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Application of Electrodialysis for the treatment of almond industry wastewater.

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Keywords

Electrodialysis

Industrial wastewater

Fouling control

Abstract

In this work, electrodialysis has been proved to be a suitable technique for decreasing the conductivity of a real wastewater from an almond industry, which has been previously treated by electrocoagulation (EC) and electrooxidation (EO). A seven-cell electrodialyzer, with total active membrane area of 1400 cm^2, was employed and several parameters, as the limiting current density, were determined. A method for measuring voltage across the membranes was developed, in order to control membrane fouling. The method consisted of capillaries inserted into the solution compartments and connected to a high impedance voltmeter. A study of the reuse of the concentrate solution was made, and it was stated that it can be concentrated ten times. The treatment of the wastewater was performed at different voltages (7-16 V) to reach values of conductivity of the diluate of 0.5 mS cm^{-1}. After that, the scaling up to a pre-industrial scale was performed by using a seventy-cell electrodialyzer, with total active membrane area of 3.5 m^2. The process was performed by applying voltages of 20-70 V and a final conductivity of the diluate of 0.5 mS cm^{-1} was achieved. The electric energy consumption was calculated in every case.

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1. Introduction

Food industry generates large volumes of wastewater containing high concentrations of suspended solids (SS), chemical oxygen demand (COD), conductivity, turbidity or colour among other pollutants. Among these, almond industry has a high relevance in Spain, especially in the south-east of the country. Spain is the second producing country in the world, and we calculate that the flow of wastewater generated by this industry in Spain is higher than 500000 m^3 $year^{-1}$. This kind of wastewater has been treated by conventional physico-chemical and biological methods. Nevertheless, traditional methods have not been able to perform the treatment properly and that is the reason why our research group have studied the implementation of electrochemical methods in order to develop a feasible treatment of this kind of wastewater.

Electrocoagulation (EC) and Electrooxidation (EO) have proved to be suitable methods for reducing pollutants up to 99 % of COD, SS, turbidity or colour, but they are not able to reduce electric conductivity [1-2]. Spanish law establishes 3 mS cm^{-1} as the limit of conductivity for a wastewater to be dumped to the sewage system [3-4]. As the value of conductivity for the treated wastewater after EC and EO is near 7 mS cm^{-1}, it needs to be reduced before dumping. Another electrochemical technique, Electrodialysis, has been successfully employed for different purposes [5-10] such as desalting brackish water [11-13], purifying solutions in food industry [14], or producing acids and alkalis from industrial streams [15]. In this work, electrodialysis (ED) is proposed to be the technique employed for reducing conductivity by removing ions from almond industry wastewater.

The aims of this work are to demonstrate that electrodialysis is a suitable technique for desalting almond industry wastewater, after the application of other electrochemical techniques; to study the suitable conditions for the treatment at laboratory scale; to minimize the volume of concentrate solution to be discharged and to perform the scaling-up to a pre-industrial scale.

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2. Materials and Methods

2.1. Analytical techniques

Total organic carbon (TOC) was measured with a SHIMADZU TOC-V analyser. COD and suspended solids were measured with a HACH DR 2000 spectrophotometer. The concentration of ions was measured by a Metrohm 850 ProfIC AnCat MCS ion chromatography system.

2.2. Wastewater description

The wastewater samples used came from a company located in the south-east of Spain and were taken from a homogenization tank placed after the blanching process. The colour of this murky wastewater was brown and it contained a large amount of suspended solids and a high COD value. Previous to the electrodialysis treatment, an Electrocoagulation and an Electrooxidation treatment were applied to the wastewater in order to decrease COD, SS and turbidity. The conditions of the EC and EO treatments were stated in previous works [1-2]. Table 1 shows the analytical parameters of the wastewater after EC and EO treatment, which are the initial analytical parameters for the wastewater employed for both, laboratory and pre-industrial scale ED processes.

Table 1. Analytical parameters of the wastewater employed in this work.

pH	6.7
Conductivity (mS cm^{-1})	7.2
TOC (mg L^{-1})	296
Suspended Solids (mg L^{-1})	5
Cl^- (mg L^{-1})	730
SO_4^{2-} (mg L^{-1})	1035
Na^+ (mg L^{-1})	2089
Ca^{2+} (mg L^{-1})	21
Mg^{2+} (mg L^{-1})	45
K^+ (mg L^{-1})	230

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2.3. Laboratory scale experimental system

The electrodialyzer employed at this stage of the work was provided by Eurodia and consisted of seven pair cells, with AMX anion-exchange alternating with CMX cation-exchange Neosepta membranes, as it can be seen in figure 1. Table 2 shows the main characteristics of the membranes, according to the data provided by the manufacturer [16]. The active membrane area was 200 cm^2 per cell, thus the total active area was 1400 cm^2. The ED system consisted of three 3 L identical cylindrical tanks for the concentrate, diluate and electrolyte solutions. An independent pump was used for every liquid line. Two Crison conductivity meters were employed for measuring conductivity of diluate and concentrate solutions. A Krauser K2904 SRD-I power supply was employed to power the reactor. In order to control temperature of the solutions, when needed, a Selecta Frigiterm refrigerated recirculation bath was used. The flow rate was 300 L h^{-1} for the diluate and the concentrate solutions and 150 L h^{-1} for the electrolyte.

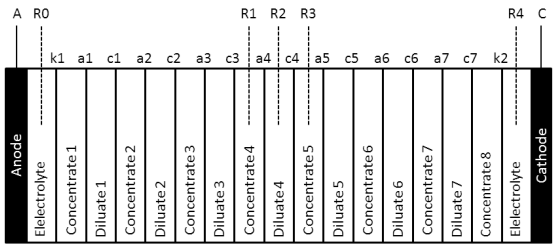

Figure 1. Scheme of the ED reactor for laboratory scale, where the position of the membranes and the capillary tubes inserted into the compartments is shown. A: measuring point at the anode; C: measuring point at the cathode; R0-R4: reference electrodes measuring inside the specified compartments; a1-a7: anion-exchange membranes; c1-c7: cation-exchange membranes; k1-k2: end cation-exchange membranes (Neosepta CMX).

Table 2. Membrane characteristics provided by manufacturer.

Membrane	Characteristics	Electric resistance (Ω cm^2) [a]	Burst strength (MPa)	Thickness (mm)	Temperature (ºC)	pH
CMX	High mechanical strength	3.0	≥ 0.40	0.17	≤ 40	0-10
AMX	High mechanical strength	2.4	≥ 0.25	0.14	≤ 40	0-8

a. Measured in 0.5 M NaCl solution at 25 ºC.

