Desalination and Water Treatment

57 (2016) 14317–14335 July



www.deswater.com

doi: 10.1080/19443994.2015.1072585

Membrane operations for produced water treatment

Enrico Drioli^{a,b,c,d}, Aamer Ali^b, Young Moo Lee^{e,f}, Sharaf F. Al-Sharif^g, Mohammed Al-Beirutty^h, Francesca Macedonio^{a,b,*}

^aNational Research Council - Institute on Membrane Technology (ITM–CNR), via Pietro BUCCI, c/o The University of Calabria, cubo 17C, 87036 Rende CS, Italy, Tel. +39 0984 492039; email: e.drioli@itm.cnr.it (E. Drioli), Tel. +39 0984 492012; Fax: +39 0984 402103; email: francesca.macedonio@unical.it (F. Macedonio)

^bDepartment of Environmental and Chemical Engineering, The University of Calabria, Rende CS, Italy, Tel. +39 0984 492014; email: amir_hmmad@hotmail.com (A. Ali)

^cWCU Energy Engineering Department, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133791, South Korea ^dCenter of Excellence in Desalination Technology, King Abdulaziz University, Jeddah, Saudi Arabia

^eDepartment of Energy Engineering, Hanyang University, Seoul 133791, Republic of Korea, email: ymlee@hanyang.ac.kr ^fSchool of Chemical Engineering, Hanyang University, Seoul 133791, Republic of Korea

⁸Centre of Excellence in Desalination Technology, King Abdulaziz University, Jeddah, Saudi Arabia, email: sfalsharif@kau.edu.sa ^hFaculty of Engineering, Department of Thermal Engineering and Desalination Technology, King Abdulaziz University, Jeddah, Saudi Arabia, email: mbeirutty@kau.edu.sa

Received 9 January 2015; Accepted 12 June 2015

ABSTRACT

Growing energy demand associated with improved living standards and rising population has increased the consumption of petroleum-based energy sources. To bridge the gap between demand and supply of petroleum-based energy resources, enhanced oil recovery and exploration of new nonconventional resources including shale gas, coal bed methane gas, and tight gas have gained popularity. These new techniques, however, use relatively fresh water and produce huge volumes of highly contaminated produced water. From compositional and potential treatment options, bilge water can also be included in the category of produced water. This work provides an overview of the investigations carried out for the removal of oil and greases using a membrane bioreactor and various other membrane operations. An analysis of a current and future scenario of produced water generated through conventional and nonconventional sources of energy and the perspective of produced water treatment in Saudi Arabia are also given. Finally, a cost estimation for the treatment of produced water using membrane operations is discussed.

Keywords: Produced water; Produced water treatment; Membrane operations

1. Introduction

Despite the increasing emphasis on the use of alternative and renewable resources for energy, the

role of oil and gas in modern civilization is well known and demand for them has even accelerated. It has been estimated that the daily consumption of petroleum will increase to 106.6 million barrels by 2030. Like all other industrial activities, the production of oil and gas is also associated with the generation of liquid waste

^{*}Corresponding author.

^{1944-3994/1944-3986 © 2015} Balaban Desalination Publications. All rights reserved.

Table 1

streams, mainly wastewater that accounts for 80% of the wastes for newly drilled oilfield wells and up to 95% for the mature wells [1]. The wastewater produced by the oil and gas industry is referred to as oilfield produced water or natural gas produced water or produced water (Fig. 1). Global produced water production is 250 million barrels per day [2], whereas in the US the reported average production is 10 bbl/bbl of oil [3]. Recent and forecasted surge in volume of produced water in the world and in North America since 1990 and forecast in 2025 has been addressed in some recent studies [2,4]. By 2030, an investment of 1 trillion dollars will be required to maintain the production of oil and the major part of this investment will be spent for handling the waste [4,5].

At the moment, the most documented information about volume, characteristics, and management strategies of produced water (and in particular of shale gas-based produced water) is based on the reservoir established in the US.

Regarding produced water composition, this is determined by its source, geographical location and also varies with the life period of the well.

Table 1 summarizes natural gas and oilfield produced water parameters.

The main sources of oilfield produced water are the water injected into the reservoir to maintain the high hydraulic pressure and the water that breaks through from the outside into the reservoir as the oilfield gets mature. Additionally, it contains all the chemicals added during the production process. In general, oilfield produced water is a complex mixture of different components including organic and inorganic fractions, dissolved and dispersed oils and greases, production chemicals, formation water, dissolved gases, and production solids. Benzene, toluene, ethylbenzene, xylene (BTEX), polyaromatic hydrocarbons, and phenols constitute the main fractions of dissolved and dispersed oils, whereas the mineral or

	Minimum value (ppm)		Maximum value (ppm)		
Parameter	OFPW	GFPW	OFPW	GFPW	
pН	4.3	3.1	10	7	
Conductivity	_	42,00	_	586,000	
TDS	_	2,600	_	360,000	
TSS	1.2	14	1,000	5,484	
BOD	_	8	_	2,870	
COD	_	2,600	1,220	120,000	
Aluminum	310	0	410	83	
Arsenic	0.005	0.004	0.3	151	
Barium	1.3	0	650	1,740	
Bromide	_	150	_	1,149	
Chromium	0.02	0	1.1	0.03	
Copper	0.002	0	1.5	5	
Iron	0.1	0	100	1,100	
Lithium	3	18.6	50	235	
Magnesium	_	0.9	_	4,300	
Nickel	_	0	_	9.2	
Potassium	24	149	4,300	3,870	
Silver	0.001	0.05	0.15	7	
Sodium	132	520	97,000	120,000	
Strontium	0.02	0	1,000	6,200	
Zinc	0.01	0	35	5	
Benzene	0.03	0.01	35	10.3	
Oil/greases	2	2.3	565	60	

Constituents of natural gas and oilfield produced water [2]

Notes: (-) not given, OFPW: Oilfield produced water, GFPW: Gas field produced water.

inorganic components include various anions and cations, heavy metals, and radioactive elements [6].

Produced water from gas wells is enriched in small molecular aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (Table 1) and is, therefore, considered more toxic than that from oil wells. The toxic ratio of gas and oilfield produced

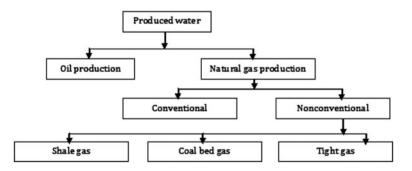


Fig. 1. Main sources of produced water.

water proves to be 10 [7]. The difference in volume from the two resources (60% of the produced water in the world comes from the oilfields) is however significantly large, thus counterbalancing the overall harmful impact. Besides the toxicity, the other characteristics of the water including pH and chloride contents from two sources may also significantly differ.

In both cases, the elevated concentrations of heavy metals (including beryllium, cadmium, chromium, copper, iron, lead, nickel, silver, and zinc) along with the natural radioactive radionuclides and the hundred ppm of organic matters speak fairly about the toxic nature of the produced water. The diluted and treated form of produced water mixed with seawater does not create environmental hazards; however, in the case of discharge near to the coastal areas or onshore, the high toxicity of the components of produced water creates serious hazards to human and other living beings. Moreover, the long-term discharge of the water containing even small fractions of hydrocarbons has serious consequences. According to the US Environment Protection Agency, the presence of benzene can cause cancer and other diseases; therefore, special attention must be focused on the treatment of produced water before discharging into the environment.

Another type of wastewater that can be considered a subcategory of produced water is "bilge water." Bilge is the term used to describe the lowest compartment on a ship where water and oil mainly leaked from the ship accumulate besides the piping and other mechanical and operational resources. The composition of bilge water comprises oil, lubricants, cleaning fluids, solvents, urine, and other similar wastes. Both gravity separable and emulsified phases are present in bilge water and both require attention for successful treatment. The off-board discharge of bilge water is forbidden by law. Bilge water can be either accumulated within the ship in holding tanks and discharged to the reception facilities or can be treated on board, according to the availability of the facility. Tomaszewska et al. [8] have estimated bilge water production as 0.5–50 m³ per day per boat and contributes as much as 20% of the total production of oily water worldwide.

Taking into account that most of the oil- and gasproducing regions lie in the water-stressed zones (which is particularly true for the Middle East, Africa, and southern parts of North America, www.data pages.com, and Inter Press Services, www.ipsnews.net), the general tendency is to treat and reuse produced water, focusing on efforts to find efficient and cost-effective treatment methods to remove pollutants as a way to supplement their limited fresh water resources. Reuse and recycling of produced water include underground injection to increase oil production, use for irrigation, livestock or wildlife watering and habitats, and various industrial uses (e.g. dust control, vehicle washing, power plant makeup water, and fire control) [2]. The management decision is purely based on economics and a detail of various considerations affecting the final decision can be found in reference [9].

The state-of-the-art practice for wastewater treatment includes various physical, chemical, and biological methods, leaving produced water disposal as the final option. The main demerit of discharge is its environmental impact due to the pollution of soil, fresh and underground water caused by the dissolved organic compounds, and chemicals and heavy metals present in the produced water; however, their longterm effects on the environment are not fully documented and understood so far. On the other hand, the new stringent rules and regulations emphasize more effective treatments.

