Energy consumption in membrane capacitive deionization and electrodialysis of low salinity water

Krzysztof Mitko, Adam R. Rosiński, Marian Turek*

Analytical Chemistry and Electrochemistry, Faculty of Chemistry, Department of Inorganic, Silesian University of Technology, ul. B. Krzywoustego 6, 44-100 Gliwice, Poland, email: Marian.Turek@polsl.pl (M. Turek)

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Abstract

Membrane capacitive deionization (MCDI) is a promising new technology for brackish water treatment. Although many authors show the advantages of MCDI by comparing its energy consumption with pressure driven-methods, such as reverse osmosis or nanofiltration, membrane capacitive deionization should rather be compared to electrodialysis (ED), widely considered the most economical desalination technology for low salinity brackish water treatment. In this paper, MCDI is compared with ED by desalting model sodium chloride solutions (0.7–1.0 g/dm³). The results show higher energy consumption of MCDI than of ED when generating 0.5 g/dm³ product: 0.428–0.499 kWh/m³ for MCDI and 0.034–0.230 kWh/m³ for ED, depending on the feed concentration and used membrane.

Keywords: Membrane capacitive deionization; Electrosorption; Electrodialysis; Brackish water desalination; Energy consumption

1. Introduction

The increasing demand for clean water requires further improvement in desalination technology. One of the emerging desalination methods is capacitive deionization (CDI), in which the separation of salt and water is achieved by electrosorption of ions on porous carbon electrodes. Membrane capacitive deionization (MCDI) is a process, which integrates CDI with ion-exchange membranes [1]. The principle of MCDI is presented in Fig. 1. Feed solution flows between porous carbon electrodes with ion-exchange membranes placed on top of them. During the sorption step, ions migrate towards the electrodes through the ion-exchange membranes, causing a decrease in solution salinity. When the electrodes are fully loaded, the electrode polarity is reversed or the power is switched off, causing ion desorption. The ion-exchange membrane acts as a barrier, preventing ions desorbed on one electrode from sorption on the second electrode during the desorption step. Recently, a concept of flow electrode has been introduced: the electrode is a suspension of carbon particles, circulated from cathode to anode compartments of the CDI unit [2]. Such arrangements allow a fully continuous operation; however, most of the work focuses on a conventional, batch mode (M)CDI.

CDI and MCDI have some advantages over well-established desalination methods, mainly much easier energy recovery than for instance reverse osmosis. The energy in CDI and MCDI can be recovered during desorption, as the ions desorb from the electrode even if no external electric field is applied. However, there are some issues that need to be addressed in order for CDI and MCDI to become competitive with other desalination methods. The crucial problem in the MCDI application is the electrosorption capacity of the carbon porous electrode, which should be as high as possible. The electrosorption capacity may vary between 0.63 and 14.9 mg/g [3] for review on different
materials and methods used for increasing the capacities. Other problems include fouling and scaling of electrodes – highly porous carbon can adsorb organic material, leading to bacterial growth [4]. Electrode fouling can strongly increase energy consumption. Zhang et al. [5] have operated a pilot CDI plant and showed that total dissolved salts (TDS) removal efficiency dropped after 15 d of operation; chemical cleaning with 0.01 mol/dm³ citric acid or 0.01 mol/dm³ sodium hydroxide was enough to restore the electrode capacity. Omosebi et al. [6] have shown that the electrosorption capacity of carbon aerogel electrode decreased by about half in 50 h of CDI operation, but was constant during MCDI operation. CDI and MCDI are not effective methods for seawater desalination [4]; however, its application for brackish water desalination remains investigated.

