

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**DATA DRIVEN IDENTIFICATION OF INDUSTRIAL REVERSE
OSMOSIS MEMBRANE PROCESS**

PELİN DÖLOĞLU
A THESIS SUBMITTED FOR THE DEGREE OF
MASTER OF SCIENCE
DEPARTMENT OF CHEMICAL ENGINEERING

GEBZE
2021

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

DATA DRIVEN IDENTIFICATION OF
INDUSTRIAL REVERSE OSMOSIS
MEMBRANE PROCESS

PELİN DÖLOĞLU
A THESIS SUBMITTED FOR THE DEGREE OF
MASTER OF SCIENCE
DEPARTMENT OF CHEMICAL ENGINEERING

THESIS SUPERVISOR
ASSIST. PROF. DR. HASAN ŞILDIR

GEBZE
2021

T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

ENDÜSTRİYEL TERS OZMOZ MEMBRAN
SÜRECİNİN VERİ ODAKLI
TANIMLANMASI

PELİN DÖLOĞLU
YÜKSEK LİSANS TEZİ
KİMYA MÜHENDİSLİĞİ ANABİLİM DALI

DANIŞMANI
DR. ÖĞR. ÜYESİ HASAN ŞILDIR

GEBZE
2021

GEBZE TEKNİK ÜNİVERSİTESİ	YÜKSEK LİSANS JÜRİ ONAY FORMU
----------------------------------	--------------------------------------

GTÜ Fen Bilimleri Enstitüsü Yönetim Kurulu'nun 27/05/2021 tarih ve 2021/06 sayılı kararıyla oluşturulan jüri tarafından 10/06/2021 tarihinde tez savunma sınavı yapılan Pelin DÖLOĞLU'nun tez çalışması Kimya Mühendisliği Anabilim Dalında YÜKSEK LİSANS tezi olarak kabul edilmiştir.

JÜRİ

ÜYE

(TEZ DANIŞMANI) : Dr. Öğr. Üyesi Hasan ŞILDIR

ÜYE : Doç. Dr. Devrim Barış KAYMAK

ÜYE : Dr. Öğr. Üyesi Özgün YÜCEL

ONAY

Gebze Teknik Üniversitesi Fen Bilimleri Enstitüsü Yönetim Kurulu'nun
...../...../..... tarih ve/..... sayılı kararı.

İMZA/MÜHÜR

SUMMARY

A dynamic Artificial Neural Network (ANN) is developed for the identification of a complex industrial reverse osmosis membrane process to characterize the major fouling causes and their impacts using online measurements. The historical data used, for the ANN training and validation, includes 4-year-data on some feed properties and measured process variables in the plant, which have an interacting and nonlinear impact on the ultimate permeate flow, in turn fouling. The ANN formulation takes the current and previous week's online measurements to account for the dynamic regime and provides one-week and two-week ahead permeate flow predictions. The model performance is satisfactory at new and regenerated membranes in process lifetime, including early, middle and late of the cycle. A sensitivity analysis is provided to determine the variables with high impact on the permeate flow, and thus the fouling. Based on the sensitivity analysis, cartridge filter pressures and pH have the highest impact on the permeate flow rate. Plant operating window is also calculated to demonstrate the impact of the changes of those for a typical range under such complex multivariable and nonlinear nature. The results show quantitative and intuitively parallel conclusions to existing literature and provide significant insight on the major components of fouling in an industrial and large-scale process.

Keywords: Artificial Neural Networks, Process Identification, Reverse Osmosis Membrane, Sensitivity Analysis, Operating Window.

ÖZET

Çevrimiçi ölçümler kullanılarak başlıca kirlenme nedenlerini ve etkilerini karakterize etmek için karmaşık bir endüstriyel ters ozmoz membran işleminin tanımlanması için dinamik bir Yapay Sinir Ağı (YSA) geliştirilmiştir. YSA eğitimi ve doğrulaması için kullanılan tarihsel veriler, tesisteki bazı besleme özellikleri ve ölçülen proses değişkenleri hakkında 4 yıllık verileri içerir ve bunlar nihai ürün suyu akışı üzerinde etkileşimli, doğrusal olmayan ve sonucunda kirlenmenin meydana geldiği bir etkiye sahiptir. YSA formülasyonu, kısa vadede dinamik rejimi hesaba katmak için mevcut ve bir önceki haftanın çevrimiçi ölçümlerini alıp bir ve iki hafta sonraki ürün suyu akış tahminini yapmaktadır. Model performansı, ters ozmoz membranların yıkama döngüsünün başı, ortası ve sonları dahil olmak üzere yeni ve rejenere membranlarda proses ömrü boyunca tatmin edicidir. Membranlarda kirliliğin göstergelerinden biri olan ürün suyu akışının üzerinde yüksek etkiye sahip değişkenleri belirlemek için bir duyarlılık analizi yapıldı. Duyarlılık analizine göre, kartuş filtre basınçları ve pH, ürün suyu akışı üzerinde en yüksek etkiye sahiptir. Karmaşık, çok değişkenli ve doğrusal olmayan yapıdaki değişkenlerin, belirli bir aralıkta prosese etkisini göstermek amacıyla tesisin çalışma çerçevesi hesaplanmıştır. Sonuçlar, mevcut literatüre nicel ve sezgisel olarak paralel sonuçlar gösterir ve büyük ölçekli endüstriyel proses için kirlenmenin temel sebepleri hakkında önemli bilgiler sağlar.

Anahtar Kelimeler: Yapay Sinir Ağları, Proses Tanımlama, Ters Ozmoz Membran, Duyarlılık Analizi, Çalışma Çerçevesi.

ACKNOWLEDGMENTS

I would like to express my deepest gratitude to my supervisor, Assist. Prof. Dr. Hasan ŞILDIR for providing me with support, invaluable guidance, encouragement, patience, and suggestions.

I would like to express my gratitude to Fatih GÜLMEZ who is process engineer of TÜPRAŞ's Industrial Water Treatment Plant for valuable knowhow conveying about ROMU plant and comments on the results. I am also grateful to Algorithm and Software Solutions Team from R&D Department of TÜPRAŞ for their support.

Very special thanks to my family on whose constant encouragement and love I have relied throughout my life. I am deeply grateful to my parents Şeyda DÖLOĞLU and Mesut DÖLOĞLU, to my sister Selin DÖLOĞLU, and to my grandparents Emine CENGİZ and Cevat CENGİZ. I owe special thanks to my dear friend Melike Kamuran ONAT for her great friendship. I want to express my innermost thanks to my dear friend, Umut YAZGAN for his never-ending encouragement, help and faith in me.

TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	v
ÖZET	vi
ACKNOWLEDGMENTS	vii
TABLE OF CONTENTS	viii
LIST OF SYMBOLS AND ABBREVIATIONS	ix
LIST OF FIGURES	xi
LIST OF TABLES	xii
1. INTRODUCTION	1
2. PROCESS AND METHODS	9
2.1. Process Description	9
2.1.1. Online Measurements	9
2.1.2. Laboratory Data	11
2.1.3. ROMU Operation Procedure	12
2.2. Artificial Neural Networks	12
2.3. Data preprocessing and ANN performance	14
3. RESULTS AND CONCLUSIONS	18
3.1. Sensitivity Analysis	18
3.2. Operating Window	22
4. CONCLUSIONS	34
REFERENCES	36
BIOGRAPHY	42

LIST OF SYMBOLS AND ABBREVIATIONS

<u>Symbols and Abbreviations</u>	<u>Descriptions</u>
Δ	: Delta
Σ	: Sum Symbol
$^{\circ}\text{C}$	: The Degree Celsius
kg/cm^2	: Kilogram per Square Centimeter
mg/L	: Milligram per Liter
mV	: Millivolt
m^3/h	: Cubic Meters per Hour
μm	: Micrometer
$\mu\text{S}/\text{cm}$	: Micro Siemens per Centimeter
ppm	: Parts Per Million
CaCl_2	: Calcium Chloride
NaCl	: Sodium Chloride
Na_2SO_4	: Sodium Sulfate
ANN	: Artificial Neural Network
BWRO	: Brackish Water Reverse Osmosis
CIP	: Cleaning-In-Place
COD	: Chemical Oxygen Demand
CP	: Concentration Polarization
CU	: Color Unit
L-BFGS	: Limited-memory Broyden–Fletcher–Goldfarb–Shanno Algorithm
MF	: Microfiltration
NF	: Nanofiltration
NTU	: Nephelometric Turbidity Units
ORP	: Oxidizing Reduction Potential
RO	: Reverse Osmosis

ROMU	:	Reverse Osmosis Membrane Unit
SSM	:	Suspended Solid Matter
SWRO	:	Seawater Reverse Osmosis
TDS	:	Total Dissolved Solids
UF	:	Ultrafiltration

LIST OF FIGURES

<u>Figure No:</u>	<u>Page</u>
1.1: Simplified RO diagram.	3
2.1: Simplified ROMU diagram.	10
2.2: A simple ANN architecture.	13
2.3: RMSE value of changing neuron numbers.	14
2.4: Correlation matrix of input variables.	15
2.5: Predicted values and actual values of (a) train set, (b) test set.	16
2.6: Test dataset distribution of residuals.	17
3.1: Operating windows of most sensitive parameters for newly operated membrane a) early date of the cleaning cycle, b) late date of the cleaning cycle.	24
3.2: Operating windows of same parameters for newly operated membrane a) early date of the cleaning cycle, b) late date of the cleaning cycle.	26
3.3: Operating windows for old membrane a) early date of the cleaning cycle, b) late date of the cleaning cycle.	28
3.4: Operating windows of most sensitive parameters for old membrane a) early date of the cleaning cycle, b) late date of the cleaning cycle.	30
3.5: Operating window according to variance of the temperature and overall pressure difference.	31
3.6: ROMU plant performance.	33
3.7: ROMU plant performance under low fouling effect.	33

LIST OF TABLES

<u>Table No:</u>	<u>Page</u>
1.1: Pressure driven membrane processes classification.	2
2.1: ROMU sensors and descriptions.	10
2.2: Industrial Water Treatment Plant feed water characteristics.	11
2.3: ROMU laboratory analyses' sampling point, name and cyclic.	12
2.4: Train and test sets' performance metrics.	17
3.1: Sensitivity analysis for three different simulations when RO membrane is new.	19
3.2: Sensitivity analysis for three different simulations when RO membrane is old.	21

1. INTRODUCTION

Only 2.5% of water has a direct industrial, agricultural and municipal usage potential. In addition to increasing demand, both pollution and climate change have a significant impact on the water scarcity [1], [2]. From the industrial perspective, with such limited availability, water is a primary utility and feedstock for many industrial processes, for which the water usage efficiency is an important concern [3]. Significant amount of research has been conducted for alternative solutions to obtain clean water or reduce its usage and put great effort to raise awareness [1].

Obtaining clean water by desalination, which has the capability to process a variety of water sources with different process configurations, is a popular alternative [4] among many. It is a process to remove salts, minerals, and contaminants from saline water, including the seawater, the brackish water and wastewater effluent. Desalination technologies include thermal and membrane focused applications, and such applications are classified under their separation mechanism. Some examples of thermal desalination processes, which separate the salt through evaporation and condensation, are multistage flash, multiple effect distillation, and vapor compression. On the other hand, membrane desalination processes, which are mainly reverse osmosis (RO) and electrodialysis, retain the salts and other impurities on the membrane surface by forcing the transport of water to the other side [5].

With low energy requirement, no additional chemical usage, operational convenience and easy scale-up, membranes have a broad range of applications in different industries such as water treatment [5]. In practice, membranes are the selective barriers which allow the transport of only desired materials due to a particular driving force. The membrane operations can be classified under the driving force including the pressure, concentration, temperature and electrical potential. While pressure driven membrane processes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), RO and piezodialysis; concentration driven membrane processes are pervaporation, gas separation, vapor permeation, dialysis, diffusion dialysis and carrier-mediated transport. Also, thermo-osmosis and membrane distillation count as temperature driven membrane processes, and electrical potential driven membrane processes are electrodialysis, electro-osmosis and membrane electrolysis [6]. MF, UF, NF and RO membranes are pressure driven membrane processes and have a large

industry market share. Since membrane process technologies other than pressure driven membrane processes are developing or to be developed industrial membrane technologies, they have limited industry market share [7]. Pressure driven membrane processes are mainly divided into MF, UF, NF and RO membranes based on their pore size as shown in Table 1.1 [5].

Table 1.1: Pressure driven membrane processes classification.

Process	Particle Size (μm)
MF	0.1 - 1
UF	0.01 - 0.1
NF	0.001 - 0.01
RO	0.0001 - 0.001

RO membrane process, compared to the others, has the highest capacity in desalination technology [5], and RO usage in desalination has gained rapid growth and development since the 1950s [1]. In [1], the plants using such technology were classified under the feedstock they utilize such as brackish water (BWRO) and seawater (SWRO). BWRO and SWRO process 500 mg/L to 10,000 mg/L and around 30,000 mg/L saline water, respectively. BWRO has low and high salinity processes with 500 to 2500 mg/L and 2500 to 10,000 mg/L capacity.

RO desalination plant feedstock can be various types of water sources such as seawater, saline groundwater, drainage water and treated wastewater [2]. While desalination of seawater and brackish water for drinking water and industrial processes are the most common RO usage areas, RO technology is also used for wastewater including the municipal wastewater and recycled municipal wastewater desalination, a favorable method to lower the usage of fresh water, and reuse applications in zero waste concept [3], [8]. The cooling, boiler feed, processing, sanitary services, fire protection, and many other miscellaneous purposes of refinery processes are examples of such needs. Thus, the recovery of wastewater is a hot research topic for reducing freshwater demand and wastes [9]. RO membrane is a state-of-the-art technology for producing qualified water from recycled municipal wastewater in refineries, and the related process includes pretreatment steps such as UF and membrane bio-reactor [10], [11] to interfere clogging by inorganic and organic pollutants [12], which in turn increases the lifetime.

