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Investigation and comparison of the physical models performance of energy extraction from salinity gradient (PRO and RED) in Arvand river estuary

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ABSTRACT

In recent years, scientists have considered the development and utilization of sustainable and environmentally friendly energy resources to replace fossil fuels. One of the newest topics of new energies is the extraction of energy from salinity gradients in seas and oceans. One of the practical methods of energy extraction from salinity gradient is reverse electrodialysis and delayed osmosis pressure. These methods result from mixing two types of water with different salinity concentrations, which are one of the best places to extract energy in the river estuary, where freshwater is naturally mixed with seawater. In this study, using physical parameters measured in 3 hydrometric stations located in Arvand River, achievable Gibbs energy and electrical energy from reverse electro dialysis method and delayed osmosis pressure as physical model setup were investigated. The amount of Gibbs energy obtained using delayed osmosis pressure method from data from three hydrometric stations in Arvand River shows that Khorramshahr station has the highest amount of extractable energy with 0.75 MJ. By calculating the voltage of two heads of each inverse electrodialysis cell in the three studied stations on the Arvand River, it was found that the highest potential difference with the amount of 80 mV was related to Khorramshahr station. Also, the efficiency of the two devices and the selection of the appropriate geographical location for its location were examined.

1. Introduction

With the rapid economic and industrial growth of countries in the world in recent decades and their increasing and comprehensive development, the use of fossil energy resources has increased dramatically. The limitation of fossil fuel resources, diversification of energy resources, sustainable development and energy security and environmental problems resulting from fossil energy consumption on the one hand, and the clean and renewable of new energy resources, on the other hand, have led to the world has paid serious attention to the development and expansion of the use of renewable energies and increasing its share in the world's energy basket. Salinity gradient power (SGP) is one of the renewable and extractable energies from the sea. This potential is mostly in freshwater rivers estuary. Patel first presented the concept of energy production through the mixing of salty and fresh water in 1954, and he mentioned the existence of this energy source [9]. In 2014, a comprehensive and thorough study was conducted at IRENA Institute to investigate the energy gradient energy of salinity and examined how energy extraction and power generation were evaluated when the river flows into the sea by delayed osmosis pressure and electrodialysis methods [11]. He believed that the membrane is the most important factor in both approaches to increase productivity. Sabet Ahd Jahromi et al. (2015) evaluated a physical model based on the reverse electrodialysis method of power density and energy efficiency [14]. In 2016, Emadi et al. investigated the energy potential for energy generation from the intrinsic water of Zarrinehrud River to Urmia Lake and compared energy extraction processes with RED and PRO methods [10]. May et al. (2018) investigated recent developments in energy extraction by reverse electrodialysis method and considered the use of Nano membranes to increase energy and flow effectively [15]. In 2019, Young et al. investigated water treatment before entering different concentration solutions using ultrafiltration and Nano filtration membranes and increased the reverse osmosis pressure device's efficiency [12]. Iran also has several rivers along the Persian Gulf coasts with a suitable position to access this energy source. Therefore, this study aimed to investigate the salinity gradient in the estuary of Arvand River leading to the Persian Gulf and its energy absorption method, which will eventually lead to a laboratory model for energy extraction from the salinity gradient.

2. Materials and methods

2.1. Salinity gradient power (SGP)

Salinity gradient power is one of the renewable and extractable energies from the sea. This potential is mostly in freshwater rivers estuary. As shown in Figure 1, instead of direct discharge of river water into the sea, a cycle of energy generation is used by the salinity gradient's power process on its way, and electrical energy is extracted. The SGP method is based on spontaneous processes and membrane techniques. The automatic process is a kind of reaction carried out without receiving energy from an external source. For this purpose, a thermodynamic function is introduced. This function is called Gibbs' free energy (G) [6].

$$G = H - TS \qquad (1)$$

This energy follows enthalpy (H) and entropy (S). A thermodynamic process is possible when Gibbs' free energy changes are negative.

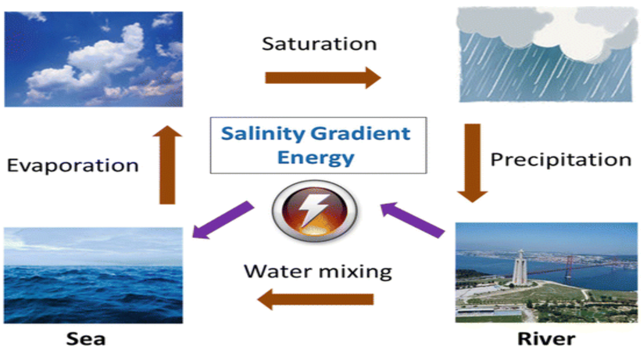

Figure 1: The location of salinity gradient power process in water cyclic for extraction of electrical energy [1]

Delayed osmosis pressure and reverse electrodialysis can be mentioned as energy extraction techniques.

