

Abstract

The produced water, which could be a complex mixture of different organic and inorganic compounds (mostly salts, minerals and oils) is a major wastewater stream generated during oil and gas production processes. Due to increase oil and gas exploration and production, especially from unconventional resources like shale oil and gas reservoirs, the volume of this effluent production is increasing around the world and its discarding to the environment is one of the global concerns. There are various physical and chemical methods to treat the produced water. However, a comprehensive and deep understanding of each issue can lead to a better and more efficient solution. In this study, various physical and chemical treatment methods for produced water have been reviewed based on the latest findings and recently published articles on this topic. Moreover, challenges and opportunities of each of these treatment methods have been fully discussed. Also potential applications for reusing the treated PW have been suggested and discussed finally.

Keywords

produced water, oil and gas production, wastewater reuse, wastewater disposal

1 Introduction

Produced water (PW) is an undesirable product of hydrocarbon production from oil and gas reservoirs. Usually the PW is in contact with hydrocarbons in reservoir, well or surface pipelines, so that it is a very complex mixture comprising of polar and non-polar organic components, cations (e.g. magnesium, calcium and iron), anions (e.g. carbonate and bromide sulfate) and other substances such as heavy metals (e.g. barium, uranium, cadmium, chromium and lead) [1]. The PW may be originated from reservoir (associate water), previously injected water into the formation for recovery purposes, the water from the aquifer or combination of them and it can contain any chemicals added during the drilling and production processes.

The physicochemical properties of PW varies considerably depending on the reservoir type (e.g. oil, gas or coal), geographic location of the field, the geologic formation and the type of produced hydrocarbon (e.g. heavy oil, medium oil, light oil, lean gas, rich gas, ...). Table 1 represents the summary of typical oil field PW characteristics. Moreover, the PW characteristics and volume of PW varies throughout the lifetime of the proposed reservoir, in which, the water production is very small as the production starts from the reservoir and it increases as the reservoir gets older.

This study reviews the conventional and current PW treatment technologies, their challenges and opportunities. Moreover, the usability of membrane separation technologies, (e.g. pressure-driven and thermally driven), coalescing filtration, fresh water generation and recovery of valuable compounds with minimal negative impact on the environment have been discussed comprehensively.

2 Characteristics of produced water

PW management is a very expensive process, which needs to be kept in-line with each specific production plan and this way, it can play an important role in determining the economic recovery of the reservoir which may lead to leaving a substantial amount of recoverable hydrocarbons in the reservoir. In the following, some of the options for managing the PW in petroleum industry, have been summarized [1, 4].

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Table 1 Characteristics of typical oil field PW [1]

Parameter	Unit	Value
Density	kg/m ³	1014-1140
Surface tension	dynes/cm	43-78
TOC	mg/l	0-1500
COD	mg/l	1220
TSS	mg/l	1.2-1000
pH	-	4.3-10
Total oil	mg/l	2-565
Volatile (BTX)	mg/l	0.39-35
Chloride	mg/l	80-200000
Bicarbonate	mg/l	77-3990
Sulphate	mg/l	2-1650
Sulphide	mg/l	10
Total polar compounds	mg/l	9.7-600
Higher acids	mg/l	1-63
Phenols	mg/l	0.009-23

As the first way, it is very desirable to find a method to avoid the PW by preventing its production from the reservoir (i.e. using polymeric gels that block water contributing fissures or fractures). Another choice can be using the Downhole-Water Separators (DWS) which enable the separation of the water from produced downhole streams and re-injecting the PW into the suitable formations. This method is not always applicable. Other alternatives can be summarized as: injecting the PW into the same formation or another suitable formation, discharging the PW in the environment by treating it to meet required onshore/offshore discharge regulations, reusing it in the well drilling and maintenance-operations after the treatment to meet the required quality, using it for commercial purposes where significant treatment is required to meet the minimum quality for irrigation, rangeland restoration and live organism consumption.

