



A REVIEW OF OILFIELD WASTEWATER TREATMENT USING MEMBRANE FILTRATION OVER CONVENTIONAL TECHNOLOGY

(Ulasan Mengenai Rawatan Sisa Medan Minyak Menggunakan Teknologi Membran Penapisan Berbanding Teknologi Konvensional)

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Abstract

The oil and gas industry has been a constant developing industry as it is of importance to the maintenance of industrial civilization in its current configuration and play vital roles in many other industries. Some oil and gas industry operations have been accountable of water contamination through by-products of refining and oil slicks. One of the biggest by-products that have raised a critical environment concern is oilfield produced water. Oilfield produced water (OPW) is coproduced aqua liquid phase which originate from well alongside oil phases in normal production process. The content of OPW consists of different type of organic and inorganic mix. Discarding this kind of wastewater can lead to surface pollution especially on water sources as well as soil. Hence, to meet environmental regulations as well as reuse and recycling of produced water, many researchers have focused on treating oily saline produced water. Conventional technologies used to treat produced water consist of clarifiers, dissolved air flotation, hydro cyclones, and disposable filters/absorbers. Typically, additional chemicals for coagulation or settling are needed which are expensive and are incapable of achieving recently required standards of cleanliness. Therefore, researchers have swung to membrane filtration plans because of their capability to minimize extra expenses and surpass issues connected with current advances. Thus, the purpose of this review is to highlight the current and developed membrane technology used in treating the oilfield produced wastewater and its current progress.

Keywords: oilfield produced water, membrane filtration, mixed matrix membrane, oily wastewater

Abstrak

Industri minyak dan gas telah menjadi industri membangun berterusan kerana ia adalah penting untuk mengekalkan tamadun perindustrian dalam konfigurasi semasa dan memainkan peranan penting dalam banyak industri lain. Sesetengah operasi industri minyak dan gas telah dipertanggungjawabkan ke atas pencemaran air melalui tindakan penapisan dan minyak tumpahan. Salah satu yang produk sampingan yang terbesar yang telah menimbulkan kebimbangan persekitaran kritikal adalah air yang dihasilkan medan minyak. Air yang dihasilkan dari medan minyak (OPW) adalah dihasilkan bersama fasa cecair dan fasa minyak yang berasal dari telaga minyak dalam proses pengeluaran normal. Kandungan OPW terdiri daripada pelbagai jenis campuran organik dan bukan organik. Pembuangan jenis air sisa ini boleh membawa kepada pencemaran permukaan terutamanya kepada sumber air dan tanah. Oleh itu, untuk memenuhi peraturan-peraturan alam sekitar serta penggunaan semula dan kitar semula air yang dihasilkan, ramai penyelidik telah memberi tumpuan kepada merawat air masin yang dihasilkan dari medan minyak ini. Teknologi konvensional yang digunakan untuk merawat air yang dihasilkan terdiri daripada clarifiers, pengapungan udara terlarut, siklon hidro dan penapis boleh guna/penyerap. Biasanya, bahan kimia tambahan untuk pembekuan

atau pemendakan yang diperlukan yang agak mahal dan tidak mampu mencapai piawaian semasa kebersihan air. Oleh itu, penyelidik telah beralih kepada teknologi membran pemisahan kerana keupayaannya untuk mengurangkan perbelanjaan tambahan dan mengatasi isu-isu yang berkaitan dengan kemajuan semasa. Oleh itu, tujuan ulasan ini adalah untuk mengetengahkan teknologi membran semasa dan maju yang digunakan dalam merawat air sisa medan minyak yang dihasilkan dan kemajuan semasa teknologi ini.

Kata kunci: sisa medan minyak, penapisan membran, membran matriks campuran, air sisa berminyak

Introduction

The fast growth of oil and gas industry is usually closely related to its vital role in the maintenance of industrial civilization in its current configuration. Virtually almost all economic sectors depend intensely on oil and gas. This ever-emerging industry has raised concern for many nations, mainly because its processes generate large volume of liquid waste [1].

Some oil and gas industry operations have overseen water contamination through by-results of refining and oil slicks. The oil and gas industry the biggest industrial source of discharges of volatile organic compounds (VOCs) which is a gathering of chemicals that add to the arrangement of ground-level ozone and this has raised many concern over the century. One of the biggest by-products that have raised a critical environment concern is oilfield produced water. Produced water is the aqueous liquid phase that is co-produced from a producing well along with oil phases during normal production process. Oilfield produced water contains different types of organic and inorganic contents. Discharging produced water can pollute surface and underground water and soil [1].

In recent years, it is found that universally produced water production is evaluated at around 250 million barrels each day. Since universally produced water production is more than production of oil, water cut has risen to 70%. Because of expanding volume of this waste everywhere throughout the world, the destiny and impact of releasing created water on natural has as of late turned into a noteworthy issue of ecological [2]. Figure 1 shows the estimation of onshore and offshore produced water production since 1990 until 2015. Ferro and Smith [3] forecasted that the production of oilfield produced water will be increased ultimately by years and this has been proven as the oil and gas industry has become a major industry since the early 2000s. The increasing demand in oil and gas industry has increased the production of wastewater which has in turned raised concern in terms of environmental safety.

