Coupling Electrodialysis with bipolar membranes with renewable energies through advanced control strategies

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Abstract

Recently, EU is directing its priorities to the implementation of innovative strategies for waste valorisation and smart use of energy, pushing towards ecological transition. Powering water treatment technologies with renewable energies, using the process buffering capacity as a way to indirectly store energy, has been recently proposed as an effective strategy for smart energy use. With this respect, electrodialysis with bipolar membranes (EDBM) can be particularly suitable due to the high energy intensity, coupled with an extreme flexibility of its operational modes. EDBM is an electro-membrane process able to convert saline wastewater into valuable products such as acids and bases, simply by supplying electric power. This work was focused on the development of advanced control systems allowing EDBM to operate under transitory regimes following the highly variable trend of renewable energy availability, adapting the operating conditions and the process targets according to the variable power input offered during a normal day. To this aim, a pilot scale EDBM unit (provided by FuMA-Tech GmbH) was operated and tested in Lampedusa island (Italy) in feed and bleed configuration under two different scenarios (summer and winter) at a fixed concentration target of acids and base (0.5 M of NaOH and HCl). In the hours of the day with an available power higher than a minimum threshold value (2.0-6.5 kW), the controller was able to keep the outlet concentration at its target (0.5 M of NaOH and HCl) by letting the outlet flowrate of the product to vary from 0.5 up to 3 l min-1. In these operating conditions, the controller was able to guarantee high product quality, still retaining high specific productivity (in the range of 0.1-0.2 kg h-1m-2) and low consumption (in the range of 1.3- 1.9 kWh kg-1 of NaOH and 1.8- 2.4 kWh kg-1 of HCl). In all cases, the parallel control logic allowed to tune the applied voltage in order to meet the electric power availability, while manipulating the outlet flowrate to meet the desired product specification. The obtained results demonstrate for the first time at the pilot scale how EDBM can be particularly suitable to valorise, in industrial relevant scenarios, available saline streams and unstable energy sources, thus pushing towards the industrial implementation according to sustainable and circular values approaches.

**Keywords**: brine mining, renewable energy, electro-membrane, circular economy, advanced control

* 1. Introduction

Nowadays, researchers are focusing their efforts to find new strategies for a sustainable exploitation of energy sources through the valorization of concentrated brines coming from industrial processes. Currently, the world desalination capacity stands at, approximatively, 100 millions of cubic meters per day (Ihsanullah et al. 2021), being dominated by membrane processes. The most used membrane technology in the world is reverse osmosis (RO) covering the 70% of the global production of desalinated water (Jones et al. 2019). However, this process has two main drawbacks: (i) the production of a desalination waste (which represents the 60% of the treated water) and (ii) the significant energy consumption. In order to make the process more sustainable and reduce its environmental foot-print, different treatment chains based on Minimum/Zero Liquid Discharge approaches have been proposed so far to valorize waste brines by extracting valuable raw materials and energy from them. With this respect, electrodialysis with bipolar membranes (EDBM) (Filingeri et al. 2023) plays a key role allowing the production of chemical reagents which can be reused in-situ in accordance to a circular economy approach. EDBM is an electro-membrane technology, enabling the synthesis of chemicals as acids and bases, from waste saline waters, applying an electrical field. The repeating unit of an EDBM stack is called triplet and consists of a sequence of three ion exchange membranes, namely cationic, bipolar and anionic one, and three channels: basic, acid and salt channel (Figure 1). Through the application of an external electric field, the cations and anions dissolved in the saline solution migrate selectively towards the cathode and towards the anode, respectively, encountering the protons and hydroxide ions generated inside the bipolar membrane in the acid and base channel, respectively (Culcasi et al. 2022). Additional information about the working principle of the EDBM unit can be found in Strathmann’s book (Strathmann 2004). The utilization of EDBM technology in MLD/ZLD treatment chain has energetic benefits due to the smart use of renewable energy sources (RESs) to produce valuable product (Virruso et al. 2023). Furthermore, the utilization of RESs could allow an off grid-spreading of this process in remote areas. Herrero-Gonzalez et al. (Herrero-Gonzalez et al. 2018) have proposed a PV-EDBM set-up coupling a lab-scale EDBM stack (Am=0.01 m2) with a PV solar array simulator. The system was operated in semi-batch configuration switching on and off the outlet flowrates according to the pH of the acid tank and the conductivity of the salt tank. They have demonstrated that the use of a rudimental control system could already lead to an improvement in the performance indicators, reducing the specific energy consumption (SEC) of the acid from 7.3 kWh kg-1 (at fixed current density) to 4.4 kWh kg-1 (at variable current density).

