1 **Powering with solar energy the anodic oxidation of soil washing wastes**

2 *M. Millán, M.A. Rodrigo, C.M. Fernández-Marchante, P. Cañizares, J. Lobato**

3 Department of Chemical Engineering, Faculty of Chemical Sciences & Technologies,
4 University of Castilla-La Mancha, Av. Camilo Jose Cela n 12, 13071 Ciudad Real,
5 Spain

6 *Corresponding author. Telf: +34 926 295 300; fax: +34 926 295 256. E-mail address:

7 justo.lobato@uclm.es

8 **Abstract**

9 This work focuses on the development of new sustainable and environmentally friendly
10 electro-oxidation processes, made by the combination of photovoltaic panels and
11 electrolytic cells equipped with diamond anodes. In order to evaluate the best operation
12 mode, three cases of study were evaluated for the treatment of synthetic wastes polluted
13 with clopyralid: 1) electrolysis at constant specific electric charge but changing intensity
14 (by following power production profile with both the flowrate and the current intensity),
15 2) electrolysis at variable specific current charge, keeping the value in the average of
16 case 1 but changing the intensity and keeping the flowrate constant and 3) electrolysis
17 at constant specific electric charge and constant intensity applied and flowrate treated
18 (by keeping the average electric charge applied in the same value than in the previous
19 case). Results obtained showed significant differences between the performance of the
20 technology in the three cases of study, pointing out that the best quality in the effluents
21 was obtained in Case 1 and the highest efficiency in the use of energy in Case 2. The
22 changes in the pH of the effluents were important and together with the changes
23 observed in the intermediates, indicate that changing the operation mode (from the

viewpoint of the power fed) may affect importantly to the performance of the system also from a mechanistic point of view.

INTRODUCTION

The development of the agrochemical industry during the 20th century has been one of the driving forces that causes an exponential growth of the planet's population. One of the key families of chemicals responsible for the necessary increase in the global food production are the pesticides. However, its use, that helps to maximize crop production, has an important drawback: nowadays, hundreds of hectares of soil are polluted with pesticides (and, in turn, the water reservoirs connected with them).

A very important fraction of the pesticides belongs to the group of organochlorinated hydrocarbons, and often they are highly toxic and persistent in the environment. Clopyralid (3,6-dichloro-2-pyridinecarboxylic acid, $C_6H_3Cl_2NO_2$) is a good model. It is an herbicide widely used in agriculture to remove weed in grass. This compound is highly-soluble in water(Pohanish, 2014) and it is not significantly adsorbed onto soil particles(Šojić et al., 2009). Consequently, it remains in soils for long periods and can reach the groundwater reservoirs by permeation processes.

Considering the characteristics of organochlorinated pesticides, electrochemical processes might be considered among the best technologies for the treatment of these organics. Thus, electrochemical advanced oxidation processes (EAOPs) have been widely studied in the mineralization of toxic and persistent organic pollutants (POPs) from wastewater effluents (Martínez-Huitl and Ferro, 2006; Oturan and Aaron, 2014; Moreira et al., 2017). These EAOPs are characterized by the in-situ generation of powerful oxidant agents, such as hydroxyl radicals (OH^*). Among the wide variety of EAOPs, it can be highlighted the conductive diamond electrochemical oxidation (CDEO),

because of its high removal efficiencies and low environmental impact(Martínez-Huitle and Ferro, 2006; Panizza and Cerisola, 2009; Rodrigo et al., 2010; Rodrigo et al., 2014; Moreira et al., 2017).

Electrochemical technologies are based on the use of electrons as the almost unique reactive. Hence, they demand electrical energy. Within the context of increasing the sustainability, in order to make these processes more sustainable and environmentally friendly, their coupling with green energies is being proposed. Solar power is one of the best options in countries such as Spain, which receives an annual average of solar radiation between 3.6 and 5.4 kWh m⁻² (Kabir et al., 2018). Thus, photovoltaic (PV) systems are able to produce energy throughout the year and even, 80% of their power range could be produced in partly cloudy days and up to 30% of energy in extremely overcast days (Mook et al., 2014). These PV systems can be operated into two mode: stand-alone and grid-connected systems (Mook et al., 2014). Nevertheless, theses operational modes need the storage of energy in batteries or the couple of them with the local grid. Previous studies in our group proposed to power electrochemical devices for the treatment of soils and wastewater polluted by persistent organic pollutant directly by renewables energies (Souza et al., 2015a; Souza et al., 2015b; Millán et al., 2018). Those works showed promising results in the treatment of wastewater effluents, however the electro-kinetic process carried out into a soil matrix shown an unexpected non-desirable behaviour (Souza et al., 2016a; Souza et al., 2016b) because the progress in the remediation obtained during daytime reversed overnight, decreasing the global efficiency of the process. In the treatment of wastewater this problem did not seem to be as severe. However, it was evaluated in batch processes and there is a lack of expertise in the understanding of what may happen in continuously operated processes.

