Investigation of Hybrid Self Regenerating Ion Exchange- Reverse Osmosis (HSIX-RO) for Low TDS and High TDS (Brackish) Water

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ABSTRACT

Recently in many regions around the world, the available source of water has a phenomenon highly saline and/or high hardness. To provide clean water with a suitable cost, Reverse Osmosis (RO) is among the most reliable technologies, however, the RO membrane is suffered from calcium carbonate and other scales available from feed causing precipitation on the membrane surface. Scaling control in RO membrane was used popular through dose antiscalant and acid. Ion exchange (IX) is one of an efficient and reliable method as a pre-softening process before RO performance. However, the applying of IX softening has had a little limited used due to higher operating and capital costs of the regenerant chemical. At this study, a combination of ion exchange method and reverse osmosis in a system together was proposed. It was called "Hybrid self-regenerating ion exchange RO (HSIX-RO) systems" that use the "free" salt from the RO reject to regenerate the resin without a need to add whichever regenerant chemical. Two operating schemes of HSIX-RO depended on the feed characteristics were proposed and further validated using high hardness with different level of total dissolved solids (TDS). Performance of ion exchange and membrane process were collected.

Keywords: Desalination, Brackish groundwater, Cation exchange resin

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Introduction

Water is the premise of human survival, however, numerous zones globally confront water deficiency issue due to contamination surface water source. So, desalination of groundwater supply daily life is becoming a necessity [1-3]. In recent year, RO membrane technology has been investigated as a reasonable innovation for desalination [4-14]. However, the issue scaling of membrane leads to flux decrease and in the long run, make shortening lifespan of the membrane [15-18]. Many contemporary studies address the need to solve membrane related issue as the following;

1. The mainly due to calcium salt obstructs RO membrane;
2. Treatment of reject water;
3. High energy use;
4. Anti-scaling chemicals need to be minimized;

Two solutions are made in RO desalination plants to resolve issue precipitation on membrane surface:

1. Quantity dosing anti-scaling or sequestering agent in the feed dosed [19-20]
2. Maintain the permeate recovery at a stable level [21-22]

According to an economical and environmentally sustainable development point of view shows that the anti-scaling agent in the reject caused the discharge problematic. Pre-softening of RO feed is one of the most reliable technologies of desalination [23] and was proposed in this study called "Hybrid Ion Exchange Reverse Osmosis" (HSIX-RO). Through utilization high concentration from RO rejects to use for regeneration that will bring results greatly reduces both economic and environmental burden of the disposal problem due to the absence of anti-scaling. The range of the HSIX-RO processes proposed for this study can be investigated into two different options as the following detail:

Option 1: For desalination high hardness groundwater with low total dissolved solids (TDS);

Option 2: For desalination high hardness groundwater with high total dissolved solids (TDS) (brackish);

Concept of system

In this study, through the incorporation of a hybrid self-regenerating ion exchange assisted reversed osmosis (HSIX-RO) processes was proposed to modification of the traditional RO process. The new process is built based on the existing equipment of the Ro process. The advantage of this process is can be avoided carbonate and sulfate precipitation without needing add anti-scaling agent. The HSIX-RO process has divided into two different options to investigate

HSIX - RO is a system to improve water quality through water groundwater desalination. Figure 1 provides a schematic of HSIX-RO processes which integrates the IX process with RO. The groundwater which contains calcium ion is pumped into the system (column A). The first set valves (V1, V2, V3, and V4) will open and the second set valves (V5, V6, V7, and V8) will close. Each option has individual step are:

Option 1: A Self-regenerating Exchange Resin in Magnesium Form for Desalination Low TDS & High Hardness Groundwater

Step 1. The hard water passes through column A (cation exchange resin in Mg^{2+} form) which is in service run, calcium ion is exchanged with magnesium ion and magnesium is released into the system.

$$\overline{(RSO_3^-)_2Mg^{2+}} + Ca^{2+} \rightleftharpoons \overline{(RSO_3^-)_2Ca^{2+}} + Mg^{2+} \tag{1}$$

The water stream rich in Mg^{2+} is feed to the membrane, water with almost no magnesium comes out as permeate and water with a high concentration of magnesium comes out as reject.