As mentioned earlier, the oil-field PW contains several impurities such as dispersed oil. Oil is one of the important contaminants in PW since it can potentially cause toxic effects along the discard line. It can significantly distribute the chemical oxygen demand (COD) and hence affect the aquatic or marine ecosystems [5]. Current treatment processes could only recover oil droplets with size up to 10 microns [6]. Other contaminants are the dissolved organic compounds including organic acids, polycyclic aromatic hydrocarbons, phenols and some volatiles, their concentrations in PW are usually higher in gas condensate production wells than oil production wells. Treatment chemicals which are usually used as corrosion inhibitors and reverse emulsion breakers (including biocides) could be highly toxic even at low concentrations (i.e. 0.1 ppm). On the other hand, some corrosion inhibitors can create stable emulsions which would be very hard to separate [7].

PWs often contain some solids including precipitated solids, sand, silt, carbonates and clays which are suspended in the streams. Furthermore, PW can contain some anaerobic bacteria, which can cause corrosion, and heavy metals which are less toxic compared to general organic constituents [8].

Factors affecting the amount of PW are very important and should be investigated for better planning of PW management. Reynolds and Kiker [9] evaluated the parameters that could potentially affect the amount of PW including the drilling method (in which horizontal wells can usually produce at a higher rate than vertical wells), location of the well, completion type, producing zones communications (e.g. single zone production or commingled zones production), type of water separation technology, water injection or water flooding for enhancing oil recovery (EOR) purposes and degree of mechanical integrity.

3 Produced water management

PW is considered as a waste stream in oil and gas production processes and its management which is usually done to decrease its environmental pollution issues, is very expensive. For the PW management, three major successive manners can be considered which could respectively be summarized as minimizing the production of PW, reusing or recycling the PW and if none of them could be applied, discarding of PW must be considered.

PW treatment process, which is used before recycling or discarding the PW, is very important to decrease the harmfulness of the PW and valuable products would be achieved through it. The main objectives of this process could be stated as the removal of the following contents of PW:

1. Free and dispersed oil
2. Dissolved organics
3. Microorganisms, algae and bacteria
4. Turbidity via elimination of suspended particles and colloids
5. Dissolved gases
6. Dissolved salts and minerals, excess water-hardness and possible radioactive materials

Usually, selection of the PW treatment method is a challenging problem that is steered by the overall treatment goal. The general plan is to choose the cheapest and most efficient method. To meet up with mentioned objectives, operators usually have applied many stands-alone in one combined technology: physical, biological and chemical treatment methods for PW management and treatment. Table 2 represents a general overview of treatment technologies which apply nowadays for PW treatment. Some of these technologies will be discussed in the next section.

Table 2 Technologies assessed for PW treatment

Treatment method	De-oiling	Suspended particles removal	Iron removal	Softening (Ca and Mg removal)	Soluble/trace organics removal	Desalting
API separator	■	■				
Deep bed filter	■	■				
Hydrocyclone	■	■				
Aeration and sedimentation		■				
Precipitation		■	■			
Ion exchange			■	■		
Biological treatment					■	
Thermal desalination		■		■		■
Activated carbon	■		■	■	■	
Chemical treatment	■				■	
Ultrafiltration	■	■			■	
Nanofiltration	■	■	■	■	■	■
Reverse osmosis	■	■	■	■	■	■
Electrodialysis			■	■		■

4 Produced water treatment methods

4.1 Physical treatment methods

4.1.1 Hydrocyclones

Hydrocyclones are used to separate solids (i.e. sand) and oil contents of PW streams based on the density difference [10]. Usually, they consist of a cylindrical section at the top where the liquid stream is fed tangentially and a conical base. The performance and separation capacity of the hydrocyclones depend on the angle of the conical section [11]. This system has two discharge streams, one at the bottom, which is called the underflow or reject stream and used for discharging the heavier phase, and one at the top, which is called the overflow or product stream and used for discharging the lighter phase of the input stream. A general scheme of the hydrocyclone system is shown in Fig. 1.

PW contains several suspended solid particles and oil droplets as well as surfactants. Depending on the model of employed hydrocyclone, it can remove the particles in the range of 5 to 15 µm; however, it cannot remove the soluble components [12]. Hydrocyclones have been extensively used to treat the PW by numerous companies [11, 12]. Hydrocyclones do not need any chemicals or energy for their operation. Also they do not require any pre or post treatment stages and the hydrocyclone is the only required piece of treatment equipment. Depending on the size and configuration of the hydrocyclone, a large pressure drop can be occurred through the hydrocyclone. The waste stream, which is the bottom output of the hydrocyclone, is a slurry of concentrated solids and it is the only residual that must be disposed. A summary of the hydrocyclone assessment is provided in Table 3.

