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Produced Water Treatment Using Ultrafiltration Membrane Process Experimental Study

A Thesis

Submitted to Department of Civil Engineering at the University of Kerbala in Partial Fulfilment of the Requirements for the Degree of Master of Science in Civil Engineering

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنْكُمْ وَالَّذِينَ أُوتُوا الْعِلْمَ دَرَجَاتٍ وَاللَّهُ بِمَا تَعْمَلُونَ خَبِير

صَدَقَ اللهُ العَلِيُّ العَظيم

سورة المجادلة/الآية١١

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Produced Water Treatment Using Ultrafiltration Membrane Process Experimental Study.

وقد قومتها من الناحية اللغوية والاسلوبية وبذلك تكون صالحة لأغراض المناقشة مع توصيتنا بالأخذ بنظر الأعتبار تصحيح بعض الملاحظات اللغوية المؤشر عليها

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Dedication

This thesis is dedicated to…

My father and mother, who first taught me the value of life and education.

A special feeling of gratitude to my husband whose words of encouragement and push for tenacity ring in my ears.

I also dedicate this work to my beloved brothers who supported me and have never left my side and are very special

I dedicate this work.

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Abstract

In recent years, research has focused on membranes technology for waste water treatment. This study deals with using polyether-sulfone (PES) ultrafiltration membrane (UFM) in the treatment of produced water generated from Al-Ahdab oil field in Wasit Iraq as a case study. In the experimental work, 8 rectangular flat sheets of prepared PES ultrafiltration membrane were used. The area of each membrane is 60 cm^2. Scanning Electron Microscopy (SEM) was used to examine the membrane morphology such as pore size, and thickness. Two types of samples were used in the study; these are, raw produced water and pre-treated water and examined for three months. Physical and chemical characteristics were analysed to determine treated water quality. The effects of trans-membrane pressure, temperature of fluid, membrane fouling was studied in detail to evaluate the efficiency of used UFM. The result show that when the trans-membrane pressure (TMP) increased from 1 bar to 5 bar, the amount of permeation flux increased from 360 to 750 $l/m^2.hr$ due to the increase in driving forces across the membrane. However, permeation flux decreased gradually as time went by due to an accumulation of pollutants on the membrane. Temperature also has effects on permeation flux. When the temperature increased from 30^o to 50^o C, the permeation flux also increases from 543 to 556 $l/m^2.hr$. Membrane efficiency decreased about 7% after the backwashing. The results indicate high removal efficiency for many parameters, about 100% removal for the three parameters (oil content, total suspended solids and heavy metal). UFM showed weakness in removing efficiency for total dissolved solid (TDS) when compared with conventional treatment (CT) methods. In this study, combining two methods (CT and UFM) showed increasing of removal efficiency. The chemical oxygen demand (COD) decreased from 380 to 68.4 mg/l by using UFM only and to

43.7 mg/l for CT and UFM together. This value is within the permissible value of Iraqi standards (IQS).

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List of Abbreviations

A	Area of The Membrane
AGF	Air Gas Flotation
alum	Aluminium Sulfate
BAF	Biological Aerated Filter
BOD	Biological Oxygen Demand
BTEX	Ethylbenzene, And Xylenes
CBM	Coal Beed Methane
CC	Chemical Coagulation
CFV	Cross Flow Velocity
COD	Chemical Oxygen Demand
CPF	Centre Production Facility
CPI	Corrugated Plate Interceptor
D	Membrane Thickness
DGF	Dissolved Gas Flotation
DMSO	Dimethyl Sulfoxide
EC	Conductivity
Fp	Permeate Flux
FTE	Freeze Thaw Evaporation
IGF	Induced Gas Flotation
k	Permeability
MF	Microfiltration
MWCO	Molecular Weight Cut-Off
NF	Nanofiltration
NORM	Naturally Occurring Radioactive Materials
NPD	Naphthalene, Phenanthrenes, Dibenzothiophene
O/G	Oil and Gas
O/W	Oil to water ratio
p	Pressure
PAHs	Polycyclic Aromatic Hydrocarbons
PAN	Polyacrylonitrile
pH	Acidity Scale
PPI	Parallel Plate Interceptor

List of Abbreviations	
PES	Polyether sulfone
PVDE	Polyvinylidene Fluoride
PVP	Polyvinyl Pyrrolidone
PW	Produced Water
q	Instantaneous flow rate
RO	Reverse Osmosis
SEM	Scanning Electron Microscopy
Sp Gr	Specific Gravity
T	Temperature
t	Time
T.O.C	Total Organic Carbone
TDS	Total Dissolved Solids
TMP	Transmembrane Pressure
TSS	Total Suspended Solid
UF	Ultrafiltration
UFM	Ultrafiltration Membrane
UFMT	Ultrafiltration Membrane Treatment
V	Voltage
Vol.	Volume
Vp	Volume Of Permeate
WHO	World Health Organization
z	Diffusion Constant

List of Symbols

Ba^{+2}	Barium
Be	Beryllium
Ca_2^{+}	Calcium
Cl-	Chloride
Co_2	Carbon Dioxide
CO_3^{2-}	Carbonate
Cr	Chromium
Cu	Copper
H_2S	Hydrogen Sulphide
HCO3-	Bicarbonate
K^{+}	Potassium
Mg^{+2}	Magnesium
Mn	Manganese
Na^{+}	Sodium
Ni	Nickel
O_2	Oxygen
Pb	Lead
SO_4^{2-}	Sulfate
Sr^{+2}	Strontium
Zn	Zinc

Chapter One

Introduction

1.1 General

One of the main challenges deals with oil and gas production are the environmental impact of generated wastes. Hydraulic fracturing used a large quantity of fluid, involved water and other chemicals added, as a result, a large amount of wastewater is generated, which known as produced water (PW). The released water, which contains high concentrations of salt such as dissolved solids, metals, and oil and grease, and can contaminate groundwater or surface waters [1].

On the other hand, hydraulic fracturing and horizontal drilling require a large amount of water which reaches three times that of the produced hydrocarbon, and most of this water is taken from groundwater, surface water, or reused water. Since water is an important issue, not only for water-deficient regions. Water scarcity is encouraging researchers to develop a new treatment technology to reuse water through typical water movement and redistribution systems for alternative water sources such as seas, oceans, municipal and industrial wastewater [2].

Water scarcity is assessed by hydrologists through knowing the population water relationship. When annual water supplies drop below 1,700 m^3 per person for some area, the region faces water stress. And, when annual water supplies dropping below 1,000 m^3 per person, the region faces water scarcity. The region faces absolute scarcity when annual water supplies dropping below 500 m^3 per person [3].

In 2014, published research at Aarhus University in Denmark, Vermont Law School showed that there will be not enough drinking water by the year 2040 to fulfil the thirst of the population [4]. On the other hand, electricity consumes the largest amount of water for many countries, due to cooling recycles of power plants in order to operate. It will be very difficult to continue to produce electricity in this way and meet the water demand by 2040. Agriculture is another sector consuming a huge amount of water, involving approximately 70% of worldwide water use, increasing to over 90% in the developing countries [5]. Reusing PW can reduce the demand for fresh water and change the waste into usable water resources. Treatment of PW is required in order to meet pre-disposal regulatory limits or to meet beneficial use specifications.

Figure 1.1 show the source of PW and where it can be used for beneficial purposes.

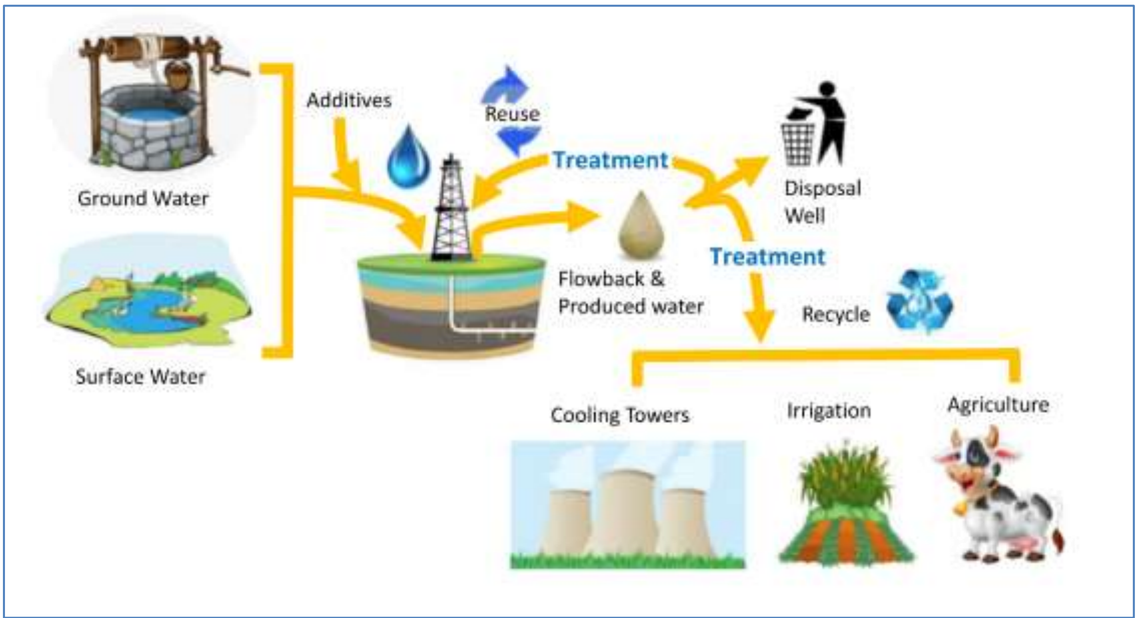


Figure (1.1): PW generation and management [6].

The treatment of PW currently centres around the removal of solids from this water. Clarifiers and coagulant addition are the mechanisms currently used for treatment, and this treatment doesn't meet the requirement of beneficial uses [7].

1.2 Problem Statement

Increasing demand for petroleum (oil and its derivatives) led to increasing oily water production, which contains complex compositions. Therefore, its treatment has been a challenge, because these undesirable components require heavy treatment technologies to treat until their final disposal, in order to meet the legal requirements for disposal in the environment or technical requirements. The water maybe used injection into oil wells to increase oil production, or other beneficial uses such as irrigation, livestock watering, and various industrial uses such as dust control, vehicle washing, power plant, and fire control.

1.3 Objective of the Study

The main objectives of the present study are:

1. Studying the physical and chemical characteristics of Al-Ahdab PW and treated water by conventional treatment plant (CT). And evaluating the management process.
2. Fabricating polyether-sulfone ultrafiltration membrane by phase inversion method and characterizing it by Scanning Electron Microscopy (SEM) to exam the surface morphology, pore size and thickness.
3. Membrane techniques are used to treat PW by polyether sulfone ultrafiltration membrane (UFM) to increasing water quality for reuse proposes

1.4 Methodology of the study

- The selected samples used in this study were from Al-Ahdab oil field, which is located between Numania and Al-Kut, about 180 km to the southeast of Baghdad/Iraq. Its area is about 300 km^2. This field was discovered in 1978, and its production began in 2011.
- Information and figures mentioned in chapter 3 about treatment processes of PW in the field were got during the visit to Al-Ahdab oil field.
- The samples of the treated PW were analysed by a physical and chemical method for the period from January to March 2020.
- The experiments were done by using a locally manufactured filter system, and its parts were explained in detail in chapter four.
- Ultra-filtration membrane is used.
- The membrane was manufactured in the laboratories of the chemical engineering department at the University of Technology Baghdad/Iraq.
- Test of Scanning Electron Microscopy (SEM) was carried out at the chemical engineering department in the University of Technology in Baghdad/Iraq.
- Samples were analysed before and after treatment at Wasit environment agency laboratory, and U-science laboratory in Diwaniyah province.

1.5 Structure of the Thesis

- Chapter one illustrates the introduction, problem statement, the objective of the study, and the scope of the work.
- Chapter two presents the literature that might be pertinent to understand the source of the PW. This section gathers many references to provide information about the components and characteristics of PW. And how to manage and be treated by conventional and unconventional treatment techniques.
- Chapter three provides background about the well including extraction method, characteristics of PW extracted from Al-Ahdab oil field, treatment methods, and chemical additives for enhancing extraction and treatment operations. The sampling and analysis of the sample are described as well, followed by the results.
- Chapter four explain the experimental work including the fabrication of the membrane, operating of the treatment system, and analysis instruments.
- Chapter five displays the results obtained from experimental work.
- Chapter six displays the conclusions and recommendations that can help provide more data for a better understanding of the recycling process.

Chapter Two

Theoretical Background and Literature Review

2.1 Introduction

In the 1850s, Edwin Darke drilled his first oil well, at that time the demand for petroleum increased and continue rising because it was considered a major source of energy. In spite of its significant aspect, it produced a large volume of wastewater, which is called produced water (PW). PW is a big issue of water and environmental pollution. The volume of this wastewater is around 70% of total wastewater produced during oil production. While 80% of this water is re-injected to the well for pressure maintenance, 30% of the total is injected into a deep well for final disposal. The water, which is not re-injected to the production well, has to be treated [8].

The volume of PW from oil and gas wells does not remain constant over time. The water-to-hydrocarbon ratio increases over the life of the well. Initially, water represents a small percentage of produced fluids. As time goes on, the amount of PW will increase, and the amount of oil/gas produced will decrease [9]. Khatib and Verbeck reported that PW generated from several wells increased from 2.1 million bbl/day in 1990 to more than 6 million bbl/day in 2002 for crude oil wells nearing the end of their products as much as 98% of the material brought to the surface can be PW. Coal Bed Methane (CBM) wells, in contrast, produce a large volume of PW early in their life, and the volume declines over time. For example, between 1999 and 2001, the amount of PW generated per well in the Powder River Basin dropped from 396 bbl/day to 177 bbl/day [10]. As shown in Figure 2.1.

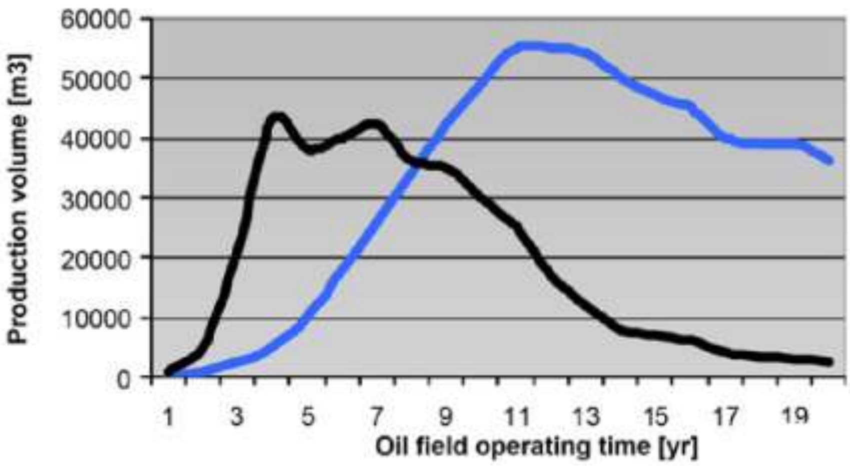


Figure (2.1): Production profile for a typical oil field [11].

2.2 Source of Produced Water

The reservoirs include natural water called formation water, which is generally permeated naturally occurring rocks with different underground fluids such as oil and gas and considers one of the main sources of the PW. The other source is the injected water into the well from the external source to sustain the pressure and achieve greater recovery levels. Both of them are withdrawing during oil and gas extraction. At the surface, PW separated from hydrocarbons [12]. Figure 2.2 shows the distribution layers of hydrocarbons oil, gas and water.

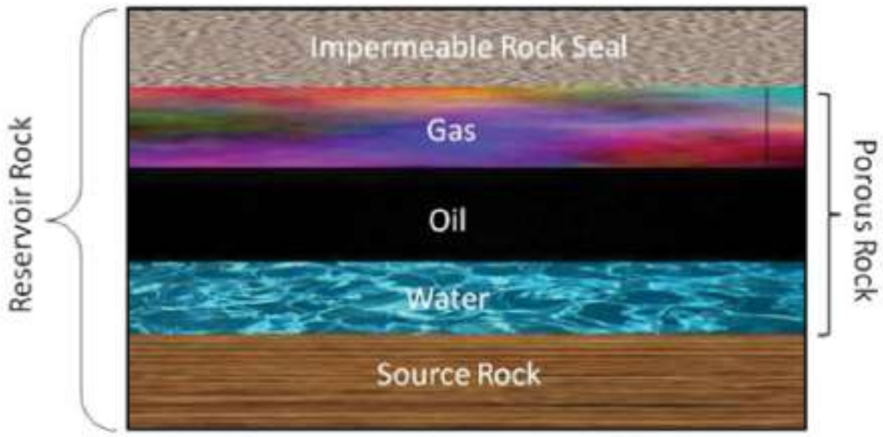


Figure (2.2): Typical reservoir components [11].

2.3 Characteristics of Produced Water

PW has distinctive characteristics due to organic and inorganic matters. It includes salts and oil hydrocarbons which may be toxic to the environment. The characteristics of PW differ from well to well and also depend on reservoir lifetime [13]. Some factors such as the geological location of the field, its geological formation, the lifetime of its reservoirs, and the type of hydrocarbon produced affect the physical and chemical properties of PW [14]. It is a variable and can be very different from well to well. Besides, the characteristics of PW from gas and oil fields also are variable. For example, extracted PW from oil production are relatively less toxic than extracted PW from gas production. That's due to the higher contents of flow molecular–weight aromatic hydrocarbons in the gas reservoir, such as toluene, benzene, and xylene [15].

Oily PW includes a complex composition that contained (polar, non-polar) organic and inorganic components. These organic matters existed in oily PW in two forms, the first is a hydrocarbon (dispersed oil), and non-hydrocarbon matters [16]. The soluble inorganic components compose both metals and non-metals. The metal constituents are calcium, magnesium, sodium, chloride, sulfate, and carbonate/bicarbonate components [17].

PW Characterization to determine major constituents is the first step to choose the optimum treatment methods for PW. Therefore, the major compounds of PW include:

- Dissolved and dispersed oil compounds.
- Dissolved formation minerals.
- Production chemical compounds.

- Production solids (including formation solids, corrosion and scale products, bacteria, waxes, and asphaltenes).
- Dissolved gases [17].

2.3.1 Dissolved and Dispersed Oil Compounds

Oil is a mixture of hydrocarbons that includes benzene, ethylbenzene, xylenes (BTEX), naphthalene, phenanthrenes, dibenzothiophene (NPD), polycyclic aromatic hydrocarbons (PAHs), toluene, and phenols. Water cannot dissolve all hydrocarbons, therefore most of the oil is dispersed in water [12]. The amounts of dissolved and suspended oil that present in PW are related to the factors that are stated bellow[18].

- Oil composition.
- Total dissolved solids (TDS), pH, salinity, temperature.
- Oil/water ratio,
- Amount and type of chemical additive.
- Amount and type of waxes, asphaltenes and fine solids that consider stability compounds

2.3.1.1 Dissolved Oil

Polar constituents in PW are soluble organic components that are found distributed in low and medium carbon ranges. One of the organic components is organic acids that are present in PW, such as formic and propionic. The solubility of organic compounds in PW is affected by PH, temperature, and pressure. Temperature alters the carbon range ratio, while pressure slightly enhances the concentration of dissolved organic compounds in water. In addition, soluble components and salinity don’t affect TDS concentration in PW. Soluble oil amount depends on the type of oil, the volume of PW, techniques of artificial life, and production age [19].

Oil/water separation techniques cannot remove aromatic compounds. These compounds are major contributors to the natural environment's toxicity [18].

2.3.1.2 Dispersed Oil

PW contains small droplets of suspended oil, find as dispersed oil. Dispersed oil amount depends on oil density, droplet shear history, oil precipitation amount, and the interfacial tension between oil and water. Other compounds of PW are less soluble but present as dispersed oil, such as polyacrylonitrile (PAH) and some heavier alkylphenols [18].

This dispersed oil increases chemical oxygen demand (COD) and damage marine and aquatic ecosystems because of its toxicity effect [20].

2.3.2 Dissolved Formation Minerals

PW contains a wide range of inorganic dissolved compounds such as cations, anions, naturally occurring radioactive materials (NORM), and heavy metals [21]. Cation ions such as Na^+, K^+, $Ca_2{}^+$, Mg^{+2}, Ba^{+2}, Sr^{+2}, Fe^{+2} and anions such as Cl^-, $SO_4{}^{2-}$, $CO_3{}^{2-}$, $HCO_3{}^-$. In addition, small dissolved sodium and chloride.

The salinity of PW is mainly due to dissolved chloride and sodium and in a less amount of magnesium, calcium, and potassium. These metals have similar concentration patterns [17].

Sometimes the concentration of heavy metals in PW is higher than in seawater. Their concentration could reach 10^2 to 10^5 times the one found on seawater. It depends on age of the wells and formation geology. PW contains trace quantities of various heavy metals such as cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc [22].

NORM is originated in geological formation and brought to the surface as dissolved solid in PW. NORM may precipitates into sludge when the temperature of water reduces as it reaches the surface [14].

2.3.3 Production Chemical Components

Some chemicals are added during the production of the oil and gas, to enhance oil/water separation and treat or prevent operation problems. Treatment chemicals (production treating, gas processing, and stimulation) and production treating chemicals (scale and corrosion inhibitors, biocides, emulsion breakers, antifoam, and water treatment chemicals) are used in these processes. The concentration of production chemicals in PW is as low as 0.1ppm [23].

2.3.4 Production Solids

Term of produced solids includes a wide range of solid organic and inorganic materials such as; sand, silt, clays, carbonates, waxes, bacteria, precipitated, corrosion, and anti-scale products for pipes and equipment. Production solid concentrations vary from one platform to another.

In anoxic PW, sulfides (polysulfides and hydrogen sulfide) are generated by bacterial reduction of sulfate. Because of different toxic chemicals in PW, few microorganisms can survive.

Biological analysis indicates that there are 50–100 cells of microorganisms per ml. The side effect of it is clogging or causing corrosion of equipment and pipelines [24].

2.3.5 Dissolved Gases

There are different types of gases formed naturally dissolved in PW. That's due to chemical reactions and bacterial activities. These gases include hydrogen sulfide (H_2S), oxygen (O_2), and carbon dioxide (CO_2). Water salinity and temperature decrease the gases solubility, and pressure increases them [11].

Fakhrul in 2009, summarized all parameters of PW from the oil field in the world [7], as shown in the Table 2.1.

Table (2.1): Characteristics of Typical PW in the World [7].

