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Case Report

A novel renewable energy powered zero liquid discharge scheme for RO desalination applications

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ABSTRACT

This work proposes a conceptual model for a Zero Liquid Discharge (ZLD) for Reverse Osmosis (RO) desalination. The model describes a Process Flow Diagram (PFD). The proposed process relies on an RO followed by electrolyser, solar evaporator and mixing tank. The water reject from the RO is split into three fractions, one to an electrolyser to produce H_2, another to solar evaporator to produce fresh water, third is remixed with water from the evaporator to reduce the salinity of the RO feed. The hydrogen produced in the electrolyser is burned and its energy is stored using cement blocks. The evaporator is operated using solar energy during the sunny period of the day. Then, the energy stored in cement will replace the solar energy during the remaining hours of the day. The proposed model is based on mass and energy balances including the performance characteristics of individual equipment. A new parameter pZLD is defined as the ratio of the brine reject from the overall plant to the fresh brackish water drawn from the wells. The minimum value of pZLD is zero. The theoretical model is tested for desalination of brackish water with 8000 ppm Total Dissolved Solids (TDS). For a small capacity of 2,000 L/d of fresh water produced, the following results were reported for 400 ppm fresh water: water from well = 2,108 L; produced H_2 = 7.40 kg/d; cement required = 2,160 kg for 14 h; solar energy = 5.04 kW for 10 h; pZLD = 5.8%. The cost of modifications to conventional desalination unit is 533,028 Egyptian Pound (EGP), (capital) and 323.49 EGP/h (operating).

1. Introduction

Freshwater shortage is one of the critical challenges that face all global economic growth plans as well as all natural environment preservation plans. Brackish water Reverse Osmosis (BWRO) desalination and Seawater Reverse Osmosis (SWRO) desalination present a reliable solution to address the freshwater scarcity challenge [1]. Recent investigations indicated that the global production of freshwater from desalination exceeds 120 million m3/d [2,3]. Two years ago, the resulting global desalination brine was estimated at 129 million m^3/d [4]. Global desalination brine disposal methods, employ rejection in marine environment, surface water and sewage disposal and deep well injection. Several authors have discussed the associated aquatic environmental pollution and the adverse effects of these brine disposal methods on both surface water and ground water recourses [5].

An emerging sustainable and environment friendly solution for brine disposal is the Zero Liquid Discharge (ZLD) approach [6,7]. Effectively ZLD is a brine treatment strategy that is designed to maximise water reuse and to produce solid salts, thus eliminating desalination environmental threats. The drivers for the implementation of Zero Liquid Discharge systems originated from the stricter environmental regulations, the stressing freshwater scarcity and the considerably high cost of wastewater treatment and disposal.

The implementation of ZLD started by the integration of a series of thermal processes [8]. Following a pre-treatment step, the brine feed is concentrated in brine concentrator which employs mechanical vapour compression for the evaporation process. The brine concentrator is followed by a brine crystalliser or an evaporation pond. The resulting distillates streams are condensed and reused as freshwater while the solids are treated as byproducts. The use of the thermal energy intensive brine concentrators and brine crystallisers is inevitable in ZLD systems. The use of RO membranes for the pre-concentration of the brine feed can allow for reduced energy consumption of these thermal processes [9]. Tong and Elimelech reported that integrating a secondary RO unit for treating the brine of an inland RO desalination unit resulted in 58–75% energy saving and 48–67% of treatment cost saving as compared with a ZLD system containing brine concentrator and evaporation pond [10]. RO membranes fouling and scaling as well as the limited brine upper salinity impose constraints on employing RO units in ZLD systems.

Bond and Veerapaneni reported a pilot ZLD project that employed RO with ultra-filtration pretreatment which allowed the subsequent RO stage to be operated at relatively high recovery ratio [11].

