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Treating High Salinity Produced Water Using Hybrid Membrane Processes: Electrocoagulation-Microfiltration/Ultrafiltration-Membrane Distillation-Crystallization

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Treating High Salinity Produced Water Using Hybrid Membrane Processes: Electrocoagulation-Microfiltration/Ultrafiltration-Membrane Distillation-Crystallization

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Abstract

Produced water (PW) is considered the largest industrial wastewater stream in the world. PW generated from oil and gas operations generally contains a range of contaminants including high total dissolved solids, high total suspended solids, polar and nonpolar organic compounds, and low surface tension dissolved species. Treating PW is very challenging and applying only membrane-based technologies is not sufficient due to membrane fouling, which affects their long-term performance. Hence, integrated membrane processes are required to treat PW effectively. Hybrid membrane processes, which may result from combining a conventional process with a membrane separation, could be used to address the issues of fouling (and wetting), and maximize water recovery. In this dissertation, several hybrid membrane processes are reviewed and the effects of important parameters that determine the performance of these hybrid systems are discussed.

While the highly impaired PW is often deep well injected, there is a great deal of interest in treating and recovering this water for beneficial uses. However, the need to use multiple unit operations is essential if these wastewaters are to be recovered. Electrocoagulation (EC) is considered a promising pretreatment technology. In this study, the use of aluminium electrodes for electrocoagulation as a pretreatment operation was investigated. The effects of electrode arrangement, applied current, reaction time, initial pH, and inter electrode distance on the quality of the treated water have been investigated.

EC results showed good removal of turbidity (95%), total suspended solids, TSS (90%), and total organic carbon, TOC (70%) by carefully choosing the reaction conditions. Sedimentation

was used to separate the treated water from the sludge. The quality of the feed PW can strongly affect the performance of the EC.

In addition, a combined electrocoagulation – microfiltration – membrane distillation (EC-MF-MD) process had been used to treat PW. In this work, EC was followed by MF to pretreat the wastewater prior to MD. After EC, the TOC was reduced from 120 mg L^{-1} to 64 mg L^{-1}. Tangential flow MF using a 0.1 μm pore size polyethersulfone membrane was used to separate the particulate matter after EC and to further reduce the TOC to 44 mg L^{-1}. MD was used to desalinate the pretreated PW resulting in a high quality treated water (reducing the total dissolved solids (TDS) concentration from 245,300 mg L^{-1} to 56 mg L^{-1}). Three membranes with very different surface morphology were tested here: commercially available polyvinylidene fluoride, electrospun poly (vinylidene fluoride-co-hexafluoropropylene) nanofibers and multiwalled carbon nanotube coated polytetrafluoroethylene. The surface properties of an ideal membrane that is resistant to wetting and provides high flux is likely to depend on the TDS and properties of the PW.

The integrated electrocoagulation-ultrafiltration-membrane distillation and crystallization process (EC-UF-MDC) was also used to treat PW. The focus of this work was to determine the feasibility of this integrated process for increasing water recovery. The results of this work suggest that optimizing the various unit operations in this integrated process could be used to recover PW. Dissolved organic compounds are known to foul the hydrophobic membrane used in MD. In this study, a significant reduction in membrane fouling was obtained by EC pretreatment, which can lead to a long-term durability of MD system. In addition, the use of MDC can help mitigate the scale formation. Also, treating PW will preserve surface and groundwater, which form 80% of the

water utilized in hydraulic fracturing, and reduce the amount of PW directly disposed in Class II disposal wells, which further address the main cause of earthquakes.

Finally, the integrated EC-MF pilot-scale system will be used to pretreat and reuse PW. The EC reactor (37.5 L) was built based on experiences gained from working with a laboratory scale (1 L). The integrated process will be evaluated at Texas Tech University (TTU). The design and construction of the EC-MF system are discussed in this work. The pilot-scale system has a capacity of treating 3600 L/day PW. The system layout is also discussed in this study. The EC-MF process was designed based on 70% feed water recovery. Turbidity, TSS, and TOC analysis will be obtained for samples collected during the 5 days operation. The goal of this work is to achieve a reduction of 95, 90, and 70% for turbidity, TSS, and TOC, respectively, which is the pretreated PW quality needed to be further treated by TTU.

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List of Acronyms

AFM	**Atomic force microscopy**
API	**American Petroleum Institute**
BAF	**Biologically active filtration**
BOD	**Biological oxygen demand**
BPS	**Bipolar series**
BR	**Biological reactor**
CMC	**Critical micelle concentration**
COD	**Chemical oxygen demand**
DAF	**Dissolved air flotation**
DMAc	**N,N-dimethylacetamide**
DO	**Dissolved oxygen**
DOC	**Dissolved organic carbon**
EC	**Electrocoagulation**
ED	**Electrodialysis**
EDX	**Energy-dispersive X-ray**
EEC	**Electrical energy consumption**
FO	**Forward osmosis**
IAF	**Induced air flotation**
LEP	**Liquid entry pressure**
LLE	**Liquid-liquid extraction**
MD	**Membrane distillation**
MDC	**Membrane distillation–crystallization**
MF	**Microfiltration**
MPP	**Monopolar parallel**
MPS	**Monopolar series**
MSF	**Multi-stage flash**
MVC–MD	**Mechanical Vapor Compression Membrane Distillation**
MWCNT	**Multiwalled carbon nanotube**
NF	**Nanofiltration**
PAC	**Polyaluminum chloride**

PAM	**Polyacrylamide**
PP	**Polypropylene**
PS-WSF	**Precipitative softening - walnut shell filtration**
PTFE	**Polytetrafluoroethylene**
PVDF	**Polyvinylidene fluoride**
PVDF-HFP	**Poly (vinylidene fluoride-co-hexafluoropropylene)**
PW	**Produced water**
RO	**Reverse osmosis**
SBR-MBR	**Sequencing batch reactor-membrane bioreactor**
sCOD	**Soluble chemical oxygen demand**
SEM	**Scanning electron microscopy**
SLE	**Solid-liquid extraction**
TDS	**Total dissolved solids**
TOC	**Total organic carbon**
TSS	**Total suspended solids**
TTU	**Texas Tech University**
U of A	**University of Arkansas**
UF	**Ultrafiltration**
USGS	**United States Geological Survey**
VMD	**Vacuum membrane distillation**
XRD	**X-ray diffraction**

List of Published Papers

Chapter 2 (Published): M. Jebur, S.R. Wickramasinghe, Hybrid membrane processes for treating oil and gas produced water, in: Integrated and Hybrid Process Technology for Water and Wastewater Treatment, Elsevier, 2021: pp. 339–369. https://doi.org/10.1016/b978-0-12-823031-2.00019-7.

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Chapter 4 (Published): M. Jebur, Y.H. Chiao, K. Thomas, T. Patra, Y. Cao, K. Lee, N. Gleason, X. Qian, Y. Hu, M. Malmali, S.R. Wickramasinghe, Combined electrocoagulation-microfiltration-membrane distillation for treatment of hydraulic fracturing produced water, Desalination. 500 (2021). https://doi.org/10.1016/j.desal.2020.114886.

Chapter 5 (Under preparation): M. Jebur, Y. Bachynska, X. Hao, X. Qian, S.R. Wickramasinghe, Integrated Electrocoagulation–Ultrafiltration–Membrane Distillation Crystallization for Treating Hydraulic Fracturing Produced Water.

Chapter 1. Overall Introduction

Hydraulic fracturing combined with horizontal drilling is the fastest growing sector for U.S. energy supply known as unconventional shale gas and oil operations. Using hydraulic fracturing enables the recovery of abundant oil and gas from low-permeability rocks, such as tight sandstone, shale and coal beds, that were previously unreachable [1–3]. The extraction of shale gas using this advanced technique has increased from 14 % of the U.S. natural gas production in 2004 to 97 % in 2018. This increase in shale gas production has led to a drastic increase in water usage for hydraulic fracturing [4,5].

In hydraulic fracturing, water and proppant (ceramic or sand) containing about 2 % added fracturing fluid (frac fluid, such as biocides, scale inhibitors, solvents, friction reducers, corrosion inhibitors and non-ionic surfactants) are mixed and pumped at high pressure through the well pore to fracture tight rock formations [3,6,7]. Then, the pressure is reduced, and the water flows back to the surface as flowback water plus oil or gas and produced water (PW). The amount of PW generated during the extraction period of each well is around 15 to 23 million liters [8]. In general, approximately 116 billion liters of PW are formed in the U.S. annually [9].

Due to the increase in water demand, sustainable water management practices are needed to treat, recycle, and reuse PW in a wide range of applications, such as hydraulic fracturing, livestock or wildlife watering, irrigation, and various industrial uses (e.g., power plant makeup water, dust control, fire control, and vehicle washing) [10,11]. Disposal of PW is a major environmental challenge due to having the added frac fluid, oil, and contaminants from the geological formation [12,13]. Thus, treating PW, which is highly impaired, is essential. However, treating PW is very challenging because it contains a wide range of contaminants including high total dissolved solids (TDS) concentration, high total suspended solids (TSS), polar and non-polar

organic compounds, and low surface tension dissolved species, which vary in concentration due to the geographic location of the field and the type of oil or gas being produced [14,15].

In order to convert PW from wastewater to a valuable product, frequent multiple unit operations are needed to remove dispersed oil and grease (De-oiling), soluble organic compounds, TSS, bacteria (disinfection), TDS (desalination), and excess water hardness (softening) from PW [16]. The level of treatment of PW depends on the beneficial use of the treated water [7,17–20]. To result in a water sufficient for deep well injection into a geological isolated formation, primary treatment is required to remove suspended solids and free oil from PW. To further treat the water for reuse to stimulate new wells, secondary treatment is needed. To result in a water which can be discharged directly into lakes and rivers, tertiary treatment operations are applied. The work done by Jiménez et al. provides a detailed summary of the unit operations typically considered for primary, secondary, and tertiary treatment of PW [21].

The accepted current practice to manage PW is deep well injection. Deep well injection practices have several drawbacks such as the limitation of available deep well injection sites, the cost of transporting PW to the available sites (up to 4 USD per barrel of PW) [22], and the effects of deep well injection practices on enhancing earthquakes [23,24].

To treat PW, physical, chemical, thermal, and biological methods are usually used as conventional techniques. When treating PW to meet the discharged water standards, using only conventional methods (coagulation, sedimentation, multistage flash distillation, integrating evaporation-crystallization-spray drying, centrifugation and filtration) [25–27] is not sufficient due to only reduce the contaminants in PW to levels that are in general not complaint with environmental regulations. In addition, these conventional techniques still suffer from some drawbacks, such as high cost, large footprint, and the use of toxic chemicals [28].

Membrane technology is another option used to treat high TDS PW, such as microfiltration (MF) [29,30], reverse osmosis (RO) [31,32], forward osmosis (FO) [33,34], and membrane distillation (MD) [35–37]. In RO, brines with a TDS below 50,000 mg/L can be successfully treated because at high TDS (> 50,000 mg/L) the applied pressure on the feed side will be less than the osmotic pressure [38,39].

In MD, a microporous hydrophobic membrane is used as a barrier between the feed and permeate streams. Due to the vapour pressure differences resulting from the temperature difference between the feed and distillate, the water vapour molecules will transport from the feed stream (warm brine) to the distillate (cold) stream. The advantage of using MD instead of other known membrane techniques is that the feed TDS concentration has little effects on the separation process, which means MD is relatively insensitive to the feed salinity so it can be used to treat a high TDS brine [40,41]. In direct contact membrane distillation, which is used here, the feed and distillate streams are in direct contact with the two surfaces of the membrane [42]. However, MD like all other membrane technologies still suffers from fouling and scaling propensity of the membrane, which affects its long term performance [43]. Research into membranes for MD is still at a basic level and a lot of opportunities exist to improve membrane stability

In general, it is not practical or even possible using only a membrane system to treat PW given the wide range of contaminants present in PW. Hence, a pretreatment step is essential to obtain low energy consumption, low chemical cleaning requirements, and a high steady flux through the membrane. Hybrid membrane processes could be used to successfully treat PW and overcome most of the drawbacks faced by using only conventional techniques. Here we investigate the feasibility of treating high salinity PW using hybrid membrane processes, such as electrocoagulation – microfiltration or ultrafiltration (EC–MF/UF), membrane distillation –

crystallization (MDC), and electrocoagulation – microfiltration or ultrafiltration – membrane distillation – crystallization (EC–MF/UF–MDC). Integrating one or more techniques with membrane processes can address the issues of both scaling and wetting and maximize water recovery.

The integrated EC–MF/UF system could be used to successfully treat PW by achieving high removal efficiency of suspended solids, turbidity, and organic compounds and overcome most of the drawbacks faced by using other techniques. Using the integrated EC–MF/UF process can provide several advantages such as low cost, small footprint, and membrane scaling mitigation. Using the electrocoagulation (EC) as a pretreatment step is essential to reduce membrane fouling [44]. The EC unit is used as a pretreatment step in MF [45,46], UF [47], RO [48], and FO units [49]. By applying an electrical current, metal ions are released into the solution to generate a variety of metal hydroxides as shown in the following equations.

$$M_{(s)} \rightarrow M^{n+}_{(aq)} + ne^- \quad \text{(at anode)} \quad (1)$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad \text{(at cathode)} \quad (2)$$

Where M is often Al or Fe (only Al electrodes used here) [50]. Various metal complexes form; such as $M(OH)^{(n-1)+}$, $M(OH)_2^{(n-2)+}$ and $M_6(OH)_{15}^{(6n-15)+}$ [51], and can contribute in neutralizing the negatively charged organic species and suspended solids. These metal complexes can convert to amorphous $M(OH)_{n(s)}$ particles as the solution ages. Organic compounds and suspended solids can easily be adsorbed and trapped by $M(OH)_{n(s)}$ particles, which eventually are deposited as flocs [52].

MF or UF is a pressure membrane process, which can provide a high permeate flux by applying a low pressure (0.1 – 2 bar and 0.1 – 5 bar, respectively) as a driving force. The separation mechanism in MF or UF is based on particle size so the membrane works as a barrier to retain all

the particles larger than the pore size of the membrane. The constant pressure tangential flow cell is used to treat PW and obtain high water recovery. Organic (polymeric) and inorganic (ceramic) membranes are used as MF and UF membranes in this study, respectively. Using MF or UF after EC is necessary to mitigate the membrane fouling and reduce the sedimentation time required to separate sludge from pretreated water during EC.

Employing crystallization after MD can mitigate membrane scaling by reducing the formation of crystal nuclei in the bulk feed. The MDC technology can also offer a potential solution to the high TDS brine disposal by recovering both water and minerals at high rates, which can lead to a nearly zero liquid discharge [53–55]. Crystallization has been applied after membrane distillation in previous studies to treat synthetic wastewater rather than wastewater [56–58]. The critical operating conditions for MDC including the inlet temperature and flow rates of both feed and distillate streams as well as the temperature of the feed tank, has not been evaluated to treat various wastewater including PW. In this study, we evaluate the crystallization unit as a part of the integrated MDC system to treat high TDS brines.

EC–MF/UF–MDC is another hybrid membrane process that can be used to treat PW. Using EC–MF/UF as a pretreatment step before MD can help in reducing the membrane fouling by removing most of the organic compounds and suspended solids from PW. Also, using a crystallizer unit after MD can enhance the recovery rate of both water and minerals as well as mitigate scaling on the membrane by removing most of the inorganic compounds. Several studies have been done using EC–MD or MDC systems to treat high TDS brine as synthetic PW and to our knowledge, this is the first study used the integrated EC–MF/UF–MDC system to ensure long term operation of the membranes in MF/UF and MD as well as recovering both water and minerals from PW. In this part of our research, we will optimize the operating conditions in the EC–MF/UF–MDC

system. This will give us a good understanding of the performance in each step. This research evaluates the feasibility of using EC–MF/UF–MDC system as a continuous process to recover water and minerals from shale oil and gas PW.

The technology used here can have a potential impact on water resources/oil & gas companies because surface water and groundwater form about 80% of the water utilized in hydraulic fracturing [59]. Further, about 95% of the collected PW is directly disposed in Class II disposal well [60]. Using deep well injection may not be always available due to the new regulations that may be issued in the future. Some studies show that there is a strong connection between deep well injection of PW and earthquakes, which could be the main reason to apply new regulations to minimize or eliminate the deep well injection of PW. The hybrid membrane processes (EC–MF/UF, MDC, and EC–MF/UF–MDC) could be an effective solution to treat and reuse PW to achieve a high recovery of water. The data collected from treating PW can be used to evaluate the integrated hybrid membrane processes, which can further lead to the next step of establishing a pilot-scale of these hybrid membrane processes. The deliverable of this research is:

1. Fundamental understanding of the hybrid membrane processes (EC–MF/UF, MDC, EC–MF/UF–MDC).
2. Performance data for each treatment step using hydraulic fracturing PW.
3. A lab-scale of continuous EC–MF/UF–MDC system.
4. A pilot-scale of continuous EC–MF system.

The objectives of this study can be summarized as following.

1) EC–MF/UF

a) Design and establish the EC unit.

b) Determine the efficiency of batch EC at removing foulants from PW [removal of turbidity (95%), total suspended solids, TSS (90%), and total organic carbon, TOC (69%)].

c) Develop operational and design key parameters based on the dominant mechanism in EC.

d) Evaluate the continuous EC system at optimized operating conditions.

e) Establish and test the lab-scale combined EC–MF/UF processes.

f) Study the effects of using polymeric and ceramic membranes on the permeate water flux, cleaning, and long term operation.

g) Establish and test the pilot-scale EC–MF process.

2) MDC

a) Investigate the performance of MD process by testing electrospinning and commercial PVDF membranes for treating synthetic, real, and pretreated PW.

b) Study the effects of adding the crystallization unit after MD on the reduction of scalants.

c) Evaluate the operating conditions of MDC process.

3) EC–MF/UF–MDC

a) Evaluate the performance of integrated EC–MF/UF–MDC processes for treating PW.

b) Determine the water and minerals recovery rates in EC–MF/UF–MDC.

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Chapter 2. Hybrid Membrane Processes for Treating Oil and Gas Produced Water

This chapter is adapted from a published book chapter by M. Jebur, S.R. Wickramasinghe, Hybrid membrane processes for treating oil and gas produced water, in: Integrated and Hybrid Process Technology for Water and Wastewater Treatment, Elsevier, 2021.

Abstract

Produced water (PW) generated from oil and gas operations is considered the largest industrial wastewater stream in the world. It generally contains a range of contaminants including high total dissolved solids, high total suspended solids, polar and nonpolar organic compounds, and low surface tension dissolved species. Membrane-based technologies could provide new cost-effective methods to treat PW. However, membrane-based technologies suffer from membrane fouling, which affects their long-term performance. Hence, combined and integrated membrane processes will be required to treat PW efficiently. Using a hybrid membrane process, which may result from combining a conventional process with a membrane separation, could address the issues of fouling (and wetting), and maximize water recovery. In this review chapter, several hybrid membrane processes are reviewed. Emerging technologies will also be discussed. The effects of important parameters that determine performance of these hybrid systems are discussed.

2.1. Introduction

Currently, one of the fastest growing sectors for U.S. energy supply is unconventional shale gas and oil operations. The exploitation of abundant oil and gas resources that were previously unreachable has been enabled using hydraulic fracturing combined with horizontal drilling, which is considered as an emerging technology [1]. The water used for hydraulic fracturing has drastically increased in U. S. due to using this advanced technique (hydraulic fracturing)

increasing the U.S. natural gas production from 14 % in 2004 to 97 % in 2018 [2,3]. In hydraulic fracturing, the tight rock formation is fractured by pumping water mixed with chemicals at high pressure through the well bore. Then, the pressure is reduced, and the water flows back to the surface as flowback and produced water referred to here as PW. PW generated from oil and gas operations is considered as the largest industrial wastewater stream in the world [4,5]. During the extraction period of each well, about 15 to 23 million liters of PW are generated [6]. In general, the amount of PW formed in U.S. is around 116 billion liters per year [7].

Due to the increase in water demand, treating PW is essential if it is directly discharged or reused in a wide range of applications, such as hydraulic fracturing, livestock or wildlife watering, irrigation, and various industrial uses (e.g., power plant makeup water, dust control, fire control, and vehicle washing) [8,9]. PW is very challenging to treat because it contains a wide range of contaminants including high total dissolved solids (TDS) concentration, high total suspended solids (TSS), polar and non-polar organic compounds, and low surface tension dissolved species. The geographic location of the field and the type of oil or gas being produced determine the range and variety in the concentration of contaminants found in PW [10,11].

One of the accepted current practices used to manage PW is deep well injection. However, there are several drawbacks found when applying deep well injection practices such as, the cost of transporting PW to the available sites (up to 25 USD per m^3 of PW) [12], the limitation of available deep well injection sites, and the effects of deep well injection practices on enhancing earthquakes [13,14].

Removing dispersed oil and grease (de-oiling), soluble organic compounds, TSS, bacteria (disinfection), TDS (desalination), and excess water hardness (softening) from PW is required to convert PW from wastewater to a valuable product [15]. To treat PW, physical, chemical, thermal,

and biological methods are usually used as conventional techniques. Using conventional methods only, such as coagulation, sedimentation, multistage flash distillation, integrating evaporation-crystallization-spray drying, centrifugation and filtration [16], is not sufficient when treating PW to meet the discharged water standards. The conventional methods can only reduce the contaminants in PW to levels that are in general not complaint with environmental regulations. In addition, these conventional techniques still suffer from some drawbacks, such as high cost, large footprint, and the use of toxic chemicals [17].

Membrane technology is another option found to treat PW, such as microfiltration (MF) [18,19], reverse osmosis (RO) [20,21], forward osmosis (FO) [22,23], and membrane distillation (MD) [24–26]. However, using only a membrane system to treat PW is not practical or even possible given the wide range of contaminants present in PW. In addition, all the membrane technologies still suffer from fouling and wetting propensity of the membrane, which affect their long term performance. Hence, a pretreatment step is essential to obtain low energy consumption, low chemical cleaning requirements, and a high steady flux through the membrane.

Using a hybrid membrane process, which may result from integrating a conventional process with a membrane separation, can address the issues of fouling and wetting, and maximize water recovery by extending the membrane life. Hybrid membrane processes could be used to successfully treat PW and overcome most of the drawbacks faced by using only conventional techniques. The purpose of this review chapter is to summarize several hybrid membrane processes and describe the effects of important parameters on the overall performance.

2.2. Membrane Separation Processes

A membrane is generally defined as a physical barrier existing between two homogeneous phases which enables one or multiple components to cross the membrane more readily than others.

The transport of components through the membrane is achieved by applying a driving force across the membrane. In general, increasing the driving force across the membrane will lead to an increase in the permeation rate (flux) through the membrane as described in equation (1) [27].

$$J = -A \times \frac{dX}{dx} \quad (1)$$

where J, A, dX/dx, X, and x are the flux, a phenomenological coefficient, the driving force given, the gradient (temperature, concentration, pressure etc.), and the coordinate perpendicular to the transport barrier respectively. Membrane processes can be classified according to their driving force, for example, pressure, temperature (partial pressure), concentration, and electrical [28]. The flux can be described as mass, volume, heat, and electrical flux by phenomenological equations; Fick's law (Jm = - D * dc/dx), Darcy's law (Jv = - Lp * dP/dx), Fourier's law (Jh = - λ * dT/dx), and Ohm's law (Ji = - 1/R * dE/dx), respectively [27].

In pressure driven membrane processes, such as MF, ultrafiltration (UF), nanofiltration (NF), and RO, the driving force is the difference in the applied pressure across the membrane. Here, the solvent is the continuous phase passing the membrane to concentrate or purify an aqueous or non-aqueous solution, while the solutes and particles are rejected to an extent, which depends on the pore size of the membrane. The separation mechanism in pressure driven membrane processes is mainly determined by the particle or molecular size of the solute. Figure 1 illustrates the separation principles of the four pressure driven membrane processes. Going from MF to UF and NF to RO membranes, the pore size is in the range of 0.1 – 10, 0.01 – 0.10, 0.001 – 0.01, and < 0.001 µm, respectively [29]. The characteristics of MF membranes can be summarized as highest permeability [>1000 L/(h.m^2.bar)], low pressure, largest pore size, and rejection of large suspended particles. In the case of MF and UF membranes transport is by convective flow through the membrane pores. However, transport through RO membranes occurs by a solution diffusion

mechanism [28]. Transport through high permeability NF membranes is often a combination of solution diffusion and convective flow through the membrane.

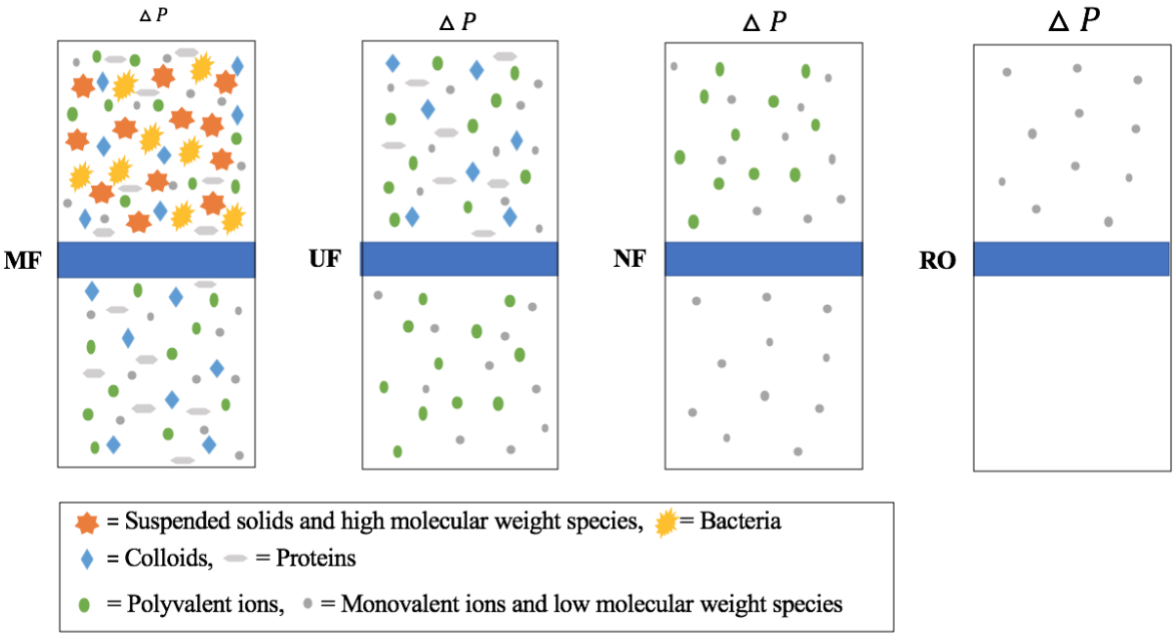

Figure 1. Schematic representation of separation principles in pressure driven membrane processes. MF, microfiltration; UF, ultrafiltration; NF, nanofiltration; and RO, reverse osmosis.

UF membranes have a permeability in the range of 10 – 1000 L/(h.m^2.bar) and can be used to remove emulsions, colloids, and proteins from wastewater. Small organic compounds and polyvalent ions can be separated using NF membranes having a permeability of 1.5 – 30 L/(h.m^2.bar). RO membranes have the lowest permeability [1.5 – 30 L/(h.m^2.bar)] and can be used to retain monovalent ions (NaCl) [30]. Thus, an RO system can be used as a final step to produce drinking and process water. RO can be used successfully to treat wastewater with a TDS below 50,000 mg/L because at high TDS (> 50,000 mg/L) the applied pressure on the feed side will be less than the osmotic pressure [31,32]. The transmembrane pressure is in the range of 0.1 – 2 bar and 0.1 – 5 bar when using MF and UF membranes, respectively. On the other hand, when utilizing NF and RO membranes, the transmembrane pressure is much larger in the range of 3 – 20 bar and

5 – 120 bar [30], respectively, which is directly related to the pore size of the membrane and the particle or dissolved solute being retained.

Concentration driven membrane processes can be applied when the activity (solute concentration) difference across the membrane is the driving force, such as forward osmosis (FO). The concentration difference can lead to osmotic pressure differences between a pure solvent or a dilute solution and a concentrated solution. Here, the solvent (water) transports through a semipermeable membrane from the dilute side (high chemical potential) to the concentrated side (low chemical potential) until reaching osmotic equilibrium. The separation mechanism in these membrane processes is solution-diffusion. In FO, the water flows through a selectively permeable membrane from the feed (dilute) solution to the draw (concentrated) solution resulting in concentration of the feed stream and dilution of the draw solution (highly concentrated solution). The relationship between the osmotic pressure (π) and the solute concentration Cj is described by the Van't Hoff equation [27] equation (2).

$$\pi = C_j \times R \times \frac{T}{M} \tag{2}$$

where R, T, and M are the ideal gas constant, the temperature and molecular weight.

In thermally driven membrane processes, such as MD, the driving force is the temperature difference across the membrane. In this case, two solutions kept at different temperatures are separated by a membrane. In MD, the transport of water vapour molecules from the feed stream (hot side) to the permeate stream (cold side) through a non-wettable microporous hydrophobic membrane is achieved by two compensating phase transitions to concentrate and purify an aqueous solution. The driving force in MD is the vapour pressure differences induced by the temperature difference between the feed and permeate streams [27]. Figure 2 describes the principles of MD. The highest permeation rate is related to the component with the highest partial pressure. A very

high selectivity is obtained when using a salt solution (NaCl in water) in MD because the salt has a negligible vapour pressure in comparison with water. Thus, the transport of water occurs from the feed (salt solution) to the permeate (pure water) [33].

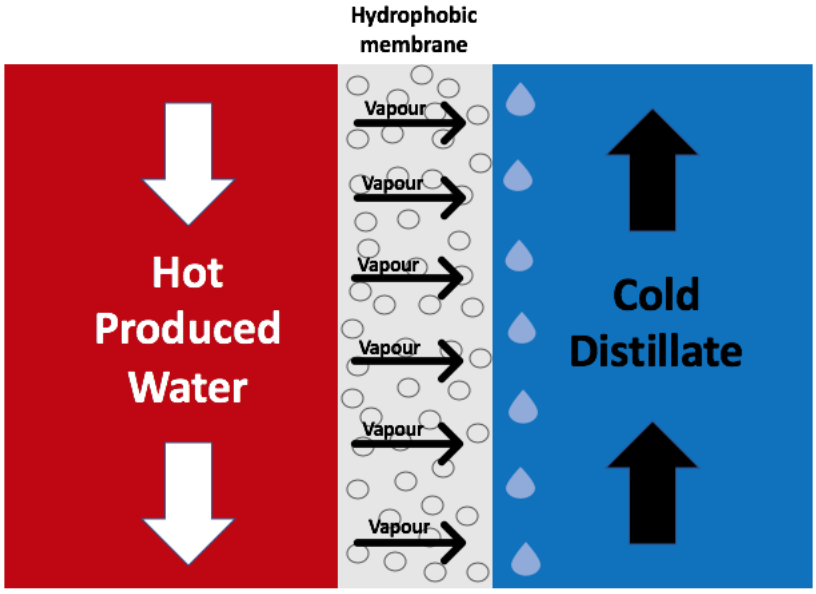

Figure 2. Schematic principles of MD. MD, Membrane distillation.

When an electrical potential difference is applied as a driving force, the membrane processes are known as electrically driven membrane processes such as electrodialysis (ED) and membrane electrolysis. Here, the transport of ions can only occur when both charged membranes and molecules are present. When applying an electrical potential difference to a charged solution (a sodium chloride solution), anions (negative ions Cl^-) migrate to the anode (positive electrode), while cations (positive ions Na^+) migrate to the cathode (negative electrode). The migration of these ions is controlled by electrically conductive membranes, such as cation-exchange membranes and anion-exchange membranes [34]. The mechanism used to describe the transport of ions through a charged membrane is Donnan exclusion [27].

In ED, ions are removed from a salt solution by electrically charged membranes. An alternating pattern of a number of cation- and anion-exchange membranes arranged between a

cathode and an anode is used here as shown in Figure 3. When applying a direct current in ED, the formation of alternate concentrated and dilute solution is observed. In addition, hydrogen (H_2) and hydroxyl ions (OH^-) are generated at the cathode (negative electrodes), while at the anode (positive electrodes), chlorine (Cl_2) oxygen (O_2) and hydrogen ions (H^+) are formed. The electrical current or current density applied is proportional to the amount of ions that move through the membrane. To obtain the current density needed to transfer the ions present in the solution, equation 3 can be used [27].

$$i = z * F * Q * dc/e \quad (3)$$

where i, z, F, Q, dc, and e are the electrical current, the valence of the ion, Faraday constant, the flow rate, the concentration difference between the feed and the permeate (diluate) (eq/L), and the current efficiency, respectively.