RO might be adapted to different processes once underlying mechanism is

exploited in detail. While osmosis is a process that water in low concentrated solution flows through a semipermeable membrane to high concentrated solution due to already existing driving forces, RO requires greater amount of osmotic pressure on high concentrated solution side to transport water from high to low concentrated solution. A simplified process diagram is shown in Figure 1.1 [8].

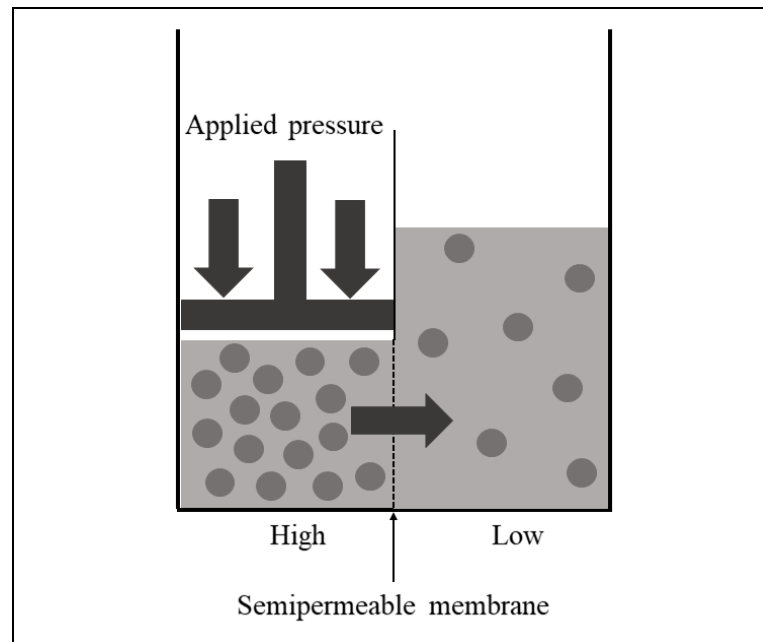


Figure 1.1: Simplified RO diagram.

Dead-end and cross-flow filtration are two filtration types based on the flow direction to membrane surface in RO processes. In the dead-end filtration, both the solution and the permeate flow vertically to the membrane surface. In cross-flow filtration, solution flow direction is parallel to membrane surface unlike permeate flow. There are different types of RO membrane modules such as spiral wound, plate and frame, tubular and hollow fiber. Membrane module type is related to filtration type and it directly affects membrane performance [8].

RO transport mechanism is complex and many proposals are available [13]. In one of them, the RO mass transportation occurs through two mechanisms: alignment type diffusion by the help of hydrogen bonding association between membrane and molecules, and hole type diffusion of molecules that can not enter any association with membrane. Pores in the membrane cause salt leakage through permeate side, which is an undesired phenomenon on this mechanism. Another proposal is the solution-diffusion mechanism, which is the most widely accepted theory for the RO transport

mechanism. In this mechanism, there are three steps for saline water desalination. Sorption of both water and salt at one side of membrane; diffusion through the membrane; and desorption at the other side of membrane, respectively. Sorption and diffusion coefficients are individual for every membrane, once the membranes are quite nonporous and perfect. When any deterioration occurs on the pores, salts in the feed pass through permeate side of membrane. Alternatively, Banks and Sharples [14]–[16] considered the diffusive flow through the pore free layer on membrane surface. For water desalination, there is another proposal with the combination of both molecular diffusion of water transportation through membrane polymer matrix and parallel mechanisms for solute transportation, which are sorption, diffusion and hydrodynamic flow [17]. Also, both diffusion and pore flow processes carry out together according to another theory for water and solute filtration [18]. Lastly, the proposal in [19]–[21] is related with non-equilibrium thermodynamics. With the help of transport models, RO membrane performance can easily express mathematically in terms of operating conditions and feed properties.

The solution-diffusion model proposed by Lonsdale et al. [22] have found wide interest in the literature and industrial applications. In this model, there are two transport mechanisms for solvent and solute. The flux for solvent (J_w) and the effective pressure difference across the membrane are linearly proportional and given by:

$$J_w = A(\Delta P - \Delta \pi) \quad (1.1)$$

where A is the water permeability coefficient and it is a function of the diffusivity of water through the membrane; ΔP is the applied pressure driving force which is also a function of the feed, concentration and permeate pressure; $\Delta \pi$ is the osmotic pressure of the solution that is function of the feed, concentrate and permeate concentrations.

Similarly, the flux for solute (J_s) across the membrane is proportional to the effective solute concentration difference. Equation (1.2) shows the solute flux through membrane.

$$J_s = K(C_{A2} - C_{A3}) \quad (1.2)$$

where K is the salt permeability coefficient, and it is a function of the diffusivity of

salt through the membrane; C_{A2} and C_{A3} are molar concentrations of solute at boundary level and in the permeate, respectively.

Equations (1.1) and (1.2) are elegant equations and validated using the experimental data [8]. Water flux and salt rejection are the two parameters to evaluate the RO membrane performance. While water flux can be calculated from Equation (1.1), salt rejection is the membrane separation ability of solute from the feed solution and observed rejection (R_o) formula is Equation (1.3).

$$R_o = 1 - \frac{C_p}{C_f} \quad (1.3)$$

where C_p and C_f represent permeate concentration and feed solution concentration, respectively [23].

Convective flow of solutes from feed stream in the direction of membrane occurs during RO desalination. Therefore, this phenomenon causes maximum solute concentration on the membrane surface and boundary layer where the solute concentration is higher than the bulk solute concentration. Solutes are transported back from the membrane because of higher solute concentration within the boundary layer. On the other hand, the solutes accumulate in the boundary layer and on membrane surface due to stronger convection compared to diffusion. Therefore, the solute concentration in the bulk feed water is always lower than concentration on the membrane surface. Accumulation of solutes on the surface of membrane is called concentration polarization (CP). Decreased permeate flux and increased solute flux across the membrane are two main negative effects of CP. Decreased permeate flux can be associated with membrane fouling which is the undesired consequence of CP. In parallel, permeate solute concentration increases, membrane solute rejection decreases [1]. Therefore, CP has severe undesired effects on membrane performance.

Adverse consequence of CP is membrane fouling that is an accumulation of undesired impurities (foulants) on the membrane surface or inside the membrane pores. There are different classifications for fouling based on foulants and their locations. Surface and internal fouling are two types of location based classifications. Since RO membranes are nonporous membranes, surface fouling is a more common problem than other membrane types. However, internal fouling is more problematic rather than surface fouling which can be handled by chemical cleaning or improving

feed water hydrodynamic conditions, to some extent. In addition, fouling can be classified as biofouling, organic fouling, inorganic scaling and colloidal fouling in terms of foulants types. Microorganism adhesion and proliferation on membrane surface is biofouling. Organic fouling occurs by organic matters such as humic substances, polysaccharides, proteins, lipids, nucleic acids and amino acids, organic acids, and cell components. While feedstock is surface water or seawater, organic foulant is generally natural organic matter. On the other hand, organic fouling is severe problem in wastewater treatment and the main organic foulant is called wastewater effluent organic matter. Inorganic scaling, which is the common issue for every type of water feedstock in treatment, is caused by deposition of inorganic materials. Furthermore, colloids or particles build up on the host particle in colloidal fouling. In practice, membrane fouling occurs by a combination of various foulants, and membrane autopsy should be applied to determine the actual source of fouling [24].

The fouling decreases the permeate flow and salt rejection; whereas increases pressure differences at desalination plants. Therefore, energy demand due to increased operational pressure, frequency of cleaning, chemical consumption during cleanings, membrane replacement due to permanent fouling increase, as well. Thus, once membrane fouling is not managed, water treatment costs can rise significantly [25]. Consequently, it is crucial to understand which parameters have an impact on membrane fouling, and how fouling indicators of RO desalination plant performance (permeate flow, salt rejection and pressure differences) are affected in time.

Although a significant amount of research has been conducted in the field of RO membrane fouling for the last three decades, there is still much more to be explored in this area. Current researches can be gathered under six areas: foulant characterization by membrane autopsy, figuring out how fouling works, prediction of fouling indices, full-scale system modeling, pretreatment and cleaning optimization, membrane substance and module design optimization. As the first four fields are related to fouling mechanism and prediction of fouling, the other fields focus on the fouling mitigation and prevention [26]. Modeling fouling of RO membrane approaches can be classified as physics-based, data-driven and hybrid models.

Physics-based approach generally uses a physical model for describing the behavior of RO membrane fouling to represent the underlying driving forces and interactions. Hoek et al. [27] proposed a model for fouling effects on full-scale RO process that considers system properties, water quality, and transport phenomena. Flux

dependent resistance modeling approach for organic gel fouling of RO desalination is developed by Karabelas et al. [28]. In addition, there are different fouling indices for scaling potential such as silt density index and modified fouling index [25]. For such purposes, membrane autopsy is a common method for characterization of membrane fouling, and Fourier transform infrared spectroscopy, inductively coupled plasma atomic emission spectrometry, X-ray photoelectron spectroscopy and X-ray diffraction are generally used [29]–[31].

Although physics-based models have a wide range of descriptive capability, both theoretical and practical limitations exist. Firstly, the complexity of fouling mechanism due to feed composition and the interactions of variables are challenging to derive through first principles expressions. Secondly, disturbances and changing operating conditions result in significant amount of uncertainty. Next, the industrial processes lack the potential of sufficient data for the identification of precise role of the membrane surface properties and different foulants. Finally, for proper fouling characterization might be required for the membrane element sacrificed during autopsy [32], [33]. Based on these drawbacks, data driven approach for RO membrane fouling is favorable method. There are different data driven methods in RO membrane fouling such as artificial neural networks (ANNs) and support vector regression. ANN-based quantitative structure–property relations models are used for creating a set of solute and membrane variables that represent and describe rejection [34], [35]. ANN model is a common method for RO desalination plant performance modeling and prediction [36]–[38]. These ANN models use plant operation parameters that have effect on fouling such as temperature and total dissolved solids (TDS), and predict operation parameters, which is also fouling indicator such as permeate flux, pressure difference and salt rejection. Also, trained ANN models can be used for the optimization of desalination plant [37]. Roehl et al. [39] developed an ANN model from six-year historical data to evaluate causes of membrane fouling. Water permeability coefficient can be calculated with neural network based correlation [40] and superposition of two exponential functions for long term performance prediction [41]. Support vector regression model for the prediction both of steady state and transient operations is developed by Pascual et al. [42]. Park et al. [43] proposed deep neural network for modeling fouling growth and flux decline of RO membrane. Multilayer perceptron hybridized with particle swarm optimization which is the new hybrid data intelligence technique is developed for investigation of the RO process efficiency based on TDS

and permeate flow rate prediction [44]. Also, there is a comprehensive study from antifouled membrane synthetization to prediction of flux using the ANN model [45]. There is another study for performance prediction of SWRO desalination plant, which is compared support vector machines, random forests and ANN models [46]. Furthermore, neural networks and optimization algorithms such as genetic algorithm are preferred as combined strategy for simulation and then optimization of RO performance of obtained models and to calculate a control strategy [47]–[50]. In addition, Lee et al. [51] studied on optimal control to maximize the RO permeate production. Park et al. [52] proposed a modified regression model for optimization of cleaning of RO membrane.

Besides physics-based and data-driven models, hybrid models combine two approaches. Since hybrid model approaches are not mature yet in modeling concept, there are few studies in the field of RO membrane fouling. Zhao et al. [53] developed a combined model of a modified solution diffusion model and two artificial neural network models for modeling membrane mass transfer.

This study focuses on long-term industrial RO membrane process identification using ANNs in order to calculate the impact of the feed properties and process variables on the permeate flow rate, which in turn delivers a significant insight into the fouling rate. To the best of the authors' knowledge, there are limited data-driven studies on the long-term operation of a large-scale industrial plant. In Section 2, process description and identification using ANN are explained. Next, the ANN model is used to calculate the sensitivities of the variables and the plant operating window. Final part concludes the study and provides the discussions on the current method.

2. PROCESS AND METHODS

2.1. Process Description

Industrial Water Treatment Plant, in this study, utilizes Kocaeli/Turkey's treated municipal wastewater for refinery water demand. In our case, the wastewater goes through multimedia filters, activated carbon filters, UF membranes and RO membranes, successively, before usage in refinery processes. Among different processes in the treatment, RO membranes have an important impact on the ultimate water quality since they are the last part of the treatment and ensure the removal of impurities to a great extent; thus, fouling by the feed impurities would harm the succeeding refinery operations. Such membranes are a part of Reverse Osmosis Membrane Unit (ROMU) which includes cartridge filters, high pressure pump, and reverse osmosis membrane trains, respectively. RO membranes are composed of two stages with 36 and 18 membrane modules respectively. In more detail, one membrane module contains 6 spiral wound polyamide membranes as shown in Figure 2.1. First stage's concentrate flow stream is fed to the second stage. The permeate streams from the stages are stored in RO Permeate Tank, whereas the concentrate stream of second stage membranes is stored in RO Concentrate Tank. All these operations are physical treatments with negligible chemical reactions.

2.1.1. Online Measurements

A simplified ROMU is shown in Figure 2.1 with pressure, conductivity, oxidizing reduction potential (ORP), pH, temperature and flow rate sensors through which online measurements are collected on the minute basis.

