On the selection of the anode material for the electrochemical removal of methylparaben from different aqueous media

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Abstract

Parabens are widely used industrial preservatives, routinely found in wastewater along with major inorganic ions like sulfate and chloride. This work investigates the oxidation ability of three electrochemical processes in tank reactors equipped with an air-diffusion cathode to electrogenerate H_2O_2 on site, namely electro-oxidation (EO-H_2O_2), electro-Fenton (EF) and UVA photoelectro-Fenton (PEF), to degrade aqueous solutions of methylparaben (MeP) at pH 3.0. Their performance using boron-doped diamond (BDD), Pt or two kinds of dimensionally stable anodes (DSA®) has been compared from the analysis of mineralization profiles and decay kinetics in the presence of sulfate and/or chloride ions. The use of BDD ensured the overall mineralization in all three processes according to the sequence: PEF > EF > EO-H_2O_2, thanks to the contribution of BDD($^{\bullet}$OH), $^{\bullet}$OH and UVA light. Pt and DSA® became an interesting alternative in PEF, with slower organic matter removal but similar final mineralization percentages, being much less powerful than BDD in EO-H_2O_2. The presence of Cl^- was beneficial in the latter process, due to the formation of active chlorine as an additional oxidant that caused a much faster decay of MeP. Conversely, it became significantly detrimental in EF due to the partial destruction of H_2O_2 and $^{\bullet}$OH in the bulk by active chlorine and Cl^-, respectively. The oxidation power of PEF was so high that similar fast, complex decay kinetics was found in all media regardless of the anode, although the mineralization was decelerated owing to the accumulation of chlorinated by-products. GC-MS and HPLC analysis allowed the identification of up to seven aromatic MeP derivatives in sulfate + chloride mixtures, including three non-chlorinated compounds also found in pure sulfate medium. These molecules were gradually transformed into oxalic acid, along with four chlorinated aliphatic carboxylic acids in Cl^--containing media.

Keywords: BDD; DSA®; Methylparaben; Pt; Wastewater treatment

1. Introduction

Nowadays, it is quite well established that the endocrine-disrupting chemicals cause adverse effects on the endocrine system of living beings, since they disrupt the physiological function of endogenous hormones [1,2]. Several industrial additives suspect of acting as endocrine disruptors are massively used in food and beverage commodities as well as in personal care products. Among them, parabens are ubiquitous in cosmetics and toiletries like tooth pastes, deodorants, beauty creams, solar filters, and bath gels [3-5].

Parabens are esters of *p*-hydroxybenzoic acid (*p*-HBA) routinely added as industrial preservatives due to their antibacterial and antifungal properties. They are characterized by their low volatility and high stability, liposolubility and hydrophilicity, which together promote their facile absorption as well as their efficient dispersion and bioaccumulation in the environment [6]. Therefore, concerns have been raised on safety of parabens and its metabolites owing to their environmental effects [7] as well as their role as endocrine disruptors and their association with human cancers and allergic contact dermatitis [8-12], although this is still controversial [13]. As a result, they are banned or restricted, as regulated by the Cosmetic Directive announced in the Official Journal of the European Union [14], and paraben-free labels are popping up on beauty products recently.

Due to their widespread use, parabens have been routinely found in water, soil, sediment and fish [15]. In particular, they are found in samples from wastewater treatment facilities, being methylparaben (MeP) and *p*-HBA the dominant pollutants [16]. Although many current plants are thought to remove a large percentage of parabens from aqueous phase, it is unclear if a certain amount is discharged with the effluent. Overall, there exists a lack of information on the behavior of parabens during advanced water treatment. Based on such uncertainty, along with the ever increasing water deficit and demand, continuous development and optimization of highly reliable water reclamation technologies is mandatory. Although several technologies have been

satisfactorily tested for the removal of organic pollutants from water, the advanced oxidation processes (AOPs) have shown the largest detoxification ability thanks to the production of a very powerful oxidant like hydroxyl radical ($^{\bullet}OH$) on site. Some of these AOPs have been scaled-up with great success, like UV/H_2O_2 from Trojan Technologies and conventional Fenton process [17]. In contrast, the use of their electrochemical counterparts (EAOPs) is much more incipient, thereby requiring further fundamental studies to reach their complete optimization before adapting them to full-scale systems.

Electro-oxidation (EO) has been the most developed EAOP for treating organic pollutants so far, due to its simplicity combined with high performance [18]. In such cases, adsorbed hydroxyl radical is formed on the anode surface (M) from water oxidation as shown in reaction (1). In the presence of Cl^-, the concomitant formation of active chlorine (Cl_2/HClO/ClO^-) as oxidant occurs in the bulk from reaction (2). Other reactive species like chlorinated radicals ($ClOH^{\bullet-}$, $Cl_2^{\bullet-}$ and $Cl^{\bullet}$) may be simultaneously formed [19]. Oxidants like O_3 and $S_2O_8^{2-}$ can also be formed in the bulk from O_2 and sulfate oxidation at the anode [18].

$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^- \quad (1)$$

$$2\,Cl^- \rightarrow Cl_2(aq) + 2e^- \quad (2)$$

The most investigated anode materials for decontamination have been boron-doped diamond (BDD) [20-24], Pt [22,25,26], dimensionally stable anodes (DSA®) with either IrO_2 [22,27-29] or RuO_2 [30-32] active layers, PbO_2 [33] and SnO_2 [18], although less attention has been paid to the latter two due to problems related to lead leaching and short service life, respectively.

