Innovative photoelectrochemical cell for the removal of CHCs from soil washing wastes

Salvador Cotillas¹, Engracia Lacasa¹, Miguel Herraiz-Carboné¹, Cristina Sáez², Pablo Cañizares², Manuel A. Rodrigo^{2*}

¹Chemical Engineering Department, School of Industrial Engineering

University of Castilla-La Mancha. Campus Universitario s/n, 02071 Albacete, Spain

²Chemical Engineering Department, Faculty of Chemical Sciences and Technologies,

University of Castilla-La Mancha, Edificio Enrique Costa Novella. Campus

Universitario s/n, 13005 Ciudad Real, Spain

Abstract

This work presents a novel photoelectrochemical cell concept for the treatment of soil washing effluents polluted with chlorinated hydrocarbons (CHCs). This cell combines the use of low current densities and the direct irradiation of UV light to the electrodes and the bulk, being easy to be scaled up. To evaluate its performance, the treatment of a soil washing effluent polluted with clofibric acid ($\sim 50 \text{ mg dm}^{-3}$) was carried out. The prototype evaluated was equipped with two boron doped diamond (BDD) plates as anodes, two stainless steel (SS) plates as cathodes and a UV lamp located at the bottom. Results show that it was possible to attain a complete abatement and mineralization of the organochlorinated compound at applied electric charges lower than 5 Ah dm^{-3} , regardless the irradiation of UV light. Nevertheless, the removal rate was higher during photoelectrolysis, specially at the beginning of the treatment, which indicates important advantages for the removal of aromatic compounds. In addition, the toxicity of the effluent was dramatically reduced at the end of the process. These results point out the

high performance of the novel photoelectrochemical reactor proposed for the complete remediation of soils polluted with CHCs.

Keywords: soil remediation; photoelectrolysis; clofibric acid; toxicity; diamond

*Corresponding author e-mail: manuel.rodrido@uclm.es. Tel.: +34-926-29-53-00 Ext. 3411; fax: +34-926-29-52-56

Highlights

- Novel photoelectrocatalytic cell for the remediation soil washing fluids.
- Complete removal of clofibric acid at 10 mA cm^{-2} , with less than 5 kAh m^{-3} .
- Efficient mineralization and detoxification regardless light irradiation.
- Complete reduction of toxicity during the electrolysis and photoelectrolysis

1. Introduction.

The occurrence of organic micropollutants (pharmaceuticals, dyes, pesticides...) in wastewater has become a serious challenge for the scientific community. These compounds are not only responsible to produce several environmental damages but also, they are hazardous for human health, even at low concentrations [1]. Among them, it can be highlighted the chlorinated hydrocarbons (CHCs), because they can accumulate in food chains, causing several health problems for living beings [2]. Likewise, they are very stable and difficult to be removed by conventional processes that are found in Wastewater Treatment Plants (WWTPs). These compounds can be also found retained in soils after an accidental discharge, or bad practice in industrial activities, since organochlorinated species are generated or used in many different sectors, such as solvents, agrochemicals, pharmacy...[3, 4]. In this case, the pollution becomes more harmful, because it can move through the soil until reaching reservoirs, making them unsuitable for human consumption [5]. For this reason, it is necessary to search novel treatment technologies that allow a complete and efficient abatement of these pollutants in soils and wastewater, in order to avoid their spreading in the environment.

Within soil remediation processes [6, 7], soil washing is considered as an easy and efficient technology that allows to move the pollutants retained in soils to the washing fluid used [8, 9]. It needs a vigorous stirring that guarantee the mixture between both phases (soil and washing fluid), followed by a sedimentation stage that helps to separate the treated soil and polluted washing fluid. The washing fluid used depends on the nature of the pollutant and the addition of surfactants will be required if the pollutant is non-soluble in water [10, 11]. Opposite to that, hydrosoluble pollutants can be easily removed from soils using only water without any other further chemical.

