1 **IS IT WORTH USING THE COUPLED ELECTRODIALYSIS/ELECTRO-**
2 **OXIDATION SYSTEM FOR THE REMOVAL OF PESTICIDES? PROCESS**
3 **MODELLING AND ROLE OF THE POLLUTANT**

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

5 Chemical Engineering Department, Facultad de Ciencias y Tecnologías Químicas.
6 University of Castilla-La Mancha, Edificio Enrique Costa Novella. Av. Camilo José
7 Cela nº 12, 13071 Ciudad Real, Spain

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

9 **Abstract**

10 This work presents the development of the electrodialysis/electro-oxidation (EDEO)
11 technology, assessing the role of the pollutant and the modelling of the system in order to
12 look for the key aspects for the development of the technology. According to the results
13 obtained, it can be concluded that electrodialysis can be properly used to concentrate
14 clopyralid, having the selected ionic exchange membranes (AMX) an adsorption capacity
15 of $1.64 \pm 0.26 \text{ mg cm}^{-2}$. Moreover, it was observed that BDD anodes exhibit a higher
16 degradation and mineralization current efficiencies than MMO when using electro-
17 oxidation (EO). The role of the supporting electrolyte was also assessed, observing a
18 slight better performance of BDD with sulphate (maximum mineralization current
19 efficiency of 80%) and a much superior degradation efficiency with chloride when
20 selecting MMO as anode material. Regarding the EDEO technology, it was checked that
21 this process only overcomes the performance of EO when using MMO anodes, a result
22 that is explained by the ratio between degradation and transport rates. Finally, a simple
23 model was presented and successfully used to predict the degradation rate constants and
24 to simulate the performance of EDEO under different scenarios. These simulations

confirm that the transport rate needs to overcome the degradation rate in order to assure a better performance of the EDEO system compared to the conventional EO. Moreover, the simulations explain the results obtained in the present and previous works revealing the key for a further development of the EDEO technology in the future.

Keywords: Electrodialysis; electro-oxidation; concentration; organochlorine; modelling

1. Introduction

Clopyralid is an organochlorine herbicide used for controlling a wider range of weeds than other similar compounds. Commercially, it can be found as emulsified concentrate mixed with other chemicals (fluroxypyr, benazolin, cyanazine, bifenox, mecoprop, ioxinil, bifenox, triclopyr, etc) under the following names: Cyronal, Lontrel, Matrigon, Reclaim or Dow Shield. It is persistent in soil and its high solubility makes it very dangerous because it can reach the surface water by rainfall, spilling, leaching or the groundwater by infiltration.

Although it can be degraded by microorganisms, clopyralid does not bound with suspended particles found in water and in absence of a substrate the biodegradation becomes difficult (Mandy Tu, 2001).

The treatment of wastewaters containing this type of organochlorine compounds became a matter of interest because of the restrictive limits for its concentration in both surface water (50 µg/L for Sweden, 75 µg/L for Holland) (Contreras López, 2003; Vagi and Petsas, 2019) and drinking water (0.1 µg/L for European Union) (Kuhlmeier and Sherwood, 1996).

The goals of the new treatment technologies should be focused in achieving a higher removal degree in less time and with less energy consumption. The development of new technologies and the use of new materials and different energy sources has been intensively studied (Celis et al., 2012; Orellana-García et al., 2014; dos Santos and Scialdone, 2018; Rajah et al., 2019; Sedlazeck et al., 2019). Now, the attention is focused on the improvement of the existing technologies by combining them in order to achieve superior performances.

Electrochemical techniques arise once again due to the good results obtained (Rodrigo et al., 2014; Garcia-Segura et al., 2018). Besides, the energy source used can be solar, eolic, or even from a fuel cell powered by the hydrogen obtained by water electrolysis (Souza et al., 2015a; Souza et al., 2015b). The anodic material also has an important influence in the efficiency of the treatment and it must be chosen taking into account the desired reactions or specific oxidant species that need to be electrogenerated (Lizhang et al., 2016).

The integration of electrochemical oxidation with UV light, ultrasounds or Fenton (Özcan et al., 2008; Tizaoui et al., 2011) are exhibiting satisfactory results on the treatment of wastewater contaminated with clopyralid or similar compounds. Many studies have proved the efficiency of photodegradation of clopyralid, showing the influence of the water purity in the photodegradation of clopyralid (Orellana-García et al., 2014) or focusing on the photodegradation of clopyralid on TiO₂ suspensions (Šojić et al., 2009).