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Some authors have employed different techniques for measuring membrane resistance and voltage [17-21]. In this work a method for measuring potential drops between different points in an electrodialyzer has been developed, in order to allow a simple and feasible method for monitoring voltages in a continuous mode of operation during the experiments [20-21]. By means of this method, it is possible to measure the voltage between both sides of a membrane in order to control the behaviour of the system along experiments, and monitoring these values in a continuous way. The system employed for measuring the voltage between different points of the reactor consisted of capillary tubes (0.78 mm out diameter) inserted in the geometrical centre of the compartments and connected to Ag/AgCl reference electrodes via a syringe, as shown in figure 2.

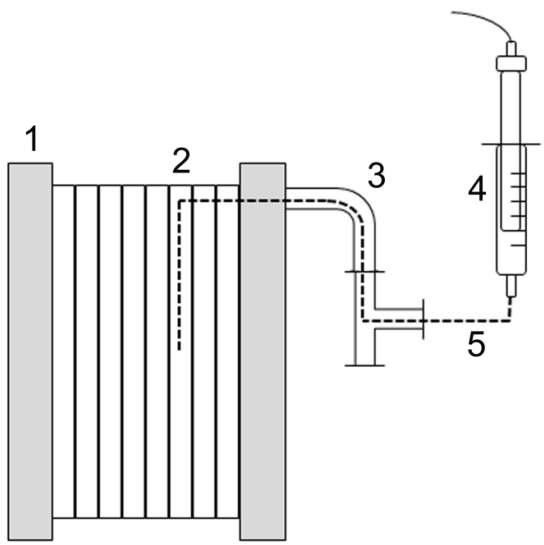

Figure 2. Scheme showing the insertion of capillary tubes into the ED reactor. 1. End plates. 2. Liquid compartments. 3. Pipes. 4. Ag/AgCl reference electrode and syringe. 5. Capillary tube (---).

The capillary tubes and the syringe were filled with a NaCl 50 g L^{-1} solution in order to achieve high conductivities and minimize IR drops along them. The internal resistance of this system was measured to be 8.5 MΩ, which is a value of the same order of magnitude than the internal resistance of commercial voltmeters (10 MΩ). For this reason, measurements made by using a commercial voltmeter are expected to be unstable and to introduce errors. In order to obtain acceptable measures, a new customized high impedance (1 TΩ) voltmeter was built.

The capillaries were introduced into both electrode compartments and the three middle compartments, in order to measure the voltage at the electrodes and across a cation and an anion-exchange membrane (figure 1). By using this system it is possible to measure the

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following voltage drops: $V_{reactor}$, between electrodes (A-C); V_{an}, between the anode and the capillary inside its compartment (A-R0); V_{stack}, all the membrane stack (R0-R4); V_{cat}, between the cathode and the capillary inside its compartment (R4-C); V_{cell}, in a pair cell (R1-R3); $V_{m,a}$, in an anion-exchange membrane (R1-R2); $V_{m,c}$, in a cation-exchange membrane (R2-R3). The IR drop of the solutions are included in the measured voltage values, i.e. the $V_{m,a}$ measure includes:

$$Vm,a = \frac{1}{2} diluate\ IR\ drop + anionic\ membrane\ voltage + \frac{1}{2} concentrate\ IR\ drop \quad (1)$$

These voltage values have a strong dependence on the conductivity of the solutions, but they allow knowing the behaviour of the system at every moment of the treatment.

2.4. Pre-industrial scale experimental system.

The experimental system employed at pre-industrial scale is described in figure 3. The electrodialyzer supplied by Eurodia was a EUR 5B70 with 70 pair cells. Cation-exchange membranes were Neosepta CMX, whereas anion-exchange membranes were AMX, all of them made by Tokuyama. The active area per cell was 500 cm^2, and the total active area was 3.5 m^2. Stainless steel SUS-316 was used as the cathode, whereas the anode was a platinized titanium plate (Ti/Pt). The reactor was powered by a SABAR 100V-50A power supply. A solution of NaCl 5 g L^{-1} was employed for the test experiments, whereas the wastewater previously treated by EC and EO was the water for the treatment experiments. In every experiment, sets of 40 L of sample were used, 6 L as the concentrate and 34 L as the diluate solution. Electrolyte solution was $NaSO_4$ 0.05 M. Flow rate for both solutions was 750 L h^{-1} and 350 L h^{-1} for the electrolyte.

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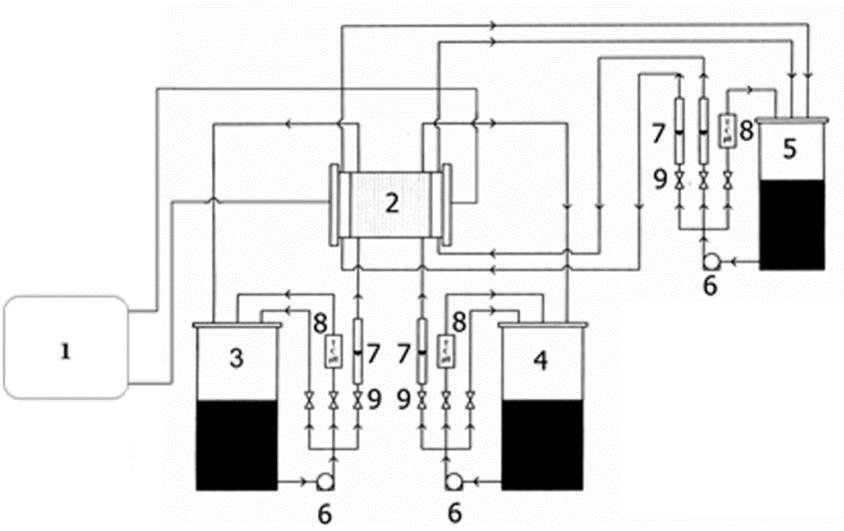

Figure 3. Scheme of the pre-industrial ED experimental system. 1. Power supply. 2. Electrodialyzer. 3. Diluate tank. 4. Concentrate tank. 5. Electrolyte tank. 6. Pumps. 7. Flow rate meters. 8. Thermometer, conductimeter and pHmeter. 9. Valves.

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3. Results and discussion

3.1. Laboratory scale

Characterization of the system

A first series of experiments was performed in order to assess the accuracy of the measurements made by the high impedance voltmeter as well as to determine the optimal value of the electrolyte concentration. A typical value for the concentration of the electrolyte solution is 0.1 M Na_2SO_4, nevertheless when working with a low number of pair cells the IR drop of the electrolyte solution may introduce errors in the voltage measurements. Thus, to minimize those errors, two different electrolyte concentrations were tested: 0.1 and 0.5 M Na_2SO_4. For these test reactions, 2 L of the electrolyte solution were used, whereas the diluate and concentrate solutions were 1.5 L NaCl 5 g L^{-1}. The experiments were performed at 25 ºC and constant voltage of 9 V.

