

# Sustainable Design and Synthesis of Hybrid RO-PRO Systems for Industrial Wastewater Treatment

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Pressure retarded osmosis (PRO) is a new technology can provide sustainable power to many processes. However, the optimal design methods of integrating this technique in practical processes are rarely reported in literatures. This work addresses the problems of sustainable design and synthesis of reverse osmosis (RO)-based wastewater treatment process powered by PRO. A novel superstructure optimization method is proposed to solve the problem, where the superstructure for a RO-PRO hybrid system is enhanced with additional features from industrial wastewater streams. The problem addressed is formulated as a mixed-integer nonlinear programming (MINLP) model. A case study on industrial wastewater desalination is carried out to show that the proposed approach can identify optimal designs for reducing the specific energy consumption of membrane-based treatment systems, especially in desalination applications. Besides, from the standpoint of life cycle assessment, the global-warming potential (GWP) has a 34.8 % of CO<sub>2</sub> reduction (from 1.299 kgCO<sub>2eq</sub>/m<sup>3</sup> for the stand-alone RO system to 0.963 kgCO<sub>2eq</sub>/m<sup>3</sup>) for the hybrid system.

## 1. Introduction

In recent years, a global shift in the process industries is toward more sustainable production. It is critical to minimize wastewater discharge and reduce greenhouse gas emissions. Meanwhile, the freshwater scarcity is becoming an increasingly significant problem in many water-stressed regions in the world. Industrial wastewaters (IWs), such as the waste streams discharged from power, chemical, pharmaceutical, and refinery industries, can vary broadly in solution composition and have more stringent treatment goals. In the most extreme example, some industrial plants must operate the scheme of zero liquid discharge because water must be extracted from the solid waste before disposal.

High pressure-driven reverse osmosis (RO) treatment process has become an increasingly important and widespread technology to provide salt-free water from IWs. But the main issue impeding the wider use of RO desalination technology is the high economic cost involved, especially caused by intensive energy consumption (Li, 2011). Meanwhile, another membrane-based technology, pressure retarded osmosis (PRO), can harvest sustainable power from mixing water streams with different salinities (Straub et al., 2016). It is an emerging approach with enormous potentials. Researchers have begun to propose several conceptual designs which integrated the stand-alone RO process with other sustainable processes (Efraty, 2016). The PRO process utilizes a semipermeable membrane placed between the feed solution (low concentration) and the draw solution (high concentration). Freshwater can permeate from the unpressurized feed solution to the pressurized draw solution (DS). After that, the pressurized permeation is expanded in a hydro-turbine to generate shaft electricity. In light of the above complementary natures of RO and PRO processes, a new integration opportunity arises for reducing the net specific energy consumption (NSEC) of RO desalination (Senthil and Senthilmurugan 2016). More specifically, an RO wastewater treatment process can be driven by the sustainable energy generated by a PRO-based power plant. The principle of this RO-PRO hybrid system can be described by a pressure-flow (P-Q) diagram see Figure 1 (He et al., 2015). Herein, a positive value of theoretical net energy consumption ( $\Delta e_{hd}$ ) indicates that the hybrid system can be sustainably operated as a stand-alone desalination system.

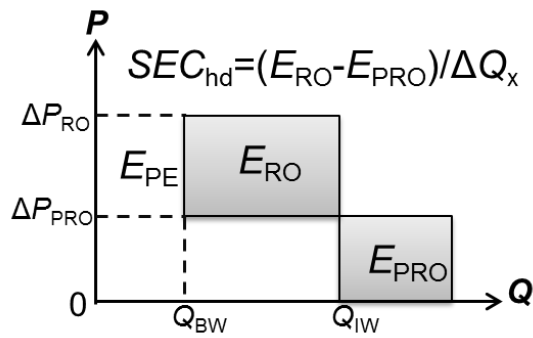


Figure 1:  $P$ - $Q$  representation of the RO-PRO hybrid system.  $E$ ,  $P$ , and  $Q$  denote the energy, pressure, and flow rate. The subscripts  $IW$  and  $BW$  are permeate product and brine water.

This work addresses the problems of sustainable design and synthesis of RO-based wastewater treatment process powered by PRO. A superstructure optimization method is proposed to solve the problem, where the superstructure for a RO-PRO hybrid system is enhanced with additional features from IWs. We formulate the problem as a mixed-integer nonlinear program model. A case study on desalination is considered in this work. The numerical results obtained by our approach are further analysed based on the aspect of water-energy nexus.

