1 Exploring the applicability of a combined electrodialysis/electro-
2 oxidation cell for the degradation of 2,4-dichlorophenoxyacetic
3 acid

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8
9 **Abstract**

10 The improvement in the treatment efficiency of diluted effluents is one of the great
11 challenges faced by electrochemical technology nowadays. In the present work, it is
12 aimed to develop an electrochemical cell for the simultaneous concentration and
13 degradation of ionic organic pollutants. This combined cell (so called EDEO device)
14 integrates the concentration of the organic by electrodialysis (ED) with its electro-
15 oxidation (EO). For the particular case of the 2,4-dichlorophenoxyacetic acid (2,4-D), the
16 performance of the cell has been tested with two anode materials (boron-doped diamond,
17 BDD and mixed mineral oxides, MMO) and with two supporting electrolytes in order to
18 explore four combinations that are expected to cover a wide range of possible actual
19 scenarios. Results demonstrate that the combined EDEO process exhibits a degradation
20 rate and a mineralization current efficiency markedly higher than the equivalent EO
21 device when working with MMO anodes, either with NaCl or with Na₂SO₄. It was
22 checked that the use of a BDD anode clearly increases the efficiency and the rate of the
23 treatment due to the formation of strong oxidants. In this case, the effect of working with

the combined EDEO in the rate of 2,4-D degradation is negligible because the 2,4-D transport rate becomes comparable to the degradation rate, being the combined process unable to generate a concentration greater than that accounted in the single EO device.

Keywords: Electrodialysis; organochlorine pesticide; electro-oxidation; applicability; anode material

1. Introduction

The treatment of wastewater containing pesticides and organochlorine compounds has recently attracted a growing commitment from the scientific community because of their high toxicity and persistent character [1-6]. Despite the fact that the use of many of these hazardous compounds has been forbidden or restricted, an intensive or inappropriate use in the past, an inappropriate storage or transportation and even some accidental spills are still causing serious problems. Due to their high water solubility and adverse effect, even at very low concentrations, organochlorine compounds become hazardous pollutants in aquatic ecosystems.

A specific example of organochlorine pesticide widely used in the past in gardens and faring to control broadleaf weeds is 2,4-dichlorophenoxyacetic acid (2,4-D). The World Health Organization (WHO) considers this pesticide as moderately toxic and several degradation technologies have been evaluated for its degradation, including fenton-related technologies [7, 8], photocatalytic degradation [9] or electrochemical technologies [10, 11].

One of the main limitations that degradation technologies must overcome is the low concentration in which pollutants are usually found in the environment. For the particular case of electrochemical degradation technologies, it is well assumed that the lower the concentration of the pollutant, the poorer is the efficiency of the degradation process, due to the appearance of mass transfer limitations and the occurrence of competing oxidation reactions (as it is the case of oxygen evolution) [12-14].

To face the challenge of increasing the efficiency of degradation technologies, several alternatives have been explored. One of the most applied is the combination of electrochemical advanced oxidation processes with UV irradiation or ultrasound

sonication, in order to improve either the activation of oxidants or the mass transfer of the pollutant to the anode surface [15-18]. Among these strategies, photoelectrocatalytic technologies have received a special attention lately due to their good results obtained in the degradation of organic compounds, as this technology combines photogeneration of strong oxidants (such as hydroxyl radicals) along with the photoactivation of the electrogenerated oxidants [19].

Another option consists of coupling concentration technologies, as it is the case of membrane separation techniques, with electrochemical or advanced oxidation processes to concentrate the pollutant prior to its degradation [20-22]. In all these cases, either the cost of the equipment and/or the energy requirements are increased due to the necessity of additional equipment and energy sources different from electricity.

Based on these limitations, our research group presented a system for the simultaneous concentration and degradation of ionic pesticides, and successfully performed a proof of concept of this device for the particular case of the degradation of 2,4-D [23]. In that work, it was confirmed that it is possible to improve the degradation rate of 2,4-D by using a combination of electrodialysis (ED) and electro-oxidation (EO) in a combined electrochemical cell (EDEO), which exhibited a removal rate from 2.3 to 2.5 higher than that observed for an equivalent electro-oxidation cell. The designed device consisted of an electrodialysis cell with an *ad-hoc* arrangement of the membranes, allowing the mixing of the concentrate and the electrode rinsing solutions and, thus, the simultaneous concentration and electrochemical degradation of the pollutant.