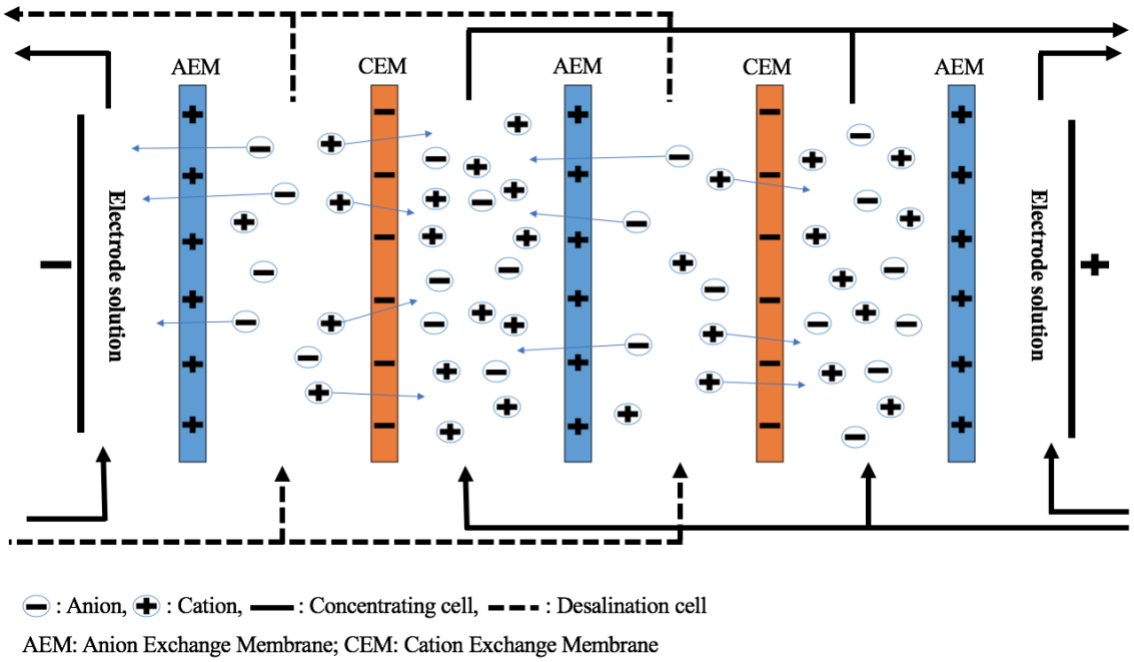

Figure 3. Schematic representation of ED principles. ED, Electrodialysis. Source: From Akhter, M., Habib,G., & Qamar, S. U. (2018). Application of electrodialysis in wastewater treatment and impact of fouling on process performance. Journal of Membrane Science & Technology, 8(2). https://doi.org/10.4172/2155-9589.1000182

2.3. Treatment Trains (Primary, Secondary, and Tertiary)

Three main treatment stages are applied to manage PW once it is recovered during hydraulic fracturing. Primary treatment involving gravity separation and centrifugation can be used effectively to remove suspended solids and free oil from PW resulting in water sufficiently treated for deep well injection. Secondary treatment units such as coagulation and flocculation, filtration, membrane separations, air flotation, and electrocoagulation (EC), are applied to treat PW to a level accepted for reuse to stimulate new wells. Finally, tertiary treatment operations including evaporation can treat PW to generate freshwater, which can be discharged directly into lakes and rivers etc. Therefore, choosing the type of treatment or treatment trains is essential to determine the quality of the treated PW. Figure 4 describes different PW treatment stages [35–39].

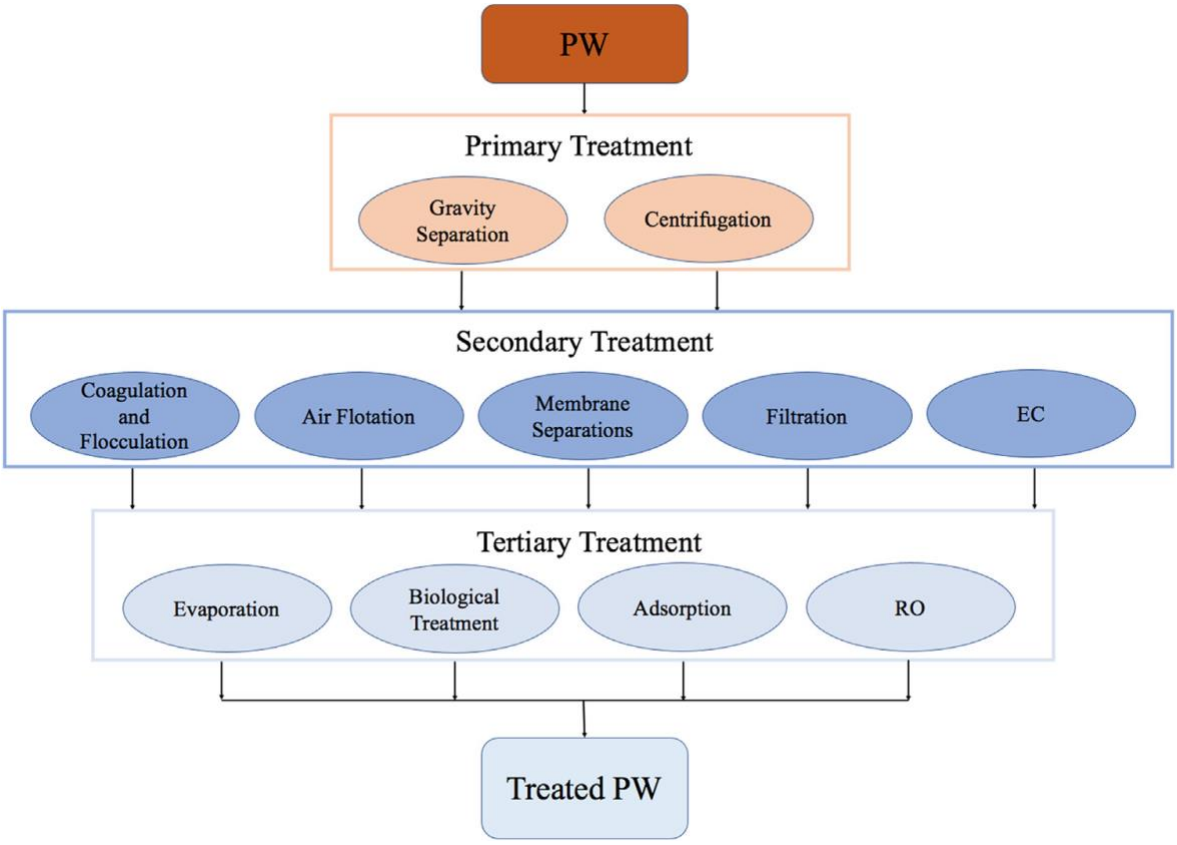

Figure 4. Schematic representation of PW treatment stages. EC, Electrocoagulation; PW, produced water; RO, reverse osmosis.

2.3.1. Primary Treatment

Since TSS, insoluble organic compounds, and free oil and grease are the most common contaminants generally found in PW, primary treatment is essential to reduce the levels of these contaminants. Gravity separation and centrifugation are the most common techniques used in primary treatment, based density differences [15,40]. Through sedimentation, the suspended solids and insoluble organic compounds settle to the bottom, while the free oil and grease rise to the surface to be removed by a surface skimmer. Gravity separation can be effectively used to remove particles or free oil with a diameter equal or more than 150 μm [15]. Proper hydraulic design and the retention time of wastewater are the key parameters for approaching a high removal efficiency using gravity separators. American Petroleum Institute (API) separators and coalescing plate separator units are the most common equipment used commercially as gravity separators.

The API separator designed by the API involves a rectangular clarifier, a surface skimmer, and a bottom rake as described in Figure 5. All free oil in PW is accumulated on the surface as a layer skimmed off using a surface skimmer, while the large suspended particles settle at the bottom making a sediment layer removed by a sludge pump or scraper. The presence of particulate matter and surfactants, feed flowrate, and the type, concentration and viscosity of oil are the key parameters for accomplishing a high removal efficiency of free oil using the API separators. Approximately 90 – 95 % and 80 – 90 % removal efficiency of free oil and suspended particles, respectively, are achieved using the API separators with effluent quality of 15 – 20 mg/L free oil and 20 – 30 mg/L suspended solids [29]. The retention time of PW passing the API separator is an essential design parameter enabling the separation of both free oil and suspended particles from wastewater [41,42]. The design parameter of the API separator, such as the minimum horizontal

area (A_H) can be calculated using equation 4, while the required length (L), and minimum cross-sectional area (A_C) are obtained by equations 5, 6 and 7.

$$A_H = F * Q_m/V_t \quad (4)$$

$$L = F * V_H/V_t * D \quad (5)$$

$$A_C = Q_m/V_H \quad (6)$$

$$F = F_1 * F_2 \quad (7)$$

where Q_m, D, V_H, V_t, F_1, and F_2 are the wastewater flowrate, the oil droplet diameter, the horizontal velocity of the oil droplets, the terminal velocity of the oil droplets, the short circuiting factor, and the turbulence factor, respectively. API separators can handle wastewater with a capacity in the range of 100 to 600 m^3/h. The main drawback when using the API separator is the poor separation efficiency of oil droplets smaller than 30 µm [29].

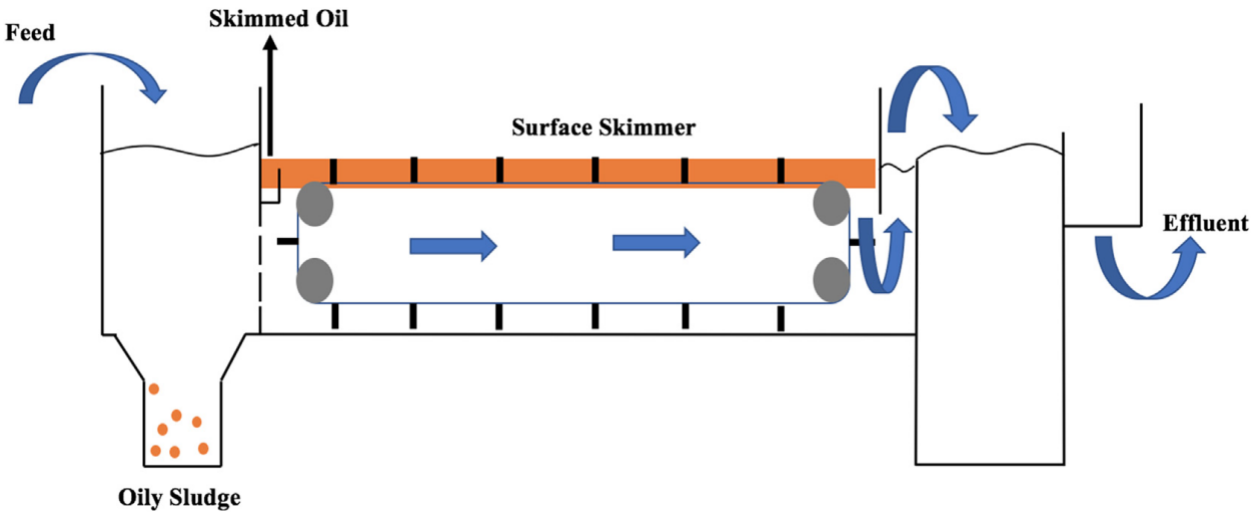

Figure 5. Diagram of an API separator. API, American Petroleum Institute.

Coalescing plate separators are also used as primary treatment units to remove both free oil and suspended solids from wastewater at high efficiency. The only difference between the coalescing plate separator and the API separator is the addition of parallel angled plates that help the coalescence of oil droplets into larger aggregates as shown in Figure 6. When the wastewater

enters the coalescing plate separator passing the parallel angled plates, a laminar flow is established in the area between the parallel angled plates, which allow sufficient time for the small oil droplets (≥40 μm) [15] to reach the upper plate. Then, these small droplets are continuously aggregated to make a large oil globule, which can finally escape to the surfaces [43,44]. Here, the removal efficiency of both free oil and suspended solids is in the range of 90 – 95 % with effluent quality of 10 – 15 mg/L (free oil) and 5 – 10 mg/L (suspended solids). The coalescing plate separator has a capacity to treat wastewater in the range of 15 to 250 m^3/h [29]. When there are suspended particles present in the wastewater as an oily sludge, the possibility of plugging the stream between the parallel angled plates is high, which is considered as a drawback leading to a poor separation efficiency [45].

Centrifugal separators are also employed as a primary treatment to remove free oil and suspended particles based on density differences. Centrifuges or hydrocyclones are the most common units used as centrifugal separators to achieve high removal efficiency of both free oil and suspended solids [46,47]. Centrifuges require less space and operating time in comparison with gravity separators [48]. The centrifugal force is about 3500 to 6000 times the gravity force, which can enhance the separation of free oil and suspended particles having a minimum size of ≥2 μm. In centrifuges, the rotating motion of the device can enhance the separation of liquids to heavy phase (the outer region) and light phase (near the vortex core). The main disadvantage when applying centrifuges for separation is the high maintenance rate due to the moving parts present [15]. Tubular centrifuge and disc-stack centrifuges are the most common continuous centrifuges utilized for industrial applications.

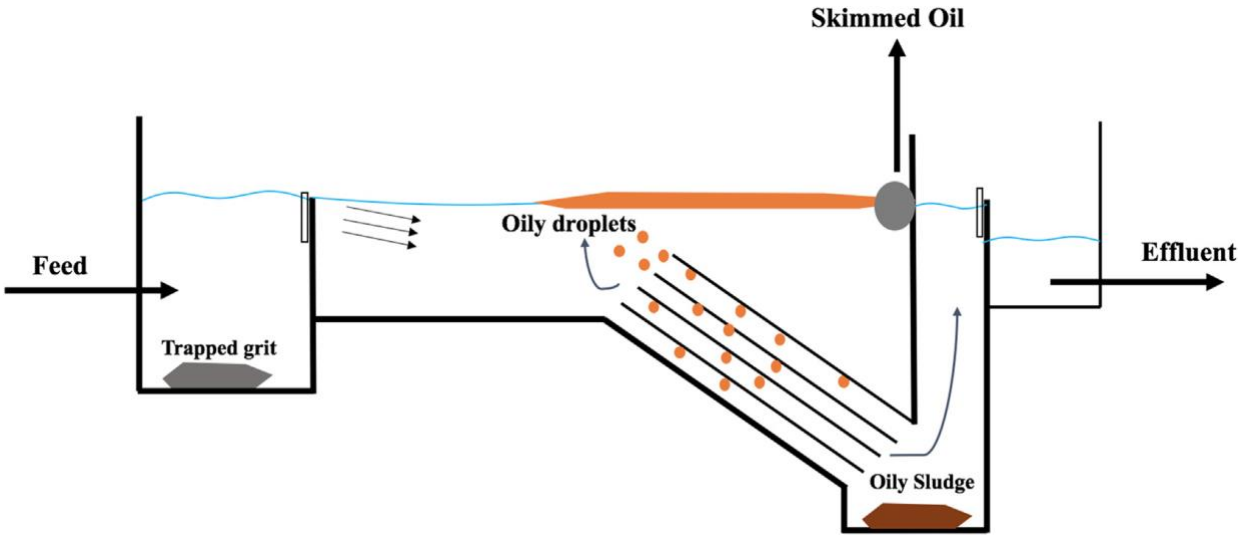

Figure 6. Diagram of a coalescing plate separator.

In the tubular centrifuge, a bowl rotates at a high speed to provide a centrifugal force separating the feed, which enters from the bottom, into a lighter phase (the inner layer) and a heavier phase (the outer layer). Two separate outlets placed at the top of the tubular centrifuge are employed to discharge the separated phases. In disc-stack centrifuge, solid-liquid and liquid-liquid separations are performed effectively. Here the feed enters the unit at the top and 30–50 closely spaced conical disks rotate forming the bowl. The lighter phase is continuously raised up through several holes spaced uniformly in each disc [49]. The light phase leaves the centrifuge from the center, while the heavy phase is discharged from the outer region of the centrifuge. The minimum oil droplet size removed from the continuous phase is calculated by equation 8 [46].

$$Dc = \sqrt{\frac{27*Q*\mu*\tan\theta}{\pi*n*w^2*dP*(r_2^3 - r_1^3)}} \quad (8)$$

where D_c, Q, r_1, r_2, θ, n, w, μ, and dP are the critical droplet diameter, the volumetric flow rate, the distances from outlet of the fluid to the disc, the distances from the rotating axis to the inlet, the disc half angle, the number of discs, the angular velocity of the centrifuge, the viscosity of the continuous phase, and the difference in density between the continuous and dispersed phases. The

disc-stack centrifuge has a capacity of 5 – 10 m^3/h with a removal efficiency of free oil, emulsified oil, and suspended solids in the range of 60 – 90 %, 40 – 80 %, and 90 – 95 %, respectively [29].

The hydrocyclone is another primary treatment unit used to separate oil having a minimum size of 10 – 15 µm from water and solids [15]. In the hydrocyclone, the feed is injected tangentially against the circular configuration of the hydrocyclone to form a circular motion. Two separated phases are formed; heavier phase collected at the bottom (underflow) and lighter phase accumulated in the center and removed from the top (overflow) [50,51]. Figure 7 is a schematic diagram of the hydrocyclone unit. The capacity of the hydrocyclone is in the range of 1 – 50 m^3/h, which can highly affect the separation performance [52]. In this unit, 80 – 90 % and 90 – 95 % removal efficiency of free oil and suspended solids, respectively, is achieved with effluent quality of 20 – 30 ppm free oil and 5 – 10 ppm suspended solids. The hydrocyclone design parameters involving dimensionless correlations, such as Reynolds (Re), Stokes (Stk), and Euler (Eu) numbers are shown in equation 9 10, and 11 [29,53,54].

$$Stk * Eu = 0.0474 * \left[ln\frac{1}{R_f}\right]^{0.742} * e^{8.96C} \quad (9)$$

$$Eu = 371.5 * R_e^{0.116} * \ e^{-2.12C} \quad (10)$$

$$R_f = 1218 * \left(\frac{D_u}{D}\right)^{4.75} * \ Eu^{-0.3} \quad (11)$$

where R_f, C, D_u, and D are the underflow-to-throughput ratio (flow ratio), the feed oil concentration (fraction by volume), the underflow diameter, and the hydrocyclone body diameter. The main advantage of applying hydrocyclones in industrial applications is providing less space and a lower foot print and capital cost as well as producing a lower oil content sludge [55].

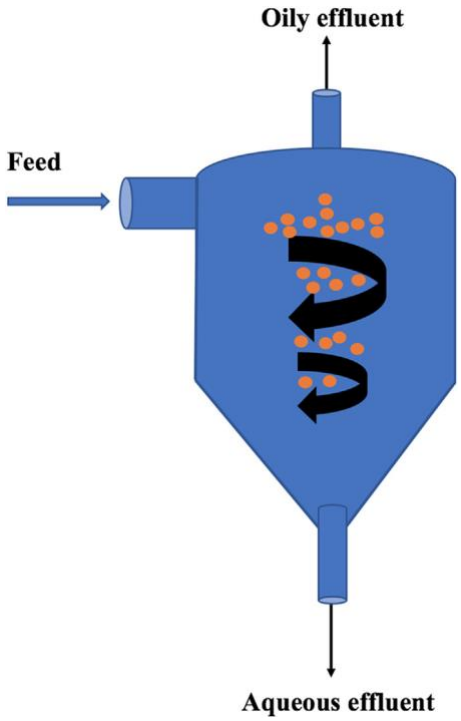

Figure 7. Diagram of a hydrocyclone.

2.3.2. Secondary Treatment

Secondary treatments including chemical, physical, or electrical methods are applied to treat PW by breaking the emulsion to remove mainly dispersed oil. The most common techniques used as secondary treatments are coagulation and flocculation (chemical methods) [56–58], filtration [59–61] and membrane separations [62–65] (physical methods), air flotation (mechanical method) [66,67], and EC (electrical method) [68]. Suspended or colloidal oil droplets can be removed from PW using chemical methods. In coagulation and flocculation, the chemical dose (inorganic salts and organic polymers) can help generate larger oil droplets resulting in better performance of the physical separation. Due to the surface charge of the oil droplets in an aqueous medium, these droplets cannot form larger aggregates. To reduce the charge on the surface of the oil droplets, chemical additives (coagulants or flocculants) are added to help in destabilizing the dispersed phase, breaking the emulsion, and enhancing droplet coalescence [69]. The most

common coagulants used in coagulation are inorganic salts of high valence cations such as aluminium chloride, ferric chloride, calcium chloride, aluminum sulfate and ferrous sulfate, while polyelectrolytes and organic polymers are commonly utilized in flocculation [70,71].

Flotation is another technique considered as a secondary treatment method. Here, the oil droplets or the light solids in suspension are raised to the surface by introducing fine air bubbles in the wastewater to enhance gravity separation of two phases having an insufficient density differential [66]. Flotation is known as a physico-chemical method because chemicals are usually added as coagulants or flocculants in this technique. Induced air flotation (IAF) and dissolved air flotation (DAF) units are the most commercially used flotation processes [15]. Figure 8 is a schematic diagram of the induced air flotation unit. In this unit, air bubbles are formed in the liquid due to mechanical mixing of air and liquid. Diffusers, recycle of a slip stream through venturi nozzles, or high-speed rotating impellers are employed in this process to produce air bubbles in the liquid [72]. The IAF includes rectangular tank with several air flotation stages, diffusers, and a skimmer.

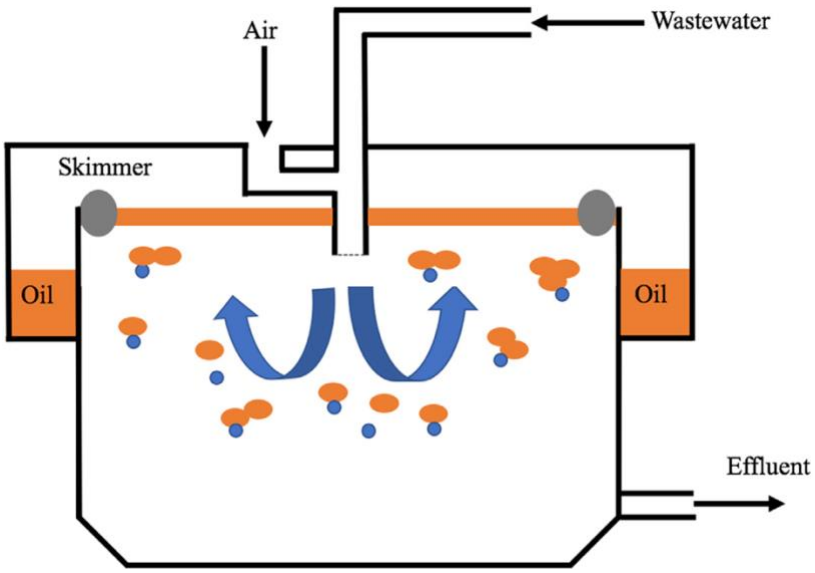

Figure 8. Diagram of an induced air flotation unit.

In dissolved air flotation, pressurized air is dissolved in the liquid. Then fine air bubbles are formed once the pressure is released. These bubbles attach to the oil and suspended solids to help carry them to the surface of the tank [72,73]. The DAF unit involves a rectangular flotation tank, flocculation chamber, a skimmer, and a compressed air tank as shown in Figure 9. The bubble size and mixing conditions are the main factors that differentiate IAF and DAF units. About 50–60 μm is the bubble size in DAF, while an order of magnitude larger bubble sizes is used in IAF [66]. Several parameters play a significant role in determining performance such as liquid residence time, air pressure, bubble and oil droplet size distributions, and feed oil concentration. The air/oil dimensionless ratio (G/S) is calculated using the design equation for a flotation system as given by equation 12 [74].

$$\frac{G}{S} = \frac{R * C_S * f * (P/101.3)}{Q * S_o - R * S_e} \quad (12)$$

where R, Cs, f, P, Q, So, and Se are the pressurized liquid flow rate, the gas saturation concentration at atmospheric pressure (mg/L), the air saturation efficiency (usually 0.5–0.8), the saturation pressure, the raw wastewater flow rate, the oil in wastewater (mg/L), and the oil in the pressurized liquid stream (mg/L). Using DAF as a secondary treatment method can lead to a high removal efficiency of free oil, emulsified oil, or suspended solids (95 – 98 %) with an effluent quality of 5 – 10 ppm. The capacity of using a flotation is in the range of 10 – 500 m^3/h.

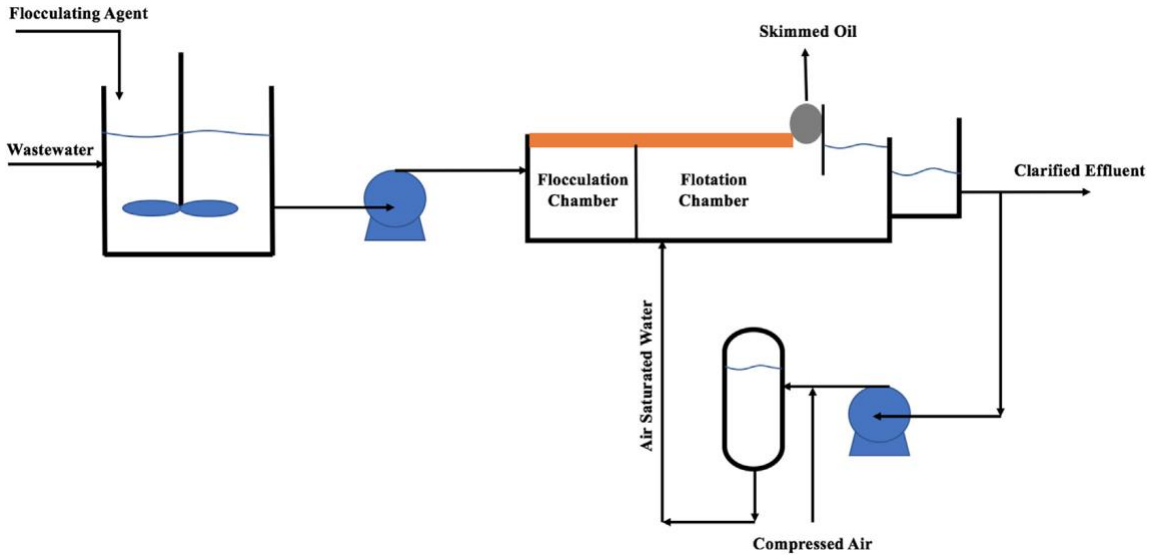

Figure 9. Diagram of a dissolved air flotation unit (recycled stream).

Membranes (MF [75,76] and UF [63,77]) can be successfully applied as a secondary treatment to remove emulsified and dissolved oil from oily wastewater. As in all membrane technologies, both MF and UF membranes still suffer from fouling and concentration polarization caused by adsorbing oil or surfactant, which lead to a reduction in permeate flux with time [78]. A higher permeate flux can be observed when using MF, which may increase the possibility of oil passing through the membrane. In UF, a steady permeate quality can be successfully achieved due to membranes having a tight pore structure [27]. The filtered liquid throughput rate and the choice of the membrane are the major key parameters used to determine the economic feasibility of membrane operations. Both lower energy costs and high quality permeate are the main advantages of using membrane distillation instead of any other techniques. However, scale-up and membrane life are the main limitations when applying membrane technologies.

Filtrations such as deep-bed filtration and filtration-coalescence known as secondary treatment units are also used to remove free and emulsified oil from wastewater [61,79]. Here, granular material is applied as a filter bed to enhance droplet coalescence or adsorb oil droplets. Droplet size, physical adsorption, and induced coalescence are the main principles of the oil

removal. The filtration performance is determined by several operating parameters, such as feed flowrate, pressure drop through filter media, oil concentration, and porosity, granularity and composition of the filter material [80,81]. The filtration performance is enhanced by decreasing granule size of the filter medium, while working at high flowrates leads to decrease the filtration performance due to the reduction in the residence time of the oil in the filter bed. High flowrates can result in observing no coalescence in filtration-coalescence unit [79,82], while the removal efficiency is enhanced when using deep-bed filtration at high feed flowrate due to improving the oil adsorption. The major drawback of filtration is the accumulation of solids and oil, which leads to pressure drop built up with time. A constant oil concentration after filtration, indicates that breakthrough has occurred, which requires backwashing of the bed or renewal the filter material [29,83].

EC is also applied as a secondary treatment to remove contaminants from PW [84]. Here, metal ions are released into the solution by applying an electrical current to generate a variety of metal hydroxides as shown in equations 13 and 14.

$$M_{(s)} \rightarrow M^{n+}_{(aq)} + ne^- \quad \text{(at anode)} \tag{13}$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad \text{(at cathode)} \tag{14}$$

where M is often Al or Fe [84,85]. Various metal complexes form; such as $M(OH^{)(n-1)+,}$ $M(OH)_2^{(n-2)+}$ and $M_6(OH)_{15}^{(6n-15)+}$ [86], which can contribute to neutralizing the negatively charged organic species and suspended solids. These metal complexes can convert to amorphous $M(OH)_{n(s)}$ particles as the solution ages. Organic compounds and suspended solids can easily be adsorbed and trapped by $M(OH)_{n(s)}$ particles, which eventually are deposited as flocs [87]. Figure 10 is a schematic diagram of an EC unit with a power supply working in a reverse polarity mode,

electrodes, and an EC reactor. The EC performance is determined by system parameters such as the current, time, initial pH, electrode arrangements, and inter electrode distance.

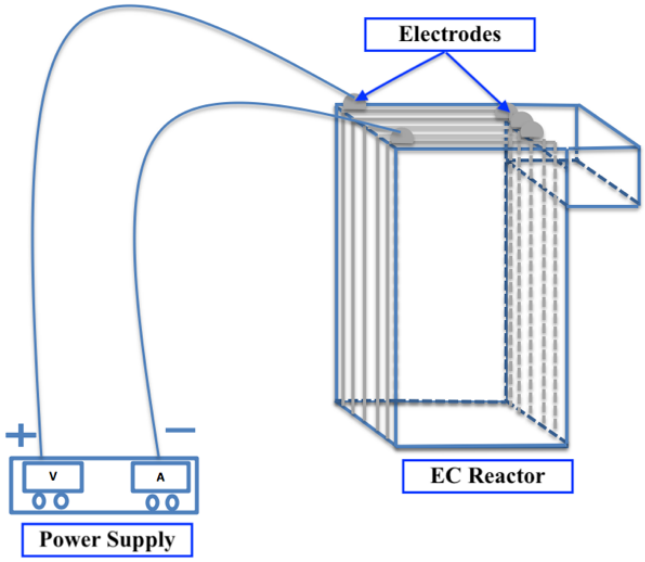

Figure 10. Diagram of an EC unit. EC, Electrocoagulation.

Electrochemistry, coagulation, and flotation are the basic steps describing the EC process as shown in Figure 11. Electrochemistry takes place when both oxidation and reduction reactions occur at the anode and cathode, respectively. Coagulation involving charge neutralization, double layer compression, bridging and sweep is obtained in the solution [88]. The type of contaminants and the EC operating conditions determine the dominant coagulation mechanisms in EC. In flotation, the suspended particles and aggregating coagulants are lifted to the surface by gases produced as by-products during EC (hydrogen and oxygen microbubbles). Studying the interaction between all the mechanisms in EC is essential to obtain the operational and design key parameters, which can determine the dominant pollutant removal path.

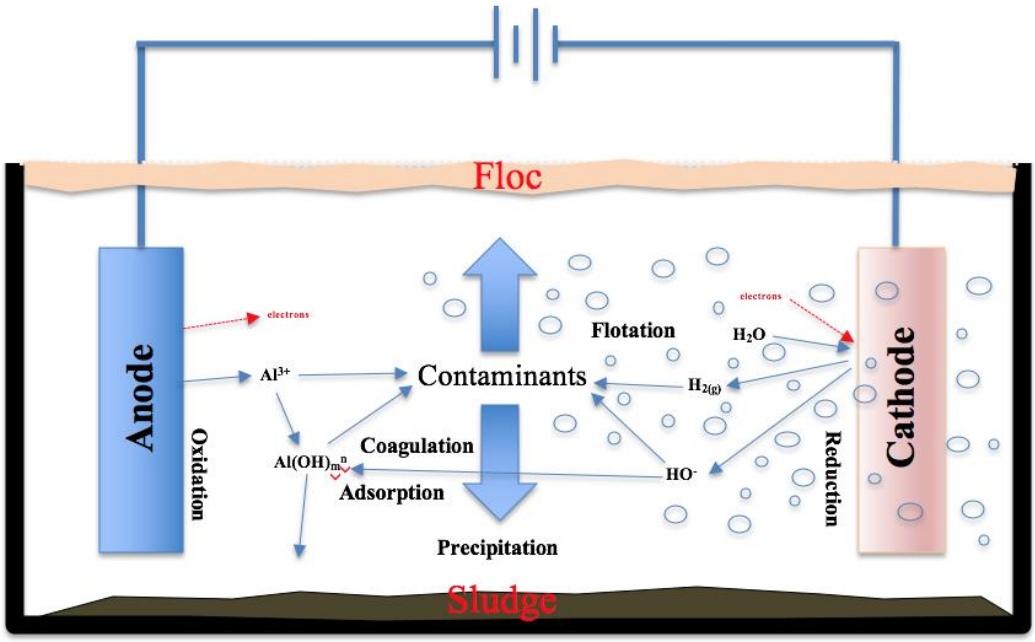

Figure 11. Mechanisms occurring during EC. EC, Electrocoagulation. Source: Modified from Coday, B. D., et al. (2014). The sweet spot of forward osmosis: Treatment of PW, drilling wastewater, and other complex and difficult liquid streams. Desalination, 333(1), 23 35. https://doi.org/10.1016/j.desal.2013.11.014.

2.3.3. Tertiary Treatment

To produce a high quality freshwater from oil and gas PW, tertiary treatment is needed such as evaporation techniques. Evaporation is a thermally driven process that requires a phase change of one or more components in a liquid mixture. The volatile liquid is separated from the residual (liquid or/and solid) by applying a large amount of energy. Thus, using evaporation is more favorable for treating small volumes of PW. Evaporators can be classified according to their heat transfer mechanism: horizontal tube evaporator, long vertical tube evaporator, agitated film evaporator, multiple-effect evaporator, vacuum evaporator, and vapor compression evaporator. The electrostatic repulsion forces and coalescence of the oil droplets are the major factors affecting the evaporation rate of water from oily wastewater [29,89]. Even though evaporation based techniques are used to treat high TDS brines with significant recovery, they still suffer from some

drawbacks, such as high cost, large foot print, and intensive cleaning requirements. Therefore, using evaporators is considered when applying other techniques is not possible.

Organic compounds can be removed effectively using biological treatment (activated sludge plants). The performance of the biological treatment depends on several key parameters including pH, dissolved oxygen (DO) concentration, and temperature. The optimized operating conditions in the biological treatment are 6 – 7 pH, 1 – 3 mg/L DO, 40 ^{o}C temperature, and 0.22 – 0.63 feed to microorganism ratio [90]. One of the challenges here is to maintain a stable microorganism population present in activated sludge plants, which may lead to a high maintenance rate [29,91].

Adsorption is another technique used to remove dissolved organic compounds from oily wastewater pretreated by primary and secondary treatment. The activated carbon bed is the most common unit used in adsorption [92]. Both activation and reactivation procedures are required when using activated carbons, which can lead to an increase in their cost. However, several materials, such as sewage sludge, may be used to produce activated carbons, which can decrease the cost of the adsorption process. Furthermore, functional groups have been introduced onto the matrix of ordinary adsorbents to be modified chemically. The adsorption capacity and selectivity of the chemically modified adsorbents have been increased to obtain better performance [29,93].