Parameter	Values	Parameter	Values
Density	1014–1140 (kg/m^3)	Calcium	13–25800 (mg/L)
Surface Tension	43–78 (dynes/cm)	Sodium	132–97000 (mg/L)
TOC	0–1500 (mg/L)	Potassium	24–4300 (mg/L)
COD	550 - 1220 (mg/L)	Magnesium	8–6000 (mg/L)
TSS	1.2–1000 (mg/L)	Iron	<0.1–100 (mg/L)
pH	4.3–10	Aluminium	310–410 (mg/L)
Total oil	2–565 (mg/L)	Boron	5–95 (mg/L)
Volatile (BTX)	0.39–35 (mg/L)	Barium	1.3–650 (mg/L)
Salinity	1.000- 400.000 (mg/L)	Cadmium	<0.005–0.2 (mg/L)
Bicarbonate	77–3990 (mg/L)	Chromium	0.02–1.1 (mg/L)
Sulfite	10 - 15 (mg/L)	Copper	<0.002–1.5 (mg/L)
Sulfate	<2–1650 (mg/L)	Lithium	3–50 (mg/L)

Ammoniacal nitrogen	10–300 (mg/L)	Manganese	<0.004–175 (mg/L)
Phenols	0.009–23 (mg/L)	Lead	0.002–8.8 (mg/L)
Total polar	9.7–600 (mg/L)	Strontium	0.02–1000 (mg/L)
Higher acids	<1–63 (mg/L)	Titanium	<0.01–0.7 (mg/L)
Silver	<0.001–0.15 (mg/L)	Zinc	0.01–35 (mg/L)
Mercury	<0.001–0.002 (mg/L)	Chloride	80–200,000 (mg/L)

2.4 Environmental Effect of Produced Water

PW effects agricultural resources and the life of aquatic. One of the main contaminants is salinity. Salinity which is the concentration of salt in PW, in which it effects the environment. It approximately ranges from (1.000-400.000 mg/L)[7].

Sodium causes substantial degradation of soils. It alters clay texture, soil texture, and subsequent erosion. In addition, it is a major dissolved constituent in PW. A high concentration of sodium with magnesium, calcium, and potassium that are uptake by plant roots. Therefore, high levels of sodium led to a deficiency of other cations and cause the structure of poor soil and inhibit infiltration of water in soil. High levels of these contaminants and toxic constituents that discharged into the aquatic environment pose a critical threat to agricultural resources and the life of aquatic by altering the natural state of the aquatic environment. In addition, organic materials in PW, also cause potential damage to the environment[25, 26].

2.5 Produced Water Management

Mantell in 2011, states that the three most important factors in PW management are quantity, rate of production, and quality of PW [27]. Arthur in 2005, states some of the options available for PW management [28].

1. Preventing water leak to the surface by using polymer gels to block fractures and fissures.
2. Injecting the PW into the well to get rid of environmental pollution and to improve oil recovery and pressure maintenance before that, PW must be treated to reduced fouling, bacteria and scaling agent.
3. Reusing in oil and gas operations: Treat the PW to meet the quality required to use it for drilling, stimulation, and workover operations.
4. Consuming in beneficial use: In some cases, significant treatment of PW is required to meet the quality required for beneficial uses such as irrigation, rangeland restoration, cattle and animal consumption, and drinking water for private use or in public water systems.
5. Discharging PW: Treat the PW to meet onshore or offshore discharge regulations. PW must be cleaned before discharge to sea. Often this water contains sand particles bound to the oil/water emulsion. The environmental regulations in most countries are quite strict.

2.6. Requirement of PW Treatment

1. De-oiling: Removal of free and dispersed oil and grease.
2. Soluble organics removal: Removal of dissolved organics.
3. Suspended solids removal: Removal of suspended particles, sand, turbidity.
4. Disinfection: Removal of bacteria, microorganisms, algae, etc.
5. Dissolved gas removal: Removal of light hydrocarbon gases, carbon dioxide, hydrogen sulfide, etc.

6. Desalination: Removal of dissolved salts
7. Softening: Removal of excess water hardness.
8. Miscellaneous: Naturally occurring radioactive materials (NORM) removal [28].

2.7 Produced Water Treatment (PWT)

Multiple technologies are using for PW treatment. Pre-treatment flowed by post- treatment is the best way to treat highly polluted water as PW to decrease the amount of PW pollutants in order to meet the acceptable level of PW reuse. Different methods may be used include physical, chemical, biological and thermal treatments method [7].

Several methods are available to remove the suspended solids filtration, coagulation, gravity separation, and biological treatment. Many methods are available to remove the dissolved and dispersed hydrocarbons such as adsorption, volatilization, oxidation, ultraviolet, irradiation, precipitation, and biological processes.

The dissolved solids which include salt, hardness ions and heavy metals can be treated by processes like ion exchange, precipitation, evaporation, distillation, electrodialysis, and membrane treatments [29]. Some of these technologies are reviewed below.

2.7.1 Hydro-cyclones

Hydro-cyclones are a physical treatment process used for separated suspended solid as sand and oil content based on density different principle. Commonly it consists of a conical base and at the top a cylindrical section, the liquid stream-fed tangentially. The angle of the conical base affects the performance and capacity of hydro-cyclones separation. It includes two discharge streams, first called reject stream or underflow located at the bottom and used for heavier material discharge.

Other called produced stream or overflow located at the top and used for the lighter phase. Hydro-cyclones can remove particles size about 5 to 15 µm, depending on the design of the cyclone; they efficiency range approximately 60-75% for oil content. However, they cannot remove the soluble components [30].

2.7.2 Thermal Treatment Technologies

Thermal treatment technologies are desirable in places where energy cost is comparatively low. This technology was used for the desalination of water before membrane technology releasing. Thermal treatment technologies for distillation include multistage flash (MSF) distillation, multi-effect distillation (MED), and vapor compression distillation (VCD) [11].

MSF includes a series of stages; each stage operates at a decreasing combination of temperature and pressure. For example, when feed water is heating, and the pressure is decreasing to evaporate the water. The resulting steam is used for the process of desalination.

MED is consisting of multiple stages, in each stage, the feed water is heated and passes through a series of evaporator tubes. The resulting steam is subsequently used in each evaporator tube to evaporate water in the next tube. MED and MSF processes need pre-treatment, anti-scaling agents, thermal and electrical energies. The overall cost of MED is lower than MSF.

VCD is a process used for the evaporation of contaminated saline water, in which the compressed vapors release latent heat. In the vapor compression distillation process, the function of the compressor is to compress the vapors, to increase both their temperature and pressure. Therefore, the latent heat released during the condensation process can be reused to create more vapor[31].

2.7.3 Adsorption Treatment Processes

The principle of adsorption based on the contact between a solid surface and a fluid. Solute molecules are accumulated on the solid surface as a layer, this is because of existing surface forces imbalanced. The adsorption materials include different materials such as zeolites, activated carbon, chitosan, organoclays, and activated alumina. Efficiency of these type approximately from 60-98 %.

Normal adsorption treatment processes don't require chemicals additives, but it might be used for cleaning operation of adsorbent martials. Performance of the adsorbents is affected by pH, temperature, suspended solids and oils, the concentration of dissolved contaminants, and salts [32].

2.7.4 Flotation

Flotation technology is used as a conventional method to treat PW in many oilfields. This method uses fine air or gas bubbles to separate particles that are suspended in PW. Flotation technology consists of the following four steps:

1. Gas and air bubbles generation.
2. Contacting between suspended particles and generated bubbles.
3. Join suspended particles to the generated bubbles.
4. removing particles from the surface when bubbles are lifting to the surface [33].

In general, flotation technology has two types based on gas bubbles generation and bubbles size. The first type is dissolved gas flotation (DGF) and the second types is induced gas flotation (IGF).

In DGF units, used a pressure drop or vacuum method to introduce the gas in to the flotation tank. While, in IGF units' propellers or mechanical shear are used to create bubbles of gas.

This method is effective for removing the particle size with a range of 3-25 mm. Important to know the particles with small sizes need a pre-treatment as coagulation. Soluble oil constituents in water cannot be removed from PW by this technique. Flotation is most effective when gas bubbles size is less than oil droplet size and it is expected to work best at low temperature since it involves dissolving gas into water stream [34].

2.7.5 Biological Aerated Filters

Biological aerated filter (BAF) is a class of technologies which includes five types; fixed film and attached growth processes, conventional trickling filters, roughing filters, intermittent filters, and packed bed media filters. Rocks, gravel or plastic considered the best permeable media in BAF.

PW flows downward over the media and as time going on generates a microbial film on the media surface. This media facilitates oxidation of biochemical and remove organic constituents

Pumps and fans are used in this technology to maintain aerobic process and aerobic conditions. BAF can remove oil, ammonia, suspended solids, nitrogen, COD, biological oxygen demand (BOD), heavy metals, iron, soluble organics, trace organics and hydrogen sulphide from PW. It is most effective for PW with chloride levels below 6600 mg/l. This process requires upstream and downstream sedimentation to allow the full bed of the filter to be used. Removal efficiencies of up to 70% nitrogen, 80% oil, 60% COD, 95% BOD and 85% suspended solids have been achieved with BAF treatment. It does not require any chemicals or cleaning during normal operations. Solid's disposal is required for accumulated sludge in sedimentation basins [25].

2.7.6 Chemical Treatment Methods

Chemical treatment methods used coagulation and flocculation processes for removing suspended particles, oil droplets, and colloids while these processes cannot remove dissolved material. Chemical oxidation is considered a developed technology of chemical treatment methods. It is effective in removing BOD and COD content ranges about 90 % [20].

2.7.7 Freeze Thaw Evaporation

In 1992, freezing, thawing, and conventional evaporation used in a process called Freeze-thaw evaporation (FTE) for PW management. The freezing point of the PW drops to 32 F due to the presence of salts and dissolved constituents. At 32 F, crystals of pure ice and unfrozen solution are formed. This solution contains dissolved constituents in high concentrations, and it is separated from the ice. Finally, the collect ice melt to obtain pure water.

In winter, about 50% of water is recovered by using this process. While at other seasons, FTE works as an evaporation pond. Therefore, water doesn't recover. The advantages of this method include removal efficiency is high about 90% for TDS, heavy metals, and organics material, the operating and monitoring are easy, it does not need chemicals additives, and the average lifetime of it is about 20 years.

However, the disadvantages of FTE are generating a large amount of concentrated oil and brine that must be a disposal of, works only at low climate temperature, and requires high spaces[28].

2.8 Membrane Treatment Technology

In most cases, the exclusion based on the size is the principle of membrane separation of constituents by using a layer of a selective barrier. which are thin films with specific pore ratings, which selectively separate fluid from its components. membrane allows the passage of certain components and retains others in the liquid or gas mixture. The stream that enters the membrane is called feed-stream, the fluid that passes through the membrane is known as the permeated while the fluid that contains the retained components is named recant or concentrate.

A membrane can be homogeneous / heterogeneous and symmetric/ asymmetric in structure. From the material point of view, a membrane could be made of organic (e.g. polymeric membranes) or inorganic materials [35].

1. **Polymeric Membranes:** Made of polyvinylidene fluoride (PVDE) and polyacrylonitrile (PAN). It can reject the particles, emulsified and dispersed oil, and particles, with an efficiency of 85% for dead-end and 100% for cross-flow. It's cheaper than inorganic membranes, and their lifetime is about seven years. [36].
2. **Inorganic Membranes:** Made of ceramic material, it considers better than polymeric membranes due to its stability for chemical and thermal. They proved to be effective in treating PW by removing TDS, suspended oil. The main drawback of this type of membrane are its relatively high capital cost, together with the high energy required for the cross-flow recycle rate needed for fouling management, which contributes to operating costs [37].

Distinct advantages of membrane technology for the treatment of PW include reduced sludge, high-quality permeate, and the possibility of total recycle water systems. These advantages, when considered along with the small space requirements, moderate capital costs, and ease of the operation make membrane technology an economically competitive alternative or addition to traditional wastewater treatment technologies [38].

2.8.1 Membrane Classification:

There are four types of membranes classified according to the pore size. It includes (micro-filtration (MF), ultra-filtration (UF), nano-filtration (NF), and reverse osmosis (RO)). MF has the largest pore size, and the pore size decreases respectively for UF, NF, and RO. as shown in Table 2.2. [39] Therefore, the hydrodynamic resistance increases due to increasing of the pressure when the pore size decrease[40].

Table (2.2): Classification of Membrane According to its Pore Size [39].

Membrane type	Pore size
Microfiltration MF	0.03-10 µm
Ultrafiltration UF	(0.002 to 0.1µm) or (2 to 100 *Nm)*
Nanofiltration NF	(0.001-0.0001µm) or (1 to o.1 *Nm)*
Reverse Osmosis RO	(< 0.0001µm) or (o.1 *Nm)*

Where: $\mu m = 10^{-6} m$, and $Nm = 10^{-9} m$.

A Molecular Weight Cut-off (MWCO) is the ability of the membrane to reject a specific molecular weight measured as Dalton [28]. The principle of MF and UF membrane is Darcy's law (a convective pore-flow mechanism). Whereas, RO membrane principle is Fick's law (solution diffusion mechanism). NF membrane is called loose RO membrane because it is in between diffusion and pore-flow mechanism. [41].

Darcy's law state that the discharge rate q is proportional to the gradient in the hydraulic head and the hydraulic conductivity [42]. His equation as below:

$$q = -\frac{k}{\mu} * \nabla p \qquad (2.1)$$

Where:

q = instantaneous flow rate per unit area.

k = permeability.

$\Delta\, p$ = pressure drops.

μ = dynamic viscosity of the fluid.

Fick's law of diffusion depends on the concept that, molecules tend to move from a higher concentration to a lower concentration where the rate of diffusion across a membrane is directly proportional to the concentration gradient and inversely related to the thickness of the membrane [43]. The equation is:

$$rate\ of\ diffusion = Z * A * \frac{Ch - Cl}{D} \qquad (2.2)$$

Where:

Z = Diffusion constant.

A = Membrane surface area.

$Ch - Cl$ = Different in Pressure.

D = Membrane thickness.

2.8.1.1 Microfiltration

Microfiltration (MF) MF is used as a primary treatment for oily wastewater to remove turbidity and suspended solids (silt, clays, sand, algae, and some microbial types). Microfiltration does not remove viruses, but it prevents viruses when used with the disinfection. The pore size of MF ranges from 10 to 0.1 microns, MWCO (of more than 100,000 Daltons, and a fairly low operating pressure of about 15 to 60 psi is required[44].

2.8.1.2 Ultrafiltration

Ultrafiltration (UF) is a membrane technology treatment method. UF considers an effective method to treat PW [45]. The pore size of UF range from 0.002 to 0.1µm, an MWCO of about 10,000 to 100,000 Daltons and operating pressure of around 2 to 6 bar[28]. The advantages of UF are; the high ability to remove oil, low energy cost, no chemical additives are required, operating at low transmembrane pressure and space requirements is small[46]. It removes colour, colloidal organic matter, odour, and viruses. In addition, it removes all microbiological matters that removed by using MF[44].

2.8.1.3 Nanofiltration

NF membranes are generally designed to be selective for multivalent ions rather than for univalent ions [47]. The nominal pore size of NF membranes is about (0.001 microns =1.0 nm), and MWCO is about from 1,000 to 100,000 Dalton [28]. NF requires higher pressure than UF and MF to push water through the mini membrane pores.

NF operates at a pressure range from 6 to 10 bar, and it can remove approximately all bacteria and viruses, and also, it can remove alkalinity of water[41].

2.8.1.4 Reverse osmosis

Reverse osmosis (RO) is the separation of dissolved and ionic components. It can remove contaminants as small as 0.0001 mm [32]. RO is typically designed to reject all matters other than water. In addition, it rejects natural organic substances, radium, ionic species, cysts, viruses, and bacteria. RO membranes are unable to remove dissolved gases and certain low weight organic molecular [47].

RO is similar to NF membrane, in which it is operating at higher pressure when compared with UF and MF membrane. In RO, water permeation flux increases when operating pressure increases, even though, it still can reject slat. Therefore, RO membranes selectivity is more effectively at high pressure, which is a major difference with NF membranes. The limitations of RO are: High capital and operating costs, high level of pre-treatment are required in some cases [48]. Figure 2.3 illustrates membrane type, pore size, requirement pressure and material removal for all types of membrane technologies.

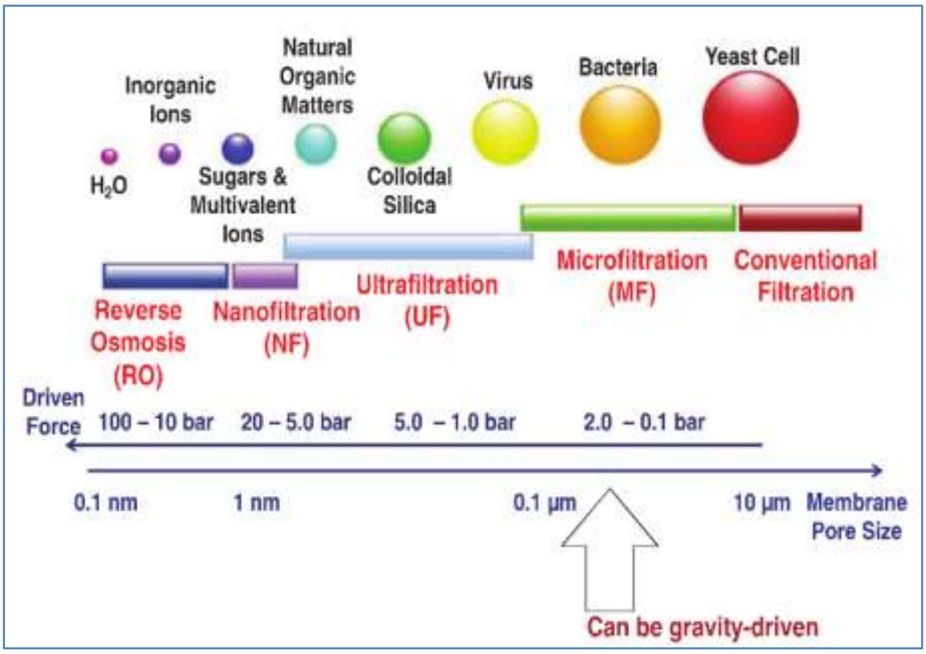


Figure (2.3): Membrane type, pore size, requirement pressure and material removal [2].

2.8.2 Separation Mechanism

Membranes employed in the present separation processes are characterized by their capacity to control the permeability of number of different materials. In tiny membranes, that are easy to permeate, the separation mechanism is done with the aid of the pressure that motivates the water motion via the small pores till the separation process is completed, and the dirt stays on the membrane surface with the flow from the outlet in the opposite aspect [49]. There are two elements that determine the performance of the membrane:

The flux: The flux depicts the quantity of liquid passing across the membrane, which is the rate of the volumetric flow of the permeate. This determines the membrane productivity that is referred to as the rate at which the molecules of the solute are transferred to the membrane. Darcy's law states that the permeate flux across the membranes is that in which the flux (J) across the membrane is directly proportional to the implemented pressure.

$$J = \frac{V}{A.t} \tag{2.3}$$

Where:

J: The flux (L/m^2.hr).

V: The volume (m^3).

A: effective membrane area (m^2).

t: The period during which the permeate is aggregated (h).

The selectivity: The membrane selectivity determines whether this membrane can be beneficial or not because it is a demonstration of the purity of the product stream and the quantity that is recovered with the required purity. The selectivity is often expressed as either retention or rejection. The solute is partly kept on the surface of the membrane, whereas the solvent particles pass freely across the membrane. The rejection is given by

$$R = 100 * \left(1 - \frac{C1}{C2}\right) \quad (2.4)$$

Where:

R: Is the rejection ratio.

$C1$: Solute concentration in permeate (mg/l).

$C2$: Solute concentration in feed (mg/1) [49].

2.8.3 Mass balances over a membrane

By considering a control volume that includes the whole membrane module it is possible to impose the total and single species mass balance constraints.

- Overall mass balance:

$$nf = np + nr = \sum nf\ xi, f = \sum np\ xi, p = \sum nr\ xi, r \quad (2.5)$$

Where

nf = the total molar flow-rate in the feed stream;
np = the total molar flow-rate in the permeate stream;
nr = the total molar flow-rate in the retentate stream;
xi = the molar fraction of component i [50].

- Single species overall mass balance:

$$nf\ xi, f = np\ xi, p = nr\ xi, r \quad (2.6)$$

$$\sum xi, f = \sum xi, p = \sum xi, r = 1 \quad (2.7)$$

By considering a control volume that includes the whole membrane module it is possible to frame the total mass flux across the membrane into the mass balance.

$$nf = nr = np = nr + \int jdA \qquad (2.8)$$

Where:

$j = \sum ji$ is the total molar flux of permeating species. ji represents the molar flux equation for species i across the membrane.

A represents the membrane section area where mass transfer occurs.

Figure 2.4 is a section of a membrane module showing the input data which represents the design specifications.

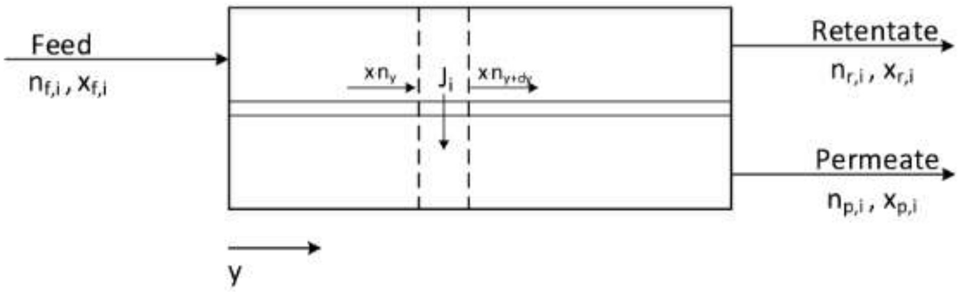


Figure (2.4): Mass balance over a membrane [50].

2.8.4 Membrane Scanning

SEM is a test process that scans a sample with an electron beam to provide a high-resolution representation of the surface (1 nm), and gives information such as roughness, pore size, pore density and/or pore size distribution. This method is also known as SEM analysis and SEM microscopy, and is used very effectively in microanalysis and failure analysis of solid inorganic materials [51].

2.8.5 Membrane Fouling

Membrane fouling is a process where the substances are deposited at the surface of the membrane, such as droplets of oil or solid particles. It is an indirect measuring way of fouling on the membrane. The deposition of substances causes flux decline. Fouling mechanisms can be categorized as shown in Figure 2.4.

- Complete pore-blocking occurs when the pore clogs with large particles. Therefore, water cannot pass through the pore.
- Standard blocking occurs when the small particles enter inside the pores. The channels become narrow causing a decrease in the flux.
- In intermediate blocking the droplets or particles build as a layer at the surface of the membrane and clog the pores partially.
- Cake filtration is similar to intermediate blocking where the particles form as a layer at the surface and decrease the pore size. Therefore, only the small particles are allowed to pass through. These types of blocking may be occurred at the same time [52].

