Journal of Environmental Chemical Engineering 13 (2025) 117752

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Carboxylic acids selective recovery from wastewater using electrodialysis

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ARTICLE INFO

Keywords:
Electrodialysis
Selective carboxylate separation
Purification
Electro-refinery
Anionic exchange membrane
MMO electrode
Oxalic acid

ABSTRACT

Carboxylic acids (CAs), such as oxalic acid and acetic acid, are valuable by-products formed during the partial oxidation of organic matter in wastewater treatment. Conventional advanced oxidation processes focus on mineralization, often at high costs, without recovering these useful compounds. This study aims to explore electrodialysis (ED) as a sustainable alternative to separate and purify these acids, adding value to wastewater treatment processes. To do this, in this work, the influence of current density on the efficient purification of oxalic acid from a mixture of four carboxylic acids was studied. Experiments were conducted using a four-compartment electrodialysis cell equipped with the appropriate anion and cation exchange membranes. Key parameters were validated by examining the migration and recovery rates of acids under controlled experimental conditions. A current density of 25 mA/cm^2 was found to be the most effective for the purification of oxalic acid, achieving higher recovery than other higher and lower current densities. With these results, this study highlights electrodialysis as a viable approach for the selective separation and purification of carboxylic acids. Careful optimization of operational parameters enables efficient acid recovery, enhancing the economic and environmental sustainability of wastewater treatment systems.

1. Introduction

In recent decades, developing environmental technologies to tackle the critical issue of wastewater discharge—particularly wastewater containing organic pollutants—has been a significant focus in research [1–5]. The most direct approach has often involved the complete elimination of these compounds by converting them into carbon dioxide, aiming for total mineralization [6–12]. A wide range of methods have been proposed to achieve this target, including biological treatments and various advanced oxidation processes.

Electrochemical environmental technologies have been aligned with these sustainability goals for years, advancing toward greater efficiency in terms of selectivity and energy use [8,13–21]. On one hand, emphasis has been placed on achieving high faradaic efficiency, where electron flow is optimized for target reactions, particularly through the design of advanced electrode materials [8,22–25]. On the other hand, improvements in cell designs such as reducing voltage losses and integrating renewable energy sources have also been critical. These developments have shown that electrochemical systems can operate primarily on electricity, making them compatible with sustainable energy [26–29].

A more recent development in this field is the concept of electro-refinery, which draws inspiration from biorefinery principles while utilizing the distinctive advantages of electrochemical processes [30]. Among its many potential applications, one of the most promising involves the oxidative transformation of organic contaminants coupled with their separation and purification via electrodialysis, followed by further upgrading through organic electrosynthesis.

This approach is feasible because oxidative breakdown of organic compounds typically involves an intermediate stage before full mineralization into CO_2 and H_2O: their conversion into carboxylic acids [13,31]. While this step is common to many treatment methods, including biological ones, electrochemical systems offer a unique level of control over the types of acids produced. By carefully selecting electrocatalytic anodes and adjusting parameters such as current density and cell voltage, the formation of specific carboxylates can be directed and optimized [31].

There are multiple methods available for isolating organic compounds from aqueous solutions, but electrodialysis is particularly notable for its precision and performance. By utilizing anion exchange membranes, this approach facilitates the efficient separation of carboxylates [23,32]. By harnessing the differences in pKa values among acids, electrodialysis enables highly selective separations, optimizing the recovery and usability of valuable streams. This underscores its dual role—not just as a method for isolating compounds but also as a

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https://doi.org/10.1016/j.jece.2025.117752
Received 2 May 2025; Received in revised form 23 June 2025; Accepted 24 June 2025
Available online 25 June 2025

powerful tool for purification, ensuring that recovered materials meet high standards of composition and quality.

However, producing solutions enriched with carboxylic acids is merely an intermediate step in broader refinement processes. These compounds hold significant potential for further transformation through reductive electrosynthesis, a technique that can upgrade them into more valuable derivatives. The success of this valorization phase, however, is strongly contingent on the thorough purification of carboxylates before proceeding with electrosynthetic modifications. Insufficient purification could hinder subsequent reactions, reducing efficiency and limiting the yield of desired products.

Thus, the integration of electrodialysis into chemical refinement pathways offers a strategic advantage, ensuring not only effective separation but also setting the stage for advanced processing methods that maximize resource utilization and enhance product quality. As research continues to refine these techniques, electrodialysis may pave the way for more sustainable and economically viable chemical recovery and conversion strategies.

This research aims to validate the feasibility of the technology while evaluating the impact of different current densities on the separation and purification of carboxylate-containing solutions. The results are essential for the development of the electro-refinery concept, as this purification step plays a key role in improving both the efficiency and the overall value of the technological framework. This study examines four representative carboxylic acids: oxalic acid (OA) formic acid (FA), acetic acid (AA) and propionic acid (PA). These compounds have been identified as predominant byproducts, alongside other acids, in the oxidation of organic matter based on prior research [13,31]. Furthermore, these carboxylates frequently appear in key oxidative degradation pathways of organic material, reinforcing the significance of this investigation.

2. Materials & methods

2.1. Membranes

Fumasep FAB-PK-130 (FAB) commercially available anion exchange membrane (AEM) was purchased from the Fuel Cell. A cation exchange membrane (CEM) was also used to separate the electrodes from the process compartment of the cell: Fumasep FKS-50 (FKS). Their main data are shown in Table 1. These membranes were selected for their properties and potential applicability in electrodialysis processes.

2.2. Chemicals

Oxalic acid (OA) (> 99 %), acetic acid (AA) (> 99 %), formic acid (FA) (>99 %) and propionic acid (PA) (>99 %) were used as model carboxylic acids and were purchased from Fisher Scientific (Madrid, Spain). Sodium hydroxide (NaOH) from Scharlab (Madrid, Spain) and sulfuric acid (H2SO4) (> 98 %) form Panreac (Madrid, Spain) were used to adjust pH. Sulfuric acid was also used as the mobile phase in liquid chromatography. Sodium sulfate (Na2SO4) (Fisher Scientific, Madrid, Spain) was used as catholyte and anolyte solution. All aqueous solutions were prepared using ultrapure deionized water (MilliQ) with a conductivity of less than 1 $\mu S \cdot cm^{-1}$.

Table 1
Physical and chemical properties of the membranes.