Membrane technologies, such as RO, are commonly used as tertiary treatments to obtain high quality freshwater. The RO membrane has a low membrane pore size and requires high operating pressures. Both monovalent and divalent ions can be removed by RO resulting in a huge reduction in the TDS concentration for the RO effluent stream [94]. The main disadvantage in RO is the decline in flux due to membrane fouling. Thus, RO is usually integrated with other primary and secondary treatment as a hybrid membrane processes to obtain a high water quality with less

fouling tendency. In general, membrane technologies can be used as secondary and tertiary treatment, which in most cases are integrated with other conventional methods. The integrated hybrid membrane processes will be discussed in the next section.

2.4. Hybrid Membrane Processes

Treating PW using only conventional methods (coagulation, sedimentation, centrifugation, or filtration) is frequently insufficient to meet discharge water standards, while using only membrane technologies (MF, UF, NF, RO, or MD) is not desirable due to the high fouling and wetting propensity of the membrane, which affects its long term performance. To meet the most severe discharge standards and obtain a high and steady flux when treating PW, combined and integrated processes are essential. Hybrid membrane processes resulting from integrating a conventional process with a membrane separation are considered as desirable alternative methods to address the issues of fouling and wetting, and maximize water recovery. Reduction in the total production cost, energy consumption, and capital cost may be observed when using integrated processes, which can lead to a high oil separation efficiency [95,96]. Hybrid membrane processes are successfully used to treat PW and overcome most of the drawbacks faced by using only conventional or membrane processes. Here, the most common hybrid membrane processes used are described.

2.4.1. Hybrid Pressure Driven Membrane Processes

The removal of suspended solids and free-floating oil prior to membrane treatment is essential to prevent membrane fouling and obtain a high, steady flux through the membrane. Here, several pressure driven membrane processes, such as MF, UF, NF, or RO can be integrated with one or more conventional techniques to treat PW. PW can be treated and reused by applying a coalescer bed integrated with MF membranes (hybrid membrane processes). In this work, the

operational problems and limitation of treating PW using each technique separately were addressed [97]. Cationic exchange resins were used to form the coalescer bed in up flow mode, while a submerged polyetherimide hollow fiber model was utilized as MF cell.

The hybrid coalescer bed – MF system was challenged with synthetic PW having 200 – 400 mg/L oil concentration in the range of 3 to 8 μm oil droplet diameters. The oil concentration was reduced to the range of 0.1 – 14.8 mg/L in treated PW after using the integrated system resulting in an overall efficiency of 93 – 100 %. Several advantages are gained when applying coalescer bed upstream of MF, such as improving the quality of the effluent stream by reducing the effect of oil peak on MF, mitigating frequent chemical cleaning of the membrane, and decreasing the flux decline through the membrane. A hybrid MF – powdered activated carbon system was applied to treat synthetic oily wastewater. The performance of the MF unit in terms of flux decline, rejection of total organic carbon, and membrane fouling was evaluated in the presence of powdered activated carbon. It was found that the permeate flux increased when adding a low concentration of powdered activated carbon (200 – 400 ppm), while adding a high concentration up to 1200 ppm decreased the permeate flux [98].

Combined coagulation – UF is another hybrid membrane processes used to remove oil from PW. The main reason for adding coagulant salts such as $CaCl_2$ is to break the oil/water emulsion and increase the droplet size. The effect of coagulant doses on the droplet size distribution was investigated to evaluate the final water quality after the integrated coagulation – UF processes. It was found that a $CaCl_2$ concentration of 0.05 M is the critical coagulation concentration resulting in a turbidity decrease because of the coalescence of the oil droplets [95]. In addition, the integrated API separator – UF can be used to enhance oil removal efficiency to 98%. The effects of operating parameters (transmembrane pressure, temperature, cross flow

velocity, pH, and salt concentration) on permeation flux were investigated to evaluate the performance of the hybrid API separator – UF system [99].

An integrated coagulation-UF-NF processes has also been considered to treat and reuse PW as reported in Chang et al. [100]. Several parameters were evaluated to study the performance of the integrated hybrid membrane processes such as the types of NF membrane, working pressure (100 – 400 psi), different coagulant salts (aluminum sulfate octadecahydrate and ferric chloride hexahydrate), and coagulant dosages (5 – 1200 mg/L). A high removal efficiency of turbidity (99.9%), chemical oxygen demand (COD) (94.2%), and most of the divalent ions (72.8% of Ca^{2+}, 86.3% of Mg^{2+}, 80.1% of Sr^{2+} and 91.7% of SO_4^{2-}) was achieved by using Coagulation-UF-NF at 900 mg/L iron dosage with a working pressure of 200 psi [100]. Using coagulation in the upstream of UF can help reduce UF membrane fouling by more than 60 %. Also, the coagulation-UF process is considered as a pretreatment step, which helps enhance the permeate flux in NF by removing most of the suspended particles and organic matter from PW.

PW can also be treated by using an integrated EC- RO processes. In this work, Zhao et al. [101] investigated the efficiency of using EC as a pretreatment step before RO to reduce fouling and scaling of the RO membranes. The removal of hardness, COD and turbidity from PW was evaluated at different operating conditions such as current density, reaction time, and initial pH. About 85.81%, 66.64%, and 93.80% removal efficiency of hardness, COD, and turbidity, respectively, was obtained when applying EC at 7.36 initial pH, 5.90 mA/cm^2 current density, and 30.94 min reaction time. The water recovery was about 87.83%. Furthermore, a pilot-scale hybrid RO-constructed wetland system was employed to treat PW as reported by Murray-Gulde et al. [102]. In this study, the toxicity, outflow water conductivity, and TDS were evaluated to investigate the efficacy of the hybrid system. In this system, a pretreatment step involving a series

of initial filtration steps, a sodium-form of cation exchange softener, a virgin polypropylene (PP) cartridge filter 0.45 µm was applied to mitigate fouling and scaling of the RO membrane. A reduction in conductivity and TDS by 95% and 94%, respectively, was observed when treating high salinity PW by the hybrid RO-constructed wetland system.

Biological treatment has also been integrated with pressure driven membrane processes for treating PW such as biologically active filtration (BAF) combined with UF-NF. The BAF was mainly applied to evaluate the degradation of organic matter present in PW. In this study, about 75–90 % dissolved organic carbon (DOC) removal efficiency was achieved via BAF treating PWs varying in salinity (12.6 to 31.2 g/L TDS). After BAF, UF was employed to reduce the turbidity from 24 (BAF effluent) to 0.2 NTU presenting a low fouling effect. Then the treated PW by BAF-UF was further desalinated via NF to decrease the TDS concentration from 12331 mg/L (UF permeate) to 685 mg/L at 2070 kPa [103]. Overall, the organic compounds and TDS were removed using the integrated BAF-UF-NF system to > 99 % and 94 %, respectively, forming high quality treated water.

Another study done by Frank et al. [104] demonstrated the treatment of oil and gas PW using a pilot-scale hybrid sequencing batch reactor-membrane bioreactor (SBR-MBR). The removal of soluble chemical oxygen demand (sCOD) and ammonia was evaluated at different PW dosage (6 % and 20 % by volume). In the SBR effluent, the sCOD removal efficiency was 90.4 ± 2.8 % at 6 % PW dosage, while it was about 79.5 ± 6.8% at 20 % PW dosage. A significant decrease in the removal efficiency of ammonia from 88 % to 24 % was observed when increasing the PW dosing from 6 % to 20 %, respectively. Finally, the effluent of the SBR was pumped to the membrane tank to be further treated using a UF membrane in a side stream MBR to improve the

removal of organic compounds. In membrane bioreactor, the biological treatment (activated sludge) is combined with MF or UF unit.

The offshore oilfield wastewater was also treated by an integrated MF-biological reactor (BR). The concentration of COD, total organic carbon (TOC), O&G and phenols in the permeate of MF was reduced by 35%, 25%, 92% and 35%, respectively. Following MF, the BR (1-L air-lift reactor containing 2 mm diameter polystyrene particles) was tested to further treating the offshore oilfield wastewater at three different hydraulic retention times (48, 24 and 12 h). The removal efficiencies of COD, TOC, phenol, and ammonium using BR was 65%, 80%, 65%, and 40%, respectively, at 12 h hydraulic retention time [105]. From these results, the hybrid MF-BR system gained much interest as an alternative technology for treating PW.

2.4.2. Hybrid Partial Pressure Driven Membrane Processes

Treating high salinity PW using partial pressure driven membrane processes, such as MD, is promising because these techniques are relatively insensitive to the feed salinity so they can be used to treat high TDS brines. Due to the wide range of contaminants found in PW, a pretreatment step integrated with the membrane processes is essential to minimize the membrane fouling. Sardari et al. [106] studied the feasibility of treating high salinity PW using the integrated EC–MD system. PW containing 135 g/L total dissolved solids was treated first using EC. A high removal of turbidity (96 %), TSS (91 %), and TOC (61 %) was obtained by applying 3 A current, and 30 sec reaction time with aluminium electrodes in the EC reactor. The pretreated PW was further concentrated to 265 g/L (TDS) in the MD unit operating in a continuous mode with stable water flux and minimal fouling for 434 h. About 57 % freshwater was recovered from high salinity PW using the hybrid EC–MD system in a long term experiment.

Shale oil and gas PW collected from Wattenberg field in Colorado was also treated using the integrated precipitative softening (PS) - walnut shell filtration (WSF) – MD. In this study conducted by Zhang et al. [107] the feed PW was pumped to PS unit to remove different particulate, organic, and inorganic contaminants from PW reducing the membrane tendency to foul and scale. Then, the softened PW was filtered by WSF to reduce several toxic volatile compounds such as benzene, ethylbenzene, toluene, and xylenes by more than 95 %. Finally, the pretreated PW was desalinated by MD to recover about 82.5 % freshwater. It was found that applying a pretreatment step before MD enhanced the water quality (less contents of volatile organic compounds), the membrane robustness and reusability, and the stability of the water vapor flux. The costs and energy consumption of shale oil and gas wastewater treatment was reduced by employing an on-site and mobile system (hybrid PS-WSF-MD system).

In addition, the combination of MD with crystallization (MDC) was evaluated to treat shale gas PW. Using MDC system can recover both water and minerals. The energy consumption, water production, and solids recovery rate were determined to evaluate the feasibility of the integrated MDC in treating shale gas PW pretreated by MF. Under optimized operating conditions of feed cross-flow velocity (0.2 m/s) and crystallization temperature (30 °C), the recovery rate of both water and minerals was 84 % and 2.72 kg/m^2day, respectively, with a low energy consumption of 28.2 kWh/m3 [108].

The organic compounds such as oil and grease, were the major reason for membrane wetting resulting in a water recovery in the range of 20 % to 25 % as reported by Kim et al. [109]. When testing PW containing only inorganic compounds, the membrane wettability and the poor permeate water quality caused by multivalent inorganic ions (barium and calcium) was effectively diminished by the integrated MDC due to the reduction in scalant loading. By applying MDC, a

total freshwater recovery of 62.5 % was obtained from PW having no organic contaminants [109]. This study demonstrated that a pretreatment step is essential to protect MD membranes from the wetting effect of organic compounds present in PW.

2.4.3. Hybrid Concentration Driven Membrane Processes

Hybrid concentration driven membrane processes such as the integration of FO with EC [110–112] or chemical treatment and filtration [113] has gained interest for treating PW due to their low energy consumption and high water recovery. The hybrid EC-FO system was applied to treat hydraulic fracturing PWs collected from Southwestern Energy operations in Fayetteville Shale as reported by Sardari et al. In this work, a high removal efficiency of both suspended solids (96 %) and organic compounds (82 %) was obtained via EC pretreatment of PWs at optimized operating conditions (0.5 A current and 2 min reaction time). The water recovery increased from 38 % to 45 % and from 55 % to 70 % when using sodium chloride and ammonium bicarbonate, respectively as a draw solution for a long term FO experiment challenged with PW pretreated by EC [110]. This increase in recovery was a result of the fouling mitigation of the FO membrane due to the use of EC as a pretreatment step. The membrane lifetime, the cost of the recovered water, and recovery and reuse of the draw solute can determine the economic feasibility of the hybrid EC-FO process.

Furthermore, Al Hawli et al. [111] evaluated the feasibility of treating PW by the integrated EC-FO system as well. In this work, EC was optimized by testing several operating conditions such as current densities (10, 30 & 60 mA/cm^2) and reaction time (10 and 30 min). Then, PW pretreated with EC was applied as a draw solution in the FO unit at three different flow rates (0.8, 1.2 and 2 L/min) and two membrane configurations (active layer facing draw solution or feed solution). The removal efficiency of total organic carbon, oil and grease and total suspended solids

was 91 %, 97.4 %, and 97 %, respectively, after EC at a current density of 10 mA/cm^2 and a reaction time of 10 min. At a flow rate of 1.2 L/min for both feed and draw solutions, the highest water flux (5.5 L/m^2.h) was recorded when FO was operated with the active layer facing draw solution. In general, about 99%, 98% and 16% removal of TSS, turbidity and conductivity were achieved using the hybrid EC-FO system in comparison to 97.0 %, 91.6 % and 5.4 % using EC only.

A pilot scale FO integrated with chemical treatment and filtration was also tested for the treatment and reclamation of oil and grease wastewater as well as high salinity brines [113]. Chemical oxidizer, caustic soda, and soda ash were added to PW in a chemical reactor to produce organic flocs and mineral precipitates. Then, a green sand media filter followed by a cartridge filter was applied to separate iron and particulate matter from the pretreated PW. Finally, the filtered PW was further desalinated by FO to reach a concentrated PW in the range of 150,000 to 250,000 mg/L TDS. The draw solution used in FO was prepared by dissolving a mixture of ammonium bicarbonate with ammonium hydroxide in water providing a high osmotic pressure driving force. A thermolytic reconcentration was successfully employed after FO to recover the diluted draw solution by evaporating the thermolytic draw solution solutes due to the lower vapor pressure of these solutes compared with water. Figure 12 describes the hybrid chemical treatment-filtration-FO system.

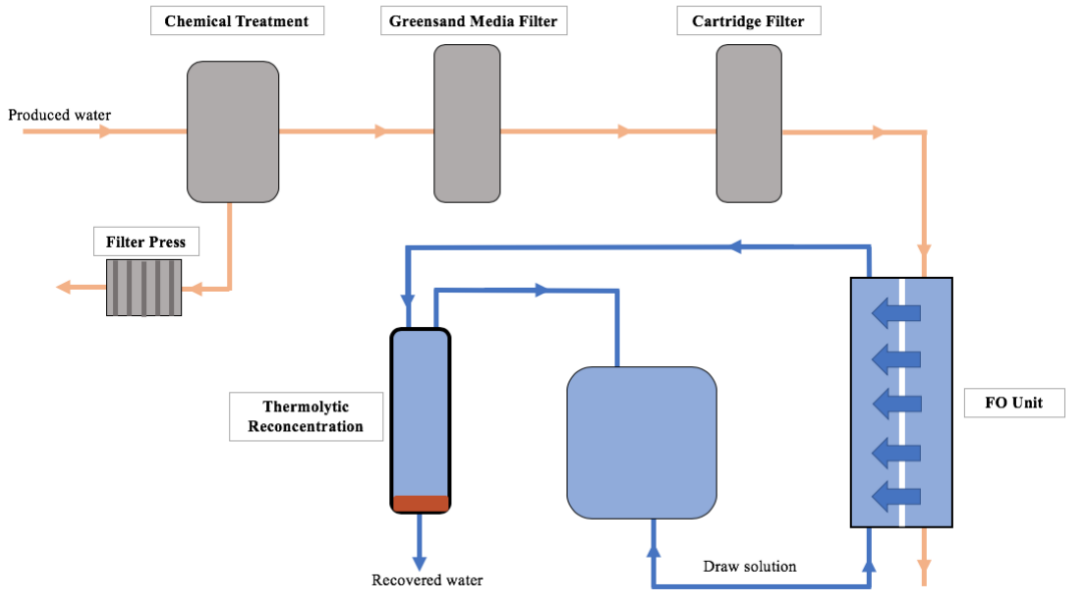

Figure 12. Schematic diagram of the integrated chemical treatment filtration FO processes. FO, Forward osmosis. Source: From Coday, B. D., et al. (2014). The sweet spot of forward osmosis: Treatment of PW, drilling wastewater, and other complex and difficult liquid streams. Desalination, 333(1), 23 35. https://doi.org/10.1016/j.desal.2013.11.014.

2.4.4. Hybrid Electrically Driven Membrane Processes

PW can also be treated using hybrid electrically driven membrane processes such as the combination of coagulation and ED [114]. Most of the organic contaminants are removed by applying coagulation prior to ED. Polyaluminum chloride (PAC) and polyacrylamide (PAM) were used as coagulation and coagulation aid, respectively. In coagulation, all the experiments were conducted at pH 7 for 90 min coagulation time using 150 ml beakers at different coagulation (PAC: 120, 200, 300, 400, 500 mg/L) and coagulation aid (PAM: 1.5, 3.5, 4.5, 6.5 mg/L) dosages. About 93.4, 94.3, and 99 % removal efficiency of COD, biological oxygen demand (BOD), and the turbidity, respectively was obtained via the coagulation pretreatment of PW at optimized operating conditions (400 mg/L PAC and 4.5 mg/L PAM). However, coagulation displayed poor removal of total hardness, which required further desalination by ED. After ED, three different flow rates (5, 15, 20 L/h) were first tested in the circulation mode to reduce the conductivity of the treated PW

from 22.3 to 1 mS/cm. To optimize the ion removal efficiency and the energy consumption, ED was carried out at different voltages (20, 30, 35, and 40 V). A total ion removal rate of up to 99.8 % was obtained when applying ED after coagulation at 15 L/h flow rate, 30 min reaction time, and 35 V voltage [114].

In addition, ED was integrated with one or a combination of BAF, UF, and MF to evaluate the effect of organic compounds present in PW on the performance of the ED membrane and effluent quality. In this study, different pretreatment techniques were applied prior to ED such as BAF-UF, BAF-MF, and MF. All the ED experiments were carried out at 7 volts with an initial current of 4 A using two membranes (ASTOM Neosepta AMX/CMX and GE Water AR204/CR67 ion exchange membrane IEM) challenged with pretreated PW. It was found that about 23-61 % of the initial TOC passed the GE IEMs to the concentrate channel using different pretreatment methods, while it was about 32-52% using Neosepta IEMs. The initial TOC concentration was found to have no significant effects on the removal of salinity from PW via ED [115].

2.4.5. Dual Membrane Processes

To achieve a high water quality for treating oil and gas PW, the integration of two or more membrane processes known as hybrid membrane processes is desirable. Several hybrid membrane processes can be used to treat PW such as UF-RO, MF-UF, NF-RO, MF-MD, FO-NF, FO-RO, and FO-MD. In a study conducted by Guo et al. [116] a combined UF-RO system was tested for treating flowback and PW from Weiyuan shale gas play in China. A decrease in the concentrations of COD, TDS, and Cl^- from 530, 18,900, and 11,000 mg/L to 7.5, 192, and 97 mg/L, respectively, was observed when using a combined UF-RO system to treat PW. The permeate flux and quality after RO was studied as a function of operating pressure and the rate of water recovery. It was

found that increasing the operating pressure increased both permeate flux and quality, while increasing the recovery rate decreased the permeate flux and quality.

The hybrid MF-UF system has also been tested at different operating parameters such as feed oil concentration (500, 700, 1,000, 2,000 and 3,000 ppm), transmembrane pressure (1 to 3 bar MF, 3 to 8 bar UF), and cross-flow velocity (presented as Reynolds number of 500, 1,500 and 2,500), to treat oily wastewater [117]. In general, the results showed a better water quality from the MF-UF effluent compared with the effluent using MF or UF separately. Increasing both transmembrane pressure and cross-flow velocity can enhance the permeate flux and reduce the oil rejection. Another study illustrated that treating PW can be obtained by integrating NF as a pretreatment step with RO to mitigate the fouling on the RO membrane and increase the water quality [118]. Ali et al. [119] reported that the recovery of both freshwater and minerals from PW was carried out by integrating MF with direct contact membrane distillation (DCMD) / membrane crystallization (MCr). The integrated MF - MD / MCr system showed a better performance in terms of productivity / size ratio and productivity / weight ratio in comparison with conventional multi-stage flash (MSF) process.

In addition, FO has been integrated with other membrane processes (NF, RO, and MD) to treat PW. In a recent study Maltos et al. [120] developed a pilot scale FO-RO system for the treatment of more than 10,000 L of PW collected from Denver-Julesburg basin (Colorado). The rejection of most of the elements and hydrocarbons found in PW was more than 99 % and 95 %, respectively when applying the integrated FO-RO system. After operation for 500 hours, a drastic decline in the water flux by 68 % was observed in the combined FO-RO system resulting from the severe fouling of the FO membrane by the high concentration of organic compounds present in PW.

Another study demonstrated the integration of FO with vacuum membrane distillation (VMD) for treatment of shale gas drilling flow-back fluid. Here, FO was applied as a pretreatment step before VMD to obtain a high removal efficiency of the contaminants causing fouling and scaling on VMD membranes. In FO, the water was extracted from the feed (PW) resulting in a diluted draw solution. Then, VMD was employed to concentrate the diluted draw solution and produce high quality freshwater as shown in Figure 13. About 90% water recovery from shale gas drilling flow-back fluid was obtained using the hybrid FO-VMD system as reported by Li et at. [121]. High salinity PWs were also treated using the integrated FO-MD system in a work done by Sardari et al. [112]. The performance of the hybrid FO-MD system was evaluated at different experimental conditions (draw solution concentration, temperature, and flow velocity) in short and long term experiments. Also, EC was used as pretreatment step before the integrated FO-MD to maintain a continuous high water flux in the long term experiments. It was found that the removal efficiency of total organic carbon and total suspended solids was around 78% and 96%, respectively, when using EC to treat high salinity PWs.

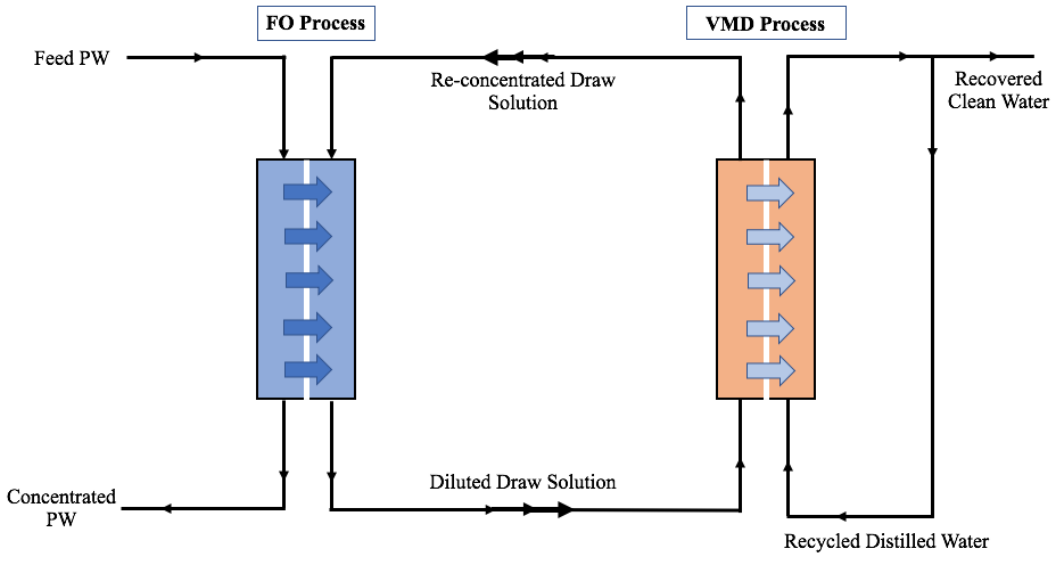

Figure 13. Schematic diagram of the hybrid FO VMD. FO, Forward osmosis; PW, produced water; VMD, vacuum membrane distillation.

2.5. Conclusion

Oil and gas PW generated from hydraulic fracturing is a highly impaired wastewater due to the presence of a wide range of contaminants including high TDS concentration, high TSS, polar and non-polar organic compounds, and low surface tension dissolved species. To preserve water resources and manage wastewater disposal, recycling, and reuse of PW from hydraulic fracturing operations is essential. Treating PW is very challenging. Several primary, secondary, and tertiary separations are usually used as conventional techniques to treat PW for deep well injection, reuse to stimulate new wells, and discharge into lakes and rivers etc, respectively. Using only a single unit operation to treat PW is not sufficient to meet the discharged water standards and not possible for long term operation at high performance.

Integrating one or more conventional processes with a membrane separation, called hybrid membrane processes, can successfully address most of the drawbacks faced by using only conventional techniques. Here, hybrid membrane processes are summarized based on the membrane driving force to hybrid pressure, partial pressure, concentration, and electrically driven membrane processes as well as dual membrane processes. The performance of different hybrid membrane processes is addressed under several design and operating parameters. A decrease in the total production cost, energy consumption, and capital cost may be accomplished via hybrid membrane processes to produce high quality freshwater from highly impaired PWs.

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Chapter 3. Treating Hydraulic Fracturing Produced Water by Electrocoagulation

This chapter is adapted from a published paper by M. Jebur, Y. Cao, M. Malmali, X. Qian, S.R. Wickramasinghe, Treating Hydraulic Fracturing Produced Water by Electrocoagulation, Separation Science and Technology, 2022.

Abstract

Hydraulic fracturing oil and gas produced water is frequently highly impaired. While it is often deep well injected, there is a great deal of interest in treating and recovering this water for beneficial uses. However multiple unit operations are needed if these wastewaters are to be recovered. Electrocoagulation is considered a promising pretreatment technology. Herein, we have investigated the use of aluminium electrodes for electrocoagulation as a pretreatment operation. The effects of electrode arrangement, applied current, reaction time, pH, and inter electrode distance on the quality of the treated water have been investigated.

The results obtained here indicate that electrocoagulation can obtain good removal of turbidity (95%), total suspended solids, TSS (90%), and total organic carbon, TOC (69%) by carefully choosing the reaction conditions. Sedimentation was used to separate the treated water from the sludge. The performance of the electrocoagulation process depends strongly on the quality of the feed water. The viability of a practical continuous electrocoagulation process will depend on the volume (footprint) of the reactor which in turn will depend on operating conditions and the quality of the feed water.

3.1. Introduction

The largest waste stream from oil and gas production is highly contaminated produced water [1]. Here we focus on hydraulic fracturing flow back and co-produced water (produced water, PW). Disposal of PW is a major environmental challenge [2]. PW contains relatively high

concentrations of hydrocarbons, heavy metals, and other pollutants. The level of treatment of the PW depends on the beneficial use of the treated water. Typically, three levels of treatment are used to treat PW [3–7].

Primary treatment is used to remove suspended solids and free oil from PW resulting in water sufficiently treated for deep well injection. Secondary treatment is used to further treat PW to a level acceptable for reuse to stimulate new wells. Finally, tertiary treatment operations result in treated water which can be discharged directly into lakes and rivers. Jiménez et al. provide a detailed summary of typical unit operations used for primary, secondary, and tertiary treatment of PW [8]. Developing an appropriate treatment train is essential for the specific beneficial use of PW such as reinjection to stimulate new wells, discharge into streams, agricultural uses etc. [9–13]. Today this highly impaired wastewater is frequently deep well injected into geologically isolated formations [14]. Recovering and reusing this highly impaired wastewater will promote a more sustainable approach to recovering oil and gas form these non-conventional resources.

Here we focus on electrocoagulation (EC) for pretreating PW. Interest in electrolysis based electrochemical processes to treat wastewater is increasing [15]. Electrolysis processes may be categorized based on where the reaction takes place: directly on the electrode surface or indirectly by ions supplied by the electrode [16]. EC is essentially an indirect process where the ions are supplied by a sacrificial electrode. However, depending on the electrode potential, direct reaction with species in the water can occur on the electrode surface. Charged species in the wastewater are removed by reaction with oppositely charged ions or with flocs of metallic hydroxide generated in the wastewater.

EC is a complex process involving a number of sequential steps. At the anode metal ions, iron or aluminum, are released. These ions generate the coagulant in situ rather than by external

addition in the case of coagulation. Simultaneously gases such as hydrogen are generated at the cathode. Often the hydrogen bubbles help the forming flocs rise to the surface of the liquid. Coagulation of the particles occurs due to a reduction in the net surface charge allowing colloidal particles to approach close enough to each other for van der Waal's forces to hold them together in an aggregate. Efficient separation of the densified floc e.g., by sedimentation is essential.

EC has been widely used to remove suspended solids, metals, oil and grease from both water and wastewater sources. Compared to chemical coagulation, EC has many advantages [17–21] such as no addition of flocculants, easy operation, easily separable flocs, lower sludge volume, and efficient removal of the smallest colloidal particles. EC has been investigated by many researchers for treating hydraulic fracturing flowback and PW from shale oil and gas operations [2,22–28]. After EC, the treated water can be reused in frac fluids, which can greatly eliminate the cost of transportation and the use of fresh water. To obtain high quality recovered water from PW for other beneficial applications, further processing by unit operations such as forward osmosis (FO) [2,23], membrane distillation (MD) [25] and reverse osmosis (RO) [29] have been investigated.

In our previous work, we demonstrated that EC is an efficient pretreatment step prior to FO/MD when treating PW [23,25,30]. However, optimizing the EC process will be essential when developing a commercially viable process. In this work the operating conditions of a batch EC unit have been investigated in order to obtain high removal in terms of turbidity (95%), total suspended solids, TSS (90%), and total organic carbon, TOC (69%) after sedimentation of the densified floc.

3.2. Theoretical Background

Assuming no side reactions occur, the theoretical number of aluminium ions required for a current efficiency of 1, may be calculated using Faraday's law as shown in Eq. (1) [31–33]:

$$m = \frac{I*t*M}{z*F} \quad (1)$$

where m is the total mass (g) of released metal ions dissolved during electrolysis time t (s), M is the molecular weight (g/mol), I is the current (A), z is the number of electrons involved in the reaction, and F is the Faraday constant (96485.34 A s/mol).

The energy consumption for this process was determined using Eq. (2) [34]

$$Energy\ consumption = \frac{V*I*t}{\mathrm{v}} \quad (2)$$

where V is the voltage applied to the reactor, I is the current (A), v is the volume of the feed in m^3, and t is the reaction time (h). The energy consumption is expressed in kWh/m^3.

Having been released from the anode, the metal ions usually form metal hydroxides that have low solubility and can precipitate. However especially for aluminium ions, various equilibrium acid/base, complexation, precipitation, and redox reactions occur. Water soluble pollutants typically organic species in the PW adsorb onto the precipitates. Colloidal suspensions are destabilized during EC. Coagulation of these particles occurs due to interactions between the soluble ions generated by metal dissolution from the sacrificial electrodes. This leads to a reduction in the repulsive forces between particles resulting in aggregation [35].

Charge neutralization by adsorption of metal ion species will also lead to aggregation. Finally, entrapment of colloidal particles within a hydroxide precipitate will lead to aggregation. The destabilization processes occur in parallel. The extent to which any one process dominates depends on the prevailing conditions. After destabilization, flocculation occurs, the rate of which depends on the degree of destabilization of the colloidal particles as well as the particle collision rate. The flocs can rise due to the rising hydrogen gas produced. The flocs eventually age, densify and settle to the bottom. The flocculated material or sludge can be removed by sedimentation [36].

In the EC process investigated here both the cathode and anode consisted of aluminium electrodes. In addition, electrode arrangement, current, reaction time, pH as well as inter electrode distance were investigated. Bipolar series (BPS), monopolar parallel (MPP), and monopolar series (MPS) were the electrode arrangements used in this work as shown in Figure 1. Currents in the range of 0.5 to 8 A were applied at a variety of reaction time of (5, 20, 60, and 90 min), pH values (5, 7, and 9), and interelectrode distances (5 and 10 mm). Other variations have been proposed by previous investigators where changes are made to the cathode material [16,37,38].

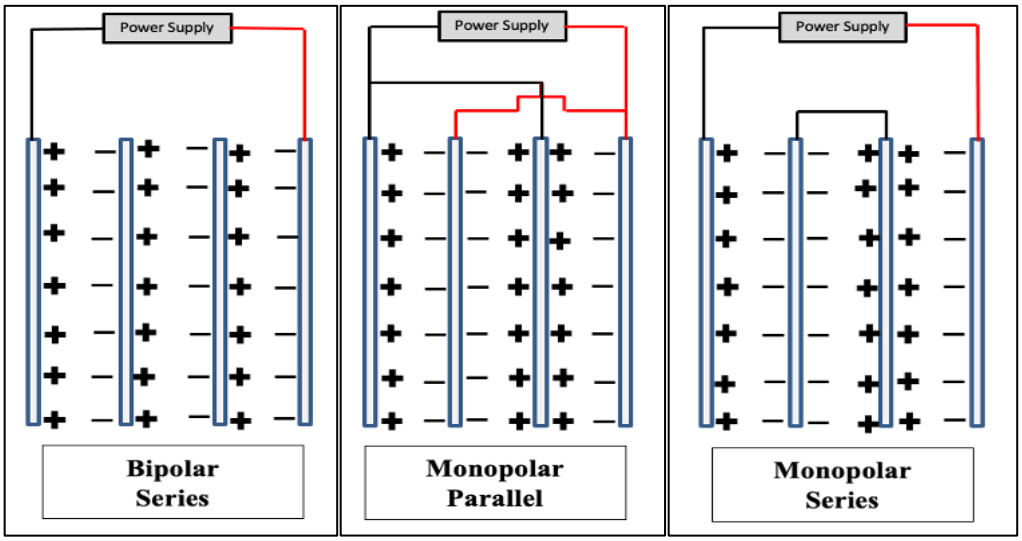

Figure 1. Schematic representation of the electrode arrangement during EC.

3.3. Experimental Section

3.3.1. Materials

PW samples were collected from an oil field in Texas, USA. These samples were treated with ClO_2 prior to receival. Deionized (DI) water used throughout the investigation was collected from Thermo Fisher 18 MΩ Barnstead Smart2Pure system (Schwerte, Germany). Aluminum sheets with thickness of 0.04" were purchased from OnlineMetals.com (Seattle, WA, USA).

