



Image caption: Produced water collected from a hydraulic fracturing facility in Texas, USA. Photo courtesy of Mahmood Jebur.

Integrated Electrocoagulation/Ultrafiltration-Membrane Distillation-Crystallization for Treating Hydraulic Fracturing Produced Water

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Abstract: In this work, produced water (PW) generated from hydraulic fracturing was treated using an integrated electrocoagulation/ultrafiltration, membrane distillation and crystallization processes (EC/UF-MDC). 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. All membrane based separation processes suffer from membrane fouling. Pretreatment of the feed is essential to suppress fouling of the membrane. Here electrocoagulation (EC) followed by ultrafiltration (UF) was used to achieve high removal efficiency of both total suspended solids (TSS) and total organic carbon (TOC). Dissolved organic compounds are known to foul the hydrophobic membrane used in MD. In this study, a significant reduction in membrane fouling was obtained, which can lead to a long-term durability of MD system. In addition, the use of membrane distillation crystallization (MDC) can help mitigate the scale formation. Crystallization in the feed tank was used to suppress scale formation on the MD membrane. The integrated EC/UF-MDC process can have a potential impact on Water Resources/Oil & Gas Companies. By treating and reusing PW, preservation of surface and groundwater forming 80% of the water utilized in hydraulic fracturing could be achieved. In addition, treating PW will reduce the amount of PW directly disposed in Class II disposal wells, which further address the main cause of earthquakes.

Key Points:

- A high TOC removal efficiency was obtained using the combined EC/UF system by reducing the TOC concentration from 395 to 23.3 mg/L.
- Applying crystallization after MD (described as MDC) can lead to an increase in water recovery and reduce scale formation caused by inorganic compounds.
- A long-term MDC experiment with regeneration showed that the polyvinylidene fluoride (PVDF) membrane can be totally recovered with more than 95% membrane regeneration by simply running DI water on both sides of the membrane for 1 hour.

Introduction

Currently, unconventional shale gas and oil is the fastest growing sector for U.S. energy supply. Hydraulic fracturing combined with horizontal drilling is a technology used to enable the exploitation of abundant oil and gas resources that were previously unreachable (Warpinski et al., 2008). 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. A drastic increase in water usage for hydraulic fracturing has been observed due to this increase in shale gas production (Perrin, 2019; Vidic et al., 2013). In hydraulic fracturing, water is mixed with chemicals and pumped at high pressure through the well bore to fracture tight rock formations. Then, the pressure is reduced, and the water flows back to the surface as flowback and PW. The amount of PW generated during the extraction period of each well is around 15 to 23 million liters (Malakoff, 2014). In general, approximately 116 billion liters of PW are produced in U.S. annually (Rosenblum et al., 2016). In the Fayetteville shale, about 20.06 million liters of water was used per well (A. Kondash & Vengosh, 2015).

Due to the increase in water demand, PW needs to be treated and reused. 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 (Luek & Gonsior, 2017; Orem et al., 2014). Deep well injection is the current accepted practice to manage PW. 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, and the effects of deep well injection practices on enhancing earthquakes. There are few options available to treat PW. Distillation based technologies such as multistage flash distillation or integrating evaporation, crystallization, and spray drying is an option to treat PW (Baig et al., 2011). Even though these techniques can treat high TDS brines with significant recovery, they still suffer from some drawbacks, such as high cost, large footprint, and the use of chemicals (Morillo et al., 2014).

Membrane technology is another option used to treat high TDS brines, such as reverse osmosis (RO). Brines with a TDS below 50,000 mg/L can be successfully treated using RO. However, at a high TDS (> 50,000 mg/L) RO cannot be used because the applied pressure on the feed side is less than the osmotic pressure (Duong et al., 2015; Pérez-González et al., 2012). Membrane distillation (MD) is a promising technique 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. Due to the vapour pressure difference resulting from the temperature difference between the feed and permeate, the water vapour molecules

will transport from the feed stream (warm brines) to the permeate (cold) stream. The advantage of using MD instead of other known membrane techniques is that the feed TDS concentration has little effect 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 (Deshmukh et al., 2018; Yun et al., 2006). In direct contact membrane distillation, which is used in this study, the feed and permeate streams are in direct contact with the two surfaces of the membrane (Lin et al., 2014).

However, MD like all other membrane technologies still suffers from fouling and wetting propensity of the membrane, which affect its long-term performance (Kafuku & Mbarawa, 2013). While development of new high performance membranes is essential, our focus here is on development of an integrated process that maximizes water recovery. Consequently, we use commercially available polyvinylidene fluoride (PVDF) membranes. Here, we evaluated the feasibility of using the integrated EC/UF-MDC to address the issues of both scaling and wetting and maximize water recovery. The integrated EC/UF-MDC system could be used to successfully treat PW and overcome most of the drawbacks faced by using other techniques. Using the integrated EC/UF-MDC operation can provide several advantages such as low cost, small footprint, treating high TDS brines, and mitigating the membrane wetting and scaling.

