

Produced Water Treatment Technologies: An Overview

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Abstract

This chapter provides an overview of produced water (PW) characteristics and treatment technologies. PW constituents are numerous and typically include oil and grease, suspended solids, dissolved solids, heavy metals, radioactive materials, bacteria, dissolved gases, and many other chemicals. These constituents influence the selection of treatment technologies, govern the scope of PW management process and determine the impacts of various factors on PW treatment practices, particularly in onshore and offshore (oil and gas) production facilities. PW from treatment processes can be reinjected into reservoir, beneficially reused, and/or safely disposed in accordance with prevailing (local) regulations. PW treatment technologies typically focus on removal of residual oil (and grease), suspended solids, dissolved solids and other contaminants. Treatment technologies for PW management include a pre-treatment step (e.g.: crude oil separator), primary treatment (e.g.: desander, skim tanks, plate pack interceptors, API separator and/or liquid-liquid or solid-liquid hydrocyclone), secondary treatment (e.g.: induced gas flotation, dissolved gas flotation, etc.) and the tertiary/advanced treatment step (e.g.: dual media filters, cartridge filters, membranes, etc.). Treating PW for beneficial reuse has gained significant attention, leading to various emerging technologies that are

briefly discussed (e.g., biological treatment technologies, capacitance deionization, humidification dehumidification, mechanical vapor recompression, crystallization). The basic mechanisms of each technology and their respective uses for PW treatment are discussed, along with their advantages, disadvantages, and waste streams generated. Thus, this chapter provides an overview of current and emerging technologies for treating PW, to facilitate their safe disposal, reinjection and beneficial reuse.

1.1 Introduction

Produced water (PW) is the wastewater separated from production fluid during oil and gas (O&G) production (Larson, 2018; WEF, 2018b; Jimenez et al., 2018). PW is generated from both conventional and unconventional sources such as the coal-bed methane, tight sands, and gas shale (Jimenez et al., 2018). PW includes formation/connate water, flowback water (injected water), and condensation water. Amount of PW generated during production of crude oil and natural gas can be as high as ten times the volume of hydrocarbon produced. Produced water volume can rise to as much as 98% of production fluids (e.g., at late stage of oil (gas) production), when production is no longer economical (Larson, 2018; Gray, 2020; Lusinier, 2019). Thus, the ratio of PW to oil varies from well to well, and over the life of the well. Typically, PW to oil volume ratio is over 3:1, and can be as high as over 20:1 (Larson, 2018; Jimenez et al., 2018). The global PW production is approximately 10.44 billion gallons/day (Jimenez et al., 2018), whereas the U.S. produced an estimated 890 billion gallons/year of PW in 2012 (GWPC, 2019).

PW contains numerous chemicals, some of which are toxic organic and inorganic compounds (Jimenez, 2018). Physical and chemical properties of PW vary, depending on the geographic location of the field, the geological formation, the extraction method, and the type of hydrocarbon product being produced. Furthermore, PW may include chemical additives, which are dosed in during drilling to treat or prevent operational problems and to enhance subsequent oil/water separation (Jimenez et al., 2018). Thus, both the flow rate and PW composition change over time, leading to varying PW management strategies (WEF, 2017). Multiple separation steps are typically required to

separate oil and water from PW (WEF, 2017). Most regulatory policies and technical requirements focus on treatment of O&G content; salt content is also critical in onshore operations (Jimenez, 2018). The major PW constituents of concern may be categorized in the following groups: salts, expressed as salinity, total dissolved solids (TDS) or electrical conductivity; oil and grease; BTEX (benzene, toluene, ethylbenzene and xylenes); PAHs (polyaromatic hydrocarbons); organic acids; phenol; natural inorganic and organic compounds, e.g., chemicals that cause hardness and scaling such as calcium, magnesium, sulfates, and barium; and chemical additives used in drilling, fracturing, and operating the well (e.g., biocides, corrosion inhibitors, etc.) (Arthur et al., 2011).

The degree of PW management depends on the site's treatment requirements and typically includes deep well injection/disposal, reinjection, evaporation ponds, surface water discharge, treatment and reuse (WEF, 2017; Does, 2012). Local water scarcity, legislation, risk of formation plugging, high costs associated with PW disposal, quality of water used in enhanced oil recovery (EOR) and increasing demand for water in production operations are some of the drivers for appropriate PW management techniques. Due to scarcity of water resulting from climate change-induced drought, regulations have become more stringent, disposal method costs have increased, and beneficial reuse is becoming a more viable option (Larson, 2018; WEF, 2018). PW disposal includes deep well injection and discharge into surface water, which requires treatment to remove dispersed and dissolved oil, solids, and toxic compounds. In offshore operations, the common practice is to discharge treated PW to the sea. hence the main treatment objective is to reduce oil and grease to levels required to meet discharge regulations and environmental standards (Does, 2012).

Reinjection into petroleum formations for hydraulic fracturing, water flooding to maintain the pressure in the reservoir and displace the petroleum fluids, and enhanced oil recovery (EOR) are the most widely used PW management strategies practiced in the industry. Reinjection of PW is generally considered the most environmentally friendly option because it substantially reduces the freshwater or seawater consumption (Lusinier, 2019). Reinjection of PW requires removal of suspended solids (SS), to avoid formation

plugging. In addition, scale forming constituents such as Barium (Ba) and Calcium (Ca) must also be removed to minimize scaling.

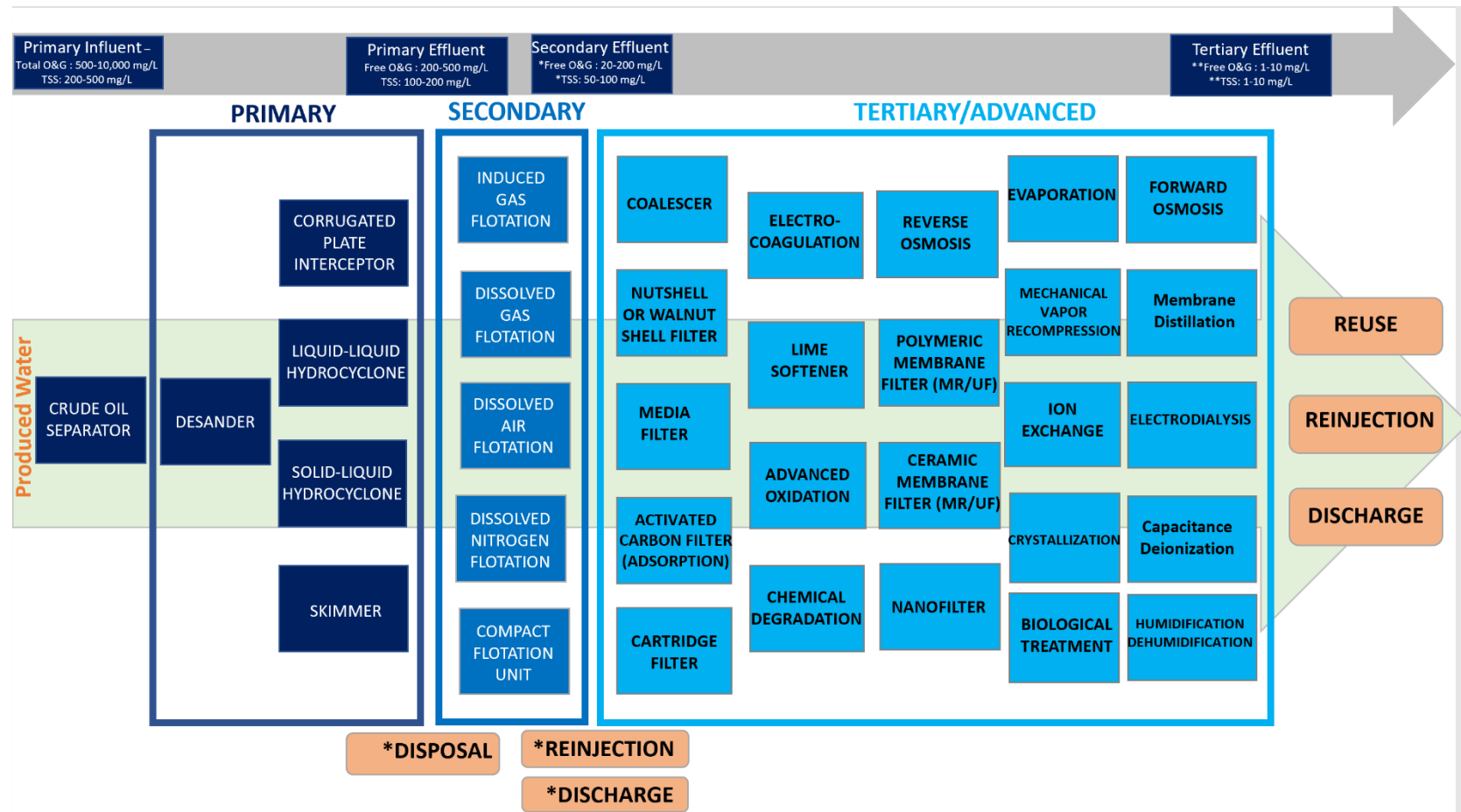
Water injection is usually utilized as a secondary oil recovery technique in oil fields when reservoirs deplete. By contrast, water is not typically injected in gas reservoirs; hence, PW from gas fields is mostly formation water and condensed water. PW from gas reservoirs is generally much less in volume than that produced from oil fields (Ahmadun, 2009). However, due to the higher concentrations of volatile hydrocarbons, PW discharged from gas fields is much more toxic than the PW from oil wells (Duraismy, 2013; Jimenez, 2018).

