the Cu(II)-oxamate complexes with BDD(\*OH) in competence with the photolysis of Fe(III)-oxamate ones. These findings support the study of the homo-SPEF treatment of organic pollutants with  $Fe^{2+}$  and  $Cu^{2+}$  as co-catalysts to clarify its oxidation power,

The effect of the electrolyte composition has been studied by Burgos-Castillo et al. (2018) using a BDD/carbon-PTFE GDE tank reactor illuminated with a 6 W UVA light for homo-EF or sunlight for homo-SPEF. Synthetic solutions of 150 mL of 0.556 mM of bisphenol A with 0.050 M Na<sub>2</sub>SO<sub>4</sub> or 0.008 M NaCl +0.047 M Na<sub>2</sub>SO<sub>4</sub> and 0.50 mM Fe<sup>2+</sup> at pH = 3.0, 35 °C were treated at *j* = 33.3–100 mA cm<sup>-2</sup> lasting 240 min. Table 1 remarks that in both media, the mineralization increased in the order: EO-H<sub>2</sub>O<sub>2</sub>< homo-EF < homo-PEF ≤ homo-SPEF. Moreover, at *j* = 100 mA cm<sup>-2</sup>, the latter process also yielded near 98% TOC removal with MCE close to 13% in both matrices, despite that in the chloride matrix, a strong oxidant such as active chlorine (HClO) was formed from the anodic oxidation of Cl<sup>-</sup> according to reactions (29) and (30):

$$2\mathrm{Cl}^- \to \mathrm{Cl}_2 + 2\mathrm{e}^- \tag{29}$$

$$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+$$
 (30)

The authors identified 8 primary aromatic by-products in sulfate medium and 13 aromatics and chlorinated aromatics in chloride matrix by GC-MS, confirming the oxidative action of homogeneous •OH in the former medium and of this radical alongside HClO in the second one. Fig. SM-1 presents the initial reaction sequence for bisphenol A degradation proposed from these by-products involving oxidation with •OH and chlorination reactions.

The homo-SPEF processes carried out with solar pre-pilot flow plants with isomers of cresols (Flox et al., 2007a) and several parabens (Steter et al., 2018) revealed their large efficiency and cost-effectiveness. For 2.5 L of each cresol with 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 1.0 mM  $Fe^{2+}$  at pH = 3.0and 30 °C treated with a solar plant like of Fig. 1c with a BDD/carbon-PTFE filter-press cell upon liquid flow rate  $= 180 \text{ Lmin}^{-1}$ and at i = 50 mA cm<sup>-2</sup>, similar performance was found regardless of the isomer tested. For 128 mg  $L^{-1}$  of pollutant, total degradation was achieved in 70-80 min and TOC was reduced by 87-90% in 120 min with excellent values of MCE = 118–122%,  $EC_{TOC} = 0.155$  kWh (g TOC)<sup>-1</sup>, and EC = 15 kWh m<sup>-3</sup> (see Table 1). Using the same plant with BDD or DSA (Ti|RuO<sub>2</sub>) anode, 2.5 L of an equimolar mixture of methyl-, ethyl-, and propyl-paraben (0.33 mM each) spiked in a WWTP effluent was treated with 0.20 mM Fe<sup>2+</sup> at pH = 3.0, 30 °C, and j = 5-30 mA cm<sup>-2</sup>. In this case, organics were oxidized with homogeneous <sup>•</sup>OH and HClO. Slightly better results were found with the BDD anode, where the application of a low  $j = 10 \text{ mA cm}^{-2}$  yielded overall abatement of all parabens in 150 min and a TOC reduction of 65% with MCE = 200% and  $EC_{TOC} = 0.084$  kWh (g TOC)<sup>-1</sup>) in 240 min (see Table 1). These impressive findings suggest the good viability of homo-SPEF that can be expected for the remediation of real wastewaters.

Aiming to improve the oxidation ability of homo-SPEF, Ye et al. (2019) prepared a novel GDE cathode coated with CoSxPy|multi-walled carbon nanotubes (MWCNTs) as electrocatalyst to potentiate H2O2 electrogeneration (see Table 1). This cathode confronted to a BDD anode was placed in the filter-press cell of solar flow plant like of Fig. 1c for homo-SPEF or using an annular photoreactor with an inner 160 W UVA light for homo-PEF. The tests were made by recirculating 2.5 L of 0.28 mM of the brominated pollutant bronopol with 0.050 M  $Na_2SO_4$  and 0.50 mM Fe<sup>2+</sup> at pH = 3.0, 35 °C, and liquid flow rate = 180 L min<sup>-1</sup> by applying a j = 40 mA cm<sup>-2</sup>. Bronopolol was completely abated in 360 min with a small  $k_1 = 0.015 \text{ min}^{-1}$  for homo-PEF and slightly more rapidly in 300 min with  $k_1 = 0.016 \text{ min}^{-1}$  for homo-SPEF. After 360 min of electrolysis, TOC was reduced by 79% for homo-PEF < 85% for homo-SPEF, but in the latter case a small value of MCE = 5% and a high  $EC_{TOC} = 2.6 \text{ kWh} (g \text{ TOC}^{-1})$  were determined (see Table 1), according to the large recalcitrance of the parent molecule to be oxidized by homogeneous •OH. Its mineralization was accompanied by the formation of formic acid and the release of toxic ions like Br<sup>-</sup>, BrO<sub>3</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup>.

# 4.2. Herbicides

The study with herbicides from wastewaters in a two-electrode tank reactor like of Fig. 1a was carried out with diuron (Pipi et al., 2014), bentazon (Guelfi et al., 2019), and triclopyr (Da Costa Soares et al., 2021). Mecoprop (Flox et al., 2007b), 4-chloro-2-methylphenoxyacetic acid (Garcia-Segura et al., 2011), diuron (Pipi et al., 2014), and tebuthiuron and ametryn (Gozzi et al., 2017) were treated in solar pre-pilot flow plants. A mixture of fungicides and insecticides has also been assessed with this system (Salmerón et al., 2019).

The pioneering work of Flox et al. (2007b) with homo-SPEF was carried out with a solar pre-pilot flow plant like of Fig. 1c with a BDD/carbon-PTFE GDE filter-press cell, and compared with homo-PEF using an annular reactor with an inside 160 W UVA light. Synthetic solutions were prepared with 2.5 L of 100–634 mg L<sup>-1</sup> of the herbicide mecoprop, 0.050 M Na<sub>2</sub>SO<sub>4</sub>, and 0.25–5.0 mM Fe<sup>2+</sup> at pH = 3.0, 25 °C, and liquid flow rate = 180 L h<sup>-1</sup>, and were treated at *j* = 50–150 mA cm<sup>-2</sup>. The best conditions were obtained with 0.50 mM Fe<sup>2+</sup> as catalyst and *j* = 50 mA cm<sup>-2</sup>. Fig. SM-2a shows an enhancement of TOC reduction for the treatment of 100 mg L<sup>-1</sup> of the herbicide in such conditions in the order: EO-H<sub>2</sub>O<sub>2</sub> < homo-EF < homo-PEF < homo-SPEF. The superiority of the two photo-assisted processes with respect to homo-EF is due to the fast photolysis of the final Fe(III)-carboxylate complexes from reaction (7), much rapid for homo-SPEF by the higher effective UV intensity of solar irradiation, which was confirmed by

following the evolution of final acetic and oxalic acids by ion-exclusion HPLC. This phenomenon was more significant at the beginning of the process, as can be seen in the change of the % MCE given in Fig. SM-2b. At the end of these treatments at 540 min, 97% of TOC was removed with MCE = 14% for homo-PEF and MCE = 15% for homo-SPEF (see Table 1). The high oxidation power of homo-SPEF was evidenced from the overall abatement of the more concentrated 634 mg L<sup>-1</sup> of the herbicide in only 50 min with  $k_1 = 1.4 \times 10^{-3} \text{ s}^{-1}$  (see Fig. SM-2c) giving a high TOC removal of 95% at 540 min (see Fig. SM-2d). These findings encouraged us for a deeper investigation of the homo-SPEF process, much more cost-effective than homo-PEF.