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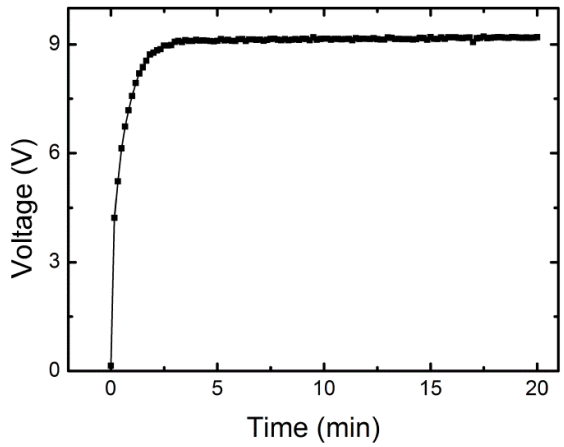

Figure 4. Curve of voltage vs. time, showing the initial ramp of voltage of the power source employed at laboratory scale.

The power source employed for this part of the study needs to perform a ramp from 0 to 9 V, because its internal circuit doesn´t allow giving 9 V from the initial instant of the experiment. The ramp takes around 3 minutes to supply the required voltage. For this reason, figures show an initial slope before reaching the required constant voltage value. Fig. 4 shows an example of voltage vs. time curve, obtained by using this power source, during the experiments corresponding to Fig. 5. This figure helps to better understanding how the power source supplies power, and the behaviour of the related curves. At t: 3 min the constant 9 V voltage is achieved. Until that moment, changes in the curves from figure 5 and 6 are caused by the increase of voltage supplied. After that point (3 min), changes in the rest of the parameters are caused by changes in the conductivity values of the solutions.

As conductivity of the diluate solution decreases, the amount of ions able to transport electrical charge also decreases and this causes the decrease of intensity. As intensity decreases, the overpotential at the electrodes also decreases and that is the reason why V_{an} and V_{cat} decrease. $V_{m,a}$, $V_{m,c}$ and V_{cell} are measurements of potential drop between both sides of membranes. These values include the measurement of IR drop of the solutions. As conductivity of the diluate decreases, the IR drop increases and that is the reason why $V_{m,a}$, $V_{m,c}$ and V_{cell} increase along the experiments.

Figure 5 shows the evolution of current intensity, i, and several voltages versus time. Figure 5.a. shows the variation of the current intensity registered during the ED experiments. The intensity current value reached distinctly depends on electrolyte conductivity, as the higher concentration of electrolyte the higher conductivity in the electrolyte compartment and the lower IR drop, so i is higher when Na_2SO_4 0.5 M is used as electrolyte. On the other hand, the voltages measured

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at the electrodes are lower when working with 0.5 M electrolyte, as observed in figure 5.b. In both cases V_{an} is higher than V_{cat}.

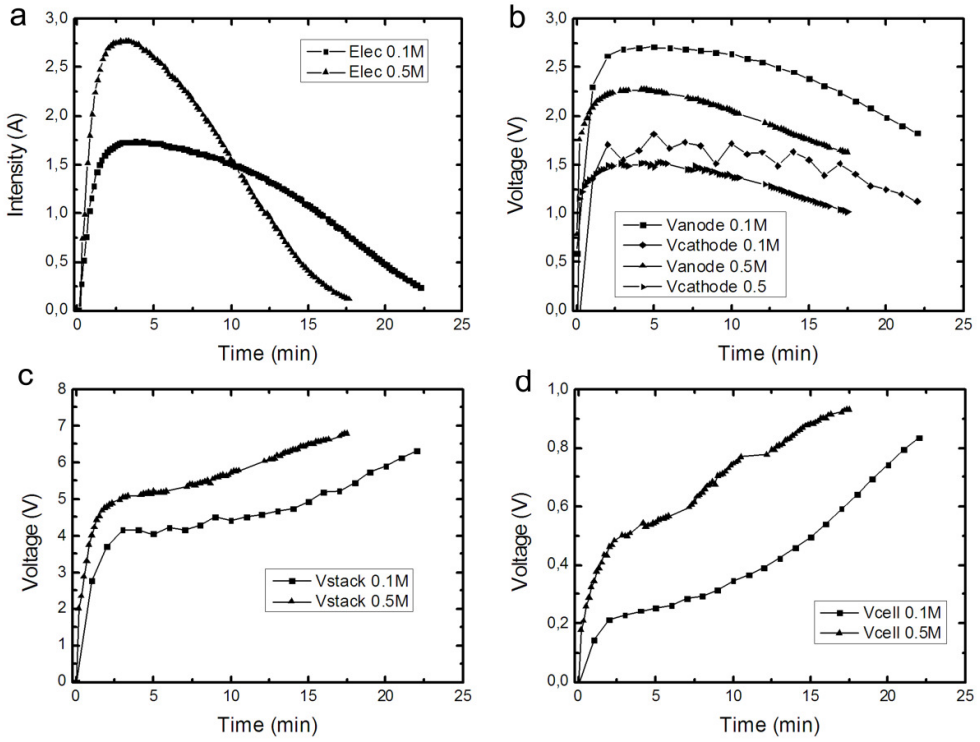

Figure 5. Curves of **a)** Current intensity vs. time; **b)** Electrodes voltage (V_{an} and V_{cat}) vs. time; **c)** Membranes stack voltage (V_{stack}) vs. time and **d)** Pair cell voltage (V_{cell}) vs. time in ED laboratory experiments for different electrolyte concentration values: 0.1 y 0.5 M Na_2SO_4.

$V_{reactor}$ is equal to the addition of V_{an}+V_{cat}+V_{stack}, thus as the experiments were performed at constant total voltage ($V_{reactor}$), the observed decrease in V_{an} and V_{cat} when working with more concentrated electrolytes, implies a higher value of voltage at the membrane stack (V_{stack}), as it is observed in figure 5.c. In both cases V_{stack} increases its value along the experiment, due to the fact that the IR drop of the diluate solution increases as its conductivity decreases. Figure 5.d shows the variation of the voltage in a pair cell (V_{cell}) along the experiments. V_{cell} is higher when the electrolyte solution is more concentrated, and increases along the experiment because of the decrease of the diluate conductivity. As a result of these experiments, the chosen value of electrolyte concentration was 0.5 M Na_2SO_4, because higher values of $V_{membrane}$ and V_{cell} cause less noise and errors in the signal and a better precision of the measurements.