Currently, the majority of PW generated at onshore O&G facilities is reinjected underground either for disposal or for EOR processes. Thus, the major focus of onshore facilities is the types of treatment technologies mainly designed for dispersed O&G and SS to avoid plugging and pumps damage (WEF, 2017; WEF, 2018). The common practice for offshore operations is to discharge the treated PW to the sea, leading to the main treatment objective of reducing O&G to acceptable levels and mitigating toxicity impacts on aquatic fauna and flora. Moreover, the requirement for fracturing fluid has changed over the years, leading to different treatment requirements (WEF, 2017). Depending on the location of the onshore O&G facilities, different types of treatment technologies are available, including primary (e.g., hydrocyclone, corrugated plate separator, American Petroleum Industry (API) separator, or similar) and secondary (e.g., flotation units, such as induced gas flotation [IGF], dissolved gas flotation [DGF], dissolved air flotation [DAF, dissolved nitrogen flotation [DNF] and compact flotation unit [CFU]), to support the goal of reducing O&G concentrations in treated PW to 30 or 40 mg/L (Dores et al., 2012; Veil et al., 2004). Nonetheless the combination of these primary and secondary treatment technologies is unable to produce an effluent that meets the quality standard for beneficial reuse in irrigation or industrial processes (Dores et al., 2012).

There is an increasing push for PW recycling for irrigation, livestock watering, aquifer storage, municipal and other industrial uses due to climate-induced water scarcity

(Al-Ghouti et al., 2019). In addition, highly treated PW may be used for other beneficial uses such as in irrigation and industrial processes.

There is need for tertiary treatment of PW or a polishing treatment for the reduction of O&G content, total dissolved solids (TSS) and other concerning substances depending on the end use. Apart from the O&G and TSS concentrations, those tertiary/polishing treatment technologies focus on treatment of micro and nanoscale particles, salinity (9% or greater), volatile compounds, extractable organics (acidic, basic, and neutral), ammonia and hydrogen sulfide. API has assessed several proven tertiary or polishing treatment technologies to reduce the pollutants in PW to desirable effluent quality or almost undetectable levels. These technologies include carbon adsorption (modular granular activated carbon systems), air stripping (packed tower with air bubbling through the PW stream), membrane filtration (nanofiltration and reverse osmosis polymeric membranes), ultra-violet light (irradiation by UV lamps), chemical oxidation (ozone and/or hydrogen peroxide oxidation) and biological treatment (aerobic system with fixed film bio-tower or suspended growth) (Igwe et al., 2013). The types of primary, secondary, and tertiary treatment applicable for PW treatment are shown in Figure 1.1. Overall, the specific treatment process or train depends on the characteristics of PW and desired end-use of the treated PW. Typical onshore and offshore treatment trains, focused on O&G and TSS removal, are shown in Figure 1.2.



*Disposal, reinjection and direct discharge are practiced at the end of primary and secondary treatment as well.

Figure 1.1: Primary, secondary, and tertiary treatment technologies applicable for PW treatment (Larson, 2018; WEF, 2018; Jimenez, 2018).

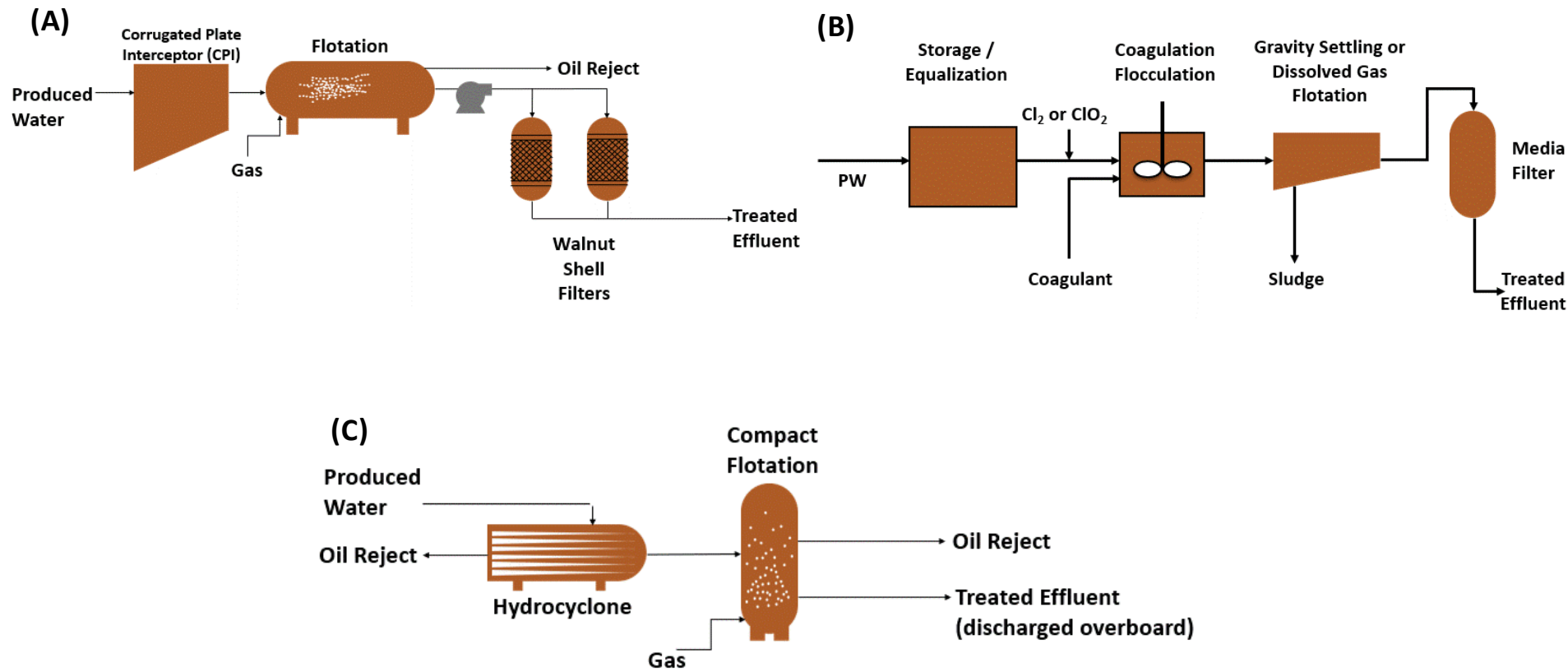


Figure 1.2: (A) Typical onshore conventional Produced Water (PW) treatment, (B) Typical unconventional PW treatment, and (C) Typical offshore PW treatment (Adopted from Larson, 2018).