Our preliminary results showed that using the electrocoagulation (EC) as a pretreatment step is essential to mitigate fouling and wetting. In fouling, a deposition of suspended or dissolved substances on the membrane surface and/or within its pores will occur resulting in a decrease of the membrane permeability. However, in wetting, the water will start flowing into the membrane pores causing a deterioration of permeate quality (Sardari et al., 2018). In electrocoagulation a sacrificial electrode (anode) is frequently used. By applying an electrical current, metal ions are released into the solution to generate a variety of metal hydroxides as shown in the following reactions $M_{(s)} \rightarrow M_{(aq)}^{n+} + ne^{-}$ (at anode) and $2H_2O + 2e^{-} \rightarrow 2OH^{-} + H_2$ (at cathode), where M is often Al or Fe (Fayad, 2018). Various metal complexes form; such as $M(OH)^{(n-1)+}$, $M(OH)_2^{(n-2)+}$ and $M_6(OH)_{15}^{(6n-15)+}$, 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 floc (Gamage & Chellam, 2014). The EC unit was directly followed by Ultrafiltration (UF) unit to remove all formed particulate matter more quickly than by sedimentation of the floc particles.

Employing crystallization after EC/UF-MD can mitigate membrane fouling and scaling by reducing the formation of crystal nuclei in the bulk feed, specifically when using

PW having a high TDS concentration, which is more likely causing scale formation. The EC/UF-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 (G. Chen et al., 2014; Edwie & Chung, 2013). In this research, we did test the optimized operating conditions in the EC/UF-MDC system. This research evaluated the feasibility of using EC/UF-MDC system to recover water and minerals from shale gas PW. This technology 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 (H. Chen & Carter, 2016). Further about 95% of the collected PW is directly disposed in Class II disposal well (A. J. Kondash et al., 2017). 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 (Rubinstein, n.d.). To preserve water resources, reduce the cause of earthquakes and manage fracturing wastewater, treating and reusing PW is very essential. The EC/UF-MDC could be an effective technology to treat and reuse PW to obtain high water recovery.

The overall objective of this research is to achieve high recovery rates of water and minerals from shale gas PW. Integrating EC/UF-MDC is essential to address the problem of scaling and wetting in MD. EC unit can provide high removal efficiency of TSS and total organic carbon (TOC). This can mitigate the wetting problems and providing a long-term durability of the membrane in MD system. Crystallization unit can reduce scaling in the membrane cell by decreasing the formation of crystal nuclei in the feed bulk. This can provide an attractive technical advancement capable for treating shale gas PW. Figure 1 shows the concept of a combined EC/UF-MDC processes for PW treatment.

Methods

PW Characterization

Two types of PW (A and B) collected from a hydraulic fracturing facility in Texas, USA was analyzed at the Arkansas Water Resources Center, University of Arkansas (Fayetteville, AR, USA). The EPA standard methods 160.1, 160.2, 415.1 and 180.1 were used to measure TDS, TSS, turbidity and TOC (Metcalf et al., 1991), respectively. In addition, the EPA methods 200.7 and 300.0 were also used to measure cations and anions, respectively. Conductivity was measured using conductivity meter (VWR, Radnor, PA).

Membrane characterization

The membrane 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 used in water contact angle was 2 μL introduced at a rate of 0.5 $\mu\text{L/s}$. In water contact angles, the measurements were applied after allowing the droplet to stabilize for 10 sec. For each membrane, the average value of three contact angle measurements obtained at three different locations was reported and 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).

EC/UF pretreatment

Figure 2 shows a diagram of the EC/UF system. In this work, the custom-built polycarbonate continuous reactor having a total volume of 1078 cm^3 (dimensions of 7 cm x 11 cm x 14 cm) was designed and fabricated, which was used to conduct all the continuous EC experiments. Five aluminum electrodes were fitted vertically inside the reactor with a 10 mm inter-electrode spacing. A DC power supply (Hewlett Packard, Palo Alto, CA, USA) was connected to a reverse

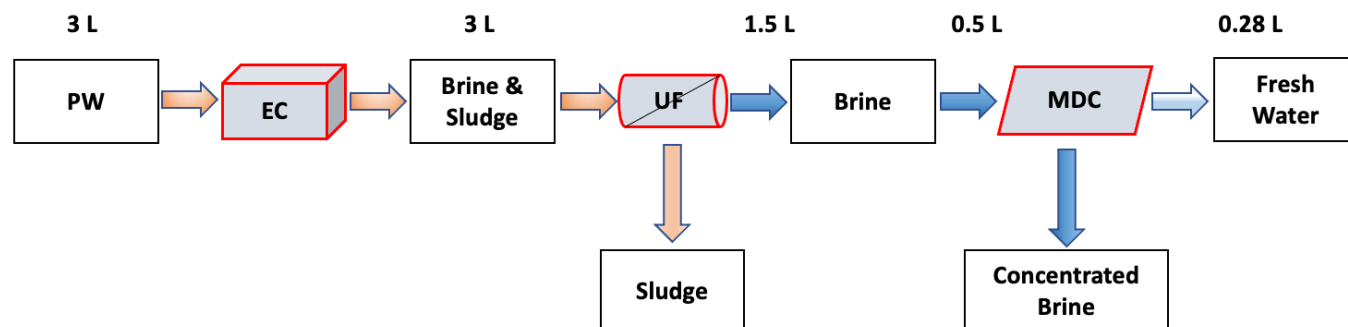


Figure 1: Diagram of the combined EC/UF-MDC process investigated in this work.