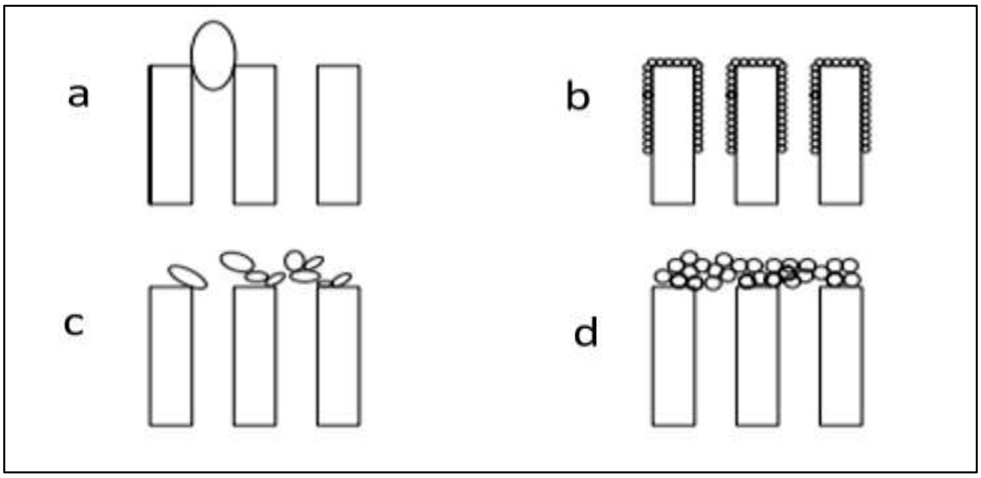


Figure (2.5): Schematic diagram of membrane fouling (a) Complete blocking, (b) Standard blocking, (c) Intermediate blocking, (d) Cake layer blocking [52].

2.8.6 Membrane Cleaning

The backwash process used to clean the membrane and remove contaminants accumulated. It was done by reversing the direction of flow for a period of time. The force and direction of the flow dislodge the contaminants at the membrane surface and wash accumulated solids out through the discharge line. Membrane filtration systems are 15 to 60 min between backwash events. The backwash process reduces the efficiency of the membrane by 5 to 10 %. Backwashing is limited to UF and MF membranes. Despite its benefit in increasing the flux, but it decreases membrane productivity after each one of backwashing.

In general, when Transmembrane Pressure (TMP) increase or permeation flux decrease, which indicates accumulation of contaminants on the pores. Therefore, membrane cleaning becomes very necessary to retrieve its clean level. Chemical cleaning use to remove these foulants. Some methods use filtered water in combination with chlorine or pressurized air to improve backwash effectiveness.

However, most recleaned membranes show a decline in their effectiveness, due to the accumulation of contaminants that cannot be removed by the backwash process. Because spiral-wound membranes generally do not permit reverse flow, NF and RO membrane systems are not backwashed. For these systems, membrane fouling is controlled with chemical cleaning, flux control, and cross-flow velocity. The inability of spiral-wound membranes to be backwashed is one reason that NF and RO membranes are seldom applied to directly treat water with high turbidity and/or suspended solids [49].

2.9 Previous Studies

(Lee and Frankiewicz, 2005) tested a hydrophilic UF membrane of 0.01 micrometre pore size, in crossflow mode, to treat oilfield PW. A hydro cyclone was first used to de-sand and de-oil the wastewater. The hydro cyclone pre-treated the raw PW removing solids and oil content by 73% and 54%, respectively. Oil and gas concentration after UF could be reduced to less than 2 mg/l[53].

(2006, Lia et al., 2006) studied a tubular model of UF membrane equipped with polyvinylidene fluoride (PVDF) and inorganic aluminium particles for PVDF membranes modification to treat the PW. The results showed that the removal efficiencies of COD 90% and oil content less than 1%[54].

(SU Delin et al., 2007) used a biological aerated filter (BAF) to treat Jiang Han oil field PW. They found that the removal efficiency for oil, COD, BOD and suspended solid was (76.3-80.3)%, (31.6-57.9)%, (86.3-96.3)%, and (76.4-82.7)%, respectively[55].

(S.Mondal et al., 2008) used two NF and one low-pressure RO membrane to treat three different PW from Colorado, USA. Significant fouling by organic compounds present in the PW was detected when assessing membrane fouling. The results found out, depending on the quality of the PW and the water quality requirements for the beneficial uses being considered, NF may be a viable process for PW treatment[56].

(M. Ebrahimi et al., 2009) studied the characterization and application of cross-flow MF process as a pre-treatment step and, partly in combination, with cross-flow UF, and NF systems as final-treatment techniques using ceramic membranes. Under 1bar TMP and 60^{o} C temperature, the result showed that it is economically attractive for the removal of oil[44].

(Ayad A. Al Haleem et al., 2010) used two samples of PW from Rumaila oil field / in the south of Iraq that were treated using RO membranes which showed that the obtained water quality is suitable for many different usages such as irrigation and other human purposes[29].

(Abbasi et al., 2010) studied the use of ceramic MF membranes made with mullite–alumina, which is a corrosion and heat-resistant mineral. The obtained results showed that ceramic MF membranes is used as an advanced pre-treatment method for oily wastewater[57].

(Hussein Basim Oleiwi, 2014) studied combined coagulation-adsorption-ion exchange treatment for the removal of some main contaminants like turbidity, oil content, and total dissolved solids from PW. The wastewater used in this work was taken freshly from Al-Ahdab oilfields. The coagulants used in this study were aluminium sulfate (alum) as a primary coagulant and calcium hydroxide (lime) as a coagulant aid. using organoclay (prepared by combination of Iraqi bentonite with quaternary amine (tetraethylammonium chloride)) for adsorption of oil content from produced water. The analysis results showed that the turbidity reading was reduced from 92 to 2.1 NTU and the organoclay adsorbent was very effective in removing oil content from PW[58].

(Jessica M. et al., 2014) studied the impact of salinity on coagulation and dissolved air flotation (DAF) treatment for oil and gas PW by using ferric chloride ($FeCl_3$), and DAF treatment for PW samples achieved high removals of dispersed oil and grease, but had limited impact on dissolved aromatics[59].

(Tutuk D. K. et al., 2018) used integrated activated carbon-bentonite adsorbent and double stages membrane process NF. This system increased rejection of TDS, turbidity, and salinity to 72%, 6%, and 90%, respectively.

It is verified that the proposed concept can achieve a higher membrane performance and extends the membrane lifetime in PW treatment [60].

(Zuoyou Zhang et al., 2019) studied effective treatment of oil and gas PW from the Wattenberg field in northeast Colorado by membrane distillation (MD) coupled with precipitative softening and walnut shell filtration. WSF displayed exceptional efficiencies (≥95%) in eliminating volatile toxic compounds including benzene, ethylbenzene, toluene, and xylenes (BTEX). The use of pre-treatment also led to robust membrane reusability within three consecutive treatment cycles, with MD water flux fully restored after physical membrane cleaning [61].

(Mahith Nadella et al., 2020) suggested treatment of PW with iron and polymeric coagulant. Highly saline and turbid PW from the Permian Basin was treated by adding chlorine as an oxidant, $FeCl_3$ as the primary coagulant, and an anionic polymer to remove suspended solids and iron. The result showed that removal of turbidity is very high (98%) and total iron removal (97%) were accomplished even with very short flocculation and sedimentation times of only 6 minutes suggesting the feasibility of this approach to reuse PW for hydraulic fracturing [62].

Table (2.3), shows the using of membrane technologies for treated different types of produced water.

Table (2.3): Summary of Membrane Treatment Technologies for Produced Water [7].

Produced water	Initial characteristics	Pretreatment	Characteristics after pretreatment	Membrane type	Pressure	Flux (L/m2 h)	Pore size	Effluent characteristics
Oilfield	-	Sedimentation, coagulation sand filtration	COD = 637; O&G = 15.5; TOC = 214.9; SS = 15.8	Tubular UF module equipped with polyvinylidene fluoride membranes modified by inorganic nano-sized alumina	0.1 MPa = 1 ba	170	MWCO = 35 kDa	COD removal = 90%; TOC removal = 98%; O&G < 1 mg/L; SS < 1 mg/L
Oilfield	-	Hydro cyclone	Total HC = 50 ppm; BTX = 2.6 ppm; Cu = 9.1 ppm; Zn = 2.8	Tubular PVDF-U	6–10 bar	309–598	MWCO = 100 kDa	otal HC removal = 95%; BTX removal = 54%; Cu removal = 96; Zn removal = 9
Oilfield	TSS = 6.1–158 ppm; O&G = 100–1000 ppm	De-oiling hydro cyclone; desanding hydro cyclone; membrane prefilter	TSS = 3–27.6 ppm; O&G = 80	UF + .45 m cartridge filter	50 psi = 3.4 bar	17	0.1 m	O&G < 2 ppm
Oilfield	-	Dissolved air flotation	COD = 985 ppm; O&G = 230	Cellulose acetate hollow fiber membrane	1 bar	119	MWCO = 130 kDa	COD = 23 mg/L; O&G = 4 mg/L
Synthetic produced water	250 and 1000 ppm crude oil	-	-	a-Alumina ceramic membranes	10 and 20 psi	15–66	0.2 and 0.8 m	Oil removal 99.3–99.9%
Synthetic produced water	250 and 1000 ppm crude oil	-	-	Surface-modified polyacrylonitrile (PAN)	10 and 20 psi	5–37	0.1 m	Oil removal 99.3–99.9%
Oilfield	SS = 30–150 ppm; O&G = 50–200 ppm; COD = 400–500 mg/L	Chemical treatment + aeration + sand filter	SS = 4–8 mg/L; O&G < 1.5 mg/L; COD = 111	PVC alloy hollow fiber	-	-	5–7 nm	SS = <0.6 mg/L; O&G < 0.5 mg/L; COD = 73

2.10 Summery

Produced water (PW) considers the largest waste stream in the world. Contains toxic components that may cause damage to the surrounding environment when discharging it without treatment. On the other hand, the treated water can be used for re-injection in the well for pressure maintenance or benefit used such as irrigation, drinking livestock, wildlife watering, and various industrial uses dust control, vehicle washing, power plant, and fire control. Traditional treatment methods of produced water Limited to gravity separation, coagulation and flocculation, filtration with gravel, sand, nutshells filters, these processes do not meet the requirement of benefit used. In recent years, research has focused on membranes technology which provides higher efficiency and lower cost.

Chapter Three

Characteristic and Treatment of Produced Water in Al-Ahdab Oil Field

3.1. Introduction:

To explain the steps of experimental work, more information about the characteristics of Al-Ahdab PW and current treatment methods should be knowing. All the information that are stated below have been taken form Al-Ahdeb authority oil field during the survey visits in research time[63].

The field is located between Numania and Kut, about 180 km to the south-east of Baghdad/Iraq. Its area is about 300 km^2. The field was discovered in 1978 and its production began in 2011, as presented in Figure 3.1.

It produces more than 100,000 cubic meters of waste from drilling operations every year, and the total amount will reach nearly one million cubic meters during production lifetime[64]. This amount of waste can cover the entire oil area (300 km^2) by approximately 3 mm when spread it. The toxic chemical substances contained in the waste considered as environmental pollution. At present, the general industrial practice is to naturally dry the waste mud and then bury it. This practice, nevertheless, will cause harm to the sustainable use of the land due to the harmful substances remaining in the waste. Wassit Governorate, where Al-Ahdab oilfield is situated, is a traditional agricultural area in Iraq. In this area, it is very important to protect land resources during oilfield operations.

In 2011, the treatment technology for Al-Ahdab project was upgraded. The second-generation technology featured better adaptability to changes in waste components, higher automation of processing equipment, and more stable treatment. The treatment capacity of waste mud increased from 5,000 cubic meters per year in 2009 to 120,000 cubic meters per year afterward.

Wells drilled using a horizontal drilling technique. From seven wells, the initial production of hydrocarbon was approximately 11 thousand barrels/day. By increasing the number of wells, the production increased to reach 135 thousand barrels/day. In the past few years, the Al-Ahdab project has treated nearly 500,000 cubic meters of waste.

Figure (3.1): Al-Ahdab oil field location [65].

3.2. Extraction Method

Driving a surface hole down is the first step to drill an oil well, about 100 feet below the deepest aquifer. Then, a steel casing is cemented to prevent polluting of aquifer water. Advancing the hole is the second step which drilled vertically to a depth of 1000 feet[62]. Then the direction of drilling changes horizontally where oil, gas, and water are trapped. Horizontal drilling is an advanced technology to reduce the disturbance effect on the surface by using one drill pad instead of multiple pads for multiple wells. Finally, The drill pipe is removed, and the steel pipe is pushed to extract the hydrocarbon. As shown in Figure 3.2.

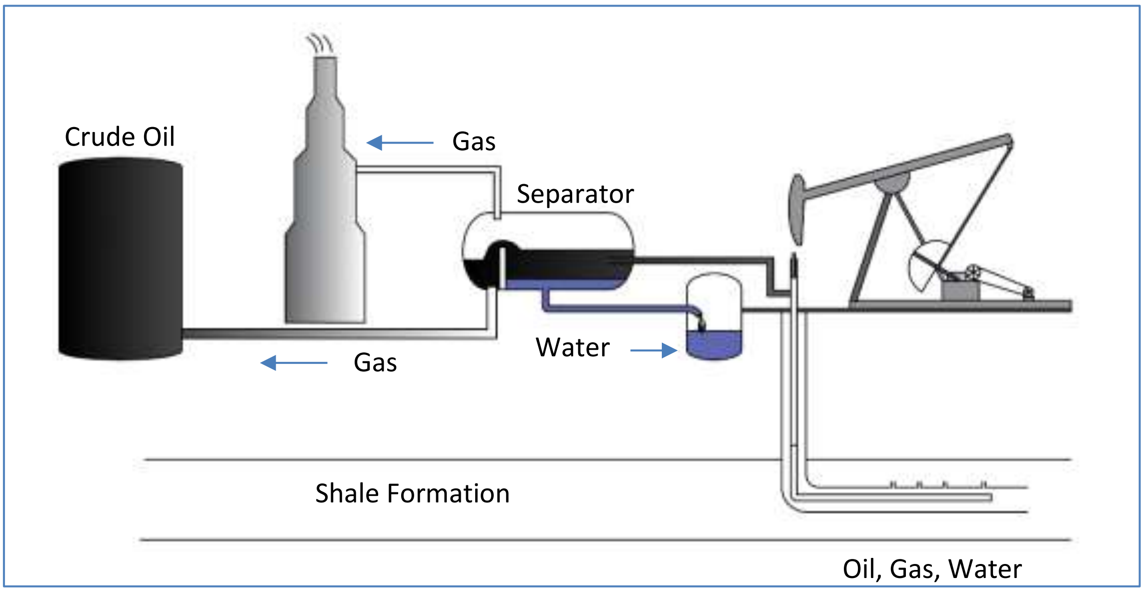


Figure (3.2): General extraction processing[62].

Once the well starts to produce hydrocarbone, the mixed fluid stream flowing from the well consists of oil, gas, and wastewater. This wastewater is separated at the surface from the recovered petroleum products. At this point, it is typically referred to as ‘produced water’, as opposed to ‘flowback’. This water is a combination of the fluid used to fracture the well and the formation water that resided.

In the first of extraction processes, the confined gas pressure is sufficient to extract the oil up to the surface; nevertheless, the oil extracted does not exceed 15 to 20% of liquid extraction, where the liquid includes gas, oil and water.At the central production facility (CPF), separation of oil, gas, and water that are achieve in the past less attention was given to the PW, it was considered as waste. Then, the bad effects of PW became understandable that without treatment, it is harmful to the environment, especially at the ground surface. Therefore, treatment of this water may be advanced in the re-injection process for many purposes such as increase petroleum production and control land subsidence by maintaining constant pressure. To inject these waters into reservoir rocks, suspended solids and oil must be removed to an appropriate degree to prevent plugging. Therfore, PW is sent to water treatment system. as illustrated in Figure 3.3.

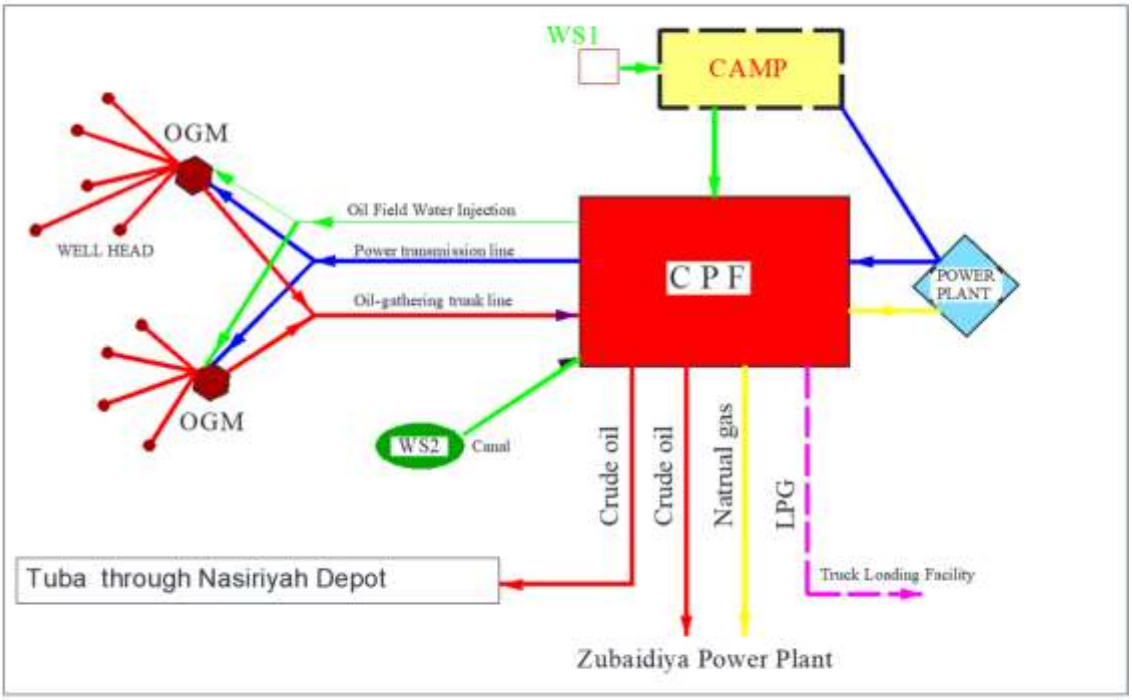


Figure (3.3): Schematic flow diagram of Al-Ahdab field facilities [63].

3.3. Characteristic of Al-Ahdab Produced Water

Produced water from Al-Ahdab oil field contains organic and inorganic component. In nature, the inorganic compounds are specific and the majority of them are existing as dissolved cations and anions. The common constituents' cations in the PW are: Na^{+1}, Ca^{+2}, K^{+1}, Mg^{+2}, Fe^{+2}, Al^{+3}, Ba^{+2}, Cu^{+2}, Li^{+1}, Zn^{+2}, Mn^{+2}, and also toxic Cd^{+2}, Cr^{+3}, Pb^{+2}, Hg^{+2}, Ag^{+1}, Sr^{+2}, Be^{+2}. The major anions in the PW are: Cl^{-1}, So_4^{-2}, Co_3^{-2}, No_3^{-1}, No_2^{-1}, etc. The organic components of PW are oil, grease, and others produced by Bactria, which considered very complex for nature.

Table (3.1): Max value of raw PW Characteristics in Al-Ahdab oil field during years (2018 - 2021) [63].

No.	Parameters	AL-Ahdeb PW
1.	Density (kg/m^3)	1,100
2.	Oil content (mg/L)	10,000
3.	PH	5.8
4.	EC (ms/cm)	227
5.	T.D.S (mg/L)	243,199.47
6.	T.S.S (mg/L)	2,500
7.	So_4^{-2} (mg/L)	160
8.	Fe^{+2} (mg/L)	5.84
9.	CL^{-} (mg/L)	132,937
10.	Na^{+1} (mg/L)	68,500
11.	Mg^{2+} (mg/L)	5,687
12.	Zn^{+2} (mg/L)	1
13.	Ni^{+2} (mg/L)	0.2
14.	Cr^{+3} (mg/L)	0.2
15.	Ca^{+2} (mg/L)	7840
16.	COD (mg/L)	375

As shown in the Table 3.1, PW from Al-Ahdeb oil field contains a high range of oil contents as compare to the typical oil field that mentioned in Table 2.1. The high range of oil content is due to the traditional methods used to separate the hydrocarbon and produced water. The high range of TSS are due to geologic formation of the field, treatment method used to extract the oil from underground, and method of separation as stated earlier.

During extraction, separation and processing operation, many chemicals are added to enhancement these operations. These chemicals have an effect on the properties of the extracted PW; these chemicals are mentioned in Table 3.2.

Table (3.2) Chemical additives in Al-Ahdab treatment facility.

Type	Benefits
Biocides	To reduce bacterial fouling
Scale inhibitors	That limits deposits of the mineral crust
Corrosion inhibitor	Reduce the risk of corrosion of equipment
Reverse emulsion breakers	Destroy water emulsion in oil
Flotation reagent	Facilitate the attachment of air bubbles to and levitation of select particles
pH control (Sodium Hydroxide)	Increase pH value
IGF (Nitrogen Gas bubble)	Increasing oil drops and suspended solid separation
Back wash (Methyl Alcohol)	Clean the filters

3.4. Produced Water Treatment System in Al-Ahdab

In order to reuse PW for pressure maintenance of the well by injection, it must be treated following the stages shown in Figure 3.4.

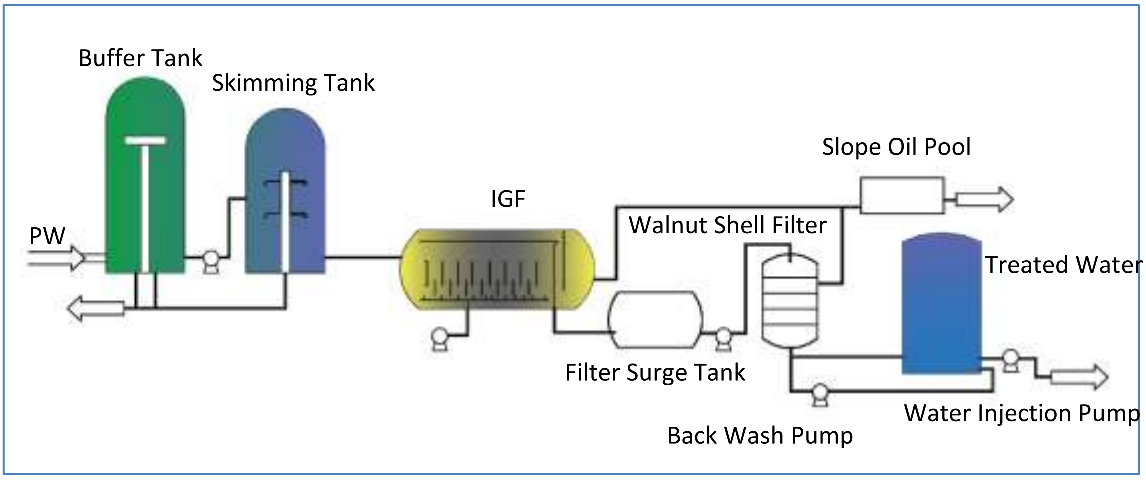


Figure (3.4): Schematic flow diagram of treatment system [63].

I.Buffer Tank:

It is a cylindrical tank, shown in Figure 3.5. Its capacity about 5000 m^3 with dimensions 23.7 m diameter and 12.87 m height. The design of the tank is based on density differentiation between water, oil, and solids. Most suspended solids will be collected at the bottom of the tank as a layer of sediment, the oil will float in the upper part of the tank, and the water will be at the middle layer between oil and solids. Oil is collected by a funnel. The funnel is located at a specific height of the tank depending on the amount of the oil in water. Reverse emulsion breakers substance is used to increase the separation between oil and water. The PW will still have amount of oil.