Based on that background, this work aims to evaluate new strategies to power electrooxidation processes by evaluating the influence of the operational mode (power supply and flow rate) on the performance of the electrooxidation of an organochlorinated compound operated in continuous mode. To do this, within a period of three days, the electrolysis in continuous mode of clopyralid (used here as a model herbicide) is going to be evaluated using three different approaches or case studies: 1) electrolysis at constant specific electric charge but changing intensity (by following power production profile with both the flowrate and the current intensity), 2) electrolysis at variable specific current charge keeping the value in the average of case 1 but changing the intensity and keeping the flowrate constant and 3) electrolysis at constant specific electric charge and constant intensity applied and flowrate treated (by keeping the average electric charge applied in the same value than in the previous case). It is important to note that case 1 did not treat wastewater overnight, because flowrate follows the patterns of sunlight irradiation while cases 2 and 3 the cell is fed with a constant flowrate over the complete three days of the tests. It is also important to point out the continuous operation mode which is a realistic approach to a potential treatment and remarks some of the characteristics of this mode of operation, which is not typically evaluated in scientific literature.

EXPERIMENTAL SECTION

- Chemical

Clopyralid was supplied by Zymit Química (Spain). Methanol HPLC and formic acid (Sigma-Aldrich, Spain) were used for the mobile phase. Mili-Q water (Resistivity: 18.2 MΩcm at 25 °C) was used to prepare all the solutions.

- Analysis procedures and methods

In the three tests shown in this work, the anodic oxidation of a solution containing 100 mg dm⁻³ clopyralid and 300 mg dm⁻³ Na₂SO₄ as a supporting electrolyte was carried out. The concentration of clopyralid and intermediates was measured by high performance liquid chromatography, HPLC (Agilent 1260 Infinity). The detection wavelength was 280 and the volume injection was set at 20 µL. A Zorbax Eclipse Plus C18 analytical column from Agilent was used. The mobile phase consisted of 30% methanol/70% water with 0.1% of formic acid (flow rate: 1 mL min⁻¹). The total organic carbon (TOC) concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer.

- **Experimental setup**

A bench-scale plant working in continuous mode was used to carry out the electrooxidation of clopyralid. The electrolysis was conducted in a DiaCell® cell supplied by Adamant (Switzerland). Three different operation modes were evaluated:

- Case 1: flowrate and energy powered follow the solar irradiation profile keeping the specific current charge passed constant.
- Case 2: power dosed follows the solar irradiation profile, but flowrate is kept constant throughout the tests (changing applied electric charge)
- Case 3: flowrate and power are kept constant over the whole tests, maintaining the average power applied constant with respect to cases a and b but applied during the whole experimental period

The solar profile (corresponding to three days of winter) used to power electrically the anodic oxidation reactor in cases a and c was that received by PV panels located on the roof of the Electrochemistry and Environmental Engineering Laboratory (E3L) of the University of Castilla-La Mancha (3.59N 3.55O) from 17th to 18th of February 2018, and

it was chosen because the very different profiles obtained in each of the days. Further information can be found elsewhere (Millan et al., 2018).

In the typical galvanostatic operational mode (case 3) the cell was powered with an applied current density of 61.52 mA cm^{-2} , which is the average current density resulting from current density profiles of cases 1 and 2. On the other hand, considering previous results of our group, where the electrooxidation of clopyralid was studied in discontinuous mode (Cotillas et al., 2017; Martín de Viales et al., 2018), the flow through the cell was adjusted with the aim of working at a typical charge of 10 Ah dm^{-3} , value for which a very important degree of oxidation has to be obtained but not the total mineralization, allowing to compare in this way the efficiency of the different strategies proposed. Thus, the reactor was fed with a flow of 8.05 mL min^{-1} in cases 1 and 3, when the reactor was running at constant flow. In case 1, the average value of the profile of

132 flowrate also corresponds to this value, because the system was also adjusted to work at
 133 10 Ah dm⁻³.