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 (Cañizares et al., 2007; Timmes et al., 2010).

UF was conducted immediately after EC using a UF ceramic membranes cell purchased from CeraMem® (Waltham, MA, USA). Honeycomb-like ceramic membrane module having a nominal average pore size of 10 nm with active membrane area of 0.13 m² was used in crossflow mode. The entire 3 L of EC treated PW was placed in the UF feed tank. Initially, the feed was recirculated through the membrane module by means of a diaphragm pump (P800, King-Kong, Taiwan) while the permeate outlet was closed. The permeate side pressure was essentially at atmospheric pressure, while the feed pressure was 70 kPa at a feed flow rate of 2.5 L/min. The permeate outlet was opened once steady state had been reached. Then, the permeate water 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 50% of the EC treated water was recovered. After each experiment, the membrane was cleaned by circulating hot DI water for 1 hour prior to starting a new experiment.

MDC treatment

Figure 3 shows the diagram of the direct contact membrane distillation (MD) system used in this work. The MD module is a custom-made acrylic membrane cell with 2 mm deep channels and 40 cm² effective membrane area. For mechanical support and mixing, PTFE spacers (ET 8700, Industrial Netting, Minneapolis, MN, USA) were applied in the membrane module. By using two peristaltic pumps (Masterflex I/P, Cole Parmer, Vernon Hills, IL), the feed and permeate streams were pumped on opposite sides of the membrane at 0.5 L/min in counter current flow. A computer-connected analytical balance (Mettler Toledo, Columbus, OH, USA) was used to measure and record the weight of the permeate. The temperature of the permeate and feed tanks was maintained at 20°C and 60°C using an external chiller and heater, respectively (PolyScience, Niles, IL, USA).

In crystallization, the feed tank was placed in a water bath after recovering 10% of the feed volume to maintain the temperature at 20°C for 5 min and induce precipitation in the feed tank to suppress scale formation on the membrane surface due to supersaturation of the feed. Then, the feed water was filtered using a paper filter (10 µm) to remove the formed salt crystals in the feed water. In this way,

we may help increasing water recovery and limit scale formation on the membrane surface. After that, the feed water was returned to the MD system and pumped through a heat exchanger to increase the temperature of the feed entering the MD module to 60 °C.

Based on the weight change of the permeate tank, the water flux was calculated and normalized using the initial average flux during the first 15 min of operation. The permeate conductivity was continuously monitored using a conductivity meter (VWR, Radnor, PA, USA). Each MD or MDC experiment was conducted using 500 ml of real or pretreated EC/UF PW. A membrane regeneration cycle was conducted during the long-term MDC experiment once 40% of the feed volume was recovered 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 for 1 hour. A commercial superhydrophobic PVDF membrane having a pore size of 0.65 µm was used in all the MD and MDC experiments conducted in this study. The PVDF membrane was purchased from MilliporeSigma (Billerica, MA, USA).

Results and Discussion

Wastewater characterization

Two types of PW (A and B) were treated with chlorine dioxide at the hydraulic fracturing facility to remove bacteria and iron prior to receipt. The water quality parameters of both PW A and B as received from the hydraulic fractur-

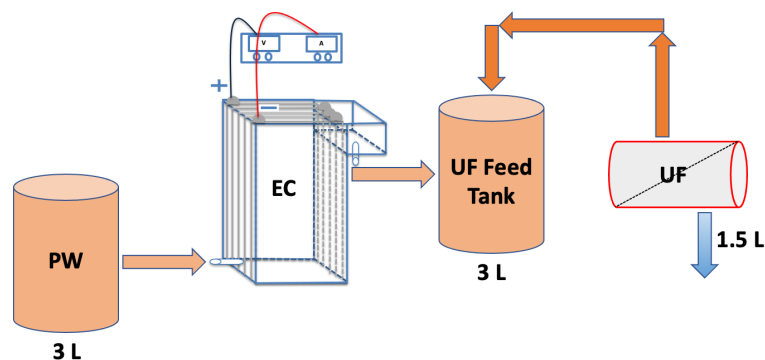


Figure 2: Diagram showing the EC/UF system investigated here.