If the electrolytic cell incorporates a carbonaceous air-diffusion cathode, which has large ability to generate H_2O_2 as additional oxidant from O_2 reduction, the process is so-called EO-H_2O_2 [34]. The performance of this method is greatly enhanced in the presence of Fe^{2+} ions at pH ~ 3.0, since hydroxyl radicals can also be formed in the bulk from Fenton's reaction (3). Further enhancement is reached under UVA irradiation because photolytic reactions yield an extra amount of $^{\bullet}OH$, allow

the continuous Fe^{2+} regeneration and lead to photodecarboxylation of refractory complexes of aliphatic by-products. The extraordinary results obtained under the so-called electro-Fenton (EF) and photoelectro-Fenton (PEF) conditions, respectively, have been demonstrated for several organic pollutants [35-41].

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

Some authors have compared the performance of the EAOPs upon use of different anodes in various aqueous media. For example, BDD, Pt, IrO_2-based and/or RuO_2-based anodes have been use to degrade naproxen in perchlorate [42], phenanthrene and ranitidine in sulfate [22,43], and dyes like Acid Red 14 and Rhodamine in various electrolytes [44,45]. But, studies on the performance of at least two anodes in various electrolytes are more rare [26,46]. A complete investigation comparing the performance of the four main anodes in Cl^- and Cl^--free media is then needed, with a view toward the application to treatment of real water, where chloride and sulfate are major anions.

This work addresses the degradation of aqueous solutions of MeP at pH 3.0 by EO-H_2O_2, EF and PEF. The electrochemical trials were conducted in undivided tank reactors equipped with an air diffusion cathode at constant current density (j = 66.7 mA cm^{-2}) in media containing 158 mg L^{-1} MeP in Na_2SO_4, NaCl or Na_2SO_4 + NaCl as electrolyte. The performance of the three EAOPs using BDD, Pt, IrO_2-based and/or RuO_2-based anodes was compared from the analysis of mineralization profiles and decay kinetics. Primary and final reaction by-products were identified by chromatographic techniques. To date, only two studies have reported the electrochemical degradation of MeP in sulfate medium, focusing on its conversion to various by-products in EO with BDD at very low j [47,48]. Previous research also assessed the treatment of MeP by conventional Fenton and UV-driven AOPs [49]. However, Fenton process was inefficient for MeP degradation, whereas UV-based methods like photo-Fenton yielded better but still partial conversion values. In contrast, solar photocatalysis with Aeroxide TiO_2 P-25 was able to completely

remove 1 and 10 mg L^{-1} MeP from water after 35 and 240 min, respectively [50], but, under the latter conditions, only 42% mineralization was attained and 6 products were identified. A larger TOC removal of 80% at 360 min was reported by conventional UV photocatalysis [51]. Several degradation products, with hydroxylation as major transformation route, were also found upon ozonation of various parabens including MeP [52].

2. Materials and methods

2.1. Chemicals

MeP with ≥ 99% purity was supplied by Sigma-Aldrich. Anhydrous sodium sulfate and sodium chloride, used as supporting electrolytes, and iron(II) sulfate heptahydrate, used as catalyst in EF and PEF, were of analytical grade from Fluka and Sigma-Aldrich. Analytical grade perchloric acid from Merck was used to regulate the solution pH. Organic solvents, carboxylic acids and other chemicals were of HPLC or analytical grade from Sigma-Aldrich and Panreac. All the solutions were prepared with ultrapure water from a Millipore Milli-Q system (resistivity >18 MΩ cm).

2.2. Electrolytic systems

The electrolytic treatments were conducted in an open, undivided, cylindrical, water-jacketed glass cell containing 100 mL of solution vigorously stirred with a magnetic bar at 800 rpm. The cell was equipped with a 3 cm^2 anode and a 3 cm^2 carbon-PTFE air-diffusion cathode from E-TEK (Somerset, NJ, USA), separated about 1 cm. The cathode was mounted as described elsewhere [38] and was fed with air pumped at 1 L min^{-1} for H_2O_2 generation. Four anode materials were employed: (i) a BDD thin-film electrode, deposited onto *p*-Si, from NeoCoat, (ii) a Pt sheet (99.99% purity) from SEMPSA, (iii) a DSA®-O_2 plate (IrO_2-based anode) from NMT Electrodes and (iv) a DSA®-Cl_2 plate (RuO_2-based anode) from NMT Electrodes. In most of the EF and PEF trials, 0.50 mM Fe^{2+} was added as catalyst because it was found optimal for analogous treatments of other organic contaminants [37]. All trials were carried out at constant *j* provided by an Agilent

6552A (0-25 A, 0-20 V) DC power supply that directly provided the potential difference between electrodes. For PEF, a Philips TL/6W/08 fluorescent black light blue tube placed 7 cm above the solution was used, emitting UVA light at λ_{max} = 360 nm with a photoionization energy of 5 W m^{-2}, measured on a Kipp&Zonen CUV 5 radiometer.

Solutions with 158 mg L^{-1} MeP (1.04 mM MeP, 100 mg L^{-1} TOC) in different media at pH 3.0, initially adjusted with $HClO_4$, were comparatively treated at 35 ºC and j = 66.7 mA cm^{-2}. This current density was selected for comparison since it allowed an almost total mineralization upon PEF within a reasonable time period, as will be discussed below. Three different media with the same specific conductivity (7.40-7.60 mS cm^{-1}) were tested as background electrolyte: 0.050 M Na_2SO_4, 0.070 M NaCl and 0.025 M Na_2SO_4 + 0.035 M NaCl. Note that a high MeP concentration was chosen in order to assess the mineralization rate of each system. Before the assays, cleaning of the anode and activation of the cathode were ensured under polarization in 0.050 M Na_2SO_4 at 100 mA cm^{-2} for 180 min.