134
 135 **Figure 1.** Current density applied and flow rate fed to the electrochemical reactor in the
 136 three tests carried out a) case 1, b) case 2, c) case 3.

137 Table 1 shows the average volumes treated as well as the average intensities applied in
 138 each day of the three tests carried out and the treatment times.

139 **Table 1.** Flowrate and operation parameters in each of the operation days of the three
 140 tests carried out in this work

Case	Day	Average Current (A)	Average Voltage (V)	Treatment time (min)	Total flow treated (L)
1	1	5.52	7.49	450	4.14
	2	3.17	5.85	235	1.24
	3	5.41	7.71	364	3.35
2	1	5.52	6.88	450/1440*	11.56
	2	3.17	5.86	235/1440*	11.56

	3	5.41	7.68	264/450*	3.61
	1	4.83	7.12	1440	11.56
3	2	4.83	7.17	1440	11.56
	3	4.83	6.48	450	3.61

* First value corresponds to electrolysis time/second value to time in which flowrate was flowing through the cell

As seen, the average values of current applied and voltages are nearly the same in the three tests during the time in which current is applied to the cell. As a consequence, so does the power applied to the system. However, the application time is different, as it only corresponds to the daylight time in cases 1 and 2 and to the full day in case 3. Consequently, the total electric charge passed is the different and much higher in the last case. Therefore, the energy passed is expected to be also higher and results have to be normalized with this value.

RESULTS AND DISCUSSION

Figure 2 informs about the degradation of clopyralid during the cases evaluated in this work (each of them consisting of a three-day test). Part b shows the changes observed in the mineralization during those tests. As expected, profiles in the concentration of pollutant and TOC are related to the transient inputs applied in the power and flowrate. The higher the current density applied, the higher the removal efficiency in all cases, as it could be initially expected according to the literature (Panizza and Cerisola, 2009; Rodrigo et al., 2010; Oturan and Aaron, 2014; Moreira et al., 2017). Thus, for cases 1 and 2, the highest daily removal is obtained when the solar radiation was maximum (around noon). In case 2, during nights no current is applied and, consequently, no degradation is obtained. Opposite, in case 1, no treatment results are obtained, because no flow is passed throughout the cell overnight (zone marked in grey). Regarding case 3, during the first day is observed that concentrations settled down to the steady-state values, which may be explained by the constant flowrate and current charge applied. In every case, changes in the concentration of clopyralid and TOC are parallel.

Figure 2. Clopyralid and TOC degradation during the three electrolytic tests

Table 2 shows the total removal of TOC during the three days and the value normalized to the electric current application time for each of the days in each of the tests. Table 3 shows the average concentrations of TOC and clopyralid (calculated taking into account the volume treated) in the influents and effluents.

177

178 **Table 2.** Net removal of TOC and average removal rate, taking into account treatment
 179 time

180

Case	Day	Total mg TOC removed	mg TOC min ⁻¹
1	1	133.4	0.30
	2	34.91	0.15
	3	88.08	0.24
2	1	114.67	0.25
	2	44.33	0.19
	3	94.8	0.25
3	1	260.56	0.18
	2	391.93	0.27
	3	123.74	0.27

181

182

183 **Table 3.** Average values of the TOC and Clopyralid and the inlet and outlet of the

184 treatment

Case	Day	TOC ₀ (mg L ⁻¹)	TOC _{out} (mg L ⁻¹)	Clopyralid ₀ (mg L ⁻¹)	Clopyralid _{out} (mg L ⁻¹)
1	1	41.28	8.93	93.78	16.58
	2	40.44	13.41	92.54	26.04
	3	39.74	13.73	94.3	22.16
2	1	41.59	25.67	96.79	56.46
	2	40.46	29.89	96.88	66.2
	3	39.8	24.31	95.71	57.37
3	1	46.92	22.22	97.36	41.87
	2	44.78	9.90	93.46	16.44
	3	43.64	9.07	92.17	16.32

185

186

187 In general terms, case 1 and 2 lead to the almost same removal of TOC (in mass), which

188 can be explained because the total energy dosed is the same. In specific values, this also

189 applies to case 3 with average TOC removal rates of 0.23 mg /min in the three cases of

study. This indicates a robust behaviour of the electrolytic system, regardless of the operation conditions applied because it always lead to the same average removal.