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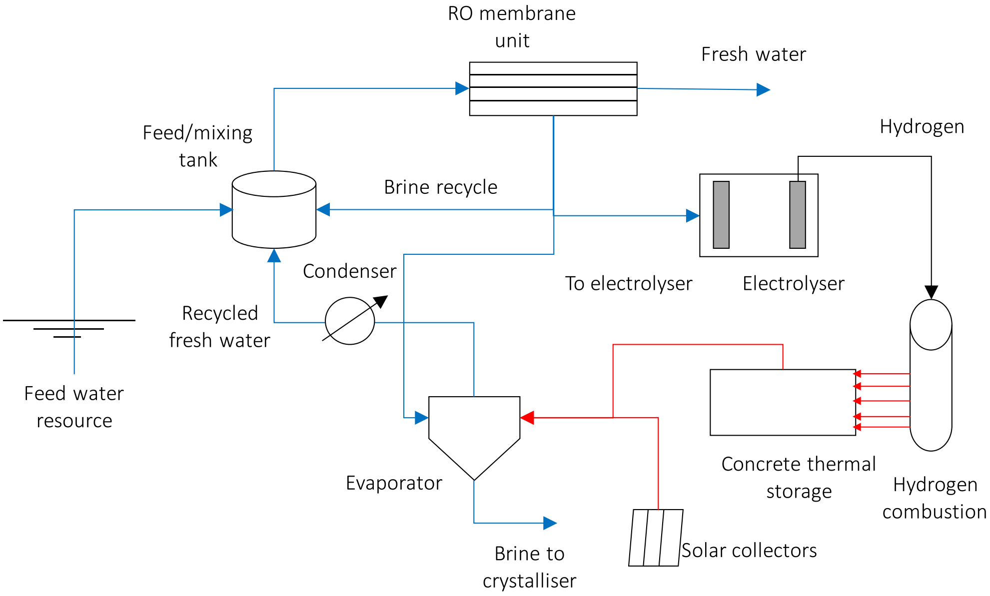

Fig. 1. Process flow diagram for conceptual model adopting ZLD approach of BWRO.

Bond and Veerapaneni reported the Electrodialysis (ED) technology for brine concentration. This technology employs electric potential and ion exchange membranes for moving cations towards a negatively charged electrode through cation exchange membranes [12]. Through anion exchange membranes, anions move in the opposite direction. In this case, a reduced salinity stream as well as a concentrated brine stream are generated. Wu et al. addressed some challenges in electrolysis of high salinity wastewater treatment [13]. In this work, experimental and theoretical analysis of byproduct formation in electrolysis were presented. To minimise fouling and scaling of the membranes, Loganathan et al. described an Electrodialysis Reversal (EDR) process where the polarity of the electrodes is reversed at predefined frequency [14]. A main advantage of the Electrodialysis process is that it can concentrate the brine up to 100,000 ppm. The associated Specific Energy Consumption (SEC) is 7–15 kwh/m^3. Korngold et al. reported a pilot integrated 79%–98% water recovery Reverse Osmosis- Electrodialysis Reversal (RO-EDR) system for Brackish Water (BW) desalination [15]. The achieved concentration of RO brine by EDR was 200,000 ppm prior to a brine crystalliser. The resulting salt diluted stream from EDR is returned to the RO unit for further desalination such that the system water recovery is reached.

Panagopoulos reported a study for ZLD system combining an RO unit, a brine concentrator, and a brine crystalliser [16,17]. Two RO desalination cases were considered. The first case is Brackish Water RO desalination (BWRO) with feed TDS of 5000 ppm and a recovery ratio of 80%. The second case is Sea Water RO desalination (SWRO) with feed TDS of 38,000 ppm and a recovery ratio of 39%.

The current work aims at proposing conceptually a new scheme to modify an existing RO desalination unit towards a zero-liquid-discharge system. The scheme proposed comprises an electrolyser powered by PV panels, an evaporator whose energy supplied by solar panels combined with thermal heat stored in cement blocks. The scheme is modelled using mass and energy balance equations, together with cost estimation models.

