Novel integrated electrodialysis/electro-oxidation process for the efficient degradation of 2,4-dichlorophenoxyacetic acid

Raschitor, A.; Llanos, J.*; Cañizares, P.; Rodrigo, M. A.

Chemical Engineering Department, Facultad de Ciencias y Tecnologías Químicas.

University of Castilla-La Mancha, Edificio Enrique Costa Novella. Av. Camilo José

Cela nº 12, 13071 Ciudad Real, Spain

***Corresponding author:** javier.llanos@uclm.es

Abstract

This work presents a novel approach of wastewater treatment technology that consists of a combined electrodialysis / electro-oxidation process, specially designed to allow increasing the efficiency in the oxidation of ionic organic pollutants contained in diluted waste. Respect to conventional electrolysis, the pollutant is simultaneously concentrated and oxidized, enhancing the performance of the cell due to the higher concentration achieved in the nearness of the anode. A proof of concept is tested with the ionic pesticide 2,4-D (2,4-dichlorophenoxyacetic acid) and results show that the efficiency of this new technology overcomes that electrolysis by more than double, regardless the supporting electrolyte used (either NaCl or Na₂SO₄). Moreover, the removal rate of 2,4-D when using NaCl was found to be more efficient, due to the best performance of the electrode material selected (DSA®) towards the formation of oxidants in chloride supporting electrolyte. These results open the way for overcoming the efficiency limitations of electrochemical treatment processes for the treatment of solutions with low concentrated ionic pollutants.

Keywords: ionic pollutant; electrodialysis; electro-oxidation; integrated process; high efficiency

1. Introduction

The research efforts devoted to the development of environmental applications of electrochemical technologies has notably increased within the last decades (Rodrigo et al., 2014; Feng et al., 2016). For the particular case of pesticide removal, many studies have been conducted in the recent years, looking for operation conditions or combination of processes that helps to attain high degradation efficiencies (Muff et al., 2009; Fontmorin et al., 2012; Kukurina et al., 2014; Souza et al., 2016) in the depletion of these hazardous species.

Despite these important efforts, several drawbacks need still to be overcome. The most important are the diffusion limitations found for the treatment of low concentrated wastes. It is well-known that the higher the concentration of pollutant, the higher is the current efficiency of the electrochemical treatment processes (Panizza et al., 2001b; Martínez-Huitle and Ferro, 2006; Panizza and Cerisola, 2009; Scialdone, 2009). Thus, mass transfer control is expected when low concentrated wastes are treated, limiting the maximum removal rate and thus lowering the current efficiency due to the appearance of parasitic reactions, such as oxygen evolution (Panizza et al., 2001a; Comninellis et al., 2008; Martín de Viales et al., 2012).

Another important drawback is the necessity of a minimum conductivity in the target waste, in order to avoid the necessity of application of excessively large cell potentials, which would increase unnecessarily the cost of the treatment. This drawback is typically solved in research studies with the addition of high concentrations of salts (Martínez-Huitle et al., 2015). This is not a good practice for real applications because, in a certain way, added salts can also be considered as pollutants, with much lower hazardousness but with a much higher persistence.

This work presents the proof of concept of a new electrochemical process designed to face both drawbacks for the treatment of ionic pesticides. It consists of an electrodialysis cell in which the concentration and the abatement of the ionic pesticide is performed simultaneously due to an *ad hoc* arrangement of the ionic exchange membranes by a combination of electrodialysis and electro-oxidation (EDEO process). In this process, the supporting electrolyte is concentrated together with the pesticide, being the latter oxidized in the concentrate compartment and thus overcoming the two drawbacks previously exposed. To validate this proof of concept, the behavior of the selected pesticide (2,4-

dichlorophenoxyacetic acid, 2,4-D) in the electrodialysis cell is first studied. Next, it is demonstrated that the 2,4-D removal in the integrated system clearly overcomes the performance of a conventional electro-oxidation process.

2. Materials and methods

The experiments were conducted in an electrodialysis setup described elsewhere (Llanos et al., 2014). It basically consists of an electrodialysis cell equipped with DSA ® (Industrie de Nora) as both anode and cathode and auxiliary equipment (pumps, tanks, measuring devices). The membranes were provided by Astom Corp. The anion exchange membrane (a standard grade AMX) has a thickness of 0.14 mm, an IEC between 1.4 – 1.7 meq g⁻¹ and an electric resistance of 2.4 Ω cm². The cationic exchange membrane (a standard grade CMX) has a thickness of 0.17 mm, an IEC of 1.5 – 1.8 meq g⁻¹ and an electrical resistance of 3 Ω cm².

