Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2021.27481

231 (2021) 101–112
August

Experimental analysis of hybrid electrodialysis (ED)-reverse electrodialysis (RED) process for the desalination of brackish waters and generation of renewable energy in a pilot scale

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Received 21 November 2020; Accepted 2 June 2021

ABSTRACT

In this study, the possibility of preparing fresh water through environmental friendly process of hybrid electrodialysis (ED)-reverse electrodialysis (RED) has been investigated. Therefore, the process performance has been evaluated with regard to both desalination and energy generation. Besides, the process has been modeled with real and synthetic concentrated brine with high salinity of up to 200,000 ppm from Persian Gulf seawater and synthetic and real brackish water with the salinity of up to 7,240 ppm from rivers in Bushehr province, Iran. Results demonstrated that the RED system was capable of generating the energy needed to desalinate brackish water with the salinity of less than 1,000 ppm, while for higher salinities, an extra amount of electrical energy is required. It was also revealed that the best desalination performance (salt removal percentage) for brackish water with initial concentration of 1,000; 2,000 and 4,000 ppm was 42%, 53% and 52%, respectively. Moreover, due to high level of salinity along with the presence of a variety of minerals in river waters, the rate of electricity production and desalination was less than that of the synthetic water samples on a pilot scale; for example, for the Mond River with an initial salinity of 2,690 ppm, the salinity reduction was around 27.17%.

Keywords: Electrolysis; Reverse electrodialysis; Desalination; Brackish water; Renewable energy

1. Introduction

Nowadays, population growth and per capita global demand for fresh water, droughts arising from global changes, and the growing need for water in industry and agriculture highlight the importance of dealing with water crisis. Ground waters and low-salinity rivers (brackish waters) are among the main sources of drinking water around the world, which are required to be desalinated to meet predetermined drinking water standards. In this respect, various desalination processes have been developed so far to obtain fresh water from saline resources of water such as seawater and brackish water [1]. These processes are divided into two main categories including thermal and membrane methods. For the thermal methods, multi-stage distillation, multi-stage flash distillation and vapor condensation can be typically exemplified, and reverse osmosis, electrodialysis (ED), and membrane distillation are some examples of membrane methods. Different desalination processes have their own advantages and disadvantages, and determining factors such as economy, environmental impacts, energy requirements, and feed water quality should be taken into account in order to choose the most appropriate method. ED is a membrane separation process, which is prevalently used for the desalination of brackish

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1944-3994/1944-3986

water. In this process, the difference in electrical potential works as the driving force to transfer ions, leading to the passage of ions through the ion-exchange membranes [2].

From the energy perspective, social, environmental and economic challenges in the energy sector have directed the attention of many scientists to innovative sources of renewable energy [3–6]. In this respect, Patel et al. [5] measured the energy consumption associated with the brackish water desalination through ED and reverse osmosis processes. They assessed the effects of changing feed salinity over salt removal, water recovery, and productivity to eventually identify the operational sweet spots of each technology. Accordingly, the best performance was observed for ED in low level of feed salinity (<3 g L^{-1}). They also perceived that increased employment of ED process demands considerable reduction in the expenses related to the ion-exchange membranes.

Electricity generation deriving from the difference in salinity of river and sea water has long been presented as a renewable power generation technique. By way of illustration, reverse electrodialysis (RED) is an alluring choice to be used for the energy generation, which is in fact the opposite of ED in terms of ion transformation. In 1954, Pattle [7] proposed the theory of electricity production based on the difference in salt concentration between the river and sea waters as a renewable energy source, and used ion-exchange membranes to generate electricity using RED. In recent years, some efforts have been made to design RED membranes, which have shown the potential for the development of ion-exchange membranes to produce energy economically. These studies have focused on examining the electrochemical and physical properties of ion-exchange membranes, which can directly affect the RED performance. Even though in the mentioned studies, the key features of membranes have been pointed out, further analyses regarding physical and electrochemical properties of membranes are still required. In the latest studies dealing with such processes, Karimi et al. [8] examined the efficiency of an ED process and modeled the effects of voltage and velocity through power functions and temperature through Arrhenius function. In another study, Doornbusch et al. [9] analyzed the performance of a multi-stage ED system for desalination. They used a four-stage system whereby it was feasible to desalinate synthetic saline water with an energy consumption of around 3.6 kWh/m^3 of water.

In recent years, researchers have seriously been working on finding optimal operating conditions to maximize the energy production and desalination rate simultaneously. They have also dealt with building appropriate and cost-effective ion-exchange membranes, utilizing the produced energy in the desalination process, as well as generating renewable electrical energy using the difference in salinity of sea and river waters. In this regard Veerman et al. [10] investigated the electricity generation through an RED system on a pilot scale where river water and seawater with the salinity of 1 and 30 g/L, correspondingly, were used as the feed water. They used platinum-reinforced titanium electrodes to examine the counter-current and co-current ED processes, realizing that the efficiency of the co-current process was greater than that of counter-current one. By combining the two processes of ED and RED, Chen et al. [11] could provide an efficient solution for preparing drinking water from brackish waters, especially in rural areas of small islands. The prominent feature of their study was that the utilized system was self-sufficient in energy while using the least number of external apparatuses, making the whole process cost-effective. The system was comprised of a pair of RED cells generating electricity, and ED pairs caring out water desalination, all integrated in a stack. Weiner and McGovern [12] also examined the effect of feed flow rate, residence time, and potential difference on the amount of energy produced in the RED process, and accurately estimated the costs associated with the electricity production. The results showed that by optimizing the operating conditions, costs could be lowered by up to 40% although the RED was basically more expensive relative to other conventional processes due to the high costs involved in membrane fabrication. In a review paper prepared by Hong et al. [13] there were some studies conducted into novel membrane fabrication and evaluation of cationic and anionic commercial membranes in the ED and RED processes. Accordingly, some of the most important evaluating parameters were mechanical, thermal and chemical stability, type and amount of transferring, costs, etc. Tedesco et al. [14] examined the impacts of different membranes, chamber sizes, and operating conditions on the RED performance where two RED units with different sizes were applied. Results showed that increasing the flow rate could increase the power output, while lowering the flow rates could boost the efficiency. They also realized that by regulating the feed temperature to below 40°C, the unit performance improved. Their team also built the first pilot plant of the RED in southern Italy using natural feed stocks (e.g., brackish water and salty water) [15]. The ion-exchange membranes had a surface area of about 50 m^2 (125 cell pairs, 44 cm^2), which was tested for 5 months using natural and synthetic feed solutions. Accordingly, using real brackish water samples, the output power was obtained to be around 40 W, whereas this was around 65 W for the synthetic feed sample (i.e., 0.03 M and 4–5 M NaCl solutions). The difference in the obtained output power reflects the presence of other ions such as Mg^{2+} in the water, which contributed to a reduction in energy production.

