

THESIS

TREATMENT OF SHALE OIL AND GAS PRODUCED WATER USING MEMBRANE  
DISTILLATION COMBINED WITH EFFECTIVE PRETREATMENT

Submitted by

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In partial fulfillment of the requirements

For the Degree of Master of Science

Colorado State University

Fort Collins, Colorado

Spring 2019

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## ABSTRACT

### TREATMENT OF SHALE OIL AND GAS PRODUCED WATER USING MEMBRANE DISTILLATION COMBINED WITH EFFECTIVE PRETREATMENT

Fossil energy is indispensable for society development. Shale oil and gas as unconventional energy resource plays an important role in improving the energy security of U.S. But the exploitation of shale oil and gas is accompanied by substantial freshwater consumption and wastewater generation. The wastewater generated from shale oil and gas production contains large amounts of salts, particles, and petroleum-associated pollutants, inevitably imposing harmful consequences to the ecological environment if not properly treated. Effective treatment of shale oil and gas wastewater, ideally for beneficial reuse, is essential in promoting sustainability of shale oil and gas production at the water-energy nexus.

In this thesis, I am focusing on developing an integrated treatment train that enables effective treatment of shale oil and gas produced water. Membrane distillation (MD), an emerging membrane desalination technology, was performed in tandem with simple and inexpensive pretreatment steps, namely precipitative softening (PS) and walnut shell filtration (WSF). A laboratory-scale MD system was designed and built at Colorado State University, and produced water generated from the Wattenberg field in northeast Colorado was collected and treated by the PS-WSF-MD system. My results demonstrated that PS removed various particulate, organic, and inorganic foulants, and thus mitigate fouling and scaling potential of the produced water. WSF displayed exceptional efficiencies ( $\geq 95\%$ ) in eliminating volatile toxic compounds including benzene, ethylbenzene, toluene, and xylenes (BTEX) along with additional gasoline and diesel range

organic contaminants. With pretreatment, the water vapor flux of MD decreased by only 10% at a total water recovery of 82.5%, with boron and total BTEX concentrations in the MD distillate meeting the regulatory requirements for irrigation and typical discharge limits, respectively. The use of pretreatment also led to robust membrane reusability within three consecutive treatment cycles, with MD water flux fully restored after physical membrane cleaning. The results of this thesis highlight the necessity of pretreatment prior to MD treatment of produced water and demonstrate the potential of the developed treatment train to achieve a cost-effective and on-site wastewater treatment system that improves the sustainability of the shale oil and gas industry. At last, an economic and technical assessment of MD-based wastewater treatment system was performed. The cost of the treatment system developed in this thesis was evaluated, and the results indicated that the cost of MD-based treatment system is around \$0.29-\$0.87/barrel. Further investigation is needed to validate the economic feasibility of MD-based treatment system when applied at full-scale in the oil and gas fields.

## ACKNOWLEDGEMENTS

I would like to express my gratitude to all those who helped me during my experiments and the writing of this thesis. My deepest gratitude goes first and foremost to Dr. Tong, my advisor, for his constant encouragement and guidance. He has walked me through all the stages of M.S. education. Without his consistent and illuminating instruction, this thesis could not have reached its present form.

Second, I would like to express my heartfelt gratitude to Dr. Carlson, who provided me the convenience to get access to the shale oil and gas produced water which from the production well in Colorado. Dr. Carlson gave me valuable technical advice and encouraged the work of this thesis spiritually. And I want to thank Dr. Zahran for taking time out of his busy schedule to participate in my M.S. defense and give me advice.

Last my thanks would go to my family for their financial and physical help and great confidence in me all through these years. My parents Yuanhong Feng and Yongjun Zhang took care of our family including my son for a long time, and they didn't ask for anything in return. My wife Yuchen has always supported my decision and helped me in every way. I also owe my sincere gratitude to my teammate Xuwei Du who gave me her help and time in experiment and data processing.

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## CHAPTER 1 INTRODUCTION

Fossil energy is the most important energy source and accounts for the vast majority of the total energy consumed in the world. According to the EIA outlook published in 2018<sup>1</sup>, oil and natural gas are still the vastly dominant energy sources in 2017 and will continue to be the case until 2050.(Figure 1) Due to the global dependence on oil and natural gas, geologists and related enterprises began to search for new oil reservoirs in tight shale formation in addition to conventional sandstone formation.[1, 2] Shale oil and gas in low permeability formation were not effectively extracted until horizontal drilling and hydraulic fracturing techniques were developed.[3-5] In 2000, shale gas production in the United States accounted for only 2 percent of total natural gas production, but ten years later this number increased to 23 percent in total natural gas production or 0.14 TCM (Trillion Cubic Meter).[4] Horizontal drilling and hydraulic fracturing are responsible for fast development in this industry. In addition, the sharp increase in shale oil production reversed the long-term decline of American oil production since 2008. As of March 2014, the shale oil production in the U.S. was 3.6 million barrels per day, accounting for almost half of national crude oil production.[6] As shown in Figure 2, shale plays are distributed in 48 states in the U.S., with Pennsylvania, Texas, Colorado, Oklahoma, North Dakota, Wyoming as the major regions of shale oil and gas production.

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<sup>1</sup> Source from: [www.eia.gov/pressroom/presentations/Capuano\\_02052018.pdf](http://www.eia.gov/pressroom/presentations/Capuano_02052018.pdf)

### Energy production (Reference case)

quadrillion British thermal units

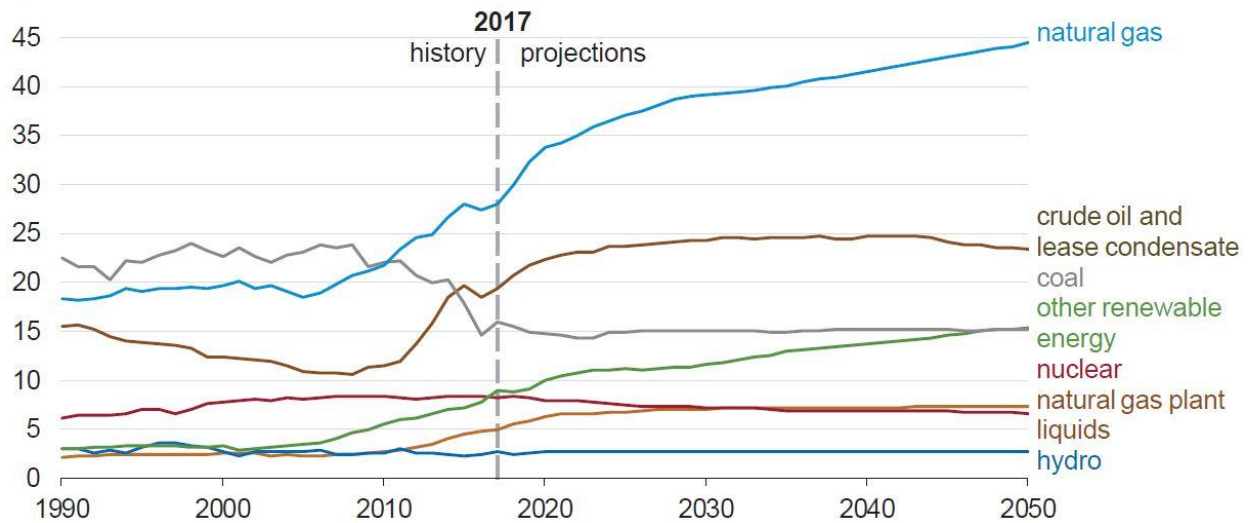


Figure 1. EIA energy production accounting and prediction, natural gas accounts for the largest share of total energy production. Source from EIA - Annual Energy Outlook 2018.

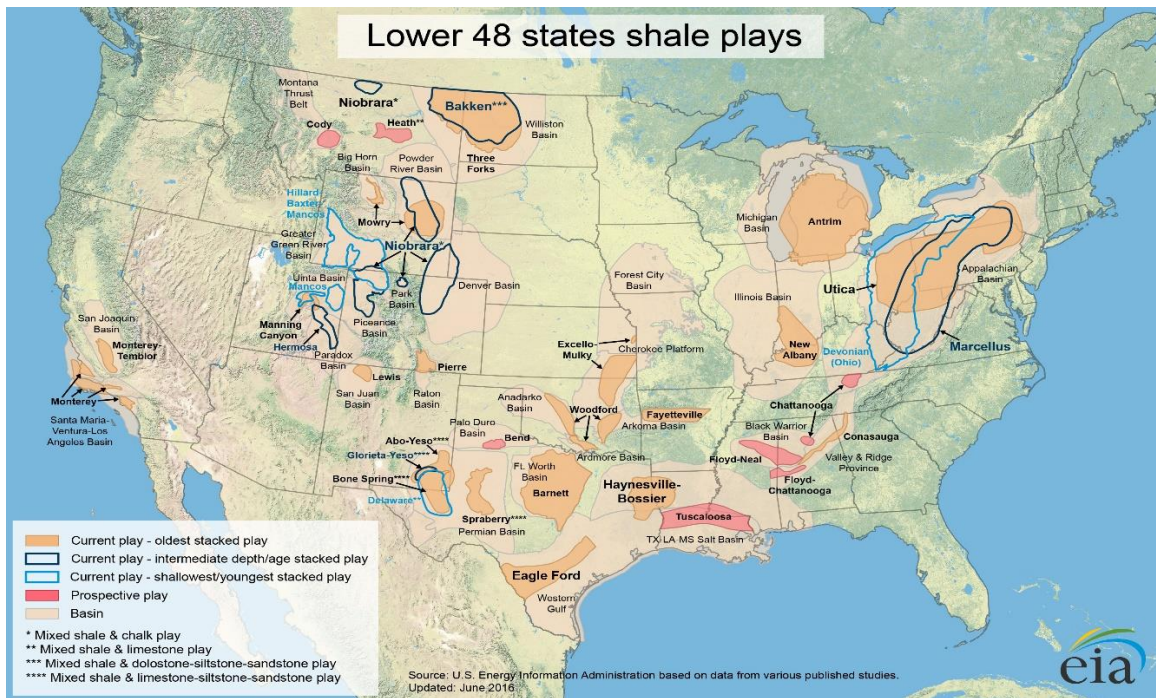


Figure 2. Lower 48 states shale plays, and lots of unconventional oil and gas resources are present in those shale plays. Source from EIA oil and gas exploration, resources and production maps (6/30/2016), [www.eia.gov/maps/maps.htm](http://www.eia.gov/maps/maps.htm).

The booming development of shale oil and gas industry has brought about related water resources problems. Hydraulic fracturing requires a large amount of fresh water as the main component of fracturing fluid. The backflow of fracturing fluid and the subsequent produced water will pollute water resources and soils if not treated accordingly.[7-11] Produced water is referred to the aqueous brine found in the same formations as oil and gas. When the oil and gas flow to the surface, the produced water is brought to the surface with the hydrocarbons. Produced water contains some of the chemical characteristics of the formation from which it was produced. Up to 20,000 cubic meters of fresh water can be used to create one fracture in one well. Figure 3 shows the volumes of water consumed by fracking one well in the US during 2011-2014 according to U.S. Geological Survey (USGS). In the shale oil and shale gas producing regions of Colorado, such fresh water is obtained from surface water and groundwater as well as a small amount of recycled wastewater from the same industry.[12] Therefore, the development and production of shale oil and gas have undoubtedly increased the pressure on the environment.