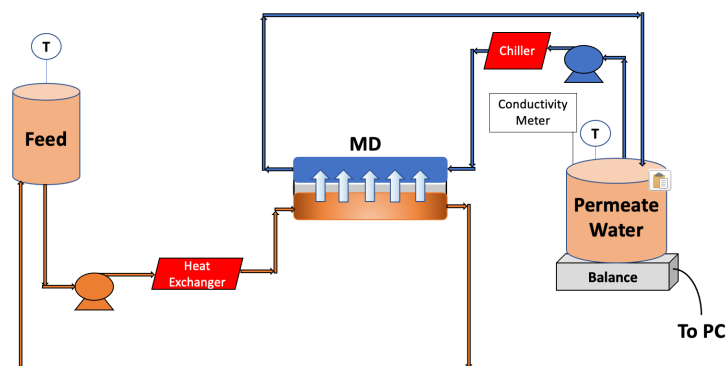


Figure 3: Diagram of MD system used in this study.

ing facility as well as after the pretreatment step of EC/UF are shown in Table 1. The TDS is very high, being about 4 times and 7 times more than seawater for PW A and PW B, respectively. Chlorine, calcium, magnesium potassium and sodium are the majority of the inorganic ions present in PW. Membrane scaling can be caused by a high concentration of calcium ions due to the precipitation of calcium sulfate (Sardari et al., 2019). The TOC and TSS are also high about 395 mg/L and 187 mg/L, respectively for PW A. The quality of the PW in general is highly variable, which affects the efficiency of the treatment operations.

Table 1: Water quality analysis for PW received from the hydraulic fracturing facility and after the EC/UF pretreatment operation.

Parameter	Unit	PW A*	EC/UF PW A**	PW B*	EC/UF PW A**
TDS	mg/L	137247	121037	245300	239760
TOC	mg/L	395	23.3	120	44
TSS	mg/L	187	76.4	131	48
Turbidity	NTU's	147	0.6	6	0.3
pH	----	7.4	7.3	6.7	3.9
Chloride	mg/L	83117	94350	156820	166170
Sulfate	mg/L	545	786	478	430
Aluminum	mg/L	0	0	0	64
Iron	mg/L	0.7	0	0.2	0.7
Calcium	mg/L	2396	N/A	30500	31700
Magnesium	mg/L	383	419	5454	5335
Potassium	mg/L	1089	906	4331	4680
Sodium	mg/L	55902	44308	63600	68100
Conductivity	μ S/cm	166300	312000	323400	229000
Total Phosphorus	mg/L as P	4.9	7.3	0.015	N/A

Note: * is real produced water received from the hydraulic fracturing facility; ** is pretreated produced water using electrocoagulation followed by ultrafiltration.

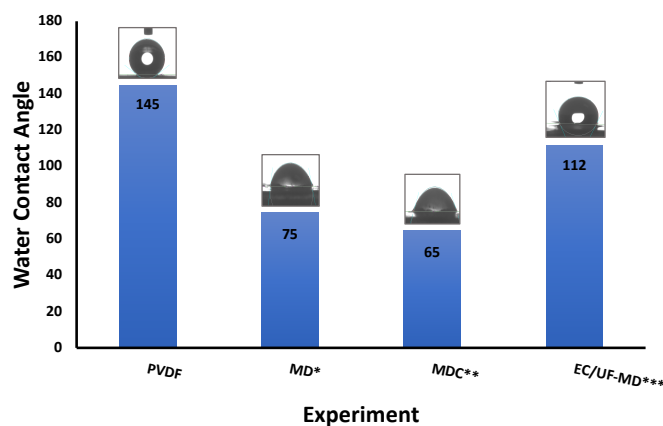


Figure 4: The water contact angle measurements of PVDF membranes before and after MD or MDC experiment.

Note: PVDF is a fresh membrane before MD or MDC experiment; * is PVDF membrane after membrane distillation of real PW A; ** is PVDF membrane after membrane distillation crystallization of real PW A; *** is PVDF membrane after membrane distillation crystallization of EC/UF pretreated real PW A.

Membrane characterization

The water contact angle of PVDF membranes before and after MD and MDC experiments is shown in Figure 4. As can be seen the PVDF fresh membrane before MD and MDC has a large water contact angle of 145 indicating a superhydrophobic membrane. 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, Figure 4 shows that the adsorption of dissolved organic compounds on the membrane surface could lead to a significant decrease in the water contact angle as obtained in PVDF membranes after MD (water contact angle of 75) and MDC (water contact angle of 65) of real PW A. These compounds could lead to scale deposition on the layer of adsorbed organic compounds if they are polar (Sardari et al., 2018). Therefore, applying a pretreatment step using EC/UF to remove most of the organic compounds and suspended solids can help in mitigating the decrease in contact angle as shown in Figure 4. The PVDF membrane after MD of EC/UF pretreated real PW A has a high water contact angle of 112.

Figure 5 shows the SEM images of all the PVDF membranes before and after MD and MDC. Table 2 shows a list of the MD and MDC experiments. In this study, we did focus on presenting the MD and MDC results using PW A at 0.5 L/min flow rate. The SEM images of unused PVDF membrane as well as membranes after, MD, MDC, EC/UF-MD, and EC/UF-MDC are given in Figure 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 minimum deposition is observed after MDC and specifically MDC of EC/UF pretreated PW A. This means that applying a pretreatment step using EC/UF followed by MD and then crystallization can successfully suppress scale formation on the membrane surface due to supersaturation of the feed and scale deposition on the layer of adsorbed organic compounds.