1.2 Characteristics of Produced Water

PW is a very complex mixture of water and up to several thousand other constituents similar to those found in crude oil. The physical and chemical properties of PW is variable (Al-Ghouti et al., 2019; Jimenez et al., 2018), and the complex composition, concentrations and toxicity of PW are influenced by geographic location of the field, composition of the fracking fluid, the geological formation, extraction method, the lifetime of the reservoir, reservoir conditions (e.g., pressure and temperature), and the chemical characteristics of the hydrocarbon being produced. In the O&G industry, the O&G content is generally regulated along with salt contents, total suspended solids (TSS) and other constituents (Jimenez et al., 2018). The toxicity of PW discharged from gas platforms is many times higher than the toxicity of discharge from oil wells, but the volumes of PW are less than those from oil production. These constituents can be a) organic compounds including oil and grease, b) suspended solids (SSs), c) dissolved solids/salts, d) heavy metals, e) radioactive materials, f) bacteria, g) dissolved gases etc.

Typical concentrations of constituents found in PW are shown in Table 1.1. Dissolved and dispersed oil compounds composed of hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (BTEX), naphthalene, phenanthrene, dibenzothiophene (NPD), polyaromatic hydrocarbons (PAHs), phenols, organic acids, etc. (Al-Ghouti et al., 2019; Jimenez et al., 2018). Most of the hydrocarbons do not dissolve in water and mainly disperse as an emulsion, or clearly separate into two phases. Therefore O&G in PW can be in the form of free, dispersed and emulsified oil. Suspended solids (SSs)/insoluble produced solids include sand, clays, slit, proppants, carbonate and sulfate scales, corrosion products, etc. Some other inorganic crystalline substances such as SiO_2 , Fe_2O_3 , Fe_3O_4 , and BaSO_4 can also be found in produced water. Large amounts of SSs could lead to serious problems such as clogging flow lines and plugging the well bore downhole, thereby reducing production. The concentration of total suspended solids (TSS) ranges from a few milligrams per liter up to ~ 5000 mg/L (Al-Ghouti, 2019, 54). PW may also contain deposited high-molecular-weight components as solid precipitates, such as paraffin waxes and asphaltenes.

Dissolved natural salts and minerals are present in PW as cations and anions such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Cl^- , SO_4^{2-} , and CO_3^{2-} . Sodium and chloride are the main ions responsible for the salinity of PW. The TDS varies considerably and is usually higher than seawater, ranging from a few parts per million (ppm) to approximately 400,000 ppm (Ahmadun, 2009; Jimenez, 2018). The high salinity (i.e., high TDS) of PW makes it unsuitable for reuse, and generally requires an expensive and energy intensive treatment to reduce the TDS to acceptable levels where the PW can be reused. In addition, concentrated brine often results in the formation of scales such as calcite (CaCO_3) and barite (BaSO_4) upon temperature and pressure changes, causing serious problems such as plugging of reservoir rock pores, production losses, and equipment damage.

Produced Water may contain trace quantities of heavy metals, such as iron, nickel, copper, zinc, arsenic, cadmium, mercury, and lead (Ahmadun, 2009, 2011), which are classified as dissolved inorganic compounds. Naturally occurring radioactive materials/radionuclides such as ^{226}Ra and ^{228}Ra may also be present in oilfield PW (Ahmadun, 2009). Like heavy metals, naturally occurring radioactive materials are also classified as dissolved inorganic compounds. There can be bacteria/viruses present that require treatment, such as sulfur oxidizing anaerobic bacteria, which can cause corrosion and scaling, and thereby clog the pipelines and formation pores. Large quantities of dissolved gases are contained in oilfield brines mostly volatile hydrocarbons, but also CO_2 , O_2 , and H_2S are commonly found in PW.

In addition to its natural components, PW may include chemical additives dosed in drilling to treat or prevent operational problems and enhance oil/water separation. Such additives include gas hydrate inhibitors, corrosion inhibitors, oxygen scavengers, scale inhibitors, biocides to mitigate bacterial fouling, asphaltene dispersants, paraffin inhibitors, defoamers, emulsion breakers, clarifiers, coagulants, flocculants, etc. (Daigle, 2012). Some of these chemicals are highly toxic even at low concentrations.

Table 1.1: Main Components and Reported Concentrations in Produced Water
(Al-Ghouti et al., 2019; Jimenez et al., 2018; Nasiri et al., 2017)

Parameter/Heavy metals (mg/L - otherwise shown)	Reported ranges of values	Heavy metals (mg/L)	Reported ranges of values
Density (kg/m^3)	1014-1140	Calcium (Ca)	13-25800
Conductivity ($\mu\text{S/cm}$)	4200-58,600	Sodium (Na)	132-97000
Surface tension (dyn/cm)	43-78	Potassium (K)	24-4300
pH (unitless)	4.3-10	Magnesium (Mg)	8-6000
COD	1220-2600	Iron (Fe)	<0.01-100
TOC	0-1500	Aluminium (Al)	310-410
TSS	1.2-1000	Boron (B)	5-95
TDS	100-400,000	Barium (Ba)	1.3-650
Total oil (IR) (O&G)	2-565	Cadmium (Cd)	<0.005-0.2
Benzene	0.032-778.51	Copper (Cu)	<0.02-1.5
Ethylbenzene	0.026-399.84	Chromium (Cr)	0.02-1.1
Toluene	0.058-5.86	Lithium (Li)	3-50
Xylene	0.01-1.29	Manganese (Mn)	<0.004-175
Volatile compounds (BTEX)	0.39-35	Lead (Pb)	0.002-8.8
Chloride	800-200,000	Strontium (Sr)	0.02-1000
Bicarbonate	77-3990	Titanium (Ti)	<0.01-0.7
Sulphate	<2-1650	Zinc (Zn)	0.01-35
Ammonium (as N)	10-300	Arsenic (As)	<0.005-0.3
Sulphite	10	Mercury (Hg)	<0.005-0.3
Phenol	0.009-23	Silver (Ag)	<0.001-0.15
Total organic acids	0.001-10000	Beryllium (Be)	<0.001-0.004
Volatile fatty acids (VFA)	0.009-4900	Palladium (Pd)	0.008-0.88

Table 1.2: Typical Concentrations of Produced Water Chemical Additives (Ahmadun et al., 2009)

Chemical Name	Concentrations in oil field		Concentrations in gas field	
	Typical (mg/L)	Range (mg/L)	Typical (mg/L)	Range (mg/L)
Corrosion inhibitor (contains amide/imidazoline compounds)	4	0.3-10	4	0.3-10
Scale inhibitor (contains phosphate ester/phosphate compounds)	10	0.2-30
Demulsifier (contains oxylated resins/polyglycol ester/alkyl aryl sulphonates)	1	1-2
Polyelectrolyte (e.g. polyamine compounds)	2	0-10
Methanol	2000	1000-15,000
Glycol (DEG)	1000	7.7-2000

1.3 Treatment Methods for Produced Water

Since PW contains several different contaminants with varying concentrations, numerous treatment technologies with a series of individual unit processes are required to remove contaminants that might not be removed through a single process. Prior to disposal or any form of PW reuse, proper contaminant removal treatment is required to comply with environmental regulations and to meet the requirements and standards for reuse applications. The treatment required depends on the PW composition and how the PW is disposed or reused. Onshore PW is usually discharged into deep disposal wells, and only dispersed hydrocarbons and SS are removed to prevent formation plugging (Hussain, 2014). On the other hand, PW in offshore operations, is often discharged to sea, and only hydrocarbons are treated to acceptable concentrations to meet the environmental regulations and standards. Reuse in oilfield operations such as in waterflooding, drilling, and hydraulic fracturing, may require only limited PW treatment to meet the needs for these operations. However, reuse in beneficial applications such as in agriculture irrigation and industrial processes might require more extensive treatment to comply with more restrictive limitations and meet the quality required (Gray, 2020).