2.3. Apparatus and analytical procedures

The solution pH and conductance were determined with a Crison 2000 pH-meter and a Metrohm 644 conductometer, respectively. The H_2O_2 concentration accumulated from cathodic O_2 reduction was obtained from the absorbance of the titanic-hydrogen peroxide colored complex at λ = 408 nm [53], using a Shimadzu 1800 UV/Vis spectrophotometer at 35 ºC. The active chlorine produced in experiments carried out in the presence of Cl^- was determined by the *N*,*N*-diethyl-*p*-phenylenediamine (DPD) colorimetric method according to Standard Methods [54]. To do this, the same spectrophotometer was set at λ = 515 nm. For total organic carbon (TOC) analysis, samples were withdrawn from raw and treated solutions, filtered with 0.45 µm PTFE filters from Whatman and directly injected into a Shimadzu VCSN TOC analyzer.

Assuming the following reaction for total mineralization of MeP:

$$C_8H_8O_3 + 13\ H_2O \rightarrow 8\ CO_2 + 34\ H^+ + 34\ e^- \quad (4)$$

the mineralization current efficiency (MCE) values for each trial were estimated as follows [44,55]:

$$\text{MCE (\%)} = \frac{n\,F\,V\,\triangle(\text{TOC})_{\text{exp}}}{4.32 \times 10^{7}\,m\,I\,t} \times 100 \qquad (5)$$

where n = 34 is the number of electrons for the mineralization, F is the Faraday constant (96,487 C mol^{-1}), V is the solution volume (L), $\Delta(TOC)_{exp}$ is the experimental TOC decay (mg C L^{-1}), 4.32 × 10^7 is a conversion factor to homogenize the units (3600 s h^{-1} × 12,000 mg C mol^{-1}), m = 8 is the number of carbon atoms of MeP, I is the applied current (A) and t is the electrolysis time (h).

The specific energy consumption per unit TOC mass (EC_{TOC}) was estimated as follows [44]:

$$EC_{TOC}\ (\text{kWh (g TOC)}^{-1}) = \frac{E_{\text{cell}}\,I\,t}{V_{\text{s}}\,\Delta(\text{TOC})_{\text{exp}}} \qquad (6)$$

where E_{cell} is the potential difference of the cell (V) and the rest of parameters have been already defined. The average E_{cell} values were 15.0 V for EAOPs with BDD and 12.5 V with the other three anodes.

The decay kinetics of MeP was determined by analyzing the degraded solutions by reversed-phase high-performance liquid chromatography (HPLC) through a Waters 600 LC fitted with a BDS Hypersil C18 6 μm, 250 mm × 4.6 mm, column at 35 ºC and coupled to a Waters 996 photodiode array detector set at λ = 258 nm. In the EF and PEF experiments, the aqueous samples were diluted with the same volume of acetonitrile to stop the degradation process. These measurements were made by injecting 20 μL aliquots into the LC after microfiltration with the 0.45 μm PTFE filters using a 40:60 (v/v) acetonitrile/water mixture at 1 mL min^{-1} as mobile phase. The chromatograms displayed a well-defined peak related to MeP at retention time (t_r) of 5.2 min.

Short-chain linear carboxylic acids were detected by ion-exclusion HPLC using a Waters 600 LC fitted with a Bio-Rad Aminex HPX 87H, 300 mm x 7.8 mm, column at 35 ˚C and coupled to a Waters 996 photodiode detector selected at λ = 210 nm. A 4 mM H_2SO_4 solution eluted at 0.6 mL min^{-1} was used as mobile phase. An absorption peak appeared at t_r of 6.7 min related to oxalic acid.

To enhance the identification of aromatic and aliphatic intermediates in the presence and absence of Cl^-, various samples were withdrawn during short treatments of MeP solutions in 0.050 M Na_2SO_4 or 0.025 M Na_2SO_4 + 0.035 M NaCl at pH 3.0. The treated solutions were lyophilized, the organic components were extracted with CH_2Cl_2 and ethyl acetate, and then the supernatant was concentrated up to ca. 1 mL with $N_{2(g)}$ to be analyzed by gas chromatography-mass spectrometry (GC-MS). This was made with an Agilent Technologies system composed of a 6890N gas chromatograph equipped with a 7683B series injector and coupled to a 5975XL mass spectrometer operating in electron ionization mode at 70 eV. A nonpolar Teknokroma Sapiens-X5 ms capillary column, 0.25 µm, 30 m × 0.25 mm, was used. The temperature ramp was: 36 ºC for 1 min, 5 ºC min^{-1} up to 320 ºC, and hold time of 10 min. The temperature of the inlet, source and transfer line was 250, 230 and 280 ºC. The analysis was made by splitless (0.7 min) injection mode. Masses ranging from 50 to 550 units (*m/z*) were analyzed, employing a NIST05 MS library to identify the mass spectra.