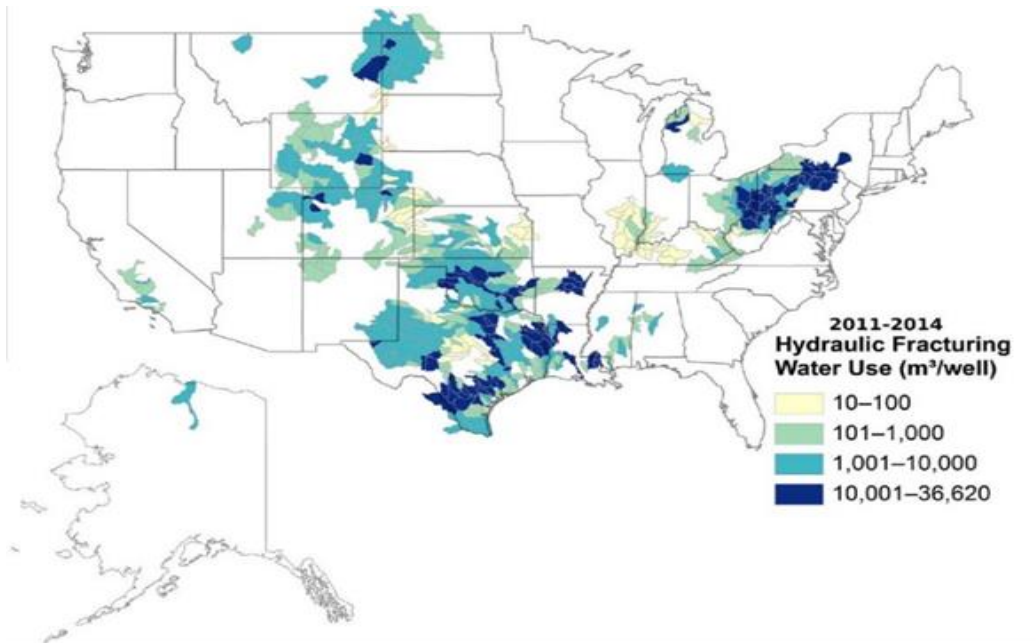


Figure 3. USGS map showing water use from hydraulic fracturing between 2011 and 2014. Hydraulic fracturing consumes large amount of water in most production area. One cubic meter of water is 264.172 gallons. Source from USGS (6/30/2015), [www.usgs.gov/media/images/percentage-hydraulic-fracturing-use](http://www.usgs.gov/media/images/percentage-hydraulic-fracturing-use)

Hydraulic fracturing is followed by a backflow production period, which can last up to four weeks, and approximately 10 to 70 percent of the fracturing fluid will flow back to surface.[4, 9, 13] The early flowback fluids will most likely be chemically similar to fracturing fluids and will not have high total dissolved solids (TDS).[14] Also, the development and implementation of new fracturing technologies, such as foam fracturing and anhydrous fracturing, have the potential to reduce or eliminate the use of fracturing fluid in the future. After entering the formal production process, the produced water in the formation will be discharged together with a small percentage of a remaining fracturing fluid. The intensity of wastewater generation in this period is far less than the flowback period, but it will accompany the entire life of the production of oil and gas wells. Thiel et al.[15] made a rough estimation that in 2015 the volume of the unconventional oil and gas produced water was around 570 million cubic meters per year. With the boom of shale oil and gas industry, the amount of produced water will undoubtedly continue to increase. More

importantly, produced water is often hypersaline, containing even more salts than seawater.[15] This special wastewater also contains petroleum pollutants and minerals including normal occurring radioactive materials (NORMs) from the tight shale and near production formation.[10, 16] Figure 4 shows the shale oil and gas produced water collected in Wattenberg field, Colorado. The brown color and high turbidity indicate the high level of contaminants in the wastewater. When comparing with the conventional oil and gas produced water, this hazardous produced water possesses higher contents of TDS, suspended particles and NORMs, and must be properly treated to minimize their environmental impact. The unconventional oil and gas industry has consumed a large amount of fresh water for fracturing, while producing a large volume of hazardous wastewater. This creates a dual challenge of water scarcity and pollution, and effective treatment of shale oil and gas wastewater for beneficial reuse will address this important issue at the water-energy nexus.

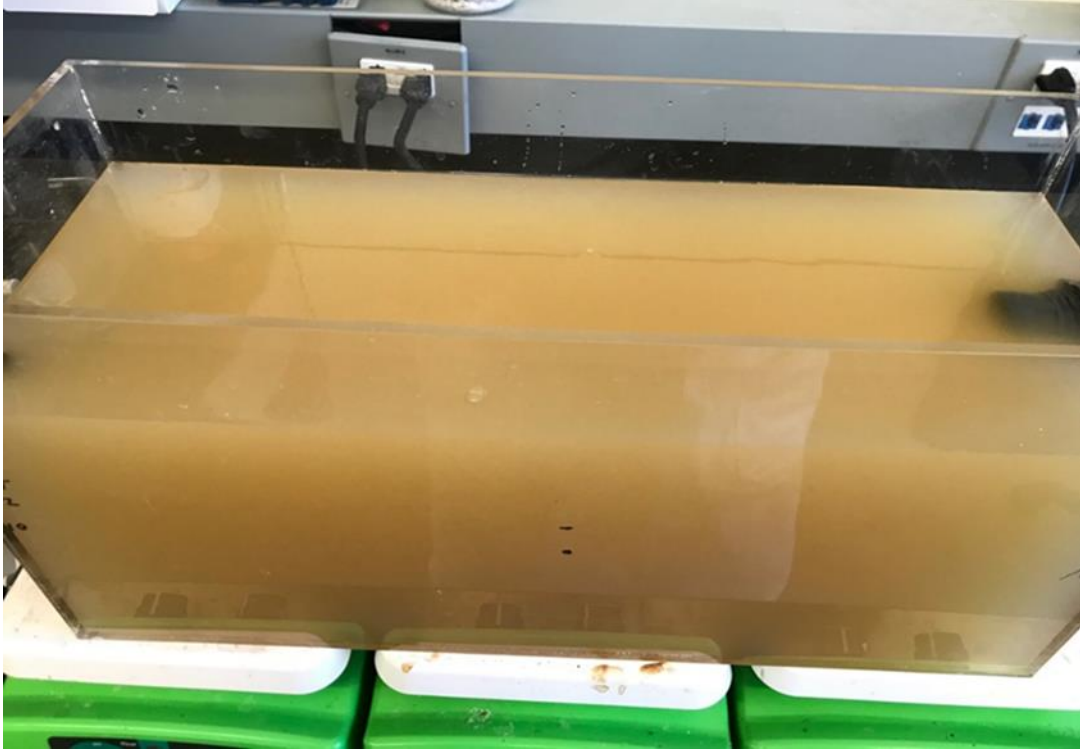


Figure 4. Shale oil and gas produced water collected in Wattenberg filed located in Colorado's Denver-Julesburg Basin. The photo is taken by Zuoyou Zhang at Colorado State University.

As for shale oil and gas produced water, the daily output of each well is not very high according to professionals and publications.[9, 15] Most wells only produce less than 100 cubic meters of water per day,[9, 15] which is perfectly suited for on-site produced water treatment equipment. At present, there are several treatment or disposal methods (off-site treatment) potentially for produced water of shale oil and gas: (1) Collect the production water together and inject it into deep wells after simple treatment; (2) Transfer shale oil and gas produced water to municipal wastewater treatment plant followed by discharging to a local waterway, but this strategy is inhibited by US EPA now; (3) Transfer produced water to industrial wastewater treatment plant followed by reusing of the treated effluent or discharging into a local waterway.[2, 4, 17] For deep-well injection, there are risks that produced water can contaminate groundwater (through aged broken well casing and contaminant move between ground layers) and induce

seismic activities.[18-20] The associated transportation, pre-treatment, and well maintenance costs can be significant. For municipal wastewater treatment plant which is used before US EPA inhibited, the high salinity, NORMs and oil contaminants of produced water, cannot be effectively removed when it was discharged into the natural water bodies. For example, the level of TDS in Monongahela River in Pennsylvania rose to 900 mg/L in 2008 compared to the standard quality of 500 mg/L, partly due to shale gas produced water disposal into municipal wastewater treatment facilities.[3] For industrial wastewater treatment plant, the disadvantages include the high costs of wastewater treatment facilities and the following produced water transportation. Therefore, more effective, more economical, and safer shale oil and shale gas produced water treatment-and-reuse technologies are urgently needed, in order to reduce environmental problems and make the development of oil and gas industry sustainable.

In general, there are two reasons for utilizing the current off-site disposal methods as mentioned. Firstly, different from conventional produced water from sandstone reservoirs, the difficulty of dealing with physical and chemical properties of shale oil and gas produced water is related to their hydrocarbon source rock that is tight shale formation (shale oil and gas are also oil and gas resources with low maturity and no migration). The complex composition of shale oil and gas produced water hinders the development of on-site methods and renders treatment technologies for conventional produced water not applicable to shale oil and gas produced water. Secondly, conventional shale oil and gas wells are relatively less dispersed and produce much more water compared to shale oil and gas oil and gas wells. The high yields of conventional oil and gas produced water make large-scale treatment with conventional techniques such as CFU (compact flotation unit) and hydro cyclones a suitable approach.



In terms of the physical and chemical properties of shale oil and shale gas produced water, it contains dissolved solids (dissolved minerals), petroleum organic pollutants, fine dissolved particles (suspended solids) and NORMs in the formation. It is common that the TDS of produced water exceeds 100,000mg/L (e.g., in Marcellus gas production areas and shale oil production areas in the western United States), which is well above the salinity limit that conventional high-efficiency desalination device (e.g., reverse osmosis, RO) could deal with (the salinity limit of RO treatment is only 60,000 - 70,000 mg/L of TDS).[16, 21] Shale oil and gas produced water also contains petroleum organic pollutants, such as toxic volatile benzene, toluene, ethylbenzene, and xylenes (BTEX). The concentrations of these pollutants commonly exist in the produced water in the order of mg/L,[22-24] which are significantly higher than the water quality standards of national pollutant discharge elimination systems (NPDES) (i.e., less than 100 µg/L according to USEPA). Also, the fine suspended particles in shale gas produced water are very different from those in conventional oil and gas produced water. Through my observation, it is found that these particles are difficult to precipitate in the short term at room temperature and higher temperatures, which brings difficulties to the treatment of this kind of wastewater. So the physical settlement is very difficult to make the suspended solids settling down in a short period of time. Considering the economic cost of oil companies and the interests of the local residents, an effectiveness wastewater treatment system for shale oil shale gas produced water should have the following features. First, an on-site treatment system is favorable to avoid long-distance transportation. Second, this treatment system should have a small energy footprint and a low maintenance cost. Further, the selected treatment technologies should be able to effectively remove harmful organic and inorganic pollutants from the produced water, in order to meet the regulatory requirement for

environmental protection. Additionally, this system will ideally recover a maximum amount of freshwater for beneficial reuse.

In this thesis, I propose an integrated on-site treatment process to effectively treat shale oil and shale gas produced water while producing high quality water product. This process includes a series of steps including precipitative softening (PS), walnut shell filtration (WSF), and membrane distillation (MD) processing. After the pretreatment of PS and WSF, the high-TDS produced water will flow into the MD system for final desalination, so as to obtain fresh water that meets potential requirements of surface discharge or irrigation. As a desalination component in the system, MD is an emerging thermal hybrid membrane distillation facility that can use thermal energy to desalinate at a lower temperature. At present, this technology has shown great potential in the fields of hazardous wastewater treatment.[25-27] Due to its thermal nature, MD can tolerate higher salinity and have low sensitivity to feedwater concentration (advantage over RO), requiring lower equipment cost and temperature than these desalination equipment such as FO (forward osmosis), MVC (mechanical vapor compressor), MED (multiple-effect distillation) and MSF (Multi-stage flash distillation).[3, 28, 29] Using MD as a field treatment equipment, where the produced water temperature is still high (approximate over 50 °C, normal MD feed temperature is about 70 °C), it can utilize this part of heat energy for desalination, which undoubtedly decreases the main heat energy consumption and thus reduces the economic cost and carbon footprint associated with this technology.[27] In addition, compared with the FO (forward osmosis) and MVC (mechanical vapor compressor) desalination equipment, MD equipment is simpler since it can increase or decrease the number of parallel membrane modules based on the corresponding production water treatment volume in the oil field. Therefore, the application of MD in the treatment system design has great potential and industrial adaptability.

However, the performance of the MD system is often limited by membrane fouling and scaling,[30] which will reduce the flux of water vapor as well as the efficiency of thermal energy usage. Previous studies have revealed that fouling and scaling of the membrane would affect the performance of MD desalination.[31-33] When MD membrane is treating shale oil and shale gas produced water with the high salinity, complex non-volatile organic components, numerous suspended solids, a high extent of fouling and scaling would occur on the membrane surface. Moreover, a recent study by Winglee et al.[34] found that volatile organic compounds potentially present in produced water were able to permeate into the distilled water of MD with water vapor. These toxic compounds deteriorate the water quality of MD distillate, constraining the reuse applications of the treated water product. Thus, pretreatment is needed before introducing the raw produced water to the MD system, in order to remove foulants, scalants, and volatile contaminants from the produced water. With such pretreatment, the rate of water vapor through the membrane, the durability of the membrane, as well the quality of treated water can be improved, which is important for the use of MD systems in the oil and gas fields.

In order to remove organic foulants and inorganic scalants in the pretreatment of shale oil and gas produced water, softening and coagulation are good pretreatment methods, which have demonstrated efficient performance in removing colloids and reducing turbidity.[35-37] Softening and coagulation also have the ability to remove a variety of inorganic pollutants from produced water.[35] Sardari et al. (2018)[38] demonstrated that the fouling problem of the membrane was effectively alleviated when Marcellus shale gas produced water was pretreated with electrical coagulation (EC) prior to MD desalination as the main treatment process. Esmailirad et al. (2015).[35] investigated methods of pretreatment of shale oil and gas produced water by using softening followed by EC, which was able to effectively remove the hardness and suspended

particles in the wastewater. Also, the authors tried the method of EC followed by softening, but this approach failed to achieve good results as before. Semblante et al.(2018)[37] pointed out that sludge generated by chemical softening will absorb part of organic matter, and chemical coagulation will reduce organic matter and remove inorganic matter such as silicon. USEPA points out in the drinking water treatment database that precipitative softening (PS) can decrease the turbidity of water, and with the increase of pH, arsenic and natural NORMs decrease significantly. However, since the softening and coagulation processes cannot remove a large percent of organic pollutants and volatile organic pollutants, adsorption filtration device can be introduced for further pretreatment. Compared with activated carbon, naturally derived walnut shell filtration (WSF) has a lower cost and longer durability, which has been used to adsorb petroleum oil and heavy metals.[39-41]

Through the above analysis, I decided to apply PS, WSF, and direct contact membrane distillation (DCMD) in sequence to create an integrated on-site shale oil and gas produced water treatment system. Figure 5 shows the schematic description of this proposed on-site wastewater treatment system. In my preliminary experiment, it was found that adding a small amount of aluminum coagulants after the softening process is indeed better than the single coagulation treatment of the produced water during oil production. Consistently, Esmailirad et al. (2015)[35] was softening first then using the EC approach to treat produced water from shale oil and gas with high oil component, which yielded good results. The EC devices are bigger, more complicated, and more expensive to build than chemical treatment methods in the reaction pool, although it produces a relatively small amount of sludge.[37] In my approach, using the precipitative softening process, a small amount of aluminum coagulants was added after the pH has increased to 10. In order to meet the requirement of the fieldwork, this relatively convenient chemical method was

used along with chemical softening by using caustic soda (sodium hydroxide). This approach has the potential to outperform EC considering the equipment size, complexity, reliability, and cost. After the PS treatment, the produced water is clarified, and the upper clear water goes into a pair of simple walnut shell filter columns. The effluent of the walnut shell filter will flow into the MD system for desalination treatment.