Coupling concentration strategies with electrochemical degradation technologies (Muñoz et al., 2017; Soriano et al., 2017; Pan et al., 2019) gained a special attention lately because this way it is possible to increase the rate and efficiency of electrochemical processes, avoiding or limiting mass transfer limitations. The concentration technology selected depends on the nature of the organochlorine pesticide to be treated, being electrodialysis a suitable option to concentrate polar organochlorine compounds.

In previous works, our research group presented a novel process that performs the concentration by electrodialysis and the degradation by electro-oxidation in one single stage. This process, so called as EDEO system, was successfully applied to the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D), demonstrating that the combined process presents a superior performance when compared to the conventional electro-oxidation (Raschitor et al., 2017; Llanos et al., 2018). Nevertheless, in those works it was

hypothesized that the transport rate of the pollutant through the electrodialysis cell may be a key parameter and may be the bottleneck for the future development of the technology.

Based on this background, the main aim of the present work is exploring the applicability of the EDEO technology to the treatment of a wider spectra of organochlorines different from 2,4-D. Moreover, a model of the system is proposed and used to obtain the degradation rate constants and to evaluate the performance of the EDEO process under a wide range of degradation vs transport rate ratios. The main aim of this model is confirming the hypotheses launched in previous works and identifying bottlenecks to be overcome to the development of the EDEO technology in the treatment of ionic organochlorine pollutants.

2. Experimental

The experimentation took place in a lab scale setup, described in detail in previous works (Raschitor et al., 2017; Llanos et al., 2018). Basically, it consists of a commercial electrodialysis cell provided by PcCell (Germany), in which it is possible to work under electrodialysis (ED), electro-oxidation (EO) or EDEO technology by properly setting the number and configuration of the ion exchange membranes.

Electrodialysis tests, made in order to characterize the transport of the pollutant throughout the cell, were performed at constant potential (ranging from 3 V to 9 V) and at discontinuous mode (no solution being fed to or extracted from the system) with the same volume of both concentrate and diluate compartments (1 dm³). The measurements used to calculate the adsorption capacity of the anion exchange membranes were performed in triplicate by immersing increasing areas of membranes in 200 cm³ of 100 ppm clopyralid solutions.

EDEO and EO were performed in continuous operation mode at a constant current density of 177.7 A m⁻². BDD (Condias GmbH, Germany) and MMO (titanium coated with mixed metal oxides, IrO₂-RuO₂) squared grid shaped electrodes were used as anode materials and NaCl and Na₂SO₄ as supporting electrolytes. Cathode was a MMO squared grid electrode in all cases. Although the influence of current density is fully described in previous works and will not be discussed here, to validate the proposed model several tests were performed varying the current density from 35.54 to 177.7 A m⁻². The volumes of the different compartments and the sampling procedure was the same as in previous works and it is fully described elsewhere (Llanos et al., 2018).

The fresh synthetic wastewater had an initial concentration of 100 mg dm⁻³ clopyralid provided by Cymit Quimica, 3000 mg dm⁻³ of salt (NaCl or Na₂SO₄) provided by Panreac and ultrapure MiliQ water.

The anion exchange membranes used in the EDEO tests (AMX from Astom Corp.) were previously saturated by immersion in a 500 ppm clopyralid solution during 48 h prior to their use. The installation setup was rigorously cleaned after each assay using Na₂SO₄ (5000 mg dm⁻³; pH 2) for 15 min at 300 A m⁻² and subsequently rinsed with deionized water in order to remove any traces of acid.

The concentration of clopyralid was measured by HPLC (Agilent 1100). The detection wavelength was 280 nm and the column temperature was 30 °C. The volume injection was set at 20 µL, and a Phenomenex Gemini 5 µm C18 analytical column was used. The mobile phase used was water (containing 0.1% formic acid)/methanol (70/30, v/v) with a flow rate of 0.8 cm³ min⁻¹. All samples were filtered with 0.45 µm Nylon filters prior analysis. The mineralization degree was estimated by TOC measurements (Analytik Jena Multi N/C 3100).