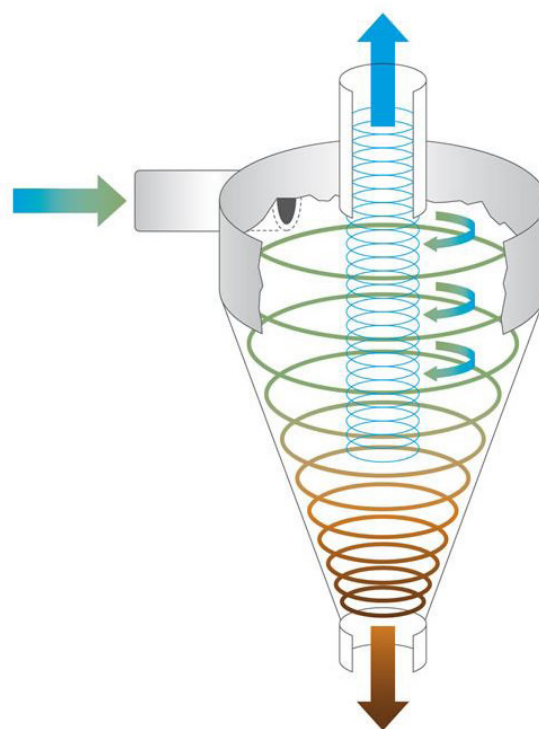


Fig. 1 A general scheme of the hydrocyclone

It must be noted that the use of compact hydrocyclones (with small and light specifications) is more favourable in offshore platforms because of the space limitations in those environments.

The Epcor compact floatation unit is a vertical three phase separator cyclone which is capable of separating the oil, gas and water phases with separation efficiency of from 50 % up to 70 % for dispersed oil content of PW [13].

Table 3 Assessment of hydrocyclone technology

Criteria	Description
Industrial status	Hydrocyclones have been widely used for PW treatment. They are mainly used for oil-water separation and can also be used for particulate removal.
Feed water quality bins	Applicable for all TDS bins, independent of salt type and concentration. High oil, particulate or organic concentrations.
Production efficiency	Can reduce the oil concentrations to 10 ppm. High water recovery.
Energy usage	The hydrocyclone does not require any energy itself; but a pump may be required to deliver the PW to the hydrocyclone or to recover pressure loss through the hydrocyclone.
Chemicals usage	None.
Expected lifetime of critical components	Long, no moving parts, may suffer from erosion.
Infrastructure considerations	Minimal. Forwarding pump.
Pre-treatment of feed water	Not required.
Post-treatment of output water	Hydrocyclone is usually used as a part of treatment stages. So, post-treatment may be required to remove other constituents of feed water.
Operator & maintainer considerations	Inlet solid block and scale formation can be occurred and frequent cleaning is required.
Overall costs	-
Waste disposal	Disposal is required for output slurry.

4.1.2 Thermal separation processes

Thermal separation technologies were traditionally used for large desalting plants, which included PW treatment processes [14]. Thermal separation techniques are still applied in plants where energy resources are readily available, such as the Middle East region, where the cost of energy is relatively low [15].

Figure 2a represents a general scheme for an MSF unit which is a mature and robust desalination/PW treatment method. In MSF, the feed water is heated and the pressure is lowered to evaporate the water and this steam is used for desalination process. This process consists of a series of stages, each operating at a decreasing combination of temperature and pressure. It can be used for desalting of water with high TDS (total dissolved solids) up to 40,000 mg/l. Some anti-scaling chemicals, such as EDTA and acids are also used to prevent the scaling. Moreover, Screening and rough filtration can be used for removing large suspended solids. The capital costs and required electrical energy of the MSF unit, completely depends on the type of feed water and desalination capacity [16].

Figure 2b represents a general scheme of the MED desalting unit in which the feed water passes through a series of evaporators in the way that produced vapour in each evaporator is subsequently used to evaporate the water in the next evaporator. Same as the MSF process, the MED process is a mature and robust technology for desalination which needs both thermal and electrical energies and pre-treatment and anti-scaling agents are also required but its overall cost is relatively lower than the one of the MSF process. The life cycle of this unit is about 20 years [17].