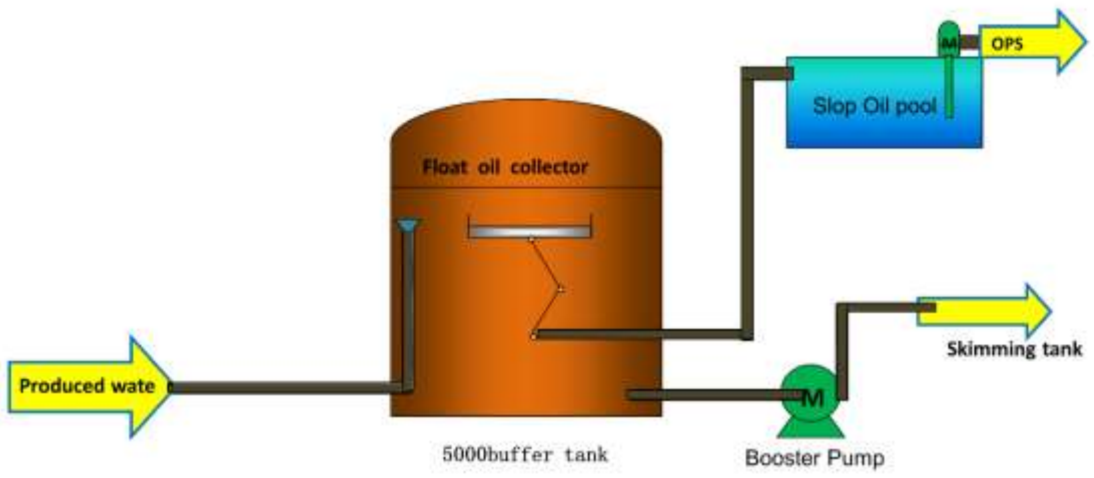


Figure (3.5): Buffer tank [63].

II.Skimming Tank:

A skimming tank is similar to the buffer tank in the principle of density differentiation to reduce the content of dispersed oil in PW. For a sufficient amount of time, the low density of oil compared with water density make oil float to the surface and skim by a skimmer. Its capacity is 3000 m^3. Sodium hydroxide is added to the tank to increase PH value. This method is efficient for dispersed components such as dispersed oil with proper large size of a particle.

This tank or the modified version of its such as PPI (parallel plate interceptor) or CPI (corrugated plate interceptor) is commonly used as part of a set of several techniques for the removal of dispersed oil.

III.Induced Gas Flotation Unit (IGF):

These units use gas bubbles to float out the oil to the surface of the PW, its capacity 600 m^3/h, uses nitrogen gas to create fine bubbles through hydraulic or mechanical systems. When gas is injected into PW, suspended particulates and oil droplets are attached to the gas bubbles as it rises. This results into the formation of foam on the surface of the water which is skimmed off as froth.

Nevertheless, efficiency is limited to the size of the oil droplet. High-performance efficiency is achieved when smaller droplets are present (should be greater than 25 microns), and flocculants and coagulants are added for better improvement. These small bubbles enhance the process of the separation of oil from the produced water, which results in low skim volume. More details are shown in Figure 3.6.

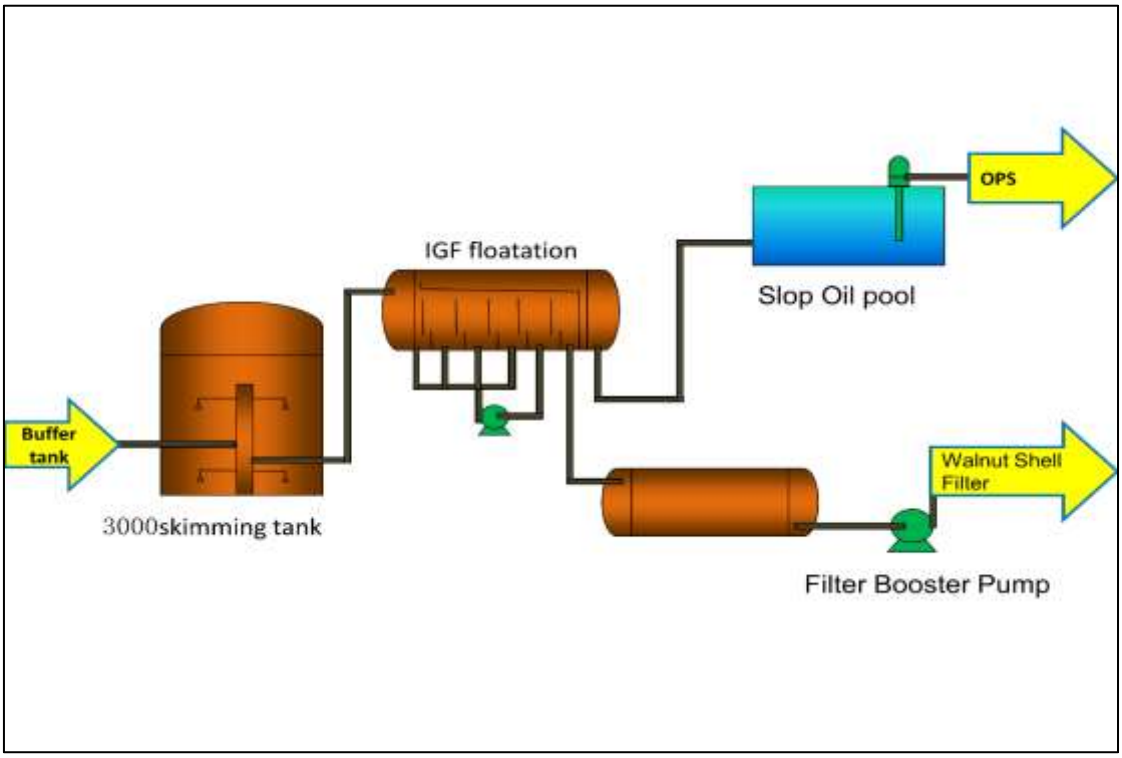


Figure (3.6): Skimming and IGF tank [63].

IV.Filtration:

This system is created by hybrid technology to remove oil and solids by using three layers of filtration.

- Top layer: this layer consists of nutshells to remove oil droplets.
- Middle layer: this consists of fine gravel to remove the fine solids.
- Bottom layer: this third layer act as a bed that supports the upper layers which made of coarse gravel.

Filter requires periodic backwash by using methyl alcohol as shown in Figure 3.7.

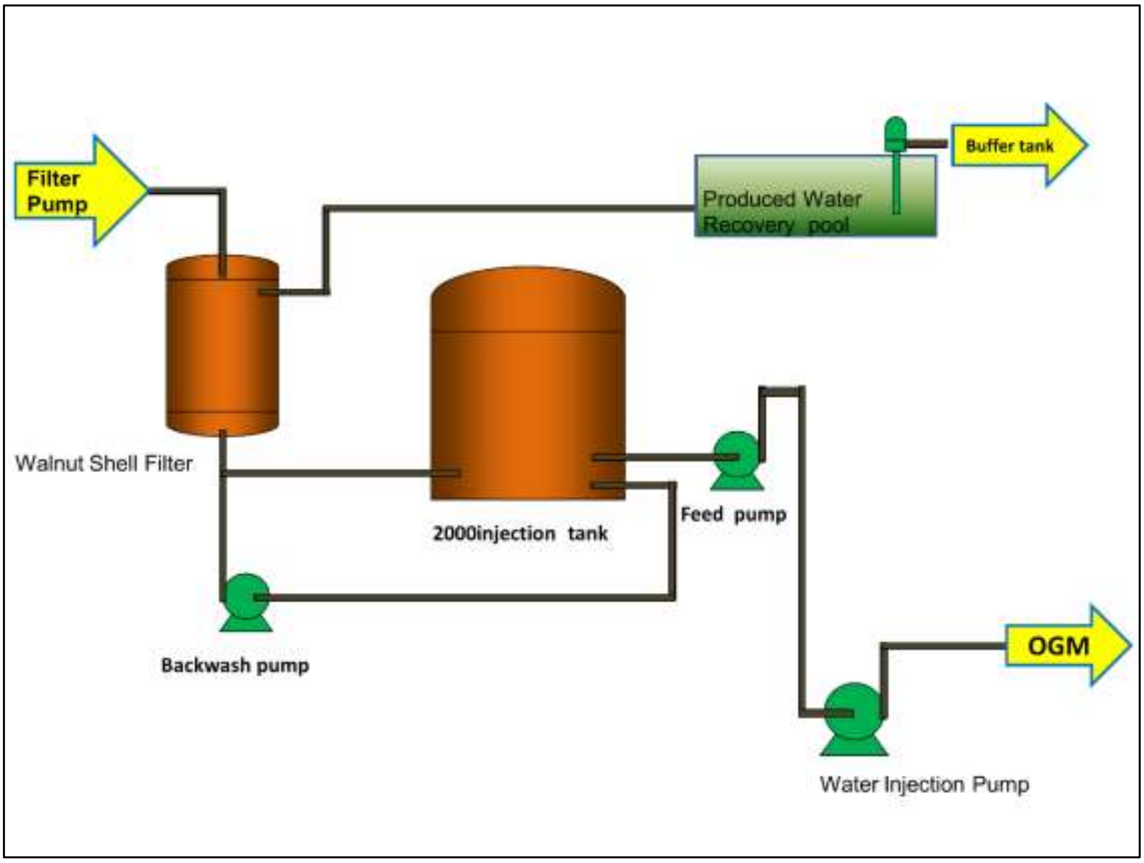


Figure (3.7): Filtration unites [63].

3.5. Treatment Mechanism in Al-Ahdab

PW are treated with several processing stages. De-oiling is one of them, which is achieved by buffer and skimming tank. A buffer tank is used to isolate the oil component from incoming PW as mentioned earlier. The retention time of feed water in this tank about 3-5 hr, which reduced the oil content from 10,000 ppm to 500 ppm and impurity to 500 ppm. The next stage is skimming tank. It is a complement of the de-oiling principle to overcome the remaining content of scattered oil. the same principle of the buffer tank is used.

When the retention time is adequate, the oil moves upward to the surface, which would be skimmed by an overwhelming and can be skimmed by an overflow. The retention time in skimming tank about 2-3 hr which reduce the oil content to 200 or 300 ppm and impurity become 400 ppm. Dissolved material such as benzene and heavy elements cannot be separated using this technique.

The following stage is IGF flotation unit, which uses the nitrogen gas to remove the suspended particles, sand and dissolved gas. Floatation agents are added in this stage to increase removal efficiency, but the side effect of this substance is reducing the PH which, must be increased. Therefore, it may be ignored in some cases. In this process, the oil contents become 100 ppm and impurity reduced to 50 ppm. The last stage of the treatment process is filtration with three layers of filter (gravel, sand and walnut). In this process, the oil content becomes 15 ppm and the impurity reduced to 10 ppm. Methyl Alcohol are used for the purpose of backwashing.

3.6. Water sampling

Samples of treated PW from Al-Ahdab treatment facilities for the period from January to March/ 2020 were analysed by physical and chemical method to evaluate the efficiency of this treatment.

3.7. Characteristics of Treated Water from Al-Ahdab Oil Field

Table 3.3 shows the characteristics of treated PW of AL-Ahdeb oil field. The average of three samples of treated water were analysed as shown in table.

Table 3.3 Characteristics of treated PW of Al-Ahdab oil field during 3 months from January to March/ 2020.

Parameter	Treated water	Method of test	Type of test
PH (value)	7.32	PH meter	Physical test
E.S (ms/cm)	18.89	Conductivity meter	
T.D.S (mg/L)	11,328	Weight analysis	
T.S.S (mg/L)	36.48	Weight analysis	
Sp.Gr	1.02	Densitometer	
Salinity (PPT)	10.41	Conductivity meter	
Ca^{+2} (mg/L)	1,021	Volumetric analysis	Cations tests
Mg^{+2} (mg/L)	208	Volumetric analysis	
Na^{+1} (mg/L)	1,165	Flame photometer	
K^{+1} (mg/L)	50.85	Flame photometer	
So^{-2} (mg/L)	2,260	Spectrophotometer	Anion’s test
Co_3^{-2} (mg/L)	3,398	Volumetric analysis	
HCo_3^{-1} (mg/L)	200	Volumetric analysis	
Cl^{-1} (mg/L)	1,993.32	Volumetric analysis	

Oil content	<= 15	Weight analysis	
T.O.C (mg/L)	0.082	IR photometer	Organic test
COD (mg/L)	87.6	Spectro photometer	
Cd^{+2} (mg/L)	0.012	Atomic Absorption	
Cu^{+2} (mg/L)	0.3297	Atomic Absorption	
Fe^{+2} (mg/L)	0.0866	Atomic Absorption	
Zn^{+2} (mg/L)	0.1119	Atomic Absorption	Heavy metals test
Cr^{+3} (mg/L)	N. D	Atomic Absorption	
Ni^{+2} (mg/L)	N. D	Atomic Absorption	
Pb^{+2} (mg/L)	0.078	Atomic Absorption	

PW testing laboratories help researchers understand the chemistry of the oil and any potential impact on the environment. In general, the PW naturally contains some oil and other products. Therefore, additional substances and elements may be present in the PW.

As shown in Table 3.3, samples of treated water were analysed. Physical tests including (PH value which it represents the acidity function of the produced water, conductivity and salinity using conductivity meter) were determined. Salinity is the total concentration of all dissolved salts in water. Salts dissolve in water to produce an anion (negatively charged) and a cation (positively charged). These ions make up the basis of conductivity in water. Conductivity is a measure of water's capability to pass electrical flow. This ability is directly related to the concentration of ions in the water.

Many heavy metals are identified as carcinogenic and toxic items which have negative effects to the environment.

The obtained results of PW from conventional treatment (CT) are suitable for re-injection into a well for improved oil recovery, but, these results are not compatible for Iraqi quality standard (IQS) for beneficial reused [66].

The current treatment technology of PW in Al-Ahdab oil field cannot remove small suspended oil particles and dissolved elements. Besides, the chemicals have a high running cost and produce hazardous sludge. Therefore, to obtained high-quality water for beneficial used, membrane technologies can be used. The proposed system based on membrane technologies by using polymeric ultrafiltration membrane.

Chapter Four

Proposed Treatment System

4.1 Introduction

The membrane technology is one of the most important techniques that is currently used in water treatment, either for drinking purposes or for reuse of water in daily consumption. A simplified model of this treatment system will be used in this study.

The experimental work included two steps: the first was preparing polyether sulfone ultra-filtration membrane then analysis it by using scanning electron microscopy SEM. The second was treating samples of PW from Al-Ahdab oil field and determine their chemical and physical characteristic.

4.2 Description of Proposal System

A schematic diagram of the PW treatment technology used in the experimental work are shown in Figure 4.1. It consists of the following systems:

1. Treatment system: contains (feed tank No.1, mixer, heater, pump, and thermometer).
2. Membrane cell: contains (cell body, and membrane sheet).
3. Washing system: contains (tank No.2, mixer, heater, pump, and thermometer).
4. Tank No.3: collects the treated produced water.

Plate 4.1 shows the form of the treatment technology while in Table 4.1 the explanation of its parts is shown.

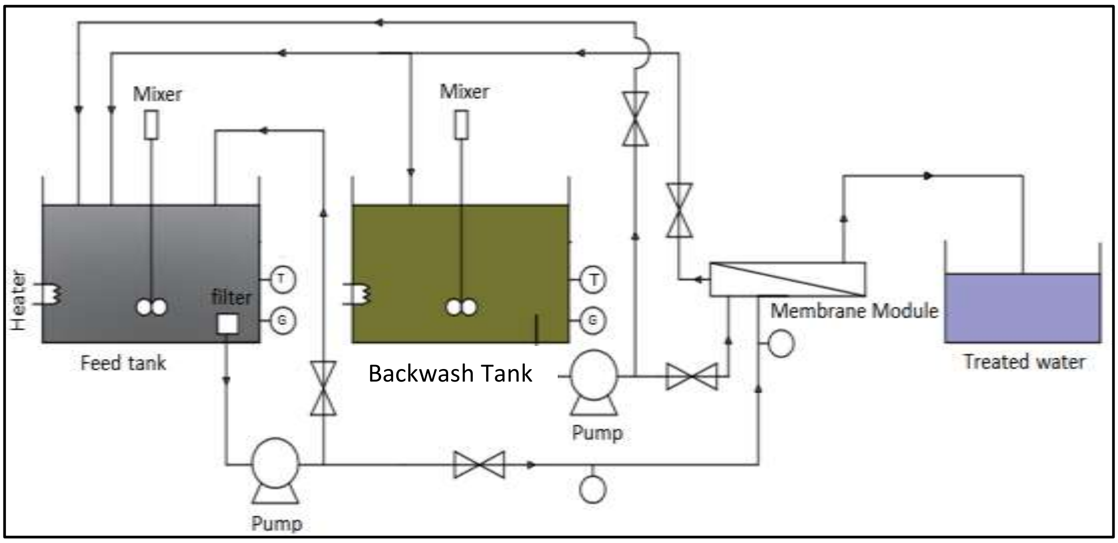


Figure (4.1): Schematic Flow Diagram of The UF Experimental Apparatus.

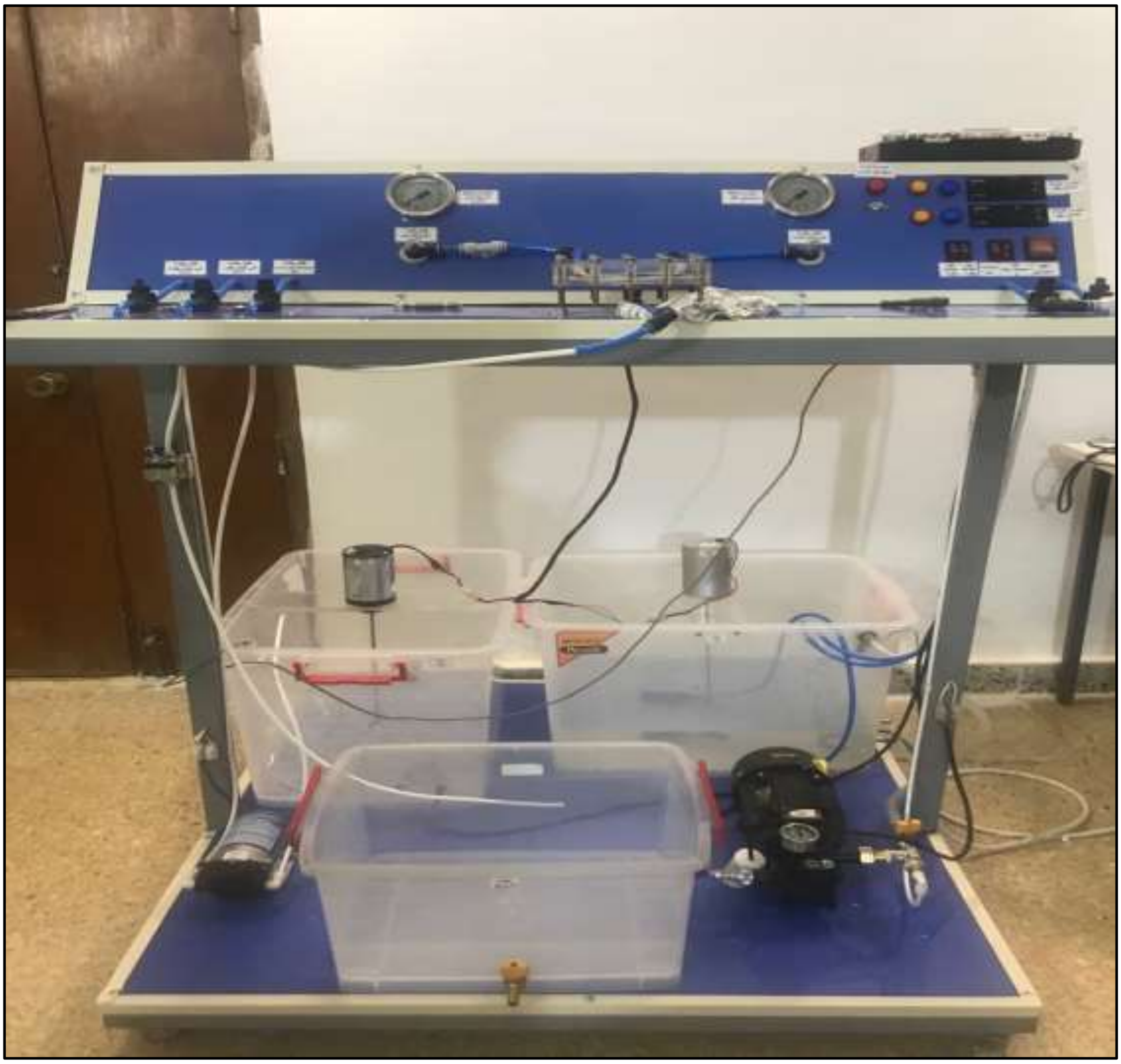
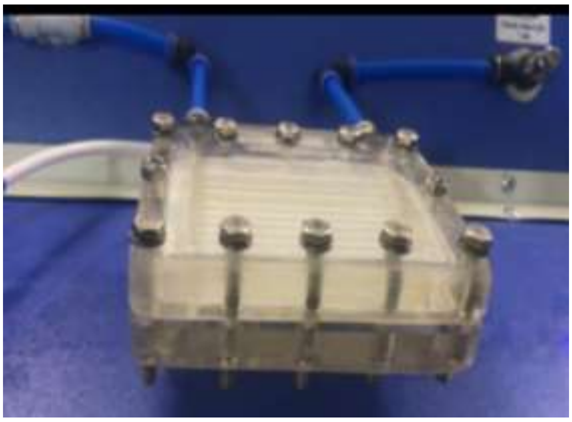
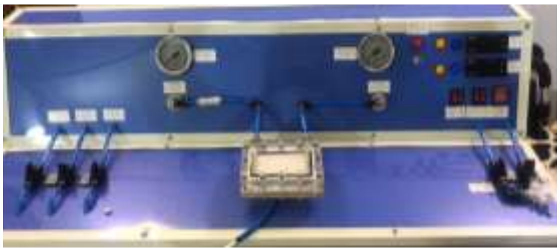
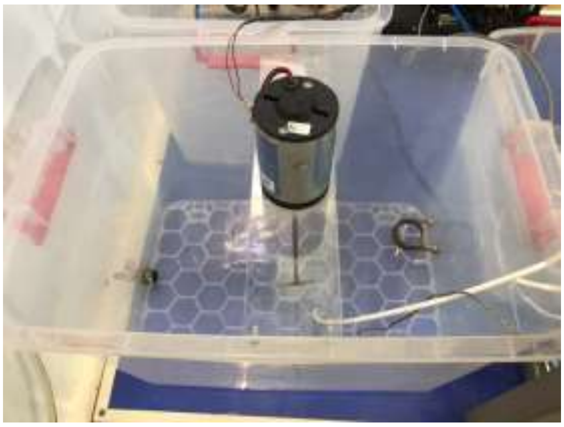


Plate (4.1): Photographic View of Cross Flow UFM System.