Step 2. Magnesium ions are detached from RO to prepare a regeneration solution**.**RO membrane start producing drinking water

Step 3. The concentrated reject water from the membrane is pumped to column B which is in regeneration run where magnesium ion is exchanged for calcium ions and calcium ion is released into the stream. Note that theoretically, Mg^{2+} ion is in the closed-loop system.

$$\overline{(RSO_3^-)_2Ca^{2+}} + Mg^{2+} \rightleftharpoons \overline{(RSO_3^-)_2Mg^{2+}} + Ca^{2+} \tag{2}$$

Option 2: A Self-regenerating Cation Exchange Operated in Sodium form for Desalination for High TDS (Brackish water) & High Hardness Groundwater

The same operating mechanism of the case for low TDS, however at this option for brackish water desalination

Step 1. The brackish groundwater passes through column A (cation exchange resin in Na^+ form which is resin form) which is in service run, calcium ion is exchanged with sodium ion and sodium is released into the system.

$$\overline{(RSO_3^-)Na^+} + Ca^{2+} \rightleftharpoons \overline{(RSO_3^-)_2Ca^{2+}} + Na^+ \tag{3}$$

The water stream rich in Na^+ which can define total dissolved salt (TDS) (units are either ppm or mg/L) is feed to the membrane, water with almost no sodium comes out as permeate and water with high concentration of TDS comes out as reject

Step 2. This step, the resultant solution from the reject water membrane is containing sodium ions mainly that will use to regenerate and reverse osmosis will produce drinking water**.**

Step 3. The concentrated reject water from the membrane is pumped to column B which is in regeneration run where sodium ion is exchanged for calcium ions and calcium ion is released into the stream.

$$\overline{(RSO_3^-)_2Ca^{2+}} + Na^+ \rightleftharpoons \overline{(RSO_3^-)Na^+} + Ca^{2+} \tag{4}$$

This method repeated as a cyclic process in continuous mode. When the column A reaches its breakdown point and calcium concentration is more than permissible then first set valves (V1, V2, V3, and V4) close and the second set valves (V5, V6, V7, and V8) open up. Influent hard water is alternately pumped to the column B which is in service run and reject concentrated water is pumped to column A which is in regeneration run. The HSIX-RO process is better as it does not use external salt for regeneration of column after service run. The reject water is concentrated and used for regeneration which is normally drained out. This method removes calcium with high efficiency and prevents the clogging of the membrane. The reject water, which is normally drained out, is concentrated and used for regeneration. This method removes calcium with high efficiency and prevents the clogging of the membrane. Selectivity sequence cation exchange resin is $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Na^{+}$. Further enhances the efficiency of the proposed process. Note, the process does not require the changing of the column from the system and hence can be used to treat a large amount of water without any additional costs.

Objectives of the study

The specific objectives to fulfill in the research for a sustained desalination process of two options are:

1. To study the efficiency of resin for desalination high hardness groundwater.
2. To investigate the performance of the membrane

Methodology

Materials

The study uses cation exchange resin which was a shallow shell structured (SSTC 65) for removing hardness cations and regeneration ion exchange. The resin was selected for this study is representative sort of strong-acid has an inner–core structure. This one has sodium (Na) form, a macroporous structure, polystyrene composition, sulfonic acid functional groups [24]. For option 1, the resin was loaded in magnesium form by passing the magnesium chloride salt of the respective cation 3.4 % of $MgCl_2.6H_2O$ solution corresponding to 2X of resin capacity and stir by a rotary shaken machine for 24 hrs. For option 2, the resin was used in sodium form as initial. The membrane used in this study was a spiral wound (Film Tec ™ TW30-1812-50) RO membrane, provided by Dow's company where the active membrane surface area was 0.32 m^2 [25]

Experiment fixed-bed column operation

The process was conducted at the same conditions – 30 mL resin have the same feed solutions were carried out using 50 mm-diameter glass columns (Kimble Chase, USA) was packed top and below to avoid any loss of ion exchange resin during used feed was pumped through the column by peristaltic pump BT100-2J with flow 5ml/min.

