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**EFFECT OF PRETREATMENT ON MEMBRANE
SCALING IN THE REVERSE OSMOSIS PROCESS OF
GEOHERMAL WATER-PILOT-SCALE STUDIES**

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Chemical Engineering Second Cycle Programme

İZMİR
2024

Mustafa Burak DOĞANAY tarafından yüksek lisans tezi olarak sunulan “Effect of Pretreatment on Membrane Scaling in the Reverse Osmosis Process of Geothermal Water-Pilot-Scale Studies” başlıklı bu çalışma EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliği ile EÜ Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 19/12/2024 tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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EGE ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ**ETİK KURALLARA UYGUNLUK BEYANI**

EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliğinin ilgili hükümleri uyarınca yüksek lisans tezi olarak sunduğum “Effect of Pretreatment on Membrane Scaling in the Reverse Osmosis Process of Geothermal Water-Pilot-Scale Studies” başlıklı bu tezin kendi çalışmam olduğunu, sunduğum tüm sonuç, doküman, bilgi ve belgeleri bizzat ve bu tez çalışması kapsamında elde ettiğimi, bu tez çalışmasıyla elde edilmeyen bütün bilgi ve yorumlara atıf yaptığımı ve bunları kaynaklar listesinde usulüne uygun olarak verdiğimi, tez çalışması ve yazımı sırasında patent ve telif haklarını ihlal edici bir davranışımın olmadığını, bu tezin herhangi bir bölümünü bu üniversite veya diğer bir üniversitede başka bir tez çalışması içinde sunmadığımı, bu tezin planlanmasından yazımına kadar bütün safhalarda bilimsel etik kurallarına uygun olarak davrandığımı ve aksinin ortaya çıkması durumunda her türlü yasal sonucu kabul edeceğimi beyan ederim.

19/12/2024

İmzası

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ÖZET**JEOTERMAL SUYUN TERS OZMOZ İŞLEMİNDE ÖN
ARITMANIN MEMBRAN TIKANMASINA ETKİSİ-PILOT ÖLÇEKLİ
ÇALIŞMALAR**

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ARALIK 2024, 62 Sayfa

Bu çalışmada ısı enerjisi alınmış geotermal suyun ters osmoz (RO) yöntemiyle arıtılması sırasında oluşan membran tıkanmasının problemini azaltmak ve membran ömrünü arttırmak üzere antiskalant ve ultrafiltrasyon ile ön arıtım etkisi incelenmiştir. Antiskalantın türü ve konsantrasyonu membran tıkanmasını önlemede önemli faktörlerden biridir. Yüksek konsantrasyonlarda antiskalantlar biyolojik tıkanmalara sebep olurken düşük konsantrasyonlarda da tıkanıklıkları önlemezler. Çalışmanın ilk aşamasında, Yenikale Jeotermal Isıtma Merkezinde jeotermal su için yapılan mini pilot ölçekli tuzdan arındırma çalışması sırasında farklı konsantrasyonlarda kullanılan ticari olarak temin edilebilen iki antiskalantın membran tıkanmasına karşı etkisinin gözlenmesi amaçlanmıştır. Her bir membran için tuzdan arındırma çalışmasından sonra jeotermal sudaki geçirgenlik değerleri hesaplanmıştır. En uygun antiskalant ve konsantrasyonu belirlenmiştir.

İkinci aşamada ise, jeotermal suyun geri kazanımı için RO işleminin ön arıtma adımı olarak kullanılan ultrafiltrasyonun (UF) etkisini görmek amaçlanmıştır. Deneyle, birinci aşamada kurulan mini pilot ölçekli membran arıtma sistemi kullanılarak gerçekleştirilmiştir. Membran geçirgenlik değerleri,

UF ön arıtma işlemi yapıldığında ya da olmadan hesaplanmıştır. Ayrıca, bu çalışmada antiskalant kullanımının etkisi de araştırılmıştır.

Çalışmanın son adımında, jeotermal ısıtma merkezine kurulan mini pilot sistemde ters ozmoz (RO) membranı kullanılarak elde edilen konsantre akımın yönetilmesi amaçlanmıştır. Konsantredeki çok değerlikli iyonların konsantrasyonunu azaltmak için öncelikle nanofiltrasyon (NF) ve ters ozmoz (RO) membranı ile ön arıtma işlemi yapılmıştır. NF ve RO süzütüsünün daha ileri arıtımı için ters elektrodializ (EDR) yöntemi uygulanmıştır. EDR yönteminin tuzdan arındırma performansı farklı elektrik potansiyeller kullanılarak araştırılmıştır.

Anahtar sözcükler: Jeotermal su, Ters ozmoz (RO), Ultrafiltrasyon(UF), Nanofiltrasyon (NF), Antiskalant, Ters-Elektrodializ (EDR), Konsantre atık yönetimi

ABSTRACT**EFFECT OF PRETREATMENT ON MEMBRANE SCALING IN
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MSc in Chemical Engineering

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December 2024, 62 Pages

In this work, the effect of pretreatment using antiscalant and ultrafiltration was investigated to reduce the membrane scaling problem that occurs during the treatment of used geothermal water by reverse osmosis (RO) method and to increase the life of the membrane. The type and concentration of antiscalant is one of the important factors in preventing membrane scaling. Antiscalants cause biofouling at high concentrations, while they do not prevent scaling at low concentrations. In the first phase of the study, it was aimed to observe the effect of two commercially available antiscalants used at different concentrations against membrane scaling during a mini pilot scale desalination study for geothermal water in Izmir. After each membrane desalination test, the permeability values in geothermal water were calculated. The most suitable antiscalant and its concentration were determined.

In the second stage, it is aimed to observe the effect of ultrafiltration (UF) used as pre-treatment for reclamation and recovery of geothermal water by RO process. A membrane test system installed at Yenikale Geothermal Energy Center in Izmir, on a mini-pilot scale, was used for the experiments. Membrane

permeability values were calculated by applying and not applying of UF process. In addition, effect of antiscalant usage was also investigated in this study.

In the last step of the study, it is aimed to manage the concentrate stream obtained by using a reverse osmosis (RO) membrane in the small pilot system installed at the geothermal energy center. In order to reduce the concentration of multivalent ions in the concentrate, first of all, a pre-treatment by a nanofiltration (NF) and reverse osmosis (RO) membranes was carried out. For further treatment of the NF permeate, electro dialysis reversal (EDR) method was applied. Desalination performance of the EDR method was investigated by using different electrical potentials.

Keywords: Geothermal water, Reverse osmosis (RO), Ultrafiltration (UF), Nanofiltration (NF), Antiscalant, Reverse-Electrodialysis (EDR), Concentrate waste management.

ÖNSÖZ

Bu çalışmada, Yenikale jeotermal ısı tesisindeki kullanılmış jeotermal atık suyun arıtımı sırasında oluşan membran tıkanmalarının önlenmesi amacıyla antiskalant kullanımı ve UF ön arıtım işlemi uygulanmış, böylece en uygun ön arıtma metodunun belirlenmesi hedeflenmiştir. Buna ek olarak arıtma sonrası oluşan konsantre atığın yönetilmesi amacıyla öncelikle NF ve RO ile ön arıtım ve ardından ters elektrodiyaliz (EDR) yöntemi kullanarak konsantreden de kullanılabilir su eldesi sağlanmıştır. Bu tez çalışmasında incelenen konular üç ana başlık altında verilebilir. Birinci bölümde membran tıkanmalarına karşın iki farklı antiskalantın dört farklı konsantrasyonda kullanarak antiskalant etkisi incelenmiştir. İkinci başlıkta ise UF ön filtrasyonun membran tıkanmasına etkisi antiskalantlı ve antiskalantsız olarak incelenmiştir. Üçüncü adımda ise jeotermal suyun arıtımı sonrası oluşan konsantre akımının yönetilmesi amacıyla NF ve RO yöntemi ile ön arıtım sonrasında ters elektrodiyaliz yöntemi ile ileri arıtım dört farklı elektriksel potansiyel uygulanarak incelenmiştir. Yeni kale jeotermal ısı merkezi sahasında gerçekleştirilen mini pilot ölçekli çalışmaları TÜBİTAK-NCBR projeleri kapsamında desteklenmiştir.

İZMİR

12/09/2024

Mustafa Burak DOĞANAY

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NOMENCLATURE

<u>Symbol</u>	<u>Explanation</u>
J_v	Permeate Flux (L/m ² h)
J_{25}	Permeate Flux Value at 25 °C (L/m ² h)
A	Active Area (m ²)
h	Hour
P	Pressure (bar)
π	Osmotic Pressure
T	Temperature (°C)
V	Electrical Potential (V)
W	Electrical Power (W)

Abbreviations

EC	Electrical Conductivity
EDR	Electrodialysis-Reversal
EPA	United States Environmental Protection Agency
GW	Geothermal Water
IEA	The International Energy Agency

NOMENCLATURE (continued)

IEM	Ion Exchange Membrane
IRENA	The International Renewable Energy Agency
RO	Reverse osmosis
NF	Nanofiltration
UF	Ultrafiltration
SW	Sea Water
XLE-RO	Extreme Low Energy Reverse Osmosis
PV	Photo Voltaic
MTA	General Directorate of Mineral Science and Exploration
AC	Alternate Current
DC	Direct Current
TDS	Total Dissolved Solid (mg/L)

1. INTRODUCTION

1.1. Renewable Energy

Nowadays, it has been proven that fossil fuels and nuclear energy create problems in terms of environmental health and that they are not ecologically and environmentally clean and sustainable. Local, national and global environmental health problems caused by energy production from nuclear and fossil fuels and the very high costs of measures to be taken to eliminate them have brought to the agenda the search for energy end-use efficiency and clean and renewable energy production (Goldemberg, 2000).

According to the definition of the The International Renewable Energy Agency (IRENA), renewable energy comes from naturally occurring processes that replenish themselves continuously. As shown in Figure 1.1, solar, wind, biomass, geothermal, hydraulic power, marine energy and hydrogen energy are resources defined as renewable energy. In addition to being environmentally friendly, such renewable energies are inexhaustible energy sources that renew themselves as long as the world exists (Ghandriz et al., 2021).

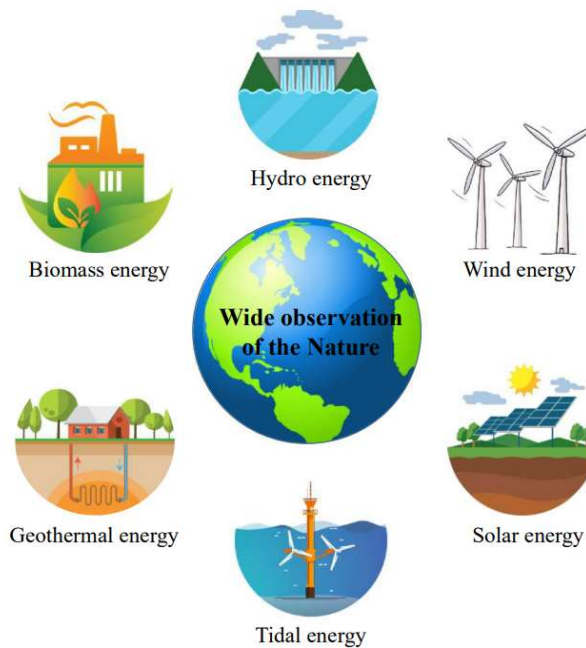


Figure 1.1. Renewable energy sources (Ghandriz et al., 2021).

One could argue that the primary benefits of using energy from green sources are that they are ecological, do not cause soil and water pollution, are inexhaustible, and reduce the country's energy dependence because they are domestic resources (Ghandriz et al., 2021).

Table 1.1. Classification of renewable energy sources according to their main sources (Zielińska, 2010).

RENEWABLE ENERGY SOURCES				
Main Source	Primary Energy Sources	Natural Energy Conversion	Technical Energy Conversion	Area of Usage
Solar	Water	Evaporation, rainfall	Water power facilities (Hydroelectric Power Plants)	Electrical energy
	Wind	Air movement	Wind power turbines	Electrical and mechanical energy
		Wave motion	Wave Energy Facilities	Electrical and mechanical energy
	Sunlight	Warming of the earth and atmosphere	Heat pumps	Heat energy
			Collectors	Heat energy
		Sunlight	Solar cells (photovoltaics)	Electrical energy
	Biomass	Biomass production	Heat power plants	Electrical and heat energy
			Conversion facility	Fuel energy
World	Earth Centre Temperature	Geothermal energy	Geothermal heat facility	Electrical and heat energy
Moon	Gravity of the Moon	Tidal phenomenon	Tidal plant facilities	Electrical energy

Renewable energy sources can be examined in three groups according to the main source of energy: solar source, earth source and lunar source. Table 1.1 makes clear that the sun is the primary source of the energy from biomass, wind, sunlight, and hydraulic sources. The earth provides geothermal energy, which is produced by the heat from the planet's center. The tidal phenomenon that occurs due to the power of lunar gravity is the energy whose main source is the moon (Zielińska, 2010).

The world's annual energy need is increasing rapidly in parallel with population growth. Along with developing technology, increases in pricing for petroleum products, and adverse consequences coal-using facilities and nuclear energy on the environment have made it necessary to use renewable energy resources more effectively. Pollutant emissions such as CO₂, SO_x, NO_x, which are produced as a result of the burning of fossil fuels and released into the atmosphere, negatively affect the environment by creating a greenhouse effect and causing climate change. In particular, the use of poor quality domestic lignite with low thermal capacity and high ash and sulfur contents increases air pollution. These negative effects increase the importance of using renewable energy resources (Asghar et al., 2021).

Today, within the limits of their economic capacity, developed or developing nations prioritize the consumption of sources of clean energy. At the beginning of the 21st century, as prices rise and environmental concerns worsen, using fossil fuels to generate energy will become unprofitable and the trend towards alternative energy sources will continue to increase (Ghandriz et al., 2021).