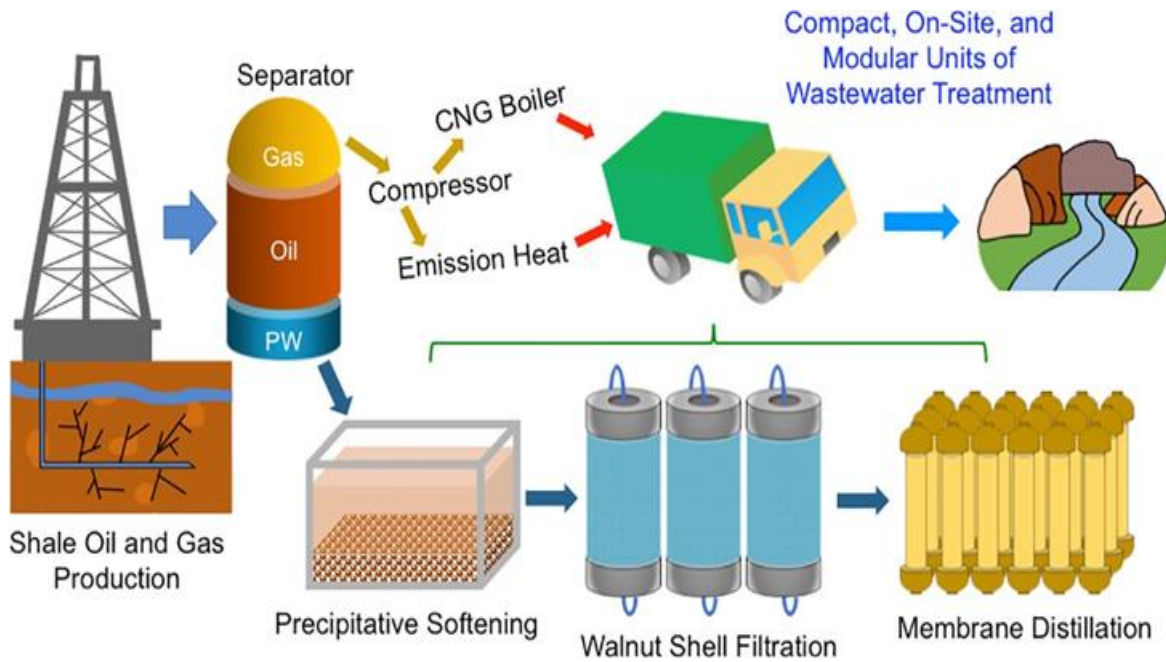


Figure 5 Schematic description of an on-site, off-grid, and mobile treatment package tailored to shale oil and gas production, utilizing the treatment chain composed of precipitative softening, walnut shell filtration, and membrane distillation. This figure is adopted from Zhang et al. (2019)[42]

The raw produced water and pre-treated produced water after PS and WSF were collected for further water quality analysis and MD desalination. The water products from MD desalination were also sampled. All of these water samples were sent to a third-party and certified laboratory (Technology Laboratory, Inc., Fort Collins, CO) for water quality analysis. The water vapor fluxes and salts rejection rates in MD desalination of produced water with and without pretreatment were compared, with a commercial flat-sheet polyvinylidene fluoride (PVDF) membrane. Three cycles

of MD treatment integrated with physical membrane cleaning were also performed to evaluate the robustness of the treatment system. Through the comparison of results, PS and WSF combined with MD was found to significantly reduce the fouling and scaling potential of produced water for the PVDF membrane and to effectively removed volatile organic pollutants. So that MD performance was more stable, and the water quality of distilled water was improved. The results show that the treatment scheme designed in this thesis was able to transform the hazardous production water of shale oil and shale gas into safe freshwater that can be discharged and reused. This treatment design has great potential to be further applied to the shale oil and gas produced water treatment in the oil field. My ongoing work is to set up a pilot-scale processing system and to evaluate this system's operating parameters and treatment efficiency in order to lay the foundation for the final field application.

In this thesis, I also analyzed the economic efficiency of this integrated treatment process. For the entire processing system, its capital expenses include the equipment cost of PS, WSF, MD, as well as the cost of related facilities such as storage tanks, control system, and site development. The operating and maintenance expenses for the treatment system include the cost of sodium hydroxide and aluminum sulfate used in the PS process, the consumption and replacement cost of the walnut shell in the WSF, the heat and electricity consumption in the MD system, and the cost of membrane replacement. The operating costs also include the sludge disposal cost of the PS process, the disposal cost of the walnut shell materials for WSF, the disposal of concentrated brine generated from MD systems, and the labor cost of the on-site operation. The cost of chemicals, filter materials, membrane, waste disposal, and labor can be estimated with relatively small uncertainties. However, the estimation of costs for MD desalination of produced water was challenging. I have gathered some literature focusing on the cost analysis of desalination of

seawater and shale gas produced water using MD system, and the authors have conducted a cost analysis on different modes of operations like the inclusion of a waste heat recovery system or different kinds of heating energy resources.[43-46] According to the estimation made by the literature, I estimate a rough treatment price of the developed wastewater treatment system.

## CHAPTER 2 The SET-UP OF A LAB-SCALE MEMBRANE DISTILLATION TREATMENT SYSTEM

Membrane distillation (MD) is an emerging technology of membrane separation. MD process uses a hydrophobic microporous membrane to separate water (vapor) from an aqueous solution containing high concentrations of solutes. Due to the surface tension of water, liquid water cannot pass through the hydrophobic pores of the membrane under normal pressure, while water vapor can pass through the pores freely. In MD aqueous solutions with different temperatures are separated by the hydrophobic microporous membrane. Since the water vapor pressure is higher on the hot side than the cold side, the water vapor generated from the hot side (i.e., typically feedwater) will go through the membrane pores to reach the cold side and achieve water separation (Figure 6). Due to its relatively low temperature needed for water purification (60 - 80 °C), this process can make full use of the waste heat and cheap thermal energy (natural gas, solar energy, geothermal energy, etc.) together with easy automation and simple equipment. As a result, MD has become an attractive separation process for water and wastewater treatment. The advantages of membrane distillation are described as follows. First, the MD process is almost carried out under normal pressure, which has inherent advantages for equipment cost and maintenance cost. Second, in MD desalination of aqueous solutions with non-volatile solutes, the distilled solution is very pure because only water vapor can pass through the membrane pores. Further, the MD process can be used to deal with an extremely high concentration of an aqueous solution. If the solute is easy to crystallize, the solution can be concentrated to a state of oversaturation. Also, the membrane modules used in MD can be easily designed in the form of latent heat recovery and have the flexibility for adapting to the fluctuation of wastewater quality and quantity, which often occurs at the oilfield. In addition, there is no need to heat the solution to the boiling point in the MD process.



As long as the appropriate temperature difference is maintained on both sides of the membrane, the MD process can be carried out.

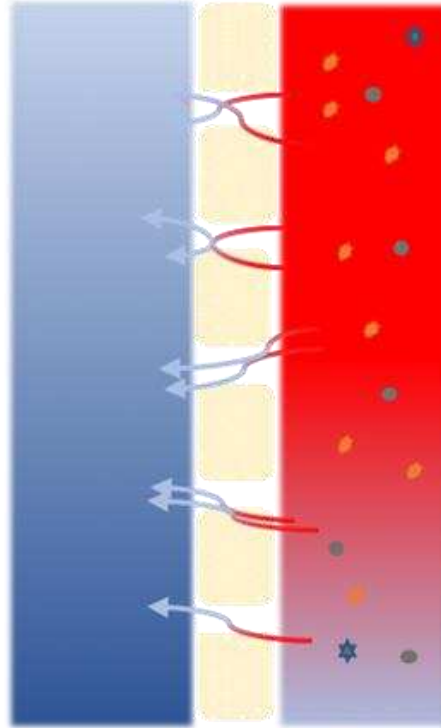


Figure 6. The mechanism of water vapor (indicated by the arrows) passing through the micro-scale pores of the membrane (white channel) from hot feedwater (red side) to cold distillates (blue side). Yellow circles stand for oil-related organic matters, gray circles stand for suspended solids, and blue stars stand for dissolved solids in the feed water.

The MD system is the core treatment process of the shale oil and gas produced water treatment chain. The first step of my thesis, therefore, is to set up a lab-scale MD system at Colorado State University. Figure 7 shows a schematic diagram of the lab-scale MD system. In this system, No.1 and No.2 are heat exchangers, No.3 and No.4 represent the chiller and heater, respectively. No.5 and No.6 are the gear pumps for the cold distilled side and hot feed side, respectively. No.7 and No.8 are the flow meter for the distilled water and feedwater flow meter, respectively. No.9 is a distilled water tank, while No.10 is a feed water tank. No.11 is a digital precise scale to measure the weight of solutions in the distillate water tank, with the recorded

values used to calculate the water vapor flux. No.12 is a conductivity meter that is used to evaluate the desalination performance of the treatment system. No.13 is membrane flow cell, with a dimension of 77mm×26mm×3 mm. No.14 is a personal computer with automatic data recording software (Winwedge).

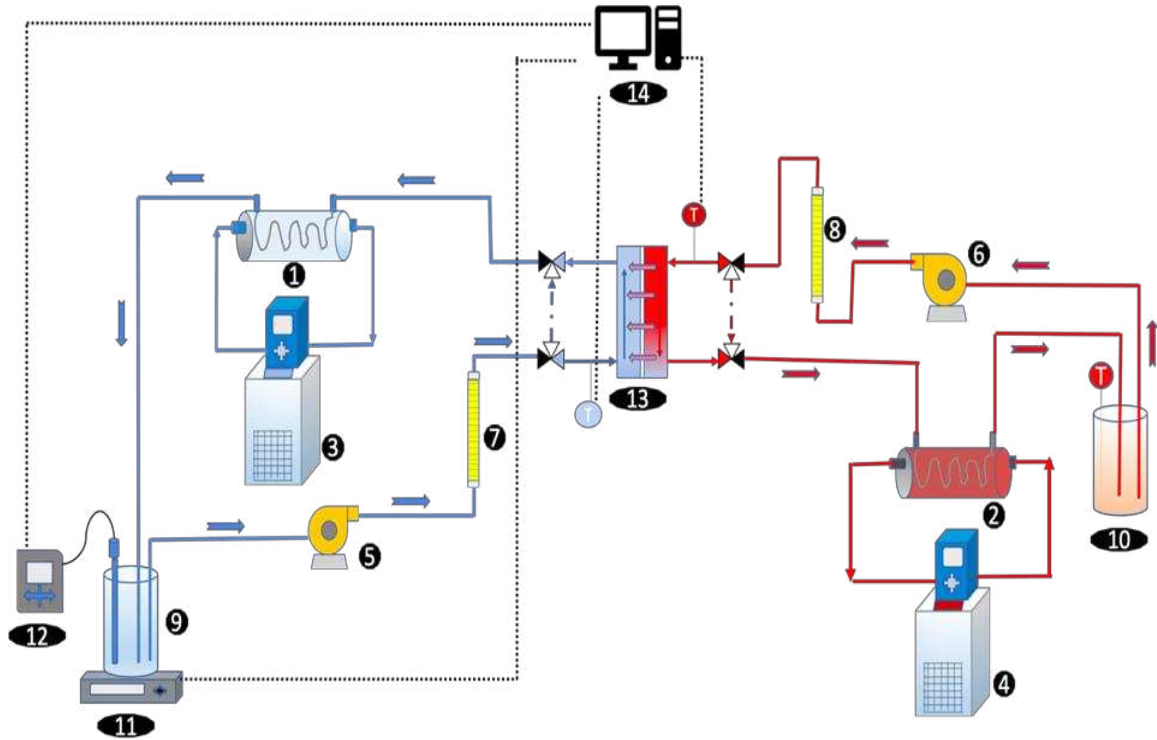


Figure 7. Equipment, pipelines and flow direction diagram of the MD system. No. 1 and 2: heat exchangers; No. 3: chiller; No.4: heater; No.5: distilled side water pump; No. 6: feed side water pump; No.7: distilled water flow meter; No.8: feedwater flow meter; No.9: distilled water tank; No.10: feed water tank; No.11: digital precise scale; No.12: conductivity meter; No.13: membrane flow cell; No. 14: personal computer with automatic data recording software.

In the MD system, the water in the right (hot) side is transformed into distilled water in the left (cold) side through the PVDF membrane in the membrane flow cell (No.13). In the flow cell (No.13), the bottom side of the membrane is facing the hot produced water while the top side of the membrane encountered the cooled permeate water. The pores in the membrane provide channels for water vapor transportation. The water vapor passes through the membrane from the

bottom (hot) side to the top (cold) side. Therefore, the weight of the distillate side increases accompanied by a decrease in the weight of the feedwater side during the MD treatment process.