3.3.2. EC Reactor Design and Operations

Table 1 lists the experimental conditions used for the batch EC experiments conducted here. The batch EC experiments were conducted as described in our previous work [36]. A polycarbonate batch reactor was designed having dimensions of 7 x 11 x 14 cm with a total volume of 1078 cm^3. Th electrodes were fitted vertically inside the reactor with a 5 or 10 mm inter electrode spacing. A DC power supply (Hewlett Packard, Palp Alto, CA) connected to a reverse polarity switch was used with cathode and anode attached to electrodes in three different electrode arrangements. The formation of passivation layers on the electrodes was mitigated by using a reverse polarity switch, which alternated the direction of current flow every 30 s. These passivation layers, consisting of aluminum oxide, can suppress further reactions if the reverse polarity is not used [39,40]. Before each experiment, the electrodes were cleaned, sandpapered, and dried. Figure 2 is a schematic diagram of the batch EC reactor.

Table 1. EC conditions investigated.

Run #	Current (A)	Reaction Time (min)	Number of Electrodes	Inter Electrode Distance (mm)	pH	Electrode Arrangement
1	1	5	5	10	7	BPS
2	1	5	5	10	7	MPP
3	1	5	5	10	7	MPS
4	0.5	5	5	10	7	BPS
5	1	5	5	10	7	BPS
6	2	5	5	10	7	BPS
7	3	5	5	10	7	BPS
8	4	5	5	10	7	BPS
9	5	5	5	10	7	BPS
10	8	5	5	10	7	BPS
11	8	20	6	5	7	BPS
12	8	20	3	10	7	BPS
13	8	60	6	5	7	BPS
14	8	60	3	10	7	BPS
15	8	90	6	5	7	BPS
16	8	90	3	10	7	BPS
17	8	20	6	5	5	BPS
18	8	20	3	10	5	BPS
19	8	20	6	5	9	BPS
20	8	20	3	10	9	BPS

Initially, three different electrode configurations (BPS, MPP, and MPS) were investigated using 5 aluminium electrodes with a current of 1 A, 5 min reaction time and 10 mm inter electrode distance at pH 7. Based on these results, BPS configuration was selected as it displayed the highest TOC removal. Then, the effect of current was investigated in the range of 0.5 to 8 A. Based on these results, the most suitable current was selected, and the effect of reaction time was investigated using 5, 20, 60, and 90 min reaction times. In order to ensure a constant current, as Al ions are released the voltage was adjusted. Once the reaction time was selected, the effect of pH was investigated. In addition, both reaction time and pH were investigated at two different inter electrode distance (5 and 10 mm) to evaluate their effect on the removal of turbidity, TSS, TOC as well as the electrical energy consumption. In each experiment, 0.6 L of PW were used. The

treated PW was collected and allowed to sediment for 60 min. Then the supernatant was separated from sludge.

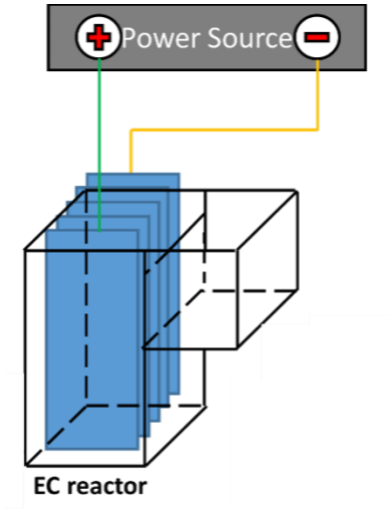

Figure 2. Schematic representation of the batch electrocoagulation setup.

3.3.3. Material Characterization

3.3.3.1. PW Characterization

The PW was analyzed by the Arkansas Water Resources Center, University of Arkansas (Fayetteville, AR, USA). Table 2 shows the results in terms of total dissolved solid (TDS), TOC, TSS as well as inorganic compounds. EPA standard methods 160.1, and 160.2 were used to measure TDS and TSS, respectively [41]. A Shimadzu TOC-Vcsh (Shimadzu scientific instruments, Colombia, MD, USA) was employed to measure TOC. Spectro Genesis ICP OES (Kleve, Germany) and Dionex DX-120 ion chromatograph (Sunnyvale, CA, USA) were used to measure the cations and anions present.

3.3.3.2. GC-MS Analysis

Liquid-liquid extraction (LLE) of the PW and solid-liquid extraction (SLE) of sludge generated after EC of PW was conducted to identify the organic compounds present. In LLE, 100

ml of PW was adjusted to pH 2 using 37% concentrated HCl and extracted using 4 sequential volumes of 5 ml hexane. The extracted phase (hexane) was concentrated under He, volumetrically diluted with hexane, and finally transferred to GC-MS vials for analysis. In SLE, 1 g of each sludge sample was mixed with 10 ml of hexane using a vortex mixer for 5 min. The supernatant was collected after centrifuging the slurry for 5 min. The same procedure was repeated twice to collect two more extracts. The three extracts were combined and concentrated under Helium. Then, the combined extract was volumetrically diluted with hexane, and finally transferred to a GC-MS vial for analysis.

GC-MS analyses were conducted using a Shimadzu QP 2012 GC-MS equipped with headspace sampler (Shimadzu scientific instruments, Colombia, MD, USA), and a Restek (Bellefonte, PA) VMS column (30 m, 0.32 mm ID, and 1.8 µm film thickness) using helium as a carrier. All samples were taken using an Automatic Liquid Sampler with inlet split of 1:5 using an automated injector temperature set at 120 ^{o}C and a constant flow of 1.07 mL/min. The GC oven temperature set at 35 ^{o}C for 4 min. Then it was increased to 230 ^{o}C (10 ^{o}C min $^{-1}$) and held at 230 ^{o}C for 5 min. The National Institute of Standards and Technology mass spectrum library (NIST 08 MS Library) was used to identify all the peaks, which were processed using the Automated Mass Spectroscopy Deconvolution and Identification System (AMDIS). A match was considered as a reliable identification by setting the NIST library agreement to greater than 90% for all peaks.

3.4. Results and Discussion

3.4.1. PW Characteristics

Table 2 shows water quality parameters for the PW used here. As can be seen the TDS of the PW was 98,250 mg L^{-1}, which is very high compared to the seawater. This PW has high TOC due to contaminants, such as suspended oil emulsion and dissolved organic compounds from the

crude oil, while mud or sand particles contribute to the high turbidity and TSS. Most of the inorganic ions present in the PW are chlorine, calcium, magnesium, sulfate, potassium, and sodium. Comparing the quality of this PW with other PWs investigated in our previous work [25,30,36], it is observed that the quality of PW is highly variable.

Table 2. Characterization of PW samples.

Parameter	Unit	PW
TDS	mg L^{-1}	98250
TOC	mg L^{-1}	280
TSS	mg L^{-1}	346
Turbidity	NTU's	300
pH	--	7.1
chloride	mg L^{-1}	67330
Nitrate	mg L^{-1}	--
sulfate	mg L^{-1}	500
Aluminum	mg L^{-1}	--
Iron	mg L^{-1}	3
Boron	mg L^{-1}	27
Calcium	mg L^{-1}	1075
Magnesium	mg L^{-1}	165
Manganese	mg L^{-1}	3.5
Nickel	mg L^{-1}	0.1
Potassium	mg L^{-1}	1035
Sodium	mg L^{-1}	16790
Conductivity	μS/cm	137100
Total Nitrogen	mg L^{-1}	66

3.4.2. Batch EC Performance

3.4.2.1. Effect of Electrode Arrangements

Initially the effect of electrode arrangement was investigated for a reaction time of 5 min and a current of 1 A using 5 aluminium electrodes with 10 mm inter electrode distance at pH 7.

Figure 1 gives the three electrode arrangements investigated. In the BPS configuration, only the first and last electrodes are directly connected to the power supply, while in the MPP configuration, all the electrodes are connected directly to the power supply. In the MPS configuration, the first and last electrodes are connected directly to the power supply, while the middle electrodes are connected to each other. After 60 min sedimentation, the efficiency of the different electrode arrangements for removal of TOC, TSS, and turbidity was determined. In addition, the electrical energy consumption (EEC) was also determined.

The removal of turbidity, TSS and TOC for the three different electrode arrangements is given in Figure 3. As can be seen, the removal of TOC is highest in the BPS arrangement. However, BPS arrangement consumes more electrical energy than the MPP and MPS arrangements. The electrical energy consumption was determined using Equation 2. Since the current is kept constant, the voltage will change as the conductivity of the solution changes. Any passivation of the electrodes will also lead to an increase in the voltage for a constant current. However, for a 5 min reaction time, no change in voltage was observed.

The potential difference across the EC unit is greatest for the BPS arrangement hence the electrical energy consumption is the greatest for the three electrode arrangements. This is not surprising as this is the only arrangement in which only the outermost electrodes are connected to the power supply. No other electrodes are connected to each other. The MPP arrangement will have the lowest voltage between the cathode and anode as every electrode is connected to the power supply. The MPS arrangement will have an intermediate voltage as all internal electrodes are connected to each other thus providing a lower resistance to current flow than the BPS arrangement.

We decided to conduct all further testing using the BPS configuration as removal of TOC is typically very important especially if the PW is to be further treated after EC. The removal for the MPP configuration is likely to be too low if EC is to be used as a pretreatment step for a subsequent treatment operation.

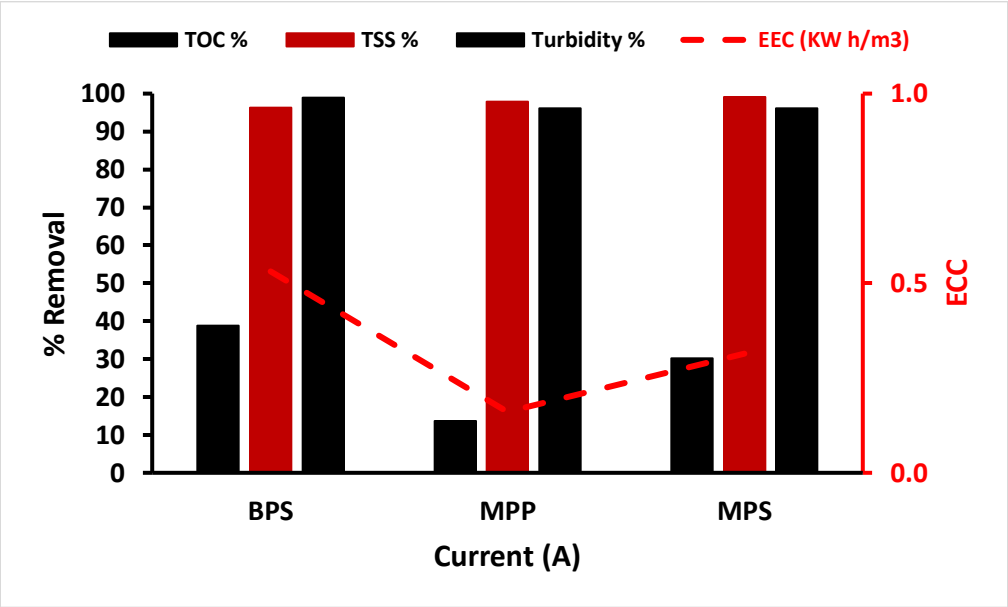

Figure 3. EC performance for different electrode arrangements (BPS; MPP; and MPS) at 1 A current and 5 min reaction time with 10 mm inter electrode distance at pH 7.

3.4.2.2. Effect of EC Current for BPS configuration

The effect of the applied current on the removal of turbidity, TSS and TOC, was investigated in the range 0.5 to 8 A using 5 aluminium electrodes with 10 mm inter electrode distance, 5 min reaction time at pH 7. As is shown in Figure 4, increasing the current from 0.5 to 8 A does lead to an increase in TOC removal from 40 to about 47%. However, turbidity and TSS removal remain around 90 to 95%. There is a slight variation in the values which is typical when working with PW samples unlike model feed streams. As expected from Equation 2, the electrical energy consumption increases with increasing current.

It was also observed that the treated water fraction after 1 hour sedimentation is less at higher currents. This observation is in agreement with the fact that when excess Al ions are added to the solution, a longer sedimentation time for the floc is needed to achieve a high water recovery due to the formation of polyaluminum hydroxides (gel formation) that hinder destabilization of the colloidal matter [42]. In this work, we chose to use a current of 8A as high TOC removal is often essential. Further due to the variability of water depending on the time of year the sample is tested; a higher TOC could lead to a lower TOC removal [43].

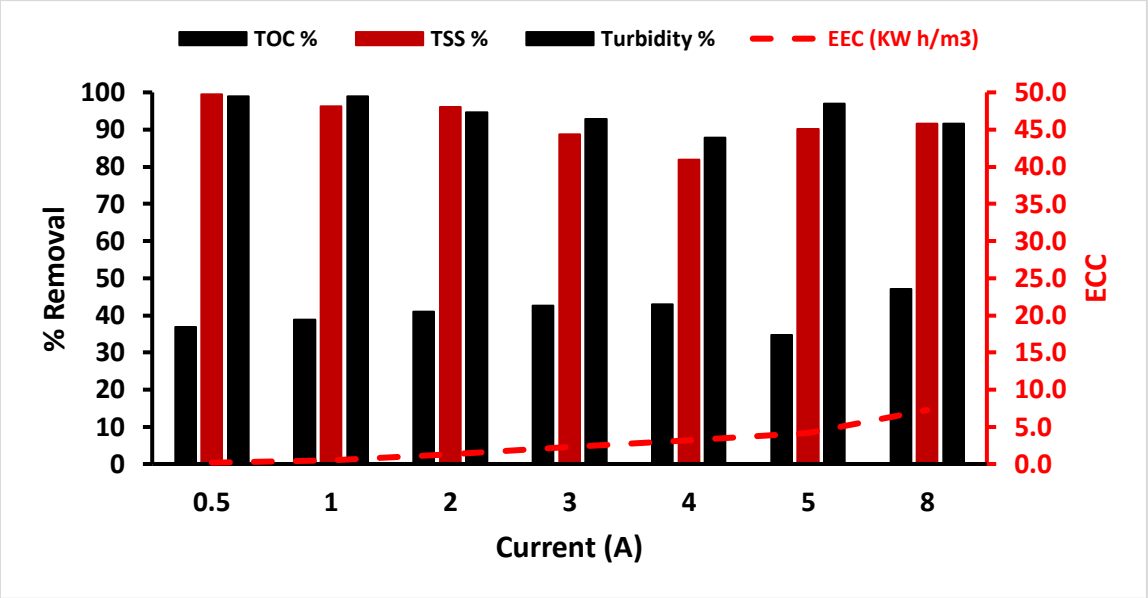

Figure 4. The EC performance as a function of current for PW treated using BPS configuration at 5 min reaction time using 5 aluminium electrodes with 10 mm inter electrode distance at pH 7.

3.4.2.3. Effect of Reaction Time, pH, and Inter Electrode Distance

Based on the BPS arrangement and a current of 8 A, the effects of reaction time over the range 5-90 min, pH values of 5, 7 and 9 and inter electrode distances of 5 and 10 mm were investigated. Figure 5 shows the effect of increasing the reaction time on the removal of turbidity, TSS and TOC at two inter electrode distances at pH 7. As can be seen increasing the reaction time leads to an increase in TOC removal but the change in turbidity and TSS removal is much less

significant. Inter electrode spacings of 5 and 10 mm have no effect on the treated water quality parameters.

As expected, increasing the reaction time will lead to an increase in energy consumption. For reaction times above 20 min an increase in the voltage was observed for a constant current. This could be due to changes in the conductivity of the solution as well as any passivation of the electrodes. It can be seen that a smaller inter electrode distance leads to a higher electrical energy consumption due to a higher potential difference for a fixed current. This is probably due to changes in the electrical conductivity of the solution due to a higher number of Al ions being released per volume of feed water.

From a practical perspective, long reaction times lead to high aluminum ion concentrations in the treated water which may be undesirable depending on the beneficial use for the water. Further the consumption of aluminum electrodes will be high. In addition, for a continuous process the reactor volume may be impractically large in order to ensure a long reaction time. Here a reaction time of 20 minutes was chosen as longer reaction times could lead to very large reaction vessels [44].

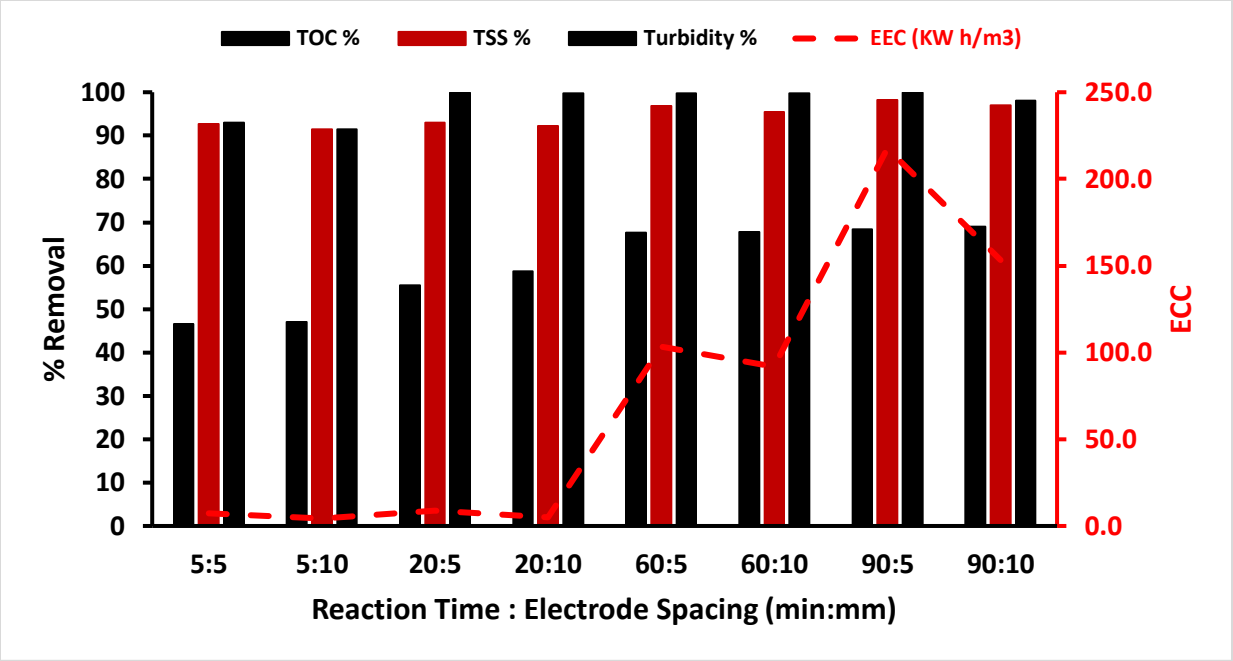

Figure 5. EC performance as a function of reaction time using the BPS configuration at 8 A and pH 7. Note: the first number in the x-axis is reaction time, and the second number is inter electrode distance.

The removal of turbidity, TSS and TOC as well as electrical energy consumption were determined for different initial pH values at inter electrode distances of 5 and 10 mm. At pH 7, the lowest electrical energy consumption was obtained being about 5 KW h/m^3. pH values of 5 and 9 lead to an increase in the electrical energy consumption. This is most likely due to changes in the conductivity of the feed. Again, a smaller inter electrode spacing leads to a higher electrical energy consumption. As can be seen again, inter electrode spacing has little effect on turbidity, TSS and TOC removal.

The pH values tested here also had little effect on the treated water quality parameters. This could be due to the formation of insoluble amorphous $Al(OH)_3(s)$ via complex polymerization processes or precipitation kinetics. Three clear zones have been described when using aluminum electrodes during EC at pH range from 1 to 14; the first one is the free aluminum ions (Al^{3+}) formed in the pH range of 1 to 3.5, the second and third zones are related with $Al(OH)_3$ (pH range from 4

to 10.5) and $Al(OH)_4^-$ (pH range from 12 to 14), respectively. The large surface area amorphous $Al(OH)_3(s)$ flocs formed at the pH range used in this study can lead to a quick adsorption of organic soluble compounds and trapping of colloidal particles, which result in no change in the removal of turbidity, TSS and TOC [45]. Consequently, we conducted further testing at pH 7. From a practical perspective, the footprint of the EC unit should be minimized. Therefore, we decided to conduct further experiments using an inter electrode spacing of 10 mm. These conditions were used and the samples analyzed by GC/MS.

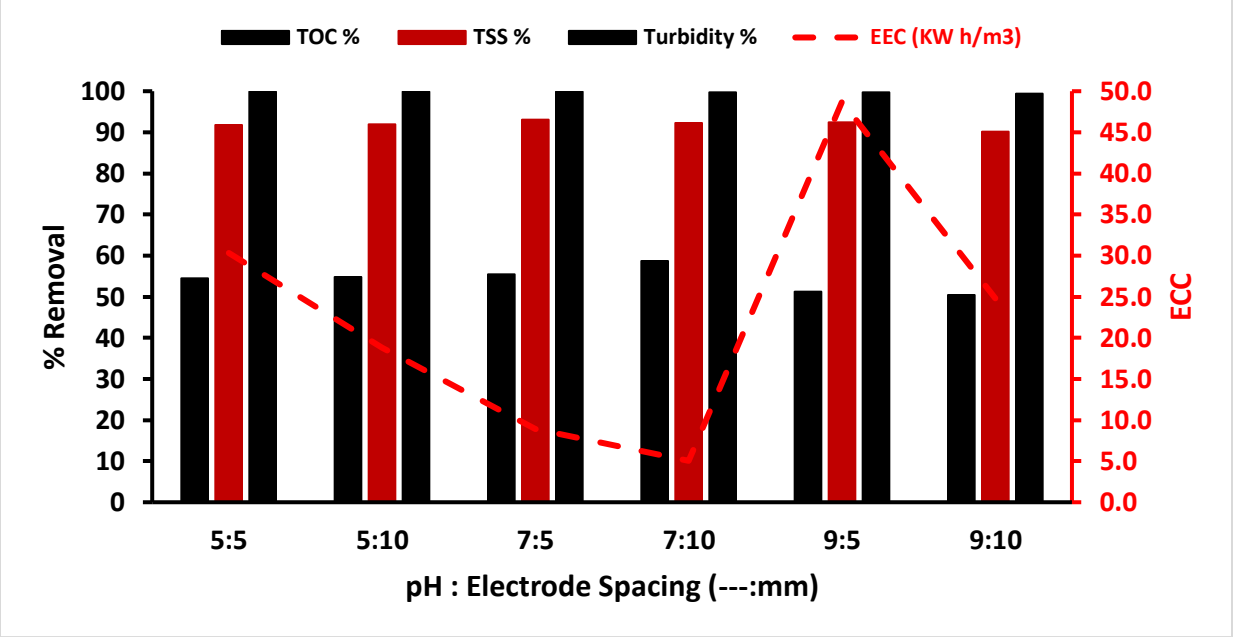

Figure 6. EC performance as a function of pH and inter electrode distance for PW treated using a current of 8 A current, and 20 min reaction time. Note: the first number in the x-axis is pH and the second number is inter electrode distance.

3.4.3. PW Composition Analysis by GC/MS

GC/MS analysis was performed to detect the organic compounds present in the PW and trapped in the sludge generated after EC. The results show that a wide range of saturated alkanes (C5 to C23) are observed in the GC-MS analyses of the extractables from the sludge samples. The compounds found in the PW are similar (see Table 3). The organic compounds as a percentage of

total organic compounds present in PW and sludge were determined indicating a high removal of TOC as we have observed. It confirms that the alkanes present in PW were adsorbed in the sludge generated after EC.

Table 3. Organic compounds identified the PW and sludge

Compounds	% in PW	% in sludge
2,6,10-Trimethyltridecane	4.5	1.1
Pentadecane	9.8	4.0
Nonadecane	10.0	8.5
Heptadecane	10.2	11.0
Pentadecane, 2,6,10,14-tetramethyl-	8.4	12.7
Pentadecane, 2,6,10,14-tetramethyl-	0.9	2.9
Octadecane	9.3	10.6
Hexadecane, 2,6,10,14-tetramethyl-	9.7	9.1
Heneicosane	1.4	3.0
Heneicosane	10.3	12.4
Heneicosane	9.8	10.5
Heneicosane	8.0	7.5
Docosane	7.8	6.8

Here we present an approach to determine appropriate operating conditions for an EC process that is used to pretreat PW. Optimization of the EC process depends on the quality of the PW and the subsequent unit operations. If membrane based unit operations are to be used, removal of organic compounds as given by TOC is essential. Further removal of suspended solids as measured by TSS and turbidity is important in order to suppress membrane fouling. In addition, it is essential that the electrocoagulation process is viable. Long reaction times leads to high consumption rates of the aluminium electrodes and large reactor volumes which may not be practical.

3.5. Conclusion

We have developed a batch EC method for determining appropriated operating conditions for an EC pretreatment operation to treat hydraulic fracturing PW. EC parameters such electrode arrangements, current, reaction time, pH, and inter electrode distance were investigated. BPS electrode configuration consumed more electrical energy while it had better TOC removal than MPP and MPS electrode configurations. For the PW tested here, high removal of turbidity, TSS and TOC was achieved using a current of 1 A current with 5 min reaction time. The pH of the feed PW was pH 7 and a 10 mm inter electrode distance was used. When identifying appropriate reaction conditions, it is essential to ensure the process is practical. Long reaction times, lead to large reactor volumes and high levels of electrode consumption which may not be feasible. The level of turbidity, TSS and TOC removal depends on the quality of the PW.

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Chapter 4. Combined Electrocoagulation-Microfiltration-Membrane Distillation for Treatment of Hydraulic Fracturing Produced Water

This chapter is adapted from a published paper by M. Jebur, Y.H. Chiao, K. Thomas, T. Patra, Y. Cao, K. Lee, N. Gleason, X. Qian, Y. Hu, M. Malmali, S.R. Wickramasinghe, Combined Electrocoagulation-Microfiltration-Membrane Distillation for Treatment of Hydraulic Fracturing Produced Water, Desalination. 500 (2021).

Abstract

Hydraulic fracturing flowback and produced water is a highly impaired wastewater containing dissolved salts, polar and non-polar organic compounds, oil, and surfactants. Here a combined electrocoagulation – microfiltration – membrane distillation process has been used to treat this wastewater. Electrocoagulation followed by microfiltration was used to pretreat the wastewater prior membrane distillation. The initial total dissolved solids (TDS) concentration was extremely high being 245,300 mg L^{-1}. After electrocoagulation, the total organic carbon (TOC) was reduced from 120 mg L^{-1} to 64 mg L^{-1}. Tangential flow microfiltration using a 0.1 μm pore size polyethersulfone membrane was used to separate the particulate matter after electrocoagulation and to further reduce the TOC to 44 mg L^{-1}. Membrane distillation was used to desalinate the pretreated produced water resulting in a high quality treated water (TDS of 56 mg L^{-1} and TOC 1 mg L^{-1}). Three membranes with very different surface morphology were used: commercially available polyvinylidene fluoride, electrospun poly(vinylidene fluoride-co-hexafluoropropylene) nanofibers and multiwalled carbon nanotube coated polytetrafluoroethylene.

The TDS in the retentate increased to over 350,000 mg L^{-1}. During membrane distillation, the temperature of the feed tank was maintained at 36 °C while the feed entered the module at 60

°C in order to minimize scaling on the membrane. The surface properties of an ideal membrane that is resistant to wetting and provides high flux is likely to depend on the TDS and properties of the wastewater.

4.1. Introduction

Water that is co-produced during oil and gas production, known as produced water (PW), is a major waste stream. The United States produces about 21 billion barrels of PW per year [1]. The amount of PW that is generated depends on the geological formation and the type of energy resource being developed. Here we focus on hydraulic fracturing and horizontal drilling which has enabled the recovery of oil and gas from shale and other tight rock formations [2]. However, this technology requires the use of a large amount of water [3].

Treating hydraulic fracturing flowback and co-produced water referred to here collectively as PW is very challenging and expensive. Fracking fluid is pumped into the well at high pressure in order to fracture the rock formation [4–6]. The fracking fluid consists of 98% water and sand. However, a number of chemicals such as friction reducers, surfactants, corrosion inhibitors and flow improvers are added [7]. After fracturing the rock formation, the pressure is reduced, and the fracking water flows back to the surface with oil/gas and co-produced water [3].

The composition of the PW water depends on the geological formation where it is trapped. In general, the PW contains high concentrations of dissolved salts referred to as total dissolved solids (TDS). In addition, there are dissolved polar and nonpolar organic compounds (total organic carbon, TOC), as well as oil, grease, fuels and additives associated with the fracking fluids that make up the total suspended solids (TSS) [1,8].

Partially treating PW onsite or transporting PW to a centralized water treatment facility is the most common practice in United States. Recycling and reusing PW from hydraulic fracturing

operations is essential to preserve water resources and manage wastewater disposal. Most often the PW is transported to a deep well injection site where it is injected deep underground into a geologically isolated formation. Nevertheless, the PW could escape from the formation and contaminate surface or groundwater [2]. Further the United States Geological Survey (USGS) found that deep-well injection is the main cause of earthquakes, not the hydraulic fracturing process itself [9]. New technologies for treating PW from hydraulic fracturing operations in an affordable manner are necessary.

Once the PW is recovered it is treated using a number of different unit operations which can be divided into three treatment stages [10]. Primary separation treats the water sufficiently for deep well injection. Secondary separation units treat the water for reuse to stimulate new wells. Finally, tertiary separation operations treat the water for discharge into lakes and rivers etc. The aim of this work is to develop a combined primary, secondary and tertiary treatment process for PW using membrane-based separation processes.

All membrane-based separation processes suffer from fouling. This is particularly problematic for PW from hydraulic fracturing operations as it contains dissolved organic and inorganic compounds as well as surfactants and other low surface tension compounds [11–13]. Rejected species will accumulate in the membrane pores and on the membrane surface, which compromises performance.

Common primary and secondary treatment processes consist of chemical precipitation and dissolved air flotation, or electrocoagulation (EC) followed by media filtration. Here we use EC as the primary unit operation. EC is an alternative to chemical coagulation. EC can effectively remove organic compounds and other contaminants by generation of an electrical current which leads to dissolution of a metal electrode such as aluminum or iron [14].

The setup of an EC system includes metal anode(s) and cathode(s) placed inside the EC cell which contains the PW. Multiple reactions occur simultaneously in the feed PW. Metal ions are driven from the anode to the water. Water is hydrolyzed on the surface of the cathode creating hydrogen gas and hydroxide ions. The hydrogen gas bubbles rise up in the solution while the metal ions and hydroxide ions react to create metal-hydroxide complexes [15]. These metal complexes can polymerize and trap organic compounds and suspended particles. Some of the aggregated particles sink to the bottom of the system forming a sludge. EC is already used by companies such as Haliburton [16] and Baker Hughes [17]. Use of EC can lead to a more easily disposable sludge reducing disposal costs [10]. Further we have combined EC with forward osmosis and membrane distillation (MD) in the past [18,19] and shown that it is effective at reducing the TOC of the feed which suppresses membrane fouling.

Numerous unit operations are used as secondary treatment processes such as filtration and oxidation. Here we use microfiltration (MF). In our earlier work [18,19] after EC we allowed the flocs to sediment. We then recovered the supernatant water and desalinated it using forward osmosis or MD or a combination of both unit operations [20]. However, sedimentation times could be as long as 24 hours which is impractical. In addition, low pressure membrane processes such as microfiltration are attractive as they can remove particulate matter as well as microorganisms.

Typically, thermal desalination technologies are used as the tertiary treatment process. Due to the very high TDS of the PW, pressure driven membrane desalination processes such as reverse osmosis and nanofiltration are not commonly used. Here we use MD to desalinate the PW. MD is an emerging membrane-based technology that could find applications in the treatment of highly impaired brackish wastewater. It is a thermally driven separation process that makes use of a hydrophobic membrane. Consequently, only vapor molecules (water and volatile species that are

dissolved in the PW) are able to pass through the membrane [21]. Here, we have investigated direct contact membrane distillation. The hot feed flows on one side of the membrane. The membrane is a thermal insulator as well as a physical barrier between the hot feed and the cold permeate (distillate). The feed and permeate streams are in direct contact with the membrane [22,23].

MD is attractive for treatment of high TDS wastewater as very high rejection of dissolved salts and nonvolatile species is possible. While the feed temperature must be elevated compared to the permeate temperature the feed need not be at its boiling point as is the case with thermal distillation. MD can take advantage of the low-grade waste heat that is produced at industrial sites [20]. All that is needed is a vapor pressure difference between the feed and permeate sides of the membrane ensuring passage of water vapor from the feed to the permeate. However, since the MD membrane is hydrophobic, it has a poor resistance to hydrophobic foulants due to hydrophobic-hydrophobic interactions. Dissolved organic compounds, surfactants and low surface tension compounds containing hydrophobic functional groups can easily adsorb on the membrane. In order to mitigate membrane fouling we propose a combined EC–MF process to pretreat the PW prior to MD, which can extend membrane life.

Figure 1 shows the concept of a combined EC–MF–MD processes for PW treatment. In this work the process was operated in batch mode. EC leads to flocculation of much of the contaminants (suspended solids and insoluble organic compounds) into a sludge. The volume of PW treated was 3 L. Next the EC treated PW was immediately filtered using MF to separate the brine from the sludge. As indicated in Figure 1, 3 L of treated PW resulted in about 0.6 L of sludge and 2.4 L of filtered brine. Finally, MD is used to desalinate the brine. Each MD run consisted of a feed volume of 0.8 L. For a feed volume of 0.8 L about 0.25 L of water was recovered.

In this work, three different MD membranes were evaluated using the EC–MF–MD process developed here: a commercially available polyvinylidene fluoride (PVDF) membrane, an electrospun copolymer membrane consisting of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and multiwalled carbon nanotube (MWCNT) coated polytetrafluoroethylene (PTFE) membrane. The three membranes had different morphologies and surface properties. The focus of this study was to evaluate the combined EC–MF–MD processes for treating PW and to understand the effects of water quality and operating conditions on fouling and scaling of three different MD membranes.