3. Results

3.1 Transport of the pollutant through the electrodialysis cell

The first stage in order to assess the viability of the EDEO technology for the treatment of a polar organochlorine is evaluating the mobility of the pollutant in a single electrodialysis step. With this aim, the electro-migration of the pollutant within the electrochemical cell was characterized by two consecutive ED tests performed with the same membranes, using a synthetic water with 100 mg dm^{-3} of clopyralid. Results are shown in Figure 1.

Figure 1. ED of clopyralid solutions: a) Performance of AMX membranes with two consecutive uses at constant current of 1 A: □■ 1st use; ○● 2nd use. Full symbols – concentrate; empty symbols – dilute. $[\text{Clopyralid}]_0 = 100 \text{ mg dm}^{-3}$, $[\text{Na}_2\text{SO}_4] = 3000 \text{ mg dm}^{-3}$, $[\text{Anode}] / [\text{Cathode}] = [\text{BDD}] / [\text{MMO}]$

As it can be observed, the increase in the concentration of the concentrate is clearly lower than the decrease in the concentration of the diluate throughout the first ED test. This situation changes in the second test, being the degree of concentration attained much closer to the dilution reached in the other compartment. Taking into account that the volumes of concentrate and diluate were equal (1 dm^3 each) and that no reaction can

take place in these compartments, the only plausible explanation for this behavior is the adsorption of clopyralid on the anion exchange membrane. In order to characterize the interaction between the membrane and the pollutant, the adsorption capacity was calculated to be $1.64 \pm 0.26 \text{ mg cm}^{-2}$. This adsorption affinity is approximately half of that obtained for 2,4-D, which was equal to $3.41 \pm 0.24 \text{ mg cm}^{-2}$ (Raschitor et al., 2017).

In order to avoid confusion between the amount of the pollutant degraded and that adsorbed by the anion exchange membranes in the EDEO tests, the membranes used in the following tests were previously saturated following the procedure described in the experimental section. Thus, the saturated membrane would loss its capacity to further adsorb the pollutant and the decrease in the concentration of the organochlorine would correspond only to the degraded fraction. To characterize the mobility of the pollutant with the saturated membrane, Figure 2 shows the influence of the applied voltage in the evolution of the concentration of clopyralid in ED tests using saturated anion exchange membranes.

Figure 2. Influence of applied potential in electrodialysis tests performed with saturated anion exchange membranes. Δ ▲ - 3V; $\square$ ■ - 6V; $\circ$ ● - 9V. Full symbols – concentrate; empty symbols – dilute. $[\text{Clopyralid}]_0 = 100 \text{ mg dm}^{-3}$, $[\text{Na}_2\text{SO}_4] = 3000 \text{ mg dm}^{-3}$, $[\text{Anode}] / [\text{Cathode}] = [\text{BDD}] / [\text{MMO}]$

As it can be observed in Figure 2, at low applied potential the electro-migration of ions is negligible, as it has been previously reported in many works, due to the high electrical resistance of the ion exchange membranes (Ben Sik Ali et al., 2013; Karimi et al., 2018). As the potential increases, so does the driving force and thus the transport of the pollutant through the membrane until it reaches the maximum concentration gradient, as it was also previously reported in many previous works that use electrodialysis for the concentration of inorganic ions (Strathmann, 2010; Karimi and Ghassemi, 2016). Thus, it can be concluded that the electro-migration of clopyralid through the electrodialysis device follows a similar behavior than that described for inorganic ions, allowing the implementation of the EDEO device to perform the simultaneous concentration and degradation of the target pollutant.

3.2 Degradation of clopyralid by EO and EDEO technologies

Once it is checked the ability of the system to concentrate clopyralid by electrodialysis, EO and EDEO tests were performed comparing BDD and MMO anodes and two supporting electrolytes (sodium chloride and sodium sulphate). Figure 3 compares the results obtained for both materials and supporting electrolytes, working at a constant current density of 177.7 A m^{-2} .

Figure 3. Influence of the anodic material and supporting electrolyte on the removal of clopyralid for EO (a) and EDEO (b) processes. $j = 177.7 \text{ A m}^{-2}$, full symbols: BDD, empty symbols: MMO; $\square \blacksquare \text{ NaCl}$, $\circ \bullet \text{ Na}_2\text{SO}_4$; $[\text{Na}_2\text{SO}_4] / [\text{NaCl}] = 3000 \text{ mg dm}^{-3}$.

