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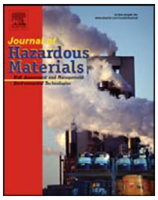

# Solar photoelectro-Fenton degradation of the herbicide 4-chloro-2-methylphenoxyacetic acid optimized by response surface methodology

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ABSTRACT

A central composite rotatable design and response surface methodology (RSM) were used to optimize the experimental variables of the solar photoelectro-Fenton (SPEF) treatment of the herbicide 4-chloro-2-methylphenoxyacetic acid (MCPA). The experiments were made with a flow plant containing a Pt/air-diffusion reactor coupled to a solar compound parabolic collector (CPC) under recirculation of 10 L of 186 mg $L^{-1}$ MCPA solutions in 0.05 M $Na_2SO_4$ at a liquid flow rate of 180 L $h^{-1}$ with an average UV irradiation intensity of about 32 W $m^{-2}$. The optimum variables found for the SPEF process were 5.0 A, 1.0 mM $Fe^{2+}$ and pH 3.0 after 120 min of electrolysis. Under these conditions, 75% of mineralization with 71% of current efficiency and 87.7 kWh $kg^{-1}$ TOC of energy consumption were obtained. MCPA decayed under the attack of generated hydroxyl radicals following a pseudo-first-order kinetics. Hydroxyl radicals also destroyed 4-chloro-2-methylphenol, methylhydroquinone and methyl-*p*-benzoquinone detected as aromatic by-products. Glycolic, maleic, fumaric, malic, succinic, tartronic, oxalic and formic acids were identified as generated carboxylic acids, which form Fe(III) complexes that are quickly photodecarboxylated by the UV irradiation of sunlight at the CPC photoreactor. A reaction sequence for the SPEF degradation of MCPA was proposed.

## 1. Introduction

Several electrochemical treatments have been recently proposed for the decontamination of wastewaters containing inorganic [1,2] and organic pollutants [3–8]. Among them, electrochemical advanced oxidation processes based on Fenton chemistry such as electro-Fenton (EF) and photoelectro-Fenton (PEF) are being developed because they generate oxidant hydroxyl radical ($^{\bullet}OH$) for an effective mineralization of toxic organics to $CO_2$, water and inorganic ions [3,5,9]. In these techniques, $H_2O_2$ is supplied to an acidic solution by the two-electron reduction of $O_2$ gas from reaction (1), which is efficiently produced at carbonaceous cathodes like carbon felt [10–17], activated carbon fiber [18], carbon-polytetrafluoroethylene (PTFE) [3,8,12,19] and carbon nanotubes-PTFE [20–22] gas ($O_2$ or air) diffusion and boron-doped diamond (BDD) [23].

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

The oxidizing power of electrogenerated $H_2O_2$ is then enhanced by adding small amounts of $Fe^{2+}$ to produce $Fe^{3+}$ and $^{\bullet}OH$ in the bulk from Fenton reaction (2) [24]:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\bullet}OH + H_2O \quad (2)$$

The catalytic reaction (2) is propagated from $Fe^{2+}$ regeneration, primordially by $Fe^{3+}$ reduction at the cathode [5,11], allowing the dehydrogenation or hydroxylation of organics by non-selective attack of $^{\bullet}OH$ until mineralization. When an one-compartment cell is utilized, organics can also be degraded by adsorbed hydroxyl radical ($M(^{\bullet}OH)$) formed as intermediate of water oxidation to $O_2$ on the anode M from reaction (3) [6,25]:

$$M(H_2O) \rightarrow M(^{\bullet}OH) + H^+ + e^- \quad (3)$$

The BDD anode is usually preferred for wastewater remediation since it provides $BDD(^{\bullet}OH)$ radicals with higher oxidizing power than those of other anodes due to its higher $O_2$-overpotential [6,26,27]. Nevertheless, the Pt anode yielding less potent $Pt(^{\bullet}OH)$ radicals is widely used since it allows more inexpensive treatments by the lower cell potential applied [6,8,9,28].