1.2. Geothermal Energy

The heat that exists in the interior of the Earth is known as geothermal energy. The physical processes taking place within our planet's interior structure are the source of this energy. Through a carrier, significant volumes of heat can be extracted and used. Geothermal fluids and other carriers, like them, are used to transport heat to accessible depths under the earth's surface. In essence, geothermal fluids are raindrops that enter the earth's crust from recharge areas, come into touch with hot rocks, and heat up as a result. After then, these heated fluids condense at high pressures as well as temperatures in aquifers. These aquifers are numerous and play a significant role in geothermal fields (Barbier, 2002).

If the temperature of a geothermal energy source is between 20 and 70 °C, it is a source of medium enthalpy if temperature range between 70 and 150 °C, or

higher than 150 °C, it is considered high enthalpy source (Kamila et al., 2021). Low and medium enthalpy geothermal resources are used primarily for heating purposes such as greenhouses, buildings, thermal facilities, industrial areas such as food product drying, paper and textile industry, cooling facilities. High enthalpy geothermal resources are widely preferred in electrical energy production (Carapezza et al., 2022).

1.3. Geothermal Energy in the World

Since the Roman era, hot water and hot steam sources close to the soil have been utilized to heat buildings and thermal springs as well as for cooking and bathing. Iceland then started to use primarily hot water as a geothermal fluid for household heating, making it one of the first nations to do so (Jalilinasrabady and Itoi, 2013).

Geothermal energy has just recently become a significant source of electricity production. In 1904, geothermal energy was produced for the first time in the Larderello area of Tuscany, Italy. A 350 MWe of primary output was produced there in 1970. Geothermal energy has caught the interest of many nations because it is a local energy source and the only source in certain countries, especially in light of the economic competition over other forms of energy following World War II (Jalilinasrabady and Itoi, 2013).

Depending on geological factors, the global distribution of thermal energy is not constant. Three regions dominate the geothermal resource distribution profile on a global scale. The first is the circum-Pacific belt's west coast, which is made up of China, Taiwan, West Indonesia, Australia, and the Philippines. The second zone is the Mid-Atlantic Ridge reaches the northern tip of Iceland and is mostly ocean; the Mediterranean to Himalayan region, the third zone, comprises Italy and Tibet in China (Sharmin et al., 2023).

Table 1.2. The ten countries that use geothermal energy the most and their capacities (Sharmin et al., 2023).

Country	Installed Capacity (MWe)
United States	3700
Indonesia	2289
Philippines	1918
New Zealand	1604
Türkiye	1549
Kenya	1193
Mexico	1105
Italy	916
Iceland	755
Japan	550

The ten countries that established the highest number of plants that use thermal energy on 2020 and energy capacities are shown in Table 1.2. Apart from developed countries such as America, Japan and Italy, developing countries such as Türkiye, Kenya and Indonesia also attach great importance to geothermal power since it lessens reliance on foreign energy sources and is a green energy source (Sharmin et al., 2023).

1.4. Geothermal Energy in Türkiye

Türkiye is situated on the Turkish Peninsula, which is positioned between the northern Mediterranean and the Black Sea. Because of the frequent volcanic activity and the tectonic changes of rock formations, this region is considered geologically active. Considering faults and volcanic activities, Türkiye is a country rich in geothermal resources (Hepbasli and Canakci, 2003).

In the 1960s, the General Directorate of Mineral Science and Exploration, or MTA, started looking into Türkiye's thermal resources. Geothermal technology has advanced significantly in Türkiye recently. 17 Turkish cities currently make use of geothermal energy. The majority of Türkiye's geothermal facilities are located in Western Anatolia, as seen in Figure 1.2 (Mertoglu et al, 2021).

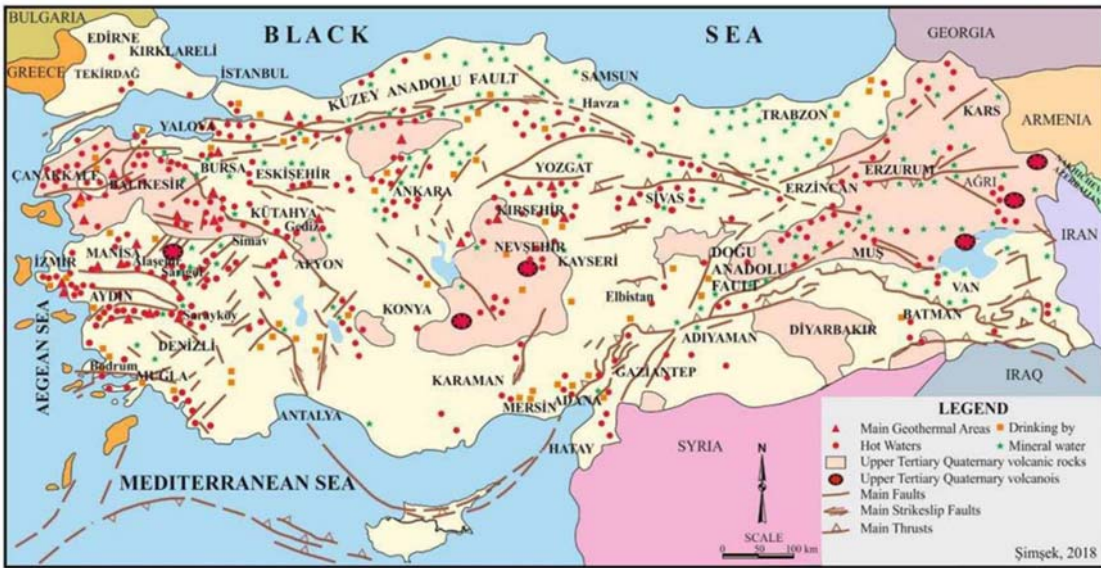


Figure 1.2. Türkiye's active faults and geothermal resource distribution (Mertoglu et al, 2021).

1.5. Geothermal fluid

The chemical content of geothermal fluids may vary depending on the area where the geothermal field is located and even over time within the same geothermal field. Liquid and gaseous forms are the two categories into which geothermal liquids fall.

1.5.1. Geothermal fluid liquid phase

The composition of geothermal water is determined by its interaction with large-scale components found in the reservoir rocks and the subterranean environment. The amount of chemical species dissolved is influenced by both temperature and local geology. Low-temperature sources have lower total dissolved solids (TDS) contents than sources with higher temperatures. TDS content varies between 2500 and 81000 mg/L in geothermal liquids with temperatures over 150 °C along with 1100 and 8200 mg/L in fluids about 90 and 150 °C (Finster et al., 2016).

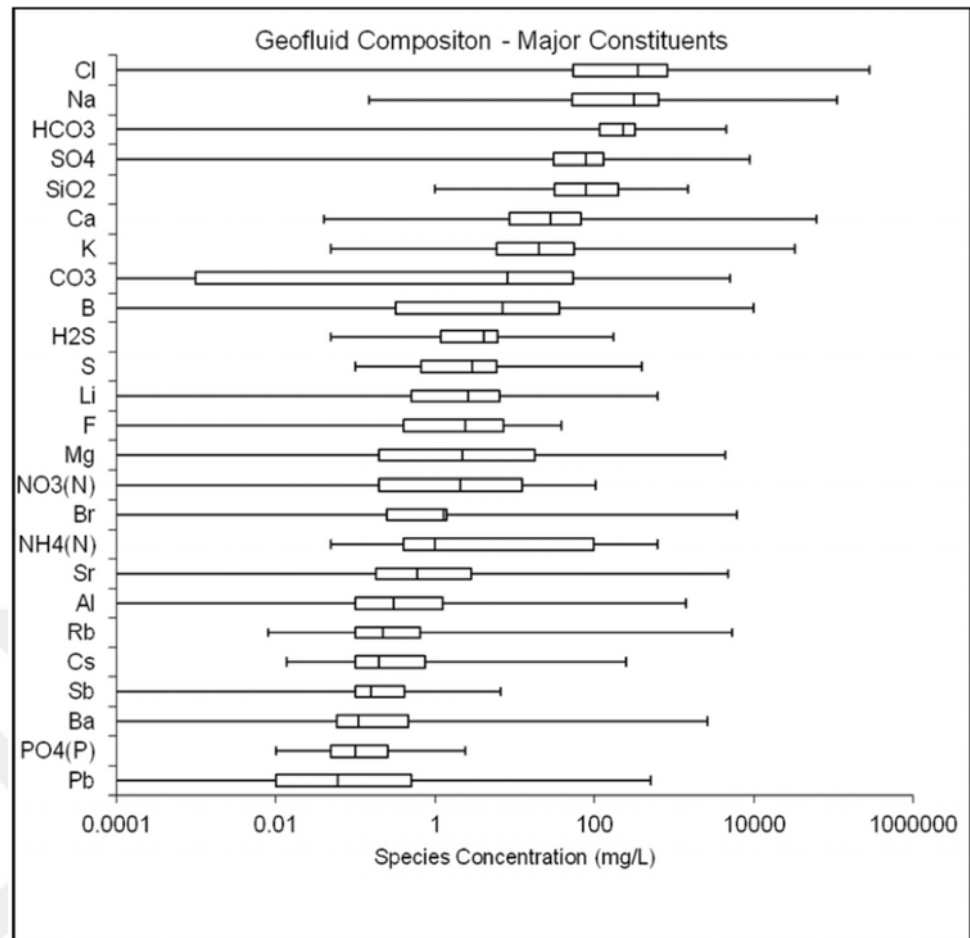


Figure 1.3. Main components and concentration ranges of geothermal fluids (Clark et al., 2010).

The pH range of geothermal resources is between 5.5 and 8.5, where 8.5 is highly alkaline and somewhat acidic. Figure 1.3 shows the elements that are most frequently detected in high concentrations: Magnesium (Mg^{2+}), bicarbonate (HCO_3^-), fluoride (F^-), sodium (Na^+), carbonate (CO_3^{2-}), chloride (Cl^-), sulfate (SO_4^{2-}), calcium (Ca^{2+}) and silicon (Si). NaCl is the most common salt that adds to the salinity of geothermal waters when it is dissolved. Essential micropollutants include elements including arsenic (As), mercury (Hg), manganese (Mn), lithium (Li), lead (Pb), boron (B). At high concentrations, As, B, F, and Hg may have a negative effect and gravely damage the ecosystem (Clark et al., 2010).

1.5.2. Geothermal fluid gas phase

Geothermal fluids can have different gas compositions from source to location and even well to well within the same region. Traces as hydrogen sulfide

(H₂S) and carbon dioxide (CO₂) make up 90% of the gas composition in high-temperature systems. In addition, trace amounts of oxygen (O₂), noble gases, volatile hydrocarbon species, and nitrogen (N), ammonia (NH₃), methane (CH₄), hydrogen (H₂) might be found in geothermal resources, though in trace amounts. These gases may exist in low-temperature systems as well, although their concentrations may differ from those in high-temperature systems (Clark et al., 2010).

1.6. Geothermal Energy's Effects on the Environment

Geothermal energy is no exception; some technical and operating practices can have an adverse impact on the environment. Despite being a clean and sustainable energy source, geothermal energy nevertheless has certain (controllable or small) environmental effects. These effects could appear while mining for resources, conducting production trials, or building and running facilities (Sharmin et al., 2023).

1.6.1. Physical effects

Ground subsidence is the main effect that the building and managing a geothermal power plant station has on ground geophysics. When the velocity of liquid extract exceeds the speed of flow in the reservoir, the reservoir may contain less fluid. Consequently, the ground level decreases due to a decrease in the internal pressure within the rock pores. Ground sinking is evident in the majority of geothermal areas that have been studied, however the problem's severity varies widely (Sharmin et al., 2023).

Another possible physical consequence is landslides, which can worsen erosion and completely destroy surrounding flora. These problems can be mitigated while using less land by implementing revegetation projects, appropriate road drainage techniques, and modern drilling equipment. Geothermal energy utilizes less land than other forms of energy because most of the activities are underground (Sharmin et al., 2023).

Apart from the occasional noise caused by drilling, construction, and borehole maintenance, geothermal power plant sound can usually be controlled at reasonable levels. With the right silencers, noise pollution can be reduced even further (Sharmin et al., 2023).

1.6.2. Effect on Atmosphere

The geothermal fluid's chemical makeup is determined by the host rock's geographical features. A large amount of fluid may be discharged into the atmosphere during the evaluation of geothermal energy, as well as while digging and sampling from wells and combustion turbines in power plants. Non-condensable gas, mostly carbon dioxide (CO₂), but also varying amounts of nitrogen (N₂), ammonia (NH₃), methane (CH₄), hydrogen (H₂), hydrogen sulfide (H₂S), and mercury (Hg) are present in this vapor (Leontidis et al., 2023).

1.6.3. Impact on the Pollution of Water

When managing geothermal fluids used to produce power, polluting of rivers and lakes poses a risk. When the geothermal fluid has recovered its heat, it is either pushed back into the interior of the earth or released (into receiving water zones or evaporation pools). If it is disposed of in surface waters, the following elements may cause pollution problems (Sharmin et al., 2023).

- Large amounts of fluid content,
- Water resource temperature imbalance disruption,
- Waste liquid is toxic.

In a day of growing water resource scarcity, preventing the harm this water will do to the environment and treated geothermal waters may provide a new challenge.

1.7. Water Treatment Methods

Water contamination varies based on the source of the pollution. Depending on where the water comes from, there are three types of water management: natural source water management, home wastewater management, and industrial wastewater management. Reuse or disposal of each system necessitates a different work strategy based on the water quality. In most water treatment procedures, physical, chemical, and biological techniques are employed (Mulder, 1996).

The foundation of biological processes is the breaking down of organic materials and the biologically assisted reactions that change inorganic materials. Membrane processes are instances of physical processes, whereas coagulation, oxidation, and ion exchange are examples of chemical processes (Mulder, 1996).

1.8. Membrane processes

The membrane processes are relatively fresh techniques for separation. Therefore, until the last 25 years, membrane filtration did not have a considerable technological role in separating operations. Membrane processes are employed in many different applications nowadays, and their number is growing. Current developments from an economic perspective include carrier media processes like gas separation (GS), vapor permeation (VP), pervaporation (PV), membrane distillation (MD), and so forth, as well as first generation membranes like microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), electrodialysis (ED), membrane electrolysis (ME), diffusion dialysis (DD), and dialysis (Mulder, 1996).