3. Results and discussion

3.1. Mineralization of methylparaben solutions in different media using BDD, Pt and DSA

A series of electrolytic trials was carried out in the absence and presence of MeP at j = 66.7 mA cm^{-2} in pure Na_2SO_4 (0.050 M), pure NaCl (0.070 M) and a Cl^-/SO_4^{2-} mixture (0.025 M Na_2SO_4 + 0.035 M NaCl). Preliminary tests were performed in the raw electrolytes aiming to quantify the concentration of active chlorine and/or H_2O_2 accumulated in the bulk from direct Cl^- oxidation at the anode and O_2 reduction at the cathode, respectively. First, the optimization of the amount of Fe^{2+} added as catalyst to the solution in the Fenton-based EAOPs was done through a series of H_2O_2 electrogeneration experiments by EF with a BDD anode in Na_2SO_4 at pH 3.0. As shown in Fig. S1, the concentration of H_2O_2 reached a plateau after a given electrolysis time in all the 0.15-1.00 mM Fe^{2+} range, when its production and destruction rates equated. A lower steady state content was

attained when increasing the Fe^{2+} concentration, due to the progressively greater destruction of H_2O_2 from Fenton's reaction (3). The minimum steady content at 360 min was 26 mM H_2O_2, attained at 0.50 mM Fe^{2+}, whereas greater iron concentrations enhanced the accumulation up to 44 mM H_2O_2. The behavior at 0.50 mM Fe^{2+} can thus be explained by the efficient reaction between both Fenton's reagents, yielding the largest amount of $^{\bullet}OH$ from reaction (3). This oxidant would then be readily available for decontamination in the presence of organic pollutants, whereas the presence of an excess of Fe^{2+} ions would be detrimental because of the partial consumption of $^{\bullet}OH$ in parasitic reactions.

Once optimized the Fe^{2+} content, the effect of chloride ion on the H_2O_2 electrogeneration was investigated by electrolyzing the raw Cl^-/SO_4^{2-} mixture with 0.50 mM Fe^{2+} at pH 3.0 under EF conditions with BDD. As observed in Fig. 1, the steady H_2O_2 concentration at 360 min was about half the value attained in the absence of chloride (see Fig. S1), which means that in the mixture H_2O_2 not only disappears due to Fenton's reaction but to some additional reagent that causes its destruction. Fig. 1 reveals the accumulation of active chlorine, which attained a steady value of 7.2 mg L^{-1} from 180 min. Therefore, the additional destruction of H_2O_2 may be accounted for by its reaction with HClO [44]:

$$HClO + H_2O_2 \rightarrow Cl^- + O_{2(g)} + H_2O + H^+ \quad (7)$$

The presence of chloride ion is detrimental in terms of $^{\bullet}OH$ formation in the bulk, not only indirectly from reaction (7), but also due to the direct destruction of this oxidizing radical ($^{\bullet}OH$ and/or $M(^{\bullet}OH)$) as follows [44]:

$$Cl^- + {}^{\bullet}OH + H^+ \rightarrow Cl^{\bullet} + H_2O \quad (8)$$

The bright side in the mixture would be thus related to the formation of radicals like $Cl^{\bullet}$ (as well as $ClOH^{\bullet-}$ and $Cl_2^{\bullet-}$) and, mainly, the accumulation of active chlorine, which may act as an oxidant. In Fenton-based systems like EF performed in the presence of chloride, reactivity of

oxidizing species presents some particularity. Indeed, $^{\bullet}OH$ can also be formed in the bulk from Fenton-like reaction between active chlorine (assuming the role of H_2O_2) and iron ions [56,57]:

$$HClO + Fe^{2+} \rightarrow Fe^{3+} + {}^{\bullet}OH + Cl^{-} \quad (9)$$

Note that [26] reported the accumulation of a much greater active chlorine concentration, up to 7 mM, upon electrolysis of a 0.05 M NaCl solution by EO with a BDD/stainless steel cell at 100 mA cm^{-2}. This supports the active role of H_2O_2 and Fe^{2+} in the disappearance of HClO by reactions like (7) and (9) under the tested conditions.

Once clarified the ability of these systems to produce H_2O_2 and active chlorine, as well as the role of these species in the formation of $^{\bullet}OH$ in the bulk, solutions of 158 mg L^{-1} MeP in each of the three media at pH 3.0 were treated by EO-H_2O_2 (no iron), as well as by EF and PEF (0.5 mM Fe^{2+}). Fig. 2a illustrates the comparative performance of the three EAOPs with a BDD anode using the Cl^{-}/SO_4^{2-} mixture. A gradual TOC abatement with 89.0% removal at 360 min was achieved in EO-H_2O_2 owing to the combined action of BDD($^{\bullet}OH$) and active chlorine on MeP and its reaction intermediates. EF yielded a very similar trend, with only 3%-7% larger mineralization at each given time and a final TOC abatement of 91%. The slightly better results may be explained by the formation of $^{\bullet}OH$ in the bulk from Fenton's reaction (3). However, its concentration is reduced as a result of the large destruction of H_2O_2 from reaction (7), despite the simultaneous co-generation from Fenton-like reaction (9). The formation of chloroderivatives and refractory complexes between Fe(III) and some by-products, which are hardly oxidizable by the low amount of available $^{\bullet}OH$, is responsible for the similarity between EO-H_2O_2 and EF at 360 min. In contrast, a significantly quicker and larger TOC removal was achieved by PEF, reaching 97% mineralization. This means that this EAOP is powerful enough to progressively degrade MeP and all the refractory by-products, either uncomplexed or complexed with Fe^{3+}. UVA radiation allows: (i) the continuous regeneration of Fe^{2+} from Fe(III) photoreduction, thus enhancing the production of $^{\bullet}OH$ in the bulk

from reactions (3) and (9), and (ii) the photodecarboxylation of persistent complexes, which upgrades the TOC removal and regenerates Fe^{2+} as well [34,38].