## 2. RO-PRO model development

### 2.1 Model description

Figure 2(a) shows the state-space based superstructure of the proposed RO-PRO hybrid system which includes a RO subsystem and a PRO subsystem, as well as a stream network connecting the subsystems. The feed streams of this hybrid system are multiple industrial wastewaters (IWs) discharged from different process units and auxiliary production units, thus they contain distinct properties like total dissolved solids (TDS). Likewise, different permeate streams are extracted from the pressure vessel and directed either to another pass for further processing or to the final product collection points. In industrial processing, the basic element of each subsystem is membrane-based modules (e.g., spiral wound module). These modules are connected in a series arrangement within a high pressure vessel (RO- $n$  and PRO- $m$ ). A single RO/PRO stage includes several number of high pressure vessels operating at the same conditions of flow rate, chemical composition, and pressure. In order to enhance the recovery efficiency, each subsystem can be assembled for any number of RO/PRO stages (Lin and Elimelech, 2015).

The detailed unit operation of a single RO stage is shown in Figure 2(b). This RO subsystem employs a split partial second pass (SPSPRO) concept (Saif, Almansoori et al. 2014), in which permeate stream are extracted at different location along the length of the pressure vessels. In general, each stage has a set of mixer (MX) and splitter (SP) nodes. For example, in this Figure, the first mixer node ( $MX_{1,RO}$ ) that mixing different streams coming from other RO stages and/or the PRO subsystem, will provide a feed stream to the RO stage. Another mixer node ( $MX_{2,RO}$ ) receives high pressure stream like RO reject streams, which is a feed stream to the pressure exchanger (PE) unit. The splitter nodes  $SP_{1,RO} \sim SP_{i,RO}$  in the RO stage provide locations for permeate extraction, while the splitter nodes  $SP_{i+1,RO}$  and  $SP_{i+2,RO}$  are the high and low pressure reject splitters. Meanwhile, the high-pressure pump (HPP) and booster pump (BP) are used to pressurize the feed streams prior to RO stages in order to facilitate the desalination. Energy extraction from HPP by PE serves to reduce the energy consumption.

Figure 2(c) shows the unit operation of a PRO stage based on a multi-feed solution multi-draw solution (MFMD) concept (Altaee et al., 2014). The high-salinity draw solution (DS) exiting from the splitter node  $SP_{i+2,RO}$  enters the first pressure vessel, where the water transmembrane movement driven by the osmotic pressure occurs between feed solution (FS) and draw solution (DS). This operation leads to a decrease in DS's concentration and an increase in FS's concentration along the tube channel, further reducing the transmembrane driving force across the membrane due to concentration polarization (CP) phenomenon. In order to enhance the driving force, the MFMD concept allows multiple external streams with higher solute concentrations to mix with the inter-stage FS stream at the mixer nodes  $MX_{2,PRO} \sim MX_{j,PRO}$ . Likewise, multiple external streams with lower solute concentrations are designed to mix with the inter-stage DS stream at the mixer nodes  $MX_{j+1,PRO} \sim MX_{2j-1,PRO}$ . These operations can enrich the inter-stage DS stream and dilute the inter-stage FS stream, easing the detrimental effect of CP. The pressure energy of the final DS outlet can be

harvested by a hydro-turbine (HT). The depressurized HT outlet enters a splitter node  $SP_{1, PRO}$  in which a portion of this outlet is split and sent to the RO subsystem as the input stream. The other portion, namely DS discharge (DSD), together with the final FS discharge (FSD) is considered as an exhaust stream.