2. Methodology

Given that the brine reject of the RO desalination unit is challenging, a conceptual approach is proposed in this work to relax the environmental problems of brine reject disposal. The concept of ZLD suggested relies on the approach of splitting the brine reject of an RO desalination unit into a number of fractions, for example 3 splits. A process flow diagram PFD for the ZLD approach is shown in Fig. 1.

2.1. Conceptual model description

The conceptual process model of this work focuses on a modification to BWRO desalination units to adopt the concept of ZLD. The brine reject from the RO desalination module is split into 3 fractions. One fraction (r_{el}) is fed to an electrolyser to generate hydrogen. The electrolyser is run by electricity from renewable PV panels and the H_2 produced can be used for several applications. One of these can be to provide heat to concrete thermal storage. This option is preferable particularly when the amount of H_2 generated is in surplus. The hydrogen produced is burned to provide heat that can be used in the ZLD process. The heat of combustion of hydrogen can be thermally stored in concrete and thus the stored heat is exploited to run an evaporator system. Another fraction (r_{ev}) enters an evaporation system run by solar energy and heat from hydrogen to produce fresh water and concentrate the brine reject further. The fresh water vapour produced in the evaporator is condensed and then recycled to the RO module. The third split (r_{re}) of brine reject is recycled with the saline source water before the RO desalination unit. The recycled fresh water impacts reducing the salinity of the brine feed to the RO module. This results in reducing the volume of brackish water drawn from wells. The mixing of the fresh brackish water from wells, recycled water from evaporator and the remixed split from the RO unit defines the feed volumetric rate/load and salt concentration on the RO unit. The evaporator concentrates the fraction leaving the RO unit and thus the salt concentration increases enough to be sent to evaporation ponds or crystallisation units. If available and feasible, reinjecting the concentrated brine back into surface water (or deep wells) is considered less expensive than environmentally treating and disposing dry salts. This is highly dependent on the environmental costs. Evaporator unit can be single effect or in the design of multiple effect evaporators. An alternative to evaporators, electro dialysis ED can be employed to concentrate brine to approximately typical 20% NaCl brine solutions. The overall product streams of the conceptual process are fresh water stream, hydrogen, and salts leading to ZLD approach. Below is a full description of the conceptual process models employed within the new process configuration adopting ZLD approach.

2.2. Conceptual model equations

2.2.1. RO membrane unit

The equations describing the conceptual model include mass and energy balance, and salt concentration balances around the individual units presented in Fig. 1. In addition to the balance equations, the model involves also characteristic performance of individual equipment. An RO module is essential to produce fresh water stream from the brackish water feed stream with a recovery rate R based on the volume of the brine/saline source water (70–90%). Salt concentration of brackish water in this study is taken as 8,000 ppm, while that for fresh water produced is of 400 ppm. The volume of brine reject and fresh water generated from the RO desalination unit can be calculated by the following equation:

$$V_{br} = V_{bw} \times \left(1 - \frac{R}{100}\right) \tag{1}$$

$$V_{fw} = V_{bw} \times \left(\frac{R}{100}\right) \tag{2}$$

where V_{br} is the volumetric flow rate (L/d) of brine reject from RO unit, V_{bw} is the volumetric flow rate of saline brackish water source feed (L/d), and V_{fw} is the volumetric flow rate (L/d) of fresh water. The salt concentration of the brine reject is determined through salt balance around the RO unit, providing the brackish water and the fresh water salinities are given, as shown by the below equation:

$$X_{br} \times V_{br} \times \rho_{br} = X_{bw} \times V_{bw} \times \rho_{bw} - X_{fw} \times V_{fw} \times \rho_{fw} \tag{3}$$

where ρ_{bw} is the density of brackish water (1015 kg/m^3), and ρ_{fw} is the density of fresh water (kg/m^3). X_{bw}, X_{br} and X_{fw} are the salt concentrations (ppm) in brackish water feed, brine reject stream and fresh water stream produced respectively.