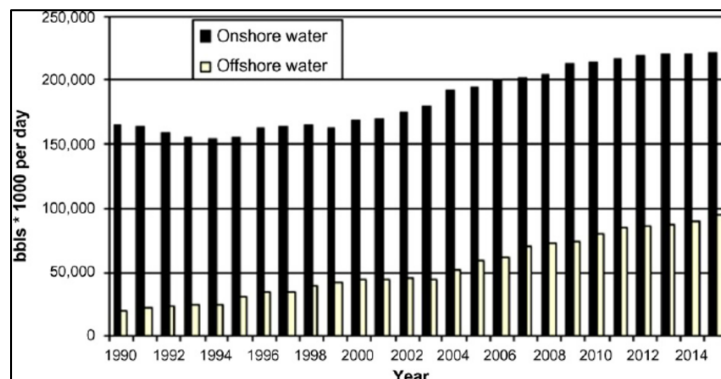


Figure 1. The estimation of produced water since 1990 until 2015 [3]

Historically, produced water was discarded in vast evaporation ponds. In any case, this has turned into an undeniably inadmissible disposal technique from both ecological and social viewpoints. Generally, produced water is often viewed as an industrial waste and coal seam gas (CSG) producers which are currently required to employ

any type of useful re-utilization for it. Currently, more-exacting environmental standards have led to greater efforts being made to treat produced water. Per Malaysia's Environmental Law, Environmental Quality Act, 1974, the Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, 1999, 2000, the limit for oil and grease disposal in the water is 10 mg/L whereby the COD limit is 100 mg/L.

Hence, to meet environmental regulations as well as reuse and recycling of produced water, many researchers have focused on treating oily saline produced water [1]. There are several main contaminants of concern in the produced water which include high level of total dissolved solids (TDS), oil and grease (O&G), suspended solids (SS), dispersed oil, dissolved and volatile organic compounds, heavy metals, radionuclides, dissolved gases, and bacteria.

Generally, treatment of produced water from oilfield involved several stages that include pre-treatment to remove the bulk oil and gas as well as other coarse particle, main treatment that remove small droplets and particles, polishing treatment to remove ultra-small particles and finally optional tertiary treatment to removed dissolved matters and gases. There are different types of treatment that can be employed to achieve those treatments. The treatment of produced water is conventionally expensive and time consuming as capital cost of physical methods and cost of chemicals for chemical treatment of hazardous sludge is high [1]. The main aim in treatment of oilfield produced water is to remove hydrocarbon components. Table 1 shows the summary of type of treatment used in stages involved in treatment of produced water in a simple water treatment plant.

In produced water technologies, there are a few requirements that needed to be addressed to achieve high performance and separation. High recovery is desirable to decrease waste volume and disposal. Besides that, high rejections of contaminants are favored to meeting the stringent discharge requirements. In addition to that, a dynamic treatment should be very robust and comprises of low maintenance to reduce labor and supervision requirement. The treatment should also be flexible whereas it can handle high variation in water quality and quantity. Furthermore, in modular aspect, the technology should have small footprint as well as minimal disturbance.

Table 1. General overview of stages of oily wastewater treatment

Stages	Treatment
Primary	Physicochemical
Secondary	Biological combined with physicochemical
Tertiary	Treating the sample for reuse
Finishing	Sludge treatment (natural/mechanical)

Thus, with environmental regulations in concern and in effort to reduce cost, more researchers are focusing in coming up with novel technique in treating the oily wastewater which aims to reduce the cost as much as possible [4]. Domestic and foreign research institutions have tirelessly studied the matter in-depth and discussed on oily wastewater treatment methods, and the goal is both include of removal of a large amount of oil, considering the removal of dissolved organic matter, suspended solids, soaps, pH, sulfide, ammonia, etc. [5]. Customary physical-chemical strategies utilized for the treatment of oilfield produced water are frequently inadmissible since they are centered around the division of the dispersed oil or the expulsion of disintegrated organic pollutants from the aqueous stage with no synthetic change [6]. Although the produced water is a complex mixture of different contaminations, but, by using suitable and effective technologies it can be treated for various reclamation and re-use alternative options [7].

The environmental concerns regarding oilfield produced water usually due to the polluting impact which caused by numerous aliphatic and aromatic hydrocarbons, polycyclic aromatic hydrocarbons, phenols, and other chemical products. Current technologies used to treat produced water consist of clarifiers, dissolved air flotation, hydrocyclones and disposable filters/absorbers. Typically, without using the technologies, additional expensive

chemicals for coagulation or settling, these technologies are not capable of achieving recently required standards of cleanliness. Thus, operating expenses that enhanced and increased volumes of hazardous waste are produced. Even after a primary process of separation from the oil, the water still contains drops of oil in emulsion in concentrations as high as 2000 mg/L, necessitating further treatment before it may be discharge [8].

Conventional treatment methods of oilfield produced water

There are several conventional methods used to treat oily produced water that has been employed since decades before. The methods include flotation, coagulation, and biological treatment. Both flotation and coagulation are physicochemical method whereas biological treatments make use of anaerobic and aerobic method to reduced COD and BOD levels in the wastewater. However, the conventional treatment methods mentioned are not efficient enough especially when the sample involved has oil droplets that dispersed finely and low in concentration. The conventional way of produced water purification before was primarily involve the separation of oil and water physically by making use of gravity and the effluent was subsequently dump to the environment [9].

