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Mineralization of herbicide mecoprop by photoelectro-Fenton with UVA and solar light

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Abstract

The photoelectro-Fenton degradation of 2.5 l of solutions containing herbicide mecoprop (2-(4-chloro-2-methylphenoxy)-propionic acid) up to 0.64 g l^{-1}, 0.05 M Na_2SO_4 and 0.5 mM Fe^{2+} of pH 3.0 has been studied using a flow plant with a one-compartment filter-press electrolytic reactor with a boron-doped diamond (BDD) anode and an O_2-diffusion cathode, both of 20-cm^2 area, coupled to either a UVA or solar photoreactor. Electrolyses performed in batch at low constant current density yield overall mineralization in both methods, although the process is much faster and less expensive with solar light. Under these conditions, the degradation rate and efficiency increase strongly with rising mecoprop content. The kinetics for the herbicide decay follows a pseudo-first-order reaction. Mecoprop reacts rapidly with hydroxyl radical ($^\bullet OH$) produced from Fenton's reaction between Fe^{2+} and H_2O_2 electrogenerated at the cathode to yield 4-chloro-*o*-cresol, 2-methylhydroquinone and 2-methyl-*p*-benzoquinone as primary reaction products. Fe^{3+}-oxalato and Fe^{3+}-acetato complexes are detected as the most persistent final products. Overall mineralization is attained because Fe^{3+}-oxalato complexes are efficiently photodecomposed by solar irradiation, whereas Fe^{3+}-acetato complexes are slowly destroyed by $^\bullet OH$ formed at the BDD anode from water oxidation. The initial chlorine is released as Cl^-, which is slowly oxidized to Cl_2 on BDD. Photoelectro-Fenton with solar light appears to be a viable method to remove chlorophenoxy herbicides in wastewaters at industrial scale.

Keywords: Chlorophenoxy herbicides; Photoelectro-Fenton; Solar light; Mineralization; Water treatment

1. Introduction

An increasing accumulation of chlorophenoxy herbicides in US and European ground waters and surface waters at relatively high contamination levels has been recently documented [1–7]. This pollution comes from their widespread use for agricultural and non-agricultural purposes generating continuously rinsate, waste product and contaminated soil in application sites. To avoid the potential adverse health effects on humans and animals of such toxic and biorefractory herbicides, powerful oxidation processes are being developed to remove such compounds and their products from wastewaters.

Mecoprop (2-(4-chloro-2-methylphenoxy)-propionic acid or MCPP) is a translocatable postemergence chlorophenoxypropionic herbicide, widely used for control of cleavers, chickweed and other weeds in cereal crops. It has been detected as minor pollutant in US and European soils, as well as in ground waters and surface waters, being the most often found herbicide in drinking water [1]. Fletcher et al. [7] determined concentrations of MCPP of 1.8 mg g^{-1} after 138 days of its application in soil and close to 0.4 mg l^{-1} in water samples. Several authors have described the quick removal of MCPP from waters by O_3 [8], UVC irradiation [9] and advanced oxidation processes (AOPs) with generation of oxidant hydroxyl radical ($^\bullet OH$) such as O_3/H_2O_2 [8] and TiO_2/UV [10,11]. However, these methods do not yield its overall mineralization, i.e., its total conversion into CO_2, water and inorganic ions, and hence, more potent oxidation processes are needed to be applied to destroy this compound in wastewaters.

The recent use of indirect electrooxidation methods such as electro-Fenton (EF) and photoelectro-Fenton (PEF) for water remediation has attracted great interest [12–26]. These powerful AOPs are environmentally friendly electrochemical techniques based on the continuous supply of H_2O_2 to a

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contaminated solution from the two-electron reduction of O_2:

$$O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (1)$$

Reaction (1) can efficiently take place at reticulated vitreous carbon [12,13,26], activated carbon fiber [23], carbon-felt [4,14,16,19,20,22,25] and O_2-diffusion [15,17,18,21,24] cathodes. In the EF method a small quantity of catalyst Fe^{2+} is added to an acidic solution to produce $^{\bullet}OH$ and Fe^{3+} from the classical Fenton's reaction [27]:

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

Reaction (2) is propagated from Fe^{2+} regeneration, mainly by reduction of Fe^{3+} at the cathode [4]. $^{\bullet}OH$ is a non-selective strong oxidant able to react with organic pollutants to give dehydrogenated or hydroxylated derivatives until total mineralization. The PEF process involves the solution irradiation with UVA light to favor: (i) the photodecomposition of complexes of Fe^{3+} with generated carboxylic acids [15,17,24,28] and (ii) the additional regeneration of Fe^{2+} from photoreduction of $Fe(OH)^{2+}$, which is the predominant Fe^{3+} species in acid medium [27]:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \qquad (3)$$

Mineralization of organics can also be enhanced by the production of $^{\bullet}OH$ from reaction (3).

The EF treatment of several chlorophenoxy herbicides, including MCPP, has been reported by Oturan et al. [4]. These authors degraded 100-ml solutions with 1 mM of substrate and 2 mM Fe^{2+} in 0.01 M HCl, describing its decay kinetics and the detection of initial aromatic products. In previous work we have studied the EF process of chlorophenoxyacetic herbicides such as 2,4-dichlorophenoxyacetic [15,21] and 4-chlorophenoxyacetic [17,21] using a one-compartment cell of 100-ml capacity with a Pt or boron-doped diamond (BDD) anode and a carbon-polytetrafluoroethylene (PTFE) O_2-diffusion cathode. At pH 3.0, near the optimum pH of 2.8 for Fenton's reaction (2) [27], complete mineralization is found for EF with BDD and 1.0 mM Fe^{2+}, whereas stable carboxylic acids such as oxalic remained in the solution using Pt. The greater oxidation power of EF with BDD can be related to the higher O_2-overpotential of this anode allowing destroying pollutants with reactive hydroxyl radical (BDD($^{\bullet}OH$)) adsorbed on its surface coming from water oxidation [21,29–33]:

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

In contrast, the same 100-ml solutions of chlorophenoxyacetic herbicides with 1.0 mM Fe^{2+} can be totally mineralized by means of PEF under irradiation with a 6-W UVA light using a Pt anode due to the effective photodegradation of complexes of Fe^{3+} with final carboxylic acids [15,17].