Membrane capacitive deionization can outperform reverse osmosis in a low concentration range. Zhao et al. [7] have compared energy consumption in reverse osmosis and membrane capacitive deionization. They have found that MCDI can consume less energy than reverse osmosis (RO) when the feed salinity is below 3 g/dm³. Oren [4] has found that CDI is more economical than RO for brackish water desalination; however, Qin et al. [8] showed that RO is significantly more energy-efficient than CDI, particularly when targeting higher salinity feed streams and higher salt rejection values. For brackish water with a salt concentration of 2,000 mg/dm³, achieving 50% water recovery and 75% salt rejection, with an average water flux of 10 dm³/m²·h using CDI requires a specific energy consumption of 0.85 kWh/m³, one order higher that of RO (0.09 kWh/m³).

Mossad and Zou [9] have investigated the energy consumption of a single-pass CDI module, equipped with activated carbon electrodes working at 1.5 V per electrode pair. Energy consumption was found to be 3–6 kWh/kg of transported salts at feed TDS range 0.5–3.5 g/dm³. Lee et al. [10] compared MCDI with CDI for the treatment of 1 g/dm³ NaCl solution, showing that the former had a 19% higher salt removal rate. The energy consumption was 1.96 kWh/m³. The better desalination performance of MCDI than that of CDI is mainly due to the minimized ion resorption during electrosorption [11]. Zhang et al. [5] have estimated energy consumption in a pilot-scale CDI plant to be 1.8 kWh/kg of transported salt (feed TDS 1.5 g/dm³). They have also observed that scaling on the electrodes increased the energy consumption to 5.16 kWh/kg of transported salt. VanLimpt and van der Wal [12] have calculated the energy consumption of a MCDI unit desalting cooling tower water. At 70% salinity removal, the energy consumption was found to be 0.105 and 0.234 kWh/m³ for feed TDS of 0.186 and 0.329 g/dm³, respectively. Dlugolecki and van der Wal [13] claim that up to 83% of energy can be recovered and the energy consumption in MCDI can be 0.26 kWh/m³ when salinity is decreased by 10 mmol/dm³ of NaCl. Zhao et al. [14] have calculated the energy requirements for ion removal in MCDI; within the range 10–200 mmol/dm³ energy consumption of 54.56 kJ/mol was found. They have also mathematically tested the influence of operating parameters (feed salinity, adsorption/desorption current, desorption voltage, flow rate, process time) on the MCDI performance in both constant current and constant voltage modes [15]. Choi [16] have found that constant voltage MCDI shows higher electrosorption capacity and lower charge efficiency than constant current operation; in addition, the energy consumption is significantly lower when operating the MCDI in constant current mode. Membrane capacitive deionization has also been utilized for selective removal of species, such as nitrate ions [17] or lithium [18], or for the production of highly purified water [19]. Dykstra et al. [20] tested two modes of operation: constant voltage and constant current without energy recovery and with 50% energy recovery and found energy consumption to be, respectively, 89.2, 93.4, 65.6, and 56.3 kJ/mol. When recalculated for removal of 0.5 g/dm³ of NaCl, the energy consumption was in the range 0.222–0.134 kWh/m³.