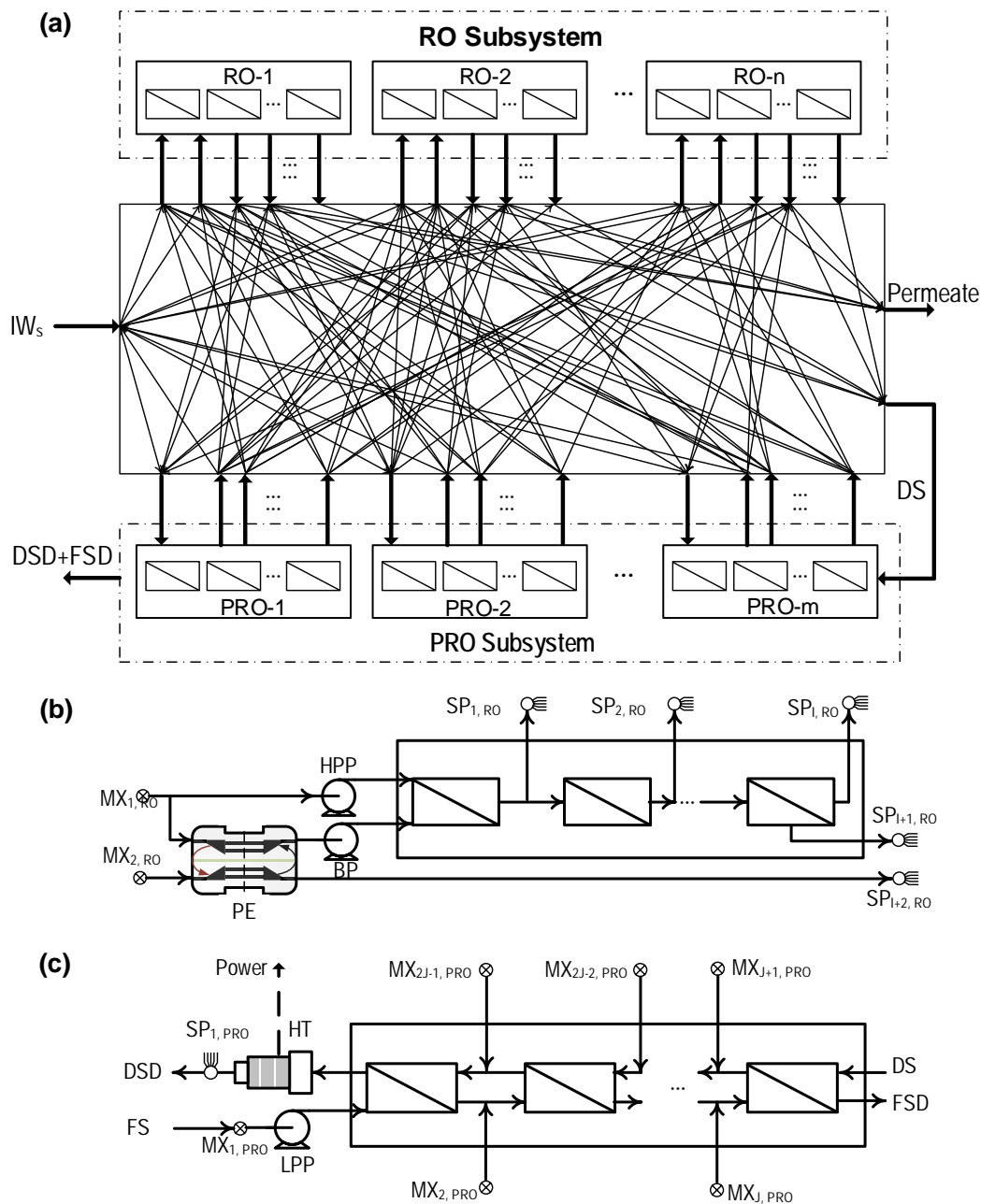


Figure 2: Superstructure representation of the design problem. (a) RO-PRO hybrid system, (b) RO sub-system, and (c) PRO sub-system.

## 2.2 Model

The mathematical programming model formulation for the RO-PRO water treatment network is a mixed integer nonlinear program (MINLP). The objective function of this MINLP model is to minimize the total annualized operating cost (AOC) of the RO-PRO network through searching the optimal process configuration, treatment capacity, and the operating parameters like the pressures of RO and PRO pressure vessel, split ratio, pump outlet pressure, etc. Only a brief model is introduced due to the page limits.

$$\begin{aligned}
 \text{Min } AOC &= AT \times P_e \left( \sum_{m=1}^M W_{LPP,m} + \sum_{n=1}^N (W_{LPP,n} + W_{BP,n}) - \sum_{m=1}^M W_{HT,m} \right) \\
 \text{s.t. } & \text{Mass balance} \\
 & \text{Energy balance} \\
 & \text{Unit efficiency constraints} \\
 & \text{Salt concentration constraints} \\
 & \text{Operating conditions constraints}
 \end{aligned} \tag{1}$$

where the  $AT$ ,  $P_e$ , and  $W$  is annualized operating time, price of electricity, and power consumption. The unit efficiency constraints considered herein refer to the thermal efficiencies of LPP, HP, BP, and PE. The salty concentration constraints include the bounds of inlet IWs' TDS and the specification on permeate quality. Besides, the last constraints specify the variations of key operating variables such as the pressure of PRO and RO, flow rates of DS and IWs.