A typical PW treatment process has three main stages a) primary treatment, b) secondary treatment step, and c) tertiary/advanced treatment steps with a pre-treatment step (Figure 1.1). The pre-treatment step is done to remove large oil droplets, coarse particles and gas bubbles with the goal of reducing the amount of dispersed contaminants

that would otherwise pass through the crude oil separator. The primary treatment step involves removing small oil droplets and particles using desanders, skim tanks, plate pack interceptors, API separators, and/or liquid-liquid or solid-liquid hydrocyclones. The secondary treatment involves removal of much smaller oil droplets and particles using gas flotation (e.g., induced gas flotation, dissolved gas flotation, etc.) and, sometimes, hydrocyclones and centrifuges. The tertiary/advanced treatment step is usually employed to remove ultra-small droplets and particles and dispersed hydrocarbons (<10 mg/l) using techniques like dual media filters, cartridge filters, membranes, etc. (WEF, 2017; WEF 2018; Al-Ghouti et al., 2019).

Different physical, chemical, and biological processes are employed at different stages (e.g., primary, secondary, and tertiary/advanced step) of PW treatment. A well-designed combination (hybrid method) of two or more treatment technologies is commonly used to achieve a high degree of treatment and to reduce energy consumption. In general, a viable treatment method should have low operating costs and high efficiency. Additionally, in offshore uses, the technology should also be compact to accommodate space and weight limitations (Nonato, 2018). Typical onshore and offshore O&G and TSS treatment trains are shown in Figure 1.2.

The treatment methods can be broadly classified into basic separation methods designed to remove suspended solids and dispersed oil and grease, and more advanced techniques tailored for the removal of dissolved solids and hydrocarbons to achieve a higher degree of treatment (Lin, 2020). Basic separation methods include gravity separation, media filtration, flotation, coagulation-flocculation, and cyclonic/centrifuge separation. Commonly used advanced treatment methods include membrane filtration, adsorption, distillation, ion exchange, advanced oxidation processes, etc. The detailed description of treatment methods, their advantages and drawbacks can be found in several recent excellent reviews on the treatment of PW (Al-Ghouti, 2019; Jimenez, 2018; Nasiri, 2017; Nonato, 2018; Wei, 2020).

In general, the treatment technologies are selected and recommended based on the following factors: a) source of PW: onshore and offshore, b) PW composition and concentration of pollutants, c) regulations and environmental standards associated with

discharge and reuse, d) space requirements, e) cost of treatment. An overview of the separation technologies in use or with potential to treat PW is presented in Table 1.3 and Figure 1.1.

Table 1.3. Summary of Existing and Emerging Technologies for Produced Water

Treatment Technology	Dispersed Oil & Grease	Dissolved Hydrocarbons	Suspended Solids	Dissolved Solids
Physical Methods				
Gravity Separator	X		X	
Hydrocyclones	X		X	
Microfiltration			X	
Ultrafiltration	X	X	X	
Nanofiltration	X	X	X	X
Reverse Osmosis	X	X	X	X
Membrane Distillation	X	X	X	X
Thermal Separators				X
Flotation	X		X	
Activated Carbon Adsorption	X	X	X	X
Chemical Methods				
Chemical Precipitation	X		X	X
Ion Exchange				X
Advanced Oxidation Processes		X		
Electrodialysis				X
Electrochemical Processes		X		
Biological Methods				
Aerated Filtration	X	X		
Activated Sludge		X		
Membrane Bioreactors	X	X	X	X

This chapter briefly describes some treatment techniques, including physical, chemical or biological processes, for separating different types of contaminants from PW. Biological methods such as the activated sludge process, aerated filtration, and membrane bioreactors are not extensively utilized in PW treatment, but interest is increasing due to recycling and beneficial reuse of PW. Biological treatment processes are generally mostly used in refineries, petrochemical and other downstream facilities to remove dissolved organic compounds by biodegradation, in which aerobic or anaerobic microorganisms decompose the dissolved hydrocarbons into smaller molecules that can then be converted into water, CO₂, and biomass through biological oxidation. In general, when compared to physical and chemical treatments, biological treatments have higher removal efficiencies for dissolved hydrocarbons and are relatively less expensive. However, they suffer from serious challenges such as large footprints, which make biological treatments unsuitable for offshore applications. Other major challenges are the toxicity of some dissolved compounds, such as BTEX, and the high salinity of PW, which may strongly limit biological activity. Interested reader is referred to the comprehensive recent reviews on biological treatments of PW (Lusinier et al., 2019; Camarillo and Stringfellow-, 2018; Wei et al., 2019).

As discussed earlier, PW treatment processes focus on the removal of oil and grease and other contaminants. PW treatment equipment (e.g., API gravity separator; corrugated plate separator; induced gas floatation, etc.) have different capacities for particles size removal. Table 1.4 shows the list of different de-oiling technologies with respect to their particle size.

Table 1.4: Summary of Different Oil Removal Technologies for Produced Water (Arthur et al., 2005; WEF 2019)

Oil Removal Technology	Minimum size of particles removed (μm)
API gravity separator	150
Corrugated plate separator	40
Induced gas floatation (no flocculants)	25
Induced gas floatation (with flocculants)	3-5
Hydrocyclone	10-15
Mesh coalescer	5
Media filter	5
Centrifuge	2
Membrane filter	0.01

Treatment technologies such as corrugated plate separator, centrifuge, hydrocyclone, gas floatation, etc., can be used effectively to recover oil from emulsions and/or water with high oil content prior to discharge. Produced water from water-drive reservoirs and water flood production are the most likely feedstocks, containing oil and grease in excess of 1000 mg/L (Arthur, 2005). Treatment processes such as extraction, ozone/hydrogen peroxide, oxygen, adsorption, etc., can remove oil from water with low oil and grease content (<1000 mg/L) or remove trace quantities of oil and grease prior to membrane processing. Oil reservoirs and thermogenic natural gas reservoirs usually contain trace amounts of liquid hydrocarbons. Biogenic natural gas, such as coal-based natural gas (CBNG), may contain no liquids in the reservoir but when pumped to the surface, the water takes up lubricating fluids from the pumps. The basic description of de-oiling technologies, their respective advantages and disadvantages, together with their types of waste stream are described in Table 1.5.