Previous work at laboratory scale of 100 ml showed that EF and PEF methods can be useful to decontaminate wastewaters containing chlorophenoxy herbicides. To assess the possible viability of these AOPs at industrial scale, we have undertaken a study on the degradation of the chlorophenoxypropionic herbicide MCPP in a flow plant containing a one-compartment filter-press electrochemical cell with a BDD anode and an O_2-diffusion cathode, coupled to a UVA or solar photoreactor to apply the PEF process. Comparative treatments of solutions containing up to 0.64 g l^{-1} of this herbicide and 0.5 mM Fe^{2+} as catalyst of pH 3.0 were then made by PEF with UVA or solar light operating in batch at constant current density. The same solutions were also degraded without light irradiation by EF and without catalyst by anodic oxidation (AO) to clarify the oxidation power of PEF procedures. The effect of current density and Fe^{2+} and MCPP concentrations on the degradation rate of PEF with solar light was explored. The herbicide decay and the evolution of intermediates were followed by chromatographic techniques. The results obtained in this study are reported herein.

2. Experimental

MCPP (95% purity) from Lancaster was recrystallized in a 50:50 (v/v) ethanol/water mixture before use. 4-Chloro-*o*-cresol, 2-methylhydroquinone, 2-methyl-*p*-benzoquinone, pyruvic acid, acetic acid and oxalic acid were reagent or analytical grade from Sigma, Fluka and Merck. Sulfuric acid, anhydrous sodium sulfate and heptahydrated ferrous sulfate were analytical grade from Merck and Fluka. All solutions were prepared with pure water obtained from a Millipore Milli-Q system (resistivity > 18 MΩ cm at 25 °C). Organic solvents and other chemicals used were HPLC or analytical grade from Panreac and Aldrich.

The concentration of accumulated H_2O_2 in electrolyzed solutions was determined from the light absorption of the titanic-hydrogen peroxide colored complex at λ = 408 nm [34], using a Unicam UV/Vis UV4 spectrophotometer thermostated at 25 °C. All samples withdrawn from treated solutions were filtered with 0.45 μm PTFE filters from Whatman before analysis. The degradation of MCPP solutions was monitored from the removal of their total organic carbon (TOC), determined with a Shimadzu 5050 TOC analyzer. Reproducible TOC values, with an accuracy of ±1 mg l^{-1}, were obtained using the standard non-purgeable organic carbon method. Cl^- concentration in treated solutions was determined by ion chromatography using a Shimadzu 10Avp HPLC chromatograph fitted with a Shim-Pack IC-A1S, 100 mm × 4.6 mm (i.d.), anion column at 40 °C, and coupled with a Shimadzu CDD 10Avp conductivity detector. In this technique the mobile phase was a solution with 2.5 mM phtalic acid and 2.4 mM tris(hydroxymethyl)aminomethane) of pH 4.0 at 1.5 ml min^{-1}. The herbicide decay and the time-course of aromatic products were followed by reversed-phase HPLC chromatography using a Waters 600 HPLC liquid chromatograph fitted with a Spherisorb ODS2 5 μm, 150 mm × 4.6 mm (i.d.), column at room temperature, and coupled with a Waters 996 photodiode array detector, which was selected for each compound at the maximum wavelength of its UV-absorption band. These analyses were performed by injecting 20-μl aliquots into the chromatograph and circulating a 50:45:5 (v/v/v) methanol/phosphate buffer (pH 2.5)/pentanol mixture at 1.0 ml min^{-1} as mobile phase. Carboxylic acids were detected by ion-exclusion chromatography using the above HPLC chromatograph fitted with a Bio-Rad Aminex HPX 87H, 300 mm × 7.8 mm (i.d.), column at 35 °C. For these measurements, 20-μl samples were analyzed, the photodiode detector was selected at 210 nm and the mobile phase was 4 mM H_2SO_4 at 0.6 ml min^{-1}.

Comparative treatments of 2.5 l of MCPP solutions in 0.05 M Na_2SO_4, adjusted with H_2SO_4 to pH 3.0, were carried out by AO, EF and PEF with UVA or solar light at constant current density. In the three later methods 0.5 mM Fe^{2+} was added to the starting solution as catalyst. A scheme of the flow plant designed for PEF with solar light is depicted in Fig. 1. The electrolytic cell was a one-compartment filter-press reactor with a BDD anode from CSEM and a carbon-PTFE O_2-diffusion cathode from E-TEK. This cathode was fed with pure O_2 at an overpressure of 8.6 kPa to produce continuously H_2O_2 from reaction (1). The separation of both electrodes was 1 cm and their area in contact with the effluent was 20 cm^2. The solution was introduced in the reservoir and recirculated through the cell by means of a peristaltic pump. Its temperature was then regulated at 25 °C by two heat exchangers and its flow rate was adjusted to 180 l h^{-1} by a flowmeter. The current was supplied by an Agilent 6552A DC power supply, which directly displayed the applied cell voltage. In PEF with solar light the solution was irradiated when it circulated through a polycarbonate box of 240 mm × 240 mm × 25 mm (irradiated volume 600 ml), connected to the outlet of the cell (see Fig. 1). The solar photoreactor was built-up with a mirror at the bottom and inclined 30° from the horizontal to collect better the direct sun rays. These trials were made in sunny and clear days during the spring of 2006 in Barcelona, Spain (longitude: 41°21′N, latitude: 2°10′E). In PEF with UVA light the solution was illuminated with a 160-W Philips black light blue lamp of $\lambda_{max} = 360$ nm, placed inside an annular Schott-Duran glass photoreactor of 210 mm height, 110 mm external diameter and 10 mm thickness (irradiated volume 640 ml), connected to the outlet of the cell. This device was also used in the dark in AO and EF to keep the same residence time of the effluent in the cell.