The waste stream of these processes is a solution with a high degree of salinity. By using hybrid thermal technologies, zero liquid discharge can be achieved through a brine concentrator and crystallizer [16]. Moreover, the hybrid systems of MED-RO/NF or MSF-RO/NF are under investigation to increase the water recovery and decrease the hyper-saline waste discharge to the environment [18, 19].

Vertical tube/falling film evaporation and vapour compression evaporation (VCE) are the other effective thermal processes for PW treatment. The advantages of these methods could be summarized as follows:

- No sludge production
- No need of chemicals for treatment
- Lower costs of waste and life cycle
- Lower requirement of maintenance and human power
- No requirement for oil separation apparatus

It must be noted that about 95 % of the operating cost for thermal treatment processes in industrial scale is related to the energy consumption.

4.1.3 Adsorption treatment processes

Adsorption can be accomplished by using a variety of materials, including organoclays [20], zeolites [21], chitosan and activated carbon [22]. In the adsorption based treatment methods, chemicals are not required for normal operation; however, they may be used to regenerate the medium when all active sides of the adsorbents are occupied [23].

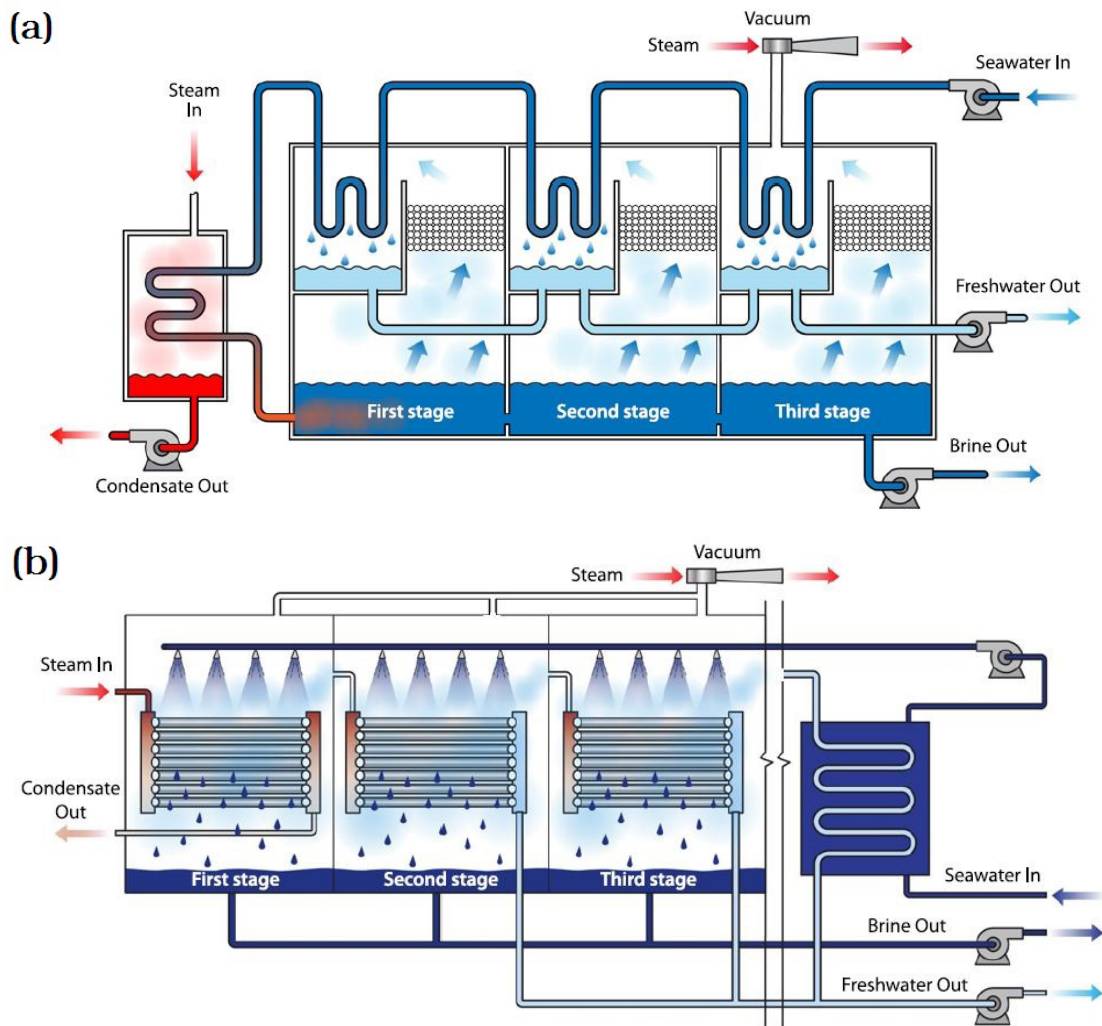


Fig. 2 General scheme of the (a) MSF and (b) MED processes [15]

Performance of the adsorbents is affected by pH, temperature, amount of suspended solids and oils, concentration of dissolved contaminants and salts. For example, the removal efficiency could be decreased because of plugging the adsorption medium by the suspended oil/particles of PW. For this reason, the medium is backwashed periodically to remove large particulates which blocked the void spaces of the medium. The input stream can be fed to the adsorption medium by gravity, so it does not require any energy supply except during the backwash process. Adsorbents are capable of removing iron, total organic carbon, heavy metals, and the oil content of the PW [24]. Adsorption process is generally utilized as a unit process in a treatment plant rather than used as a stand-alone process. The adsorbents in the adsorption process, can be easily overloaded for handling large concentrations of organics, so this process is better to be used as a polishing stage rather than a primary treatment stage [25].