Table 1.5: Description, Advantages, Disadvantages and Waste Streams of Different De-oiling Technologies (adapted from Arthur et al., 2005)

Treatment	Description	Advantages	Disadvantages	Waste Stream
Corrugated plate separator	Separation of free oil from water under gravity effects enhanced by flocculation on the surface of corrugated plates	(a) No energy required, (b) Cheaper & effective for bulk oil removal, (c) No moving parts (d) robust & resistant to breakdowns	(a) Inefficient for fine oil particles, (b) Requirement of high retention time, (c) Maintenance	Suspended particles slurry at the bottom of the separator
Centrifuge	Separation of free oil from water under centrifugal force generated by spinning the centrifuge cylinder	(a) Efficient removal of smaller oil particles and suspended solids, (b) lesser retention time, (c) High throughput	(a) Energy requirement for spinning, (b) High maintenance cost	Suspended particles slurry as pre-treatment waste
Hydrocyclone	Free oil separation under centrifugal force generated by pressurized tangential input of influent stream	(a) Compact modules (b) Higher efficiency and throughput for smaller oil particles	(a) Energy requirement to pressurize inlet, (b) No solid separation, (c) fouling, (d) Higher maintenance cost	
Gas Floatation	Oil particles attached to induced gas bubbles and float to the surface	(a) No moving parts, (b) Higher efficiency due to coalescence, (c) Easy operation (d) Robust and durable	(a) Generation of large amount of air, (b) Retention time required for separation, (c) Skim volume	Skim off volume, lumps of oil
Extraction	Removal of free or dissolved oil soluble in lighter hydrocarbon solvent	(a) No energy required, (b) Easy operation (c) Removes dissolved oil	(a) Use of solvent (b) Extract handling (c) Regeneration of solvent	Solvent regeneraton waste
Ozone/hydrogen peroxide/oxygen	Strong oxidizers oxidize soluble contaminant and remove them as precipitate	(a) Easy operation (b) Efficient for primary treatment of soluble constituents	(a) On-site supply of oxidizer, (b) Separation of precipitate (c) Byproduct CO ₂	Solids precipitated in slurry form
Adsorption	Porous media adsorbs contaminants from the influent stream	(a) Compact packed bed modules (b) Cheaper and efficient	(a) High retention time (b) Less efficient at higher feed concentration	Used adsorbent media, regeneration waste

Removal of bacteria, viruses, microorganisms, algae, etc., from PW is necessary to prevent scaling, water contamination (to protect potability), or fouling of the reservoir, tubulars, and surface equipment. Microorganisms can occur naturally in PW or may be added during de-oiling treatments. Advanced filtration techniques are one effective technology used to remove microorganisms. UV light treatment, chlorine or iodine reaction, ozone treatment and pH reduction are other treatments available to disinfect PW (Arthur, 2005). The basic description, advantages, disadvantages, and waste streams of major disinfection techniques are shown in Table 1.6.

Table 1.6: Description, Advantages, Disadvantages and Waste Streams of Different Disinfection Technologies (adapted from Arthur et al., 2005)

Treatment	Description	Advantages	Disadvantages	Waste Stream
UV light/ozone	Passing UV light or ozone produce hydroxyl ions that kills microbes	(a) Simple and clean operation (b) Highly efficient disinfection	(a) On-site supply of ozone, (b) Other contaminants reduce efficiency	Small volumes of suspended particles at the end of the treatment
Chlorination	Chlorine reacts with water to produce hypochlorous acid which kills microbes	(a) Cheaper and simplest method	(a) Does not remove all types of microbes	

Removal of dissolved solid, salts or impurities is one of the key functions of the water treatment systems. TDS in PW ranges from <2000 ppm to >150,000 ppm. The choice of desalination method depends on TDS content and the treatment system's compatibility to function in the presence of extra contaminants in the PW. O&G operators have attempted evaporation, distillation, membrane filtration, electric separation and chemical treatments to remove TDS from PW. Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO) utilize high pressure across the membranes to accomplish filtration of contaminants from PW. Cations such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Sr^{2+} , Fe^{2+} and anions such as Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- affect PW chemistry in terms of buffering capacity, salinity, and scale potential as well as subsequent removal efficiency of the treatment technologies. PW also contains trace quantities of various heavy metals such as cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc, mostly from natural origins, that affects relevant treatment

technologies. Table 1.7 and Table 1.8 provide descriptions, advantages, disadvantages, and waste streams of different desalination technologies and membrane processes. Technologies shown in Table 1.7 typically require less power and less pre-treatment than membrane technologies. Suitable PW feed will have TDS value between 1,000 and 10,000 mg/L. Some of these treatment processes remove oil and grease contaminants, while others require oil and grease contaminants to be reduced before their operation. Removal of trace oil and grease, microbial, soluble organics, divalent salts, acids and trace solids are possible via membrane-based technologies. Contaminants can be targeted by the selection of the membrane. Removal of sodium chloride, other monovalent salts, and other organics can be achieved via a RO membrane, although some organic species may require pre-treatment. While energy costs increase with higher TDS, RO can efficiently remove salts in excess of 10,000 mg/L.

Table 1.7: Description, Advantages, Disadvantages, and Waste Stream of Different Desalination Technologies (adapted from Arthur et al., 2005)

Treatment Methods/ Technology	Description	Advantages	Disadvantages	Waste Stream
Lime Softening	Addition of lime to remove carbonate, bicarbonate etc hardness	Cheaper, accessible, can be modified	chemical addition, post treatment necessary	used chemical and precipitated waste
Ion Exchange	Dissolved salts or minerals are ionized and removed by exchanging ions with ion exchangers	low energy required, possible continuous regeneration of resin, efficient, mobile, treatment possible	pre and post treatment required for high efficiency, produce effluent concentrate	Regeneration chemicals
Electrodialysis	Ionized salts attract and approach to oppositely charged electrodes passing through ion exchange membranes	clean technology, no chemical addition, mobile treatment possible, less pretreatment	less efficient with high concentration influent, require membrane regeneration	Regeneration waste
Electro-deionization	Enhanced electrodialysis due to presence of ion exchange resins between ion exchange membranes	removes weakly ionized species, high removal rate, mobile treatment possible	Regeneration of ion exchange resins, pre/post treatment necessary	Regeneration waste, filtrate waste from post-treatment stage
Capacitive deionization	Ionized salts are adsorbed by the oppositely charged electrodes	low energy required, higher throughput	expensive electrodes, fouling	Regeneration waste
Electrochemical Activation	Ionized water reacts with ionized chloride ion to produce chlorite that kills microbes	Simultaneous salt and microbial removal, reduce fouling	expensive electrodes	Regeneration waste
Rapid spray evaporation	Injecting water at high velocity in heated air evaporates the water which can be condensed to obtain treated water	high quality treated water, higher conversion efficiency	high energy required for heating air, required handling of solids	waste in sludge form at the end of evaporation
Freeze thaw evaporation	Utilize natural temperature cycles to freeze water into crystals from contaminated water and thaw crystals to produce pure water	no energy required, natural process, cheaper	lower conversion efficiency, long operation cycle	N/A

Table 1.8: Description, Advantages, Disadvantages, and Waste Stream of Membrane Technologies (adapted from Arthur et al., 2005)

Treatment	Description	Advantages	Disadvantages	Waste Stream
Microfiltration	membrane removes micro-particles from the water under the applied pressure	higher recovery of fresh water, compact modules	high energy required, less efficiency for divalent, monovalent salts, viruses etc	Concentrated waste from membrane backwash during membrane cleaning, concentrate stream from the filtration operation
Ultrafiltration	membrane removes ultra-particles from the water under the applied pressure	higher recovery of fresh water, compact modules, viruses and organics etc.removal	high energy, membrane fouling, low MW organics, salts etc	
Nanofiltration	membrane separation technology removes species ranging between ultrafiltration and RO	low MW organics removal, hardness removal, divalent salts removal, compact module	high energy required, less efficient for monovalent salts and lower MW organics, membrane fouling	
Reverse Osmosis	pure water is squeezed from contaminated water under pressure differential	removes monovalent salts, dissolved contaminants etc, compact modules	high pressure requirements, even trace amounts of oil and grease can cause membrane fouling	

