Transforming membrane technologies as appropriate technologies through cost-effective enhancements

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Received 24 July 2016; Accepted 10 April 2017

ABSTRACT

Utilisation of solar ponds in the operation of membrane distillation (MD) could improve the costeffectiveness of water production from inland brackish water sources. Similarly, capacitive deionisation with renewable energy would also provide cost-effective water production. While, solar ponds could help to run either MD alone or MD coupled with reverse osmosis (RO), capacitive de-ionisation will be cheaper to operate when brackish water to be treated. This study discusses details of (i) Optimal footprint of a solar pond for the operation of MD or RO/MD system, and (ii) Appropriate configuration of capacitive de-ionisation system.

Keywords: Brackish water; Capacitive de-ionisation; Membrane distillation; Reverse osmosis; Solar ponds

1. Introduction

Conserving fresh water and recovering resources from concentrates have become essential for a sustainable future. Increasing the water recovery in seawater desalination through the incorporation of membrane distillation (MD) would help to conserve fresh water. Incorporation of membrane crystallisation (MCr = MD + crystalliser) would both increase the water recovery and recover minerals. Literature shows a system comprised of microfiltration (MF), nanofiltration (NF) coupled with MCR and reverse osmosis (RO) coupled with MCr would not only produce water and salts but also will run on positive in terms of operations when energy recovery systems for RO in place and waste thermal energy is available for the operation of MD. Table 1 shows the cost comparison of various systems under such conditions for a feed flow rate of 25,188 m³/d [1]. While a MF-NF-RO system would cost \$0.46/m³ of produced water (\$0.39/m³ if

Pelton turbine is used as energy recovery device) at 49.2% water recovery, a MF-NF(/MCr)-RO(/MCr) would yield a profit of \$0.68/m³ of produced water at 92.4% water recovery when the following are incorporated in the desalination plant:

- 1. Pelton turbine is used as energy recovery device
- 2. Thermal energy is available in the plant or the stream is already at the operating temperature of the MCr
- 3. Produced salts are sold in the market.

2. Membrane distillation

Membrane distillation (MD) is one of the effective processes to separate water from salts that are present in liquid concentrates. MD utilises the vapour pressure difference between the feed (liquid concentrate with high vapour pressure) and permeate (with low vapour pressure) streams by

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Presented at the EDS conference on Desalination for the Environment: Clean Water and Energy, Rome, Italy, 22–26 May 2016.

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Table 1

Operating cost of different membrane desalination systems for a 25,188 m³/d feed flow (adapted from [1])

Process	Water recovery factor (%)	Amount of salt recovered (kg per m ³ of feed)	Total annual cost (\$)	Total annual profit of salts sale (\$)	Unit cost* (\$/m ³)	Unit cost ^{*,b} (\$/m³)
MF-NF-RO	49.2		1,871,000		$0.46/0.39^{a}$	$0.46/0.39^{a}$
NF-RO	52		2,005,000		$0.47/0.40^{a}$	$0.47/0.40^{a}$
RO	45		2,040,000		$0.61/0.40^{a}$	$0.61/0.40^{a}$
MF-NF (/MCr)-RO	71.9	5.4	4,024,000	6,398,000	$0.68/0.63^{a}$	$0.55/0.51^{a}$
MF-NF-RO (/MCr)	70.6	14.2	3,440,000	2,991,000	$0.59/0.54^{a}$	$0.47/0.43^{a}$
MF-NF (/MCr)-RO (/MD)	88.4	5.4	5,445,000	6,398,000	$0.74/0.71^{a}$	$0.55/0.51^{a}$
MF-NF (/MCr)-RO (/MCr)	92.4	19.5	5,593,000	9,389,000	$0.73/0.69^{a}$	$0.54/0.51^{a}$

*-desalted water unit cost without considering the gain from the sales of salts

a-if Pelton turbine is used as energy recovery device

b-if thermal energy is available in the plant or the stream is already at the operating temperature of the MCr