2.2. The theory of delayed osmosis pressure process (PRO)

In the PRO process implementation, finding a stable process with constant pressure and energy production is one of the main energy extraction goals. The high-concentration lethal solution (higher salinity) enters the membrane modulus after passing through a pressure converter, which increases the pressure applied in the flow to reach a constant pressure. Feed flow is pumped at ambient pressure in the opposite direction of the membrane modules. Due to osmotic pressure difference throughout the membrane, which is larger than hydraulic pressure difference, water molecules move from feed solution to lethal solution, which increases concentration flow and dilution of concentration solution and decreases feed flow and concentrates of feed solution. The concentration solution is then pushed towards a current that passes through the turbine, creating a current that passes through the pressure transducer and transmits pressure and re-converts into concentration current [7]. Figure 2 describes a view of this process. Gibbs' energy from mixing two solutions with various concentrations in delayed osmosis pressure will be calculated according to 1 equation [5]. G_{mix} is the energy change of Gibbs energy, where G_S represents the energy from saline water and G_r denotes Gibbs energy from fresh water and G_B is the energy from the mixture of two water at different concentrations.

$$\Delta G_{mix} = G_B - (G_s - G_r) \qquad (2)$$

$$-c_{i,B} V_B \ln(x_{i,B})]$$

$$= RT \sum_i [C_{i,S} V_S \ln(x_{i,S}) + C_{i,r} V_r \ln(x_{i,r})$$

$$\Delta G_{mix} = \sum_i (G_{i,S} + G_{i,r} - G_{i,B})$$

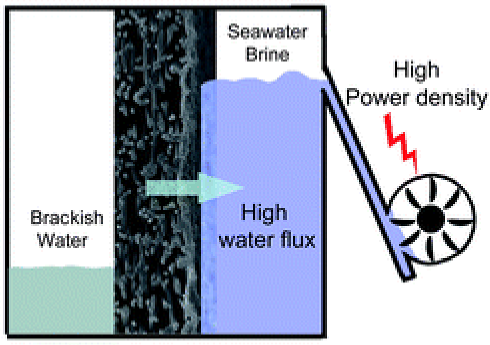

Figure 2: shows the delayed osmosis pressure process [2]

2.3. Inverse electrodialysis process theory (RED)

In this method, concentration difference between successive cells is used. In this case, after the membranes separate the ions, they enter the electrode chamber on both sides of the system, whereby performing oxidation-reduction reactions, an ion current becomes an electron current. This phenomenon causes a potential difference between the electrodes and leads to the charge of a battery. Two types of membranes are used in this battery. One is a cation exchanging membrane (CEM), and the other one is Anion exchanging membrane (AEM). By emitting ions through the membranes, an ion current is produced. This ion current is converted to electron current with suitable reduction reactions in electrodes [4]. Figure 3 describes a view of this process. The theoretical calculation of Gibbs energy derived from the entropy of mixing two solutions with different concentrations is calculated from the following relationship [8].

$$\Delta G = -2RT\left[C_S V_S \ln\frac{C_S}{C_M} + C_R V_R \ln\frac{C_R}{C_M}\right] \quad (3)$$

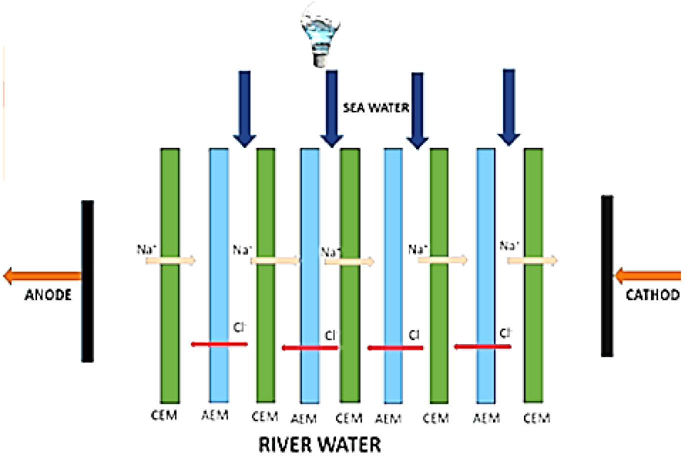

Figure 3: shows the reverse electrodialysis process [3]