The resulting soil washing effluents can be treated by different physical-chemical processes. Among them, it is worth to mention conductive-diamond electrochemical oxidation (CDEO) [12, 13]. This is an electrochemical advanced oxidation process (AOP) that favors the production of large amounts of hydroxyl radicals by water oxidation on boron doped diamond (BDD) anodes [14]. Likewise, other powerful oxidants can be generated from the oxidation of the ions naturally contained in real effluents (chloride, sulfate, phosphate, ...), which also contribute to the removal of organic pollutants [15, 16]. However, one of the main drawbacks of this technology is the mass transfer limitations of pollutant to the electrode surface, where most of the generated hydroxyl radicals are concentrated (because their very low lifetime prevents their transport to the bulk)[14]. For this reason, recent studies have focused on the improvements of CDEO by the coupling of UV light irradiation or application of ultrasounds to promote the formation of large amounts of oxidants and free radicals in the bulk, favoring the removal of organic pollutants by mediated oxidation mechanisms [17-21]. Nonetheless, the electrochemical reactor design that enhances the removal of organochlorinated pollutants in wastewater still remains a key challenge to scientists [22].

With this background, the main aim of the present work is to evaluate a new photoelectrochemical cell prototype for the remediation of soils polluted with a CHC compound. This cell allows the direct irradiation to the electrode surface and can be easily scale-up, simply by multiplication of the electrodes, although in this first work a very simple configuration with only two anodes is evaluated. Specifically, the new photoelectrochemical reactor consists of a tank (2 dm^3) equipped with a UV lamp at the bottom, two BDD plates as anodes and two stainless steel plates as cathodes, set parallel between them and perpendicular to the UV lamp. The final aim is to allow the use of the more efficient low current densities while keeping a reasonable intensity using a large

electrode surface, in agreement with the conclusions of previous works [23, 24] that demonstrated that these operation conditions are ideal for this technology. To test the performance of this new prototype a soil washing fluid polluted with clofibric acid (CA) and without any supplemental addition of salts was tested. This compound has been selected as a model of organochlorine pollutant because it is an herbicide commonly used in agricultural uses. Tests were carried out using the new photoelectrochemical reactor using 10 mA cm^{-2} because this low value was found to be very suitable for reaching high efficiencies in previous works about the degradation of organics [25, 26]. Formation of powerful oxidants during single electrolysis and, the improvements of coupling UV light irradiation to CDEO for the removal of organochlorinated pollutants by the occurrence of free radicals from the photoactivation of electrogenerated oxidants are evaluated in this new cell.

2. Material and methods.

2.1. Chemicals.

Clofibric acid ($\text{C}_{10}\text{H}_{11}\text{ClO}_3$), sodium chloride, magnesium sulfate, sodium nitrate, potassium iodide and calcium carbonate were analytical grade and used as received (Sigma Aldrich, Spain). Formic acid and acetonitrile HPLC grade (Sigma Aldrich, Spain) were used for the mobile phase to determine clofibric acid concentration. Acetone, 2,6-pyridinedicarboxylic acid and nitric acid (Sigma Aldrich, Spain) were used for the mobile phase to determine the ions concentration. Double deionized water (Millipore Milli-Q system, resistivity: $18.2 \text{ M}\Omega \text{ cm}$ at 25°C) was used to prepare all solutions.

2.2. Preparation of spiked soil.

Soil was polluted with a concentrated solution of clofibric acid that it was dissolved in ultrapure water due to its high solubility (polar compound). This solution was homogeneously sprayed to soil and then, soil was aerated for 24 h to evaporate the water used as solvent. The main characteristics of the soil used in this work has been reported elsewhere [18] and, the final concentration of organochlorinated compound in soil was 100 mg kg⁻¹ approximately.