The main purpose of the present paper is to summarize current technologies and in particular membrane technologies available to treat produced water, underlining advantages and drawbacks, and to discuss future development needs to meet discharge, reuse, and recycle standards.

2. Case study: produced water management perspectives for Saudi Arabia

A large amount of produced water is present in Saudi Arabia. In this country, a better understanding of the produced water characteristics, the present management practices, the technical challenges, and the potential areas for future technology development can be gained by first reviewing briefly its origin.

Large quantities of seawater are treated at a central plant in Qurayyah. The present capacity of the Qurayyah seawater treatment plant is 1,40,00,000 barrels per day (16,70,000 m³/d) [10]. The treated seawater is then transported through six large cross-country pipelines over great distances, passing through a number of intermediate stations, to a system of more than 600 injection wells along the flanks of two major oil fields, Ghawar and Khureis, where it is used for oilfield pressurization [10].

The raw crude oil mixture coming out of the production wells is sent to a gas oil separation plant, where a series of operations is carried out in order to separate the various phases present. Since the water used for oil field pressurization is seawater, the salinity of the produced water is typically very high. An indication of the quality of the produced water can be gleaned from the typical water analysis presented in Table 2, taken from Alkhudhiri et al. [11].

Sodium (ppm)	65,372	Chloride (ppm)	119,437
Calcium (ppm)	14,161	Sulfate (ppm)	573
Magnesium (ppm)	2,773	**	
Potassium (ppm)	2,671		
Strontium (ppm)	409	TDS (ppm)	187,440
Barium (ppm)	5.52	Hardness (ppm)	53,621
Boron (ppm)	31.7	Alkalinity as CO_3^{-2} (ppm)	0
Lithium (ppm)	5.6	Alkalinity as HCO_3^- (ppm)	82.4
Silicon (ppm)	2.96	Total alkalinity (ppm)	119

 Table 2

 Representative analysis of produced water from the Arabian Gulf [11]

The high salinity of produced water in Saudi oil fields makes it very challenging to desalinate or reuse for anything other than re-injection into the oil field. Re-injection decreases the quantity of seawater needed, which is the main management strategy practiced at present. Even this reuse purpose, however, places certain demands on the quality of the injected water for safe continuous operation of the production wells and the prevention of blockages at various stages. The prevention of scale formation is one of the quality requirements. Often there can be significant quantities of barium and strontium in the formation rocks, and when seawater is used for injection, the high levels of sulfate typically present in seawater can lead to precipitation of the sparingly soluble Ba and Sr sulfates. This can lead to scale formation and associated problems. In such cases, there may be a need to lower the levels of sulfate in the water before injection. This can be achieved by various means, notably nanofiltration is particularly effective for this purpose.

The pore size characteristics of the reservoir formation and the need to preserve its permeability can be translated into specifications on the maximum allowable particle size in the injected water. Suspended particles larger than the allowed size can lead to blockage of the formation pores and consequent decrease in production, and thus must be removed from the produced water if it is to be re-injected. Similarly, oil suspended in water can have a detrimental effect on the process of re-injection, and must therefore be reduced and controlled.

With the increasing adoption of enhanced oil recovery technologies, the composition of oilfield produced water will increasingly contain additional components that need to be treated. For example, in the practice of polymer flooding long chain polymers are added to the injected water in order to increase the viscosity, thus achieving a better sweep of the oil in the formation. Along these lines, the Industry Technology Facilitator (ITF), a nonprofit organization owned by a group of major oil and gas companies,

whose objectives include the identification of technology needs for the industry, issued a call for proposals (CFP) in May 2012 [12] focusing on produced water management in the GCC states. The CFP issued by ITF identified several key challenges related to produced water management, the first of which related to the treatment of water with back produced polymer where polymer flooding is used. The oil industry is interested in the development of a treatment technology that can separate the back produced polymer from the produced water, preferably without degrading the polymer, thus allowing it to be reused. The treatment technology sought needs to be robust in terms of the range of viscosities it can handle (up to 60 cP). In addition to the separation and recovery of injected polymers, there is also a need for desalination technologies that can cope with the presence of back produced polymer in the feed water.

The other major challenge, or group of challenges, identified by the ITF relates to the safe disposal or re-injection of produced water in order to comply with local legislation. The industry acknowledges the potential risk of contaminating the water table if the produced water is not treated effectively before disposal, and current treatment technologies have not been entirely satisfactory in meeting set limits [12]. The Regional Organization for the Protection of the Marine Environment (ROPME) protocol for overboard discharge is 15 mg/L oil in water (OIW), and local Environment Ministries set a limit of 40 ppmv OIW.

The huge volumes of water that will need to be treated, expected to reach 100,000 bpd in the next 3 years [12], makes this a formidable task. Notably, increasing volumes of water that must be handled by produced water treatment systems means that these systems can become bottlenecks for increasing or continued oil production. This demands treatment technologies that are reliable and robust enough to be implemented on a large scale while minimizing disruptions to the oil production process.

There is also a need, on a smaller scale, to develop technologies capable of desalinating very high salinity produced water for use in steam generation. Typical salinities of produced water in region exceed 50,000 mg/L, with the maximum often being much higher than 120,000 mg/L.

3. Produced water management

Different operations can be applied to remove various components from produced water including oil and greases, dissolved organic compounds, soluble salts, bacteria and viruses, and other miscellaneous impurities. A description of the treatments applied to remove various types of contaminants is reported in the following section.

3.1. Oil and grease removal

Oil and greases in produced water are present in the form of free oil, dispersed oil, and emulsified oil. The stringent environmental regulations and laws put quantitative restrictions on the discharge of water containing oil and greases [13]. A number of techniques have been practiced to remove oil and greases from produced water (Fig. 2). The choice of the treatment technology is determined by the size of the oil droplets rather than the final quality of the treated water. Free oil and dispersions with large oil droplets favor the floating of oil droplets on the surface due to their large size and high rise velocity. Small size particles can form an emulsion that complicates the separation of the two phases. It is often the combination of more than one technique that is fruitful for the treatment of emulsions. In general, in a first step, the emulsions are destabilized by the coalescence of small particles. The latter can be removed in subsequent steps through various conventional methods. Therefore, droplet size distribution of the oil plays a decisive role in dictating the final separation technique for oil removal [14].

The commonly used treatment methods include API gravity separator, hydrocyclones, corrugated plate separator, media filters, induced gas floatation centrifuge, membrane filters, etc. [17,18]. However, each technique has its associated drawbacks: gravity separation is usually applied to remove oil from a mixture; however, it is basically effective only in removing free oil. Hydrocyclones cannot remove oil droplets smaller than 10–15 microns and require a gas floatation vessel at the downstream end. But gas floatation involves the use of a large amount of air and needs high retention time. Membrane filters can remove particles as small as 0.01 microns.

It is also important to note that the final selection of the treatment method is also according to the location of the plant, whether offshore or onshore. In the case of offshore installations, the treatment method should be fast, as the accumulation of water in ponds for a long period of time is not feasible. Moreover, the addition and storage of chemicals can cause extra problems of disposal methods and availability of storage place, respectively. Additionally in the case of offshore discharge, the performance of the plant can

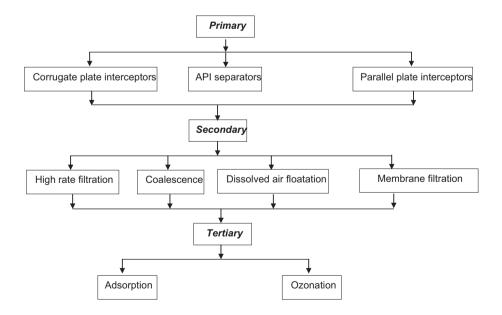


Fig. 2. Separation of oil/water emulsion from produced water [15,16].

be strongly determined by the weather conditions [19].

3.2. Dissolved organics removal

The extraction of heavy hydrocarbons using light hydrocarbons has been used by some oil producers to remove the dissolved organics from the produced water [20]. Adsorption is another widely used technique for the removal of soluble organics [21]. The adsorption columns containing adsorbent media retain the hydrocarbon on the surface of the adsorbent. Highly porous solid materials with a large surface area are the preferred adsorbents. The commonly used adsorbents include nutshell media, activated carbons, and different organic clays [22]. The requirement of high retention time is the main concern regarding the adsorption technique as it limits the efficiency of the entire process. Moreover, the carbon granules are susceptible to fouling and require backwashing, a waste stream of carbon is produced and some pretreatment is required before introducing the feed into the system. The soluble organics can also be oxidized to convert them into carbon dioxide that can be easily removed. Ozone and hydrogen peroxide are the most commonly used oxidizers [23]. The use of peroxide, however, may result into the toxic residue. On the other hand, the energy input for ozone system is considerably high. Ultraviolet light and some advanced oxidation processes have also been tested for removal of soluble organics. Ultraviolet technique is not effective in removing heavy metals, dispersed oil, salinity, and ammonia. The energy requirement of the process is also high and UV lamp can foul. The plants and micro-organisms can also be applied to treat the water containing dissolved organics. The main drawbacks of biological treatments include large surface area, high residue times, the buildup of oil, and iron hinder the biological activities, formation of the calcium deposits, and resultant gases and sludge require treatment. Membrane bioreactor (MBR) has been also investigated to remove oil and greases, chemical oxygen demand (COD), and total organic from the produced water as it will be described in Section 4.