The purpose of this work was to pair a pre-industrial scale EDBM plant (Herrero-Gonzalez et al. 2023) with a renewable energy source. To reach this aim, advanced control systems were developed and tested firstly through the Matlab dynamic simulation toolbox (Simulink). Subsequently, the controllers were implemented in LabVIEW software and tested in the real plant mimicking a PV array. The objective of the control system was to allow continuous operation of the equipment in highly transitory regimes, to reach and maintain the set-point concentration for both, acid and base. At the same time, the controller ensured stability over time maximizing the use of the available energy in terms of performance indicators.



Figure 1. Schematic representation of the repetitive unit (triplet) of an EDBM stack

* 1. Description of the pilot and its control schemes
		1. The EDBM pilot plant

The EDBM pilot, built within the framework of the Water Mining project, consists of two fundamental parts: the hydraulic pumping station and the EDBM stack itself. The pumping station housed all the hydraulic lines as well as the monitoring and control instrumentation such as flowmeters, conductivity meters, pressure transducers, pumps and electro-actuated valves. Furthermore, the hydraulic skid included the electrical cabinet where the acquisition and command hardware were located. More precisely, a chassis with analog acquisition and command cards was employed to collect data and provide signals to the actuators. The acquisition and command hardware were provided by National Instrument. LabVIEW was employed as software to develop the Programmable Logic Controller (PLC) and the Human Machine Interface (HMI) of the plant. The EDBM stack was an FT-ED1600-3 unit provided by FuMA-Tech GmbH (Germany). The stack consisted of 40 triplets divided into two modules with 20 triplets each, reaching a total active membrane area of 19.2 m2. These two modules were put in communication in series using as internal staging the channels derived in the anode plate.

The EDBM was powered using a Rectifier (GIUSSANI Srl) able to release a maximum power of 17.5kW corresponding to 80V and 200A. Additional information were reported in a previous work (Cassaro et al. 2023). The plant was operated in feed and bleed configuration, feeding continuously acid, base and salt solutions, while the electrode rinse solution was always operated in closed-loop mode.

* + 1. Advanced control strategies

Several control systems were designed and implemented inside the PLC to make the EDBM plant able to work automatically under dynamic conditions. Particularly, the dynamic behavior of the uncontrolled system was investigated, in order to understand the dynamic features of main variables involved in the process. The dynamic trends collected from the experimental campaign were fitted, using first order transfer function model, to obtain reliable relationships having the outlet variables as a function of the inlet ones. This investigation led to the development of four advanced controllers: (i) the recirculation flowrate-maximum pressure using override logic to prevent from possible clogging phenomena which could damage the stack; (ii) the product quality cascade control, where the slave controller was an outlet flowrate controller with split range logic while the master was a conductivity control, to manage the concentration of the acid and base products; (iii) the ratio control between the salty and alkaline streams to guarantee the desired molar ratio among feed and product;(iv) the DC drive control for PV maximum power point tracker (MPPT). The latter was realized to operate the system with dynamic power set-point, through the use of a gaussian function fitting the real power produced by a solar field (EU 2023) as showed in Figure 1.



Figure 2. a) Comparison between the real and the simulated power; b) DC drive feedback control.