2.3. Analytical techniques.

The concentration of clofibric acid was measured by liquid chromatography using an Agilent 1200 series chromatograph equipped with a DAD detector. A ZORBAX Eclipse Plus C18 analytical column was used for the determination and the mobile phase consisted of 60:40 v/v aqueous solution acetonitrile/0.1 % of formic acid (flow rate: 0.6 cm³ min⁻¹). The DAD detection wavelength was 230 nm, the injection volume was 20 µL and the temperature was kept at 25°C. Total Organic Carbon (TOC) was monitored using a Multi N/C 3100 Analytik Jena analyzer. Inorganic ions were measured by ion chromatography using a Metrohm 930 Compact IC Flex coupled to a conductivity detector. The experimental conditions for the determination of different anions and cations has been reported elsewhere [27]. Oxidants were determined iodometrically according to Kolthoff & Carr [28]. Toxicity of clofibric acid and their metabolites were monitored using the Microtox® method [29, 30]. It consists on the bioluminescence inhibition of marine bacteria *Vibrio fischeri*. Bioluminescence measurements were carried out after 5 and 15 minutes of samples exposure at 15°C.

2.4. Experimental set-up.

A new concept of electrochemical cell is tested in this work. The key ideas for its conceptual design are (1) keeping a reasonable oxidation reaction rate by using low

current densities and high electrode surface areas and (2) improving performance by direct irradiation of UV light to the bulk and electrode surface as indicated in Figure 1a. To evaluate its performance this cell concept was developed with the prototype proposal shown in Figure 1b. Thus, electrolysis and photoelectrolysis were carried out in a double-BDD anode photoreactor under galvanostatic conditions. Circular BDD (WaterDiam, France) and stainless steel (SS) plates, with a geometric area of 78 cm² each one, were used as anodes and cathodes, respectively. The inter electrode gap between both electrodes was 10 mm. A UV lamp VL-215MC (Vilber Lourmat, 254 nm) was placed at the bottom of the reactor, irradiating 15 W directly along the system. The electric current was provided by a Delta Electronika ES03010 power supply.

Figure 1. Detail of the photoelectrochemical reactor. (a) Concept; (b) prototype.

3. Results and discussion.

Soil washing (SW) process was carried out for the treatment of 2 kg of soil polluted with 100 mg kg⁻¹ of CA using a synthetic groundwater as washing fluid (4 dm³). The composition of this effluent has been previously reported elsewhere [5]. The process was

operated for 24 h and, after that moment, all the pollutant retained in soil was considered to be completely moved to the liquid phase. Then, photolysis, electrolysis and photoelectrolysis with diamond anodes were carried out for the removal of CA in the resulting soil washing effluent ($[CA]_0$ near to 50 mg dm^{-3}). The soil washing fluid was treated as produced, without any addition of salts to improve ionic conductivity.

Figure 2 shows changes in CA concentration with the applied electric charge during the electrochemical and photoelectrochemical oxidation of the soil washing effluent. Single photolysis shows an almost null pollutant depletion during the same reaction time than the electrochemical systems were operated (data not shown).

Figure 2. Clofibric acid concentration as function of the applied electric charge during the treatment of soil washing effluents polluted with 100 mg kg^{-1} . (■) electrolysis; (□) photoelectrolysis; j : 10 mA cm^{-2} ; $UV_{254 \text{ nm}}$: 15 W .

As can be observed, the concentration of CA decreases with the applied electric charge until reaching a total pollutant depletion at values lower than 5.0 Ah dm^{-3} , regardless the technology employed. This reveals the main advantage of the proposed electrochemical reactor for the treatment of organochlorinated pollutants, since other conventional

electrochemical reactors require electric charges higher than 10 Ah dm^{-3} to achieve a complete removal of this concentration of this type of pollutants during electrolysis and photoelectrolysis with diamond anodes [5, 31, 32]. Hence, the energy consumption will be expected to be lower with the reactor used in this work.

The removal is faster during photoelectrolysis which indicates that the irradiation of UV light along the reactor improves the process performance. This can be directly related to the different mechanisms for the removal of CA with the two technologies studied. In this context, the pollutant degradation can take place by direct oxidation on the anode surface or mediated oxidation through oxidant species previously electrogenerated [23]. This last one (mediated oxidation) can be favored since the synthetic groundwater used as washing effluent contains different amounts of chloride, sulfate or carbonate which can be oxidized on the diamond surface, favoring the production of powerful oxidants (Eqs. 1-5) [5, 15, 33]. These species are known to efficiently contribute to the removal of organics pollutants from wastewater [34].