Mass balance and salt balance calculations around the RO unit are determined according the following equations:

$$V_{sc} \times \rho_{bw} = V_{br} \times \rho_{bw} + V_{fw} \times \rho_{fw} \tag{4}$$

$$X_{bw} \times V_{sc} \times \rho_{bw} = X_{br} \times V_{br} \times \rho_{bw} + X_{fw} \times V_{fw} \times \rho_{fw} \tag{5}$$

where V_{sc} is the volumetric flow rate (L/d) of the saline combined feed to RO. It is reasonably assumed that the brackish water density does not change with salt concentration.

The volumetric flow rate of the combined stream (V_{sc}) fed to RO and its salt concentration are calculated from balancing the mixing tank as demonstrated by the following relationships:

$$V_{sc} \times \rho_{bw} = V_{bw} \times \rho_{bw} + V_{br} \times (1 - r_{el} - r_{ev}) \times \rho_{bw} + V_{br} \times r_{ev} \times R_{ev} \times \rho_{fw} \tag{6}$$

$$X_{sc} \times V_{sc} \times \rho_{bw} = X_{bw} \times V_{bw} \times \rho_{bw} + X_{br} \times V_{br} \times (1 - r_{el} - r_{ev}) \times \rho_{bw} \tag{7}$$

where, R_{ev} is the evaporation rate fraction achieved in the evaporator leading to pure water vapour. It must be noted that the salt concentration of the water vapour leaving evaporator is zero.

2.2.2. Electrolyser

Electrolysis is an effective and major technique for hydrogen production from salty water (sea water/brackish water). A challenge of this technology is found simply in the evolution of chlorine and oxygen at the anode. In addition, brine water contains different ions such as Na^+, Cl^-, Mg^+, Ca^+, etc. which troubles the seawater electrolysis. For example, high concentration of Cl^- can cause chloride evolution at the anode. Also the Ca+ and Mg + may precipitate at the cathode producing $Ca(OH)_2$ and $Mg(OH)_2$ It was investigated that the evolution activity of hydrogen is decreased with increasing concentration of OH^-. On the other hand, the oxygen evolution is enhanced by the presence of Cl^- (He et al., 2023). The produced chlorine at the anode can be for sale or used for several applications, among which it can oxidise bromine ions into bromine. In electrolysis technology, water is split directly into hydrogen and oxygen without prior desalination step. Electricity required for this technology is provided by renewable energy sources, e.g. photovoltaic cells (PV cells) and wind, or conventional grid. The basic splitting equation for electrolysis is shown as follows:

$$H_2O + Electircity = H_2 + \frac{1}{2}O_2 \tag{8}$$

This implies for every mole of water electrolysed, 1 mol of hydrogen is produced and correspondingly a half-mole of oxygen is released. Therefore, a mass balance on the electrolyser results in the following equations:

$$m_{H2} = \frac{m_{H2O}}{M_{H2O}} \times M_{H2} \tag{9}$$

$$m_{H2O} = (1 - X_{br}) \times V_{br} \times (r_{el}) \times \rho_{bw} \tag{10}$$

where m_{H2O} is the mass flow rate of brackish water fraction from brine reject of RO, m_{H2} is the mass flow rate of hydrogen produced, and M_{H2O}, and M_{H2} are the molecular mass of water and hydrogen respectively. Typical energy demand (ΔE_{el}) for electrolysis ranges from 33 to 56 kWh/kg of hydrogen produced. Therefore, the total energy required (ΔE_{tot}) for procuring hydrogen with mass flow rate m_{H2} can be determined by:

$$\Delta E_{tot} = m_{H2} \times \Delta E_{el} \tag{11}$$

In case this energy is provided by solar photovoltaic cells, the number of cells, n_{cell}, is calculated providing the power produced from each PV cell (P_{cell}) and the sunny-hours-per-day (θ_{sun}), according to the following equation:

$$n_{cell} = \frac{1}{P_{cell}} \times \frac{1}{\theta_{sun}} \times \Delta E_{tot} \tag{12}$$

It must be noted that the electrolyser is employed to provide hydrogen necessary as heat source for evaporation. In some cases, where large fraction of brine reject is directed to electrolyser, the hydrogen produced will exceed the necessity of the evaporation. Thus the surplus hydrogen can be sold or used in fuel cells for other purposes.

