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Performance Evaluation of an Electrodialysis with Bipolar Membranes Pilot Plant Operated in Feed & Bleed Mode

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Electrodialysis with bipolar membranes (EDBM) has been recently proposed as a promising strategy for the valorization of desalination waste brine. This process enables the production of chemicals (i.e., acids and bases) starting from a salty stream via the application of an electric field. Several process configurations have been reported in the literature, operating both in continuous and discontinuous mode. The continuous feed & bleed configuration has resulted the best option for the process scale-up. In this work, a performance evaluation of a large scale EDBM unit (19 m^2 of total membrane area) operated in feed & bleed mode is presented. Time profile of acid and base concentrations as well as of voltage applied to the stack are reported, thus proving the stability of the process in galvanostatic condition. Four tests have been conducted at four different current density (200-500 A m^{-2}) and the results have been analysed utilizing appropriate performance parameters (i.e., Current Efficiency, Specific Energy Consumption and Specific production). Results suggest that increasing the current density, the acid concentration rises at fixed base concentration of 1 mol l^{-1}. Furthermore, increasing the current density, the current efficiency of base remains fairly constant (60-63 %), while for acid a growth is observed. Specific energy consumption and specific production show an increasing trend with the current density: at 500 A m^{-2}, values of 3.6 and 2.7 kWh kg^{-1} and 0.94 and 1.3 ton y^{-1} m^{-2} were obtained, respectively.

1. Introduction

Valorization of waste brines represents an important step towards the sustainability of industrial processes. Desalination facilities supply freshwater in areas affected by water scarcity, but, as a drawback, a hyper-saline solution, called brine, is generated (Panagopoulos, 2022). Seawater reverse osmosis (SWRO) technology dominates the present desalination scenario based on the installed capacity (Amy et al., 2017). The brine generated by SWRO process accounts approximately for the 50% of the treated seawater, with a doubled salt concentration (Reig et al., 2016). Many efforts have been dedicated to the recovery of valuable minerals from these streams to reduce, or totally eliminate, the volume discharged (Ghyselbrecht et al., 2014). New technologies have been proposed to this end, such as Electrodialysis with bipolar membranes (EDBM) (Badruzzaman et al., 2009), calcium and magnesium hydroxide crystallizer (Vassallo et al., 2021) and calcium and sodium sulphate crystallizer (Randall et al., 2011). Among these, EDBM represents one of most promising technology, due to the useful chemicals produced (acids and bases) and its low environmental impact (only water and electrical energy are needed). EDBM is an electromembrane process capable of producing acid and base streams from the corresponding salty solution (Strathmann, 2004). This process employs conventional cation- and anion- exchange membranes, to selectively separate cations and anions coming from the salt. In addition, a bipolar membrane is used to allow the dissociation of water into protons and hydroxide ions, under the application of an electric field. The repetitive unit of an EDBM stack is named triplet and is composed of three channels (i.e. salt, acid and base) and three different charged membranes (i.e., cation-exchange membrane, anion exchange membrane and bipolar membrane). The conversion of electrical current into ionic current is accomplished through two electrodes and an electrode rinse solution (ERS).

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The EDBM process has been extensively studied at laboratory scale (low number of triplets and small membrane area) for the production of inorganic acids and bases. (Ibáñez et al., 2013)evaluated the performance of a laboratory scale (2 triplets of 0.01 m^2 membrane area) EDBM unit, using,as feed, a solution that mimicked the brine generated from a desalination plant located in Las Aguilas (Spain). The stack was operated in a closed-loop mode, supplying a current density between 250 and 1000 A m^{-2}. Concentrations ranging from 0.6 to 1 mol l^{-1} and current efficiencies between 45 - 80% were found for the produced chemicals. (Herrero-Gonzalez et al., 2020)utilized a lab scale unit (1 triplet of 0.01 m^2 membrane area) to produce HCl and NaOH from 1 mol l^{-1} of NaCl solution. Tests were performed in closed-loop mode, powering the system with a constant current (1000 $A \cdot m^{-2}$) and using a volume ratio (salt to base) of 20. A concentration of 3.2 and 3.6 mol l^{-1} was reached for acid and base, respectively, and a SEC value of 41 $kWh \cdot kg^{-1}$ for the acid was recorded.