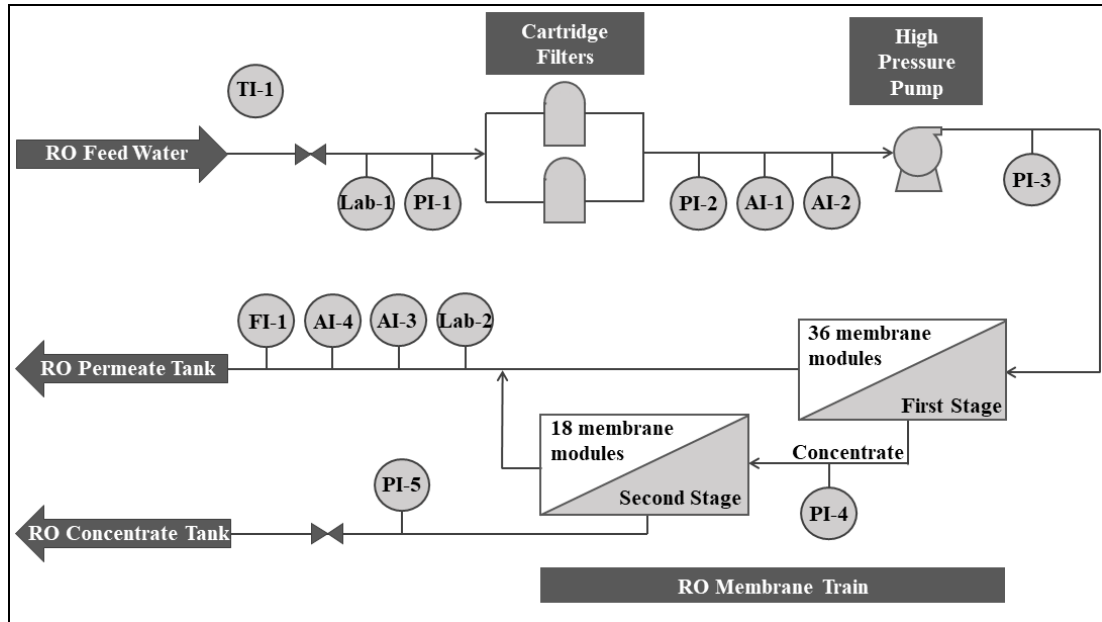


Figure 2.1: Simplified ROMU diagram.

The sensors in Figure 2.1 are described in Table 2.1.

Table 2.1: ROMU sensors and descriptions.

Tag	Description	Range	Unit
PI-1	The inlet pressure value of cartridge filters	2.5-4	kg/cm ²
PI-2	The outlet pressure sensor of cartridge filters	1-4	kg/cm ²
PI-3	The outlet/first stage inlet pressure sensor	8.5-13	kg/cm ²
PI-4	First stage outlet/second stage inlet pressure sensor	6-9.5	kg/cm ²
PI-5	Concentrate pressure sensor	1.5-8	kg/cm ²
AI-1	The feed stream conductivity sensor	635-2400	μS/cm
AI-2	The feed stream ORP sensor	110-575	mV
AI-3	The permeate conductivity sensor	5.5-230	μS/cm
AI-4	The permeate pH sensor	5-7.5	-
FI-1	The permeate flow rate sensor	140-255	m ³ /h
TI-1	The atmosphere temperature sensor	0-40	°C

Since there is no sensor for monitoring feed water and RO membrane's feed tank temperatures, TI-1 is used to approximate the water temperature by measuring the air temperature. Also, there is no pressure sensor for permeate water which is crucial for indicator of fouling. Since water, that cannot pass through the membrane due to the fouling, sends to concentrated stream, PI-5 is considered for revealing pressure difference and permeate water relations.

2.1.2. Laboratory Data

When Kocaeli/Turkey's treated municipal wastewater is delivered to the refinery, some laboratory analyses are done on wastewater. Typical wastewater feed characteristics are summarized on Table 2.2 according to laboratory analyses.

Table 2.2: Industrial Water Treatment Plant feed water characteristics.

Experiment Name	Typical Characteristic	Unit
pH	7.5	-
Sulfate	90.5	ppm
Chemical Oxygen Demand (COD)	25	ppm
Turbidity	1.8	NTU
Conductivity	1282	$\mu\text{S}/\text{cm}$
Suspended Solid Matter (SSM)	3.6	ppm
Chloride	246.5	ppm
Oil and Grease	1.6	ppm
Total Hardness	253	ppm
Calcium Hardness	209.5	ppm
Color	20	CU
Total Iron	0.3	ppm
Alkalinity	195.2	ppm
Ammonium	0.02	ppm
Silica	3.3	ppm

After wastewater arrives at the refinery, wastewater enters multimedia filters and multimedia filters remove suspended solids. Then, wastewater goes through activated carbon filters and this step helps adsorbing components which cause the odor and tastes [54]. Next step is the ultrafiltration, which removes 0.01-0.1 μm particle size colloidal particles, viruses and macromolecules. The last step is the ROMU and RO membranes remove 0.0001-0.001 μm particles which generally refer salinity, minerals and micropollutants [55].

ROMU feed stream and permeate stream are the sampling places and some laboratory analysis are done on these samples with different time periods. First sampling line Lab-1 is on feed stream and second sampling line Lab-2 is on permeate stream can be seen from Figure 2.1. Laboratory analysis names, typical characteristics, analyses' cyclic and sampling points are summarized on Table 2.3 for ROMU. Laboratory measurements have not been used in the process identification since they have infrequent experiment cyclic according to online sensors.

Table 2.3: ROMU laboratory analyses' sampling point, name and cyclic.

Sampling Point	Experiment Name	Typical Characteristic	Unit	Experiment Cyclic
Lab-1	SSM	1.4	ppm	Daily
Lab-1	COD	20.2	ppm	Twice a week
Lab-1	Total Iron	0.5	ppm	Once a week
Lab-2	pH	6.6	-	Daily
Lab-2	Conductivity	66.8	$\mu\text{S}/\text{cm}$	Daily
Lab-2	Chloride	14.2	ppm	Daily
Lab-2	SSM	0.2	ppm	Daily
Lab-2	Sulfate	0.8	ppm	Daily
Lab-2	Turbidity	0.2	NTU	Daily
Lab-2	COD	15.8	ppm	Three times a week
Lab-2	Total Iron	0.1	ppm	Once a week
Lab-2	Oil and Grease	1	ppm	Twice a week
Lab-2	Alkalinity	15.6	ppm	Once a week
Lab-2	Silica	0.7	ppm	Twice a month

2.1.3. ROMU Operation Procedure

ROMU contains both online and offline operations. Offline operations include system flush, membrane cleaning, and membrane lay-up. Offline operations are accomplished mostly for upgrading system performance and decreasing operational cost. System flush is done while shutting-down and starting-up as well as during stand-by. When membranes get fouled, membrane cleaning is required for longer membrane life and upgrading operating conditions to save money and time. Membrane lay-up can be required for any reason that causes membranes to shut-down. Online operations for RO membranes correspond to trouble-free operations while taking proper data [8]. For this study, only online operating conditions are considered since the online prediction of permeate flow in real time is the major concern.

2.2. Artificial Neural Networks

ANNs are complex mathematical expressions to infer the interactions among a complex process with a comprehensive historical dataset [56]. Such expressions, with a high number of various activation function types and architectural modifications, transform the input information to the outputs through successive hidden layers which have a pre-specified number of neurons. Once more neurons and layers are introduced, in general, the fitting performance is increased since more parameters are defined and

might yield to poor test performance once overfitting occurs [57]. In addition, such correlated and high number of parameters significantly increase the training computational load with many local optimum parameter values which provide a similar fitting performance.

Feedforward ANNs are special architectures in which the information in the inputs propagates to the outputs only in forward direction during the evaluation of a particular input. A demonstration of feedforward ANN is shown in Figure 2.2.

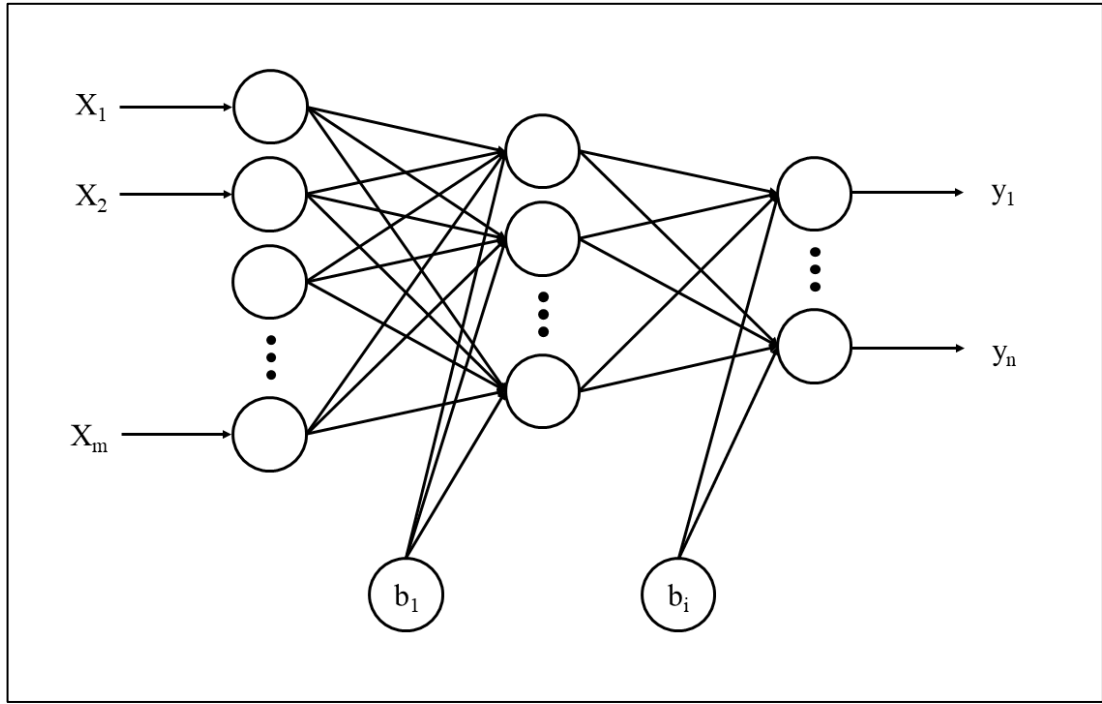


Figure 2.2: A simple ANN architecture.

A typical ANN prediction, y_i which is the prediction of a particular layer is calculated from:

$$y_i = f_i (\sum W_i X_{i-1} + b_i) \quad (2.1)$$

where f_i is the activation function of the layer to process the inputs from the previous layer; X_{i-1} is the input to the i^{th} layer; W_i is the weight matrix; and b_i is the bias vector. m and n in Figure 2.2 are number of inputs and outputs, respectively. In our case, the ANN model contains single hidden layer with 3 neurons using the logistic activation function. A neuron number of 3 is selected according to test set RMSE value depending on neuron number from Figure 2.3. Considering computational time and complexity,

3 neurons have relatively high but still negligible RMSE value. Associated weight matrices and bias vectors are obtained via L-BFGS [58] algorithm. In this study, Python 3.7 is employed for training of ANN model and further applications of ANN model.

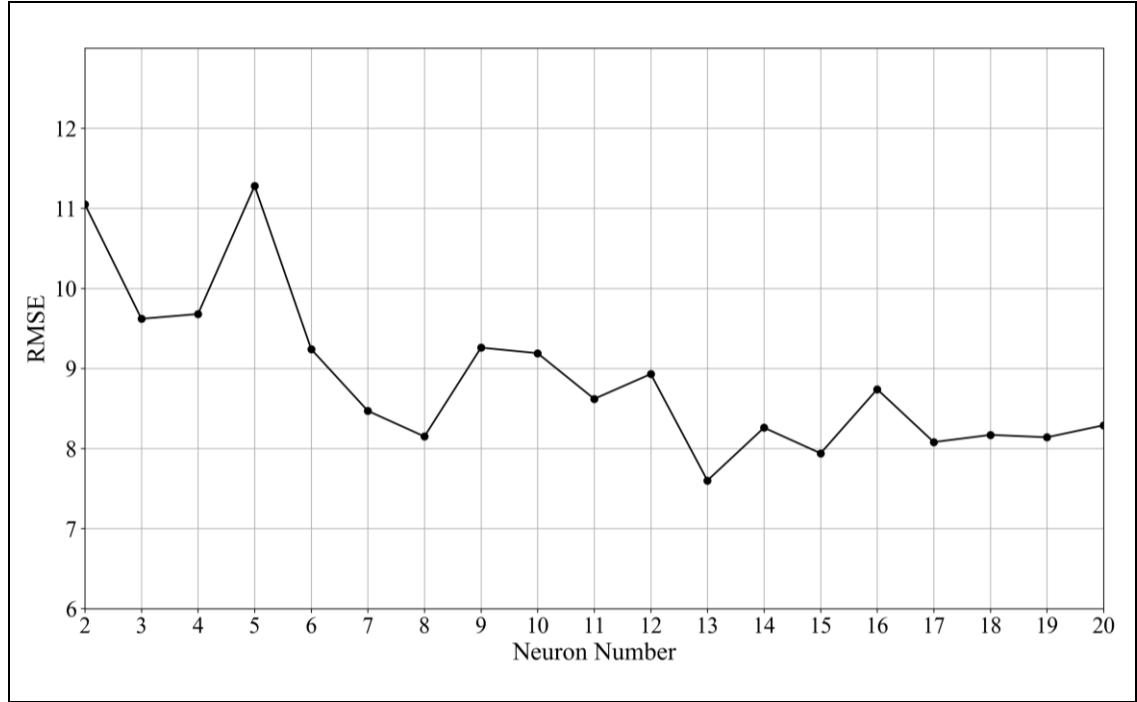


Figure 2.3: RMSE value of changing neuron numbers.

2.3. Data preprocessing and ANN performance

Historical measurements of sensor variables in Table 2.1 from the last 4 years are used for the training and validation of ANN model to identify the impact interactions of corresponding process variables. To the best of authors' knowledge, there are limited studies that consider as many parameters as in this study for such a complex industrial plant. All the sensors in the ROMU were used to simulate the operation of a complex industrial plant in the closest to the real process. Data is fetched hourly considering the time constant of the plant. In the preprocessing step, firstly, the data related to offline operation was removed according to typical range values of every sensor in Table 2.1. Next, daily averages of such measurements were computed; thus a longer time horizon calculation is more manageable. A major contribution from the developed ANN model is the impact of the recent feed and operating conditions on the near-future permeate flow rate, primarily one-week and two-week ahead

permeate flows from the reference date. Thus, a cumulative fouling impact can also be evaluated when recursive simulations are performed. In parallel, the input to the model contains the measurements from the last two weeks. For the training and validation, only a complete set of data with four successive weeks constitute a sample.