Due to different content in oily wastewater, the traditional methods are often failed in obtaining high separation result [10]. Besides that, most of the conventional techniques are only suitable for pretreatment of wastewater for in-situ reuse. It is not as versatile and dynamic hence there's a need for greater and more reliable treatments methods. The refractory nature of oily wastewater has made it difficult for the traditional technique to fully treat it and high success rate is often impossible.

Flotation

Flotation is a process of separating small particles of various materials by treatment with chemicals in water to make some particles adhere to air bubbles and rise to the surface for removal while others remain in water. The conventional dissolved gas flotation system is as depicted in figure 2. Flotation has shorter retention time and higher loading rate. This method has better separation efficiency in removing smaller and lighter particles [11].

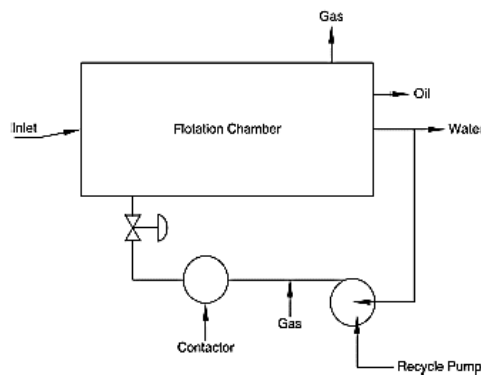


Figure 2. Conventional dissolved gas flotation systems [12]

However, for wastewater containing emulsified oil it is difficult to separate small bubble. There are several factors that is sensitive to the process and can affect the effectiveness of the process which includes pH, pressure, and feed rate. To improve the performance of floatation process, the process parameters and conditions or characteristics of floatable particles need to be determined properly [13]. This made the method more tedious, time consuming and multiple use of instruments and mechanism will increase the cost greatly.

Coagulation

Coagulation is a method which makes use of coagulants which destabilized the colloids by neutralizing the forces that keep them apart as depicted in Figure 3. This method usually coupled with flocculation which aims to agglomerate the fine particles and colloids into larger particles to reduce turbidity. The process comprised of two

stages which involve rapid mixing of dispersed coagulant into water and followed by flocculation for agglomeration of small particles into well define flocs via gentle agitation. This method has simple design, low energy consumption, easy operation and quite versatile as it can be used in different stages of wastewater treatment [14]. This method employed the usage of coagulants and the most extensively used coagulants in wastewater treatment include aluminium sulphate and polyaluminium chloride. Table 2 shows the most widely used coagulants in treatment of oily wastewater. Its mechanism is determined greatly on coagulant selection, dosage, wastewater characteristics and treatment technique.

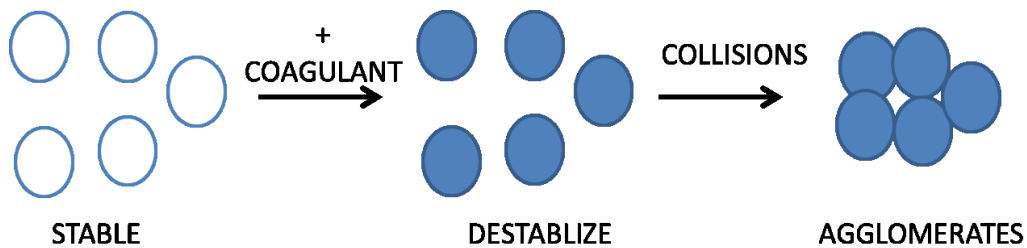


Figure 3. Basic mechanism of coagulation [15]

Table 2. Commonly used coagulant for treatment of oilfield produced water

Coagulant	Properties
Aluminium sulfate	Inorganic salt, water soluble and act as medium strong acid which reacts with alkalis and attacks many metals in presence of water
Ferric chloride	Inorganic salt, water soluble, FeCl_3 in slightly basic water reacts with the hydroxide ion to form a floc of iron(III) hydroxide, or more precisely formulated as $\text{FeO}(\text{OH})^-$, that can remove suspended materials
Polyaluminum chloride	polymeric structure, totally soluble in water, work extremely well at low raw water temperatures

Dosage plays large roles in effectiveness of this method as overdosing the coagulant can cause the particles to restabilized. The use of chemical coagulant can rise another concern in terms of toxicity of alum and polymeric based coagulant whereby it has posed hazard to health. Overdosing of alum in wastewater treatment may lead to high residual of aluminium concentration [16].

Zhang Jin et al. [17] has employed coagulant utilization in treatment of oily wastewater and found that the coagulant has affected the filtration flux in their combined experimental methods. They found that by using coagulant, the filtration flux improved which mainly due to coalescence between the droplets taken together and the consequent the size of emulsion. However, the excess dosage of coagulant has also found to be the reason behind flux decrement.

Biological treatment

Biological treatments make use of microbial metabolism so that the water was dissolved colloidal organic pollutants into harmless substances. The use of anaerobic and facultative digestion has been employed to overcome the oily effluent pollution. Activated sludge process has been the mainstay of wastewater treatment however it is a very energy consuming process. Biological conversion of organic wastes which includes oily wastewater involves four fundamental phenomena which are hydrolysis, fermentation, acefogenesis and methanogenesis [18].

