CARITAS UNIVERSITY AMORJI-NIKE, EMENE, ENUGU STATE
Caritas Journal of Engineering Technology
CJET, Volume 4, Issue 1 (2025)
Article's History: Received: 20th December, 2024 Revised: 23rd January, 2025 Accepted: 10th February, 2025

Assessment of Oil and Gas Waste Water Treatment Technologies. A Review

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Abstract
The rapid growth of the oil and gas industry has led to an increase in the production of wastewater containing contaminants such as hydrocarbons, heavy metals, and salts. These contaminants pose significant environmental and health risks if not properly treated. Therefore, various technologies have been developed to treat oil and gas wastewater. This review article aims to assess the various treatment technologies available and their efficiency in treating these wastewater. The technologies reviewed include physical, chemical, and biological treatments. Physical methods including flocculation, sedimentation, and filtration techniques are effective in removing suspended solids. Chemical methods, such as coagulation and advanced oxidation processes, are effective in removing hydrocarbons and heavy metals. Biological treatments, including microbial fuel cells and constructed wetlands, have also shown promising results in treating oil and gas wastewater. The review found that a combination of two or more of these technologies can provide efficient and cost-effective treatment of oil and gas wastewater. However, further research is needed to determine the best treatment approach for various types of oil and gas wastewater.

Keywords: ***Wastewater; Oil and gas; Heavy metals; Technology; Produced water***

1.0 Introduction

Oil and gas extracted from oilfields in many areas of the world are accompanied by (mainly salty) water called produced water. Produced water is defined by the U.S. EPA as the water (brine) brought up from the hydrocarbon-bearing formation strata during the extraction of oil and gas. It can include formation water which is a natural water layer that, being denser, lies under the hydrocarbons, injection water, small volumes of condensed water, and residues of treatment chemicals that have been added to assist in the separation of oil/water (Produced Water Facts), to avert unfavourable effects. These can include solvents or chemicals such as hydrate inhibitors, dehydrators, scale inhibitors, corrosion inhibitors, bactericides, emulsion breakers, coagulants, flocculants, deformers and paraffin inhibitors (Farajzadeh 2017). Moreover, the properties of the formation water are almost the same as produced water from oil or ordinary gas production, but its composition may be quite different (Veil et al. 2016), as the formation water usually has higher salt concentration, with the cationic composition generally resembling seawater, also it is more acidic.

In subsurface formation, naturally occurring rocks are generally permeated with fluid such as water, oil, or gas (or some combination of these fluids). Thus, reservoir rocks normally contain both petroleum hydrocarbons (liquid and gas) and water. Sources of this water may include flow from above or below the hydrocarbon zone, flow from within the hydrocarbon zone, or flow from injected fluids and additives resulting from production activities. This water is frequently referred to as "connate water" or "formation water" and becomes produced water when the reservoir is produced and the fluids are brought to the surface (Kevin and Juniel 2003).
Water occupies 71% per cent of the Earth's surface, however, only 2.6 % of that amount is fresh water and even a smaller percentage is accessible for consumption (Farajzadeh 2004). Water scarcity is a growing problem due to the increase in population and it affects all the countries around the world (Debra et al. 2002). By 2030 is predicted that the global population will experience a rise of 40% with a water demand increase of 55%, which also includes the industry water requirement (Hawboldt and Adams 2005). According to this situation, urgent action is required to tackle this problem. Besides, the existing freshwater access is worsening as the plants reject brine to the sea and soil, requiring action on wastewater management to save

the planet. Industries such as mining and oil face problems with clean production because of water consumption and brine rejection (Hongzhu and Wang 2006) As an example, the oil and gas industry has a production of 250 million barrels and more than 40% of this is discharged to the environment (Kevin and Juniel 2003).

Petroleum is a major source of energy and revenue for many countries today, and its production has been described as one of the most important industrial activities in the twenty-first century (Farajzadeh 2004). Since the late 1850s when Edwin Drake drilled the first oil well, demand for petroleum has continued to rise. It is estimated that world daily petroleum consumption will increase from 85 million barrels in 2016 to 106.6 million barrels by 2030 (Grini, et al. 2002). Despite its significance, petroleum is produced with large volumes of waste, with wastewater accounting for more than 80% of liquid waste (Godshall 2006) and as high as 95% in ageing oilfields (Hongzhu and Wang 2006). Generally, the oil/water volume ratio is 1:3 (Tibbetts et al. 1992).

Produced water has a complex composition, but its constituents can be broadly classified into organic and inorganic compounds Hayes T., Arthur D., (2016), including dissolved and dispersed oils, grease, heavy metals, radionuclides, treating chemicals, formation solids, salts, dissolved gases, scale products, waxes, microorganisms and dissolved oxygen [5–8]. Globally, 250 million barrels of water are produced daily from both oil and gas fields, and more than 40% of this is discharged into the environment. Consequently, desalination technologies have received a lot of attention and development to overcome the water scarcity problem and brine management. Produced water is the largest volume waste stream in the oil and gas exploration and production processes. It is a by-product of the production of oil and gas hydrocarbons from underground reservoirs, which consists of the formation of water that is naturally present in the reservoir and/or in the case of gas production called condensed water. Produced water is any water that is present in a reservoir with hydrocarbon resources and is brought to the surface together with crude oil or natural gas. Produced water in any particular reservoir increases as the oil and gas field reaches maturity. To transfer and utilize the product, Produced water must be removed from the petroleum product as fully as possible (Rabalais et al. 2015). At the surface, the output of an oilfield is separated into an oil stream, a gas stream and a water stream (Kevin and Juniel 2017). This is normally done by pressurization and gravity separation (Rabalais et al. 2014).

On the other hand, oil fields usually start producing reservoir water at a rather early stage of production at low water-to-oil ratios. Later, as the field matures, the ratio between water and oil could reach high values (thus up to 10:1) and the composition of the produced reservoir water changes. In addition, oil field production is often enhanced by the injection of water, to maintain the reservoir pressure. When this injected water breaks through into the production stream it dilutes the formation water and the discharged produced water progressively approaches the injected water in composition and character.

However, in general terms, produced water is composed of organic constituents, inorganic constituents, production and processing chemicals and other substances and properties.

Around 17 million cubic meters of water are produced daily in offshore operations worldwide together with the 120 million barrels of oil equivalent. About 40 % of the daily water production (7 million cubic meters) is discharged offshore. When hydrocarbons are produced, they are brought to the surface as a produced fluid mixture. The composition of this produced fluid is dependent on whether crude oil or natural gas is being produced and generally includes a mixture of either liquid or gaseous hydrocarbons, produced water, dissolved or suspended solids, produced solids such as sand or silt, injected fluids and additives that may have been placed in the formation as a result of exploration and production activities Daniel Arthur J, (2015).