The influence of the anode material on the performance of the EAOPs is shown in Fig. 2b. In EO-H_2O_2, the use of IrO_2-based, Pt and RuO_2-based anodes led to a rather poor mineralization at 360 min, being much larger with the latter two anodes (43%) than with the former one (1.9%). This behavior arises from the lower oxidation power of IrO_2($^{\bullet}$OH), Pt($^{\bullet}$OH) and RuO_2($^{\bullet}$OH) formed from reaction (1) compared to BDD($^{\bullet}$OH), since they are chemisorbed rather than physisorbed radicals. The superiority of the Pt and RuO_2-based anodes compared to the IrO_2-based one may arise from the larger O_2-evolution overpotential of Pt and the great ability of the RuO_2-based anode to produce active chlorine [58]. On the other hand, the trends in PEF with these three anodes were much more similar, with 85% TOC removal using the RuO_2-based anode and 89%-91% with the other ones. The larger production of active chlorine with the former anode causes a higher destruction of H_2O_2 from reaction (7) and results in a poorer concentration of $^{\bullet}$OH in the bulk, which justifies the lower oxidation power. In conclusion, PEF with BDD was the optimum process in the Cl^-/SO_4^{2-} medium as a result of the best balance between active chlorine, $^{\bullet}$OH and M($^{\bullet}$OH) formed as main oxidants. These species, along with UVA photons, ensured the almost total degradation of refractory by-products. However, the systems equipped with BDD have to be carefully optimized because, otherwise, toxic ClO_4^- may be formed, as reported during the electrochemical oxidation of Cl^- at this anode [59-61], which occurs to a lower extent using less oxidant ones like Pt [61].

Fig. 3a depicts the comparative TOC-time trends for the different EAOPs with BDD in Na_2SO_4. A slower mineralization, reaching a final value of 77%, was found in EO-H_2O_2 from the main action of BDD($^{\bullet}$OH). The synergistic occurrence of active chlorine in the previous Cl^-/SO_4^{2-} mixture was thus beneficial to attain a larger TOC abatement, although in that medium the final solution probably contained a certain number of toxic, chlorinated by-products. In contrast, the mineralization percentages at 360 min in EF and PEF (89% and 97%, respectively) were very close

to those achieved in the presence of chloride ion. This means that $^{\bullet}OH$ formed in the bulk are highly effective for degrading the chlorinated derivatives in the Cl^-/SO_4^{2-} mixture. Nevertheless, note that the TOC removal rates were somewhat higher in Na_2SO_4. For example, at 180 min of EF and PEF, the mineralization was 78% and 92% (see Fig. 3a) instead of 69% and 80% (see Fig. 2a), which confirms the slower accumulation of $^{\bullet}OH$ and M($^{\bullet}OH$) in the presence of chloride ion due to parasitic reactions. The same occurred in PEF with Pt, IrO_2-based and RuO_2-based anodes, since significantly greater TOC abatements were attained at any given time up to reach 98% mineralization at 360 min in all cases (see Fig. 3b). The quicker and larger TOC decay compared to that in Cl^--containing medium, along with the almost identical profiles of the four PEF treatments in Na_2SO_4, allows inferring the preponderant role of homogeneous $^{\bullet}OH$ over M($^{\bullet}OH$) in the latter medium, as well as their lower destruction by parasitic reactions. Fig. 3b also shows the very poor performance of EO-H_2O_2 with the three anodes, attaining 6.9%-8.5% with DSA ones and 17% with Pt. These results are worse than those obtained with either BDD (see Fig. 3a) or with the same three anodes in the Cl^-/SO_4^{2-} mixture (see Fig. 2b), which confirms the low oxidation power of the M($^{\bullet}OH$) (especially the DSA($^{\bullet}OH$)) formed on their surface compared to BDD($^{\bullet}OH$) and the consequent importance of active chlorine contribution to oxidation in those cases. Hence, PEF with a low cost anode like DSA is the treatment of choice in Cl^--free medium like sulfate, since $^{\bullet}OH$ formed in the bulk along with UVA light are the main agents to transform the organic matter into innocuous by-products.

The clear effect of chloride ion on mineralization was confirmed by comparing the trends of EO-H_2O_2, EF and PEF with BDD in pure NaCl shown in Fig. 4. It can be seen that, as expected, the oxidation power increased in the order: EO-H_2O_2 < EF < PEF. However, the presence of chloride ion and the formation of active chlorine unified the degradation results at long electrolysis time, yielding 86%, 90% and 93% at 360 min, respectively. These values confirm the positive contribution of chloride in EO-H_2O_2, as compared with Fig. 3a, whereas in EF and PEF this anion

leads to slightly slower mineralization rates and/or final TOC abatements. Despite this deceleration in the presence of chloride, a large decontamination was achieved again by PEF.

Several authors have recently reported interesting results on other EAOPs such as electro-peroxone [62] and photoelectro-peroxone [63,64], which involve the generation of $^{\bullet}OH$ from injected O_3 and electrogenerated H_2O_2 at a carbonaceous cathode and/or the photolysis of the latter species upon UVC irradiation. During the treatment of benzene derivatives and 1,4-dioxane, no significant influence of the anode nature (Ti/Pt, Ti/RuO_2-IrO_2 and BDD) on TOC removal was found in sulfate medium, owing to the high oxidation power of O_3 on $^{\bullet}OH$ generation. In contrast, in Cl^- medium, a strong inhibition of mineralization was observed due to the removal of H_2O_2 with generated HClO from reaction (7), which was more significant using a DSA anode owing to its larger production of active chlorine. The addition of Fe^{2+} to the solution caused a decrease in mineralization rate in electro-peroxone, being related to the formation of Fe(III)-carboxylate complexes, but in photoelectro-peroxone such species were photolyzed by UVC light [64].