MILP-based iterative methods proposed by Pan et al. (2014) can be used to solve the MINLP problems. An iteration algorithm (two iteration loops) is used to find the optimal solution. In the first loop, the MILP-based model is solved repeatedly to obtain a feasible solution under certain objective value. In the second loop, the minimum objective value is searched, and the feasible solution under the minimum objective value can be found by using the procedure proposed in the first loop.

### 3. Case study

Due to the limitation on content, the proposed superstructure is tested by a simple case study which is taken from ref. (Senthil and Senthilmurugan 2016) The problem is to design a hybrid RO-PRO wastewater treatment process with a single RO/PRO stage that is able to produce  $0.130 \text{ m}^3 \cdot \text{s}^{-1}$  of on-specification permeate with less than 200 TDS. Two IWs are considered as the system feed streams, one is originally derived from the gasification wastewater with a high concentration of 35,000 TDS, while the other one is a low-salinity sanitary wastewater with a concentration of 100 ~ 1,000 TDS. BW30LE-440 membranes are used for the PRO and PRO pressure vessels. The relevant process input parameters and bounds are updated from Karuppiyah et al. (2012), and some of important model parameters are listed in Table1.

Table 1: Key input parameters used in model formation

Parameters	Value	Unit
Hydro dynamic permeability	$1.593 \times 10^{-11}$	$\text{m}^3/(\text{N} \cdot \text{s})$
Salt permeability	$2.440 \times 10^{-7}$	m/s
Multiplying constant in mass transfer coefficient	$3.800 \times 10^{-3}$	$/(\text{m} \cdot \text{s})^{0.5}$
Power constant in mass transfer coefficient	0.500	–
Area of one PRO/RO membrane	7.432	$\text{m}^2$
Length of one PRO/RO membrane	0.963	m
No. of PRO/RO membranes per pressure vessel	5/7	–
Number of pressure vessels per train	291	–
Reflection coefficient	0.999	–
Water permeability coefficient of membrane	$5.016 \times 10^{-12}$	$\text{m}^3/(\text{N} \cdot \text{s})$
Salt permeability coefficient of membrane	$4.340 \times 10^{-7}$	m/s
Permeate pressure	101325	$\text{N/m}^2$
PE efficiency	98	%
PE friction coefficient	0.050	%
Cost of electricity	0.08	\$/kwh

Figure 3 shows the optimal configuration of the proposed RO-PRO system where a part of  $IW_1$  is pressurized to  $5.070 \times 10^5 \text{ N/m}^2$  by LPP1 followed by PE. The other part mixed with DS outlet at  $MX_1$  is pressurized to  $5.580 \times 10^6 \text{ N/m}^2$  by HPP. After that, the high pressure HPP outlet is dehydrated at the RO subsystem at the same operating pressure. The product of the RO subsystem is PP1 containing a very low TDS concentration. The other effluent is split at  $SP_2$  where most proportion is sent to the PE and BP for the next closed-circulation. In the PRO subsystem, the incoming DS indirectly and reversely contacts with the low-salinity FS exiting from LPP2. Meanwhile, the overwhelming majority of the volume-enlarged DS outlet is introduced to the HT for power generation. The optimal solutions of pressure, flow rate, and concentration are detailed in Table 2.