There are different technologies among the desalination methods, some very well studied, and others in progress. They can be grouped into two main categories: membrane desalination, and thermal desalination. Reverse osmosis (RO) is the most commonly used desalination method as membrane desalination. Multistage flash (MSF) and Multiple effect distillation (MED) are types of thermal desalination. RO is applied to 65% of the total desalination, while MSF and MED follow next with each being 21% and 7% of the total desalination process Arthur D., (2016). RO has been used because of its simple concept and feasibility to handle large-scale systems. However, there are some disadvantages such as water acidity, high

operation time, and waste of pure water in the process. On the contrary, thermal plants can be a solution if the energy input can be extracted from other industrial plants.
However, the main disadvantage is the complexity of operating continuously and the feasibility of building large-scale systems. This review intends to provide a solution to overcome those limitations and apply it to the treatment of produced water.

2.1 Produced water composition
Hydrocarbons can be present in produced water as suspended droplets or dissolved in the aqueous phase and represent the greatest environmental concern when discharged with produced water, because of their toxicity, oxygen demand and their resilience over time in the receiving environment, be it on water or soil bodies. Organic components that can be found in produced water include suspended oil, organic acids, polycyclic aromatic hydrocarbons, phenols, and volatiles. The toxicity of these compounds is additive, which means that even if individually their toxicity is insignificant, combined they represent a serious risk for the environment. The type of organic matter found in produced water will depend on the type of hydrocarbon and the type of operation to extract it.

Petroleum hydrocarbons represent the highest concern environmentally. The most abundant hydrocarbons in produced water are aromatic hydrocarbons such as benzene, toluene, ethylbenzene, xylenes (BTEX), and low molecular weight alkanes, the latter of which are usually found in concentrations much lower than BTEX, mainly because of the higher solubility in water of BTEX and the volatility of low molecular weight alkanes. Polycyclic aromatic hydrocarbons represent the highest risk due to their toxicity and persistence in marine environments. The phase in which these oil particles can be found is key to their management because oil/water separators are efficient in removing suspended oil droplets, but not dissolved organic matter. The volatility of some compounds, such as BTEX means they are rapidly released from the water steam during stripping and mixing into the ocean. As no treatment procedure is 100% effective, some dissolved oil is still discharged with produced water streams.

2.2 Dissolved minerals
Inorganic compounds dissolved into the water due to the extended contact time with the formation include a variety of ions such as sodium, chloride, calcium, magnesium, potassium, sulfates, sulfides, and ammonia. The concentrations of these vary greatly from source to source, and they affect the solubility, salinity, and scale potential of the stream. Sulfides are highly corrosive. They can be generated by the bacterial reduction of sulfates in the anoxic conditions of the formation and are more common in sour gas or oil with high concentrations of sulfur. Hydrogen sulfide and ammonia possess high levels of toxicity, which must be monitored to avoid damage to marine organisms. Produced water may also contain dissolved metals with extremely variable concentrations in every case, but commonly higher than in seawater. The most common metals present at high concentrations include barium, chromium, copper, iron, lead, nickel, and zinc, but it is possible to find more toxic metals such as mercury and arsenic. Metals can also cause production problems and deposits at discharge sites. Bacteria in produced water streams can cause clogs or the creation of strong emulsions, as well as hydrogen sulfide as previously mentioned.

2.3 Global onshore and offshore produced water production
Global produced water production is estimated at around 250 million barrels per day compared with around 80 million barrels per day of oil. As a result, water to water-to-oil ratio is around 3:1 that is to say water cut is 70%. The global water cut has risen since a decade ago and continues to rise. Produced water is driven up by the maturing of old fields but driven down by better management methods and the introduction of new oil fields.

Fig. 1 gives an estimate of onshore and offshore produced water production since 1990, and forecast in 2015.

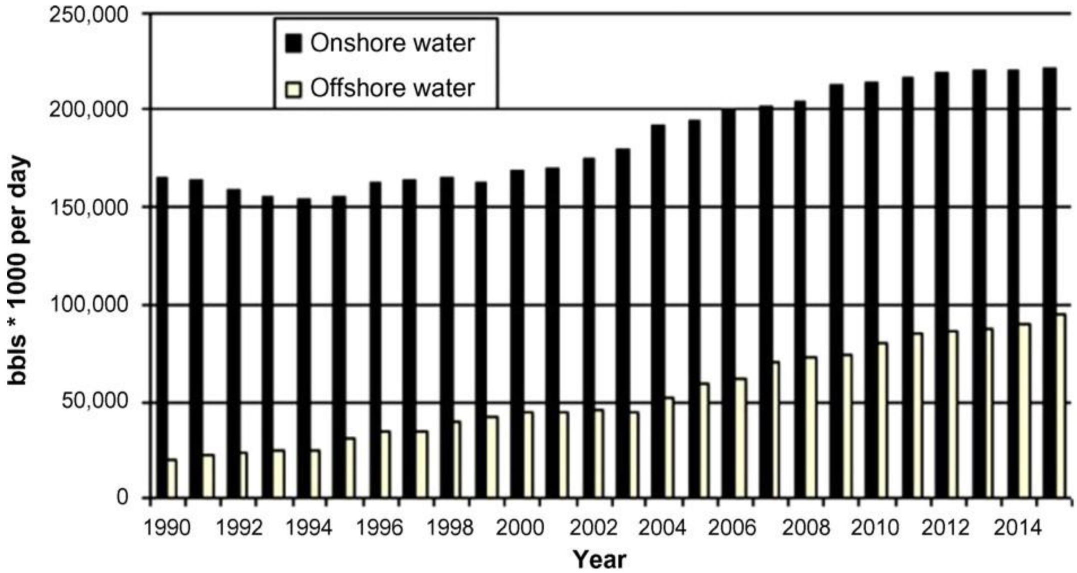

Fig. 1. Global onshore and offshore water production

2.4 Produced water composition: Average ranges

The following tables 1 and 2 show the values for different parameters measured and averaged from multiple samples around the world by Costa et al. (2021).

Table 1: Range of parameters characterization from produced water around the world (Costa et al., 2021).

Parameter	Oil field	Gas field	Unit
Density	1.01–1.14	1.02–1.13	g/cm^3
pH	4.3–10	3.1–8.8	–
Alkalinity	300–380	0–285	mg/L
Conductivity	4,200-58,600	4,200–586,000	*µS/cm*
Salinity (NaCl)	0.033–300	n.d.-250	g/L
Chemical Oxygen Demand – COD	1,220–2,660	2,600–120,000	mg/L
Total Suspended Solids – TSS	1.2–1,000	8–5,484	mg/L
Total Dissolved Solids – TDS	100–400,000	2,600–360,000	mg/L
Total Organic Carbon – TOC	0–11,000	67–38,000	mg/L
Total Naphthenic Acids	23.6–88	6.0–56	mg/L
BTEX	0.39–35	0.01–48	mg/L
PAHs	40–3,000	25–2,000	mg/L
Phenols	0.001–10,000	n.d.-1,160	mg/L
Volatile Fatty Acids	2–4900	n.d.	mg/L
Total Organic Acids	0.001–10,000	n.d.	mg/L
Oil and Grease Content	2–565	2.3–60	mg/L
Corrosion inhibitor	0.3–10	2–10	mg/L

Table 2.: Range of average concentration of ions and solids from different produced waters around the world (Costa et al., 2021).