3.3. Desalination

Produced water contains high amount of suspended and dissolved solids. Total dissolved solids vary from less than 2,000 ppm to more than 150,000 ppm [24]. The treatment method applied depends upon the amount of solids and the compatibility of the operation with the other impurities present into the water. The commonly used techniques include evaporation, distillation, membrane operations, electrical methods, and ion chemical techniques.

Thermal techniques have been the main players on the market for the removal of solids from wastewater. Evaporation can eliminate several steps of physical and chemical treatment. Falling film evaporators have gained significant popularity. Rapid spray evaporation and freeze-thaw evaporation are two commercial versions of the evaporation technique. Thermal distillation is another commonly applied technique. Other thermal techniques include vapor compression, multieffect distillation, combination of multieffect distillation and vapor compression, and multistage flash. However, all these thermal operations are energy consuming, require a large footprint and scaling is present. In Section 4, membrane-based operations for the treatment of produced water will be described.

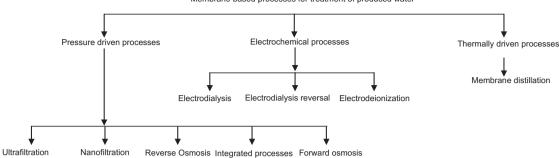
3.4. Disinfection

Micro-organisms including bacteria, viruses, and algae are either naturally present in produced water or they are introduced to achieve de-oiling of the produced water. They can cause the scaling or contamination downstream. Advanced filtration is the most commonly used technique applied for disinfection. Other techniques include ozone treatment, chlorination, ultraviolet treatment, and pH reduction.

4. Membrane-based treatments

The conventional operations employed for the treatment of produced water have certain limitations including the use of toxic chemicals, a large footprint, and the creation of secondary pollution. Moreover, conventional methods might be not sufficient to fulfill the new tight environmental regulations. Membranebased operations have been declared to be the promising candidates for wastewater treatment and reuse in the twenty-first century. They are also showing growing potentialities in solving all the problems related to the purification of produced water due to their intrinsic characteristics of efficiency and operational simplicity, high selectivity and permeability for the transport of specific components, low energetic requirement, easy control and scale-up. Fig. 3 summarizes the membrane processes that can be utilized for produced water treatment.

A summary of the membranes applied for the treatment of produced water with different objectives is reported in Table 3. It is evident from the table that different membrane operations have been tried for



Membrane based processes for treatment of produced water

Fig. 3. Schematic of membrane processes for produced water treatment.

produced water from various sources. The mentioned studies also point out that these operations are technically and economically feasible for produced water treatment by applying both polymeric and ceramic membranes. The table indicates that for pressure-driven membrane processes for produced water treatment, the availability of the membranes is not an issue as most of the membranes mentioned are commercially available. It implies that more focus should be devoted on process improvement (mainly fouling reduction) to enhance the process performance.

A comparison of some treatment techniques on the basis of the energy consumption, the handleable and achievable salinity level is shown in Fig. 4. The horizontal length of each bar represents the salinity level the technologies are able to handle, while the thickness of each bar indicates the range of corresponding energy requirement. A common look at Fig. 4 and Table 1 indicates that state-of-the-art RO-based desalination technologies may not be sufficient to treat produced water with high salinity content. Brine concentrator and crystallizer are able to treat solution with very high TDS, but their energy consumption is very high. This scenario highlights the importance of using advanced membrane operations discussed in Sections 4.4–4.6 for produced water treatment.

4.1. Pressure-driven membrane processes: microfiltration and ultrafiltration

Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) are well-established membrane-based operations and can be applied for the removal of species with specific range of sizes. MF is generally implied for the removal of suspended solids, whereas UF can be used to remove color, odor, viruses, and colloidal organic matters. UF is effective also in the removal of oil from produced water. Both ceramic and polymeric membranes can be employed for MF and UF. All these processes can be used either as pretreatment or as a final treatment step according to the required quality of the produced permeate.

Various studies can be found in the literature related to the application of MF and UF to produced water treatment and a comprehensive review has been recently published by Alzahrani and Mohammad [33]. Mueller et al. [34] studied the performance of crossflow microfiltration using ceramic and polymeric membranes. The membranes showed excellent performances in terms of oil removal; however, they were prone to fouling. In ceramic membranes, both internal and external fouling were observed and the membrane character was altered from hydrophilic to hydrophobic as a result of fouling. The addition of suspended solids reduced the intensity of fouling. Campos et al. [35] used the combination of microfiltration and air-lift reactor containing polystyrene particles as support. The reactor was operated at three different hydraulic retention times. The removing efficiency of only microfiltrated sample for COD, TOC, O&G, and phenols was 35, 25, 92, and 35%, respectively, whereas for the combined process removal efficiencies of 65% COD, 80% TOC, 65% phenols, and 40% ammonium were attained even at the lowest retention times. Deriszadeh et al. [36] used the combination of UF and micellar-enhanced ultrafiltration (MEUF) to remove the organic contaminants from the natural produced water. Simple UF was applied to remove free oil droplets and suspended solids, whereas MEUF was tested to check its feasibility in the removal of dissolved organics. A treatment train consisting of two-stage UF followed by a third-stage MEUF was able to remove free oil droplets, suspended solids, and rejected more than 95% of the soluble organics. Faibish and Cohen [27] modified a zirconia-based ultrafiltration membrane with poly (vinylpyrrolidone) and compared the performance of modified and unmodified membrane against an oil/ water microemulsion and a commercial cutting oil

		Membranes			
Operation	Feed	Trade name	Material	Supplier	Refs.
RO	Natural gas produced water	TFC-HR		Koch Membrane Systems	[25]
ULPRO	Natural gas produced water	TFC-ULP		Koch	[25]
ULPRO	Natural gas produced water	TMG10		Toray America	[25]
NF	Natural gas produced water	NF-90		Dow/Filmtec	[25]
UF	Model oily and bilge wastewater	FP 100 membrane		n.m	Tomaszewska et al. 2005 [8]
RO	Model oily and bilge wastewater	BW 3,040 and SW 30,404		n.m	[8]
MF	Oilfield produced water	-	Cellulose Acetate	n.m	[26]
UF	Oilfield produced water	-	Ultrafilic	Osmonics	[26]
NF	Oilfield produced water	NF200	Polyamide thin-film composite	Film Tech	[26]
RO	Oilfield produced water	ST10, AG	Thin-film Composite	Osmonics	[26]
UF	Microemulsion and cutting oil	-	Ceramic zirconia	Rhodia Orelis	[27]
UF NF	Oilfield wastewater	- NE 270 NE 00	PVC alloy hollow fiber	Litree Co. China	[28]
	CBM and oilfield produced water	NF 270, NF 90	Polyamide thin-film composite	FilmTec	[29]
RO	CBM and oilfield produced water	BW 30	Polyamide thin-film composite	FilmTec	[29]
UF	Metalworking o/w emulsion	Carbosep M308 and Carbosep M309	Ceramic (ZrO ₂ /TiO ₂ supported on carbon active layer)	Rhodia Orelis, Miribel, France	[30]
RO	Produced water extracted from sandstone aquifer	TFC-HR	2	Koch Membrane Systems	[31]
ULPRO	Produced water extracted from	XLE, TFCULP, TMG-10		Dow/Filmtec, Koch, Toray	[31]
NF	sandstone aquifer produced water extracted from candstone aquifer	NF-90, TFC-S, ESNA		America) Dow/Filmtec, Koch, Hudropoutice	[31]
MD	sandstone aquifer produced water from an oilfield		Lab-made polyvinylidene fluoride (PVDF) hollow fiber	Hydranautics	[32]
MD	produced water from an oilfield	MD020CP2 N	membranes Polypropylene (PP) hollow fiber membranes	Microdyn-Nadir	[32]

Table 3

Membranes used for produced water treatment in various investigations

emulsion. Both the fluids caused irreversible fouling of the unmodified membrane which was not observed for the modified one. The improved stability of the modified membranes was attributed to the narrowing of pore defects as a result of modification. Li et al. [37] developed and characterized a hydrophilic cellulose acetate-based UF hollow fiber membrane with antifouling characteristics for oil water separation. The membrane showed an oil retention of 99%. A flux reduction was observed during the tests and was associated with

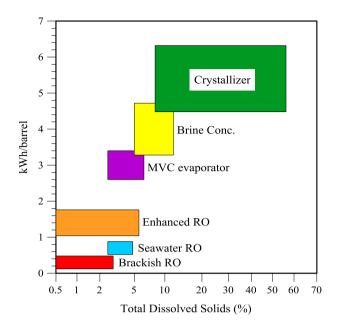


Fig. 4. A comparison of desalination technologies on the basis of energy consumption, feed concentration, and maximum achievable salinity level (Source: GWI, 2011).

the concentration polarization phenomena. Additionally, the membrane could function over a wide range of pH. In another study, Li et al. [38] tested a PVDF UF membrane modified with inorganic nanosized alumina particles. The claimed retention of COD and TOC was 90 and 98%, respectively, whereas the oil content in the permeate stream was below 1 ppm. The recovery of the modified membrane after washing was reported at 100%.