In order to check the reproducibility of the measurements, a series of 4 experiments under identical conditions was performed. As initial diluate and concentrate solution, 1.5 L NaCl 5 g L^{-1} (7 mS cm^{-1}) were used, whereas 2 L Na_2SO_4 0.5 M were employed for the electrolyte solution. The total voltage applied to the reactor was 9 V and the experiments were performed until the

diluate solution achieved a conductivity of 0.5 mS cm^{-1}. For these experiments, V_{stack}, $V_{m,a}$, $V_{m,c}$ and V_{cell} were registered and the values are shown in figure 6, where it can be seen that the values were reproducible.

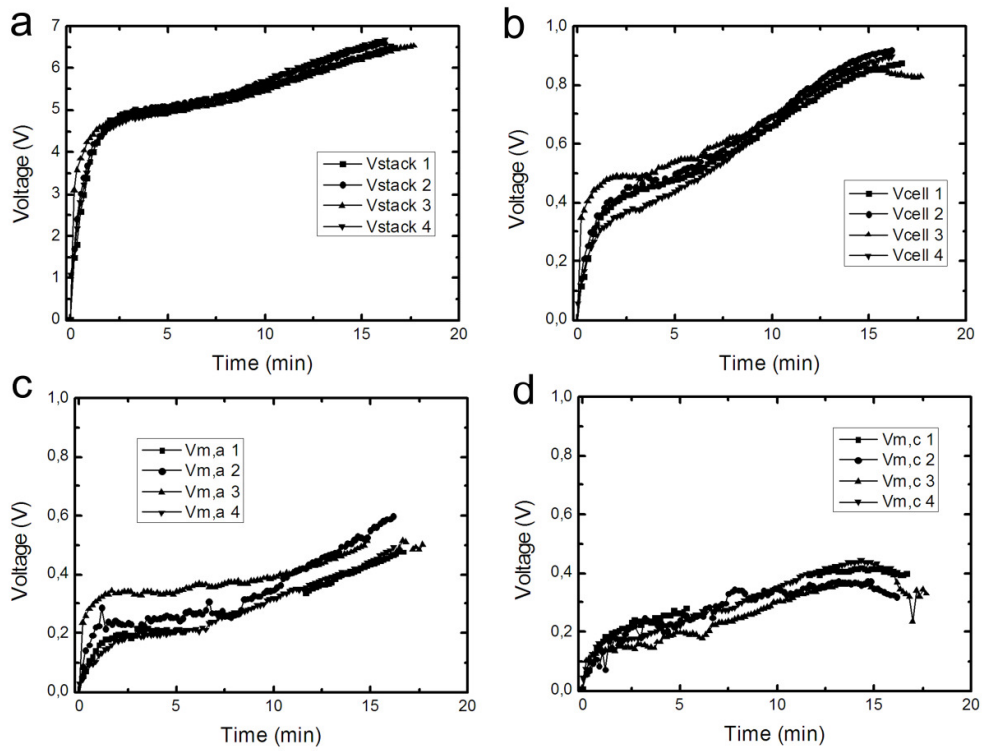

Figure 6. Voltages measured in 4 experiments under identical conditions: 1.5 L NaCl 5gL^{-1} in diluate and concentrate, 2 L Na_2SO_4 0.5M in electrolyte. Constant $V_{reactor}$: 9V. **a)** Membrane stack voltage (V_{stack}) vs. time; **b)** Pair cell voltage (V_{cell}) vs. time; **c)** Anion-exchange membrane voltage ($V_{m,a}$) vs. time; **d)** Cation-exchange membrane voltage ($V_{m,c}$) vs. time.

Determination of limiting current density

To complete the characterization of the reactor it is necessary to know the limiting current density (j_{lim}) [5, 22-28]. To this aim, polarization curves at different conductivity of the solutions were carried out. The conductivity of diluate and concentrate must be the same and remain constant, because differences between the conductivity of the solutions at both sides of the membrane may cause the appearance of Donnan potentials and as a consequence, they will provoke errors in the measurements. To this aim, a single solution was employed to feed diluate and concentrate compartments, re-mixing them in a 3 L tank after they cross the reactor.

The chosen conductivities for plotting the polarization curves were: the initial value, 9 mS cm^{-1}, and two possible target values for the conductivity at the end of the treatment, 1 and 0.5 mS cm^{-}

[1]. The solutions employed were 3 L of NaCl 5, 0.6 and 0.3 g L^{-1} respectively, and as the electrolyte solution, 2 L Na_2SO_4 0.5 M were employed in every case.

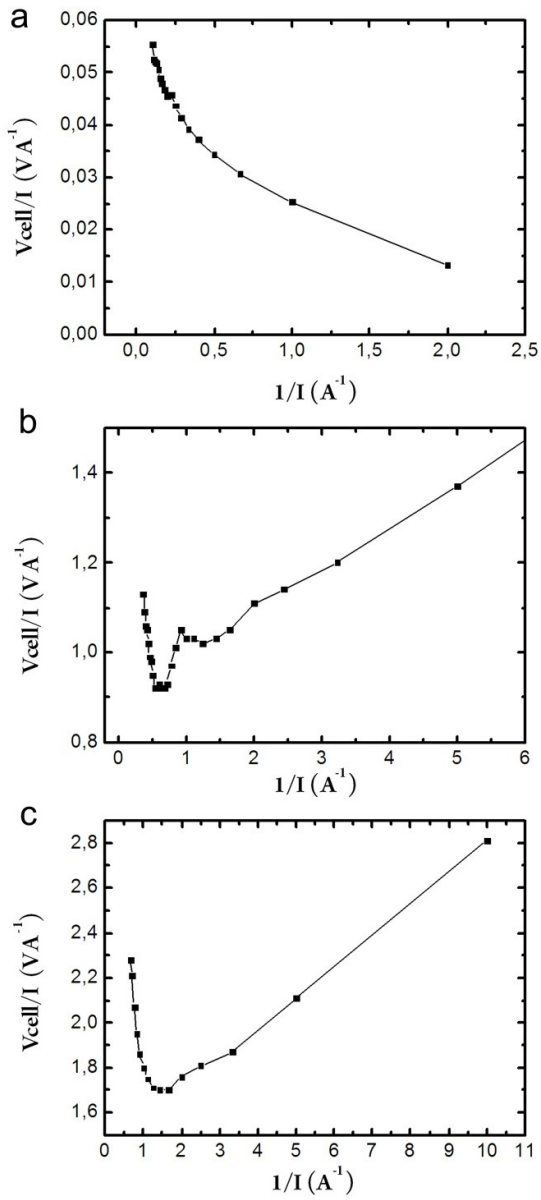

Figure 7. V_{cell}/I vs. 1/I curves for different values of electric conductivity of the solution: **a)** 9 mS cm^{-1}; **b)** 1 mS cm^{-1}; **c)** 0.5 mS cm^{-1}.