Parameter	Oil field	Gas field	Unit
Ammonium (NH_4+)ˆ	10–300	0–2.74	mg/L
Bicarbonate (HCO_3^-)	77–3,990	n.d.-4,000	mg/L
Bromide (Br^-)	46–1,200	150–1,149	mg/L
Carbonate (CO_3^{2-})	30–450	20–300	mg/L
Chloride (Cl^-)	80–270,000	1,400–190,000	mg/L
Iodide (I^-)	3–210	n.d.	mg/L
Sulphate (SO_4^{2-})	$< 2 - 1,650$	n.d.-3,663	mg/L
Aluminium (Al)	0.4–410	n.d.-83	mg/L
Arsenic (As)	0.002–11	0.004–151	mg/L
Barium (Ba)	0–850	n.d.-1,740	mg/L
Beryllium (Be)	< 0.001–0.02	*n.d.*	mg/L
Boron (B)	5–95	n.d.-56	mg/L
Cadmium (Cd)	0.005–2	n.d.-1.21	mg/L
Calcium (Ca)	13–25,800	n.d.-25,000	mg/L
Chromium (Cr)	0.02–1.1	n.d.-0.03	mg/L
Copper (Cu)	0.002–1.5	n.d.-5	mg/L
Iron (Fe)	0.1–1,100	n.d.-2,838	mg/L
Lead (Pb)	0.002–8.8	0.2–10.2	mg/L
Lithium (Li)	0.038–64	18.6–235	mg/L
Magnesium (Mg)	8–6,000	0.045–4,300	mg/L
Manganese (Mn)	0.004–175	n.d.-96.5	mg/L
Mercury (Hg)	0.001–26	n.d.	µg/L
Nickel (Ni)	0.02–0.3	n.d.-9.2	mg/L
Palladium (Pd)	0.008–0.88	n.d.	mg/L
Potassium (K)	24–4,300	0.21–5,490	mg/L
Radium (226Ra)	0–1.66	0.65–1.031	Bq/L
Silver (Ag)	0.001–0.15	0.047–7	Bq/L
Sodium (Na)	0-150,000	10.04–204,302	mg/L
Strontium (Sr)	0–6,250	0.03–6,200	mg/L
Titanium (Ti)	0.01–0.7	n.d.-1.1	mg/L
Zinc (Zn)	0.01–35	n.d.-20	mg/L

The values shown in tables 2.1 and 2.2 were derived from multiple samples coming from different wells around the world, and the ranges for concentration obtained vary by some orders of magnitude for most components, which is an indicator of one of the main problems with produced water management: every stream is different, and composition may vary significantly even from well to well in the same reservoir. In further chapters, the challenges associated with these differences will be discussed.

2.5 Primary Treatment

Physical methods include gravity separation, adsorption, the use of hydrocyclone separators, and membrane filtration-based techniques, including osmosis processes and thermal evaporators.

2.5.1 Gravity Separation

Gravity forces can be used to separate oil droplets from a continuous water phase; as oil is less dense than the volume of water they displace, a buoyancy effect is exerted over them, causing oil-dispersed droplets to flow up and, eventually, form a free phase separate from water. Gas, if present, will follow the same effect and float up to the top part of the vessel.

The effectiveness of this gravity separation depends on the composition of the oil in the produced water: density, viscosity, temperature, turbulence, droplet sizes, etc. Usually, in the oilfield, this separation is performed by methods of a separator tank (Fig 2), whose design varies depending on the number of phases to be separated (water, oil and/or gas), their characteristics, and their volumes.

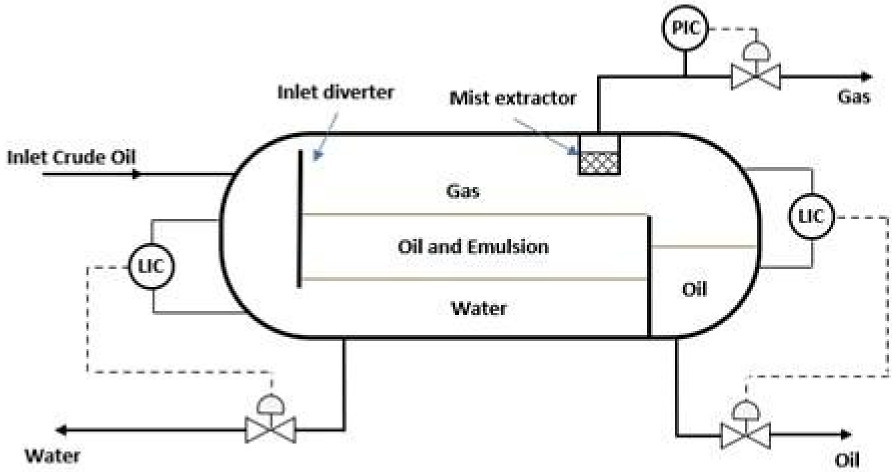

Figure 2: Basic diagram of a horizontal 3-phase separator

2.5.2 Corrugated Plate Interceptors (CPI)

In a CPI unit, the water stream flows through corrugated parallel plates to help gravity-induced separation. The plates are packed in a specific arrangement that provides tortuous channels for the fluids to flow through, which enhance the coalescence of dispersed droplets and help their separation by directing the separated particles out of the water stream thanks to their inclination angle (60° to the horizontal); sediments migrate down, and coalesced oil droplets float up, where they can be removed by specific outlets from the separation device (Fig 3). Corrugated plate separation is important due to its low energy consumption, high efficiency, and absence of secondary pollution, so research is constantly evolving in the interest of creating equipment and internal structures that improve the separation without reducing simplicity of use and durability (Han et al., 2017).

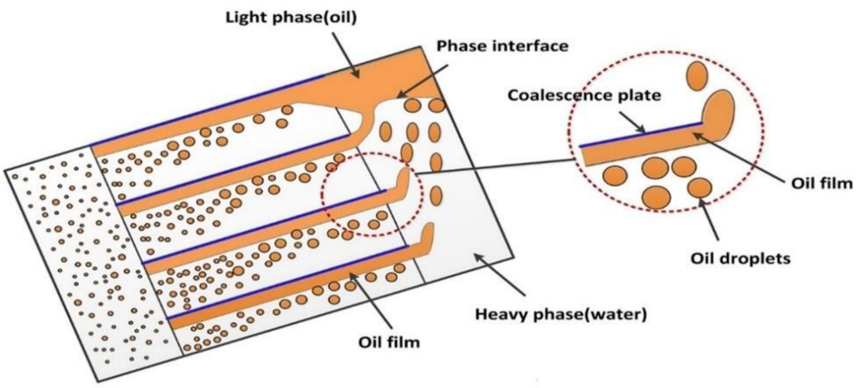

Figure 3: Principle of coalescence and phase separation used for CPI separation (Han et al., 2017).