* 1. Results

In this section, a summary of the obtained results relevant to the summer and winter scenario was reported. In both cases, the quality of the product, for both acid and base, was controlled via cascade composition controller (i.e. controller (ii)). As a consequence, the flowrates of the outlet streams were varied by the controller according to the power availability in the two investigated cases (Figure 2). The summer scenario, in the month of July, guaranteed the highest peak irradiation in Lampedusa, equal to 980 W m-2 at midday. On the other hand, the winter scenario, in the month of December provided the lowest peak irradiation of the year, equal to 600 W m-2. Moreover, the sunny hours decreased significantly from 12h in July down to 8h in December. Furthermore, it was observed a significant drop in the maximum power available, going down from a maximum of 6.5 kWp in July to 3.2 kWp in December. This power reduction dramatically affected the maximum current density reached in the winter scenario, equal to 265 A m-2 compared to the summer scenario, equal to 435 A m-2.

Notwithstanding this effect, the control system was found always able to guarantee the conductivity set-point during the working day for both acid and base. However, acid and base in the summer scenario reached values slightly different compared to the set-point. As a matter of fact, in the summer scenario, the power changed rapidly, generating abrupt variations in the current density (disturbance) both, before and after the maximum value (Figure 3a). Under these conditions, the control system was unable to delete the off-set completely, since the time required to reach the set-point value was greater than the disturbance variation time. On the other hand, in the winter scenario, even though the power varied as well, the controller kept the concentration fixed to the set-point value, throughout the working day (Figure 3b). Table 1 showed an overall comparison of the average parameters obtained in both scenarios, in terms of performance indicators, power, voltage and current density, for the base, which represented the product with higher added value. The average available power was found equal to 3.2 and 2.0 kW for the summer and winter scenarios, respectively. This means that the DC drive control system supplied an 11% higher external voltage in the summer scenario compared to the winter scenario to follow the available power. Consequently, the average value of current density was higher in the summer scenario (250 A m-2) respect to the winter one (180 A m-2). Looking at the performance parameters, concerning the current efficiency (CE), high average values were reached in both scenarios, both higher than 60%. However, CE in the summer scenario was 7% higher since the EDBM stack operated in feed and bleed configuration performed better at higher current densities (Cassaro et al. 2023). As regards the specific energy consumption (SEC), it was found the same value for both, summer and winter, likely due to the lower reduction of the average external voltage than the average current efficiency. Last, but not the least, the average specific productivity (SP) resulted 25% lower in the winter scenario compared to the summer one. This effect is related to the higher values of current density and current efficiency in summer compared to winter.



Figure 3. Comparison between a) Power and b) concentrations temporal trends, for base and acid, in summer and winter scenarios

Table 1. Summary of the average performance parameters in the summer and winter scenarios for the alkaline stream.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Scenario** | **Power****(kW)** | **Voltage****(V)** | **Current density****(A m-2)** | **CE****(%)** | **SEC****(kWh kg-1)** | **SP****(kg h-1 m-2)** |
| Summer | 3.2 | 35.8 | 250 | 70 | 1.6 | 0.08 |
| Winter | 2.0 | 31.9 | 180 | 65 | 1.6 | 0.06 |

* 1. Conclusions

The aim of this work was the development of advanced control systems allowing to operate the EDBM technology powered by renewable energy. The synergy of these control schemes and the automation logic (PLC) implemented in the LabVIEW environment allowed to test the EDBM pilot plant powered by simulated solar panels in two different scenarios, namely summer and winter. The control system guaranteed, in both scenarios, a concentration equal to the target of 0.5 mol l-1 (fixed at set-point value). During the dynamic operation of the unit, valuable information were obtained in terms of performance indicators. Concerning CE, very high values were achieved, exceeding 65% for the base, in both scenarios. Moreover, the control system enabled to obtain very low values of SEC for the base, always lower than 2.0 kWh kg-1. In terms of specific productivity, high values were obtained. In particular, in the summer scenario a value of 0.2 kg h-1 m-2 was reached for the base. These results confirmed the EDBM technology particularly suitable to operate in highly dynamic regimes such those established in presence of renewable energy availability. Following works will be focused on the potentiality of this coupling, on its viability at a higher scale and on the implementation of further advanced controllers achieving an overall optimization of the process.