Certain challenges might include a broad range of sizes, from particles to molecules, and membrane procedures are based on various separation concepts and methods. The membrane is what all membrane processes have in common, notwithstanding these variations. A semi-selective barrier or contact between two phases, the membrane is the central component of all membrane processes. Figure 1.4 provides with an example of the membrane separation mechanism (Van De Merbel et al., 1993).

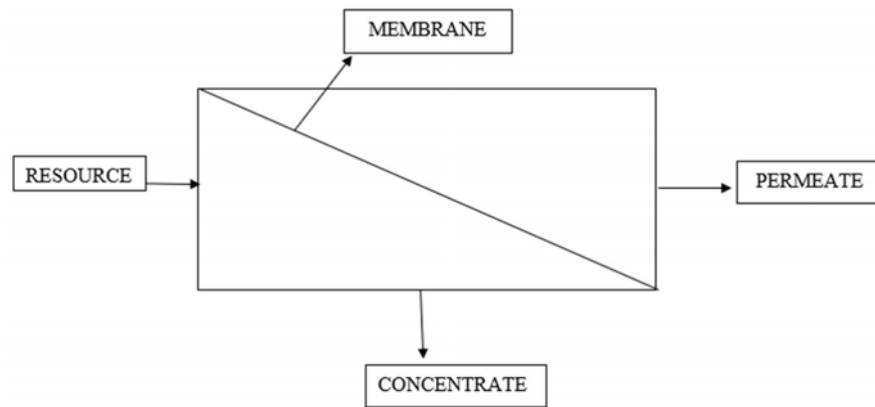


Figure 1.4. General mechanism of membrane process (Van De Merbel et al., 1993).

1.8.1. Membrane Types

The most general definition of a membrane is a selected barrier between two phases, yet this is difficult to describe precisely. The membrane or membrane processes are necessarily selective. It should be mentioned that this definition is macroscopic even though the separation mechanism is thought to be at the small level. The term makes no mention of the membrane's composition or purpose (Mulder, 1996).

The transport can be either active or passive, the membrane can be thick or thin, its structure can be homogenous or heterogeneous, and the driving forces for passive transport can be differences in temperature, pressure, or concentration. The membrane may either be neutral or charged, natural or artificial. In summary, membranes may be categorized in a number of ways based on different viewpoints (Mulder, 1996).

1.8.1.1. Microporous membranes

Conventional filters and microporous membranes have structural and functional similarities. Their very porous structure consists of randomly dispersed solid pores that are coupled to one another. But what sets these holes apart from traditional filters is their minuscule size, which ranges from 0.01 to 10 μm in diameter. Every particle larger than the biggest holes is unable to flow through the membrane. The membrane partially blocks particles that are larger than the

smallest pores but smaller than the biggest pores, depending on the membrane's pore size distribution. The membrane may readily let through particles that are considerably smaller than the smallest pore (Baker, 2004).

As a result, the distribution of pore sizes and molecular size largely determine how well particles are separated by microporous membranes. Generally speaking, microporous membranes, such as those used in microfiltration and ultrafiltration, can only successfully separate molecules with significant size differences (Baker, 2004).

1.8.1.2. Non-porous dense membranes

In nonporous dense membranes, a pressure, concentration, or electrical potential gradient acts as the driving force, and the dense membrane is permeable to diffusion. Different components' relative rates of transit through the membrane, which are dictated by their diffusivity and solubility in the membrane material, are directly connected to how well they separate from a mixture. Consequently, materials of comparable size can be separated by nonporous dense membranes if their concentrations (i.e., solubilities) in the membrane material differ considerably. The majority of gas separation procedures employ dense membranes to carry out the pervaporation and reverse osmosis separation operations. To improve flux, these membranes often feature an anisotropic structure (Baker, 2004).

1.8.1.3. Electrically charged membranes

Electrically charged membranes can be dense or microporous, but the most often used ones have extremely excellent microporosity, meaning that the pore walls contain fixed ions that are either positively or negatively charged. Since it binds anions into the surrounding liquid, a membrane containing fixed positively charged ions is known as an anion exchange membrane. When charged membranes are used for separation, ions with the same charge as those fixed in the membrane structure are removed; this is accomplished with pore sizes that are significantly smaller. The concentration and charge of ions in the solution have an

impact on separation. For instance, monovalent ions are not included in the selectivity drop with high ionic strength solutions since they are less efficient than divalent ions. Electrolyte solutions used in electrodialysis are separated by electrically charged membranes (Baker, 2004).

1.8.1.4. Anisotropic membrane

There exists an inverse relationship between the thickness of the membrane and the rate at which a species is transported across it. For financial reasons, high transport rates are desirable in membrane operations, hence the membrane should be as thin as feasible. A thickness of around 20 μm is the maximum thickness at which mechanically robust, perfect films may be produced using conventional film manufacturing procedures. A significant advancement in membrane technology over the past three decades has been the creation of novel membrane synthesis methods for anisotropic membrane production. On a little thick porous substrate, an incredibly thin surface layer makes up anisotropic membranes. Either one step or several stages can be taken to build the surface layer and the underlying support (Baker, 2004).

Composite membranes often have a surface layer composed of several polymers. The surface layer, which is the support structure utilized to provide the membrane additional mechanical strength, largely determines the membrane's permeability and separation characteristics. Anisotropic membranes are used in practically all industrial processes due to their high flux as a benefit (Baker, 2004).

1.8.1.5. Ceramic metal liquid membranes

Since most commercial membranes are polymer-based, the debates so far have suggested that membranes are organic polymers. The creation of membranes from unconventional materials has, nonetheless, drawn more attention in recent years. Ceramic membranes are a unique kind of microporous membranes that have started to be employed in microfiltration and ultrafiltration applications where thermal stability and solvent resistance are necessary. In order to separate

hydrogen from gas mixtures, dense metal membranes—mostly palladium membranes—have started to be explored, and supported liquid films have been created for carrier-facilitated transport procedures (Baker, 2004).

1.9. Membrane Separation Techniques

There are five different kinds of membrane technology that are frequently used to wastewater or water. These are;

- Reverse osmosis (RO)
- Electrodialysis (ED)
- Microfiltration (MF)
- Ultrafiltration (UF)
- Nanofiltration (NF).

These procedures can be used to separate particles or compounds that have not dissolved from the liquid phase. Table 1.3 compares the elements influencing the performance of these five membrane separation strategies and identifies their driving forces (Cheremisinoff, 2019).

Table 1.3. Comparing of membrane separation technique (Cheremisinoff, 2019).

Technology	Driving Force	Influencing Factors			
		Size	Diffusibility	Ionic charge	Solubility
Microfiltration	Pressure	+++	-	-	-
Ultrafiltration	Pressure	+++	-	+	-
Nanofiltration	Pressure	+++	+	+	-
Reverse osmosis	Pressure	+	+++	+	+++
Electrodialysis	Electricity	+	+	+++	-

Each type of membrane process has distinct features and may be categorized based on the kind of driving forces it uses and the characteristics of the

membranes. These driving factors are the variations in electrical potential (ΔE), concentration (ΔC), temperature (ΔT), and pressure (ΔP) between the two phases (Cheremisinoff, 2019).

1.9.1. Microfiltration (MF)

The membrane technique that is most similar to the conventional coarse filtration method is MF. MF membranes with pore sizes ranging from 10 to 0.05 μm are appropriate for holding onto emulsions and suspensions. Numerous materials, including inorganic (ceramic, metal, glass) and organic (polymer), can be used to create microfiltration membranes (Mulder, 1996).

Compared to other separation methods, MF uses membranes with more pores. As a result, this method produces a comparatively higher flux. This method can take the place of the conventional granular filtration process and is helpful in eliminating substances that cause turbidity (Mulder, 1996).

Due to their superior chemical and thermal resistance, inorganic membranes are typically chosen over polymeric ones. Ceramic membranes are produced by sintering, sol-gel processes, and anodic oxidation techniques, whereas membranes made of polymeric materials are produced by stretching, trace etching, sintering, and phase inversion techniques (Mulder, 1996).

Pharmaceutical and beverage cold sterilization, cell harvesting, fruit juice, beer, and wine clarification, semiconductor industry particle removal in pure water production, metal recovery (e.g., colloidal oxides or hydroxides), wastewater management, continuous fermentation, oil-water emulsion separation, and latex dehydration are some of the industrial uses for microfiltration membranes (Mulder, 1996).

With minimal impact on the treated water's quality, MF membranes might be used to remove extremely low turbidity. Membrane disinfection procedures necessary for chlorination should be evaded since microorganisms and other are eliminated. To enhance membrane performance, metal salts of iron and aluminum

can be added. For instance, soluble species like As and P are precipitated by adding iron and aluminum coagulants, which also improves their removals of particles (Cheremisinoff, 2019). Table 1.4 provides a few instances of MF utilized in industry.

Table 1.4. Applications of MF membranes in industry (Koyuncu, 2018).

Industry	Applications
Metalworking industry	Recovery of emulsions used in metalworking
Food industry	Elimination of fat molecules; elimination of bacteria from fermentation products; Colloidal particles including casein, serum protein molecules, and milk/fat separation are used in the dairy sector. recovery of important substances from the leftovers of the processing of yeast and starch.
Paper industry	Wastewater treatment
Pharmaceutical industry	Sterile filtration of solutions or water
Water treatment	Before NF or RO, pre-treatment is used to treat water directly. Taking out organic materials

Effects like coagulation of small colloidal particles, decreased contaminant penetration into the membrane pores, the creation of an extra porous cake structure on the outer layer of the membrane, decreased material aggregation on the membrane because of the impact of particle size on component transfer, and enhanced membrane backwash characteristics all contribute to an increase in the permeate flux. MF membranes on a pilot scale yield permeate levels that are superior to or on par with those obtained through traditional filtration (Cheremisinoff, 2019).

The removal of coliform microbes from secondary wastewater can also be accomplished with MF just as well as with chlorination. The main benefits are that it has the ability to filter and disinfect microorganisms without the need for further dechlorination. In MF, there are certain drawbacks but no benefits if the

flow type is cross-flow. The membrane pressure drop and filtrate quality evaluations for the dead-end flow type were found to be on par with or better than those for cross-flow (Cheremisinoff, 2019).

1.9.2. Ultrafiltration (UF)

Between NF and MF, UF is another membrane technique. Membranes with pore sizes ranging from 0.05 μm (MF size) to 1 nm (NF size). Solutes with a molecular weight of several thousand Daltons are the lower limit for UF, which is typically employed to remove colloids and macromolecules from solutions (Baker, 2000).

Both MF and UF membranes are regarded as porous membranes, with the solute transport being directly influenced by the applied pressure and the sieving being mostly dictated by the size and shape of the solute, which depends on the membrane's pore size. Similar membrane methods with the same separation principle are used in MF and UF. A significant distinction between them is that ultrafiltration membranes contain a substantially denser top layer (smaller pore size and lower surface porosity) and an asymmetric structure, which leads to a significantly greater hydrodynamic resistance (Baker, 2000).

Recently, commercial UF membranes are mostly made from polymeric materials using the phase inversion method. Polyvinylidene fluoride, polyacrylonitrile, cellulose, polyimide, aliphatic polyamides, polyether ketone, polysulfone, and polyether sulfone are a few examples of these materials. These polymeric materials are also utilized in UF membranes, as are inorganic (ceramic) materials, particularly zirconia and alumina (Baker, 2004).

Table 1.5. Applications of UF membranes in industry (Koyuncu, 2018).

Industry	Applications
----------	--------------

Automotive and household appliances	Separation of electrophoretic paints from rinse water
Metalworking	Recovery of emulsions used in metalworking
Textile industry	Wastewater treatment
Food industry	Recovery of proteins from whey; recovery of substances from starch and yeast processing residues; diet milk production, concentration of egg white; sterilization and clarification of beverages
Paper industry	Wastewater treatment
Pharmaceutical industry	Sterile filtration of solutions or water, isolation, purification and concentration of biologically active substances (enzymes, viruses, nucleic acids, specific proteins) and fractionation of blood
Water industry	Pretreatment before NF or RO, use for direct water treatment and organic matter removal

Among the many uses for UF are circumstances in which it is necessary to separate high molecular weight from low molecular weight components. These kinds of applications are commonly employed in the paper, leather, metallurgy, textile, chemical, pharmaceutical, food, and dairy industries. UF is utilized in the food and dairy industries for procedures including manufacturing cheese and milk concentrate, recovering whey proteins, recovering potato proteins and starch, concentrating egg products, and clarifying fruit juice and alcoholic drinks and some other applications shown in Table 1.5 (Baker, 2004).

1.9.3. Nanofiltration (NF)

RO membranes and UF membranes are separated by NF membranes. FilmTec coined the term "NF" to describe a selective "RO process" that purposefully permits specific ionic compounds in the input stream to flow through. Organic solutions with low molecular weights, such 200–1000 Da, are

often separated using NF membranes, which are made to have a molecular weight barrier of around 1–10 nm. They are sometimes referred to as partial demineralization procedures because of their efficacy in eliminating multivalent salts. In contrast to UF membranes, they are able to hold onto organic colors, low molecular weight chemical compounds, and dissolved salts (Fane et al., 2010).

However, compared to RO membranes, the removal efficiency is lower. NF membranes work with both sieving and diffusion transport processes at the porous and nonporous membrane interface, in contrast to reverse osmosis membranes, which have a nonporous structure and a solution-diffusion transport mechanism. Consequently, NF membranes fall in between "tight" ultrafiltration and "loose" RO (Fane et al., 2010).

NF membranes' "loose" characteristic enables them to function at lower pressures while achieving larger water fluxes (water recovery) than RO membranes. There are considerable energy savings as a result. The transport and selectivity characteristics of NF membranes are further influenced by electrical interactions since the majority of NF membranes are surface charged. The elimination of multivalent ions also involves electrostatic interactions. For monovalent salts, NF membranes have a high permeability. They are able to eliminate organic molecules with a relatively modest molecular weight and retain a significant amount of multivalent salts (Fane et al., 2010).