Clogging and sedimentation of membranes are also important issues in this area, which should necessarily be dealt with, as they may cause a significant reduction in the power density. Numerous studies have been performed regarding this issue so far. To illustrate, Vermaas et al. [16] proposed periodic replacement of feed water (e.g., changing the seawater sample instead of the river water and vice versa, as the feed water). This maintains a high power density in the early hours of the process owing to the removal of polyvalent ions and sediments of organic matter. However, with the passage of time, colloidal deposition starts to form, which is not completely reversible. To address this problem, they used a compressor by which pressurized air was injected periodically every 30 min for 30 s under the pressure of 1 bar. They could significantly prevent sedimentation and reduction of the power density. Chen et al. [11] coupled the ED and RED processes to develop a primary method by which drinking water could be prepared from brackish water with a salinity of 1,000 ppm. The proposed system did not require external input power, providing an energy self-sufficient process using minimum number of additional accessories. The generating chamber consisted of 11 pairs of RED cells and 4 pairs of ED cells. The reason for choosing more cells in the RED unit was to provide the required energy for desalination to the desired level in the ED unit.

Likewise, in another study carried out by Luo et al. [17] ED and RED processes were combined to desalinate brackish water, yielding encouraging results. To supply the electrical energy, the electricity generated by RED was connected to both ends of the ED stack via a wire. First, the performance of each of the two processes was examined separately. Next, the coupled process was evaluated for both continuous and batch ED processes. Accordingly, in the optimal operating conditions and discontinuous state, the salinity of 250 mL of water sample with an initial concentration of 9,000 µs/cm reached below 100 µs/cm after 200 min of operation.

Gurreri et al. [18] numerically modeled an RED cell using Navier–Stokes and continuity equations, giving better results in comparison with laboratory results. Also, Olkis et al. [19] used a new RED-desalination system with surface adsorption to generate electricity from wasted energy and exergy efficiency of 44.6% was observed. Hu et al. [20] revealed that the performance of the counter-current RED system was superior to co-current one. They also stated that the effect of increasing feed salinity was greater than that of increasing feed flow rate.

The results of research by Choi et al. [21] demonstrated that the integrated process of RED and reverse osmosis was economically effective for the treatment of seawater with high salinity (such as Persian Gulf water) relative to the two-stage reverse osmosis process. In addition, in 2019 and 2020, some research has been undertaken into the exergy of the RED process to optimize the production of electrical energy as well as numerical modeling of the process. However, further studies are still needed to optimize the operating conditions, and thereby reducing the electrical resistance of the system, specifically on pilot scales [18,22–25].

However, there is no comprehensive research in the literature dealing with the integrated ED-RED system. Specifically, the mathematical modeling of ED-RED system with the purpose of identifying the effect of feed salinity over the energy efficiency and desalination rate with commercial membranes on a pilot scale is still lacking in the literature. Therefore, in this study, by selecting brackish water samples (TDS of up to 4,000 ppm) and brine samples (TDS of up to 200,000 ppm), performance of hybrid ED-RED system has extensively been evaluated. Besides, the process has been modeled to measure open circuit voltage, internal resistance, power density and membrane perm-selectivity by changing the salt concentration and feed flow rate with commercial membranes on a pilot scale. In other words, the novelty of this research is the intensive study of combined ED-RED process on a pilot scale to gain a deeper insight into the effects of various operating parameters over the desalination rate and energy production with the use of synthetic brackish and saline waters as well as real sea and river waters using Fujifilm commercial membrane (The Netherlands). Therefore, the purpose of this article is to answer the following questions:

- What are the most effective operating parameters among open circuit voltage, internal resistance, power density and membrane perm-selectivity?
- What are the most important resistances of the system and their values?
- What is the amount of energy produced and the quality of desalinated water using saline and brackish waters with different concentrations on a pilot scale?

2. Materials and methods

The governing relations and equations in the study of integrated ED and RED systems are defined as follows. To compare the flow rates of brackish water and concentrated brine streams and compare them with that of other studies, it is necessary to express them in linear velocity. The calculation of the linear velocity is in accordance with Eq. (1) [26]:

$$V = \frac{Q}{N \cdot \delta \cdot b \cdot \varepsilon} \tag{1}$$

where Q is the volumetric flow rate (mL/min), δ is the spacer thickness, N is the number of cells, b is the spacer width, ε is the spacer porosity.

The amount of open circuit voltage that can be obtained from the RED system can be calculated from the Nernst relation as follows [27]:

$$\text{OCV} = N\frac{2\alpha RT}{ZF}\ln\left(\frac{a_c}{a_d}\right) \tag{2}$$

where N is the number of cells, α is the apparent perm-selectivity of the membrane, Z is the ion exchange capacity (equal to 1 for NaCl salt), R is the gas constant (8.814 J/mol K), T is the absolute temperature (K), F is the Faraday constant (96,485 C mol^{-1}), a_c is the activity (mol/L) of concentrated brine and a_d is the activity of dilute saline. Assuming $\alpha = 1$ and NaCl solution (monovalent), the Nernst equation is written as Eq. (3) [15]:

$$\text{OCV} = N\frac{2RT}{F}\ln\left(\frac{\gamma_c m_c}{\gamma_d m_d}\right) \tag{3}$$

In the above equation, γ is the mean ionic activity coefficient and m is the molal concentration of solution. Regarding the fact that the concentration of water-soluble salt is high, the activity cannot be assumed one, so for each concentration, the activity is calculated using the Pitzer equation (Eq. (4)), according to literature [27,28].

$$\ln\gamma_{\pm}^{(m)} = \left|z_+ z_-\right| f^{\gamma} + m\left(\frac{2v_+ v_-}{v}\right)B_{\text{MX}}^{\gamma} + m^2\left[\frac{2\left(v_+ v_+\right)^{3/2}}{v}\right]C_{\text{MX}}^{\gamma} \tag{4}$$

