Application of electrodialysis for the treatment of almond industry wastewater

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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 10 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 70-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 color 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 0.5 h m^3 yr^{-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 has 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 color, 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.

2. Materials and methods

2.1. Analytical techniques

Total organic carbon (TOC) was measured with a SHIMADZU TOC-V analyzer. 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

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placed after the blanching process. The color 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 treatments, which are the initial analytical parameters for the wastewater employed for both, laboratory and pre-industrial scale ED processes.

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 Fig. 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.

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 behavior 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 center of the compartments and connected to Ag/AgCl reference electrodes via a syringe, as shown in Fig. 2.

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 (Fig. 1). By using this system it is possible to measure the 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

$$V_{m,a} = \frac{1}{2}\text{diluate IR drop} + \text{anionic membrane voltage} + \frac{1}{2}\text{concentrate IRdrop}$$

(1)

These voltage values have a strong dependence on the conductivity of the solutions, but they allow knowing the behavior 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 Fig. 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 were 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 100 V 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.

3. Results and discussion

3.1. Laboratory scale

3.1.1. 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$_2$SO$_4$, nevertheless when

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

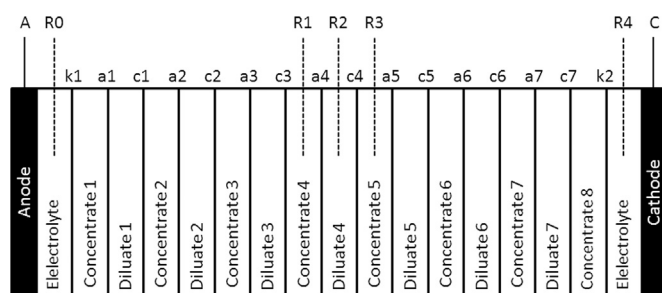|	
pH	6.7
Conductivity (mS cm^{-1})	7.2
TOC (mg L^{-1})	296
Suspended solids (mg L^{-1})	5
Cl$^-$ (mg L^{-1})	730
SO$_4^{2-}$ (mg L^{-1})	1035
Na$^+$ (mg L^{-1})	2089
Ca^{2+} (mg L^{-1})	21
Mg^{2+} (mg L^{-1})	45
K$^+$ (mg L^{-1})	230

Fig. 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).