Name	Type	Supplier	Thickness (μm)	Proton Transfer Rate (μmol min^{-1} cm^{-2})	Ion Exchange Capacity (meq g^{-1})
Fumasep FAB-PK−130	AEM	Fuel CellStore	110–141	60–400	0.7–1.0
Fumasep FKS−50	CEM	Fuel CellStore	45–55	-	1.2–1.4

2.3. Experimental setup

The core of the purification device is an electrodialysis cell composed of four compartments (Fig. 1), two of them hosting the electrodes (named as electrode compartments) and separated from the operative compartments by Cation Exchange Membranes (CEM) type FKS-50. Main characteristics of this membrane are summarized in Table 1. In one of these compartments the anode was a mixed metal oxide (MMO) electrode, comprising a ruthenium oxide coating on a titanium substrate (Tiaanode, India), while in the other a stainless-steel AISI 304 plate was used as the cathode. Both electrodes were square-shaped and measured 2.5 × 2.5 cm, resulting in an active surface area of 6.25 cm^2 each. In turn, the two operative compartments were separated by an Anion Exchange Membrane type FAB-PK-130. Details about this membrane are also provided in Table 1.

The custom-designed four-compartment electrodialysis cell was developed and fabricated using stereolithographic 3D printing. Special attention was given to the mechanical design of the inlet and outlet nozzles, as well as the structure of the electrode, feed, and purified product compartments. The design promotes a swirling flow pattern within each compartment, enhancing mass transfer and generating sufficient shear stress to minimize solid deposits on the membranes and electrodes. The cell was printed using a Form 3 printer (Preform) with Clear V4 resin, and the design was created using Autodesk® Fusion software.

Each compartment of the electrodialysis cell, with an internal volume of 10 mL, was connected in a recirculation loop to external reservoirs: 150 mL tanks for both the anolyte and catholyte, 500 mL for the feed (raw) solution, and 100 mL for the product (purified) stream. The electrolyte used in the anolyte and catholyte tanks consisted of a 100 mM sodium sulfate solution. A Heidolph Pumpdrive 5001 peristaltic pump (Heidolph Instruments GmbH & Co. KG, Germany) was employed to maintain a recirculation flow rate of 10 mL/min between the reservoirs and the corresponding compartments in the electrodialysis setup.

2.4. Experimental procedure

To investigate the effect of the current density on the separation and purification of oxalic acid from solutions containing oxalic, acetic, formic and propionic acid, different experiments were conducted using the FAB PK 130 AEM to separate the feed and purified compartment. In the

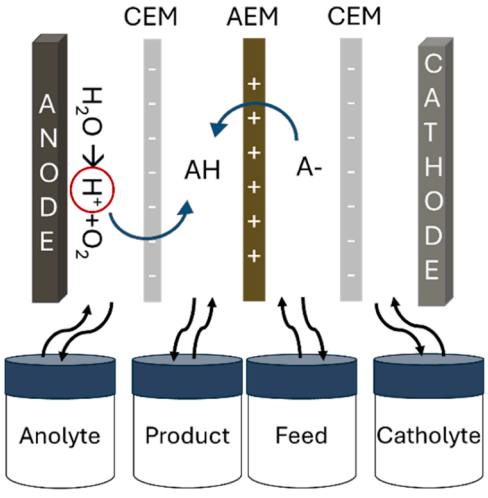

Fig. 1. Scheme of the experimental setup for the selective recovery of carboxylic acids.

tanks that collects the feed and purified compartment, a solution with an equimolar concentration of each acid was carried out (100 mM). The pH in feed compartment was selected at 1.5, for all experiments, to obtain the separation of oxalic acid from the mixtures considering the pK_a of all acids in the mixture. In the tank that collects the purified compartment, a solution with 10 mM of each acid was carried out and the pH was 1.9 and it was not adjusted during the test. Electrolytic tests were carried out at three different current densities (12.8, 25.0 and 37.5 mA cm^{-2}) for a total duration of 9 h with samples collected at different times from feed and purified product tanks to monitor acid concentrations. An additional experiment in the absence of electric current was performed as a blank.

Additionally, a series of four experiments was conducted, each utilizing a different acid (OA, FA, AA, and PA), to evaluate whether the tests from prior sections remained within or exceeded the system's current density threshold. In the tank linked to the feed compartment, a solution containing the relevant carboxylic acid (500 mM of OA, FA, AA, or PA) was introduced, with the pH adjusted to 1.5. Meanwhile, the tank connected to the product compartment also received a solution with the same acid but at a lower concentration (10 mM), and no pH adjustments were made. The experiments were carried out under varying voltage conditions, ranging from 0 V to 30 V, and the system's resulting intensity was recorded. Each test was repeated twice, and the values presented represent the average of the obtained results.

2.5. Analytical methods

Conductivity was measured using a GLP 31 conductometer, and pH readings were taken with a GLP 22 pH meter, both supplied by Crison Instruments S.A. (Spain). The concentrations of carboxylic acids in the feed and purified product compartments were quantified using high-performance liquid chromatography (HPLC) on an Agilent 1100 system. Analysis was carried out with a Hi-plex H column from Agilent, using a 100 mM H_2SO_4 solution as the mobile phase. The system operated at a temperature of 50 °C with a flow rate of 0.6 mL min^{-1}. Prior to analysis, samples were filtered to eliminate any solid particles and avoid analytical interferences.

3. Results and discussion

As mentioned above, in this work four different experiments have been carried out with the same acid mixture. These mixtures have up to four different compounds OA, FA, AA and PA (Table 2). These acids were used because they are common intermediates in the degradation of organic compounds by oxidation [33]. The experiments carried out aim to maximize the concentration of OA, to the detriment of the other acids, through electrodialysis. Within this aspect, a system with a single separation stage is tested. Different acids have been selected for their separation, which act as model compounds as they are the main acids obtained in the electro-oxidation of organic matter [13,31]. The selected acids were oxalic (OA), formic (FA), acetic (AA) and propionic (PA). These acids have sufficiently different pKa values (1.27, 3.75, 4.76 and 4.87, respectively) to allow separation by pH adjustment. Depending on the pH of the feed solution, the ionization (to the corresponding carboxylate) of one of the acids (OA) will be maximized over the rest. Thanks to the installation of an AEM, the migration of anionic species through the AEM can be accelerated by increasing the applied current density. Although AEMs primarily facilitate the movement of ionized species when an electric field is applied, neutral molecules can still interact with the membrane through adsorption or diffuse across it due to concentration gradients. By regulating the pH, the transport of the ionized (carboxylate) forms can be favoured over another, leading to an accumulation of the less ionized acids in the feed compartment and the more ionized carboxylates in the product compartment.

Fig. 2 shows the changes in the concentration of the different organic compounds contained in the solutions circulated through the two operative compartments of the cell during the 9 h of the electrodialysis test carried out applying a constant current density of 25 mA cm^{-2}, as well as the changes observed in the purity of the two streams generated ("feed raw" and "purify product" solutions) during the treatment, expressed in terms of percentage of the different compounds contained in the solutions.