Regarding concentrations in the effluent, as expected, case 2 shows the worst results because there is no treatment overnight and flow is not stopped. The average removal of clopyralid and mineralization are 76.89, 37.80 and 70.45 %, respectively for cases 1, 2 and 3. The average mineralization percentages were 70.22, 34.40 and 66.48%. These values agree with those reported in a previous study in which the technology was evaluated in discontinuous mode and indicates that the parameter Q (applied current charge) can give a good indication of the progress of the treatment, regardless of the conditions in which it is used.

In comparing the values of clopyralid oxidation and mineralization, it can be stated that there are very small differences between the oxidation of the clopyralid and the mineralization, suggesting that once the molecule start its oxidation, it proceeds very efficiently up to its complete degradation. This result is expected for electrolysis with diamond anodes, in which the occurrence of intermediates is known to be not very important and often negligible (Panizza and Cerisola, 2009; Rodrigo et al., 2010).

Anyway, differences between corresponding values of clopyralid and TOC removal stand for those intermediates, which, in this work, were monitored by HPLC. Figure 3 shows the intermediate species generated during the electro-oxidation powered by the different operation modes studied in terms of intermediate areas. 17 different intermediates were observed in total, but not all of them were presented in all studied cases. The highest number of intermediates species was attained when the electrooxidation reactor worked under the traditional operation mode (case 3). By contrast, this operation mode showed the lower areas, below 300 a.u. Nevertheless, this variable is not directly related to the concentration of compound. Each intermediate

must be identified to confirm that this operation mode generated the lower amount of intermediate species. On the other hand, the operation mode which generated the lowest number of intermediates was the case 1, when the reactor was running at constant charge and powered by solar energy profile. This operation mode allows to work at the desired charge which can achieve the complete mineralization of the organic compounds and the lower generation of intermediate species. The use of high current densities favours the formation of oxidants from the salts present in the water and consequently, the generation of intermediates species (Cotillas et al., 2017; Lan et al., 2017). Thus, the number of intermediates species generated at solar peak hour should be huge. However, great differences were not found which could be due to the high current density values were applied during short periods of times. Among the different intermediate species which were generated, some of them could be identified. Results show that different intermediates were identified depending on the operation mode, which indicates that the degradation pathway is different in each case. 6-chloropicolinic acid (i_{15}) was identified in the three operational modes at a retention time of 3.794 min. On the other hand, when the reactor was powered by green energy, the pathway showed oxalic acid (i_8 , 1.485 min) in both cases. Nevertheless, this species was not identified when electrolysis was powered at constant current density. In this case, the picolinic acid (i_5) and the 3-chloropicolinic acid (i_{12}) were also identified at 1.167 and 1.840 min, respectively. Other studies reported different intermediates compound in the degradation pathway of clopyralid when photocatalytic processes are used to remove this herbicide from wastewater effluents (Šojić et al., 2009).

238

239 **Figure 3.** Chromatographic areas of intermediate species generated during the three
 240 different operation modes studied

241 Figure 4 shows the maximum chromatographic areas of each intermediate for the
 242 different operational modes studied. Thus, the maximum areas of the generated
 243 intermediates can be compared qualitatively for the three operation modes studied.
 244 Results show higher maximum chromatographic areas for most of the intermediate
 245 species generated when the reactor was powered by solar energy. Nevertheless, the
 246 operation mode 2 showed lower maximum chromatograph areas than the operation mode
 247 a for the same intermediate specie. In addition, if the areas of the identified intermediates
 248 are compared, the results show a generation of oxalic acid (i_8 , 1.485 min) almost three
 249 times greater when the reactor worked under the second operational mode. On the other
 250 hand, the generation of 6-chloropicolinic acid (i_{15} , 3.794 min) was much higher when the
 251 reactor was electrically supplied by the traditional operational mode. However, it is
 252 important to highlight that the chromatographic areas do not correspond to the
 253 concentration of compound and all the intermediate species must be identified to quantify
 254 them. In addition, their identification is essential to know their nature and consequently
 255 their harmfulness.

Figure 4. Maximum chromatographic area of intermediate species during the electrooxidation of clopyralid supplied by solar power and constant flow (■), solar power and non-constant flow (□) and galvanostatic mode and constant flow (■).