Few information could be found in literature regarding higher scale EDBM unit (both in terms of number of triples and membrane area) and, especially, adopting a continuous operating mode. Recently, (Cassaro et al., 2023) analyzed three process configurations (closed-loop, feed & bleed and fed-batch) for the production of a target base concentration (1 mol l^{-1}) using a semi-industrial scale EDBM unit. They claimed that, at higher current densities, the feed & bleed operating mode presents significant advantages and more attention should be dedicated to the evaluation of this process configuration. However, the analysis focusing only on the base product and no information could be found regarding the acid product.

Following such indications, the promising feed & bleed configuration has been examined in detail, focusing on both products (i.e., acid and base), at four different current densities (200-500 A m^{-2}). Firstly, the steady-state functioning of the system was evaluated, reporting concentration and voltage profiles. Secondly, the trend of the main performance indicators as function of the current density were evaluated for acid and base.

2. Materials and Methods

The EDBM unit analyzed in this work was designed and built as part of the demonstrative treatment chain of the Horizon 2020 Water-Mining project Case Study 1 (European Commission, 2020).It is composed of two skid-mounted structures: i) the pumping station; ii) the stack unit (Figure 1). The pumping station was realized using polypropylene pipes (¾ inches) and equipped with all the instrumentation needed to monitor and control the main variables involved in the process, such as flowrates, conductivity, temperatures, pH and pressures. These variables are checked, both at the inlet and outlet of the EDBM stack, by using magnetic induction flowmeters (OPTIFLUX 4100C, KROHNE Messtechnik GmbH), conductivity sensors (OPTISENS IND 1000, KROHNE Messtechnik GmbH) for conductivities and temperatures, pH sensors (SMARTPAT PH 8320, KROHNE Messtechnik GmbH) and pressure transducers (OPTIBAR P 1010 C, KROHNE Messtechnik GmbH). All materials adopted in the pumping station were chosen to resist in highly aggressive environments. The stack unit, on the other hand, houses the EDBM stack and the DC drive, which has been suitably isolated from the rest of the container, by means of PVC panels, to guarantee operator safety. The EDBM stack is an FT-ED1600-3 module provided by FuMA-Tech GmbH (Germany) and it is composed of 40 triplets. The repetitive unit (triplet) is constituted of FUMASEP® FAB-PK, FKB-PK and FBM-PK as anion, cation and bipolar membrane, respectively. Moreover, the cell pack, is divided into two modules of 20 triplets each, arranged hydraulically in series and electrically in parallel. In this way, the stack was able to reach, in a single pass, a higher concentration, thanks to an active membrane area of 2x0.16 m^2. To power the system, a DC drive (GIUSSANI S.r.l.) was installed, which is able to provide up to 200 A (i.e., 550 A m^{-2}).and 80 V The two skids are connected through flexible PVC hoses, in order to reduce mechanical vibration of the stack.

The pilot plant was also equipped with a total number of six IBC tanks of 1 m^3 each, for acid, base and salty solution, while, for the electrode rinse solution a cylindrical tank of 0.125 m^3 was employed. Magnetic-driven centrifugal pumps with a regenerative turbine (PTM 2.5x6, made in PP, TEOREMA S.r.l.), provided with inverter, were installed to feed the electrolytic solutions inside the stack. The system was designed to work under different process configurations such as, closed-loop, open-loop and feed & bleed (Strathmann, 2004). The latter configuration is more complex, and therefore, requires an additional instrumentation. Specifically, to recirculate part of the outlet flowrate at the inlet one, electrically actuated valves (VKDIV/CE DN15, made in PP, FIP – Formatura Iniezione Polimeri S.p.A.) were installed. Furthermore, to guarantee the desired outlet flowrate, for the acid and the alkaline solution, two gear pumps were adopted in the exit lines. All measuring and control devices were connected to the data acquisition hardware, which is composed of a chassis (NI cDAQ-9179), where acquisition (C series: NI-9203, NI-9208) and command cards (C series: NI-9264, NI-9265 and NI-9266) are located. To monitor and control the main variables involved in the process, LabVIEW software (National Instrument®) was used.