They function extremely well at retaining divalent salts having Ca^{+2} and Mg^{+2} , but they are less effective than the RO method in eliminating monovalent salts having Na^{+} and Cl^{-} ions. Their driving force pressure needs are lower than those of the RO membrane but greater than those of the UF membrane. They function at pressures ranging from 3 to 15 bar (Fane et al., 2010).

In industry, NF membranes are used to treat salty cheese water, recover materials from wastewater from the dairy sector, remove color and organic matter from textiles, clean food, textiles, and pharmacies, and remove salt and organic matter concentration. NF membranes can be used in conjunction with UF and TO

membranes to treat a variety of industrial wastewaters, including leachate, textile, and others (Fane et al., 2010).

1.9.4. Reverse osmosis (RO)

Membranes having a dense active surface are employed in the reverse osmosis process to separate salts and tiny organic compounds. Diffusion and dissolution are the carriers. The high density of active surface means that operating pressures are significantly greater than in MF and ultrafiltration procedures. The osmotic transport phenomena that takes place in a semi-permeable barrier in the natural environment must be understood before one can comprehend the RO process (Koyuncu, 2018).

The process of osmosis occurs naturally. As seen in Figure, water diffusion from the low-solute solution to the salty solution with high-solute concentration takes place when water with the same amount of salt and low solute concentration is put in a container divided by a semipermeable membrane. Until the water concentration is the same on both sides, this diffusion process keeps happening. As water may move across the semipermeable barrier between these two liquid phases but dissolved compounds cannot, the level on the side with the low solute concentration ultimately drops while the level on the salty side rises (Koyuncu, 2018).

The term osmotic pressure of the solution refers to the level differential on either side of the semi-permeable membrane. The amount of pure water in this instance drops. However, the amount of clean water may be raised and the amount of filthy water can be lowered using an external engineering application. First, the osmotic pressure needs to be reset to zero in order to promote water diffusion in the other direction. It is therefore possible to produce reverse diffusion flow by applying the additional reverse pressure. A pressure greater than the osmotic pressure causes pure water to start moving from the solution with a high concentration to the one with a low concentration (Koyuncu, 2018).

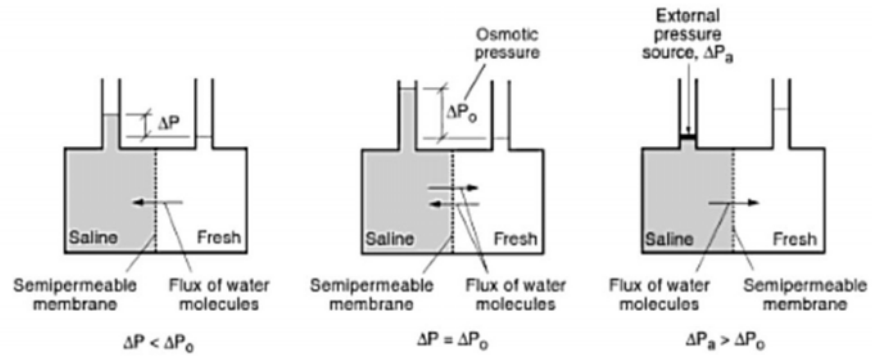


Figure 1.5. General mechanism of reverse osmosis (Asano, 2007).

Water molecules can pass through the polymeric network structure that makes up the membrane surfaces, where the solvent can dissolve. A "pore" effect is produced in the polymeric dense film by the gaps between the networks of polymers. RO membranes are typically classified as thin film composite membranes and asymmetric membranes (Koyuncu, 2018).

The thin-film selective permeable layer that makes up the asymmetric RO membrane is held up by a porous substrate. This thin film selective permeable layer has a thickness of less than one micrometer and has a direct impact on selectivity and flux. The separation process is significantly aided by the porous support layer at the bottom. Typically, the phase transformation approach is used to create asymmetric membranes. Thin film composite membranes are made by covering a second polymer thin film on top of a highly porous support layer. They contain two or more polymer components. Because of its very thin selective layer, the newly developed thin film membrane has a low water resistance and high water flow values (Koyuncu, 2018).

The desalination of salt and saltwater is the primary application for the RO technique. For ultrapure water, it is also often utilized in industry. These membranes are utilized in home purifying systems that resemble kitchens. It is possible to remove even monovalent salts quickly. As was already established, the osmotic pressure varies depending on the salinity of the feed water, which alters the necessary pressure. Depending on how salinized the membrane and feed water are, it can function at pressures ranging from 15 to 60 bar (Koyuncu, 2018).

1.9.5. Electrodialysis (ED)

The electrical potential gradient, which allows molecules that are charged to diffuse at a rate far higher than what they can achieve in a given medium by the chemical attraction between two liquids, as in classical dialysis, is the foundation of the electrodialysis idea. Cations move toward the negative pole, or cathode, and anions move toward the positive pole, or anode, when a direct current (DC) is run through a salt solution. Therefore, by varying the ability to conduct or electrical current among the poles or layers, the speed at which ions are carried between them may be altered (Cheremisinoff, 2019).

In industry, ED is used as a constant flow type. Concentration polarization is among the most significant technical issues with the ED process. Other issues include membrane fouling from organic species and membrane scaling brought on by inorganic molecules in the feed solution. In order to accomplish effective separation and minimize these drawbacks, activated carbon is employed as a pretreatment procedure (Cheremisinoff, 2019).

Applications for ED include:

- In processes related to the protection, concentration, cleaning and separation of the desired substances in a mixture and in the recovery of materials in liquid wastes.
- In the process of purifying water supplies
- In managing wastewater for reuse and in fulfilling the requirements to guarantee suitable water quality (Cheremisinoff, 2019).

In this system, a layer of cation or anion exchange membranes is positioned between the outer layers to control the movement of ions. Figure 1.6 illustrates this. These resins that are selective for cations and anion let the appropriate ions in the solution pass through. When a DC current is applied, anions and cations will gather on one face of the membrane and be carried or released on the other. In order to reduce the salt ions in the center of the cell, Na^+ ions will move towards the membrane if NaCl is applied there (Cheremisinoff, 2019).

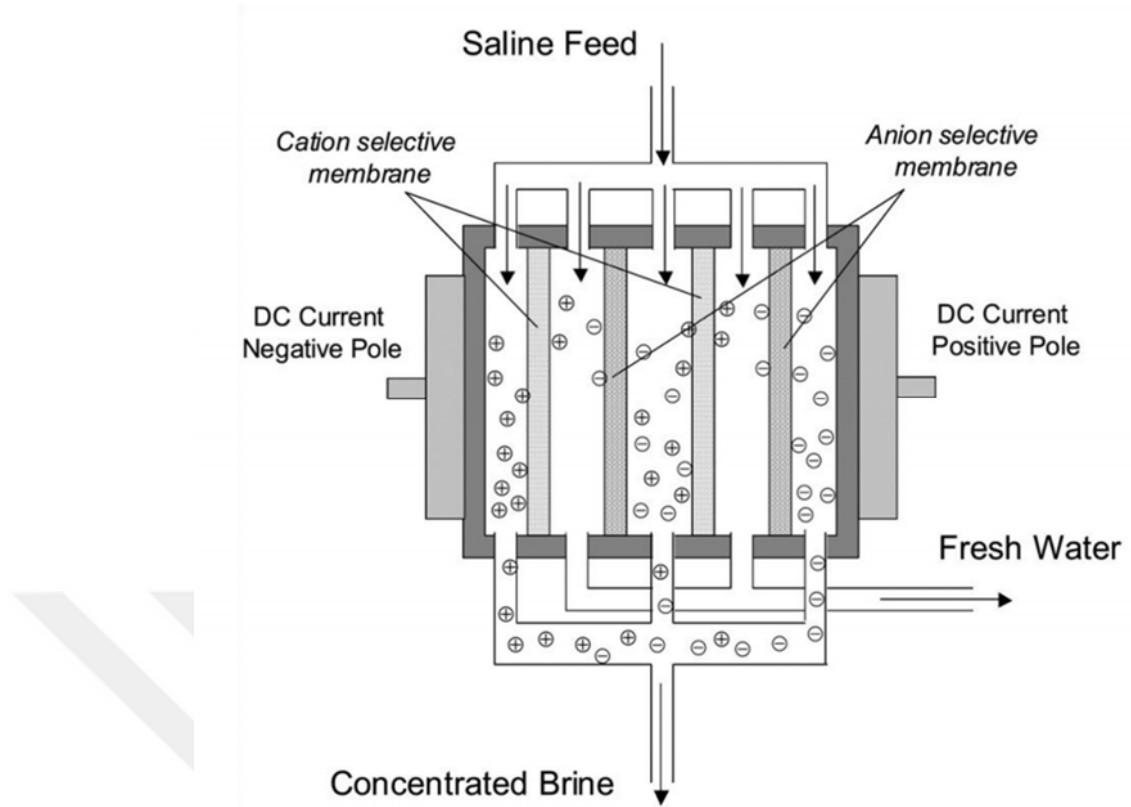


Figure 1.6. Mechanism of ED operation (Islam et al., 2018).

Producing drinkable water from slightly salted water is one of the most significant uses of ED for water treatment. Three key factors that impact the ED process's cost are the facility's size, the total amount of TDS in the feed solution, and the effectiveness of TDS removal (Cheremisinoff, 2019).

1.10. Operating model in membrane processes

Two categories of operating types can be distinguished in membrane processes. These types of operations are known as dead-end and cross-flow. Figure 5 depicts these two operating modes. In the cross-flow mode, the fluid to be filtered passes through the membrane as a result of the pressure differential, flowing parallel to the membrane surface. This operating mode has the benefit of lessening the development of filter cake. In this operating mode, filter cake formation is kept to a minimum (Kirschner et al., 2018).

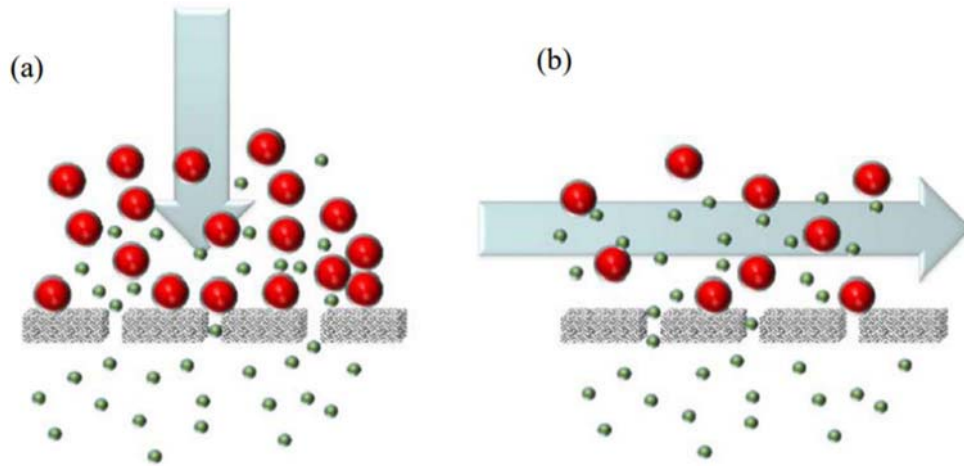


Figure 1.7. Dead end (a) and crossflow (b) design (Kirschner et al., 2018).

When using the dead-end filtering mode, water is supplied straight onto the membrane's surface from one side. Substances in the water that are bigger than the membrane's pore size create a cake layer that slowly expands on the membrane's surface. The retentate flow is absent in the dead-end filtering mode. Frequently stirring the fluid creates turbulence on the membrane, preventing the creation of this thick cake layer and maintaining high flux rates (Kirschner et al., 2018).

Significant restrictions are brought on by the fouling issue that arises in both cross-flow and dead-end operating modes. However, as was already indicated, the surface flow in the cross-flow mode delivers more appropriate flux values and less fouling (Kirschner et al., 2018).

1.11. Concentration polarization

When the concentration of the precipitant is higher than the concentration in the feed solution, solutes accumulate on the membrane surface, a phenomenon known as concentration polarization. As water flows across the membrane in this situation, the flux of solutes on the membrane surface is significantly higher than the flux of solutes returning to the feed solution, which raises the solute concentration on the membrane surface (Koyuncu, 2018).

Possible negative effects of concentration polarization on reverse osmosis;

- Increasing of osmotic pressure on the membrane surface causes a decrease in water flow.
- There is an increase in the solute flux,
- If the concentration at the surface surpasses its solubility limit, solute precipitation may result in obstruction in the membrane pores, which would lower the water flux.
- The membrane's separation characteristics change (Koyuncu, 2018).

Mixing the membrane surface solution with the feed solution can lessen the detrimental effects of concentration polarization. By altering the membrane modules to enhance mixing, adding turbulent flow amplifiers to the feed channel, raising the feed flow to raise the axial velocity, and increasing the turbulent flow, this procedure can be carried out (Koyuncu, 2018).

Concentration polarization makes it difficult to sample membrane systems because the concentration on the membrane walls is difficult to determine. At very high flow rates, sufficient mixing occurs that the concentration on the membrane walls is assumed to be equal to the concentration of the feed solution. At low flow rates, this assumption is incorrect. To calculate the concentration on the membrane walls accurately, the Navier-Stokes diffusion convection equation must be solved (Koyuncu, 2018).

1.12. Biological Fouling

Bacterial growth on the membrane surface causes biological fouling. The membrane's susceptibility to biological fouling is crucial. For instance, germs can easily penetrate cellulose acetate membranes. Thus, it is necessary to sterilize feed water to prevent these membranes. Furthermore, compared to cellulose membranes, hollow fibers made of polyamide exhibit greater bacterial resistance. By using the proper pretreatment and UV disinfection to eradicate bacteria and germs from the feed water, biofouling can be successfully managed (Ho & Sirkar, 2012).

1.13. Organic Fouling

Numerous organic materials found in nature have the potential to seriously impair membrane performance. The chemical and biological breakdown of plant and animal waste in surface waters produces humic and fulvic chemicals, which are naturally occurring organic molecules. Nearly every source of surface water contains fulvic and humic chemicals. Because they are absorbed by the membrane pores, organic materials with tiny molecular structures are efficient in membrane fouling, even while dissolved organic matter is ineffective on its own (Ho and Sirkar, 2012).