2.2.3. Concrete thermal storage

Concrete recently is examined to store energy generated by thermal power plants as it can provide storage capacity for longer durations at lower cost. In this work, concrete blocks are used to store energy provided by the combustion of hydrogen. During the period of no-sun shine, steam is produced inside the concrete and then applied to provide thermal heat to evaporator to concentrate the brine reject.

The heat released by the combustion of hydrogen amount m_{H2} (Q_{H2}, kW) can be calculated by knowing the calorific value or heat of combustion of H_2 (ΔH_{CH2}, kW /kg):

$$Q_{H2} = m_{H2} \times \Delta H_{CH2} \tag{13}$$

The heat stored in concrete (Q_{cncr}, kJ), mass of concrete (m_{cncr}, kg) required and steam produced (m_{stc}, kg/s) can be calculated as follows:

$$Q_{cncr} = Q_{H2} \times (24 - \theta_{sun}) \times 3600 \tag{14}$$

$$m_{cncr} = \frac{Q_{cncr}}{CP_{cncr} \times (T_{H2} - T_{cncr})} \tag{15}$$

$$m_{stc} = \frac{Q_{cncr}}{CP_{fw} \times (T_{stc} - T_{cw}) + \Delta H_{stc}} \times \frac{1}{3600 \times (24 - \theta_{sun})} \tag{16}$$

where, CP_{cncr} is specific heat or heat capacity of concrete (kJ/kg·K), T_{H2} and T_{cncr} are temperature of H_2 (500 ^oC) and concrete respectively (30 ^oC), T_{stc} is saturation temperature of steam generated (for example 160 ^oC), T_{cw} is temperature of inlet water, and ΔH $_{stc}$ is latent heat of vaporisation of steam generated at T_{stc} in concrete (kJ/kg).

2.2.4. Evaporator

Evaporation equipment can be used as single effect or as multiple effects. Heat source is applied to produce water vapour from a brine solution or salty water. If a pound of steam is supplied to an evaporator (single effect), it can be used to produce about 0.9 lb of water vapour or steam from a pound of water (Kern). The remaining 0.1 lb of water contains the bulk of salt. The water vapour produced is condensed and recycled to RO unit to reduce the salt content of the brackish water source stream, while the brine concentrate is sent to crystallisers or evaporation ponds. In this work, a combination of heat from concrete storage and solar collectors. The model of the evaporator is described in below equations:

$$m_{ev} = V_{br} \times r_{ev} \times \rho_{bw} \tag{17}$$

$$m_{wv} = m_{ev} \times R_{ev} \tag{18}$$

$$m_{brc} = m_{ev} - m_{wv} \tag{19}$$

$$X_{sl} = \frac{m_{ev} \times X_{br}}{m_{brc}} \tag{20}$$

where m_{ev} is the mass flow rate of brine feed to evaporator, m_{wv} is the mass flow rate of water vapour produced in the evaporator, m_{brc} is the mass flow rate of brine concentrate from the evaporator, and X_{sl} is the salt concentration in brine concentrate leaving the evaporator. The heat required in the evaporator (Q_{ev}) to produce the amount m_{wv} (kg/s) is the energy necessary to heat the brine feed m_{ev} (kg/s) to the saturation temperature and then vaporise the amount $m_{wv},$ as shown in energy balance equation.