In addition, the application of UV light irradiation during the treatment promotes the photoactivation of these electrogenerated oxidants, both on the anode surface and in the bulk, favoring the production of free radicals (Eqs. 6-8). These radicals are more powerful than electrogenerated oxidants and, therefore, they can help to explain the higher removal

efficiency for CA. For example, sulfate radical is known to react 10^3 - 10^5 times faster than peroxodisulfate [35].

To check the role of the electrogenerated oxidants and free radicals on the removal on CA from soil washing effluents, Figure 3 shows the evolution of oxidants species measured as function of the applied electric charge during the electrolysis and photoelectrolysis with diamond anodes. It is important to mention that the oxidants generated are expected to be higher than the concentration measured, because these species are continuously reacting with the organic matter contained in the effluent and even among them. This is expected to be more important in the case of the irradiated process, because in this case the formation of non-stable radicals is promoted.

Figure 3. Electrogenerated oxidants as function of the applied electric charge during the treatment of soil washing effluents polluted with 100 mg kg⁻¹ clofibric acid. (■) electrolysis; (□) photoelectrolysis; j: 10 mA cm⁻²; UV_{254 nm}: 15 W.

The main oxidant that it is expected to be generated during the electrolysis of wastewater with diamond anodes is the hydroxyl radical [36, 37]. Because of its very low lifetime it is not accounted in the oxidants measured in Figure 3. This species is formed from water oxidation (Eq. 9) and it presents a noteworthy oxidant capacity (E⁰: 2.8 V) for the non-selective removal of organic matter in wastewater [38]. However, it is necessary to apply a minimum current density value to guarantee the generation of large amounts of this oxidant in the effluent [14] and, the current density applied in this work (10 mA cm⁻²) is too low to ensure the massive production of this species in the system. This is not bad, as the higher efficiencies typically observed at low current densities during CDEO are explained because the rate of production of hydroxyl radicals and the mass transport rate of pollutants from the bulk towards the nearness of the anode surface are more balanced and less hydroxyl radicals are wasted by side reactions that ends up with the formation of oxygen.

However, in the new cell, the production of hydroxyl radicals can also take place by the reaction of oxygen radical generated by the photoactivation of hypochlorite (Eq. 6) and water during photoelectrolysis (Eq. 10) [39, 40]. Likewise, hydrogen peroxide and ozone can be electrochemically generated during the electrolysis (Eqs. 11-12) and, they can be also photoactivated both in the nearness of the electrode surface and in the bulk, favoring the production of hydroxyl radicals (Eqs. 13-14) [25]. These hydroxyl radicals are more valuable, because they are not confined in the nearness of the electrode surface, but they are distributed in the bulk, being less affected by diffusion control.

239 Regarding oxidants with a longer lifetime, results plotted in Figure 3 show that the
 240 concentration of oxidants increases with the applied electric charge for all the
 241 technologies tested. Specifically, the trend observed shows an initial increase followed
 242 by a plateau zone or even a decrease in their concentration. This indicates that the
 243 production rate of these compounds is higher at the beginning of the treatment and then,
 244 at electric charges higher than 2 Ah dm⁻³ (>75 % CA removal), the generation and
 245 elimination rates are similar, which reveals that oxidants are mainly consumed during the
 246 process for the degradation of organics. Hence, this points out that the removal of CA
 247 during electrolysis and photoelectrolysis with diamond anodes occurs by the combination
 248 of direct and mediated mechanisms. On the other hand, the concentration of oxidants is
 249 higher during photoelectrolysis at higher electric charges. This is an unexpected behavior
 250 taking into account that the electrogenerated oxidants are photoactivated during the
 251 process to produce free radicals and, therefore, their concentration is expected to be lower
 252 [41]. Nonetheless, the generation of large amounts of hydroxyl radicals during
 253 photoelectrolysis favors the indirect production of oxidant species. In this context,
 254 hydroxyl radical can react with chloride, sulfate or carbonate contained in the effluent,
 255 favoring the production of oxidants (Eqs. 15-17). Likewise, free radicals can also react
 256 with hydroxyl radicals and the result of this reaction is the production of oxidants (Eqs.