The experimental process always divides to 2 options:

1. Ca^{2+} concentration inlet for option 1 ~ 8 meq/l, Conductivity = 1168 mS/cm, the exhausted material regenerated using 113.21 meq/L of Mg^{2+} of $MgCl_2$ solution

2. Ca^{2+} concentration inlet for option 2 ~ 12 meq/l, Conductivity = 3181 mS/cm, the exhausted material regenerated using 1% NaCl solution

The effluent was collected periodically using an ELDX fraction collector (ELDEX Model U200, USA). EDTA titrimetric method based on techniques mentioned in the book for standard techniques of water and wastewater experiment was used to measure water sample hardness [26].

Measurement of regeneration efficiency: [27]

$$\%\, Regeneration = \frac{Mass\ leached\ from\ the\ resin}{Mass\ loaded\ on\ the\ resin} \times 100\% \quad (5)$$

Experimental RO setup

The experimental studies were carried out at different operating conditions. The first experiment, RO system under high hardness low TDS desalination conditions using 8 meq/L Mg^{2+} solution. The second experiment, feed conditions using a 2,000 ppm NaCl solution. Both experiment performance at temperature (25 ± 0.5 ^{0}C) at15 minutes at each an operating pressure of 70, 80, 90, 100 psi to estimate the water flux (L/m^2hr, LMH) and recovery (%). RO experiment was done for each of the pressure of pump under conditions the same salt concentration in the feed, the composition of the salt which was drowned from the same feed tank.

At the end of the RO operation, quality of product water was determined by some measurements such as electrical conductivity (EC), total dissolved solids (TDS), salinity. The measurements of EC were performed by a portable conductivity meter. TDS (mg/L) values were calculated by multiplication of salinities with their densities after salinity measurements were done with the conductivity meter [28]

$$\mathrm{TDS\ (mgL^{-1})} = \mathrm{k_e} \times \mathrm{EC\ (\mu S\ cm^{-1})} \quad (6)$$

Where k_e is a constant of proportionality, the k_e value was varied 0.55-0.85 and the extremes (0.7) is widely used and was selected to calculation on this study

Measurement of RO operation efficiency: [29]

The water flux (J_w- LMH) across the RO membrane was calculated follow equation

$$Jw = \frac{\Delta V}{A \times \Delta t} \quad (7)$$

Where ΔV (L) is the volume change of feed solution during predetermined time Δt (h), and A is surface area (m^2) of the RO membrane.

Furthermore, the recovery was calculated by measuring the overall production of the system

$$R(\%) = \left(\frac{Q_{permeate}}{Q_{feed}}\right) \times 100\% \quad (8)$$

Where R is recovery (%) as a difference of the initial solution flow and the permeate solution flow, $Q_{permeate}$ (Lhr^{-1}) is the permeate flow, Q_{feed} (Lhr^{-1}) is the feed flow. That means R% of the feed flow is produced as permeate.

Results

Option 1: Desalination of High Hardness Groundwater with Low Total Dissolve Solids (TDS) using Cation Exchanger Operated in Magnesium Form

The results fixed-bed column operation

From the fixed-bed column studies, in Figure 2-1 show that SSTC65 resin in Magnesium can treat high hardness water low TDS containing Ca^{2+} 8 meq/L and TDS 818 mg/L at approximately 200 volumes (BVs). Figure 2-2 indicate that the result of a regeneration run in which water was rejected from the membrane containing 1,358.52 mg/L of Mg^{2+} was pumped through the resin column and the effluent was tested for concentrations of Ca^{2+} at different BV, each at an interval of 5BV. The resins were regenerated from the highest solute reject results of membrane operation at 100 psi. The experiment indicate that the concentration of Ca^{2+} follow a nonlinear distribution with the concentration reaching a peak value at 20 BV. The recovery of calcium after the regeneration run is calculated by dividing the area under the graph in this figure. That shows percentage recovery very high achieved 97.78%**.**