$$Q_{ev} = m_{wv} \times H_{wv} + m_{brc} \times CP_{brc} \times (T_{ev} - T_r) - m_{ev} \times CP_{br} \times (T_2 - T_r) \tag{21}$$

where H_{wv} is the enthalpy of the water vapour stream (kJ/kg) at the evaporation temperature T_{ev}, CP_{brc} is the specific heat of brine concentrate (kJ/kg·K), T_2 is the temperature of brine feed to evaporator (K), and T_r is reference temperature (0 ^{o}C). If the first evaporator runs at atmospheric conditions, then $T_{ev} = 100\ ^{o}$C. The expected heat transfer area for the evaporator A_{ev} (m^2) can be calculated from heat balance around the heat source provided, as shown below:

$$A_{ev} = \frac{Q_{ev}}{U \times \Delta T_{ev}} \tag{22}$$

where U is the overall heat transfer coefficient (kW/m^2·K), and ΔT_{ev} is the temperature difference between the evaporation temperature and the energy source temperature (K).

2.2.5. ZLD performance

Within the proposed ZLD flowsheet, a new parameter *pZLD* is defined as the ratio of the brine reject from the overall plant to the fresh brackish water drawn from the wells.

$$pZLD = \frac{m_{brc}}{V_{bw} \times \rho_{bw}} \tag{23}$$

The *pZLD* parameter evaluates the performance of the new modified unit with respect to being ZLD process. The absolute value for this parameter is zero; however, this value is not necessarily an optimum. The performance of the new modified RO desalination unit can be measured by analysing the cost implications and profit due to modifications.

2.2.6. Costs analysis performance

In order to assess the performance of the new modified RO unit, economics of process modifications and profit need to be analysed. The modifications proposed incur capital investments, including the costs of the evaporator, cement blocks, electrolyser, solar preheater, PV panels, and the exchanger equipment. The following table reports the capital costs of the equipment of the modified RO plant and the calculations of heat transfer equipment areas. Cost values of equipment and utilities are provided by local providers in Egypt. The total capital investment equals the purchase costs of all equipment, while the total operating cost includes those for water used and electricity. On the other hand, process profit comes from the selling fresh water from RO and the surplus H_2. Payback time is estimated from the ratio of total capital investment to the profit. Flows of water streams, utilities, hydrogen etc. are calculated from mass balance equations presented above.

Table 1
Capital and utilities costs/prices.

Equipment	Price	Price unit
Solar preheaters	5,000	EGP
Evaporator	50,000	EGP
Electrolyser	10,000	EGP
PV panels (350 W/panel)	3,000/panel	EGP
Concrete storage	5,780	EGP/m3
Electricity	0.85	EGP/kWh
Water for cooling	41.65	EGP/kg
Water produced for sale	3	EGP/L
Hydrogen produced for sale	2.4	$/kg
Steam for heating	850	EGP/MW
Heat exchanger	6,000 + 200 × (heat transfer area)	$

3. Case study and results

The theoretical model is tested for desalination of brackish water with 8,000 ppm TDS. For a small desalination unit with a capacity of 2,000 L/d of fresh water with 400 ppm salt concentration; this unit corresponds to a lab scale desalination unit located at the British University in Egypt. The recovery of RO unit is set to 60%. The conventional unit before modification (not adopting ZLD concept) consumes 3,347 Litre-per-day brackish water from well in order to supply the capacity of 2,000 L/d fresh water. Solving the presented model equations above resulted in the following results:

- Water drawn from well = 2,108 L
- Fraction of RO reject to electrolyser = 5% of total reject from RO unit.
- Fraction of RO reject to evaporator = 58% of total reject from RO unit.
- Fraction of RO reject recycled to feed/mixing tank = 37% of total reject from RO unit.
- Recycled salt concentration = 8054 ppm
- RO mixed feed flow rate = 3347 L/d
- H_2 produced = 7.4 kg/d
- Electricity required = 317 kWh
- Energy content of H_2 combustion = 7.11 kW
- Cement blocks required = 2,160 kg (thermal storage period = 14 h)
- Solar energy = 5.04 kW (solar energy period = 10 h)
- Brine to evaporation pond = 78 L
- Salt concentration of final brine = 195,360 ppm
- pZLD = 3.6%

The capital costs of equipment required for modifications are calculated as proposed in Table 1 and found to be 533,028 EGP. On the other hand, the operating costs of electricity and water needed for cooling/evaporation are 323.49 EGP/h leading to an annual costs of 2,587,915 EGP. The annual profit generated will be the selling price of 2,000 Litre-per-day of fresh water, resulting in 2,190,000 EGP.