The pH and the conductivity in the inlet and outlet stream were also measured during the tests and figures 5 and 6 show the values recorded, respectively for each parameter in the influent and effluent of the treatment. Table 4 shows average values of these parameters for comparison purposes. The pHs in the influent were close to neutral. As expected, a drop was observed in all cases when the electrolysis process was running due to the acid nature of the intermediate species produced in the three operational modes. Changes were of 10.3, 6.9 and 19.7%, respectively for cases 1, 2 and 3. The changes do not follow the same patterns of the TOC decrease, which was higher in case 1 instead of case 3 (which shows the maximum change in pH) and together with the changes observed in the intermediates, they indicate that changing the operation mode may affect importantly to the performance of the system at least from a mechanistic point of view.

Figure 5. Values of pH in the influent (■) and effluent (□) during the three electrolytic tests.

On the other hand, changes in the conductivity of the solution were not observed (always below 5%), despite the changes in the pH, that are expected to affect the conductivity. It is important to note that average values of conductivity increases in cases 1 and 3 by 1.8 and 1.1 % and decreases in case 2 by 4.6%, although not a clear explanation was found for this observation.

Figure 6. Conductivities in the influent (▲) and effluent (△) during the three electrolytic tests

Table 4. Daily average values of pH and conductivity in the three cases of study.

Case	Day	Inlet pH	Outlet pH	Inlet conductivity (mS cm ⁻¹)	Outlet conductivity (mS cm ⁻¹)
------	-----	----------	-----------	---	--

1	1	4.72	3.76	4.03	4.15
	2	4.8	5.13	4.13	4.14
	3	4.69	3.86	4.2	4.29
2	1	4.92	3.84	4.37	3.87
	2	4.95	4.53	3.87	3.80
	3	4.95	5.42	3.79	3.81
3	1	5.19	3.96	3.73	3.83
	2	5.03	4.32	3.45	3.44
	3	5.22	3.94	3.25	3.24

A last point to be discussed in this work is related to the energy dosed in each of the tests. Table 5 shows the key values related to this topic.

Table 5. Current charge and energy spend in each of the three cases of study.

Case	Day	Current charge passed (Ah/L)	Specific energy applied (Wh/L)	Total electric charge passed (Ah)	Total Energy passed (Wh)	Ratio TOC /Energy (g TOC kWh)
1	1	10	74.91	41.41	310.18	0.43
	2	10	58.51	12.41	72.63	0.48
	3	10	77.11	33.54	258.62	0.34
2	1	11.46	78.82	41.41	296.67	0.39
	2	6.58	38.35	12.41	66.72	0.66
	3	11.23	86.24	33.54	275.76	0.34
3	1	10	71.23	115.92	825.75	0.32
	2	10	71.71	115.92	831.24	0.47
	3	10	68.42	36.23	247.84	0.50

As it can be observed the specific values are very similar in the three tests, with applied current charges near the design parameter selected for these three tests (10 Ah dm⁻³) and daily specific energy applied in the range 38.35 to 86.24 Wh/L, with average values close to 69.5 Wh/L in the three tests. Conversely, changes in the total amount of charge and energy applied were motivated by the different application time in the three tests and they should correlated with the changes in the removal of pollutant. Thus, here is it important to compare the relation between the TOC removed (g) and the total energy passed (kWh). This ratio is also shown in Table 5, where it can be seen that they fluctuated between 0.32 and 0.66 g/kWh, and that test 2 is the most efficient with an average value of 0.46 g/kWh. which is slightly over the 0.42 and 0.43 g /kWh obtained by tests 1 and 3,

respectively. The higher concentration at the outlet of the reactor (with lower diffusion limitations) can help to understand this better result.

ACKNOWLEDGMENTS

Financial support from the Spanish Ministry of Economy, Industry and Competitiveness and European Union through project CTM2016-76197-R (AEI/FEDER, UE) is gratefully acknowledged. M. Millán wishes to thank to the UCLM for the pre-doctoral contract within the framework of the Plan Propio I+D.