Table 1 shows that the works in two-electrode tank reactors were performed with different anodes and a carbon-PTFE GDE cathode by homo-PEF with a 6 W UVA light and homo-SPEF. Guelfi et al. (2019) electrolyzed 130 mL of 0.208 M of the herbicide bentazon in 0.050 M Na<sub>2</sub>SO<sub>4</sub>, 0.025 M Na<sub>2</sub>SO<sub>4</sub> + 0.035 M NaCl, or WWTP effluent with 0.25–1.00 mM Fe<sup>2+</sup> at pH = 3.0 and 30 °C using a BDD, Pt, or Ti|RuO<sub>2</sub> anode at j = 3,33-100 mA cm<sup>-2</sup>. Fig. 3a and b highlight that the performance of homo-EF with 0.50 mM Fe<sup>2+</sup> at j = 16.6 mA cm<sup>-2</sup> increased in the sequence: Pt < Ti|RuO<sub>2</sub> < BDD in both synthetic sulfate and chloride media. The homo-SPEF process always upgraded the homo-PEF one, as can be deduced by comparing the above figures with Fig. 3c and



**Fig. 3.** Effect of the anode and current density on the change of: (a) bentazon concentration and (b) percentage of TOC removal with time for the homo-PEF treatment with a 6 W UVA light of 130 mL of 0.208 mM of pollutant in pure water with 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 0.50 mM Fe<sup>2+</sup> at pH = 3.0 and 30 °C filling a two-electrode cell like of Fig. 1a with a BDD, Pt or Ti|RuO<sub>2</sub>, anode and a carbon-PTFE GDE cathode upon a 6 W UVA light at j = 16.6 mA cm<sup>-2</sup>. Effect of current density and aqueous matrix over the variation of (c) bentazon concentration and (d) percent of TOC decay with time for the homo-SPEF treatment upon the above conditions in pure water with 0.050 M Na<sub>2</sub>SO<sub>4</sub> + 0.035 M NaCl, or a WWTP effluent with a BDD anode. The initial TOC was 25 mg L<sup>-1</sup> in pure water and 37 mg L<sup>-1</sup> in the WWTP effluent. (e) Percentage of MCE for the above assays. (f) Time course of carboxylic acids (( $\blacktriangle$ ) tartaric, ( $\blacklozenge$ ) oxamic, ( $\blacksquare$ ) malonic, ( $\bigcirc$ ) formic, ( $\Box$ ) oxalic, ( $\bigcirc$ ) maleic, and ( $\triangle$ ) fumaric) detected by ion-exclusion HPLC during the assay of graphic (c) with 0.050 M Na<sub>2</sub>SO<sub>4</sub> at j = 16.6 mA cm<sup>-2</sup>. Adapted from Guelfi et al. (2019).

d for the herbicide decay and the percentage of TOC removal, respectively. It can also be observed in the latter two figures that higher *j* caused faster degradation and mineralization in sulfate medium using BDD. This yielded a decrease of the corresponding %MCE value due to the expected acceleration of the parasitic reactions (26)-(28), as can be seen in Fig. 3e. At j = 16.6 mA cm<sup>-2</sup>, homo-SPEF with BDD yielded total bentazon abatement in 20 min ( $k_1 = 0.16$  min<sup>-1</sup>), 15 min ( $k_1 = 0.15$ min<sup>-1</sup>), and 45 min ( $k_1 = 0.11 \text{ min}^{-1}$ ), with TOC removal of 89.2% (MCE = 21%), 80.2% (MCE = 19%) and 60.3% after 240 min for sulfate medium, chloride or mixed matrix, and WWTP effluent, respectively (see Table 1). The quicker degradation in chloride matrix than in sulfate medium is due to the faster parallel oxidation with HClO originated in the former case. This produced more recalcitrant chloro-derivatives that were more slowly mineralized (see Fig. 3d). The enlargement of the herbicide degradation with lower TOC abatement with the WWTP effluent can be ascribed to the parallel oxidation of its organic components decelerating that of herbicide. Fig. 3f presents the evolution of the 7 final carboxylic acids detected during the mineralization process of homo-SPEF in sulfate medium, which were totally removed in about 120 min by the fast decarboxylation of their Fe(III)-complexes from reaction (7). The GC-MS analysis of treated solutions in pure water allowed identifying 7 non-chlorinated and 16 chlorinated aromatic by-products, along with 2 chlorinated aliphatics. Fig. SM-3 shows the initial reaction sequence proposed for bentazon degradation from such intermediates, involving reactions of demethylation, hydroxylation, and chlorination.

Da Costa Soares et al. (2021) explored the use of ethylenediamine-N, N'-disuccinic acid (EDDS) as chelating agent of Fe<sup>3+</sup> to stabilize this ion in homo-SPEF at neutral pH. This treatment as well as homo-EF and homo-PEF were made with the above systems equipped with BDD or Ti IrO2 anode by treating 150 mL of 0.12 mM triclopyr in 0.050 M Na2SO4 with 0.06 mM of Fe(III):EDDS at pH = 7.0, 35 °C, and j = 16.7 mA cm<sup>-2</sup> lasting 300 min. A superior performance for BDD was found as well, raising in the sequence: EO-H<sub>2</sub>O<sub>2</sub> < homo-EF < homo-PEF  $\approx$  homo-SPEF (see Table 1). For the two latter processes, total degradation was achieved in 180 and 80 min, respectively, but TOC was finally reduced by 62–65% with an acceptable  $EC_{TOC} = 1.31-1.33$  kWh (g TOC)<sup>-1</sup>. These excellent results at neutral pH are explained by the rapid photolysis of the stable Fe(III)-EDDS to form Fe(II)-EDDS that regenerates the parent molecule by reaction with  $H_2O_2$ , this originating homogeneous •OH as strong oxidant. The authors also detected 3 aromatic by-products and 4 aliphatic acids by GC-MS and 2 final carboxylic acids by ion-exclusion HPLC.

The homo-SPEF treatment of highly recalcitrant herbicides has also been tested with solar pre-pilot flow plants with BDD/carbon-PTFE filter-press cells. An example is the case of the removal of tebuthiuron and ametryn reported by Gozzi et al. (2017). The results of Table 1 show that at pH = 3.0 and after 360 min at j = 50 mA cm<sup>-2</sup>, 70% and 52% of TOC decay with 11.2% and 11.2% of MCE and high 2.23 and 2.61 kWh (g TOC)<sup>-1</sup> of EC<sub>TOC</sub> were found for 2.5 L of 0.180 mM tebuthiuron and ametryn alone, respectively. For their mixture, TOC was only reduced by 51% but with a higher MCE = 20.9% and lower EC<sub>TOC</sub> = 1.51 kWh (g TOC)<sup>-1</sup>. This indicates that the composition of the pollutants is determinant to characterize the oxidation ability of homo-SPEF and its viability in practice.

#### 4.3. Pharmaceuticals

Synthetic solutions polluted with pharmaceuticals like salicylic acid (Guinea et al., 2008), ibuprofen (Skoumal et al., 2009), enrofloxacin (Guinea et al., 2010), ciprofloxacin (Antonin et al., 2015b), trimethoprim (Zhang et al., 2016), a mixture of sulfamethoxazole and trimethoprim (Murillo-Sierra et al., 2018), and captopril (dos Santos et al., 2020a) have been remediated with a two-electrode tank reactor. Other pharmaceuticals such as paracetamol (Almeida et al., 2011), atenolol, metoprolol tartrate, and propranolol hydrochloride (Isarain-Chávez et al., 2011), sulfanilamide (El-Ghenymy et al., 2013), chloramphenicol (Garcia-Segura et al., 2014), trimethoprim (Moreira et al., 2014), ranitidine (Olvera-Vargas et al., 2015), metronidazole (Pérez et al., 2015), erythromycin (Pérez et al., 2017), and ampicillin, sulfamethazine, tetracycline, and salicylic acid (Bugueño-Carrasco et al., 2021), have been treated with a solar pre-pilot flow plant. A three-electrode filter-press cell has been used in the case of levofloxacin (Coria et al., 2018),

Huge efforts have been made to show the suitability of homo-SPEF to remove pharmaceuticals in synthetic wastewaters with a two-electrode cell such as Fig. 1a with a carbon-PTFE GDE cathode. It is remarkable the work of Skoumal et al. (2009) over the treatment of 100 mL of 41 mg  $L^{-1}$ of ibuprofen in 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 0.10–1.0 mM  $Fe^{2+}$  at pH = 3.0 and 25 °C using a BDD or Pt anode at i = 3.33-66.7 mA cm<sup>-2</sup>. The best performance by homo-SPEF was attained with 0.50 mM Fe<sup>2+</sup> and a higher TOC abatement with smaller % MCE was obtained with increasing *j*, as pointed out above for other kinds of pollutants. Little effect was observed for both anodes by homo-EF and homo-PEF with a 6 W UVA light, since at  $j = 33.3 \text{ mA cm}^{-2}$ , a quick and similar total degradation in 40 min with  $k_1$  near  $2 \times 10^{-3}$  s<sup>-1</sup> was determined for Pt and BDD (see Table 1). These point to consider that the main oxidant was the homogeneous <sup>•</sup>OH formed from Fenton's reaction (1), with scarce relevance of the hydroxyl radicals formed from the photo-Fenton reaction (6) of  $Fe(OH)^{2+}$  species. In contrast, the higher UV intensity of sunlight accelerated strongly the latter photolytic process and ibuprofen was completely abated in only 20 min with both anodes by homo-SPEF. In this case, 84% and 88% of TOC was removed with Pt and BDD, respectively, after 240 min of electrolysis (see Table 1). The superior oxidation power with BDD can be related to the production of higher amounts of BDD(<sup>•</sup>OH) from reaction (4) that destroy more organic intermediates during the long mineralization process. The authors also detected 4 important aromatic derivatives by GC-MS and quantified 4 final carboxylic acids by ion-exclusion HPLC.