3.2. Mineralization current efficiency and energy consumption

The MCE and EC_{TOC} values corresponding to the TOC-time profiles presented in Fig. 2-4 were calculated using Eq. (5) and (6), respectively. Fig. 5 illustrates the MCE curves obtained in the Cl^-/SO_4^{2-} mixture, which resulted from TOC trends of Fig. 2. As can be seen in Fig. 5a, at any given time, the current efficiency with BDD increased in agreement with the larger oxidation power in the order: EO-H_2O_2 < EF < PEF, since the production of reactive species was accelerated upon use of Fe^{2+} and UVA light. The highest MCE values with this anode were obtained at short electrolysis time (20-40 min), reaching 11.0%, 15.6% and 17.7%, respectively. Afterwards, the MCE underwent a progressive decay in all cases up to a final value around 7.0%-7.6% (see Table 1), in accordance with the close TOC values found at 360 min (see Fig. 2a). The current efficiency fall over time can be accounted for by: (i) the increasing mass transport limitations due to organic matter removal, which enhances the role of parasitic reactions involving the reactive species, and

(ii) the formation of more hardly degradable by-products, including chlorinated derivatives and Fe(III) complexes with short aliphatic compounds [18,44]. All these findings were confirmed using Pt, IrO_2-based and RuO_2-based anodes. As shown in Fig. 5b, PEF was much more efficient than EO-H_2O_2, especially at short time with MCE values of ~ 20% and < 10%, respectively. The current efficiency of the three PEF treatments was analogous to that of PEF with BDD (see Table 1), whereas the EO-H_2O_2 treatments were less efficient than that with BDD during all the electrolysis time. Table 1 summarizes the MCE values obtained at 360 min by EO-H_2O_2, EF and PEF in Na_2SO_4 and NaCl media. Note that a similar current efficiency around 7% was achieved in all the PEF treatments.

Fig. 6a illustrates that, using BDD in the Cl^-/SO_4^{2-} mixture, a higher energy consumption was required as the oxidation power of the EAOP diminished in the order: PEF < EF < EO-H_2O_2, in correspondence with a less efficient process (see Fig. 5a). Moreover, EC_{TOC} always increased over time up to final values of 1.54-1.86 kWh (g TOC)$^{-1}$. This is reasonable, since constant current and E_{cell} were ascertained during the experiments, whereas the gradually lower mineralization rate led to a more difficult removal of TOC content (see Fig. 2a). Similar trends can be observed in Fig. 6b for the EAOPs with the other three anodes, with significantly greater energy consumption in EO-H_2O_2 due to their lower degradation performance (see Fig. 2b). In particular, very high energy consumptions were needed when using the RuO_2-based anode, up to 60 min, because of its small oxidation power. The EC_{TOC} values at 360 min for the trials carried out in Na_2SO_4 and NaCl are summarized in Table 1. It can then be concluded that, unless renewable energy is used to power the systems, the treatments become significantly more expensive at long electrolysis times, but coupling with less expensive post-treatments can be envisaged to reduce operation expenses.

3.3. Comparison of MeP decay kinetics

The influence of the EAOP and anode nature on the decay of MeP concentration with electrolysis time was assessed for the previous treatments of solutions containing 158 mg L^{-1} of

pollutant in each medium at pH 3.0. Fig. 7 shows the decays upon use of BDD in the Cl^-/SO_4^{2-} mixture and the corresponding kinetic analysis when feasible. In EO-H_2O_2 and EF, MeP disappeared completely at 120 min. Both trends agree well with a pseudo-first-order reaction, as shown in the inset, yielding very close apparent rate constants (k_1) of 3.43 x 10^{-2} and 4.07 x 10^{-2} min^{-1} in EO-H_2O_2 and EF, respectively. The existence of such reaction kinetics suggests that MeP reacts with a constant concentration of reactive species. Based on the poor difference between both EAOPs, it can be concluded that BDD($^{\bullet}$OH) and active chlorine act as main oxidants, being the contribution of $^{\bullet}$OH in the bulk much less relevant. This confirms the comments made for the mineralization trends of Fig. 2a, with a large amount of the H_2O_2 required for Fenton's reaction being destroyed by HClO. In contrast, the profile of the MeP decay in PEF, shown in Fig. 7b, presented two major differences from those of Fig. 7a: (i) a complex kinetics appeared, not corresponding to a pseudo-first-order reaction, and (ii) a faster MeP removal was obtained, with a disappearance of 66% instead of 41% after 10 min. Since MeP was photostable under UVA irradiation (not shown), these two facts can be explained by the contribution of additional $^{\bullet}$OH in the bulk. Indeed, the continuous Fe^{2+} regeneration thanks to Fe(III) photoreduction enhances the accumulation of $^{\bullet}$OH from Fenton's reaction (3), as compared to EF. But, even more relevant, such a great Fe^{2+} availability promotes the formation of $^{\bullet}$OH from Fenton-like reaction (9). Consequently, PEF in the presence of chloride entails a very complex and powerful reaction environment with multiple oxidants of variable concentration over time. This finding is highly interesting because, to our knowledge, the decay kinetics of organic pollutants in Fenton-based EAOPs in chloride medium has not been reported yet, only existing studies that report the effect of chloride ion on TOC and color removal [26]. The use of Pt and DSA instead of BDD led to similar MeP decays, with a removal percentage around 60-65% (not shown). This means that, in PEF, the preponderant oxidizing role corresponded to bulk oxidants (active chlorine and $^{\bullet}$OH), being less important the influence of the adsorbed M($^{\bullet}$OH).