Pearson correlation coefficients of input variables can be seen in Figure 2.4 as correlation matrix. Subscript 0 represents the reference week, whereas -1 is the previous week. There are some strong correlations between previous and reference weeks' variables as expected. Since membrane pressure differences represent binary difference between combinations of three pressure values (PI-3, PI-4, PI-5), there are some strong correlation between these pressure differences.

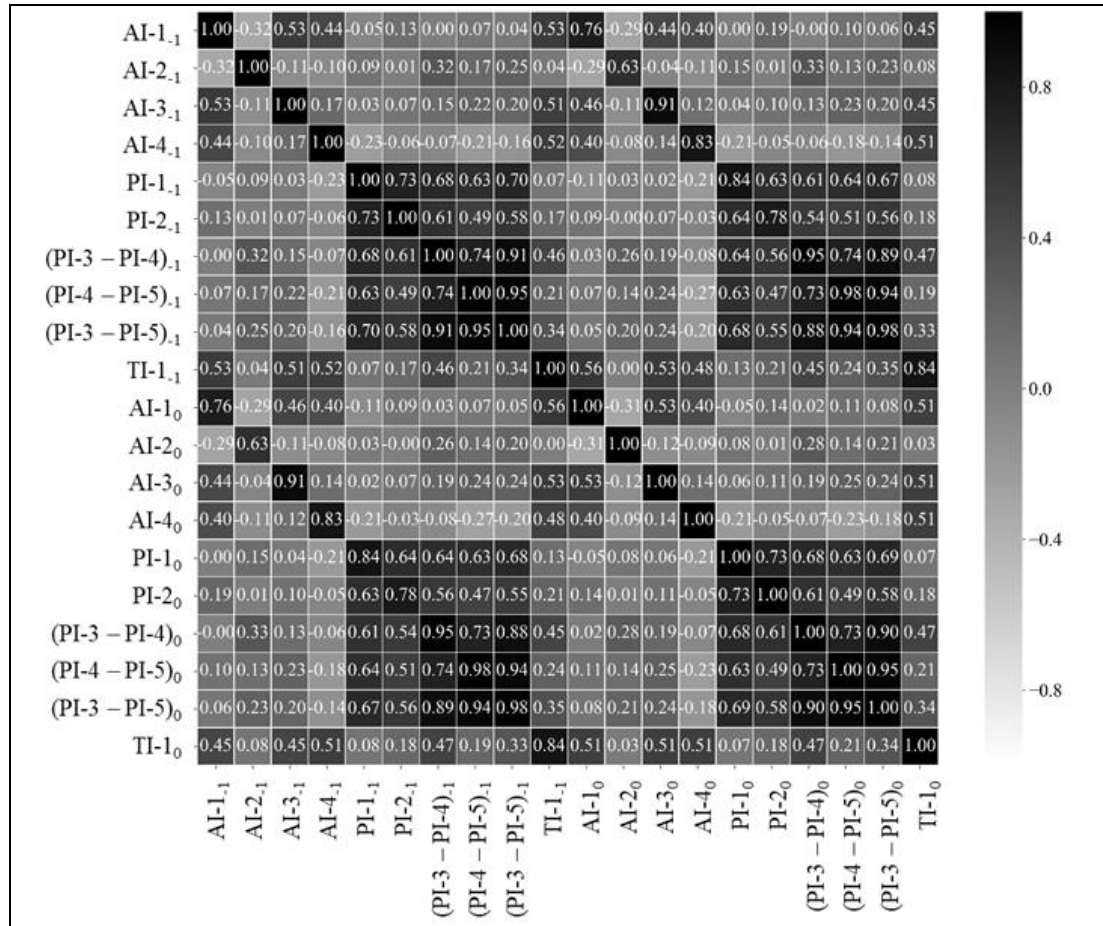


Figure 2.4: Correlation matrix of input variables.

Once the dataset was prepared, the training was performed using 70% of the data. ANN training and test performances are shown in Figure 2.5.

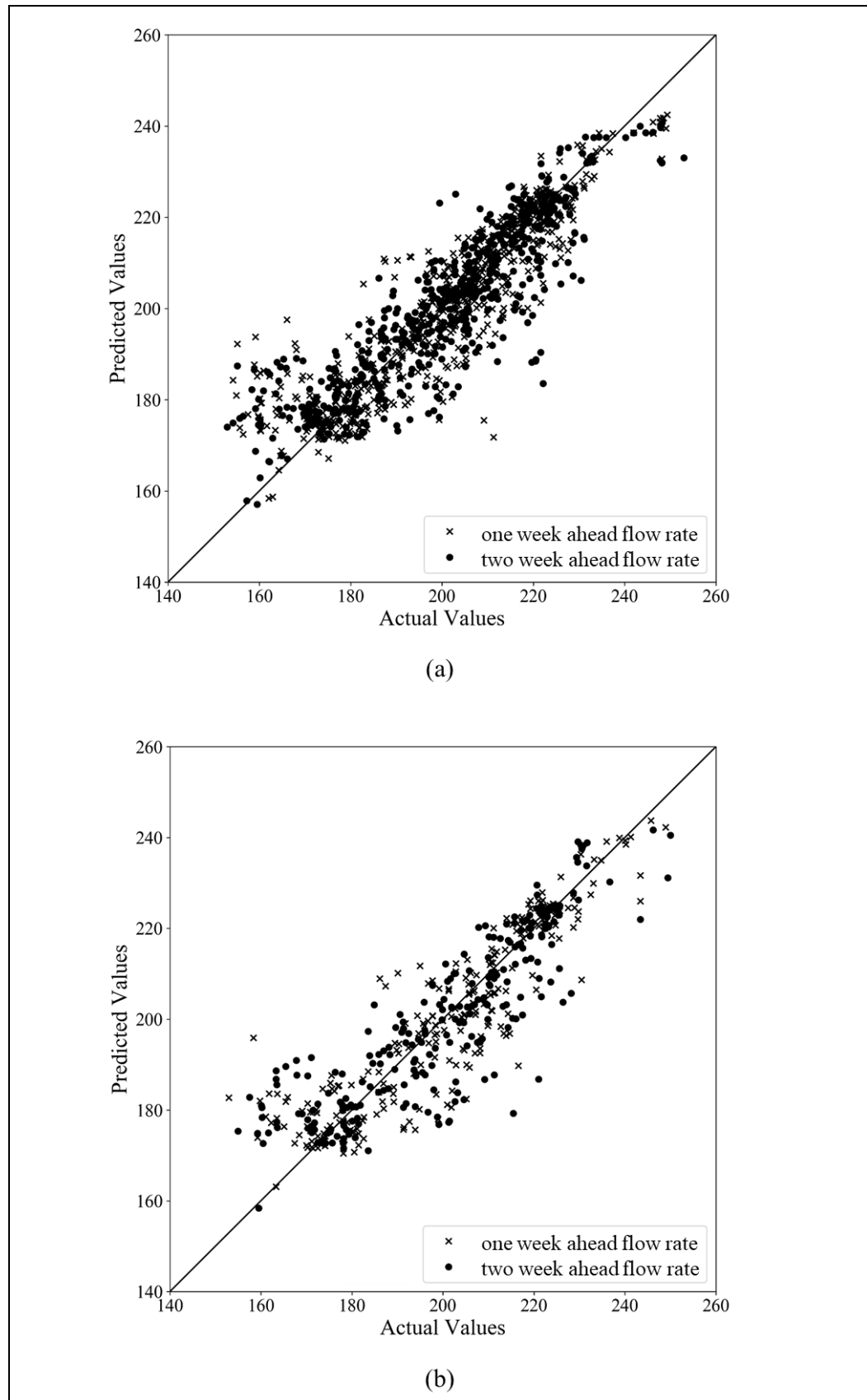


Figure 2.5: Predicted values and actual values of (a) train set, (b) test set.

Mean absolute error (MAE), mean squared error (MSE) and root mean squared error (RMSE), which are ANN model success metrics, of both train and test results are in Table 2.4 . In Figure 2.6, most of the residuals, the model prediction error, of test set vary between -5 and 5. This interval, in which the sensor data also changes daily in ROMU, shows success of the ANN prediction model.

Table 2.4: Train and test sets' performance metrics.

Performance Metric	Train Set	Test Set
MAE	6.78	6.99
MSE	84.09	92.45
RMSE	9.17	9.62

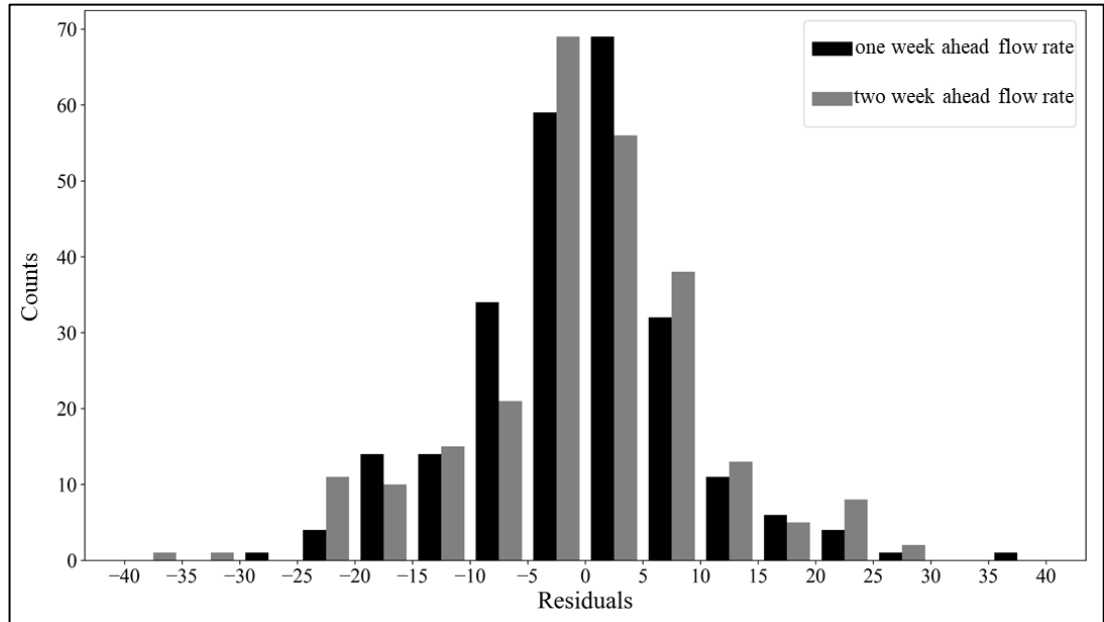


Figure 2.6: Test dataset distribution of residuals.

3. RESULTS AND CONCLUSIONS

3.1. Sensitivity Analysis

Once the impacts on the fouling and their quantitative contribution are known and the outcome is predictable through a model, the maintenance of RO process is more sustainable and scheduled considering the permanent fouling. Sensitivity analysis is a mathematical approach to determine how the change in the model outputs adhere to change in the inputs [59] and can be performed to infer input variables, including the feed properties and other measured disturbances, impact on the fouling. Here the feedforward ANN model, derived in Section 2.3, has been used for such purpose.

Since the sensitivity analysis is a local approach, the results from such analysis are immune to conditions at the evaluation operating regime and might yield different conclusions due to plant nonlinearities over a wider range. On the other hand, the time constant of the fouling process is large and thus such analysis would still deliver a valuable insight. To avoid the theoretical issue, three different operating conditions from a different process operating regimes with different membrane fouling have been used for the evaluation.

For a particular input sample, each variable is perturbed by the same percentage based on their nominal value. The permeate flow rates of three successive dates in one cleaning cycle, when membrane is new, are calculated by ANN using such inputs. The results for 3 different simulations, which are taken from early, middle and late date of the longest cleaning cycle, are shown in Table 3.1 for a new operated RO membrane. Subscript 0 represents the reference week; and -1 is the previous week.

Table 3.1: Sensitivity analysis for three different simulations when RO membrane is new.