A more recent work of Murillo-Sierra et al. (2018) considered the removal of a mixture of 50.0 mg  $L^{-1}$  of sulfamethoxazole + 11.1 mg  $L^{-1}$ of trimethoprim in 0.050 M Na<sub>2</sub>SO<sub>4</sub> or 0.070 M NaCl with 0.50 mM Fe $^{2+}$ at pH = 3.0 and 35 °C using a BDD, Pt, or Ti $|IrO_2$  anode at j = 33.3 mA  $cm^{-2}$  during 240 min. In sulfate medium, similar k<sub>1</sub>-values of 0.30 min<sup>-1</sup> were found for the component sulfamethoxazole by homo-EF, homo-PEF with 6 W UVA light, and homo-SPEF for all anodes because the main oxidant homogeneous •OH was formed from Fenton's reaction (1). However, the drug removal was largely accelerated in chloride medium with  $k_1 = 0.90 \text{ min}^{-1}$ , indicating that the generated HClO from reactions (29) and (30) reacted with the drug more quickly than homogeneous <sup>•</sup>OH. The other component trimethoprim followed the same trends, although it was abated more rapidly. For the mixture, higher TOC decay of 87.4% with MCE = 7.9% was obtained by homo-SPEF with BDD in 0.050 M Na<sub>2</sub>SO<sub>4</sub>, dropping down to 65.8% TOC with MCE = 6.0% in 0.70 M NaCl, i.e., the opposite tendency to the drug degradation. This is indicative of a large formation of chloroderivatives by the attack of HClO that are slowly destroyed. The remediation of real wastewaters with sulfate and chloride ions then needs to be accurately investigated to clarify the role of the different oxidants (\*OH and HClO) formed. Zhang et al. (2016) have also described a total degradation in 90 min with 80% mineralization in 360 min for 125 mL of 200 mg  $\rm L^{-1}$  of trimethoprim with 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 1.0 mM  $Fe^{2+}at pH = 3.0$  and 25 °C using the cell of Fig. 1b powered with a photovoltaic cell at j = 18mA  $cm^{-2}$  (see Table 1). Note that renewable-energy-driven electrochemical technologies have been recently used to power bench-scale reactors based on different electrochemical processes (Ganiyu et al., 2020).

The homo-SPEF process of pharmaceuticals performed with a solar pre-pilot flow plant confirmed its large effectiveness and low cost needed for its feasible application at industrial scale. An interesting work of El-Ghenymy et al. (2013) was centered in the treatment of 2.5 L of 239–1195 mg L<sup>-1</sup> of sulfanilamide in 0.050 M Na<sub>2</sub>SO<sub>4</sub> with 0.25–5.0 mM Fe<sup>2+</sup> at pH = 3.0, 35 °C, and liquid flow rate = 200 L h<sup>-1</sup>. The trials

were made with the plant of Fig. 1c with a Pt/carbon-PTFE GDE filter press cell for homo-SPEF and without solar irradiation for homo-EF. Fig. 4a depicts the quicker removal of 239 mg L<sup>-1</sup> of sulfanilamide with 0.50 mM Fe<sup>2+</sup> by homo-SPEF as compared to homo-EF at j = 50mA cm<sup>-2</sup> due to the formation of more amount of homogeneous <sup>•</sup>OH from photo-Fenton reaction (6). In both EAOPs, the drug abatement raised at higher *j* as result of the generation of more homogeneous <sup>•</sup>OH from Fenton's reaction (1) by the acceleration of H<sub>2</sub>O<sub>2</sub> production from reaction (2). The influence of Fe<sup>2+</sup> concentration on TOC decay for the homo-SPEF treatment at j = 50 mA cm<sup>-2</sup> is presented in Fig. 4b. A faster mineralization can be observed from 0.2 to 0.5–2.0 mM Fe<sup>2+</sup>, which can be related to: (i) the formation of more homogeneous <sup>•</sup>OH by the rise in rate of Fenton's reaction (1), and (ii) the faster production of final Fe (III)-carboxylate complexes that are more quickly photolyzed from reaction (7). In contrast, the process was inhibited for 5.0 mM Fe<sup>2+</sup> owing to the Consumption of this radical by the excess of catalyst from reaction (28). Fig. 4c makes evident the influence of sunlight largely enhancing homo-SPEF with respect homo-EF. TOC removal was more rapid by increasing *j*, but with lower % MCE and higher EC<sub>TOC</sub> (see Fig. 4d) due to the decrease of the oxidant homogeneous •OH by the acceleration of its parasitic reactions (26)–(28). The best conditions were then obtained at *j* = 50 mA cm<sup>-2</sup> with a TOC reduction = 91%, MCE = 59.9%, and EC<sub>TOC</sub> = 0.155 kWh (g TOC)<sup>-1</sup> after 240 min of electrolysis (see Table 1). Fig. 4e and f reveal the high oxidation power of homo-SPEF with ability enough to destroy a 91% of TOC after 300 min of treatment of a concentrated solution with 1195 mg L<sup>-1</sup> of sulfanilamide at *j* = 100 mA cm<sup>-2</sup>, with a greater MCE = 122.7% and a lower EC<sub>TOC</sub> = 0.110 kWh (g TOC)<sup>-1</sup>. A more recent paper of



**Fig. 4.** (a) Effect of current density on sulfanilamide concentration vs. time for the homo-EF and homo-SPEF processes of 2.5 L of 239 mg L<sup>-1</sup> of pollutant in pure water with 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 0.50 mM Fe<sup>2+</sup> at pH = 3.0, and 35 °C using a solar pre-pilot flow plant like of Fig. 1c with a Pt/carbon-PTFE GDE filter-press cell at j = 50 and 150 mA cm<sup>-2</sup>. (b) Influence of Fe<sup>2+</sup> concentration over the TOC removal of the above homo-SPEF assay at j = 50 mA cm<sup>-2</sup>. (c) Effect of current density on TOC vs. time under the conditions of graphic (a). (d) Percentage of MCE and energy consumption per unit TOC mass at the end of these assays. (e) Influence of sulfanilamide concentration over TOC abatement for the homo-SPEF treatment with 0.50 mM Fe<sup>2+</sup> at j = 100 mA cm<sup>-2</sup> , nd (f) percentage of MCE and energy consumption per unit TOC mass at the end of these trials. Adapted from El-Ghenymy et al. (2013).

Olvera-Vargas et al. (2015) described worse performance of ranitidine upon similar conditions due to its highly recalcitrant heteroaromatic structure (see Table 1).

Almeida et al. (2011) also reported a fast degradation and good mineralization of paracetamol using a plant like of Fig. 1d with a Pt/carbon-PTFE GDE filter-press cell. A synthetic solution of 10 L with 157 mg L<sup>-1</sup> of this pharmaceutical in 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 0.33–1.17 mM Fe<sup>2+</sup> at pH = 1.38–4.36, 35 °C, and liquid flow rate = 180 L h<sup>-1</sup>, were electrolyzed at I = 3.5–8.5 A. The analysis of homo-SPEF by response surface methodology allowed establishing that the optimum performance was reached with 0.40 mM Fe<sup>2+</sup>, pH = 3.0, and I = 5.0 A. Under these conditions, paracetamol was completely destroyed in 55 min with  $k_1 = 1.04 \times 10^{-3} s^{-1}$ , whereas 80% of TOC was removed with MCE = 59%, EC<sub>TOC</sub> = 0.114 kWh (g TOC)<sup>-1</sup>, and EC = 9.1 kWh m<sup>-3</sup> in

150 min (see Table 1). The authors quantified the evolution of some intermediates and proposed the reaction sequence of Fig. SM-4 for paracetamol mineralization with 5 aromatic by-products and 7 carboxylic acids detected. It is noticeable the formation of oxamic acid from acetamide, as well as oxalic and formic acids from longer carboxylic acids. These short acids form Fe(III) complexes that are directly converted into  $CO_2$  with release of Fe<sup>2+</sup> according to reaction (7).

