Ultrafiltration Membrane Technology for Oily Wastewater Treatment

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Abstract. Oil and gas sectors generate large amounts of oily wastewater, which is called produced water. In which, it contains high concentrations of hazardous organic and inorganic pollutants. This paper attempts to evaluate the performance and quality of using a polyethersulfone ultrafiltration membrane (UFM) to treat the produced water of Al-Ahdab oil field (Wassit, Iraq). 8 rectangular flat sheets of polyethersulfone ultrafiltration membrane were used. The area of each is 60 cm² and pore size about 15 nm used in the experimental work. Prepared UFM is characterized by determining the surface morphology by scanning electron microscopy (SEM). The result showed that the UFM indicated high removal efficiency in all parameters and especially oil and grease and total suspended solid but in general it still less than the requirement of water reuse. The results showed that, a combination of a conventional treatment method and UFM technology have higher efficiency than using UFM only.

1. Introduction
Oily wastewaters are produced in huge quantities by many different industries with the main contributor being the petrochemical sector. The oil/gas industry generates a large amount of wastewater during the operation of extract the hydrocarbons, processing and refining [1]. Therefore, the water called produced water (PW), which comprises both formation water and injected water. Formation water naturally occurs with the hydrocarbons in the reservoir, while injected water is being withdrawn from an external source and injected in the well to improved oil recovery [2]. As a result of the increasing volume of produced water all over the world, it becomes a big concern on the environment, that’s due to a complex composition of toxic organic and inorganic compounds [3]. Organic matter of the produced water includes dispersed oil (hydrocarbon) and non-hydrocarbon organic material [4]. The inorganic compounds exist as dissolved anions and cations, cations such as Na+, K+, Ca2+, Mg+2, Sr+2, Ba+2, Fe+2, anions SO42−, Cl−, CO32−, HCO3 and other substances such as heavy metals (e.g., barium, uranium, cadmium, chromium and lead), and can contain any chemicals added during the drilling and production processes [5]. See table 1.
Table 1: Characteristic of produced water from Al-Ahdab oil field comparing with Typical oil field In the world.

| Parameter       | AL-Ahdb oil field | Typical oil field [6] |
|-----------------|-------------------|-----------------------|
| Density (kg/m³) | 1,100             | 1,014-1,140           |
| Oil content (mg/L) | 10,000          | 2-565                 |
| pH              | 5.8               | 4.3-10                |
| EC (µs/cm)      | 227,000           | 4,200-58,600          |
| T.D.S (mg/L)    | 243,199.47        | 100-400,000           |
| T.S.S (mg/L)    | 2,500             | 1.2-1,000             |
| So₄⁺ (mg/L)     | 160               | 77-3,990              |
| Fe (mg/L)       | 5.84              | 0.1-100               |
| Cl⁻ (mg/L)      | 132,937           | 80-200,000            |
| Na (mg/L)       | 68,500            | 132-97,000            |
| Mg (mg/L)       | 5,687             | 8-6,000               |

Table 1 shows the optimum range of physical and chemical analysis for raw produced water from Al-Ahdab oil field. Located between Numania and Kut about 180 km to the south-east of Baghdad/Iraq. Oil and grease are the most important constituent in produced water. It’s not referring to a single chemical, but many families of organic chemicals. Another important constituent is the salt content of produced water which it effects on soils, water quality, and ecosystems [7].

Treatment of the produced water conventionally done by physical and chemical processes. Principles of these treatments including (de-oiling, desalination, sand and suspended particles removal, soluble organics removal, gases removal, and NORM removal) [8]. These principles were applied using several methods such as (gravity separation, adsorption, electrochemical process, filtration, and flotation) [9]. These methods may be costly and generate a burden on producing companies. Therefore, membrane technologies can be used for produced water treatment, which considers an efficient and widely used treatment method. Its advantages are decreasing sludge, require a small space, ease of operation, reasonable capital costs and possibility of total recycle water systems. All of these advantages make membrane treatment an economical alternative to traditional treatment methods or addition for it [10,11].

Membranes classified into four types according to pore size. It includes microfiltration (MF), ultrafiltration (UF), Nano filtration (NF) and reverse osmosis (RO). MF has the largest pore size and decreases in UF then NF and RO at the end. Therefore, hydrodynamic resistance for the liquid passage increases from MF to RO [12]. UF is one of these types, Its pore size about (2-100 nm). It discards virus and macromolecular colloids. Unfortunately, almost more dissolved ionic species may pass through the membrane [13]. Also, UF is considered an effective method for produced water and oily wastewater treatment. The efficiency of oil removal, no chemical additives needed, energy cost is low, operate at low transmembrane pressure about 1–30 psi and space requirements small are the main advantage of it use [14].