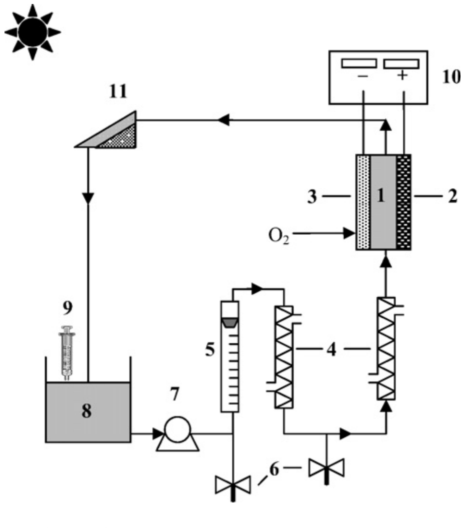


Fig. 1. Setup of the flow plant used for the photoelectro-Fenton (PEF) degradation with solar light of mecoprop (MCPP) solutions. (1) One-compartment filter-press electrochemical cell, (2) 20-cm^2 BDD anode, (3) 20-cm^2 O_2-diffusion cathode, (4) heat exchangers, (5) flowmeter, (6) purge valves, (7) peristaltic pump, (8) reservoir, (9) sampling, (10) power supply and (11) solar photoreactor. In the PEF treatment with UVA light, the MCPP solution was directly irradiated with a 160-W lamp ($\lambda_{max} = 360$ nm) inside an annular photoreactor that replaced the solar one.

3. Results and discussion

3.1. H_2O_2 accumulation

The ability of the electrolytic system to accumulate H_2O_2 supplied by the O_2-diffusion cathode from reaction (1) was tested by electrolyzing 2.5 l of a 0.05 M Na_2SO_4 solution of pH 3.0 at different current densities, 25 °C and liquid flow of 180 l h^{-1} for 9 h. Fig. 2 shows a gradual rise in H_2O_2 concentration in solution at 150 mA cm^{-2} (curve a), 100 mA cm^{-2} (curve b) and 50 mA cm^{-2} (curve c) up to reach steady values of 54, 36 and 16 mM, respectively. This indicates that the increase in current density causes the electrogeneration of more H_2O_2 from reaction (1), together with its faster decomposition in the system. The steady H_2O_2 content is attained just when it is electrogenerated and destroyed at the same rate. H_2O_2 is expected to be mainly oxidized to O_2 at the BDD anode via hydroperoxyl radical ($HO_2^{\bullet}$) as intermediate, a much weaker oxidant than $^{\bullet}OH$ [15]:

$$H_2O_2 \rightarrow HO_2^{\bullet} + H^+ + e^- \qquad (5)$$

$$HO_2^{\bullet} \rightarrow O_2 + H^+ + e^- \qquad (6)$$

Reactions (5) and (6) compete with water oxidation to O_2 initiated by reaction (4). Note that low concentrations of other weak oxidants such as peroxodisulfate and O_3 can also be produced at the BDD anode, as detected during the electrolyses of Na_2SO_4 solutions [32].

In the PEF process, however, H_2O_2 is expected to be more rapidly destroyed due to its additional consumption in Fenton's reaction (2), which can be accelerated by reaction (3), as well as in other homogeneous reactions, for example, with Fe^{3+} and

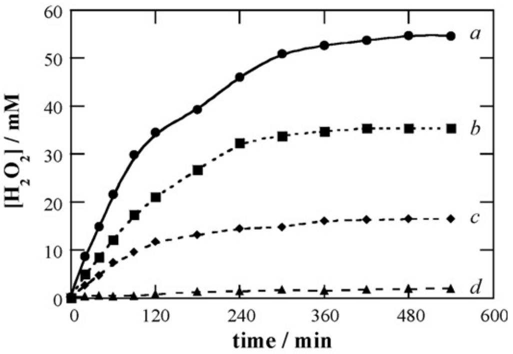


Fig. 2. Variation of accumulated H_2O_2 concentration with time during the electrolysis of 2.5 l of a 0.05 M Na_2SO_4 solution of pH 3.0 in the flow plant at: (a, ●) 150 mA cm^{-2}, (b, ■) 100 mA cm^{-2} and (c, ◆) 50 mA cm^{-2}, 25 °C and liquid flow of 180 l h^{-1}. In curve (d, ▲), a 100 mg l^{-1} MCPP solution with 0.5 mM of Fe^{2+} of pH 3.0 was degraded under the same conditions at 50 mA cm^{-2} by PEF with solar light.

$^{\bullet}$OH [27,35]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (7)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad (8)$$

To confirm this behavior, the H_2O_2 content during the treatment of a 100 mg l^{-1} MCPP solution with 0.5 mM Fe^{2+} of pH 3.0 by PEF with solar light at 50 mA cm^{-2} was determined. The lowest current density used in the trials of Fig. 2 was chosen to reduce the energy cost needed for the degradation process. As can be seen in curve d of Fig. 2, H_2O_2 is always present in excess in the medium (<2 mM), indicating that the system maintains the maximum production of $^{\bullet}$OH from Fenton's reaction (2) during the PEF process, thus allowing the fastest destruction of pollutants with this oxidant.