Table 2
Protonation states of the CA at pH 1.5 based on their dissociation constants.

Carboxylic acid	Dissociation constant	Speciation	Speciation for pH 1.5 (%)
Oxalic acid	$Ka_1 = 5.37{\cdot}10^{-2}$ $pKa_1 = 1.27$ $Ka_2 = 5.25{\cdot}10^{-5}$ $pKa_2 = 4.28$	$[(COOH)_2] = \frac{C_t}{1+\frac{Ka_1}{[H^+]}+\frac{Ka_1Ka_2}{[H^+]^2}}$ $[HOOC-COO^-] = \frac{Ka_1[(COOH)_2]}{[H^+]}$ $[(COO^-)_2] = \frac{Ka_2[HOOC-COO^-]}{[H^+]}$	37.02 % 62.87 % 0.104 %
Formic acid	$Ka_3 = 1.78{\cdot}10^{-4}$ $pKa_3 = 3.75$	$[HCOOH] = \frac{C_t}{1+\frac{Ka_3}{[H^+]}}$ $[HCOO^-] = \frac{Ka_3[CH_3-COOH]}{[H^+]}$	99.44 % 0.56 %
Acetic acid	$Ka_4 = 1.74{\cdot}10^{-5}$ $pKa_4 = 4.756$	$[CH_3-COOH] = \frac{C_t}{1+\frac{Ka_4}{[H^+]}}$ $[CH_3-COO^-] = \frac{Ka_4[CH_3-COOH]}{[H^+]}$	99.94 % 0.055 %
Propionic acid	$Ka_5 = 1.35{\cdot}10^{-5}$ $pKa_5 = 4.877$	$[CH_3-CH_2-COOH] = \frac{C_t}{1+\frac{Ka_5}{[H^+]}}$ $[CH_3-CH_2-COO^-] = \frac{Ka_5[CH_3-COOH]}{[H^+]}$	99.95 % 0.043 %

As seen, despite conditions of both streams were specifically selected for a purification of oxalate from the raw mixture of carboxylic acids/carboxylates contained in the feed solution by fixing the initial pH in the feed and purification compartments at 1.5, unexpectedly all compounds contained in the feed solution are transported to the purify product solution, although the different values reached indicate that with a rather different rate.

Thus, according to the pKa_i values of the four compounds contained in the raw feeding solution, at pH 1.5 the ionization of the four compounds should be very different with oxalate being the primary ionic species (with one deprotonation) and the other three compounds being mainly in their acidic molecular forms, as shown in Table 2, in which it can be seen that ionization of formic, acetic and propionic acid is expected to be nearly negligible, being several logs below that of oxalate.

This implies that oxalate is the only species initially expected to be transported to the product purified compartment. However, what can be observed is an increase in the concentration of all compounds in the product solution, that is, that all the compounds pass through the membrane at not negligible rates. Although it is true that the proportion in which they pass through seems to be related to the pKa_i of each compound, and, for this reason, the purified product increases its concentration in oxalate over time to a greater extent than the other components reaching concentrations as high as 218 mM, more than twice the value contained in the initial feeding solution, while the concentration of the others carboxylates in this product stream increases to much lower values, even below those contained initially in the feed stream after the application of electric field for 9 h (electric charge passed 1.41 Ah.

Meanwhile, in the feed stream, the concentration of carboxylates decreases, although this change is less important in the acids with a higher pKa_i value. Mass balance is kept, because no reactivity is