The problem with comparisons between (M)CDI and RO as brackish water desalination technology is that reverse osmosis, albeit the most popular desalination technology [21], is not necessarily the most economical method of brackish water desalination. Electrodiagnosis can be cheaper than RO for low salinity feeds [22,23]. Electrodiagnosis is based on the phenomena of ion migration in the electric field and the exclusion of co-ions by the charged group fixed in the polymeric matrix of the ion-exchange membrane. A salt solution flows between the alternately placed cation- and anion-exchange membranes. When an electric field is applied in the direction perpendicular to the solution flow, cations migrate through the cation-exchange membranes and are retained by the anion-exchange membranes, whereas the anions migrate through the anion-exchange membranes and are retained by the cation-exchange membranes. Thus, a salt solution stream is being split into a desalinated stream (diluate) and concentrated stream (concentrate). Schoeman and Steyn [24] have shown that electrodiagnosis reversal (EDR) can replace RO in desalination of mine water of TDS 2.7–3.8 g/dm³. Hsu et al. [25] have compared sand filtration (SF) – ultrafiltration (UF) – reverse osmosis (RO) pilot plant to a SF-EDR pilot plant used in desalination of a waste treatment plant effluent from TDS of ca. 300 mg/dm³ down to ca. 50 mg/dm³. Based on the results, the unit costs for large-scale plants – from 15,000 to 60,000 m³/d – was calculated as $0.77–0.59/m³ for SF-UF-RO and $0.65–0.52/m³ for SF-EDR. There are several reasons why the electrodiagnosis (ED) can outperform RO in brackish water desalination. Passanisi et al. [23] have observed that during the first year of desalination plant operation, EDR showed less maintenance and cleaning downtime than RO and nanofiltration units. The ion-exchange membranes are more resistant to biofouling than RO membranes, less sensitive to chlorine, able to operate at higher feed SDI and are easier to clean up [22]. The basis of the process is different: in reverse osmosis and nanofiltration, the energy is proportional to the amount of solvent that needs to be transported across the membrane; in electrodiagnosis, it is quite the opposite – the required energy is proportional to the amount of ions that is needed to be transferred. Because brackish water desalination requires the removal of a relatively small amount of salt, the ED can be economically competitive. Thus, in order to reliably assess the membrane capacitive deionization as brackish water desalination technology, one should compare it with electrodialysis. The aim of this study is to find which of these two methods consumes less energy in a chosen case study; desalination of model solutions resembling low salinity brackish water (0.7–1.0 g/dm³ as NaCl) down to 0.5 g/dm³ level.
2. Experimental

2.1. Membrane capacitive deionization

A bench-scale, single-pair MCDI module (Fig. 1) was used. The module consisted of current collectors (platinum-covered titanium), two porous carbon electrodes (total mass of 0.413 g), a cation-exchange membrane, an anion-exchange membrane, and a 0.26 mm thin intermembrane spacer. The effective electrode area was 9 cm². The module was operated in batch mode, at a linear flow velocity of 1 cm/s, and a constant voltage of 0.75 V, both during sorption and desorption steps. The total volume of the working solution was 5 cm³. Both Neosepta CMX/AMX [24] and Fujifilm Type I CEM/AEM [25] membranes were tested with two model feed solutions (1 and 0.7 g/dm³ of NaCl). Porous carbon electrodes were made of powdered active carbon, mixed with poly(vinylidene fluoride), and smeared over graphite plate.

2.2. Electrodialysis

An electrodialyzer consisting of four membrane pairs, separated by a 0.26 mm thin intermembrane spacer, was used. The effective membrane area was 4.5 cm², the module was operated in a batch mode, at 1 cm/s linear flow velocity in both diluate and concentrate, and a constant voltage of 0.75 V. Diluate and concentrate volume was 70 cm³ each. Both Neosepta CMX/AMX and Fujifilm Type I CEM/AEM membranes were tested with two model feed solutions (1 and 0.7 g/dm³ of NaCl). The electrode rinse solution was sodium sulfate of concentration 1.21 and 0.85 g/dm³ for the experiments with 1 and 0.7 g/dm³ sodium chloride solutions, respectively.

3. Results

During MCDI sorption/desorption steps, changes in applied current were observed – Fig. 2 – which indicated loading and unloading of electrodes, as confirmed by conductivity changes. The changes of current and voltage were similar between each sorption/desorption step, which indicates a stable MCDI operation is possible in the tested conditions. Table 1 presents the observed changes in conductivity during MCDI desalination of model NaCl solutions (0.7 and 1.0 g/dm³), both when Neosepta CMX/AMX and Fujifilm Type I CEM/AEM membranes were placed inside the module. The increased conductivity after the first step of sorption/desorption may indicate that electrodes were not fully unloaded during the first desorption, an effect that was not affected by the longer desorption step (20 min instead of 5 min). The product conductivity, however, was similar after subsequent sorption steps. There was no significant difference in the quality of the product between 3 min sorption and 20 min sorption time, which is in agreement with current/voltage curves and indicates the majority of ions are adsorbed during the first 3 min. The sorption time an important parameter from the practical point of view, as shorter sorption/desorption steps mean the overall capacity of MCDI can be increased or – when used in continuous mode – modules having short hydraulic residence time can be used.