The red part on the right of Figure 7 is the feed water loop. Since the feed water temperature is higher than 60 °C during the operation of the MD system, the feed water loop is marked in red in the figure. The red dotted arrow between the three-way (L port) valves on the right represents an inner circulation within which the water flow does not pass through the flow cell. Note that inner circulation is only used when flushing the system (so the temperature could be raised to the required value without affecting the MD process) and replacing the membrane. Similarly, the blue part in the left is the cycle of the distilled water loop and is marked in blue as the temperature of the entire distilled water loop is around 20 °C. The blue dotted arrow between the three-way (L port) valves on the left also represent inner circulation within which the water flow does not pass through the flow cell.

In the feedwater loop, pump No.6 will pump the hot feed solution from feed tank (No.10) into the flow meter (No.8), after which the feed solution flows into the bottom side of the flow cell (No.13) through the three-way (L port) valve. As mentioned above, the temperature in the loop is above 60 °C, and there will be steam (i.e., water vapor) being generated and penetrating through the membrane to the top side of the flow cell (No.13). Finally, the rest of the feed water will flow out from the flow cell (No.13). The water vapor penetrating to the top side of the membrane will be carried by cold clean permeate water loop, where the condensation of water vapor occurs. Once the feed water leaves the flow cell (No.13), it will go through another three-way (L port) valve which lies below the previous one, go into the heat exchanger (No.2), and return to where it starts—feed water tank (No.10) to finish the whole feedwater loop. An outside heater (No.4) will provide

the heat to the heat exchanger (No.2) through hot fluid media, and hot fluid media makes a counterflow thermal exchange with feed water in the tubes.

In the permeate water loop, pump (No.5) will pump out cold and deionized water from the distilled water tank (No.9) into flow meter (No.7), where the permeate water will further go to the top side of the flow cell (No.13) through the three-way (L port) valve. While in the flow cell (No.13), the cold permeate water will carry and condense the water vapor that penetrates through the pores of the membrane from the bottom channel of the flow cell, and flow out together through the topside channel of the flow cell (No.13). In the end, they will go back to the distilled water tank (No.9), and on its way back water's heat is exchanged through the exchanger (No.1) after passing the three-way (L port) valve left above. Similarly, the outside chiller is connected with the heat exchanger (No.1) and makes counter-flow heat exchange with the flow of permeate water. Now the permeate water loop is finished and readers should be aware that all the equipment in the process is linked through the usage of the plastic pipeline which requires thorough post-experiment cleaning.

The weight of distillate (note that the volume of permeate in the distilled water tank is calculated through the weight of distillate) and the distillate conductivity will be collected by a digital precise scale (No.11) and calibrated conductivity meter (No.12). The data will be sent to a data-receiving computer (No.14) in every minute for further analysis. Two temperature detectors were placed on the inlet of the feedwater side and the outlet of distillate side. The temperature data will be sent to the computer (No.14) in real time in every minute and will detect whether the temperatures of the system is in the required range.

When we set up the MD system ready, we tested this system's stability and performance using 1800 ml 35 g/L NaCl solutions and the commercial PVDF membrane (HVHP, Durapore, Millipore Sigma) with effective membrane area is 20.02 cm<sup>2</sup>. The test has terminated once the collected distilled water reached 1000 mL. The temperatures of the feed solution and deionized distillate were kept at 60 °C and 20 °C, respectively. The cross-flow velocities of the feed and distillate streams were 8.5 cm/s (0.4 L/min) and 7.4 cm/s (0.35 L/min), respectively. The weight and conductivity of the solution in the distillate tank were monitored continuously to calculate the flux of water vapor flux and assess membrane wetting. As shown in Figure 8, the MD system set up in this system performed steadily. The water vapor flux remained near 30 L m<sup>-2</sup> h<sup>-1</sup> (LMH) during the test from 0 h to 16.5 h (with cumulative permeate volume of 1000 mL), and the conductivity of distilled water did not increase, indicating a remarkable salt removal efficiency of this system.

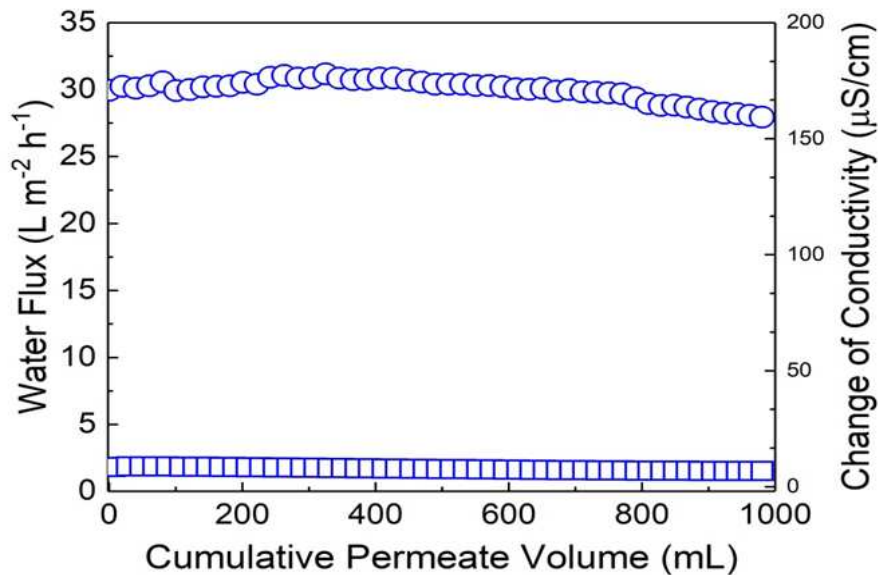


Figure 8. Test results of sodium chloride solution in the MD system, water flux and change of conductivity keep steady during the test.

## CHAPTER 3 PRETREATMENT OF SHALE OIL AND GAS PRODUCED WATER USING PRECIPITATIVE SOFTENING AND WALNUT SHELL FILTRATION

In this chapter, precipitative softening (PS) and walnut shell filtration (WSF) were used in sequence as the pretreatment process, followed by membrane distillation (MD) as the core treatment step. Figure 9 shows the pretreatment procedure and the following MD treatment. The contents of Chapter 3 and 4 have been published in the peer-reviewed journal *Desalination* (Zhang et al., 2019, *Desalination*, 454, 82-90).

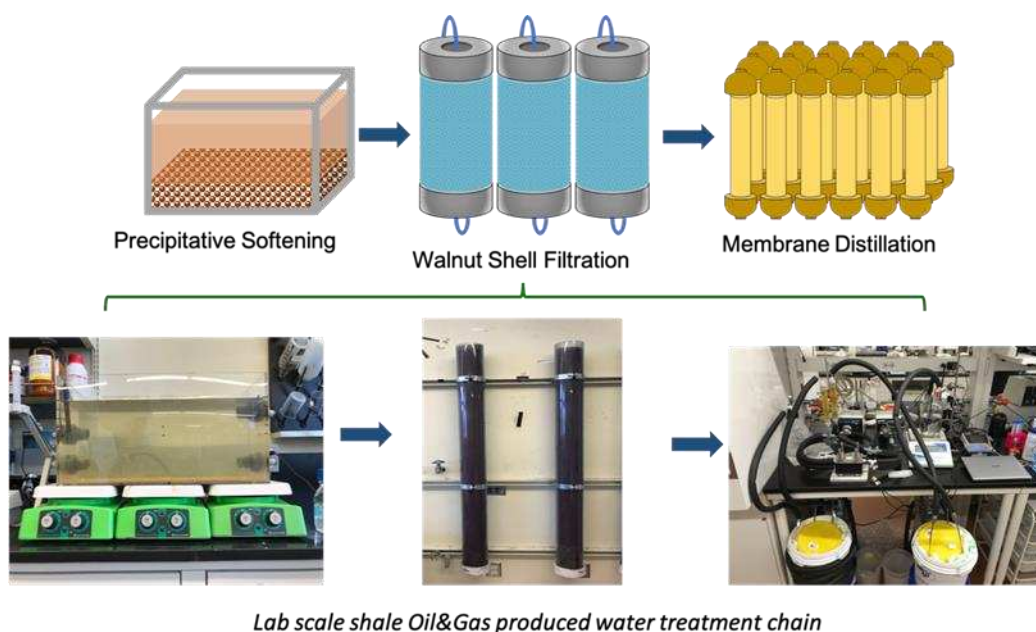


Figure 9. Lab scale shale oil and gas produced water treatment chain. Precipitative softening, walnut shell filtration, and membrane distillation are used in the sequence and form an integrated lab scale treatment chain.

As for the chemical agents, membranes and shale oil and gas produced water used in the experiment is as follows. Aluminum sulfate octadecahydrate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) and sodium hydroxide (NaOH) were both purchased from VWR BDH Chemicals. Hydrochloric acid (HCl, 36.5–38%) was provided by Fisher Chemical. Blast media walnut shells with an average grain size of 1.6mm were supplied by the Eastwood Company. Deionized (DI) water was produced from an

ultrapure water purification system ( $> 18\text{M}\Omega$  cm, Millipore). Shale oil and gas produced water samples were collected on March 21th, 2018 from a production site located in the Wattenberg field of northeast Colorado. The well was drilled and hydraulically fractured with its flowback beginning on October 24th, 2017. The produced water was transported to our laboratory located at Colorado State University (Fort Collins, CO) within 2 h after collection and stored at  $4\text{ }^{\circ}\text{C}$  until use.

In the process of PS, a transparent plastic rectangular tank with a volume of 20 L was used as a precipitative softening reaction pool. There are level markers on the tank, which can indicate the fluid volume in the reaction pool. The fluid in the rectangular tank was stirred using three magnetic stirrers. The magnetic stirrers could mix raw produced water and dosing chemicals very quickly in the tank. Also, there are four fast valves on the left and right walls of the tank which can introduce the raw produced water into the pool and export the pre-treated produced water to the next treatment stage. Shale oil and gas produced water (18 L) was placed in a rectangular container and the pH was adjusted to  $\sim 10$  by adding NaOH solution, then a small amount of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  (alum, 15 mg/L as coagulant) was added into the produced water to facilitate the precipitation process. After mixing the produced water with  $\text{Al}_2(\text{SO}_4)_3$  for 1 min at room temperature, the formed flocs were allowed to settle for 30 min. Then the supernatant was decanted into a clean polyethylene bucket for further treatment and analyses. The collected supernatant was either used as the influent in the following WSF or stored in  $4\text{ }^{\circ}\text{C}$  for future analyses and MD desalination tests.

For the WSF pretreatment, the industrial walnut shell filter was downsized to two lab-scale walnut shell filter columns as shown in Figure 9. Two cylindrical filter columns (10.4 cm in diameter and 103.5 cm in height) were packed with walnut shell particles. In order to ensure that

the small walnut shell particles would not leak from the bottom of the filter, a nylon mesh was added to the bottom of each filter. And a mixture of stones with different sizes was also added between the walnut shell media and the nylon mesh. These two walnut shell filters were used in sequence in the pretreatment. The filter columns were cleaned and stabilized by filtering 50 L of DI water per day for 10 days. The after PS produced water was filtered by these two filter columns in sequence at a constant flow rate of 4.5 L/min, and the filtered solution was collected into a clean polyethylene bucket and stored at 4 °C for future analyses and MD desalination tests. As shown in Figure 10, the effluents of both PS and WSF were much clearer than the raw produced water, indicating that PS and WSF were effective to remove contaminants from the produced water (more detailed results will be described below). The detailed water qualities of the effluents from PS and WSF were analyzed and compared to that of the raw produced water.

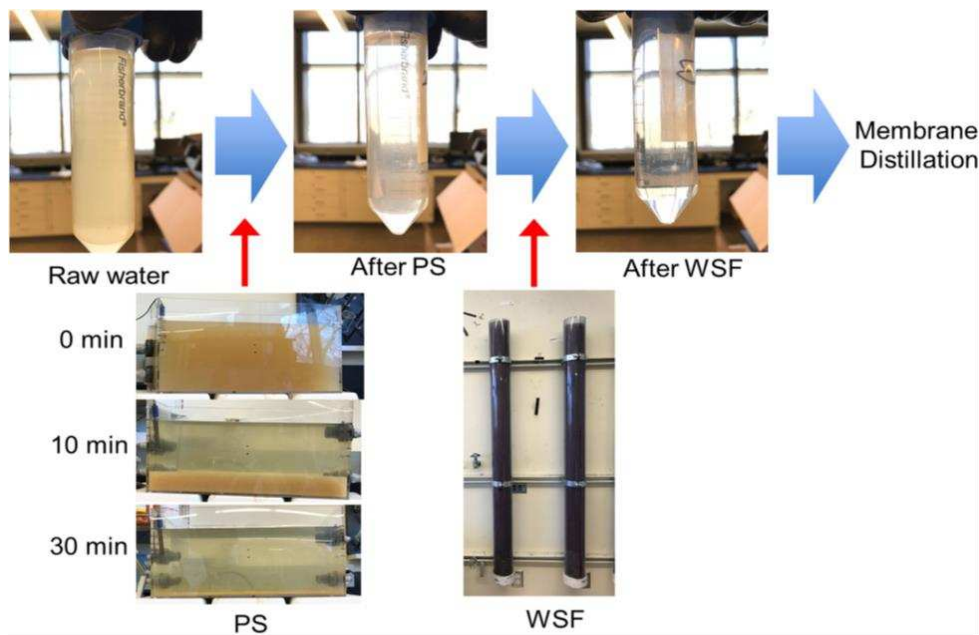


Figure 10. Schematic of pretreatment procedure prior to membrane distillation of shale oil and gas produced water. The raw wastewater will go through precipitative softening (PS, with 30 min settling time) and walnut shell filtration (WSF) in sequential. The improvement of water quality is visible as indicated by the decrease of turbidity.



