Membrane selection for the desalination of bio-refinery effluents using electrodialysis

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ABSTRACT

Electrodialysis (ED) has the potential to cost-effectively separate ions from organics in bio-refinery effluents, thereby simplifying downstream treatment and producing streams for possible valorisation. However, there is little information in the open literature regarding the impact of membrane selection for such systems. In this study, we have examined the effect of ion exchange membrane selection on key performance parameters (i.e. desalination rate, specific electrical energy consumption and the transfer of organics) using three commercially available anion and cation exchange membranes with bio-refinery effluents. It was found that the choice of anion exchange membrane had a significant impact, particularly after depletion of those anions having a high membrane permeability (e.g. chloride). The apparent stack resistance (and therefore the specific electrical energy consumption) was found to depend on the choice of anion exchange membrane (from 68 Ω for a PCSA/CMX membrane pair to 188 Ω for an AHA/CMX membrane pair with a cane molasses effluent); additionally the apparent stack resistance was also closely correlated with the amount of organics crossing the membrane. Collectively, these results show that careful membrane selection is critical, particularly when a high desalination rate is desired.

1. Introduction

Bio-refineries can produce a wide range of products (e.g. glutamic acid, citric acid, baker's yeast and ethanol) [1–4]. One characteristic all molasses based bio-refineries share is that they typically generate large amounts (8–34 L L^{-1} of ethanol produced) [5,6] of highly coloured wastewater (6000–570,000 PtCo), rich in both organic material (Chemical Oxygen Demand (COD) = 5–380 g L^{-1}) and salts (conductivities from 4 to 72 mS cm^{-1}) [5,7,8]. The treatment of such streams can be a considerable challenge using existing technologies; for example, the high levels of salt present in these effluents inhibit anaerobic digestion [5,9,10]. Identifying a cost-effective method of separating salts from organics could potentially allow the salts to be used as a high-grade fertilizer while improving the amount of bio-gas produced from the resultant organic stream.

Electrodialysis (ED) is a technology with the ability to separate ionic from non-ionic compounds under an applied current [11–14]. ED has been found to efficiently separate salts from organics in bio-refinery effluents [7,15–17]. As ED is a membrane based process, selection of the most appropriate membranes is a critical consideration in optimising overall process performance [18]. A number of reviews of ion exchange membranes (IEMs) can be found in the literature; for example, those by Strathmann [11], Xu [19] and Ran et al. [20].

Ion exchange membranes (IEMs) are typically made of hydrophobic polymers such as polystyrene, polyethylene or polysulphone. Commercially available anion exchange membranes (AEMs) usually contain quaternary ammonium ($-NR_3^+$), guanidinium ($-NH-C(NH_2)_2^+$) or imidazole groups while cation exchange membranes (CEMs) typically contain sulphonate ($-SO3^-$), carboxyl ($-COO^-$) or phosphoric (PO_3^{2-}) groups [11,19,20]. Commercial membranes are usually homogeneous but porous in nature. The fixed charged group is evenly distributed within the polymer [21] with the uptake of mobile counter-ions (via Donnan equilibrium adsorption) providing low electrical resistance which in ED results in low electrical energy consumption [19]. Fabrication procedures for homogeneous membranes can be found in the literature [11,19,21].

The choice of a suitable CEM and AEM pairing is essential from an economic perspective. In particular, membrane resistance is an important parameter in any ED application, especially in cases where the membrane can be contaminated/fouled by any organic compounds

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present [22]. Such a possibility would directly impact membrane resistance, ion flux and membrane life, leading to a reduction in separation efficiency and increased operational costs [22]. ED generally utilises a stack of IEM pairs and the rise in stack resistance (or in voltage over time across the ED stack) should also be considered as part of the membrane selection process. Lee et al. [23] and El Khattabi et al. [22] investigated the voltage rise for a range of IEMs. They found a higher voltage rise for the AEMs and concluded that these membranes are more susceptible to fouling relative to CEMs. Additionally, El Khattabi et al. [22] measured the resistance of each individual membrane before and after ED to examine the impact of organic contamination/fouling with the highest membrane resistance increase being found for the AEMs. These results were wholly consistent with previous studies into the impacts of membrane fouling [24–27].

Specific electrical energy consumption is a key parameter in the design of any ED system, and several authors [23,28] have examined the effect of membrane selection on this parameter. Lee et al. [23] examined the power required for salt removal using two commercial CEMs (Tokuyama Corp., Japan) and found the CMB membranes gave a 10% lower specific electrical energy consumption than the CM-1 membranes, although no technical reason was given. Specific electrical energy consumption values were also measured by Boucher et al. [28] who found that the energy required was some 30% higher for a monovalent cation selective membrane than for other non-selective exchange membranes (0.34–0.37 compared to 0.22–0.24 kWh kg^{-1}). Hence, employing a monovalent perm-selective membrane would be a compromise between high ion selectivity and low specific electrical energy consumption if the stream being treated contained a mixture of monovalent ions, polyvalent ions and organics.