A different solar pre-pilot flow plant with a three-electrode FM01-LC filter-press reactor with a Pt anode and a carbon cloth|grafite felt (GF) GDE cathode connected to a CPC photoreactor has been checked by Coria et al. (2018) for the treatment of 6 L of 30–60 mg L<sup>-1</sup> of TOC of levofloxacin in 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 0.50 mM Fe<sup>2+</sup> at pH 3.0 and 35 °C. For the lower content of 30 mg L<sup>-1</sup> of TOC by applying an  $E_{cat} = -0.3$  V/SCE, the solution was completely mineralized with a smaller EC<sub>TOC</sub> =



**Fig. 5.** Effect of Fe<sup>2+</sup> concentration on the variation of (a) the percentage of color removal and (b) Congo Red concentration with time for the homo-SPEF treatment of 2.5 L of 0.260 mM of the diazo dye in pure water with 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 0.25–2.0 mM Fe<sup>2+</sup> at pH = 3.0 and 35 °C with a solar pre-pilot flow plant like of Fig. 1c with a Pt/carbon-PTFE GDE filter-press cell at j = 150 mA cm<sup>-2</sup>. Influence of diazo dye content and current density on the change of (c) the percentage of color removal and (d) dye concentration with time under the above conditions with 0.50 mM Fe<sup>2+</sup>. (e) TOC removal for the above assays and (f) percentage of MCE and energy consumption per unit TOC mass at the end of these trials. The inset panels of graphics (b) and (d) present the corresponding pseudo-first-order kinetic analysis. Adapted from Solano et al. (2015).

0.015 kWh (g TOC)<sup>-1</sup> in 180 min (see Table 1). This opens the doors to promote the study of different kinds of plants to better optimize the destruction of organics from wastewaters by homo-SPEF.

#### 4.4. Synthetic organic dyes

More attention has received the destruction of synthetic organic dyes from synthetic wastewaters. The studies with Sunset Yellow FCF (Moreira et al., 2013), food color additives E122, E124 and E129 (Thiam et al., 2015a), Acid Blue 29 (Fajardo et al., 2019), Acid Orange 7 (Paz et al., 2020), and Erythrosine B (Clematis and Panizza, 2021) have been performed with a two-electrode tank reactor. Solar pre-pilot flow plants have been used for treating Acid Yellow 36 (Ruiz et al., 2011a), Acid Red 88 and Acid Yellow 9 (Ruiz et al., 2011b), Disperse Red 1 and Disperse Yellow 3 (Salazar et al., 2011), Disperse Blue 3 (Salazar et al., 2012), Sunset Yellow FCF (Moreira et al., 2013), Direct Yellow 4 (Garcia-Segura and Brillas, 2014), Evans Blue (Antonin et al., 2015a), Congo Red (Solano et al., 2015), Allura Red AC (Thiam et al., 2015b), Acid Orange 7, Acid Red 151, and Disperse Blue 71 (Garcia-Segura and Brillas, 2016), Acid Yellow 42 (Espinoza et al., 2016), Tartrazine, Ponceau SS, and Direct Blue 71(dos Santos et al., 2018b), and Acid Blue 29 (Salazar et al., 2019).

For the removal of synthetic organic dyes, the solution discoloration is determined instead of their concentration decay (degradation) because of its difficulty to be measured by reversed-phase HPLC. However, many researchers confuse both terms despite the apparent difference between them. Discoloration involves the loss of the color by the breaking of the conjugated bonds for the dye, e.g., of azo groups with aromatics and heteroaromatics, but this usually promotes the production of colored intermediates that absorb in the same light region than the parent dye. The slower destruction of such Colored intermediates causes the enlargement of the discoloration process with respect to degradation. This fact has been clarified for the homo-SPEF treatment of some synthetic organic dyes with solar pre-pilot flow plants. Solano et al. (2015) assessed the remediation of 2.5 L of 0.065-0.520 mM of the diazo dye Congo Red with 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 0.25–2.0 mM Fe<sup>2+</sup> at pH = 3.0 and 35 °C using a plant like of Fig. 1c with a Pt/carbon-PTFE GDE filter-press cell. Fig. 5a depicts the influence of  $Fe^{2+}$  concentration on the change of the percentage of color removal with time for 0.260 mMdye at  $j = 150 \text{ mA cm}^{-2}$ . The faster discoloration occurred at 0.50 mM  $\mathrm{Fe}^{2+}$  where the color was lost in 150 min. The process was enhanced from 0.25 to 0.50 mM  ${\rm Fe}^{2+}$  due to the faster  ${\scriptstyle \bullet OH}$  production from Fenton's reaction (1), but it was progressively inhibited at higher catalyst content by the loss of this oxidant from its parasitic reaction (28). As expected, the same tendency can be observed in Fig. 5b for the abatement of dye concentration, where it disappeared more rapidly, in 90 min, with  $k_1 = 0.081 \text{ min}^{-1}$  according to the pseudo-first-order kinetics shown in its inset panel. This behavior was also found for all dyes contents between 0.065 and 0.520 mM and *j* between 50 and 150 mA cm<sup>-2</sup>, as can be deduced from Fig. 5c and d. For example, for 0.520 mM dye at  $i = 150 \text{ mA cm}^{-2}$ , total removal was attained in 120 min, whereas 94% of discoloration was achieved in 150 min due to the formation of colored by-products, as pointed out above (see Table 1). Lower percent of color removal with better performance was obtained at higher dye content, increasing with *j*. These trends were followed for the mineralization parameters given in Fig. 5e and f. The best results were found for the higher dye content of 0.520 mM dye at j = 150 mA cm<sup>-2</sup>, and 74% TOC decay with MCE = 38.8% and  $EC_{TOC} = 0.110$  kWh (g TOC)<sup>-1</sup> at 240 min can be observed. The optimization of operating variables is then required to obtain the better homo-SPEF treatment for organic removal. LC-MS analysis of electrolyzed solutions revealed 21 aromatic by-products and their ion-exclusion HPLC analysis, 5 final carboxylic acids. Fig. SM-5 shows the reaction sequence proposed for the initial degradation of Congo Red with homogeneous 'OH involving the consecutive breaking of the two azo bonds to form the aromatic derivatives detected with loss of  $NH_4^+$ ,  $NO_3^-$ , and  $SO_4^{2-}$ .

Another work of Garcia-Segura and Brillas (2016) considered the effect of the number of azo bonds over the homo-SPEF treatment of azo dyes with a plant like of Fig. 1d with a Pt/carbon-PTFE GDE filter-press cell. The azo dyes tested were the monoazo Acid Orange 7, the diazo Acid Red 151, or the triazo Disperse Blue 71 in 10 L of solutions with the same TOC content (50 mg  $L^{-1}$ ) in 0.050 M Na<sub>2</sub>SO<sub>4</sub> with 0.50 mM Fe<sup>2+</sup> at pH 3.0, 35 °C, and j = 33.2-77.6 mA cm<sup>-2</sup>. At j = 33.2 mA cm<sup>-2</sup>, Fig. SM-6a and b show less abatement of both, the percentage of color removal and the dye concentration with increasing the number of azo bonds since the dyes were more recalcitrant. Moreover, the degradation was always faster than discoloration, indicating the production of colored by-products. For example, the monoazo Acid Orange 7 disappeared of the solution in 30 min with  $k_1 = 2.6 \times 10^{-3} \text{ s}^{-1}$ , whereas 97% of color removal was reached more slowly in 60 min (see Table 1). The same behavior was observed at higher *j* with enhancement of the destruction of all azo dyes. Fig. SM-6c and d disclose that the monoazo dye was the most easily mineralized attaining 96% TOC reduction with MCE = 63%, and  $EC_{TOC} = 0.100 \text{ kWh} (g \text{ TOC})^{-1}$  in only 180 min.