Based on the results, the number of ions adsorbed on the porous carbon electrodes, \( n \) (mmol), was calculated as:

\[
 n = C_{\text{ads},0} - C_{\text{ads},k} V
\]

where \( C_{\text{ads},0} \) and \( C_{\text{ads},k} \) denote concentration at the beginning and at the end of sorption step, respectively, and \( V \) denotes the total volume of the desalted solution (5 cm³). The electro-sorption capacity, \( q \), was calculated as:

\[
 q = \frac{n}{m}
\]

where \( m \) denotes the mass of the electrode. Direct current (DC) energy consumption per mass of transported salt, \( E_{\text{DC,MCDI}} \), was calculated as:

![Fig. 1. A scheme of membrane capacitive deionization MK – cation-exchange membrane; MA – anion-exchange membrane; C – porous carbon electrode; (a) sorption and (b) desorption.](image-url)
where $I_{ads}(t)$ and $I_{des}(t)$ denote the applied current during sorption and desorption step, respectively, $U$ denotes applied voltage of 0.75 V and $M$ denotes the molar mass of sodium chloride. Salt removal, $\eta$, was defined as:

$$\eta = \frac{C_{ads,0} - C_{ads,k}}{C_{ads,0}} \times 100\% \quad (4)$$

Table 2 presents the results of energy consumption, salt removal and electrosorption capacity calculations. The calculated energy consumption is similar to the results reported elsewhere: Zhao et al. [7] reported MCDI energy consumption as 0.6–0.8 kWh/kg (feed TDS range of 1–5.2 g/dm$^3$, product TDS of 0.5 g/dm$^3$); Mossad and Zou [9] reported CDI energy consumption as 4 kWh/kg for 1 g/dm$^3$ feed. Similarly, the electrosorption capacities – 0.063–0.104 mmol/g, which corresponds to 3.69–6.08 mg/g – are comparable with the typical results in (M)CDI [3].

Fig. 3 presents an example of applied current and concentration changes observed during electrodialysis. DC energy consumption in electrodialysis was calculated as:

$$E_{DC,ED} = \frac{U \left[ \int_{t=0}^{t'} I_{ads}(t)dt + \int_{t=0}^{t'} I_{des}(t)dt \right]}{nM} \quad (5)$$

where $C_{ads,0}$ and $C_{ads,k}$ denote diluate concentration at the beginning and at the end of electrodialysis. Table 3 presents the results obtained from electrodialysis of 0.7 and 1 g/dm$^3$ sodium chloride solutions using Neosepta CMX/AMX and Fujifilm Type I CEM/AEM membranes.

### 3.1. Comparison of energy consumption in ED and MCDI

Figs. 4 and 5 present the influence of salt removal on DC energy consumption for MCDI and ED, respectively. Alternating current (AC) energy consumption of electrodialysis was calculated, assuming 85% pump efficiency, as:

$$E_{AC,ED} = \frac{(Q_{dil} + Q_{kon}) \cdot 10 \cdot \Delta P}{0.85 \cdot V_{dil}} \quad (6)$$

where $Q_{dil}$ and $Q_{kon}$ denote the volumetric flow of diluate and concentrate, respectively, $V_{dil}$ denotes diluate volume and $\Delta P$ denotes pressure drop on each of 10 intermembrane spacers of the electrodialyzer, which was measured with a mercury manometer. AC energy consumption of membrane capacitive deionization was calculated, assuming 85% pump efficiency, as:

$$E_{AC,MCDI} = \frac{Q_{MCDI} \cdot \Delta P (t_{ads} + t_{des})}{0.85V_{dil}} \quad (7)$$