In this work, the EDBM pilot plant was operated in feed & bleed configuration for acid and base and in closed loop mode for salt solution and ERS. The flowrates at the stack inlet were kept constant, and equal to 5 l min^{-1}, for acid, base and salt (corresponding to a channel velocity of 2.6 cm s^{-1}). Instead, a higher flowrate was fixed

for the ERS (20 l min^{-1}) to guarantee an effective removal of gases produced by the electrodes. The current density range was properly selected to assess the most interesting operating conditions for industrial applications. The outlet flowrate was set according to the current density supplied to the stack, to maintain constant the concentration of base (1 mol l^{-1}), while the acid concentration was let to vary. In this way, it is possible to analyze the effect of current density on the acid stream. Notably, only an inlet flowrate of demineralized water was fed in the acid and base compartments. Salty feed solution was prepared from demineralized water, adding 58.44 g l^{-1} of NaCl (>99.5% purity, Saline di Volterra S.r.l), mimicking the concentration of SWRO brine, after removing bivalent ions. The ERS was also prepared using demineralized water and adding 35.5 g l^{-1} of Na_2SO_4 (technical grade, CR GRUPO CRIMIDESA).
During the tests, acid and base samples were collected every 15-30 minutes and analyzed for analytical characterization by titration. To do this, a standard solution of Na_2CO_3 (0.05 mol l^{-1}) and HCl (0.1 mol l^{-1}) were employed to determine the H^+ and OH^- concentration, respectively, using methyl orange as pH indicator.