Based on these preliminary but promising results, the present work describes a comprehensive work about the performance of this technology with two different supporting electrolytes (sulphate and chloride) and two anode materials (mixed mineral

oxides, MMO and boron-doped diamond, BDD) trying to shed light on the operational mechanisms. The main aim of the present work is to explore the applicability and the possible bottlenecks for the future development of this technology for the treatment of wastewater containing ionic organic pollutants.

2. Materials and methods

2.1. Experimental

The installation setup employed in this work was described in detail elsewhere [23]. It consists of a commercial electrodialysis cell provided by PCCell (Germany) equipped with MMO (titanium coated with mixed metal oxides, $\text{IrO}_2\text{--RuO}_2$) as both anode and cathode. The electrodes have a square grid-shaped geometry, of 7.5 x 7.5 cm and a thickness of 0.2 cm. In order to explore the applicability of the process, a similar mesh coated by a BDD layer (3D-mesh Diachem® diamond electrode supported on niobium) was acquired from Condias GmbH (Germany). The surface area of both electrodes was calculated using a Rexcon DS3 silver 3D scanner equipped with EZScan 8 and the Geomagic Wrap 2015 software, resulting a ratio of 1.5 of surface/geometric area. To maintain uniformity with previous works, the current densities presented here are referred to the geometric area of the electrodes.

The ion exchange membranes (ASTOM Corp) have a square geometry of 11x11 cm and a thickness of 0.17 mm for cationic and 0.14 mm for anionic. The anion exchange membranes were saturated prior to their use by immersing them into a solution of 500 mg dm^{-3} of 2,4-D for 48 hours.

The synthetic wastewater was prepared with 2,4-D (Alfa Aesar) with concentrations of 100 mg dm^{-3} and a concentration of 3000 mg dm^{-3} of sodium chloride or sodium sulphate (Sigma Aldrich). The initial concentration of 2,4-D was selected to work under conditions

at which mass transfer limitations are expected. Before starting the experiments, the electrodes were polarized for 15 min at 300 A m^{-2} with a Na_2SO_4 solution of 5000 mg dm^{-3} at pH 2 and subsequently rinsed several times with deionized water.

ED tests were performed at constant voltage and at discontinuous mode of operation to characterize the behaviour and the transport of the pollutant through the anion exchange membrane. The same volume of concentrate and diluate was used ($V = 1\text{L}$).

EO and EDEO tests were conducted in continuous mode and at constant current ($I = 1 \text{ A}$, $j = 177.8 \text{ A m}^{-2}$). In this case, continuous mode avoids the formation of a high concentration gradient between both compartments (and consequently an excessive cell potential), meanwhile galvanostatic is the most common mode of operation when working in electro-oxidation processes.

EO tests were performed without ion exchange membrane (IEM) and with a total volume in the system of 2L. EDEO tests were conducted with two membranes, a cation IEM facing the cathode and an anion IEM facing the anode. This way, there were two compartments in the EDEO trials, one diluate and a second one (1L each) that mixes concentrate and electrode rinsing solution. In both cases, the same total flow rate was fed and purged to and from the system: 60 mL every 10 minutes during the first hour and the same volume every five minutes during the rest of the tests. For EDEO tests, this total volume was divided into 10 mL fed to the concentrate and 50 mL fed to the diluate. This is equivalent to a specific charge of 2.78 Ah L^{-1} for the first hour and of 1.39 Ah L^{-1} for the rest of the tests. The different modes of operation of the cell are schematically presented in a Figure appended as supplementary material (Fig. sup.1). All tests lasted 4 hours, resulting in a total mass of 2,4-D and TOC fed to the system (including the mass initially loaded in all compartments) of 452 mg and 196.3 mg, respectively.