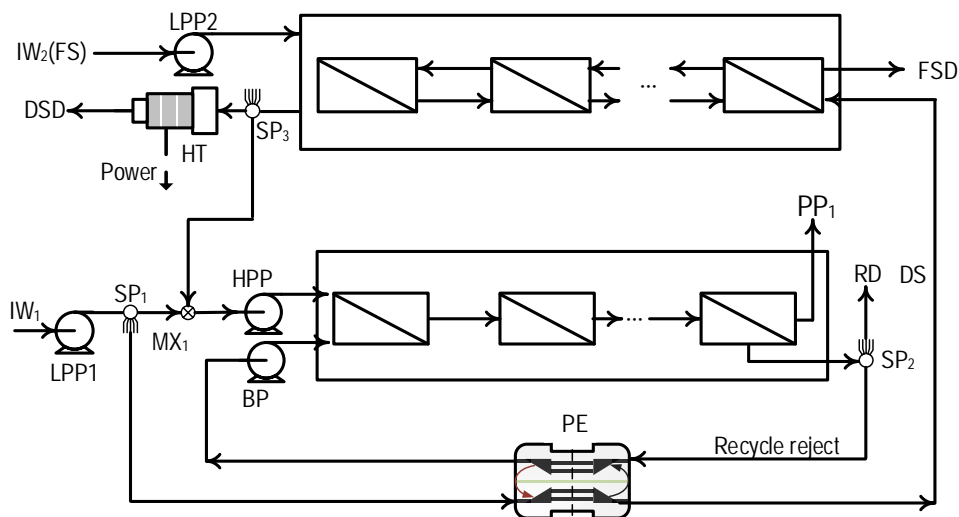


Figure 3: Optimal RO-PRO hybrid system configuration

Table 2: Optimal flow rate, pressure, and concentration

Stream	Flow rate (m <sup>3</sup> /s)	Pressure (×10 <sup>3</sup> N/m <sup>2</sup> )	Concentration (g/m <sup>3</sup> )
IW1	0.269	101	35,000
IW2 (FS)	0.308	101	800
Permeate (PP1)	0.116	101	45
DS	0.154	507	35,000
DSD	0.249	101	21,679
FSD	0.194	150	1,273
Recycled reject	0.174	5,289	54,294
Recycled DS	0.020	489	21,679

In Table 3, we compare the major performance metrics of the optimal process with those of conventional RO system. Given the same recovery of permeate (40.2%), the optimal NSECs are 1.72 and 2.32 kWh/m<sup>3</sup> for the RO-PRO hybrid system and the RO stand-alone system, resulting in a 34.8 % of energy saving. Accordingly, for the investigated desalination process, a lower NSEC leads to the reduction in GHG emissions from the standpoint of life cycle environmental footprint. In this work, we measure the environmental footprint using 100 year-based global-warming potential (GWP) which focuses on the global warming effects caused by CO<sub>2</sub>, CH<sub>4</sub>, SO<sub>2</sub>, and NO<sub>x</sub>. The calculation results show that the GWP is 0.963 kgCO<sub>2eq</sub>/m<sup>3</sup> for the RO-PRO hybrid system and 1.299 kgCO<sub>2eq</sub>/m<sup>3</sup> for the RO stand-alone system. Thus, the GHG emissions reduction, also, is 34.8%.

Although the RO-PRO hybrid system is found to be energy efficient and environment-friendly for wastewater desalination application, the major barrier is the high capital cost and system uncertainties. For example, the RO-PRO hybrid system requires double amount of process equipment (pump, PE, pressure vessels, etc.) compared with the RO stand-alone system, significantly increasing the investment cost. Therefore, further studies on determining the trade-off between energy efficiency and capital cost would provide a more credible design.

Table 3: Model performance metrics

Performance metrics	RO-PRO hybrid system	RO stand-alone system
Equipment number	8	4
Recovery, %	40.2	40.2
Power density, W m <sup>-2</sup>	5.68	-
NSEC, kWh m <sup>-3</sup>	1.72	2.32
FS/DS ratio	2	-
Energy saving, %	34.8	-
GWP, kgCO <sub>2eq</sub> m <sup>-3</sup>	0.963	1.299
GHG emissions reduction	34.8	-

#### 4. Conclusions

In this work, we proposed a superstructure-based sustainable design and synthesis of RO-based wastewater treatment process powered by PRO. It mainly included a RO subsystem and a PRO subsystem, as well as a stream network connecting both the subsystems. The feed streams of this hybrid system were multiple IWs discharged from different process units. We formulated the problem as a MINLP which was globally solved to yield optimal results. A simple case study on desalination was considered in this work, and the optimization results showed that the optimal RO-PRO hybrid system was highly useful for identifying energy efficient designs for reducing the specific energy consumption of membrane-based purification systems. Besides, compared with the stand-alone RO system, the optimal hybrid system can reduce 34.8 % of greenhouse gases emissions through life cycle assessment of per kg permeate generated.

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