The related variables are defined as follows:

$$f^{\gamma} = -A_{\varphi}\left[\frac{I^{1/2}}{1+bI^{1/2}} + \frac{2}{b}\ln\left(1+bI^{1/2}\right)\right] \tag{5}$$

$$B^{\gamma}_{\mathrm{MX}} = 2\beta^{(0)}_{\mathrm{MX}} + \frac{2\beta^{(1)}_{\mathrm{MX}}}{\alpha^2 I}\left[1-\left(1+\alpha I^{1/2}-\frac{\alpha^2}{2}\right)\exp\left(-\alpha I^{1/2}\right)\right] \tag{6}$$

$$C^{\gamma}_{\mathrm{MX}} = \frac{3}{2}C^{\varphi}_{\mathrm{MX}} \tag{7}$$

$$I = \frac{1}{2}\sum_i m_i Z_i^2 \tag{8}$$

$$v = v^{+} + v^{-} \tag{9}$$

where Z is the valency of ion (valency of both anion and cation is 1 for NaCl), v is the number of ions which is written as subscript in the chemical formula (for NaCL is 1 for both ions), m_i is the molality of species i (for solute ion), $A\varphi$ is the Debye–Hückel constant, which is 0.392 $\mathrm{kg}^{1/2}\,\mathrm{mol}^{-1/2}$ at atmospheric pressure and temperature of 25°C, b is equal to $\mathrm{kg}^{1/2}\,\mathrm{mol}^{-1/2}$, and for most electrolyte solutions including NaCl, α is equal to 2 $\mathrm{kg}^{1/2}\,\mathrm{mol}^{-1/2}$. The constants $^{0}\beta$, $^{1}\beta$ and $C\varphi$ are specific to the type of electrolyte solution. Here, Weber-modified constants are used for aqueous NaCl solution, which are 0.06743, 0.3301 and 0.00236, respectively.

The ratio between the experimental open circuit voltage and the theoretical one is called the apparent membrane perm-selectivity ($\bar{\alpha}$) as shown in Eq. (10) [29,30].

$$\bar{\alpha} = \frac{\mathrm{OCV}^{\mathrm{experimental}}}{\mathrm{OCV}^{\mathrm{theoretical}}} \tag{10}$$

The internal resistance of the RED system can be expressed as Eq. (5) [31].

$$R_{\mathrm{in}} = \frac{N}{A}\left(R_{\mathrm{ohmic}} + R_{\Delta\mathrm{C}} + R_{\mathrm{BL}}\right) \tag{11}$$

where R_{ohmic} includes the resistance of cationic and anionic membranes, the resistance of the brine and brackish channels and the resistance of the electrodes, which are collectively equivalent to the resistance of a cell. $R_{\Delta\mathrm{C}}$ is the resistance arising from the reduction of driving force as a result of the change in the concentration of the solution bulk. R_{BL} is the resistance of the boundary layer due to the concentration polarization arising from penetration into the boundary layer close to the membrane surface, particularly at relatively low flow rates.

Eq. (6) can be used to calculate the internal resistance of the RED system. The required data are obtained through OCV measurement test, the measured voltage in the presence of external resistance and the amount of external resistance [13,32,33].

$$R_{\mathrm{in}} = \frac{\mathrm{OCV} - V}{V} \times R_{\mathrm{out}} \tag{12}$$

where R_{in} (Ω) and R_{out} are internal and external resistance, respectively, OCV (V) is the open circuit voltage and V is voltage in the presence of external resistance.

According to Kirchhoff's law, the output power (watts) of the RED chamber is measured through Eq. (13) [34].

$$P = I^2 R_{\mathrm{out}} = \frac{\mathrm{OCV}^2 R_{\mathrm{out}}}{\left(R_{\mathrm{in}} + R_{\mathrm{out}}\right)^2} \tag{13}$$

The output power is a function of the total resistance of the chamber R_{in} (Ω) and the external resistance R_{out}, so the output power (W) reaches its maximum when these two are equal, which is given as Eq. (14):

$$P_{\max} = \frac{\mathrm{OCV}^2}{4R_{\mathrm{in}}} \tag{14}$$

If the power density is defined as the output power per unit area of the membrane surface, the maximum power density P_d (W m^{-2}) is calculated as Eq. (15).

$$P_d = \frac{\mathrm{OCV}^2}{4AR_{\mathrm{in}}} \tag{15}$$

where A is the effective membrane surface area (m^2).

In order to assess the performance of the ED-RED system at different concentrations of brine and brackish water, first the experiments are performed with synthetic concentrated brine and brackish water and the results are analyzed using the presented equations. Then, in the best operating conditions of the pilot system, two real samples including brackish water of rivers in Bushehr province of Iran and sea water of the Persian Gulf are examined in order to evaluate the pilot performance in terms of desalination and renewable energy generation.

To build the integrated ED-RED system including 11 cells in RED and 1 cell in ED, different types of valves, fittings, pressure gauges, flow meters, various diaphragm pumps, 25 anionic and cationic membranes with effective surface area of each membrane equal to 918 cm^2 (Type 2 from FUJIFILM company, The Netherlands) with electrodes made up of 316 stainless steel, spacer, 100-L polyethylene tanks, PVC pilot body, electrolyte liquid glass tank, direct power supply are used. According to the required capacity, two pumps with a maximum flow and pressure of 4 L per minute and 130 psi, respectively, for brine, and two pumps (model KJ-4000 made by KOJINE company of Taiwan) with a flow and a maximum pressure of 1.6 L/min and 130 psi, correspondingly, for brackish water are used. Also, according to different flow inputs, Fischer brand flowmeters are utilized to determine the amount of fluid entering the integrated ED-RED system. In addition, to determine the inlet and outlet pressure of the system and calculate the pressure drop due to fluid passage in the system, pressure gauges made by Nuova Fima, (Italy) company with a maximum pressure of 140 psi are used. Due to the use of brine, and consequently corrosion, corrosion-resistant paint and 20 mm thick PVC coatings are applied. In order to use the pilot for the real river and Persian Gulf water samples, activated carbon and microfiltration filters are used to remove sludge and bacteria, correspondingly. Fig. 1 and Table 1 present specification of the pilot plant of ED-RED. Also, Fig. 2 illustrates the process flow diagram of ED-RED process.

Conductivity of saline solutions entering and leaving the system is estimated using the electrical conductivity measuring device made by WTW company, inoLab Multi 9620 IDS model.