The elemental analysis of all PVDF membranes used in this study was obtained using energy-dispersive X-ray (EDX). The average elemental ratios of carbon/fluorine (C/F) and oxygen/fluorine (O/F) are shown in Table 3.

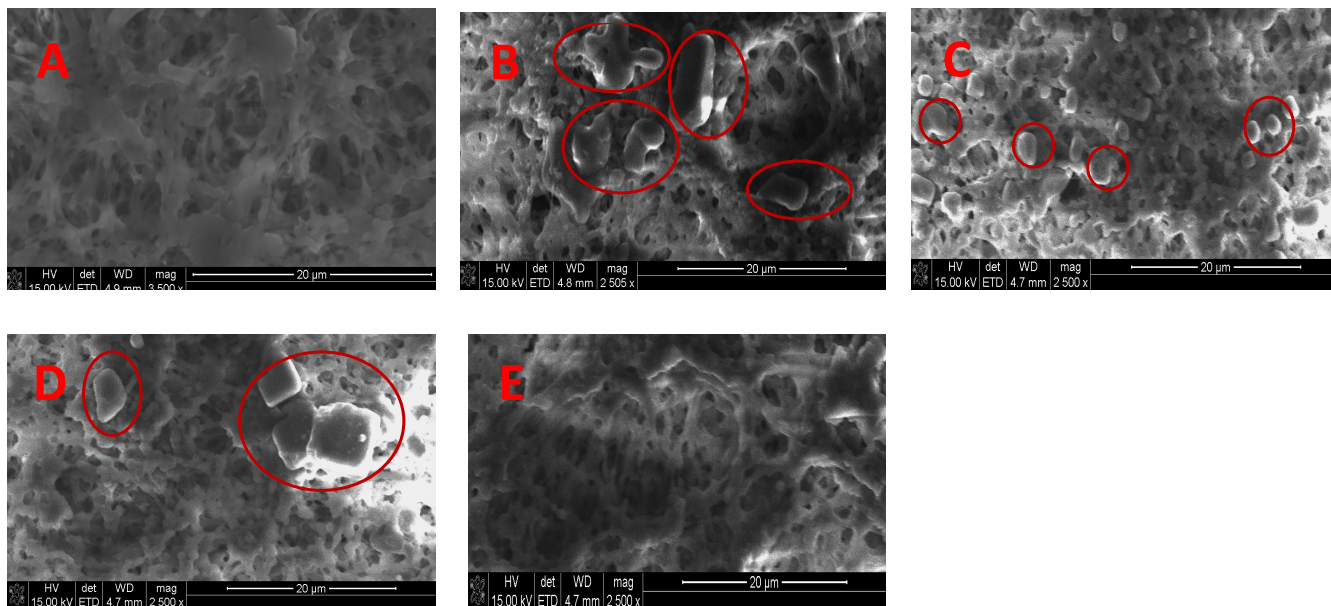


Figure 5: SEM images of the membrane surface before (fresh PVDF) and after MD or MDC: 5A is fresh PVDF membrane; 5B is PVDF membrane after MD of real PW A; 5C is PVDF membrane after MDC of real PW A; 5D is PVDF membrane after MD of pretreated EC/UF PW A; and 5E is PVDF membrane after MDC of pretreated EC/UF PW A.

Table 2: Lists of the MD and MDC experiments conducted here.

#	Experiment Type	PW Type	Flux	XRD	SEM/EDX	Whole Analysis
1	MD of real PW at 0.5 L/min flow rate*	A	Done	Done	Done	
2	MDC of real PW at 0.5 L/min flow rate*	A	Done	Done	Done	
3	EC/MF-MD of real PW at 0.5 L/min flow rate*	A	Done	Done	Done	Done
4	EC/MF-MDC of real PW at 0.5 L/min flow rate*	A	Done	Done	Done	
5	MD of real PW at 0.14 L/min flow rate	A	Done		Done	
6	MDC of real PW at 0.14 L/min flow rate	A	Done		Done	
7	Regeneration MDC of real PW at 0.5 L/min flow rate*	A	Done			
8	MD of real PW at 0.14 L/min flow rate	B	Done	Done	Done	
9	MDC of real PW at 0.14 L/min flow rate	B	Done	Done	Done	
10	EC/MF-MD of real PW at 0.14 L/min flow rate	B	Done	Done	Done	Done
11	EC/MF-MDC of real PW at 0.14 L/min flow rate	B	Done	Done	Done	
12	Regeneration MDC of real PW at 0.5 L/min flow rate*	B	Done			

Note: * means the experiments that are used in this report

rine (O/F) for 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 of real PW A with no pretreatment, which is mainly due to the organic fouling. However, the C/F and O/F ratios are low for PVDF membranes used in MDC of EC/UF pretreated PW A due to the high removal efficiency of organic compounds achieved by EC followed by UF.

EC performance

In EC, the reduction of water takes place at the cathode forming hydroxide ions, while aluminum ions are gen-

erated continuously at the anode. A variety of aluminum hydroxides are produced in the solution when coagulating ions (aluminum and/or hydroxide ions) undergo hydrolysis in water. 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. The aggregated aluminum hydroxides will adsorb soluble organic compounds. 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.