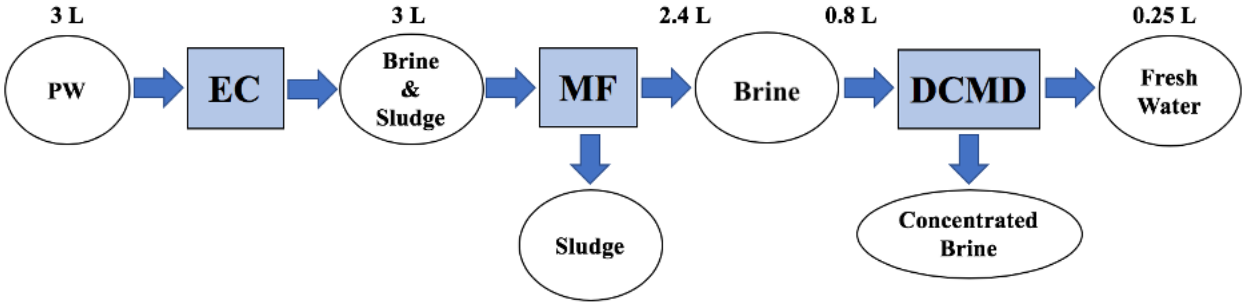

Figure 1. Diagram of the combined EC–MF–MD process investigated here.

4.2. Materials and Methods

4.2.1. PW Characterization

PW was obtained from a hydraulic fracturing facility in Texas, USA. Prior to testing the water was analyzed at the Arkansas Water Resources Center, University of Arkansas (Fayetteville, AR, USA). Total dissolved solid (TDS), total suspended solids (TSS), turbidity and total organic carbon (TOC) were measured using EPA standard methods 160.1, 160.2, 415.1 and 180.1 [24], respectively. Cations and anions were measured using EPA method 200.7 and 300.0, respectively [25]. Conductivity was measured using conductivity meter (VWR, Radnor, PA).

4.2.2. Materials

Acetone and N,N-dimethylacetamide (DMAc) were purchased from Alfa-Aesar (Ward Hill, MA, USA). Deionized (DI) water used throughout the investigation was collected from Thermo Fisher 18 MΩ Barnstead Smart2Pure system (Schwerte, Germany). Sodium hydroxide and PVDF-HFP were purchased from Sigma Aldrich (St. Louis, MO, USA). Commercial PVDF membranes were obtained from MilliporeSigma (Billerica, MA, USA). PTFE membranes were purchased from Shengju Environmental Science and Technology Co., Ltd (Hangzhou, China). Multi-walled carbon nanotubes (MWCNTs) were purchased from Chengdu Organic Chemicals Co. Ltd. (Chinese Academy of Sciences, Chengdu, China). The MWCNTs have a diameter of ~8 nm, a length of 10~20 μm, and purity ~98%. Mineral oil was obtained from Walmart Inc. (Bentonville, AR, USA).

4.2.3. Fabrication of Electrospun Membranes

The solvent used was a 7:3 (wt%) acetone: DMAc solution. The PVDF-HFP was dried at 70 ^{o}C overnight then dissolved under mixing (200 rpm) at a temperature of 45 ^{o}C in the solvent to form a 10 wt.% polymer solution. The homogeneous polymer solution was placed in a fume hood overnight for degassing. A diagram of the electrospinning system is shown in Figure 2. The polymer solution was ejected from a syringe at a specified flow rate. The needle was connected to a high voltage supply. The rotating collector was grounded. The distance between the needle and the rotating collector was 15 cm. The electrospun membranes were fabricated at 23 ^{o}C and 50% relative humidity.

Briefly, a droplet sits at the end of the needle and is slowly pushed by the plunger. The liquid becomes charged due to the electric field between the tip of the needle and the collector plate. A Taylor cone forms. The droplet stretches and a jet erupts from the cone at the critical point

where electrostatic repulsion overcomes the surface tension of the liquid. The jet heads for the point with a lower potential (the collector plate). The solvent evaporates as the jet reaches the collector plate. The jet does not break up as the polymer chains are entangled. The mat that forms at the collector is a distribution of continuous nanofibers [26,27]. The electrospinning conditions were as follows: voltage 16 kV, flow rate 1 ml/hour, collector rotation speed 90 rpm, spinning time 10 hours. After electrospinning, the membranes were dried in a fume hood for 24 hours to remove the residual solvent. Then the electrospun membranes were subjected to 3 min hot-press post treatment at 130 ^{o}C to further remove solvent and improve stability.

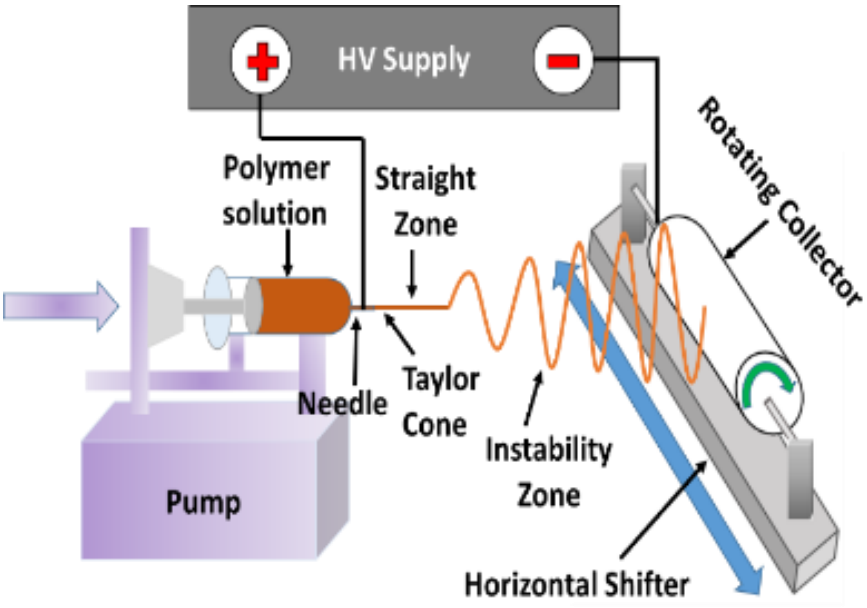

Figure 2. Diagram of electrospinning set up.

4.2.4. Fabrication of the MWCNT-Coated Membrane

An ethanol dispersion of 0.4 g·L^{-1} MWCNTs was prepared immediately before coating the PTFE membrane. MWCNTs were dissolved in ethanol for 10 min. The suspension was stirred at 100 rpm using a magnetic stirrer followed by sonication for 2 hours using a probe sonicator (JY 92-IIDN, Scientz, Ningbo, China) at room temperature. Spray coating was conducted using a spray

gun (LPH-50-S9, Anestiwata, Yokohama, Japan) having a nozzle size of 0.8 mm at a pressure of 1 bar. The distance between the nozzle and the membrane was 20 cm. After spraying, the MWCNT-coated membrane was dried at 50 ^{o}C in an oven for 1 hour. Then, the MWCNT-coated membrane was heat-treated in air at 250 ^{o}C for 2 hours in a muffle furnace to firmly bind the MWCNTs and substrate.

4.2.5. Membrane Characterization

The mean pore diameter on the membrane surface and the thickness of skin layer were measured using Nano Measure software based on the scale bar of the SEM images. For each set of data, more than 50 pores were randomly selected from the SEM images of three individual parallel specimens [28]. Liquid entry pressure (LEP) was determined as described by Smolder and Franken [29]. A Sterlitech HP4750 (Kent, WA) stainless steel cell was filled with deionized (DI) water and pressurized to 13.8 kPa. Then the feed pressure was gradually increased at 13.8 kPa/min. A continuous flow of DI water through the membrane is first observed and the pressure was recorded as the LEP [30].

A sessile drop contact angle goniometer (Model 100, Rame-Hart Instrument Company, Netcong, NJ, USA) was used to measure membrane static water and oil contact angles. For the water contact angle, the volume of the DI water droplet was 2 µL which was introduced at a rate of 0.5 µL/s. For the oil contact angle, the underwater oil (mineral oil) droplet volume was 5 µL which was introduced at a rate of 0.5 µL/s. Both water and oil contact angles were measured after allowing the droplet to stabilize for 10 sec. The contact angle measurement for each membrane was obtained at three different locations and the average value is reported.

Both scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy were used to determine the surface morphology and elemental analysis, respectively,

for each membrane before and after MD using Nova Nanolab 200 Duo-Beam Workstation (FEI, Hillsboro, OR, USA). Atomic force microscopy (AFM) images were acquired using Bruker Dimension icon instrument (Santa Barbara, CA, USA) to obtain detailed information on the surface roughness. AFM tapping mode was conducted using Antimony-loaded Si-based probes. AFM images were obtained for membranes before and after MD.

4.2.6. EC–MF Pretreatment

A diagram of the combined EC–MF system is shown in Figure 3. A custom-built polycarbonate reactor having dimensions of 4 cm x 32 cm x 40 cm with a total volume of 5120 cm^3 was used to conduct all the EC experiments. Six aluminum electrodes were fitted vertically inside the reactor with a 5 mm inter-electrode spacing and a total effective surface area of 3760 cm^2. A DC power supply (Hewlett Packard, Palo Alto, CA, USA) was connected to a reverse polarity switch which enabled the direction of the current to alternate every 30 sec. This is essential to prevent formation of a passivation layer on the electrode which would suppress further reactions [31,32].

Immediately after EC, microfiltration was conducted using a custom-built MF cell developed in previous work [33]. The entire 3 L of EC treated feed water was placed in the MF feed tank. Initially the permeate outlet was closed and feed was recirculated through the membrane module by means of a diaphragm pump (P800, King-Kong, Taiwan). The membrane surface area available for filtration was 33.75 cm^2. The feed flow rate was 1.8 L min^{-1} and the feed pressure was 110 kPa. The permeate side pressure was essentially at atmospheric pressure. Once steady state had been reached, the permeate outlet was opened and permeate was collected in the permeate tank which was placed on a computer-connected analytical balance (Mettler Toledo, Columbus, OH). The permeate flux was calculated based on the rate of permeate collection in the permeate

tank. About 80% of the EC treated water was recovered (see Figure 1). After each cycle, the membrane was cleaned by circulating DI water for 1 hour prior to starting a new cycle. A commercially available PES membrane purchased from Membrane Science Inc. (Hsinchu, Taiwan) and having a porosity of 80.4%, 0.1 µm pore size and 43.7° air contact angle was used.

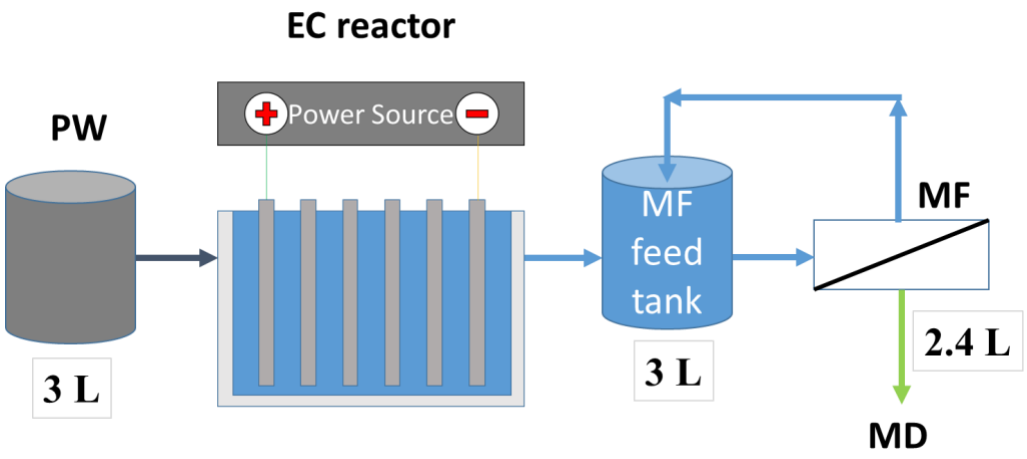

Figure 3. Diagram showing combined EC–MF system investigated here.

4.2.7. MD

A diagram of the MD system is shown in Figure 4. A custom-made acrylic membrane cell with 40 cm^2 effective membrane area and 2 mm deep channels was used as the membrane module. PTFE spacers (ET 8700, Industrial Netting, Minneapolis, MN, USA) were used for mechanical support and mixing. Feed and permeate streams were pumped on opposite sides of the membrane at 0.05 L min^{-1} using two peristaltic pumps (Masterflex I/P, Cole Parmer, Vernon Hills, IL) in counter current flow. The weight of the permeate was measured and recorded by a computer-connected analytical balance (Mettler Toledo, Columbus, OH, USA). The temperature of the permeate tank was maintained at 20 °C using an external chiller (PolyScience, Niles, IL, USA). The feed tank was placed in a water bath to maintain the temperature at 36 °C. The feed water was pumped through a heat exchanger in order to increase the temperature of the feed entering the MD

module to 60 ºC. From our previous work, we found that cooling the feed tank relative to the temperature of the feed entering the MD module induces precipitation in the feed tank and suppresses scale formation on the membrane surface due to supersaturation of the feed. In this way we increase water recovery and limit scale formation on the membrane surface [34].

The water flux was calculated based on the weight change of the permeate tank. The permeate conductivity was continuously monitored using a conductivity meter (VWR, Radnor, PA, USA). Each MD experiment was conducted using 800 ml of pretreated PW. It was assumed that pore wetting and membrane failure occurred once the permeate conductivity increased above 50 µS cm^{-1}. A regeneration cycle was conducted once the permeate conductivity reached 50 µS cm^{-1} or there was no weight increase of the permeate for 20 min. Regeneration of the membrane involved pumping DI water on both sides of the membrane at 0.5 L min^{-1} for 1 hour.

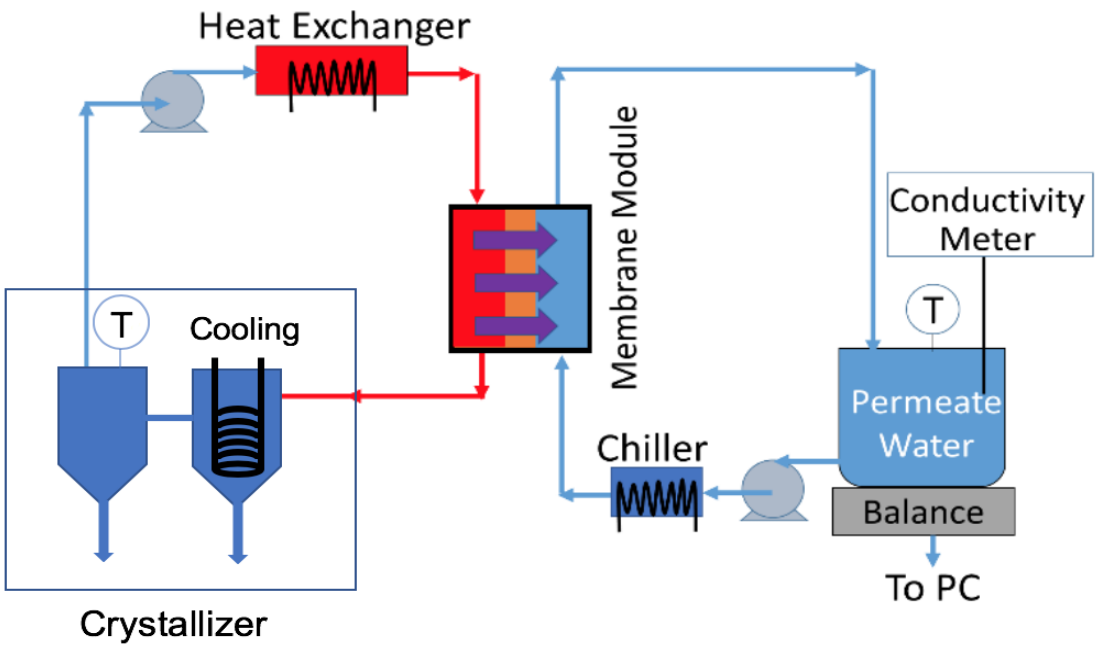

Figure 4. Diagram of MD system investigated here.

4.3. Results and Discussion

4.3.1. Wastewater Characterization

Prior to receival the PW was treated with chlorine dioxide at the hydraulic fracturing facility. Table 1 shows the water quality parameters of the PW as received from the hydraulic fracturing facility as well as after each treatment step. As can be seen the TDS is very high, being about 7 times more than seawater. The majority of the inorganic ions present are chlorine, calcium, magnesium potassium and sodium. A high concentration of calcium ions (30500 mg L^{-1}) can potentially lead to membrane scaling due to the precipitation of calcium sulfate [20]. The TOC and TSS are 120.0 mg L^{-1} and 131 mg L^{-1}, respectively. The water is highly impaired. It is important to note that the quality of the PW in general is highly variable, and this will affect the efficiency of the treatment operations. By comparison with previous studies [18,20,25,35], this PW contains much higher TDS. The percent difference (electroneutrality) between the sum of the cations and anions was 4.1% indicating that the analysis of the PW is of sufficient accuracy.

Table 1. Water quality analysis for PW received from the hydraulic fracturing facility and after each water treatment operation.

Parameter	Unit	PW	PW treated by EC	PW treated by EC–MF	PW treated by EC–MF–MD
TDS	mg L^{-1}	245300	238400	239760	56
TOC	mg L^{-1}	120	64	44	1
TSS	mg L^{-1}	131	186	48	1
Turbidity	NTU's	6	13	0.3	0.4
pH	--	6.7	3.8	3.9	7.1
Chloride	mg L^{-1}	156820	160250	166170	5
Sulfate	mg L^{-1}	478	419	430	0
Iron	mg L^{-1}	0.2	0.6	0.7	0
Boron	mg L^{-1}	97	87	85	0
Calcium	mg L^{-1}	30500	30300	31700	1
Magnesium	mg L^{-1}	5454	5500	5335	0
Manganese	mg L^{-1}	0.1	0.3	0.4	0
Nickel	mg L^{-1}	0.2	0.4	0.4	0
Potassium	mg L^{-1}	4331	4800	4680	0.4
Aluminium	mg L^{-1}	0	97	64	0
Sodium	mg L^{-1}	63600	68600	68100	4
Conductivity	µS/cm	323400	228000	229000	35

4.3.2. Membrane Characterization

4.3.2.1. Bulk Membrane Properties

Table 2 lists the characteristics of the MD membranes, including mean pore size, thickness, contact angle and LEP. As can be seen all three membranes have a large water contact angles and are hydrophobic. This is essential for MD as only water vapor should pass through the membrane pores. The membrane should be resistant to wetting by water. However, Table 1 suggests that the dissolved organic compounds present in PW could adsorb on the membrane surface. If these compounds are polar, they could lead to scale deposition on the layer of adsorbed organic compounds [18]. Consequently, an oleophobic membrane surface is desirable. As indicated by Table 2, the electrospun membrane has the highest oil contact angle.

Table 2. Bulk membrane properties.

Membrane	Porosity	Thickness (µm)	Mean pore size (µm)	LEP (kPa)	Water Contact Angle (°)	Oil Contact Angle (°)
Commercial PVDF		103 ± 5	0.45	233.7	144.6 ± 3	71.8 ± 2
Electrospun PVDF-HFP		100 ± 7	0.60	155.1	137.7 ± 1	82.8 ± 1
MWCNT PTFE		63 ± 1	0.21	96.5	150.0 ± 4	33.7 ± 3

4.3.2.2. SEM Images

SEM images of all three membranes before and after MD are given in Figure 5. Figure 5A, 5B and 5C are for commercial PVDF, electrospun PVDF-HFP and MWCNT PTFE membranes before MD. Figure 5D, 5E and 5F are for commercial PVDF, electrospun PVDF-HFP and MWCNT PTFE membranes after MD. As can be seen some deposition (highlighted with circle) on the membrane surface is observed after MD.

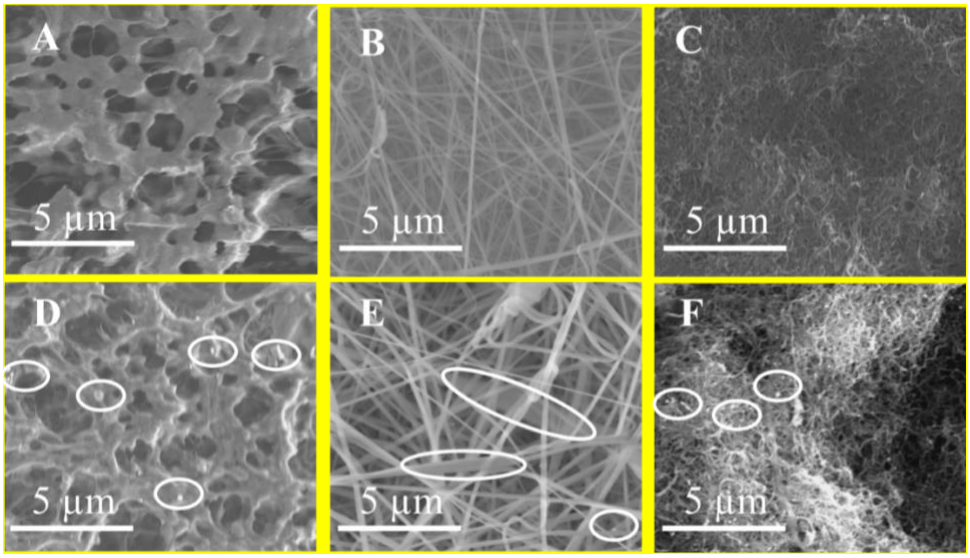

Figure 5. SEM images of the membrane surface before and after MD: 5A, 5B 5C are for commercial PVDF, electrospun PVDF-HFP and MWCNT PTFE membranes before MD and 5D, 5E, 5F are after MD.

4.3.2.3. AFM Images

The surface morphology of the membranes before and after MD was imaged by AFM as shown in Figure 6. Average roughness values are given in Table 3. As can be seen the surface pore morphology changes for all three membranes after MD. In addition, Table 3 indicates an increase in surface roughness after MD for all membranes.

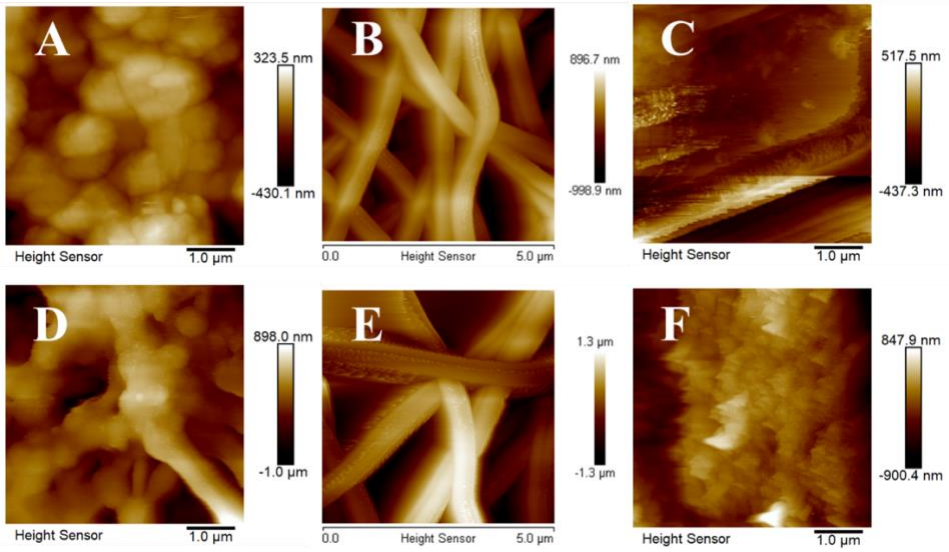

Figure 6. AFM images (A, B and C) for commercial PVDF, electrospun PVDF-HFP and MWCNT PTFE membranes before MD. Images D, E and F are for commercial PVDF, electrospun PVDF-HFP and MWCNT PTFE membranes after MD.

4.3.2.4. EDX Results

The EDX spectra of commercial PVDF, electrospun PVDF-HFP and MWCNT PTFE membranes before and after MD are given in Figure 7. The average elemental ratios of carbon/fluorine (C/F) and oxygen/fluorine (O/F) for all three membranes before and after MD are given in Table 3. As can be seen the C/F and O/F ratios of all the membranes increased after MD, which is mainly due to the organic fouling.

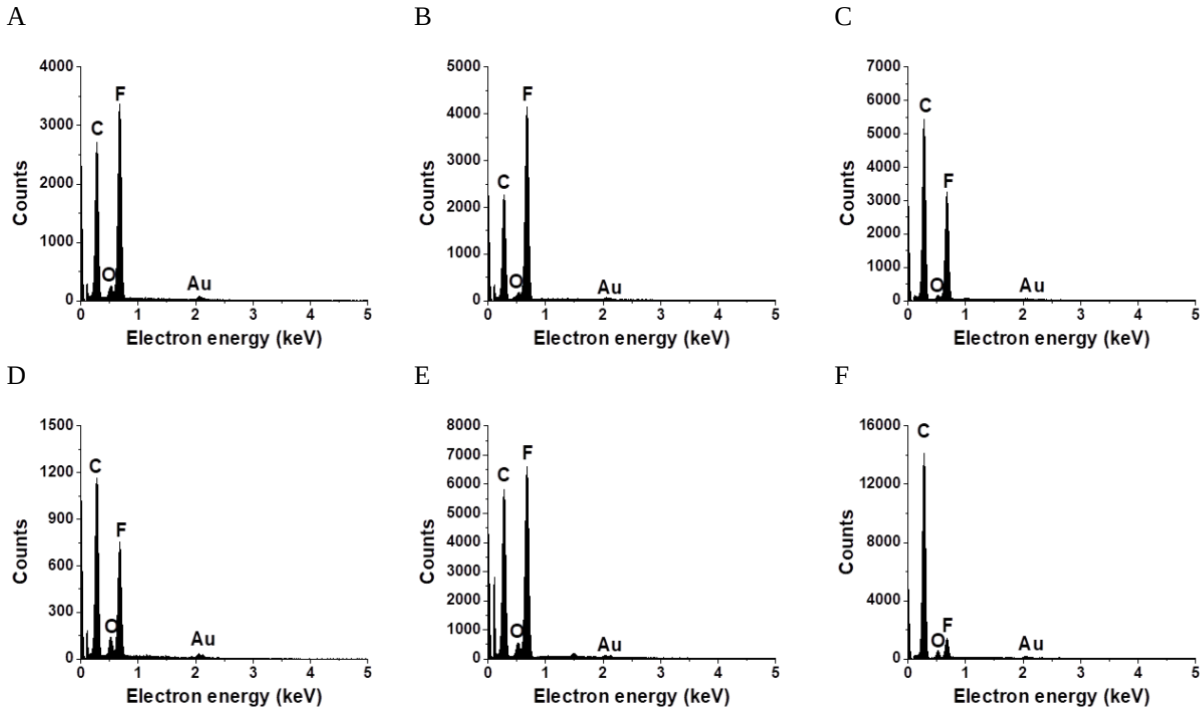

Figure 7. EDX spectra of the membrane surface before and after MD: A, B, and C are for commercial PVDF, electrospun PVDF-HFP and MWCNT PTFE membranes, respectively, before MD and D, E, and F are after MD.

Table 3. Average roughness and C/F and O/F atomic percent ratios for the three membranes before and after MD.

Membranes	Average roughness Ra (nm)		C/F atom percental ratio		O/F atom percental ratio	
	Before MD	After MD	Before MD	After MD	Before MD	After MD
Commercial PVDF	77	236	2.21	3.36	0.17	0.35
Electrospun PVDF-HFP	275	404	1.61	2.32	0.08	0.14
MWCNT PTFE	89	202	3.45	21.79	0.10	1.28

4.3.3. EC Performance

In the presence of an aluminum electrode, the main electrode reactions that occur are as follows [36].

At the anode:

$$Al \rightarrow Al^{3+} + 3e^{-} \quad (5)$$

At the cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (6)$$

In the solution:

$$Al^{3+} + H_2O \rightarrow AlOH^{2+} + H^+ \quad (7)$$

$$AlOH^{2+} + H_2O \rightarrow Al(OH)^+_2 + H^+ \quad (8)$$

$$Al(OH)^+_2 + H_2O \rightarrow Al(OH)^0_3 + H^+ \quad (9)$$

$$Al(OH)^0_3 + H_2O \rightarrow Al(OH)^-_4 + H^+ \quad (10)$$

During EC, the aluminum ions are generated continuously at the anode. The reduction of water takes place at the cathode forming hydroxide ions. In the solution, a variety of aluminum hydroxides are produced when coagulating ions (aluminum and/or hydroxide ions) undergo hydrolysis in water. Reactions (7)-(9) are the dominant reactions at pH 6.7, the pH of the PW. Introducing aluminum hydroxides can help destabilize suspended, emulsified and dissolved contaminants, which can further aggregate and precipitate as sludge or lift up to the surface as flocs. Soluble organic compounds can be adsorbed by the aggregated aluminum hydroxides. This adsorption phenomenon is a result of the liquid-solid intermolecular attraction forces between the adsorbable solute in the solution and the large surface area of the porous floc that form.

The bipolar series (BPS) configuration was used in this work because only the first and last electrodes are connected to the power supply, simplifying the electrical connections (see Figure 3). Further previous studies indicated that using BPS configuration can enhance the TOC removal [37,38]. Initial experiments focused on determining an appropriate EC current and reaction time. A range of currents (1 to 9.5 A) and reaction times of 5 min and 20 min were studied. Each EC experiment was conducted using 600 ml of PW. After EC, the treated water was allowed to sediment for 6 hours. Treated water was removed from the sludge and settled floc. The TOC removal for the recovered water was defined as,

$$\text{TOC removal } (\%) = \frac{\chi_{pw} - \chi_{rw}}{\chi_{pw}} \times 100 \quad (1)$$

where, χ_{pw} and χ_{rw} are the TOC in the PW and recovered water after EC, respectively.

The TOC removal is given on Table 4. As can be seen, the TOC removal increases from 17.9 % to 29.3 % as the current increases from 1 to 5 A. To obtain higher TOC removal, higher currents and longer reaction times were investigated. However, increasing the current above 8A for a reaction time of 20 min provided only a small increase in TOC removal. On the other hand, increasing reaction time and current leads to an increase in power costs. Consequently, all EC experiments consisted of treating 3 L of PW for 20 min using a current at 8A. The TOC in the treated PW that was the feed for MF was 64 mg L^{-1} as shown in table 1.

Table 4. Percentage removal of TOC for different currents and reaction times.

EC Operating Conditions	% TOC Removal
1 A, 5 min	17.9
5 A, 5 min	29.3
8 A, 20 min	46.4
9.5 A, 20 min	48.45

4.3.4. MF Performance

Figure 8 shows the variation of permeate flux with time. Results are shown for two repeat runs. For the first run the initial flux was 28 L m^2 h^{-1}. The flux gradually decreased to 10 L m^2 h^{-1} after 320 min. The decrease in flux with time is due to the deposition of flocs on the membrane surface [39]. The membrane was regenerated and tested with a second batch of EC treated PW. The flux profile is very similar. The initial flux was 26 L m^2 h^{-1}. The result suggests that there is minimal irreversible fouling. After 10 runs the initial permeate flux was regenerated by simply recirculating the DI water for 1 hour. The result suggests that EC was effective at flocculating the dissolved organic compounds and particle matter that could plug the pores of the MF membrane.

A digital photo of the MF membrane after filtration is shown in Appendix A Figure A.1A, and the MF membrane after regeneration with DI water is shown in Appendix A Figure A.1B. It can be seen that most of the flocs that had adhered on the membrane surface were removed after circulating DI water for 1 hour. SEM images of the unused and regenerated MF membranes are given in Figure 9. As can be seen from Figure 9 A and B, most of the regenerated membrane appears to have an open structure similar to the structure of the unused membrane. This suggests that regenerating the MF membrane by circulating DI water is sufficient to remove flocs from the membrane surface resulting in minimal irreversible fouling. There were tiny pieces of flocs residual left on the regenerated membrane, which was observed by the SEM (shown in Figure 9C). The gap between the flocs shows nice open pore structure (Figure 9D), which would be occupied by the flocs cake before regeneration and was cleaned by circulating DI water. It is further confirmed the pore structure was not irreversibly blocked by the flocs.

Particle floc size distribution (Appendix A, Figure A.2) was determined after EC for 20 min with an 8 A current using a Beckman Coulter (Indianapolis, IN) LS 13 320 Laser Diffraction Particle Size Analyzer. Particle with a diameter larger than 0.1 μm, contributed to 97.6% of the total sludge volume (based on the cumulative volume percentage). Although 31.5% of the particles have a diameter smaller than 0.1 μm based on the number percentage, they represent only 2.4 % volume of the fouling layer on the surface of the MF membrane. In fact, a cake layer may be formed very quickly by large size particles. Thus, most of the smaller particle will be rejected by the cake layer through size exclusion. This can help prevent small particles entering the membrane pores leading to irreversible pore blockage and fouling. The EDX result for the MF membrane (Appendix A Figure A.3) indicates that fouling may be mainly caused by $Al(OH)_3$, the major floc compound generated during EC.

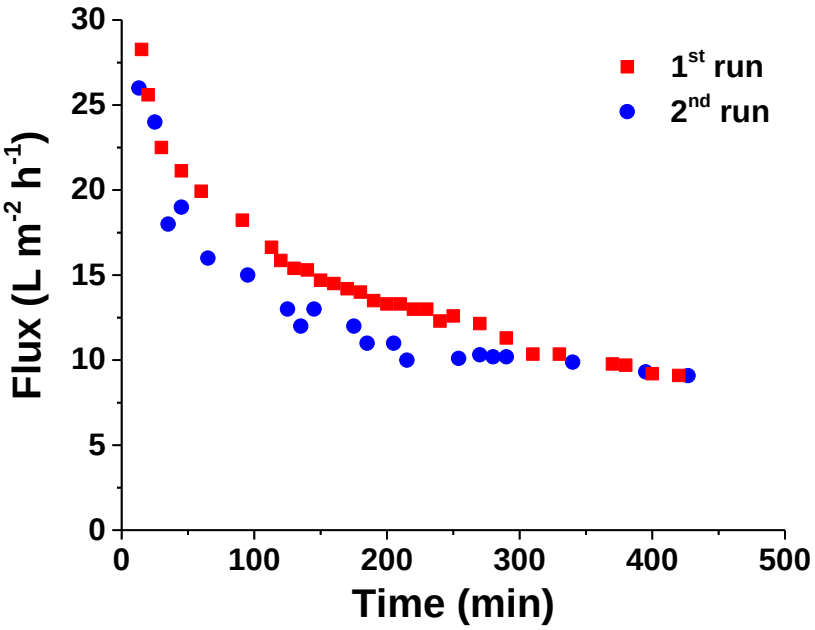

Figure 8. Variation of MF permeate flux with time.