Effect of pressure on RO membrane

The values of the permeate fluxes were taken at each 15 min from starting of the cross-flow filtration process. The experimental results of permeate and reject water flux were shown in (table 1) and Figure 3. Increasing the membrane pressure will increase the concentration difference between the permeate flux and reject flux. The results data in (table 1) show that the permeate flux increased from 39.72 ($L\ hr^{-1}\ m^{-2}$) to 96.13 ($L\ hr^{-1}\ m^{-2}$) as the membrane pressure was increased from 70 to 100 psi. Under the same conditions, the reject flux decreased from 63.72 ($L\ hr^{-1}\ m^{-2}$) to 7.33 ($L\ hr^{-1}\ m^{-2}$). So, Figure 3 signifies the pair effect between the pressure and flux. It also shows the solute reject salinity effect on reject water. With synthetic feed water at 8 meq/L of magnesium solution, the solute reject was 38.4 % at 70 psi. With increasing pressure, the solute reject was increased from 38.4% to 92.91% which indicated that almost solute in the feed that has rejected at high pressure.

Option 2: For Desalination Brackish Groundwater which is high Total Dissolve Solids (TDS) operated in Sodium form

The results fixed-bed column operation

In this case, Figure 4-1 also have the same result is possible with processing capability to treat brackish water containing Ca^{2+} 12 meq/L and TDS 2227 mg/L at approximately 80 (BVs) for service run. Then the resins were regenerated by containing 1% NaCl that approximately TDS 10,000 mg/L. Figure 4-2 shows the outlet history regeneration for a run of the resin column. The breakthrough point of the column for regeneration run is at the value 40 (BVs). It is clear that at 1% of NaCl concentration affect greatly recovery and calcium removal as well that percent recovery approach over 99.88 %.

Effect of pressure on RO membrane

The values of the permeate fluxes were taken at each 15 min from starting of the cross-flow filtration process. The experimental results of permeate and reject water flux were shown in table 2 and Figure 5. Figure 5 shows the schematic and the results of a run in which effluent from the resin column were pumped to the membrane at four different pressures and reject flux from the membrane was noted. From the table 2, it is clear that at a pressure of 70 psi the recovery rate of water was less than 40% with low concentration of salt in reject whereas when the water was pumped at a pressure of 100 psi the recovery rate was greater than 70% with very high concentration of salt in reject. This reject is concentrated and used for the regeneration run of the other column. The figure shows that as the increasing operation pressure from 70 to 100 psi, the concentration of reject increased near linearly. It was explained by the permeate flux is directly proportional to the net driving force. Pressure does not affect the diffusion of solute through the membrane. Therefore, the increase in salt rejection due to the permeate concentration was diluted by the higher water flux. Hence, Figure 5 shows the permeate flux and observed rejection for RO membrane under different operating pressure conditions for a brackish solution (2,000 mg/L). At 0.2% concentration, the permeate flux increase and reject flux decrease with increasing operating pressure. The findings show that the permeate flux decreases while rejecting flux increase with an increase in operating pressure. Studies show that for pressure-driven membrane separation process, the permeate flux depends on the net pressure across the membrane. Thus, increasing operation pressure increases the net pressure as well consequently the permeate flux. Note that, the available RO pressure pilot unit in the lab, just service for this research.

Discussion and Conclusions

High hardness water is pumped into the system in which water passes through a column in the service run. The effluent from the service run column is pumped into the membrane, permeate is used for drinking purposes and the reject is pumped back into the system. The reject contains high amounts of solute reject salts are pumped to an exhausted column and its regeneration takes place. The effluent after the regeneration containing high amounts of calcium is thrown as waste. The development of a pilot scale HSIX-RO system for desalination high hardness groundwater has been assessed during the treatment of feed solutions. It was shown that the resin in magnesium form can remove calcium hardness at approximately 200BVs and the HSIX-RO system with original resin in sodium form can desalination brackish water which can remove hardness approximately 80BVs. The RO system has percent solute reject recovery of regeneration more than 70% recovery depends on operating pressure.