In order to study the simultaneous concentration and removal of 2,4-D, three cell configurations were proposed as shown schematically in Fig. 1, using as model of waste to be treated a solution containing 100 mg L⁻¹ of 2,4-D and 3000 mg L⁻¹ of NaCl or Na₂SO₄. The first arrangement is a conventional electrodialysis configuration (ED) in which an anion exchange membrane was placed between two cation exchange membranes to form 3 compartments: a diluate, a concentrate and an electrode rinse. This configuration can attain the concentration of the pesticide in one stream and a waste with a much lower concentration in the other.

Fig. 1

The second configuration (namely electrochemical oxidation, EO) does not involve the use of membranes and the oxidation of the pollutant takes place in only one compartment. The third set up brings the novelty of combining the previous two configurations by performing simultaneously electrodialysis and electro-oxidation in the same cell (EDEO process). In this case, two membranes were used in order to obtain two compartments: a dilute compartment and a mixed compartment in which the electrode rinse and the concentrate are brought together. In this way, it is possible to improve the degradation

process and to favor the direct and indirect oxidation mechanisms. The anionic membrane was previously saturated by immersing it in a concentrated 2,4-D solution (500 mg L^{-1}) during 48 h in EDEO tests in order to avoid the contribution of adsorption in the removal of 2,4-D during the EDEO tests.

At this time, it is worth mentioning that ED is usually operated at constant voltage meanwhile EO is commonly performed under galvanostatic conditions. In the present work, ED tests were performed to characterize the transport of 2,4-D through the anionic membranes and to evaluate its behavior in the ED cell. For this, the most simple and common mode of operation was selected for ED trials: discontinuous mode and constant voltage. Conversely, EO and EDEO tests were run under galvanostatic conditions (typical of EO processes) and at continuous mode. This mode of operation was selected mainly for two reasons: 1) a real treatment plant is expected to be operated at continuous mode; 2) with this mode of operation the formation of excessive concentration gradients between both compartments is avoided, allowing to operate the tests throughout sufficient time to observe noticeable differences between the two configurations proposed.

To run the system in continuous mode, volumes of 50 mL from the diluate compartment and 10 mL from the concentrate compartment were replaced every ten min during the first h. After this (and until the end of the experiments) the same volumes were replaced every five min. It has to be mentioned that in the case of using NaCl as supporting electrolyte, the volumes added after the first h needed to be doubled due to the higher reactivity of the DSA electrodes in chloride media. This dissimilar feeding flow rate allows working with similar 2,4-D concentrations with both supporting electrolytes. An average applied electric charge of 0.64 Ah L^{-1} was passed to the runs with NaCl as supporting electrolyte and 1.08 Ah L^{-1} to the synthetic wastes with Na_2SO_4 .

High performance liquid chromatography system used was an Agilent 1100 equipped with an UV detector (280 nm) and column Phenomenex Gemini $5 \mu\text{m}$ C18. It used a mobile phase that consisted of 60% acetonitrile and 40% water to 2% acetic acid with a flow rate of 0.4 mL min^{-1} , an oven temperature of $25 \text{ }^\circ\text{C}$, and volume injection of $20 \mu\text{L}$.

3. Results and discussion

First, conventional electrodialysis tests were performed in order to characterize the mobility of the pesticide and the driving force needed to achieve the maximum allowable transfer rate in ED. Therefore, Fig. 2 shows the evolution of 2,4-D concentration in both diluate and concentrate compartments for cell potentials ranging from 1.0 to 10.0 V.

Fig. 2

At 1.0 V there is no ionic mobility, which means that this cell voltage is not high enough to promote the transport of 2,4-D through the anionic membrane. As the potential increases, so does the mass transfer, being able to dilute the synthetic wastewater from 100 mg L⁻¹ down to approximately 10 mg L⁻¹ and concentrate it from 100 up to 130 mg L⁻¹. No significant differences were found between the results obtained in the tests carried out at 5.0 and 10.0 V.

Hence, ED can be used to treat waste polluted with 2,4-D. However, a noteworthy difference between the degree of dilution and the degree of concentration should be pointed out in both ED tests. This difference does not depend on the cell voltage applied and it has been explained in terms of the adsorption of 2,4-D onto the anionic membranes, which is compatible with the behavior of the pesticide during the first 40 min of experiments. As it can be observed, during this time the concentration of the concentrate compartment remains practically the same, while the concentration of the dilute decreases. To confirm this hypothesis, batch 2,4-D adsorption tests were conducted by immersing membranes into 2,4-D solutions, revealing that the membrane has a capacity to retain up to 3.41±0.24 mg cm⁻² of 2,4-D.