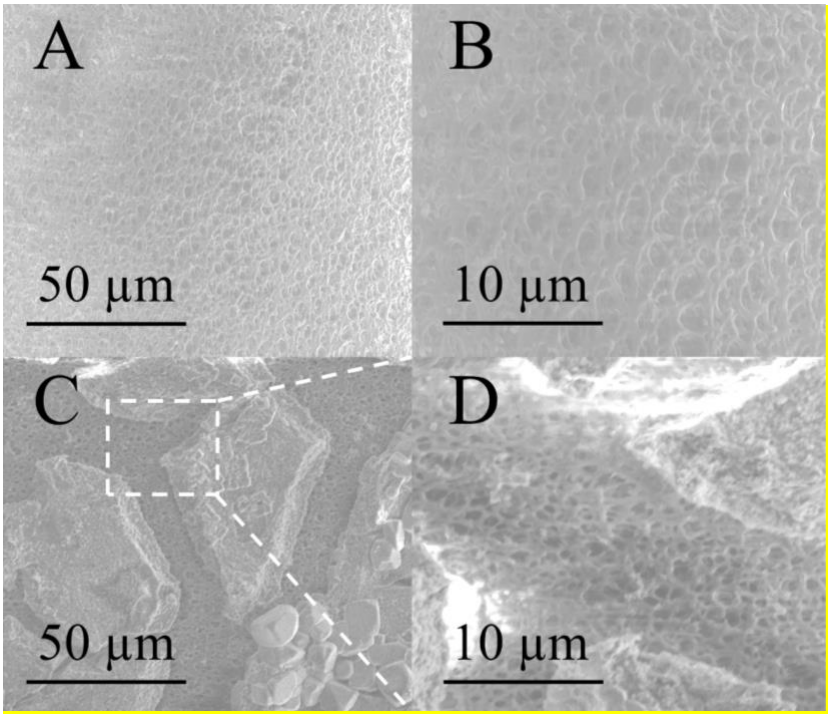

Figure 9. SEM images of MF membranes: A and B) unused; C and D) specific area with flocs after regeneration.

4.3.5. MD Performance

Figure 10 (A), (B) and (C) give the cumulative permeate volume versus time for the commercial PVDF membrane, the electrospun PVDF-HFP membrane and the MWCNT PTFE membrane, respectively. Figure 11 (A), (B) and (C) give the variation of permeate flux with permeate volume for the commercial PVDF membrane, the electrospun PVDF-HFP membrane and the MWCNT PTFE membrane, respectively. Table 5 summarizes the initial permeate flux and the volume of the feed water recovered for the three membranes.

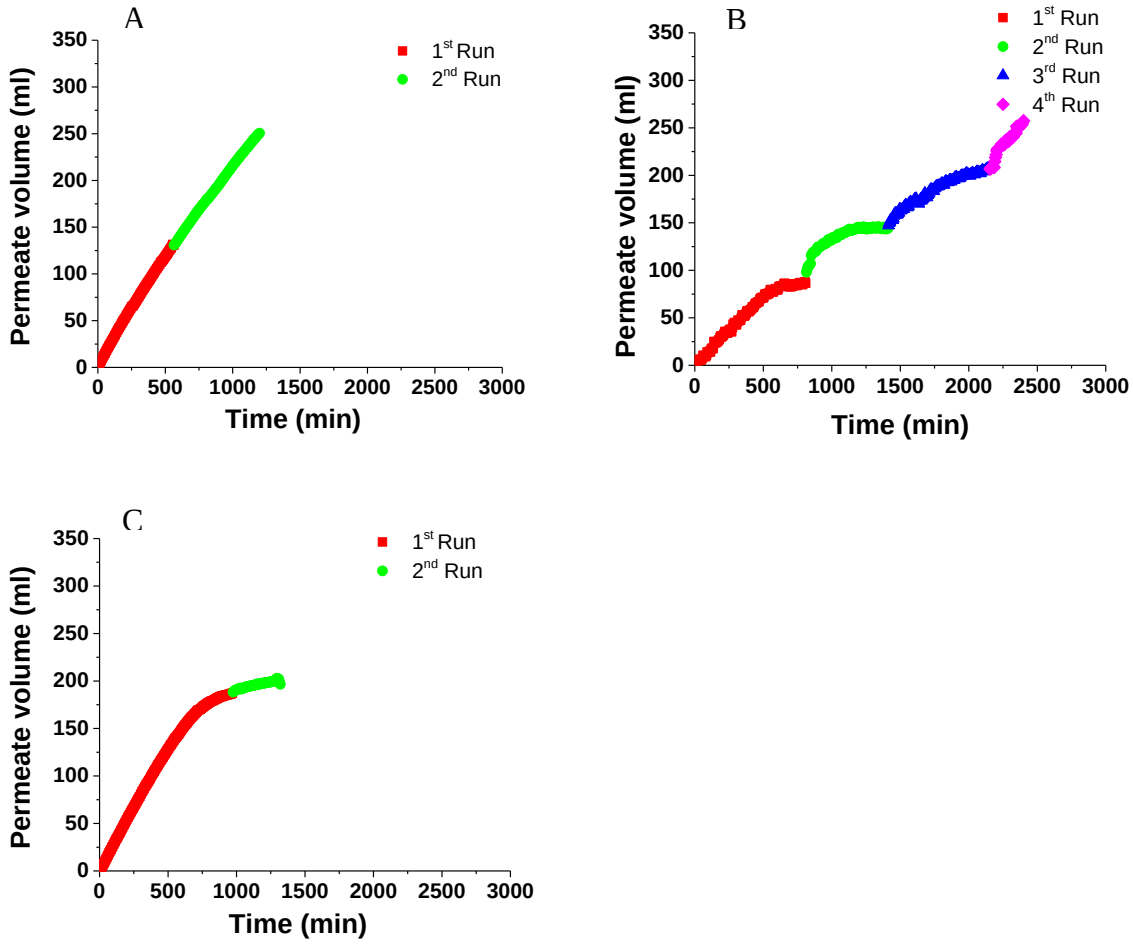

Figure 10. Cumulative permeate volume versus time for the (A) commercial PVDF membrane, (B) electrospun PVDF-HFP membrane, (C) MWCNT PTFE membrane.

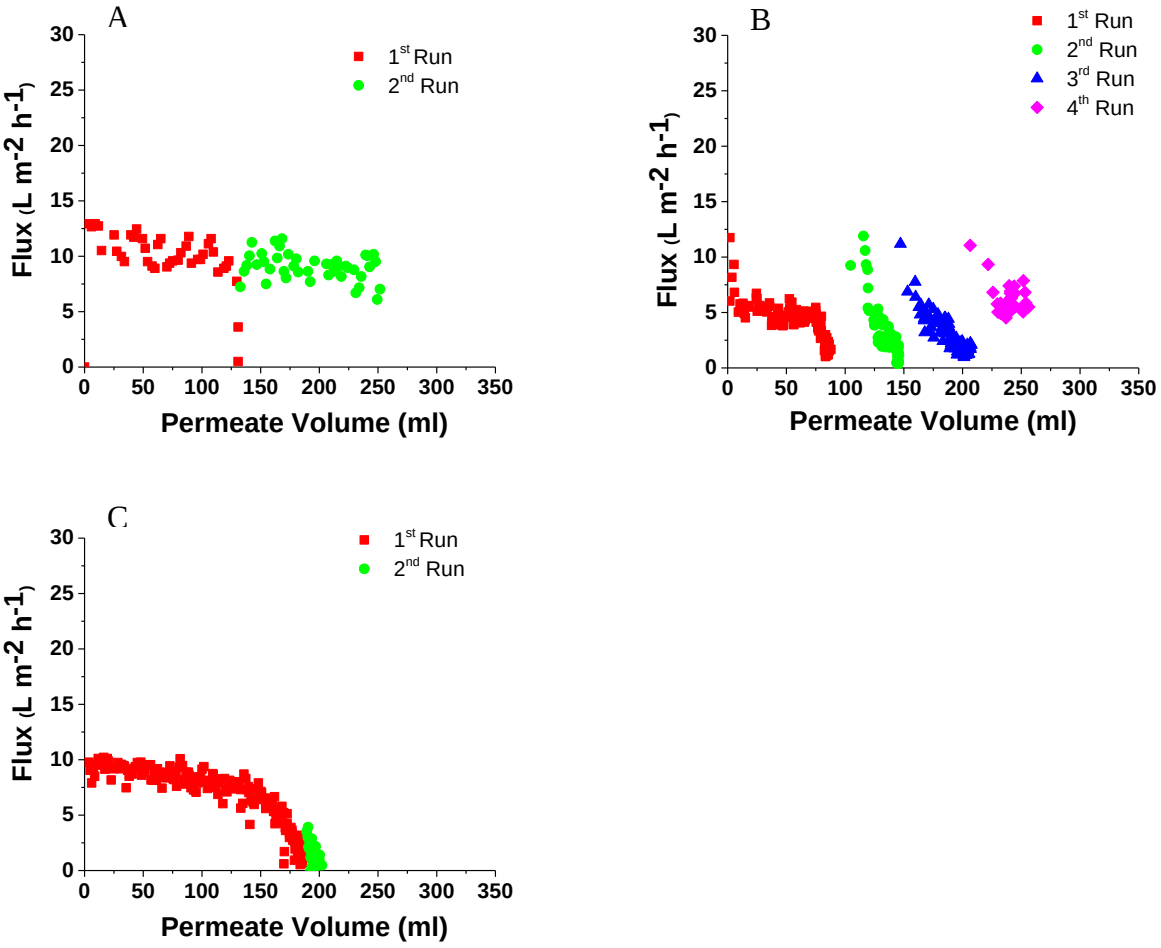

Figure 11. Variation of permeate flux with permeate volume for (A) commercial PVDF membrane, (B) electrospun PVDF-HFP membrane, (C) MWCNT PTFE membrane.

As noted in Table 1 the feed TDS is 245,300 mg L^{-1} which is extremely high. The solubility of NaCl is around 360,000 mg L^{-1} at 30 °C [30,40]. We aim to recover 250 ml of permeate (30% water recovery) which would result in a feed TDS of 356,800 mg L^{-1}. Given the number of organic and inorganic compounds in the PW it is likely precipitation will occur at a TDS below 360,000 mg L^{-1}. The feed tank was kept at 36 °C while the temperature of the feed to the MD module was increased to 60 °C in order to minimize the risk of supersaturation and precipitation on the MD membrane. Precipitation was observed in the feed tank. Though the combined EC–MF pretreatment step reduced the TOC in the PW to around 44 mg L^{-1}, deposition of polar organic

compounds on the membrane surface will increase the likelihood of precipitation of dissolved salts on this layer of adsorbed organic species.

Table 5 Summary of membrane performance results.

Membrane	Run 1 initial water flux ($l\ m^{-2}\ h^{-1}$)	Run 1 water recovery (ml)	Run 2 initial water flux ($l\ m^{-2}\ h^{-1}$)	Run 2 water recovery (ml)	Run 3 initial water flux ($l\ m^{-2}\ h^{-1}$)	Run 3 water recovery (ml)	Run 4 initial water flux ($l\ m^{-2}\ h^{-1}$)	Run 4 water recovery (ml)	Total water recovery (ml)
Commercial PVDF	13	131	10.0	121	-----	-----	-----	-----	252
Electrospun PVDF-HFP	12	87	12	59	11	56	11	50	252
MWCNT PTFE	10	186	4	17	-----	-----	-----	-----	203

Figure10 (A) and Table 5 indicate that 131 ml of permeate were removed in the first run for the commercial PVDF membrane before the flux dropped to zero and the membrane was regenerated. The membrane was regenerated by simply running DI water on both sides of the membrane for 1 hour. The flux for the second run was a little lower than the first run indicating some adsorbed species could not be removed by simply flushing the membrane with water. During the second run the desired total permeate volume of 250 ml was recovered.

The electrospun PVDF-HFP membrane behaved differently. Though the initial flux was similar to the commercial PVDF membrane, the flux dropped much more rapidly. In fact, the membrane had to be regenerated 3 times before the desired permeate volume of 250 ml was reached. As indicated in Figure 10B, 11B and Table 5, for each subsequent run though the initial permeate flux was similar the rate of decrease of the flux was faster and the volume of recovered

permeate was less. However, the membrane could be regenerated, and the conductivity was always less than 50 μS cm^{-1}.

The MWCNT PTFE membrane displayed the highest constant flux out of all three membranes during the first run. In fact, during the first run 186 ml of water were recovered. However, after regeneration the conductivity during the second run reached 50 μS cm^{-1} very quickly. In fact, it was not possible to recover 250 mL of permeate. The results indicate the importance of membrane surface properties when treating PW.

Table 2 indicates that the water contact angle for the commercial PVDF membrane is a little greater than the electrospun PVDF-HFP membrane, but the reverse is true for the oil contact angle. However, Table 3 indicates the increase in roughness for all three membranes after MD is significant. Thus, for all three membranes significant deposition occurs after MD. The oil contact angle of the MWCNT PTFE membrane is very low.

Our results indicate that a very low oil contact angle is undesirable if the PW contains dissolved organic compounds. The MWCNT membrane contains carbon nanotubes which provide channels for water vapor transport. Hence the membrane displays a much higher flux over a longer period of time which results in much greater water recovery during the first run before regeneration. Given the low oil contact angle, dissolved organic compounds can easily adsorbed onto the channels of carbon nanotubes, which leads to eventual flux decline. However, regeneration by flushing both sides of the membrane with DI water did not lead to release of the adsorbed foulants as evidenced by the low permeate flux at the start of the second run.

In MD, the feed is typically kept at the same temperature in both the feed tank and the MD cell. However as one approaches the solubility limit of the lest soluble components in the feed, scale formation on the membrane is likely [38]. In fact, both concentration and thermal polarization

will provide a driving force for precipitation on the membrane surface. In order to maximize the water recovery and membrane life, we would like to promote precipitation in the feed reservoir, not the membrane surface.

Here, we cooled the feed reservoir relative to the temperature of the feed entering the MD module. Thus, we promoted precipitation in the feed reservoir but the least soluble component in the feed entered the MD module below its solubility limit due to the increases in temperature of the entering feed. Evidence of the fact that scale formation on the MD membrane was minimal is provided by EDX results (Figure 7). No metallic elements were detected except for gold due to coating the samples. However, the change in C:F and O:F ratios given in Table 3 as well as the observed decline in flux indicate that fouling by organic compounds is significant [19,39]. Fluorine is present in all three membranes but not the PW (Table 1). After MD, the C/F ratios of the commercial PVDF, electrospun PVDF-HFP, and MWCNT PTFE membranes have been increased by 52.0%, 44.1%, and 531.6%, respectively. As can be seen, the greatest increase in the C/F ratio was for the MWCNT PTFE membrane due to the adsorption of the organic compounds by the carbon nanotubes.

Hydrophobic and oleophobic surfaces will not suppress adsorption of low surface tension liquids as wetting by these liquid remains thermodynamically favorable [13]. Low surface tension compounds commonly found in PW include oils, alcohols and surfactants [7]. In addition, as shown in Figure 12, micelles can form in the feed solution once the concentrations of the surfactants exceeded their critical micelle concentration (CMC), which could lead to blockage of the membrane pores [41]. These micelles can grow from spherical aggregates to an elongated structures with an increase in concentration, which can lead to more severe fouling [42]. The proposed fouling mechanism is shown in Figure 12A. There is also a chance of bilayer sheet

formation on top of the membrane surface, as shown in Figure 12B, leading to an increased roughness of the membrane as observed in the AFM images (Figure 6(D), (E), and (F).

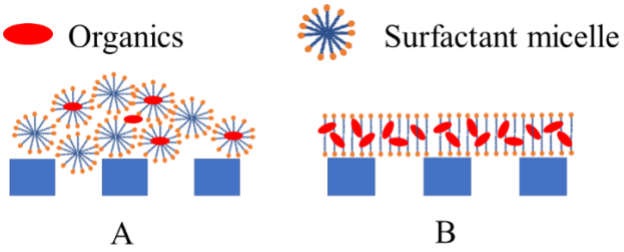

Figure 12. Fouling layer caused by surfactant: A) micelle; B) bilayer.

Organic foulants (surfactant [43] and organic contaminants [44]) built up on the membrane surface during the MD forming an adsorbed layer. The presence of polar groups in the layer of deposited organic compounds can lead to scale formation on the adsorbed layer. This will lead to a decrease in permeate flux. Simply flushing both sides of the membrane with DI water may remove deposited scales but will be less effective at removing adsorbed organic compounds. Hence the flux is always lower after membrane regeneration. Given the very low oil contact angle for the MWCNT PTFE membrane as well as the much higher permeate flux, it is likely that adsorption of organic compounds was more rapid. In fact, during the second run the permeate conductivity increased above 50 μS cm^{-1}, indicating breakthrough of water through the membrane pores.

In this work we have attempted to recover water from an extremely high TDS PW. Under these challenging conditions we show that a combined EC–MF–MD process can recover water up to the solubility limit of NaCl. The concentration of CaSO4 is around 677 mg/L in the PW (calculation based on sulfate present). Thus, while CaSO4 scale could form in this case, removal of 250 ml of permeate will not reach the solubility limit of CaSO4 (>4000 mg/L with 1mol/L NaCl) [45]. Further we show that a combined EC–MF–MD system where the feed reservoir is

cooled relative to the feed entering the MD module will increase water recovery and move closer to a zero liquid discharge process. However, the energy cost will also be increased.

Here we have evaluated three different membrane structures. Our results suggest that simply optimizing the membrane surface properties is insufficient. It is important to consider the properties of the PW and the operating conditions. The MWCNT PTFE provided the highest flux and best performance as long as there are no organic compounds that can adsorb onto the membrane surface. On the other hand, the electrospun PVDF-HFP membrane appears to be easy to regenerate. AFM mad SEM images appear to show less absorption on the nanofibers. In reality it is unlikely a single membrane will be used to concentrate the reject from a low TDS to above the solubility limit of the salts present. A staged process with inter-stage heat exchange is more likely. In addition, one can optimize the membrane for the TDS of the stage. Our future work will focus on development of an EC–MF–MD process that could be used to treat at a side stream at a hydraulic fracturing facility.

4.4. Conclusion

We have investigated a combined EC–MF–MD process for treating hydraulic fracturing PW. The PW investigated here had a very high TDS. Nevertheless, the process developed here could concentrate the reject to the solubility limit of the dissolved salts. By reducing the temperature of the feed tank relative to the feed entering the MD module, precipitation on the membrane is suppressed and occurs in the feed tank. We show that EC can lead to adequate reduction in the PW TOC (67 mg L^{-1}) and MF can efficiently remove the particulate matter. The stability of the MD membrane is critical. Three different membranes with different surface properties were tested. An ideal membrane is one which provides a high flux at high TDS and is

resistant to breakthrough. It is likely that ideal membrane will depend on the TDS and other properties of the PW.

Acknowledgements

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Appendix A

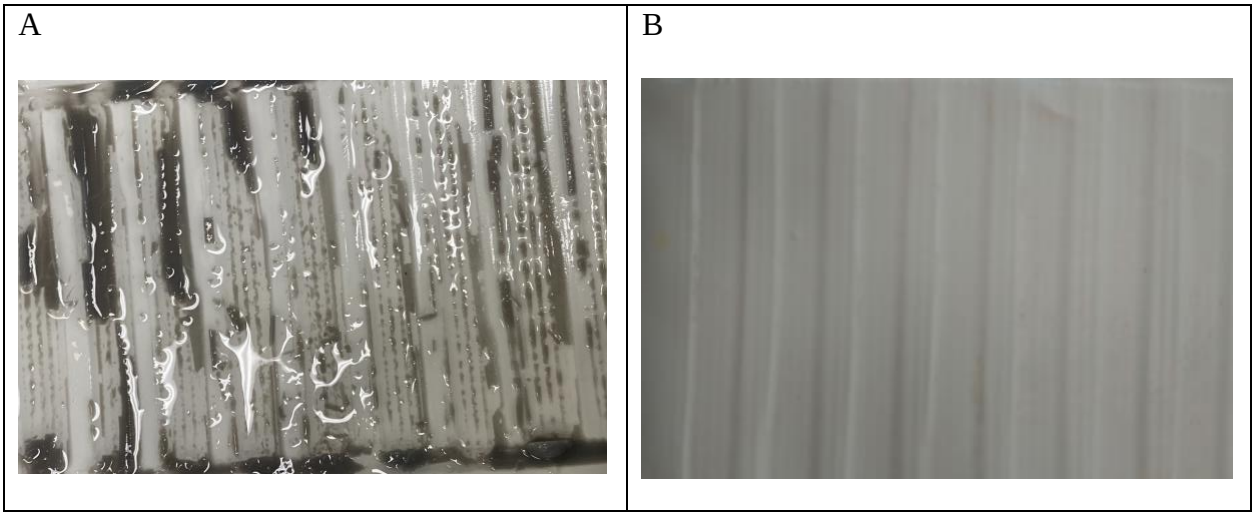

Figure A.1. Digital photos of the MF membrane: A) after MF filtration; B) after regeneration by recirculation.

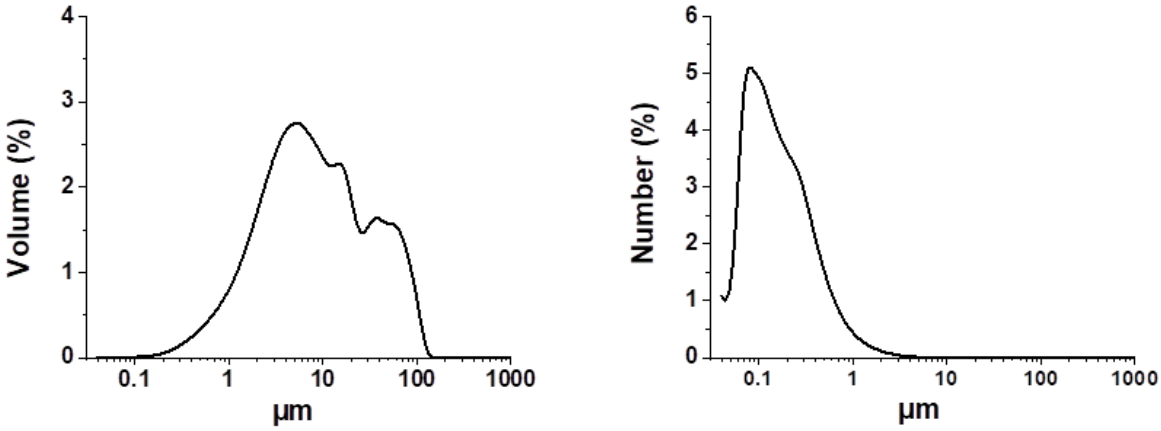

Figure A.2. Particle size distribution in the EC treated water (8 A, 20 min, Al, BPS).

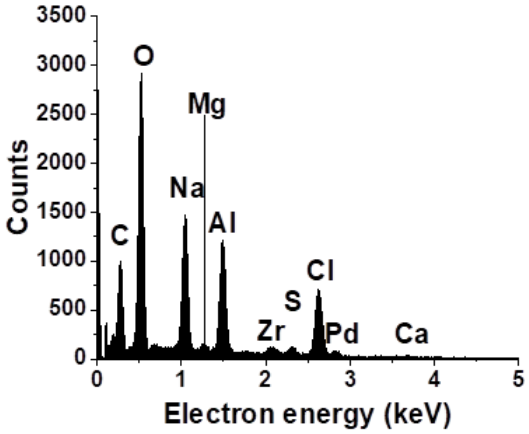

Figure A.3. EDX results of the flocs residual on regenerated MF membrane surface.

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Chapter 5. Integrated Electrocoagulation Ultrafiltration Membrane Distillation Crystallization for Treating Produced Water

This chapter is adapted from a submitted paper by M. Jebur, Y. Bachynska, X. Hao, X. Qian, S.R. Wickramasinghe, Integrated Electrocoagulation Ultrafiltration Membrane Distillation Crystallization for Treating Produced Water, 2023.

Abstract

In this work, produced water generated from hydraulic fracturing was treated using an integrated electrocoagulation ultrafiltration, membrane distillation and crystallization process (EC UF MDC). The focus of this work was to determine the viability of this integrated process for maximizing water recovery. The results obtained here indicate that optimizing the various unit operations used here could lead to increased recovery of produced water.

Membrane fouling limits all membrane separation processes. Membrane processes require a pretreatment step to suppress fouling. Here removal of total suspended solids (TSS) and total organic carbon (TOC) was achieved by electrocoagulation (EC) followed by ultrafiltration (UF). The hydrophobic membrane used in membrane distillation may be fouled by dissolved organic compounds. Reducing membrane fouling, is essential to increase the long-term durability of the MD system. In addition, combining membrane distillation with crystallization (MDC) can help reduce scale formation. By inducing crystallization in the feed tank scale formation on the MD membrane was suppressed. The integrated EC UF MDC process can impact Water Resources/Oil & Gas Companies. Conservation of surface and groundwater which forms 80% of the water used in hydraulic fracturing is possible by treating and reusing the PW. Additionally, treating the PW reduces the amount of PW disposed in Class II disposal wells, which has been shown to be the main cause of earthquakes and promotes more environmentally sustainable operations.

5.1. Introduction

The fastest growing energy sector in the US is unconventional shale gas and oil production. Hydraulic fracturing combined with horizontal drilling is used for exploitation of tight rock formations containing abundant oil and gas resources that were previously unreachable [1]. The extraction of shale gas using advanced hydraulic fracturing has increased from 14% of U.S. natural gas production in 2004 to 97% in 2018. However, this has led to a concurrent increase in water usage [2,3]. In hydraulic fracturing, water, mixed with chemicals, is pumped at high pressure through the well bore to fracture the tight rock formation. Then, the pressure is reduced, and the water flows back to the surface as flowback and produced water (PW) known collectively as PW. Around 15-23 million liters of PW is generated during the extraction period of each well [4]. Approximately 116 billion liters of PW are produced in U.S. annually [5]. About 20.06 million liters of water was used per well in the Fayetteville shale [6].

Water is a very scarce and valuable natural resource. Promoting circularity in water usage is essential in order to develop sustainable manufacturing processes. Recovery and reuse of PW is essential. PW is highly impaired, thus treating this water is very challenging. It contains a range of contaminants as well as high total dissolved solids (TDS) concentration, high total suspended solids (TSS), polar and non-polar organic compounds, and low surface tension dissolved species [7,8]. Currently the PW is frequently deep well injected. However, deep well injection practices are non-sustainable and have several drawbacks including the limitation of available deep well injection sites, cost of transporting PW to the available sites, and the possibility of creating earthquakes. Importantly it does not lead to recycle and reuse of the water.

Limited options exist to treat PW. Some investigators have considered distillation-based technologies such as multistage flash distillation or integrating evaporation, crystallization, and

spray drying to treat PW [9]. Though successful in treating high TDS brines, these technologies suffer from some drawbacks, such as high cost, large footprint, and the use of chemicals [10].

Here membrane technology is considered to treat high TDS brines. Conventional membrane processes such as reverse osmosis (RO) can be used to treat brines with TDS values below 50,000 mg/L. However, as the osmotic back pressure increases, the amount of water that can be recovered using RO, especially as the TDS increases over 50,000 mg/L is limited [11,12]. Membrane distillation (MD) is an emerging technology that can be used to treat high TDS PW. In MD, a microporous hydrophobic membrane is used as a barrier between the feed and permeate streams. The feed stream is heated relative to the permeate stream. This imposed temperature gradient leads to a vapour pressure gradient across the membrane. Water vapour passes down the vapour pressure gradient from the feed to the distillate. Importantly non-volatile solutes cannot pass through membrane pores. Unlike reverse osmosis the depression of the feed vapour pressure with increasing feed TDS is much less than the increase in osmotic back pressure [13,14]. Here direct contact membrane distillation is used where the feed and permeate streams are in direct contact with the two surfaces of the membrane [15].

However, MD like all other membrane technologies suffers from fouling of the membrane by rejected species. In the case of hydraulic fracturing PW, dissolved polar and non-polar organic species can easily adsorb onto the hydrophobic membrane surface. In addition, low surface energy compounds such as surfactants can adsorb on to the membrane. Scaling by dissolved salts at high TDS can also occur. Fouling leads to a drop in permeate flux. However, it can also lead to failure of the membrane whereby water together with dissolved non-volatile solutes pass directly through the membrane pores [16].

Here the aim is to develop an integrated process to maximize water recovery and suppress membrane fouling. Commercially available polyvinylidene fluoride (PVDF) membranes have been used to evaluate the feasibility of the integrated electrocoagulation ultrafiltration membrane distillation crystallization EC UF MDC process to address both scaling and wetting of the membrane and maximize water recovery. Electrocoagulation (EC) is used to pretreat the feed and remove dissolved organic compounds that could foul the membrane. UF is used to rapidly separate the permeate from the EC sludge. MD is used to recover treated water. By linking this with crystallization, we maximize water recovery while suppressing scaling on the MD membrane.

EC is an electrolysis process where, a sacrificial electrode (anode) is used to generate metal ions. These metal ions generate a variety of metal hydroxides as follows $M_{(s)} \rightarrow M^{n+}_{(aq)} + ne^-$ at the anode. Water is reduced at the cathode by the reaction $2H_2O + 2e^- \rightarrow 2OH^- + H_2$, where M is often Al or Fe [17]. Metal complexes such as $M(OH)^{(n-1)+}$, $M(OH)_2^{(n-2)+}$ and $M_6(OH)_{15}^{(6n-15)+}$ are produced. These metal complexes contribute to neutralization of the negatively charged organic species and suspended solids. As the solution ages they convert to amorphous $M(OH)_{n(s)}$ particles. $M(OH)_{n(s)}$ particles can easily adsorb and trap organic compounds and suspended solids.

Crystallization after EC UF MD can minimize membrane fouling and scaling by reducing the formation of crystal nuclei in the bulk feed. This is particularly important when using hypersaline PW which has a high TDS concentration. In addition, the EC UF MDC process can also offer a potential solution to high TDS brine disposal by recovering both water and minerals, which can lead to a nearly zero liquid discharge [18,19]. Here the feasibility of using EC UFMDC to recover water and minerals from hypersaline shale gas PW has been investigated. In addition, we compare the increase in water recovery when adding a crystallization unit by comparing EC UF MDC with EC UF MD. As about 80% of the water utilized in hydraulic fracturing is surface

water and ground water the process developed here could have an impact on hydraulic fracturing operations [20]. Further about 95% of the collected PW is directly disposed in Class II disposal well [21]. Fig. 1 shows the concept of the combined processes. The feed consisted of 3 L. After UF about 1.5 L of permeate is recovered. Table 1 shows previous studies focused on treating synthetic and actual wastewater including PW, sea water, and RO brines. Previous studies have been conducted using EC MD or MDC systems to treat low TDS brines as well as synthetic PW. To our knowledge, this is the first study that has considered an integrated EC UF MDC system to treat hypersaline PW from unconventional oil and gas wells.

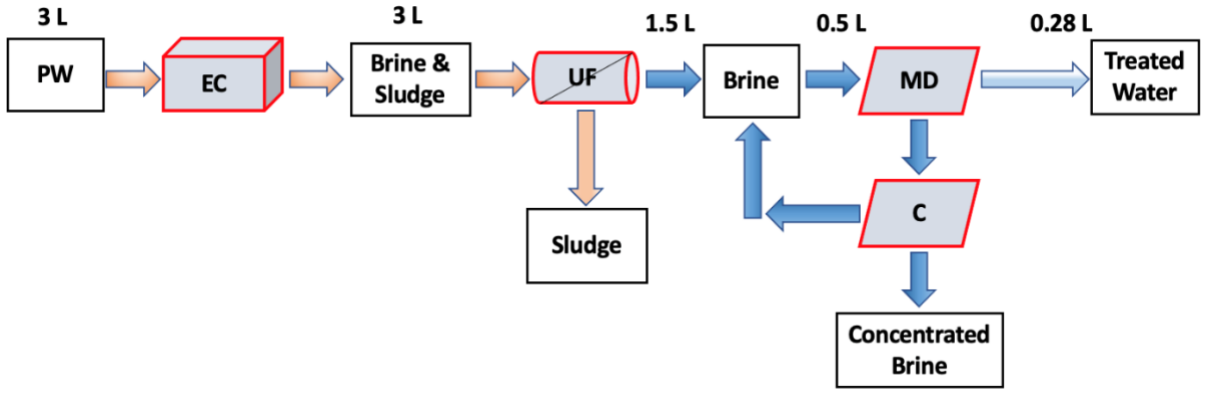

Fig. 1. Schematic diagram of the EC UF MDC process studied here. C refers to the crystallization unit

Table 1. Overview of the previous studies available in the current literature

Treatment Configuration	**Feed Water**	**TDS (mg/L)**	**Reference**
MDC	Actual RO Brines	50,000	[22]
MDC	Synthetic PW	150,000	[23]
MDC	Actual PW	30,000	[24]
MDC	Synthetic RO Brines	65,000	[25]
Ultrasound-Assisted MDC	Synthetic NaCl Solution	350,000	[26]
MDC	Actual RO Brines	45,000	[27]

5.2. Methods

5.2.1. PW Characterization

PW samples were collected from a hydraulic fracturing facility in Texas, USA. The sample were analyzed at the Arkansas Water Resources Center, University of Arkansas (Fayetteville, AR, USA). The received PW had been treated with chlorine dioxide at the hydraulic fracturing facility to remove bacteria and iron. EPA standard methods 160.1, 160.2, 415.1 and 180.1 were used to measure TDS, TSS, turbidity and total organic carbon (TOC) [28]. EPA methods 200.7 and 300.0 were used to measure cations and anions, respectively. Conductivity was measured using a conductivity meter (VWR, Radnor, PA).

5.2.2. Membrane Characterization

Static water contact angles were measured using a sessile drop contact angle goniometer (Model 100, Rame-Hart Instrument Company, Netcong, NJ, USA). The DI water droplet volume was 3 µL introduced at a rate of 0.5 µL/s. Each droplet was allowed to stabilize for 10 sec prior to measurement. For each membrane, the average value of three measurements obtained at three different locations was used in this study.