Twenty-three parameters were measured and compared between produced waters with and without pretreatment. Those parameters include seventeen inorganic constituents (alkalinity, chloride, dissolved aluminum, dissolved barium, dissolved boron, dissolved calcium, dissolved iron, dissolved magnesium, dissolved silica, dissolved sodium, dissolved strontium, pH, sulfate, sulfide, TDS, and turbidity), which were closely associated with salinity and scaling potential of the produced water. A set of organic constituents (seven parameters), including BTEX (containing four organic compounds), total organic carbon (TOC), total recoverable petroleum hydrocarbons (TRPH), and total volatile petroleum hydrocarbons (TVPH), were also measured to represent the contents of organic foulants and contaminants. All the measurements were performed following standard methods[47], and stringent quality control was provided by Technology Laboratory, Inc. The scaling potential of the produced water with and without pretreatment was estimated by thermodynamic calculation using the software PHREEQC and the database MINTEQ (version 4).[48, 49]

The influences of pretreatment steps (i.e., PS followed by WSF) on the 23 inorganic and organic constituents of shale oil and gas produced water were evaluated. As shown in Table 1, PS effectively reduced the turbidity of produced water by 94%, as indicated by the much clearer softening supernatant compared to the raw produced water (Figure 10). PS also decreased the concentrations of multiple scale-forming species, as the concentrations of alkalinity, dissolved barium (Ba), calcium (Ca), magnesium (Mg), silica, and strontium (Sr) dropped by 45%, 48%, 46%, 19%, 32%, and 20%, respectively. These scale-forming species were responsible for a wide spectrum of mineral scales occurring in membrane desalination (e.g., barium sulfate, calcite, gypsum, silica, and strontium carbonate),[50-53] indicating that PS reduced scaling potential of the produced water. Thermodynamic calculation indicated that with pH of 10 and a relatively high

concentration of alkalinity (5.5 mM), dissolved Ca could be removed by forming sparingly soluble calcite ( $\text{CaCO}_3$ ), while dissolved Sr and Ba were precipitated in the forms of strontianite ( $\text{SrCO}_3$ ) and witherite ( $\text{BaCO}_3$ ). Also, the observed removal of silica was likely due to its co-precipitation with aluminum salts, which are well-known reagents for silica removal.[54] The partial removal of dissolved Mg was consistent with what was reported by Esmailirad et al.,[35] because pH of 10 was insufficient for significant Mg softening (requiring  $\text{pH} > 11$ ). However, PS was ineffective in removing boron from the produced water (only 5% removal efficiency). At the experimental pH, boron was in the forms of borate ions ( $\text{B(OH)}_4^-$ , dominant species) and boric acid ( $\text{B(OH)}_3$ ), both of which were unable to form removable precipitates during the softening process.[55, 56]

Furthermore, PS was also able to remove multiple organic contaminants (Table 1). The concentrations of TOC, TRPH, and TVPH were reduced by 39%, 44%, and 9%, respectively, while the contents of BTEX were decreased by 7%–45% depending on the specific compound. Since softening was not intentionally designed to remove organic matter, the observed removal of organic substances was mainly because of their adsorption onto the precipitates formed during softening.[57] Due to the chemical complexity of the produced water, the mechanisms underlying the variation of removal efficiency for different organic contaminants are still not fully understood and require further investigation. The higher removal efficiencies for ethylbenzene and total xylenes (32%–45%) compared to benzene and toluene (7%–9%) were likely attributed to their higher octanol/water partition coefficients ( $K_{ow}$ ). WSF was employed to further reduce the levels of organic contaminants present in the produced water after PS. This naturally derived approach notably removed >95% of BTEX (Table 1) from the feedwater, thereby substantially reducing the potential of these toxic and volatile compounds in penetrating into the distilled water product of the MD process. WSF also removed 66% of boron from the incoming produced water, and further

reduced the concentrations of all the scale-forming species except for dissolved calcium. The removal of inorganic constituents by WSF was likely due to adsorption, and future investigation (e.g., on adsorption isotherms and binding of specific ions with walnut shells) is needed to elucidate the mechanisms and selectivity of inorganic removal by WSF. The increase of calcium concentrations and TOC in the walnut shell filtrate was probably due to the release of calcium ions and organic substances from the walnut shell media. After pretreatment with a combination of PS and WSF, the fouling and scaling potential of the produced water was significantly reduced. Considering a water recovery of 80%, thermodynamic calculations showed that the saturation indices (defined as the common logarithm ( $\log_{10}$ ) of the ratio of ion activity product to solubility product) of calcite, silica, and strontianite were decreased from 1.25, 0.37, and 0.62 in the raw produced water to 0.03,  $-0.14$ , and  $-0.70$  in the pretreated produced water.

Table 1. The inorganic and organic composition of shale oil and gas produced water with and without pretreatment steps.

Parameter	1.Raw Water		2.After PS		3.After WSF		1-2 Change	2-3 Change	1-3 Change
Alkalinity	555	mg/L	306	mg/L	183	mg/L	45%	40%	67%
Dissolved Aluminum	10.9	mg/L	6.92	mg/L	6.95	mg/L	37%	0%	36%
Dissolved Barium	42.1	mg/L	21.8	mg/L	14.7	mg/L	48%	33%	65%
Dissolved Boron	32.9	mg/L	31.1	mg/L	10.6	mg/L	5%	66%	68%
Dissolved Calcium	878	mg/L	470	mg/L	601	mg/L	46%	-28%	32%
Chloride	23292	mg/L	20901	mg/L	16724	mg/L	10%	20%	28%
Dissolved Iron	<0.007	mg/L	<0.007	mg/L	<0.007	mg/L	N/A	N/A	N/A
Dissolved Magnesium	129	mg/L	105	mg/L	102	mg/L	19%	3%	21%
Dissolved Silica	26.1	mg/L	17.7	mg/L	11.9	mg/L	32%	33%	54%
Dissolved Sodium	11000	mg/L	11100	mg/L	8760	mg/L	-1%	21%	20%
Dissolved Strontium	99.7	mg/L	79.7	mg/L	55.7	mg/L	20%	30%	44%
Sulfate	<0.05	mg/L	<0.05	mg/L	<0.05	mg/L	N/A	N/A	N/A
Sulfide	0.081	mg/L	0.1	mg/L	0.094	mg/L	-23%	6%	-16%
TDS	41420	mg/L	37290	mg/L	31290	mg/L	10%	16%	24%
TOC	720	mg/L	440	mg/L	540	mg/L	39%	-23%	25%
GRO (TVPH)	55.8	mg/L	50.8	mg/L	4.1	mg/L	9%	92%	93%
TRPH	70.9	mg/L	39.8	mg/L	11.2	mg/L	44%	72%	84%
Turbidity	322	NTU	20.1	NTU	18.1	NTU	94%	10%	94%
pH	6.6	Units	9.72	Units	5.77	Units	N/A	N/A	N/A
Benzene	9	mg/L	8.38	mg/L	0.412	mg/L	7%	95%	95%
Toluene	4.29	mg/L	3.89	mg/L	0.103	mg/L	9%	97%	98%
Ethylbenzene	0.479	mg/L	0.327	mg/L	0.009	mg/L	32%	97%	98%
Total Xylenes	1.67	mg/L	0.911	mg/L	0.034	mg/L	45%	96%	98%

PS = precipitative softening; WSF = walnut shell filtration



## CHAPTER 4 MEMBRANE DISTILLATION TREATMENT PERFORMANCE

### 4.1 Membrane Distillation Performance in The Treatment of Shale Oil and Gas Produced Water Within A Single Cycle

Shale oil and gas produced water with and without pretreatment was treated in a laboratory-scale, custom-built DCMD unit equipped with a transparent acrylic flow cell. The feedwater and distillate channels of the flow cell had a dimension of 77mm×26mm×3 mm, corresponding to an effective membrane area of 20.02 cm<sup>2</sup>. Three types of produced water were used as MD feedwater: (1) raw produced water without any pretreatment; (2) produced water pretreated by only PS; (3) produced water pretreated by both PS and WSF. The produced water (2000 mL) was placed in the reservoir of feed solution, while DI water (600 mL) was added into the reservoir of distillate. The hot feed and cold distillate streams were circulated using two variable gear pumps (Cole-Parmer), and the temperatures were maintained at 60 °C (feed) and 20 °C (distillate), respectively. The crossflow velocities of the feed and distillate streams were 8.5 cm/s (0.4 L/min) and 7.4 cm/s (0.35 L/min), respectively. The mass and conductivity of the solution in the distillate reservoir were monitored continuously in order to calculate the water vapor flux and assess membrane wetting. When 1650 mL of distillate was collected (corresponding to a water recovery of 82.5%), the DCMD tests were terminated to complete one treatment cycle. A higher water recovery could be reached in the experiments, but a maximum water recovery of 82.5% was used to protect the gear pump from potential damage by the highly concentrated brine.

Figure 11 presents the normalized water vapor fluxes in the DCMD treatment of different produced water in a single cycle. When the raw produced water without any pretreatment was used as the MD feedwater, the water vapor flux decreased rapidly by ~60% at a water recovery of only

40% (i.e., collecting 800 mL of distillate). The high concentrations of suspended solids, organic foulants, and inorganic scalants present in the raw produced water caused severe fouling and scaling on the membrane surface, which blocked membrane pores and increased membrane resistance to water vapor transport. When pretreatment was applied, MD demonstrated much more stable water productivity and achieved higher water recoveries. The water flux was reduced by only ~18% at a water recovery of 82.5% (i.e., collecting 1650 mL of distillate, Figure 11), when PS was employed as the only pretreatment step. At this point, the TDS of MD concentrate was as high as 213,000 mg/L (initial TDS of produced water at 37,290 mg/L, Table 1), which exceeded the salinity limit of RO significantly and was comparable to those of concentrated brines generated by MVC and thermolytic FO. This remarkable improvement of MD performance was due to the effectiveness of PS in reducing both fouling and scaling potential of the produced water (Table 1). When WSF was performed following PS, MD exhibited the most stable water productivity, with the water vapor flux dropping by only ~10% at a water recovery of 82.5% (the TDS of MD brine was ~180,000 mg/L, considering the initial TDS of the pretreated produced water at 31,290 mg/L). Since the activity of water in NaCl solution was 0.88 at NaCl concentration of 3M (with similar TDS as my MD brine), this decrease of water flux was mainly due to the increase in salinity of the MD feedwater (which reduced solution vapor pressure) rather than membrane fouling and scaling. Therefore, my results demonstrated that coupling MD with appropriate pretreatment steps (i.e., PS and WSF in the current study) is an adequate and valuable approach to mitigate membrane fouling and scaling in MD desalination of shale oil and gas produced water, thereby increasing both water productivity and membrane lifespans effectively.

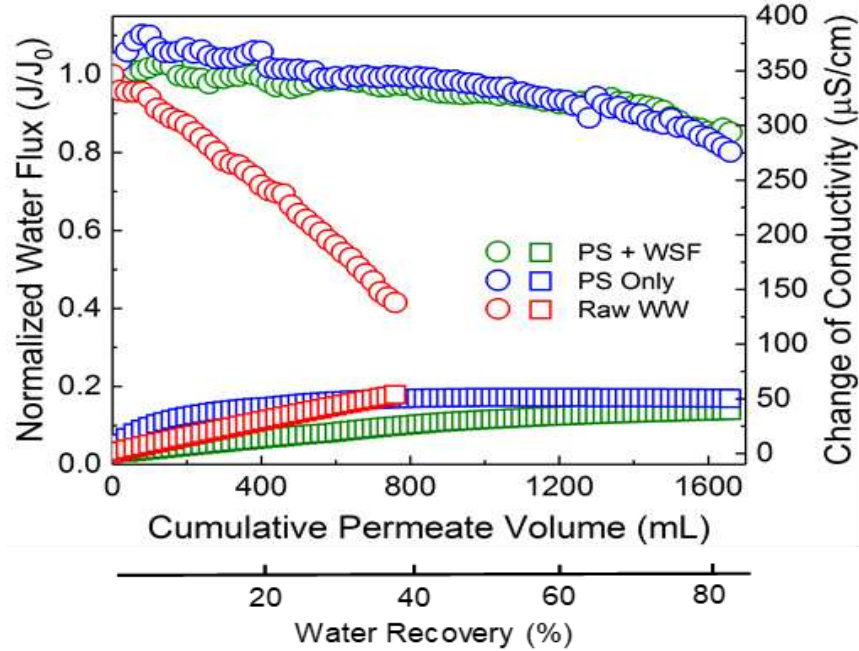


Figure 11. Normalized water (vapor) flux during single-cycle DCMD desalination of shale oil and gas produced water with and without pretreatment. Precipitative softening (PS) and walnut shell filtration (WSF) improved the performance of downstream DCMD significantly. The crossflow velocities in the feed and distillate streams were 8.5 cm/s and 7.4 cm/s, respectively. The feed and distillate temperatures were 60 °C and 20 °C, respectively. The feed volume was 2000 mL. The initial water fluxes for treating raw wastewater (WW), WW after PS only, and WW after PS and WSF were 30.48, 30.06, and 31.38 L m<sup>-2</sup> h<sup>-1</sup>, respectively.