2.5.3 Hydrocyclones:

Hydrocyclones are compact equipment originally developed for solid-solid separation but can also be used for liquid-liquid and gas-liquid separation. These devices traditionally consist of a cylinder with an inlet at the upper and two outlets, one at the bottom called underflow, and one at the top called overflow. The flow through the device generates a spinning motion of the inflow fluid, which causes the separation of the heavier water from the lighter oil due to centrifugal forces. The less-dense phase flows up and is collected at the overflow, while the heaviest phase flows down to the underflow, although different configurations exist.

Cyclonic separators (Fig 4) are widely used in the industry to remove solids and oil from produced water; the absence of mobile parts makes them simple to use while requiring small space, energy, and maintenance, with high efficiency.

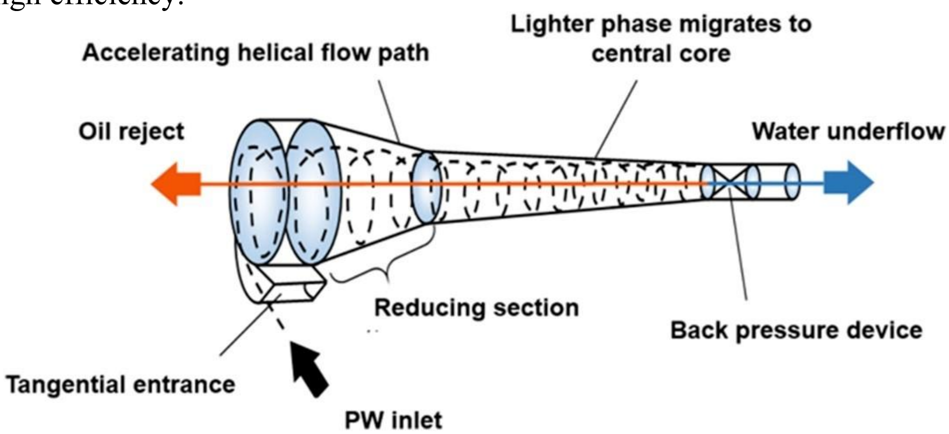

Figure 4: Separation mechanism of hydrocyclones (Liu et al., 2021).

2.5.4 Flotation Devices

A technique involving flotation processes uses the introduction of fine gas bubbles to separate small, suspended particles which are difficult to remove by sedimentation from the produced water; called Induced Gas Flotation (IGF), this process works by injecting a gas (air, nitrogen, natural gas, or other inert gas) into the water stream, causing oil particles and some suspended solids to attach to the bubbles created, and enhancing their floatability. This results in the creation of a foam on the surface, which can be removed by skimming. Efficient performance depends on the optimization of parameters like bubble size (100-1000 micrometres), gas flow rate, feed flow rates, temperature, and the content of oil and the size of oil droplets.

Upon coalescence, the difference in density between agglomerates and water enhances separation, where particle flotation at a velocity that can be described by Stokes' Law for particles that experience only their own weight and buoyancy forces, as expressed in the following equation:

$$\mathbf{v} = \frac{2}{9}\frac{R^2 g(\rho_w - \rho_o)}{\mu} \quad (1)$$

Where v is the velocity of oil droplets rising to the surface, R is the radius of oil droplets, is the density of oil and water, g is the gravitational constant and μ *is* the viscosity of water. Therefore, the larger the size of oil droplets the difference between oil and water densities, and the lower the viscosity of water, the faster the separation of phases will occur (Figures 5 and 6).

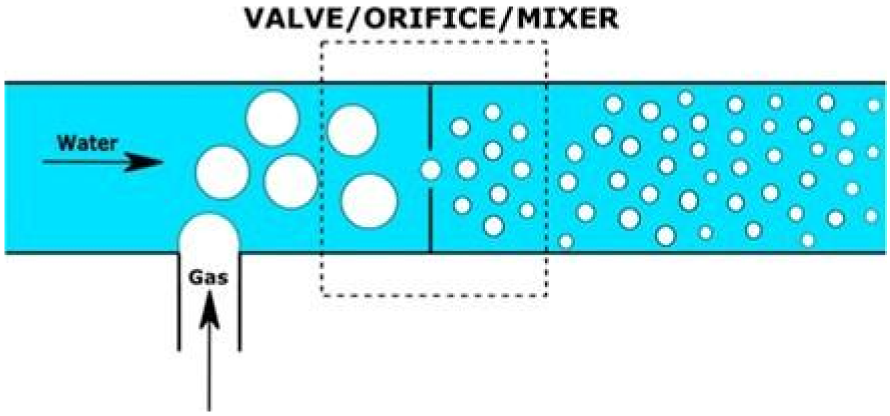

Figure 5: Induced Gas Flotation method scheme (Piccioli et al., 2020)

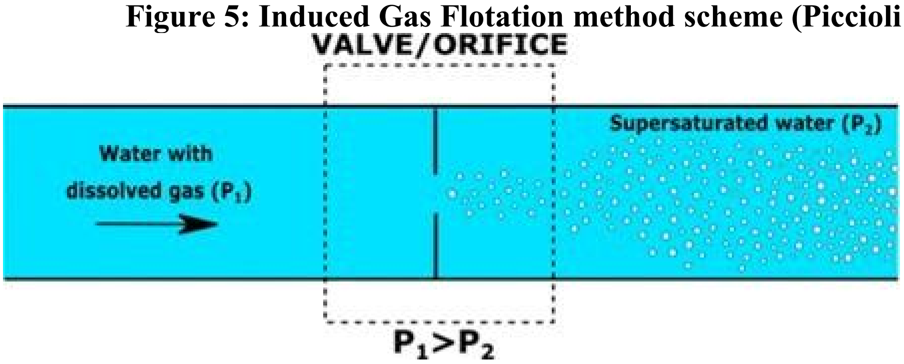

Figure 6: Dissolved Gas Flotation method scheme (Piccioli et al., 2020)

2.5.5 Medium Filtration

This method uses filter media to remove pollutants and is widely used in the treatment of drinking and industrial water. Medium filtration in produced water allows for the extraction of oil and suspended solids, although some soluble organic compounds, like aromatic hydrocarbons, can also be removed.

Media used for filtration include walnut shells, fibre balls, ceramic particles, and quartz sand. The mechanisms through which these media allow for the separation of compounds are the inertial diffusion and gravity precipitation of particles, as well as mechanical sieving and interception, adhesion based on the characteristics of the filter media or their interface with particles, including electrostatic forces, Van der Waals force and chemical bonds, and the coalescence based on coarse-graining, mainly aimed at removing oil, allowing for the fusion of small particles into larger droplets which can be separated (Figure 7).

