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Novel graphene nanoplatelets-coated polyethylene membrane for the treatment of reject brine by pilot-scale direct contact membrane distillation: An optimization study

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ABSTRACT

In this research study, a direct contact membrane distillation (DCMD) system was used in the concentration of raw brine from a full-scale reverse osmosis desalination plant for further zero-liquid discharge (ZLD) applications. Several operating conditions such as feed inlet temperature (T_f), feed (Q_f) and permeate (Q_p) flow rate, and feed concentration (C_f) were tested to obtain the optimum permeate flux across the membrane, salt rejection and specific thermal energy consumption (STEC). The highest flux of 16.7 LMH, salt rejection of 99.5% and STEC of 152 kWh/m^3 were achieved at T_f, Q_f, Q_p, and C_f of 85 °C, 75 L/h, 48 L/h and 57,500 ppm, respectively. Furthermore, this study was carried out for a long term operation of 77 h in which the membrane was found to be prone to significant fouling thereby resulting in a flux decline across the membrane of 69%. To mitigate fouling, novel membranes were prepared through the surface coating of commercial membranes with graphene nanoplatelets (GNPs) at 0.08, 0.16 and 0.2 wt%. Over a 10 h operation, membranes coated with 0.08 and 0.16 wt% GNP reduced membrane fouling by 59 and 78%, respectively.

1. Introduction

In recent years, membrane processes are being used in desalination applications due to their competitive benefits over thermal distillation. This includes advantages such as lower energy consumption and reduced environmental impact. Reverse osmosis (RO) is one of such membrane processes that have been established for the commercial use in saline water desalination processes [1]. Currently, more RO desalination plants exist worldwide than other plants that employ other desalination technologies where it is the fastest growing desalination technology in terms of the number of installed plants [2]. However, one of the main problems associated with RO desalination is the discharge of its highly saline by-product known as RO brine or concentrate [3]. The salinity of brine rejected from seawater RO (SWRO) might be greater than that of seawater by about 1.3 to 1.7 times. SWRO brine is a major threat to the environment because it contains pretreatment chemicals at elevated temperatures [4], which can disrupt the ecological interactions among organisms in the biosphere. Sodium hypochlorite (NaOCl), ferric chloride ($FeCl_3$) and sulfuric acid (H_2SO_4) are all examples of pretreatment chemicals that might be present in SWRO brines [5,6]. Additionally, pretreatment chemicals and high temperatures might alter the metabolism of aquatic life and cause species mortality at long exposure times [7].

RO brine production continues to increase at an exponential rate due to the spatial and temporal expansion of RO technology. As a result, the need for cost-effective brine management solutions has become essential to further concentrate brine through enhanced recovery of pure water, using low-grade energy sources [8]. This concentrated brine can be converted to a zero-liquid product through the recovery of the solids in the concentrated brine. This principle is known as zero-liquid discharge (ZLD) and is used to prevent the discharge hazardous liquid brine into the environment [9]. This process allows for the further recovery of water from brine while further separating concentrated brine into solid and liquid phases [3,10]. The ZLD process is composed of two stages, the first is used to reduce the volumetric load of brine while the second involves the recovery of solids from the concentrated brine via crystallization or evaporation. The results and findings reported in recent studies on ZLD are shown in Table 1.

Brine concentration is a crucial ZLD stage due to its significant influence on the overall energy consumption of the process as well the cost of brine management [3]. The SWRO brine concentration stage serves as the pre-treatment stage and the optimum recovery of salt in the succeeding stage. This stage is termed as the “life wire” of the SWRO ZLD process. Brine concentration has been achieved in a number of previous studies through the use of different methods such as multi-

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Table 1
Results reported in recent studies on ZLD.