The above findings confirm that the oxidation power of homo-SPEF depend on the nature of the synthetic organic pollutant and its byproducts. This fact can also be concluded from the data collected in Table 1 for other dyes treated with solar pre-pilot flow plants under similar conditions. Thus, high TOC removals of 98% with MCE = 20%have been reported by Ruiz et al. (2011b) for 2.5 L of 50 mg  $L^{-1}$  of the azo dyes Acid Red 88 and Acid Yellow 9 with a BDD anode after 360 min at  $j = 50 \text{ mA cm}^{-2}$ , but with high EC<sub>TOC</sub> values of 0.48 and 0.38 kWh (g TOC)<sup>-1</sup> due to their recalcitrance. In the case of 200 mg L<sup>-1</sup> of Disperse Blue 3, Salazar et al. (2012) described total discoloration of 2.5 L solutions with a BDD anode after 150 min at i = 50 mA cm<sup>-2</sup>, whereas 96% of TOC was reduced for 0.50 mM  $Fe^{2+}$  in 240 min (see Table 1). The use of 0.50 mM  ${\rm Fe}^{2+} + 0.10$  mM  ${\rm Cu}^{2+}$  yielded a slightly larger mineralization with 98% TOC abatement due to the more rapid oxidation of the final Cu(II)-carboxylate complexes with BDD(\*OH) than the competitive photolysis of their Fe(III) ones. An acceptable  $EC_{TOC} = 0.18$  kWh (g TOC)<sup>-1</sup> was determined for both catalysts. The study performed with Allura Red AC by Thiam et al. (2015b) also pointed out to the decay of more amount of dye at its higher concentration, although linked to a smaller degradation, because more oxidant homogeneous 'OH was formed from the deceleration of the parasitic reactions (26)-(28). For 2.5 L of 230 mg L<sup>-1</sup> of this dye with a Pt anode at j = 50 mA cm<sup>-2</sup>, a rapid discoloration was found in 20 min along with 92% of TOC abatement with MCE = 94% and lower  $EC_{TOC} = 0.12$  kWh (g TOC)<sup>-1</sup> than the above works (see Table 1). In contrast, operating at a double *i* of  $100 \text{ mA cm}^{-2}$ , TOC reduction was weakly improved (97%) but MCE was drastically reduced to 45% and EC<sub>TOC</sub> largely increased to 0.31 kWh (g TOC)<sup>-1</sup>. This loss of performance of homo-SPEF with *j* indicates that it should be chosen with the maximum value to offer a minimum electrolysis time for enough TOC removal related to a high % MCE and low EC<sub>TOC</sub>. In this way, Salazar et al. (2019) found 100% of color removal, 100% of TOC decay, and a very low  $EC_{TOC} = 0.057$  kWh (g TOC)<sup>-1</sup> in 300 min for the homo-SPEF process of 10 L of 233 mg  $L^{-1}$  of the azo dye Acid Blue 29 with a DSA anode at a lower  $j = 25 \text{ mA cm}^{-2}$  (see Table 1). It is noteworthy that all the papers related to the homo-SPEF with solar pre-pilot flow plants described the detection of aromatic intermediates and final carboxylic acid, with the proposal of reaction sequences for the removal of the dyes such as shown in Fig. SM-5 for Congo Red.

Potent homo-SPEF processes have been reported for the discoloration and mineralization of some synthetic organic dyes in synthetic solutions using two-electrode tank reactors like of Fig. 1a with a carbon-PTFE GDE cathode. Fajardo et al. (2019) explored the influence of different anodes on the treatment of 130 mL of 118 mg L<sup>-1</sup> of Acid Blue 29 with 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 0.50 mM Fe<sup>2+</sup>at pH 3.0, 35 °C, and j =33.3 mA cm<sup>-2</sup> for 360 min. They confirmed that the H<sub>2</sub>O<sub>2</sub> accumulated in the medium decreased in the order: EO-H<sub>2</sub>O<sub>2</sub> > homo-EF > homo-SPEF for any anode as result of its faster destruction with more quantity of initial and regenerated Fe<sup>2+</sup>, thus explaining the increasing discoloration and COD decay in the opposite sequence (see Table 1). They also found a growing oxidation power of the process for Ti|RuO<sub>2</sub> < Pt < BDD. The latter anode yielded excellent results with  $k_{\rm dis} = 0.153$  min<sup>-1</sup>, total COD removal, ACE = 22.1%, and EC<sub>COD</sub> = 0.103 kWh (g COD)<sup>-1</sup> (see Table 1). However, a lower EC<sub>COD</sub> = 0.087 kWh (g COD)<sup>-1</sup> was determined for the less potent Ti|RuO<sub>2</sub> due to its lower  $E_{\rm cell}$  value.

Interesting comparative homo-PEF and homo-SPEF treatments have been studied by Paz et al. (2020) and Clematis and Panizza (2021). The first authors reported a similar oxidation ability of homo-PEF with a UVC light and simulated homo-SPEF with Xe lamp giving rise to  $k_{dis} =$ 0.041–0.044 min<sup>-1</sup> as well as 90% TOC abatement with MCE = 7.5%after 360 min of electrolysis at i = 150 mA cm<sup>-2</sup> of 350 mL of 0.260 mM of the azo dye Acid Orange 7 with  $0.10 \text{ M K}_2\text{SO}_4$  and  $0.50 \text{ mM Fe}^{2+}$  at pH 3.0 and 20 °C filling a BDD (non-stoichiometric) WO<sub>2'72</sub>/C GDE tank reactor like of Fig. 1a (see Table 1). The additional photolytic destruction of organics by UVC light can explain the similar performance of both processes. The second authors presented a more detailed study over the dye Erythrosine B (see its chemical structure in Fig. SM-7a) with a BDD/CF cell like of Fig. 1b illuminated with 100 W UVA light or direct sunlight. Fig. SM-7b depicts the slower discoloration achieved by homo-EF, which needed 50 min to make colorless 300 mL of 100 mg  $L^{-1}$ of dye in pure water with 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 0.10 mM Fe<sup>2+</sup> at pH 3.0 and  $i = 20 \text{ mA cm}^{-2}$ . This time was shorted to 20 min with homo-SPEF, the same time as required for homo-PEF with 100 W UVA light, although it was enlarged to 35 min for homo-PEF with 25 W UVA light. Fig. SM-7c and d highlight a similar normalized COD abatement and % ACE, respectively, for homo-PEF with 100 UVA light and homo-SPEF, attaining total COD removal with ACE = 13-14% in 120 min. Moreover, the change of EC with the percentage of COD removal depicted in Fig. SM-7e shows a better performance for homo-PEF with 100 UVA light, requiring about 21 kWh m<sup>-3</sup> for a large mineralization as in homo-SPEF. However, if the power of the UVA lamp was taken into account the EC value of homo-PEF rose up to 556 kWh m<sup>-3</sup>(see Table 1), i.e., the energy consumption grew 26.5-fold to equilibrate the oxidation power of homo-SPEF. This justify the preferred use of homo-SPEF with respect homo-PEF for the remediation of wastewaters polluted with organic pollutants.

#### 4.5. Real wastewaters

The homo-SPEF process has been explored to remove organic pollutants from complex real wastewaters. While a washing machine effluent of jeans has been tested in a two-electrode tank reactor (dos Santos et al., 2018a), a sanitary landfill leachate (Moreira et al., 2016), aa slaughterhouse effluent (Páramo-Vargas et al., 2016), and greywater (dos Santos et al., 2023) have been treated with a solar pre-pilot flow plant. An interesting study has been reported for an elderberry agro-industrial wastewater with a solar pilot flow plant (Ferreira et al., 2020).

The treatment of a washing machine effluent of jeans was performed with a BDD/carbon-PTFE GDE tank reactor like of Fig. 1a filled with 100 mL of effluent with 315 mg L<sup>-1</sup> of TOC after adding 0.50 mM Fe<sup>2+</sup> and operating at pH 3.0, 35 °C, and j = 16.6-100 mA cm<sup>-2</sup> (dos Santos et al., 2018a). It was confirmed an enhancement of the discoloration and mineralization with raising j owing to the greater generation of homogeneous °OH by the acceleration of H<sub>2</sub>O<sub>2</sub> formation. After 180 min at j =66.6 mA cm<sup>-2</sup>, the percentage of color removal reached a 95% by homo-EF and 100% by homo-SPEF, as expected if the main oxidant was the homogeneous °OH formed from Fenton's reaction (1) with small induction by photo-Fenton reaction (6). The effect of sunlight to photolyze Fe(III) species was well observed on TOC decay that only attained a 68% by homo-EF increasing up to a 97% by homo-SPEF (see Table 1). These excellent results encourage the remediation of real wastewater by homo-SPEF to obtain final effluents that could be reused at least for agriculture purposes.

A recent study of dos Santos et al. (2023) was centered in the

treatment of greywater with a solar pre-pilot flow plant like of Fig. 1d with a Pt/carbon-PTFE GDE filter-press cell. Response surface methodology was applied to optimize the homo-SPEF process of 10 L of this effluent with 80.8–100.6 mg L<sup>-1</sup> of TOC after adding 20 mg L<sup>-1</sup> of TOC of dodecyl-benzene sulfonic acid as surfactant. The best mineralization conditions of 55% TOC removal with  $EC_{TOC} = 0.32$  kWh (g TOC)<sup>-1</sup> were obtained for 5 mg L<sup>-1</sup> Fe<sup>2+</sup>, pH 3.0, and j = 77.5 mA cm<sup>-2</sup> lasting 240 min (see Table 1). In contrast to this poor TOC decay, the authors described a 60% reduction of the acute toxicity to *Artemia salina*, suggesting that a biological post-treatment could be used to more largely purify the resulting wastewater.