3.2. Comparative degradation

A solution of 2.5 l of 100 mg l^{-1} MCPP (corresponding to 56 mg l^{-1} TOC) with 0.5 mM Fe^{2+} and 0.05 M Na_2SO_4 of pH 3.0 was treated in the flow plant by EF and PEF with UVA or solar light at 50 mA cm^{-2}, 25 °C and liquid flow of 180 l h^{-1} for 9 h to assess their comparative oxidation power. The same solution without Fe^{2+} was also degraded by AO under comparable conditions. In all these experiments the solution pH remained practically constant, reaching a final value of 2.8–2.9. The change in solution TOC with consumed specific charge (Q, in Ah l^{-1}) for such trials is depicted in Fig. 3a. As can be seen, AO possesses the lowest oxidizing ability since TOC drops slowly yielding 49% mineralization at 9 h after consuming 3.6 Ah l^{-1}. That means that MCPP and its products are progressively oxidized by BDD($^{\bullet}$OH) formed at the anode surface from reaction (4). A faster TOC decay can be observed in Fig. 3a for the EF process, attaining 69% decontamination at the end of electrolysis. The acceleration of the degradation rate in EF can be ascribed to the parallel destruction of pollutants in the medium with $^{\bullet}$OH generated from Fenton's reaction (2). In contrast, Fig. 3a also shows that the two PEF treatments destroy much more rapidly all organics, leading to overall mineralization (>96% of TOC removal) in 9 h. This enhancement of the mineralization process can be related to the quick photodegradation of complexes of Fe^{3+} with final carboxylic acids [15,17,24,28]. In PEF with solar light, however, TOC is very slowly removed after being reduced to 82% at 100 min (Q = 0.67 Ah l^{-1}), suggesting the presence of other final species in the remaining solution that can only be oxidized with BDD($^{\bullet}$OH) and/or $^{\bullet}$OH, but not photodecomposed. The monotonic TOC decay found under UVA irradiation can then be accounted for by the parallel destruction of all final products via either oxidation or photodecomposition. This point has been confirmed from the analysis of generated carboxylic acids, as will be discussed below.

Although the intensities of UVA and solar irradiation, as well as the geometry of their corresponding photoreactors, are different, a similar action of oxidants BDD($^{\bullet}$OH) and $^{\bullet}$OH produced in the electrolytic reactor is expected in both PEF treatments of MCPP at a given current density, independent of the light source. The kinetic differences between both methods can then be mainly related to the different photodecomposition rate of complexes of Fe^{3+} with final carboxylic acids by UVA or solar light. Results of Fig. 3a show that PEF with solar light is able to destroy more rapidly these products, yielding the highest oxidation power under the experimental conditions tested.

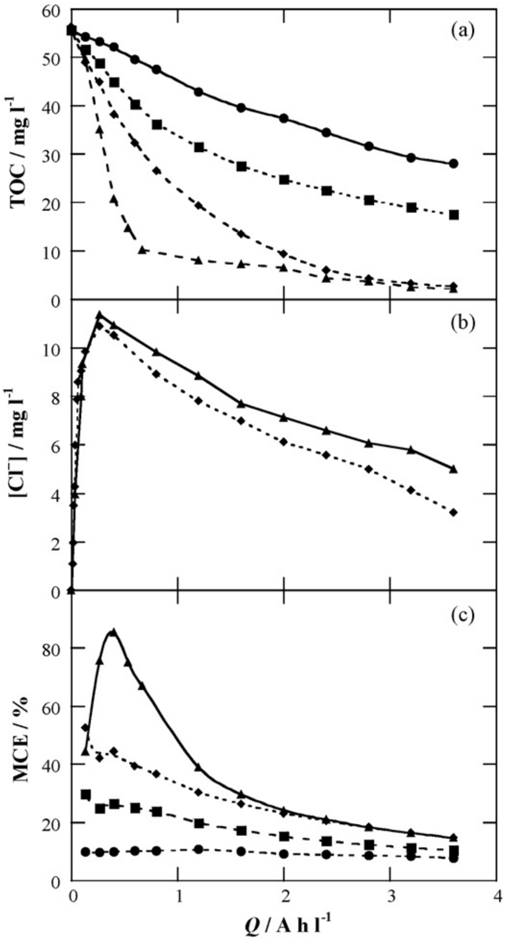


Fig. 3. Dependence of (a) TOC, (b) chloride ion concentration and (c) mineralization current efficiency on specific charge for the degradation of 2.5 l of 100 mg l^{-1} MCPP solutions in 0.05 M Na_2SO_4 of pH 3.0 at 50 mA cm^{-2}, 25 °C and liquid flow of 180 l h^{-1}. Method: (●) AO, (■) EF, (◆) PEF with UVA light and (▲) PEF with solar light. In the three latter methods the starting solution contained 0.5 mM Fe^{2+} as catalyst.

Ion chromatograms of the above treated solutions exhibited a well-defined peak related to Cl^- ion coming from the initial chlorine of MCPP. The possible formation of other chlorine–oxygen ions such as ClO_3^- and ClO_4^- was not detected by this technique. Fig. 3b shows a progressive and similar accumulation of Cl^- for 1 h (Q = 0.40 Ah l^{-1}) of both PEF processes, where it attains approximately 11 mg l^{-1} corresponding to 67% of the initial chlorine content (16.5 mg l^{-1}). At longer time, however, this ion is gradually removed at similar rate in both treatments to reach about 3–5 mg l^{-1} at the end of electrolysis. These findings indicate that the dechlorination process of MCPP involves the loss of most of its chlorine atoms in the form of Cl^-, which is unstable since it is slowly oxidized to Cl_2 at the BDD anode [30].