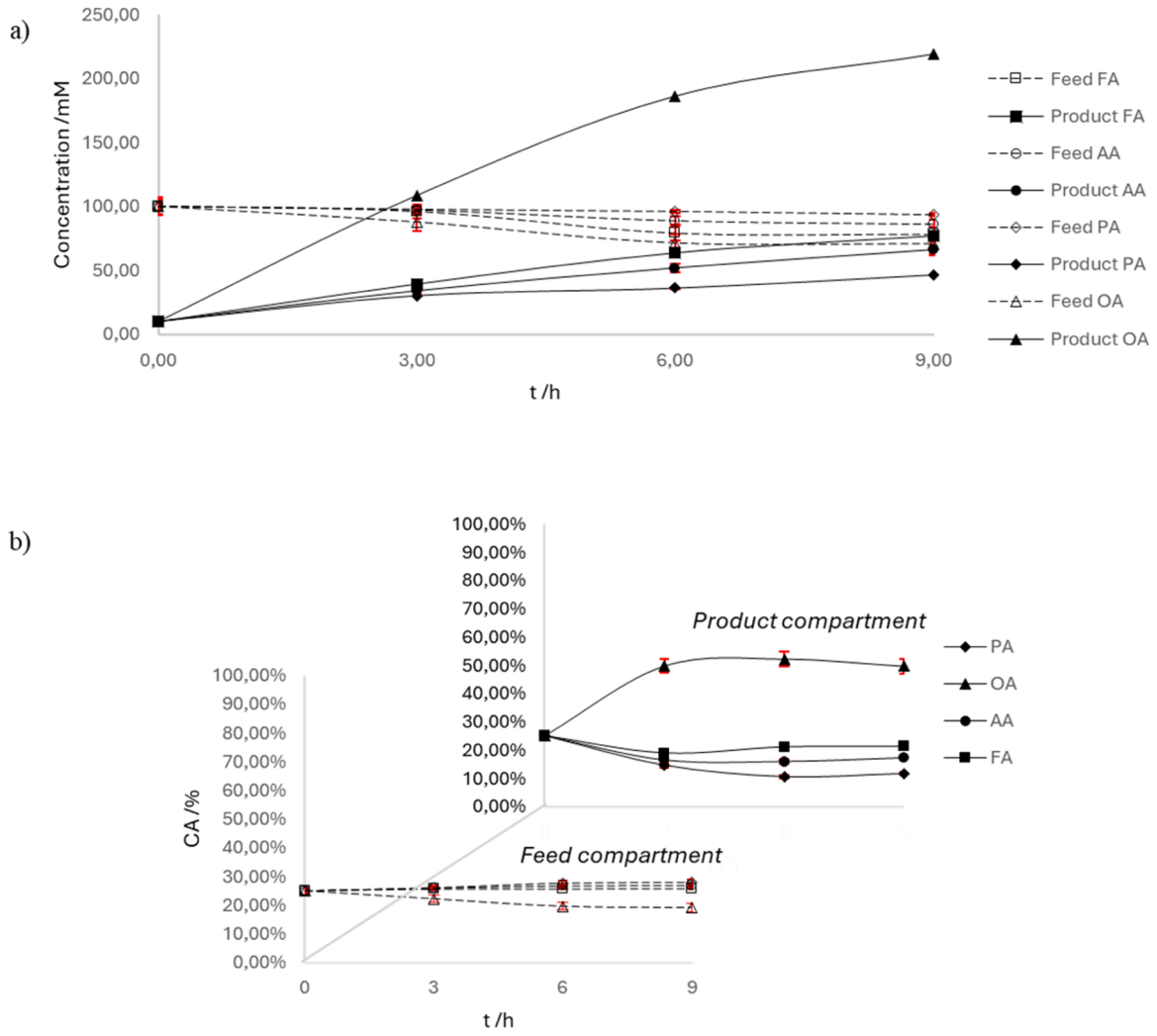

Fig. 2. a) Variation of the concentration of the 4 acids during a 9-hour ED test at 25 mA cm^{-2} and pH 1.5 in the feed and product compartments. b) Variation in the purity (as percentage of the total amount of CA) of acids in the feed raw and product compartments in the test carried out at pH 1.5 and 25 mA cm^{-2}.

produced in the purify product and feed compartments and no carboxylates crossover through the cation exchange membranes is detected.

This implies that although the desired theoretical purification is not completely achieved with this system, significant partial purification is obtained, which means that after the batch treatment, the feed stream is concentrated in propionate/propionic acid (the acid with the highest pKa_i), while the product stream is concentrated in oxalate/oxalic acid (the acid whose first protonation is reached at the lowest pKa_i).

This can be clearly seen in Part b of Fig. 2 in which the relative proportion of the different compounds are shown in the product and feeding solutions. Regarding the degree of purification obtained, it is noteworthy that a good value is achieved in the concentrated stream, reaching approximately 50 % for the component with the lowest pKa_i (oxalic acid/oxalate), while in the feed stream, the component with the highest pKa_i (propionic acid/propionate) is concentrated, reaching a concentration of 28 % of the organics contained. The lower changes observed in the feeding solution ratios are explained in terms of the higher volume of this stream as compared to that of the product stream (ratio 1:10). No important changes in the volumes of both solutions were detected during the test.

Fig. 3 shows the changes observed in the total amount of carboxylates transported between both operating compartments, cell voltage and pH and during this test. As seen, during the process, the pH of the product solution increases up to a stabilization value trend, which can only be explained by the interaction of the carboxylates (not only oxalates but the other three carboxylates that also passes at lower rates) passing through the membrane with these protons to fix the protons transported from the anodic compartment, which, in turn, have been formed on the electrode surface by the oxidation reaction of water to form oxygen (Eq. 1).

$$H_2O \rightarrow 2\ 0.5H_2 + 4H^+ + 4e^- \quad (1)$$

These protons should pass through the cation exchange membrane (CEM) that separates the anodic and purified compartments by electromigration according to the electric field established between the anode and cathode (also by diffusion due to their higher concentration in the anodic compartment than in the purification compartment, although this process is expected to be much less significant) and should contribute to a theoretical decrease in pH in the purification compartment. Therefore, neutralization (and consequent deionization of the arriving species) must be significant based on this observed result. Regarding the pH in the feed compartment, it remains at a value close to the initial one, with a moderated increase which can be explained by being connected to the cathodic compartment through a cationic membrane. For each carboxylate that crosses the anion exchange membrane into the purification compartment, to maintain the charge balance in the feed compartment, either protons or sodium ions must pass into the cathodic compartment, where water reduction to produce hydrogen (Eq. 2) is the primary reaction expected on the surface of the electrode.

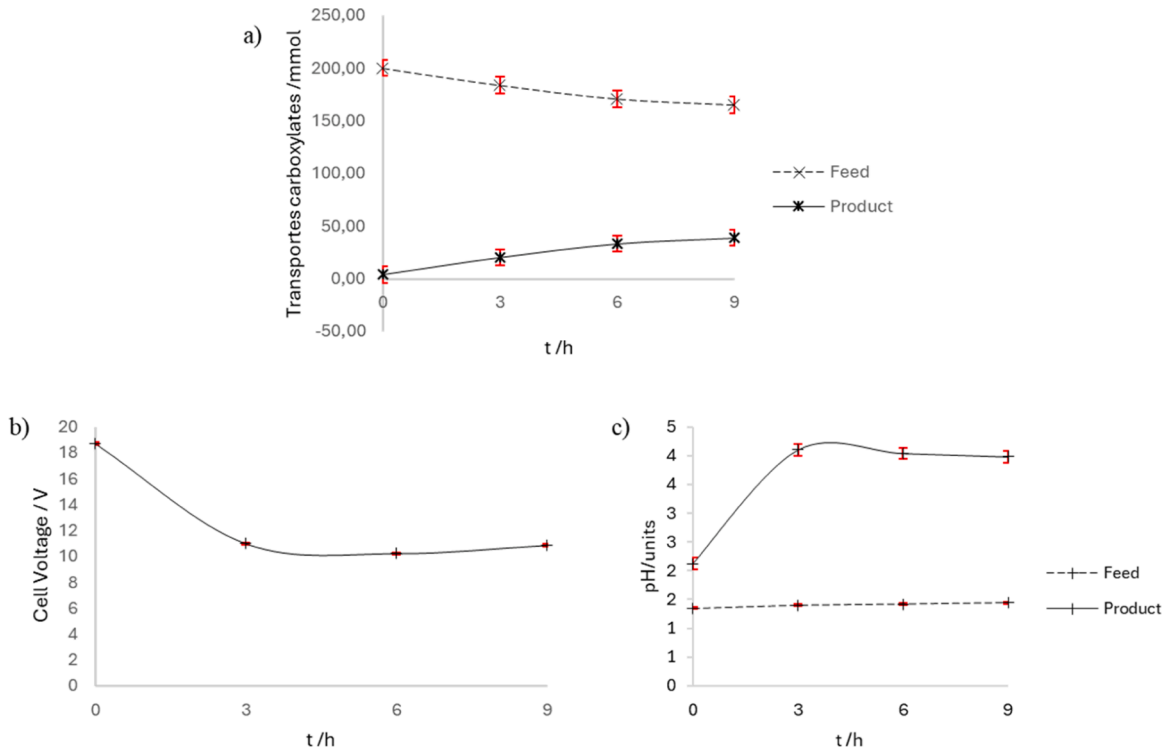

Fig. 3. a) Variations of the total amount of carboxylates transported between the feed and product compartment during a 9-hour ED test at 25 mA cm^{-2} and initial feed pH 1.5. b) Variation of the cell voltage during the ED at 25 mA cm^{-2}. c) Variation of the pH of the feed and product compartment during the ED at 25 mA cm^{-2}.

$$H_2O + \quad e^- \rightarrow \quad 2 \quad 0.5H_2 + OH^- \tag{2}$$

The effects of carboxylate transport are also observed with the conductivity, which increases from 3.30 mS cm^{-1} to 19.28 mS cm^{-1} in the purified product compartment during the test, while it decreases from 18.91 mS cm^{-1} to 13.79 mS cm^{-1} in the feed compartment. The important increase in the ionic conductivity of the product tank can be responsible for the observed decrease in the cell voltage. Because of the prospective character of this work, with still a low technology readiness level (TRL), cell design was not yet considered for being optimized in order to obtain low values as a target, and the large gaps used in the four compartments (1 cm) help to understand that a change in the conductivity of the liquid may explain an important decrease in the cell voltage (and hence in energy consumption) of more than 40 %. Obviously, in increasing TRL in future developments, this will be one of the most important aspects to be tackled.