After preparing the brine and brackish water tanks with a certain concentration, the inlet and outlet pipes as well as the auxiliary energy generating device, which also shows


Fig. 1. Integrated system of ED-RED on pilot scale.

the voltage and amperes, are connected to the system. After turning on the inlet feed pumps, the fluid flow rate is set to its specified value. It should be noted that the system reaches a steady-state condition after around 20 min, and therefore the data are measured after the stability of the system. Due to the use of 0.5 M NaCl solution as the electrolyte liquid and inexpensive stainless steel electrodes to simulate the industrial conditions and reduce the costs, in addition to the electrical energy generated in the system, a supplementary voltage is provided to complete the electrical power required. According to literature, to conduct the experiments, for the brine, the flow rate is set at 100 L/h (equal to the linear velocity of 4 cm/s), and for the brackish water, it is set at a flow rate of 3.1 L/h (equivalent to the linear velocity of 0.1 cm/s) [15,16,17,18]. Three salinity levels of 1,000; 2,000 and 4,000 ppm are chosen for the synthetic brackish samples, while for the brine samples, the same levels, but with salinity ratios (the salinity of brackish water to brine) of 1 to 15, 1 to 30 and 1 to 50 are selected to be examined. Three different levels including 3, 5 and 7 V are considered for the auxiliary voltage (external driving force) and tested for every level and ratio of salinity.

The external driving force is applied by the generator to both ends of the stack. Here, for each pair of RED cells, the applied voltage is as follows:

- 3 V:0.272 V/cell pair
- 5 V:0.454 V/cell pair
- 7 V:0.636 V/cell pair

Since experimental errors are inherent part of the pilot-scale research, the experiments were repeated twice. The uncertainty analysis was performed and the whole

Table 1
Layout and material of membrane components of ED-RED system in pilot scale

Size (number)	Component
Number of ionic membranes	25 Type 2 from FUJIFILM company (The Netherlands)
Thickness of membranes	160 micrometer
Type	Homogenous
Perm-selectivity of membranes (Perm-selectivity measured at 0.05–0.5 M NaCl)	96%
Water permeation of membranes	3 for AEM and 3.5 for CEM (mL/bar m^2 h)
Electrical resistance in 2 M NaCl	6.1 for CEM and 3.5 for AEM
Electrode size	30 × 36 cm^2
Number of spacer	24
Thickness of spacer	0.3 mm
Porosity of spacer	85%
Size of each membrane (inner section)	30 × 36 cm^2
Size of each membrane (outer section)	40 × 46 cm^2
Effective area of each membrane	918 cm^2
Overall size of the system	50 × 56 cm^2
Brine flow rate	100 L h^{-1}
Brackish water flow rate	3.1 L h^{-1}
Brine linear velocity	4 cm s^{-1}
Brackish water linear velocity	0.1 cm s^{-1}
Temperature	30°C

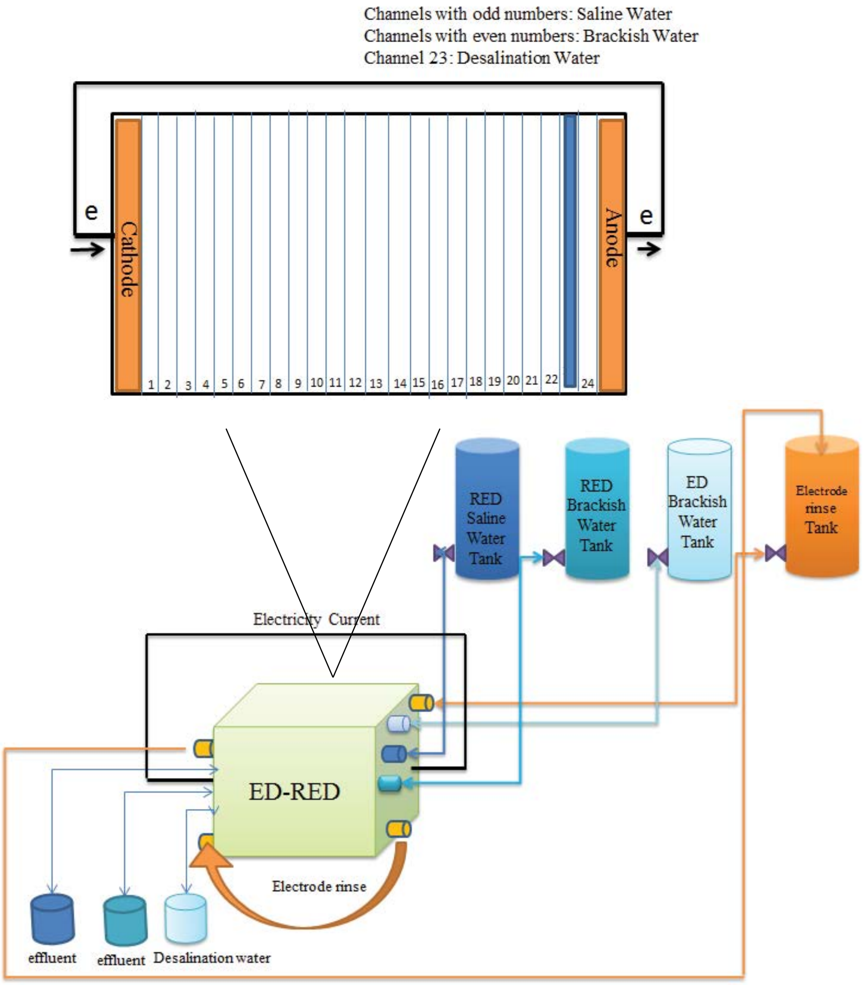

Fig. 2. Process flow diagram of ED-RED process.

experimental data were plotted with 95% confidence intervals.

Table 2 shows the design of experiments performed at the pilot scale.

3. Results and discussion

3.1. Desalination and energy production through synthetic brackish and brine

Fig. 3a represents the desalination performance of the ED-RED system on a pilot scale for the brackish water with the salinity of 1,000 ppm and brine with the salinity of 15,000–50,000 ppm. The best desalination performance is observed at the voltage of 7 V (0.636 V/cell pair), giving the minimum salt concentration of 587 ppm in the outlet, which is equivalent to 42% salt removal.

In fact, the system gives the highest salt removal percentage for the brackish water with minimum salinity of 1,000 ppm under the maximum driving force of 7 V (0.636 V/cell pair). This can be attributed to the higher driving force in the cell side of the ED, which contributes to higher salt removal percentage. Besides, since the concentration difference for 1,000 ppm (brackish) and 50,000 ppm (brine) is higher than other cases, the highest amount of electrical energy is produced in RED, which is subsequently transferred to ED system to perform the desalination. Indeed, by increasing the salinity of brine from 15,000 to 50,000 ppm, due to the increase in the energy production, the salinity of brackish water (1,000 ppm) lowers from 883 to 587 ppm. Thus, it can generally be concluded that increasing either salinity or applied voltage exerts a positive effect over desalination performance. By increasing the voltage, the driving force at both ends of the system increases, accelerating transformation of ions. In addition, increasing the salinity lowers the resistance of the system, and consequently the presence of more ions in the boundary layer to be transferred through the membrane. These results are in agreement with those reported by Chen et al. [11] and Liu et al. [17] for desalination of brackish water with the salinity of around 1,000 ppm through ED system.