For each membrane before and after MD or MDC, both the surface morphology and elemental analysis were obtained using scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy, respectively, using Nova Nanolab 200 Duo-Beam Workstation (FEI, Hillsboro, OR, USA).

5.2.3. EC–UF Pretreatment

Fig. 2 shows the EC UF system. Here, a custom-built polycarbonate reactor with a volume of 1078 cm^3 (dimensions of 7 cm x 11 cm x 14 cm) was used to conduct all EC experiments. Five aluminum electrodes were fitted vertically inside the reactor. The inter-electrode spacing was 10

mm. The residence time in the reactor was 5 min. A DC power supply (Hewlett Packard, Palo Alto, CA, USA) was connected to a reverse polarity switch which enabled the direction of the current to alternate every 30 sec. This is essential to prevent formation of a passivation layer on the electrode surface which would suppress further reactions [29,30].

The first and last electrodes were connected to the power supply in a bipolar series (BPS) configuration to simplify the electrical connections. In previous studies, the BPS configuration was shown to lead to an enhancement in TOC removal [31]. In earlier studies, several EC experiments were conducted to determine the appropriate current and reaction time [31,32]. Based on these earlier studies, a range of currents from 1 to 3 A and a reaction time of 5 min were studied here.

Firstly, three standalone EC experiments were conducted to optimize the current based on achieving a high TOC removal. After each EC experiment, treated water was removed from the sludge and settled floc after sedimentation for 30 minutes. After optimizing the current, the EC reactor was run to treat 3 L of PW. This takes about 15 min, which leads to an average aging floc of 7 min. Next the supernatant from the EC became the feed to the UF process.

UF was conducted after EC using a ceramic membrane from CeraMem® (Waltham. MA, USA). Crossflow filtration was conducted using a 10 nm nominal pore size ceramic membrane module. The active surface area was 0.13 m^2. After EC, the 3L of PW was placed in the UF feed tank. The feed was recirculated through the module using a diaphragm pump (P800, King-Kong, Triwin, Taichung City, Taiwan) keeping the permeate outlet closed. The permeate outlet was opened after 5 min. The transmembrane pressure (TMP) was 65 kPa at a feed flow rate of 2.5 L/min. The permeate water was collected in the permeate tank, which was placed on a balance (Mettler Toledo, Columbus, OH). The permeate flux was calculated based on the weight of

permeate. About 50% of the EC treated water was collected as permeate. After each experiment, the membrane was cleaned by pumping hot DI water for 1 hour prior to starting a new experiment.

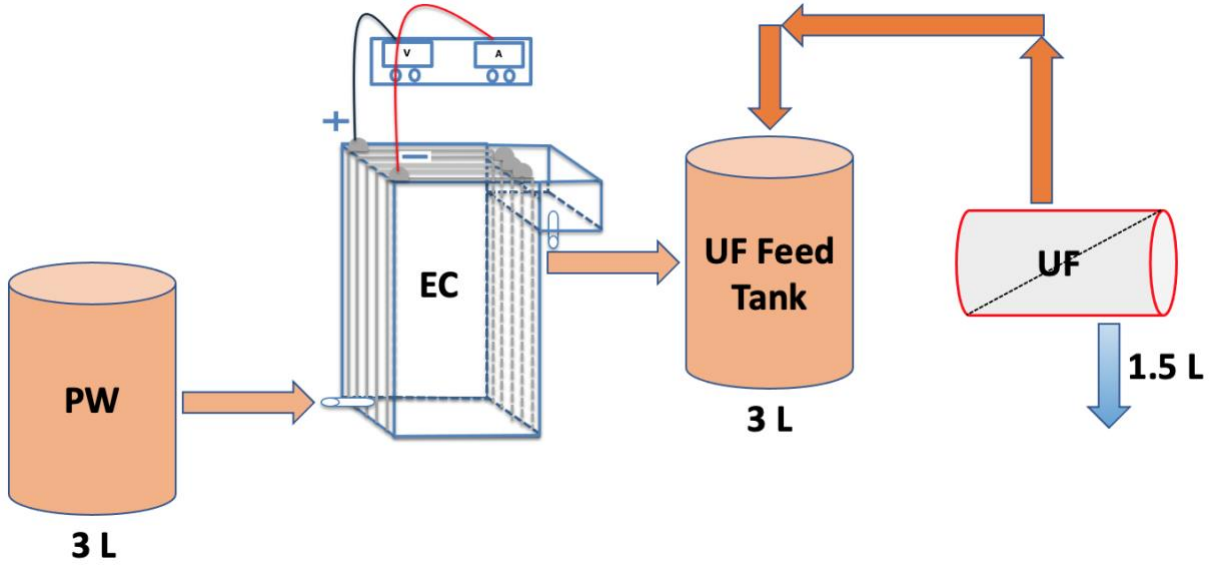

Fig. 2. Schematic representation of the EC UF system investigated here.

5.2.4. MD Testing

The MD system used here is shown schematically in Fig. 3. A custom-made acrylic module was used. The total membrane surface areas was 40 cm^2. The flow channel was 2 mm deep. A commercial 0.65 μm pore size PVDF membrane (Millipore, Billerica , MA, USA) was used. PTFE spacers (ET 8700, Industrial Netting, Minneapolis, MN, USA) provided mechanical support and also promoted mixing. Peristaltic pumps (Masterflex I/P, Cole Parmer, Vernon Hills, IL) were used to pump the feed and permeate streams at 0.5 L/min on opposite sides of the membrane. The temperature of the permeate and feed tanks was maintained at 20 ^oC and 60 ^oC using an external chiller and heater, respectively (PolyScience, Niles, IL, USA). Experiments were run for about 8 hours. We aimed for about 40% water recovery.

5.2.5. MDC Testing

MDC experiments were conducted in four stages. Initially MD was run till about 10% of the feed was recovered in the permeate (about 115 min operation). The feed tank was then placed in a water bath containing ice that was constantly replaced. After about 15 min the temperature of the feed reached 20 ^{o}C. It was then kept in the water bath for an additional 5 min. After removal of the precipitate, the feed tank was returned to the MD system, and MD recommenced once the temperature reached 60 ^{o}C. The precipitate was recovered and analyzed for the feasibility of mineral recovery. Precipitation occurs in the feed tank and rather than on the membrane, increasing water recovery.

Using the weight change of the permeate tank, the water flux was calculated and normalized using the average flux during the first 15 min of operation. The permeate conductivity was measured using a conductivity meter (VWR, Radnor, PA, USA). Each MD and MDC experiment was conducted using 500 ml of PW with no pretreatment or with PW pretreated using EC UF.

An experiment was also conducted where the membrane was regenerated and reused. A membrane regeneration cycle was applied once 40% of the feed volume was recovered or there was no permeate weight increase for 20 min. During regeneration, DI water was pumped on both sides of the membrane at 0.5 L/min for 1 hour.

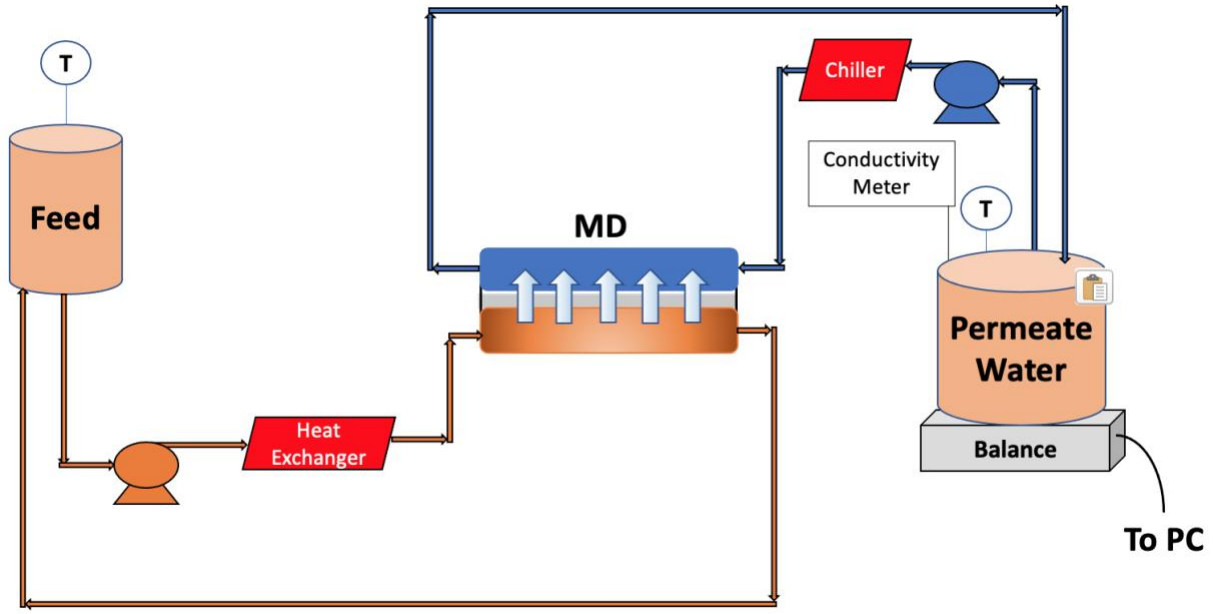

Figure 3. Diagram of MD system used in this study.

5.3. Results and Discussion

5.3.1. Wastewater Characterization

Table 2 gives the water quality parameters of the PW received from the hydraulic fracturing facility as well as after EC UF. The TDS is about 4 times higher than seawater. The major inorganic species present are chlorine (83,117 mg/L), sulfate (545nmg/L), calcium (2,396 mg/L), magnesium(383 mg/L), potassium (1,089 mg/L), and sodium (55,902 mg/L). A high concentration of calcium ions could lead to membrane scaling due to the precipitation of calcium sulfate [33]. Here the TOC and TSS are also high being about 395 mg/L and 187 mg/L, respectively. The quality of the PW in general is highly variable, which affects the efficiency of the treatment operations. As can be seen EC UF pretreatment leads to a 94% decrease in TOC and 59% decrease in TSS. A corresponding decrease in turbidity is also observed. However as expected, EC does not lead to a significant change in the concentration of dissolved ions.

Table 2. Water quality for PW as received and after EC UF pretreatment operation.

Parameter	Unit	PW*	EC/UF PW**
TDS	mg/L	137,247	121,037
TOC	mg/L	395	23.3
TSS	mg/L	187	76.4
Turbidity	NTU's	147	0.6
pH	-----	7.4	7.3
Conductivity	µS/cm	166,300	312,000

Note: *PW as received; ** PW after EC UF pretreatment.

5.3.2. Membrane Characterization

The water contact angles are given in Fig. 4. before and after MD and MDC. Initially the PVDF membrane is hydrophobic as the water contact angle is 145°. As water vapor and not water should pass through the membrane pores this is important for MD operation. During MD, Fig. 4 indicates that the water contact angel decreases. This is due to adsorption of dissolved organic compounds on the membrane surface. The water contact angle is 75° after MD and 65° after MDC in the absence of pretreatment. This could enhance scale deposition on the layer of adsorbed organic compounds, especially if they are polar [34]. Thus, reduction of the TOC and TSS by EC UF is important to reduce membrane fouling. As shown in Fig. 4. when the PW is pretreated with EC UF after MD and MDC the contact angle is 112° and 119°, respectively. This significantly higher than in the absence of pretreatment.

Fig. 5 gives corresponding SEM images of the membranes before and after MD and MDC. The feed flow rate was 0.5 L/min, which results in a Reynolds number of 200 (laminar flow). The SEM images of membrane before MD as well as after, MD, MDC, in the absence and presence of pretreatment are given in Fig. 5A, 5B, 5C, 5D, and 5E, respectively. As can be seen some deposition (highlighted with circle) on the membrane surface is observed after MD, while very minimal deposition is observed after MDC and specifically MDC with pretreated feed PW. Thus,

pretreatment using EC UF followed by MD and then crystallization appears to suppress fouling on the membrane surface.

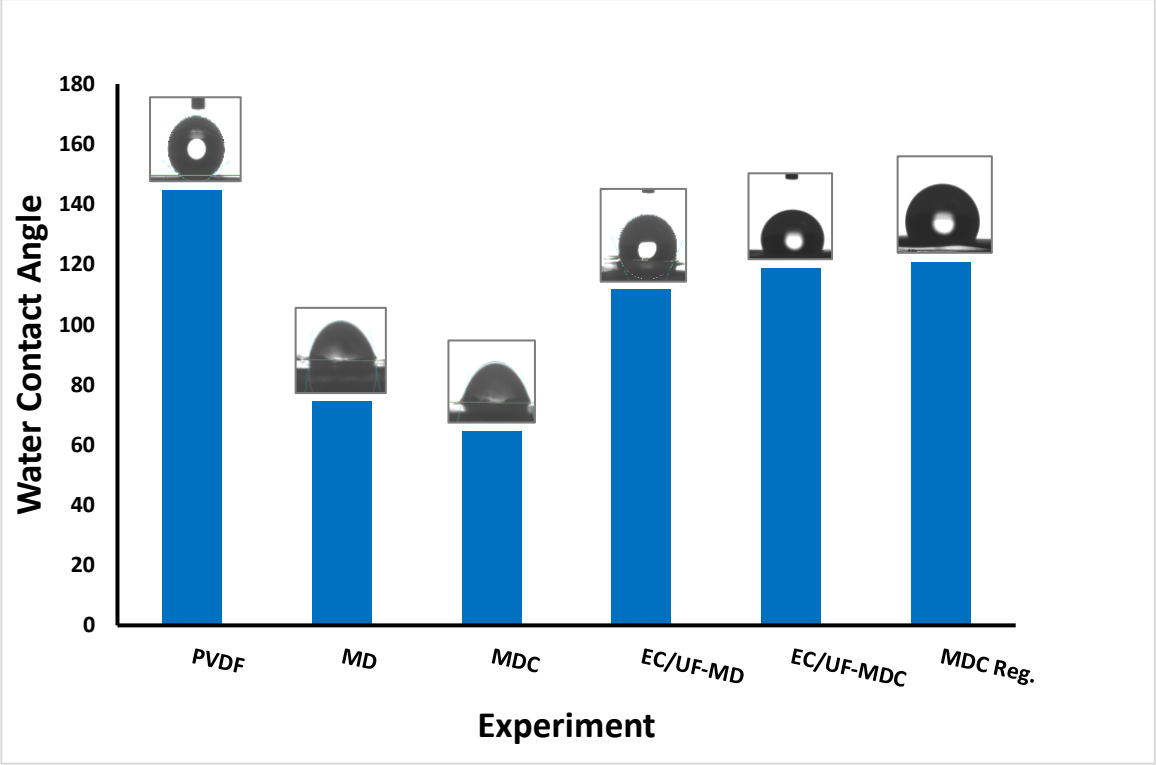

Fig. 4. Water contact angle measurements. PVDF refers to virgin membrane; MD and MDC refer to PVDF membranes after MD and MDC, respectively, whereas EC/UF-MD and EC/UF-MDC refer to the same unit operations where the feed is pretreated using EC/UF; MDC Reg. is for the membrane after regeneration.

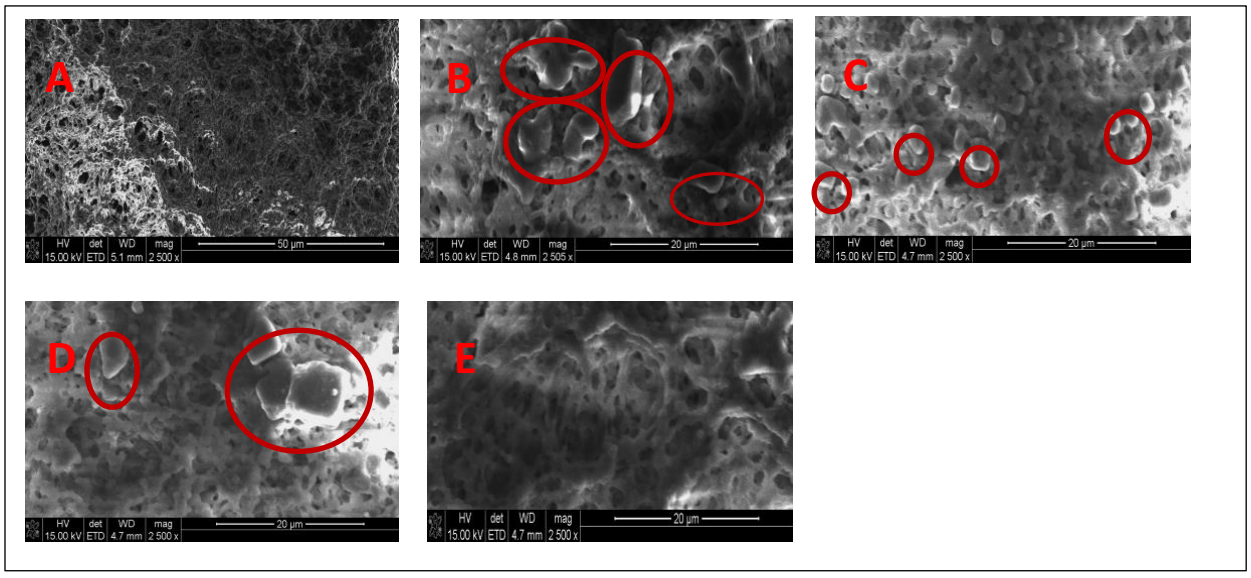

Fig. 5. SEM images for (A) virgin membrane; (B) after MD; (C) after MDC; (D) after MD using EC/UF pretreated PW; (E) after MDC using EC/UF pretreated PW.

Results for elemental analysis of the membranes using EDX are given in Table 3. The average elemental ratios of carbon/fluorine (C/F) and oxygen/fluorine (O/F) for the PVDF membranes after MD and MDC are given in Table 3. As can be seen the C/F and O/F ratios are high for PVDF membranes after MD and MDC in the absence of pretreatment, which is mainly due to the organic fouling. The contact angle, SEM, and elemental analysis results indicate that reducing both TOC and TSS by EC UF leads to a significant decrease in deposition of colloidal material and organic compound on the membrane surface. The results highlight the importance of using an integrated pretreatment step to minimize membrane fouling when treating highly impaired wastewaters such as hydraulic fracturing PW.

Table 3. The C/F and O/F atomic percent ratios for PVDF membranes

Membranes	C/F atom percental ratio	O/F atom percental ratio
After MD (no pretreatment)	2.4	0.37
After MDC (no pretreatment)	1.8	0.23
After EC/UF-MD	1.7	0.19
After EC/UF-MDC	1.6	0.12

5.3.3. EC Performance

EC is an electrolysis process where aluminium ions are continuously generated at the anode while reduction of water takes place at the cathode leading to the formation of hydrogen gas and hydroxide ions. A range of polyaluminum hydroxides are produced in the solution when coagulating ions (aluminum and/or hydroxide ions) undergo hydrolysis in water. These aluminum hydroxides can help destabilize suspended, emulsified, and dissolved contaminants, which can aggregate and precipitate as sludge or lift up to the surface as flocs. The aggregated aluminum hydroxides will adsorb soluble organic compounds. The low-density flocs that rise to the surface, age, densify and sediment. This adsorption phenomenon is a result of the liquid-solid intermolecular attractive forces between the organic solutes in solution and the large surface area of the porous flocs that form. TOC removal is calculated using the following equation (TOC%) $=((X_{pw}-X_{rw})/X_{pw}) \times 100$, where, X_{pw} and X_{rw} are the TOC in the PW and the treated water after EC, respectively.

Table 4 gives the TOC as well as removal for different currents. TOC removal increases from 65% to 74% as the current increases from 1 to 3 A. To obtain higher removal, higher currents and longer reaction times are needed [31,32]. However, it is also important to ensure the EC process is practical. Based on our earlier studies [31] long reaction times are undesirable as they lead to holding very large volumes of water. This leads to a rapid increase in the capital cost for the process as well as an increased footprint. Based on the higher TOC removal a current of 3 A

is used here. Reduction of TOC is essential in order to minimize adsorption of organic species that will lead to fouling of the membrane and reduced fluxes. Further when working with hypersaline solutions, it increases the risk of scale formation on the membrane surface which in turn can increase the likelihood of water passing through the membrane pores and the membrane surface will be much more hydrophilic. This will lead to failure of the process.

Table 4. TOC removal at different currents (1, 2, and 3), 5 min reaction time and using 5 Al electrodes in BPS configuration.

Current (A)	TOC ppm	RE of TOC %
1	140	65
2	124	68
3	102	74

5.3.4. UF Performance

While sedimentation may be used to recover the treated water from the sludge, it is unlikely to be practical. Long sedimentation times will lead to the need for very large holding tanks. This in turn will lead to higher capital costs and footprint. Further given the high variability in the quality of the PW, even from the same well, the sedimentation time is likely to be highly variable [32]. Here UF is used to rapidly remove the EC sludge from the supernatant. It should be noted that floc aging is necessary in order to allow the coagulation processes to occur whereby dissolved organic compounds and colloids are adsorbed onto the growing aluminium hydroxide flocs. Here the average floc aging time is about 7 min. In a continuous process a holding tank will be required after the EC unit to allow the floc to age.

EC was conducted on the entire 3 L feed after which UF was conducted at a TMP of 65 kPa. The variation of permeate flux with operating time is shown in Fig. 6. First, the membrane was tested with DI water to determine the initial DI water flux of 270 L m^{-2} h^{-1} bar^{-1}. Then, the membrane was used to treat EC pretreated PW using constant pressure filtration. The flux

gradually decreased to 71 L m^{-2} h^{-1} bar^{-1} and stabilized at 70 L m^{-2} h^{-1} bar^{-1} even after 100 min. The decrease in flux with time is due to the deposition of flocs on the membrane surface. The membrane was regenerated after 50% recovery of the feed water by simply recirculating the hot water for 1 hour. The DI water flux was determined again. The DI water flux is similar to water flux during the first run (within 5%). The result suggests that EC was effective at flocculating the dissolved organic compounds and particle matter that could plug the pores. Further, regenerating the UF membrane by circulating hot water is sufficient to remove flocs from the membrane surface resulting in a minimal irreversible fouling.

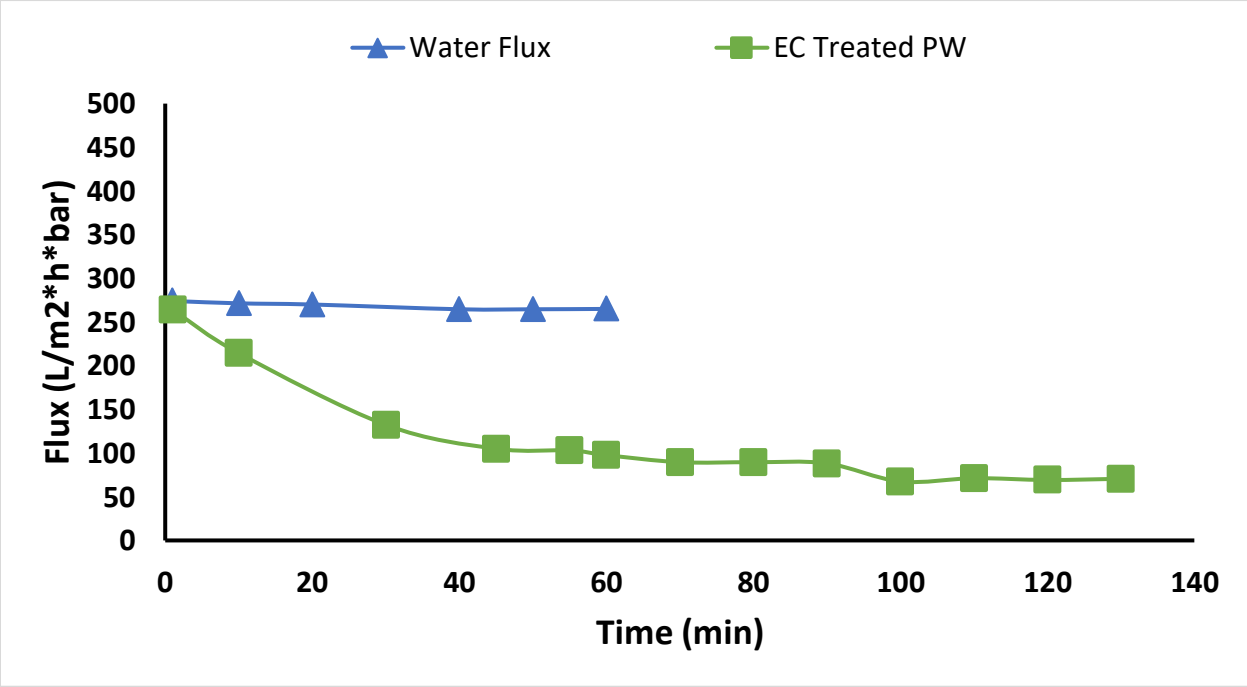

Fig. 6. DI water flux and flux of permeate stream after EC.

5.3.5. MD and MDC Performance

Normalized flux versus time for MD and MDC of PW in the absence pretreatment is shown in Fig. 7. Total water recovery is shown in Table 5. As can be seen the flux for MDC shows 4 slight jumps. This is due to the mode of operation used here. After 10% of the feed volume was

recovered as permeate MD was stopped and the feed was cooled to promote precipitation as described in the methods section. The jump in permeate flux occurs when MD recommences. However as can be seen in Fig. 7, the permeate flux and water recovery are higher for MD integrated with crystallization. The conductivity of the permeate samples collected from both MD and MDC experiments gradually increased. For both MD and MDC, they were within 5% of each other. The average value is shown in Fig. 7. The maximum value reached was about 90 μS/cm. This is due to passage of volatile inorganic compounds such as ammonium chloride from the feed stream to the permeate stream [35]. The concentration of ammonium ions in the permeate samples was in the range of 10 to 18 mg/L. Table 5 summarizes the volume of feed water recovered. As can be seen water recovery is significantly enhanced using MDC. Here, the use of MDC reduced the risk of supersaturation and precipitation on the membrane surface.

Crystallization showed no significant differences in membrane performance when comparing MDC and MD of EC UF pretreated PW (see Fig. 8,). This is probably due to first reducing the layer of adsorbed organic species, which further decreases the likelihood of precipitation of dissolved salts on the membrane surface. The conductivity for both MD and MDC experiments increased. The values were within 5% of each other.

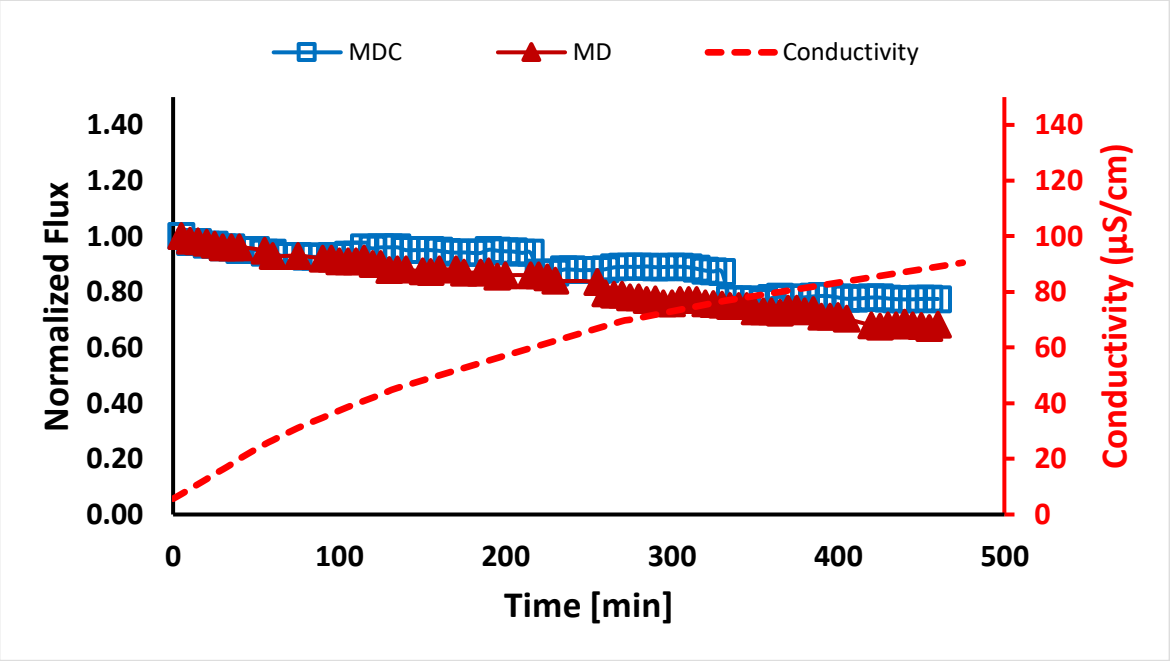

Fig. 7. Normalized flux versus time for the membrane using MD and MDC for PW at 0.5 L/min flow. MDC was conducted in four stages, each running for about 115 min.

Table 5. Summary of water and salt recovery after MD and MDC at 0.5 L/min flow

Experiment	**Water Recovery (ml)**
MD of PW	175
MDC of PW	205
MD of EC/UF Pretreated PW	220
MDC of EC/UF Pretreated PW	215
MDC of PW with regeneration (1st Cycle)	200
MDC of PW with regeneration (2nd Cycle)	201

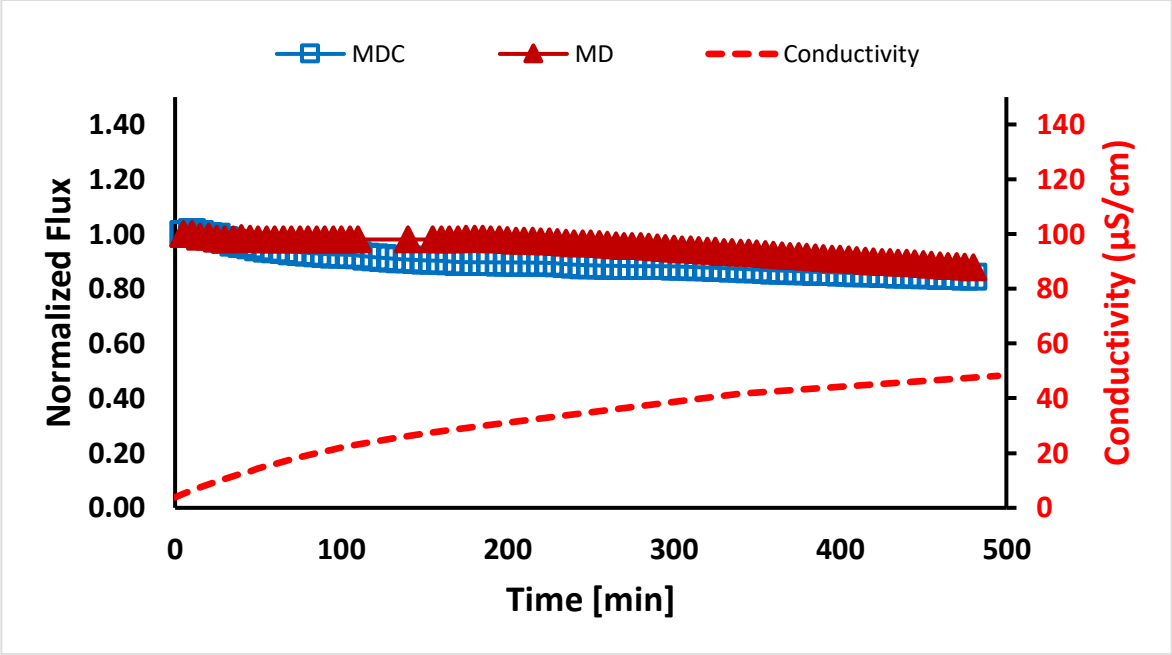

Fig. 8. Normalized flux versus time for MD and MDC for EC UF pretreated PW at 0.5 L/min flow. Note: MDC was conducted in four stages, each running for about 115 min.

An average salt recovery of 42 kg/m^3 was obtained after cooling the feed to 20 ^{o}C for 5 min. X-ray diffraction (XRD) was used to identify the purity of the salts produced. Fig. 9 shows the XRD patterns of the crystals produced during MDC. The results indicate that the main salts formed are halite (sodium chloride), a monovalent ion of low crystallinity, as shown in Fig. 9.

Finally in order to determine if membrane fouling is reversible and to determine the feasibility of membrane regeneration the membrane was regenerated after 40% of the feed volume was recover and then run with a new batch of 500 mL feed. As can be seen in Table 5, during the second run 40% water recovery was achieved. The normalized fluxes for the two runs were within 10% of each other as shown in Fig. 10. The membrane could be easily regenerated simply by pumping water on both sides of the membrane for 1 hr. Importantly the conductivity for both runs was with 5% of each other. The average values are given in Fig. 10.

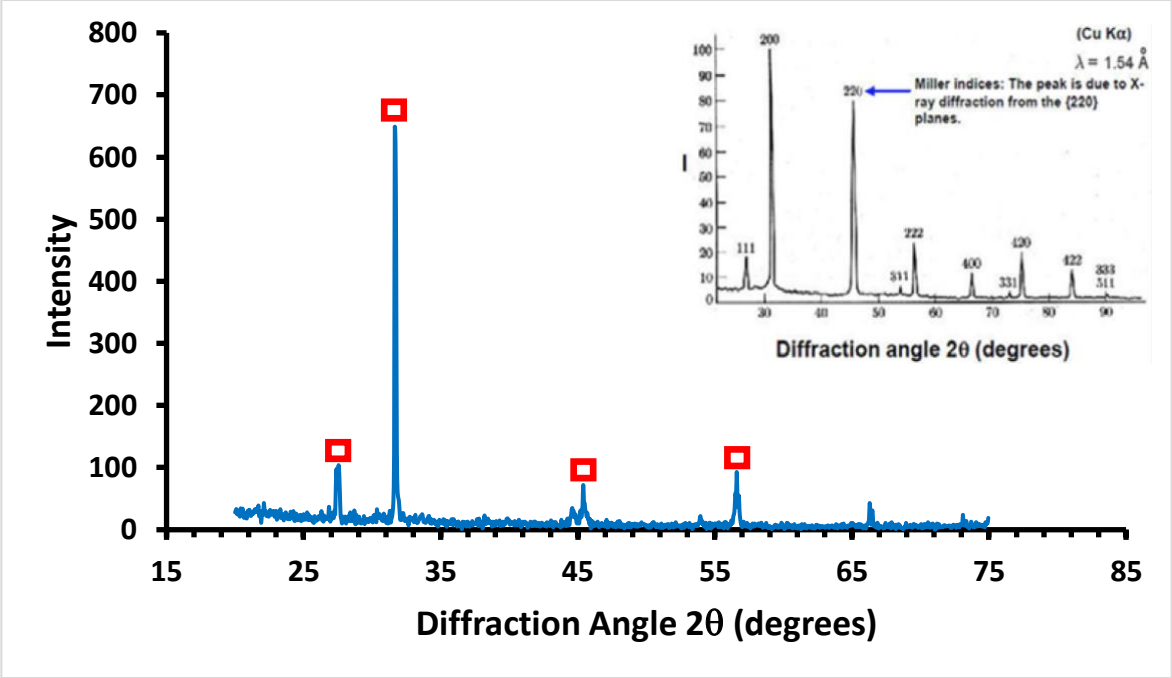

Fig. 9. XRD analysis of the salts produced during MDC. The XRD spectrum of NaCl (standard) is shown in the inset.