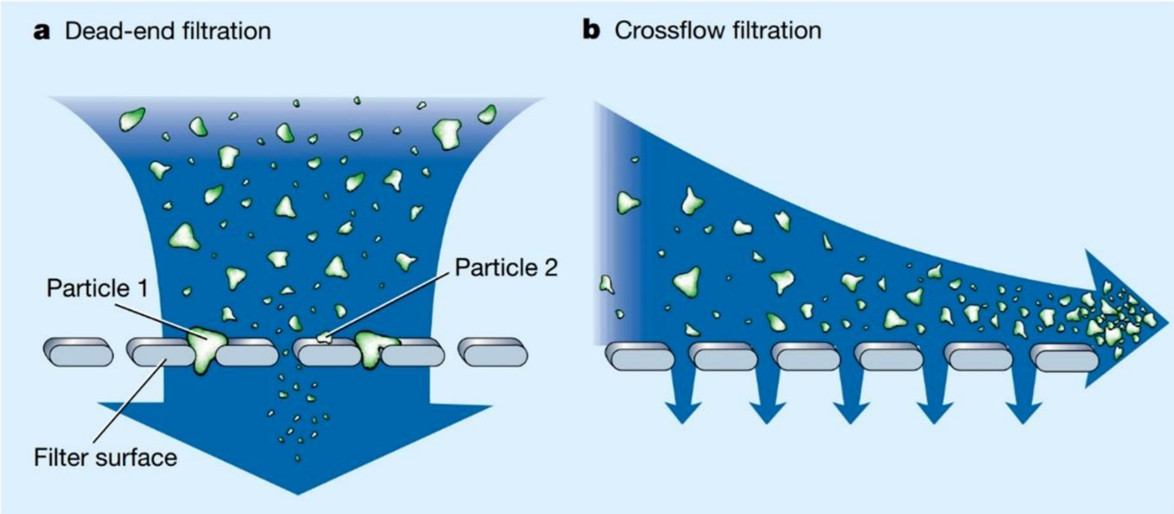

Figure 7: Filtration techniques for separation (Liu et al., 2021)

The focus of current research on the subject is directed at developing new composite materials and the modification of existing ones to maximize their efficiency. (Liu et al., 2021)

2.5.6 Adsorption

Adsorption is the ability of a solid material (adsorbent) to attract molecules of solutes dissolved in a liquid or gaseous phase (adsorbates) onto their surface, mainly due to Van der Waals and electrostatic forces, but also from chemical bonding. (35) This process forms the basis of separation by adsorption technologies, which are widely used in many industrial processes, including produced water treatment; the water stream flows through a column packed with a porous and adsorbent material specifically chosen for the targeted pollutant, resulting in an effluent with little to no pollutant molecules. The adsorption capacity of a material and its performance depend on different factors, including (The International Adsorption Society, 2020):

- Their specific surface area, as a larger area of contact within the pores results in more adsorption,
- pore size and its distribution, which determines the accessibility of adsorbates into the internal adsorption surface,
- surface polarity, which defines their affinity to polar substances such as water, allowing to creation of polar adsorbents called hydrophilic, and non-polar adsorbents called hydrophobic,
- salinity and amount of suspended particles in the stream, which can plug porous media and reduce the efficiency of the desired adsorption due to the presence of other dissolved salts,
- Temperature and pH, among others.

The benefits of treatment by adsorption include flexibility of design, no generation of toxic products and ease of recovery, as the media can be regenerated through contact with chemicals to wash particulates trapped (Hedar, 2018).

2.5.7 Membrane Filtration

Membranes are microporous films of synthetic materials which can separate a fluid from its components.
There are four processes that use membrane filtration for separation:

1. Microfiltration (MF): Process of sieving of particulates based on the pore size of the membrane. Pore sizes range from 0.1 to 3 micrometres, and are useful as a pretreatment stage to enhance the effectiveness of UF, NF or RO.
2. Ultrafiltration (UF): Pore sizes range between 0.01 and 0.1 micrometres. It is more effective for oil removal in produced water than traditional methods, and better at removing hydrocarbons and suspended solids than MF. UF has proven to be capable of meeting effluent standards, as opposed to MF which cannot be used by itself.
3. Reverse osmosis (RO): RO membranes are designed to reject all compounds other than water. Osmotic pressure is suppressed by applying hydraulic pressure which forces clean water to diffuse through a non-porous membrane. RO can remove particles as small as 0.0001 micrometres. It requires adequate

pretreatment and regular membrane cleaning to be effective, as scaling and fouling are generated which causes an unavoidable clogging of the membrane.

4. Nanofiltration (NF): Similar to RO, is also operated at relatively high pressure. It is as effective in removing inorganic materials, but instead of blocking all ions like RO, has a selectivity for divalent ions and allows monovalent ions to flow.

To remove accumulated fouling on the membranes, a process called backwashing is performed. During this process, the transmembrane pressure is reversed, causing the produced permeate to flow back and wash away the accumulated fouling.

3.0 Chemical Treatment

Processes of separation such as precipitation due to gravity or degradation can be enabled and enhanced by the addition of specific chemical compounds that alter the behaviour of naturally occurring compounds in produced water. An aspect of chemical treatment to be taken into serious account is the calculation of chemicals needed for a complete coalescence or reaction, as excess chemicals will add to the total contaminants in water, which is a complete drawback from its objective.

3.1 Precipitation

Precipitation is considered one of the conventional processes of chemical treatment. It allows for the removal of a large part of the suspended and colloidal particles. Colloid refers to any substance present in very fine particles, ranging from 10 nm to 10 μm (Koohestanian et al., 2008) with an electrostatic charge similar to the particles surrounding them which causes them to be repelled, stabilizing them, and therefore avoiding the coalescence of particles into larger particles, impeding their sedimentation. This makes colloidal particle removal the most difficult aspect of conventional water treatment. Coagulation and flocculation, achieved by chemical agents, help destabilize colloids to facilitate the formation of larger and heavier particles which can be removed by physical treatment.

Coagulation is the process of decreasing or neutralizing the negative charge on the particles to allow the particles to start accumulating. Rapid, high-energy mixing is necessary to ensure that the coagulant is fully mixed into the flow.

Flocculation is the process of bringing together the particles to finally form the large agglomerations expected through the use of coagulant aids such as polymers. The adequate addition of chemical agents to allow for the coalescence of suspended solids allows for the removal of a large part of contaminants in water through simple physical methods.
AOPs are based on the in-situ generation of highly reactive radicals with low selectivity, such as hydroxyl radicals (HO·), hydrogen peroxide ($H2O2$), or ozone ($O3$), which can virtually attack and mineralize all oxidizable substances, including organic contaminants, transforming them into CO_2 and mineral salts. Even in case of partial degradation, it results in electronically poorer, smaller (in terms of molecular mass), more hydrophilic and often biodegradable compounds compared to the original contents, which can then be handled by the subsequent treatment step.