4.2. Pressure-driven membrane processes: nanofiltration and RO

RO and NF are high-pressure-driven processes and can be used to remove dissolved salts and other species as small as 0.0001 µm. However, in the case of RO, there are certain challenges which can considerably affect the efficiency of the process if not properly controlled: the fouling and scaling of the membrane. These problems can be minimized using an appropriate pretreatment of the process. The integration of different membrane processes can be an efficient tool to deal with these problems. An example can be found in the work carried out by Xu and Drewes [31] investigating potentialities and the fouling tendency of low-pressure RO and NF, with and without MF as pretreatment, in the purification of produced water. The authors found that the membranes with high permeability show more fouling. Furthermore, the hydrophobic and rough surfaces also accelerate the fouling. The pretreatment including MF, pH adjustment, and addition of antiscalant decreases the fouling significantly. The use of anionic surfactant and caustic cleaning restores the permeability more effectively than hydraulic or acid cleaning.

Mondal and R. Wicramasinghe [29] proved that an NF membrane with large pore size, smooth, and hydrophilic surface presents less fouling but also lower flux than that of an RO membrane.

NF and ultra-low pressure reverse osmosis (ULPRO) were compared with conventional RO by Xu et al. [25]. The rejection of various constituents was tested at low and high recoveries. The specific flux was highest in the case of NF, whereas the rejection was poor. The permeate quality from the ULPRO process was similar to the conventional RO process, whereas the specific flux was even higher. The operating and maintenance cost for the ULPRO was slightly less than RO for drinking standard water and less than NF for irrigation quality water.

4.3. Pressure-driven membrane processes: MBR

Another membrane operation suitable both as NF/ RO pretreatment and as produced water treatment is the MBR. It combines the properties of a membrane with that of a biological treatment providing a considerable high level of physical disinfection. This makes MBR especially suitable for reuse and recycling of wastewater.

Some research activities have been devoted to investigating the potential of MBR as a treatment step to remove organics present in produced water. Pendashteh et al. [39] applied MBR for the treatment of real and synthetic produced water. The performance of MBR for biodegradation of hydrocarbons with different organic loads was examined. The effect of salt concentration on biological treatment of the pollutants was scrutinized. The removal efficiencies achieved for COD, TOC, and oil and greases were greater than 97% for synthetic produced water. These values, however, were slightly less for real produced water. The performance was also determined by the salinity level of the feed. Kose et al. [40] studied the effect of the severe environment that bacteria are exposed to during treatment of produced water. The overall removal efficiency for COD was found to be more than 80-85% for all the analyzed sludge retention times, though a slight increase in COD removal was observed at shorter retention times. The hydrocarbon removal efficiency achieved was more than 99%. Kurian and Nakhla [41] investigated the effect of hydraulic

Permeation propert	Permeation properties of membrane bioreactor systems based on the configuration of the membranes	systems b	ased on the con	figuration of	the membr	anes				
			Feed characteristics	stics		Removal efficiency (%)	ncy (%)			
Membrane system Configuration	Configuration	COD HRT(h) (mg/L)	COD (mg/L)	TOC O&G (mg/L) (mg/L)	O&G (mg/L)	TDS (mg/L)	COD removal TOC		O&G	Refs.
MSBR	Tubular cross-flow ultrafiltration	24–96	562.5-6,750	137–1,650 15–1,050	15-1,050	35,000–250,000 86.2–97.	86.2–97.	90.8–97.2 90–98.9	90–98.9	[39]
IMBR SBR	Tubular membranes Hollow fiber membranes	24 2–8	200–460 495–607	n.m	150-600		100 89.9–95.5	>95%	97.6–99.9	[45] [15]
Aerobic MBR	Module ZW-1, Zenon environmental, Oakville	120–240	10,025–50,500		600-6,000		78–96		92–95	[41]
SMBR	Hollow fiber		$2,371 \pm 521$		140 ± 118	$140 \pm 118 8,367 \pm 1,689$	80-85		60-85	[40]
MBR	FS PE MF	48	600-1,800		115–346 64,400	64,400	~83		89.2–95.5	[42]

Table 4

retention time on COD, BOD₅, ammonia, oil, and grease removal using an aerobic coupled MBR. A considerable increase in removal efficiencies was obtained when the hydraulic retention time was increased from 5 to 10 days. Sharghi et al. [42] applied halophilic bacterial consortium in a submerged MBR for the treatment of high salinity oilfield produced water. The MBR maintained low turbidity of the produced water throughout the operational time of 112 d. An increase in removal efficiency of O&G from 89.2 to 95.5% was observed when the organic loading was increased from 0.3 to 0.9 kg COD m^3/d , while COD stayed approximately constant at 83%. Kwon [43] proved the superiority of MBR to treat BTEX and carboxylates present into produced water as compared to the vapor phase biofilter. Kose et al. [40] found that a hollow fiber submerged MBR is particularly affective in removing light hydrocarbons from natural gas oilfield produced water. Zhang et al. [44] investigated a novel method of treating produced water from polymer flooding consisting of a combination of hydrolysis acidification dynamic MBR-coagulation process. The authors concluded that the water after treatment meets the class 1 requirements for discharge established by the National Wastewater Discharge Standard of China.

The above discussion indicates that MBR technology possesses an excellent potential to treat produced water with various levels of BOD, COD, oil, and greases. A summary of the MBR systems used, feed characteristics, and permeate quality quoted in various studies is provided in Table 4. The table shows that MBR technology is capable to treat the produced water containing a broad range of TOC, BOD, and oil and greases. However, the major challenge in the case of MBR was the fouling of the membrane, especially when working with real produced water. Application of innovative fouling reduction techniques practiced for traditional MBRs can be useful to mitigate the fouling in MBR applied for produced water treatment.

4.4. Electrochemical processes

Besides the pressure-driven membrane-based processes, electrochemical charge-driven membrane-based processes have been applied to treat the produced water. Electrodialysis and electrodialysis reversal are the two main examples in this context which involve the separation of ions using an ion permeable membrane to separate the dissolved ions under the influence of an electrical potential gradient. The ion exchange membranes can selectively transport positively or negatively charged ions while restricting the passage of the opposite ones. Thus in an electrodialysis stack, consisting of arrays of alternating negatively and positively charged membranes, the density of charged ions in one compartment increases, while dilution occurs in the consecutive one. In electrodialysis reversal, the polarity of the membranes can be changed to control the membrane fouling and scaling [21]. The critical factors affecting the efficiency of electrodialysis or electrodialysis reversal process for the treatment of brackish water or desalination include the current density of the membrane, the ionic concentration of the solution, counter effects due to the transport of co-ions, diffusion, and osmosis. The main drawbacks include high treatment cost, fouling and the limitation to treat relatively high salinity water [46]. The membrane must be cleaned using dilute acidic and alkali solutions to restore its performance. These challenges must be addressed for successful competitive application of these processes for produced water treatment.

4.5. Forward osmosis

Forward osmosis or natural osmosis utilizes a dense membrane to separate two solutions with different concentrations. The water from low concentrated solution migrates to the high concentrated solution due to the osmotic pressure gradient across the membrane. The solvent moves due to its natural tendency to migrate from the solution of high osmotic pressure to the lower one, eliminating the need to apply hydraulic pressure. The elimination of applied hydraulic pressure attributes far less fouling in FO than its counterpart RO. Moreover, the developed fouling can be removed by hydraulic washing or chemical cleaning. FO can remove all the particulate matters and almost all the dissolved matters. The theoretical recovery factor obtainable is quite high and, at the same time, the associated energy consumption and chemical demand is very low. The processes based on the osmotic energy have not been practiced yet for the treatment of produced water. However, the lab-scale and pilot plant studies of this process have shown a good potential to treat the water with different levels of salinity gradient [47-50]. Hickenbottom et al. [51] used forward osmosis to treat the water from drilling wastes. A commercially available cellulose triacetate-based semipermeable membrane casted over a polyester support was used in the study. A highly concentrated (260 g/L) NaCl solution served as draw solution. The authors concluded that the use of FO can greatly concentrate the produced water (up to 80% recovery) and can reduce the demand for a freshwater source. The rejection of both organic and inorganic contaminants was very high. The reduction in flux over the period of time was associated with the dilution of the draw solution. The fouling could be removed by osmosis backwashing to restore the initial flux. FO possesses great potential for produced water treatment. The issues of internal concentration polarization, relatively low flux, and recovery of draw solutions, however, need to be addressed.

4.6. Membrane distillation

Membrane distillation is an emerging thermalbased membrane process with the potential to be operated with waste or low-grade energy. The process has several advantages over the state-of-the-art thermal- and pressure gradient-based processes, the most important of which are the possibilities of going beyond the concentrations achievable through conventional techniques and using alternative energy sources (solar, wind, or geothermal). This is because typical MD processes can be conducted at temperatures below 70°C and driven by low temperature difference (20°C) between the hot feed and the cold permeate. Taking into account the waste grade heat available with warm produced water, the latter can provide the thermal energy needed to drive the MD separation process for a cost- and energy-efficient liquid separation system [52]. Moreover, produced water coming from steam-assisted gravity drainage can have a temperature even higher than 100°C. The treatment of water with such a high temperature using RO requires cooling as prerequisite step, thus adding costs to the process and at the same time causing the waste of the energy associated with this water. Several studies have revealed the potential of membrane distillation to achieve a high recovery factor from various types of brine and other concentrated solutions. Similarly, it was demonstrated through several investigations that membrane distillation has the potential to compete with the RO process if the source of waste grade heat or energy is available [32,53-56]. In the case of produced water, membrane distillation can be used to achieve water of high purity due to the capability of MD to reject theoretically all the salts, metals, and other nonvolatile components [9].