Calculation of MCE and power consumption

Considering the following reaction for the total mineralization of 2,4-D (Eq. 1), mineralization current efficiency (MCE, %) can be calculated by Equation 2 [24]

$$\text{MCE, \%} = \frac{m_{\text{TOC}} \cdot n \cdot F}{I \cdot t \cdot 96} \cdot 100 \quad (2)$$

where m_{TOC} is the mass of TOC degraded (g), n the number of electrons needed for the complete mineralization ($n=30$), F the Faraday constant (96500 C mol^{-1}), I the intensity (A), t the time (s) and 96 the mass of carbon atoms per molecule of 2,4-D (g mol^{-1}). Obviously, there is not a direct 30 e^- transfer, being this parameter used only for comparison purposes. The power consumption (PC, $\text{kWh kg}^{-1} \text{ TOC}$) has been calculated by Equation (3)

$$\text{PC, kWh kg}^{-1} \text{ TOC} = \frac{I \cdot V}{m_{\text{TOC}}} \quad (3)$$

where V is the average applied voltage (V) and m_{TOC} is the mass of TOC removed throughout the test. At this point, it is worth noting that both parameters have been calculated as discontinuous process, as the stationary state was not reached in none of the tests presented in the present work.

2.2. Analytical techniques

For the measurement of 2,4-D it was used the Agilent 1100 HPLC equipped with a UV detector (280 nm) and a Phenomenex Gemini $5 \mu\text{m}$ C18 column. The mobile phase consists of 60% acetonitrile and 40% water with 2% acetic acid at a flow rate of $0.4 \text{ cm}^3 \text{ min}^{-1}$, an oven temperature of 25°C and an injection volume of $20 \mu\text{L}$. The total organic carbon quantification was made with the Multi N / C 3100 Analytik Jena equipment.

3. Results and discussion

3.1. Transport of 2,4-D through electrodialysis cell

As a first step, the electro-migration of the pollutant within the electrochemical cell was characterized by two consecutive electrodialysis tests performed with the same IEM. Figure 1 shows the evolution of the concentration of 2,4-D in both diluate and concentrate compartments within these consecutive tests.

Fig.1. Evolution of 2,4-D concentration throughout two consecutive ED tests in discontinuous mode at 10V using NaCl as supporting electrolyte. Full symbols – concentrate; empty symbols – diluate; □ I use, ○ II use.

As it can be observed, the dilution is clearly lower than the concentration throughout the first ED test. This situation changes in the second test, being the concentration attained much closer to the dilution reached in the other compartment. Taking into account that the volume of concentrate and diluate was equal (1 L each) and that no reaction can take place in both diluate and concentrate compartments, the only plausible explanation for this behaviour is the adsorption of 2,4-D on the anion exchange membrane. This

phenomenon was described and explained in our previous work [23], where the adsorption capacity of 2,4-D by this anion exchange membrane was determined to be $3.41 \pm 0.24 \text{ mg cm}^{-2}$.

Taking into account this behaviour, the following tests were performed with saturated anion exchange membranes, thus avoiding the influence of the degree of saturation of the membrane on the degradation results and the confusion between the amount of 2,4-D degraded and the mass of pollutant adsorbed.

3.2. EO and EDEO performance with MMO anode

Figure 2 shows the influence of the cell configuration (EO vs. EDEO) on the 2,4-D and TOC removal (Figure 2.a) and on the mineralization current efficiency (MCE) at 177.8 A/m^2 using NaCl as supporting electrolyte and MMO anode.

Fig. 2. Influence of the intensity and cell configuration on the 2,4-D and TOC removal rate (a) and efficiency (b) at 177.8 A/m^2 using NaCl as supporting electrolyte and MMO anode; $\square$ 2,4-D, $\circ$ TOC. Full symbols: EDEO; Empty symbols: EO

As it can be observed, the removal efficiency considerably improves for both 2,4-D (161.52 vs 43.18 mg at 240 min) and TOC (30.30 vs 3.35 mg at 240 min) by using the integrated system with respect to the conventional EO configuration. This means that, by

concentrating and oxidizing at the same time, not only a higher removal efficiency of the pollutant can be achieved but also a higher degree of mineralization. This higher mineralization rate of EDEO system is clearly observed in Figure 2.b, in which the mineralization current efficiency of the EDEO system is approximately nine times higher at the end of the test than the equivalent MCE for the EO cell (7.05% of EDEO vs. 0.78% of EO).