Table (4.1): Parts of The Membrane Treatment System.

1. Feed tank: The capacity of the feed tank was 50L with a heater and mixer to stabilize the temperature of the feed water at constant and similar conditions.	 plate (4.2)
2. High pressure pump: The pump used in the system with a maximum flow rate = 480 L/h, temperature = 60^{o} C, P_{max} = 15bar and V = 230 volt.	 Plate (4.3)

3. Membrane cell: The membrane was made of epoxy resin with rectangular shape chamber. A flat sheet membrane with dimensions 60*100 mm is fixed in the cell with an additional sub-layer to save the membrane from damage.	 Plate (4.4)
4. Control board	 Plate (4.5)
5. Pressure gauges: It approximately ranges from 0-10 bar.	 Plate (4.6)

6. Low pressure pump: A low-pressure pump has been using with the following details (flow rate = 28L/h, P max = 135 PSI and V = 24 volt).	 Plate (4.7)
7. Waste water valve: This valve is sensitive to the sudden increasing of the flow passing through the membrane (when the membrane ruptures, the lock will be closed automatically).	 Plate (4.8)
8. Washing tank: The capacity of this tank was 50L, a heater and mixer have used to stabilize the temperature of cleaning water at the constant conditions.	 Plate (4.9)

4.3 Membrane

In this work, the membranes used in the experiments were (8) rectangular sheet Polyether sulfone ultrafiltration with dimensions of 100*60 mm. It's prepared in the Chemical Engineering Laboratory at the University of Technology. These membranes were asymmetric and porous, and consist of a skin layer that supported by a porous sub-layer.

4.3.1 Membrane Composition

Polyether sulfone are non-hydrophilic; they are stable chemically, mechanically, and thermally. It has a molecular weight cut-off of (800-100000) Dalton. Molecular weight cut-off (MWCO) is a method of characterization used in filtration to describe pore size distribution and retention capabilities of membranes. It is defined as the lowest molecular weight (in Daltons) at which greater than 90% of a solute with a known molecular weight is retained by the membrane [66].

The polymers of this family (standard PSU, polyaryl sulfone, polyether sulfone, polyphenyl sulfone) are characterized by extraordinary, inherent flame retardancy and high transparency. Plate 4.10 and Figure 4.2 shows polysulfone pellets and chemical structure [66].

Plate (4.10): Polysulfone pellets

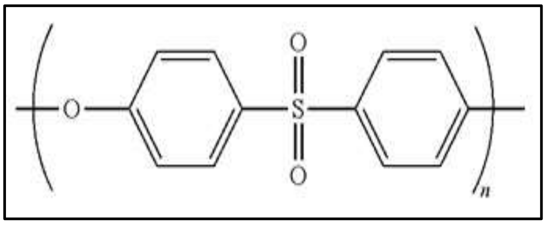


Figure (4.2): Molecular Structure of Polyether sulfone

Molecular Formula: ($C_{12}H_8O_3S$)

Dimethyl sulfoxide (DMSO) is an organosulfur compound with the formula $(CH_3)_2SO$. This colourless liquid is an important polar aprotic solvent that dissolves both polar and nonpolar compounds and is miscible in a wide range of organic solvents as well as water, as shown in Plate 4.11 and Figure 4.3. It has a relatively high boiling point. DMSO has the unusual property that many individuals perceive a garlic-like taste in the mouth after contact with the skin

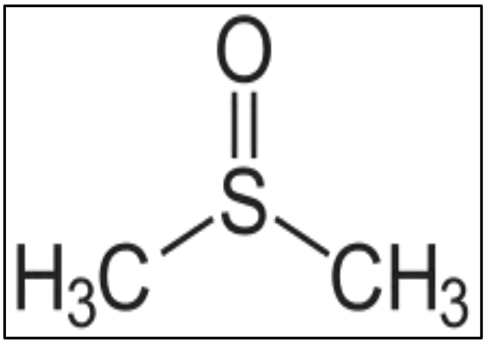


Figure (4.3): Molecular Structure of Dimethyl sulfoxide

Plate (4.11): Dimethyl Sulfoxide

4.3.2 Membrane Preparation

By using the method of phase inversion casting, the preparation of ultrafiltration membrane has been achieving. The following steps show this method of membrane preparation.[67].

1. 21 gm of polyether sulfone pellets were heated for 5 hours at 150^o C to degas. The pellets were provided from (Sigma–Aldrich, St. Louis, MO, USA).

2. It was melted with 79 gm of DMSO (Dimethyl sulfoxide). DMSO were provided from (Sigma–Aldrich, St. Louis, MO, USA).
3. Polyvinyl pyrrolidone (PVP) was added to polyether sulfone solution with a ratio equal to 1% of this solution weight. PVP was provided from (Sigma–Aldrich, St. Louis, MO, USA).

Figure 4.4 shows all the necessary laboratory tools required to prepare a polymer solution.

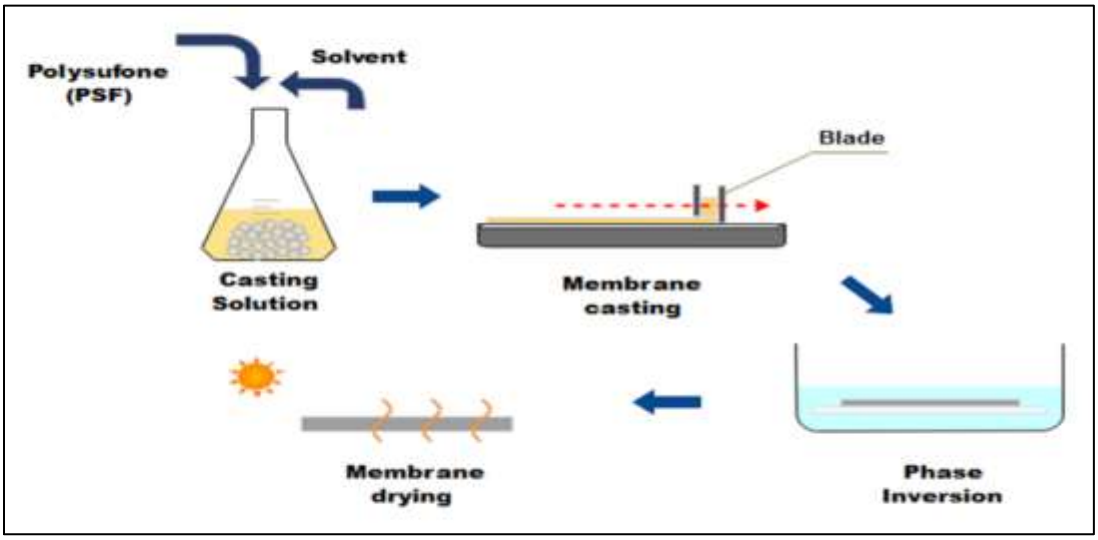


Figure (4.4): Tools Used for Preparing Solution of Membrane[67].

4. The mixer was rotated with (500 r/min) for 24 hours at a temperature of 50° C to ensure that polyether sulfone was dissolved in DMSO and formed a homogeneous solution.
5. The solution was kept in the dark to reduce the number of bubbles in its.
6. The nonwoven polyester fabric was fixed onto a glass plate, and then the solution casting using a stainless-steel knife. The thickness of cast model was approximately 200 µm.

7. It was let for 1 minute to get a uniform surface of the support layer.
8. The glass plate was put into a water bath for 1 hour at 23^{o} C.
9. The membrane was stored in distilled water 18.2 MΩ. cm (that is high purification and poor for an electrical conductor). The temperature is 40^{o} C. These conditions preserve the properties of the membranes and prevent them from dehydration, thus causing a defect in the structure, which affects the filtration process.

   Plate 4.12 shows the casting of polyether sulfone layer.

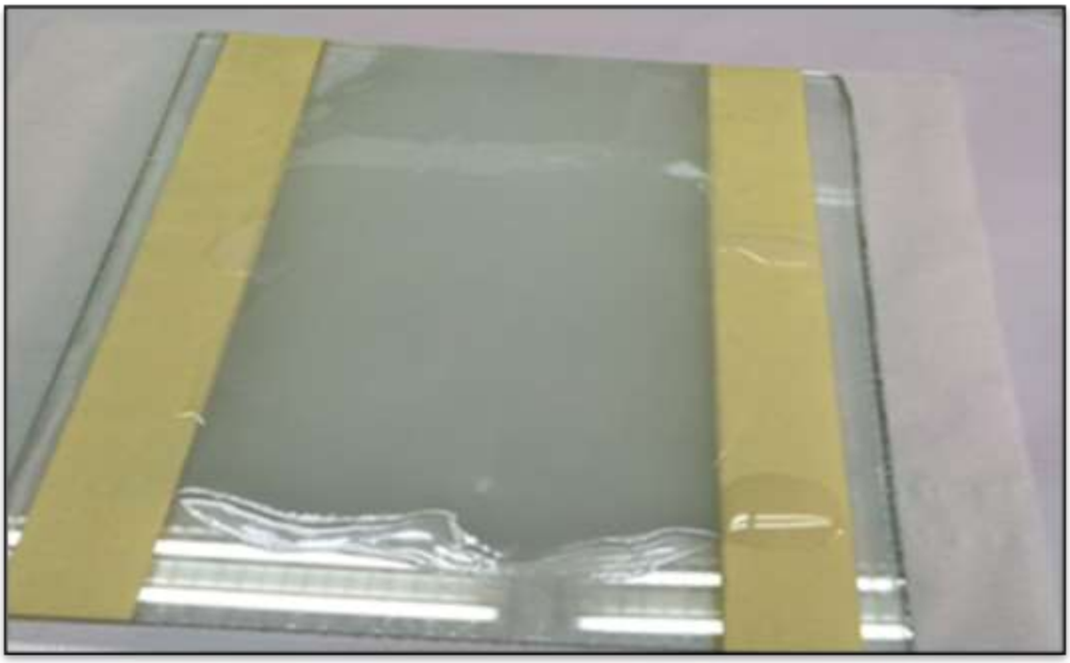


Plate (4.12): Polyether Sulfone Membrane After Casting [67].

4.3.3 Scanning Electron Microscopy (SEM)

Integrity test of polymeric membranes is an important consideration to ensure operating and damage. SEM was used to characterize the surface Ultrafiltration flat-sheet polyether sulfone (PES) membranes with surface area (10mm*10mm). The obtained information is the pore sizes and the skin layers. It seems to have pores shaped like a finger, and it has dense top skin layers, a porous sub-layer and a sponge-like bottom layer. Plates 4.13 shows SEM analysis of membrane used in the experimental work. Plate 4.13 a and Plate 4.13 b shows the top surface, while Plate 4.13 c and Plate 4.13 d shows a cross-sectional view of the membrane.

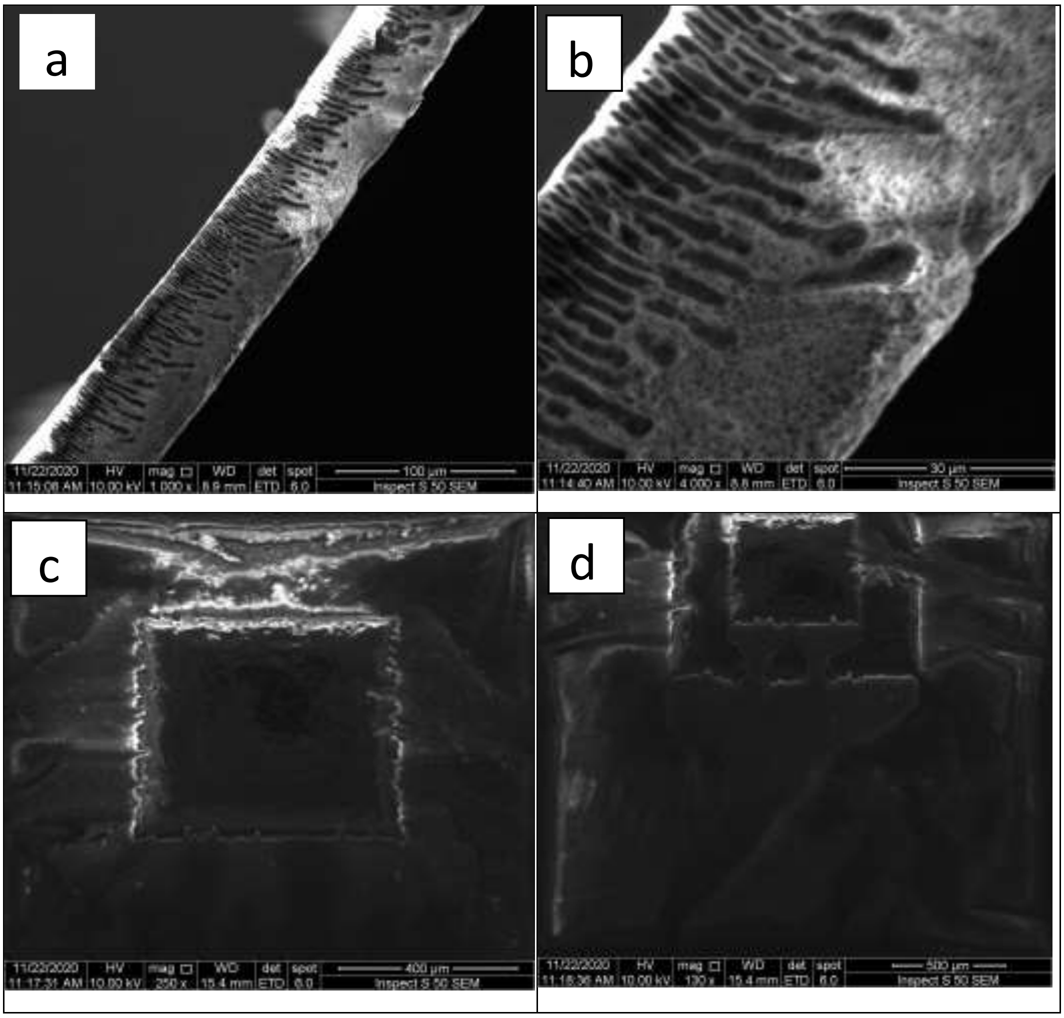


Plate (4.13): SEM images of membrane: (a) Outer surface view of membrane with magnification×1000. (b) Outer surface view of membrane with magnification×4000. (c) Cross-sectional view of membrane with magnification×250. (d) Cross-sectional view of membrane with magnification×130.

Table 4.2 show the composition and design of the membrane by using Scanning Electron Microscopy (SEM).

Table (4.2) Characteristic of UF membranes used in proposal system.

Characteristic	Amount
Polyether-sulfone (PES)	21%
Dimethyl sulfoxide (DMSO)	79%
Membrane thickness	220 μm
Mean pore diameter	15 nm

4.4 Feed water

Three types of samples were taken from Al-Ahdab oil field for the purpose of conducting the laboratory experiment as shown in Plate 4.14.

- Sample 1: PW before treatment.
- Sample 2: PW after skimming (physical treatment for sample No.1 by removing the oil).
- Sample 3: Treated PW in the field (by using the treatment methods mentioned in Chapter 3).

Plate (4.14): Samples of PW.

4.5 System Operation

This section includes two stages, the treatment method and membrane back wash.

4.5.1 Treatment Method

The experiments were carried out with the cross-flow membrane system. And according to the following steps.

- 30 L of feed water was placed in the feed tank No 1.
- The heater was operated to keep the temperature equal to 40^o C.
- The mixer was operated to improved distribution of temperature.
- The tested sample was pumped from the feed tank of PW to the inlet of the membrane cell by using high pressure pump.
- Operating pressure and flow rate were controlled by the valves.
- Five levels of pressure were applied on the membrane (1, 2, 3,4 and 5 bar), 30 min of working for each level to evaluate the effect of pressure on permeate flux.

- The water that passed through the membrane was collected in tank No. 3 (treated water).
- The permeation flux of filtered water from the membrane was gathered every 10 min for 3 hr. The experiment is done under a constant pressure equal to 3 bar, and constant temperature equal to 40° C. This experiment evaluates the effect of membrane fouling on permeate flux.
- The surplus feed was recycled back through the by-pass stream to the feed PW tank.
- The collected treated water was measured with a volumetric unit = ml.
- The permeation flux volume was measured after attaining flow stabilization. Permeation flux was calculated from the following equation 4.1:

$$Fp = \frac{Vp}{A\,.\,\Delta t} \qquad (4.1)$$

Where:

Fp = Permeate flux ($l/(m^2.hr)$).

Vp = Volume of permeate (l).

A = Area of the membrane (m^2).

Δt = Time taken to collect the measured amount of permeate collected at different trans-membrane pressures (hr).

Plate (4.15) Treated water by UFM.

- Treated water samples were analysed to calculate the physical and chemical parameters.
- These samples were taken during three months (Sep., Oct., Nov.)2020 in the experimental work.

4.5.2. Membrane Back Wash

Cleaning the membrane from contaminants is achieve by using washing system. Deionized water is feed in the tank of back wash (No.2), then the system is operated for 2-3 hr under 40^0 C of temperature and 5 bar pressures.

This procedure is performed at the end of each experiment, when the membrane contamination is significant which lead to decrease the flow rate, or when the pressure increased above the required limits. Plates 4.16 shows accumulation of contaminants on the membrane during 200 minutes of filtration.

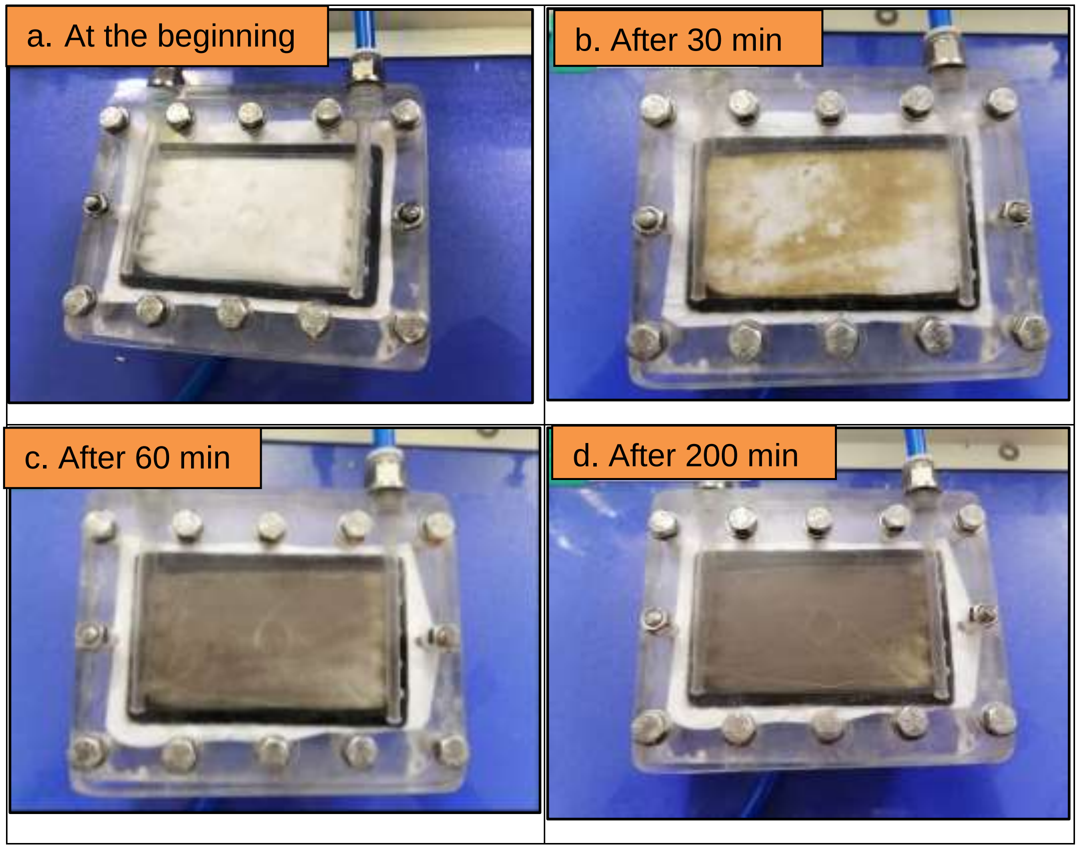


Plate (4.16): Membrane Fouling (a)Clean membrane (b)Accumulation of pollutants after 30 min (c)Accumulation of pollutants after 60 min (d)Accumulation of pollutants after 200 min.

4.6 Water Analysis Instruments

In order to determine the efficiency of the treatment method, quality of the permeate water, and to decide whether the PW can be reused, physical-chemical parameters must be determined by using the following instruments:

4.6.1 PH meter

It is an instrument used to measure acidity or alkalinity of a solution. pH is a measure that describes the degree of acidity or alkalinity. It is measured on a scale of 0 to 14. pH was measured by Jenway 3320 pH Meter as shows in Figure (4.17).

Plate (4.17): pH metre / Jenway 3320.

4.6.2 Conductivity Metre

Conductivity is the electrical current in a solution, but that value depends on which ions are present and in what concentration. Ions carry a negative or positive electrical charge: anions are negative and cations are positive, the ions that contribute to high conductivity result from dissolved minerals and salts. The meter converts this reading to milli- or micro-Ohms or milli- or micro-Siemens per centimetre.

Salinity is the measure of dissolved salts in a solution. Conductivity meters equipped with a salinity option internally convert the conductivity reading to one of salinity. The electricity and salinity of the samples was measured by conductivity metre 556 MPS shown in Plate 4.18.

Plate (4.18): Conductivity metre 556 MPS.

4.6.3 Densitometer

Densimeter, which is a specific gravity tester, is an advanced density testing equipment for measuring solid and liquid samples with high precision sensor and auto-weighing function. As shown in Plate 4.19.

Plate (4.19): Densimeter device.

4.6.4 Flame Photometry

Flame photometry, or more properly is called flame atomic emission spectrometry, is a device used in inorganic chemical analysis to determine the concentration of certain metal ions, that are easily excited and do not require very high temperatures (Na^{+1}, K^{+1}, Li^{+1}, Ca^{+2}). Flame photometry works by measuring the intensity of light emitted (which is measured using a wavelength of a colour) when the element is exposed to a flame. The intensity of the colour will depend on the energy that had been absorbed by the atoms and was sufficient to vaporise them. As shown in Plate 4.20.

Plate (4.20): Flame photometric.

4.6.5 Spectrophotometer

A spectrophotometer is an optical device that can determine the concentration of a compound or particles in a solution as shows in plate 4.21. A light of pre-selected wavelength is shone through a chamber that houses the sample. The sample particles will absorb some of the light. The amount of light that is absorbed increases with the increasing numbers of molecules. The percent of light that has been absorbed can be determined and, by comparing this absorption to a graph of the absorption of known numbers of molecules.

Plate (4.21): Spectrophotometer T70 UV/VIS.

Chapter Five

Results and Discussion

5.1 Introduction

This chapter presents the results obtained using polyether sulfone ultrafiltration membrane. The physical and chemical characteristics of the treated water were analyzed in laboratories of Wasit Environmental Agency.