The analogous MeP decays in Na_2SO_4 depicted in Fig. 8 exhibit significant differences from those obtained in the electrolyte mixture. The profile in EO-H_2O_2 was still exponential (see Fig. 8a), but showing a much slower MeP removal with only 80% of disappearance at 360 min. Accordingly, a k_1 = 4.96 x 10^{-3} min^{-1} (one order of magnitude lower compared to results of Fig. 7a) was achieved. This much slower degradation, with BDD($^{\bullet}$OH) as the main oxidant, justifies the decisive contribution of active chlorine in EO-H_2O_2 in the Cl^-/SO_4^{2-} mixture (see above). In contrast, Fig. 8b shows that straight decays were obtained in EF and PEF, with an analogous profile in both cases, not corresponding to a pseudo-first-order reaction but to a complex kinetics. Furthermore, the removal of MeP was much faster compared to EO-H_2O_2, and was also quicker than any other EAOP performed in the previous medium. For example, in only 10 min, the MeP content decreased by 94%. In these cases, the great amount of $^{\bullet}$OH produced in the bulk from Fenton's reaction (3), along with adsorbed M($^{\bullet}$OH), is the main responsible for the particular reaction kinetics, without much influence of UVA light. Interestingly, also the PEF treatments with Pt and DSA led to a complex kinetics with similar decay rate, with MeP removal at 10 min ranging between 93% and 95% (not shown).

3.4. Elucidation of reaction routes for MeP mineralization

In previous sections, some of the profiles have been explained on the basis of the formation of specific reaction by-products. A GC-MS analysis of treated solutions was then carried out in order to identify as many products as possible, aiming to elucidate the preeminent degradation routes. Since, in a given medium, the same kinds of reactive species contribute to MeP transformation in all the EAOPs regardless of the anode used, BDD was chosen to perform this thorough study.

Table S1 summarizes the characteristics of aromatic and aliphatic intermediates detected during the degradation of solutions with 158 mg L^{-1} MeP in the Cl^-/SO_4^{2-} mixture at pH 3.0. From these 13 by-products, the reaction sequence of Fig. 9 is proposed. MeP (**1**) is transformed into three different primary aromatic by-products as a result of: (i) direct attack of $^{\bullet}$OH or BDD($^{\bullet}$OH) to yield

a hydroxylated MeP (**2a**), (ii) nucleophilic attack of hydroxyl radicals onto the carbon atom of the carbonyl group, causing the release of the $–OCH_3$ group to yield 4-hydroxybenzoic acid (**3a**), and (iii) chlorination to form a chlorinated MeP (**4a**). Decarboxylation of **3a** upon attack of hydroxyl radical yields hydroquinone (**11a**), whereas hydroxylation in concomitance of chlorination leads to several polychlorinated phenols (**5a**, **6a** and **7a**). On the other hand, consecutive action of active chlorine on **4a** causes its cleavage to yield aliphatic polychlorinated compounds (**8a**, **9a** and **10a**). These by-products can be mineralized, or may undergo further transformations under the action of hydroxyl radicals and active chlorine as occurs with the aromatic molecules. Various short-chain aliphatic carboxylic acids (**12a**, **13a** and **14a**), either complexed with Fe(III) or uncomplexed, are produced and further converted into CO_2, Cl^- and H_2O. As shown in Fig. 2a, mineralization of all these intermediates is almost total in PEF with BDD.

An analogous study performed in Na_2SO_4 under the same conditions resulted in the 7 by-products summarized in Table S2, giving rise to the reaction sequence of Fig. 10. Primary intermediates **2a** and **3a** are also formed in this medium. In addition, hydroxylation of MeP yields products **4b** and **5b**, which may end in **6b**. On the other hand, the attack of hydroxyl radicals on the benzenic C atom of MeP bonded to carbonyl group, or on some of the by-products, yields hydroquinone (**11a**), which might be further transformed into malonic acid (**7b**) prior to overall mineralization.

These findings agree with recent literature. For example, Steter et al. [47,48] reported the formation of 4-hydroxybenzoic acid (**3a**) as the first transformation step of MeP by EO with BDD in K_2SO_4. This was converted to phenol, and further to hydroquinone (**11a**) and *p*-benzoquinone. The formation of hydroquinone has also been ascertained in solar photocatalysis [50]. Finally, during the ozonation of various parabens, **3a** and **11a** were also found as major breakdown products [52].

As observed in Fig. 9 and 10, carboxylic acids were the final by-products before reaching the total mineralization, as also reported by Steter [48]. HPLC analysis revealed that the greatest accumulation corresponded to oxalic acid, attaining 17, 30 and 42 mg L^{-1} as maximal in EO-H_2O_2, EF and PEF with BDD in Na_2SO_4, respectively (see Fig. 11a). An almost total removal was achieved at 360 min in PEF thanks to photodecarboxylation of Fe(III)-oxalate complexes under UVA irradiation [38], in agreement with the overall mineralization shown in Fig. 3a, whereas the acid was more refractory to attack by BDD($^{\bullet}$OH) and $^{\bullet}$OH in EO-H_2O_2 and EF, respectively. In PEF with chloride ion, a much lower content of oxalic acid was attained, being further mineralized. Finally, it can be noted in Fig. 11b that PEF with Pt and DSA in Na_2SO_4 led to very similar profiles and values of oxalic acid, also close to those obtained with BDD, which agrees with the TOC-time trends commented from Fig. 3b, corroborating the powerful action of UVA irradiation onto its Fe(III) complexes.