This study is a practical application for using polymeric ultrafiltration membrane in the treatment of produced water from Al-Ahdab oil field, Wassit, Iraq.
2. Material and Methods

2.1. Proposal System

Figure 1 shows a schematic diagram of the produced water treatment system used in experimental work. It consists of the following parts.

- Treatment system contains: (feed container, mixer, heater, pump, and thermometer).
- Membrane cell.
- Washing system contains: (container, mixer, heater, pump, and thermometer).
- Container (3) used for collecting the treated produced water.

![Figure 1 Schematic diagram of membrane treatment system.](image)

2.2. Membrane Preparation

The membranes used in their experiments were (8) rectangular sheet polyethersulfone ultrafiltration with a pore size of 15 nm, and dimensions of $10 \times 6$ cm, prepared in the chemical engineering laboratory of the university of technology. The membrane is porous and asymmetric.

The phase inversion casting method used to prepare a polyethersulfone ultrafiltration flat sheet membrane. 15 gm. of polyethersulfone pellets (Sigma–Aldrich, St. Louis, MO, USA) heated for 5 hours at 150°C to degas. Further, it melted with 85 gm. of DMSO (Dimethyl sulfoxide) (Sigma–Aldrich, St. Louis, MO, USA) for the 15.0 wt. % concentrated solution. 1.0 wt. % of polyvinyl pyrrolidone (PVP) (Sigma–Aldrich, St. Louis, MO, USA) added to the polyethersulfone solution as additive. Figure (2) shows the solution mixing glass flask and all the necessary laboratory tools required to prepare a polymer solution. The mixer was rotating at (500r/min) for 24 hours at a temperature of 50°C to sure that polyethersulfone was dissolved in DMSO and formed a homogeneous solution. To reduce the number of bubbles in the solution it kept in the dark. Nonwoven polyester fabric fixed onto a glass plate and then the solution casting using a stainless-steel knife. Then lets for 1 minute to get a uniform surface of the support layer. The glass plate was put into a water bath for 1 hour at 23°C. The membrane was stored in distilled water 18.2 MΩ cm at 40°C. Figure 3 shows the casting of polyethersulfone layer. The thickness was approximately 200 μm [15].
Figure 2. Tools used for preparing the solution of membrane.

Figure 3. Polyethersulfone membrane after casting.

2.3. Scanning Electron Microscopy (SEM)
A scanning Electron Microscopy (SEM) also known as SEM microscopy is a test using an electron beam to scans a sample of the membrane to get a high-resolution superficial image (1 nm) and provide information about pore size, pore size distribution, pore density, roughness. It is efficiently in microanalysis solid inorganic materials. Figure 4 a, b, c and d below show SEM analysis of membrane used in experimental work [16].

Figure 4 (a). Cross-sectional view of membrane with magnification×1000.

Figure 4 (b). Cross-sectional view of membrane with magnification×4000.
2.4. Feed water

Two Type of the samples are taken from Al-Ahdab oil field to use in the experiment:

- Raw produced water.
- Treated water by conventional treatment method in the field [17].

2.5. System operation

The experiments were carried out based on the cross-flow membrane system. The schematic flow diagram of the membrane treatment system shown in Figure 1. The system consists of the membrane treatment system and membrane wash system every one includes (feed container, mixer, heater, pump and thermometer), membrane cell and container (3) used for collecting the treated produced water. The feed water pumped from the container of produced water to the inlet of the membrane cell. The pump used in the system with a maximum flow rate = 480 L/h, temperature = 60 °C and transmembrane pressure = 100 bar. A heater in the feed produced water container used to stabilize the temperature of it about 40 °C. Operating pressure and flow rate controlled by the valves. The membrane cell was epoxy resin rectangular chamber. Flat sheet membrane with an area of 60 cm² fixed in the cell with sub-layer to save the membrane from damaged under the applied pressure. Variation of the oil pressure gauge about (2 bar) before and after the membrane cell. The surplus feed is recycled back through the by-pass stream to the feed produced water container. The permeation flux from the membrane was measured for 2000 min and collected in the container (3). Five levels of pressure were used (1, 2, 3, 4 and 5 bar).
3. Results and Discussion

3.1. Evaluating Of Ultra-Filtration Membrane flux

Effect of TMP On Permeation Flux

Under a constant period of filtration equal to 30 min and when increase TMP gradually from 1 bar to 5 bar amount of permeation flux were increase significantly due to the increase in driving forces across the membrane, as seen in figure 5. 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](image_url)

**Figure 5.** Relationship between TMP and permeation flux.

Effect Of Membrane Fouling On Permeation Flux

Under constant TMP (3 bar) and as time go on, permeation flux decreased gradually, it indicates accumulation of pollutants on the membrane. Due to oil droplet adsorption at the membrane surface and pores. See figure 6.