### Table 2

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Fujifilm</th>
<th>Neosepta</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorption time (min)</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>Desorption time (min)</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>Initial feed concentration (g/dm$^3$)</td>
<td>0.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Initial feed conductivity (mS)</td>
<td>1.46</td>
<td>2.05</td>
</tr>
<tr>
<td>Conductivity after each of sorption/desorption steps (mS)</td>
<td>1.71</td>
<td>2.53</td>
</tr>
</tbody>
</table>

Fig. 2. An example of applied current density changes during sorption/desorption steps of MCDI (Neosepta membranes, feed concentration 0.7 g/dm$^3$).
where \( Q_{\text{MCDI}} \) denotes the volumetric flow of the solution flowing through MCDI module, \( t_{\text{ads}} \) and \( t_{\text{des}} \) denote sorption and desorption step length, respectively, and \( V \) denotes the total volume of solution being desalted by MCDI.

Based on the results, the energy required to decrease the concentration of 1 m\(^3\) of 0.7 or 1 g/dm\(^3\) sodium chloride solution down to 0.5 g/dm\(^3\) was calculated for both ED and MCDI. The results are presented in Table 4.

3.2. Required membrane area

To estimate how are the investment costs in MCDI in comparison to the ED, one can compare salt flux across the membrane pair. For MCDI, it was calculated as:

\[
J = \frac{nV}{(t_{\text{ads}} + t_{\text{des}})A}
\]

where \( n \) is the number of moles of salt removed from the solution (Eq. (3)), \( V \) is the total volume of the desalted solution (5 cm\(^3\)), \( A \) is the membrane area (9 cm\(^2\)), \( t_{\text{ads}} \) and \( t_{\text{des}} \) represent a time of adsorption and desorption steps, respectively. Since the fluxes did not differ much between each of the desorption cycles, the mean values were calculated. To compare it with ED, the following procedure was applied: (1) determine the salt removal for a given MCDI experiment, (2) interpolate the salt flux for at same salt removal level knowing the experimentally observed relationship between salt removal in ED and salt flux across the membranes, and (3) divide the result by four to account for the different number of membrane pairs in ED and MCDI. The results are presented in Table 5.

The results suggest that MCDI may need a smaller membrane area installed; however, the issue with MCDI is that it requires a pair of electrodes per each membrane pair, whereas the electrodialysis requires the only pair of electrodes per the whole membrane stack, which may contain hundreds of membrane pairs.

4. Discussion

A comparison of Neosepta CMX/AMX and Fujifilm Type I CEM/AEM membranes shows that the module equipped with the former has lower energy consumption.
MCDI showed higher energy consumption than ED, both in terms of DC energy and pumping energy. Both MCDI and ED modules used the same membranes and intermembrane spacers, and the flow velocity was the same. The energy consumption in MCDI is not substantially higher than the values obtained by other researchers. During the experiments, there was no energy recovery in the MCDI module. Długołecki and van der Wal [13] have claimed that thanks to energy recovery, the energy required to decrease the solution salinity by 10 mmol/dm$^3$ (0.585 g/dm$^3$ as NaCl) in MCDI can be decreased down to 0.26 kWh/m$^3$. According to Dykstra et al. [20] energy consumption in the range 0.222–0.134 kWh/m$^3$ with energy recovery is achievable which is still higher than the energy consumption obtained in electrodialysis especially in the case of Neosepta membranes. The energy consumption in ED is also typical, given the low current density applied in the process. Based on the results, we conclude that in terms of energy consumption, membrane capacitive deionization is not the best method for low salinity brackish water desalination. The presented experimental results are in agreement with a theoretical study by Patel et al. [26], who compared the performance of an electrodialyzer equipped with 50 pairs of ion-exchange membranes and 0.3 mm spacers with the performance of 50 cell MCDI stack working in series. The authors have found specific energy consumption of ED to be about an order of magnitude lower than the specific energy consumption of MCDI throughout all range of tested parameters (feed concentration 1–10 g/dm$^3$ as NaCl, salt removal 30%–90%) – in our experimental study we also found ED energy consumption to be the order of magnitude lower than MCDI. The ED also exhibits higher energy efficiency than the MCDI. Patel et al. [26] contribute this difference to electrosorption.
inherently consuming more energy than ion transport. Taking into account both presented experimental data and theoretical studies available in the literature, we do not believe MCDI can outperform ED as a brackish water desalination method.