Fig. 2 summarises the impact of split fraction to electrolyser within the range 2–14% on both the salt concentration and volume of feed to RO membrane unit at constant split fraction to evaporator (58%). It is

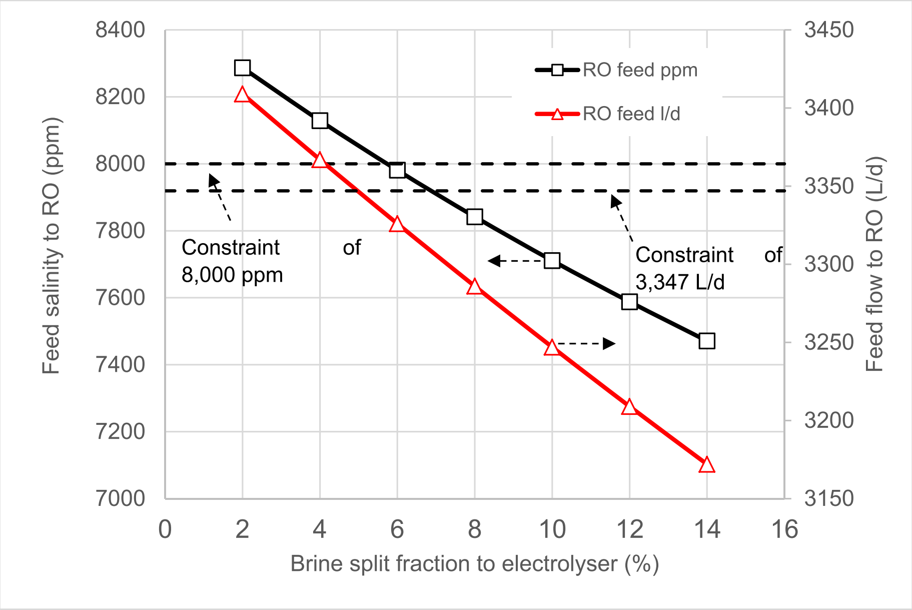

Fig. 2. Effect of brine split to electrolyser on salt concentration and flow of RO feed (at 58% to evaporator).

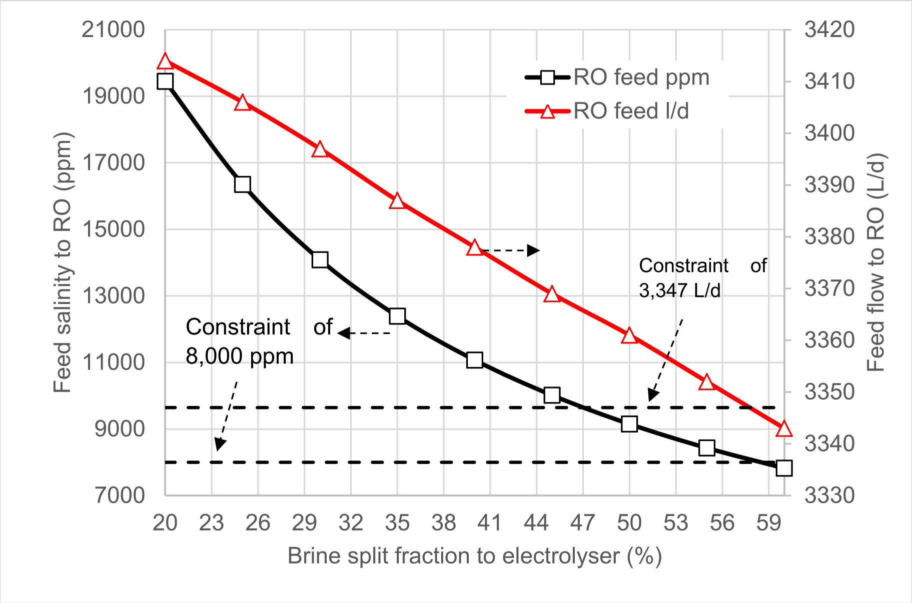

Fig. 3. Effect of brine split to evaporator on salt concentration and flow of RO feed (at 5% to electrolyser).