New Advanced Oxidation Processes continue to be developed and evaluated by researchers at the time; the research by Coha et al. (2021) describes the following five families of AOPs:

1. **Fenton-based reactions:** Based on the use of H_2O_2 and Fe2+/Fe3+ as catalysts and oxidants. The nature of the reactions allows for the constant recycling of Fe(III) to FE(II) The most important factors determining degradation efficiency are pH and the catalyst/oxidant ratio, although other parameters such as the presence of sulfate ions, dissolved organic compounds and inorganic dissolved solids can significantly reduce efficiency. Best efficiency was reported with a pH of 3.5, whereas produced water streams usually are in the 6-8 range, which means the process requires acidification of the stream. An acidic pH limits the precipitation of Fe(III) as hydroxide during the process, allowing it to be recycled to Fe(II). Efficiency can be further increased by the application of a UV light source (photoFenton process) which has proven to increase oil and grease and phenol removal as reported in Table 3.1. Another alternative is the generation of hydroxyl radicals through electrochemical processes, called the electro-Fenton technique, and the combination of both (photo-electro-Fenton) has proven to further increase efficiency, although optimal parameters are different for each.

2. **Heterogeneous photocatalysis:** works through the photoactivation of a chemical reaction through the adsorption of a quantum of light (photon) from a photocatalyst. Their use in the treatment of produced water has been widely researched, with titanium dioxide (TiO_2) as the most adopted catalyst, although others such as iron oxide can also be used. This process does not require pH adjustments and its efficiency is mainly regulated by the catalyst concentration.
3. **Ozonation:** Ozone (O_3) is a strong oxidant which can be used to directly oxidize contaminants or as a precursor of other reactive compounds (OH) but is too unstable and reactive to be stocked or transported, meaning it must be produced on-site from dry air (to avoid reactions with water vapour) or pure O_2. Ozone reactions are especially useful for breaking double carbon bonds in alkenes, although they can also react with other classes of organic compounds like alcohols and aldehydes. For contaminants that do not react to O_3, it can be used as an OH precursor.

Table 3 compares the maximum efficiencies of the application of the different advanced oxidation methods aimed at the removal of different pollutants, as a result of the analysis of the available research up to date by Coha et al. (2021). These removal efficiencies are the highest reported throughout multiple experiments by different authors, which allow in turn to identify the optimal configurations to maximize treatment efficiency.

Table 3: Maximum reported removal efficiency for different methods of advanced oxidation processes, based on information collected by Coha et al. (2021)

Process	Targeted substance	Maximum removal Efficiency
Fenton	COD	91%
	Naphthalene	98%
	Oil and Grease	58%
	Phenol	80%
	TOC	58%
Photo-Fenton	TOC	96%
	Oil and Grease	84%
	Phenol	95%
	TOC	96%
Electro-Fenton	COD	78%
	Oil	90%
Photo-electro-Fenton	COD	86%
Heterogeneous Photocatalysis	BTEX	97%
	Naphthalene	85%
	Oil and Grease	100%
	COD	88%
Ozonation	PAH	100%
	TOC	85%
	COD	73%
Anodic Oxidation	BTEX	98%
	Phenol	47%
	PAH	95%
	COD	98%

Chemical oxidation and advanced oxidation processes have been proven to be able to achieve large levels of water cleaning overall. However, the main drawback with the application of chemical oxidation processes is related to their high cost, and the constant requirements of calibration and maintenance to maintain their efficiency to the maximum, as scaling, fouling, and efficiencies are always time-increasing.

3.2 Biological Treatment

Biological treatment of water consists in the biodegradation of organic matter into simpler substances and biomass with the use of microorganisms, followed by removal of the resulting mass through sedimentation. Water is then washed out of the reactor for clarification leaving behind solid sludge containing both live and dead bacteria at the bottom. The main obstacle to biological treatment comes from the fact that oil field-produced water contains toxic substances that can inhibit bacterial activity, which makes it necessary to pre-treat water and select adequate bacteria. (Kardena et al., 2017) Biological treatment has been mostly used in the treatment of oily and salty wastewater from refineries, shipping, agricultural and textile industries, but recent research by Camarillo and String fellow (2018) recollected proof from multiple studies, mostly on a small scale, about the efficiency of biological treatment for oil and gas industry produced water.

Different metrics were compared to evaluate performance, such as Biochemical Oxygen Demand (BOD) which represents the amount of oxygen required by microorganisms when decomposing organic matter and therefore, is an index of the degree of organic pollution (United States Geological Survey, 2020), Chemical Oxygen Demand (COD), total organic carbon (TOC), or oil and grease concentration (OG). Different methods based on biological action exist and have been reviewed:

- Fixed-film treatment: This method is the most commonly used as microorganisms bound in films can be retained and resist extreme conditions of pH, temperature, and salinity. Nutrients can be added to the process to support microbial growth, increasing COD removal from 20% without nutrients to 65-80% when phosphorus and carbon substrates where added. Different configurations showed variable retention times (4 to 48 hours) and COD removals of around 60-80%, with some scaling reported, which did not inhibit biological activity or growth.
- Membrane bioreactors: Membrane bioreactors have the advantage of not requiring settling times as membranes take care of solid separation and therefore have a smaller footprint as they do not require external clarifiers. COD removal was typically higher than 80%, which indicates similar efficiency to fixed-film treatment, requiring retention times varying from 6 to 96 hours. Membrane fouling and scaling were observed in membrane bioreactor studies, which caused reduced membrane permeability.
- Wetland and pond treatment: This method consists in the creation of an artificial wetland where biodegradation of nitrogen and metals is performed by plant life such as cattails, reeds, or bulrush. Studies have been performed only in small, simulated pilots, but have proven positive outcomes with COD removal of ¿70%, provided an adequate pre-treatment is conducted. Constructed wetland treatment systems require lower costs and maintenance, as well as creating new wildlife habitats.
- Activated sludge: Consists of an aeration tank and a settling tank with a system for the return of the sludge collected in the latter. The system works as a cycle, where activated sludge (loaded with organisms) collected in the settling tank from the removal of organic and dissolved compounds, is returned and mixed with the water influent and loaded with oxygen for some time in the aeration tank, where the organisms use the organic matter as nutrients and continue to grow, being removed as a sludge with the products of the biodegradation in the settling tank, and returned to the beginning of the system, only requiring a periodical remove of excess solids and organisms (Figure 8) (Mountain Empire Community College, 2020). It is a mature technology which provides effective removal of oxygen demand, with a low cost and lower environmental impact than other methods.