The total amount of carboxylates transported does not increase linearly; instead, the transport rate decreases over time until it reaches a practically constant value after 9 h. This indicates that, although the driving force is maintained and there is still a sufficient amount of carboxylate in the feed compartment to not limit the transport rate, an equilibrium must be reached between what passes by electromigration and what passes in the opposite direction by diffusion. In this context, it is important to note that the concentrations reached in the purified compartment for certain carboxylates (especially for oxalate) are much higher than those reached in the feed compartment and that the diffusion rate through the membrane is determined by Eq. 3, which indicates that it is proportional to the concentration difference between both compartments, where $C_{feed,i}$ and $C_{product,i}$ stand for the concentration of carboxylate *i* in the feed and purified compartments, respectively, and k is the mass transfer coefficient (which accounts not only for diffusion but by other transport mechanisms). On the other hand, the total electromigration rate does not initially depend on the ion concentration and can be approximated by Eq. 4, as according to Eqs. 1 and 2 each electron transferred through the external circuit from the anode to the cathode produces one proton in the anodic compartment and one hydroxyl ions in the cathodic compartment, which have to be compensated, in a very simplistic way by its transport to the purified compartment (CEM that separates the anodic and purification compartments) or by the transport of protons coming from the dissociation of carboxylates to the cathodic compartment (CEM that separates the cathodic and feed compartments), where water is regenerated (Eq. 5). Therefore, while the former increases over time, the latter remains constant until they reach an equilibrium value where both rates balance (solving simultaneously Eqs. 3, 4 and 6, which is the mass balance of the carboxylate *i*).

$$r = k \quad . \quad A \quad (C_{feed,i} - \quad C_{product,i}) \tag{3}$$

$$r_{charges} = \quad \frac{I}{F} \tag{4}$$

$$H^+ + \quad OH^- \rightarrow H_2O \tag{5}$$

$$C_{feed,i} \quad . \quad V_{feed} - \quad C_{product,i} \quad . \quad V_{product} = 0 \tag{6}$$

Fig. 4 shows the influence of the applied current density on the total amount of carboxylates transported from the feed compartment of the crude product to the purified product compartment, as well as the changes in the cell voltage achieved after 9 h of operation. As it can be observed, increasing the applied current density results in a greater passage of carboxylates through the AEM, due to the higher driving force applied.

In fact, the average cell voltage increases in this proportion, as shown in Part b of Fig. 4, where the time course of this variable is shown in the four tests and in which the changes in each experiment can be explained in terms of the increase in the conductivity of the product solution over time that increase from 3.66 to 13.97 mS cm^{-1} in the test made at 12.8 mA cm^{-2} and from 3.43 to 25 mS cm^{-1} in the test made at 37.5 mA cm^{-2}. Obviously, this change is not observed in the tests in which the electric current was not applied, in which not an increase but a slight decrease is observed from 5.98 to 4.61 mS cm^{-1}, corresponding to the changes in the concentration produced by non-electrochemically assisted transport processes.

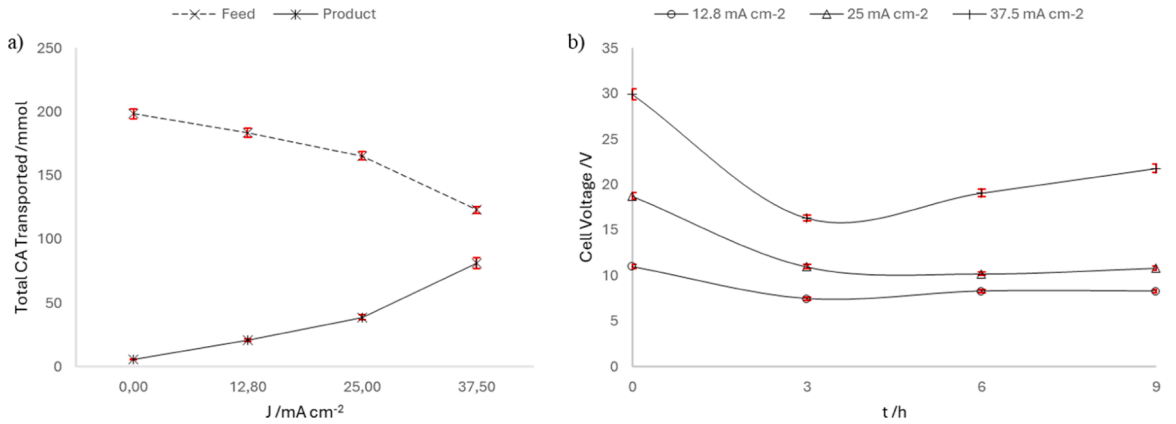

Fig. 4. a) Effect of the current density on the transport of carboxylates from the feed to the product compartment after a 9-hour ED test. b) Variation of the cell voltage during a 9-hour ED test at different current densities: 12.8 mA cm^{-2}, 25 mA cm^{-2}, and 37.5 mA cm^{-2}.

Fig. 5 shows the changes during the operation of the purification process in the purity of the different streams, as well as the changes in the pH of the two solutions processed by the electrodialysis cell.

In the first test, no electric field was applied between the electrodes meaning that diffusion is the primary mechanism that can be used to explain the transport of carboxylates through the AEM. As seen, in this test, the concentration of all carboxylates increases linearly in the product solution in 0.14 mM for acetate, 1.36 mM for oxalate, 2.7 mM for formate and 3.92 mM for propionate after the 9 h of treatment. Considering this constant rate, that area of the AEM is 6.25 cm, a value of the mass transfer rate in the absence of electric field of 0.0025, 0.0242, 0.0480 and 0.0697 mmol cm^{-2} h^{-1} can be proposed respectively for the four compounds. Differences in the transport rate makes that the resulting products enriched in propionate, while the proportion of acetate in the feeding solution increases during this test. In addition, it is observed that the change in the pHs is lower, but it is still observed in both compartments pointing out the importance influence of the ionization equilibrium in both compartments, even in the absence of electrochemical processes on the electrodic compartments.