Various current studies have investigated the potential of membrane distillation to treat produced water. Singh and Kamlesh [57] used porous PTFE flat sheet membranes and simulated produced water with temperature ranging from 80 to 130°C (corresponding to feed pressure of 2–3 atm). The salinity level of the utilized water was 10,000 ppm and phenol, cresol, and naphthenic acid were added to reproduce produced water composition closely. It was found that the water

vapor flux remains unchanged with respect to the presence of phenol, cresol, and naphthenic acid; however, the quantity of these compounds in the permeate increases as the feed temperature is increased, whereas no sodium chloride traces were found. It was concluded that the utilized membrane maintained its hydrophobic character throughout the experimentation. The quantity of phenol and cresol in distillate was assumed due to the volatile nature of these compounds. The highest flux achieved was as high as 195 kg/m² h. Macedonio et al. [32] tested different polyvinylidene fluoride (PVDF) and polypropylene (PP) hollow fiber membranes in direct MD contact for desalting real high saline oilfield produced water. Analysis of the collected permeates indicated that overall salt rejection factor greater than 99% and total carbon rejection higher than 90% were achieved. Alkhudhiri et al. [11] proved also the feasibility of air gap MD for the treatment of produced water. Recently, Lee et al. [58] developed thermally rearranged polybenzoxazole membranes. Initially developed for gas separation application due to the extraordinary gas permeability of small gas molecules, the thermally rearranged membranes exhibited very hydrophobic characteristics, flux of about 65 L/m^2 h and virtually no sodium chloride in the permeate of direct MD contact. Moreover, the membrane maintained the hydrophobicity for a prolonged period of time.

A membrane technology similar to membrane distillation and with great potential in produced water treatment is membrane crystallization (MCr). The latter is an extension of membrane distillation and is able to promote crystals nucleation and growth in a wellcontrolled pathway, starting from under-saturated solutions. The experimental evidence that can be found in several published articles [59-61] validates the effectiveness of MCr as an advanced method for performing well-behaved crystallization processes. One of the main advantages of MCr is that it does not suffer significant limitations due to the osmotic pressure of highly concentrated streams; therefore, MCr could be employed in produced water treatment processes for the production of freshwater and crystalline compounds from waste streams, transforming the traditional disposal cost in a potential new profitable market. This technology was already tested in desalination where it was proved that the integration of MCr on NF and/or RO brine offers the possibility of enhancing the water recovery factor, to produce solid materials (such as NaCl and epsomite) and to minimize brine disposal problem [62-69]. Moreover, other products such as LiCl can be produced when further increasing the concentration factor.

Taking into account the high concentration of produced water, MCr could represent an additional option for completely re-designing produced water treatment processes, where the introduction of MCr might determine substantial improvements in terms of water quality, product recovery factor, overall cost, and environmental impact.

5. Multitechnology processes

These processes are based upon the integration of different operations (both thermal- and membranebased processes). An example can be found in the plants of the petroleum industry using steam injection for the enhancement of oil recovery. Thermal technologies are usually used to produce steam. Treated produced water is used as feed for the steam generator. To facilitate and improve its life period, the feed to the steam generator is treated through lime softening followed by filtration to remove silica, calcium, and magnesium. Iron and hardness can be further removed using weak acid cation. To obtain steam of the required quality, in addition to the use of chemicals and filtration, also liquid–vapor separator may be required (such as mechanical vapor compression).

Conventional physiochemical processes have also been combined with membrane-based treatment to enhance the treatment quality of produced water. Dual RO process with chemical precipitation can be utilized to enhance the recovery of conventional RO process by treating and concentrating the retentate of primary or first-stage RO process [70]. The physicochemical processes are used to treat the RO retentate of the first stage before introducing it into the second stage. The chemical step includes the use of chemical agents for the precipitation of sparingly soluble salts followed by the filtration to remove the precipitated salts. The total recovery of the entire process has been reported as high as 95%. The main drawbacks of the technique include excessive use of the chemicals associated with the large footprint.

Different membrane- and nonmembrane-based combinations to treat oilfield produced water were examined by Çakmakce et al. [26]. The studied systems include dissolved air floatation (DAF), acid cracking, coagulation (CA) with lime and precipitation, cartridge filters (5 and 1 μ m), microfiltration (MF), and ultrafiltration (UF) as pretreatment steps, whereas NF and RO were used as final separation technologies. The use of NF brings the COD to the required level; however, the effluent contains unacceptable high level of salts that require the use of RO after an appropriate pretreatment. They found

experimentally that primary + oil/water separator + DAF system + 1 μ m ceramic or metallic cartridge filter + 0.2 μ m ceramic or metallic MF gave the best pretreatment option in terms of permeate flux and water quality before RO membranes.

Ozgun et al. [71] investigated the effect of different pretreatment options including MBR and pressurized MF and UF on the treatment of produced water using NF and RO. The authors observed that the maximum flux is obtained with MF/UF pretreatment combined with NF, while MBR combined with RO gives the best quality of the permeate in terms of conductivity and COD.

Also Ebrahimi et al. [72] studied various pretreatments (including MF, UF, and DOF) combined with NF (as final treatment step). The study showed that MF combined with NF can reduced the oil content to 93%, while UF + NF can reduce it up to 99.5%. However, removal of TOC was limited to 49% in both cases. Zhong et al. [73] reported an oil removal efficiency of ceramic UF membranes combined with flocculation as high as 99%.

Tomaszewska et al. [8] investigated the integration of UF and RO processes to treat the bilge wastewater. UF effectively removed oil down to 95%, all suspended solids, and turbidity. The authors claimed the removal of more than 70% of TOC and 90% of cations and sulfates, whereas all the free oil was removed. It was found that the treated water complies all the wastewater treatment standards.

Qiao et al. [28] investigated the performance characteristics of a hybrid system consisting of aeration tank, air floatation system, sand filter, and UF membranes for the treatment of produced water. It was witnessed that the new design can reduce the oil and solid contents down to 0.5 ppm and 1 ppm, respectively. In addition, iron and various types of bacteria can also be reduced down to an acceptable level for the discharge standards.

6. Produced water treatment costs

The costs associated with managing and treating produced water are greatly determined by the composition of the raw water and the required finished water quality. Therefore, estimating the costs for managing these waters is complex at best given the wide variability in the chemistry of produced waters. In some cases, the cost of treating the produced water can be prohibitive to energy development ventures.

For inland production facilities, more than 60% of produced water is commonly re-injected back into the

wells that are geologically isolated from underground sources of drinking water. Mondal and Wickramasinghe [29] report that re-injection costs vary from \$0.40 to \$1.75 per barrel, while installation costs vary from \$4,00000 to \$30,00,000 per well. In Table 5, various cost estimates for produced water disposal methods can be found.

It has to be considered that the discharge of produced water can have different potential impacts on environment depending on where it is discharged. It can be a potential environmental risk for soil, surface, and underground waters. On the other hand, as clean water is a scarce resource, treating and reusing these waters for beneficial applications (i.e. for irrigation, industrial processes, or other nonpotable purposes) can have significant economic benefits. Therefore, the development and implementation of effective produced water treatment systems are vital both for providing a viable source of "potable or semipotable" water and for preventing serious environmental damage and for minimizing costs.

Cost estimates of different technologies for treating produced water from coal bed methane and oil fields are provided by [75,77]. The latter report that costs for treatment of produced water ranges from 0.0016 to 1.75 \$/bbl depending on the initial composition of the produced water, the treatment technology, and the desired final composition of the output water (Table 6).