Feed type	Removed pollutants	Technology	System configuration	Operating conditions	Pollutant removal efficiency	Ref.
SWRO brine (1 M NaCl RO retentate)	NaCl	DCMD and reverse electrodialysis	50 microporous polypropylene hollow fiber membranes	The inlet temperature of the distillate stream was set constant at 20 °C, while inlet feed temperature was varied within 40 and 50 °C. Flow velocity: 0.7, 0.9 and 1.1 cm/s	Volume Reduction Factor (VRF) up to 83.6%	[9]
Aqueous NaCl solutions at concentration of 35 g/L	N/A	DCMD to estimate the mass flux and the heat efficiency	Crosscurrent flow	The temperature at the permeate side: 15 °C; mass flow rate of 0.055 kg/s at feed side and 0.028 kg/s at permeate side; feed temperatures: (25, fluxes of 3.1 × 10–4 and 2.7 × 10^{-4} kg/m^2 s for natural and synthetic brines, respectively.40, 55, 60, 70 °C)	N/A	[21]
SWRO brines	NaCl	MDC	Polypropylene hollow fiber membranes	The temperatures in the distillate reservoir and jacketed retentate/crystallization tank = 20 and 30 °C respectively; Crystallization tests at almost constant transmembrane fluxes of 3.1 × 10^{-4} and 2.7 × 10^{-4} kg/m^2 s for natural and synthetic brines, respectively	Final water recovery factor increased up to 90%.	[22]
Red sea saline water	N/A	Solar-powered membrane distillation (SPMD)	Spiral wound PTFE membranes in crosscurrent configuration	N/A	Recovery ratio: 30 to 50%; distillate conductivity: 20–250 µS/cm	[23]
Wastewater containing HLW (high-level waste) and LLW (low level waste) nuclear wastes	Inorganic salts such as nickel, zinc, iron, europium, and cerium	Precipitation/ membranes desalination system with: MD stage and single-stage precipitation system	Flat sheet membranes	(25–93 °C) feed temperatures and atmospheric pressure for membrane desalination	Up to 11,000 ppm in the concentrate stream	[24]
Several RO brines	Precipitated inorganic salts	Integrated system of solar evaporation, MD, and electrodialysis	Flat sheet membranes; countercurrent flow configuration	Several operating conditions were reviewed	99–100% rejection	[4]
Basal water	Inorganic salts (suspended solids)	Electrodialysis RO, and low-temperature crystallizer	Cross flow configuration	Feed water temperature: 17 ± 2 °C; RO feed pressure: 55 kPa	95–99% water recovery	[25]
Two types of RO brine streams: Brine A (concentrate from primary brackish water RO desalter); Brine B (concentrate from secondary RO desalter)	Silica and calcium sulfate	Vacuum-enhanced direct contact membrane distillation (VEDCMD) and forward osmosis (FO)	Laminated membrane PTFE active layer over a polypropylene support mesh; flat sheet 0.22 µm polypropylene membrane; flat-sheet cellulose triacetate FO membrane; crosscurrent flow	ΔT = 20 and 40 °C; FO experiments at constant temperature of 23 ± 2 °C	Total recovery > 89% for brine A and > 98% for brine B	[26]
Synthetic NaCl brine solution	NaCl	Continuous membrane distillation crystallization (CMDC)	MD was integrated with a cooling crystallization unit in a crosscurrent configuration; Hollow fiber MD membrane was used	Feed flow rate: 0.64 L/min; permeate flow rate: 0.35 L/min; feed temperature: 338 K; permeate temperature: 303 K	Water flux: 72.66 kg/m^{2}d; NaCl solid production flux: 26.06 kg/m^{2}d	[27]
Synthetic brine solution containing Na_2SO_4, NaCl, $MgCl_2$, $CaCl_2$, $MgSO_4$ and $NaHCO_3$	Cl^-, Na^+, SO_4^{2-}, Mg^{2+}, Ca^{2+}, HCO^{3-}	MF–NF–RO membrane system integrated with MD/ crystallization units	Polypropylene	Inlet retentate and distillate temperatures: 35 ± 1.58 °C and 15 ± 18 °C, respectively	Cl^- (NF = 12.8%); (RO = 98.95%); Na^+ (NF = 22%); (RO = 98.9%); SO_4^{2-} (NF = 90%); (RO = 99.6%); Mg^{2+} (NF = 88.98%); (RO = 99.6%); Ca^{2+} (NF = 88.4%); (RO = 99.7%); HCO_3^-(NF = 62%); (RO = 98.4%)	[28]
	Sodium sulfate; sodium, and chloride ions			MD flux of 15–20 LMH at feed temperature (TF) of 60 °C, permeate (TP) temperature of 20 °C; average MD flux of 4 LMH from RO brine (TF = 45 °C; TP = 25 °C)		[29]

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