On the other hand, the results of the test made at 12.8 mA cm^{-2} are rather similar to those obtained at 25 mA cm^{-2} and indicate that under that current it is possible to purify importantly oxalate. However, the main discrepancy occurs in the test made at 37.5 mA cm^{-2}, where the purification observed is appreciably worse than that obtained when applying 12.8 and 25 mA cm^{-2}, despite the total amount of carboxylates transported underwent a significant increase. Likewise, it can be observed that pH increases up to three hours and then it decreases continuously marking a progression in which the pH after the first three

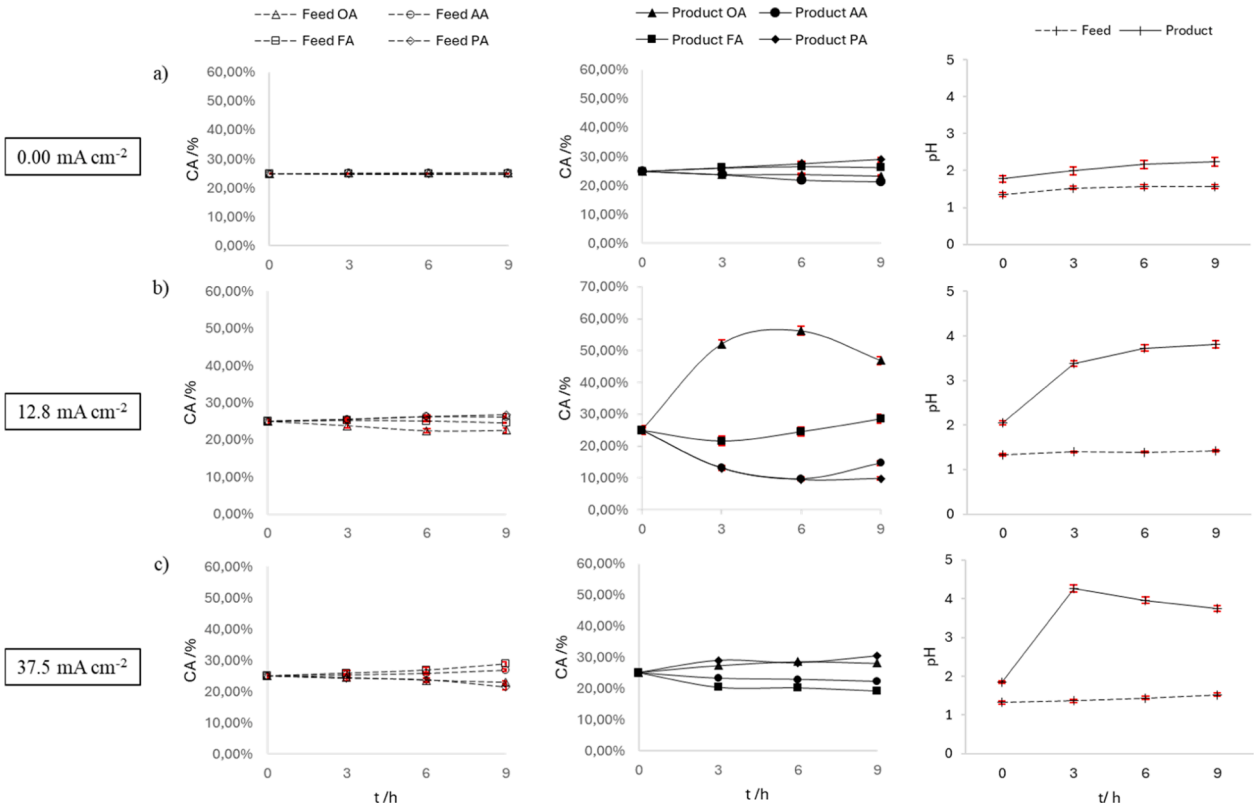

Fig. 5. Variation of the purity of the feed and product solutions and pH during a 9-hour ED test at different current densities: a) 0 mA cm^{-2}, b) 12.8 mA cm^{-2} and c) 37.5 mA cm^{-2}.

hours increases at 12.8 mA cm^{-2}, remains constant at 25 mA cm^{-2}, and decreases at 37.5 mA cm^{-2}. These results are initially difficult to explain, but Fig. 6 shed light on a plausible mechanism responsible for such discrepancies.

In this Figure, the influence of the current density on the rate of transport of the different carboxylates is represented, and it can be seen that while formic and oxalic acids follow the linear trend expected, acetate and propionate, both species with higher pKa, undergo a higher unexpected increase in the rate which help to explain the lower capacity of purification reached in applying higher current densities.

The current efficiency (CE) and the specific energy consumed (SEC) for the OA separation by using FAB-PK-130 AEM were calculated according to Eqs. 7 and 8, respectively, and results are shown in Table 3.

$$CE = \frac{u \cdot F}{I \cdot 3600} \cdot 100 \quad (7)$$

$$SEC = \frac{V \cdot I}{u} \quad (8)$$

Where, u is the molar migration rate ($molh^{-1}$) of the OA, F is the constant of Faraday ($Cmol^{-1}$), I is the current intensity (A) and V is the voltage (V).

As can be seen, the current efficiency increases from 33.4 to 35.5 when going from 12.8 to 25.6 mA/cm2 of applied current density. It is important to note that at 25.6 mA/cm2 the highest OA separation efficacy was obtained (Figure xxx where the purity is shown). It is, therefore, an optimal value, according to the conditions tested, since it is the most effective and efficient for the electrodialysis system. The specific energy consumed increases with the current density applied. However, it is a considerable increase when increasing from 25.6 to 37.5 mA/cm2. This is because the OA migration velocity begins to reach an asymptotic value (Fig. 6). CE and SEC were also calculated for the rest of the acids (FA, AA and PA), however, the passage of these acids across the membrane was not desirable and therefore the consumption referred to each mole of these acids migrated across the membrane increases considerably inversely proportional to their migration velocity. However, by considerably increasing the molar migration velocities of FA, AA and PA to 37.5 mA/cm2 this consumption begins to moderate and assimilate to that specific to OA.