From an application viewpoint, the developed hybrid desalination process, HSIX-RO, for desalination high hardness groundwater from low to high TDS is one of the promising methods to eliminate antiscalants. Besides, the HSIX-RO system was investigated for this research by use cation exchange instead of anion exchange as previous research. This process will cost saving due to the cost of cation resin about 3 times lower than the cost of anion resin. However, the research stop at designing a diagram without building an up-scale. So, the HSIX-RO system for up-scale should be investigated in future work.

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Table 1 Permeate and reject water flux at different operating pressure valves

Pressure	Permeate		Reject		Mg^{2+} in Reject	Recovery
(Psi)	Volume (mL)	Flux (L $hr^{-1}m^{-2}$)	Volume (mL)	Flux (L $hr^{-1}m^{-2}$)	(mg/L)	(%)
70	1536	39.72	2640	63.72	155.88	38.4
80	2496	64.40	1505	38.81	255.36	62.4
90	3508	90.65	492	12.71	780.36	87.7
100	3706	96.13	284	7.33	1358.52	92.91

Operating condition: temperature: 25°C, C_0 = 96 mg L^{-1}(8 meqL^{-1}), V= 4L

Table 2 Permeate and reject water flux at different operating pressure valves

Pressure	Permeate		Reject		Salt in Reject	Recovery
(Psi)	Volume (mL)	Flux (L $hr^{-1}m^{-2}$)	Volume (mL)	Flux (L $hr^{-1}m^{-2}$)	(mg/L)	(%)
70	1145	35.5	2645	68.9	3819	34.13
80	1372	42.2	2080	54.2	3839	40.50
90	2290	59.6	1040	27.1	4740	57.25
100	2840	74.0	567	14.8	7059	71.00