Membrane filtration is a process that should be applied for the removal of most of the natural organic substances. Due to their large size, it is possible to separate natural organic substances with membrane filtration. However, since they are adsorbed in the membrane pores, it causes a decrease in membrane performance. In order for organic substances not to block the membrane pores, they can be adsorbed with active carbon and different adsorbents beforehand (Ho & Sirkar, 2012).

Numerous organic materials found in nature have the potential to seriously impair membrane performance. The chemical and biological breakdown of plant and animal waste in surface waters produces humic and fulvic chemicals, which are naturally occurring organic molecules. Nearly every source of surface water contains fulvic and humic chemicals. Because they are absorbed by the membrane pores, organic materials with tiny molecular structures are efficient in membrane fouling, even while dissolved organic matter is ineffective on its own (Ho & Sirkar, 2012).

1.14. Inorganic Scaling

On the membrane surface, undissolved metal salts from the feed water precipitate to produce the crust. Ion concentration in the feed solution rises as the salts in the water are eliminated in the filter, eventually surpassing the solubility limit. After then, a crust of salts forms on the membrane's surface. It is possible to ascertain a feed water's propensity to produce a crust by analyzing it and figuring

out the concentration factor in the brine. Recovery ratio is defined as the product flow rate divided by the input solution flow rate (Baker 2004).

Scaling is not an issue in reverse osmosis systems with a 50% recovery rate. On the other hand, recovery rates for salt water reverse osmosis systems range from 80% to 90%. After that, the concentration of salt on the membrane's salt water side can shift away from the solubility limit. salts that serve as crust binders, in general (Baker 2004);

- Calcium carbonate (CaCO_3)
- Calcium sulfate (CaSO_4)
- Barium sulfate (SrSO_4)
- Strontium sulfate (BaSO_4)
- Silicon Dioxide (Silica) (SiO_2).

1.15. Concentration management in RO process

The creation, control, and treatment of concentrates are the primary factors influencing the viability of membrane applications. Increased environmental consciousness and stringent laws have made concentrate management unavoidable, while recent advancements in membrane technology have resulted in large amounts of concentrate discharges. Both discharge without treatment and technologies for treatment and/or recovery are included by concentrate management. For membrane processes, focused removal accounts for a large amount of operational costs, particularly when treatment is carried out. Sometimes the choice of location for the facility is also influenced by membrane concentrate management (Koyuncu, 2018).

When this technique is used, the concentration of pollutants in the concentrate at the application site pollutes the receiving environment, and the high pollution causes the dissolved oxygen value in the receiving environment to drop. Discharging the concentrate stream into the sewage is the second. This approach increases the amount of pollutants and salt load in the home wastewater treatment plant, which is where the last stage of treatment is completed. In contrast to direct

discharge into the receiving environment, this procedure is thought to be a better way to dilute the concentrate (Koyuncu, 2018).

After treatment in urban wastewater treatment facilities, concentrate streams discharged as a result of membrane operations in desalination plants can also be controlled via evaporation, land spreading, or injection into groundwater. One area where concentrated flow is troublesome is the management of membrane concentrates created by membrane treatment of industrial wastewater, where it is noted that technologies other than evaporation are not frequently employed (Subramani and Jacangelo, 2014).

Evaporation is a step in the concentrate removal process that is based on mechanical or natural thermal means. Wet salt and water vapor are the byproducts of mechanical evaporation, or evaporation that is accomplished by heating the concentrate. Only evaporation ponds are involved in the natural evaporation process. Due to the energy-intensive nature of evaporation processes, highly efficient vapor condenser systems that lower energy requirements have been developed and put into use (Subramani and Jacangelo, 2014).

Evaporation systems with reduced energy use are still required, though. Evaporation tanks demand a lot of area and the process cost has not yet been established because it is not a real-scale application, despite being less expensive and requiring less equipment than mechanical evaporation (Koyuncu, 2018).

The literature's studies and the outcomes of real-world systems demonstrate that the above-summarized techniques were created and implemented especially for desalination plants, and some of them have been effective in treating and managing membrane concentrates. However, more research should be done to create low-cost, long-lasting technologies. The literature's studies and the outcomes of real-world systems demonstrate that the above-summarized techniques were created and implemented especially for desalination plants, and some of them have been effective in treating and managing membrane concentrates. However, more research should be done to create low-cost, long-lasting technologies. Thermal-based concentrate removal techniques and

membrane processes (electric potential driven and pressure driven) can be combined in membrane concentrate treatment/management studies with a zero liquid discharge approach in industrial applications (Koyuncu, 2018).

1.15.1. Evaporation ponds

Evaporation ponds are an appropriate disposal technique for regions with higher evaporation than precipitation and hot, dry climates. The salinity of the water, air and water temperatures, wind speed, and barometric pressure all have an impact on evaporation rates. Evaporation ponds can often be used without a special permit. Ponds utilized as leach pads may have requirements that the concentration must fulfill (Shafi et al., 2018).



Figure 1.8. Some of example of evaporation ponds (Koyuncu,2018).

Evaporation ponds are simple to build and need little upkeep. Additionally, they don't need a lot of operator care. They might work well in places with low land costs and high rates of evaporation. Large regions, however, can occasionally be needed, necessitating isolation using synthetic material or layers of impermeable clay. The expense of building goes up as a result. Concentrate streams with comparatively small volumes can benefit from this method. Figure provide examples of how evaporation ponds are used (Shafi et al., 2018).

1.15.2. Deep well injections

Injections into deep wells are another technique for concentrated trash. This technique entails injecting liquid waste between 305 and 2440 meters into porous subsurface rock formations. Class I wells are typically designated for the dumping

of concentrates from water treatment plants. The categorizations are significant. The construction and monitoring standards for Class I wells are more demanding than those for Class II wells. Class I wells are defined as those that must be injected down below the lowest formation that contains a supply of drinking water underneath. To stop injection fluids from migrating upward, a hydrologically impermeable structure should be placed between injection sites and subterranean drinking water sources. The possibility of injected fluid contaminating potable water bodies is the method's biggest environmental risk (Koyuncu, 2018).

For the purpose of injecting garbage into the ground, authorities ought to publish regulations that are prioritized and adopted by each region. Criteria include standards for building, operation, monitoring, and reporting. Typically, deep well injection is an expensive procedure. The cost of building the well and the requirement for close observation are incurred (Koyuncu, 2018).

1.16. Electrodialysis Reversal (EDR)

The EDR procedure uses the ED cell in its original form, but it is made to clean its membrane on its own without the need of acid or other chemicals. Membrane cleaning is accomplished in the EDR process by switching the location of the concentrated and diluted compartments by reversing the direct current applied to the electrodes in the cell at specific times. This results in a higher rate of recovery in the feed water, a lower load on the source water, and a lower potential amount of trash at the conclusion of the operation (Valero & Arbós, 2009).

The cell membranes are impacted by the EDR process in four major ways (Valero & Arbós, 2009);

- It causes the polarization film to break.
- The precipitated chemicals are prevented from growing and causing damage to the membrane.
- By electrically reversing the colloidal particles' direction, it stops films from forming.

- Prevents the formation of complexes that may occur as a result of continuous acid addition

In the EDR process, where the polarity is reversed at certain intervals, the hydraulic flow is also reversed. Thus, the dilute compartment in the cell becomes the concentrated compartment, while the concentrated compartment replaces the dilute compartment. In this direction, three main flows are recovered, namely the concentrated flow, dilute flow and electrode flow. The recovery of these product waters and their re-feeding to the process prevents waste formation (Valero & Arbós, 2009). The change in ion movement during polarity change in the EDR process is shown in Figure 1.9.

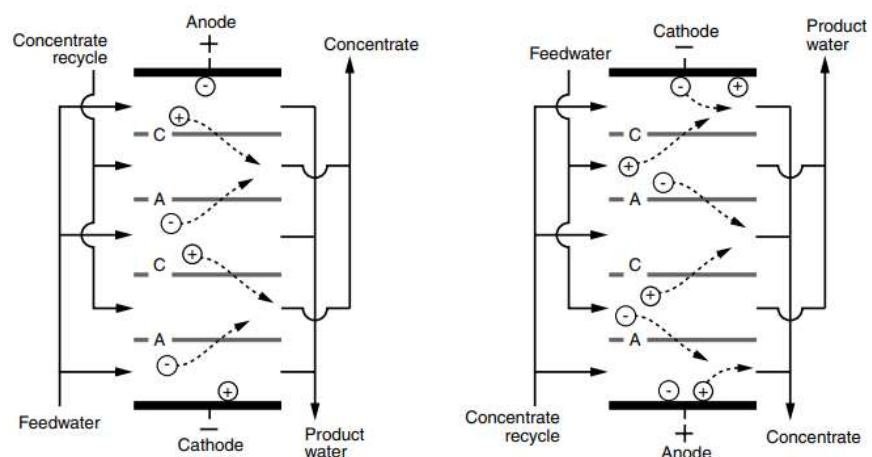


Figure 1.9. Working mech of EDR (Zhao et al., 2019).

Heavy metal-containing industrial effluent is frequently treated and metal recovered using the EDR process. Research has been done on the elimination of heavy metals like nickel and cadmium (Benvenuti et. al., 2014) (Marder et. al., 2003). The biomedical industry is another application. Protein in the blood can be recovered when ultrafiltration is employed in conjunction with it. The EDR procedure has also been used in research to remove salt from household wastewater and recover it for use in garden irrigation (Goodman et al. 2013).

Flow rate, membrane structure, polarity reversal duration, and feed water quality are some of the factors that impact the EDR process's efficiency.

According to Kabay et al. (2016), it is crucial to ascertain the impact of these parameters on the process and run it with the most suitable settings.

1.17. Aim of study

Membrane scaling is one of the major problems for membrane processes for geothermal water desalination. The impurities in the geothermal water will create layers on the membrane surface and decrease the permeate flow, decrease the energy efficiency by causing pressure loss, and increase the operating cost and shorten the membrane life due to more frequent membrane cleaning. Chemical additives known as antiscalants are used to prevent the buildup or deposition of scale. These chemical additives are used almost exclusively in desalination plants due to their desirable qualities, which include ease of handling, low cost, low dose rate, avoidance of corrosion issues caused using mineral acids, and the capacity to affect the formation of hard scale. Dosing rate and scale inhibitor type are crucial operating factors in desalination. Scale formation is caused by scale inhibitors being dosed below optimally, whereas overdose is thought to accelerate sludge formation and biofouling.

In this thesis study, it is aimed to observe the effect of two commercially obtained antiscalants at different concentrations against membrane scaling using a pilot scale membrane test system installed at Yenikale Geothermal Heating Center. Ultrafiltration (UF) can be also considered as a pre-treatment system for either reverse osmosis and nanofiltration systems if the feed water contains some colloidal substances such as silica. In the second part of this thesis study, effect of pretreatment using UF will be also investigated. The mini-pilot system was integrated with solar panels. Thus, the energy production by solar panels will be also investigated. The study's third section dealt with the handling of waste concentrate that was produced following RO treatment. The EDR model's ability to produce water from waste was examined. NF and RO membranes were used as a first pre-treatment for the waste water. The production of pure water was then targeted with four potential variations.

2. EXPERIMENTAL

2.1. Geothermal water

Samples of geothermal water were supplied for membrane testing by the Izmir Geothermal Power Corporation in Izmir, Turkey. Geothermal water, which had reached about 100°C, was taken into a polyethylene container and refrigerated in the laboratory. Table 2.1 provides a list of the characteristics of the geothermal water utilized in laboratory experiments. The geothermal heating center's geothermal reinjection line provided the geothermal water samples that were used in the outdoor experiments.

Table 2.1. Characteristics of the geothermal fluid this thesis uses (Jarma, 2022).

Spent geothermal water properties			
pH	8.52	K (mg/L)	32
Conductivity ($\mu\text{S}/\text{cm}$)	1807	Mg (mg/L)	7.7
TDS (mg/L)	1230	Ca (mg/L)	25
Alkalinity (mg CaCO_3/L)	509	Li (mg/L)	1.4
HCO_3 (mg CaCO_3/L)	475	Sr (mg/L)	0.65
HCO_3 (mg/L)	580	B (mg/L)	12
CO_3 (mg/L)	21	Si (mg/L)	55
Cl (mg/L)	199	SiO_2 (mg/L)	118
SO_2 (mg/L)	164	Fe (mg/L)	164
F (mg/L)	7	Ba (mg/L)	0.13
Na (mg/L)	411	As (mg/L)	0.17

2.2. Membranes

Table 2.2 presents general features of the membranes utilized in the antiscalant investigations, which were conducted using FilmTech SW-30-2540 membranes.

Table 2.2. Properties of SW30 Membranes (Dupont, 2024).

Membrane type	Polyamide thin-film composite
Maximum operating temperature (°C)	45
Maximum operating pressure (bar)	69
pH range	1-13

In the case of test of pretreatment with UF, Vontron membrane was employed. Upon closer inspection, the characteristics of the Vontron membrane listed in Table 2.3. indicate that it works best with brackish water.

Table 2.3. Properties of Vontron BW-RO membrane (Vontron, 2024).

Active area (m ²)	2.8
Maximum operating temperature (°C)	45
Maximum operating pressure (bar)	41.4
pH range	3-11

The properties of the UF membrane ACM-20, which is owned by the Akkim corporation, was displayed in the Table 2.4.

Table 2.4. Properties of ACM-20 UF membrane (Akkim, 2024).

Membrane type	Hollow fiber UF
Maximum operating temperature (°C)	40
Maximum operating pressure (bar)	5
pH range	2-11

Table 2.5 depicts the general characteristics of the NF and XLE-RO membranes utilized for pretreatment in the EDR tests. The characteristics of NF90 membrane, a nanofiltration membrane, seem to be similar to those of RO membranes.

Table 2.5. Properties of NF90 and XLE-RO membrane (Dupont, 2023).