Annual sales of salts: CaCO₃ = \$478,700, NaCl = \$4,693,000; MgSO₄:7H₂O = \$4,218,000 and therefore total annual profit = \$9,389,000; total annual cost = \$5,593,000; total annual cost per m³ of fresh water produced = $$-0.49/-0.68^{\circ}$

allowing the water vapour to pass through a hydrophobic membrane. The feed stream is heated in order to increase the vapour pressure. Out of the four configurations (direct contact membrane distillation (DCMD), sweeping gas membrane distillation (SGMD), vacuum membrane distillation (VMD), and air gap membrane distillation (AGMD)) of MD, AGMD was found to be the best configuration for a small-scale, energy-efficient seawater desalination process in remote areas due to its thermal efficiency and less design complexity [2]. In another study, Duong et al. [3] found that optimal thermal efficiency for DCMD could be achieved at water recoveries ranging from 20 to 60%.

Fouling is one of the major factors affecting the performance of the MD membrane and it was found cleaning the membrane that was fouled when processing feed streams with high temperature was difficult [2]. Depression of solubility of $CaSO_4$ due to concentration polarisation at the feed side and the morphology of the scaled layers at high feed temperatures were important factors for the fouling of the membrane. Further, Nguyen et al. [4] found that the deposition of organic mass onto the membrane increased the overall fouling potential due to the interactions with the membrane surface and salt ions. Seawater reverse osmosis brine tends to reduce the MD flux mainly due to the precipitation of $CaCO_3$ and $CaSO_4$ and this could be reduced by the introduction of anti-scalants and the introduction of inline cartridge filters in a DCMD [5].

2.1. Applications of MD

Doung et al. [6] has utilised a DCMD and membrane electrolysis (ME) in series to produce water and NaOH respectively from the concentrate generated by RO when treating coal seam gas produce water. Such system was capable of reducing the thermal energy requirement of ME by 3 MJ per kg of NaOH produced and the thermal energy consumption of MD by 22 MJ per m³ of clean water extracted when the feed and coolant temperatures were 60°C and 50°C, respectively. Another study conducted by Duong et al. [7] found that an AGMD system used for small-scale and off-grid seawater desalination system where solar thermal or low-grade heat sources are readily available will require a specific thermal and electrical energy consumption of 90 and 0.13 kW h/m3, respectively. Dao et al. [8] has found that removing As(III) from brackish water was effective when using VMD. A removal of more than 99.7% was found for a feed with 2000 ppb of As(III) with 10 g/L of NaCl concentration at 40°C of feed temperature. In another study by Jia et al. [9], Sr²⁺ was removed from aqueous solution by VMD and the removal efficiency reached 99.60% for a Sr²⁺ concentration of 10 mg/L in the feed solution and the membrane flux could be maintained at 6.71 L m⁻² h⁻¹. Polypropylene hollow fibre membrane was used in that study. Thus, the recent studies reveal that all types of MD configurations can be used to produce water from concentrates which could possibly present in remote locations. However, the MD process to be energy efficient, a renewable heat source is essential which can be readily provided by salt gradient solar ponds (SGSPs)[10].

3. Salt gradient solar ponds (SGSPs)

Utilisation of solar ponds in the operation of MD could improve the cost-effectiveness of water production from inland brackish water sources as it provides the required thermal energy for the MD process. A schematic of such application is shown in Fig. 1. A salt gradient solar pond (SGSP) will have three zones namely upper convective zone (UCZ), non-convective zone (NCZ) and the lower convective zone (LCZ). The thickness of the UCZ should be kept to a minimum in order to have efficient thermal storage at the LCZ. The depth of the LCZ can be varied depending on the desired operating temperature. UCZ varies in thickness between 0.15–0.30 m which has a low and almost uniform salt content. Beneath, the NCZ which varies in thickness between 1.0–1.5 m and has a salt content that increases with depth. The LCZ also called the storage zone, which has thickness varying between 1.0-2.0 m and has a nearly uniform high salt concentration. A typical temperature and salt gradient in a SGSP is shown in Fig. 2. A maximum of 40 W/ m² of thermal flux can be generated from a solar pond [11] and 1500 and 6250 m² ponds were constructed in the past to



Fig. 1. Application of salt-gradient solar pond to provide thermal energy for membrane distillation process.