Input	Early Date		Middle Date		Late Date	
	One week ahead	Two week ahead	One week ahead	Two week ahead	One week ahead	Two week ahead
AI-1 ₋₁	0.00	0.00	0.00	0.00	0.02	0.02
AI-2 ₋₁	-0.01	-0.01	-0.01	-0.01	-0.02	-0.02
AI-3 ₋₁	0.07	0.06	0.08	0.07	-0.21	-0.24
AI-4 ₋₁	-1.46	-1.44	4.02	4.67	30.28	33.71
PI-1 ₋₁	6.57	7.21	13.14	14.60	16.26	18.43
PI-2 ₋₁	-0.59	-0.46	0.22	0.51	7.49	8.57
(PI-3 – PI-4) ₋₁	4.23	2.06	-0.94	-4.76	1.47	-1.99
(PI-4 – PI-5) ₋₁	-8.53	-7.81	-11.63	-10.69	-8.90	-7.63
(PI-3 – PI-5) ₋₁	-1.11	-1.31	-2.49	-2.90	-1.58	-1.92
TI-1 ₋₁	-0.04	-0.08	-0.20	-0.27	-0.31	-0.40
AI-1 ₀	0.00	0.00	0.00	-0.01	-0.02	-0.02
AI-2 ₀	0.00	0.00	0.01	0.02	0.01	0.02
AI-3 ₀	-0.07	-0.04	0.02	0.08	0.26	0.35
AI-4 ₀	9.59	7.60	10.14	6.79	0.80	-3.42
PI-1 ₀	-53.46	-46.06	-52.97	-43.15	-31.87	-18.75
PI-2 ₀	-10.68	-12.12	-21.42	-24.37	-4.62	-5.73
(PI-3 – PI-4) ₀	-8.79	-6.47	-5.77	-1.80	20.76	28.09
(PI-4 – PI-5) ₀	1.56	-0.10	-2.69	-5.63	-0.65	-3.40
(PI-3 – PI-5) ₀	-0.70	-0.89	-1.55	-1.91	1.38	1.32
TI-1 ₀	-0.18	-0.17	-0.30	-0.30	-0.49	-0.51

The most sensitive input parameters at the early and middle of cleaning cycle for a new membrane are the inlet pressure value of cartridge filters and the outlet pressure value of cartridge filters at the reference week, respectively. Both output flow parameters are affected negatively by the inlet pressure value of cartridge filters at the reference week, but magnitude of impact that input decreases as fouling becomes significant through cycles. A similar conclusion is given in [39] where cartridge filter pressure difference is determined as an indicator of fouling and has a high negative impact on fouling indicator parameter. The second sensitive parameter, which is the outlet pressure value of cartridge filters at the reference week, has a negative impact on both output parameters until the late date of the cycle. On the other hand, at the late of the cleaning cycle, the outlet pressure value of cartridge filters at the reference week impact on the outputs decreases significantly. However, the outlet pressure value of cartridge filters at previous week has negative sensitivity at an early date of the cleaning cycle and sensitivity results turns to positive and larger with the cleaning cycle. This is in line with the process operations in which cartridge filters used as

pretreatment of RO membrane to filter any fouling material [12]. Therefore, if any change occurs at the cartridge filters, it directly affects to RO membrane fouling. Moreover, permeate water pH at previous week is the second most sensitive input parameter for the late date of cleaning cycle, since RO membranes are generally used for removing ions from the solution and pH is an indicator of ions, pH change in water directly affects RO membrane's flux. While the permeate water pH at previous week for early date of a cleaning cycle has negative sensitivity result, sensitivity result for a middle of a cleaning changes to positive and also late date of the cleaning cycle is positive with significant increasing rate, as well. In addition to that, permeate water pH at reference week has a positive and relatively big effect on permeate flow rates for early and middle date of a cleaning cycle. However, it significantly decreases for late date of a cleaning cycle. This is a typical example of nonlinear behavior of RO process due to the fouling and feed properties and shows the complexity of daily operations due to changing magnitudes and even signs of the gains of process variables as operation proceeds. This nonlinear behavior has been investigated in the literature as well. Hoang et al. [60] showed that normalized permeate flow rate increases with increasing pH level for CaCl_2 solution and Na_2SO_4 solution. However, the study showed that normalized flow rate first increases and then decreases with increasing pH level for NaCl solution. On the other hand, Childress et al. [61] reported that, there was a peak in relatively constant permeate flow instead of a constant feed flow with varying pH range. There may be two reasons for peak in permeate flow rate according to authors: polymer structure change in membrane can cause pore size increasing and decreasing electroviscous effects can cause water permeation increasing. The third most sensitive input at the late date of cleaning cycle is the first stage pressure difference at reference week. In addition, the first stage pressure difference at reference week for early and middle date of the cleaning cycle have negative effect on output parameters, but they have relatively small sensitivity at the late date of cleaning cycle of membrane. When membranes get fouled in time and permeate flow rates, which are model's outputs, decrease, the input pressure of first stage is increased to provide a temporary increase in permeate flow. Therefore, sensitivity increases when membrane fouling is most intense. Also, these time periods are taken from different seasons. Early, middle and late date of the cleaning cycle period are taken from November, April and August, respectively. Seasonal change also has a great effect on membrane, and thus the permeate flow rate. Previous week and reference week temperature

parameters have negative and small effects on permeate flow rates. However, seasonal change may affect feed water conductivity and in turn permeate conductivity. That situation causes sensitivity of conductivity change positive to negative or negative to positive for both previous week and reference week.

Next, a newly operated RO membrane and 4 years old RO membrane, another relatively long cleaning cycle for old membrane, is compared to show the impact of regeneration procedures on the process. Same steps are done for 4 years old membrane for three different particular simulations: early, middle and late date of the cleaning cycle period. Sensitivity analysis results are shown in Table 3.2.

Table 3.2: Sensitivity analysis for three different simulations when RO membrane is old.

Input	Early Date		Middle Date		Late Date	
	One week ahead	Two week ahead	One week ahead	Two week ahead	One week ahead	Two week ahead
AI-1 ₋₁	0.03	0.03	0.00	0.00	0.02	0.02
AI-2 ₋₁	-0.03	-0.03	-0.01	-0.01	-0.01	-0.01
AI-3 ₋₁	-0.36	-0.42	-0.15	-0.18	-0.11	-0.13
AI-4 ₋₁	30.24	33.70	3.56	4.19	1.18	1.27
PI-1 ₋₁	12.78	14.64	-4.91	-5.62	18.97	21.76
PI-2 ₋₁	11.23	12.77	2.36	2.87	3.05	3.42
(PI-3 – PI-4) ₋₁	0.70	-4.13	14.35	12.70	-13.76	-16.14
(PI-4 – PI-5) ₋₁	-9.50	-7.85	-9.69	-8.40	-1.38	-1.44
(PI-3 – PI-5) ₋₁	-1.82	-2.24	0.69	0.69	-3.21	-3.67
TI-1 ₋₁	-0.44	-0.55	0.11	0.09	-0.51	-0.58
AI-1 ₀	-0.03	-0.04	0.01	0.00	-0.03	-0.03
AI-2 ₀	0.02	0.02	-0.02	-0.01	0.04	0.04
AI-3 ₀	0.40	0.52	-0.12	-0.08	0.42	0.48
AI-4 ₀	-5.20	-12.31	-29.39	-36.69	-48.62	-55.15
PI-1 ₀	-41.01	-29.01	-80.42	-73.78	37.48	43.61
PI-2 ₀	-8.17	-9.96	3.25	3.55	-18.32	-20.94
(PI-3 – PI-4) ₀	27.32	36.02	-11.81	-8.61	29.32	33.51
(PI-4 – PI-5) ₀	-1.30	-4.92	10.43	9.38	-13.28	-15.40
(PI-3 – PI-5) ₀	2.44	2.42	1.76	1.82	-2.23	-2.58
TI-1 ₀	-0.69	-0.72	-0.32	-0.31	-0.22	-0.24

The most sensitive parameters for early date of cleaning cycle are the inlet pressure value of cartridge filters at the reference week, permeate water pH at previous week and first stage pressure difference at reference week. All these parameters are also the same with the most sensitive parameters for late date of the cleaning cycle of new membrane. This situation may be the cleaning cycle that is before the selected

cleaning cycle, was not efficient and membrane have permanent fouling. The inlet pressure value of cartridge filters at the reference week is also the most sensitive parameter for middle and late date of the cleaning cycle same as the newly operated membrane. The only difference is the sensitivity value changes sign to positive for old membrane late date of the cleaning cycle. In addition, flow rates have high sensitivity to first stage pressure difference through membranes for early date of cleaning cycle, which is same for middle and late date of cleaning cycle, as well. However, sensitivity for middle of cleaning cycle is negative unlike early and late date of cleaning cycle. Permeate flow rates sensitivities to first stage pressure difference at previous week are increased with the fouling occurrence. Also, the other pressure parameters such as second stage pressure difference and the outlet pressure of cartridge filters at reference week, and the inlet pressure at previous week highly affect flow rates. Since more pressure parameters affect flow rates for old membrane, it is showed that old RO membrane is more affected with permanent fouling. Permeate flow rate is decreased by fouling, and high-pressure pump power is increased to compensate the decreased flow rates. In addition to that, system hydraulics affect permeate flow rates with varying pressures. Fayaz et al. [62] also explained that fouling formation leads to increase in pressure differences thorough RO membranes and decrease in permeate flow rates. Furthermore, the results for old membrane show that high sensitivity to permeate water pH level is observed for old membrane, similar to the late date of cleaning cycle of newly operated RO membrane. This similarity implies that, salts cause permeant deterioration to RO membrane. In addition, temperature has negative and small effect on permeate flow for both new and old membrane. Roehl et al. [39] indicate that temperature is one of the least predictive parameters for scale and biofilm growth. Since sensitivity analysis is a local analysis as mentioned above, change in feed flow affects the fouling characteristic of RO membrane for secondary treatment of municipal wastewater [63]. Therefore, operational parameters have different effects on flow rate behavior considering new or old RO membrane even in a cleaning cycle.

3.2. Operating Window

The complex interactions between the ROMU operation parameters and the permeate flow rate must be well understood in order to select the most efficient ROMU configuration and processing regimes. Using the trained ANN model, ROMU plant

operating windows are plotted as binary combination of input parameters with varying minimum and maximum operation values while all other parameters are constant at their nominal values. Constant values are obtained from a typical day to enable ANN evaluation and thus for the plotting local operating windows. The resulting operation windows of the most sensitive input parameters for newly operated RO membrane, which were the inlet and outlet pressure of cartridge filters at reference week (PI-1₀ - PI-2₀), permeate water pH level at previous week (AI-4₋₁) as described in Section 3.1, is shown in Figure 3.1.

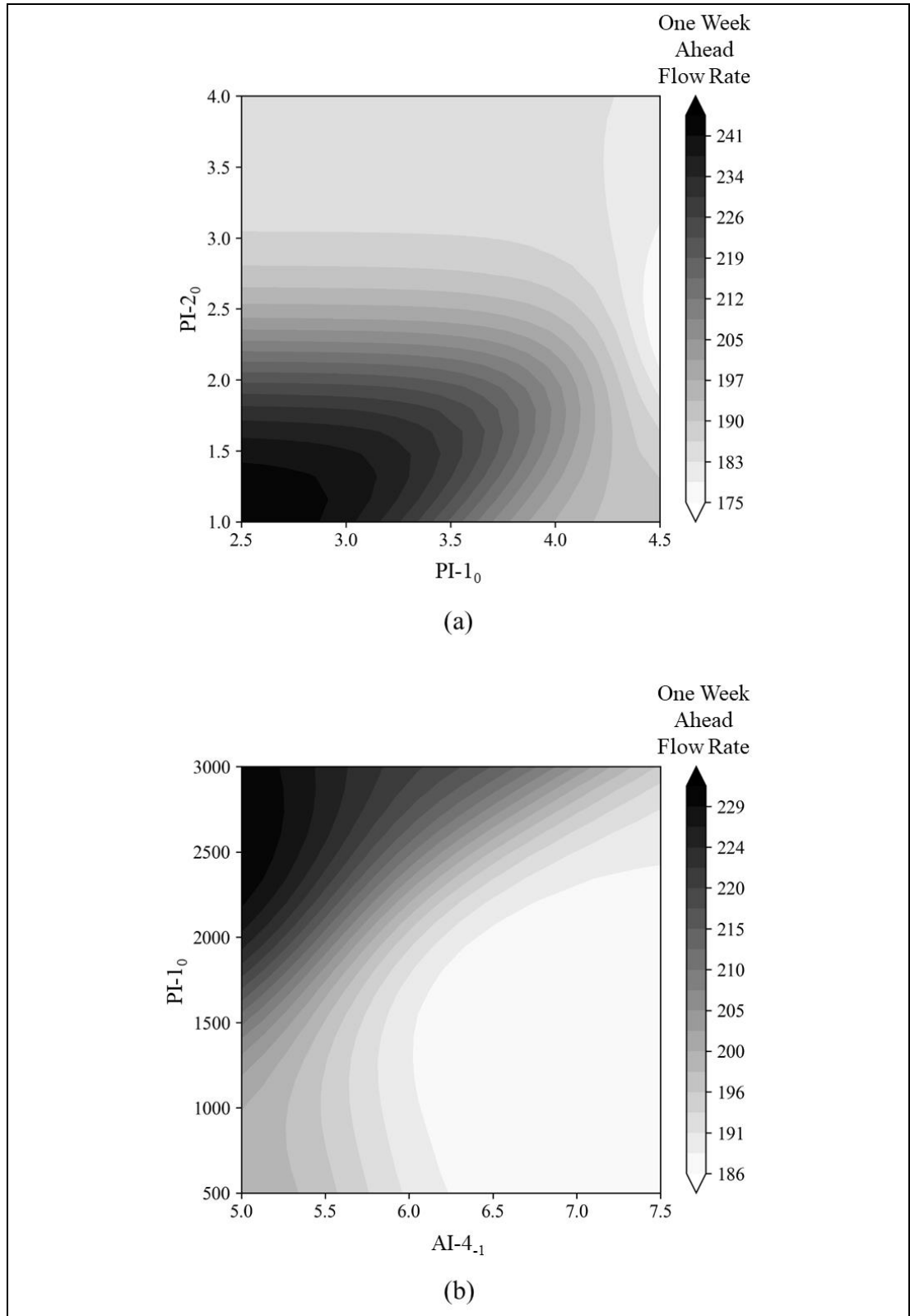


Figure 3.1: Operating windows of most sensitive parameters for newly operated membrane a) early date of the cleaning cycle, b) late date of the cleaning cycle.

Similar to the conclusions in the sensitivity analysis, the outlet pressure of cartridge filters is increased with the increasing inlet pressure of cartridge filters. One

week ahead permeate flow rate has the maximum value with decreasing inlet and outlet pressure of cartridge filters at reference week as shown in Figure 3.1a. In parallel, minimum one week ahead permeate flow rate has reached with maximum inlet pressure and moderate outlet pressure of cartridge filters at reference week. Also, Figure 3.1b shows that maximum one week ahead permeate flow rate is obtained when permeate water is more acidic and the inlet pressure of cartridge filters at reference week is maximum level. For RO membrane cleaning, Cleaning-In-Place (CIP) procedure is followed. CIP solution that used for RO membrane cleaning is generally acidic solution [64], and in treatment unit new membranes are cleaned with acidic CIP solution. Operation with low pH level may cause mitigation of fouling effect during operation.

Also, same parameters from early and late date of newly operated RO membrane in Figure 3.1 are used for ROMU plant performance when membranes are clean and fouled without permanent fouling. The resulting operating windows are in Figure 3.2.