In this chapter, two types of samples that were collected from Al-Ahdab oil field during three months (Sep., Oct., and Nov. 2020) were investigated. The first is raw PW (Sample No.2), and the second is treated water using conventional treatment (CT) (Sample No.3).

The obtained results were using three different methods of treatment. they include treated water by CT in Al-Ahdab field, treated water by membranes technology, and combining of the two previous methods.

Finally, study the effects of the pressure, fouling of the membrane, membrane cleaning, and fluid temperature on the permeation flux.

5.2 Characteristics of PW Samples

Table 5.1 shows the characteristics of PW (Sample No.1) for three months (Sep., Oct., Nov / 2020). This table shows high concentration of TDS, TSS, oil content, and heavy metal concentration.

Table (5.1): Characteristics of raw PW from Al-Ahdab oil field.

No.	Parameters	Unit	Sep.	Oct.	Nov.
1	PH	-	6.62	6.6	5.8
2	EC	ms/cm	132.47	150.83	112.7
3	TDS	mg/l	111200	121785	101215
4	TSS	mg/l	2060	3460	1975
5	Sp Gr	mg/l	1.048	1.0848	1.053
6	Salinity	mg/l	162	193	103
7	Ca^{+2}	mg/l	5680	6502	5008
8	Mg^{+2}	mg/l	1138	1721	567
9	Na^{+1}	mg/l	11542	13284	9854
10	K^{+1}	mg/l	1957	2135	1488
11	So_4^{-2}	mg/l	9865	16234	12481
12	Co_3	mg/l	16730	19414	18535
13	Cl^{-1}	mg/l	13396	17470	9430
14	Oil Con.	mg/l	547	1005	380
15	T.O.C	mg/l	109	167	87
16	Cd^{+2}	mg/l	0.014	0.013	0.033
17	Cu^{+2}	mg/l	0.366	0.69	0.398
18	Fe^{+3}	mg/l	0.213	0.414	0.31
19	Zn^{+2}	mg/l	1.623	2.15	0.067
20	Cr^{+2}	mg/l	0.0055	0.0078	0.005
21	Ni^{+2}	mg/l	0.0749	0.0367	0.051
22	Pb^{+2}	mg/l	0.021	0.045	0.028
23	COD	mg/l	381	387	375

5.3 Chemical and Physical Analysis of Treated Water

In this section, PW was tested and analysed using different treatment methods (conventional treatment (CT), Ultrafiltration membrane (UFM), and combination of them (CT+UFM)).

The samples were analysed to evaluate the efficiency of treatment methods. Physical and chemical parameters were measured in the Wasit environmental laboratories of Iraqi science and technology.

Properties that have been measured in the study are hydrogen number (pH), electrical conductivity (EC), total dissolved solid (TDS), total suspended solid (TSS), oil content, chemical oxygen demand COD, specific gravity, and cation and anion concentration. Then, a comparison was made between the results and Iraqi standard and international standard.

5.3.1. Conventional Treatment (CT)

Table 5.2 illustrates the characteristics of PW (Sample No.3) after conventional treatment in Al-Ahdab oil field.

Table (5.2): Characteristics of treated PW by CT method for sample No.3.

No.	Parameters	Unit	Sep.	Oct.	Nov.
1	PH	-	7.5	7.56	6.9
2	EC	ms/cm	16.8	25.3	14.57
3	TDS	mg/l	9864	16237	7883
4	TSS	mg/l	30.52	52.42	26.5
5	Sp Gr	mg/l	1.01	1.047	1.003
6	Salinity	mg/l	9.3	14.2	7.75
7	Ca^{+2}	mg/l	974	1296	793

8	Mg^{+2}	mg/l	212	236	176
9	Na^{+1}	mg/l	1573	1488	433
10	K^{+1}	mg/l	48.2	63.3	41.05
11	So_4^{-2}	mg/l	2015	2787	1978
12	Co_3^{-2}	mg/l	3532	3660	3002
13	Cl^{-1}	mg/l	2147	2345	1488
14	Oil Con.	mg/l	21.3	26	15
15	T.O.C	mg/l	0.052	0.134	0.06
16	Cd^{+1}	mg/l	0.013	0.004	0.019
17	Cu^{+2}	mg/l	0.256	0.54	0.19
18	Fe^{+2}	mg/l	0.0367	0.18	0.043
19	Zn^{+2}	mg/l	0.074	0.216	0.043
20	Cr^{+3}	mg/l	0.0011	0	0
21	Ni^{+1}	mg/l	0	0	0
22	Pb^{+2}	mg/l	0.15	0.051	0.034
23	COD	mg/l	87.6	92.5	82.7

5.3.2. Ultra-filtration Membrane Treatment (UFM).

In this section, sample No.2 has been treated using UFM, as mentioned in Chapter 4, and the results are shown in Table 5.3.

Table (5.3): Characteristics of treated water by using UFM method.

No.	Parameters	Unit	Sep.	Oct.	Nov.
1	PH	-	6.77	6.35	6.1
2	EC	ms/cm	75.1	67.4	45.47
3	TDS	mg/l	42468	43745	26830
4	TSS	mg/l	0.015	0.021	0.006
5	Sp Gr	mg/l	1.007	1.031	1.025
6	Salinity	mg/l	39.6	42.6	34.104
7	Ca^{+2}	mg/l	1833	2167	1688

8	Mg^{+2}	mg/l	370	427	358
9	Na^{+1}	mg/l	3205	4981	2758
10	K^{+1}	mg/l	452	487	507
11	So_4^{-2}	mg/l	3689	4868	4373
12	Co_3^{-2}	mg/l	6456	6570	6456
13	Cl^{-1}	mg/l	4620	5640	3468
14	Oil Con.	mg/l	0	0	0
15	T.O.C	mg/l	0.072	0.103	0.054
16	Cd^{+1}	mg/l	0	0	0.001
17	Cu^{+2}	mg/l	0.163	0.19	0.075
18	Fe^{+2}	mg/l	0.242	0.293	0.257
19	Zn^{+2}	mg/l	1.572	2.07	0.054
20	Cr^{+3}	mg/l	0	0	0
21	Ni^{+1}	mg/l	0	0	0
22	Pb^{+2}	mg/l	0	0	0
23	COD	mg/l	66.6	70.4	68.2

5.3.3. CT & UFM Treatment.

Table 5.4 illustrates the characteristics of water after treatment using both conventional and ultrafiltration membrane.

Table (5.4): Characteristics of treated water by using CT + UFM.

No.	Parameters	Unit	Sep.	Oct.	Nov.
1	PH	-	7.4	7.5	6.64
2	EC	ms/cm	5.07	6.58	4.78
3	TDS	mg/l	2681	4789	2388
4	TSS	mg/l	0.0002	0.0016	0
5	Sp Gr	mg/l	1.009	1.034	1.005
6	Salinity	mg/l	2.17	3.16	1.84
7	Ca^{+2}	mg/l	249	376	209
8	Mg^{+2}	mg/l	87.7	83.8	57.7
9	Na^{+1}	mg/l	278	344	176
10	K^{+1}	mg/l	12.46	15.89	9.6

11	So_4^{-2}	mg/l	715	735	476
12	Co_3^{-2}	mg/l	1063	1146	977
13	Cl^{-1}	mg/l	523	583	389
14	Oil Con.	mg/l	0	0	0
15	T.O.C	mg/l	0.051	0.08	0.043
16	Cd^{+1}	mg/l	0	0	0
17	Cu^{+2}	mg/l	0.0033	0.0081	0.0012
18	Fe^{+2}	mg/l	0.026	0.1236	0.046
19	Zn^{+2}	mg/l	0.054	0.1194	0.027
20	Cr^{+3}	mg/l	0	0	0
21	Ni^{+1}	mg/l	0	0	0
22	Pb^{+2}	mg/l	0	0	0
23	COD	mg/l	46.2	44.1	40.8

5.4. Removal Efficiency

The efficiency of using membrane technologies for PW treatment depends on the membrane removal efficiency for many parameters.

5.4.1. TDS Removal Efficiency

Total dissolved solids (TDS) combine the sum of all ion particles that are smaller than 2 microns (0.0002 c). This includes all of the disassociated electrolytes that make up salinity concentrations, as well as other compounds such as dissolved organic matter [68]. It is noticed that the removal efficiency of TDS is increased when the membrane is contaminated. This is due to the clogging of the membrane that courses rejection of smaller contaminants over time.

In Sep., the removal efficiency for CT is 91 %, UFM is 62%, and CT+UFM is 98%, this result indicates higher removal efficiency.

In Oct., the removal efficiency for CT is 87 %, UFM is 64%, and CT+UFM is 96%, this result indicates higher removal efficiency.

In Nov., the removal efficiency for CT is 92%, UFM is 73%, and CT+UFM is 98%, which indicates higher removal efficiency.

These results indicate that UFM had the lowest removal efficiency when comparing it with CT and CT+UFM as shown in Figure 5.1. Depending on the ionic properties, excessive TDS can produce toxic effects on the environment.

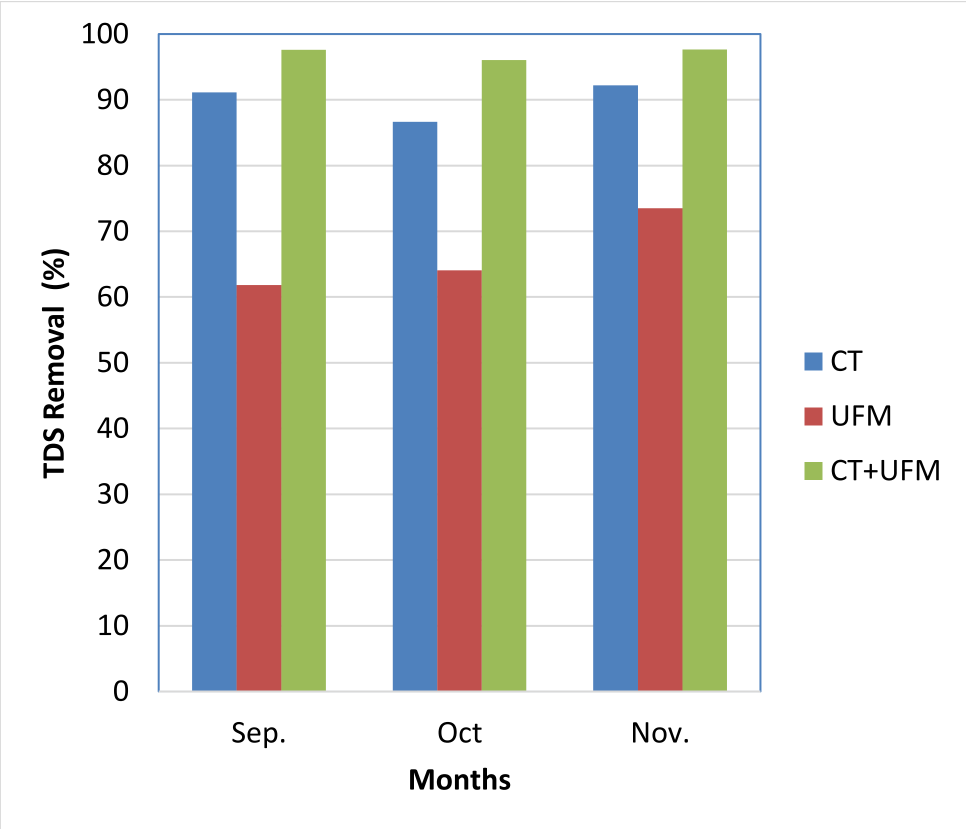


Figure (5.1): Effect of treatment technology on TDS removal % (TMP=3 bar,T=40° C).

5.4.2 TSS Removal Efficiency

Figure 5.2 shows the efficiency of TSS removal. The results show that UFM treatment was very effective in removing suspended solids, with very high removal ratios reached 100% for all three months. In spite of the effectiveness of the membrane, the suspended solid increases the fouling of the membrane due to the accumulation of these solid at the surface of the membrane.

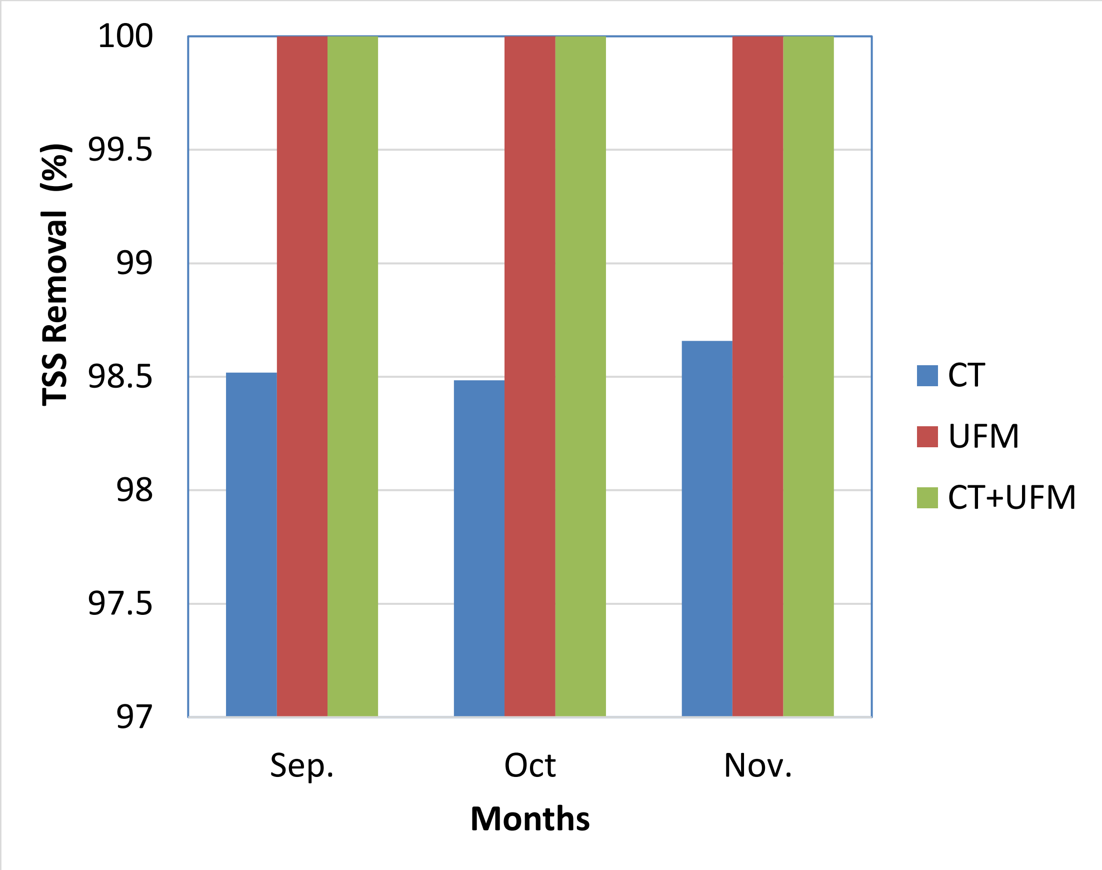


Figure (5.2): Effect of treatment technology on TSS removal % (TMP=3 bar, T=40° C).

5.4.3 Oil & Grease Removal Efficiency

Removal efficiency is related to two important factors T and TMP. Oil rejected ratio decreases when T&TMP increase which effect on fluid viscosity and membrane pore size. Therefore, at TMP = 3 bar and T=40° C, UFM treatment method shows high efficiency in terms of rejecting oil content, which reached approximately 100% for three months. The average removal efficiency for oil and grease by using CT for the three months is about 96%, which indicates less efficiency as compared with UFM and CT+UFM. As shown in Figure 5.3.

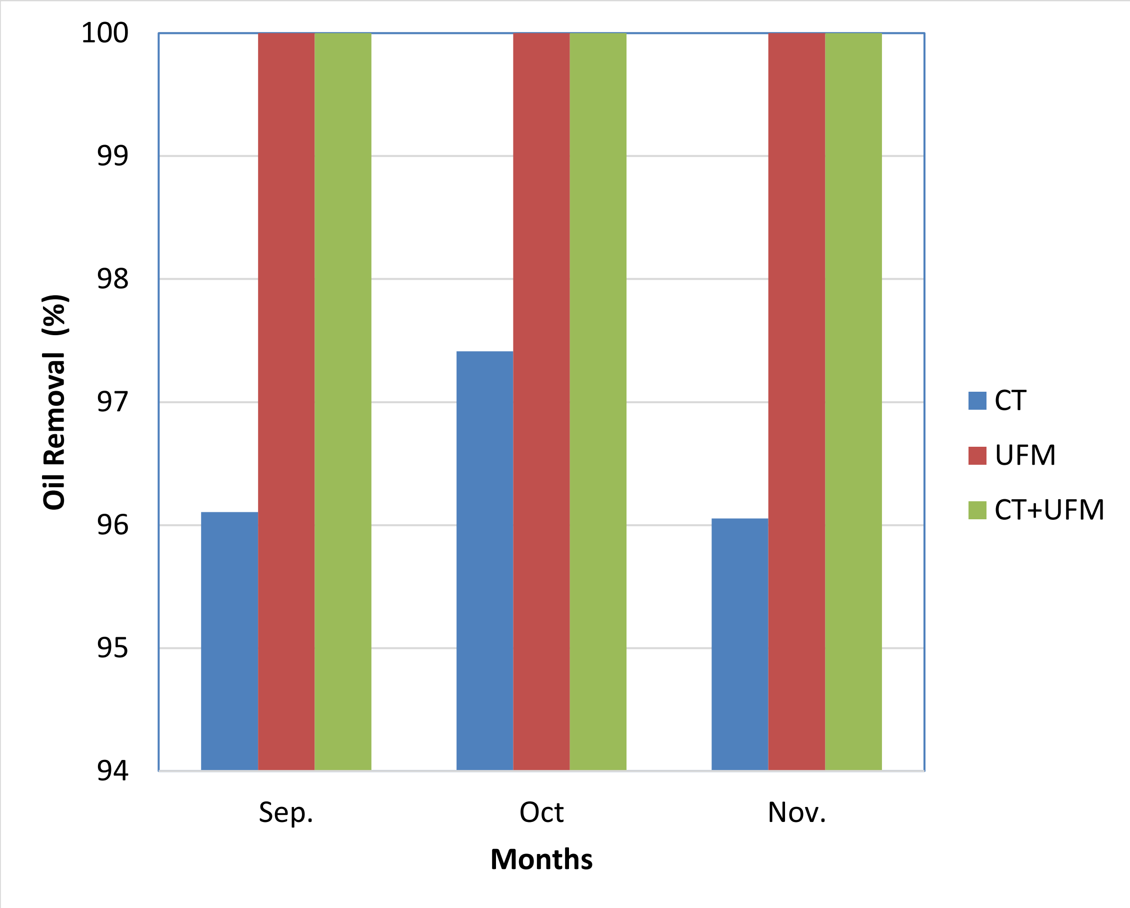


Figure (5.3): Effect of treatment technology on oil removal % (TMP=3 bar, T=40º C).

5.4.4 Salinity Removal Efficiency

Salinity is the total concentration of all dissolved salts in water. It is a strong contributor to conductivity. There are many different dissolved salts that contribute to the salinity of water, which are chloride, sodium, magnesium, sulfate, calcium, potassium, and bicarbonate. In Sep., the removal efficiency of salinity for CT is 94 %, UFM is 76%, and CT+UFM is 99%. In Oct., the removal efficiency for CT is 93 %, UFM is 78%, and CT+UFM is 98%. In Nov., the removal efficiency for CT is 92%, UFM is 67%, and CT+UFM is 98%, which indicates higher removal efficiency.

According to these results, it is obvious that, UFM is not effective method to remove minerals. CT is more effective than UFM. But using both methods showed higher efficiency. Figure 5.4 shows the removal efficiency of salinity.

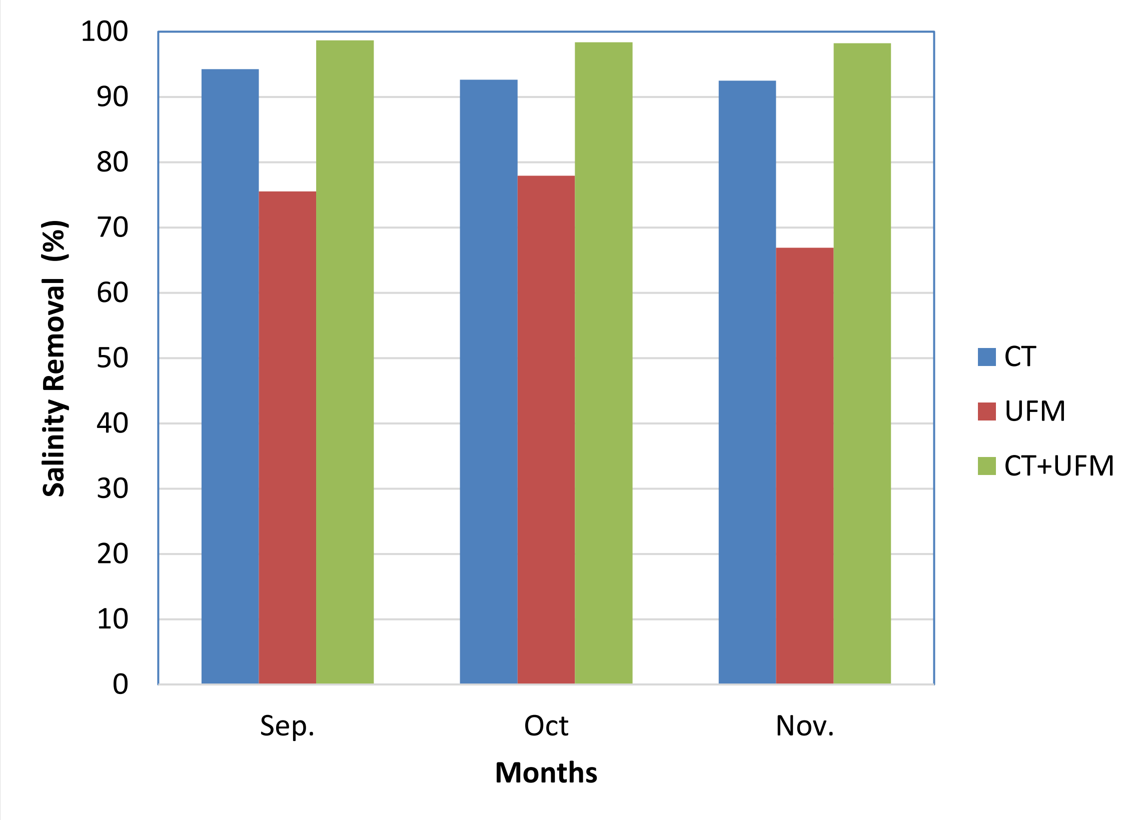


Figure (5.4): Effect of treatment technology on salinity removal % (TMP=3 bar, T=40^o C).

5.4.5 Heavy Metal Removal Efficiency

The presence of heavy metals in the aquatic ecosystem has far-reaching implications directly to the biota and indirectly to man. Because of its toxic effect on plants, animals and human, heavy metals are listed in environmental pollutant category, when it exceeds the permissible limits of WHO standards.