In this work, only the first and last electrodes are con-

Table 3: The C/F and O/F atomic percent ratios for PVDF membranes after MD and MDC of both real PW A and pretreated EC/UF PW A.

Membranes	C/F atom percental ratio	O/F atom percental ratio
PVDF after MD*	2.4	0.37
PVDF after MDC*	1.8	0.23
PVDF after MD**	1.7	0.19
PVDF after MDC**	1.6	0.12

Note: * is PVDF for MD or MDC of real PW A; ** is PVDF for MD or MDC of EC/UF pretreated real PW A.

nected to the power supply in a bipolar series (BPS) configuration to simplify the electrical connections. Also, the BPS configuration was used in previous studies, which show an enhancement in the TOC removal. In our previous work, several batch EC experiments were conducted to determine the appropriate EC current and reaction time. A range of currents (1 to 3 A) and a reaction time of 5 min were studied in this work. Each EC experiment was conducted continuously using 3 L of real PW A. After EC, treated water was removed from the sludge and settled floc. The recovered pretreated water samples were analyzed and the TOC removal for the recovered water was defined as, TOC removal (%) = $((X_{pw} - X_{rw}) / X_{pw}) \times 100$. Where, X_{pw} and X_{rw} are the TOC in the PW A and recovered water after EC, respectively.

Table 4 describes the TOC removal at different applied current using EC in continuous mode. As can be seen, the TOC removal increases from 65 % to 74 % as the current increases from 1 to 3 A. To obtain higher TOC removal, higher current and longer reaction time were required. A long continuous EC experiment was also conducted at 3 A current and 5 min reaction time to evaluate the feasibility of EC in obtaining a consistent TOC removal. Figure 6 shows that a consistent TOC removal (> 70%) was achieved when conducting EC in continuous mode even after 100 min. The TOC in the treated PW A that was the feed for UF and MD was 102 mg/L and 23.3 mg/L, respectively.

UF performance

The variation of permeate flux with time is shown in Figure 7. First, the ceramic membrane was tested with DI water to determine the initial DI flux of $270 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. Then, the ceramic membrane was used to filter an EC pretreated PW A. The flux gradually decreased to $71 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and stabilized at $70 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ 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 by simply recirculating the hot water for 1 hour and tested with DI water. The DI water flux shows a similar initial flux value. The initial flux was about $300 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. The result suggests that EC was effective at flocculating the dissolved organic compounds and particle

Table 4: The TOC removal of PW A treated using EC in continuous mode at different operating conditions current (1, 2, and 3), 5 min reaction time and using 5 Al electrodes in BPS configuration.

No.	Sample Name	TOC ppm	RE of TOC %
1	EC continuous, PW A at 1A current	140	65
2	EC continuous, PW A at 2A current	124	68
3	EC continuous, PW A at 3A current	102	74

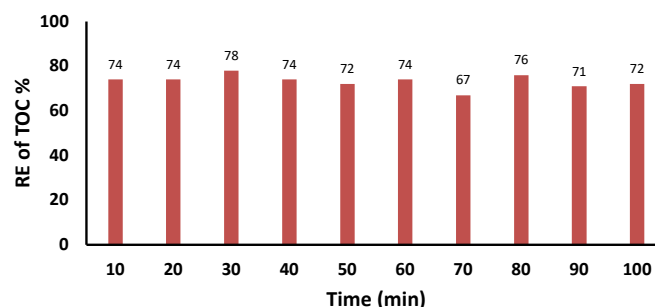


Figure 6: Total organic carbon (TOC) removal efficiency of EC treated PW A in continuous mode at 3 A current and 5 min reaction time (Long-term continuous EC experiment).

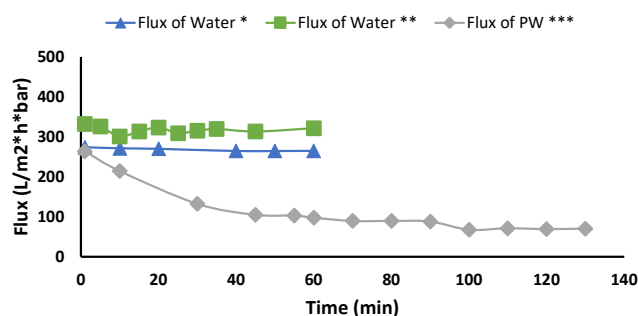


Figure 7: UF flux of water and EC treated PW A. Note: * is water flux before using EC pretreated PW A; ** is water flux after using EC pretreated PW A and cleaning with hot water; *** is the permeate flux of using EC pretreated PW A to recover about 50% of the feed volume.

matter that could plug the pores of the UF ceramic membrane. Also, regenerating the UF membrane by circulating hot water is sufficient to remove flocs from the membrane surface resulting in a minimal irreversible fouling.