Biological treatments are usually considered as secondary treatment whereby it involves aerobic and anaerobic processes. The employment of mixed bacterial culture has demonstrated to be more advantageous in comparison with pure culture due to synergistic interactions among members of the associations [19]. Due to characteristics of poor nutrients of nitrogen and phosphorus, low BOD/COD ratio, high toxicity, oilfield produced water is difficult to be treated by a simple biological treatment [20].

Lu et al. [21] has developed a field pilot treatment system that employed hydrolysis acidification/bio-contact oxidation system (HA/BCO) as shown in Figure 4 at which air used to produce oxygen-saturated conditions was supplied to the two aerobic tanks through air diffusers, located at the bottom of the tanks, to supply sufficient oxygen to the biomass and to stir the liquid as well as to exfoliate the aged biofilm. The system can achieve the ratio of BOD₅ to COD of 0.24 which is around 65% COD removal efficiency and showed an overall hydrocarbon waste removal efficiency of 68%. Their study proved that biological treatment can be a cheap alternative however yet to prove its efficiency in overall treatment of oilfield produced water.

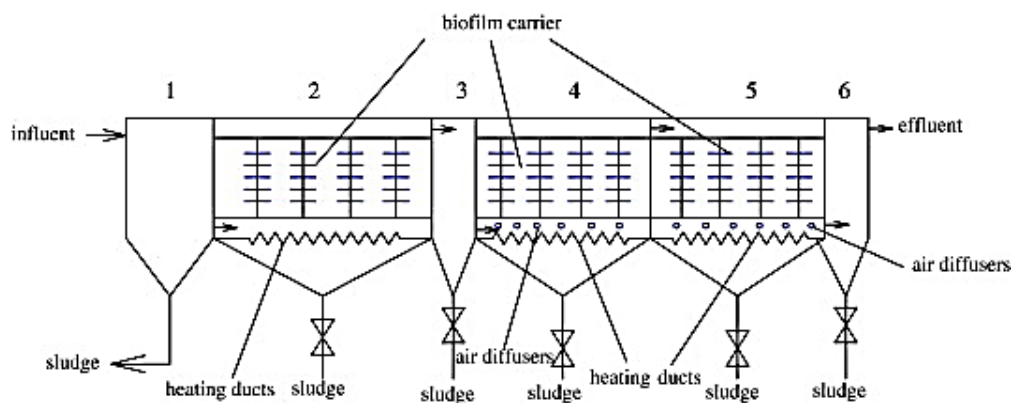


Figure 4. Schematic diagram of the HA/BCO setup. 1. Settling tank a; 2. Anoxic tank; 3. Settling tank b; 4. Aerobic tank a; 5. Aerobic tank b; 6. Settling tank [21]

Membrane technologies in oilfield produced water treatment

Precise investigations of membrane marvels can be followed to the eighteenth century rationalist researchers. Through the nineteenth to mid twentieth hundreds of years, membranes had no modern or business utilizes, however were utilized as research center instruments to create physical/synthetic speculations [26].

Preparatory tests utilizing membrane innovation included isolating certain gasses and were at first led in 1950 [22]. The success of these membrane applications prompted the improvement and use of 219 membrane units in refineries around the globe until roughly 1993 [33], after which extra applications have been produced and utilized. Table 3 shows the advancements of membrane technologies utilization in treatment of OPW. For oilfield produced water treatments, there are many studies that have been conducted showing promising results via application of membrane technology which further details and examples are discussed in next sections.

Type of membrane filtration process

Researchers have swung to membrane filtration plans because of their capability to minimize extra expenses and transfer issues connected with current advances. Polymeric and ceramic membranes are found to be effective in separating the oils, emulsions, and silts from the produced water [8]. The membrane pressure driven procedure depends on the pore size of the layer to isolate the sample segments as indicated by their pore sizes [24]. membrane based operations tested so far include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Also, the coalition of membrane based procedures has been examined as an effective device to treat the produced water to meet the quality benchmarks of environmental standards [25].

Table 3. Advancement in membrane utilizations for OPW purification

Reference	Study	Inference
White et al. [27]	Polyimide membrane for separation of solvents from lube oil	Separate small molecules of methyl ethyl ketone solvent from lube oil
Buffle et al. [28]	A generalized description of aquatic colloidal interactions: The three-colloidal component approach	Utilization of UF Membrane for the development of filtration process that led to the upgrade visbroken residual products by UF during thermal cracking
Yu et al. [29]	Treatment of oily wastewater by organic–inorganic composite tubular ultrafiltration (UF) membranes	After UF treatment, there's significant decrement of oil and suspended solid content
Zhang et al. [30]	Development of a sulfated Y-doped nonstoichiometric zirconia/polysulfone composite membrane for treatment of wastewater containing oil	Oil retention is 99.16% and oil concentration in the permeation is 0.67 mg/L
Salahi et al. [31]	Nano-porous membrane process for oily wastewater treatment: Optimization using response surface methodology	Nano-porous membrane is efficient for the treatment of petroleum refinery waste water
Huang et al. [32]	Treatment of oily waste water by PVP grafted PVDF ultrafiltration membranes	Ultrafiltration performance of oil wastewater was improved greatly and flux recovery of PVDF–PVP membranes cleaned using NaOH solution exceeded 90%.