The limiting current density can be determined by plotting V/I vs. 1/I [5, 28]. The appearance of the limiting current density is a phenomenon of the individual membranes, caused by the concentration polarization. Nevertheless, in this case the value monitored was the potential drop in a pair cell, in order to know the maximum value of V_{cell} that can be applied, so V_{cell}/I vs. 1/I

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was monitored [27]. The value of j_{lim} measured does not correspond to the pair cell, but to the cation-exchange membrane. When j_{lim} is achieved the curve shows an inflexion point that evidences a sharp change of the resistance of the cation-exchange membrane and must be understood as the starting point of new undesired processes, due to the insufficient ion transport rate from bulk solution to the membrane surface. The curves registered are shown in figure 7. For high conductivity solutions (9 mS cm^{-1}), no j_{lim} appears. Nevertheless, when conductivity is 1 mS cm^{-1} a change in the slope of the curve is observed. By fitting each region of the curve to a straight line, the intersection point represents the value of j_{lim}. In this case, it happens when I= 2A, V_{cell}= 1.9V, $V_{reactor}$= 20V and j_{lim}:= 10 mA cm^{-2}. Finally, when conductivity decreases to 0.5 mS cm^{-1} this phenomenon appears at lower voltage and intensity, I=1 A, V_{cell}= 1.8 V, $V_{reactor}$=18 V and j_{lim} =5 mA cm^{-2}. The last values are the most restrictive and, as the usual mode of operation for ED is at constant voltage, $V_{reactor}$ must not exceed 18 V for this reactor.

Wastewater treatment

With the aim of performing the treatment of the wastewater, a series of experiments at constant voltage ($V_{reactor}$) of 7, 9, 12 and 16 V were carried out. In every case the solutions employed were 2.5 L of the wastewater as the diluate, 1.5 L of NaCl 5 g L^{-1} as the concentrate and 2 L of Na_2SO_4 0.5 M as the electrolyte solution. The treatment was applied until the conductivity of the diluate was lowered to 0.5 mS cm^{-1}.

Figure 8.a shows the current intensity (*i*) vs. time curves for the different total voltages ($V_{reactor}$) applied. It can be seen that the higher $V_{reactor}$ the higher current intensity is achieved and as a consequence, the time needed to achieve the target conductivity value decreases. Figure 8.b shows the variation of the conductivity of concentrate and diluate for the experiments, where it can be seen that the target value (0.5 mS cm^{-1}) in diluate conductivity was achieved in every case. The main difference between treatments at different $V_{reactor}$ applied is the time needed to decrease conductivity to the target value, because the total electric charge passed to achieve it is similar, as shown in figure 8.c. The voltage of a pair cell (V_{cell}) and the membranes that form it ($V_{m,a}$ and $V_{m,c}$) were also measured and they are shown in figures 8.d-f, where it is observed that V_{cell} raised along the experiments. The main contribution to this variation comes from the anion-exchange membrane $V_{m,a}$, which has a similar shape as V_{cell}, whereas $V_{m,c}$ just shows a slight variation.

The real wastewater employed had previously been treated by EC and EO processes, but the organic matter had not been completely removed. The organic matter was oxidized to short-chain acids, which can also cross the membrane. Ion chromatography revealed the presence of acetate, pyruvate and oxalate. Different mobility between anions and cations provoke differences in the resistance of the membranes [29]. The larger organic anions show lower mobility, so they may find higher resistance when crossing the membrane. This is the reason

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why the voltage at the anion-exchange membrane is higher than at the cation-exchange membrane, where the inorganic cations will find less resistance for crossing the membranes.

The TOC analysis of diluate and concentrate at the initial and final time confirms the fact that the organic anions are moving across the membrane. For example, TOC of the diluate solution decreases from 272 to 93 mg L^{-1}, whereas TOC of the concentrate rises from 12 to 268 mg L^{-1}, for the experiment at $V_{reactor}$ = 12.5 V. This fact means that the most organic matter is passing across the membrane and the diluate solution is decreasing not only its conductivity, but also its organic matter content.