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References

Cassaro, Calogero, Giovanni Virruso, Andrea Culcasi, Andrea Cipollina, Alessandro Tamburini, and Giorgio Micale. 2023. “Electrodialysis with Bipolar Membranes for the Sustainable Production of Chemicals from Seawater Brines at Pilot Plant Scale.” *ACS Sustainable Chemistry and Engineering* 11 (7). https://doi.org/10.1021/acssuschemeng.2c06636.

Culcasi, A., R. Ktori, A. Pellegrino, M. Rodriguez-Pascual, M. C.M. van Loosdrecht, A. Tamburini, A. Cipollina, D. Xevgenos, and G. Micale. 2022. “Towards Sustainable Production of Minerals and Chemicals through Seawater Brine Treatment Using Eutectic Freeze Crystallization and Electrodialysis with Bipolar Membranes.” *Journal of Cleaner Production* 368. https://doi.org/10.1016/j.jclepro.2022.133143.

EU. 2023. “PV-GIS.” 2023. https://joint-research-centre.ec.europa.eu/photovoltaic-geographical-information-system-pvgis\_en.

Filingeri, Antonia, Julio Lopez, Andrea Culcasi, Tamara Leon, Alessandro Tamburini, José Luis Cortina, Giorgio Micale, and Andrea Cipollina. 2023. “In-Depth Insights on Multi-Ionic Transport in Electrodialysis with Bipolar Membrane Systems.” *Chemical Engineering Journal* 468 (July): 143673. https://doi.org/10.1016/J.CEJ.2023.143673.

Herrero-Gonzalez, Marta, Pedro Diaz-Guridi, Antonio Dominguez-Ramos, Raquel Ibañez, and Angel Irabien. 2018. “Photovoltaic Solar Electrodialysis with Bipolar Membranes.” *Desalination* 433. https://doi.org/10.1016/j.desal.2018.01.015.

Herrero-Gonzalez, Marta, Julio López, Giovanni Virruso, Calogero Cassaro, Alessandro Tamburini, Andrea Cipollina, Jose Luis Cortina, Raquel Ibañez, and Giorgio Micale. 2023. “Analysis of Operational Parameters in Acid and Base Production Using an Electrodialysis with Bipolar Membranes Pilot Plant.” *Membranes* 13 (2). https://doi.org/10.3390/membranes13020200.

Ihsanullah, Ihsanullah, Muataz A. Atieh, Muhammad Sajid, and Mazen K. Nazal. 2021. “Desalination and Environment: A Critical Analysis of Impacts, Mitigation Strategies, and Greener Desalination Technologies.” *Science of the Total Environment*. https://doi.org/10.1016/j.scitotenv.2021.146585.

Jones, Edward, Manzoor Qadir, Michelle T.H. van Vliet, Vladimir Smakhtin, and Seong mu Kang. 2019. “The State of Desalination and Brine Production: A Global Outlook.” *Science of the Total Environment*. https://doi.org/10.1016/j.scitotenv.2018.12.076.

Strathmann, H. 2004. *Ion-Exchange Membrane Separation Processes, First Ed.* *Elsevier Science*. Vol. 9. Amsterdam: Elsevier. https://doi.org/10.1007/s13398-014-0173-7.2.

Virruso, Giovanni, Calogero Cassaro, Alessandro Tamburini, Andrea Cipollina, and Giorgio D M Micale. 2023. “Performance Evaluation of an Electrodialysis with Bipolar Membranes Pilot Plant Operated in Feed & Bleed Mode” 105 (February): 73–78. https://doi.org/10.3303/CET23105013.