The water qualities of MD distillate were analyzed and compared among experimental conditions with and without pretreatment of produced water (Figure 12 and 13). Regardless of the prior pretreatment steps, MD demonstrated excellent rejection of salt and boron. The conductivities of the distilled water product were increased by ~30–50 μS/cm (Figure 11 and 12A) at the conclusion of the DCMD tests. This increase corresponded to conductivities of ~50–90 μS/cm in the MD permeate, which were three orders of magnitudes lower than that of the untreated produced water (40–50 mS/cm). Hence, no significant membrane wetting occurred in my study. Since neither borate ions nor boric acids are volatile, MD was able to effectively remove >99.5% of boron (Figure 12B) from the produced water. This exceptional removal efficiency was higher than that of RO (the boron rejection by single-pass RO in seawater desalination has been reported

to be ~90% at near neutral pH).[58] The concentrations of boron in the MD distillate (0.04–0.15 mg/L, depending on the applied pretreatment steps) met the regulation standard required for irrigation (< 0.5 mg/L).[58, 59] In addition, the TRPH concentrations were below the detection limit of 5 mg/L after MD treatment (Figure 12C), despite a high TRPH concentration of 70 mg/L in the raw produced water.

Since volatile contaminants are able to transport through microporous membranes along with water vapor during the MD process, the concentrations of TVPH and BTEX were measured to assess the environmental and health risks of the distilled water product. As shown in Fig. 12D, 23.6% of volatile petroleum hydrocarbons from the raw produced water was able to penetrate through the PVDF membrane, resulting in a TVPH concentration of ~13 mg/L in the MD water product. The employment of pretreatment steps reduced the concentrations of TVPH in the MD distillate significantly. The concentration of TVPH dropped to ~6 mg/L in the distillate when PS was used, and additional pretreatment using WSF further decreased the TVPH concentration to only 0.9 mg/L. The same trend was observed in the removal of BTEX (Figure 13). In the MD treatment of raw produced water, the concentrations of benzene, ethylbenzene, toluene, and xylenes in the distillate were 3.08 mg/L, 0.93 mg/L, 0.05 mg/L, and 0.16 mg/L, corresponding to 34.2%, 21.7%, 10.4%, and 9.6% of the compounds passing through the DCMD system, respectively. Those concentrations were much higher than the typical local discharge limit (100 µg/L of total BTEX) regulated by the NPDES,[60-62] indicating that MD treatment alone was unable to generate water product suitable to be discharged into the POTWs. When PS was applied prior to MD desalination, the concentrations of benzene, ethylbenzene, toluene, and xylenes in the MD distillate dropped by ~60% to 1.02 mg/L, 0.35 mg/L, 0.02 mg/L, and 0.06 mg/L, respectively. WSF, which demonstrated exceptional efficiencies in adsorbing BTEX (> 95%, Table 1), further



decreased the BTEX concentrations to ultra-low levels (0.001 mg/L–0.06 mg/L), with total BTEX concentration meeting the typical NPDES discharge limit ( $< 100 \mu\text{g/L}$ ).<sup>[60-62]</sup> My results, therefore, are among the first to reveal the concentrations of representative volatile contaminants in the distillation products of MD desalination of shale oil and gas produced water. Along with the results of TVPH as mentioned before, a combination of PS and WSF as a pretreatment was shown to effectively prevent the intrusion of those volatile contaminants into the distillate of the MD process, thereby largely reducing the potential environmental and health risks of the treated wastewater.

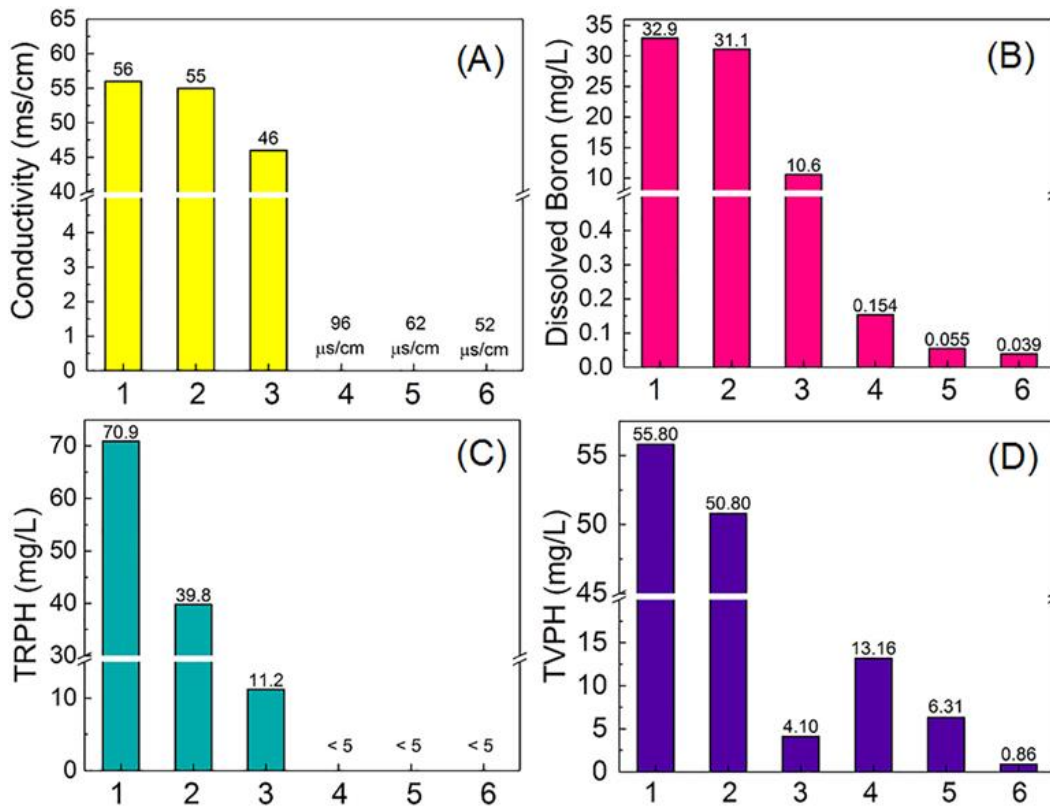


Figure 12. The concentrations of (A) conductivity, (B) dissolved boron, (C) total recoverable petroleum hydrocarbons (TRPH), and (D) total volatile petroleum hydrocarbons (TVPH) at different stages of shale oil and gas produced water treatment: (1) raw wastewater (WW), (2) raw WW after precipitative softening only, (3) raw WW after precipitative softening and walnut shell filtration; (4) DCMD product when using water (1) as the feed solution, (5) DCMD product when using water (2) as the feed solution, (6) DCMD product when using water (3) as the feed solution.

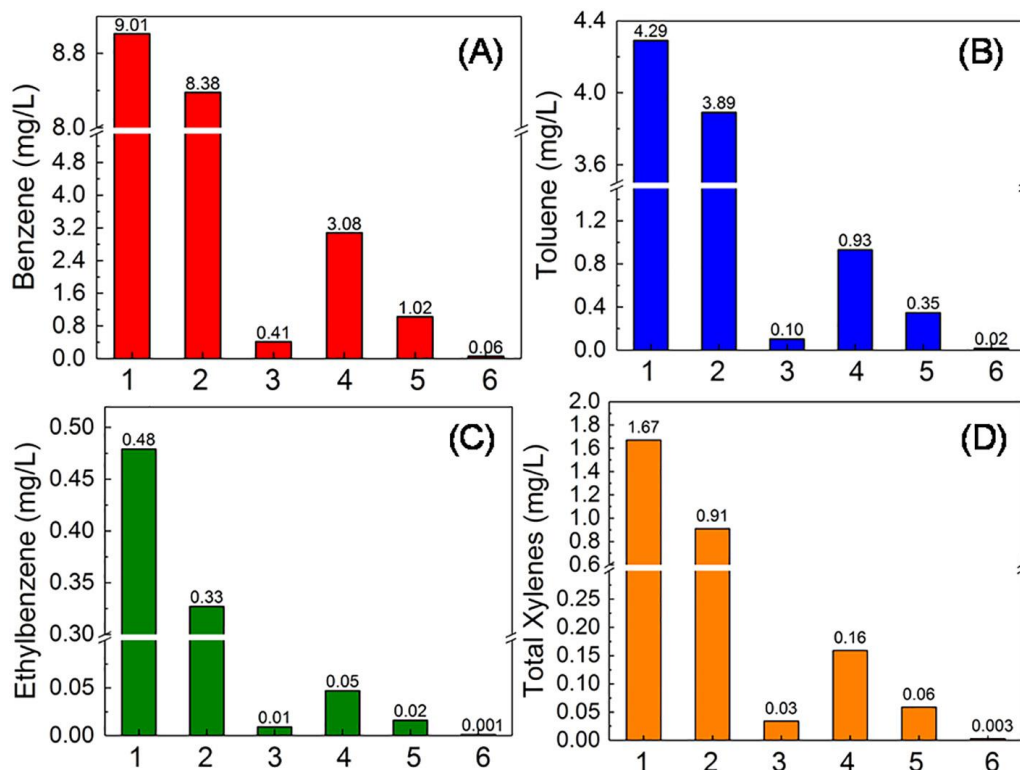


Figure 13. The concentrations of (A) benzene, (B) toluene, (C) ethylbenzene, and (D) total xylenes at different stages of shale oil and gas produced water treatment: (1) raw wastewater (WW), (2) raw WW after precipitative softening only, (3) raw WW after precipitative softening and walnut shell filtration; (4) DCMD product when using water (1) as the feed solution, (5) DCMD product when using water (2) as the feed solution, (6) DCMD product when using water (3) as the feed solution.

#### 4.2 Fouling Reversibility and Membrane Reusability Within Multiple Treatment Cycles When MD Treating After Pretreatment Produced Water

Fouling reversibility and membrane reusability were evaluated within three continuous treatment cycles, in which the produced water pretreated by both PS and WSF was used as the feed solution. After collecting 1650 mL of distillate (i.e., one full treatment cycle), the membrane coupon was taken out of the flow cell and rinsed thoroughly with DI water (2 L/min, for 20 s) on both sides. This physical cleaning procedure removed inorganic and organic foulants that were loosely attached to the membrane surface. The membrane coupon was then reinserted into the

DCMD unit after being dried in air, and 2000 mL of new pretreated produced water was added into the feed reservoir to start another DCMD treatment cycle. The initial water vapor fluxes and flux decline rates in different treatment cycles were measured and compared.

Fouling reversibility and membrane reusability of the MD treatment were investigated within three consecutive treatment cycles, in order to evaluate long-term MD performance for produced water treatment. My recent study has demonstrated the importance of evaluating membrane reusability, not only membrane fouling and wetting, in the assessment of membrane performance in the MD process.[33] The produced water pretreated by both PS and WSF was used as the MD feedwater because it led to the most stable water vapor flux and the best water product quality (Figures 11–13). Physical membrane cleaning was performed after each treatment cycle (i.e., collecting 1650 mL of distillate with a water recovery of 82.5%).

As shown in Figure 14, the water productivity of MD treatment remained relatively stable within the three treatment cycles, with a water flux decline of <20% observed for every cycle. The water vapor flux was fully restored after physical cleaning regardless of the treatment cycles (Figure 14). Further, the change of conductivity in the MD distillate remained at low levels (< 50  $\mu\text{S}/\text{cm}$ ) for all the treatment cycles, which corresponded to consistent salt rejection rates of >99.8%. Hence, no significant membrane wetting was observed during the three treatment cycles. The above results indicate that treatment train was able to achieve high water recoveries (> 80%, with MD concentrate TDS of ~180,000 mg/L) during multiple runs of MD desalination of shale oil and gas produced water, and the PVDF membranes used in the current study were reusable after applying a simple cleaning procedure.