The adsorption medium usage rate is one of the main operational costs for adsorption processes. When all active sites of the adsorption agents have been occupied, the adsorbents must be regenerated or disposed. Regenerating the medium will

result in a liquid waste which must be disposed. Also, solid waste disposal is necessary when the adsorption agents need to be completely replaced [26, 27].

4.1.4 Coalescing filtration

In the case of PW, which is oil contaminated wastewater, fine oil droplets have been dispersed in hyper-saline water as the continuous phase. Liquid-liquid coalescing filtration is a versatile method which could be used to accelerate the merging of small droplets to form bigger droplets [28]. This phenomenon can be explained by the well-known law of Stokes which expresses that the falling or rising velocity of droplets can be defined as follows:

$$v_d \propto \frac{R^2 g (\rho_d - \rho_f)}{9\mu} \quad (1)$$

where v_s is the falling or rising velocity, R is droplets radius, ρ_d is the droplets density, μ is dynamic viscosity and ρ_f is the bulk fluid density. Based on Eq. (1), the settling or rising of the larger droplets in the coalescing system, requires considerably less residence time rather than of smaller droplets. So that by

creating the larger droplets, the separation process can be done more quickly.

Droplets coalescing involve three major steps including: droplets strike and adhere together, Coalesce of several captured droplets on the medium, and formation of larger drops which are trickled down/up and become separated. Therefore, the coalescing medium is the most important part of a coalescing filtration system. Shirazi et al. [6] used a pilot plant (Fig. 3) to study the coalescing filtration of oil contaminated wastewater using a novel filter medium in which an electrospun nanofibrous filter made of polystyrene was used as the coalescing filtration medium. They investigated the effect of thermal treating on the characteristics and performance of as-spun filters. They found that thermal treated filters had better oil droplets separation performance; so, this process can be effectively used for the separation of oil content of PW stream.

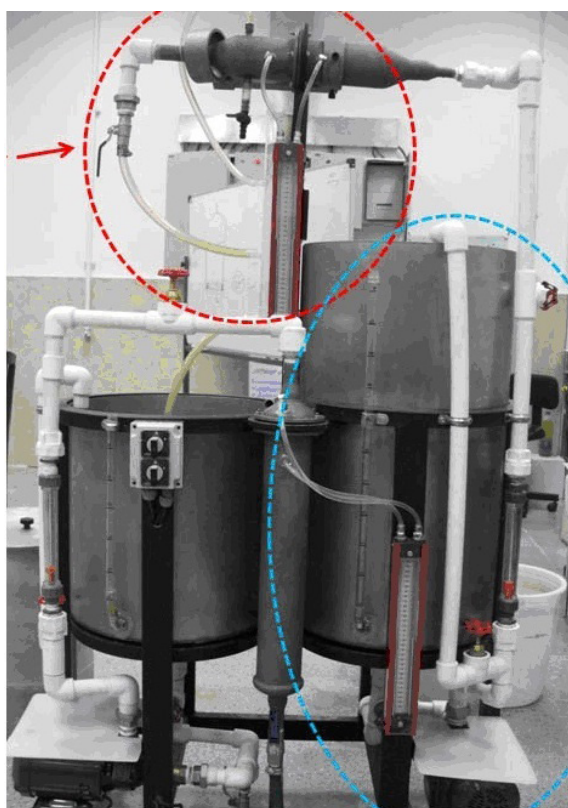


Fig. 3 Shirazi et al. coalescing filtration pilot plant [6]