3.3. Mineralization current efficiency

The above results allow establishing that the mineralization of MCPP gives carbon dioxide and Cl^- as primary inorganic ion, which can be written as follows:

$$C_{10}H_{11}ClO_3 + 17H_2O \rightarrow 10CO_2 + Cl^- + 45H^+ + 44e^- \quad (9)$$

The mineralization current efficiency (MCE) for treated solutions at a given time was then calculated from the following equation:

$$\mathrm{MCE} = \frac{\Delta(\mathrm{TOC})_{\mathrm{exp}}}{\Delta(\mathrm{TOC})_{\mathrm{theor}}} \times 100 \quad (10)$$

where $\Delta(\mathrm{TOC})_{\mathrm{exp}}$ is the experimental solution TOC removal and $\Delta(\mathrm{TOC})_{\mathrm{theor}}$ is the theoretically TOC decay calculated considering that the applied electrical charge (=current × time) is only consumed in reaction (9).

Fig. 3c shows the MCE-Q plots thus obtained for the different treatments reported in Fig. 3a. The efficiency of these methods rises according to their relative oxidation power, following the sequence: AO < EF < PEF with UVA light < PEF with solar light. At 1 h ($Q = 0.40$ Ah l^{-1}), for example, increasing MCE values of 9.8%, 27%, 45% and 86% are found for such treatments. For anodic oxidation, the initial efficiency of 9.8% decays slightly to 7.7% at the end of electrolysis, reaching a maximum value of 11% at 3 h ($Q = 1.20$ Ah l^{-1}), as expected if all pollutants are oxidized by BDD($^{\bullet}$OH) at similar rate. The much greater efficiency of 29% found at the beginning of the EF process indicates that initial organics are much more rapidly destroyed with $^{\bullet}$OH formed from Fenton's reaction (2) than with BDD($^{\bullet}$OH). However, this parameter falls to 10% at 9 h ($Q = 3.60$ Ah l^{-1}), due to the generation of products that are more difficultly oxidized with $^{\bullet}$OH. A progressive decay in MCE from 53% to 14% can also be observed in Fig. 3c for PEF with UVA light. The increase in efficiency of this method with respect to EF can be explained by the quick parallel photodecomposition of complexes of Fe^{3+} with final carboxylic acids under the action of UVA light. In contrast, for PEF with solar light, this parameter attains a maximum value of 86% at 1 h, whereupon it undergoes a dramatic drop up to a final value of 15%. This trend evidences a very rapid removal of products easily photodegradable under solar irradiation, further remaining in solution other species that are slowly mineralized with BDD($^{\bullet}$OH) and/or $^{\bullet}$OH, as pointed out above.

3.4. Effect of experimental parameters in photoelectro-Fenton with solar light

The effect of current density and Fe^{2+} concentration on the degradation rate of PEF with solar light was investigated to clarify its optimum operative conditions. The TOC-t plots obtained for a 100 mg l^{-1} MCPP solution with 0.5 mM Fe^{2+} treated at 25, 50 and 150 mA cm^{-2} are depicted in Fig. 4a. At the end of these trials, 92% of TOC is only removed at 25 mA cm^{-2}, whereas overall decontamination is attained at 50 and 150 mA cm^{-2}. The rise in current density mainly causes a gradual increase in degradation rate up to 100 min of electrolysis. At 60 min, for example, TOC is reduced by 41%, 62 % and 70% at 25, 50 and 150 mA cm^{-2}, respectively. This trend can be ascribed to the faster destruction of organics due to the greater production of BDD($^{\bullet}$OH) from reaction (4) and $^{\bullet}$OH from Fenton's reaction (2), since more H_2O_2 is electrogenerated from reaction (1) (see Fig. 2). On the other hand, Fig. 4a also evidences a very little influence of Fe^{2+} concentration in the range 0.25–5.0 mM on TOC abatement of the above solution degraded at 50 mA cm^{-2}. A small quantity of this catalyst is then sufficient to yield the maximum generation of oxidant $^{\bullet}$OH from Fenton's reaction (2).

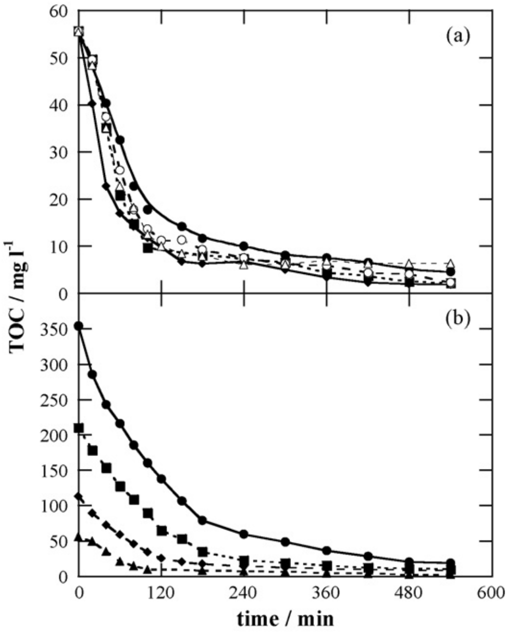


Fig. 4. Effect of experimental parameters on TOC removal with time for the degradation of 2.5 l of MCPP solutions in 0.05 M Na_2SO_4 of pH 3.0 at 25 °C and liquid flow of 180 l h^{-1} by PEF with solar light. In plot (a), degradation of 100 mg l^{-1} mecoprop: with (○) 0.25 mM, (■) 0.5 mM, and (△) 5.0 mM Fe^{2+} at 50 mA cm^{-2}; with 0.5 mM Fe^{2+} at (●) 25 mA cm^{-2} and (◆) 150 mA cm^{-2}. In plot (b), treatment of: (●) 634 mg l^{-1}, (■) 375 mg l^{-1}, (◆) 200 mg l^{-1} and (▲) 100 mg l^{-1} of herbicide with 0.5 mM Fe^{2+} at 50 mA cm^{-2}.