The adsorption of 2,4-D onto the anionic membranes may hinder the analysis of its degradation throughout the EDEO tests, as the removal of this pollutant would be a combination of both oxidation and adsorption mechanisms. For this reason, the EDEO tests were performed with anionic membranes previously saturated in pesticide, as described in the experimental section. Fig. 3 shows the amount of 2,4-D removed by EO and by EDEO, as well as the influence of the supporting electrolyte in the removal rate.

Fig.3

154

155 From the analysis of the results shown in Fig. 3a, it can be stated that the average removal
156 rate of EDEO system is 2.5 times than of EO when using Na₂SO₄ as supporting electrolyte
157 (53.53 mg 2,4-D in EO vs. 133.65 mg in EDEO after 480 min of electrolysis). A similar
158 behavior is observed when using NaCl as supporting electrolyte (Fig. 3b), showing
159 removals of 2,4-D of 138.4 mg for EO and 320.79 mg for EDEO after the same
160 electrolysis time. This means an increase in the efficiency of more than double. Hence,
161 as expected, the removal efficiency increases when the concentrate and the electrode rinse
162 share the same compartment because the efficiency of anodic oxidation depends on the
163 mass transfer of pollutants from the bulk to the anode surface or its vicinity (Sharma et
164 al., 2007). It is well-known that the electrolysis of diluted wastes fits well to a pseudo-
165 first order kinetic and this means that the higher the concentration of pollutant, the higher
166 is the efficiency expected (Cañizares et al., 2004a, b). Electrochemical processes occur at
167 the nearness of the electrodes (direct on the surface and mediated near to it) and, for this
168 reason, when the concentration of the pollutant decreases mass transfer control is
169 expected, causing a decrease in the degradation efficiency due to the appearance of
170 competitive oxidation reactions (Martin de Vidales et al., 2012, 2017). Thus, it is
171 consistent that the use of concentrated solutions leads to the removal of higher amounts
172 of pollutants per unit of charge applied (Hamza et al., 2009; Cavalcanti et al., 2013; Da
173 Silva et al., 2014; Madsen et al., 2015; Moreira et al., 2015).

174 Moreover, in comparing Fig. 3a and b, it can be concluded that the nature of the
175 supporting electrolyte highly affects the degradation kinetics, being the removal rate
176 higher in the case of using NaCl, even when applying a lower specific charge as
177 previously described in the experimental section. This result is explained on the basis of
178 the reactivity of the DSA® in chloride media. Thus, it has been previously demonstrated
179 that the removal of target compounds and mineralization occur more rapidly using NaCl
180 compared to Na₂SO₄ (Sharma et al., 2007; Kümmerer, 2009; Thiam et al., 2014) due to
181 the formation of active chlorine species produced by direct oxidation of chloride at the
182 anode (Eq. (1) to (3)) (Cotillas et al., 2016; Llanos et al., 2016). Thus, the higher
183 concentration reached in the EDEO configuration near to the anode surface also enhance
184 the mediated oxidation mechanisms and so the overall degradation rate.

This is not the case when the electrolyte support is sulfate because DSA® anodes are not effective in the oxidation of sulfate to peroxosulfate. In this case, mediated processes are not as favored as in the other case but even that, the EDEO process is much more efficient than the single electrolysis.

Apart from the higher degradation rate with both anodes in chloride media, it is worth mentioning the potential formation of chlorinated by-products as it has been widely reported in literature (García et al., 2013; Antonin et al., 2015; Garcia-Segura et al., 2015). This matter will be studied in detail in future works.

4. Conclusions

The main conclusion of this work is that the EDEO cell permits the concentration and simultaneous degradation of an ionic organic pesticide in a single electrochemical cell. This novel approach more than doubles the removal rate of 2,4-D compared to a conventional EO cell working at the same experimental conditions. This configuration is directly applicable to the removal of several ionic pollutants, overcoming the limitation of efficiency characteristic of electrochemical treatment processes that work under mass transfer control.

Acknowledgments

The authors acknowledge funding support from the Spanish Government through the MINECO Project CTM2016-76197-R.