The results obtained from laboratory analyses for concentration of heavy metals in treated water show that the removal efficiency reaches the highest value when UFM preceded by CT as shown in Figures 5.5, 5.6, 5.7, 5.8, and 5.9, and it achieved approximately 100% for Ni^{+1}, pb^{+2}, and Cr^{+3}.

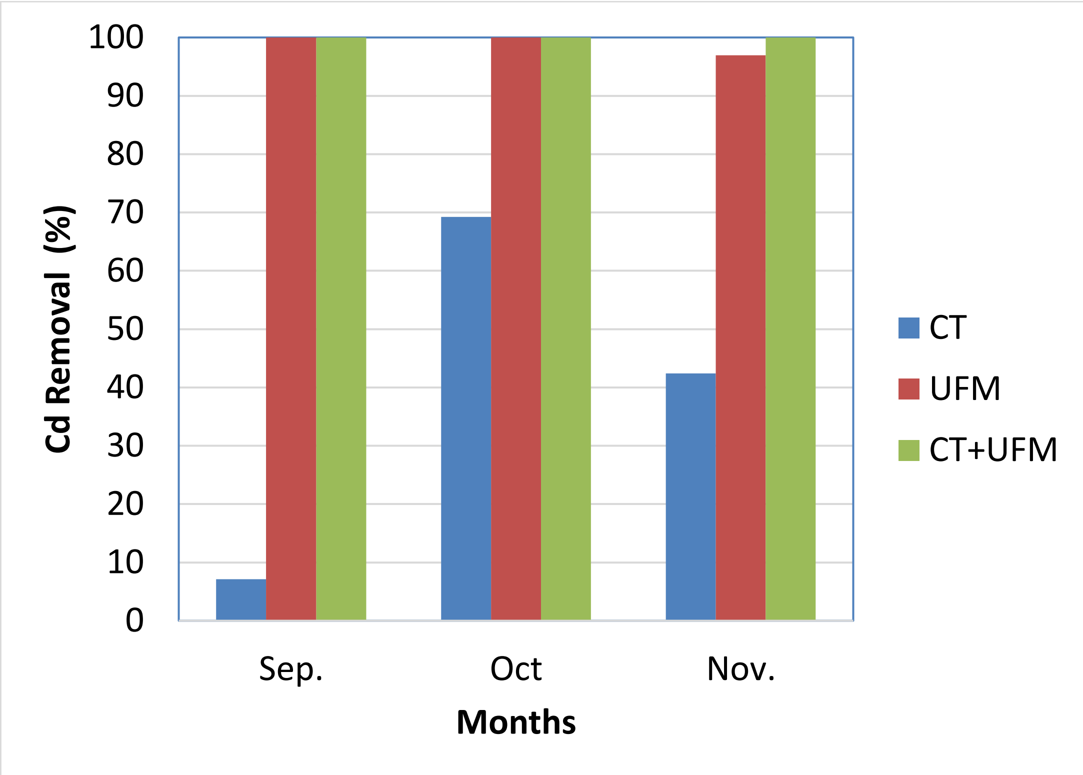


Figure (5.5): Cd removal (%).

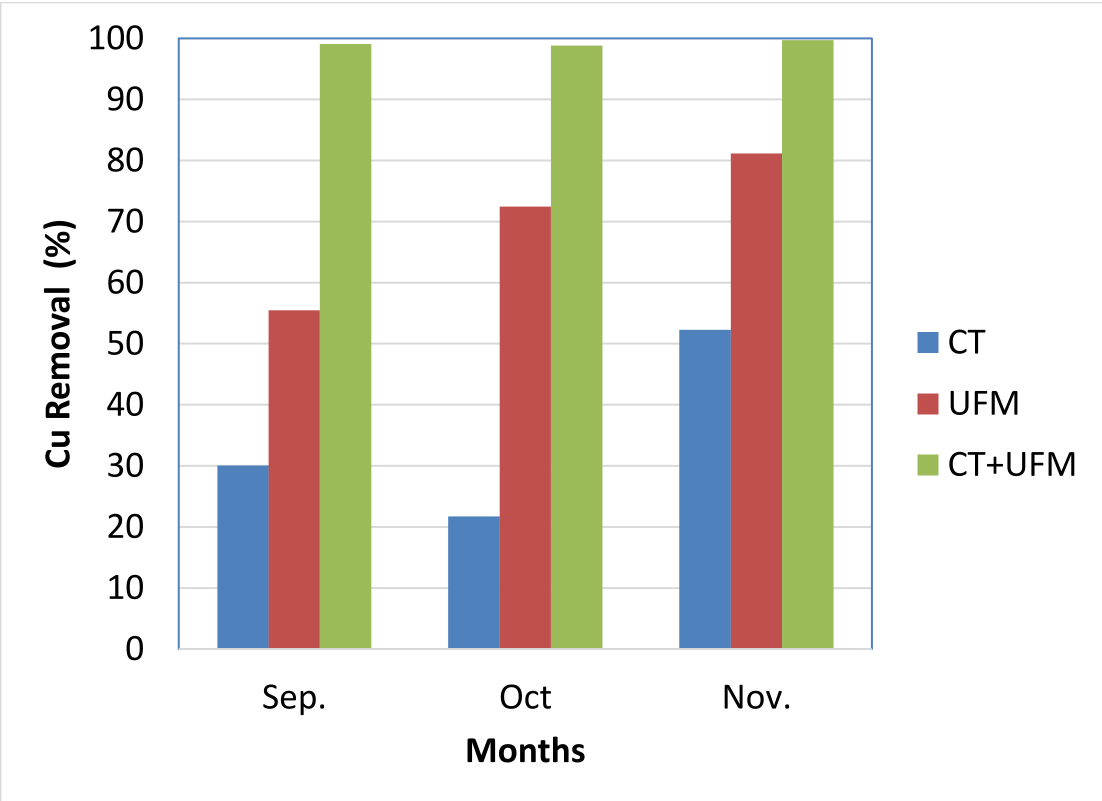


Figure (5.6): Cu removal (%).

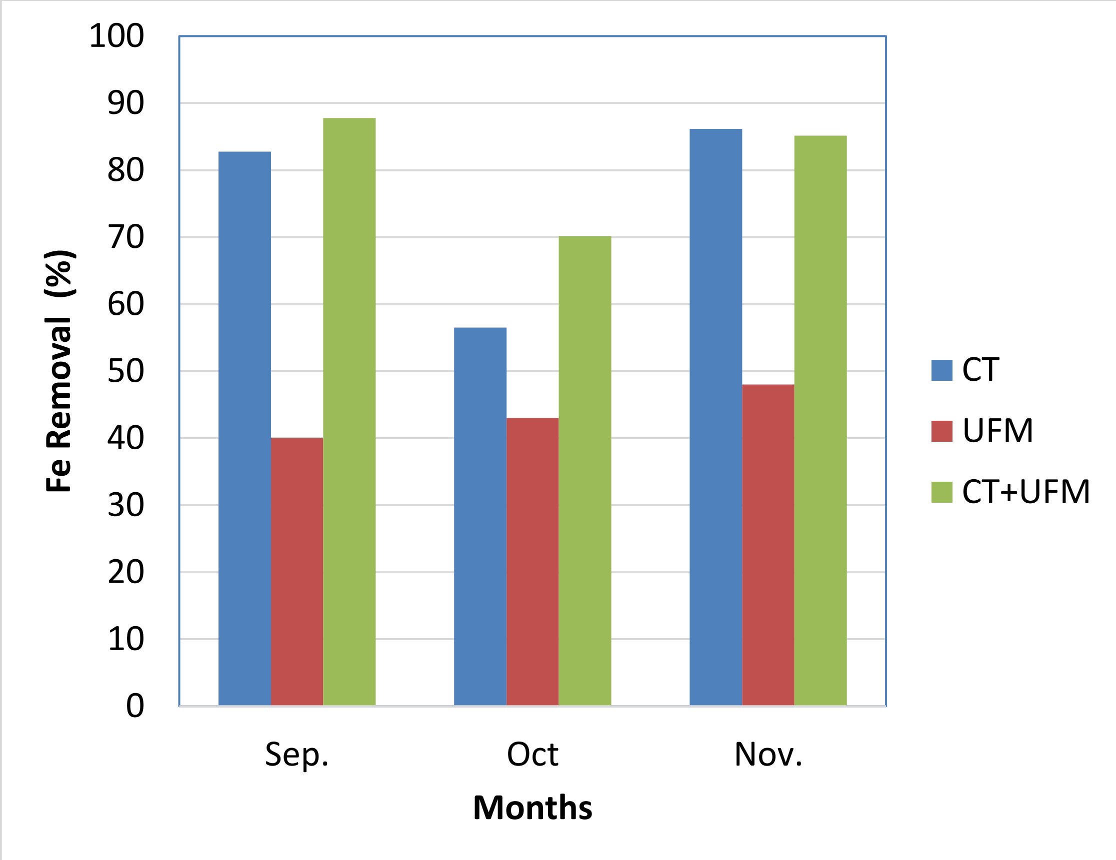


Figure (5.7): Fe removal (%).

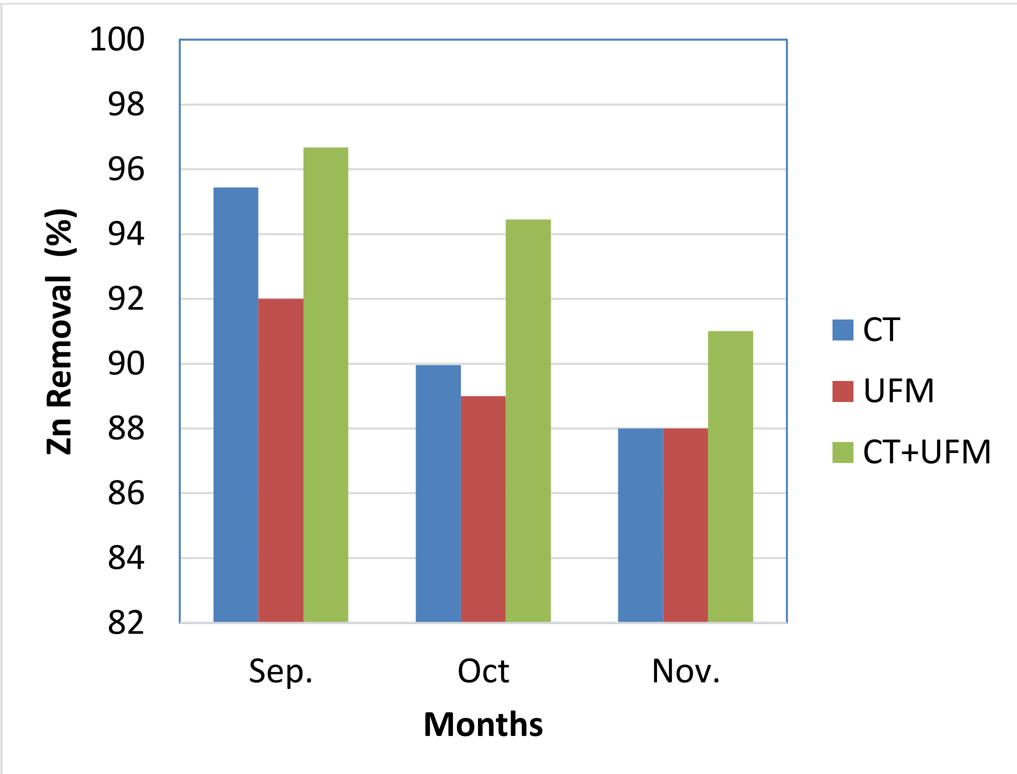


Figure (5.8): Zn removal (%).

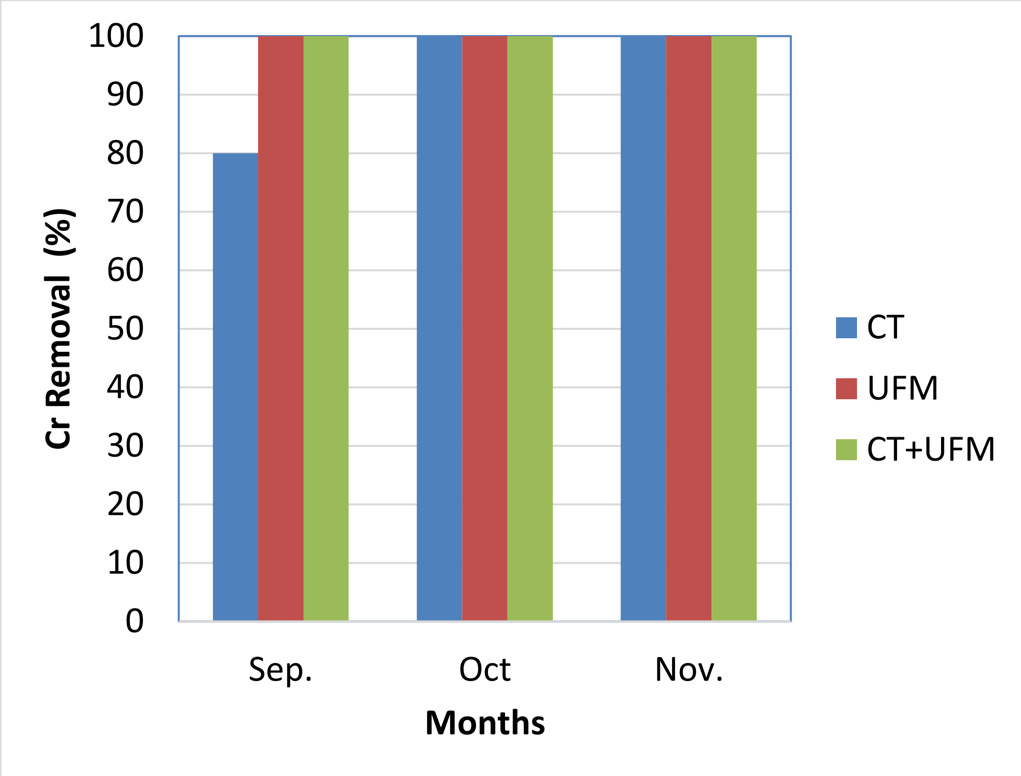


Figure (5.9): Cr removal (%).

5.4.6. COD Removal Efficiency

Chemical Oxygen Demand (COD) is another important water quality parameter that industrial and municipal authorities should be familiar with to determine the best wastewater treatment methods for their needs. The results obtained showed COD removal efficiency when using CT+UFM, see figure (5.10).

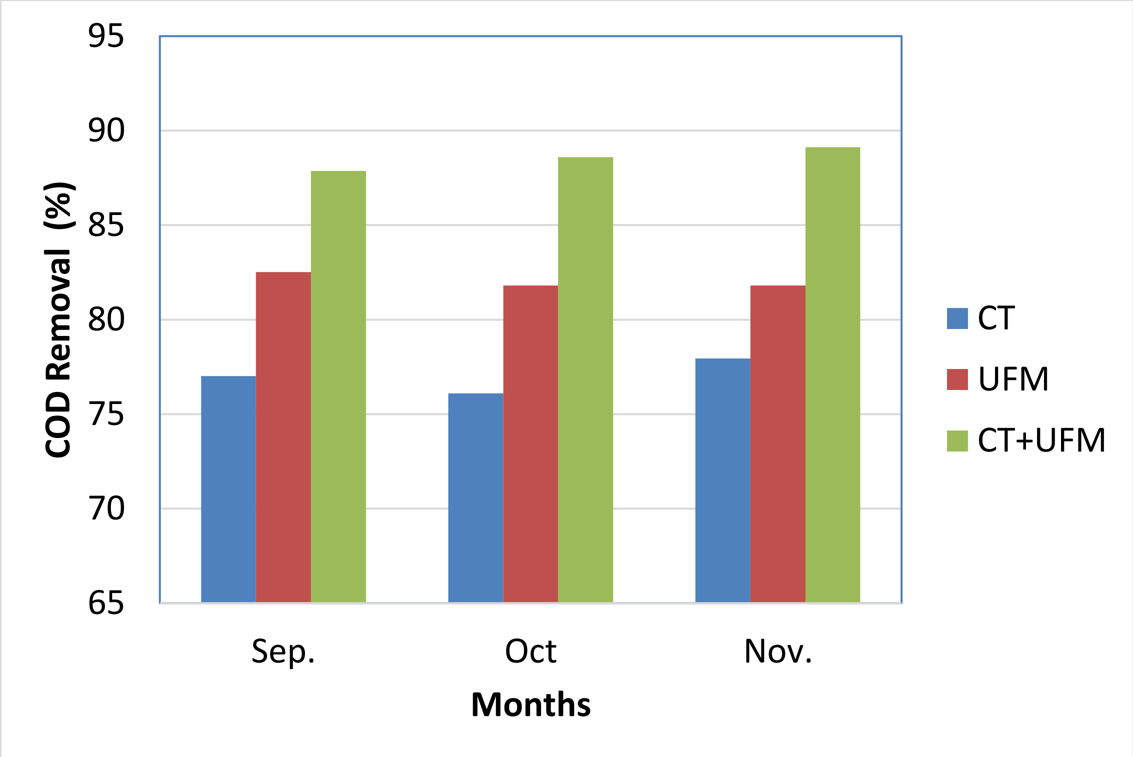


Figure (5.10): COD removal (%).

5.4.7. TOC Removal Efficiency.

TOC is short for Total Organic Carbon, which within water treatment is referring to the total amount of organic carbon found in water. The reduction of TOC in water is critical in applications such as microelectronics and semiconductors, pharmaceutical, food and beverage, and processing wastewater, to ensure ultrapure water. The obtained results as shown bellow.

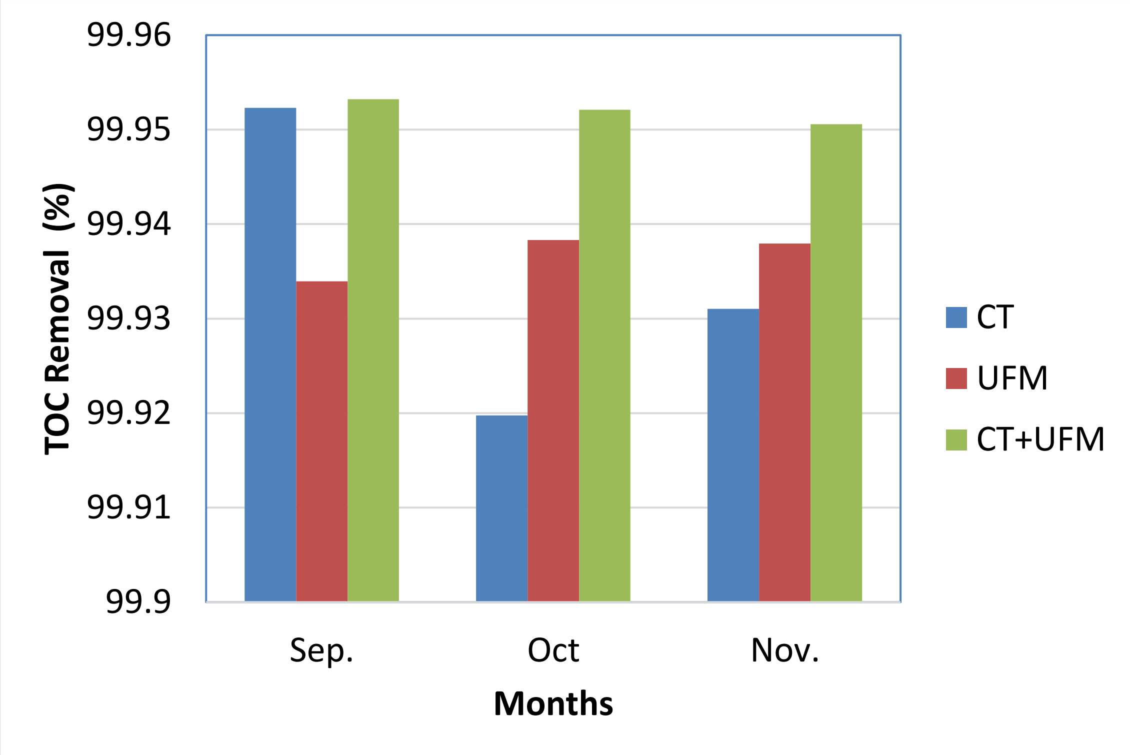


Figure (5.11): TOC Removal Efficiency.

5.5. Results Analysis and Discussion

From the result shown in Table 5.3, UFM showed high removal efficiency in many parameters, and it nearby 100% for oil content, a TSS and heavy metal which consider a big concern of environment and human body. It can be noticed that all the results obtained for heavy metal are in the range of allowed limits. But they don't meet the requirement of irrigation or other benefit used, and when comparing them with the conventional treatment method results that show in Table 5.2, its be not effective way because of the lower efficiency and membrane fouling problem. Therefore, using the combination of two previous methods gives results of treatment with high removal efficiency and quality than using one of them only, as shown in Table 5.4.

When the salts dissolve in water to produce an anion and a cation, salinity relates to the amount of salt in the water, where the salt can be in many different forms (salt used in food is sodium chloride). Typically, waters can contain two or more of the following salts (Na^{+1}, Mg^{+2}, Ca^{+2}, k^{+1}, So_4^{-2}, Co_3^{-2}, and Cl^{-1}). There are two main methods of defining the concentration of salt in water: EC and TDS.

The values of conductivity obtained from UFM are (75.1, 67.4, and 45.4) mS/cm for (Sep., Oct., and Nov.) respectively. While from CT+UFM is (5.07, 6.58, and 4.78) mS/cm for (Sep., Oct., and Nov.), respectively. The last values may consider in acceptable range for surface and ground water that limited to (5-50) mS/cm and for the most livestock[69].

The recommended TDS for beneficial uses such as stock ponds or irrigation about 1000–3000 mg/L[70]. While the average values of TDS obtained from UFM are (42468, 43745 and 26830) m/L for (Sep., Oct., and Nov.) respectively, and from CT+UFM are equal to (2681, 4789, and 2388) m/L for (Sep., Oct., and Nov.) respectively, which mean the last result close to acceptable range which is suitable only for crops that have ability to tolerate high salinity such as wheat and barley.

COD is widely used as a measure of the susceptibility to oxidation of the organic and inorganic materials present in the produced water [66]. It can be noticed that the COD of the raw PW is decreased from (381, 378, and 375) mg/l for (Sep., Oct., and Nov.) respectively to (66.6, 70.4, and 68.2) mg/l by UFM method, and to (46.2, 44.1, and 40.8) mg/l using CT+UFM together. and all these values with in the permissible values of Iraqi Standards (IQS) which is 100 mg/l [66].

Heavy metal concentrations of water samples with standards as followed. Pb is a very toxic heavy metal even at low concentration. The standard value is given for Pb by IQS is 0.015 mg/L. The standard value of Ni is 0.07 mg/L. IQS stated that the value of Cr is 0.01 mg/L for standard use. Cd is highly toxic to freshwater, the IQS guideline (0.005 mg/L). The tested samples from UFM and also from CT+UFM, proved to be free of all previous heavy metal parameters stated above, in which achieving 100% removal efficiency [66].

The obtained average results of Cu, Fe, and Zn are (0.142, 0.26, and 1.23) mg/L respectively for using UFM method, and average results (0.0042, 0.0652, and 0.0668) mg/L respectively for CT+UFM. The standard values of Cu, Fe, and Zn are (1.3, 0.3, and 5) mg/L [66], which means that, all the obtained results are acceptable for IQS standard.