As described in the previous sections, different treatment technologies can be used to treat wastewater (i.e. physical or membrane separation, chemical or biological methods). The main drawbacks of chemical and biological methods are the high treatment cost, the toxic chemical usage, and the space requirements for installation [11]. Moreover, low efficiency, high operating costs, corrosion, and possible recontamination are the disadvantages of conventional oily wastewater treatment methods. Low-energy consumption, low use of chemicals, and low susceptibility toward feed composition are instead the advantages of membrane operations. Camacho et al. [52] report that electrodialysis treatment of produced waters containing up to 10,000 mg/L of TDS requires only \$0.06/m³ for power consumption (based on an electricity price of \$0.6/kWh), certainly lower than the current cost for well disposal. However, above 10,000 mg/L of TDS, the power cost of electrodialysis can increase exponentially [76]. Cost analysis carried out for MD operating at 50°C and with a recovery of 70% indicate a water cost of 0.72\$/m³ when the temperature of the produced water fed to the MD plant is 50°C and 1.28\$/m³ when 20°C is the temperature of the produced water fed to the plant [32]. Moreover,

14330

Table 5

Produced water	r disposal	methods and	costs	(adapted	from [74])
----------------	------------	-------------	-------	----------	------------

Method	Estimated cost (\$/bbl)
Surface discharge	0.01–0.08
Secondary recovery	0.05-1.25
Shallow re-injection	0.10-1.33
Evaporation pits	0.01-0.80
Commercial water hauling	0.01-5.50
Disposal wells	0.05–2.65
Freeze-thaw evaporation	2.65-5.00
Evaporation pits + flowlines	1.00-1.75
Constructed wetland	0.001-2.00
Electrodialysis	0.02–0.64
Induced air flotation for de-oiling	0.05
Anoxic/aerobic granular activated carbon	0.083

Table 6

Treatment costs of selected produced water (adapted from [75] and [77])

Technology	Cost \$/bbl
Coal Bed Methane (CBM) disposal ^a	from 0.10 to 1.75
CBM electrodialysis ^a	from 0.29 to 1.04
CBM freeze crystallization ^a	from 0.24 to 1.04
Oilfield reverse osmosis ^a	from 0.20 to 1.68
Oilfield distillation ^a	0.67
Produced water de-oiling through API	0.0016
Produced water de-oiling through hydrocyclone	0.0028
Produced water de-oiling through API with chemical polymer	0.0908
Produced water de-oiling through induced gas flotation	0.0172
Produced water de-oiling and organic removal through API with chemical polymer and GAC	0.1517
Produced water de-oiling, iron, and organic removal through API with chemical polymer, chemical iron removal, and GAC	0.2613
Produced water organic removal and partial demineralization through forced evaporation	1.11

^aCost depending on the desired final composition of the output water.

Table 7 Total cost (US\$/1000 bal) of produced water treatment

Technology	RO	Flash	RO + Flash	Distillation	RO + Distillation	
	With con-	ventional crystalliz	zer			
	23	38	40	31	36	
	Without conventional crystallizer					
	43	41	32	33	27	

the sensitivity of changing different variables (i.e. membrane type, driving force, MD recovery, and membrane life-time) on the process economics was also analyzed [32]. The achieved results suggest that the higher are (i) trans-membrane flux, (ii) membrane module recovery, (iii) membrane life-time, and (iv)

feed temperature, the lower is the cost of the treated water.

Knutson et al. [77] estimate and compare the produced water treatment costs considering 10 different technologies: (1) RO with crystallizer, (2) RO without crystallizer, (3) multiple effect distillation (MED) with

Table 8 Comparison of technologies for produced water treatment

Technology	Objective	Advantages	Disadvantages
Biological aerated filters	Removal of organics, oil, ammonia, nitrogen, chemical oxygen demand, iron, magnesium, heavy metals, etc.	Well-established technology for produced water, informal version requires minimum equipment, nearly 100% water recovery, no chemicals or cleaning requirements, does not require skillful operators, long life	Large footprints, long operational time, limited removal capabilities
Hydrocyclone	Removal of particulate and dispersed oils	No moving parts, no post or pretreatment required, no need of chemicals or energy	Ineffective on soluble oils and greases, the pressure drop is higher, susceptible to abrasion
Flotation	Removal of small suspended particles and oil droplets, volatile organics, and oil and greases	Applicable for broader range of TOC concentrations, excellent to remove NOM, no post-treatment required	Droplet size and temperature- dependent efficiency, cannot remove soluble oils, coagulation may be required
Adsorption	Used as a unit process with the capability of removing iron, magnesium, TOC, BTEX compounds, heavy metals, and oil	No typical energy requirement except in backwashing, can be used as a good polishing step, operation independent of the brine composition	Regular back washing is required as absorbent can easily become overloaded, solid material needs to be disposed, may require chemicals for media regeneration
Settling	Removal of particles by settling,	None, except for the pumping, no requirement of the chemicals, long-life time, no pretreatment is required	Require large footprints, can be subjected to stringent environment regulations, liners are required, operational quality depends upon the retention time, solid disposal is required
Media filtration	Used for the removal of oil, greases, and TOC, only energy requirement for backwashing	Can be used for all salt concentrations and compositions, well-established technology, 100% recovery of water	Backwashing is required, frequent replacement of the media may be required, disposal of solid waste is required
Microfiltration/ Ultrafiltration	Can be used to remove suspended solids, viruses, odor, color, dispersed and emulsified oil contents, etc.	Proven and mature technology, can remove emulsified oil even with very small droplet size, removal of almost all nondissolved carbon, high expected life time, especially in case of ceramic membranes, small footprint, energy efficient	Needs periodic backwash, chemical cleaning may be required, high quantities of iron in the feed can cause irreversible fouling
Nanofiltration	Effective technology as softening treatment for the subsequent processes.	Ability to reject divalent and radionuclide, mature technology for water treatment, initial positive results with produced water, high product recovery, energy requirement is less than RO, disposal cost is minor, automation may eliminate the need for labor	May require scale inhibitors and pretreatment, not sufficient as stand-alone technology for produced water
Reverse osmosis	Possesses the capability to produce drinking quality water from produced water	Robust and well-proven technology for seawater treatment, system can be	Intensive pretreatment and process integration is required when considering for PW,

(Continued)

14332

Technology	Objective	Advantages	Disadvantages
Membrane distillation	Has the potential to produce	automated, the integration and process modifications have generated excellent results for produced water, can operate at broader ranges of pH Can utilize waste grade heat	Intensive use of scale inhibitors and cleaning agents, mineralization or pH adjustment may be required in case of produced water Not much studied process for
distillation	ultrapure water	often associated with produced water, can completely reject all nonvolatile present in the feed, the performance is only slightly dependent upon feed concentration, can be operated at downstream end of RO or as stand-alone technology for desalination, can generate the crystals from the brine	produced water treatment, the specific membranes are not available, no study comprehending the real operational problems
Forward Osmosis	Can concentrate produced water to a very high level with rejection of most of the organic and inorganic impurities	High rejection of all contaminants. Reversible membrane fouling. Can achieve high water flux. High salinity produced water can be used as draw solution.	Draw solution needs reconcentration. Periodic membrane cleaning.
Multieffect distillation (MED)	Can be used to remove the salts and other solids	Well established and mature desalination technology, applicable to wide range of TDS	Intensive energy requirement, extensive use of scale inhibitors, pretreatment is required, special focus must be placed on avoiding scale formation
MED-VC	Can handle the water of very high salinity to give a product of very high purity	A hybrid technology used to treat the water with high salinity level and to improve the recovery factor, can be used to achieve zero liquid discharge at expense of high energy consumption	Scale inhibitors and antiscalant are required, the use of chemicals for cleaning is another issue, the specific energy goes on increasing with an increase in salinity level
Multistage flash (MSF)	Can achieve very pure product from feed with high concentration	Well-established technology applicable to very high TDS level	Energy cost is high, extensive use of chemicals as scale inhibitors and cleaning agents

Table 8 (Continued)

crystallizer, (4) MED without crystallizer, (5) multistage flash distillation (MSF) with crystallizer, (6) MSF without crystallizer, (7) MED after RO with crystallizer, (8) MED after RO without crystallizer, (9) MSF after RO with crystallizer, and (10) MSF after RO with crystallizer. Crystallization has been considered for achieving zero liquid discharge (ZLD). The achieved results are reported in Table 7.

Produced water treatment with ZLD processes was found to be less expensive than treatment without ZLD, mainly owing to high costs for concentrated brine disposal (in the costs evaluation, the cost of brine disposal through underground injection in wells was assumed to be \$24 per 1,000 gal). Moreover, a membrane system was found to be cheaper than the thermal ones.

On the basis of the literature on produced water treatment technologies cited in the present article, an analysis of advantages and disadvantages has been provided in Table 8.

7. Conclusions

In conclusion, from the data presented, the scale of the produced water problem today and the growing impact on the environment and the water stress in future can be well understood. The traditional methodologies applied up to now will be less appropriate in the next few years due to the increasing demand for water treatment consistent with the process intensification strategy.

Traditional membrane technologies (such as microfiltration, ultrafiltration, nanofiltration, and RO) are already successfully competing with the other methodologies and showing growing potentialities in solving all the problems related to the purification of produced water. It is interesting, moreover, to realize that new membrane operations (such as membrane distillation, MCr, membrane reactor, and specifically MBR) might significantly contribute to minimizing environmental problems, to maximizing possible water reuse in an enhanced water oilfield or also in water purification and reuse in different alternative applications. Efforts for producing better membranes for membrane operations (and specifically in membrane distillation) are in progress and maybe, in the next few years, they will become a reality.