It is commonly accepted that the electrochemical oxidation of an organic pollutant follows a pseudo-first order kinetics as it mainly takes place in the nearness of the anode surface, either by direct or by mediated oxidation [25-29]. This implies that mass transfer control is expected at low concentration of the organic, being the maximum rate of the process directly proportional to the concentration of the target pollutant [30]. Moreover, it is well assumed that the kinetics of the mediated oxidation of an organic molecule by the active chlorine species electrochemically produced follows a pseudo-first order kinetics with respect to the pollutant concentration, once the concentration of the oxidant reaches a stationary value [31-33]. This implies a higher degradation rate for higher concentration of the pollutant, not only at the nearness of the electrode but also in the bulk. This fact All this together explains the higher rate of 2,4-D removal in the case of the combined process compared to the single electro-oxidation. The values of MCE (far lower than 100% in both cases) are consistent with systems in which the transport of the pollutant to the anode surface is controlling the rate of the process due to the low concentration of pollutant (mass transfer control) [34]. Thus, the higher concentration obtained in the EDEO system once again implies a higher value of the MCE, that is, a more efficient use of the charge passed through the system. It is worth noting that the higher MCE also implies a greater degree of mineralization and, consequently, a more limited formation of undesirable reaction intermediates.

Figure 3 shows the evolution of 2,4-D and TOC removed (Fig. 3.a), together with the values of MCE (Fig. 3.b) for the case of working with MMO electrodes and sulphate as supporting electrolyte.

Fig. 3. Influence of the intensity and cell configuration on the 2,4-D and TOC removal rate (a) and efficiency (b) at 178 A/m² using Na₂SO₄ as supporting electrolyte and MMO anode; □ 2,4-D, ○ TOC. Full symbols: EDEO; Empty symbols: EO

As observed, the rates of 2,4-D and TOC removal do not reach the values observed for the case of NaCl. As it has been discussed in literature, the degradation of organics by MMO anodes occurs at a higher rate when NaCl is used instead of Na₂SO₄ [23, 25, 35, 36] because of the production of active chlorine species, as expressed by equations 4 to 6 [37-39]. On the contrary, the production of peroxodisulfate from sulfate by MMO anodes is not effective, being the degradation of 2,4-D mainly due to direct oxidation mechanisms [40]. Although a lower degradation rate is obtained when using sulphate as electrolyte, it is worth mentioning that the potential formation of hazardous chlorinated by-products can be produced when chloride is used as electrolyte, as it is well described in literature [41]. Nevertheless, it is not the aim of the present work to evaluate the formation of chlorinated by-products but to test the performance of the new concept of EDEO cell in the most common working conditions.

251

252 In any case, it is important to point out that although the system is less efficient in sulphate
 253 medium, the degradation rate and MCE of the EDEO system clearly improves the results
 254 of the electro-oxidation process. Regarding 2,4-D degradation, the total mass of 2,4-D
 255 degraded at 240 min was 80% higher in the EDEO system (58.5 mg of EDEO vs. 32.6
 256 mg of EO). In the case of MCE, the total mineralization reached within 240 min was more
 257 than ten times higher in the EDEO system (13.24 mg of EDEO vs. 1.03 mg of EO system).
 258 As commented for NaCl, the greater rate and efficiency of the process is explained by the
 259 higher concentration of pollutant in the EDEO process. In this case, this higher
 260 concentration enhances the transport of the pollutant to the anode surface and,
 261 consequently, the rate of the direct oxidation mechanisms.