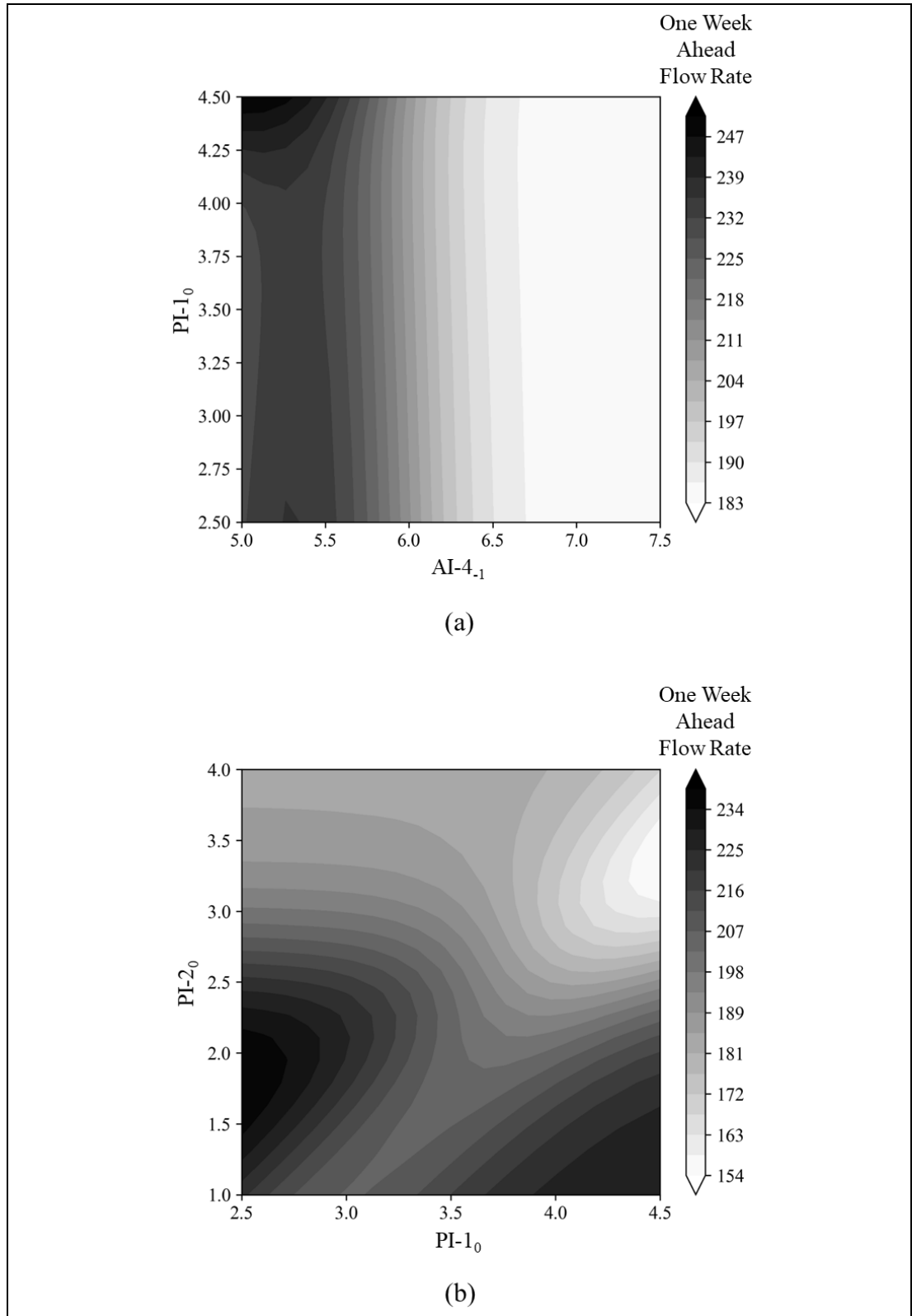


Figure 3.2: Operating windows of same parameters for newly operated membrane a) early date of the cleaning cycle, b) late date of the cleaning cycle.

From Figure 3.1a and Figure 3.2b, it is clear when membrane gets fouled, operating pressure values are higher due to system hydraulics. When membranes are

started fouling, operators set higher inlet pressure for getting higher amount of permeate flow rate. Park et al. [65] showed that applied pressure in feed pump increase over time to keep constant permeate flow rate. Furthermore, Figure 3.2a confirms that low pH level operations are followed with higher flow rate because of mitigation of fouling effect during operation.

An old RO membrane operation behavior may be different than the newly operating RO membrane. Therefore, it is also studied operating windows for 4 years old membrane for the same cleaning cycle with Section 3.1. The resulted operating windows for the most sensitive parameters during relatively long cleaning cycle for an old membrane, which are the inlet pressure of cartridge filters, first stage pressure difference and permeate water pH at reference week, are shown in Figure 3.3 and Figure 3.4.

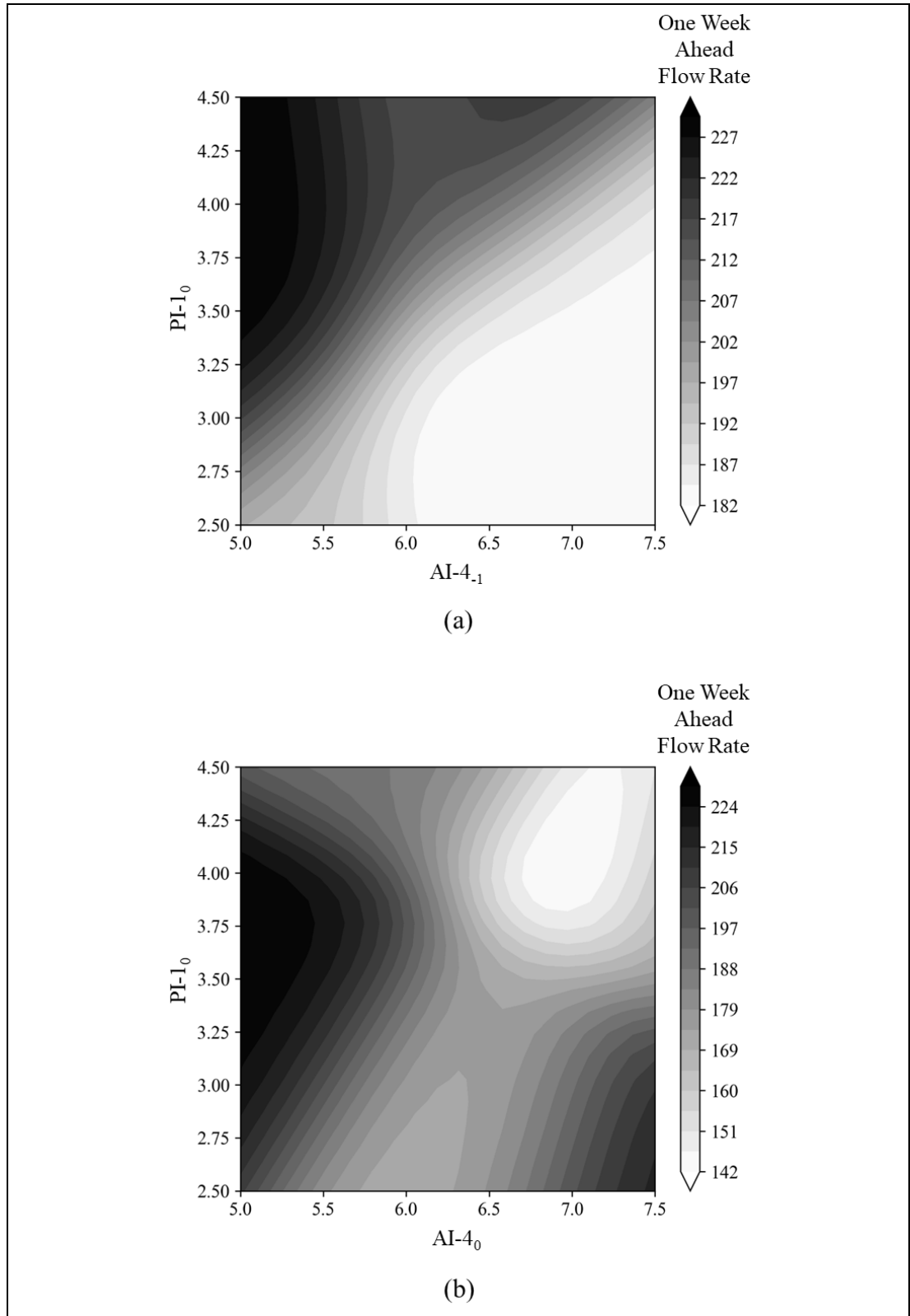


Figure 3.3: Operating windows for old membrane a) early date of the cleaning cycle, b) late date of the cleaning cycle.

From Figure 3.2a and Figure 3.3a, it is showed that plant operations for an old and clean membrane are changed. Figure 3.3a shows more nonlinear relationship and

it operated like fouled membrane in Figure 3.1b. Similarity between Figure 3.1b and Figure 3.3a show that when pH level affected RO membrane, the mitigation effect of pH is permanent even if the membrane is cleaned. For an old and fouled RO membrane in Figure 3.3b, pH level of permeate flow at reference week has similar operating window with previous week permeate flow pH level, but nonlinear relations are obvious. Since PI-1 is the inlet pressure of cartridge filter which is also outlet stream of UF membranes, Mosset et al. [66] showed that silt density index, which is the measurement of fouling potential of suspended solids, of UF pretreated seawater behaves nonlinear like Figure 3.3a and Figure 3.3b. The reason we cannot clearly see this result for new membrane is that all equipment in ROMU also were new and UF membranes were working more effective. In addition, Srivastava et al. [67] indicate that pH change has almost no effect on permeate flow for a pilot plant. Although we have observed similar trends for pH for certain local operating regimes, in addition, in our case, we have calculated a contribution also from pH in a larger range.

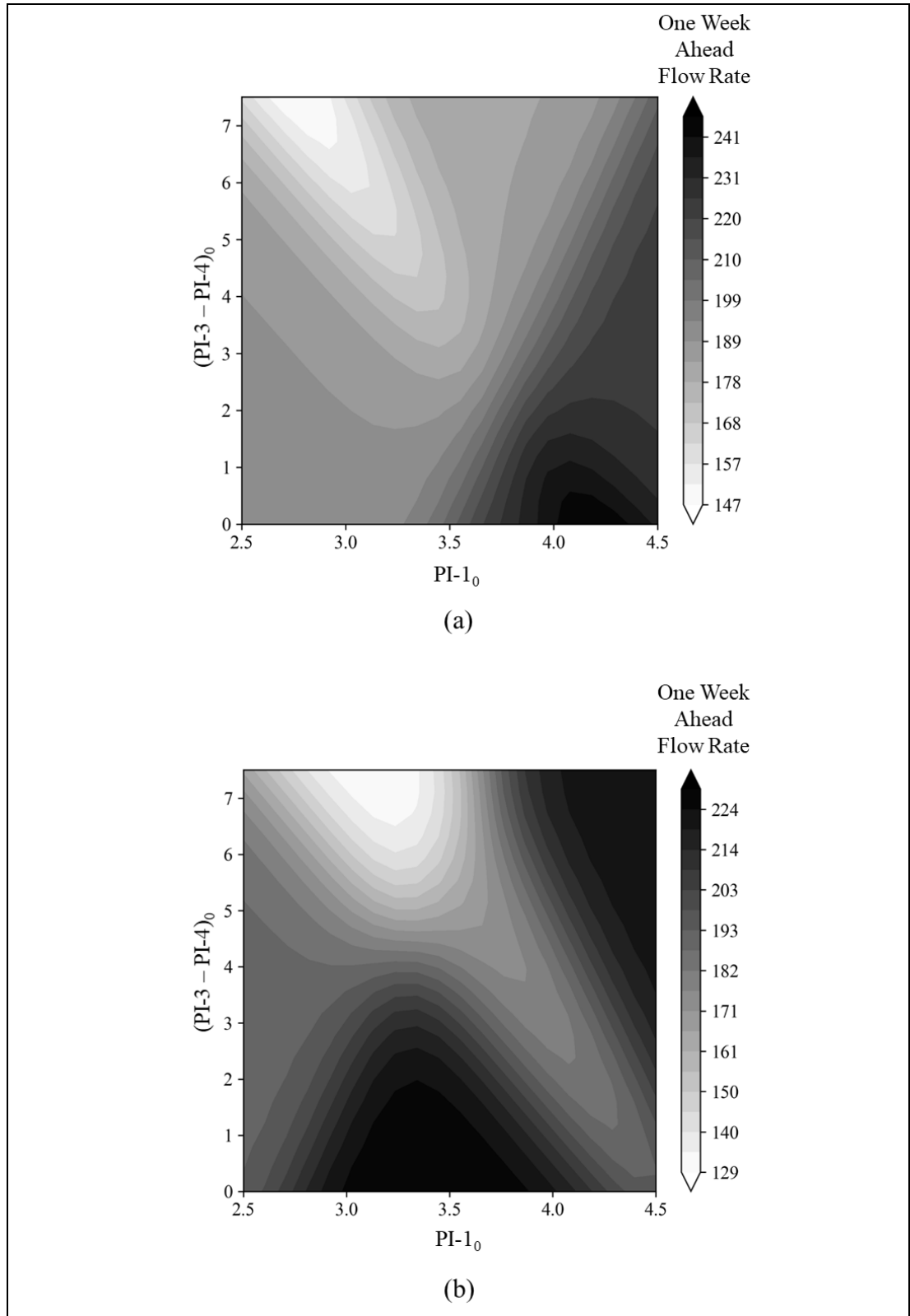


Figure 3.4: Operating windows of most sensitive parameters for old membrane a) early date of the cleaning cycle, b) late date of the cleaning cycle.