MD and MDC performance

In MDC, the experiment was conducted in several runs. Each run was stopped after recovering 10% of the feed volume. Then, the feed tank was placed in water bath and maintained at 20°C for 5 min, which is considered as a crystallization step. After that the feed water was filtered to remove any formed crystal before starting the next run. To maximize the water recovery and membrane life, we would like to promote precipitation in the feed reservoir during crystallization, not on the membrane surface. The normal-

ized flux versus time for commercial PVDF membranes used in MD and MDC of real PW A with no pretreatment is shown in Figure 8. For real PW A, applying MDC can enhance the water recovery resulting in more stabilized flux as shown in Figure 8. The conductivity of the permeate samples collected from both MD and MDC experiments gradually increased due to transporting volatile inorganic compounds such as ammonium chloride from the feed stream to the permeate stream. The concentration of ammonium in the permeate samples was in the range of 10 to 18 mg/L. Table 5 summarizes the volume of the feed water recovered as well as the salts produced. Here, the use of MDC minimized the risk of supersaturation and precipitation on the membrane surface. During crystallization, precipitation was observed in the feed tank.

Figure 9 shows the normalized flux versus time for commercial PVDF membranes using MD and MDC of EC/UF pretreated real PW A. A similar flux profile was observed when using MD and MDC of EC/UF pretreated PW A. The combined EC/UF pretreatment step reduced the TOC in PW A to around 23.3 mg/L, which can help mitigating the deposition of polar organic compounds on the membrane surface and further decreasing the likelihood of precipitation of dissolved salts on the layer of adsorbed organic species

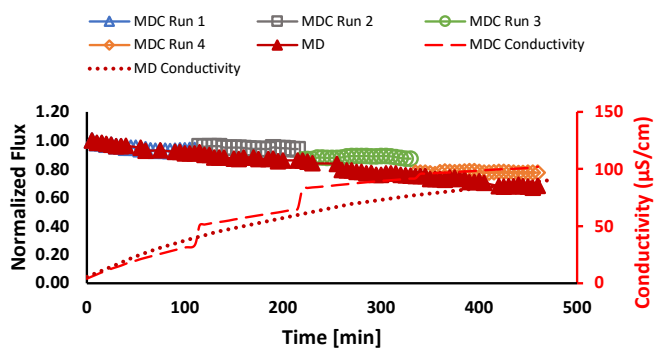


Figure 8: Normalized flux versus time for commercial PVDF membrane using MD and MDC of real PW A at 0.5 L/min flow. Note: In each MDC Run, 10 % of the feed volume was recovered.

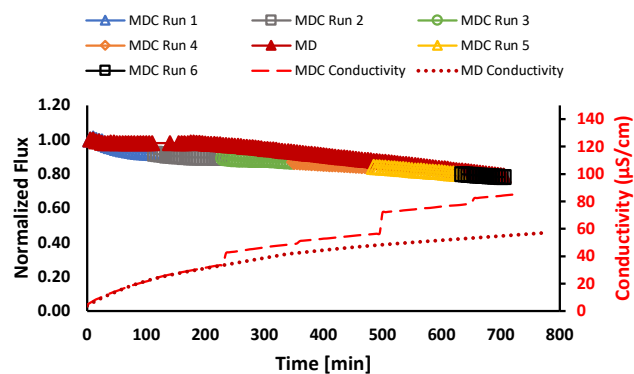


Figure 9: Normalized flux versus time for commercial PVDF membranes using MD and MDC of EC/UF treated PW A at 0.5 L/min flow. Note: In each MDC Run, 10 % of the feed volume was recovered or there was no weight increase of the permeate for 20 min.

resulting in a very similar membrane performance between MD and MDC. Crystallization showed no significant differences in membrane performance when comparing MDC and MD of EC/UF pretreated PW A, which is mainly due to first reducing the layer of adsorbed organic species, which further decreasing the likelihood of precipitation of dissolved salts on the membrane surface, and second not reaching the supersaturation limit after recovering about 55% of the feed volume.

A salt recovery of 42 kg/m³ was obtained during the MDC of PW A by cooling the feed water after each run at 20 °C for 5 min. The X-ray diffraction (XRD) analysis was conducted to identify the purity of the salts produced via MDC. Figure 10 shows the XRD patterns of crystals produced during MDC of PW A. The results indicate that the main salts formed is halite (sodium chloride), a monovalent ion of low crystallinity, as shown in Figure 10.

A high water recovery was obtained when using MDC with regeneration as shown in Table 5 indicating that 198 ml of permeate removed in the first cycle for the commercial PVDF membrane after 4 runs. Then the membrane was regenerated by simply running DI water on both sides of the membrane for 1 hour. The normalized flux for the second cycle shown in Figure 11 was similar to first cycle indicating that most of the adsorbed species were removed by simply flushing the membrane with water. During the second cycle, a desired total permeate volume of 201 ml was recovered. This means that the commercial PVDF membrane using MDC could be regenerated and reused to recover more water.

In addition, the MDC experiment with regeneration was conducted using PW B as shown in Figure 12. The first cycle was conducted for 3 runs resulting in a water recovery of 118 ml with a decrease in the normalized flux in 1st cycle run 3. However, after cleaning with water, the normalized flux increased and stabilized for two runs resulting in a water recovery of 100 ml. The conductivity of the permeate water after MDC of PW B was not high indicating that there are no volatile inorganic compounds such as ammonium chloride moved from the feed stream to the permeate stream.