262 3.3. Performance with BDD anode and comparison of anode materials

263 As demonstrated in the previous section, the performance of the EDEO system clearly
 264 overcomes a conventional electro-oxidation process in terms of degradation rate and
 265 MCE of 2,4-D. To explore the applicability of the process with a different anode material,
 266 a mesh with a BDD layer, an anode material that has exhibited an outstanding behaviour
 267 in the degradation of a wide spectra of organic molecules [42], was produced *ad hoc* by
 268 an external manufacturer (CONDIAS GmbH). Thus, Figure 4 shows the compared
 269 performance of EDEO and EO systems in terms of 2,4-D abatement and incineration rate
 270 (Fig. 4.a) and MCE (Fig 4.b), working with NaCl as supporting electrolyte.

Figure 4. Influence of the intensity and cell configuration on the 2,4-D and TOC removal rate (a) and efficiency (b) using NaCl as supporting electrolyte and BDD anode; $\square$ 2,4-D, $\circ$ TOC. Full symbols: EDEO; Empty symbols: EO

The first important point to be highlighted from these data is the higher 2,4-D removal rate and MCE with BDD, compared to that obtained for MMO (364 mg of BDD vs. 161 mg of MMO at 240 min for EDEO). This result is in agreement with the high performance of diamond-based anodes for the production of oxidants as it is the case of chlorine-based oxidant species or hydroxyl radicals, due to the non-active nature of its surface [43-45].

On the contrary, a somehow unexpected result is the similar performance of EO and EDEO systems regarding the removal of 2,4-D. To explain this result, it is important to notice that the EDEO system is based on two stages: 1) the transport of 2,4-D through the IEM and 2) the degradation of 2,4-D in the concentrate. As discussed in the previous paragraph, the degradation rate of 2,4-D has markedly increased when using BDD as anode material. As the system is operated in continuous mode, the degradation rate (mg min^{-1}), varies with time until a steady state is reached. On the other side, although the rate of transport of 2,4-D in the EDEO system depends on the applied voltage and the concentration gradient, an average value could be approximately calculated from the slope of the diluate stream in Figure 1. Thus, the value of the calculated degradation rate,

for both EO and EDEO systems, the approximate estimation of transport rate of 2,4-D and the ratio between the degradation rates of EDEO and EO processes are gathered in Figure 5 (Fig. 5.a for BDD Fig 5.b for MMO).

Fig. 5. Time course of degradation rate of EO (dotted bars) and EDEO (stripped bars) with (a) BDD and (b) MMO in NaCl media. The ratio between degradation rates of EDEO and EO systems is included as full triangles (secondary axis). Dashed line: estimation of the average transport rate of 2,4-D (0.97 mg min^{-1}).

As it can be observed, the degradation rates of both processes decrease for higher times, which can be explained by the lower concentration of 2,4-D in the electrode compartments. At the beginning of the test with BDD, it can be clearly observed that the degradation rates of EDEO and EO processes are almost equal, meanwhile the transport rate is lower than the degradation rate of both systems. As it can be observed from the evolution of the ratio between the degradation rates of both process, the rate of the EDEO process becomes to be appreciably higher than the EO only when the transport rate becomes higher than the degradation rate (ratio of 1.02 at 0 min; ratio of 1.22 at 240 min). These results exhibit a limitation in the applicability of EDEO process to systems in which the transport rate is higher than the degradation rate.

As observed in Fig. 5.b, the degradation rate was lower when the system was run with the MMO anode, being in this case the transport rate large enough to increase the

concentration of the electrode compartment of EDEO process and, thus, to give a higher rate of this configuration compared to the EO system. This behaviour is clearly observed when analysing Figure 5.b. Although the rate of both processes (EO and EDEO) is almost equal at the very beginning of the test, the EDEO process clearly overcomes the behaviour of the EO process, as the transport rate is higher than the degradation rate throughout the entire run (except for the point at $t=0$). In this case, the rate of EDEO process is from 3.7 (at 30 min) to 4.8 times (at 240 min) higher than the degradation rate of the EO system.

In line with these results, the rate of TOC degradation and MCE (Figure 4.b) of both processes is much similar than in the case of MMO anodes. Just for times greater than 50 min, it can be stated that the MCE of EDEO system is higher than that measured for EO. This latter increase in the MCE of the EDEO can be explained because of the lower volume of the electrode compartment in the EDEO system, which implies a higher concentration of the reaction intermediates and, consequently, a greater efficiency of mineralization.