Microfiltration

Microfiltration (MF) is a kind of physical filtration process where a polluted liquid is gone through an exceptional pore-sized layer to partitioned microorganisms and suspended particles from procedure fluid. It has significant applications in simple dead-end filtration for water, sterile fruit juices and wine, and aseptic pharmaceuticals [33]. However, not all applications that benefit from MF operate successfully in the dead-end mode. Recent innovation in microfiltration has mainly concerned the development of cross-flow filtration technology and membranes [26]. Thus, MF need to be coupled to other methods to achieved successful result.

There are numbers of research done in investigating the effectiveness of MF membrane on treatment of oily wastewater. Studies done by Kiss et al. [34] found that the oil emulsion can be separated with MF PTFE membrane however the retention has been decreased in presence of emulsifier due to arrest of oil coalescence.

A study done by Nandi et al. [60] confirmed that the MF membrane can be used for treatment of oil water emulsion to yield permeate containing oil concentration less than 10 mg/L. Some other research focused on the flux decline of the membrane to evaluate the effectiveness of MF membranes. Modeling of permeation flux decline during MF of oily wastewater in membrane with experimental results is important in evaluating membrane fouling [35].

Besides that, research done by Wang et al. [36] observed that for the treatment of factory emulsified oily wastewater, MF membrane could not be fully regenerated by using conventional cleaning method and combination of filtration with interval aeration would enhance the performance of the membrane. Hence, the use of MF operations would most likely result in better separation performance if coupled with other operations.

Ultrafiltration

Ultrafiltration uses a finely porous membrane to separate water and micro solutes from macromolecules and colloids. The average pore diameter of the membrane is in the 10 – 1000 Å range. Compared to conventional method, the use of ultrafiltration method is more energy saving and have consistent product quality. Typical filtration processes for emulsified oily wastewater can reach an oil rejection rate of 80 – 99% [37]. The application of ultrafiltration (UF) to the separation of oil emulsions (O/W) from oily wastewater streams has been extensively examined and it is observed that the ability of UF membranes in separating oil in water emulsions with high TOC rejection [39]. There are few researches has recorded successful application of UF membrane in treating wastewater.

Recently Abdullah et al. [40] has successfully synthesized a new type of adsorptive microporous UF membranes that were composed of an organic polysulfone (PSf) and inorganic HFO nanomaterial and has helped in removal of lead in the wastewater. Meanwhile Luo et al. [41] has employed ultrafiltration of oil-water separation using triangle-shape tri-bore hollow fibre membrane from sulfonated PSf and the result has shown that the water permeates after filtration are very clear with low turbidity. These researches show the promising ability of UF in oil-water separation and there are different opportunities in enhancing its ability even further.

Nanofiltration

Nanofiltration is a membrane filtration-based strategy that utilizes nanometer estimated barrel shaped through-pores that go through the membrane at 90°. Nanofiltration membrane has pore sizes ranging from 1 – 10 nanometers, smaller than that used in microfiltration and ultrafiltration, but just larger than that in reverse osmosis (RO). NF generally focused to expel just divalent and bigger particles. Monovalent particles, for example, sodium and chloride will go through a nanofiltration film, in this way a considerable lot of its uses include de-salting of the procedure stream.

This promising procedure has pulled in expanding consideration over late years because of the advancement of new applications in the few regions, for example, material industry (expulsion of color from waste wash water), paper, plating industry (constraining of consumption of clean water by reusing waste water similarly as the release waters don't contain too high measures of monovalent particles), drinking water generation and so forth.

Reverse osmosis

Reverse Osmosis (RO) utilizes a semipermeable film to evacuate particles, atoms, and bigger particles from drinking water. In reverse osmosis, a connected weight is utilized to overcome osmotic weight, a colligative property, that is driven by substance potential contrasts of the dissolvable, a thermodynamic parameter. The utilization of RO innovation in wastewater treatment has been accounted for since the 1970s. RO is the finest partition membrane process accessible, with pore sizes range from 0.0001 µm to 0.001 µm. RO can hold generally all atoms aside from water and because of the measure of the pores, the required osmotic weight is essentially more prominent than that for MF. Figure 5 depicts the commonly employed RO membrane used for water treatment. Due to both RO and NF small size pores, they are not preferable in treatment of oily wastewater.

Al-Jeshi et al. [42] has conducted an experiment to test the ability of RO membranes to treat water containing up to 50% (by volume) of oil and to evaluate the effect of oil contamination on membrane performance whereby it is found that the RO membrane employed can only treat wastewater with up to 50% oil contamination. Besides having questionable ability in separation of oil in water emulsion, the high-pressure pump supplies the pressure needed to push water through the membrane, even as the membrane rejects the passage of salt through it which makes the process make use of more energy compared to other separation methods.