Solar flow plants like of Fig. 1d but with commercial MicroFlowCell reactors with a carbon-PTFE GDE cathode have been checked for the homo-SPEF treatment of real wastewaters. Moreira et al. (2016) explored the process for a sanitary landfill leachate with a BDD or Pt anode using Fe(III)-oxalate complexes as catalyst to produce Fe<sup>2+</sup> from the photodecarboxylation reaction (7) at pH > 3. The assays were carried out with 1.19 L of effluent with  $337-403 \text{ mg L}^{-1}$  TOC in the presence of 20–80 mg  $L^{-1}$  of Fe<sup>2+</sup> or 1:3 Fe(III)-oxalate complex at pH 2.8–4.0, 15–40 °C, and  $i = 200 \text{ mA cm}^{-2}$  lasting 300 min. The mineralization process was practically not affected operating between 20 and 40 °C. The best conditions for homo-SPEF were obtained with 60 mg  $L^{-1}$  $Fe^{2+}$  at pH = 2.8, reaching a TOC abatement of 64% with Pt < 78% with BDD. For the best BDD anode and using the same  $Fe^{2+}$  content as 1:3 [Fe (III)]/[oxalate], the TOC removal varied with pH as 67% at pH 3.0, 83% at pH 3.5, and 75% at pH 4.0 (see Table 1). The Fe(III)-oxalate complex allowed a little improvement of homo-SPEF at pH > 3, which does not seem significant enough for practical application.

Ferreira et al. (2020) coupled the MicroFlowCell reactor with a BDD anode to a solar CPC photoreactor in a solar pilot flow plant with the same components as Fig. 1d upon recirculation of 75 L of an elderberry agro-industrial wastewater with 160–210 mg L<sup>-1</sup> TOC with 20 mg L<sup>-1</sup> Fe<sup>2+</sup> at pH 3.0, liquid flow rate = 300 L h<sup>-1</sup>, and *j* = 150 mA cm<sup>-2</sup> during 240 min. The large recalcitrance of this wastewater only allowed a 25% of TOC abatement with EC = 1.2 kWh m<sup>-3</sup>, but with an enhancement of biodegradability for further biological treatment. These authors also remediate more weakly the wastewater by homo-SPF with the same plant and by an ozonation plant at pH = 11 and determined that the total operation cost increased as:  $0.40 \in m^{-3}$  for homo-SPEF <0.80  $\in m^{-3}$  for homo-SPEF <1.86  $\in m^{-3}$  for ozonation (see Table 1). The homo-SPEF process can then be envisaged as a promising technology with greater viability than other AOPs.

# 4.6. Homogeneous solar photoelectro-Fenton-like

Based on the generation of homogeneous <sup>•</sup>OH from the reaction (31) between HClO and Fe<sup>2+</sup>, Murrieta et al. (2020) and Manrique-Losada et al. (2022) developed a novel homo-SPEF-like process that was checked in an electrolytic system without  $O_2$  or air sparging to avoid the Fenton process. In this treatment, the wastewater with Cl<sup>-</sup> is electrolyzed for the continuous production of HClO via reactions (29) and (30) without H<sub>2</sub>O<sub>2</sub> generation and so, homogeneous <sup>•</sup>OH is formed upon addition of Fe<sup>2+</sup> from reaction (31) and by the photolytic reaction (6). Organics are then mainly oxidized by this radical and HClO. The oxidation power of this homo-SPEF-like process was maintained thanks to the regeneration of Fe<sup>2+</sup> at the cathode from reaction (5).

$$Fe^{2+} + HClO \rightarrow Fe^{3+} + {}^{\bullet}OH + Cl^{-}$$
(31)

As an example, Murrieta et al. (2020) used a solar pre-pilot plant flow with an FM01-LC reactor containing a DSA anode and a stainless-steel cathode connected to a CPC photoreactor illuminated with a 15 W UVA light for homo-PEF-like or direct sunlight for homo-SPEF-like. The assays were made with 6 L of synthetic solutions of 0.096–0.385 mM of the azo dye Acid Red 1 with 0.025 M Na<sub>2</sub>SO<sub>4</sub> + 0.035 M NaCl and 0–0.50 mM Fe<sup>2+</sup> at pH 3.0, liquid flow rate = 3.2 L min<sup>-1</sup>, and j = 5-20 mA cm<sup>-2</sup>. Higher dye content and j caused faster discoloration up to 0.40 mM Fe<sup>2+</sup>, and the percentage of color removal decreased in the order: homo-EF-like > EO-HClO > homo-PEF-like > homo-SPEF-like. In EO-HClO, M(°OH) formed from reaction (4) and generated HClO were the main oxidants, which was slightly upgraded by homo-EF-like due to the extra formation of homogeneous °OH by reaction (31). The negative influence of UVA light in homo-PEF-like can be ascribed to the enhancement of Fe<sup>2+</sup> regeneration from photo-Fenton reaction (6) accelerating the homogeneous °OH destruction by its parasitic reaction with this ion via reaction (28). The higher intensity of sunlight reinforced these negative trends yielding slower discoloration with homo-SPEF-like. In contrast, homo-SPEF-like gave the fastest COD removal of 84% after 480 min, followed by 79% for homo-PEF-like. Thus, the homo-SPEF-like treatment presented a higher ACE = 25% with a lower EC<sub>COD</sub> = 0.076 kWh (g COD)<sup>-1</sup>. This behavior can be

related to the quick photodecarboxylation of the final Fe (III)-carboxylated complexes by reaction (7), as confirmed from the detection of recalcitrant maleic and acetic acids. These positive findings open the doors to further research for a better knowledge of the characteristics of homo-SPEF-like in chloride matrices.

# 5. Heterogeneous solar photoelectro-Fenton of organics removal

Only two works have used hetero-SPEF treatments to remove synthetic organic dyes with iron solid catalysts using two-electrode tank reactors like of Fig. 1a, as can be seen in Table 1. Pinheiro et al. (2020) used a cell with a Pt anode and a GDE cathode under UVA light to remediate 350 mL of 100 mg L<sup>-1</sup> of the azo dye Sunset Yellow in 0.10 M Na<sub>2</sub>SO<sub>4</sub> or 0.13 M NaCl with 0.25 g of Fe<sub>3</sub>O<sub>4</sub> as catalyst at pH 3.0 and 20 °C for hetero-PEF at I = 100 mA during 90 min Fe<sub>3</sub>O<sub>4</sub> gave a low



**Fig. 6.** (a) Percentage of color removal vs. time, (b) pseudo-first-order kinetic analysis for discoloration, and (c) percentage of TOC removal and MCE at 360 min for different treatments of 130 mL of 0.150 mM of the diazo dye Ponceau SS in pure water with 0.050 M Na<sub>2</sub>SO<sub>4</sub> and 0.018 mM Fe<sup>2+</sup> (homo-EF) or 1.0 g L<sup>-1</sup> sodium vermiculite as hetero-catalyst at pH = 3.0 and 25 °C using a BDD/carbon-PTFE GDE tank reactor like of Fig. 1a by applying a j = 33.3 mA cm<sup>-2</sup>. Effect of (d) vermiculite concentration, (e) current density, and (f) dye concentration on the percentage of TOC removal and MCE at 360 min for the hetero-PEF process with a 6 W UVA light under the above conditions. Adapted from dos Santos et al. (2020b).

amount of heterogeneous •OH from the heterogeneous Fenton's reaction (9) to remove the dye in front of the high amount of HClO formed from reactions (29) and (30). This explained that total discoloration was obtained after 15 min of hetero-EF and hetero-SPEF in 0.13 M NaCl, being much slower in 0.10 M Na<sub>2</sub>SO<sub>4</sub>, with 55% and 78% color removal, respectively (see Table 1). In contrast, similar TOC decay and % MCE and EC<sub>TOC</sub> values after 90 min of hetero-SPEF in both media were determined, suggesting an effective generation of heterogeneous •OH from Fe<sub>3</sub>O<sub>4</sub> to non-selective remove the dye and its by-products. The attack of active chlorine over the dye should be much more selective, enhancing discoloration. A good reusability of the catalyst after 8 successive cycles by hetero-PEF with Na<sub>2</sub>SO<sub>4</sub> was obtained indicating its practical application.