Fig. 3b shows the desalination performance of the ED-RED system on a pilot scale for brackish water with the salinity of 2,000 ppm and brine with variable salinity of 30,000 to 100,000 ppm. As expected from the results corresponding to the 1,000 ppm brackish water similarly

Table 2
Design of experiments of the ED-RED system

No. of experiment	Brackish water concentration (ppm)	Brine concentration	Auxiliary voltage	Ratio
1	1,000	15,000	3	1 to15
2	1,000	15,000	5	1 to15
3	1,000	15,000	7	1 to15
4	1,000	30,000	3	1 to 30
5	1,000	30,000	5	1 to 30
6	1,000	30,000	7	1 to 30
7	1,000	50,000	3	1 to 50
8	1,000	50,000	5	1 to 50
9	1,000	50,000	7	1 to 50
10	2,000	30,000	3	1 to15
11	2,000	30,000	5	1 to15
12	2,000	30,000	7	1 to15
13	2,000	60,000	3	1 to 30
14	2,000	60,000	5	1 to 30
15	2,000	60,000	7	1 to 30
16	2,000	100,000	3	1 to 50
17	2,000	100,000	5	1 to 50
18	2,000	100,000	7	1 to 50
19	4,000	60,000	3	1 to 15
20	4,000	60,000	5	1 to 15
21	4,000	60,000	7	1 to 15
22	4,000	120,000	3	1 to 30
23	4,000	120,000	5	1 to 30
24	4,000	120,000	7	1 to 30
25	4,000	200,000	3	1 to 50
26	4,000	200,000	5	1 to 50
27	4,000	200,000	7	1 to 50

in this case, increasing either salt concentration or voltage leads to an increase in desalination. Here, the best concentration of desalinated water is 948 ppm, meaning salt removal percentage of 53%, which is around 11% higher than that of 1,000 ppm brackish water. The main reason for this improvement is the higher concentration of salt in all channels of the system, both brackish and brine channels, which contributes to a decrease in electrical resistance, and thereby increasing the current intensity.

The desalination performance of the system for brackish water with the salinity of 4,000 ppm and brine with the salinity of 60,000–200,000 ppm is represented in Fig. 3c. It can be seen that the trend of variation is similar to what is observed for the 1,000 and 2,000 ppm brackish water. The maximum reduction in salt concentration is around 1,950 ppm obtaining at the brine concentration of 200,000 ppm. Indeed, the maximum obtainable removal percentage is about 52%, which is comparable with that obtained at 2,000 ppm brackish water (i.e., 53%). However, it should be noted that in terms of the amount of removal, it is nearly twice that of 2,000 ppm concentration; that is, here 2,050 ppm of salt is removed from the water, while in the previous part this amount was equivalent to 1,052 ppm. As aforementioned, the improvement of the desalination for higher brine concentrations can most presumably be attributed to the lower resistance of the system, and thus higher ion transportation. Another observation is that in all the three applied voltages, there is no substantial difference in desalination performance between the brine concentrations of 120,000–200,000 ppm. As a matter of fact, regarding the increase in the concentration of salt, and subsequently the number of ions in the system, the concentration polarization can probably occur in the vicinity of the membrane, which leads to a decrease in ion exchange capacity compared with the ideal state [17,18,20,21].

3.2. Modeling of the reverse ED-RED system

3.2.1. Generating voltage of the system

In order to evaluate the performance and efficiency of the desalination process, the generated voltage for different set of brackish and brine concentration is calculated as listed in Table 3. It should be noted that it is presumed that the generating voltage of the system is the only driving force (i.e., no auxiliary voltage or extra input power is taken into account) for the desalination of the brackish water.

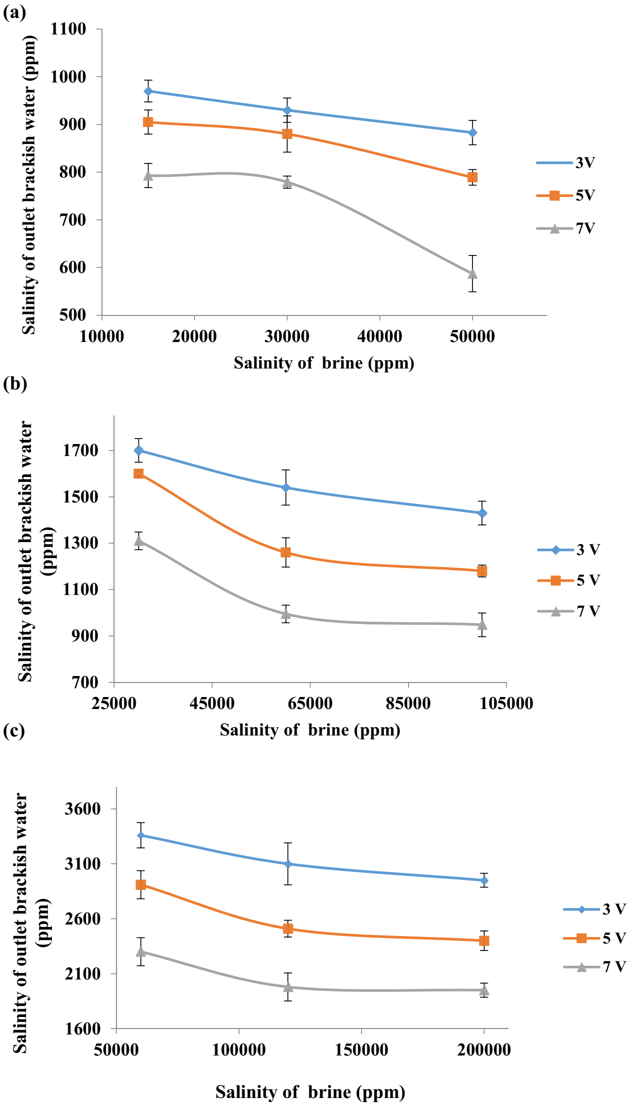

Fig. 3. Desalination performance of ED-RED process for (a) the brackish water with the salinity of 1,000 ppm, (b) the brackish water with the salinity of 2,000 ppm and (c) the brackish water with the salinity of 4,000 ppm.