PW softening, sodium adsorption ratio (SAR) adjustments and removal of trace contaminants, pollutants, naturally occurring radioactive materials (NORM), etc., are part of PW treatment in some regions, depending on the PW composition. Different biological treatment technologies (e.g., fixed-film treatment, membrane bioreactors, wetlands and ponds, activated sludge treatment, anaerobic treatment, bio-electrochemical treatment etc.) are also emerging, though not used widely yet. The desire to recycle and reuse PW has led to increased interest in its biological treatment. Technical details and their relevance to PW treatment are described below for various widely used physical and chemical PW treatment processes. Some physical treatment processes included are: a) hydrocyclones, b) API separator and corrugated plate separator/interceptor, c) media filtration (e.g., nutshell filter), d) gas flotation e) membrane filtration, f) membrane distillation, g) thermal separators, and h) activated carbon adsorption. Some chemical treatment processes included are: a) chemical precipitation, b) ion exchange, c) advanced oxidation, d) electrodialysis, and e) electrochemical processes.

1.3.1 Hydrocyclones

In the petroleum industry, cyclones are often used for desanding, for instance at the wellhead, to protect the downstream equipment. Hydrocyclones are also widely used to treat PW. A cyclone uses centrifugal acceleration to mechanically reduce or increase, depending on the process objectives, the concentration of a dispersed phase (aggregates, particles, droplets, etc.) within a dispersant media (Jimenez et al., 2019). Hydrocyclones can be classified as liquid-liquid, liquid-solid, or gas-liquid separation types (Liu et al, 2015). Hydrocyclones are mainly used to remove suspended solid particles and dispersed oil droplets based on the density difference and centrifugal force. As shown in Figure 1.3, a hydrocyclone has two sections, a cylindrical section, where the feed stream enters under pressure tangentially at the top, and a conical section. While the heavier phase is forced toward the wall of the hydrocyclone and discharged at the bottom (underflow), the lighter phase flows toward the center and leaves at the top (overflow). Three-phase cyclonic separators have also been designed to remove solids and oil from PW (Ahmadun, 2009). Hydrocyclones do not require any chemicals or pretreatment; however, hydrocyclones cannot remove dissolved components. A typical cyclone removal efficiency for dispersed oil is approximately 50–70% (Ahmadun et al., 2009).

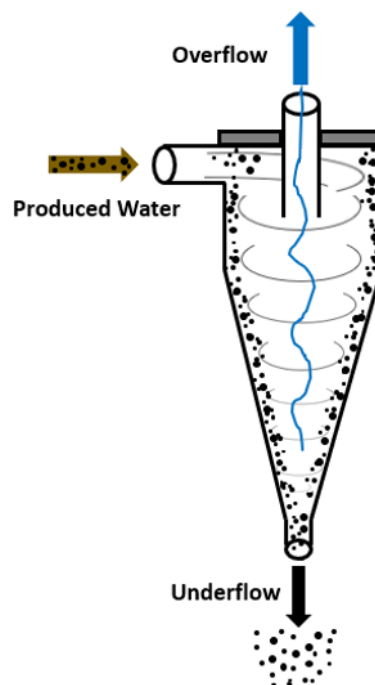


Figure 1.3. A general scheme of a hydrocyclone separator.

1.3.2 API Separator and Corrugated Plate Separator/Interceptor

The API separator (Figure 1.4) is a gravity-based device designed using Stokes Law. Most SS will settle to the bottom of the separator as a sediment layer, the oil will rise to top of the separator, and the wastewater will compose the middle layer. Any settled gross solids and trash must be periodically removed from the trash screen in the inlet chamber (Duraismy, 2013; Judd et al., 2014; Han et al., 2017). Whereas conventional oil-water separators can only remove free oil, API separators are designed to remove oil

droplets with diameters as small as 0.015 cm (150 microns). Under most operating conditions, the API separator will remove both free oil and SS down to a concentration between 50 and 200 mg/L (WEF, 2017; WEF, 2018). Chemical Oxygen Demand (COD) removals in the range of 16 to 45% and TSS removals in the range of 33 to 68% have been documented (Fuller, 2021). Removing the bulk of free oils, greases, and SS from the wastewater reduces overloading and other problems in downstream treatment processes (Duraismy, 2013; Judd et al., 2014; Han et al., 2017; Fuller, 2021). Plate separators, or coalescing plate separators (CPI), are similar to API separators and are also based on Stokes Law principles but include inclined plate assemblies (parallel packs). The underside of each parallel plate provides more surface for suspended oil droplets to coalesce into larger globules (Boraey, 2018; Ahmadun et al., 2009). Separation of free oil from water under gravity is enhanced by flocculation on the surface of corrugated plates. CPI is widely used for oil recovery from emulsions or water with high oil content prior to discharge. Water may contain oil and grease in excess of 1000 mg/L (Ahmadun et al., 2009).

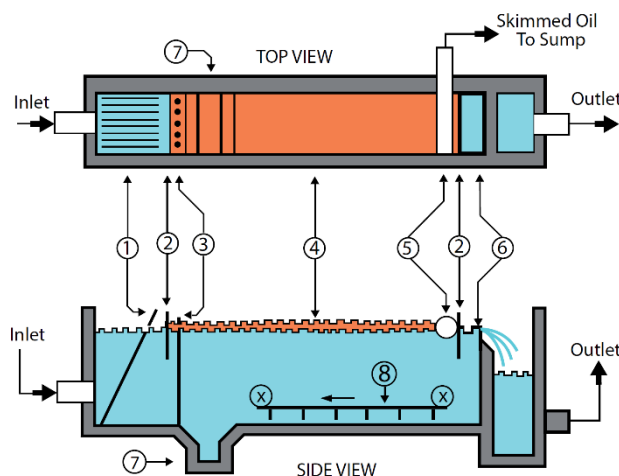


Figure 1.4. A general scheme of an API separator (Filtration+Separation, 2013). 1) Trash trap (inclined rods), 2) Oil retention baffles, 3) Flow distributors (vertical rods) 4) Oil layer, 5) Slotted pipe skimmer, 6) Adjustable overflow weir, 7) Sludge sump 8) Chain and flight scraper.

1.3.3 Media Filtration

A relatively simple technique used in O&G treatment process, filtration is based on the use of porous filter media to allow only water and not the impurities (e.g., oil and

grease) to pass through it. Filtration technology is extensively used to remove oil and grease and TOC from PW (more than 90% efficiency). Various porous materials can be used as filter media, such as sand, gravel, anthracite, walnut shell and others. However, sand is the most widely used material due to its availability, low cost and efficiency. Walnut shell filters are commonly used for PW treatment because they are not affected by water salinity and might be applicable to any type of PW. Filter efficiency can be further enhanced if coagulants are added to the feed water prior to filtration. Media regeneration and solid waste disposal are setbacks to this process (Igunnu and Chen, 2012; Ahmadun et al., 2009).

1.3.4 Activated Carbon Adsorption

Adsorption is considered one of the best techniques used in a tertiary/advanced step to achieve high water quality with nearly undetectable levels of pollutants. Activated carbon is particularly effective in removing contaminants thanks to its unique characteristics, including high surface reactivity, high adsorption ability, large surface area, and microporous structure (Al-Ghouti 2019, 114). In addition to suspended particles and insoluble free hydrocarbons, activated carbon can also be used to remove dissolved organic compounds, heavy metals, and radioactive materials. Installation and maintenance costs are the major disadvantages of activated carbon adsorption. As in other adsorption processes, the activated carbon must be regenerated after a few runs. Various chemicals such as acids and organic solvents can be used to regenerate the activated carbon, which results in liquid waste disposal and an increase in treatment costs (Al-Ghouti, 2019).