On the other hand, dos Santos et al. (2020b) checked the treatment of 130 mL of 0.075-0.225 mM of the diazo dve Ponceau SS in 0.050 M Na<sub>2</sub>SO<sub>4</sub> at pH 3.0 and 25 °C with a BDD/carbon-PTFE GDE cell, injecting 400 mL of air to the cathode, at j = 16.6-66.6 mA cm<sup>-2</sup>. The catalysts were 0.018 mM  $\text{Fe}^{2+}$  for homo-EF or 0.25–2.0 g L<sup>-1</sup> of the mineral sodium vermiculite for hetero-EF, hetero-PEF, and hetero-SPEF. A 6 W UVA light or direct sunlight was used to irradiate the solution. Fig. 6a presents the best percentage of color removal found for 0.150 mM dye, 1.0 g L<sup>-1</sup> of sodium vermiculite, and i = 33.3 mA cm<sup>-2</sup>. This parameter increased in the order: EO-H<sub>2</sub>O<sub>2</sub> < homo-EF<hetero-EF < hetero-PEF < hetero-SPEF. This means that the heterogeneous 'OH formed at the sodium vermiculite surface had greater oxidation power than homogeneous <sup>•</sup>OH proceeding from Fe<sup>2+</sup>. Total loss of color with  $k_{dis} = 0.914$ min<sup>-1</sup> was achieved after 300 min of hetero-SPEF, as can be seen in Fig. 6b and Table 1. This process also yielded faster TOC removal of 84.1%, with the higher MCE = 6.7% at 360 min (see Fig. 6c). Fig. 6d–f depict the effect of vermiculite concentration, *j*, and dye concentration on the percentage of TOC decay and % MCE at 360 min, respectively, showing the same superiority as in discoloration. The partial mineralization achieved by hetero-SPEF can be associated with the incomplete removal of the final carboxylic acids since their complexes with the surface  $\equiv$ Fe(III) species were more slowly photodecarboxylated than those with soluble Fe(III), as confirmed by the presence of large amounts of tartronic, malic, oxamic, and oxalic acids in the final solution of hetero-SPEF.

Further studies should consider the behavior of more hetero-SPEF systems with other solid catalysts and functionalized cathodes aiming to operate with near neutral polluted wastewaters at least in solar prepilot flow plants. This approach should be attractive to confirm the feasible applicability of these systems at industrial level.

#### 6. Combined processes

Hybrid treatments of homo-SPEF with SPC (Garza-Campos et al., 2014, 2016) or SPEC (Peng et al., 2016; Hernández et al., 2018; Xu et al., 2021) have been proposed. Sequential processes have been developed with the consecutive coupling of aerobic oxidation (Moreira et al., 2015a), aerobic oxidation-coagulation (Moreira et al., 2015b), anaerobic digestion (Vidal et al., 2016, 2019), or nanofiltration with homo-SPEF (Salmerón et al., 2021; Deemter et al., 2022).

Hybrid SPEF/SPC processes have been described for the removal of salicylic acid in synthetic wastewater using a BDD/BDD tank reactor with TiO<sub>2</sub>|glass spheres in suspension (Garza-Campos et al., 2014) and the solar pre-pilot flow plant schematized in Fig. SM-8a ((Garza-Campos et al., 2016). The Pt/carbon-PTFE GED filter-press cell was connected to a solar planar photoreactor for homo-SPEF followed by another planar photoreactor filled with TiO<sub>2</sub>|glass spheres for hetero-SPC. The semiconductor TiO<sub>2</sub> absorbed the UV photons of sunlight to photoexcite an electron  $e_{CB}^-$  from its valence band (VB) to its conduction band (CB) with the generation of a positive hole  $h_{VB}^+$  in the VB following reaction (32). The separated  $h_{VB}^+$  can then directly oxidize the adsorbed organics or more probably, react with H<sub>2</sub>O to form heterogeneous °OH from reaction (33) for their destruction. However, the oxidative efficiency of  $h_{VB}^+$ 

is low because the  $e_{CB}^-/h_{VB}^+$  pair is rapidly recombined from reaction (34) that minimizes the charge separation.

Semiconductor 
$$+ hv \rightarrow e_{CB}^- + h_{VB}^+$$
 (32)

$$h_{VB}^{+} + H_{2}O \rightarrow {}^{\bullet}OH + H^{+}$$
(33)

$$e_{CB}^- + h_{VB}^+ \rightarrow \text{Semiconductor} + \text{heat}$$
 (34)

Fig. SM-8b depicts the comparative normalized salicylic acid decay for different processes of 3.0 L of 165 mg  $L^{-1}$  pollutant with 0.050 mM  $Na_2SO_4$  at pH = 3.0 and 35 °C. A very poor degradation can be observed by hetero-SPC, whereas total pollutant abatement in 60 min occurred by homo-EF, homo-SPEF, and hybrid SPEF/SPC after addition of 0.50 mM  $Fe^{2+}$  upon a j = 50 mA cm<sup>-2</sup>. This indicates that homogeneous •OH generated from Fenton's reaction (1) governed the oxidation in the three later methods. A different behavior can be deduced from Fig. SM-8c, since TOC was more quickly reduced in the sequence: hetero-SPC <homo-EF < homo-SPEF < SPEF/SPC. The latter method favored that final Fe(III)-carboxylate complexes were more rapidly formed and photolyzed. Fig. SM-8d and e confirm the superior TOC removal of SPEF/SPEC over homo-SPEF in the *j* interval of 50–150 mA cm<sup>-2</sup>, and the expected greater mineralization, lower % MCE, and higher EC<sub>TOC</sub> found for the hybrid process with increasing *j*. The best results were obtained at  $j = 50 \text{ mA cm}^{-2}$  with 66% TOC abatement, MCE = 29%, and a relatively high  $EC_{TOC} = 0.249 \text{ kWh} (\text{g TOC})^{-1}$ .

SPEC offers to test a compact system with a cathode coupled to a semiconductor photoanode that is irradiated by sunlight to produce  $e_{CB}^{-}$  $h_{VB}^+$  pairs from reaction (32). The photoexcited  $e_{CB}^-$  can then circulate to the cathode though an external electric circuit largely diminishing its recombination with  $h_{VB}^+$  via reaction (34), This enhancement of charges separation largely favors the oxidation of organics at the photoanode surface with  $h_{VB}^+$  or with heterogeneous <sup>•</sup>OH produced by reaction (33), much more effective than M(°OH) formed from reaction (4). When a carbonaceous cathode is used to electrogenerate H<sub>2</sub>O<sub>2</sub> from reaction (2) and the wastewater with catalytic  $Fe^{2+}$  is illuminated with sunlight as well, the potent hybrid SPEF/SPEC is applied for its remediation. For this process, it is remarkable the recent work of Xu et al. (2021) who used a three-electrode cell with a photoanode of BiMoVO<sub>4</sub> (photoexcited with visible light) coating a transparent fluorine tin oxide (FTO) and a CF cathode to assess the removal of the herbicide simazine. The tank reactor was filled with 50 mL of 0.025 mM (2 mg  $L^{-1}$  of TOC) of this pollutant in 0.050 M K<sub>2</sub>SO<sub>4</sub> with 0.20 mM Fe<sup>2+</sup> at pH 3.0 and the treatments ran by applying an  $E_{cat} = -2.5 \text{ V/Ag}|\text{AgCl upon illumination}$ with a solar simulator of 1000 W cm<sup>-2</sup>. After 45 s of electrolysis, the simazine degradation grew as: 4% for SPEC ( $k_1 = 0.05 \text{ min}^{-1}$ ) < 89% for homo-SPEF  $(k_1 = 3.04 \text{ min}^{-1}) < 100\%$  for SPEF/SPEC  $(k_1 = 4.82)$ min<sup>-1</sup>). The hybrid process then presented a synergy between the individual ones. Analogously, total TOC removal was achieved in 120 min for SPEF/SPEC, much higher than the sum of the mineralization attained by SPEC (18%) and homo-SPEF (50%). This can be related to the quicker formation of Fe(III) complexes from the combined oxidation action of homogeneous <sup>•</sup>OH from homo-SPEF and heterogeneous <sup>•</sup>OH from SPEC, which are more quickly destroyed by sunlight. For this hybrid process, solar flow plants should be designed to show its viability for organic destruction in practice.