References

- Antonin, V.S., Santos, M.C., Garcia-Segura, S., Brillas, E., 2015. Electrochemical incineration of the antibiotic ciprofloxacin in sulfate medium and synthetic urine matrix. *Water Res.* 83, 31-41.
- Cañizares, P., García-Gómez, J., Lobato, J., Rodrigo, M.A., 2004a. Modeling of wastewater electro-oxidation processes part i. General description and application to inactive electrodes. *Ind. Eng. Chem. Res.* 43, 1915-1922.
- Cañizares, P., García-Gómez, J., Lobato, J., Rodrigo, M.A., 2004b. Modeling of wastewater electro-oxidation processes part ii. Application to active electrodes. *Ind. Eng. Chem. Res.* 43, 1923-1931.
- Cavalcanti, E.B., Garcia-Segura, S., Centellas, F., Brillas, E., 2013. Electrochemical incineration of omeprazole in neutral aqueous medium using a platinum or boron-doped diamond anode: Degradation kinetics and oxidation products. *Water Res.* 47, 1803-1815.
- Comninellis, C., Kapalka, A., Malato, S., Parsons, S.A., Poulios, I., Mantzavinos, D., 2008. Advanced oxidation processes for water treatment: Advances and trends for r&d. *J. Chem. Technol. Biotechnol.* 83, 769-776.
- Cotillas, S., Llanos, J., Castro-Ríos, K., Taborda-Ocampo, G., Rodrigo, M.A., Cañizares, P., 2016. Synergistic integration of sonochemical and electrochemical disinfection with DSA anodes. *Chemosphere* 163, 562-568.
- Da Silva, L.M., Gonçalves, I.C., Teles, J.J.S., Franco, D.V., 2014. Application of oxide fine-mesh electrodes composed of sb-sno₂ for the electrochemical oxidation of cibacron marine fg using an spe filter-press reactor. *Electrochim. Acta* 146, 714-732.
- Feng, Y., Yang, L., Liu, J., Logan, B.E., 2016. Electrochemical technologies for wastewater treatment and resource reclamation. *Environ. Sci.: Water Res. Technol.* 2, 800-831.
- Fontmorin, J.-M., Huguet, S., Fourcade, F., Geneste, F., Floner, D., Amrane, A., 2012. Electrochemical oxidation of 2,4-dichlorophenoxyacetic acid: Analysis of by-products and improvement of the biodegradability. *Chem. Eng. J.* 195-196, 208-217.
- Garcia-Segura, S., Keller, J., Brillas, E., Radjenovic, J., 2015. Removal of organic contaminants from secondary effluent by anodic oxidation with a boron-doped diamond anode as tertiary treatment. *J. Hazard. Mater.* 283, 551-557.
- García, O., Isarain-Chávez, E., Garcia-Segura, S., Brillas, E., Peralta-Hernández, J.M., 2013. Degradation of 2,4-dichlorophenoxyacetic acid by electro-oxidation and electro-fenton/bdd processes using a pre-pilot plant. *Electrocatalysis* 4, 224-234.
- Hamza, M., Abdelhedi, R., Brillas, E., Sirés, I., 2009. Comparative electrochemical degradation of the triphenylmethane dye methyl violet with boron-doped diamond and pt anodes. *J. Electroanal. Chem.* 627, 41-50.
- Kukurina, O., Elemesova, Z., Syskina, A., 2014. Mineralization of organophosphorous pesticides by electro-generated oxidants. *Procedia Chem.* 10, 209-216.
- Kümmerer, K., 2009. The presence of pharmaceuticals in the environment due to human use – present knowledge and future challenges. *J. Environ. Manage.* 90, 2354-2366.

254 Llanos, J., Cotillas, S., Cañizares, P., Rodrigo, M.A., 2014. Novel electrodialysis-
 255 electrochlorination integrated process for the reclamation of treated wastewaters. *Sep.*
 256 *Purif. Technol.* 132, 362-369.

257 Llanos, J., Cotillas, S., Cañizares, P., Rodrigo, M.A., 2016. Electrocoagulation as a key
 258 technique in the integrated urban water cycle – a case study in the centre of Spain. *Urban*
 259 *Water J.*, 1-5.

260 Madsen, H.T., Søgaaard, E.G., Muff, J., 2015. Reduction in energy consumption of
 261 electrochemical pesticide degradation through combination with membrane filtration.
 262 *Chem. Eng. J.* 276, 358-364.

263 Martín de Vidales, M.J., Millán, M., Sáez, C., Cañizares, P., Rodrigo, M.A., 2017.
 264 Irradiated-assisted electrochemical processes for the removal of persistent pollutants from
 265 real wastewater. *Sep. Purif. Technol.* 175, 428-434.