clear from the figure that the salt concentration decreases with a rate larger than that for the volume in L/d. From the figure feasible regions of operations can be identified which fall below the level of 8,000 ppm and 3347 L/d. Results imply that the fraction of brine sent to electrolyser should be more than 6%.

On the other hand, the model is tested to study the sensitivity of salt concentration of feed and the volumetric flows to RO unit to the change in brine split to evaporator at 5% brine fraction to electrolyser; results are shown in Fig. 3. The figure reveals that the salt concentration of RO feed increases sharply with decreasing the fraction of brine to evaporator. It is also obvious from results that at 5% fraction to electrolyser the brine split to evaporator should be more than 60% implying that less than this value no feasible regions for operation.

Fig. 4 shows study results obtained for testing the model to simulate the case of sea water desalination for a freshwater capacity of 2,000 L/d and salinity of water feed of 35,000 ppm. The study considers the impact of changing the brine split to electrolyser and evaporator on the salinity of the feed to the RO membrane unit.

The results show that the decrease rate of salinity decrease largely for lower brine split fractions to evaporator. On the other hand, for large split fractions to evaporator, the salinity of RO feed is almost constant. Feasible solutions can be observed from figure below the limit of 35,000 ppm of RO feed. This implies split fractions should be more than 35% in order to fulfil salinity limitations on RO feed.

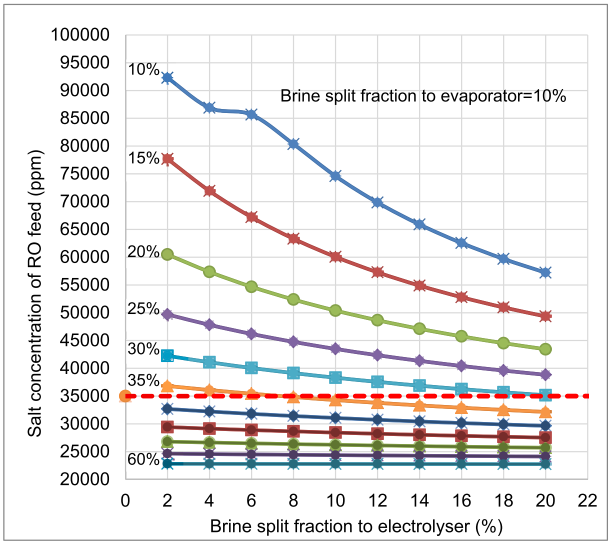

Fig. 4. Effect of brine split fraction to electrolyser on salt concentration of RO feed at different brine split fractions to evaporator (from 10 to 60%).

4. Conclusion

In the present work, a conceptual ZLD scheme has been proposed for brackish water desalination using RO membrane unit. The model considers splitting the brine reject from RO to electrolyser and evaporator. This results in relaxing the salt concentration of the recycle streams to RO unit. Model equations have been introduced covering the individual equipment in the ZLD scheme. Conceptual model can be used to analyse sensitivity of the scheme performance with several parameters in the operation. The model is tested for a small scale RO system of producing 2,000 Litres-per-day of fresh water from brackish water of 8,000 ppm salt concentration. The RO recovery was 60%. The model results resulted in reducing the brackish water withdrawn from the well from 3,347 L/d to 2,108 L/d with a reduction of 37%. The capital cost and operation expenses required were 533,028 EGP and 2,587,915 EGP/y. The annual profit generated were the selling price of 2,000 L/d fresh water, resulting in 2,190,000 EGP.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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