Parameters	NF90	XLE-RO
Membrane materials	Polyamide Thin-Film Composite	Polyamide Thin-Film Composite
Maximum operating temperature (°C)	45 °C	45 °C
Maximum operating pressure (bar)	41 bar	41 bar
pH range	2-11	2-11

Cation and anion exchange membranes from the Ralex brand, whose characteristics are displayed in Table 2.6, were used in the EDR investigation. Separators supplied by the manufacturer were positioned in between the pairs of ten membranes.

Table 2.6. Ion exchange membranes properties (Özkök et al., 2024).

Property	AMH-PES	CMH-PES
Fitting fabrics	Polyester	Polyester
Ion-exchange group	R – (CH ₃) ₃ N ⁺ (quaternary ammonium)	R – SO ₃ ⁻ (sulphonate)
Ionic form – counter ion	Cl ⁻	Na ⁺
Swelled membrane thickness (mm)	< 0.75	< 0.77
Electrical resistance (Ω·cm ²)	7.5	8.0
Permselectivity (%)	> 90	> 90

2.3. Antiscalants

Two types of antiscalants were utilized in pilot scale testing to investigate the impact of their use during the geothermal water treatment process. They are mentioned in the Table 2.7.

Table 2.7. Properties of Antiscalants.

Antiscalant	Preventing scaling by
Protek 101	High silica, calcium carbonate
Procond R624	Silica, calcium carbonate

2.4. Mini-pilot scale membrane tests

A pilot scale device was used for the field experiments. The flow chart of this system was shown in Figure 2.1. The cooling tank receives water from the reinjection line that is between 55-60 °C. Once the water cools down, it is transferred to the feed tank after being cleaned of any remaining organic and inorganic particles using sand and carbon filters. With the aid of an antiscalant

dosage pump, antiscalant was injected into the feed tank at various concentrations. Ultimately, the feed water was supplied to the mini pilot RO system after passing through the cartridge filter. Following desalination, the permeate stream was collected in a tank and the concentrate stream was returned to the reinjection line.

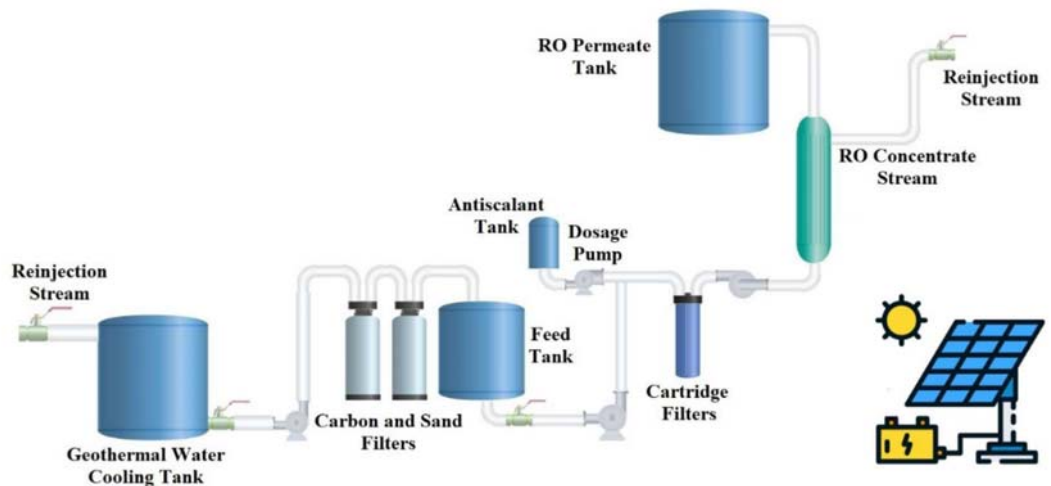


Figure 2.1. Mini pilot scale membrane system in Yenikale geothermal heating system, İzmir.

2.5. Mini-pilot scale membrane system with UF pretreatment

The UF pretreatment study made use of the same mini-pilot membrane setup. As shown in Figure 2.2, the UF membrane was added to this testing system after the carbon and sand filters. The cooled geothermal water flows via the sand and carbon filter, the UF membrane, and the feed tank, where it is collected. After that, it is treated with RO after going through the cartridge filter.

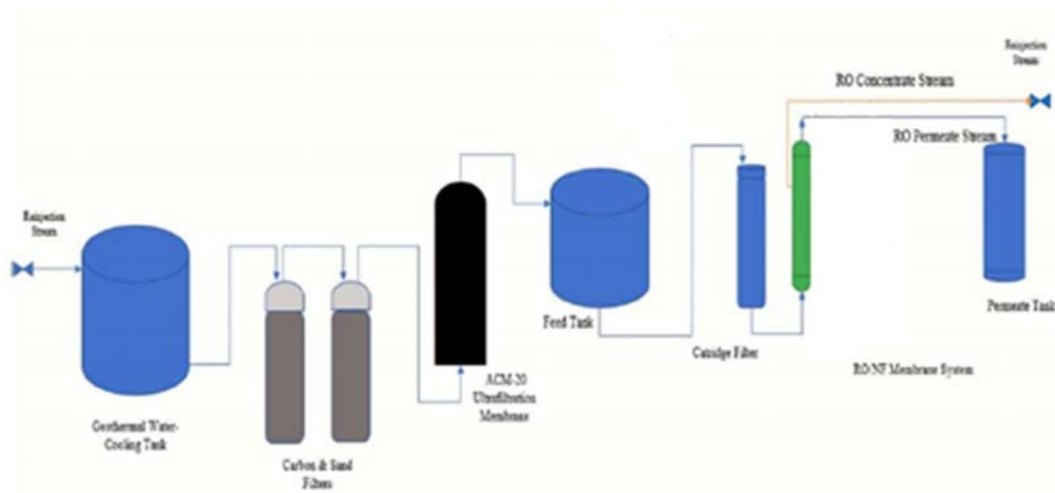


Figure 2.2. Mini pilot scale membrane system with UF pretreatment.

2.6. Pretreatment tests with lab-scale membrane system

The concentrate stream resulting from the treatment of used geothermal water with RO SW-30 membrane in Yenikale geothermal heating center was pre-treated with XLE-RO and NF90 membranes in laboratory using SEPA CF Cell membrane test system. Pre-treatment was carried out in order to prevent the concentration stream from causing clogging in ion exchange membranes to be employed with the EDR system due to high multivalent ion density in RO concentrate.

Laboratory-scale cross-flow flat sheet membrane test apparatus was used to pretreat the NF90 and XLE-RO filtration procedures. Using NF90 and XLE-RO membrane filtration was performed at an operating pressure of 15 and 20 bar. The concentrate stream's flow rate was maintained at 96 L/h.

A crossflow filtration device called the SEPA CF II Cell is used to evaluate how well flat sheet membranes work in various applications. Moreover, the flow dynamics of larger membrane elements, such as industrial spiral wrapped membrane elements, are simulated with this device as shown in Figure 2.3.

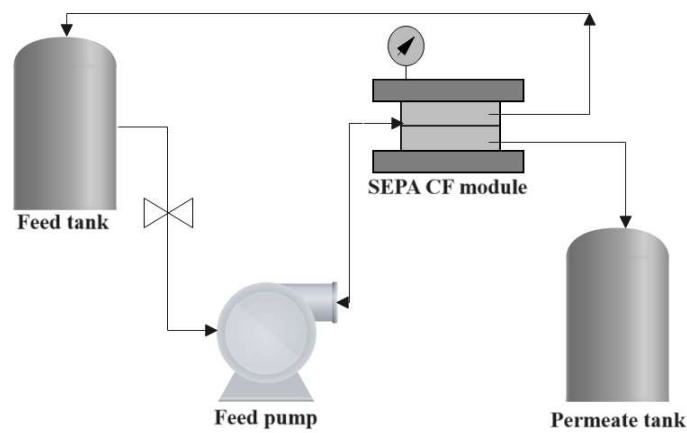


Figure 2.3. Flow diagram for the SEPA CF-2 cross-flow membrane test system.

The water that is pumped into the cell container is a high-pressure pump. The hydraulic hand pump was used to apply pressure to the cell holder. A hydraulic hand-held pump mechanism instantly sealing the cell and generates consistent pressure to ensure a precise seal. The operational pressure is changed and the system is run as a closed loop with the use of the pressure gauge.

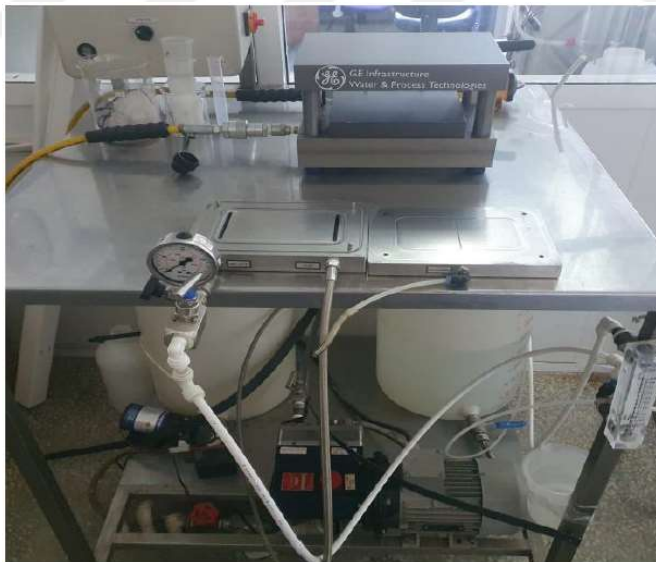


Figure 2.4. SEPA CF-2 cross-flow membrane test apparatus for flat sheet membranes.

2.7. EDR tests

In EDR experiments, the laboratory scale MEGA brand EDR test system shown in the Figure 2.5 was used. The equipment has a total of 4 compartments and 1

electrode compartment. The equipment is also suitable for use in ED, EDR and BMED experiments.



Figure 2.5. Mega EDR-Z/4x10-0.8 system.

Ralex brand membranes are arranged in ten pairs of in the membrane stack as depicted in Figure 2.6 to carry out the EDR experiment. Through these membranes, water flows and the post treatment of NF and RO permeate process is carried out.



Figure 2.6. EDR-Z/4x10-0.8 Type CA stack.

In the experiment's EDR section, the permeate of NF90 and XLE-RO membranes to get a permeate that allowed us to use four different voltage values

to lower its concentration and achieve pure water. A specified flow rate of 30 L per h was employed in the concentrate and dilute compartments for the two-hour trials for each electrical voltages value shown in Table 2.8. There were no temperature adjustments performed during the experiment, which was conducted at room temperature.

Table 2.8. Conditions for EDR tests.

Parameters	NF90 permeate	XLE-RO permeate
Applied voltage	5, 10, 15, 20 V	
Time	2 h	
Flow rate	30 L/h	
Temperature	Ambient temperature	

3. RESULTS AND DISCUSSION

3.1. Pretreatment with Antiscalants

In the first step, the pure water fluxes were measured for each membrane in the range of 5-30 bar of the applied pressure at room temperature to determine the pure water permeabilities. Next, the RO processes were carried out at 15 bar for 6 h by using Protek 101 and Procond R624 antiscalants dosed in the geothermal water with four different antiscalant concentrations (0, 5, 10 and 15 g/m³) with the help of dosing pump while maintaining a consistent water recovery as 60%. These studies were carried out separately using two different SW30-RO membranes.

Table 3.1. The effect of Protek 101 concentration on SW30 membrane permeability.

Pure water permeability (L/hm ² bar)	Concentration of antiscalant (g/m ³)	Average geothermal water permeability (L/hm ² bar)	Increase in Permeability (%)
19.0 ± 3	0	11.3 ± 0.3	-
	5	13.8 ± 0.6	18.1
	10	15.5 ± 0.8	27.1
	15	17.3 ± 0.5	34.7

Table 3.1 shows the initial pure water permeability and the average geothermal water permeability values when Protek 101 antiscalant was used at different concentrations. It was clearly seen that the geothermal water permeability increased by the increase in the antiscalant concentration although permeability of the geothermal water was less than the permeability of pure water.

Table 3.2. The effect of Procond 624 concentration on SW30 membrane permeability.

Pure water permeability (L/hm ² bar)	Concentration of antiscalant (g/m ³)	Average geothermal water permeability (L/hm ² bar)	Increase in Permeability (%)
13.7 ± 0.4	0	6.4 ± 0.3	-
	5	6.7 ± 0.7	4.5
	10	7.2 ± 0.8	11.1
	15	10.7 ± 0.3	40.2

As shown in Table 3.2 , effect of antiscalant concentration on membrane permeability was similar with Procond R624. When the antiscalant concentration was 15 g/m³, the geothermal water permeability was highest.

It was considered that the highest antiscalant concentration as 15 g/m³, which preserves the pure water permeability at a higher rate, prevents scaling more compared to lower concentrations of antiscalants. Protek antiscalant retains membrane water permeability greater than Procond antiscalant, as the Table 3.3 reveals.

Table 3.3. Antiscalants' impact on the permeability of pure water after 15 g/m³ applied.

Antiscalant	Decrease of Water Permeability (%)
Protek 101	8.9
Procond 624	21.9

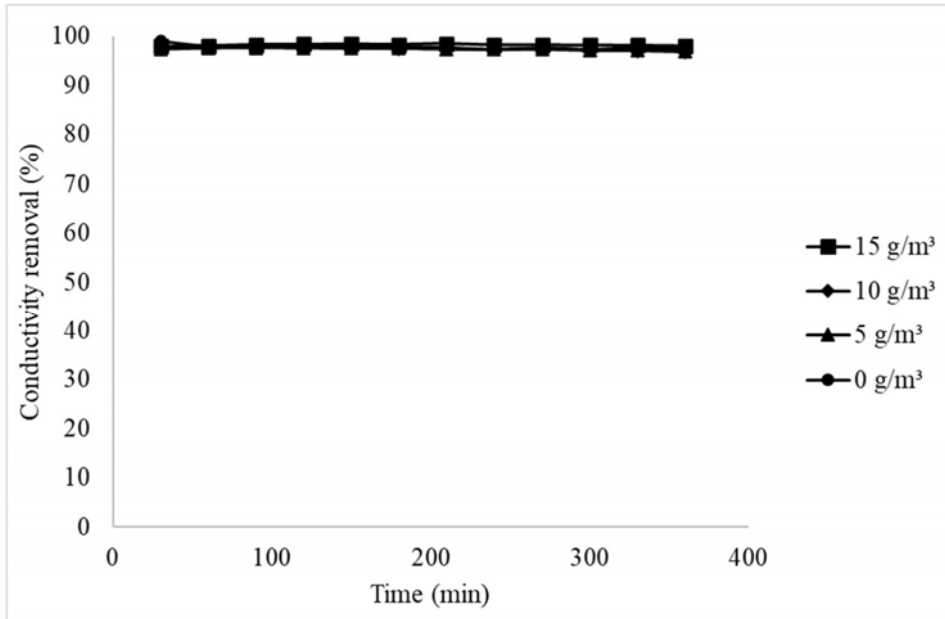


Figure 3.1. Conductivity removal from geothermal water using Procond 624 antiscalant.