First stage pressure difference and inlet pressure of cartridge filters at reference week operating windows for old membrane at the early date of the cleaning cycle show

that maximum permeate flow rate can be obtained at low first stage pressure difference and high inlet pressure of cartridge filters (Figure 3.4a). In order to obtain minimum permeate flow rate for fouled old membrane, moderate inlet pressure of cartridge filters and low first stage pressure difference is ideal. These behaviors for clean and old membrane occur because of system hydraulics. When membrane is clean, there is no need for operating at high pressures to obtain maximum permeate flow rate. However, when membrane gets fouled, there is another operating interval for obtain high permeate flow rate in Figure 3.4b: high first stage pressure differences and high inlet pressure of cartridge filters. It is necessary to work at high pressures in order to tolerate the formed fouling in the membranes and still provide high permeate flow.

In addition, according to literature, maximum flow rate can be obtained with the relatively high temperature and low pressure [37]. Therefore, it is investigated binary relationship of temperature and overall pressure difference while other variables remain at reference week and operation window of newly operated membrane for these parameters are shown in Figure 3.5.

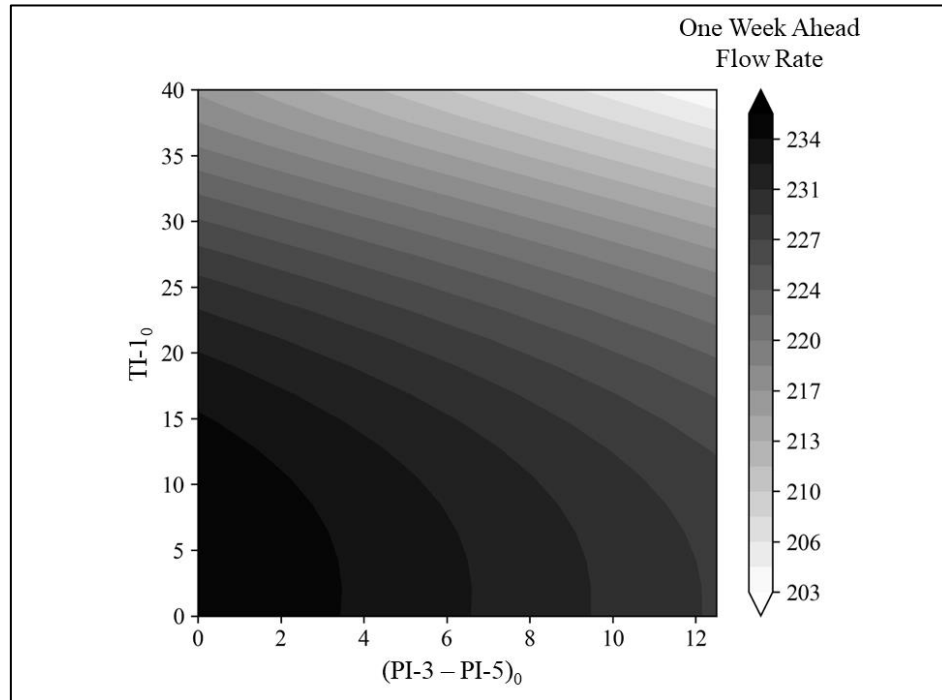


Figure 3.5: Operating window according to variance of the temperature and overall pressure difference.

Figure 3.5 shows that maximum permeate water can be reached with moderate temperature and low overall pressure difference across the membranes. Also, system

hydraulics has great effect on fouling rate, low overall pressure difference indicates no fouling and high permeate flow rate can be obtained. In [37], maximum flow rate is obtained at 30 °C which is moderate for their operating borders and they use trans membrane pressure instead of overall pressure difference (feed pressure – concentrate pressure). Note that, such observations are limited to change of two variables only and the permeate flow might behave differently once the other inputs are subjected to change. On the other hand, a pilot plant experimental study [67] shows that both increasing pressure and temperature enhance permeate flow using narrower operating regime under a relatively low flowrate. Since the permeate pressure is not measured in industrial plant using concentrate pressure instead of permeate pressure when calculating the pressure difference, may have caused differences.

Figure 3.1 to Figure 3.5 show the operating window of two important plant variables, keeping the other variables constant at a particular value. On the other hand, in the actual process, all variables are subjected to change based on the plant nature, manipulated variables and other disturbances. Such historical behavior enables the calculation of the covariance matrix for the representation of changes of corresponding variables around a mean. Cholesky decomposition is used to generate normally distributed multivariable synthetic data to deliver more input dataset to developed ANN model. Figure 3.6 includes the projection of one-week ahead flow rate on two important and easily interpretable variables. The results in Figure 3.6 show that the permeate flow is favored by increased temperature and reduced pressure difference, which is a typical observation in the literature, as well. Also, these conditions are clean membrane parameters and ROMU performance is desired to keep high which means higher permeate flow rates than fouled membrane permeate flow rates. In addition, optimum process conditions in terms of temperature and pressure difference can be inferred to maximize permeate flow rate from Figure 3.6. It is clearly seen that optimum ROMU operation conditions are between 10-20 °C and under 4 kg/cm². White space in Figure 3.6 represents out of operating conditions, and there is no data for those intervals.

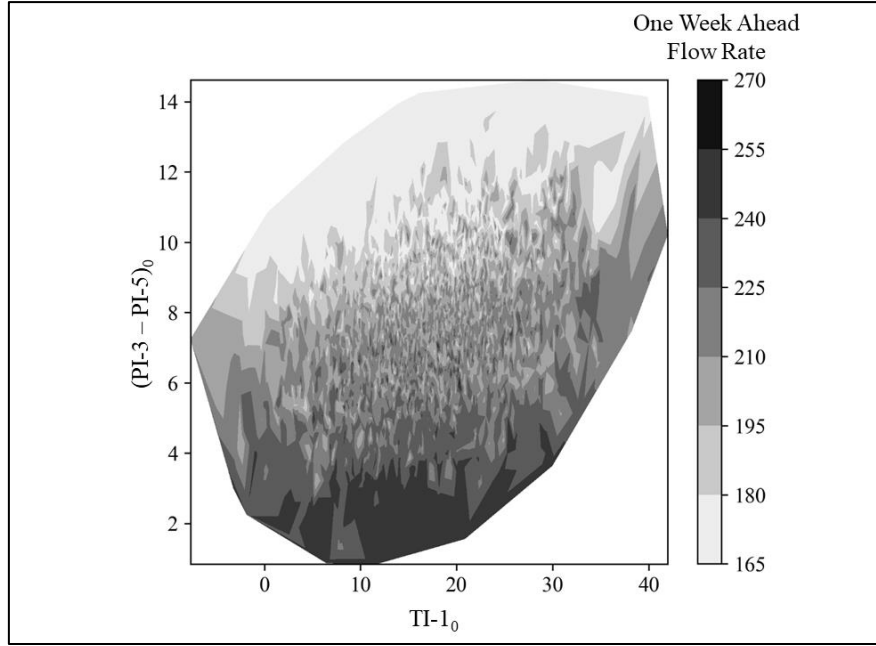


Figure 3.6: ROMU plant performance.

The conclusion from Figure 3.6 is in line with the current industrial experience from the plant, in general. However, it is not possible to validate the local nonlinearity-related complex behaviors based on industrial data. In more detail, Figure 3.7 focuses on lower right quadrant of Figure 3.6, which is expected low fouling effect.

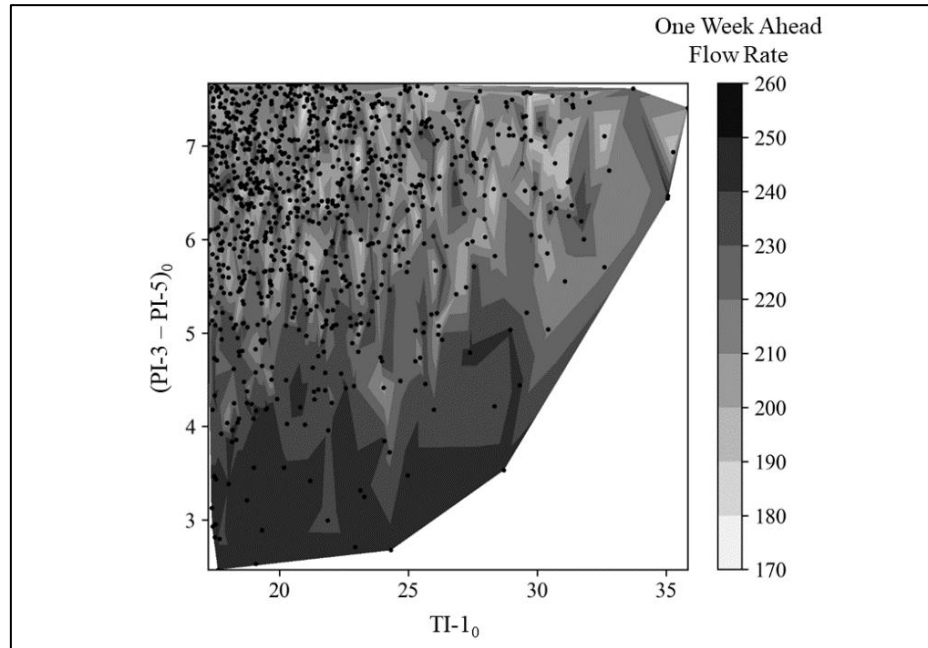


Figure 3.7: ROMU plant performance under low fouling effect.

4. CONCLUSIONS

Monitoring of ROMU plant performance is crucial to deal with fouling. Important process considerations including energy consumption due to increased operational pressure, cleaning frequency, chemical consumption during cleanings, membrane replacement due to permanent fouling are out of control, in practice. In order to decrease water treatment cost, ROMU plant performance parameters which are permeate flow, salt rejection and pressure differences are monitored to manage fouling.

Fouling of industrial RO membrane is a complex process, and physics-based models hinder the large-scale industrial applications. Data-driven modeling of fouling, in our case, is a relatively simple and satisfactory method to model the fouling and the impacts of the processes variables on the process outputs. In our case, permeate flow rate is more crucial and measurable variable for this ROMU plant to represent fouling. In addition, maximization of the permeate flow is a primary refinery concern. To model complex and nonlinear industrial ROMU plant, ANN model is used for the identification. Dynamic ANN model is developed, and it is used for predicting one and two week ahead permeate flow rates. The prediction horizon is limited to two weeks for practical purposes since the operating conditions and feed properties show a significant change over time. Therefore, built ANN model can be used for scheduling of cleaning times effectively, and plant engineers can use this model as decision support in relatively longer time horizons. In addition, this study is important due to simulate the operation of a complex industrial plant in the closest to the real process.

Further, ANN model is used for exploiting the indicator of fouling by operation parameters. For the purpose of understanding the effect of fouling behavior change of plant in time clearly, different cleaning cycles when membranes are new and old, are considered. When membranes are old, permanent fouling is occurred and fouling effect for new membrane, which has no permanent fouling, is investigated. For a new membrane without permanent fouling, the inlet pressure value of cartridge filters at the reference week and the outlet pressure value of cartridge filters at the reference week are the most sensitive parameters at the early and middle date of cleaning cycle. It is clearly showed that any change occurs at the cartridge filters, directly affects RO membrane fouling. The second most sensitive input parameter for late date of cleaning

cycle, which is permeate water pH at previous week, indicates that pH change in water directly affects RO membrane's flux since, RO membranes are generally used for removing of ions from the solution and also pH is indicator of ions. Also, early, middle and late date of the cleaning cycle period are taken from November, April and August, respectively, and it is seen that seasonal change has profound effect on membrane. In order to see permanent fouling effect, sensitivity analysis is applied for old membrane. We can assume permanent fouling occurs in RO membranes because, the most sensitive parameters for late date of the cleaning cycle of new membrane and most sensitive parameters for early date of cleaning cycle for old membrane are same. Also, more pressure parameters affect flow rates for old membrane, it is demonstrated that old RO membrane is more affected with permanent fouling. Moreover, sensitivity result for old membrane is showed that high sensitivity to permeate water pH level is calculated for both the late date of cleaning cycle of new RO membrane and old membrane. This similarity is showed that, salts that cause fouling are origin of permeant deterioration of RO membrane. It is also reminded that sensitivity analysis is a local analysis, change in feed flow characteristic affects fouling characteristic of RO membrane for secondary treatment of municipal wastewater. Therefore, operational parameters have different effect on flow rates behavior is expected result considering new or old RO membrane behavior even in a cleaning cycle.

Another usage area of ANN model is the different binary operational parameter effect on permeate flow rates while other parameters are remaining. Thus, operation windows are plotted and investigated binary parameter relations of most sensitive parameters. While other parameters are remaining during investigating binary relationship of parameters, it affects to see known relationships in plant. Therefore, it is also investigated the most interested parameters which are temperature and pressure difference. By the help of ANN model, optimized process conditions for industrial ROMU plant can be obtained. As there is no control variable in the ROMU plant, application of control system is not suitable for ROMU. However, ANN model can be used for further applications as fully automated decision support system for cleaning times. Besides, cleaning efficiency can be calculated by another model and both models can be work together.