Table 3
Generating voltage of the system in a pilot scale for different concentrations of brackish water and brine

Concentration of brackish water and brine (ppm)	Generated voltage of the system (V)
1,000–15,000	1.2
1,000–30,000	1.41
1,000–50,000	1.78
2,000–30,000	1.19
2,000–60,000	1.45
2,000–100,000	1.62
4,000–60,000	1.14
4,000–120,000	1.42
4,000–200,000	1.68

According to the Nernst equation, the output voltage is directly related to the number of cells in the RED system and the concentration gradient between brine and brackish water. As a result, increasing the dimensions of system has no effect on voltage generation, instead it increases the fluid input flow, and also affects its resistance. If it is aimed at producing the 7 V (0.636 V/cell pair) of voltage needed for the desalination of the brackish water only in the RED system with the same dimensions, the number of cells is required to be increased, which is theoretically calculated based on the concentration and using Nernst equation (Table 4).

It is observed that the number of cells in the same salinity ratios is almost equal to each other because the ratio is used in the Nernst equation. Besides, the Debye-Hückel equation is used to calculate the activity of the solutions. It must be noted that Table 4 dose not assume a constant perm-selectivity for the whole range of salinities and it is measured using Eqs. (3)–(10).

3.2.2. Open circuit voltage in the RED system

Fig. 4 shows the generated open-circuit voltage vs. different concentrations of the input feed in the RED system.

Table 4
Number of required cells for different set of brackish water and brine concentrations

Concentration of brackish water and brine (ppm)	Number of required cells in RED
1,000–15,000	55
1,000–30,000	44
1,000–50,000	38
2,000–30,000	55
2,000–60,000	44
2,000–100,000	38
4,000–60,000	55
4,000–120,000	43
4,000–200,000	36

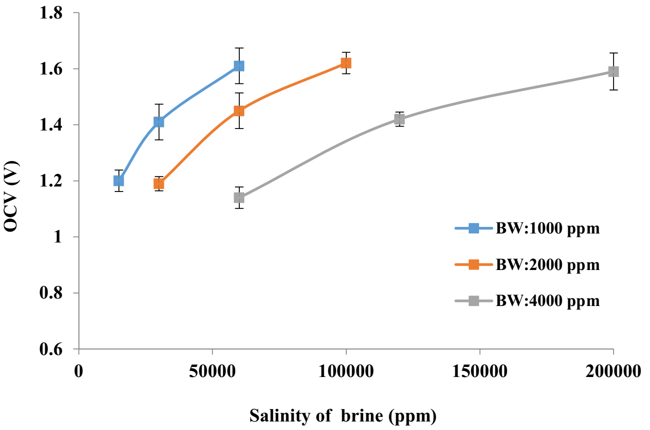

Fig. 4. Open circuit voltage of the RED system vs. concentration of input brine.

It is discernible that by increasing the concentration gradient between the brackish water and brine, the output voltage increases, which is in agreement with Nernst theory. Another observation is that in equal ratios, the output voltage of the 4,000-ppm brackish water sample is slightly lower than that of other levels (i.e., 1,000 and 2,000). This can most likely be ascribed to the relatively high concentration of ions, specifically in the brine channels, and consequently concentration polarization, interference in ion transportation and reduction of perm-selectivity for the 4,000-ppm sample. However, it should be taken into account that the effect of this factor is dependent on the membrane material as well as the type of ions, and thus for each specific case, a certain result is obtained, which cannot be generalized for other conditions.

3.2.3. Evaluation of apparent membrane perm-selectivity in different concentrations of brine and brackish water

Fig. 5 represents the results of apparent membrane perm-selectivity at three levels of brackish water concentration. It is seen that the permeability for the 1,000-ppm brackish water sample is higher than 2,000- and 4,000-ppm ones. Besides, for all the three samples, increasing the brine channel concentration leads to a decrease in permeability. In general, experiments reveal that membrane perm-selectivity decreases with increasing the concentration in both brine and brackish water channels. If the concentration gradient between these channels is large, due to the higher chemical potential and ion density on the brine channel side, membrane clogging can occur, which negatively affects the perm-selectivity of membrane. In addition, the input water flux can directly affect the permeability; thinner membrane provides higher water flux. Also, it has a direct effect on reducing infiltration; the thinner the membrane, the higher the flow rate. Nevertheless, it should be mentioned that to decrease the water flux, the thickness of membrane cannot be increased greatly because it increases the resistance of the system, and thereby exerting an adverse effect over the power generation.

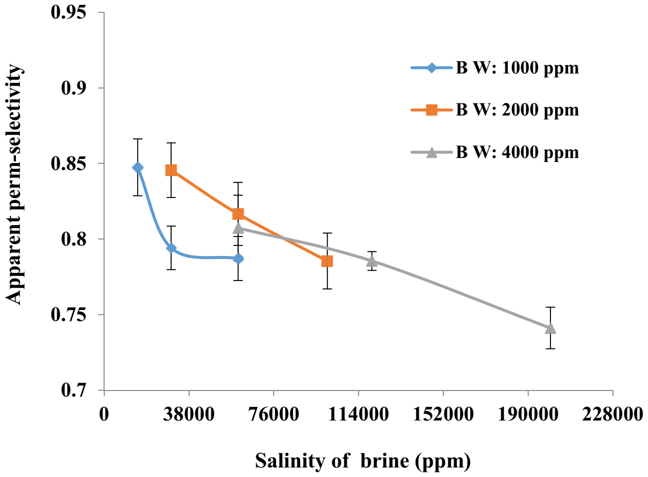

Fig. 5. Apparent perm-selectivity of membrane in the RED system vs. input feed concentration.

3.2.4. Evaluation of internal resistance of the RED system at different concentrations of brackish water and brine

To measure the internal resistance of the RED system, at each given concentration and flow rate, the internal resistance is calculated four times, and the mean internal resistance is reported. Fig. 6 illustrates the internal resistance of the RED system based on the input feed concentration. As mentioned previously, the resistance of the whole system is in fact the sum of ohmic resistance, the resistance arising from the change in the concentration of the solution bulk, and the resistance of the boundary layer. It can be seen that as the concentration of feed increases, due to the increase in the number of ions, the water conductivity increases, and subsequently the resistance to flow declines, thus the internal resistance of the whole system decreases. This negative correlation is obviously observed for the brackish water concentration of 1,000 and 2,000 ppm, while for 4,000 ppm, the internal resistance is higher at 200,000 ppm of brine relative to 120,000 ppm. This result can be explained by the occurrence of concentration polarization at high levels of feed water concentration, and consequently the resistance in the boundary layer against the mass transfer of ions.

Another observation is that although the salt concentration at the level of 2,000–100,000 ppm is collectively greater than that of 4,000–60,000 ppm, the internal resistance of the system is lower in the latter case. This is mainly because of the pronounced effects of brackish water concentration on the total ohmic resistance of the system, which have also been confirmed by other researchers [1,16]. As a result, since the brackish water concentration in the second case (4,000–60,000 ppm) is twice as much as the first one (2,000–100,000 ppm), its effect on lowering the resistance is much powerful than the effect of higher brine concentration.