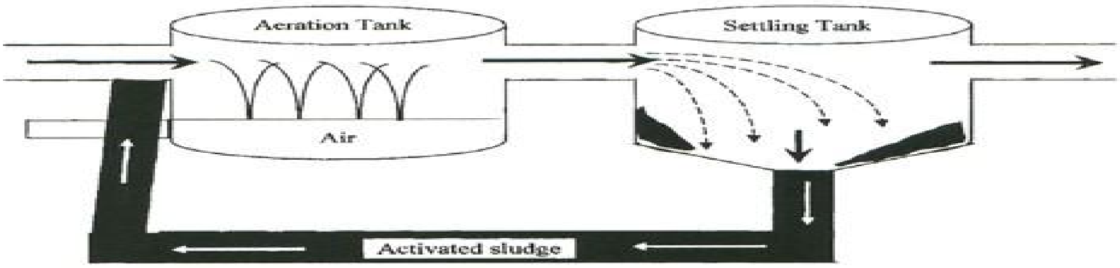

Figure 8: **Diagram describing the process of Activated Sludge treatment (Mountain Empire Community College, 2020).**

3.3 Regulations concerning produced water around the world

The petroleum industry is present in several countries, each with its own political, economic and cultural differences. Depending on the geographic location of a hydrocarbon reservoir, the government bodies that oversee the operations allowed within their authority are completely different.

Emissions and discharges are two of the most important concerns looked upon by regulatory agencies to limit and monitor the impacts that the existence of different types of industry cause in their territory; this means that for every area, operators must carefully investigate the limits applicable to comply, avoiding sanctions, and causing damage to the environment and human health. This section shows some of the limits applied in terms of discharges around the world and associated considerations.

3.4 **Selection of technologies**

Mostly, produced water characterization focuses mainly on total dissolved organic constituents which represent the heaviest environmental concern overall, whereas dissolved solid characterization commonly looks for concentration of specific components considered of high importance. Methods for other certain chemicals that are not required to be monitored may not exist currently.

The main treatment objectives are to remove free phase oil which is the main regulatory constraint to meet discharge or injection criteria, and large solids to protect the injection equipment and avoid formation pores to be blocked. Treatment refers to multiple physical, chemical, and biological methods which are used separately or combined.

The following are the objectives pursued by the treatment of produced water:

- Removal of dispersed oil and grease,
- Removal of dissolved organics,
- Removal of suspended particles and sand,
- Dissolved gas removal, which includes hydrocarbon gases, carbon dioxide and hydrogen sulfide,
- Removal of dissolved salts (desalination),
- Reduce water hardness,
- Remove naturally occurring radioactive matter.

Treatment methods can be divided into three levels (Figure 9) according to their complexity and their ability to remove more specialized pollutants from the stream to comply with regulations:

- **Primary Treatment:** Comprehends physical treatment processes which allow the elimination of solid particles and hydrocarbon from produced water. The main mechanism used at this step is gravity separation, which includes separators, hydrocyclones for desanding and deoiling, where flocculants and coagulants can be used to facilitate the coalescence of particles.
- **Secondary treatment:** Focused on removing dissolved pollutants through the combined use of various methods such as flotation, membrane filtration, and biological processes.
- **Tertiary treatment**: Also called "water polishing" refers to additional steps to further reduce organic content, turbidity, metals, and pathogens. Techniques developed for these ends include oxidation and degradation-based processes through chemical treatment, as well as Nanofiltration and Reverse Osmosis.

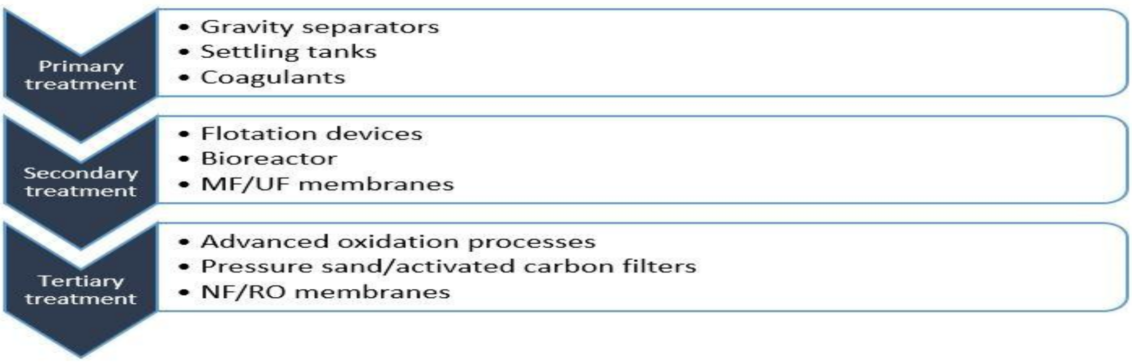

Figure 9: Treatment processes for produced water from oil and gas operations (Olajire, 2020).

3.5 Cost and energy efficiency evaluations for different strategies of treatment for Produced water

As mentioned before, it is a fact that economic rentability is a major factor in the selection of technologies applied in any operation in an oil and gas field. This is true also for waste management techniques, which include produced water. This means it is necessary to identify the management strategy for this effluent that will give the most benefit at a feasible cost. In the following section, multiple economic evaluations from different researchers were studied to obtain a descriptive framework of the operational costs of the most effective produced water management technologies applicable to oil and gas fields.

As stated before, desalination and removal of organic content are usually the main objectives of treatment to provide an effluent fit for applicable regulations. Oil and grease removal is the most essential step in producing water treatment, and it is always present in any operation. However, soluble organic compounds are often not characterized for most disposal options but are very important to remove in case reuse is intended. Desalination is another difficult step in water treatment, especially in produced water with much higher salinities than those of seawater. However, desalination is an essential step to consider reuse in applications outside the energy sector. Different factors define the capital and operational costs associated with treatment technologies, such as energy consumption, equipment required, maintenance, and chemical agents required. Desalination especially has high energy consumption overall, whereas the recently researched reverse osmosis has been proven to have the least energy requirement compared to thermal or membrane processes.

Cost assessment for each available technology varies on a site-to-site basis, as every specific location will present different issues associated with logistics, energy prices, civil work costs, brine composition, and taxes, among many other factors.