One of the most important parameters for calculating the voltage of two heads of each cell is reverse electrodialysis. Using the Nerest equation and determining the ratio of seawater concentration (C_S) to river water (Cr) in different stations, the difference in potential created between the two ends of each cell in the reverse electrodialysis battery is calculated from this equation.

$$E = E^0 - \left(\frac{RT}{zF}\right)\ln\frac{C_S}{C_R} \quad (4)$$

2.4. The site of study

Arvand River consists of joining the Tigris and Euphrates rivers in the Gharne near Basra city and then by connecting Karun river to it at a distance of 33 km from this city. This river flows into the Persian Gulf after a distance of 110 km. Arvand River basin covers an area of about 948375 km^2[14]. The location of the estuary is in the latitude N 25, 55, 29 ° N and the longitude E 33, 33 ´ 35, 48 °.

To investigate the amount of achievable energy from the average of 8 years data from 3 hydrometric stations of Khosrowabad, Dirifram and Khorramshahr located in Arvand River between 2010 and 2018 is used.

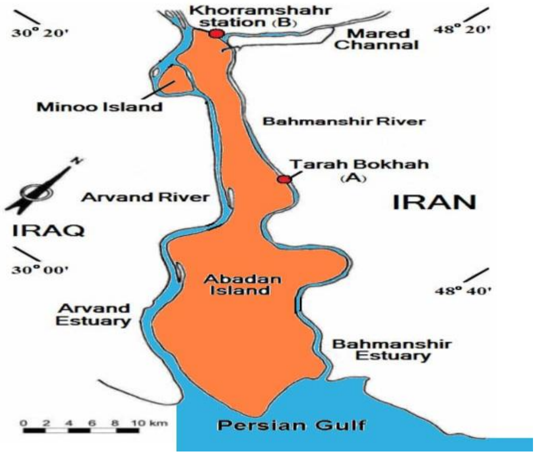

Figure 4: View of Arvand River [13]

3. Results

3.1. Gibbs energy calculation

First, we investigate the physical parameters of river water. These parameters include the total dissolved solids (TDS), electrical conductivity of water (EC) and river water flow. For this purpose, data from the last ten years (from 2010 to 2018) related to the nearest hydrometric station to the Arvandrud estuary were used. To calculate the concentration of river and seawater (C_r), the TDS parameter is divided into the mass of one mole of NaCl.

$$C_r = TDS/58.44\,(mol.m^{-3}) \quad (5)$$

For the Persian Gulf, the study area showed that seawater salinity in this area is considerable. Its annual average in this area with an appropriate approximation is 40 ppt, which can be considered based on TDS equal to 40000 mg/lit. Therefore, seawater Concentration (CS) is:

$$C_S = \frac{TDS}{58.44} = \frac{40000}{58.44} \approx 684.46\, mol/m^3 \quad (6)$$

To obtain Gibbs free energy, first, the concentrations of river and sea water were obtained in 3 hydrometric stations of Khosrowabad-Direfram and Khorramshahr in Arvandrud according to Table 1.

Table 1: Water Concentrations of Arvand River and the Persian Gulf from 2010-2018 in 3 Hydrometric Stations

Monitoring station	Latitude	Longitude	Year	$C_S = \frac{TDS}{58.44}(mol/m^3)$	$C_r = TDS/58.44$ ($mol.m^{-3}$)	$C_M = \frac{C_S V_S + C_R V_R}{V_S + V_R}$
Khosroabad	30-09-53	48-24-48	2010-2018	684.46	187.0308	500.4
Dirifam	30-22-58	48-11-09	2010-2018	684.46	85.5462	307.14
Khoramshahr	30-26-36	48-08-26	2010-2018	684.46	64.1907	293.68

Gibbs energy in equations 2 and 3 is calculated with the river and sea concentration values. Since the amount of input and output volume is very important First, Gibbs free energy (ΔG) for combining different volumes of seawater (VS) and river (Vr) is investigated. In the combination of different sea and river water ratios, increasing the amount of river water compared to seawater has a more effective role in increasing the amount of Gibbs free energy extraction. Therefore, by obtaining the best volume of input and output of Gibbs energy in 3 hydrometric stations, it was calculated according to table 2. Since its value was negative, it shows that this is a spontaneous process.