References

- E.T. Igunnu, G.Z. Chen, Produced water treatment technologies, Int. J. Low Carbon Technol. (2012) 1–21, doi: 10.1093/ijlct/cts049, (Accessed October 6, 2013). Available from: <a href="http://iilct.oxfordjournals.org/cgi/subarbolic.com/cgi/subarbol
- Available from: <http://ijlct.oxfordjournals.org/cgi/>.
 [2] A. Fakhru'l-Razi, A. Pendashteh, L.C. Abdullah, D.R.A. Biak, S.S. Madaeni, Z.Z. Abidin, Review of technologies for oil and gas produced water treatment, *J. Hazard. Mater.* 170(2–3) (2009) 530–551.
- [3] E.J. Sullivan, R.S. Bowman, L. Katz, K.K., Water treatment technology for oil and gas produced water, Abstract Presented at Identifying Technologies to Improve Regional Water Stewardship: A Conference Series Featuring Intersections of Technology and Water Management, North-Middle Rio Grande Corridor, Albuquerque, NM, vol. 216, 2004.
- [4] I.E.A., 2003. World Energy Investment Outlook 2003, (Accessed on April 27, 2015). Available from: http://www.worldenergyoutlook.org/media/weowebsite/20 08-1994/weo2003.pdf>.
- [5] Annual Energy Outlook 2010 With Projections to 2035, (Accessed on 18/June/2014). Available from: http://www10.iadb.org/intal/intalcdi/pe/2010/05499.pdf>.
- [6] Produced Water. Environmental risks and advances in mitigation technologies, in: K. Lee, J. Neff (Eds.), New York, NY: Springer New York, 2011, (Accessed on October 17, 2013). Available from: http://www.springerlink.com/index/10.1007/978-1-4614-0046-2>.
- [7] R.P.W.M. Jacobs, R.O.H Grant, J. Kwant, J.M. Marquenie, E. Mentzer, Produced water, technical/ environmental issues and solutions, in: J.P. Ray, F.R. Engelhardt (Eds.), The Composition of Produced Water from Shell Operated Oil and Gas Production in the North Sea, 1992, pp. 13–21, doi: 10.1007/978-1-4615-2902-6 2.
- [8] M. Tomaszewska, A. Orecki, K. Karakulski, Treatment of bilge water using a combination of ultrafiltration and reverse osmosis, Desalination 185(1–3) (2005) 203–212.

- [9] D.L. Shaffer, L.H. Arias Chavez, M. Ben-Sasson, S. Romero-Vargas Castrillón, N.Y. Yip, M. Elimelech, Desalination and reuse of high-salinity shale gas produced water: Drivers, technologies, and future directions, Environ. Sci. Technol. 47(17) (2013) 9569–9583.
- [10] J. Din, World's largest seawater plant helps keep the oil flowing, *Dimensions International*, 8–13, 2012. Available from: http://www.saudiaramco.com/content/dam/Publications/Dimensions_international/Dimensions_International_Fall2012/WorldsLargest_SeawaterPlant.pdf>.
- [11] A. Alkhudhiri, N. Darwish, N. Hilal, Produced water treatment: Application of air gap membrane distillation, Desalination 309 (2013) 46–51.
- [12] ITF. ITF Call for Proposals Focus: Produced Water Management in the Gulf Co-operating Council of States in the Middle East, 2012. Available from: http://www.itfenergy.com/index/cms-filesystem-action?file=/mailchimp/gcc-water-management-call-201 2.pdf>.
- [13] G.T. Tellez, N. Nirmalakhandan, J.L. Gardea-Torresdey, Performance evaluation of an activated sludge system for removing petroleum hydrocarbons from oilfield produced water, Adv. Environ. Res. 6(4) (2002) 455–470.
- [14] Maurice Stewart, Ken Arnold, Emulsions and Oil Treating Equipment. Selection, Sizing and Troubleshooting, Gulf Professional Publishing, 2008.
- [15] T.P. Thanh, Oily Wastewater Treatment by Membrane Bioreactor Process Coupled with Biological Activated Carbon Process, Master Thesis, Asian Institute of Technology School of Environment, Resources and Development, Thailand, 2002.
- [16] R.R. Reynolds, Produced Water and Associated Issues. Oklahoma Geological Survey Open-File Report, 6, 2003, (Accessed on June 16, 2014). Available from: http://karl.nrcce.wvu.edu/workshops/2003/pww/p roduced_water.pdf>.
- [17] R.A. Jaisinghani, G.S. Sprenger, A study of oil/water separation in corrugated plate separators, J. Eng. Ind. 101(4) (1979) 441–448, doi: 10.1115/1.3439534.
- [18] J.J. Seureau, Y. Aurelle, M.E. Hoyack, A three-phase separator for the removal of oil and solids from produced water, SPE Annual Technical Conference and Exhibition, 25–28 September, New Orleans, Louisiana. Society of Petroleum Engineers, 1994, (Accessed on April 27, 2015). Available from: https://www.onepetro.org/conference-paper/SPE-28535-MS>.
- [19] Using V-SEP to Treat Produced Water, (Accessed on June 16th, 2014). Available from: http://www.vsep. com/pdf/ProducedWater.pdf>.
- [20] B.L. Knudsen, M. Hjelsvold, T.K. Frost, M.B.E. Svarstad, P.G. Grini, C.F. Willumsen, H. Torvik, S.A., Meeting the zero discharge challenge for produced water, in: Paper SPE86671 Presented at the 2004 SPE International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production, Alberta, Canada, (pp. 29–31), March 2004.
- [21] RPSEA Project, 07122-12, 2009. An Integrated Framework for Treatment and Management of Produced Water, (Accessed on June 16, 2014). Available from: http:// www.rpsea.org/0712212/>.
- [22] Water Treatment Operations and Unit Processes, in: F.R. Spellman, Handbook of Water and Wastewater

Treatment Plant Operations, CRC Press, 2003, doi: 10.1201/9780203489833.ch17.

- [23] J.D. Arthur, B.G. Langhus, C. Patel, Technical Summary of Oil and Gas Produced Water Treatment Technologies, All Consulting, LLC, Tulsa, OK, 2005, p. 53 (Accessed on July 21, 2015). Available from: http://www.odinoilandgas.com/Portals/0/TreatmentOption sReport.pdf>.
- [24] J.D. Arthur, B.G. Langhus, C. Patel, Technical Summary of Oil & Gas Produced Water Treatment Technologies, ALL Consulting, LLC, (2005) 53 p. (Accessed on June 16, 2014). Available from: http://www.odinoilandgas.com/Portals/0/TreatmentOption sReport.pdf>.
- [25] P. Xu, J.E. Drewes, D. Heil, Beneficial use of co-produced water through membrane treatment: Technicaleconomic assessment, Desalination 225(1–3) (2008) 139–155.
- [26] M. Çakmakce, N. Kayaalp, I. Koyuncu, Desalination of produced water from oil production fields by membrane processes, Desalination 222(1–3) (2008) 176–186.
- [27] R.S. Faibish, Y. Cohen, Fouling and rejection behavior of ceramic and polymer-modified ceramic membranes for ultrafiltration of oil-in-water emulsions and microemulsions, Colloid Surf., A 191(1–2) (2001) 27–40.
- [28] X. Qiao, Z. Zhang, J. Yu, X. Ye, Performance characteristics of a hybrid membrane pilot-scale plant for oilfield-produced wastewater, Desalination 225(1–3) (2008) 113–122.
- [29] S. Mondal, S.R. Wickramasinghe, Produced water treatment by nanofiltration and reverse osmosis membranes, J. Membr. Sci. 322(1) (2008) 162–170.
- [30] A. Lobo, A. Cambiella, J.M. Benito, C. Pazos, J. Coca, Ultrafiltration of oil-in-water emulsions with ceramic membranes: Influence of pH and crossflow velocity, J. Membr. Sci. 278(1–2) (2006) 328–334.
- [31] P. Xu, J.E. Drewes, Viability of nanofiltration and ultra-low pressure reverse osmosis membranes for multi-beneficial use of methane produced water, Sep. Purif. Technol. 52(1) (2006) 67–76.
- [32] F. Macedonio, A. Ali, T. Poerio, E. El-Sayed, E. Drioli, M. Abdel-Jawad, Direct contact membrane distillation for treatment of oilfield produced water, Sep. Purif. Technol. 126 (2014) 69–81.
- [33] S. Alzahrani, A.W. Mohammad, Challenges and trends in membrane technology implementation for produced water treatment: A review, J. Water Process Eng. 4 (2014) 107–133.
- [34] J. Mueller, Y. Cen, R.H. Davis, Crossflow microfiltration of oily water, J. Membr. Sci. 129 (1997) 221–235.
- [35] J.C. Campos, R.M.H. Borges, A.M.D. Oliveira Filho, R. Nobrega, G. L. Sant'Anna, Oilfield wastewater treatment by combined microfiltration and biological processes, Water Res. 36(1) (2002) 95–104.
- [36] A. Deriszadeh, M.M. Husein, T.G. Harding, Produced water treatment by micellar-enhanced ultrafiltration, Environ. Sci. Technol. 44(5) (2010) 1767–1772.
- [37] H.J. Li, Y.M. Cao, J.J. Qin, X.M. Jie, T.H. Wang, J.H. Liu, Q. Yuan, Development and characterization of anti-fouling cellulose hollow fiber UF membranes for oil-water separation, J. Membr. Sci. 279(1–2) (2006) 328–335.
- [38] Y.S. Li, L. Yan, C.B. Xiang, L.J. Hong, Treatment of oily wastewater by organic-inorganic composite

tubular ultrafiltration (UF) membranes, Desalination 196(1–3) (2006) 76–83.