The above findings evidence that the use of a low current density of 50 mA cm^{-2} and a small Fe^{2+} content of 0.5 mM allows achieving the best operative conditions for PEF with solar light. The great oxidation power of this procedure was confirmed by degrading solutions containing up to 0.64 g l^{-1} of MCPP under such optimum conditions. As can be seen in Fig. 4b, the decay in TOC for these trials is so fast that it is always reduced by more than 96% in 9 h. Since the average applied cell voltage was always 11.5–11.7 V, an energy cost as low as 46 kWh m^{-3} can be determined for MCPP mineralization, practically independent of its initial content. Results of Fig. 4b also show that at a given time more amount of TOC is removed as herbicide concentration raises, enhancing the efficiency of the process. Thus, at 60 min increasing MCE values of 86%, 133%, 202% and 337% are obtained for 100, 200, 375 and 634 mg l^{-1} of MCPP, respectively. For the latter solution, the efficiency becomes as high as 93% at 9 h. This suggests that nonoxidizing reactions of BDD($^{\bullet}$OH) (e.g., its oxidation to O_2 at the anode) and $^{\bullet}$OH (e.g., reaction (8) and its reaction with Fe^{2+} [27]) become slower, favoring the reaction of these oxidants with higher amount of pollutants present in the medium. The fact that increasing MCE values >100% are calculated from Eq. (10) when MCPP content raises, can then be explained if a faster generation of complexes of Fe^{3+} with final carboxylic acids takes place, followed by their photodegradation without consuming electric charge.

3.5. Mecoprop decay and kinetic analysis

The decay of MCPP concentration in the different treatments was followed by reversed-phase chromatography, where it displayed a well-defined peak at retention time (t_r) of 7.43 min. It was previously confirmed that this compound can only react with BDD($^•$OH) and/or $^•$OH produced in the electrolytic systems because it is not directly photolyzed by UVA light (see Fig. 5a) and is not degraded by H_2O_2, since no change in its concentration with time was found by adding 20 mM H_2O_2 to a 100 mg l^{-1} MCPP solution of pH 3.0.

The decay kinetics for MCPP was comparatively studied by treating 100 mg l^{-1} herbicide solutions of pH 3.0 at 50 mA cm^{-2}. Anodic oxidation without Fe^{2+} yielded a quite slow removal of this compound, which remained in solution for more than 9 h, as expected if it reacts very slowly with BDD($^•$OH). Kinetic analysis of these data fit well to a pseudo-first-order equation, giving a rate constant (k) of 4.50×10^{-5} s^{-1} (square regression coefficient (R^2) = 0.997). In contrast, Fig. 5a shows that it is destroyed very quickly in 16 min and at similar rate by EF and PEF with UVA or solar light, with an average k-value of $(5.20 \pm 0.09) \times 10^{-3}$ s^{-1} ($R^2 = 0.998$). The fast and similar removal of MCPP in these AOPs indicates that it reacts rapidly with $^•$OH, without significant participation of BDD($^•$OH) and contribution of reaction (3).

The influence of herbicide concentration on its decay kinetics in PEF with solar light was further investigated. Fig. 5b shows that the time required for total removal of MCPP gradually increases from 16 to 50 min when its content rises from 100 to 634 mg l^{-1}. As can be seen in the inset of Fig. 5b, this species always follows a pseudo-first-order reaction with decreasing k-values of 5.27×10^{-3} s^{-1} ($R^2 = 0.998$), 3.25×10^{-3} s^{-1} ($R^2 = 0.996$), 2.43×10^{-3} s^{-1} ($R^2 = 0.998$) and 1.40×10^{-3} s^{-1} ($R^2 = 0.9990$) for increasing concentrations of 100, 200, 375 and 634 mg l^{-1}. This tendency suggests that greater amount of MCPP reacts with lower steady $^•$OH concentration and the enhancement in TOC removal found when its concentration increases (see Fig. 4b) can be related to an acceleration of the destruction of products that are more easily oxidizable with $^•$OH.

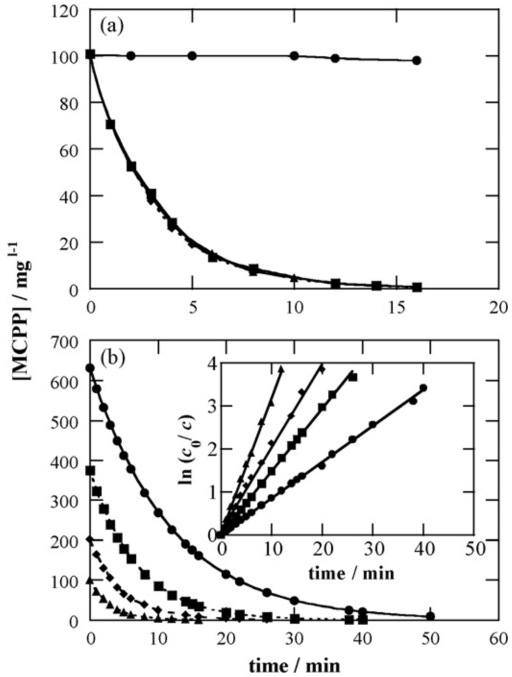
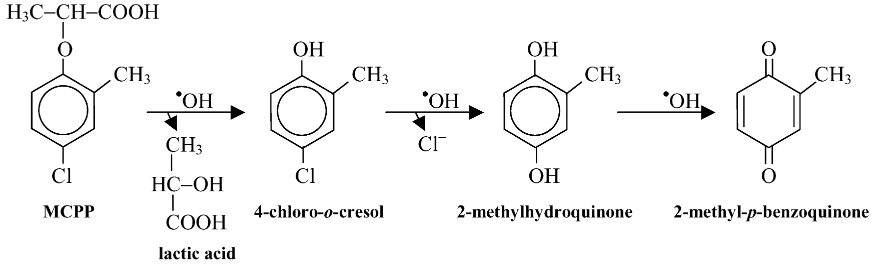