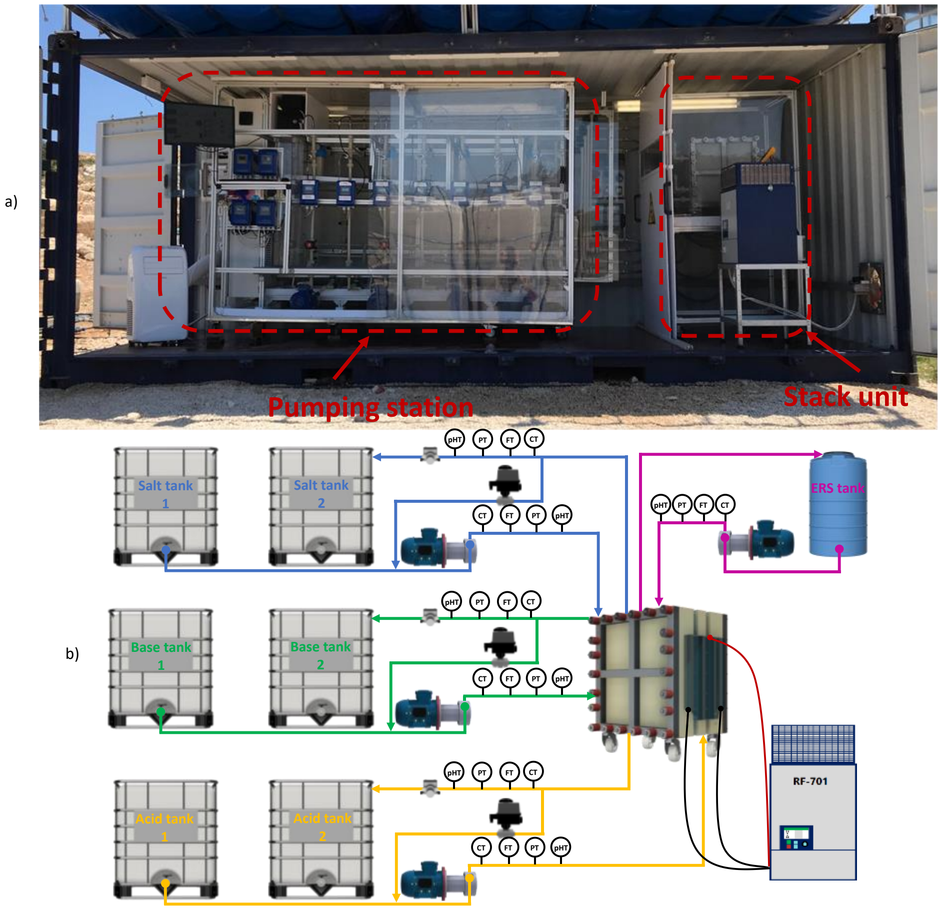

Figure 1: a) front view of the EDBM pilot plant. b) simplified process flow diagram (PFD) of the EDBM pilot plant operated in feed & bleed configuration.

To assess the stack performances three key indicators were employed.

- Current efficiency (CE, %), which represents the percentage of electrical current converted into acid and base, with respect to the total current provided to the system:

$$CE = \frac{Q_p(C_{p,out} - C_{p,in})F}{60\ N_{tr}\ i\ A_m} 100 \tag{1}$$

Where Q_p is the product outlet flowrate (acid and base) in l min^{-1}, $C_{p,out}$ and $C_{p,in}$ are the outlet and the inlet concentrations of the product (mol l^{-1}), respectively, F is the Faraday's constant (i.e. 96,485 C mol^{-1}), N_{tr} is the number of triplets, A_m is the active membrane area (m^2) and i is the current density (A m^{-2}).

- Specific energy consumption (SEC, kWh kg^{-1}), defined as the amount of energy consumed to obtain one kilogram of desired product:

$$SEC = \frac{U\, i\, A_m}{60\, Q_p (C_{p,out} - C_{p,in})\, M_p} = \frac{F\, U}{36\, M_p\, CE\, N_{tr}} \qquad (2)$$

Where U is the external voltage (V) and M_p is the molecular weight of the product (g mol^{-1}).

- Specific Production (SP, ton $y^{-1}m^{-2}$), which gives the mass of desired product obtained in a year (considering 8000 working hours per year) per unit of total membrane area:

$$SP = \frac{0.48\, Q_p\, (C_{p,out} - C_{p,in})}{3\, A_m\, N_{tr}} M_p \qquad (3)$$

3. Results and discussion

The EDBM pilot plant was operated in feed & bleed mode at different current density, in the range 200-500 A m^{-2}. A summary of the tests performed and the operating conditions adopted is reported in Table 1.

Table 1: Main operating conditions of the tests performed

Test	Current Density A m^{-2}	Salt Flowrate l min^{-1}	ERS Flowrate l min^{-1}	Outlet Acid/Base Flowrate l min^{-1}	Recirculated Acid/Base Flowrate l min^{-1}*
1	200	5	20	0.48	4.52
2	300	5	20	0.75	4.25
3	400	5	20	1	4
4	500	5	20	1.2	3.8

*The sum of the recirculated and the outlet flowrate represents the flowrate fed to the stack (5 l min^{-1}).

Figure 2 shows the profiles of acid and base concentration as well as the trends of the applied voltage as function of time at two different current density values, i.e., 300 and 500 A m^{-2}. In both tests, starting from demineralized water in the acid and base compartment, a transitory phase is observed to increase progressively the acid/base concentration at the stack inlet. Finally, a steady-state condition is reached, in which the inlet water, in the acid and base compartment, is mixed with the recirculated stream and a certain outlet concentration is obtained. It seems, from Figure 2a, that the transient phase is faster for the acid solution with respect to the base. This effect could be attributed to the lower concentration reached in the acid channel, which in turn depends on the protons diffusion in the salt channel (Herrero-Gonzalez et al., 2023).