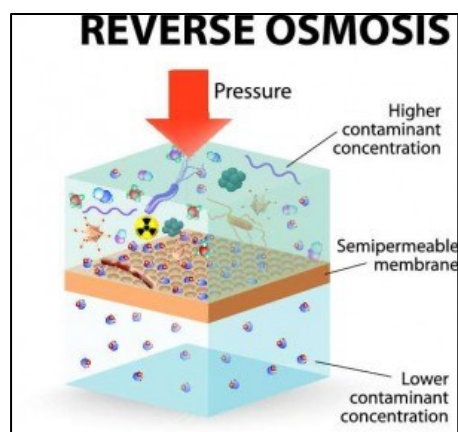


Figure 5. Mechanism of RO [42]

Type of membrane for oilfield produced water treatment: Polymeric membrane

Polymeric membrane is usually classified as synthetic membrane and is the most widely used in oil-in-water separation. Polymeric membranes, many organic polymers including crystalline and amorphous, glassy, and rubbery, are suitable membrane fabrication that targets oil-in-water separation. The preparation methods involve phase inversion, interfacial reaction, coating, stretching and etcetera [43]. Synthetic membranes such as polymeric membranes are the most commercially utilized membrane in oily wastewater separation with estimated sales of \$2 billion in 2003 worldwide. Utilization of synthetic membranes in purification of oily wastewater such as produced water has better performance compared to the organic membranes. As compared to its biological or organic counterparts, polymeric membrane possesses variety of advantages especially in industrial application such as oil-in-water separation. Due to its wide variability of barrier structures and properties, polymeric membrane has ultimately been the first choice in development of oily wastewater treatment technologies. Its robustness has given the possibility to control the density, size, size distribution, shape and vertical alignment of membrane pores making it easier to be customized to suit the need of any certain application.

The ability of the polymeric membranes to be designed accordingly and with wide rooms for customization has given it upper hand in competing with its organic counterparts. Currently, there are two commercial designs used using polymeric membrane. Membrane filters are usually manufactured as flat sheet stock or as hollow fibers and then formed into one of several different types of membrane modules [44]. Polymeric membranes are generally classified by the nature of the materials, the membrane morphology, geometry, preparation method, separation regime and processes.

The polymeric membrane possessed three significant structural magnitudes namely thermocular, microcrystalline and colloidal. Thermocular level of the membrane is like the chemical nature of the polymer and it is responsible for the membrane's microcrystalline nature. The microcrystalline is the level at which play an important part for both the transport and mechanical properties of the membrane; and finally, the colloidal that involved macromolecules aggregation and affect the pores properties such as pore size, size distribution, density, and void volume [45]. The utilization of polymeric membrane in purification of oilfield produced water is still limited and only few literatures have been done using it as sample feed. There are a few researches that have been done in applying polymeric membranes and integrating it into the treatment technologies of oilfield produced water.

Xu and Drewes [45] in their report has tested thin-film composite polyamide membranes at which was applied in two standard laboratory cross-flow membrane filtration units to purify the water sample collected at a natural gas production facility in Eastern Montana. Their research was focused on salt rejection, iodide recovery and operating performance at which they employed bench-scale filtration tests and in situ characterization techniques to examine the viability of the selected membrane in multi-beneficial use of produced water. The research has concluded that

the studied polymeric membranes having high salt rejection and permeability, provide a viable technique for produced water treatment and beneficial reuse.

Besides that, Mondal et al. [46] have employed three layers' membrane distillation system which consists of polyester, polysulfone and polyamide to purify produced water that was obtained from three different sources. The membranes have different surface roughness and rejection behavior for the oily feeds. In their study, they had determined the variation of permeate flux with time during dead end filtration. Their results conclude that the usage of different polymeric membranes have given positive output at which all three successfully displayed minimum reduction of flux after tested with produced water. They have also concluded that membrane filtration could be a viable process for produced water treatment.

Besides tested on its own, the polymeric membrane has also been integrated to different technologies to further improve the system's performance. Qiao et al. [47] has developed a pilot-scale plant involving aeration tank, air floatation, sand filter and UF has been designed and performance characteristics of the hybrid process have been studied for treatment of oilfield produced water. The UF membrane used was a PVC alloy hollow fiber membrane. Their research resulted in the SS and oil removal in the UF unit of about 70% and 90%, respectively, and their respective contents in the effluent of UF are less than 0.5 mg/L and 1.0 mg/L meet the required standard for discharging or injection water.

A. Fakhru'l-Razi et al. [7] had employed two different polymeric membranes namely polyethersulfone (PES) and polyvinylidene fluoride (PVDF) in their membrane sequencing batch reactor which their coupled with utilization of isolated tropical halophilic microorganisms. It was found that the isolated microorganisms played an important role in the biodegradation of the pollutants and membrane separation was required for ensuring a stable permeate quality. Their research has proven that it is possible to employ polymeric membrane in treatment of produced water.

Ceramic membrane

Ceramic membrane has reputable ability in treatment oily wastewater especially in oilfield produced water. It has excellent membrane reliability and stability which contribute to its high operation safety. Commonly, ceramic membrane has an asymmetrical structure with a viable top layer framed by coating or casting. Figure 2 shows the theoretical portrayals of ceramic membrane which are usually asymmetrical [48]. Sol-gel process usually produces typical ceramic membranes. In this process, particle dispersions are forced to agglomerate. To produce continuous and porous layers, particles of decreasing size are deposited and the membrane is sintered at extreme temperature. This resulted in asymmetric structure of the membrane. Pore size and characteristics of the selective layers of the membrane may be customized by using grain size and type of particles as basis.