Fig. 5. Mecoprop decay with time during the treatment of 2.5 l of herbicide solutions with 0.05 M Na_2SO_4 and 0.5 mM Fe^{2+} of pH 3.0 at 50 mA cm^{-2}, 25 °C and liquid flow of 180 l h^{-1}. In plot (a), degradation of 100 mg l^{-1} MCPP by: (●) UVA light (without current), (■) EF, (◆) PEF with UVA light, and (▲) PEF with solar light. In plot (b), treatment of: (●) 634 mg l^{-1}, (■) 375 mg l^{-1}, (◆) 200 mg l^{-1} and (▲) 100 mg l^{-1} of herbicide using PEF with solar light. The inset panel presents the corresponding kinetic analysis assuming a pseudo-first-order reaction for MCCP.

3.6. Time-course of intermediates

Reversed-phase chromatograms of 100 mg l^{-1} MCPP solutions with 0.5 mM Fe^{2+} treated by EF and PEF with UV or solar light at 50 mA cm^{-2} exhibited peaks related to aromatic intermediates such as 4-chloro-*o*-cresol (t_r = 6.68 min), 2-methylhydroquinone (t_r = 1.84 min) and 2-methyl-*p*-benzoquinone (t_r = 2.25 min). The evolution of these aromatics is presented in Fig. 6a–c, respectively. As can be seen, each product is accumulated and removed at similar rate in all treatments, rapidly disappearing in a time close to 16 min for 4-chloro-*o*-cresol, 22 min for 2-methylhydroquinone and 27 min for 2-methyl-*p*-benzoquinone, as expected if they are consecutively produced. The fact that the evolution of these aromatics is similar in the different AOPs indicates that they are mainly oxidized with $^•$OH, discarding their direct photolysis. From these considerations, the following initial reaction sequence can be envisaged:



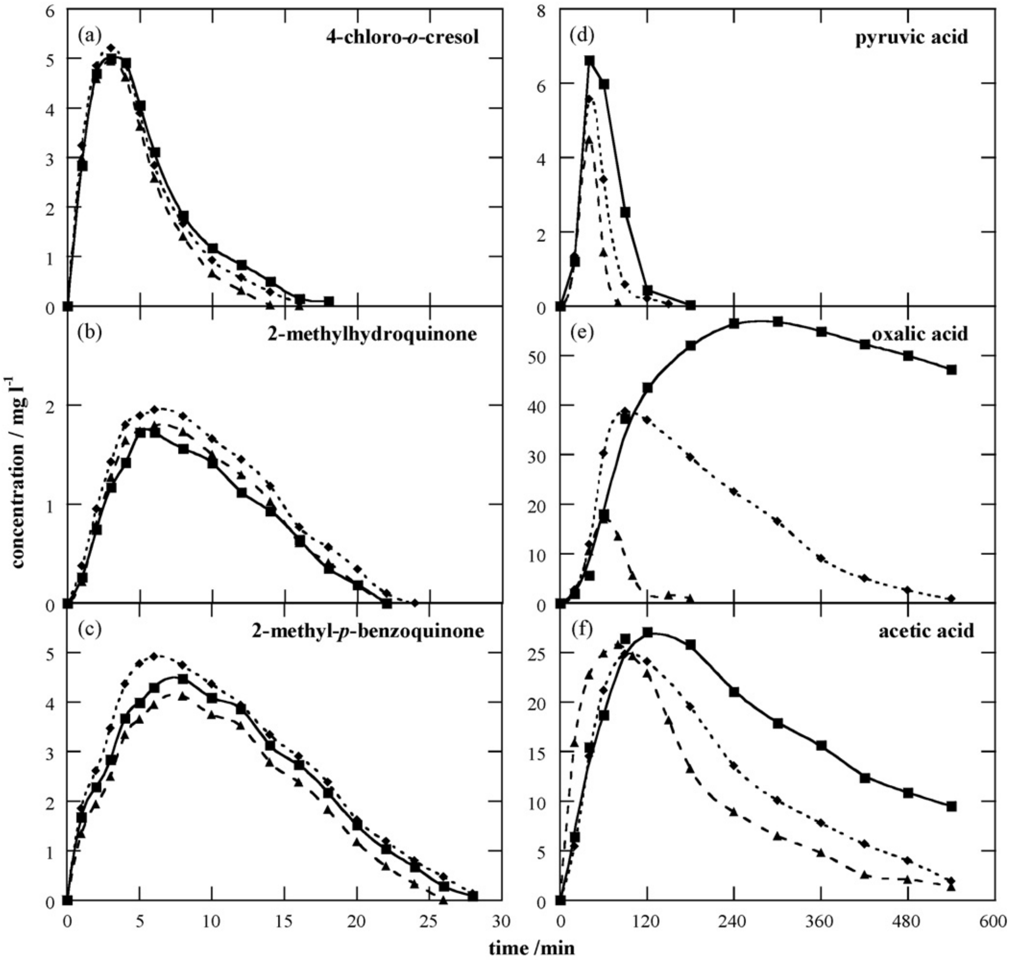


Fig. 6. Evolution of the concentration of intermediates detected during the degradation of MCPP under the same conditions of Fig. 5a. Plots correspond to compounds: (a) 4-chloro-*o*-cresol, (b) 2-methylhydroquinone, (c) 2-methyl-*p*-benzoquinone, (d) pyruvic acid, (e) oxalic acid and (f) acetic acid. Method: (■) EF, (◆) PEF with UVA light and (▲) PEF with solar light.