The SW30 RO membrane demonstrated a desalination performance of about 99% due to its superior desalination capability. As shown in Figure 3.1 and 3.2, membrane showed similar performance in the absence and presence of both antiscalant. Changing antiscalant concentration did not show any difference in conductivity removal.

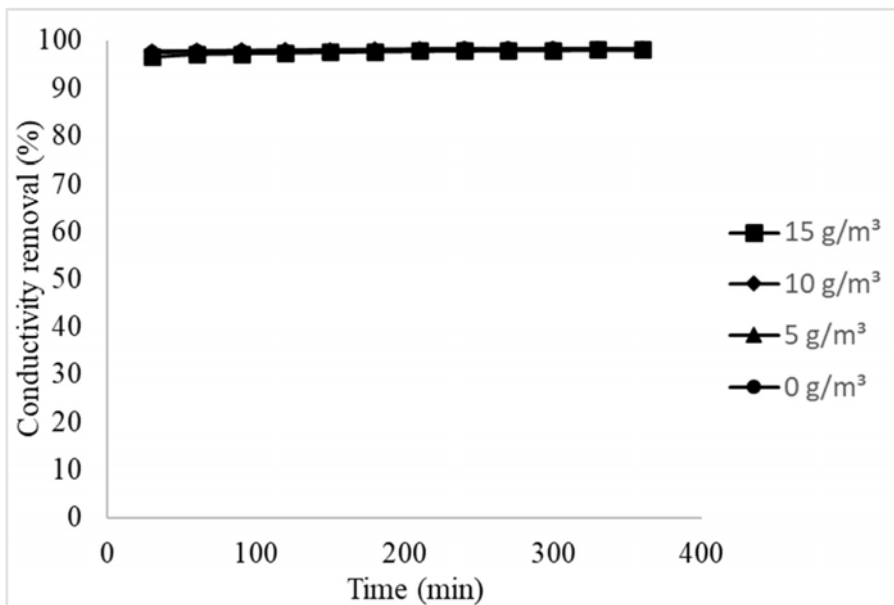


Figure 3.2. Conductivity removal from geothermal water using Protek 101 antiscalant.

On the other hand, boron removal from geothermal water influenced by use of Procond 624 as antiscalant. Although boron removal decreased by time, the highest boron removal was achieved by using 15 g/m³ of Procond 624 as shown in Figure 3.3. Therefore; boron removal by RO-SW30 were calculated for each experiment.

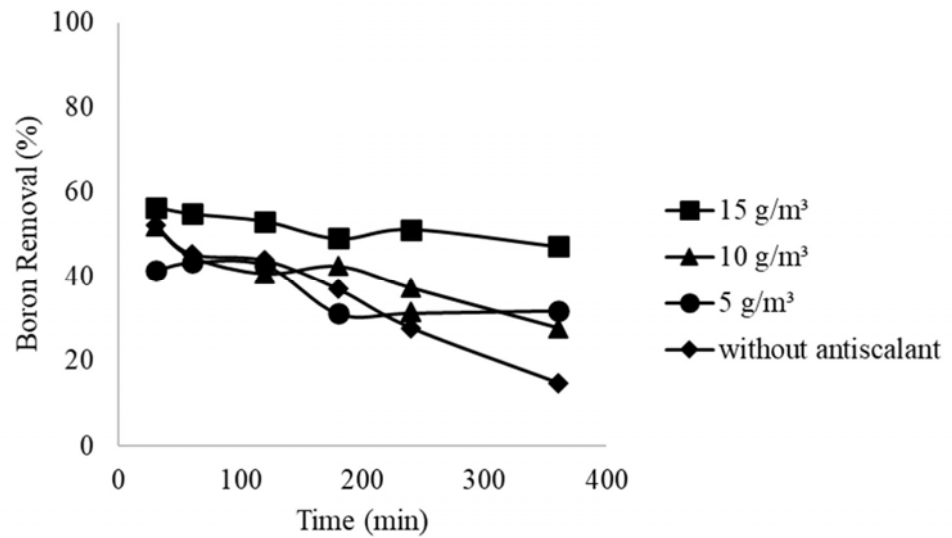


Figure 3.3. Boron removal from geothermal water using Procond 624 antiscalant.

On the other hand, there was not much differences on boron removal by time when Protek 101 was used as antiscalant. The highest boron removal was similar for both antiscalant.

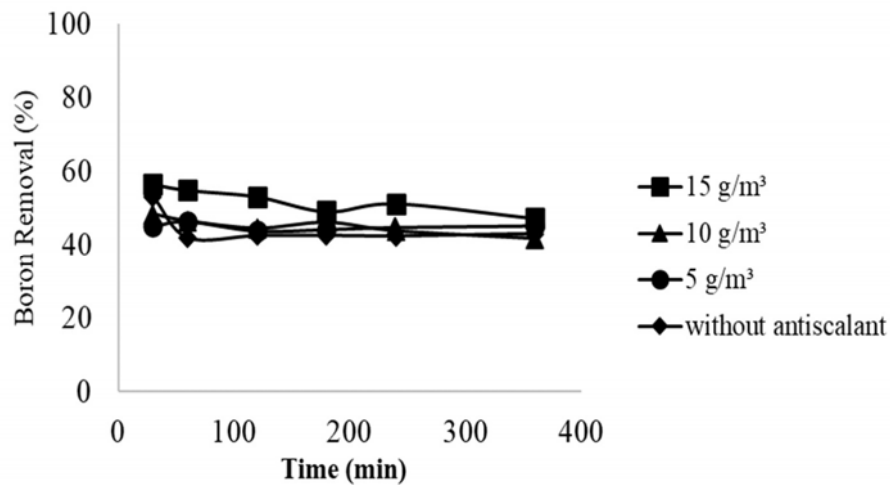


Figure 3.4. Boron removal from geothermal water using Protek 101 antiscalant.

Increasing the concentration of this antiscalant did not yield a discernible effect.

The outcomes are fairly similar to one another.

3.1.1. PV Solar Energy System Powered Desalination

The performance data of the solar panels measured during the antiscalant pretreatment studies are shown in the table. When looking at the table, the energy produced in the winter months does not match the energy consumed. On the other hand, the amount of energy produced in the summer and spring months is higher. Briefly, while solar panels alone are not enough to operate the system in the current winter months, they can operate the system in the summer and spring months.

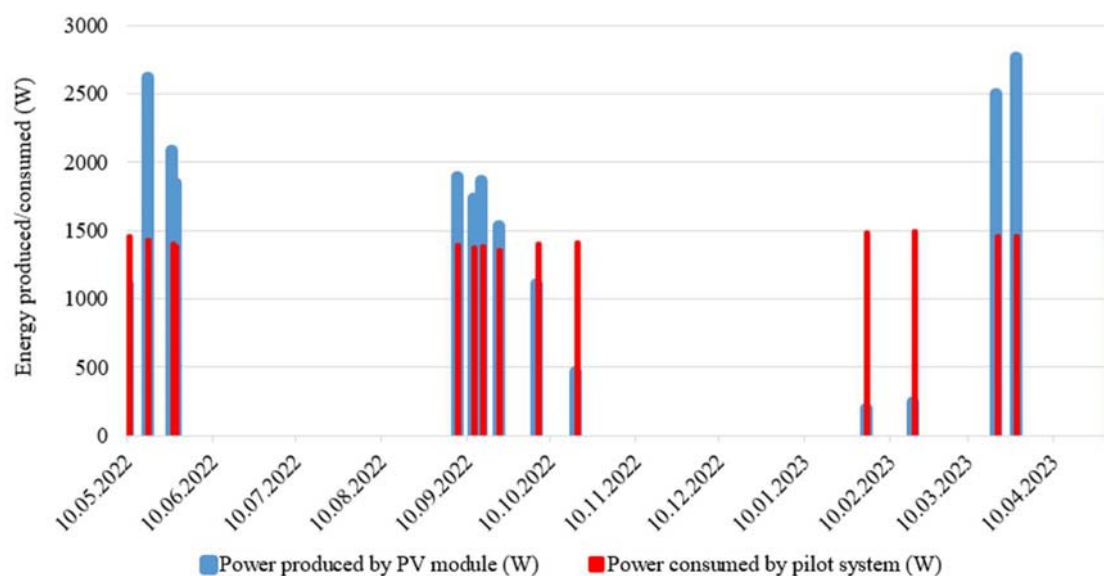


Figure 3.5. Average power produced by PV module/power consumed by pilot scale system with SW30 vs. date plot.

3.2. Pretreatment with UF

Geothermal water was treated using a mini-pilot-scale test with a Vontron BWRO membrane. ACM-20 ultrafiltration served as the pretreatment for the membrane tests, which employed Protek101 antiscalant at a concentration of 15 g/m³. UF membrane prevents silica in colloidal form while Protek antiscalant prevents blockages caused by high silica and calcium carbonate. The RO processes were carried out at 15 bar for 6 h maintaining a consistent water recovery as 60% with

four different pretreatment methods. They are follows UF and RO presence of antiscalant (UF+RO+AS), RO with antiscalant, UF and RO without antiscalant and RO with no antiscalant and UF measured permeate flux, conductivity, TDS and salinity each 30 min. To ascertain on the permeability of the membranes after each experiment, pure water fluxes were measured for the membrane in the range of 5-25 bar of applied pressure at room temperature.

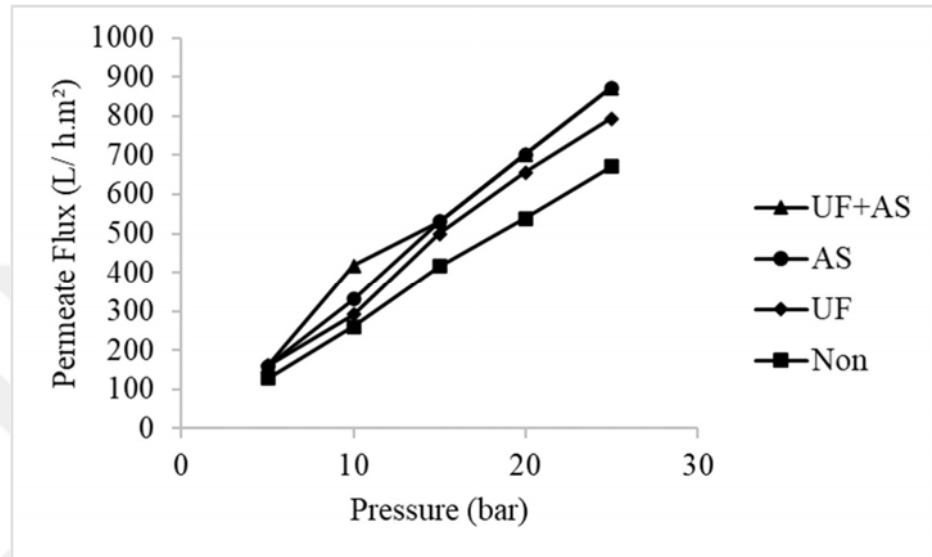


Figure 3.6. Permeate flux of pure water vs. pressure applied for Vontron BWRO membrane after treatment of geothermal water with UF+AS, antiscalant(AS),UF and without pretreatment(Non).

After 6 h RO tests using pretreatment UF and with presence of antiscalant, UF pretreatment, antiscalant and without any pretreatment, a pure water permeability test was conducted to comprehend the membrane scaling. Figure 3.5 compares the permeate flux values obtained from this test, demonstrating that using antiscalant with UF pretreatment maintains high permeate flux while reducing membrane scaling.

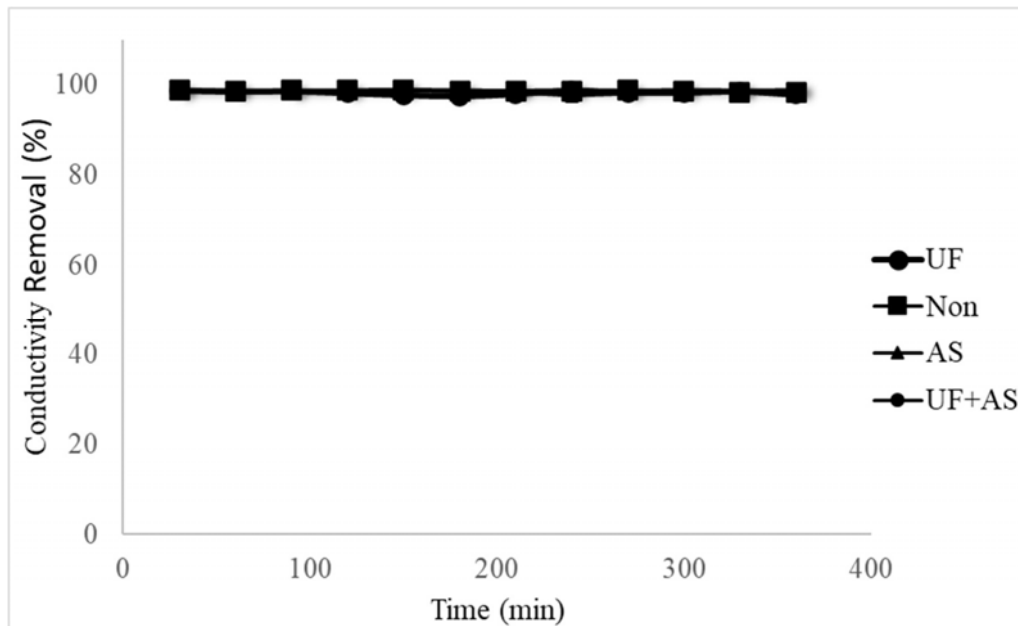


Figure 3.7. Conductivity Removal from geothermal water using UF with antiscalant, UF, antiscalant and without pretreatment.