As it can be seen, the removal rates obtained with BDD anodes are significantly higher than those reached with the MMO. This behavior is expected taking into account the well-known ability of BDD anodes to degrade organic matter (García et al., 2014; Garcia-Segura et al., 2015) and to generate oxidants from the anions of the raw solution (Sánchez et al., 2013; Song et al., 2018). The high overpotential for oxygen evolution and the weak interaction between BDD active sites and hydroxyl radicals favors the generation and availability of high concentration of reactive radicals that enhance the degradation and mineralization of organic matter (Brillas et al., 2010; Gozzi et al., 2017).

When the combined EDEO system is used, the removal degree clearly increases with respect to EO when MMO anodes are employed but slightly decreases when using BDD anodes. These results are in the line of the previous research on the removal of 2,4 – D (Raschitor et al., 2017). In that work, it was hypothesized that the balance between the degradation rate of the pollutant and its transport through the electrodialysis cell may play a key role in allowing a higher concentration in the anode compartment in EDEO with respect to EO system and thus a higher degradation rate in the former. With BDD anodes, the degradation rate is clearly higher than with MMO, as it is demonstrated by the EO tests, but the transport rate is expected to be similar in both cases. Taking this into account, the transport rate is expected to be higher than degradation rate for MMO anodes but in the same order than the degradation rate for BDD anodes, what would explain the dissimilar performance of the EDEO technology with these two electrode materials. This hypothesis will be further evaluated and discussed in Section 3.3, devoted to the modelling of the system.

Once evaluated the behavior in terms of the degradation of clopyralid, the results obtained for the TOC removal and the mineralization current efficiency (MCE) comparing the electrode materials and supporting electrolytes for both EO and EDEO process are presented in Figure 4.

Figure 4. Influence of the anodic material and supporting electrolyte on the removal of TOC for a) EO and b) EDEO processes and on the mineralization current efficiency (MCE) for c) EO and d) EDEO, $j = 177.7 \text{ A m}^{-2}$, full symbols: BDD, empty symbols: MMO; $\square$ $\blacksquare$ NaCl, $\circ$ $\bullet$ Na₂SO₄. $[\text{Na}_2\text{SO}_4] / [\text{NaCl}] = 3000 \text{ mg dm}^{-3}$.

In the line with the results of clopyralid removal, the mineralization efficiency was much higher when using BDD than when selecting MMO as anode material. Moreover, the influence of the supporting electrolyte on the mineralization efficiency depends on the anode material selected: greater with chloride when using MMO but higher with sulphate with BDD. The higher mineralization efficiency of MMO when using chloride may be explained by the ability of these anodes to promote the formation of chlorine active species from chloride (Malpass et al., 2006; Neodo et al., 2012; Cruz-Díaz et al., 2018) following mainly the reactions expressed by Equations 1 to 3. Regarding

BDD, the production and activation of persulphate, following Equation 4, explains the superior performance of this electrode when working with sulphate as working electrode (Matzek and Carter, 2016; Bu et al., 2017; Song et al., 2018).

Regarding the comparison of EO and EDEO systems, the MCE of EDEO overcomes that of EO when using the BDD-sulphate and MMO-chloride systems. At this point, it is important to bear in mind that the system can concentrate not only the target pollutant but also the ions present in the raw solution. This way, the concentration of sulphate and chloride ions in the tests performed with EDEO system is expected to be higher than that of EO, thus enhancing the formation of the oxidants that are responsible of the higher MCE of the EDEO system.

According to the results presented so far, it seems clear that the balance between transport and degradation rates plays a key role in the performance of the EDEO technology. To confirm this hypothesis and to fully understand the behavior of this new technology, the next step of the work consisted in the development of a model of the system.

3.3. Modelling of EO and EDEO systems

Before presenting the model used, it is worth mentioning that the tests were performed under continuous mode and that the data were collected in the first stage of the process, in which the system had not already reached the stationary state. Thus, the model

of a non-stationary continuous stirred-tank reactor (CSTR) was applied to both EO and EDEO cells. Figure 5 presents two schematic diagrams of the systems to be modelled, including the variables that will be used in the model.