The irradiation of the contaminated solution with UVA light ($\lambda_{max}$ = 360 nm) in PEF accelerates the degradation of pollutants in

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EF, since it promotes the photodecomposition of Fe(III) complexes with generated by-products like carboxylic acids from reaction (4) and the enhancement of $Fe^{2+}$ regeneration and $^{\bullet}OH$ production from the photolytic reaction (5) [5,9,10,18–21,29,30]:

$$Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^{\bullet} \quad (4)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \quad (5)$$

In our laboratory, we are exploring the alternative use of sunlight ($\lambda > 300$ nm) as an inexpensive and renewable energy source in the solar photoelectro-Fenton (SPEF) process. The use of solar light is expected to improve the performance of UVA lamps since photons in the UV region range of 300–400 nm, as well as in the visible region ranges of 400–450 nm [31] and 400–650 nm [32], but with much less quantum yield, can be absorbed for reactions (4) and (5), respectively. SPEF has been shown to mineralize some aromatic pollutants like cresols [3], the pharmaceutical paracetamol [8] and the azo dye Acid Yellow 36 [33]. However, more research efforts are required to know the degradation ability of this method on other kinds of pollutants to assess its possible application to industrial scale. In this way, we have studied the SPEF process of the herbicide 4-chloro-2-methylphenoxyacetic acid (MCPA), belonging to the family of phenoxyacetic acids, which are considered highly carcinogenic [34]. MCPA was chosen because it has been detected in natural and drinking waters with contamination levels up to 0.4 $\mu$g $L^{-1}$ [35,36], due to its widespread use in the selective control of perennial crops, grasslands and lawns [19,27]. At the pH of most soils the anionic form of this herbicide predominates allowing its leaching and the contamination of aquifers associated with its use [37].

This paper reports the SPEF degradation of 186 mg $L^{-1}$ MCPA solutions using a 10 L solar flow plant containing a Pt/air-diffusion cell coupled to a compound parabolic collector (CPC) under batch recirculation mode. The optimum experimental variables for this process have been determined with a central composite rotatable design (CCRD) coupled to response surface methodology (RSM) [38,39]. This statistical tool has been recently applied to the Fenton [40–42], photo-Fenton [42,43], solar photo-Fenton [44–47], peroxi-coagulation [22], EF [48,49] and SPEF [8] treatments of some organic compounds. The major advantage of RSM is that includes interactive effects among the variables to describe their complete influence on the process by means of a minimum number of assays [50]. The experiments were performed taking the current, $Fe^{2+}$ content and pH as independent variables and using the analysis of variance (ANOVA) to validate the mathematical models developed [39]. The MCPA decay and the evolution of its by-products were determined by chromatographic techniques and a reaction sequence for MCPA degradation was proposed.

## 2. Experimental

### 2.1. Chemicals

MCPA, 4-chloro-2-methylphenol, methylhydroquinone and methyl-*p*-benzoquinone were reagent grade from Merck and Sigma–Aldrich. All carboxylic acids were analytical grade from Panreac and Avocado. Heptahydrated ferrous sulphate and anhydrous sodium sulphate were analytical grade from Fluka. The MCPA solutions were prepared with deionized water and their pH was adjusted with analytical grade sulphuric acid from Merck. Organic solvents and other chemicals employed were either HPLC or analytical grade from Merck, Fluka and Sigma–Aldrich.

### 2.2. Apparatus and analytical procedures

The solution pH was measured with a Crison GLP 22 pH-meter. Before analysis, aliquots of 7 mL withdrawn from electrolyzed solutions were neutralized at pH 7–8 to stop the degradation process and filtered with 0.45 $\mu$m PTFE filters from Whatman. The mineralization process was monitored from the total organic carbon (TOC) abatement of solutions using a Shimadzu VCSN analyzer. From this data and assuming the overall mineralization of MCPA to $CO_2$ and $Cl^-$ ion via reaction (6):

$$C_9H_9ClO_3 + 15H_2O \rightarrow 9CO_2 + Cl^- + 39H^+ + 38e^- \quad (6)$$

the mineralization current efficiency (MCE) was estimated from Eq. (7) [30,33]:

$$\%\,\mathrm{MCE} = \frac{nFV_s\,\Delta(\mathrm{TOC})_{\mathrm{exp}}}{4.32 \times 10^7\, mIt} \times 100 \quad (7)$$

where $n$ is the number of electrons consumed per MCPA molecule (38), $F$ is the Faraday constant (96487 C $mol^{-1}$), $V_s$ is the solution volume (L), $\Delta(\mathrm{TOC})_{\mathrm{exp}}$ is the experimental solution TOC decay (mg $L^{-1}$), $4.32 \times 10^7$ is a conversion factor (3600 s $h^{-1}$ × 12,000 mg $mol^{-1}$), $m$ is the number of carbon atoms of MCPA (9 atoms), $I$ is the applied current (A) and $t$ is the electrolysis time (h). The energy consumption per unit TOC mass (EC) was calculated from Eq. (8) [5,33]:

$$\mathrm{EC}\,(\mathrm{kWh\ kg^{-1}\ TOC}) = \frac{1000\,E_{\mathrm{cell}}It}{V_s\,\Delta(\mathrm{TOC})_{\mathrm{exp}}} \quad (8)$$

where $E_{\mathrm{cell}}$ is the average cell potential (V) and 1000 is a conversion factor (mg $g^{-1}$).

The MCPA decay and the evolution of its aromatic intermediates were followed by reversed-phase HPLC using a Waters 600 LC fitted with a Spherisorb ODS2 5 $\mu$m, 150 mm × 4.6 mm, column at 35 °C, coupled with a Waters 996 photodiode array detector selected at $\lambda$ of 230 nm for MCPA, 229 nm for 4-chloro-2-methylphenol, 269 nm for methylhydroquinone and 248 nm for methyl-*p*-benzoquinone. Carboxylic acids were detected by ion-exclusion HPLC using the above LC fitted with a Bio-Rad Aminex HPX 87H, 300 mm × 7.8 mm, column at 35 °C and the photodiode array detector selected at $\lambda = 210$ nm. The mobile phase was 70:30 (v/v) acetonitrile/phosphate buffer (pH 3.5) at 0.3 mL $min^{-1}$ for reversed-phase HPLC and 4 mM $H_2SO_4$ at 0.6 mL $min^{-1}$ for ion-exclusion HPLC. The $Cl^-$ concentration was determined by ionic chromatography with a Shimadzu 10 Avp HPLC fitted with a Shim-Pack IC-A1S, 100 mm × 4.6 mm, anion column at 40 °C, coupled with a Shimadzu CDD 10 Avp conductivity detector, using a 2.4 mM tris(hydroxymethyl)-aminomethane and 2.5 mM phthalic acid solution of pH 4.0 at 1.0 mL $min^{-1}$ as mobile phase.

### 2.3. Solar flow plant

Fig. 1 shows the sketches of the solar flow plant and the electrolytic filter-press cell used for the SPEF degradation of 10 L of 186 mg $L^{-1}$ MCPA solutions in 0.05 M $Na_2SO_4$. The solution introduced in the reservoir was recirculated by a peristaltic pump at 180 L $h^{-1}$ adjusted by a rotameter and thermostated at 35 °C by two heat exchangers. The cell contained a Pt sheet of 99.99% purity from SEMPSA and a carbon-PTFE air-diffusion electrode from E-TEK for $H_2O_2$ electrogeneration from reaction (1). Both electrodes of 10 cm × 10 cm in dimension were separated 1.2 cm by a PVC liquid compartment with a central window of 9.5 cm × 9.5 cm (90.3 $cm^2$). The inner face of the cathode was in contact with a PVC gas chamber fed with compressed air at 4.5 L $min^{-1}$ regulated with a back-pressure gauge. The current to the Pt/air-diffusion cell was supplied by a Grelco GDL3020 power supply, which directly displayed the applied potential. The solar CPC photoreactor with a concentration