On the other hand, it is understood from Figure 3.6 that pretreatment does not make any difference on conductivity removal. Vontron membrane has been shown to successfully desalinate geothermal water without any pretreatment.

3.3. Pretreatment of Geothermal brine with NF90

Flat sheet membranes made of NF90 and XLE-RO will be used in this experiment to pre-treat the RO-treated geothermal concentrate. Throughout this process, the XLE-RO membrane was subjected to a pressure of 20 bar, while the NF90 membrane was subjected to 15 bar. Pressure differential is caused by an increase in pressure, which allows for faster collection of permeate water.

The NF90 membrane was used to pre-treat the geothermal water concentrate that was produced during the RO process. The NF90 permeate water with an average quality of 219 ($\mu\text{S}/\text{cm}$) was obtained as a result of this process as shown in Table 3.4.

Table 3.4. The feed and permeate conductivity values obtained with the NF90 of the SEPA system.

Time (min)	Feed Conductivity ($\mu\text{S}/\text{cm}$)	Permeate Conductivity ($\mu\text{S}/\text{cm}$)
30	4870	189.8
60	4910	178.5
90	4990	181.1
120	5070	193.1
150	5170	191.1
180	5220	210.0
210	5300	221.0
240	5430	234.0
270	5440	246.0
300	5530	235.0
330	5560	264.0
360	5670	286.0
Average	5263	219 ± 35

The XLE-RO membrane was used to pre-treat the geothermal water concentrate that was produced during the RO process. The XLE-RO permeate water with an average quality of 78 ($\mu\text{S}/\text{cm}$) was obtained as a result of this process as shown in Table 3.5.

Table 3.5. The feed and permeate conductivity values obtained with the XLE-RO of the SEPA system.

Time (min)	Feed Conductivity ($\mu\text{S/cm}$)	Permeate Conductivity ($\mu\text{S/cm}$)
30	4780	56.1
60	4830	65.4
90	4890	68.1
120	4940	71.0
150	5050	76.2
180	5090	79.2
210	5140	80.1
240	5210	83.9
270	5290	84.5
300	5370	88.4
330	5430	92.4
360	5510	95.7
Average	5293	78 ± 12

3.4. Pretreated geothermal water dilution with EDR

According to Figure 3.7 , conductivity removal was constant at high levels by time. Under these circumstances, the loss of conductivity was not adversely affected by membrane blockages. On the other hand, membrane blockages could negatively impact ion removal in long-term investigations.

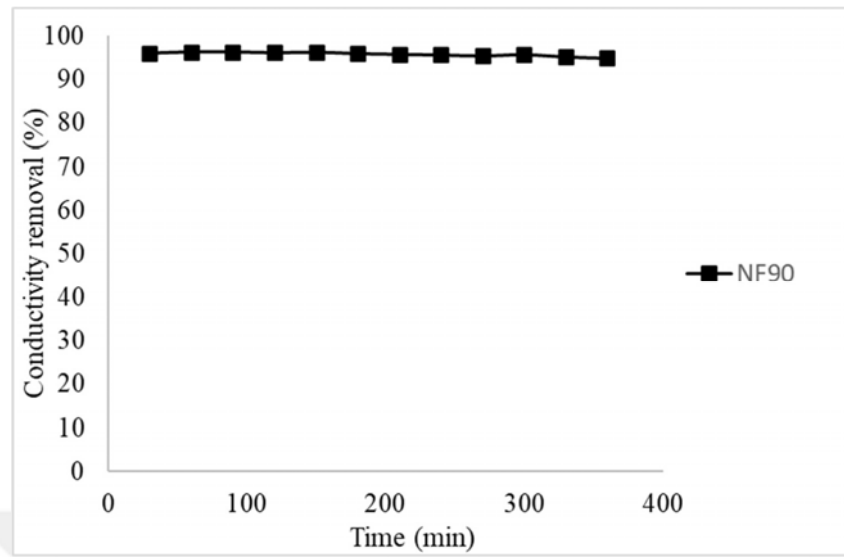


Figure 3.8. Conductivity Removal from geothermal water concentrate using NF90.

EDR Treatment with EDR at 20 V was performed after NF90 pretreatment. According to Table 3.5 the conductivity value of the water decreased to 1.44 ($\mu\text{S}/\text{cm}$) levels after 2h of EDR treatment. This shows that it provides a successful treatment for NF permeate of RO concentrate.

Table 3.6. Conductivity values of NF90 permeate water according to time with.

Time (min)	Permeate Conductivity ($\mu\text{S}/\text{cm}$)
0	189.40
10	60.30
20	26.00
30	10.54
40	5.48
50	3.28
60	2.56
70	2.17
80	2.00
90	1.74
100	1.55
110	1.59
120	1.44

In Figure 3.8 the conductivity removal rates of water applied with an electrical difference at 4 different electrical potential was shown. Treatment with EDR at 20, 15, 5 and 0 v was performed after NF90 pretreatment. According to Figure , water was purified at a high rate at each voltage value. However, when we compared the voltage values, it was seen that better purification was achieved in a faster time in 15 v and 20 v studies. This shows that it provides a successful treatment with the geothermal brine EDR method. According to these results, it was determined that the conductivity removal reached 99 percent levels in 60 minutes.

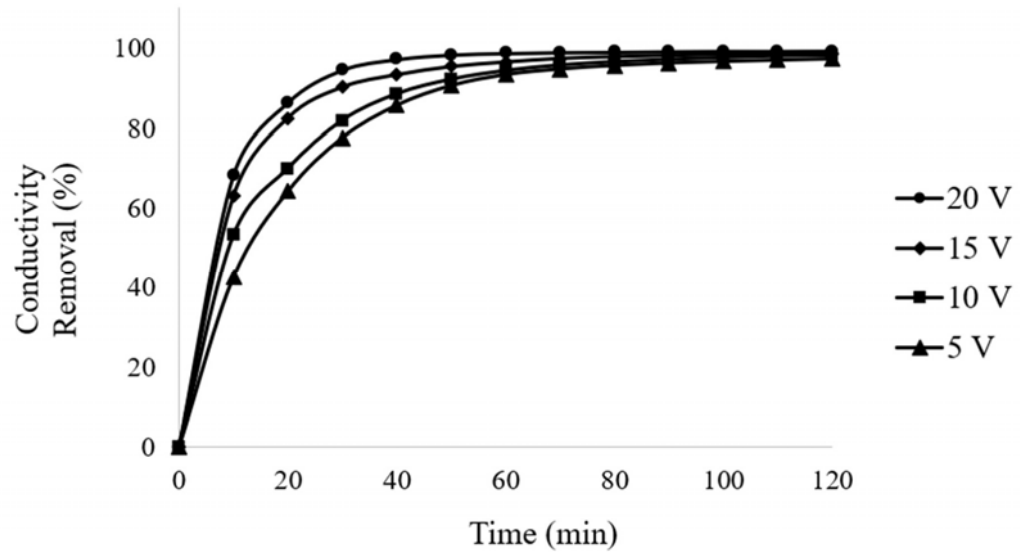


Figure 3.9. Conductivity Removal from NF90 permeate using EDR system at 20, 15, 10 and 5 V.

In the XLE-RO study, 4 different voltage values were used. In this study, water was purified at high levels with the EDR method. When we compared the voltage values, it was seen that the values of 20 V and 15 V were close to each other. The reason for this may be that the maximum level to be purified with the EDR method was reached due to the low conductivity levels reached in the pretreatment.

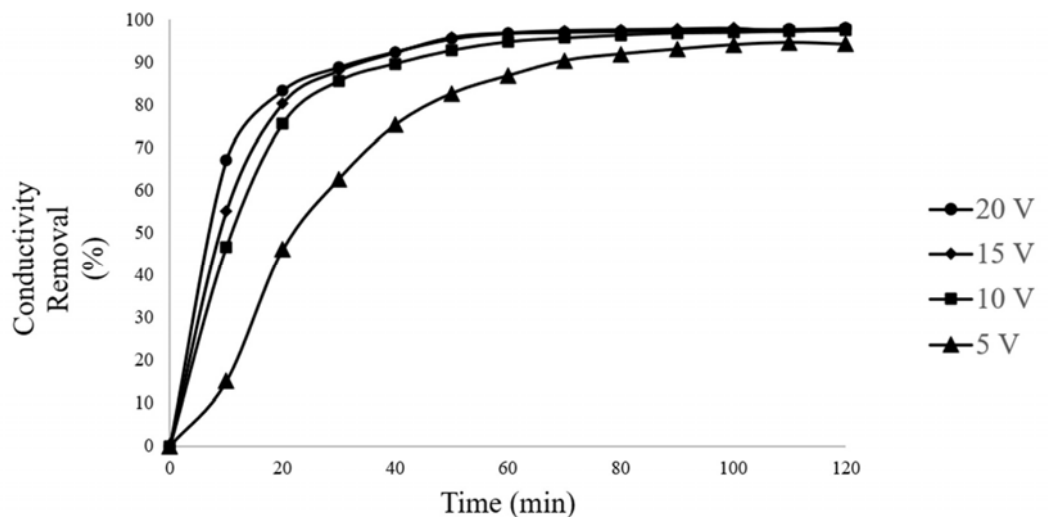


Figure 3.10. Conductivity Removal from XLE-RO permeate using EDR system at 20, 15, 10 and 5 V.

4. CONCLUSIONS

Nowadays, with the depletion of clean water resources, it is critical to enhance the sustainable usage of alternate water sources. Water and wastewaters can be purified with membrane technology. The limitations of this method, however, are the management of the concentrate that is created after purification and also membrane fouling. To come up with different answers to these issues, experimental investigations were carried out in this work.

In comparison to lower antiscalant concentrations, it was determined that the maximum antiscalant concentration of 15 g/m³ prevented scaling more and preserved the pure water permeability at a faster rate. Protek101 antiscalant has been found to be more appropriate for use as a pretreatment antiscalant used for geothermal water treated by SW30-RO membrane.

Applying UF pretreatment maintained the permeate flux higher and prevented scaling. By maintaining a high permeate flux, UF pretreatment can be an effective pretreatment technique. It has been observed that the use of only antiscalant gives better results than the use of only UF. Therefore, it has been observed that the use of appropriate antiscalant concentration together with UF pretreatment provides more effective results in preventing membrane blockages.

Using SWRO membrane, the geothermal water was greatly desalinated. It was evident that water recovery from the NF pretreated geothermal water RO concentrate could be achieved through the use of an EDR system. Concentrate management is also possible through the integration of EDR treatment with RO and NF.

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6. ACKNOWLEDGEMENT

This work was made possible by funding from an international academic project financed by TÜBİTAK-NCBR (Project No. 118Y490-POLTUR3/Geo4Food/4/2019). I am appreciative of TUBİTAK for offering the crucial financial support needed for our endeavors.

I want to express my gratitude to Prof. Dr. Nalan KABAY. my adviser, for her continuous assistance during my master's program.

I would also like to express my gratitude to Dr. Aydın CİHANOĞLU. Yakubu Abdullahi Jarma. Dr. Esra ALTİOK. Aseel ZAİD and Emmanuel BABAJİDE who guided and helped me during both field and laboratory experiments.

Without the knowledge and experience my defense committee kindly provided. I could not have continued on this adventure. I therefore like to express my gratitude to Prof. Dr. Sacide ALSOY ALTINKAYA and Doç. Dr. Tülay GÜNGÖREN MADENOĞLU.

For giving me the chance to work in TUBİTAK Project, I would like to thank Prof. Dr. Alper BABA, the project's coordinator.

I would like to thank İzmir Geothermal Co. for giving us support during field work and allowing us to use their geothermal water samples. Thanks to them, we completed our field work without any problems.

Lastly. I want to express my gratitude to my family for helping me throughout this journey.

7. CURRICULUM VITAE

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SKILLS

- English
- Microsoft Office (Word, Excel, Powerpoint) Minitab
- Driving Licence (B type)
- Laboratory experiments and data analysis
- Good technical reporting and presentation skills
- No military obligation (done)

EDUCATION

- **Masters in Chemical Engineering**

Ege University | 2021-Current

Water treatment techniques, concentrate management.

Advisor: Prof. Dr. Nalan KABAY Contact: +90 532 777 04 91

- **Chemical and Process Engineering (3.09)**

Yalova University | 2012-2019 Controlled / living radical polymerization with microemulsion. Styrenation of vegetable oils.

Advisor: Assoc. Prof. Dr. Mesut YILMAZOGLU Contact: +90 554 538 77 44

- **Chemical Engineering (Erasmus Student Exchange Program)**

Klaipeda University 2016-2017

Extraction, processing and prevention of environmental pollution of petroleum products

EXPERIENCE

- **Production Engineer (November 2023- Current)**

Responsibility for the production reaction, product processing and auxiliary facilities of expandable polystyrene and general purpose polystyrene.

- **Entrepreneurship Clarxvia (November 2020- August 2022)**

While selling handmade art products online. we also conducted e-commerce with our Cute Cat eyeglasses brands.

- **Sub-lieutenant Turkish Armed Forces (October 2019 - October 2020)**

I completed my compulsory military service as an officer. In this process. my task is to provide the necessary foods for the military and to check that they comply with the specified quality standards with physical. chemical and biochemical tests.

- **Long Term Intern DowAksa Advanced Composite Material Industries (November 2018 - June 2019)**

In the project with TAI. it is to ensure that the characterization tests are carried out in accordance with the quality criteria and that the test results obtained are documented in an understandable way.

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