The attack of $^{\bullet}$OH on the C(1)-position of MCPP leads to the formation of 4-chloro-*o*-cresol and lactic acid. Further hydroxylation in the C(4)-position of 4-chloro-*o*-cresol yields 2-methylhydroquinone with loss of Cl^{-}. This product is then oxidized to 2-methyl-*p*-benzoquinone, which is subsequently degraded to carboxylic acids.

Ion-exclusion chromatograms of the above treated solutions showed a large accumulation of carboxylic acids such as oxalic (t_r = 6.6 min), pyruvic (t_r = 9.1 min), and acetic (t_r = 15.4 min). At the early stages of the EF process, traces of maleic (t_r = 8.0 min), lactic (t_r = 12.1 min) and fumaric (t_r = 15.9 min), acids were also detected. Maleic and fumaric acids come from the oxidation of the aryl moiety of aromatics and are converted into oxalic acid [15,17,18,21,24]. To clarify the oxidative connection of the other acids, solutions with 50 mg l^{-1} of pure compounds in 0.05 M Na_2SO_4 of pH 3.0 were degraded in the flow plant by EF at 50 mA cm^{-2} and their products were identified by ion-exclusion chromatography. These trials revealed that lactic acid released when MCPP gives 4-chloro-*o*-cresol is oxidized to pyruvic acid. The latter acid is transformed into acetic acid, which is degraded to oxalic acid as the ultimate product of MCPP mineralization since it is directly converted into CO_2 [31,33].

In the AOPs tested Fe^{3+} is extensively produced from Fenton's reaction (2) and from oxidation of Fe^{2+} with $^{\bullet}$OH [27] and then, carboxylic acids are expected to form complexes with this ion in large extent. The fact that lactic, maleic and fumaric acids are detected as traces in EF brings to consider that their Fe^{3+} complexes are very rapidly destroyed with $^{\bullet}$OH. The reaction of this oxidant with Fe^{3+} complexes of their subsequent acids is much slower and then, they persist for much longer time. Fig. 6d shows that pyruvic acid is accumulated in smaller extent and disappears more rapidly in the order EF < PEF with UVA light < PEF with solar light, indicating that Fe^{3+}-pyruvato complexes can also react with BDD($^{\bullet}$OH) and photodecomposed. Since these species are removed in 90–180 min, their destruction cannot explain the different oxidation power of treatments at long electrolysis time. A very different behavior can be observed in Fig. 6e and f for oxalic and acetic acids, respectively. Fig. 6e shows that oxalic acid is hardly oxidized in EF, as expected if Fe^{3+}-oxalato complexes react slowly with BDD($^{\bullet}$OH) but not with $^{\bullet}$OH [15,21]. In PEF, however, these species are slowly photodecarboxylated for 9 h using UVA light, being this process much more rapid under solar irradiation disappearing in about 2 h. This very fast removal of Fe^{3+}-oxalato complexes in PEF with solar light explains its quickest TOC decay of 82% and highest efficiency attained at 100 min of electrolysis (see Fig. 3). Fig. 6f also evidences a poor effect of UVA and solar light on the removal of Fe^{3+}-acetato complexes, indicating that they are slowly oxidized with BDD($^{\bullet}OH$) without photodecomposition. At 3 h of PEF with solar light, for example, only 23 mg l^{-1} of acetic acid are detected, corresponding to 9 mg l^{-1} TOC, the same value as found for the treated solution (see Fig. 3a). The long time needed for total mineralization of MCPP in this method can then be related to the large persistence of Fe^{3+}-acetato complexes, which are the only remaining species in solution from 2–3 h of treatment.

4. Conclusions

It has been demonstrated that PEF with UVA or solar light yields complete mineralization (>96% of TOC removal) of mecoprop at pH 3.0 using a one-compartment cell with a BDD anode. The herbicide undergoes a similar degradation pathway in both treatments, but solar light allows a much faster and less expensive decontamination. Experiments carried out in a flow plant with an electrochemical reactor coupled to a solar photoreactor show a strong enhancement of the degradation rate and efficiency with rising herbicide concentration. MCPP and its aromatic products are rapidly converted into final Fe^{3+}-oxalato and Fe^{3+}-acetato complexes under the action of $^{\bullet}OH$ produced from Fenton's reaction (2). Fe^{3+}-oxalato complexes are very rapidly removed due to their efficient photodecarboxylation by solar light, but Fe^{3+}-acetato complexes persist for long time because they are slowly oxidized by BDD($^{\bullet}OH$) formed at the anode surface. The energy cost required for the treatment of MCPP solutions under solar irradiation is 46 kWh m^{-3} at 50 mA cm^{-2}, practically independent of herbicide content up to 0.64 g l^{-1}. These results show the viability of PEF with solar light to remove chlorophenoxy herbicides in wastewaters at industrial scale.

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