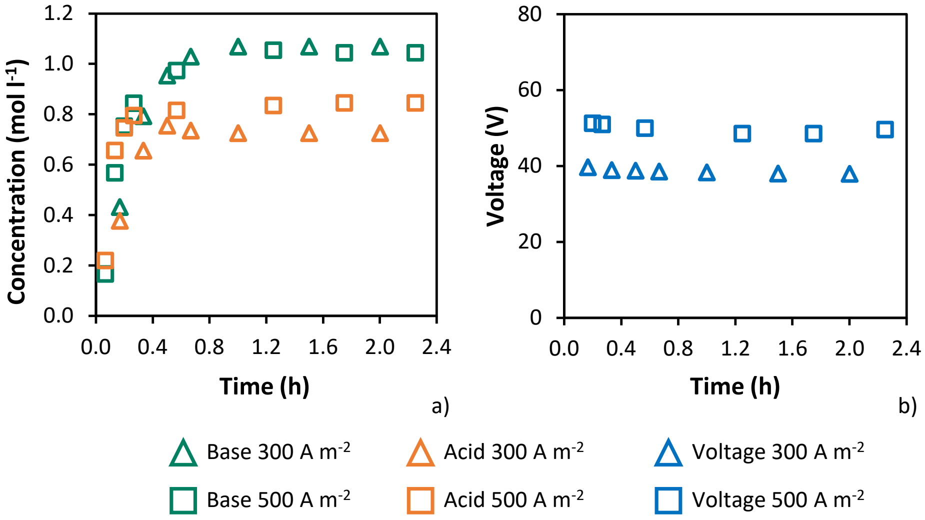

Figure 2: a) Acid and Base profile as function of time, b) external applied voltage in the EDBM stack as function of time, for the tests at 300 and 500 A m^{-2}, outlet flowrate of acid and base equal to 0.75 and 1.2 l min^{-1}, respectively.

It was also observed that the acid steady-state concentration slightly increases as the current density rises. This phenomenon could be due to the lower impact of the diffusive flux, towards the salt channel, with respect to the migrative flux of protons, generated in the inter-layer of the bipolar membrane, at higher current densities.

In Figure 2b the voltage profile for the two tests is shown. A slightly descending trend is observed in the transitory phase, due to the reduction of the stack resistance as the concentrations rise. After approximately 40 minutes, a steady-state condition is reached and the final value of voltage applied to the stack is 38 and 49.5 V for the test at 300 and 500 A m^{-2}, respectively.

In Figure 3, the concentrations as well as the main performance indicators for acid and base are reported as function of the current density. The outlet acid concentration increases as the current density rises, from 0.68 mol l^{-1} at 200 A m^{-2} up to 0.84 mol l^{-1} at 500 A m^{-2}, while the target of 1 mol l^{-1} is kept for the base. Regarding the CE, a quite stable trend is observed for the base (59-67%), while an increase in the utilization of the current is observed for the acid at higher current density. This increase could be attributed to the higher outlet concentration of acid. The SEC shows an increasing trend with current density, despite the increasing or the stable trend observed in the current efficiency for acid and base, respectively. The voltage applied to the stack, indeed, has a larger effect on the SEC then the CE (Cassaro et al., 2023). Values of SEC in the range 3-3.6 kWh kg^{-1} and 1.8-2.7 kWh kg^{-1} were found for acid and base, respectively. The SP shows a monotonous increasing trend as function of the current density, with value up to 0.94 and 1.3 ton y^{-1} m^{-2} for acid and base, respectively, at 500 A m^{-2}.