18-20) [41]. This could explain why the concentration of oxidants is higher during photoelectrolysis.

The degradation of CA contained in soil washing effluents by electrolysis and photoelectrolysis with diamond anodes can lead to the complete mineralization of the pollutant to carbon dioxide or to the formation of other intermediate organics in the effluent. These last one can be more hazardous than the initial pollutant and, for this reason, the concentration of total organic matter present in the effluent was monitored during the treatment. Figure 4 shows the evolution of TOC as function of the applied electric charge during the electrolysis and photoelectrolysis of soil washing effluents polluted with CA. In addition, TOC associated to the intermediates has been estimated taking into account the carbon of CA still remained in solution and TOC values measured according to equation 21 where $n^\circ\text{C}_{\text{CA}}$ is the number of carbon atoms in clofibric acid molecule (10), AW_{C} is the atomic weight of carbon (12 g mol^{-1}) and MW_{CA} is the molecular weight of CA ($214.645 \text{ g mol}^{-1}$).

$$\text{TOC}_{\text{intermediates}} = \text{TOC}_{\text{measured}} - ([\text{CA}]_{\text{measured}} \cdot n^\circ\text{C}_{\text{CA}} \cdot \text{AW}_{\text{C}} / \text{MW}_{\text{CA}}) \quad [21]$$

Figure 4. TOC decay as function of the applied electric charge during the treatment of soil washing effluents polluted with 100 mg kg⁻¹ clofibric acid. (■) electrolysis; (▲) photoelectrolysis; black symbols: experimental TOC; white symbols: theoretical TOC associated to intermediates; j: 10 mA cm⁻²; UV_{254 nm}: 15 W.

TOC concentration decreases with the applied electric charge for all the tests carried out until reaching mineralization percentages higher than 90 %. These results reveal that the electrochemical reactor used does not only remove the organochlorinated compound contained in soil washing effluents, but it also allows to mineralize the organic matter almost completely, applying electric charges lower than 5 Ah dm⁻³. Nonetheless, the trend observed in the Figure suggests that it would be possible to attain a complete mineralization of the organic matter at slightly higher charges.

Photoelectrolysis shows a lower efficiency for TOC removal at the end of the treatment in comparison with the results obtained during single electrolysis. Specifically, the TOC removal percentage during photoelectrolysis (at 4.0 Ah dm⁻³) was 94.58 % whereas a 96.78 % was attain without UV light irradiation. This points out that the photo-assisted

process is more effective for the degradation of aromatic intermediates formed at the beginning of the breakup of CA molecule and, the degradation of aliphatic compounds that are formed at the end of the oxidation processes is more favored during the non-irradiated electrolysis. This behavior has been previously reported in literature during the electrolysis of other organics with diamond anodes [25]. Likewise, this assumption is supported by the changes in the intermediates TOC concentration, where the higher concentrations observed during photoelectrolysis can be explained by the slower oxidation of aliphatic intermediates under light irradiation.

For comparison purposes, experimental data (CA and TOC concentrations) were fitted to a first order kinetics and the resulting kinetic constants are presented in Figure 5.

Figure 5. Kinetic constants calculated for the removal of clofibric acid and TOC during the treatment of soil washing effluents polluted with 100 mg kg⁻¹ clofibric acid. (■) pollutant; (□) TOC; j: 10 mA cm⁻²; UV_{254 nm}: 15 W.

As expected, the value obtained for the removal of CA is higher during photoelectrolysis (+ 28.81 %) whereas the constant calculated for TOC removal is higher during single

electrolysis (+ 14.75 %). Nonetheless, both constants for the removal of organochlorinated compound are higher than the values obtained for TOC removal in both technologies. This confirms the formation of intermediates more difficult to oxidize during the removal of CA.