5.6. Permeation Flux

The efficiency of using UFM treatment depends on the amount of permeation flux, which depends on the TMP, fouling of membrane and membrane cleaning, temperature of fluid.

5.6.1. Effect of TMP on Permeation Flux

Under constant time period of filtration equal to 30 min for each level of pressures (1, 2, 3, 4 and 5 bar) and when increase TMP gradually, the amount of permeation flux increased significantly due to the increase in driving forces across the membrane. Therefore, always higher flux is obtained at higher TMP as shown in Figure 5.10. It can be seen that the pressure has positive effect on the permeate flux However, with increasing TMP, fouling can occur at a faster rate when oil droplets become more compact on the membrane surface and block the pores.

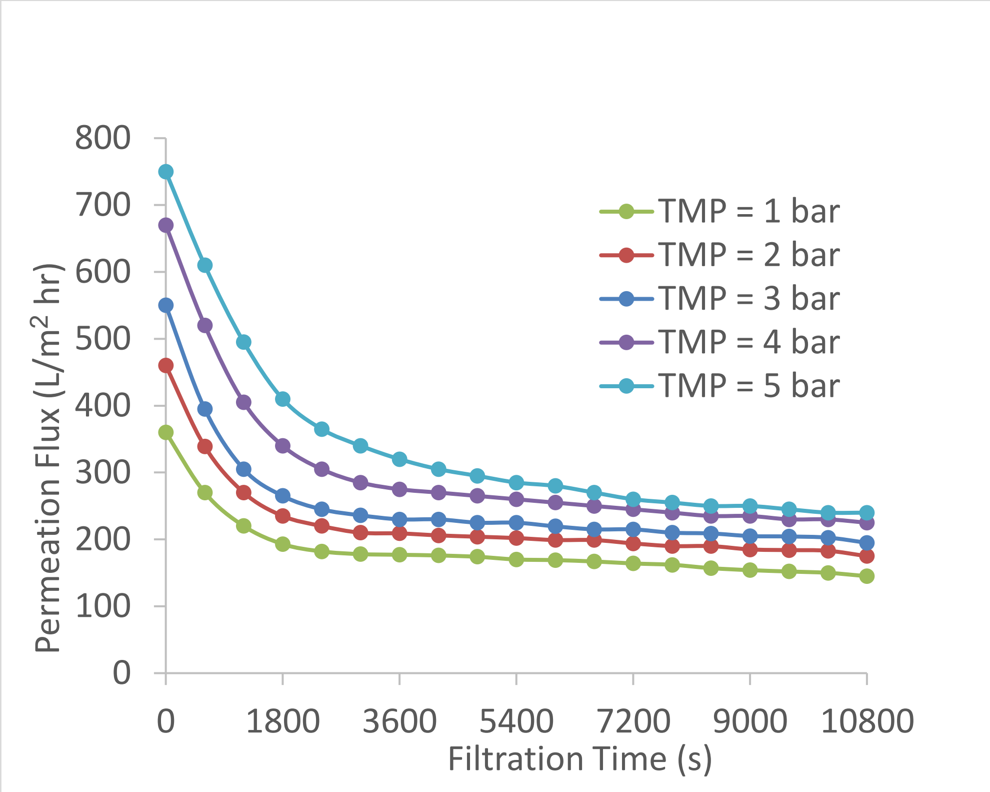


Figure (5.12): Variation of permeation flux with filtration time for different TMP.

5.6.2. Effect of Membrane Fouling on Permeation Flux

The fouling problem was occurred in all other membrane process and pollutants present in feed samples such as suspended particles, organic matters, colloids and inorganic deposits which contribute in obstruction in the treatment process, thereby cause decline in permeate flux. Therefore, under constant TMP equal to 3 bar and as time go on, permeation flux was decrease that’s indicating accumulation of foulants on membrane. It decreased gradually due to oil droplet adsorption at the membrane surface and pores. Figure 5.11, shows the effect of fouling membrane.

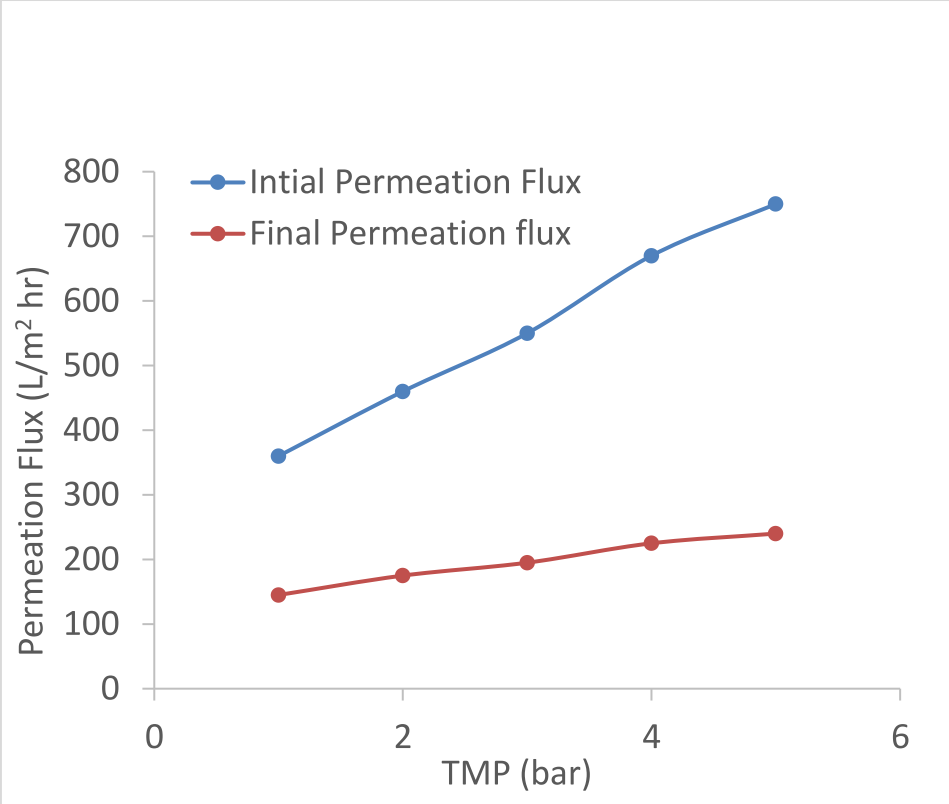


Figure (5.13): Effects of fouling membrane on permeation flux.

Figure 5.12 shows the difference between permeation flux from sample 1 (produced water) and sample 2 (pre-treated water), the last shows decreasing in permeation flux due to the high concentration of pollutant which clog the membrane pores.

The membrane surface roughness plays a very important role in membrane fouling. High roughness increases the membrane surface area, and hence, it increases the surface area to which foulants can attach.

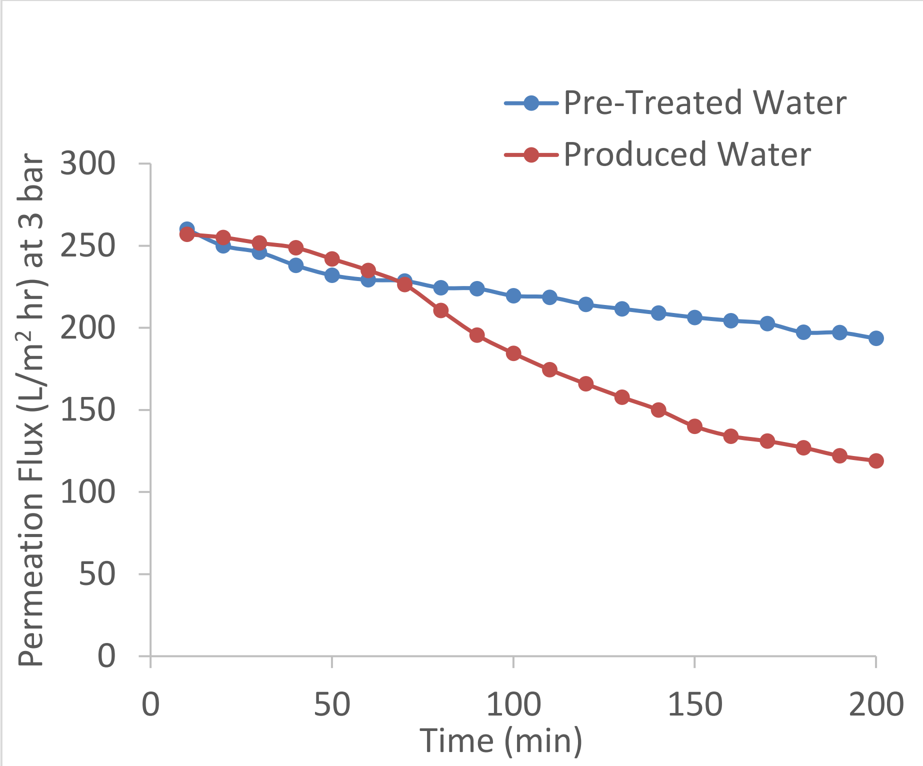


Figure (5.14) Permeation flux obtained from PW and pre-treated water at 3bar.

5.6.3. Effect of backwashing process on permeation flux

The backwashing process reduces the membrane efficiency value by more than 7 % every time. This inefficiency because of foulants accumulation that the backwash cannot remove. Figure 5.13 shows the decrease in membrane efficiency after washing.

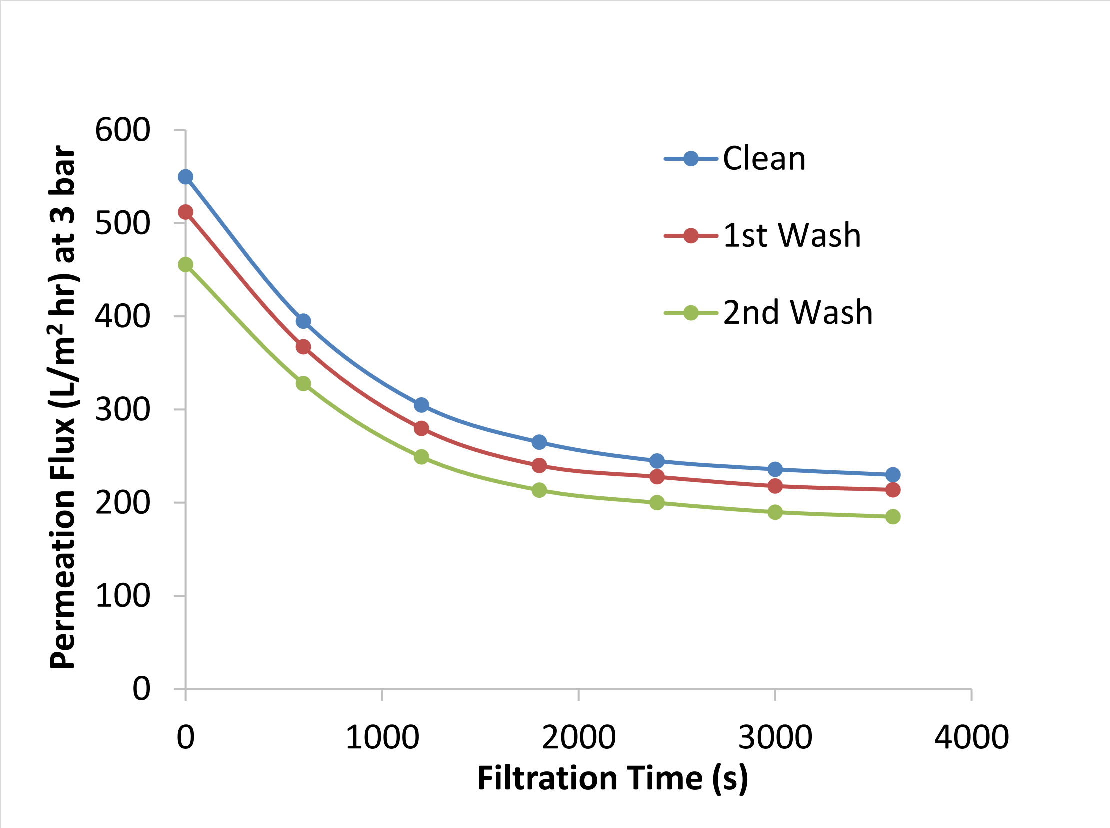


Figure (5.15): Effect of Backwash on Membrane Efficiency.

5.6.4. Effect of Temperature on Membrane.

Permeate flux is very sensitive to the feed temperature. By raising the temperature of the fluid from 30º to 50º C the water flux showed a gradual increase through the membrane as shown in Figure 5.14. This may be attributed to reducing the viscosity of the fluid and causing a high diffusion rate through the membrane surface, also this increase in temperature will increase in mean pore radius of the membrane and the permeability of water through the membrane increases. On the other hand, temperature also affects the removal efficiency in the membrane separations involving diffusion of particles through membrane pores, therefore removal efficiency decreases.

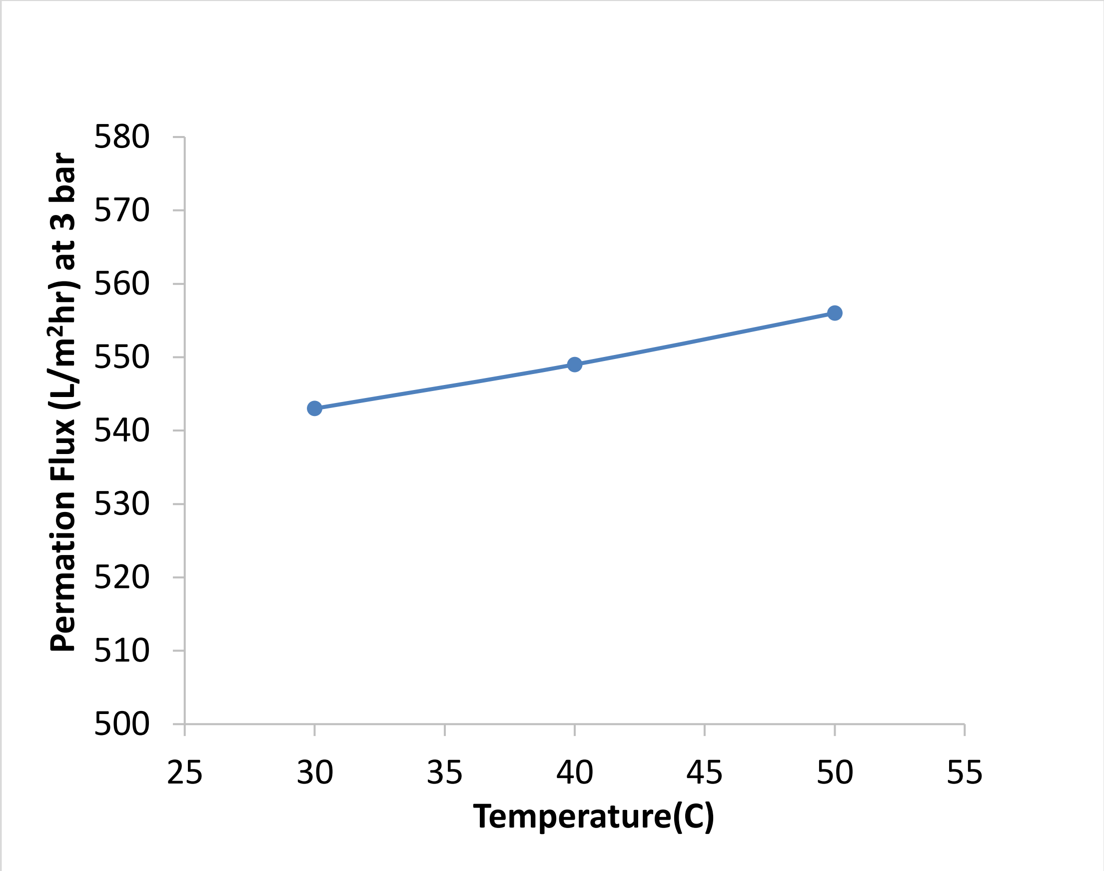


Figure (5.16): Effect of temperature on permeation flux (TMP =3 bar).

Chapter Six

Conclusions & Recommendations

6.1 Conclusions

The conclusion of the study has been given in this chapter. It is based on the results obtained in the previous chapters.

1. Physical and chemical analyses of the treated PW samples showed that PW didn't meet the requirements of irrigation water quality or other benefit use, due to the weakness of UFM treatment to remove TDS and heavy metal from the PW. Nonetheless, the obtained PW is suitable for re-injection into a well for improved oil recovery.
2. Through the current study, the use of UFM has been proven to be an effective method to remove the oil content and TSS with a ratio that reaches approximately 100%.
3. UFM showed weakness in TDS, cation and anion removal efficiency when compared with CT methods. Through this study, combined two methods CT and UFM showed increasing in removal efficiency.
4. The quality of the resulting water after using CT+UFM method does not meet the quality of potable water, but it was suitable for crops that tolerate high salinity.
5. Temperature and pressure play a big role to determine the quantity and quality of permeation flux resulted, which consider the main factor in determining the efficiency of using membrane technology.
6. When the feed temperature increased from 30^{o} to 50^{o} C the permeation flux increases from 542 to 556 (l/m^2.hr) at TMP = 3bar. And when TMP increase from 1 to 5 bar, the permeation flux increases from 450 to 750 (l/m^2.hr) at T= 40^{o} C.

7. The backwash of the membrane reduced the efficiency of filtration by more than 7% every time.
8. The results of this experimental work showed that using a UFM technology as a supplementary stage after CT, gives high efficiency.
9. The obtained results are not suitable for beneficial uses, due to increasing the pollution for Al-Ahdab oilfield PW in recent years.

6.2 Recommendations

- **Recommendations for Al-Ahdab Oil Field**

1. There is no single treatment method that treats PW to meet the standard requirements of reuse water. Therefore, three or more treatment systems might be used in series operations.
2. An economic feasibility study should be conducted to investigate whether this process of treatment can be applied in the oil and gas industry.

- **Recommendations for Future Studies**

1. In the pre-treatment stage, the complexity of organic matters must be solved and removed to reduce membrane fouling and make UFM practically a feasible treatment and economically applicable.
2. A study of using some adsorbents combined with ultrafiltration membrane to improve the properties of the treated water.
3. MF membrane may be used as a pre-treatment step for the other membrane operations such as UF membrane.
4. It is suggested to test NF membrane as a supplementary stage after UF membrane.

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اضــافة الى ذلك تؤثر درجة الحرارة أيضًــا على تدفق النفاذية عندما تزداد من 30 إلى 50 ، كمـا يزداد تـدفق النفـاذيـة من (543 إلى 556) لتر / م^2، ومن جـانـب اخر، تنخفض كفـاءة الغشــاء بحدود 7٪ بعد الغســيل العكســي في كل مرة وذلك دلالة على تراكم الملوثات التي لايمكن ازالتها بواسطة الغسل.

اخيرا، أشــــارت النتائج إلى أن كفاءة الإزالـة عاليـة لاغلب المعايير وإزالـة حوالي 100٪ للمعايير الثلاثـة (محتوى الزيت ، إجمالي المواد الصـــلبـة العالقة ، والمعادن الثقيلـة). فيمـا أظهرت اغشــية الترشــيح الفائق PES ضــعفًا في كفاءة إزالة المواد الصــلبة الذائبة الكلية (TDS) بالمقارنة مع طرق المعالجة التقليدية من خلال هذه الدراســة. انخفض الطلب على الاوكسجين الكيميائي بمعدل من 380 إلى 68.4 مجم / لتر باستخدام الغشاء فقط والى 43.7 مجم / لتر باسـتخدام الاغشـية مسـبوقة بالمعالجة التقليدية. أظهر الجمع بين المعالجة التقليدية وتقنيات الاغشية زيادة في كفاءة ازالة كافة المعايير وتقترب من الحدود المسموح بها للمياه القياسية العراقية IQS.

المستخلص

المياه المصـــاحبة هي المياه الملوثة المتولدة في جوف الخزان التي ترتفع الى الســطح خلال عمليات اســـتخراج النفط والغاز. وهي تعتبر أكبر مجرى للنفايات في العالم وتحتوي على مكونات ســامة قد تســبب ضــررا للبيئة المحيطة عند التخلص منها دون معالجه. من ناحية أخرى، يمكن استخدام المياه المعالجة لغرض اعادة الحقن داخل الخزان للحفاظ على الضغط الثابت أو لاغراض اخرى مثل الري وشـــرب الماشـــية وســـقي الحياة البرية ومختلف الاســتخدامات الصــناعية كالسـيطرة على الغبار وغســل المركبات، ومحطات توليد الطاقة والسيطرة على الحرائق. طرق المعالجة التقليدية للمياه المصاحبة تقتصر على فصل الجاذبية والتخثر والتلبيد والترشيح بواسطة الحصى والرمل ومرشحات قشور الجوز.وهذه العمليات لا تفي بمتطلبات الاســتخدام النافع. في الســنوات الأخيرة، ركزت الأبحاث على تقنيات الأغشية التي توفر كفاءة أعلى وتكلفة أقل.

تتناول هذه الدراســة اسـتخدام غشــاء الترشـيح الفائق بولي إيثر سـلفون (PES) في معالجة المياه المصـــاحبة المتولدة من حقل الأحدب النفطي في واســط / العراق كدراســة حالة في التجارب المختبرية. تم استخدام ثمانية صـفائح مستطيلة الشـكل من غشـاء الترشـيح الفائق PESالمصنع مختبريا, مساحة كل منها 60 سم^2. تم استخدام الفحص المجهري الإلكتروني (SEM)لفحص شكل الغشـاء مثل حجم المسـام والسـمك. تم فحص نوعين من العينات لمدة ثلاثة أشــهر (ايلول، تشــرين الاول، تشــرين الثاني) وهي المياه الخام المصـــاحبة والمياه المعالجة التي تمت معالجتها بواســـطة حقل الاحدب. حيث تم تحليل الخصــــائص الفيزيائية والكيميائية لتحديد جودة المياه المعالجة. وتمت دراســـة تاثير كل من الضــغط المســلط على الغشـاء ودرجة حرارة السـائل وتلوث الغشـاء وتاثير الغسـل العكسـي للغشـاء بالتفصـيل لتقييم كفاءة الغشاء المستخدم. حيث تبين ان زيادة الضغط المسلط على الغشاء (TMP) من 1 بار إلى 5 بار ، زادت كمية تدفق النفاذية من 360 إلى 750 لتر/ م^2 ســاعة، وذلك بســبب زيادة القوى الدافعة عبر الغشـــاء. ومع ذلك، انخفض تدفق النفاذية تدريجيًا مع مرور الوقت وذلك بسبب تراكم الملوثات على الغشاء.

جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة كربلاء

كلية الهندسة

قسم الهندسة المدنية

معالجة المياه المصاحبة باستخدام اغشية الترشيح الفائق

(دراسة تجريبية)

الرسالة مقدمة إلى

قسم الهندسة المدنية / كلية الهندسة في جامعة كربلاء كجزء من متطلبات نيل درجة الماجستير في علوم الهندسة المدنية

من قبل

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