REFERENCES

- [1] Qasim M., Badrelzaman M., Darwish N. N., Darwish N. A., Hilal N., (2019), "Reverse osmosis desalination: A state-of-the-art review", *Desalination*, 459, 59-104.
- [2] Quist-Jensen C. A., Macedonio F., Drioli E., (2015), "Membrane technology for water production in agriculture: Desalination and wastewater reuse", *Desalination*, 364, 17-32.
- [3] Sánchez A. S., (2021), "Toward 'Zero Liquid Discharge' industrial facilities: Reducing the impact on freshwater resources by reusing industrial and urban wastewaters", In: Chaudhery Mustansar Hussain, Editor, "Concepts of Advanced Zero Waste Tools", Elsevier.
- [4] Prihasto N., Liu Q. F., Kim S. H., (2009), "Pre-treatment strategies for seawater desalination by reverse osmosis system", *Desalination*, 249, 308-316.
- [5] Asadollahi M., Bastani D., Musavi S. A., (2017), "Enhancement of surface properties and performance of reverse osmosis membranes after surface modification: A review", *Desalination*, 420, 330-383.
- [6] Mulder M., (1997), "Basic Principles of Membrane Technology", 2nd Edition, Springer Science & Business Media.
- [7] Baker R. W., (2012), "Membrane Technology and Applications", 3rd Edition, John Wiley & Sons.
- [8] Kucera J., (2015), "Reverse Osmosis: Industrial Processes and Applications", 2nd Edition, John Wiley & Sons.
- [9] Ismail A. F., Khulbe K. C., Matsuura T., (2018), "Reverse Osmosis", 1st Edition, Elsevier.
- [10] Tam L. S., Tang T. W., Lau G. N., Sharma K. R., Chen G. H., (2007), "A pilot study for wastewater reclamation and reuse with MBR/RO and MF/RO systems", *Desalination*, 202(1-3), 106-113.
- [11] Radelyuk I., Tussupova K., Zhapargazinova K., Yelubay M., Persson M., (2019), "Pitfalls of wastewater treatment in oil refinery enterprises in Kazakhstan-a system approach", *Sustainability*, 11(6), 1618.
- [12] Wolf P. H., Siverns S., Monti S., (2005), "UF membranes for RO desalination pretreatment", *Desalination*, 182(1-3), 293-300.
- [13] Ismail A. F., Matsuura T., (2018), "Progress in transport theory and characterization method of Reverse Osmosis (RO) membrane in past fifty years", *Desalination*, 434, 2-11.

- [14] Banks W., Sharples A., (1966), "Studies on desalination by reverse osmosis", J. Appl. Chem., 16(1), 28–32.
- [15] Banks W., Sharples A., (1966), "Studies on desalination by reverse osmosis: II. The relation between the fabrication procedure and the structure of cellulose acetate desalination membranes", J. Biochem. Toxicol., 16(3), 94-99.
- [16] Banks W., Sharples A., (1966), "Studies on desalination by reverse osmosis. III. Mechanism of solute rejection", J. Appl. Chem., 16(5), 153–158.
- [17] Micheals A. S., Bixler H. J., Hodges Jr R. M., (1965), "Kinetics of water and salt transport in cellulose acetate reverse osmosis desalination membranes", J. Colloid Sci., 20(9), 1034–1056.
- [18] Sherwood T. K., Brian P. L. T., Fisher R. E., (1967), "Desalination by reverse osmosis", Ind. Eng. Chem. Fundam., 6(1), 2-12.
- [19] Jagur-Grodzinski J., Kedem O., (1966), "Transport coefficients and salt rejection in unchanged hyperfiltration membranes", Desalination, 1(4), 327-341.
- [20] Johnson Jr. J. S., Dresner L., Kraus K. A., (1966), "Chapter 8 - Hyperfiltration (Reverse Osmosis)", In: K. S. Spiegler, Editor, "Principles of Desalination", 1st Edition, New York: Academic Press.
- [21] Spiegler K. S., Kedem O., (1966), "Thermodynamics of hyperfiltration (reverse osmosis): criteria for efficient membranes", Desalination, 1(4), 311-326.
- [22] Lonsdale H. K., Merten U., Riley R. L., (1965), "Transport properties of cellulose acetate osmotic membranes", J. Appl. Polym. Sci., 9(4), 1341-1362.
- [23] Wang J., Dlamini S. D., Mishra A.K., Pendergast M. T. M., Wong M. C. Y., Mamba B. B., Freger V., Verliefde A. R. D., Hoek E. M.V., (2014), "A critical review of transport through osmotic membranes", Journal of Membrane Science, 454, 516-537.
- [24] Jiang S., Li Y., Ladewig B. P., (2017), "A review of reverse osmosis membrane fouling and control strategies", Science of the Total Environment, 595, 567-583.
- [25] Sim et al. L. N., (2018), "A review of fouling indices and monitoring techniques for reverse osmosis", Desalination, 434, 169-188.
- [26] Ruiz-García A., Melián-Martel N., Nuez I., (2017), "Short review on predicting fouling in RO desalination", Membranes, 7(4), 62.
- [27] Hoek E. M. V., Allred J., Knoell T., Jeong B. H., (2008), "Modeling the effects of fouling on full-scale reverse osmosis processes", J. Memb. Sci., 314(1-2), 33-49.

- [28] Karabelas A. J., Sioutopoulos D. C., (2015), "New insights into organic gel fouling of reverse osmosis desalination membranes", *Desalination*, 368, 114-126.
- [29] Tran T., Bolto B., Gray S., Hoang M., Ostarcevic E., (2007), "An autopsy study of a fouled reverse osmosis membrane element used in a brackish water treatment plant", *Water Res.*, 41(17), 3915-3923.
- [30] Sari M. A., Chellam S., (2016), "Reverse osmosis fouling during pilot-scale municipal water reuse: Evidence for aluminum coagulant carryover", *J. Memb. Sci.*, 520, 231-239.
- [31] Wang S., Huang X., Elimelech M., (2020), "Complexation between dissolved silica and alginate molecules: Implications for reverse osmosis membrane fouling", *J. Memb. Sci.*, 605, 118109.
- [32] Chen K. L., Song L., Ong S. L., Ng W. J., (2004), "The development of membrane fouling in full-scale RO processes", *J. Memb. Sci.*, 232(1-2), 63-72.
- [33] Goh P. S., Lau W. J., Othman M. H. D., Ismail A. F., (2018), "Membrane fouling in desalination and its mitigation strategies", *Desalination*, 425, 130-155.
- [34] Libotean D., Giralt J., Rallo R., Cohen Y., Giralt F., Ridgway H. F., Rodriguez G., Phipps D., (2008), "Organic compounds passage through RO membranes", *J. Memb. Sci.*, 313(1-2), 23-43.
- [35] Yangali-Quintanilla V., Verliefde A., Kim T. U., Sadmani A., Kennedy M., Amy G., (2009), "Artificial neural network models based on QSAR for predicting rejection of neutral organic compounds by polyamide nanofiltration and reverse osmosis membranes", *J. Memb. Sci.*, 342(1-2), 251-262.
- [36] Libotean D., Giralt J., Giralt F., Rallo R., Wolfe T., Cohen Y., (2009), "Neural network approach for modeling the performance of reverse osmosis membrane desalting", *J. Memb. Sci.*, 326(2), 408-419.
- [37] Lee Y. G., Lee Y. S., Jeon J. J., Lee S., Yang D. R., Kim I. S., Kim J. H., (2009), "Artificial neural network model for optimizing operation of a seawater reverse osmosis desalination plant", *Desalination*, 247(1-3), 180-189.
- [38] Aish A. M., Zaqoot H. A., Abdeljawad S. M., (2015), "Artificial neural network approach for predicting reverse osmosis desalination plants performance in the Gaza Strip", *Desalination*, 367, 240-247.
- [39] Roehl E. A., Ladner D. A., Daamen R. C., Cook J. B., Safarik J., Phipps Jr D. W., Xie P., (2018), "Modeling fouling in a large RO system with artificial neural networks", *J. Memb. Sci.*, 552, 95-106.
- [40] Barello M., Manca D., Patel R., Mujtaba I. M., (2014), "Neural network based correlation for estimating water permeability constant in RO desalination

process under fouling”, *Desalination*, 345, 101-111.

- [41] Ruiz-García A., Nuez I., (2016), “Long-term performance decline in a brackish water reverse osmosis desalination plant. Predictive model for the water permeability coefficient”, *Desalination*, 397, 101-107.
- [42] Pascual X., Gu H., Bartman A. R., Zhu A., Rahardianto A., Giralt J., Rallo R., Christofides P. D., Cohen Y., (2013), “Data-driven models of steady state and transient operations of spiral-wound RO plant”, *Desalination*, 316, 154-161.
- [43] Park S., Baek S. S., Pyo J. C., Pachepsky Y., Park J., Cho K. H., (2019), “Deep neural networks for modeling fouling growth and flux decline during NF/RO membrane filtration”, *J. Memb. Sci.*, 587, 117164.
- [44] Ehteram M., Salih S. Q., Yaseen Z. M., (2020), “Efficiency evaluation of reverse osmosis desalination plant using hybridized multilayer perceptron with particle swarm optimization”, *Environ. Sci. Pollut. Res.*, 1-14.
- [45] Farahbakhsh J., Delnavaz M., Vatanpour V., (2019), “Simulation and characterization of novel reverse osmosis membrane prepared by blending polypyrrole coated multiwalled carbon nanotubes for brackish water desalination and antifouling properties using artificial neural networks”, *J. Memb. Sci.*, 581, 123-138.
- [46] Cabrera P., Carta J. A., González J., Melián G., (2018), “Wind-driven SWRO desalination prototype with and without batteries: A performance simulation using machine learning models”, *Desalination*, 435, 77-96.
- [47] Khayet M., Cojocaru C., Essalhi M., (2011), “Artificial neural network modeling and response surface methodology of desalination by reverse osmosis”, *J. Memb. Sci.*, 368(1-2), 202-214.
- [48] Madaeni S. S., Shiri M., Kurdian A. R., (2015), “Modeling, optimization, and control of reverse osmosis water treatment in kazeroon power plant using neural network”, *Chem. Eng. Commun.*, 202(1), 6-14.
- [49] Cabrera P., Carta J. A., González J., Melián G., (2017), “Artificial neural networks applied to manage the variable operation of a simple seawater reverse osmosis plant”, *Desalination*, 416, 140-156.
- [50] Nazif S., Mirashrafi E., Roghani B., Bidhendi G. N., (2020), “Artificial Intelligence-Based Optimization of Reverse Osmosis Systems Operation Performance”, *J. Environ. Eng.*, 146(2), 04019106.
- [51] Lee S., Myung S., Hong J., Har D., (2016), “Reverse osmosis desalination process optimized for maximum permeate production with renewable energy”, *Desalination*, 398, 133-143.
- [52] Park K. B., Choi C., Yu H. W., Chae S. R., Kim I. S., (2018), “Optimization of chemical cleaning for reverse osmosis membranes with organic fouling using

statistical design tools”, Environ. Eng. Res., 23(4), 474-484.

- [53] Zhao Y., Taylor J. S., Chellam S., (2005), “Predicting RO/NF water quality by modified solution diffusion model and artificial neural networks”, J. Memb. Sci., 263(1-2), 38-46.
- [54] Spellman F. R., (2013), "Handbook of Water and Wastewater Treatment Plant Operations", 3rd Edition, CRC press.
- [55] Madsen H. T., (2014), “Membrane Filtration in Water Treatment - Removal of Micropollutants”, In: "Chemistry of Advanced Environmental Purification Processes of Water: Fundamentals and Applications", 1st Edition, Newnes.
- [56] Hassoun M. H., (1995), "Fundamentals of artificial neural networks", 1st Edition, MIT press.
- [57] Kavzoglu T., (1999), “Determining Optimum Structure for Artificial Neural Networks”, proceedings 25th Annu. Tech. Conf. Exhib. Remote Sens. Soc., UK Cardiff, UK.
- [58] Nocedal J., Wright S. J., (2006), “Numerical optimization”, In: "Springer Series in Operations Research and Financial Engineering", 2nd Edition, Springer Science & Business Media.
- [59] Al R., Behera C. R., Zubov A., Gernaey K. V., Sin G., (2019), “Meta-modeling based efficient global sensitivity analysis for wastewater treatment plants – An application to the BSM2 model”, Comput. Chem. Eng., 127, 233-246.
- [60] Hoang T., Stevens G., Kentish S., (2010), “The effect of feed pH on the performance of a reverse osmosis membrane”, Desalination, 261(1-2), 99-103.
- [61] Childress A. E., Elimelech M., (2000), “Relating nanofiltration membrane performance to membrane charge (electrokinetic) characteristics”, Environ. Sci. Technol., 34(17), 3710-3716.
- [62] Hossein Fayaz S. M., Mafigholami R., Razavian F., Ghasemipناه K., (2019), “Correlations between silt density index, turbidity and oxidation-reduction potential parameters in seawater reverse osmosis desalination”, Water Sci. Eng., 12(2), 115-120.
- [63] Zhao Y., Song L., Ong S. L., (2010), “Fouling behavior and foulant characteristics of reverse osmosis membranes for treated secondary effluent reclamation”, J. Memb. Sci., 349(1-2), 65-74.
- [64] Jafari M., D'haese A., Zlopasa J., Cornelissen E. R., Vrouwenvelder J. S., Verbeke K., Verliefde A., van Loosdrecht M. C., Picioreanu C., (2020), “A comparison between chemical cleaning efficiency in lab-scale and full-scale reverse osmosis membranes: Role of extracellular polymeric substances (EPS)”, J. Memb. Sci., 609, 118189.

- [65] Park K., Burlace L., Dhakal N., Mudgal A., Stewart N. A., Davies P. A., (2020), “Design, modelling and optimisation of a batch reverse osmosis (RO) desalination system using a free piston for brackish water treatment”, *Desalination*, 494, 114625.
- [66] Mosset A., Bonnelye V., Petry M., Sanz M. A., (2008), “The sensitivity of SDI analysis: from RO feed water to raw water”, *Desalination*, 222(1-3), 17-23.
- [67] Srivastava A., Aghilesh K., Nair A., Ram S., Agarwal S., Ali J., Singh R., Garg M. C., (2021), “Response surface methodology and artificial neural network modelling for the performance evaluation of pilot-scale hybrid nanofiltration (NF) & reverse osmosis (RO) membrane system for the treatment of brackish ground water”, *J. Environ. Manage.*, 278, 111497.

BIOGRAPHY

Pelin Döloğlu was born in Istanbul in 1995. She is R&D engineer in Algorithms & Software Development team. She joined TÜPRAŞ after completing her bachelor of science in Chemical Engineering Department of Istanbul Technical University on June 2018. She is currently enrolled in MSc program in Chemical Engineering in Gebze Technical University since 2018. Her research areas are data mining, artificial intelligence, knowledge extraction and algorithm development.