Based on these results, the synergy coefficient (SC) was calculated for CA and TOC removal according to Eq. 22.

$$SC (\%) = \frac{k_{\text{photoelectrolysis}} - k_{\text{photolysis}} - k_{\text{electrolysis}}}{k_{\text{photolysis}} + k_{\text{electrolysis}}} \cdot 100 \quad [22]$$

A synergistic effect (SC: +39.64 %) resulted for the removal of CA during photoelectrolysis whereas an antagonistic effect (SC: -15.31 %) was obtained for the mineralization of the organic matter. This clearly reveals that photoelectrolysis is an efficient technology for degrading chlorinated hydrocarbons using the proposed reactor and, single electrolysis seems to be more efficient for the abatement of intermediate organic compounds generated during the pollutant oxidation. Therefore, the photoelectrochemical reactor tested would be an excellent alternative for the removal of organochlorinated compounds since it promotes the generation of free radicals from the photoactivation of electrogenerated oxidants near the anode and in the bulk, improving the process performance.

On the other hand, the toxicity of the resulting effluents was evaluated using the Microtox® test which is based on the luminescence inhibition caused by CA and its intermediate by-products on the *Vibrio fischeri* (*V. fischeri*) bacterium. Figure 6 shows the luminescence inhibition percentage with the applied electric charge during electrolysis and photoelectrolysis of soil washing effluents polluted with CA.

Figure 6. Percentage inhibition as function of the applied electric charge during the treatment of soil washing effluents polluted with 100 mg kg⁻¹ clofibric acid. (■) electrolysis; (▲) photoelectrolysis; black symbols: after 5 min exposure to *V. fischeri*; white symbols: after 15 min exposure to *V. fischeri*; j: 10 mA cm⁻²; UV_{254 nm}: 15 W.

As can be observed, the two inhibition percentages corresponding to 5 and 15 min of exposure during electrolysis and photoelectrolysis show similar trends. There is a strong initial increase (reaching a percentage higher than 95 % for both cases) which reveals the higher toxicity associated to CA and its primary intermediate oxidation compounds. In literature, it has been reported that the electrolysis and photoelectrolysis of organic pollutants with diamond anodes lead to the formation of aromatic/cyclic intermediates at the beginning of the oxidation process which are responsible of the higher inhibition percentages achieved [42].

The maximum inhibition percentage attained is higher during electrolysis and it decreases later in comparison with the results obtained during photoelectrolysis. This is due to the presence of large amounts of aromatic/cyclic compounds in the effluent at the beginning of the treatment, as previously explained in TOC profile (Figure 4) and points out the

significance of combining UV irradiation because the effluent can be susceptible to be combined with a cheaper biological treatment. Nonetheless, the trends observed in toxicity analyses indicate that after passing a higher current charge, CA and its aromatic/cyclic intermediates are completely oxidized, reaching a null toxicity value for all the technologies tested. These results confirm that the final oxidation products of CA during the treatment of soil washing effluents by electrolysis and photoelectrolysis with diamond anodes are carboxylic acids with short chain which produce a very low toxicity for *V. fischeri*. Hence, both technologies allow to completely remove the organic matter present in the effluents and to decrease the toxicity for the subsequent discharge to the environment, being the initial values slightly lower during photoelectrolysis. For this reason, it is possible to detoxify soil washing effluents polluted with organochlorinated compounds using the proposed electrochemical reactor.

Finally, the energy consumption (W) for the removal of CA during electrolysis and photoelectrolysis with the proposed reactor was calculated by Eqs. 23 and 24, where Q is the applied electric charge (kAh m⁻³), V is the cell voltage (V), w is the UV lamp power (0.015 kW, 100 % efficiency), t is the operation time (h) and v is the volume treated (m³). Likewise, the energy consumption per TOC unit was calculated by Eq. 25 where W is the energy consumption during electrolysis (W_{electrolysis}) or photoelectrolysis (W_{electrolysis} + W_{photolysis}) and ΔTOC is the difference between initial and final TOC value.

$$W_{\text{electrolysis}} = Q \cdot V \quad [23]$$

$$W_{\text{photolysis}} = w \cdot t / v \quad [24]$$

$$W_{\text{TOC}} = W / \Delta\text{TOC} \quad [25]$$

Furthermore, the values obtained have been compared to others reported in literature for the complete removal of other organochlorinated pollutants by electrolysis and

photoelectrolysis with commercial electrochemical cells under similar operating conditions and herbicide type (Table 1).