![Figure 6](image_url)

**Figure 6.** difference between initial and final permeation flux due to fouling of membrane.
3.2. Chemical and Physical Analysis of Treated Water

Table (2) shows the results of the treatment of produced water by ultrafiltration membrane technology and conventional methods.

| Parameter       | Feed water | UFM treatment | Conventional treatment | Conventional +UFM treatment |
|-----------------|------------|---------------|------------------------|-----------------------------|
| pH (value)      | 6.34       | 6.41          | 7.32                   | 7.18                        |
| E.S (ms/cm)     | 132        | 62.66         | 18.89                  | 5.477                       |
| T.D.S (mg/l)    | 111,400    | 37,681        | 11,328                 | 3286                        |
| T.S.S (mg/l)    | 2,500      | 0.014         | 36.48                  | 0.0006                      |
| Sp.Gr           | 1.062      | 1.021         | 1.02                   | 1.016                       |
| Salinity (PPT)  | 140.5      | 38.77         | 10.41                  | 2.39                        |
| Ca+2 (mg/l)     | 5,730      | 1,896         | 1,021                  | 278                         |
| Mg+2 (mg/l)     | 1,142      | 385           | 208                    | 76.4                        |
| Na+1 (mg/l)     | 11,560     | 3,648         | 1,165                  | 266                         |
| K+1 (mg/l)      | 1,860      | 482           | 50.85                  | 12.65                       |
| So-2 (mg/l)     | 12,860     | 4,310         | 2,260                  | 642                         |
| Co3-2 (mg/l)    | 18,226     | 6,132         | 3,398                  | 1,062                       |
| Cl-1 (mg/l)     | 1,432      | 4,576         | 1,993.32               | 498.3                       |
| Oil content     | 644        | N             | 20.75                  | N                           |
| T.O.C (mg/l)    | 121        | 0.076         | 0.082                  | 0.058                       |
| Cd (mg/l)       | 0.02       | N             | 0.012                  | N                           |
| Cu (mg/l)       | 0.485      | 0.143         | 0.329                  | 0.0042                      |
| Fe (mg/l)       | 0.3120     | 0.2641        | 0.0866                 | 0.0652                      |
| Zn (mg/l)       | 1.28       | 1.232         | 0.1119                 | 0.0668                      |
| Cr (mg/l)       | 0.0061     | N             | N                      | N                           |
| Ni (mg/l)       | 0.0542     | N             | N                      | N                           |
| Pb (mg/l)       | 0.031      | N             | 0.078                  | N                           |
| COD (mg/l)      | 380        | 68.4          | 87.6                   | 43.7                        |

The results in the above table showed high removal efficiency for almost all parameter. In this issue about 100% removal for the three parameters oil content, total suspended solids and heavy metal (which consider a big concern of the environment and the human body). The results obtained for heavy metal are in the range of authorised limits. Unfortunately, it is not proper for irrigation or other beneficial used because of some dissolved materials.

Furthermore, when we compare a UF method with Current treatment methods in the field, it seems that it is an ineffective treatment. Lower efficiency and membrane fouling problem are the major drawbacks of UF. Therefore, a combination of the two previous methods was result water with high efficiency than any one of them only.

Anion and cation produced when the salts dissolve in water. These ions make up the basis of conductivity in water. The conductivity value is 5400 μS/cm may consider an acceptable range for poultry drinking water that limited to about 6000 μS/cm and 10000 μS/cm for the most livestock. The recommended TDS for beneficial uses such as stock ponds or irrigation about 1000–3000 mg/L. While the result of TDS equal to 3286 mg/l, which mean it is suitable only for crops that can tolerate high salinity such as wheat and barley.

SAR is a term of sodium adsorption ratio used to evaluate the propriety of water in irrigation. The high SAR effects on the soil by replacing the magnesium and calcium by sodium, which decrease its the ability to form stable aggregates. The permissible ratio for SAR is less than 3 while SAR for the resulting water is 1.3 that's mean there is no effect.
COD used as a measure of the oxidation of the organic and inorganic components in the produced water. COD for the raw produced water was decreased from 380 to 68.4 (mg/l) by using UFM only and, 43.7 mg/l for pre-treated produced water and this value within the permissible range.

4. Conclusion
This paper was a study of the treatment of produced water from Al-Ahdab oil field. (8) a rectangular flat sheet of polyethersulfone ultrafiltration membrane (UFM) used in the experimental work. Preparation of the membrane and Scanning electron microscopy (SEM) in the chemical engineering department in University of technology, Baghdad/Iraq.

The results show a combination of conventional treatment and UFM will improve the characteristic of the resulting water to meets the requirement of irrigation crop that tolerate high salinity and drinking for poultry and livestock. But it still not meet the quality of potable water. On the other hand, pre-treatment before membrane technology reduced fouling of the membrane. Which, considers the major setback of these technologies. Therefore, single technology cannot meet suitable effluent characteristics.

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