1.3.5 Gas Flotation

This widely used treatment process for oilfield PW can be used to remove volatile organics, oil and grease from PW (Igunnu and Chen, 2012). A gas such as nitrogen or air is injected into the PW to remove suspended particles and dispersed oil droplets. Dissolved Gas Floatation (DGF) and Induced Gas Floatation (IGF) are two subdivisions of the gas flotation technology based on the method used to generate gas bubbles and the resultant bubble size (Al-Ghouti et al., 2019). The process efficiency mainly depends on the contaminants to be removed, liquids density differences, temperature, and oil

droplet size. Particles of 25 μm can be removed by dissolved air flotation, and 3–5 μm particles can be removed when coagulation is used as pretreatment step (Al-Ghouti et al., 2019). Fine solid particles and small oil droplets attach to the micro gas bubbles and rise together to the surface due to an increase in buoyancy or a diminished aggregate density. As a result, foam forms at the water surface, which can then be removed by skimming, and the clarified water is collected at the bottom of the flotation zone. This process is simple, robust, and requires no moving parts. The disadvantages include a large amount of gas and a large skim volume (Al-Ghouti, 2019).

1.3.6 Membrane Filtration

Membrane systems can compete with more complex treatment technologies for treating water with high oil content, low mean particle size, and flowrates greater than 150m³/h and is, consequently, suitable for medium and large offshore platforms (Ahmadun, 2009). A membrane is a thin semi-permeable layer of organic (e.g., polymeric membranes) or inorganic (e.g., ceramic membranes) material that separates a pollutant from PW when an external pressure is applied across the membrane. As shown in Figure 1.5, pressure-driven membrane separation technologies are classified according to pore size (i.e., MF, UF, NF and RO). Whereas MF and UF membranes primarily remove bacteria, viruses, proteins, colloidal particles, and SS particles, NF membranes and RO can reject molecules and ions. This is because water flows through the pores of MF and UF membranes, whereas in NF and RO membranes water moves through the molecular structure (Thomas, 2019). In RO membranes, an external hydraulic pressure suppresses the osmotic pressure and forces the permeate to diffuse through the membrane. While NF membranes can remove multivalent ions such as calcium, magnesium and sulfate, RO can retain monovalent ions, such as sodium and chloride, in addition to multivalent ions (Dores, 2012; Thomas, 2019). RO osmosis membranes can achieve 99% salt rejection (Ahmad, 2020 and 99.9% organic rejection (Ahmad, 2020).

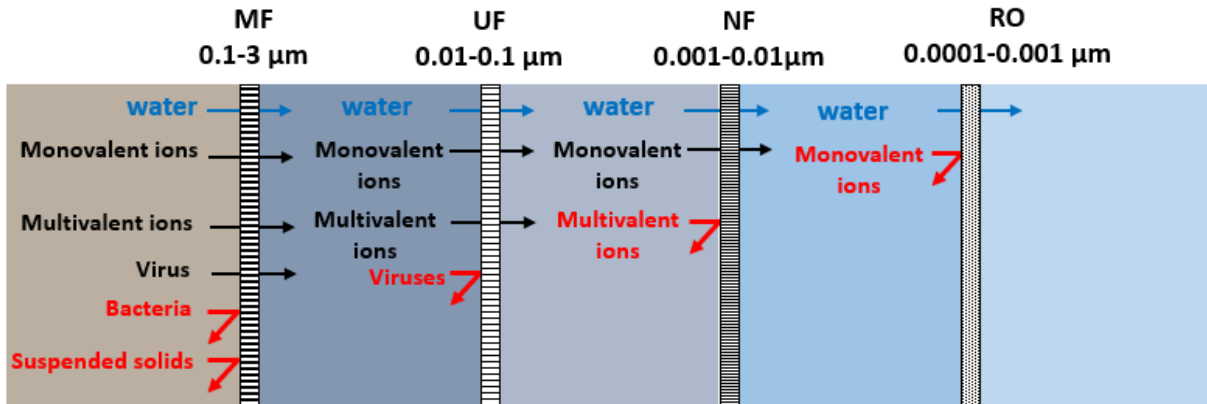


Figure 1.5. Membrane filtration technologies. (MF: microfiltration, UF: ultrafiltration, NF: nanofiltration, RO: reverse osmosis.)

Based on their material type, membranes can also be classified into polymeric, inorganic, and composite. Polymeric membranes are prepared from materials like Polytetrafluoroethylene (PTFE), polyacrylonitrile (PAN), polysulfone (PS), and polyvinylidenedifluoride (PVDF). These membranes are highly efficient for removing dispersed oil and SS particles. Inorganic membranes include ceramic membranes, metallic membranes, glass membranes, and zeolitic membranes. They have better chemical and thermal stability than polymeric membranes, but they are generally more expensive (Duraismy, 2013; Dickhout, 2017). Membranes can be operated in two modes, dead-end filtration and crossflow filtration, as shown in Figure 1.6.

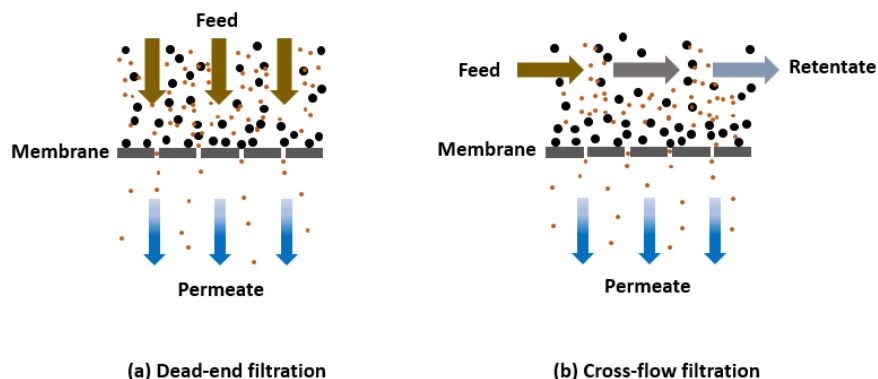


Figure 1.6. Operation modes for membranes: (a) Dead-end filtration (b) Crossflow filtration.

Compared to traditional separation methods, UF is one of the most effective methods for oily wastewater treatment, especially for PW, because of its high oil removal efficiency. UF requires no chemical additives, incurs low energy costs, and has small space requirements (Ahmadun et al., 2009). The main advantages of membrane filtration technologies for O&G treatment include their (a) small footprint, which makes membrane filtration suitable for both onshore and offshore operations, (b) modularity; easy to upgrade capacity, (c) consistent and high quality permeate, (d) ease of operation; fully automated, (e) little or no chemical requirements, (f) small sludge quantities and (g) continuous processing. The major issue with membrane filtration technologies is membrane fouling caused by the complex contaminants in PW. In membrane fouling, a layer of solids, oil and other PW constituents form on the membrane surface resulting in decreased permeate flux, selectivity, and membrane lifetime. Furthermore, fouled membranes require higher pressure during operation. Fouling in membranes can be either reversible or irreversible. Reversible fouling is due to deposited particles or dissolved components on the membrane and can be reversed by backwashing with pure water. Irreversible fouling is a result of strong sorption on the membrane surface and in the membrane pores (Duraismy, 2013).