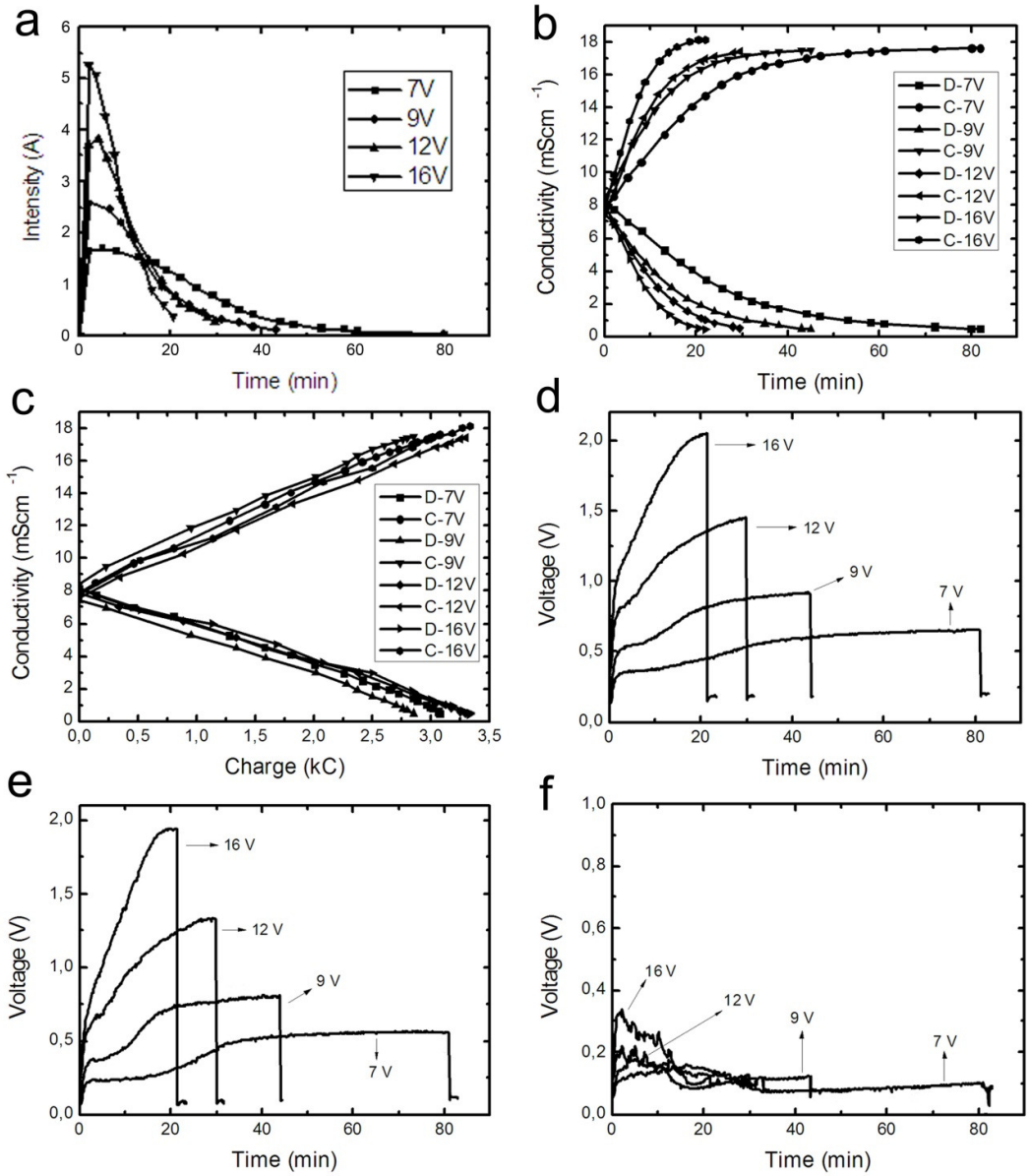

Figure 8. Curves of: **a)** Current intensity vs. time. **b)** Conductivity of diluate (D) and concentrate (C) solutions vs. time; **c)** Conductivity of diluate (D) and concentrate (C) solutions vs. electric

charge passed. **d)** Pair cell voltage (V_{cell}) vs. time; **e)** Anion-exchange membrane voltage ($V_{m,a}$) vs. time; and **f)** Cation-exchange membrane voltage ($V_{m,c}$) vs. time, for the ED experiments performed at constant $V_{reactor}$ of 7, 9, 12 and 16 V.

Study of possible membrane fouling

Large ions present in solutions may be deposited on the membrane surface or into pores, causing the so called "fouling" of the membranes [30-34]. In addition, anion-exchange membranes, which have positively charged groups on their surface, might be specially affected due to the fact that most foulants are negatively charged. For industrial applications of electrodialysis, fouling control is a parameter to be controlled in order to minimize operation costs and avoid interruptions in production. In order to assess the feasibility of the treatment by ED at an industrial scale, the possible fouling process must be studied due to the fact that it may increase operation cost and treatment time. To this aim, an experiment with one only solution and one only deposit for the diluate and the concentrate was performed. The electrolyte solution was 2.5 L Na_2SO_4 0.5 M and 2.5 L of the wastewater were used to feed the concentrate and diluate compartments. The treatment was applied at constant $V_{reactor}$ of 9 V for 100 hour. By this mode of operation the solutions were mixed after the reactor to maintain a constant conductivity and amount of organic matter. In case of fouling, the amount of organic matter within the wastewater will decrease and the voltage at the membranes will rise due to the increase of their resistance.

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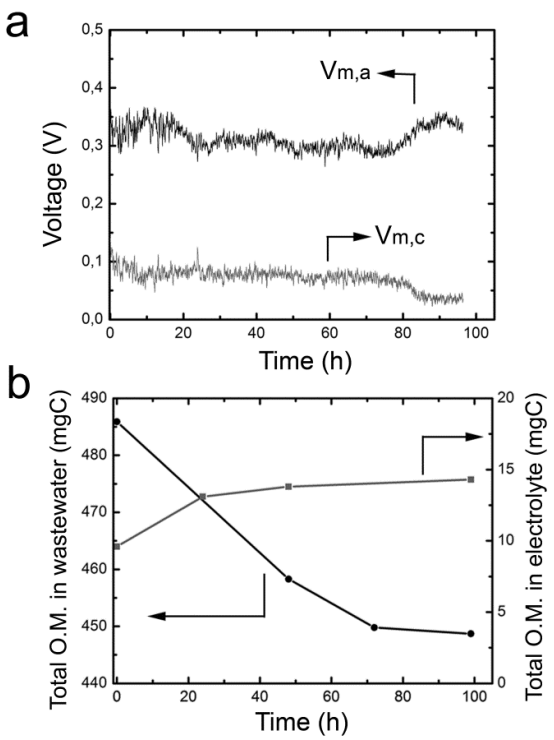

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Figure 9. Curves of **a)** Anion ($V_{m,a}$) and cation-exchange ($V_{m,c}$) membrane voltage vs. time; **b)** Total organic matter contained in the wastewater and the electrolyte vs. time, for the study of membrane fouling with $V_{reactor}$: 9 V and treatment time: 100 hour.

The voltage drop across the membranes, as well as TOC value, was measured during the experiments. These curves are shown in figure 9. The values of voltage at the membranes did not considerably vary. TOC value for the wastewater slightly decreased, while it increased for the electrolyte, what means that part of the organic matter was carried to the electrolyte. When a balance of matter is made, the loss in the total amount of organic matter is assumed to be into the membranes. This amount of matter has been calculated to be 32 mg TOC for 2.5 L of solution, 0.23 g TOC m^{-2} of membrane. The stability of the membrane voltage values and the small amount of matter trapped at the membrane evidences that membrane fouling under these experimental conditions is negligible after 100 hours of treatment.

Concentration trials in constant voltage mode

The purpose of this series of experiments was to simulate a continuous or semi-continuous industrial processing: electrodialysis was run at constant voltage and the concentrate was enriched through consecutive batches. The concentrate solution increases its content of ions and organic matter up to a maximum value of concentration, which can be measured as a maximum in conductivity. When this value is close to the maximum, some physical processes, such as back diffusion or osmosis, appear due to a concentration gradient. These effects provoke a decrease in the volume of treated wastewater and the dilution of the concentrate.

Table 3. Experimental data of the study of concentration limit of concentrate experiments.

Experiment nº	**1**	**2**	**3**
Total applied voltage ($V_{reactor}$) (V)	9	9	12
Initial diluate volume (L)	75	40	40
Initial concentrate volume (L)	1.2	1.2	1.2
Initial conductivity (mS cm^{-1})	8.20	8.20	8.27
Final concentrate volume (L)	3.0	2.1	2.5
Final concentrate conductivity (mS cm^{-1})	34.9	77.6	78.2
Final diluate conductivity (mS cm^{-1})	2.85	2.22	0.96
Water recovered (%)	96	95	94
Electric cost (kW h m^{-3})	2.7	2.8	4.5

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In order to study these phenomena with the wastewater used in this work, a series of experiments at different $V_{reactor}$ applied and volume rate between concentrate and diluate solutions was performed. The volume of concentrate remained constant and different volumes of diluate solution were used. The experimental system was modified and a 100 L tank was used for the diluate solution. Table 3 shows the experimental parameters of the experiments performed, including conductivity, initial and final volume of solutions and the percentage of water recovered as diluate from the total volume employed in each case.