4.2 Chemical treatment methods

Coagulation and flocculation are two effective methods for removing suspended oil droplets, particles and colloids but these are unable to remove dissolved contaminants. In this regard, Lime softening is the common process for PW treatment which can remove this type of water contaminants.

Advanced oxidation processes (AOPs) (e.g. chemical oxidation, electrochemical oxidation, Fenton reaction, Ozone treatment and photocatalytic oxidation) have been extensively investigated for the decades and can be considered as a fully developed technology which are enable to remove about 90 %

of BOD/COD content of PW [29]. The AOPs include a number of different reactions such as $O_3+H_2O_2$, $UV+H_2O_2$, $UV+O_3$ or $O_3+UV+TiO_2$, and Fenton reaction [30]. Furthermore, there are some other non-conventional AOPs such as wet-air-oxidation and humid-oxidation with peroxide (OHP) [31]. The important note is that there is limited information on AOPs usage for PW treatment in industrial scale.

4.3 Membrane treatment methods

High treatment costs, using toxic chemicals, space limitations for equipment installation and generation of additional pollution, have led the researchers to develop membrane-based methods for wastewater treatment purposes [32, 33]. The membrane pressure driven separation process relies on the pore size of the used membrane for separation of the feed stream components [34].

Membranes are thin films of synthetic organic and/or inorganic materials, which separate specific components from the aqueous feed stream. Membrane processes can be classified based on their applied membranes (e.g. microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO)) [35].

Microfiltration (MF) membrane can be used for separation of suspended particles, so it can only be used for the pre-treatment of PW. Cakmaci et al. [36] studied the application of membrane processes in PW treatment by use of a MF membrane made of cellulose acetate with the pore size of 0.2 microns which was used as pre-treatment stage for NF and RO membranes. Ebrahimi et al. [37] were studied the different ceramic membranes for the oil-field PW treatment.

UF is one of the membrane technologies for treating oil contaminated wastewater which is more effective than other previously mentioned conventional methods. The advantages of this method include high oil removal efficiency, no chemical requirement, low energy costs and small space requirement for installation. Another work was studied and it compared the MF and UF membranes for oil-field PW treatment by utilizing a pilot scale plant [37]. Results of this work indicated that in contrast to MF membranes, UF membranes can meet effluent standards. It was also concluded that for PW treatment, UF membranes with MWCO (molecular weight cut off) of 100 to 200 kDa would be preferred.

Experiments investigations have indicated that RO/NF membrane technologies would be perfect for PW treatment where an appropriate pre-treatment method has been used before. It must be noted that all the previously mentioned conventional methods could be used as pre-treatment stage for RO/NF membrane systems. Capital costs of RO/NF systems depend on the required separation percentage, building materials of the membrane and site location. On the other hand, energy price and TDS (total dissolved solid) level, affect the operating costs.

Table 4 Comparison of polymeric and ceramic MF/UF membranes.

Membrane type	Polymeric MF/UF membrane	Ceramic MF/UF membrane
Feasibility	Enable to treat water/wastewater with high TDS Enable to treat PW	Ceramic membranes have extensively been used for PW treatment
Pre-treatment	Both chemical (e.g. ferric chloride coagulant) and physical (e.g. cartridge filtration) pre-treatments can be used	Both chemical (e.g. ferric chloride coagulant) and physical (e.g. cartridge filtration) pre-treatments can be used
Overall costs	Capital costs depend on feed water quality and size of the membrane module	Ceramic membranes are more expensive than polymeric ones, but they have longer life cycle
Life cycle	3-7 years	≥ 10 years
Primary positive aspects	Treated stream is usually free of suspended solids 85 % to 100 % of feed stream recovery	Treated stream is usually free of suspended solids 90 % to 100 % of feed stream recovery, Have a longer lifespan than polymeric membranes
Primary negative aspects	Membrane needs periodic cleaning and Waste generation during backwash	Irreversible membrane fouling can be occurred Membrane needs periodic cleaning and Waste generation during backwash