3.2.5. Evaluation of power density of RED system at different concentrations of brackish water and brine

Fig. 7 depicts the variation of power density for the RED system at different concentrations of the input feed. As aforementioned, the power density depends on both

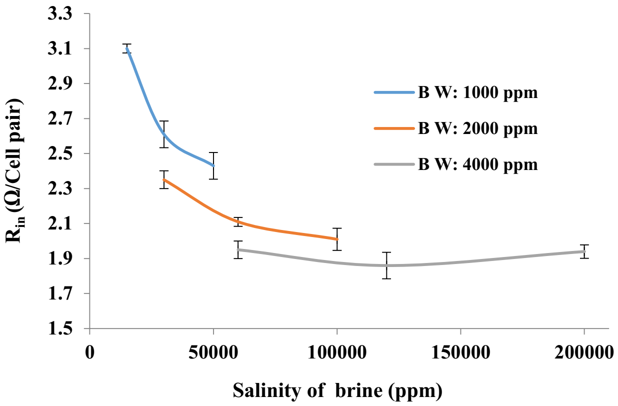

Fig. 6. Internal resistance of RED system vs. input feed concentration at fixed flow rate.

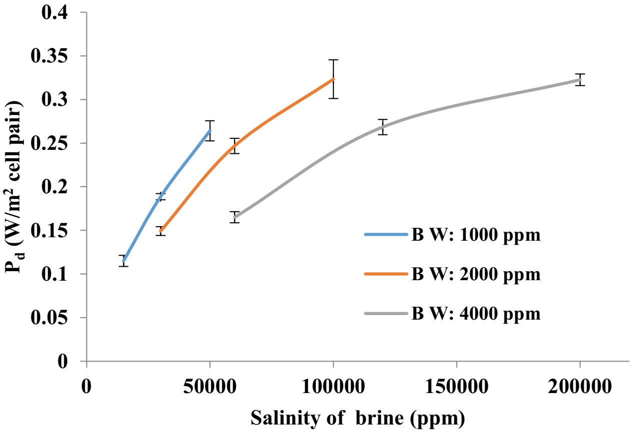

Fig. 7. Power density of RED system vs. input feed concentration at a fixed flow rate.

internal resistance and generated open circuit voltage of the output circuit. In fact, either higher output voltage or lower internal resistance results in higher power density in the system. As expected, the power density increases with increasing concentration gradient in the input feed. Although the ratio of feed concentrations (i.e., concentrations of brackish water and brine) in all three levels of brackish water is the same, the power density increases with an increase in brackish water concentration. As a matter of fact, the power density corresponding to 4,000 ppm brackish water is higher than 2,000 ppm, and that of 2,000 ppm is greater than 1,000 ppm. This is due to the lower internal resistance in higher levels of brackish water concentrations, leading to a higher power density at the same concentration difference.

It can also be seen that when the brackish water concentration increases from 2,000 to 4,000 ppm the power density does not alter noticeably in comparison with when it changes from 1,000 to 2,000 ppm. The reason for the slight change in power density in the two upper levels of brackish water is connected with concentration polarization occurring at 4,000 ppm, which increases the internal resistance.

3.2.6. Generated current intensity at different conditions of the RED systems

Wherever there is a discussion of electrical resistance and voltage, current intensity is also of paramount importance. Actually, as the resistance decreases at a constant voltage, the current intensity increases. Fig. 8 illustrates the variation of current intensity vs. voltage and brine concentration at three different levels of brackish water concentration. Accordingly, in general, increasing the voltage and salinity of water (reducing the resistance) increases the intensity of the current passing through the system, which agrees very well with what reported by other researchers such as Li et al. [26] and Tedesco et al. [15]. If the total salinity of the two channels is the same for two systems with different concentrations of brackish water, the passing currents are directly affected by the concentration of the brackish water. Therefore, in this case, a system with a higher brackish water concentration will have less resistance, and consequently higher current intensity.

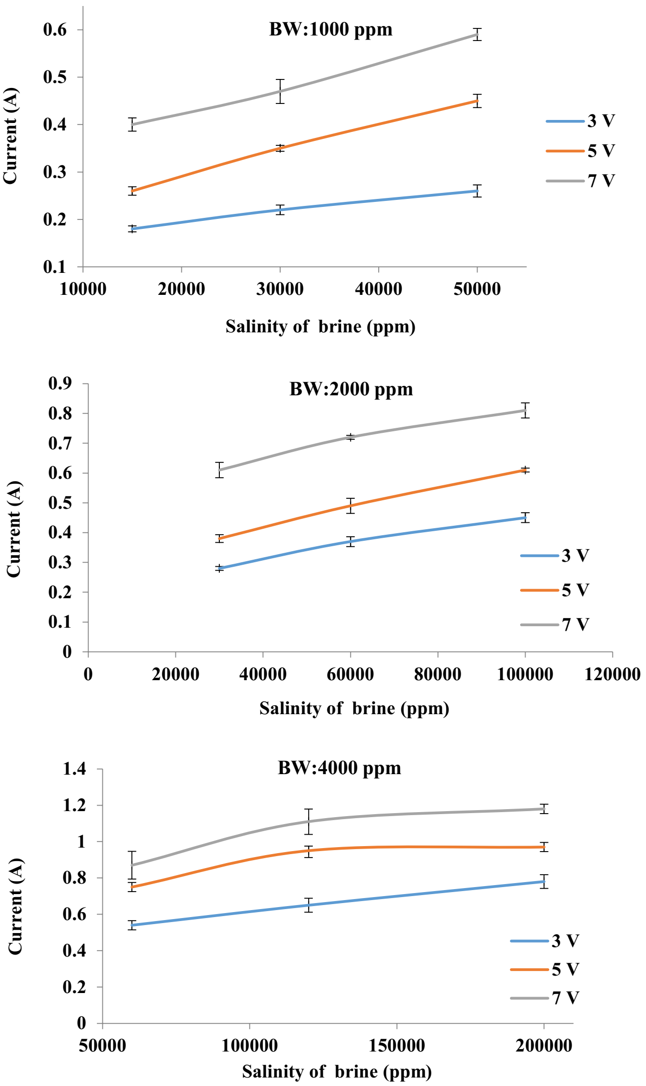

Fig. 8. Current intensity vs. voltage and brine concentration at three different levels of brackish water concentration on a pilot scale.