5. Conclusions

When it comes to brackish water desalination, membrane capacitive deionization is virtually always compared with pressure-driven methods (reverse osmosis, nanofiltration) and almost never with electrodialysis. It is not a surprise that reverse osmosis turns out to be a more expensive method for brackish water desalination – RO is not the cheapest method in this feed concentration range anyway. That is why we have compared energy consumption in membrane capacitive deionization and electrodialysis during desalination of 1 g/dm³ sodium chloride solution. As it turns out, ED is a more economical method in terms of DC energy and pumping energy requirements. There are several advantages of ED over (M)CDI. Electrodialysis and electrodialysis reversal are well-established technologies for the desalination of waters having high scaling potential while the fouling of porous carbon electrodes in (M)CDI is not widely researched. Increasing the module capacity by placing additional repeatable unit cell into the membranes stack is much easier in case of ED than it is in case of (M)CDI. Another question is the life-time of the installation. Although some authors have asserted that frequent polarity change in MCDI should cause higher membrane longevity than in case of electrodialysis reversal [27], which itself is at least a controversial claim, there is still a question of decreasing electrosorption capacity of porous carbon electrodes. ED plants have been in operation for years, long-term (M)CDI operation is not as widely studied. One of the advantages of MCDI could be the lack of electrode reactions; in electrodialysis, hydrogen, oxygen (sometimes chlorine) are always evolved on the electrodes. In CDI, this is only observed at high voltage [28].

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Symbols and abbreviations

\[\begin{align*}
C & \quad \text{Concentration, mmol/dm}^3, \text{g/dm}^3 \\
CDI & \quad \text{Capacitive deionization} \\
E & \quad \text{Energy consumption, kWh/m}^3, \text{kWh/kg} \\
ED & \quad \text{Electrodialysis} \\
l & \quad \text{Applied current, A} \\
m & \quad \text{Mass of electrodes, g} \\
M & \quad \text{Molar mass, g/mol} \\
MCDI & \quad \text{Membrane capacitive deionization} \\
\eta & \quad \text{Number of adsorbed ions, mmol} \\
\Delta P & \quad \text{Pressure drop, Pa} \\
PVDF & \quad \text{Poly(vinylidene fluoride)} \\
q & \quad \text{Electrosorption capacity, mmol/g} \\
Q & \quad \text{Volumetric flow, m}^3/\text{s} \\
RO & \quad \text{Reverse osmosis} \\
t & \quad \text{Time, s} \\
TDS & \quad \text{Total dissolved salts} \\
U & \quad \text{Voltage drop, V} \\
V & \quad \text{Volume, dm}^3 \\
\eta & \quad \text{Salt removal, \%} \\
\end{align*}\]

Subscripts

\[\begin{align*}
\theta & \quad \text{Initial value} \\
\text{AC} & \quad \text{Alternating current} \\
\text{ads} & \quad \text{Sorption step of MCDI} \\
d & \quad \text{ED diluate} \\
\text{DC} & \quad \text{Direct current} \\
\text{des} & \quad \text{Desorption step of MCDI} \\
\text{ED} & \quad \text{Electrodialysis} \\
\kappa & \quad \text{Final value} \\
\text{MCDI} & \quad \text{Membrane capacitive deionization} \\
\end{align*}\]

References