Operating condition : temperature : 25°C, C_0 = 2000 mg L^{-1}(0.2%), V = 4L

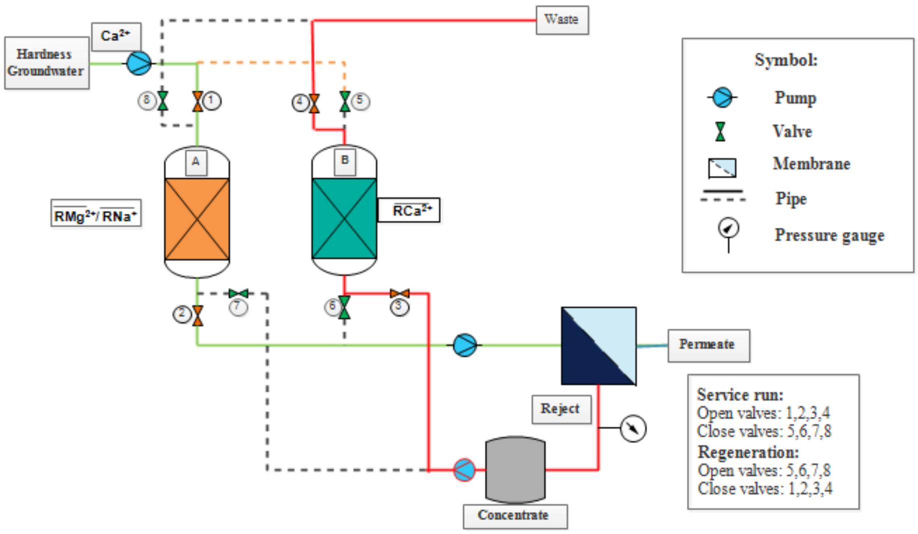


Figure 1 Proposed hybrid self-regeneration ion exchange using RO reject

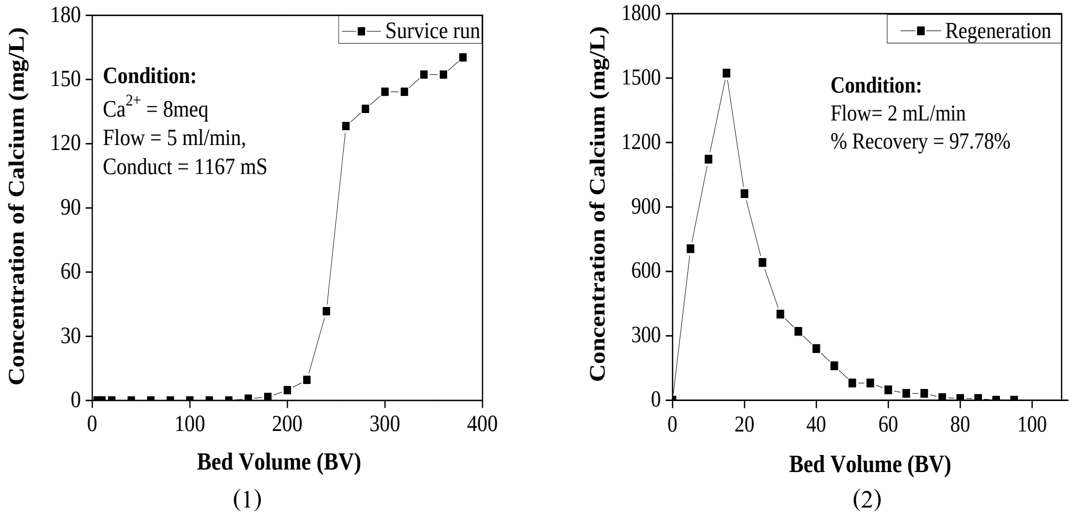
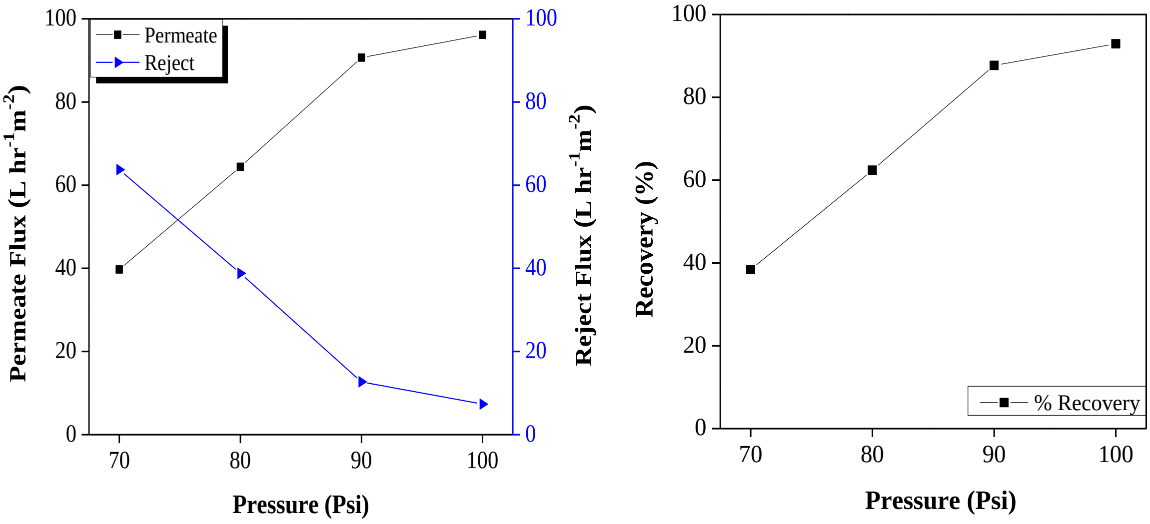
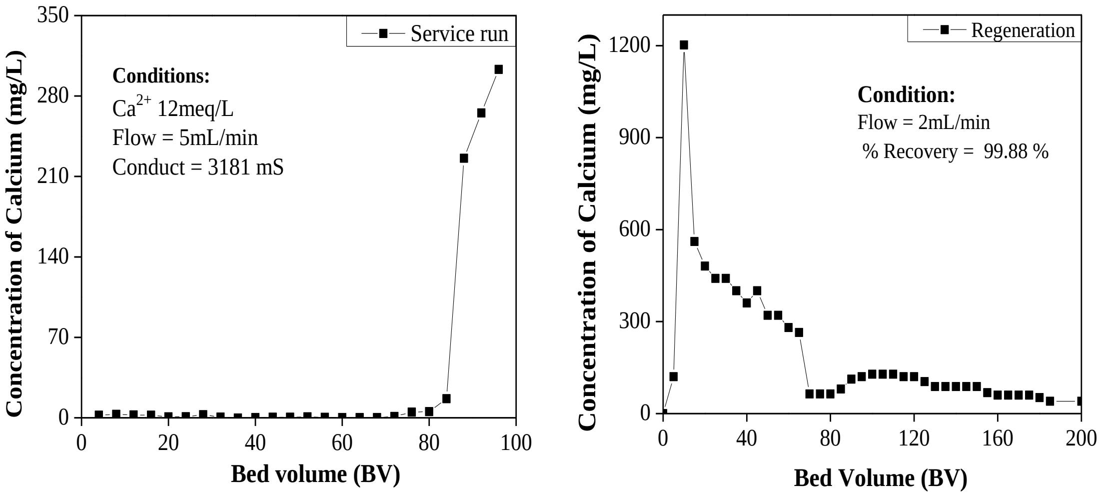