Figure 10 represents the variation of conductivity for the solutions in these experiments and the variation of the concentrate volume. In experiment 1, where the volume rate is 75:1, the conductivity of the concentrate reaches its maximum value (89 mS cm^{-1}) when the diluate conductivity is higher (5 mS cm^{-1}) than the target value. From that moment on, a reversal trend of the curve starts and the concentrate solution gets diluted due to the current intensity is not high enough to counterbalance the pass of water from diluate to concentrate, caused mainly by the higher osmotic pressure of the concentrate.

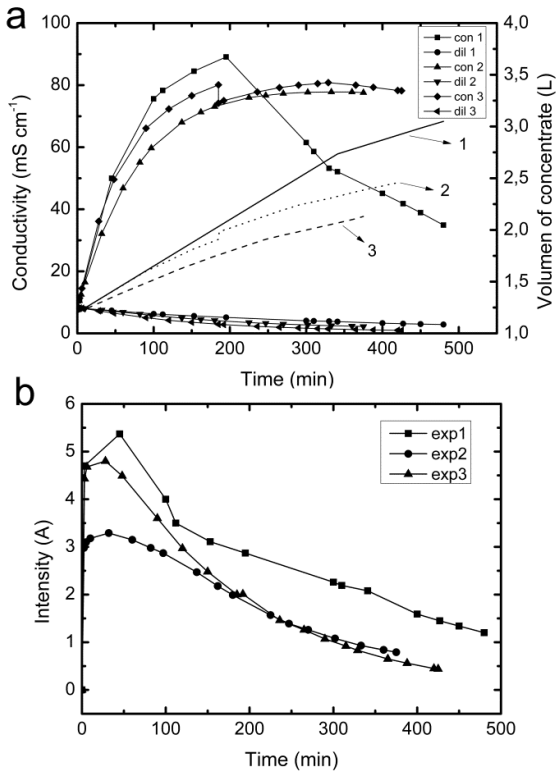

Figure 10. a) Conductivity of diluate and concentrate solutions and concentrate volume vs. time. **b)** Current intensity vs. time for the study of concentration limit of concentrate solution.

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Two possibilities were evaluated for reducing this effect and achieve the enrichment of the concentrate while diluting the diluate at least to 1 mS cm^{-1}: increasing the total voltage applied to the reactor or using a lower volume rate. In experiment 2 a lower volume rate, 40:1, was employed. In this case the conductivity of the concentrate solution rose up to an asymptotic value of 79 mS cm^{-1}, but the target value on the diluate conductivity was not achieved. With the purpose of having a lower conductivity of the diluate, experiment 3 was performed by applying a higher $V_{reactor}$ and keeping the same volume rate as in experiment 2. An asymptotic value of 78.2 mS cm^{-1} was reached for the conductivity of the concentrate when the conductivity of the diluate was lower than 1 mS cm^{-1}. The final conductivity of the concentrate was ten times the initial, and a 94 % of the total initial wastewater was recovered as treated water. The electric cost for experiment 3 is the highest, but for the other two situations the system was not able to achieve low conductivities. The steps observed at experiment 3 curves were caused by a temporary stop of the system, resulting in a slight dilution of the concentrate because of the ion diffusion from concentrate to diluate in the absence of an electric field. The final concentrate solution was the residue generated by this treatment and it had been minimized to a 6 % of the total volume introduced in the system.

3.2. Pre-industrial scale

First of all, a series of test experiments at different total voltages $V_{reactor}$ (20, 35 and 70 V) was carried out so that the typical electric parameters, treatment times and behaviour of the system, could be known. Figure 11.a-c shows the curves of conductivity and current intensity for these tests. In every case results were similar to those obtained at laboratory scale: the higher values of intensity and lower treatment time were achieved for the higher voltage values. It was also possible to achieve a diluate conductivity of 0.5 mS cm^{-1} in the three tests.

Once the main experimental parameters of the system were known, the treatment of the wastewater at pre-industrial scale was performed and experiments at $V_{reactor}$: 20, 35 and 70 V were carried out. Figure 11.d-f shows the curves of conductivity and intensity vs. time for these experiments. It can be observed that the behaviour of the treatment is similar to that observed at the test reactions, but treatment time for the real wastewater treatment was longer, probably caused by the differences in composition, as the mobility of sodium and chloride ions is higher than the mobility of larger ions present at real wastewater. Despite the increase in treatment time, it was possible to decrease the conductivity of diluate to 0.5 mS cm^{-1}. As it happened at laboratory scale, TOC in the concentrate raised along the experiments to values higher than 1000 mg L^{-1}, as it can be seen in table 4.

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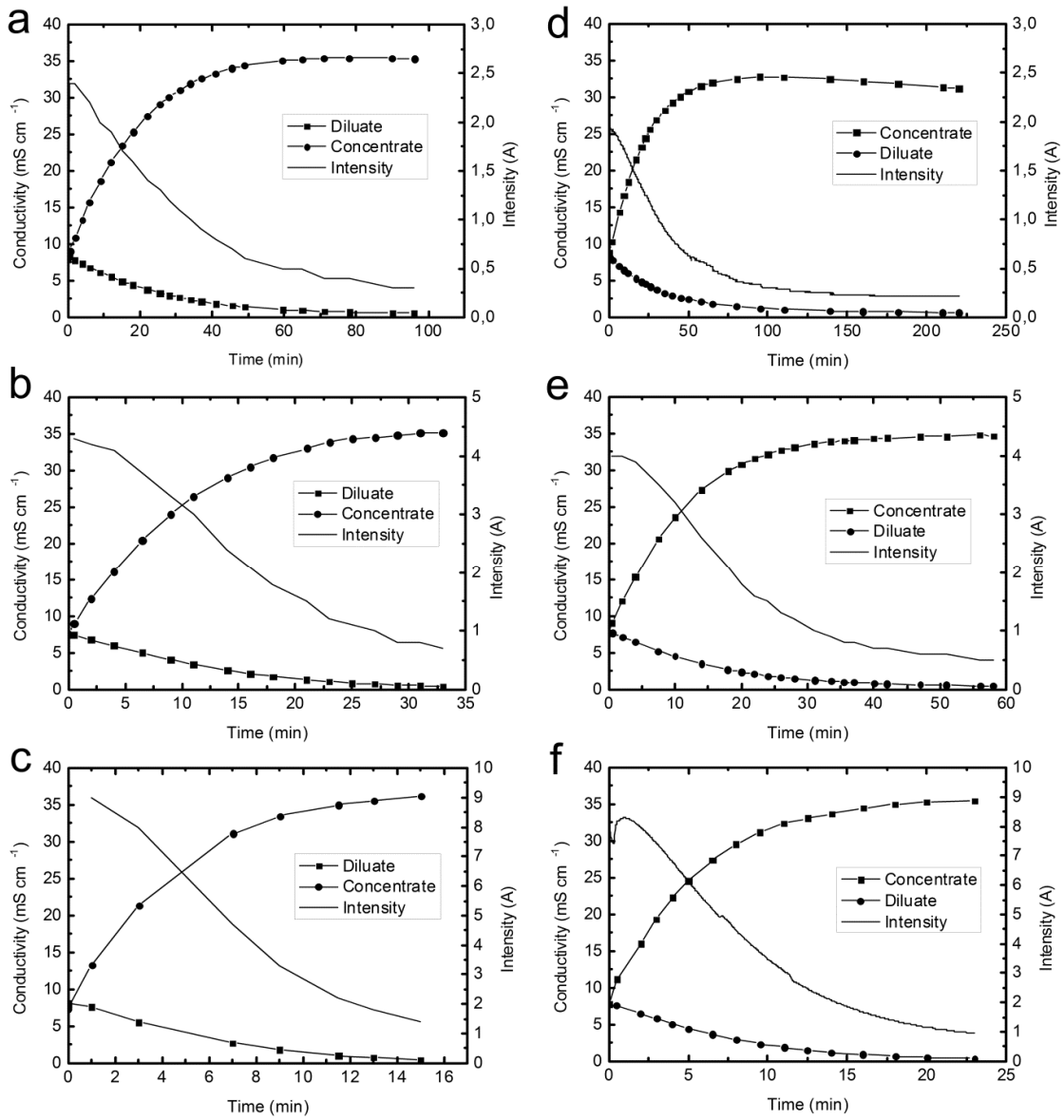