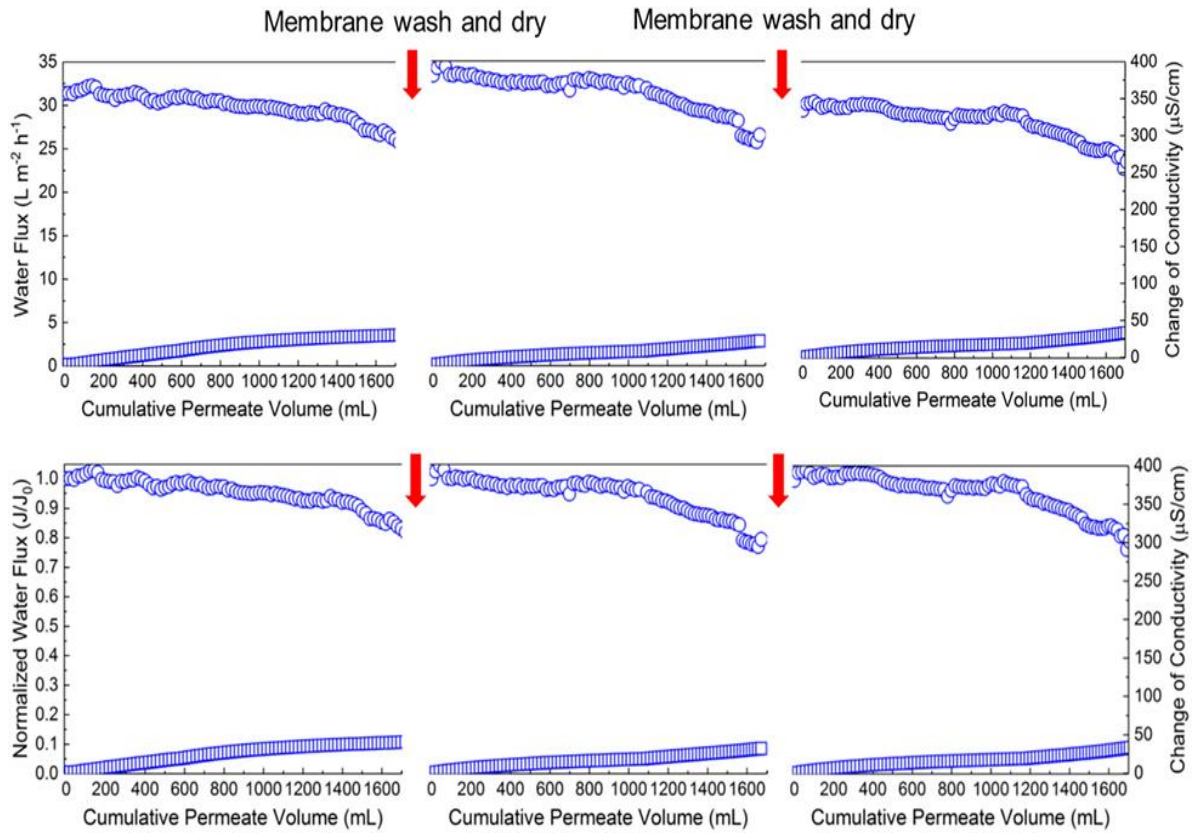


Figure 14. Fouling reversibility and membrane reusability during DCMD desalination of shale oil and gas produced water pretreated by precipitative softening and walnut shell filtration. The experimental condition of DCMD desalination was identical to that described in Figure 11, and the red arrows indicate the time when the DCMD tests were terminated and the membrane coupons were subjected to physical cleaning followed by in-air drying. The dried membrane was then re-inserted into the DCMD system to start another cycle of desalination with new pretreated produced water.

## CHAPTER 5 TECHNO-ECONOMIC ANALYSIS AND FUTURE WORK

At present, shale oil and gas produced water is mainly injected into underground saltwater disposal wells as a common approach to wastewater management. The oil and gas producers have not widely adopted new treatment methods to replace current deep-well injection practices. At least two reasons are responsible for the reluctance of the shale oil and gas industry to wastewater treatment and reuse. First, we have not proved that current wastewater treatment technologies are more convenient and economical than deep-well injection. Second, the environmental policies regarding the reuse applications of the treated wastewater are still unclear.

Although with certain disadvantages of deep well injection, this method could not be replaced right now. Texas and Pennsylvania, the main production areas of shale oil and gas, have huge amounts of produced water to be treated and pumped into deep saltwater disposal wells. In contrast, there are only eight saltwater disposal wells reported in Pennsylvania, compared with a big number of about 12000 disposal wells in Texas. Therefore, a large amount of produced water generated from Pennsylvania needs to be transported to disposal wells in other states' disposal wells. But the information was not available on the cost of shale oil and gas produced water treatment at Pennsylvania's industrial wastewater treatment plants. The cost of deep-well injection includes both injection cost and transportation cost of produced water. In general, the price of the injection depends on supply and demand and is generally between \$0.50 and \$2.50 per barrel combining observations from both Texas and Pennsylvania,[63] similarly Exxon and Halliburton estimated it at \$0.75 to \$1 per barrel in Texas. (from the news: Wastewater Recycling Part III: Costs and Challenges in Breaking Energy May 16<sup>th</sup>, 2013). The transportation price is about \$1 per barrel per hour, for areas like Texas, transportation cost may only add \$0.5 per barrel because of the high density in disposable wells, but for areas such as Pennsylvania where the nearest

commercial disposal well maybe in Ohio or West Virginia, the transportation cost can easily add \$4 to \$6 per barrel. [63] Therefore, the total cost of deep well injection could be \$1 to \$8.50 per barrel depending on the location. Moreover, these total costs are only the costs of the oil companies and do not take into account the externality to the third party such as the wear of the road and the impact of transportation vehicle emissions on the environment.

Next, I roughly estimate the cost of the onsite equipment to process an average cubic meter of shale oil and gas produced water. To calculate the produced water treatment cost by each cubic meter using my MD system, the total capital cost (equipment, site cost) plus the operation and maintenance cost to obtain the final treatment cost should be included. Relevant papers have made a detailed estimate of the cost of MD treatment of shale oil and gas produced water. According to the literature,[43, 44, 46] the cost for MD treatment of shale oil and gas produced water is \$0.64-\$0.74/m<sup>3</sup> (\$0.11- \$0.12/barrel) wastewater if waste heat is ready to use in the oil field. Considering the actual oil production, on-site waste heat generated by production equipment (like the natural gas compressor) is not easy to use, thus it is still a question whether the waste heat energy can meet the thermal energy needs of MD equipment. Therefore, it is a practical and feasible method for us to consider using natural gas to provide thermal energy that powers the MD process. Someone might consider why not use electrical energy to provide thermal energy? If we use fossil energy to generate electricity, it will reduce the efficiency of energy use as the conversion of electricity to thermal energy is not efficient, because typical thermal efficiency for utility-scale electrical generators is around 37% for coal and oil-fired plants.(From Wikipedia, Fossil fuel power station) Renewable energy such as solar and wind power is still expensive, occupies a large area and is not an all-weather energy supply. Therefore, it is an economical and feasible method to use a natural gas boiler as a direct heat source supply. Most oil and gas fields produce natural

gas, which can meet the demand of thermal energy for produced water treatment. It is assumed that the normalized capital, operation, and maintenance cost except for energy consumption is around  $\$0.4/\text{m}^3$ , and the electricity of 2 kWh and thermal heat of 100 kWh are consumed in the MD production process according to literature.[46] Considering electrical cost of  $\$0.09/\text{kWh}$ , thermal energy price (natural gas) of  $\$0.009/\text{kWh}$  (1MMBtu natural gas price is  $\$2.69$  according to U.S. National Average Natural Gas Price as of Feb 1<sup>st</sup>, 2019, and 1MMBtu = 293 kWh), the total normalized cost is  $\$1.48$  to treat  $1 \text{ m}^3$  using MD powered by natural gas ( $\$1.48/\text{m}^3 = \$0.4/\text{m}^3$  (capital, operation, maintenance and excludes thermal energy cost) +  $2 \text{ kWh}/\text{m}^3 \times \$0.09/\text{kWh}$  (electricity) +  $100 \text{ kWh}/\text{m}^3 \times \$0.009/\text{kWh}$  (natural gas)). And one literature mentioned the thermal energy consumption for the MD system may reach  $500 \text{ kWh}/\text{m}^3$ , [15] so the total normalized cost will reach  $\$5.08/\text{m}^3$ . In addition, the pretreatment use of NaOH for PS will add to the cost of  $\$0.3/\text{m}^3$  wastewater (considering 800 g of NaOH per  $\text{m}^3$  wastewater and  $\$400$  per ton of NaOH). Also, WSF will add to the cost of  $\$0.1/\text{m}^3$  for produced water treatment. After the calculations, the total costs of the service charge for the treatment of water will be  $\$0.29$ - $\$0.87$  per barrel of wastewater (corresponding to  $\$1.88$ - $\$5.48/\text{m}^3$  wastewater).

However, we need to also consider the small amount of high-pH (around pH of 9.6) sludge generated in the PS process, crystallization of the concentrated MD brine, and the disposal of walnut shell waste. Also, the end-use applications of generated distilled water still need further investigation due to the ambiguous regulation and reuse demands. Therefore, the estimated price of  $\$0.29$ - $\$0.87/\text{barrel}$  wastewater is referred to only the cost of the treatment process, and the total cost of the wastewater treatment system will be higher when applied practically. Also, the cost of our treatment system is currently not comparable with that of deep-well injection, although a total cost of  $\$1/\text{barrel}$  -  $\$8.5/\text{barrel}$  was reported in the literature as discussed above. Further



investigation is still in need to validate the economic feasibility of the proposed MD-based system for the full-scale treatment of shale oil and gas produced water. A very clear point is that the advantage of MD technology to deal with the produced water is that it has no risks of polluting the underground water source or inducing earthquakes, and that the treated water can be recycling and augmenting freshwater supply within the hydrological cycle. Therefore, from the perspective of environmental protection and water conservation, wastewater treatment and reuse (e.g., by my integrated MD treatment system) is still a wise and feasible choice by the oil and gas producers, despite its unclear economic advantages.

Currently, we are setting up a pilot-scale treatment system based on the lab-scale system described in this thesis. The new pilot treatment system will use a larger size of membrane flow cells with a larger membrane area (6 inches  $\times$  11 inches, 20 times larger than the lab-scale system). The water channels of flow cell are re-designed according to fluid mechanics. The module will work in parallel with two or three newly designed flow cells to simulate the modular processing mode in actual pure water production. The new system will be equipped with heaters and chillers with higher capacity, an industrial heat exchanger, and scaled-up reaction pool for PS and walnut shell filter. A longer-term wastewater treatment test will be performed in the oilfield of Colorado. After the completion of the test, we will be able to demonstrate the effectiveness of the treatment systems to the oil and gas producers, thereby facilitating the practical applications of my system to the shale oil and gas production.

In addition, although technical research is the focus of my future work, it will take time to address challenges in terms of policy and regulation to make this technology truly commercialized. The research directions should help regulators and oil and gas producers understand the necessity and importance of wastewater treatment and reuse in shale oil and gas production. Also, more

reasonable regulatory standards should be established clearly for wastewater treatment and reuse. The relevant regulatory requirements will be used to guide the development of wastewater treatment technologies that are tailored to specific reuse applications of treated wastewater from shale oil and gas production.

## CHAPTER 6 CONCLUSIONS

In this thesis, an integrated treatment chain, which coupled MD with PS and WSF as pretreatment steps, was developed to treat shale oil and gas produced water generated from the Wattenberg field in northeast Colorado. A lab-scale MD system was successfully built with stable desalination performance. PS decreased the concentrations of particulate, organic, and inorganic foulants, thereby reducing fouling and scaling potential of the produced water. WSF, a naturally derived approach, removed  $\geq 95\%$  volatile toxic contaminants such as BTEX, effectively preventing their intrusion into the distilled water product. Compared to the raw produced water, the pretreated produced water resulted in a remarkably more stable water vapor flux during MD desalination. Although MD demonstrated exceptional rejection of non-volatile constituents of the produced water (e.g., salts, boron, and non-volatile organics), volatile organic pollutants were able to transport through the MD membranes and compromise the quality of distilled water product. A combination of PS and WSF substantially decreased the contents of volatile organic contaminants in the MD permeate, reducing the total BTEX concentration to a level below the typical NPDES discharge limit. MD treatment of the pretreated produced water also exhibited robust performance during three consecutive treatment cycles, each of which achieved total water recovery of  $>80\%$  (TDS of MD brine at  $\sim 180,000$  mg/L). Therefore, MD in tandem with simple pretreatment is demonstrated to be a promising strategy to treat shale oil and gas produced water effectively.

Also, a techno-economic analysis of this treatment system, if applied on-site, was performed based on the data provided by the literature. A total cost of this treatment system was estimated to be \$0.29-\$0.87 per barrel (not include waste disposal fees), but further investigation is still in need to validate the economic feasibility of the proposed MD-based system for the full-scale treatment of shale oil and gas produced water. Also, such wastewater treatment system will

have lower environmental risks than deep-well injection, meanwhile augmenting freshwater supply. In the future work, a pilot-scale system will be built to obtain further field data to validate the effectiveness of the developed MD system in practical treatment and reuse of wastewater generated from shale oil and gas production.