Fig. 2. Typical temperature and salt gradients in a salt-gradient solar pond.

generate 6 and 150 kW electricity respectively [12]. Another parametric design of 500 m² SGSP estimated the optimum depths of UCZ, NCZ and LCZ to be 0.2, 1.3 and 0.9 m, respectively when 270 W/m²·h of solar radiation is available [13]. In that study, the maximum collection efficient of the pond was 0.22 to 0.17 when operated with and without heat extraction. Berkani [14] et al. has found that SGSPs using CaCl₂ to obtain the salt gradient respond quicker to reach thermal saturation and thus increase the thermal efficiency. Atiz et al. [15] has found that the turbidity caused by insects, leaves, dust particles as well as particles brought into the pond by wind can decrease the energy transmission and reduce the efficiency of the pond.

It is essential to compute the energy storage in a given pond through mathematical modelling. A model proposed by Sayer et al. [12] can be used to develop the temperature profile in the pond at different months as well as to evaluate the influence of heat loss on energy storage. Monthly average values of the following climatic conditions will be required to run the model: solar radiation (MJ/m²·month), ambient temperature (°C), relative humidity (%) and wind speed (m/s).

The heat transfer rate at the upper and lower convective zones can be expressed as below using the notations shown on Fig. 2 where the heat Q is measured in W/m^2 [12]: UCZ:

$$\rho_{u}A_{u}X_{u}c_{pu}\frac{dT_{u}}{dt} = Q_{r-in} + Q_{ub} - Q_{uc} - Q_{ur} - Q_{ue} - Q_{r-out} - Q_{w}$$
(1)

LCZ:

$$\rho_l A_l X_l c_{pl} \frac{dT_s}{dt} = Q_{rs} - Q_{ub} - Q_{ground} - Q_{load} - Q_w$$
(2)

By substituting appropriate expressions for each heat, the temperatures of upper and lower convective zones can

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be computed to develop a monthly temperature profile of a solar pond. A 50 m² solar pond is available at the Bundoora Campus of RMIT university in Australia (UCZ = 0.35 m, NCZ = 1.1 m, LCZ = 0.6 m). The following factors have to be considered in maintaining the solar pond (Fig. 3) and Fig. 4 shows the temperature variations in the UCZ and the LCZ at RMIT solar pond over a period of time:

- 1. A clear solar pond with low turbidity is desired. Therefore controlling the algae growth for maintaining the clarity has been adopted with an initial pH target of less than 4. When this was done, increased adaptability of algae to acidic environment was observed and therefore the pH of less than 3 at both NCZ and UCZ was maintained through weekly pH monitoring.
- 2. Chlorine tablets are supplied at the top of solar pond by using a chlorine tablet floater.
- 3. Salt in the LCZ is lost due to upward diffusion and therefore NaCl is added through the salt charger on a weekly basis.
- 4. the salinity at UCZ is increased and regular flushing with fresh water is required.

When operating a direct contact membrane distillation (DCMD) system, Suarez et al. [16] observed an average flux of 1 L/m^2 -h which was equivalent to 1.16 L/d per m² of solar pond. The DCMD module contained 40 capillary membranes (1.8 and 2.8 mm inner and outer diameter respectively) with

an active length of 460 mm, a surface area of 0.1 m² and a free flow area of 1 cm². The membrane material was polypropylene with an average pore size of 0.2 μ m, porosity of 70%, tortuosity of 1.43 and an average effective thermal conductivity of 0.046 W/m·°C. In another study, Suarez et al. [17] have proposed a methodology to reclaim terminal lakes by employing coupled DCMD/SGSP systems.

The advantage of this type of system is it is capable of producing drinking water even from treated wastewater. A membrane bioreactor (MBR) and forward osmosis (FO) treated wastewater can be used to produce drinking water using this system. A schematic of such concept is given in Fig. 5. MBR effluent can dilute the draw solution of the FO system which in turn can be heated by the heat exchanger connected to the LCZ of the solar pond. This heated draw solution can then be passed through the MD system to pro-



Fig. 4. Temperature profiles of UCZ and LCZ over a period of time at RMIT solar pond.