266 Martín de Vidales, M.J., Sáez, C., Cañizares, P., Rodrigo, M.A., 2012. Electrolysis of
 267 progesterone with conductive-diamond electrodes. *J. Chem. Technol. Biotechnol.* 87,
 268 1173-1178.

269 Martínez-Huitle, C.A., Ferro, S., 2006. Electrochemical oxidation of organic pollutants
 270 for the wastewater treatment: Direct and indirect processes. *Chem. Soc. Rev.* 35, 1324-
 271 1340.

272 Martínez-Huitle, C.A., Rodrigo, M.A., Sirés, I., Scialdone, O., 2015. Single and coupled
 273 electrochemical processes and reactors for the abatement of organic water pollutants: A
 274 critical review. *Chem. Rev.* 115, 13362-13407.

275 Moreira, F.C., Boaventura, R.A.R., Brillas, E., Vilar, V.J.P., 2015. Degradation of
 276 trimethoprim antibiotic by uva photoelectro-fenton process mediated by Fe(III)-
 277 carboxylate complexes. *Appl. Catal. B: Environ.* 162, 34-44.

278 Muff, J., Andersen, C.D., Erichsen, R., Søgaaard, E.G., 2009. Electrochemical treatment
 279 of drainage water from toxic dump of pesticides and degradation products. *Electrochim.*
 280 *Acta* 54, 2062-2068.

281 Panizza, M., Cerisola, G., 2009. Direct and mediated anodic oxidation of organic
 282 pollutants. *Chem. Rev.* 109, 6541-6569.

283 Panizza, M., Michaud, P.A., Cerisola, G., Comninellis, C.H., 2001a. Anodic oxidation of
 284 2-naphthol at boron-doped diamond electrodes. *J. Electroanal. Chem.* 507, 206-214.

285 Panizza, M., Michaud, P.A., Cerisola, G., Comninellis, C.H., 2001b. Electrochemical
 286 treatment of wastewaters containing organic pollutants on boron-doped diamond
 287 electrodes: Prediction of specific energy consumption and required electrode area.
 288 *Electrochem. Commun.* 3, 336-339.

289 Rodrigo, M.A., Oturan, N., Oturan, M.A., 2014. Electrochemically assisted remediation
 290 of pesticides in soils and water: A review. *Chem. Rev.* 114, 8720-8745.

291 Scialdone, O., 2009. Electrochemical oxidation of organic pollutants in water at metal
 292 oxide electrodes: A simple theoretical model including direct and indirect oxidation
 293 processes at the anodic surface. *Electrochim. Acta* 54, 6140-6147.

Sharma, K.P., Sharma, S., Sharma, S., Singh, P.K., Kumar, S., Grover, R., Sharma, P.K.,
2007. A comparative study on characterization of textile wastewaters (untreated and
treated) toxicity by chemical and biological tests. *Chemosphere* 69, 48-54.

Souza, F., Saéz, C., Lanza, M., Cañizares, P., Rodrigo, M.A., 2016. Towards the scale-
up of electrolysis with diamond anodes: Effect of stacking on the electrochemical
oxidation of 2,4 d. *J. Chem. Technol. Biotechnol.* 91, 742-747.

Thiam, A., Zhou, M., Brillas, E., Sirés, I., 2014. Two-step mineralization of tartrazine
solutions: Study of parameters and by-products during the coupling of electrocoagulation
with electrochemical advanced oxidation processes. *Appl. Catal. B: Environ.* 150–151,
116-125.

Figure Captions

Fig. 1. Schematic plot of the electrodialysis-electrolysis set up and the three proposed configurations. AEM: anion exchange membrane; CEM: cation exchange membrane; C: concentrate; D: diluate; ER: electrode rinse; CM: conductimeter

Fig. 2. Influence of the applied voltage in the time course of 2,4-D concentration in discontinuous electrodialysis tests. Full symbols: concentrate. Empty symbols: diluate. ● 10.0 V; ■ 5.0 V; ▲ 1.0 V.

Fig. 3. Influence of cell configuration in the time-course of 2,4-D removed. a) Na₂SO₄ as supporting electrolyte; b) NaCl as supporting electrolyte. ● EDEO; □ ED; Current density: 177.77 A m⁻²

Figure 1

377

378

379

Figure 2

380

381

382

383

384

385

386

387

388

389

390

391

392

393

394

395

Figure 3