Figure 11. Curves of intensity and conductivity vs. time for the test experiments at different total voltages: **a)** 20 V; **b)** 35 V; **c)** 70 V, and the wastewater treatment experiments at different total voltages: **d)** 20 V; **e)** 35 V; **f)** 70 V. All experiments were performed by the pre-industrial ED system, diluate volume: 34 L and concentrate volume: 6L.

The ending point of the experiments was chosen as the point when the conductivity of the diluate was lower than 0.5 mS cm^{-1}. Nevertheless, in the case of an industrial application, other different ending points for the treatment might be chosen, depending on the latter use of the water: i) 3 mS cm^{-1} when the water is to be discharged to sewage system; ii) 1 mS cm^{-1} when the water is to be reused for irrigation; and iii) 0.5 mS cm^{-1} for more restrictive purposes [35-36]. These values can be achieved by applying any of the voltage values studied. The main differences among them are treatment time (8 - 220 min) and electric energy needed (0.5 – 2.9

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kW h m^{-3}) to get it. When the treatment is performed at 20 V, the time needed is excessive for an industrial purpose. On the other hand, treatment at 70 V needs high rates of energy consumption, i.e., the treatment at 70 V decreases 60 % the treatment time but increases 80 % the electric cost, compared to the treatment at 35 V. Therefore, in order to choose the optimal industrial conditions, a balance among them must be taken into account and exhaustive electric cost estimation must be done in every case.

The concentration of inorganic ions was measured by ionic chromatography. Table 5 shows the values of concentration for the main inorganic ions present in the solution for the experiment carried out at a total voltage of 70 V. It can be seen that there is a high decreasement in ions concentration along the experiments, according to the decreasement in conductivity. Some organic ions such as acetate and pyruvate were detected but not quantified.

Table 4. TOC values for initial and final water, treatment time and energy consumed for the pre-industrial scale ED experiments, measured for three possible final points with conductivities 3, 1 and 0.5 mS cm^{-1}.

		Initial		Final							
				3 mS cm^{-1}		1 mS cm^{-1}		0.5 mS cm^{-1}			
Total voltage (V)	Cell voltage (V)	TOC Diluate (ppm C)	TOC Conc. (ppm C)	Time (min)	Electric cost ($kWhm^{-3}$)	Time (min)	Electric cost ($kWhm^{-3}$)	TOC Diluate (ppm C)	TOC Conc. (ppm C)	Time (min)	Electric cost ($kWhm^{-3}$)
20	0.3	261	260	40	0.5	115	0.9	97	825	220	1.1
35	0.5	295	295	16	0.9	37	1.4	91	1102	58	1.6
70	1	262	260	8	1.8	16	2.6	89	1072	23	2.9

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Table 5. Concentration of the main inorganic ions in the wastewater, measured for initial water and the three possible final points with conductivities 3, 1 and 0.5 mS cm^{-1}. Values for the diluate solution along the experiment at $V_{reactor}$= 70 V.

	Anions (mg L^{-1})			Cations (mg L^{-1})			
	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
Initial	1659	2.3	1035	2089	230	45.2	21
K=3 mS cm^{-1}	81	1.2	629	599	25	1.9	1
K=1 mS cm^{-1}	10	1	309	221	14	0.2	3
K=0.5 mS cm^{-1}	3	0.5	169	105	5	0.1	1

4. Conclusions

In this work, the conditions for the treatment of a wastewater from almond industry by electrodialysis have been studied at laboratory scale. The limiting current density was found to be 5 mA cm^{-2}, when the diluate conductivity was 0.5 mS cm^{-1}. The concentrate was enriched ten times, up to 78 mS cm^{-1} when the volume rate was 40:1, and the recovery of treated water was 94 % under these conditions.

A simple and useful method for measuring voltages between different points inside the reactor was developed and allows detecting membrane fouling by monitoring voltages at the membranes. In the case of almond industry wastewater treated by using an electrodialyzer with Neosepta ion exchange membranes, no fouling was found for a 100 hour treatment.

The treatment was successfully scaled-up to a pre-industrial electroodialysis system, and conductivity was reduced under discharge limit established by existing legislation, when treating wastewater by this pre-industrial system. So, the feasibility of these systems has been proved. Electrodialysis systems, as well as other electrochemical reactors, are suitable to be powered by photovoltaics [37-38]. Future research will be performed in order to evaluate the direct

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connexion of electrodialysis systems to photovoltaic generators and its feasibility for this kind of treatment.

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Table 1. Analytical parameters of the wastewater employed in this work.

Table 2. Membrane characteristics provided by manufacturer.

Table 3. Experimental data of the study of concentration limit of concentrate experiments.

Table 4. TOC values for initial and final water, treatment time and energy consumed for the pre-industrial scale ED experiments, measured for three possible final points with conductivities 3, 1 and 0.5 mS cm^{-1}.

Table 5. Concentration of the main inorganic ions in the wastewater, measured for initial water and the three possible final points with conductivities 3, 1 and 0.5 mS cm^{-1}. Values for the diluate solution along the experiment at $V_{reactor}$= 70 V.

Highlights

Almond industry wastewater treatment.

Fouling control by membrane voltage measurement.

Electrodialysis for wastewater treatment.

Limiting current density determination.

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