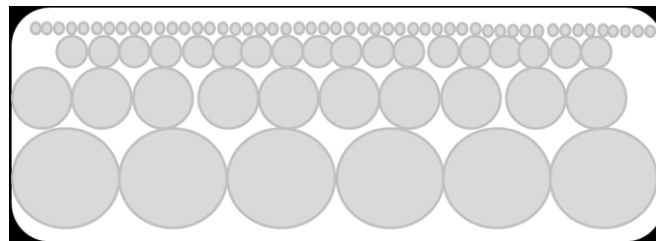


Figure 6. Theoretical portrayals of asymmetrical ceramic membrane

Lately, there is a developing enthusiasm for utilizing ceramic membrane for oily wastewater treatment since organic membranes affected by polar solvents, chlorinated solvents, and high oil fraction. Weschenfelder et al. [49] in their research have evaluated the commercialized Zirconium (ZrO_2) performance in treating oilfield wastewater using synthetic oil effluent. The membrane performance was tested in laboratory and results shows that the membrane could generate a permeate stream with an oil and grease content lower than 5 mg/L, which enables the reuse of

water. The research also shows that the cost estimation of using the ceramic membrane and it is found that there's increase of cost in using the membrane.

On the other hand, M. Ebrahimi et al. [8] has done characterization of five different ceramic membranes for oilfield produced water treatment which include MF and UF Al_2O_3 and MF and UF TiO_2 membranes and concluded that the tested membrane has been proven to be cost efficient for oil removal from oilfield produced water. However, the membranes have failed to reach an acceptable level of removed TOC. Their research has also highlighted the obstacles in treatment of produced water using membrane technologies which include membrane fouling, reduced trans-membrane flux and membrane cleaning.

Abadi et al. [50] have also employed tubular ceramic MF membrane using ($\alpha\text{-Al}_2\text{O}_3$) in treatment of refinery oily wastewater. Their research has resulted in 95% TOC removal efficiency which abides to the National Discharge Standard. They proposed the system to replace the conventional methods as it has higher efficiency rate as well as better separation for oil in water emulsions.

Li and Lee [48] in their research have also utilized ceramic membrane in purification of produced water. Their research investigates the micro- and mesoporous inorganic membranes, specifically clay membranes and zeolite membranes, on desalination of produced water. The study utilizes few ceramic membranes from different materials such as macroporous α -alumina (pore size $\frac{1}{4}$ 0.2 mm, Pall), disk-shaped stainless steel (0.5 mm, Mott), and Zr-coated stainless steel (pore size $\frac{1}{4}$ 0.1 mm, Pall), MFI-type zeolite membranes on porous α -alumina supports and laboratory fabricated clay membranes. The research concluded that microporous ceramic membranes are very effective for reducing concentrations of oil and suspended solids from produced water whereby clay and zeolite are microporous materials that show promising application in novel membrane fabrications that have potential for use in produced water deionization. MFI-type zeolite membranes formed on commercial tubular substrates give over 99% ion rejection at a water flux of approximately $10 \text{ kg/m}^2\text{h}$.

Besides using ceramic membrane on its own, there's also interest in coupling the ceramic membrane with other operation. Rahman et al. [51] has developed cross flow membrane bioreactor which utilizes hollow tubular alumina membranes in refining oily wastewater from refinery. They set up a laboratory-scale bioreactor comprised mainly of tubular ceramic membranes, aeration tank, and circulation pump. Their investigations resulted in COD removal efficiency of more than 93% and performance of the unit when operated with MLSS of 3000 mg/L was impressive with changing the influent mass loading from 30 to 65 g/day.

Different points of interest of ceramic membranes are identified with the capacity to treat slick waters without extra chemicals and its resistance against mechanical, thermal, and chemical stress, permitting a superior recovery of the layer with harsh chemical cleanings [49]. The essential preferred standpoint of utilizing ceramic membrane is the capacity to achieve the current regulatory treatment goals with no chemical pretreatment [8]. Besides that, benefits of ceramic membranes include bigger pore and enhanced hydrophilic surface which leads to higher fluxes, compared to organic membranes. The mechanical, thermal, and chemical resistance of the ceramic membrane has helps in increasing performance membrane and enhances the recovery.

Their ability to stand in harsh environment has open the way for ceramic membranes to be used in produced water purification [37]. For example, the zeolite membranes have high tolerance of organic solutions, excellent corrosion resistance, and very reliable under harsh operating conditions, i.e., high temperatures, high surface shear rates, or the presence of oxidative solvents [48].

However, utilization of ceramic membrane has its own challenges. There's always need to curb the problems regarding sealing which often caused by the thermal expansion of ceramic membrane and module housing. Besides that, its mechanical built which naturally more brittle makes it more sensitive and require a more tedious and careful handling. This diminishes its ability to be fully automated when integrated into other operation.

Notwithstanding that, the significant obstruction including ceramic film is flux misfortunes. Focused polarization frames close to the film surface amid the partition procedure which is administered by liquid science, membrane

properties and hydrodynamics [48]. Furthermore, conventionally the commercialized ceramic membranes (such as Al_2O_3 , SiO_2 , ZrO_2 , and TiO_2) are too expensive for oil in water emulsion treatment [52].

Advantages of membrane technologies and current challenge in treatment of oilfield produced water

The usage of membrane filtration technologies such as UF, MF and NF has posed several advantages in treatment of oilfield produced water. Firstly, the technology is more widely applicable across a range of industries such as off shore and on shore oil exploration. The operation is practically easy to handle and require minimal supervision. In addition to that it can be fully automated to eliminate labor and human error. Besides that, operators have turned to membrane filtration schemes due to their potential to minimize additional costs and disposal issues [8]. The transport selectivity of the membrane is a unique characteristic that draws attention for its utilization in OPW purification.