1.3.7 Membrane Distillation

Unlike pressure-driven membrane filtration processes, membrane distillation (MD) is a thermally driven process based on the temperature difference (or vapor pressure difference) between the hot brine and cold distillate streams. Hydrophobic membranes are used in membrane distillation to allow only water vapor to pass through. MD has four major configurations, including direct contact (DCMD), air gap (AGMD), vacuum (VMD) and sweeping gas (SGMD) with 100% (theoretical) solute rejection capacity (Wang and Chung, 2015; Nasiri et al., 2017). These configurations differ in how the driving force (the vapor pressure gradient) is applied. Among them, DCMD, which utilizes a hydrophobic microporous membrane, is the simplest to operate. Study results from Al-Salmi et al. show that DCMD has great potential for treatment of PW (Al-Salmi, 2020). MD exhibits several advantages, such as high selectivity, high salt rejection efficiency, no external pressure, fewer fouling issues (Ahmad, 2020). The main drawbacks include high energy consumption, long-time operation instability and membrane wetting (Ahmad, 2020).

1.3.8 Thermal Separators

Thermal separation processes are widely used for water desalting, particularly in regions where energy sources are readily available, and are mainly used for large desalting plants, which include PW treatment processes (Nasiri and Jafari, 2017). Thermal separation can be used for desalting water with high TDS, up to 40,000 mg/l. Some chemicals, such as EDTA and acids are used in conjunction with thermal separation to prevent scaling (Nasiri and Jafari, 2017). Major thermal desalination techniques include multistage flash (MSF), multi-effect distillation (MED), and vapor compression distillation (VCD). In MSF distillation, water evaporation occurs by reducing the pressure of the feed stream instead of heating. MED generally uses steam to evaporate water in a series of evaporators. In VCD, compression of vapor provides the required heat. A combination of these thermal processes such as a hybrid MED-VCD can also be used to treat PW (Iggunu, 2012). This hybrid treatment method has some advantages over the other conventical thermal technologies such as reduced overall costs and less fouling (Jimenez 2018). Various evaporator designs such as horizontal tube, vertical tube rising film, and vertical tube falling film are used to improve heat transfer rates. These evaporators offer several advantages; they are simple and require minimal

pre-treatment and substantially fewer chemicals. A major drawback is that evaporators increase the concentration of solids, which results in crystal precipitation and scaling (Dores, 2012; Nasiri, 2017). Another thermal technique is freeze-thaw evaporation (FTE®). This mature technology was developed in 1992 by Energy & Environmental Research Centre (EERC) and B.C. Technologies Ltd. (BCT). FTE is based on “freezing point depression,” a phenomenon in which salts and other dissolved constituents in PW decrease the freezing point of the solution to a temperature below the freezing point of pure water. When PW is cooled below 32°F but above its freezing point, pure water crystallizes; the ice crystals are then collected and melted to obtain cleaner water. The concentrated solution remains unfrozen (Igunnu, 2012). This technology is easy to operate and robust, but it requires large ponds and only works in cold seasons with subfreezing temperatures.

1.3.9 Chemical Precipitation

Precipitation is considered a conventional chemical treatment processes of PW (Al-Ghouti et al, 2019). Chemical precipitation is used to remove suspended solids, dispersed oil droplets, and colloidal particles from PW using flocculation and coagulation chemicals. The basic idea is to increase the size of the solid particles so they can precipitate. In coagulation, the electrostatic repulsion between the particles is reduced by chemicals called coagulants, such as aluminum sulfate, ferric chloride, and lime. These coagulants react with the suspended particles to form precipitants. In flocculation, the particles are brought together by water soluble polymeric agents. The addition of coagulation chemicals can remove almost 97% of SS and oil from PW (Al-Ghouti et al, 2019). Chemical precipitation is a simple technology for removing suspended particles, but it is ineffective in removing dissolved components. Another concern is the increased concentration of some toxic metals in the sludge that forms due to the use of chemicals (Duraismy, 2013; Jimenez, 2018).

1.3.10 Ion Exchange

Another chemical technology widely used in industrial applications for PW treatment is ion exchange technology. This technology can remove various PW

constituents such as dissolved heavy metals, arsenic, salts, radium, and uranium (Arthur et al., 2005). The method utilizes resins, in which cations or anions in the resin exchange similarly charged ions in the PW (Jimenez, 2018). Since the resin favors divalent ions (Ca, Mg, etc.) over monovalent (Na) ions for replacement, secondary treatment for SAR (sodicity) is required (Arthur et al., 2005). Ion exchange has been applied in many industrial operations including for the treatment of coal bed methane (CBM) PW (Iggunnu, 2012). Resins can be especially suitable for eliminating monovalent and divalent ions and metals present in PW, with capacity to remove boron from RO permeate of PW (Jimenez et al., 2018). Ion exchange technology has a lifetime of approximately 8 years and requires pretreatment for solids removal, as well as the use of chemicals for resin regeneration and disinfection (Jimenez et al., 2018).

1.3.11 Advanced Oxidation Processes

In oxidation processes, oxidants such as ozone (O_3), hydrogen peroxide (H_2O_2), chlorine, and ultraviolet (UV), or mixtures of these oxidants, are used to crack down dissolved organic contaminants into simple, less toxic molecules. Advanced oxidation processes (AOPs) have been extensively studied and are considered mature technologies. AOPs have received increasing interest for the treatment of PW in industrial-scale applications due to numerous advantages such as their capability to achieve complete mineralization of organic components and the minimal time (i.e., minutes) required for oxidation. Chemical oxidation (e.g., AOPs) is a well-known and consistent technology for the removal of color, odor, COD, Biochemical Oxygen Demand (BOD), organics and some inorganic compounds from PW (Jimenez et al., 2018). As recommended for wastewaters with COD below 5 g/L, the treatment of PW with a high organic load requires pretreatment operations, like dilution, coagulation and flocculation, etc., as well as optimization of reagents and energy consumption, and minimization of reaction time (Jimenez et al., 2018).

1.3.12 Electrodialysis

In electrodialysis, an electrochemical charge drives the separation process, which is used to treat PW, particularly for the removal of dissolved salts. In this process, a stack of alternating anion and cation selective membranes separated by spacer sheets is used to remove salts from PW with low TDS concentrations. When an electrical current is applied to the cell, only anions (e.g., Cl^-) can pass through the positively charged membrane (anode), and similarly, only cations (e.g., Na^+) can migrate to the negatively charged membrane (cathode), thereby producing alternating cells of diluted and concentrated solutions between the selective membranes (Al-Ghouti, 2019). Like any other process with integrated membranes, fouling is a major limitation of electrodialysis technology. Electrodialysis was successfully applied to PW from a conventional well that contained H_2S , oil, organic acids, etc. (Jimenez et al, 2018).

1.3.13 Other Electrochemical Processes

Other electrochemical technologies, including water electrolysis, electrodeposition, fuel cells, and photo-electrochemistry, can be used to treat PW through the use or generation of electricity. However, many of these treatment technologies are either rarely employed for produced water or are mainly designed to treat dissolved organic compounds. Although, most of these processes have not yet been commercially applied to treat PW, results from several studies indicate that these relatively green and low-cost technologies have a great potential for produced water treatment (Dores, 2012; Hussain, 2014; Lin, 2020).

1.4. Conclusions

Current and emerging produced water treatment technologies were briefly reviewed. These technologies enable the reinjection, safe disposal and reuse of the enormous amount of PW generated by the oil and gas industry. Produced water is a complex mixture of water and many other constituents including dispersed dissolved materials. Whilst the primary and the secondary treatment technologies may suffice for reinjection and offshore disposal, the tertiary or polishing technologies are critically essential for beneficial reuse of PW. Current research efforts in developing biological,

electrochemical and other emerging PW treatment technologies will enhance reuse and material recovery from produced water.

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