3.3. Performance evaluation of the ED-RED system in a pilot scale using real sea and river water samples

In this section, the water samples of Helleh and Mond rivers of Bushehr province are selected as the brackish water and the water of the Persian Gulf Sea is used as the concentrated brine. The salinity of river water is highly dependent on the season and seasonal rainfall. The waters tested in this project were sampled at a time (i.e., in the middle of fall) when the water had the highest amount of solutes near the river entrance to the sea. In fact, the purpose of the experiments is to evaluate the performance of the pilot-scale ED-RED system in the most severe operating conditions.

Due to the presence of mud in the natural samples of river and sea water, a pretreatment process is done prior to the entrance of the water sample to the ED-RED system. The following steps are carried out similar to what was performed for the synthetic feed. Initially, the salinity (TDS) of river and sea waters is measured, and then the experiments are performed at four voltage levels of 3 V (0.272 V/cell pair), 5 V (0.454 V/cell pair), 7 V (0.636 V/cell pair) and 9 V (0.816 V/cell pair) with the feed flow rate of 100 and 3.1 L/h for the RED and ED systems, correspondingly. Tables 5 and 6 show the results of the experiments for the brackish water of Mond and Helleh rivers, respectively, and using the Persian Gulf seawater.

According to the results, it is observed that the performance of the ED-RED system for the desalination of real river waters is not as good as that of synthetic brackish water. The best performance of the system for reducing salinity of Mond river with the initial salinity of 2,690 ppm is 27.17%, while for the synthetic feed with initial salinity of 2,000 ppm was around 53.00%. The first reason is that the ratio of brackish water to brine for the real sample is much lower than that of the synthetic sample. For example, this ratio is 1 to 5.11 and 1 to 13.7 for the Helleh and Mond rivers, respectively, which is much greater than 1 to 30 corresponding to the synthetic samples. In other words, for the real sample, the concentration gradient, which is the main driving force for the process, is not sufficiently high to give the same performance as the synthetic sample. The second reason is attributed to the presence of other salts including Ca, Mg and Si besides NaCl, which can increase the probability of membrane clogging, and thereby lowering the perm-selectivity as one of the main reasons of decrease in deionization of both ED and RED systems. This result has also been reported by Tedesco et al. [15] working on a pilot ED system in Italy. They understood that the output power and desalination performance of the real brackish water sample was around 40%–50% lower than that of synthetic feed (i.e., 0.03 M NaCl of brackish water and 4-5 M of the concentrated brine). It should be noted that in order to compare the real samples with synthetic ones, the concentration of brackish water channel should be importantly taken into account. As mentioned previously, a higher brackish water salinity contributes to a lower resistance, leading to an improved ion transport and current intensity. For the Helleh river, it is seen that the system has the ability to reduce the salinity below 2,000 ppm, which is suitable for irrigation and agriculture applications. In order to further desalinate the water of rivers to produce drinkable water, the difference in electrical potential of the RED system is needed to be improved, which can possibly be conducted by increasing the number of cells. Besides, using effluents of water desalination devices with high salinity can also be useful for increasing the electrical power of the RED system.

Table 5
Performance of desalination process using ED-RED system for brackish water of Mond river and seawater of Persian Gulf at different voltages

Item	Value
Initial salinity of the river water (ppm)	2,690
Initial salinity of seawater (ppm)	37,000
Salinity ratio of river water to seawater	1 to 13.7
Salinity of desalinated water at voltage of 3 V (ppm)	2,600
Salinity of desalinated water at voltage of 5 V (ppm)	2,510
Salinity of desalinated water at voltage of 7 V (ppm)	2,300
Salinity of desalinated water at voltage of 9 V (ppm)	1,959

Table 6
Performance of desalination process using ED-RED system for brackish water of Helleh river and seawater of Persian Gulf at different voltages

Item	Value
Initial salinity of the river water (ppm)	7,240
Initial salinity of seawater (ppm)	37,000
Salinity ratio of river water to seawater	1 to 5.11
Salinity of desalinated water at voltage of 3 V (ppm)	7,190
Salinity of desalinated water at voltage of 5 V (ppm)	7,093
Salinity of desalinated water at voltage of 7 V (ppm)	6,910
Salinity of desalinated water at voltage of 9 V (ppm)	6,734

To further enhance the system performance, complementary studies are required to be conducted in the future, specifically with regard to lowering the RED resistance by improving factors such as membrane type, spacer type, electrodes, thickness of spacer, flow direction and cell dimension. Moreover, evaluation of different methods of lowering the membrane clogging in ED-RED systems, employment of cascading systems for improving desalination and output power, as well as CFD modeling can be useful. Finally, performance measurement for integration of RED with other processes such as reverse osmosis and membrane distillation, as well as implementation of pretreatment and post treatment processes should be carried out to increase the energy production and reduce energy loss associated with pretreatment systems and pumps, and eventually boost salt removal percentage [35].

4. Conclusion

In this research, the performance of the RED-ED system on a pilot scale in terms of desalination percentage and energy production was evaluated. Results demonstrated that the RED system is capable of producing the energy required for desalination of brackish water with the salinity of less than 1,000 ppm, while for the salinity of higher than 4,000 ppm, extra input power was required.

In the best operating conditions, in terms of desalination, a decrease in the salinity of synthetic brackish water from 1,000 to 587 ppm was observed in the integrated RED-ED system. For the renewable energy production, when the salinity of brackish water decreased from 2,000 to 1,000 ppm, using the concentrated brine with salinity of 30,000 ppm, the energy production improved by 18.48%. In order to improve the desalination process and increase the electrical potential difference, the number of cells of the RED system should be increased, and also innovative membranes with lower resistance should be used.

Examining real water samples of Helleh and Mond rivers and sea water of the Persian Gulf revealed that both electricity production and desalination performance were weakened relative to synthetic samples due to the presence of various mineral salts and high salinity in the rivers of Bushehr province in summer. In fact, while the desalination percentage for the synthetic samples was around 53% with the initial brackish water salinity of 2,000 ppm, that of real samples of Mond river with the initial salinity of 2,660 ppm was about 27.17%. In the real cases, to improve the performance of the process, using auxiliary electricity, increasing the number of RED cells and serializing several ED units in a row can possibly be helpful. Another solution to increase energy production in the system is to use the brine effluent of reverse osmosis desalination plants, which can boost the performance due to having a salinity of about twice as much as seawater.

It should be noted that, to execute this project in an industrial scale, evaluating different treatment methods, recycling of ED-RED effluents, proposing solutions for the reduction or elimination of effluents to prevent environmental harms are all of vital importance.

Acknowledgment

The authors acknowledge the Water and Wastewater of Bushehr Province Company, Iran, for their financial support.

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