As previously noted, ED has the potential to be used to separate salts from organics in order to treat and valorise bio-refinery effluents. However, relatively little information is available in the open literature which examines membrane selection for such processes; in particular, there is little information about key operational parameters such as the specific electrical energy consumption and the ability of the membranes to separate salts from organics.

This work thus aims to achieve the following: (i) to explore the behaviour of the apparent stack resistance over an ED run, (ii) to examine the effect of membrane selection on the specific electrical energy consumption, (iii) to investigate achievable organic/salt separation, (iv) to explore the ion selectivity, and (v) to attempt to link observed experimental differences to the membrane characteristics. This study uses three commercially available anion and three cation exchange membranes for a set of typical bio-refinery effluents (one beet and two cane molasses effluents).

2. Materials and methods

2.1. Effluents studied

Three molasses based fermentation effluents were used in this membrane performance study. Beet effluent and cane molasses effluent (A) were collected from an industrial molasses fermentation pilot-plant, while cane molasses effluent (B) was collected from an operational molasses fermentation facility. Details on their composition are given in Table 1.

It is interesting to note that the beet molasses effluent contained around half the chloride as the cane molasses effluents, a fact that is consistent with the measured chloride levels in the beet and cane molasses feedstocks [5]. Additionally, the COD levels varied considerably; the beet molasses effluent and cane molasses effluent (A) contained, respectively, 100 and 150 g COD L^{-1} while cane molasses effluent (B) had a much lower COD level of 52 g L^{-1}.

Table 1
Effluent characteristics.

Parameter		Beet molasses effluent	Cane molasses effluent (A)	Cane molasses effluent (B)
pH		7.0	5.2	6.1
σ (mS cm^{-1})		36.9	36.0	42.1
COD (g L^{-1})		100	150	52
Colour (PtCo)		65,000	235,000	30,000
Osmolarity (mOsm)		1490	1200	1150
Ion concentration	K^+	9.7	14.0	5.8
(g L^{-1})	Na^+	6.8	0.6	8.0
	SO_4^{2-}	5.0	12.6	2.3
	Cl^-	4.3	10.3	11.4
	Ca^{2+}	1.0	3.0	0.5
	Mg^{2+}	0.2	1.8	0.1

2.2. Electrodialysis rig

A three chamber electrodialysis unit (64004 PC Cell GmbH Heusweiler, Germany) was used to run laboratory scale experiments, see Fig. 1. The ED stack was operated with 10 pairs of CEMs and AEMs in batch mode. Each membrane had an area of 0.0121 m^2 (i.e. 0.11 m × 0.11 m) and an active surface area of 0.0064 m^2 (0.08 m × 0.08 m) [29]. The flow channel width between the membranes was 5×10^{-4} m while the distance between the end membranes and the electrodes was 1.0×10^{-3} m [29]. The electrodes consisted of titanium with a platinum/iridium coating. The feed and concentrate compartment solutions were circulated through the ED rig using a peristaltic pump (model Sciq 323, Watson Marlow, USA) at a flow rate 30 L h^{-1}. This corresponds to a cross-flow velocity of 2.08×10^{-2} m s^{-1}; a retention time of 3.8 s in the cell and a Reynolds number of 10. A Masterflex easy load peristaltic pump (Cole Parmer, Australia) was used for the electrode solution. The power supply used was an HPS-13015 from Voltcraft (Germany).

A fixed current of 440 mA (68.8 A m^{-2}) was applied to the ED rig for each of the three effluents studied for 3 h, with the voltage determined by the stack resistance. The maximum voltage able to be delivered by the power supply was 30 V. Hence, when the voltage reached this value, the current was limited by the apparent stack resistance at that time. The applied current density was selected such that all experiments were conducted below the limiting current density which prior to these runs was experimentally determined to be 427 A m^{-2} for beet molasses effluent, 373 A m^{-2} for cane molasses effluent (A) and 474 A m^{-2} for cane molasses effluent (B) with PCSA/PCSK membrane pairs. Values of the limiting current density were obtained graphically using the method of Cowan and Brown [30]. Here the apparent stack resistance is plotted versus the reciprocal of the current; the limiting current density can be calculated by knowing the point at which the slope of the curve changes abruptly. Further details regarding this methodology are available elsewhere [30,31].

A data logger was used to record stack voltage at a frequency of once per minute, while the current was controlled and recorded using a QM-1324 multimeter (Digitech, Australia) at t = 0, 15, 30, 60, 90, 120, 150 and 180 min of operation.

The concentrations of key cations (potassium, sodium, magnesium and calcium) and chloride were measured in all compartments (i.e. concentrate, feed and electrode) at t = 0, 30, 60, 90, 120, 150 and 180 min. The COD and nitrate concentrations were only measured (at the same time points) in the concentrate compartment. It was only possible to measure nitrate in the concentrate solution as the high concentrations of organic and coloured compounds in the feed solution interfered with the spectrophotometric analytical technique used. The final volumes in both the feed and concentrate compartments were measured so as to estimate water transport over the ED run; these measurements were used in the calculation of both current efficiency and specific electrical energy consumption.