Table 2: Gibbs energy in 3 hydrometric stations using two methods

Monitoring station	(PRO) ΔG (MJ)	(RED) ΔG (MJ)
Khosroabad	-0.33	-1.11
Dirifam	-0.66	-1.32
Khoramshahr	-0.75	-1.88
T=298K V_s=1.46m^3 Vr=0.74m^3 C_s~684.46mol/m-3		

3.2. The physical model of PRO

To design and construct a physical model based on delayed osmosis pressure method, a plate with a diameter of 11 cm was initially considered. Then, 34 holes with an approximate area of 1 cm per hole were created. The membrane retaining plate was also cut on a 3 mm thick Plexi-glass plate using a laser cutting machine. In PRO, the active membrane layer encounters a high concentration solution (seawater) and porous support with feed solution (river water). PRO membranes are characterized by their intrinsic membrane properties such as water permeability, solute permeability, and the support layer's structural parameter. The membrane used in the physical model of TFC membrane is a nanostructure that can improve system performance by increasing the process speed and reducing sedimentation. In figure (5) the schematic design of the physical model made is shown.

To test the physical model of pure water without ion and then the solution of different concentrations was made. These solutions consisted of three different concentrations, including 50 ppm, 25 ppm, and 35 ppm, considered saltwater of the sea. Also, water with a concentration of 10 ppm was prepared under the title of river water (freshwater).

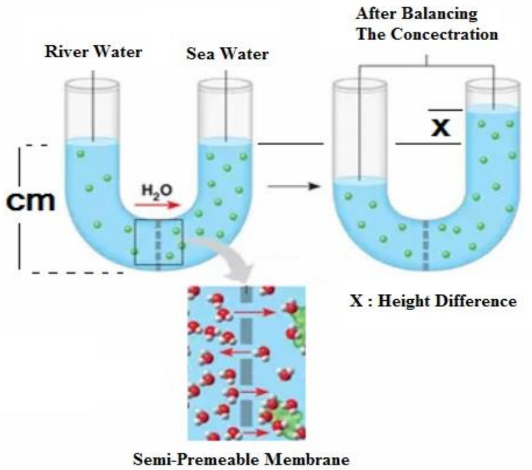

Figure 5: Schematic design of physical model PRO

Then, 3 different seawater concentrations with river water were placed alternately to test the physical model. The volume of each solution is 4000 cc. Both waters with different concentrations were placed on either side of the semi-permeable membrane with an involved surface area of 34 cm^2. In vitro and in different periods, the difference in height created in saline water solution column for different concentrations was obtained according to the table (3). The results showed that the highest height created in the mixing conditions is 50 ppm in seawater and 10 ppm in river water.

Table 3: the difference created by mixing

	25 ppm	35 ppm	50 ppm
Time(min)	H(cm)	H(cm)	H(cm)
0	0	0	0
30	1	1.2	1.5
60	1.6	2.3	4.1

90	2.4	4.1	6.2
120	3.9	5.4	7.7
150	4.6	6.3	8.2
180	4.9	6.7	8.7
210	5.2	6.9	9
240	5.6	7.3	9.2

The difference in height between the two columns of water in the U-shaped tube compared to the time for different salinity gradients shows that the height difference at the concentration of 50ppm has increased with increasing time.

Using the created height difference and increasing the water source volume with a high concentration of turbine has moved and produced flow. The higher the height difference, the higher the reservoir's energy potential and the output current from the mini-generator increases. Table 4 shows the flow rate obtained from the water micro-generator.

Table 4: the flow rate obtained from the height difference created by the salinity gradient

Current taken from a water micro-generatorI(mA)	Reservoir potential energyU(J)	Tank emptying timer(s)	Outlet flow from the tank drain valve Q(cm2/s)	Draining valve cross sectionA(cm2)	Water discharge rate from Drain valveV(cm/s)	The volume of water in the tank V(cm3)	Water tank cross section A(cm2)	Maximum height of the water columnH(cm)	Salinity gradient ppm
25.35	0.65	6.85	105.41	0.785	134.28	722.20	78.5	9.2	50
17.67	0.41	6.10	93.90	0.785	119.62	573.05	78.5	7.3	35
11.69	0.24	5.25	82.24	0.785	104.77	431.75	78.5	5.6	25

3.3. RED physical model

To evaluate the performance of designed reverse electrodialysis battery, the reverse electrodialysis battery chambers are filled with a volume of seawater Vs and river water Vr with different salt concentrations. In this system, an ion process is produced converted to electron current by reduction-oxidation reactions in electrodes. This process continues until the concentration of the solutions becomes identical on both sides. The membrane used in the physical model of nanostructure membrane. The aim of selecting nano-membranes is to help increase the process speed and reduce sedimentation.