Table 1. Energy consumptions for the removal of organochlorinated pollutants by electrochemical technologies.

Pollutant	Concentration (mg dm ⁻³)	TOC (mg dm ⁻³)	Technology*	Electrolyte**	j (mA cm ⁻²)	Q (Ah dm ⁻³)	Pollutant / TOC removal (%)	W _{TOC} (kWh g _{TOC} ⁻¹)	W (kWh m ⁻³)	Cite ***
Clofibric acid 	50	35.36	E	SWE	10	4.08	99.35 / 96.78	1.30	44.65	TW
	50	32.90	PE	SWE	10	4.08	99.88 / 94.58	4.24	131.85	TW
Clopyralid 	100	34.62	E	SGW	10	11.38	100 / 100	3.58	85.32	[5]
	5	1.64	PE	SWE	12.8	16.41	100 / 98.17	193.33	311.26	[29]

*E: electrolysis; PE: photoelectrolysis

**SWE: soil washing effluent; SGW: synthetic groundwater

***TW: this work

The values obtained during the treatment of synthetic groundwater or soil washing effluents with conventional electrochemical cells show the highest consumptions for both electrolysis and photoelectrolysis. Nonetheless, the initial pollutant concentration is higher during electrolysis process (+ 50 %) which could explain the higher energy consumption registered by the higher electric charge required for the complete removal (2 times higher: 85.32 vs. 44.65 kWh m⁻³). However, the photoelectrolysis process was carried out with a lower initial concentration (- 90 %) and, the resulting energy consumption is also higher than the value obtained during the photoelectrolysis of soil washing effluents polluted with CA using the new electrochemical cell (311.26 vs. 131.85 kWh m⁻³). This is directly related to the reactor used which required higher electric charges to attain a complete pollutant removal. In addition, the energy consumption per TOC unit shows the same results: lower values when using the proposed reactor in this work. At this point, it is important to highlight the higher energy consumption during photoelectrolysis with a conventional cell (193.33 kWh g_{TOC}⁻¹). In this case, the low initial TOC concentration reveals the mass transfer limitations of this reactor in comparison with

the system used in this work, where free radicals are directly produced on the anode surface and in the bulk, improving the mineralization performance. Hence, it can be affirmed that the proposed photoelectrochemical reactor leads to high efficiencies for the removal of organochlorinated pollutants from soil washing effluents and low energy consumptions, comparing to other commercial cells.

4. Conclusions.

From this work, the following conclusions can be drawn:

- The proposed photoelectrochemical reactor prototype for the treatment of the resulting soil washing effluents allows to completely remove the clofibric acid concentration at applied electric charges lower than 5 Ah dm^{-3} and current densities of 10 mA cm^{-2} during electrolysis and photoelectrolysis. The generation of large amounts of powerful oxidants from the oxidation of the ions naturally contained in groundwater significantly contributes to the pollutant removal. Likewise, the photoactivation of electrogenerated oxidants leads to the formation of free radicals which also favor the degradation process.
- The process efficiency is higher during the photoelectrochemical process which reveals that the production of free radicals significantly contributes to the removal of clofibric acid from soil washing wastes. Nonetheless, the applied electric charge required to attain the complete pollutant abatement is similar for both technologies.
- A mineralization higher than 90 % for current charges lower than 5 Ah dm^{-3} can be attained during both electrolysis and photoelectrolysis using the proposed reactor. The mineralization efficiency is higher during photoelectrolysis at the beginning of the treatment because this technology is more suitable for the

removal of aromatic/cyclic compounds that are the first intermediates formed from the oxidation of clofibric acid.

- The toxicity of soil washing effluents polluted with clofibric acid shows a moderate inhibition of bioluminescence to *V. fischeri* bacteria before treatment (60 %) but, the first intermediate compounds generated from the oxidation of the pollutant during electrolysis and photoelectrolysis increases the inhibition until reaching percentages of 100 %. However, the inhibition decreases down to zero at the end of the processes, which indicates that the reactor proposed for the treatment of soils polluted with organochlorinated compounds not only allows to remove the pollutant but also decreases the toxicity of treated effluents.

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