4. Conclusions

Different anode materials may be used for degrading MeP by EAOPs, being the selection dependent on the background electrolyte contained in the water matrix. If the aim is simply reaching a quick decay kinetics of the parent pollutant, PEF with DSA is the system of choice in either absence or presence of chloride ion, since it performs like PEF with BDD or Pt but DSA is much less expensive. In all media, PEF led to a complex decay kinetics, with $^{\bullet}$OH from Fenton's reaction as the main reactive species in Na_2SO_4, and active chlorine plus $^{\bullet}$OH from Fenton-like reaction between Fe^{2+} and HClO as the preeminent reactive species in the Cl^-/SO_4^{2-} mixture. Otherwise, if a large mineralization percentage is aimed, PEF with BDD must be chosen in the presence of chloride ion, whereas a less expensive PEF with DSA is enough in the absence of this anion. PEF trials presented a higher MCE and lower EC_{TOC} than EF and EO-H_2O_2 due to its larger oxidation power. Up to 13 by-products were identified in the Cl^-/SO_4^{2-} mixture, including

chlorinated and non-chlorinated ones, and 7 molecules were found in Na_2SO_4, with oxalic acid as major final short-chain aliphatic acid prior to overall mineralization of MeP.

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Figure captions

Figure 1. Variation of the concentration of: (●) active chlorine and (○) accumulated H_2O_2 with electrolysis time for 100 mL of a 0.025 M Na_2SO_4 + 0.035 M NaCl solution with 0.50 mM Fe^{2+} at pH 3.0 under EF conditions with a BDD/air-diffusion cell at 66.7 mA cm^{-2} and 35 ºC.

Figure 2. TOC removal with electrolysis time for the treatment of 100 mL of 158 mg L^{-1} methylparaben in 0.025 M Na_2SO_4 + 0.035 M NaCl at pH 3.0 by different EAOPs using cells of 3 cm^2 electrode area containing an air-diffusion cathode and operating at 66.7 mA cm^{-2} and 35 ºC. (a) (●) EO-H_2O_2, (■) EF with 0.50 mM Fe^{2+} and (▲) PEF with 0.50 mM Fe^{2+} using a BDD anode. (b) EO-H_2O_2 with a (◆) Pt, (◇) IrO_2-based and (▼) RuO_2-based anode. PEF with a (○) Pt, (□) IrO_2-based and (△) RuO_2-based anode.

Figure 3. TOC decay vs. electrolysis time for the same methylparaben solutions of Fig. 2, but using 0.050 M Na_2SO_4 as background electrolyte. (a) (●) EO-H_2O_2, (■) EF and (▲) PEF with a BDD anode. (b) EO-H_2O_2 with a (◆) Pt, (◇) IrO_2-based and (▼) RuO_2-based anode. PEF with a (○) Pt, (□) IrO_2-based and (△) RuO_2-based anode.

Figure 4. TOC abatement with electrolysis time for the same methylparaben solutions of Fig. 2, but using 0.070 M NaCl. (a) (●) EO-H_2O_2, (■) EF and (▲) PEF with a BDD anode.

Figure 5. Change of mineralization current efficiency with electrolysis time for the trials of Fig. 2. (a) (●) EO-H_2O_2, (■) EF and (▲) PEF with a BDD anode. (b) EO-H_2O_2 with a (◆) Pt, (◇) IrO_2-based and (▼) RuO_2-based anode. PEF with a (○) Pt, (□) IrO_2-based and (△) RuO_2-based anode.

Figure 6. Variation of specific energy consumption per unit TOC mass with electrolysis time for the assays of Fig. 2. (a) (●) EO-H_2O_2, (■) EF and (▲) PEF with a BDD anode. (b) EO-H_2O_2 with a (◆) Pt and (▼) RuO_2-based anode. PEF with a (○) Pt, (□) IrO_2-based and (△) RuO_2-based anode.

Figure 7. Decay of methylparaben concentration with electrolysis time for 100 mL of 158 mg L^{-1} of compound in 0.025 M Na_2SO_4 + 0.035 M NaCl at pH 3.0 using a BDD/air-diffusion cell at 66.7 mA cm^{-2} and 35 ºC. (a) (●) EO-H_2O_2 and (■) EF. (b) PEF. The kinetic analysis for a pseudo-first-order reaction for methylparaben is presented in the inset panel of (a).

Figure 8. Time course of methylparaben concentration for 100 mL of 158 mg L^{-1} of compound in 0.050 M Na_2SO_4 at pH 3.0 using a BDD/air-diffusion cell at 66.7 mA cm^{-2} and 35 ºC. (a) EO-H_2O_2. (b) (■) EF and (▲) PEF. The inset panel of (a) shows the kinetic analysis assuming a pseudo-first-order reaction for methylparaben.

Figure 9. Reaction sequence proposed from GC-MS determination for methylparaben mineralization in 0.025 M Na_2SO_4 + 0.035 M NaCl by EAOPs with a BDD/air-diffusion cell. Hydroxyl radicals, $^{\bullet}OH$, account for either adsorbed (M($^{\bullet}OH$)) or homogeneous radicals.

Figure 10. Route proposed from GC-MS determination for methylparaben mineralization in 0.050 mM Na_2SO_4 by EAOPs with a BDD/air-diffusion cell. Hydroxyl radicals, $^{\bullet}OH$, account for either adsorbed (M($^{\bullet}OH$)) or homogeneous radicals.

Figure 11. Time course of oxalic acid concentration detected during the degradation of 100 mL of 158 mg L^{-1} methylparaben at pH 3.0 by EAOPs at 66.7 mA cm^{-2} and 35 ºC. (a) BDD/air-diffusion cell using (●) EO-H_2O_2, (■) EF and (▲) PEF with 0.050 M Na_2SO_4, and (◆) PEF with 0.025 M Na_2SO_4 + 0.035 M NaCl. (b) PEF with a (○) Pt/air-diffusion, (□) IrO_2-based/air-diffusion and (△) RuO_2-based/air-diffusion cell with 0.050 M Na_2SO_4.