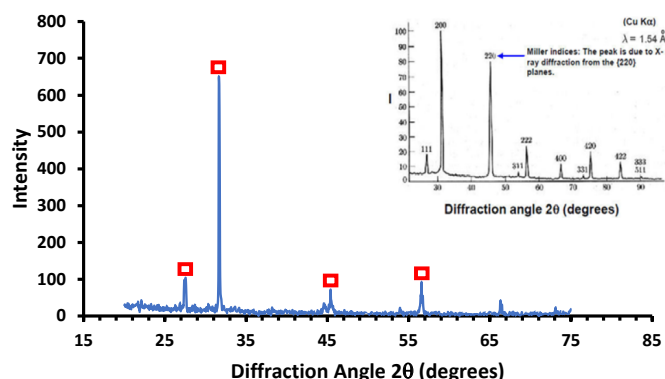


Figure 10: XRD spectra of salts produced in MDC of PW A spectra as well as XRD spectra of NaCl as standard shown in inset.

Table 5: Summary of water and salt recovery using PVDF membranes after MD and MDC of real PW

Experiment	Water Recovery (ml)	Salt Recovery (kg/m ³)
MD PW A (high flow 0.5 L/min)	183	N/A
MDC PW A (high flow 0.5 L/min)	205	42
MD EC/UF PW A (high flow 0.5 L/min)	281	N/A
MDC EC/UF PW A (high flow 0.5 L/min)	277	N/A
MDC PW A with regeneration (high flow 0.5 L/min) 1st Cycle	198	N/A
MDC PW A with regeneration (high flow 0.5 L/min) 2nd Cycle	201	N/A

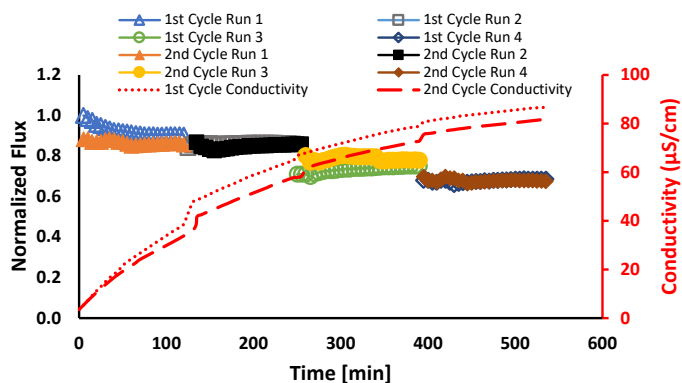


Figure 11: Normalized flux versus time for commercial PVDF membranes using MDC of real PW A at 0.5 L/min flow (long experiment with regeneration). Note: 1st Cycle was obtained by conducting MDC for 4 runs resulting in 40% water recovery; 2nd Cycle was conducted for 4 runs after cleaning the membrane.

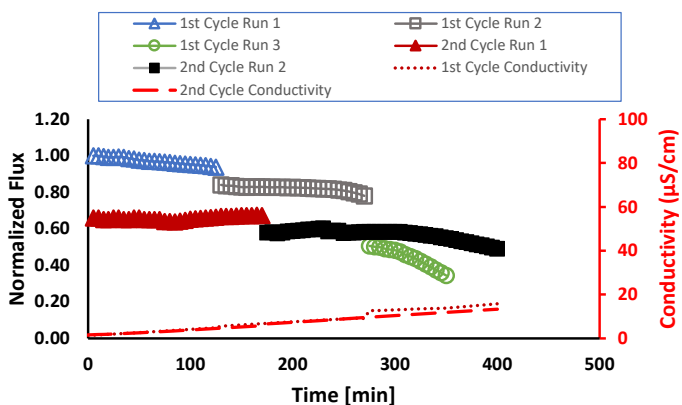


Figure 12: Normalized flux versus time for commercial PVDF membranes using MDC of real PW B at 0.5 L/min flow (long experiment with regeneration). Note: 1st Cycle was obtained by conducting MDC for 3 runs; 2nd Cycle was conducted for 2 runs after cleaning the membrane.

Conclusions

The combined EC/UF-MDC process was investigated for treating hydraulic fracturing PW. The PW investigated here had a high TDS, TSS, and TOC. Nevertheless, 55% of the feed volume was recovered using the process developed here. By applying crystallization after MD, precipitation on the membrane is suppressed when treating real PW. We found that an adequate reduction in the PW TOC can be achieved using EC, and UF can efficiently remove the particulate matter. The stability of the MDC membrane is critical and requires a membrane with high flux at high TDS and resistant to breakthrough. It is likely that the TDS and other properties of the PW will determine what train of treatment is required to achieve high water and mineral recovery.

The EC/UF-MDC technology 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. This process could be effectively used to treat and reuse PW in order to obtain about a high recovery of water. The data collected from treating real 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.

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