## REFERENCES

- [1] W. A. Ambrose, E. C. Potter, and R. J. G. Briceno, "An`unconventional"future for natural gas in the united states," vol. 53, no. 2, p. 37, 2008.
- [2] R. D. Vidic, S. L. Brantley, J. M. Vandenbossche, D. Yoxtheimer, and J. D. Abad, "Impact of shale gas development on regional water quality," *Science*, vol. 340, no. 6134, p. 1235009, May 17 2013.
- [3] D. L. Shaffer, L. H. Arias Chavez, M. Ben-Sasson, S. Romero-Vargas Castrillon, N. Y. Yip, and M. Elimelech, "Desalination and reuse of high-salinity shale gas produced water: drivers, technologies, and future directions," *Environ Sci Technol*, vol. 47, no. 17, pp. 9569-83, Sep 3 2013.
- [4] B. D. Lutz, A. N. Lewis, and M. W. Doyle, "Generation, transport, and disposal of wastewater associated with Marcellus Shale gas development," *Water Resources Research*, vol. 49, no. 2, pp. 647-656, 2013.
- [5] D. Rahm, "Regulating hydraulic fracturing in shale gas plays: The case of Texas," *Energy Policy*, vol. 39, no. 5, pp. 2974-2981, 2011.
- [6] L. Kilian, "The impact of the shale oil revolution on US oil and gasoline prices," *Review of Environmental Economics*, vol. 10, no. 2, pp. 185-205, 2016.
- [7] A. Kondash and A. Vengosh, "Water footprint of hydraulic fracturing," *Environmental Science Technology Letters*, vol. 2, no. 10, pp. 276-280, 2015.
- [8] D. J. Rozell and S. J. Reaven, "Water pollution risk associated with natural gas extraction from the Marcellus Shale," *Risk Anal*, vol. 32, no. 8, pp. 1382-93, Aug 2012.
- [9] K. B. Gregory, R. D. Vidic, and D. A. Dzombak, "Water Management Challenges Associated with the Production of Shale Gas by Hydraulic Fracturing," *Elements*, vol. 7, no. 3, pp. 181-186, 2011.
- [10] A. Vengosh, R. B. Jackson, N. Warner, T. H. Darrah, and A. Kondash, "A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States," *Environ Sci Technol*, vol. 48, no. 15, pp. 8334-48, 2014.
- [11] R. B. Jackson et al., "Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction," *Proc Natl Acad Sci U S A*, vol. 110, no. 28, pp. 11250-5, Jul 9 2013.
- [12] M. Freyman, "Hydraulic fracturing & water stress: Water demand by the numbers," *Ceres*, vol. 85, pp. 49-50, 2014.
- [13] K. Oetjen et al., "Temporal characterization and statistical analysis of flowback and produced waters and their potential for reuse," *Sci Total Environ*, vol. 619-620, pp. 654-664, Apr 1 2018.
- [14] T. Smith, "Environmental considerations of shale gas development," *Chemical Engineering Progress*, vol. 108, no. 8, pp. 53-59, 2012.
- [15] G. P. Thiel, E. W. Tow, L. D. Banchik, H. W. Chung, and J. H. Lienhard, "Energy consumption in desalinating produced water from shale oil and gas extraction," *Desalination*, vol. 366, pp. 94-112, 2015.
- [16] K. L. Benko and J. E. Drewes, "Produced Water in the Western United States: Geographical Distribution, Occurrence, and Composition," *Environmental Engineering Science*, vol. 25, no. 2, pp. 239-246, 2008.

- [17] N. R. Warner, C. A. Christie, R. B. Jackson, and A. Vengosh, "Impacts of shale gas wastewater disposal on water quality in western Pennsylvania," *Environ Sci Technol*, vol. 47, no. 20, pp. 11849-57, Oct 15 2013.
- [18] W. L. Ellsworth, "Injection-induced earthquakes," *Science*, vol. 341, no. 6142, p. 1225942, 2013.
- [19] T. Hincks, W. Aspinall, R. Cooke, and T. Gernon, "Oklahoma's induced seismicity strongly linked to wastewater injection depth," *Science*, vol. 359, no. 6381, pp. 1251-1255, 2018.
- [20] M. Weingarten, S. Ge, J. W. Godt, B. A. Bekins, and J. L. Rubinstein, "High-rate injection is associated with the increase in U.S. mid-continent seismicity," *Science*, vol. 348, no. 6241, pp. 1336-1340, 2015.
- [21] L. F. Greenlee, D. F. Lawler, B. D. Freeman, B. Marrot, and P. Moulin, "Reverse osmosis desalination: water sources, technology, and today's challenges," *Water research*, vol. 43, no. 9, pp. 2317-2348, 2009.
- [22] A. Butkovskiy, H. Bruning, S. A. Kools, H. H. Rijnaarts, and A. P. Van Wezel, "Organic pollutants in shale gas flowback and produced waters: identification, potential ecological impact, and implications for treatment strategies," *Environmental science technology*, vol. 51, no. 9, pp. 4740-4754, 2017.
- [23] N. A. Khan, M. Engle, B. Dungan, F. O. Holguin, P. Xu, and K. C. Carroll, "Volatile-organic molecular characterization of shale-oil produced water from the Permian Basin," *Chemosphere*, vol. 148, pp. 126-136, 2016.
- [24] J. Rosenblum, E. M. Thurman, I. Ferrer, G. Aiken, and K. G. Linden, "Organic chemical characterization and mass balance of a hydraulically fractured well: From fracturing fluid to produced water over 405 days," *Environmental science technology*, vol. 51, no. 23, pp. 14006-14015, 2017.
- [25] A. M. Alklaibi and N. Lior, "Membrane-distillation desalination: Status and potential," *Desalination*, vol. 171, no. 2, pp. 111-131, 2005.
- [26] J. Kim, J. Kim, and S. Hong, "Recovery of water and minerals from shale gas produced water by membrane distillation crystallization," *Water Res*, vol. 129, pp. 447-459, Feb 1 2018.
- [27] T. Y. Cath, V. D. Adams, and A. E. Childress, "Experimental study of desalination using direct contact membrane distillation: a new approach to flux enhancement," *Journal of Membrane Science*, vol. 228, no. 1, pp. 5-16, 2004.
- [28] H. Aybar, "Analysis of a mechanical vapor compression desalination system," *Desalination*, vol. 142, no. 2, pp. 181-186, 2002.
- [29] A. Deshmukh et al., "Membrane distillation at the water-energy nexus: limits, opportunities, and challenges," *Energy Environmental Science*, vol. 11, no. 5, pp. 1177-1196, 2018.
- [30] P. S. Goh, W. J. Lau, M. H. D. Othman, and A. F. Ismail, "Membrane fouling in desalination and its mitigation strategies," *Desalination*, vol. 425, pp. 130-155, 2018.
- [31] D. M. Warsinger, J. Swaminathan, E. Guillen-Burrieza, and H. A. Arafat, "Scaling and fouling in membrane distillation for desalination applications: a review," *Desalination*, vol. 356, pp. 294-313, 2015.
- [32] L. D. Tijning, Y. C. Woo, J.-S. Choi, S. Lee, S.-H. Kim, and H. K. Shon, "Fouling and its control in membrane distillation—A review," *Journal of Membrane Science*, vol. 475, pp. 215-244, 2015.

- [33] X. Du, Z. Zhang, K. H. Carlson, J. Lee, and T. Tong, "Membrane fouling and reusability in membrane distillation of shale oil and gas produced water: Effects of membrane surface wettability," *Journal of Membrane Science*, vol. 567, pp. 199-208, 2018.
- [34] J. M. Winglee, N. Bossa, D. Rosen, J. T. Vardner, and M. R. Wiesner, "Modeling the concentration of volatile and semivolatile contaminants in direct contact membrane distillation (DCMD) product water," *Environmental science technology*, vol. 51, no. 22, pp. 13113-13121, 2017.
- [35] N. Esmailirad, K. Carlson, and P. Omur Ozbek, "Influence of softening sequencing on electrocoagulation treatment of produced water," *J Hazard Mater*, vol. 283, pp. 721-9, 2015.
- [36] F. L. Lobo, H. Wang, T. Huggins, J. Rosenblum, K. G. Linden, and Z. J. Ren, "Low-energy hydraulic fracturing wastewater treatment via AC powered electrocoagulation with biochar," *Journal of hazardous materials*, vol. 309, pp. 180-184, 2016.
- [37] G. U. Semblante, J. Z. Lee, L. Y. Lee, S. L. Ong, and H. Y. Ng, "Brine pre-treatment technologies for zero liquid discharge systems," *Desalination*, vol. 441, pp. 96-111, 2018.
- [38] K. Sardari, P. Fyfe, D. Lincicome, and S. R. Wickramasinghe, "Combined electrocoagulation and membrane distillation for treating high salinity produced waters," *Journal of Membrane Science*, vol. 564, pp. 82-96, 2018.
- [39] A. Srinivasan and T. Viraraghavan, "Removal of oil by walnut shell media," *Bioresource technology*, vol. 99, no. 17, pp. 8217-8220, 2008.
- [40] S. O. Lesmana, N. Febriana, F. E. Soetaredjo, J. Sunarso, and S. Ismadji, "Studies on potential applications of biomass for the separation of heavy metals from water and wastewater," *Biochemical Engineering Journal*, vol. 44, no. 1, pp. 19-41, 2009.
- [41] A. Tripathi and M. R. Ranjan, "Heavy metal removal from wastewater using low cost adsorbents," *Bioremed Biodeg*, vol. 6, no. 1000315, p. 5, 2015.
- [42] Z. Zhang, X. Du, K. H. Carlson, C. A. Robbins, and T. Tong, "Effective treatment of shale oil and gas produced water by membrane distillation coupled with precipitative softening and walnut shell filtration," *Desalination*, vol. 454, pp. 82-90, 2019.
- [43] S. Tavakkoli, O. R. Lokare, R. D. Vidic, and V. Khanna, "A techno-economic assessment of membrane distillation for treatment of Marcellus shale produced water," *Desalination*, vol. 416, pp. 24-34, 2017.
- [44] S. Alobaidani, E. Curcio, F. Macedonio, G. Diproffio, H. Alhinai, and E. Drioli, "Potential of membrane distillation in seawater desalination: Thermal efficiency, sensitivity study and cost estimation," *Journal of Membrane Science*, vol. 323, no. 1, pp. 85-98, 2008.
- [45] R. Sarbatly and C.-K. Chiam, "Evaluation of geothermal energy in desalination by vacuum membrane distillation," *Applied Energy*, vol. 112, pp. 737-746, 2013.
- [46] U. K. Kesieme, N. Milne, H. Aral, C. Y. Cheng, and M. Duke, "Economic analysis of desalination technologies in the context of carbon pricing, and opportunities for membrane distillation," *Desalination*, vol. 323, pp. 66-74, 2013.
- [47] L. Clescerl, A. Greenberg, and A. Eaton, "Standard methods for water and wastewater analysis," ed: Washington, DC: American Public Health Association, 1998.
- [48] D. L. Parkhurst and C. J. W.-r. i. r. Appelo, "User's guide to PHREEQC (version 2)—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations," vol. 99, no. 4259, p. 312, 1999.

- [49] T. Tong et al., "Chemical interactions between nano-ZnO and nano-TiO<sub>2</sub> in a natural aqueous medium," *Environmental science technology*, vol. 48, no. 14, pp. 7924-7932, 2014.
- [50] A. Antony, J. H. Low, S. Gray, A. E. Childress, P. Le-Clech, and G. Leslie, "Scale formation and control in high pressure membrane water treatment systems: a review," *Journal of membrane science*, vol. 383, no. 1-2, pp. 1-16, 2011.
- [51] W. Cheng et al., "Selective removal of divalent cations by polyelectrolyte multilayer nanofiltration membrane: role of polyelectrolyte charge, ion size, and ionic strength," *Journal of Membrane Science*, vol. 559, pp. 98-106, 2018.
- [52] A. Rahardianto, J. Gao, C. J. Gabelich, M. D. Williams, and Y. Cohen, "High recovery membrane desalting of low-salinity brackish water: integration of accelerated precipitation softening with membrane RO," *Journal of Membrane Science*, vol. 289, no. 1-2, pp. 123-137, 2007.
- [53] T. Tong, S. Zhao, C. Boo, S. M. Hashmi, and M. Elimelech, "Relating silica scaling in reverse osmosis to membrane surface properties," *Environmental science technology* vol. 51, no. 8, pp. 4396-4406, 2017.
- [54] A. Masarwa, D. Meyerstein, N. Daltrophe, and O. Kedem, "Compact accelerated precipitation softening (CAPS) as pretreatment for membrane desalination II. Lime softening with concomitant removal of silica and heavy metals," *Desalination*, vol. 113, no. 1, pp. 73-84, 1997.
- [55] M. H. Oo and L. Song, "Effect of pH and ionic strength on boron removal by RO membranes," *Desalination*, vol. 246, no. 1-3, pp. 605-612, 2009.
- [56] K. L. Tu, L. D. Nghiem, and A. R. Chivas, "Coupling effects of feed solution pH and ionic strength on the rejection of boron by NF/RO membranes," *Chemical Engineering Journal*, vol. 168, no. 2, pp. 700-706, 2011.
- [57] S. J. Randtke, "Organic contaminant removal by coagulation and related process combinations," *Journal-American Water Works Association*, vol. 80, no. 5, pp. 40-56, 1988.
- [58] J. R. Werber, A. Deshmukh, and M. Elimelech, "The critical need for increased selectivity, not increased water permeability, for desalination membranes," *Environmental Science Technology Letters*, vol. 3, no. 4, pp. 112-120, 2016.
- [59] D. L. Shaffer, N. Y. Yip, J. Gilron, and M. Elimelech, "Seawater desalination for agriculture by integrated forward and reverse osmosis: Improved product water quality for potentially less energy," *Journal of membrane science*, vol. 415, pp. 1-8, 2012.
- [60] A. D. o. E. Quality, "Fact Sheet and Supplementary Information for General Permit Discharges from Groundwater and Surface Water Clean Up Located within the State of Arkansas," 2016.
- [61] USEPA, "Technically-based Local Limits Development Strategy," 1995.
- [62] USEPA, "Remediation General Permit Fact Sheet Excerpts," 2005.
- [63] R. McCurdy, "Underground injection wells for produced water disposal," in *Technical Workshops for the Hydraulic Fracturing Study: Water Resources Management*, US Environmental Protection Agency, Washington, DC, Paper No. EPA, 2011, vol. 600.