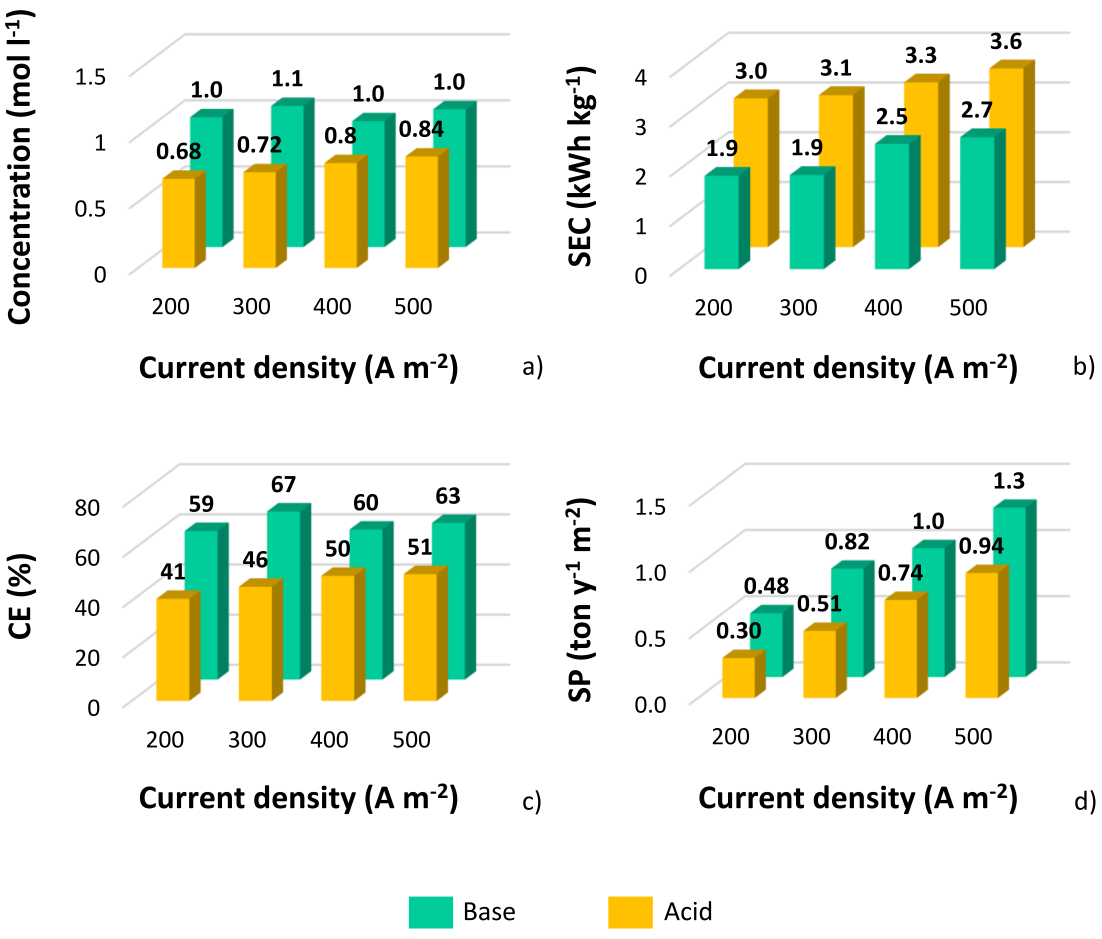

Figure 3: a) Acid and base concentrations, b) specific energy consumption, c) current efficiency and d) specific production obtained in the four tests.

4. Conclusions

This work provides an in depth analysis of the feed & bleed operation of an EDBM pilot plant for the production of hydrochloric acid and sodium hydroxide from saline solutions. Concentrations profiles as well as voltage profile were reported, during the transitory start-up phase and at steady-state. In all cases, a lower concentration of acid was found with respect to the base, though increasing the current density produces an increase in the outlet acid concentration (from 0.68 mol l^{-1} to 0.84 mol l^{-1}, when the current density goes from 200 A m^{-2} to 500 A m^{-2}). An almost constant trend was observed for the current efficiency of base (61-67%), when varying the current density from 200 to 500 A m^{-2}, while an increase was observed for the acid, with value up to 51% at 500 A m^{-2}. SEC and SP show an increasing with the current density for both product (3-3.6 and 1.8-2.7 kWh kg^{-1}, 0.3-0.94 and 0.5- 1.3 ton y^{-1} m^{-2} for acid and base, respectively). This study suggests that to promote the production of concentrated acid and base, keeping high current efficiency, it is convenient to operate the system at elevated current density of 400-500 A m^{-2}. This guarantees high levels of production with moderate energy consumption. At industrial scale, feed & bleed configuration should be adopted to guarantee a continuous production of both chemicals and reduce production costs. Future research will focus on the economic evaluation of production costs as well as on the optimization of the process configuration and operations.

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