A membrane can be homogeneous/heterogeneous and symmetric/asymmetric in structure, solid or liquid, and carry a positive or negative charge [38]. From the material point of view, a membrane could be made of organic (e.g. polymeric membranes) or inorganic materials. Among inorganic membranes, ceramic membranes have widely been used for water/wastewater treatment purposes. Ceramic membranes have high mechanical strength, high chemical compatibility, long operational life, sufficient thermal stability and potential low life-cycle cost; however, high capital cost is one of their drawbacks. This way, ceramic membrane market share is expected to grow in the following years because of its advantages related to the solvent resistant polymeric membranes which can also be used for such purposes (i.e. PW treatment) and this share can be improved by advances in materials, configuration, and operational experiences of ceramic membranes [39, 40]. Table 4 shows a comparison of MF/UF based treatments of PW with main focus on the membrane type (i.e. polymeric membrane or ceramic membrane).

5 Discussion

All mentioned treatment methods have their own advantages and disadvantages. High initial capital costs and sensitivity to the feed stream quality are the most important disadvantages of physical methods; whereas Hazardous sludge generation, high operating costs and sensitivity to the initial concentration of effluents in feed stream are disadvantages of chemical methods. On the other hand, fouling/scaling issues and high module price are the disadvantages of membrane-based treatment methods.

Prior to decision for a proper method for PW treatment, some critical questions shall be answered depending on the feed stream quality and quantity. These questions can be stated as follows:

1. Technology capability for specific contaminants removal
2. Resource consumption to achieve desired treatment
3. Necessity of pre/post -treatment
4. Level of each contaminants in the feed stream.

Furthermore, in offshore production plants, space limitations encourage the engineers to use compact treatment processes, whereas in onshore production units, where enough space is available, a wider variety of treatment methods can be used.

Reusing of PW is a promising strategy for the thirsty world. Recycled/treated PW could be used for living creations such as irrigation, and wildlife consumption purposes. This type of treated water usage is reasonably beneficial especially for arid regions but it needs a proper treatment method selection to provide the required quality of treated water. The treated water can also be used for various industrial applications such as drilling, EOR processes (e.g. water injection process), dust control (especially in the Middle East region), cleaning, cooling towers make-up, and fire-fighting. This type of treated water usage will decrease the fresh water demand but the treated water must have the minimum required quality to meet the operational standards. One important note is that the usage of treated water as make-up stream for cooling towers, where a large quantity of water is needed for continuous operation, can be one the important applications of treated water and it can eliminate the operational costs by a degree which is completely dependent to the quality of the make-up water.

As mentioned earlier (in Table 1), PW contains various concentrations of minerals and ions. Hence, feeding crystallization units with concentrated PW samples could be used as a promising strategy for specific minerals extraction and recovery.

6 Conclusions

In this work, we examined the source and characteristics of the oil field produced water. Different treating methods for this highly polluted wastewater with a high salinity level were also discussed however it must be noted that there is no single unit operation for treating the PW stream; in other words, hybrid and integrated processes should be developed and improved for such purposes. Selection of the best method for PW treatment

was also investigated which strongly depends on the PW origin, its chemical characteristics and space limitations for equipment installation. Finally, the treated PW would be a beneficial water resource for some applications, such as industrial and irrigation or even for drinking purposes.

Nomenclature

AOPs	Advanced oxidation processes
BOD	Biochemical oxygen demand
BTX	Benzene Toluene Xylene
COD	Chemical oxygen demand
DWS	Downhole Water Separators
EOR	Enhancing oil recovery
MED	Multiple effect distillation
MF	Microfiltration
MSF	Multi-stage flash distillation
MWCO	Molecular weight cut off
NF	Nanofiltration
RO	Reverse osmosis
PW	Produced water
TDS	Total dissolved solids
TOC	Total organic carbon
TSS	Total suspended solids
UF	Ultrafiltration
VCE	Vapour compression evaporation

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