Next, the results obtained using sulphate as supporting electrode and BDD as anode are gathered in Figure 6.

Fig. 6. Influence of the intensity and cell configuration on the 2,4-D and TOC removal rate (a) and efficiency (b) using Na_2SO_4 as supporting electrolyte and BDD anode; EO

b) EDEO; Full column: 2,4-D; Grid column: TOC □ 2,4-D, ○ TOC. Full symbols:
EDEO; Empty symbols: EO

The first remarkable result to be taken into account is the higher 2,4-D degradation rate and MCE than in the case of using MMO anodes. This better performance of the process can be explained in terms of the ability of BDD anodes to form peroxodisulfate from sulphate ions, according to Equation 7 [46]. Peroxodisulfate is relatively stable but it behaves as a strong oxidant, capable to degrade a wide spectra of organic molecules [47], once it is activated by the addition of iron(II) salts [48, 49], UV irradiation [50] or electrochemically by the hydroxyl radicals formed at the BDD anode from by water oxidation [46, 51]. In this latter case, the use of BDD anodes may activate peroxodisulfate, increasing its capacity of degrading organic matter, as it is schematically represented by Equation (8). Moreover, it has been recently demonstrated that the electrochemically activated peroxodisulfate may enhance the production of hydroxyl radicals and inhibit the oxygen evolution reaction, producing a greater concentration of hydroxyl radicals [51]. All together results in a higher rate in the degradation of organics.

Moreover, once again the performances of both EDEO and EO systems becomes closer. As it was the case of NaCl, the higher degradation rate, due to the formation of peroxodisulfate, explains the similar behaviour of EDEO and EO systems: the degradation rate is higher than the transport of 2,4-D through the electrodialysis membranes at the first stage of the tests so the EDEO process is not able to produce a

higher concentration, and therefore a greater degradation rate, than the electro-oxidation process.

Regarding power consumption, Table 1 gathers the values of the power consumption per unit of TOC removed, all of them calculated for 30% of TOC removal (with respect to the total TOC fed to the system). The value of $\text{kWh m}^{-3} \text{ order}^{-1}$, recently used as an interesting figure of merit for the calculation of power consumption of electrochemical degradation technologies [52], has not been used here due to the low percentage of TOC removal under the conditions tested.

Table 1. Power consumption in the mineralization of 30% of TOC

Electrode	System	Electrolyte	Electric consumption per mass ($\text{kWh kg}^{-1} \text{ TOC}$)	Average voltage (V)
BDD	EO	NaCl	320.2	5.4
		Na ₂ SO ₄	342.1	7.1
	EDEO	NaCl	293.2	7.1
		Na ₂ SO ₄	395.5	9.3

As it can be observed, the effect of EDEO process in the specific power consumption becomes negligible due to the higher voltage required when the membranes are placed inside the electrochemical cell. It is expected that, in future developments of the technology, the higher rate in TOC degradation will overcome the higher voltage required in the EDEO system.

According to these findings, the transport rate of the pollutant through the anion IEM is found to be a bottleneck for the advance of the technology. Hence, to be further developed, the experimental design and working conditions of EDEO system should assure enough transport rate to permit the concentration of the pollutant in the electrode compartment and, as a consequence, to allow higher degradation rates.

4. Conclusions

The present work explores the range of applicability of a combined electro dialysis/electro-oxidation cell (EDEO cell) for the simultaneous concentration and degradation of 2,4-D. The following main conclusions can be drawn from this work:

- The EDEO cell is capable of simultaneously concentrate and degrade a model ionic organic pollutant (2,4-D).
- The rate of removal of 2,4-D and TOC is greater when using a MMO anode and EDEO cell, with respect to the equivalent EO equipment.
- The mineralization current efficiency of the EDEO system is greater than the EO device in all the scenarios tested in the present work.
- The degradation rate of 2,4-D is not improved by the EDEO set up if the rate of degradation is higher than the transport rate of the pollutant through the membranes (case of BDD anode in the present work). Thus, the transport rate of the organic pollutant is the bottleneck for the future development of the combined technology.

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