Figs. 7 and 8 illustrate the concentrations in each compartment at different current densities (0, 12.8, and 37.5 mA/cm^2), and the differences between the concentrations of the compounds in the feed and product solutions, respectively. The loss of carboxylates and the generation of protons at the anode should lead to a decrease in the pH of the feed solution. However, a slight increase in pH is observed in all experiments. This phenomenon can be explained by proton diffusion

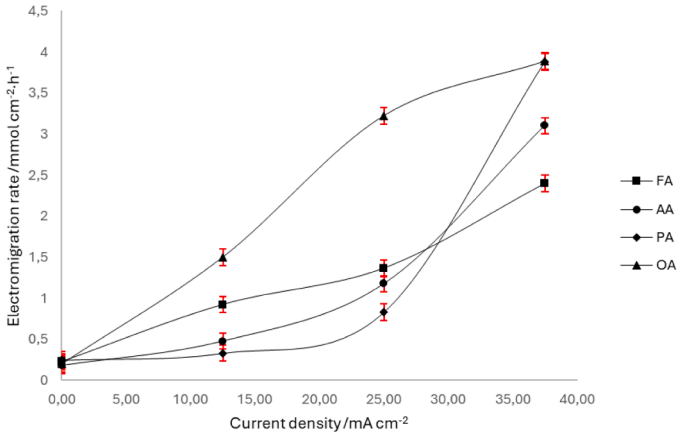

Fig. 6. Electromigration rates of the different carboxylates (OA, FA, AA, and PA) at different current densities (0, 12.8, 25, and 37.5 mA cm^{-2}).

Table 3
Current efficiency (CE) and energy consumption (SEC) of OA for the separation experiments at 12.8, 25.6 and 37.5 mA cm^{-2} of current density applied.

J (mA cm^{-2})	CE (%)	SEC (Wh mol^{-1})
12.8	33.4	663.2
25.6	35.5	818.5
37.5	27.6	2109.3

through the cation exchange membrane (CEM) into the anolyte during the 9-hour experiment, or through the anion exchange membrane (AEM) into the product via diffusion and electromigration.

Starting from a nearly neutral pH in the anolyte, after 9 h, the final pH values would be 1.10, 1.28, and 1.57, assuming 100 % efficiency. These values are similar to those measured in the feed solution (approximately 1.35, according to pH-meter analysis). Thus, proton flux must be traversing the AEM from the feed solution. Regarding the pH in the product compartment, a significant increase occurs due to the passage of carboxylates, which capture protons from the medium. However, in the experiment conducted at 37.5 mA cm^{-2}, a decline in pH is observed after 3 h. This behaviour can be explained by a reduction in the migration rate of all acids through the AEM (Figs. 2a and 7b-c), while the proton flux remains, at least, constant due to its continuous generation at the anode.

As can be observed in Fig. 7, the current density regulates the rate of carboxylate transport between the compartments of the cell, with very small, though non-zero, changes when its value is zero, highlighting that electromigration is not the only transport mechanism. Additionally, it is evident that at high current densities, significant transport still occurs, indicating that the electromigration transport mechanism is much more important than the concentration gradient-driven mechanism. This is clearly shown in Fig. 8, that shows the difference of concentration between both sides of the AEM, and where it can be seen that after three hours of testing at 25 mA/cm^2, the concentration in the product compartment began to exceed that in the feed solution only for oxalic acid (OA).

However, at 37.5 mA/cm^2, this concentration reversal occurred for all compounds. At this point, the mechanisms of diffusion reverse (as the driving force reverses), meaning that electromigration and diffusion partially compensate each other. This competition between transport mechanisms may explain not only the stabilization in concentration observed but also the loss of efficiency in producing a purer solution at the highest current density. Additionally, this behavior seems to delineate the operational current density for these purification processes.

Fig. 9 shows the current density results obtained at different voltages. As can be seen the current density obtained at a maximum voltage tested (30 V) was considerably higher than the current densities tested in the separation experiments. Within the voltage range applied in the cell, there are no observable constraints related to ion transport across the anionic membrane. Only in the case of PA were limitations observed in the migration of this acid. However, this is favourable from the perspective of retaining this acid, rather than prioritizing the attainment of the purest possible OA stream. This indicates that the membrane maintains its ability to facilitate ion movement efficiently under the tested conditions. If such a limitation were present, the system would exhibit a plateau in intensity, meaning that increasing the voltage would no longer correspond to a proportional rise in current. Instead, the observed increase in intensity with higher voltage confirms the absence of significant resistance or saturation effects, reinforcing the suitability of membrane for sustained electrochemical applications within this voltage range.

4. Conclusions

This study demonstrates the potential of electrodialysis as a selective

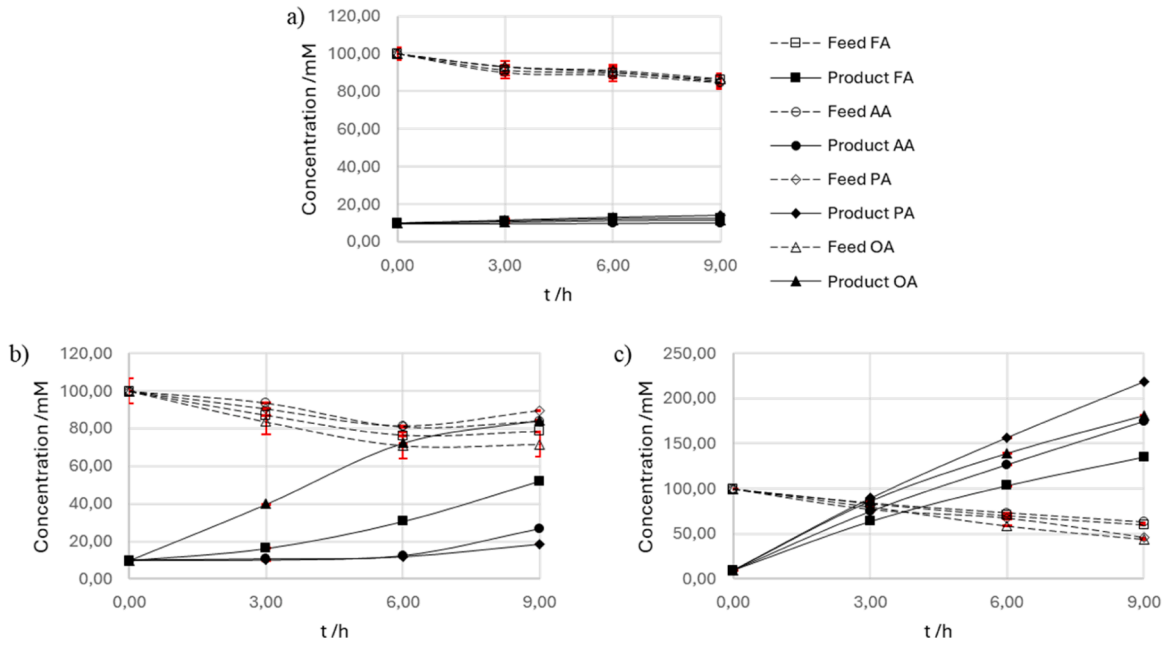

Fig. 7. Variation of the concentrations of the carboxylic acids in the feed and product compartments in mM throughout the 9-hour ED test at three different current densities: a) 0 mA cm^{-2}, b) 12.8 mA cm^{-2}, and c) 37.5 mA cm^{-2}.