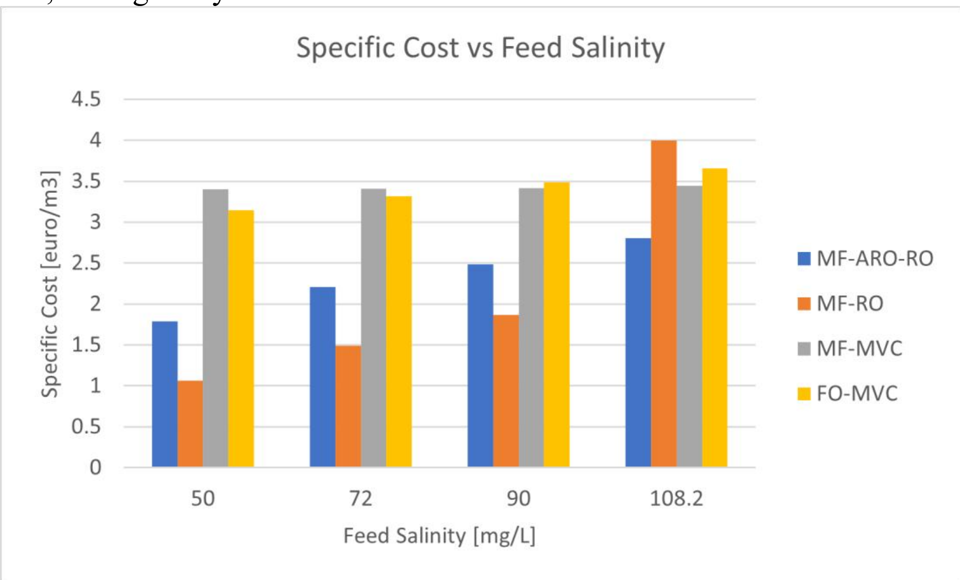

Figure 4.6: Specific price for the desalination of 1 cubic meter of water with different feed salinities through different setups: 1) microfiltration-assisted reverse osmosis reverse osmosis, 2) microfiltration-reverse osmosis, 3) microfiltration-mechanical vapour compression, 4) forward osmosis-mechanical vapour compression.

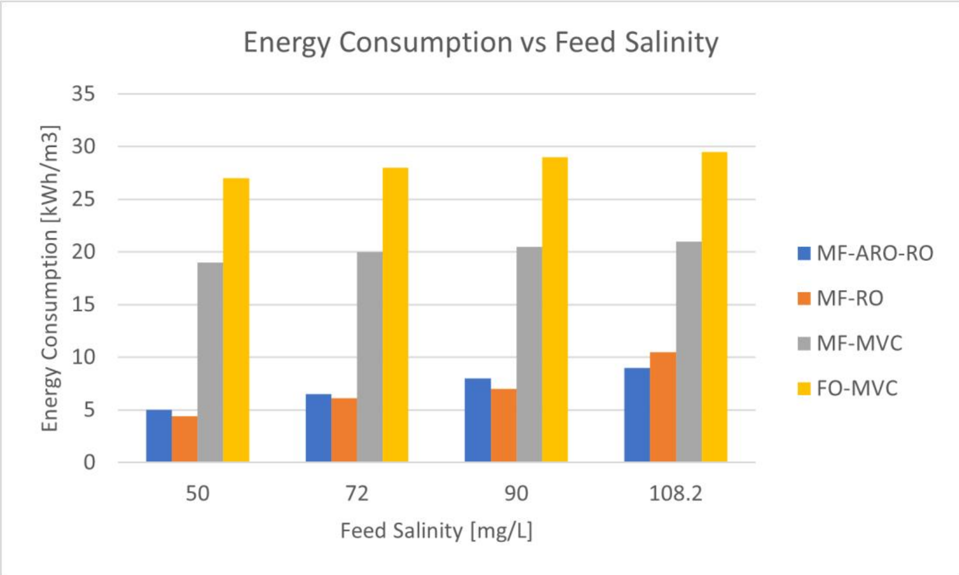

Figure 4.7: Energy Consumption in kWh/m^3 for the desalination of 1 cubic meter of water with different feed salinities through different setups: (1) microfiltration-assisted reverse osmosis- reverse osmosis, (2) microfiltration-reverse osmosis, (3) microfiltration-mechanical vapour compression, (4) forward osmosis-mechanical vapour compression.

Osipi et al. (2018) made a cost assessment of different combinations of desalination technologies for onshore treatment, involving forward osmosis (FO), reverse osmosis (RO), assisted reverse osmosis (ARO), microfiltration (MF), mechanical vapour compression (MVC) and membrane distillation (MD). This assessment was run through simulations and optimized for different reuse destinations (focusing on irrigation, with final streams with 2000 [mg/L] NaCl and 0% oil and grease), with different initial salinity; their results showed that the cheapest combination for salinities lower than 90 [g/L] was the MF-RO, while FO-RO had the highest cost; for higher salt contents, MF-ARO-RO was the cheapest alternative.

As interest in environmental protection increases and stricter limits are imposed by regulatory agencies around the world, research on emission reduction advances in every industry. The case of produced water is the same, as research on the optimization of advanced treatment strategies is fairly recent and will continue to develop over the years. The main problem when trying to make a general comparison between all strategies available is that the produced water composition is completely different from site to site, even among wells located in the same reservoir. This is important because the efficiency of every treatment technology varies greatly with the initial contents of the water to be treated, especially in terms of dissolved solids and dissolved organic compounds, as well as with the volumes to be treated, and the rates at which they are produced. Additionally, site-to-site differences include also logistic-associated costs, such as the availability of treatment plants, or the rentability of creating them, and transportation costs, space availability, maintenance required, storage costs and final disposition options. These depend heavily on the geographical location of each specific operation, which means a complete techno-economic assessment must be done at every site to select and optimize the best solutions possible.

Overall, in the literature available, certain treatment technologies are mentioned as the best option, but this varies greatly depending on the factors mentioned. For example, reverse osmosis membrane filtering is constantly referred to as the most energetically and economically efficient technology for water treatment, resulting in very high removal efficiencies. However, they are only applicable for streams with salinities lower than 40 [g/L] which means their application might require different pre-treatment steps, which would increase costs and energy consumption.

Conclusions

This study investigated the origins, nature, and degree of pollution caused by water produced by oil and gas extraction, as well as the various approaches available for its disposal and remediation. In produced water treatment, multiple treatment systems may be employed in series operations because no single technique can fulfil appropriate effluent characteristics. Based on factors including generated water chemistry, cost-effectiveness, space availability, plans for reuse and discharge, long-term operation, and byproducts, the optimal technology is chosen. Even though raw generated water is poisonous, it may be processed with the right technology to be used for many purposes, including drinking water, which is especially useful for water-stressed nations.

Treatment of Produced Water has been extensively reviewed in this paper and is proven to be an effective option for handling oil and gas Produced Water. The review has been able to identify and compile existing and recently developed technologies which are economically viable for oil and gas to Produce Water. In Produced Water treatment, two or more treatment systems might be combined as no single technology can satisfy all the water quality requirements. The choice of the best technology depends on the chemistry and origin of PW, cost-effectiveness, eco-friendliness, space limitation for equipment installation, fit-for-purpose reuse, durability of operation and by-product of the treatment process. Also, consideration of the geological and hydrologic setting for oil fields should be part of the description of applications of these technologies.

Declarations

Funding

The authors received no funding for this study.

Competing interest

The author declares that she has no competing interest

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