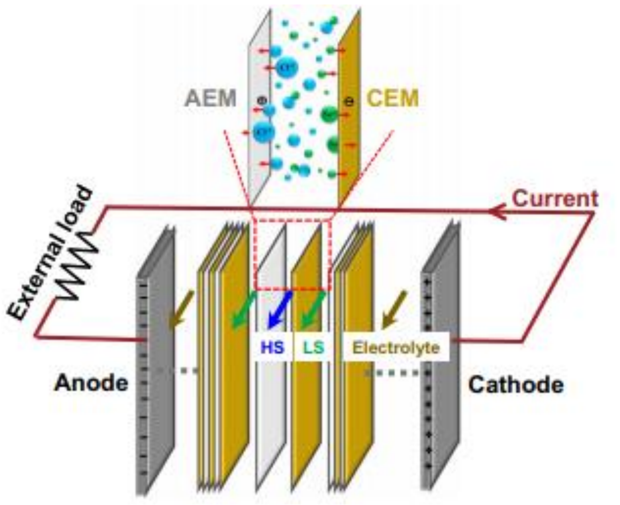

Figure (6): shows the performance of the reverse electrodialysis battery [15]

In this study, first, 4 liters of each of the diluted and thick salt solutions and electrolyte solutions were prepared. The concentration of these solutions is specified in the table (5). By injecting electrolyte solutions into the electrode chamber, dilution and thick solutions were injected into the membranes at two flux rates. In both cases, first, the system entrances are opened for a few seconds so that the salty and sweet water cells are fully filled. In this case, the system exits are completely closed. The time it takes for the system to be filled with ten ml/s flux rate is 32 seconds, and for the flux rate of 20 ml/s, it is 24 seconds.

Table 5: the concentration of used solutions

Number	Solution	Concentration
1	Dilute solution (river water)	0.017M (gNaCl / lit.)
2	Concentrated solution (sea water)	0.4 M (gNaCl / lit.30)
3	Electrolyte solution (CuSO4)	0.01 M

In table (5), the amount of potential difference between the two heads of each cell in the reverse electrodialysis system is calculated theoretically and according to the ratio of seawater to river water concentration for each hydrometric station.

Table 6: Potential difference between the two heads of each cell in the battery

River	Station	$V(mV)$
Arvand	Khosrowabad (A)	48
	Diriframe (B)	55
	Khorramshahr (C)	80

4. Conclusion and discussion

Arvand River is the largest and most important river in the Persian Gulf, so the study of gradient power is of special importance.

The amount of Gibbs energy obtained using delayed osmosis pressure method from data of three hydrometric stations in Arvand River shows that Khorramshahr station with 0.75 MJ has the highest amount of extractable energy. Since this negative value is obtained, it can be said that salinity gradient energy is a spontaneous process from which energy can be extracted. Since the investigation of energy extraction methods from salinity gradient is a new method for generating electrical energy; therefore, the results were obtained by establishing the physical model of PRO. Initially, with increasing the volume of water with high concentration, the highest height difference created in the physical model PRO with a height difference of 9.2 cm was related to the concentration of sea salinity of 50 ppm and river concentration of 10 ppm. The highest generated flow was 9.2 cm in height and ten ppm salinity concentration, which produced 26.35 mA .

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In the reverse electrodialysis method, Gibbs energy obtained from three hydrometric stations in Arvand River shows that this river has the highest amount of extractable energy in Khorramshahr station with 88.1 MJ. For the theoretical voltage of two heads of each cell, reverse electrodialysis in a RED system in three stations on the Arvand River shows that the greatest potential difference with 80 mV is related to Khorramshahr station .

By examining and comparing these two methods, it can be said that both processes can be done spontaneously, and Khorramshahr station has the best efficiency. The advantage of RED over PRO is that the electrical energy generated occurs at a lower salinity gradient, while in the PRO process, a higher salinity gradient difference is required. Therefore, placement of PRO device next to Khorramshahr desalination plant is an important step towards energy extraction. Another advantage of RED compared to PRO is that turbines are needed for electrical production in the delayed osmosis pressure method. Still, in the reverse electrodialysis method, an ion current is produced by emitting ions among the membranes.

4.1. Suggestions

The results show that the membrane system covers 50-80% of the cost of making the device according to the salinity difference level. Therefore, further development in membrane technology and identification of suitable membranes will significantly impact the possibility of processing and pathway to the market. As membrane permeability is determinative, the interaction between fluid and membrane is important in the system's permeability, so it is suggested that carbon nanotubes be used in the model in subsequent research. The physical model test in areas with output potential such as Lake Urmia; and using a delayed osmosis simultaneously with other devices related to salinity gradients, can be effective as well.

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