REFERENCES

- Cotillas, S., Cañizares, L., Muñoz, M., Sáez, C., Cañizares, P., Rodrigo, M.A., 2017. Is it really important the addition of salts for the electrolysis of soil washing effluents? *Electrochim. Acta* 246, 372-379.
- Kabir, E., Kumar, P., Kumar, S., Adelodun, A.A., Kim, K.-H., 2018. Solar energy: Potential and future prospects. *Renew.Sust. Energ. Rev.* 82, 894-900.
- Lan, Y., Coetsier, C., Causserand, C., Groenen Serrano, K., 2017. On the role of salts for the treatment of wastewaters containing pharmaceuticals by electrochemical oxidation using a boron doped diamond anode. *Electrochim. Acta* 231, 309-318.
- Martín de Vidales, M.J., Castro, M.P., Sáez, C., Cañizares, P., Rodrigo, M.A., 2018. Radiation-assisted electrochemical processes in semi-pilot scale for the removal of clopyralid from soil washing wastes. *Sep. Purif. Technol.*
- Martínez-Huitle, C.A., Ferro, S., 2006. Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes. *Chem. Soc. Rev.* 35, 1324-1340.
- Millan, M., Rodrigo, M.A., Fernandez-Marchante, C.M., Diaz-Abad, S., Pelaez, M.C., Canizares, P., Lobato, J., 2018. Towards the sustainable powering of the electrocoagulation of wastewater through the use of solar-vanadium redox flow battery: A first approach. *Electrochimica Acta* 270, 14-21.
- Millán, M., Rodrigo, M.A., Fernández-Marchante, C.M., Díaz-Abad, S., Peláez, M.C., Cañizares, P., Lobato, J., 2018. Towards the sustainable powering of the electrocoagulation of wastewater through the use of solar-vanadium redox flow battery: A first approach. *Electrochim. Acta* 270, 14-21.
- Mook, W.T., Aroua, M.K., Issabayeva, G., 2014. Prospective applications of renewable energy based electrochemical systems in wastewater treatment: A review. *Renew.Sust. Energ. Rev.* 38, 36-46.
- Moreira, F.C., Boaventura, R.A.R., Brillas, E., Vilar, V.J.P., 2017. Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters. *Appl. Catal. B* 202, 217-261.
- Oturan, M.A., Aaron, J.-J., 2014. Advanced Oxidation Processes in Water/Wastewater Treatment: Principles and Applications. A Review. *Crit. Rev. Env. Sci. Technol.* 44, 2577-2641.

340 Panizza, M., Cerisola, G., 2009. Direct And Mediated Anodic Oxidation of Organic
341 Pollutants. *Chem. Rev.* 109, 6541-6569.

342 Pohanish, R.P., 2014. Sittig's Handbook of Pesticides and Agricultural Chemicals:
343 Second Edition.

344 Rodrigo, M.A., Cañizares, P., Sánchez-Carretero, A., Sáez, C., 2010. Use of conductive-
345 diamond electrochemical oxidation for wastewater treatment. *Catal. Today* 151, 173-177.

346 Rodrigo, M.A., Oturan, N., Oturan, M.A., 2014. Electrochemically Assisted Remediation
347 of Pesticides in Soils and Water: A Review. *Chem. Rev.* 114, 8720-8745.

348 Souza, F.L., Lanza, M.R.V., Llanos, J., Sáez, C., Rodrigo, M.A., Cañizares, P., 2015a. A
349 wind-powered BDD electrochemical oxidation process for the removal of herbicides. *J.*
350 *Environ. Manage.* 158, 36-39.

351 Souza, F.L., Llanos, J., Sáez, C., Lanza, M.R.V., Rodrigo, M.A., Cañizares, P., 2016a.
352 Performance of wind-powered soil electroremediation process for the removal of 2,4-D
353 from soil. *J. Environ. Manage.* 171, 128-132.

354 Souza, F.L., Saéz, C., Llanos, J., Lanza, M.R.V., Cañizares, P., Rodrigo, M.A., 2015b.
355 Solar-powered CDEO for the treatment of wastewater polluted with the herbicide 2,4-D.
356 *Chem. Eng. J.* 277, 64-69.

357 Souza, F.L., Saéz, C., Llanos, J., Lanza, M.R.V., Cañizares, P., Rodrigo, M.A., 2016b.
358 Solar-powered electrokinetic remediation for the treatment of soil polluted with the
359 herbicide 2,4-D. *Electrochim. Acta* 190, 371-377.

360 Šojić, D.V., Anderluh, V.B., Orčić, D.Z., Abramović, B.F., 2009. Photodegradation of
361 clopyralid in TiO₂ suspensions: Identification of intermediates and reaction pathways. *J.*
362 *Hazard. Mater.* 168, 94-101.

363