- [39] A.R. Pendashteh, L.C. Abdullah, A. Fakhru'l-Razi, S.S. Madaeni, Z.Z. Abidin, D.R.A. Biak, Evaluation of membrane bioreactor for hypersaline oily wastewater treatment, *Process. Saf. Environ. Prot.* 90(1) (2012) 45–55.
- [40] B. Kose, H. Ozgun, M.E. Ersahin, N. Dizge, D.Y. Koseoglu-Imer, B. Atay, R. Kayaa, M. Altınbasa, S. Sayılıe, P. Hoshane, D. Ataye, E. Erene, C. Kinacia, I. Koyuncu, Performance evaluation of a submerged membrane bioreactor for the treatment of brackish oil and natural gas field produced water, Desalination 285 (2012) 295–300.
- [41] R. Kurian, G. Nakhla, Performance of Aerobic MBR Treating High Strength Oily Wastewater at Mesophilic –Thermophilic Transitional Temperatures, Proc. Water Environ. Fed. 2006 (2006) 3249–3255.
- [42] E.A. Sharghi, B. Bonakdarpour, P. Roustazade, M.A. Amoozegar, A.R. Rabbani, The biological treatment of high salinity synthetic oilfield produced water in a submerged membrane bioreactor using a halophilic bacterial consortium, J. Chem. Technol. Biotechnol. 88 (11) (2013) 2016–2026.
- [43] S. Kwon, Biological Pretreatment of Produced Water for Reuse Applications, ProQuest, USA, 2007.
- [44] Y. Zhang, B. Gao, L. Lu, Q. Yue, Q. Wang, Y. Jia, Treatment of produced water from polymer flooding in oil production by the combined method of hydrolysis acidification-dynamic membrane bioreactor-coagulation process, J. Pet. Sci. Eng. 74(1–2) (2010) 14–19.
- [45] A. Brookes, B. Jefferson, G. Guglielmi, S.J. Judd, Sustainable flux fouling in a membrane bioreactor: impact of flux and MLSS, Sep. Sci. Technol. 41 (2006) 1279–1291.
- [46] T. Sirivedhin, J. McCue, L. Dallbauman, Reclaiming produced water for beneficial use: salt removal by electrodialysis, J. Membr. Sci. 243(1–2) (2004) 335–343.
- [47] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, A novel ammonia—carbon dioxide forward (direct) osmosis desalination process, Desalination 174(1) (2005) 1–11.
- [48] D.K. Anderson, Concentration of Dilute Industrial Wastes by Direct Osmosis. University of Rhode Island, Providence, 1977.
- [49] R.W. Holloway, A.E. Childress, K.E. Dennett, T.Y. Cath, Forward osmosis for concentration of anaerobic digester centrate, Water Res 41(17) (2007) 4005–4014.
- [50] R.J. York, R.S. Thiel, E.G. Beaudry, Full-scale experience of direct osmosis concentration applied to leachate management, in: Proceedings of the Seventh International Waste Management and Landfill Symposium (Sardinia'99), S. Margherita di Pula, Cagliari, Sardinia, Italy. October 1999.
- [51] K.L. Hickenbottom, N.T. Hancock, N.R. Hutchings, E.W. Appleton, E.G. Beaudry, P. Xu, T.Y. Cath, Forward osmosis treatment of drilling mud and fracturing wastewater from oil and gas operations, Desalination 312 (2013) 60–66.
- [52] L.M. Camacho, L. Dumée, J. Zhang, J.D. Li, M. Duke, J. Gomez, S. Gray, Advances in membrane distillation for water desalination and purification applications, Water 5(1) (2013) 94–196.
- [53] E. Drioli, E. Curcio, G. Di Profio, F. Macedonio, A. Criscuoli, Integrating membrane contactors technology

and pressure-driven membrane operations for seawater desalination: Energy, exergy and cost analysis, Chem. Eng. Res. Des. 84(A3) (2006) 209–220.

- [54] E. Drioli, F. Macedonio, Membrane engineering for water engineering, Ind. Eng. Chem. Res. 51(30) (2012) 10051–10056.
- [55] F. Macedonio, E. Curcio, E. Drioli, Integrated membrane systems for seawater desalination: Energetic and exergetic analysis, economic evaluation, experimental study, Desalination 203 (2007) 260–276.
- [56] F. Macedonio, E. Drioli, An exergetic analysis of a Membrane Desalination System, Desalination—Special issue honoring Sidney Loeb, 261 (2010) 293–299.
- [57] D. Singh, K.K. Sirkar, Desalination of brine and produced water by direct contact membrane distillation at high temperatures and pressures, J. Membr. Sci. 389 (2012) 380–388.
- [58] J.H. Kim, S.Y. Lee, Z. Cui, M.J. Lee, K.D. Suh, E. Drioli, Y.M. Lee, Thermally rearranged polymer membranes for water application, ECI Meeting, Cetraro, Italy, September 29-October 3, 2013.
- [59] E. Drioli, E. Curcio, A. Criscuoli, G. Profio, Integrated system for recovery of CaCO₃, NaCl and MgSO₄·7H₂O from nanofiltration retentate, J. Membr. Sci. 239 (2004) 27–38.
- [60] G. Di Profio, S. Tucci, E. Curcio, E. Drioli, Selective glycine polymorph crystallization by using microporous membranes, Cryst. Growth Des. 7 (2007) 526–530.
- [61] E. Drioli, G. Di Profio, E. Curcio, Progresses in membrane crystallization, Curr. Opin. Chem. Eng 1 (2012) 1–5.
- [62] E. Drioli, E. Curcio, G. Di Profio, F. Macedonio, A. Criscuoli, Integrating membrane contactors technology and pressure-driven membrane operations for seawater desalination: Energy, exergy and cost analysis, Chem. Eng. Res. Des. 84(A3) (2006) 209–220.
- [63] F. Macedonio, E. Drioli, E. Curcio, G. Di Profio, Experimental and economical evaluation of a membrane crystallizer plant, Desalin. Water Treat. 9 (2009) 49–53.
- [64] F. Macedonio, E. Drioli, Hydrophobic membranes for salts recovery from desalination plants, Desalin. Water Treat. 18 (2010) 224–234.
- [65] F. Macedonio, E. Drioli, An exergetic analysis of a Membrane Desalination System, *Desalination—Special issue honoring Sidney Loeb*, 261 (2010) 293–299.
- [66] F. Macedonio, L. Katzir, N. Geisma, S. Simone, E. Drioli, J. Gilron, Wind-aided intensified evaporation (WAIV) and membrane crystallizer (MCr) integrated brackish water desalination process: Advantages and drawbacks, Desalination 273 (2011) 127–135.

- [67] F. Macedonio, E. Drioli, A.A. Gusev, A. Bardow, R. Semiat, M. Kurihara, Efficient technologies for worldwide clean water supply, Chem. Eng. Process. 51 (2012) 2–17.
- [68] E. Drioli, F. Macedonio, Membrane Engineering for Water Engineering, Ind. Eng. Chem. Res. 51(30) (2012) 10051–10056.
- [69] F. Macedonio, C.A. Quist-Jensen, O. Al-Harbi, H. Alromaih, S.A. Al-Jlil, F. Al Shabouna, E. Drioli, Thermodynam ic modeling of brine and its use in membrane crystallizer, Desalination 323 (2013) 83–92.
- [70] C.J. Gabelich, M.D. Williams, A. Rahardianto, J.C. Franklin, Y. Cohen, High-recovery reverse osmosis desalination using intermediate chemical demineralization, J. Membr. Sci. 301(1–2) (2007) 131–141.
- [71] H. Ozgun, M.E. Ersahin, S. Erdem, B. Atay, B. Kose, R. Kaya, M. Altinbas, S. Sayili, P. Hoshan, D. Atay, E. Eren, C. Kinaci, I. Koyuncu, Effects of the pre-treatment alternatives on the treatment of oil-gas field produced water by nanofiltration and reverse osmosis membranes, J. Chem. Technol. Biotechnol. 88(8) (2013) 1576–1583.
- [72] M. Ebrahimi, D. Willershausen, K.S. Ashaghi, L. Engel, L. Placido, P. Mund, P. Bolduan, P. Czermak, Investigations on the use of different ceramic membranes for efficient oil-field produced water treatment, Desalination 250(3) (2010) 991–996.
- [73] J. Zhong, X. Sun, C. Wang, Treatment of oily wastewater produced from refinery processes using flocculation and ceramic membrane filtration, Sep. Purif. Technol. 32(1–3) (2003) 93–98.
- [74] L.M. Jackson, J.E. Myers, Design and construction of pilot wetlands for produced-water treatment, SPE Annual Technical Conference and Exhibition Denver, Colorado, USA, 5–8 October, 2003.
- [75] AGV Technologies, Inc., Improving produced water quality for coal bed methane. RPSEA-R-518, Final report, September 30, 2004.
- [76] T. Hayes, The electrodialysis alternative for produced water management, GasTIPS, Summer 2004 (2004) 15–20.
- [77] C. Knutson, S.A. Dastgheib, Y. Yang, A. Ashraf, C. Duckworth, P. Sinata, I. Sugiyono, M.A. Shannon, C.J. Werth, Reuse of Produced Water from CO2 Enhanced Oil Recovery, Coal-Bed Methane, and Mine Pool Water by Coal-Based Power Plants. Final Report for US DOE Project DE-NT0005343, 2012, (Accessed on 12/December/2013). Available from http://www.netl.doe.gov/technologies/coalpower/ewr/water/ppmgmt/pubs/05343FSRFG043012.pdf>.