Several complex real wastewaters have been decontaminated by a biological pre-treatment followed by homo-SPEF post-treatment. The biological pre-treatment significantly reduced the biodegradable organic load of the wastewater and the sequential homo-SPEF served to complete its decontamination aiming to yield a reusable effluent. As an example, the treatment of a slaughterhouse wastewater by a sequential anaerobic digestion-homo-SPEF was first described by Vidal et al. (2016) and further, more extensively studied by Vidal et al. (2019). Fig. SM-9a schematizes the overall sequential setup consisting of an upflow anaerobic sludge blanket (UASB) reactor for anaerobic digestion and the subsequent pre-pilot flow plant equipped with a filter-press cell

with a Ti|Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> anode and a carbon-PTFE GDE cathode connected to a solar CPC photoreactor. The USB reactor was feed with an effluent of pH = 6.3–7.8 at organic load rates (OLR) of 3.94 and 8.15 g COD  $L^{-1} d^{-1}$ and hydraulic retention time (HRT) of 10 h. The influents then contained 1570 and 3450 mg  $L^{-1}$  of COD, which yielded effluents with 195 mg  $L^{-1}$ (86.6% reduction) and 867 mg  $L^{-1}$  (74.5% reduction) of COD, respectively. Fig. SM-9b and c highlight that the COD of resulting effluents was slightly more rapidly destroyed by homo-SPEF at i = 25 mA cm<sup>-2</sup> than i $= 10 \text{ mA cm}^{-2}$ , but with much higher energy consumption. For this reason, it was preferable the treatments with the lower  $j = 10 \text{ mA cm}^{-2}$ , for which 96.3% and 91.0% of total COD abatement with EC = 45.5 and 46.6 kWh m<sup>-3</sup> were found, respectively. The sequential system presented a higher decontamination power with lower organic power. The authors reported that this sequential process yielded good overall COD removal as compared to treatments with other AOPs. However, they do not determine the toxicity of the final wastewater, a knowledge necessary to establish the improvement in toxicity.

Recently, a sequential nanofiltration-homo-SPEF process has been examined by Salmerón et al. (2021) and Deemter et al. (2022) for the treatment of secondary WWTP effluents with high Cl<sup>-</sup> contents between 1100 and 2000 mg  $L^{-1}$  and addition of microcontaminants such as pentachlorophenol, terbutryn, chlorfenvinphos and diclofenac at initial concentrations of 500 and 100  $\mu$ g L<sup>-1,</sup> each. The nanofiltration ensured the reduction of the total volume of the effluent with increase of water salinity that favors the photoelectrochemical treatment. The assays were made with pilot plants for both sequential treatments. The homo-SPEF process was made with an Electro MP Cell with a BDD/carbon-PTFE GDE filter-press cell and a solar CPC photoreactor and 75 L of the nanofiltration retentate after addition of EDDS as chelating agent of Fe<sup>3+</sup> to work at pH near 8 were electrolyzed at j = 74 mA cm<sup>-2</sup>. The sequential treatment yielded 96% of removal of all micropollutants after the consumption of a low  $EC = 5.9 \text{ kWh m}^{-3}$  that validated the efficiency and cost-effectiveness of it for industrial application.

#### 7. Conclusions and prospects

It has been shown that the homo-SPEF process with soluble  $Fe^{2+}$  as catalyst under sunlight irradiation is more powerful and cost-efficient for organics removal than homo-PEF with UVA light and other nonphoto-assisted treatments like homo-EF and EO-H2O2. In homo-EF, H<sub>2</sub>O<sub>2</sub> is formed at the cathode and the main oxidants are the homogeneous <sup>•</sup>OH from Fenton's reaction (1) and the heterogeneous M(<sup>•</sup>OH) produced via reaction (4). Other weaker ROS like HO<sub>2</sub>,  $O_2^{\bullet-}$ , and  ${}^1O_2$  can also act as oxidants of organic pollutants. Homo-PEF and homo-SPEF are more potent than homo-EF due to the positive oxidative action of irradiated light originating more homogeneous 'OH from photo-Fenton reaction (6) alongside the fast photolytic destruction of Fe(III) complexes like of the final carboxylic acids via reaction (7). The use of free and renewable sunlight as energy source with higher UV intensity than expensive artificial UVA lamps explains the higher effectiveness and low energy cost of homo-SPEF. This has been well-proven in the paper of Clematis and Panizza (2021).

An important drawback of homo-SPEF is its best performance at pH = 3.0, i.e., the optimum value for homogeneous  $^{\circ}$ OH formation from Fenton's reaction (1) and photo-Fenton reaction (6) without significant Fe(OH)<sub>3</sub> precipitation. Positive attempts have been made with Fe(III)-EDDS complex as catalyst to obtain a good mineralization at neutral pH. However, this procedure is not useful in practice because more organic load is added to the wastewater making more difficult its remediation. It seems more reasonable to check in the next future the behavior of new hetero-SPEF treatments with functionalized cathodes aiming to destroy the organics with lower pH-dependent reactions and photoreactions at the cathode surface. Another relevant drawback of homo-SPEF is that it can only be applied during the daily hours of sun, being ineffective in the darkness. To solve this, it can be proposed the application of a mixed flow system using homo-SPEF in the sun hours of

a day and homo-PEF providing enough UVA light the rest of it. A system of solar photovoltaic cells could be used to accumulate electrical energy in sized batteries to power the electrochemical reactor and the UVA lamps. This arrangement may operate all the day without energy cost to remove organic pollutants not only by homo-SPEF, but also by hetero-SPEF. Current studies have already described the excellent coupling of a solar photovoltaic cell with a solar tank reactor (Peng et al., 2016) and the electrochemical cell of a pre-pilot flow plant (Garcia-Segura and Brillas, 2014). These works demonstrate that the pollutant decay and mineralization were similar upon the application of a current from a power source or a photovoltaic cell, then being the latter more cost-effective. The construction and check of the above mixed plant at least at pre-pilot flow scale then seems feasible and could serve to show the relevant interest of this EAOP at industrial level.

It has been found a rapid destruction of aromatic pollutants including industrial chemicals, herbicides, pharmaceuticals, and synthetic organic dyes in synthetic solutions by homo-SÊF. Their mineralization became more difficult due to the formation of final Fe(III)-carboxylate complexes that are slowly and completely photolyzed by sunlight. Solar prepilot flow plants gave more practical information than tank reactors, particularly by the energetic determination of EC<sub>TOC</sub> or EC<sub>COD</sub>. Higher oxidation power was found with a BDD anode than Pt and DSA ones, as result of the generation of more quantity of reactive BDD(°OH). Carbon-PTFE GDE cathodes yielded a larger H<sub>2</sub>O<sub>2</sub> production than CF and ACF ones. In the former case, about 0.50 mM Fe<sup>2+</sup> was found as optimum catalytic concentration, whereas 0.10 and 1.0 mM Fe<sup>2+</sup> were used for the two latter cathodes, respectively. Low Fe<sup>2+</sup> content was then added to the solution because it can be regenerated from reaction (5).  $\mathrm{Fe}^{2+}$  and Cu<sup>2+</sup> used as cocatalysts enhanced the mineralization of organics attained with Fe<sup>2+</sup> alone since the final Cu(II)-carboxylate complexes formed were oxidized more rapidly with M(•OH) than photolyzed the parallel and competitive Fe(III)-carboxylate species. Larger performance was always found operating at higher pollutant concentration and lower j owing to the greeater decrease in rate of the parasitic reactions (26)-(28) of homogeneous 'OH. In this way, it is better to remediate the wastewaters when produced, where the organic pollutants are more concentrated.

The electrolyte composition is a notable variable of homo-SPEF. In synthetic chloride media, active chlorine (HClO) was largely formed that can attack the parent pollutant usually more quickly than homogeneous •OH and M(•OH). However, more recalcitrant chloroderivatives are produced that persist long time, thus enlarging the mineralization process respect to sulfate matrices. This behavior occurs in the treatment of real wastewaters, although excellent results have been reported for the remediation of a washing machine effluent of jeans, sanitary landfill leachate, and greywater. An interesting study on an elderberry agro-industrial wastewater in pilot flow plants revealed the lower total operation cost of homo-SPEF than homo-SPF and ozonation. Techno-economic studies with other wastewaters are required in the next future to show the benefits of homo-SPEF in front of other technologies for its application at industrial level.

A homo-SPEF-like process with HClO generation in the presence of Fe<sup>2+</sup> for the treatment of Acid Red 1 solutions revealed a good mineralization of 84% with ACE = 25% and EC<sub>COD</sub> of only 0.076 kWh (g TOC)<sup>-1</sup>. This opens the doors to further research for a better knowledge of the characteristics of such homo-SPEF-like in chloride matrices. Few papers have reported the performance of hetero-SPEF treatments. Excellent results have been obtained using Fe<sub>3</sub>O<sub>4</sub> and sodium vermiculite as solid catalysts at pH = 3.0 to avoid the loss of catalyst as Fe(OH)<sub>3</sub> precipitation. Nevertheless, it seems more reasonable to extend the works on hetero-SPEF to functionalized cathodes aiming to operate at neutral pH of greater industrial interest.

Hybrid processes of homo-SPEF with SPC and SPEC have shown a synergistic effect respect their individual ones, a fact that should be more extensively explored in future research. Sequential homo-SPEF after anaerobic digestion or nanofiltration of real effluents have also

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achieved a large removal of their organic load. This merits more research efforts to better analyze such processes, particularly for the treatment of urban WWTPs effluents.

#### Author contribution statement

Enric Brillas is the only author of this article.

## Declaration of competing interest

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

# Data availability

Data will be made available on request.

# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.138532.

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