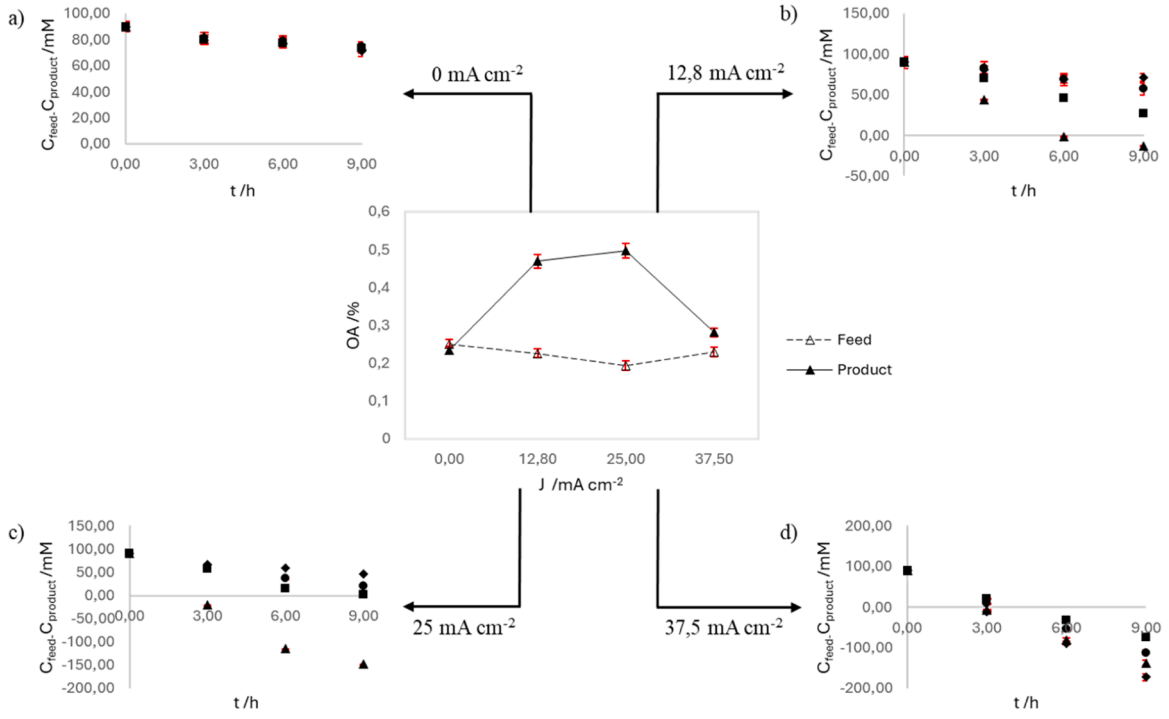

Fig. 8. The difference between the concentrations of the carboxylic acids in the feed and product compartments in mM throughout the 9-hour ED test at 4 different current densities: a) 0 mA cm^{-2}, b) 12.8 mA cm^{-2}, c) 25 mA cm^{-2}, and d) 37.5 mA cm^{-2}.

and sustainable method for the partial purification of carboxylic acids from wastewater, with a particular focus on oxalic acid. Despite the presence of multiple acids (OA, FA, AA, and PA) in the feed mixture, oxalate was preferentially transported through the membrane system, especially at a current density of 25 mA/cm^2. This behavior aligns with theoretical expectations based on acid dissociation constants and the pH conditions employed. Although complete separation was not achieved, as all acids were transported to some extent, the system effectively enriched the product stream in oxalic acid while concentrating less ionized acids, such as propionic acid, in the feed compartment. These results support the feasibility of integrating electrodialysis into broader electro-refinery systems, offering a pathway for acid recovery that adds value to wastewater treatment processes while aligning with principles of green chemistry and circular economy. Further optimization of membrane selectivity and operational parameters could enhance the purity of the target acids and broaden the applicability of this approach to other valuable organic compounds.

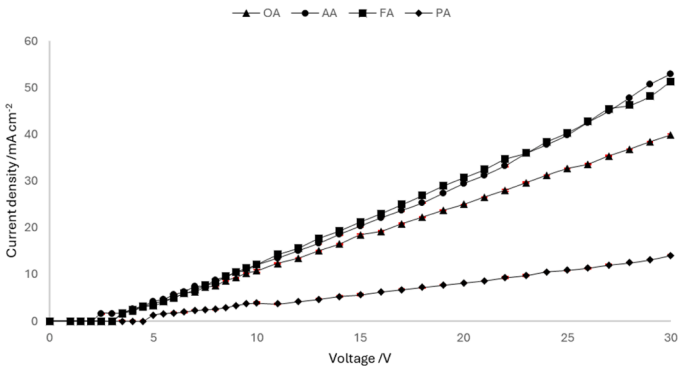

Fig. 9. Current densities at different voltages for all acids (OA, FA, AA and PA).

CRediT authorship contribution statement

M. Richa assisted with experimental work, data analysis and writing the initial draft. **R. García-Cervilla** collaborated in the research work, data analysis, supervision and writing, revising and editing. **J. Lobato** collaborated in data analysis, supervision and writing, revising, editing, conceptualization and acquisition of funding. **P. Cañizares** collaborated in supervision and acquisition of funding. **M.A. Rodrigo** collaborated in data analysis, supervision and writing, revising, editing, conceptualization and acquisition of funding.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors used Co-Pilot in order to improve English and readability. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Manuel Andres RODRIGO RODRIGO reports financial support was provided by Agencia Estatal de Investigación España. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work is part of the research project PID2022–138401OB-I00 funded by MCIN/AEI/Spain and "Unión Europea Next Generation EU/PRTR". Raúl García Cervilla is acknowledged for the Spanish Juan de la Cierva postdoctoral grant. (JDC2022–049619-I). Maya Richa is acknowledged for the Spanish predoctoral grant (FPI) supported by MCIN/AEI/Spain (PREP2022-000324) associated to the project PID2022–138401OB-I00.

Data availability

Data will be made available on request.

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