Fig. 3. Photos of the solar pond situated at the Bundoora Campus of RMIT University, Melbourne, Australia and the components of the solar pond.



Fig. 5. Application of MBR and FO in water production [18].

duce water and the concentrate can be recycled back to the FO as draw solution. Part of the produced water can be used as permeate stream for the MD process after cooling through a heat exchanger connected to the UCZ of the solar pond.

4. Capacitive deionisation (CDI)

Capacitive deionisation (CDI) is a very efficient process to demineralise brackish water. Therefore, we just wanted to emphasise, by providing a brief description to capacitive deionisation (CDI), that it will be an appropriate technology to produce potable water from brackish water in remote areas with very simple handmade CDI modules. When brackish water is passed through between a positive and a negative electrode held at a potential difference of 1.2 to 1.5 V those electrodes attract oppositely charged ions present in the brackish water (flow between electrodes). This low voltage is the key to the ease of operation as well as to produce simple CDI modules at a cheaper cost. When the electrodes are saturated with ions the operation can be stopped to clean the electrodes and collect the concentrated brackish waste stream. Porous carbon can be used as electrodes. In order to further enhance the performance of CDI process, cation and anion exchange membranes could be attached to the cathode and the anode respectively so that the brackish water is exposed to those membranes rather than the electrodes. This is termed as membrane assisted capacitive deionisation (MCDI). Currently, the architecture of CDI cells can be divided into three: One that uses static electrodes such as flow-between electrodes, flow-through electrode, MCDI and inverted CDI and the other that uses static electrodes which depart from capacitive behaviour such as hybrid CDI and desalination battery [19]. The third architecture uses flow electrodes such as feed in electrodes, feed between electrodes and membrane flow electrodes.

Studies find that CDI is better than RO in the following aspects: Reduced energy (>30%), reduced fouling (>60%), less brine (40%), low maintenance cost (>50%), higher throughput (70%) and lower capital costs (40%) [20]. Thus, there is a great scope to apply CDI for appropriate brine solutions. The specific energy consumption of CDI compared to sea water RO and brackish water RO is discussed by Oren [21] and has suggested that energy recovery in CDI is required for it to be competitive with other desalination technologies. However, it is worth noting that large scale CDI units to treat 60,000 m³/d of municipal wastewater for

the purpose of reuse as well as to treat $5,000 \text{ m}^3/\text{d}$ of coal mine wastewater for remediation have been produced by EST, China [19].

Electrodes play a significant role in storing ions and there are following carbon based electrodes can be used in CDI [22]: carbon-carbon composites (carbon nanotubes, CNTs - activate carbon, AC; CNTs - mesoporous carbon, MC; CNTs - carbon nano-fibres, CNFs; reduced graphene, RG - AC; RG - MC; RG - CNTs; carbon aerogels, CAs -AC; activated carbon fibres, ACFs - carbon black, CB; ACFs –CNFs) carbon-metal oxide composites (AC – TiO₂; AC – ZnO; nanoporous carbon, NC – MnO₂; RG – MnO₂), carbon-polymer composites (AC - chitosan, CS; CNTs -CS; carbon - RF; carbon-polyaniline, PANI; carbon - ion exchange polymer) and carbon-polymer-metal oxide composites (CNTs - polystyrene sodium sulfonate - MnO₂, RG – PANI). For example, the following maximum electrosorption capacity of NaCl by various electrode materials (mg/g)have been reported in the literature (Liu et al., 2015): CA ~ 4.51; AC ~ 13; CNFs ~ 4.6; MC ~ 0.93; RG-CNTs aerogel ~ 633; RG-TiO₂ ~ 24.2.

5. Conclusions

Solar pond assisted membrane distillation and CDI show promise in the sustainable production of clean water from concentrates. However, efficient energy transfer from the solar pond to the MD and higher efficiency membranes for the MD are critical for this hybrid system to be successful. The CDI technology will become efficient if research is concentrated into the electrochemical reactions that occur in CDI which causes change in pH and other undesirable effects. Removal of specific ions through CDI also needs research.

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