Taken together the results obtained here suggest that EC UF MDC could be a viable process to treat hydraulic fracturing PW. Our earlier studies [32] indicate that the water recovered after MD is suitable for discharge. This could lead to tremendous water savings, minimize the need for deep well injection and lead to a more sustainable process. However, it is important to realize that dissolved volatile species can pass through the membrane during MD. Consequently, the recovered water will contain these species. Thus, the quality of the recovered water will depend on the feed water quality. This work highlights the importance of integrating unit operations when developing wastewater treatment strategies.

In order to optimize the process further studies should be conducted using a continuous process. This will help determine the required floc aging time and the maximum feasible water recovery using MDC. It is essential that membrane wetting be avoided where water passes directly from the feed to the permeate. Thus, a practical upper limit for water recovery exists. Similarly,

membrane regeneration should be conducted such that irreversible fouling is avoided. It is important the regeneration leads to flux recovery. In addition, MDC could lead to sludge mining. This in turn may provide a valuable byproduct that could help offset the cost of water treatment.

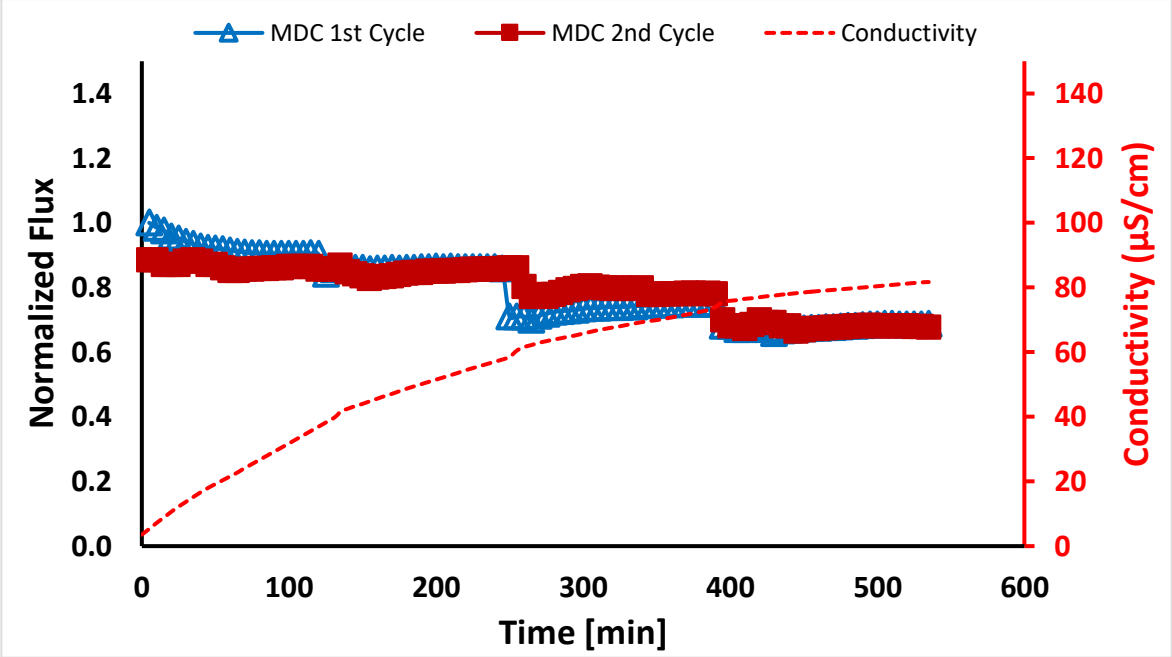

Fig. 10. Normalized flux versus time for MDC of a feed stream of PW. The membrane was regenerated and run a second time. Note: MDC 1st Cycle run till 40% water recovery, after membrane regeneration 2nd cycle run till 40% water recovery.

5.4. Conclusion

This investigation is one of the first studies to investigate the used of EC UF MDC for treating hypersaline hydraulic fracturing PW. The combined EC UF MDC process was used to treat hydraulic fracturing PW. The PW had a high TDS, TSS, and TOC. Nevertheless, 40% of the feed volume was recovered. It is likely greater water recovery is possible. By using crystallization after MD, precipitation on the membrane is suppressed. Adequate reduction in the PW TOC can be achieved using EC. UF is then used to efficiently remove the particulate matter produced during EC. The stability of the membrane is critical. Here a commercially available PVDF membrane was used. The membrane was robust and easily regenerated.

The EC UF MDC technology can have an impact on Water Resources/Oil & Gas Companies as surface and groundwater form about 80% of the water used in hydraulic fracturing. The process developed here could be used to treat and reuse PW. The possibility of mining the precipitate from the crystallization tank could lead to valuable byproducts that could help offset the cost of water treatment. The data collected from treating PW can be used to evaluate the integrated EC UF MDC process, which can guide further development of the process.

Acknowledgements

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Chapter 6. Pilot-Scale Study of EC–MF System for the Treatment of Produced Water (Design, Establishing, and Testing)

Abstract

The integrated EC–MF system is a promising technique to pretreat and reuse produced water (PW). A 37.5 L EC reactor is currently being evaluated at Texas Tech University (TTU). The EC reactor was built based on experiences gained from working with a laboratory scale (1 L) EC reactor. The design and establishment of the EC–MF system are discussed in this work. The pilot-scale system has a capacity of treating 3600 L/day PW. The system layout is also discussed in this chapter. This system is designed based on 70% feed water recovery. Samples will be analyzed for turbidity, total suspended solids, TSS, and total organic carbon, TOC. To consider PW is ready to be further treated by TTU group, a reduction of 95, 90, and 70% is required for turbidity, TSS, and TOC, respectively.

6.1. Design Specifications

Based on a 500 ml production capacity obtained using a Mechanical Vapor Compression Membrane Distillation (MVC–MD) having a 20% recovery rate of water at Texas Tech University (TTU), 2500 L/day of feed water is needed for the MVC-MD unit. Further, because the EC–MF system having a water recovery rate of 70% is required, 3600 L feed for the EC reactor per day is needed. EC reactor with 37.5 L reaction volume will be used for 8 hours/day at 5 min reaction time to obtain a total EC treated PW of 3600 L/day. In addition, 4 hours per day will be required for cleaning the aluminum (Al) electrodes used in this study. In general, 12 hours per day will be the total operation time of the EC–MF system.

Figure 1 is a schematic diagram of the EC reactor. PW will be pumped into the reactor and evenly distributed by a distribution tube connected to the EC inlet. There will be 22 individual Al

electrodes (11"×20") with 0.04" thickness installed vertically inside the EC reactor with an inlet electrode distance of 10 mm. The first and last electrodes will be directly connected to a DC power supply in bipolar series (BPS) electrode arrangement. A reverse polarity switch will also be connected to the DC power supply to enable the direction of the current to alternate every 30 s. A current range of 1 to 8 A with 5 min reaction time will be applied to treat PW. Based on the TOC removal efficiency, the current will be adjusted.

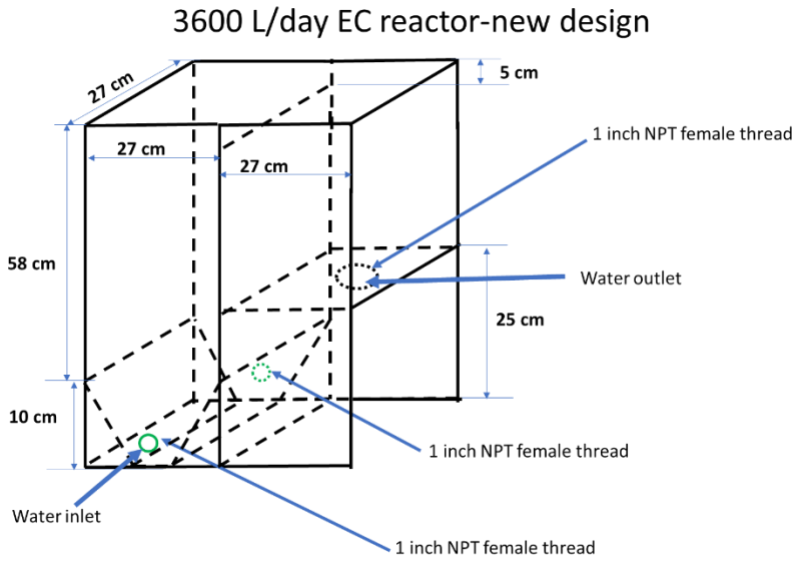


Figure 1. EC reactor schematic diagram.

To ensure the quality of the feed water entering the MVC–MD system, we proposed a secondary treatment using MF after the EC reactor. Based on our preliminary laboratory scale MF data, to produce 2500 L/day pretreated PW for the MVC–MD system, we need to use a membrane system with a surface area of 4.5 m^2. This calculation was obtained based on 100 L m^{-2} h^{-1} permeate flux of MF.

6.2. EC–MF System Layout and Operation

Figure 2 shows the entire flow chart of the integrated EC–MF process. The feed PW will be pumped into the reactor and electrocoagulation reaction will start in the reactor. The pretreated

PW will be pumped into a container (holding tank) from the overflow chamber of the EC reactor. The water in the holding tank will be pumped into two open-top tanks containing a submerged ceramic membrane system. The suction pressure generated by the peristaltic pumps used in this study will provide the vacuum pressure needed to push the clear water penetrating the ceramic membrane and the permeate will be collected in the MD feed tank, which will supply the feed water for the MVC-MD system.

The EC reactor will be used in continuous mode for 8 hours per day. The electrodes will be cleaned as needed. The electrodes will be taken out from the reactor and will be put into the acid cleaning tank as shown in Figure 3. A 10% nitric acid solution will be pumped into the acid cleaning tank (37.8 L) to soak the Al electrodes for 5 min, then the acid will be pumped back into the acid storage tank by the same pump (pump 6). Pump 7 will pump 37.8 L clean water (from the MD feed tank) into the acid cleaning tank to dilute the nitric acid residual. Then the 30% sodium bicarbonate solution will be pumped into the acid cleaning tank to neutralize the acid, which will be monitored via pH paper. The neutralized wastewater will be sent back to the EC feed tank by pump 6. Then, the cleaned electrodes will be ready to use. The operating protocol of the EC–MF system is summarized as descried in Appendix B.

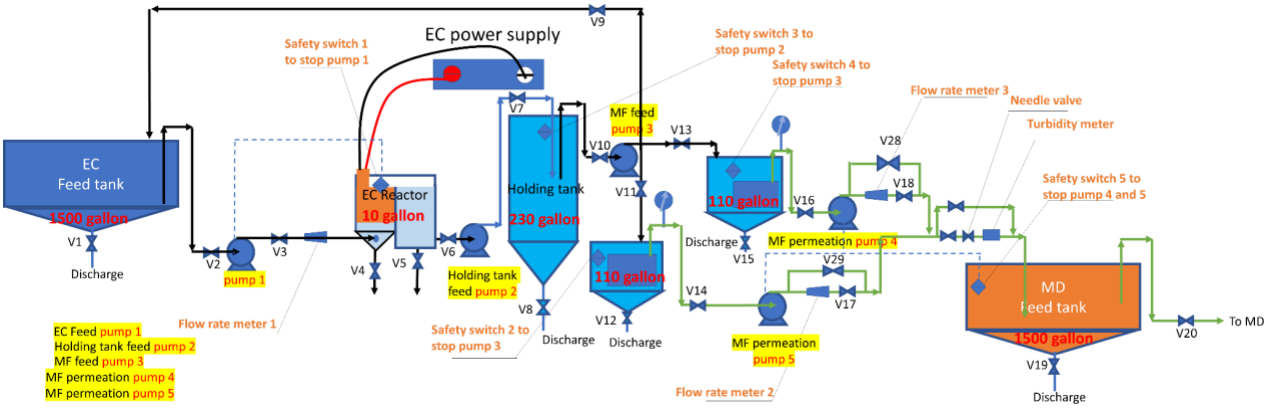


Figure 2. Flow chart of the integrated EC–MF process.

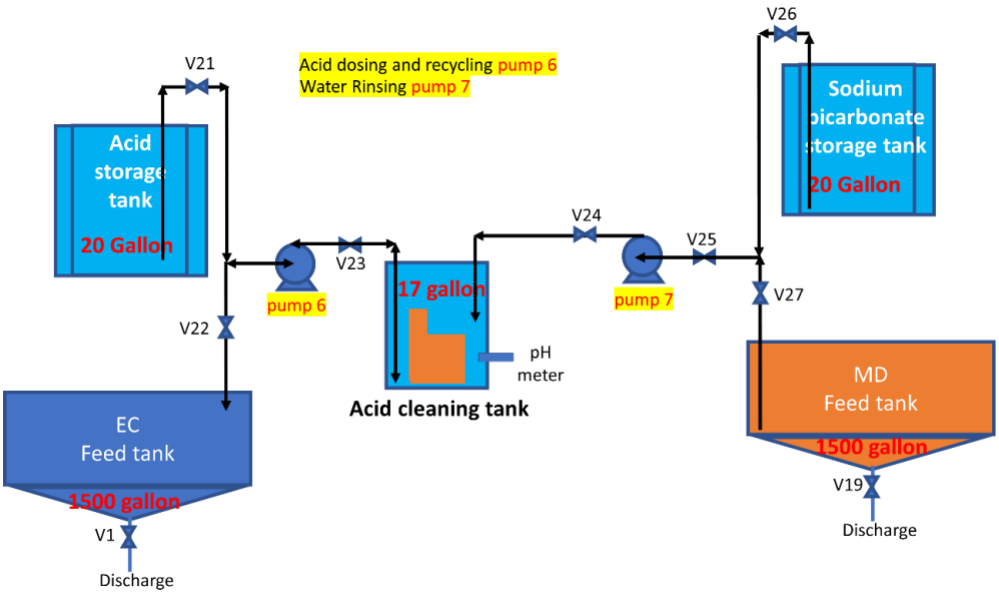


Figure 3. Acid cleaning process.

Figure 4 shows the top view of the EC–MF pilot-scale setup at TTU. The red rectangles stand for secondary containers, while blue shapes (circle and rectangle) stand for equipment units. Table A.1 summarizes all the parts ordered to build the pilot-scale EC–MF system as shown in Appendix A. All items required for establishing the EC-MF system were ordered and delivered to Oilfield Technology Center, Lubbock, TX. The EC reactor and submerged ceramic membrane system were built at University of Arkansas (U of A) and transferred to TTU. All pumps were tested and connected to level switches before transferring them to TTU. In March 2022, the EC-MF system was assembled at Oilfield Technology Center as shown in Figure 5. After establishing the whole system, a water test was performed for durability and leaks. The EC-MF system successfully passed the water test, and it is ready to be used in treating PW.

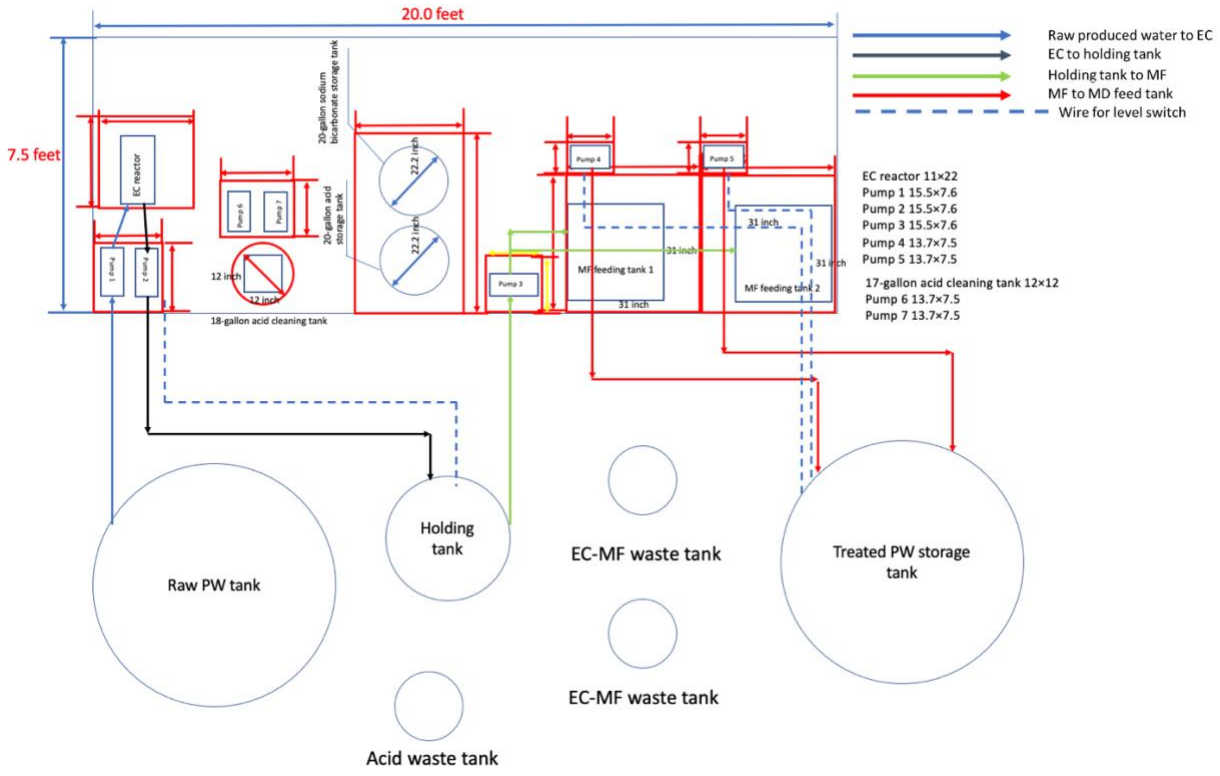


Figure 4. The EC–MF pilot-scale setup (top view in the shipping container).

Figure 5. Images of the EC-MF system assembled at OTC.

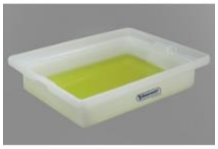
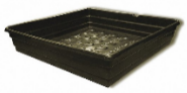
6.3. Conclusion

Based on experiences gained from working with a laboratory scale (1 L) EC reactor, the EC–MF pilot scale system was designed with a capacity of treating 3600 L/day PW. The EC–MF system was successfully passed the water test for durability and leaks. On May 20th, the EC–MF

system will be tested with PW for 5 days to evaluate the removal efficiency of turbidity, TSS, and TOC. Our aim is to treat about 3600 L/day for 5 days. The pretreated PW will be further treated using the MVC-MD. The whole system will be tested at the same time to evaluate its feasibility in effectively treating PW. During the 5 days test, we will monitor flow rate, applied current, turbidity, and pH. Several samples will be collected during the test to evaluate the TSS and TOC removal. These results will be compared to the lab results obtained at U of A. The results obtained will be evaluated on site for removal of 95% TSS, 70% TOC and 90% turbidity.

Appendix A

Table 1. List of all the items ordered to build the EC–MF pilot-scale system.

Pumps	Item	Specification	Quality	Status
Pump 1 and pump 2 (8.8inch×15.5inch) (EC feed pump and holding tank feed tank)	Drain Pan, 2 gal, Polypropylene, 22" 	https://www.zoro.com/funnel-king-drain-pan-2-gal-polypropylene-22-40092/i/G1577213/ 22inch×22inch×1.5inch	1	Arrived
Pump 3 (MF feed pump) (8.8inch×15.5inch)	Spill Tray, 5 gal Spill Capacity, 18 oz PVC fabric 	https://www.zoro.com/ultratech-spill-tray-5-gal-spill-capacity-18-oz-pvc-fabric-1330/i/G3650963/ 18inch×18inch×4.75inch	1	Arrived
pump 4 and 5 (MF permeation) (7.6 inch×13.7inch)	Rectangular Lab Tray, 7 Liter, Autoclavable PP, 10 x 15 x 3" 	https://www.calpaclab.com/rectangular-lab-tray-7-liter-autoclavable-polypropylene-10x15x3-dynalon/dl-107304	2	Arrived
Pump 6 and 7 (nitric acid and sodium bicarbonate)	**Lab Tray, Rugged LDPE, 17.5 x 23.5 x 6", 40 Liter** 	**https://www.calpaclab.com/lab-tray-rugged-ldpe-17-5x23-5x6-40-liter-bel-art/ba-162750000**	1	Arrived
EC reactor (11 inch×22inch)	**Spill Tray, Spill Capacity 17 gal, Rectangle, 30 1/2 in L x 29 1/2 in W x 6 in H** 	https://www.grainger.com/product/BLACK-DIAMOND-Spill-Tray-35LT85	1	Arrived
Acid cleaning tank (12" L x 12" W x 30" H)	**Plastic Drum with Lid - 55 Gallon, Open Top, Blue Inside: 35 1/4 x 19 7/8" (H x Diam)**	https://www.uline.com/Product/Detail/S-9945BLU/Drums/Plastic-Drum-with-Lid-55-Gallon-Open-Top-Blue?model=S-9945BLU&RootChecked=yes	1	Arrived

				
Nitric acid and sodium bicarbonate tanks Capacity: 20 Gallons Dimensions: 22.25"dia.x25.5"H	**Plastic35" x 58" x 12"Sump Capacity 75 gal. 100% High-Density Polyethylene (HDPE)** 	https://www.newpig.com/pig-utility-spill-basin/p/PAK377	1	Arrived
Plastic Drum with Lid - 55 Gallon, Open Top (wastewater and sludge storage tank from EC-MF)	DIMENSIONS: Outside with Lid: 36 x 22 3/4" (H x Diam)" 	https://www.uline.com/Product/Detail/S-9945BLU/Drums/Plastic-Drum-with-Lid-55-Gallon-Open-Top-Blue?model=S-9945BLU&RootChecked=yes	2	Arrived

Items	Specification	quantity	Status
holding tank 	**295 Gallon Vertical Plastic Storage Tank** https://www.plastic-mart.com/product/9465/houston-vt0295-42 Part Number: 9513-A-VT0295-42 Capacity: 295 Gallons Dimensions: 42" dia. x 55"H Availability: In Stock Qty. In Stock: 2 Ships From: TX	1	Arrived 
20 Gallon Double Wall Tank (For nitric acid storage) 	Part Number: PB-01-1073 Capacity: 20 Gallons Dimensions: 22.25"dia.x25.5"H Ships From: CA https://www.plastic-mart.com/product/8783/20-gallon-gemini-dual-containment-tank-system	1	**Arrived**
20 Gallon Double Wall Tank (For sodium bicarbonate storage)	Part Number: PB-01-1073 Capacity: 20 Gallons Dimensions: 22.25"dia.x25.5"H Ships From: CA https://www.plastic-mart.com/product/8783/20-gallon-gemini-dual-containment-tank-system	1	**Arrived**

			
20 Gallon Double Wall Tank (For waste nitric acid storage) 	Part Number: PB-01-1073 Capacity: 20 Gallons Dimensions: 22.25"dia.x25.5"H Ships From: CA https://www.plastic-mart.com/product/8783/20-gallon-gemini-dual-containment-tank-system	1	A**rrived**
140 Gallon Spill Containment Tray (secondary container for MF feed tank) 	Part Number: N-42771 Capacity: 140 Gallons Dimensions: 45"L x 45"W x 17"H Availability: In Stock Ships From: OK, TX https://www.plastic-mart.com/product/3356/140-gallon-spill-containment-tray-42771	2	 Arrived
Hydrogen detector	https://www.mcmaster.com/71095K71/	1	Arrived
Hydrogen detector accessories	Telephone Cord	1	Arrived
Hydrogen detector accessories	Remote with Buzzer for Early-Warning Surface-Mount Hydrogen Detector	1	Arrived
Membrane filtration feed tank	110 gallon semi-square tank Part # SST-3127 with stand https://www.polytankco.com/semi-square_tanks.html	1	Ordered
Turbidity meter	HF Scientific MTOL+ Online Process Turbidimeter	1	Arrived
Flow rate meter	Vortex flow meter SV5150 Flowrate meter for the EC feeding line https://www.ifm.com/us/en/product/SV5150 Measuring range 1.8...32 l/min	1	Arrived
Flow rate meter	Vortex flow meter SV3150 Flowrate meter for the two MF permeation lines https://www.ifm.com/us/en/product/SV3150 Measuring range 0.5...10 l/min	2	Arrived
	**CPVC 1" True Union Ball Valve Socket End ANSI** https://www.toolots.com/true-union-ball-valve-c9179-q61f-6c-25-5.html	33	Arrived
	**CPVC 2" True Union Ball Valve Socket End ANSI** **https://www.toolots.com/true-union-ball-valve-c9179-q61f-6c-50-1.html** **for discharge valves of the submerged membrane filtration tanks and the EC reactor**	5	Arrived
Tubing and fittings (by estimation)	3/4" X 10' Plain End Schedule 80 PVC Pipe https://pvcpipesupplies.com/3-4-x-10-schedule-80-pvc-pipe-h0800075pg1000.html	1	Arrived

Chemicals (HNO3, NaHCO3)			Not ordered
EC feeding pump 1 	**Model: M6-12L/YZ35-PPS** **Flow rate: 12L/MIN** www.good-pump.com	1	Arrived 
Holding tank feeding pump 2	**Model: M6-12L/YZ35-PPS** **Flow rate: 12L/MIN** www.good-pump.com	1	Arrived
MF feeding pump 3 	**Model: M6-12L/YZ35-PPS** **Flow rate: 12L/MIN** www.good-pump.com	1	Arrived
Submerged membrane filtration pumps 4 and 5/acid dosing pump6/sodium bicarbonate pump7 	**Model: M6-6L/DZ25-6L-PPS** **Flow rate: 6L/MIN** www.good-pump.com https://www.good-pump.com/cplist-41496.html	4	Arrived
Tubing for peristatic pumps	(Three rolls with two sizes)	1	Arrived 
Reactor	(0.3m L X 0.3m W X 1.1m H)	1	Arrived
DC power supply	ITech IT6953A DC Power Supply 600W 150V / 10A https://www.tequipment.net/ITech/IT6953A/DC-Power-Supplies/?gclid=CjwKCAiAmrOBBhA0EiwArn3mfLQPCfVQ9iaQ0tDTU8iFNTEFbhgOy1enC3PWHnnv7MPPYQsUGZubVhoCCCEQAvD_BwE	1	Arrived 
Reverse polarity controller		1	Fabricated
Electrodes	0.04" Aluminum Sheet (48" X 144") three full sets (63 electrodes in total)	3	Arrived
Electrode cleaning tank	17 Gallon PE Open Top Rectangular Tank Dimensions: 12"L x 12"W x 30"H	1	Arrived 

Submerged ceramic membrane	One set of membrane module contains 9 pieces of membrane elements (540*250*6mm) Total area=2.16 square meters (Two membrane modules are needed)	1	Arrived 
Membrane filtration feed tank	110 gallon semi-square tank Part # SST-3127 with stand https://www.polytankco.com/semi-square_tanks.html	1	Arrived
Vertical Mounted Chemically Compatible Liquid Level Switches	https://www.omega.com/en-us/level-measurement/level-switches/lvn60-70-series/p/LVN-70	6	Arrived
Hydrogen sulfide detector		1	Arrived
Water leakage detector in the secondary containers	Reliance Controls THP205 Reliance Sump Pump Alarm with Flood Alert, 9 V Battery, 6 Ft Wire Sensor, 105 Db, White https://www.amazon.com/Reliance-Controls-Corporation-THP205-Alarm/dp/B000IF6URO/ref=sr_1_45?keywords=pump+alarm&qid=1637617381&sr=8-45	8	Arrived

Appendix B

The operating protocol of the EC–MF system is as following.

1) For EC reaction, the valves V2, V3, V6, and V7 will be opened. Pump 1 will start to fill the reactor with water. Once the water reaches the electrodes, the power supply will be turned on. The EC treated water will be pumped from the overflow chamber of the EC reactor to the holding tank by the holding tank feed pump 2.
2) For MF, Once the holding tank reached 65% volume capacity, the MF feeding pump 3 will pump the water into MF feed tank 1 and 2, respectively. Valves V14, V16, V17 and V18 will be opened. The pumps 4 and 5 will start to run once the water levels of the MF feed tanks are high enough to soak the entire ceramic membrane elements. Back wash the membrane will be applied when the membrane flux goes lower than 50 L m^{-2} h^{-1}.
3) For Electrode cleaning, the electrodes will be placed vertically into the acid cleaning tank. Valves V21 and V23 will be opened. A 10% nitric acid solution will be pumped into the acid cleaning tank to soak the electrodes for 5 min. Then by reversing the pump flow direction, the acid will be pumped back to the acid storage tank. Valve V21 will be closed once the acid cleaning tank is empty. Valves V24, V25, and V27 will be opened, and 37.8 L of clean water will be pumped from MD feed tank to the acid cleaning tank by pump 7 to dilute the nitric acid residual. Then, valve V27 will be closed and valve V26 is opened. The sodium bicarbonate solution is slowly pumped into the acid cleaning tank till the pH of the water is closed to 7. Once the pH is closed to 7, valve V21 is closed and valve V22 is opened. Then the pump 6 will be run reversibly to empty the acid cleaning tank by pumping the water into EC feed tank.

Chapter 7. Conclusions and Future Work

The highly impaired PW generated from hydraulic fracturing contains a wide range of contaminants including high total dissolved solids (TDS) concentration, high total suspended solids (TSS), polar and non-polar organic compounds, and low surface tension dissolved species. The need to recycle, and reuse PW from hydraulic fracturing operations is essential to preserve water resources and manage wastewater disposal. It is very challenging to convert PW from wastewater to a valuable product. PW can be treated for deep well injection, reuse to stimulate new wells, and discharge into lakes and rivers etc, by applying several conventional primary, secondary, and tertiary separations, respectively. To meet the discharged water standards, using only a single unit operation to treat PW is not sufficient and not possible for long term operation at high performance.

To address most of the drawbacks faced by using only conventional techniques, the use of hybrid membrane processes is necessary. In this dissertation and based on the membrane driving force, hybrid membrane processes are summarized to hybrid pressure, partial pressure, concentration, and electrically driven membrane processes as well as dual membrane processes. The performance of different hybrid membrane processes is addressed under several design and operating parameters to produce high quality freshwater from highly impaired PWs.

The batch electrocoagulation (EC) method was used to determine appropriated operating conditions for pretreating hydraulic fracturing PW. In this work, the electrode arrangements, current, reaction time, initial pH, and inter electrode distance were investigated to optimize the EC operating conditions. The results reported here indicate that bipolar series (BPS) electrode configuration consumed more electrical energy while it had better TOC removal than MPP and MPS electrode configurations. A high removal of turbidity, TSS and TOC was achieved for PW

tested here using applied current of 1 A with 5 min reaction time at pH 7 and a 10 mm inter electrode distance. The level of turbidity, TSS and TOC removal depends strongly on the quality of the PW.

In addition, the integrated EC–MF–MD process was investigated for treating hydraulic fracturing PW having a very high TDS. This process can concentrate the rejected stream to the solubility limit of the dissolved salts. Precipitation on the membrane surface was suppressed and occurred in the feed tank by reducing the temperature of the feed tank relative to the feed entering the MD module. The results reported in this dissertation showed that EC can successfully reduce the PW TOC to 67 mg L^{-1} and MF can efficiently remove the particulate matter. Three different membranes with different surface properties were tested to evaluate the MD membrane performance and stability. The ideal membrane is the one showing a high flux at high TDS and being resistant to breakthrough. It is likely that based on the TDS and other properties of the PW the ideal membrane will be determined.

The combined EC–UF–MDC process was also evaluated for treating hydraulic fracturing PW. A recovery of 55% of the feed volume was achieved using the integrated EC–UF–MDC. Precipitation on the membrane surface was mitigated by applying crystallization after MD. A high TOC removal was obtained when using EC as a pretreatment step for PW. The particulate matter was successfully removed by applying UF directly after EC. A high flux membrane at high TDS and resistant to breakthrough is necessary to achieve a good MDC membrane stability. The TDS and other properties of the PW are essential to determine what train of treatment is required to achieve high recovery of both water and mineral. The data collected from treating PW can be used to evaluate the integrated EC–UF–MDC system, which can further lead to the next step of establishing a pilot scale process.

The pilot-scale EC–MF system was designed and established for pretreating PW. Our plan is to run the EC–MF system for 5 days and evaluate the removal efficiency of turbidity, TSS, and TOC. The EC–MF system was designed with a capacity of treating 3600 L/day of PW. The pretreated PW will be further treated using the MVC-MD. The whole system will be tested at the same time to evaluate its feasibility in effectively treating PW. During the EC–MF test, we will monitor flow rate, applied current, turbidity, and pH. Several samples will be collected during the test to evaluate the TSS and TOC removal. These results will be used to determine the feasibility of using hybrid membrane processes for treating PW in large scale running continuously for 5 days.

For future work, conducting MDC experiment in continuous mode is essential to evaluate the long-term durability of the membrane in MDC system to achieve continuous high recoveries of both water and minerals at high rates. In addition, it is necessary to extend the research on recovering sludge after MDC for sludge mining as future work. Moreover, this research indicated the necessity of making an ideal membrane that is resistant to wetting and provides high flux, which can be considered as a future focus to improve membrane properties in MDC. Development an ideal membrane for MDC will result in significant capital and operational cost savings.