Figure 5. Schematic diagram of EO and EDEO processes, F – flowrates ($\text{dm}^3 \text{min}^{-1}$); C – concentration (mg dm^{-3}); V – volume (dm^3); r_D – degradation rate (mg min^{-1}); r_T – transport rate (mg min^{-1}). Subscripts for concentration, volume and flowrate: 0 - inlet; C - concentrate; D – diluate

As it can be observed in Figure 5, the removal degree of the EO process depends on the degradation rate, which is a function of the electrode material, the composition of the target solution and the current density applied. For the combined system, it must be considered the transfer rate from the dilute compartment to the concentrate through the ionic exchange membrane, apart from the degradation rate of the pollutant.

Next, the model of both EO and EDEO systems is proposed. The model of the EO system will be used to obtain the value of the degradation rate constant for a given

electrode, composition of the target solution and current density. Once obtained the values of the constants, the model of the EDEO process will be used to perform simulations that help to understand the role of both degradation and transport rates.

i) ***Model of the EO system***

The equations 5 and 6 describe a conventional CSTR model at non-stationary state for the EO system, assuming first order kinetics for the degradation of the target organochlorine.

$$\frac{d(V \cdot C)}{dt} = F \cdot C_0 - F \cdot C - r_D \quad (5)$$

$$\frac{d(V \cdot C)}{dt} = F \cdot C_0 - F \cdot C - V \cdot K \cdot C \quad (6)$$

Where t is time (min), K is the degradation rate constant (min^{-1}) and the rest of the variables have already been defined in Figure 5. To solve this model, a constant volume can be assumed and the finite elements method applied, giving as a result Equations 7 to 9.

$$V \cdot \frac{\Delta C}{\Delta t} = F \cdot C_0 - F \cdot C - V \cdot K \cdot C \quad (7)$$

$$V \cdot \frac{C_{t+1} - C_t}{\Delta t} = F \cdot C_0 - F \cdot C_t - V \cdot K \cdot C_t \quad (8)$$

$$C_{t+1} = C_t + \frac{\Delta t \cdot F \cdot C_0}{V} - \frac{\Delta t \cdot F \cdot C_t}{V} - \Delta t \cdot K \cdot C_t \quad (9)$$

According to the Equation 9, it is possible to calculate the evolution of the pollutant concentration for given values of the flowrate, the system volume, the inlet

concentration and the degradation constant. Taking this into account, the evolution of the experimental data was adjusted to Equation 9, being the value of the degradation rate constant (K) the setting parameter to minimize the error of the adjustment by the method of least squares. Following this procedure, the values of the degradation constant (K) are depicted in Table 1 for both BDD and MMO anodes and for current densities ranging from 35.54 to 177.7 A m⁻².

Table 1. Values of degradation rate constant (K , min⁻¹) of clopyralid.

BDD			MMO		
Current density (A m ⁻²)	NaCl	Na ₂ SO ₄	Current density (A m ⁻²)	NaCl	Na ₂ SO ₄
177.7	0.0183	0.0196	177.7	0.00070	0.00039
88.85	0.0113	0.0190	88.85	0.00048	0*
35.54	0.0058	0.0089	35.54	0.00026	0*

**Nil degradation was observed within these tests.*

As it can be observed, the values presented in Table 1 are fully in agreement with the degradation rates observed and discussed in the previous section: a higher degradation rate when using BDD and a slightly greater degradation rate when using sodium sulphate, which corresponds with the larger K values observed. Moreover, it can be observed the negligible degradation performance of the system when using MMO anodes, especially when selecting sulphate as supporting electrolyte. The accurate precision of the model

and the physical meaning of the constants calculated validate it to be applied in the prediction of degradation results by this technology.