Membrane systems can dominate over more complex treatment systems in terms of treating oily wastewater that is high in oil content, small particle size with flow rates more than $150 \text{ m}^3/\text{h}$. This is much preferable especially for medium and large offshore platforms. Besides that, utilization of membrane technologies has eliminated the usage of chemical additives and coagulant making it more environmental friendly and cost effective [1].

Membranes are favored over other technologies for water treatment, such as disinfection, distillation, or media filtration because, in principle, they require no chemical additives, thermal inputs, or require regeneration of spent media [53]. In addition to that, due to simple operation and mechanism, the utilization of membrane technology has also opened the opportunities to the building of small and compact treatment plant. These possibilities are even more favorable especially in offshore facilities which often have limited space. Membrane equipment has also smaller footprints which contribute to its environmental friendly properties.

Besides having simple operational mechanism, membrane has high reusability properties which allow recycling of selected waste streams. This reduces operational cost as well as increased the sustainability in terms of resources and energy. The use of membrane operation can be independent without pre- or post-treatment which eliminates extra costs and making it more economically feasible.

In addition to that, there's vast opportunity of mixing the membrane with other technologies to further improve its performance. Its robustness allows rooms for further improvement and integration in development of better performing treatment technology. Being a versatile technology, employment of membrane can open more doors towards enhanced and excellent purification of wastewater especially produced water. Their reliability can be exploited to be adopted in the petroleum industry to satisfy the industry requirement for discharge and reuse standards [33]. Table 4 depicted the advantages of membrane technology over conventional method.

Despite its robust and versatile characteristics, membrane technology has stumbled across various challenges that hinder its performance in purification of oilfield produced water. One of the major hindrances of membrane technology is fouling. Fouling is caused by buildup of materials which can take up different form such as adsorption, pore blockage, deposition, and gel formation [55].

Fouling caused severe decline of flux which deter the membrane performance. It also contributes to the difficulties in membrane cleaning which add up extra steps in the treatment operation. Based on the sample to be treated, causes of fouling may vary. For oilfield produced water treatment, contaminants such as alumina, ammonia, organic matter, scale compounds, boron and silica can be the ones that contribute to membrane fouling during the treatment process [23].

These chemicals can lead to scaling at which concentration will increase and change the pH. This will lead precipitation of salt and hydroxide which are the main factors for scaling. Other than that, the accumulation of small molecules might tend to have strong interactions with some polymeric membranes. For instance, anti-foaming agents such as polypropylene glycols have tendency to strongly adhere to certain polymeric membrane and thus promotes pore blocking [56].

Table 4. Comparison between conventional method and membrane technology

Conventional Method	Membrane Technology
Conventional techniques are only suitable for pre-treatment of wastewater for in-situ reuse [54]	Less complex & preferable for medium and large offshore platforms. [58]
Large amount of energy and chemical additives required, economically unfit and lower size molecules difficult to settle down [54]	No chemical additives, thermal inputs, or regeneration of spent media [54]
Very slow and complex process and required more place [58]	Simple operational mechanism [59]
Often involved spent chemical that in return add on to the chemical pollutants [59]	High reusability properties which allow recycling of selected waste streams [54]
Limited room for improvement as most of the technique are rigid and exacting [59]	Robust, allows rooms for further improvement and integration in development of better performing treatment technology [60]

Besides fouling, another drawback that membrane technology possessed is sludge formation. This challenge often emerges in membrane bioreactor (MBR) which involved activated sludge removal. MBRs can be broadly defined as systems integrating biological degradation of waste products with membrane filtration [58]. This system has been integrated broadly in treatment of refinery wastewater as well as in upstream processing in oil and gas industry. The sludge form will eventually be released to the sea which in turns contribute to the severe sea pollution and pose harm to the surrounding ecosystem.

Drawbacks such as fouling and sludge formation can affect the performance of the membrane operations as it deters the transmembrane pressure as well as membrane flux. Pore blocking will also cause the membrane to function poorly after a few usages. In addition to that, there's need to add in membrane cleaning stage for the membrane to be reused. The cleaning stage might involve chemicals and additives which in turns will add on the pollutants in the final effluent from the technology.

Conclusion

Oilfield produced water has delicate and complex content and may vary depends on different factors. Each location has their own complex content making it difficult to develop technologies that can suit each one of the produced water. This has made it one of the toughest wastewater to be treated. However, with its extended versatility and vast opportunities its offer has made membrane filtration as one of the most suitable technology to be employed in purification of produced water. The readiness of membrane technology to be customized and integrated into other existing technologies making it possible to treat the complex oilfield produced water. Despite being simple in terms of operation, employment of membrane technology has greatly improved the separation of different components in oilfield produced water. It has been the greatest contender in terms of purification performance compared to other conventional and existing technologies. It has enabled the utilization of single treating unit with little to no need of pre or post treatment stage. Being highly customized, the membrane technologies offer different rooms for the development of better and enhanced purification system for reusing and filtration of oilfield produced water. It is a highly potential technology that should be explored more in future.

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