Figure 2 Experimental ion exchange of HSIX-RO process in the laboratory for option 1 (High hardnes groundwater with Low TDS): (1) Survice run; (2) Regeneration.



(1) (2)

Figure 3 (1) Permeate and Reject flux at different transmembrane pressures for solutions and (2) Percent recovery for C_0 = 96 mg L^{-1}(8 meqL^{-1}), V= 4L



(1) (2)

Figure 4 Experimental ion exchange of HSIX-RO process in the laboratory for option 12 (High hardnes groundwater with high TDS): (1) Service run; (2) Regeneration.

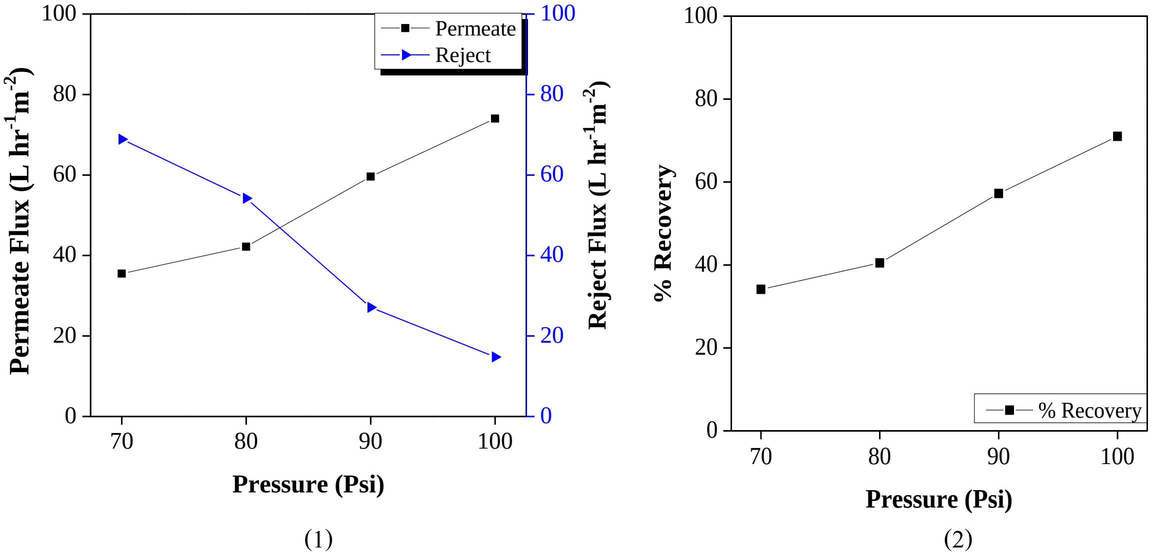


Figure 5 (1) Permeate and reject flux at different transmembrane pressures for solutions and (2) percent recovery for C_0 = 2000 mg L^{-1}(0.2%), V = 4L.