ii) *Model of the EDEO system*

Once the degradation rate constants were calculated, the model was extended to the EDEO system by adding the transport rate (r_T) to the mass balances previously presented. If the finite elements method is followed, the model is defined by the equations 10 to 14:

$$\frac{d(V_C \cdot C_C)}{dt} = F_C \cdot C_0 - F_C \cdot C_C + r_T - r_D \quad (10)$$

$$\frac{d(V_C \cdot C_C)}{dt} = F_C \cdot C_0 - F_C \cdot C_C + r_T - V \cdot K \cdot C \quad (11)$$

$$V_C \cdot \frac{\Delta C_C}{\Delta t} = F_C \cdot C_0 - F_C \cdot C_C + r_T - V \cdot K \cdot C \quad (12)$$

$$V_C \cdot \frac{C_{C,t+1} - C_{C,t}}{\Delta t} = F_C \cdot C_0 - F_C \cdot C_{C,t} + r_T - V \cdot K \cdot C_{C,t} \quad (13)$$

$$C_{C,t+1} = C_{C,t} + \frac{\Delta t \cdot F_C \cdot C_0}{V} - \frac{\Delta t \cdot F_C \cdot C_{C,t}}{V} + \frac{\Delta t \cdot r_T}{V} - \Delta t \cdot K \cdot C_{C,t} \quad (14)$$

The main difference between equations 14 (EDEO) and 9 (EO) is the presence of the transport rate. Once the degradation rate has been calculated by fitting EO tests to Equation 9 (values depicted in Table 1), Equation 14 can be used to predict the evolution of the concentration of the pollutant for a given value of the transport rate, thus allowing to study the influence of this parameter in the performance of the combined EDEO process.

If the electrode, the pollutant and the current density are maintained constant in both EO and EDEO tests, it is possible to assume that the value of the degradation rate constant will be the same in both systems. Thus, once obtained the values of the degradation rate constant (min^{-1}), it is possible to obtain the specific degradation rate ($\text{mg min}^{-1} \text{cm}^{-3}$) just by multiplying this constant by the concentration of the pollutant. Following this procedure, the expected value of the degradation rate was simulated for two increasing values of the degradation constant: a) one higher that could correspond to the use of BDD anode according to the data gathered in Table 1 ($k=0.019 \text{ min}^{-1}$); b) one 10 times lower that could represent the data obtained with MMO anodes ($k=0.0019 \text{ min}^{-1}$). The results of these simulations are gathered in Figure 6 for three increasing values of the transport rate ranging from 0.1 to 1 mg min^{-1} .

Figure 6. Simulation of the specific degradation rate for EO (continuous) and EDEO for three increasing values of r_T : (- · - ·) 0.1 mg min^{-1} ; (- · · -) 0.3 mg min^{-1} ; (- - -) 1 mg min^{-1} . a) $k=0.019 \text{ min}^{-1}$; b) $k=0.0019 \text{ min}^{-1}$

As it can be observed, in the case of the higher degradation rate (Figure 6a), the degradation expected for the EDEO system only overcomes that of EO for the higher value of the transport rate. In this case of high degradation rate, the performance of the

combined EDEO process is even worse than that of EO for the lowest value of the transport rate because, in this case, the slow transport of the pollutant would act as the limiting stage in the degradation process. On the contrary, in the system with the lowest degradation rate (Figure 6b), the performance of the EDEO system overcomes that of EO in the entire range of transport rates evaluated. This behavior is exactly that described in the tests for both 2,4 - D (Llanos et al., 2018) and clopyralid (present work): a much better improvement of the degradation rate when the EDEO process is applied to a EO system with lower degradation constant (MMO electrodes). Moreover, it is worth noting that these results strength the line in which the technology should be improved: an increasing in the transport rate would certainly improve the overall degradation observed.

4. Conclusions

The two main conclusions of the present work is that the EDEO process can be successfully applied to the degradation of clopyralid in the same line as presented in previous works with 2,4-D and that the increase in the transport rate is the key to a further development of the technology. Apart from these two general remarks, the following specific conclusions can be obtained from the present work:

- It is possible to concentrate clopyralid using electrodialysis, having the AMX membranes an adsorption capacity of this compound equal to $1.64 \pm 0.26 \text{ mg cm}^{-2}$.
- The BDD anodes present a higher degradation rate of clopyralid than MMO materials and a greater mineralization efficiency when using EO technology.
- The mineralization efficiency of BDD anodes is greater when using sulphate as supporting electrode, meanwhile MMO performs better for a supporting NaCl.

- The EDEO technology only overcomes EO process for the systems in which the transport rate overcomes the degradation rate.
- A simple model, based on the non-stationary CSTR, is proposed and used to predict the degradation rate constants. The simulations performed confirms the key role of the transport rate, a parameter that should be promoted in future works to assure the proper performance of the developed EDEO technology.

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