Long-Term Performance of a Pilot Scale Combined Chemical Precipitation-Ultrafiltration Technique for Waste Brine Regeneration at Chevron Steam Flooding Plant

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Highlights:

- Steam flooding plants generate large volumes of waste brine from the softening system
- Chemical precipitation-ultrafiltration was used for waste brine regeneration
- The combined process could remove ~100 ± 0.1% of calcium and ~99.6 ± 0.3% of magnesium
- Backwashing with an acid solution could recover UF permeability effectively

Abstract. In this work, chemical precipitation-ultrafiltration (UF) was applied for waste brine regeneration from a steam flooding plant at Duri Field, Chevron. A mixture of sodium hydroxide and sodium carbonate solution was used as chemical agent. A polypropylene (PP) UF membrane was used to remove precipitate formed in the chemical precipitation. It was found that the combined process could be used to regenerate waste brine, removing up to 100% (±0.1) of calcium and up to 99.6% (±0.3) of magnesium. High hardness removal was achieved when the chemical dosage was 1.3 to 1.7 mole of chemical/mole of hardness. Rapid permeability decline was observed in the UF membrane due to the high turbidity and TSS values of the chemically treated waste brine. Backwash with an acid solution could recover the UF membrane's permeability effectively. However, pH adjustment is needed due to the high pH value of the UF permeate (up to ~12).

Keywords: *clarification; fouling; hardness; wastewater; water softening.*

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1 Introduction

Application of a thermal method through steam injection for crude oil production is known as enhanced oil recovery (EOR). In this process, highly pressurized steam is injected to decrease oil viscosity, thus providing sufficient pressure for lifting oil to the production well. In the oil and gas industries, a large volume of water is generated [1], which contains a high concentration of minerals, especially sodium, calcium, and magnesium. Generally, the produced water is used as boiler feed water for producing injection steam. It is previously treated by a water softening process to reduce its hardness and other contaminants.

At Duri Field of PT. Chevron Pacific Indonesia (hereafter denoted as CPI), the produced water is softened by using a cation resin bed. Then, the soft water is fed to a boiler system and used to produce steam, which is re-injected into the production well. A large quantity of brine with an NaCl concentration of 8 to 9% is needed for cation resin regeneration. Currently, the cation resin regeneration at Duri Field consumes approximately 90 tons of NaCl per day. Meanwhile, the amount of waste brine coming from the process is approximately 3,180 to 4,770 m^3 per day.

The waste brine from the regeneration system contains an NaCl concentration of 4% to 5%. A large amount of waste brine with a high salt concentration may become a serious problem if discharged directly into the environment. It also contributes to scaling formation inside the plumbing system of the disposal system. Therefore, an appropriate technology to recover and reuse waste brine is urgently needed to overcome said problems.

Waste brine regeneration is similar to the water softening process itself, where hardness species are separated from the brine. One of the proposed methods for waste brine treatment is a partial reclaiming wherein the waste brine is divided into two parts [2]. The first part is discharged without treatment, while the second part is recycled and combined with fresh brine for a subsequent regeneration cycle. By using this recycling program, the cost of salt, water, and waste disposal can be reduced. However, the remaining portion of brine that is directly discharged into the environment without further treatment still poses a problem.

Chemical precipitation is a more effective method than partial reclaiming [2, 3]. Chemical precipitation may recover the brine resulting in a zero-discharge water softening process. A particular feature of this method is eliminating the conventional step of waste brine disposal. However, this process requires a large clarifier to give sufficient settling time for the sludge or precipitate formed in the chemical process.

The use of membrane separation is rapidly growing at industrial scale, especially for water and wastewater treatment [4-7]. Several membrane-based processes have been investigated for hardness removal [8-13]. The use of nanofiltration (NF) membranes has been proposed for brine regeneration [14-17]. However, NF membranes require a high operating pressure due to the high osmotic pressure of the brine. In addition, NF needs a chemical injection to avoid membrane scaling.

Another approach for waste brine treatment is by recovering pure water using membrane distillation (MD) [18,19]. Even though MD can be used to recover pure water from waste brine effectively, it requires relatively high energy associated with the high operating temperature. In addition, the application of MD is limited by the low permeating flux and membrane wetting phenomenon [20-22].

Among the available approaches, the technique oriented to regenerate waste brine by removing hardness seems to be the most profitable option. In this work, a combined chemical precipitation-ultrafiltration (UF) membrane is proposed for waste brine regeneration in a CPI steam flooding plant. The application of the combined process for softening seawater before desalination by seawater reverse osmosis has been demonstrated in [23].

Chemical precipitation is employed to remove the hardness to allow reuse of the waste brine. Meanwhile, a UF membrane is used as a post-treatment to eliminate remaining suspended solids and to produce high-quality brine. The combined process is expected to reduce fresh brine make-up and to eliminate waste brine disposal from the softening plant. In this work, the performance of the combined process during the waste brine regeneration process was investigated on a pilot scale. The performance of the process was evaluated in a long-term test. In addition, a simple techno-economic analysis was conducted.

2 Materials and Methods

2.1 Waste Brine Characteristics

A field test was conducted with real waste brine samples supplied from the Chevron steam flooding plant located in Duri Field, Indonesia. The waste brine with a total volume of 5,000 L was stored in a feed tank. The waste brine was used for 10 days of operation.

The properties of the waste brine are summarized in Table 1. In addition to salt and hardness, the waste brine also contained oil, turbidity, and total suspended solids (TSS).

Table 1 Properties of the waste brine.

Parameter	Minimum	Maximum	Average
Ca (mg/L)	1,260.0	5,500.0	3,964.6
Mg (mg/L)	224.0	717.0	466.9
Na (mg/L)	14,565.0	25,980.0	20,254.2
Cl (mg/L)	22,009.2	44,018.0	30,401.6
pH	6.6	7.2	6.9
Oil content (mg/L)	0.5	2.3	1.1
Turbidity (NTU)	16.4	76.7	36.7
TSS (mg/L)	3.1	59.0	30.0

2.2 Description of the Proposed Waste Brine Regeneration Process

The softener unit at the CPI steam flooding plant is illustrated in Figure 1(a). The softener is used to remove the hardness from the produced water. When the softener is saturated with hardness, chemical regeneration is conducted. Generally, a high concentration of NaCl solution is used in the regeneration process. The regeneration process generates waste brine that contains remaining NaCl and hardness (Ca and Mg).

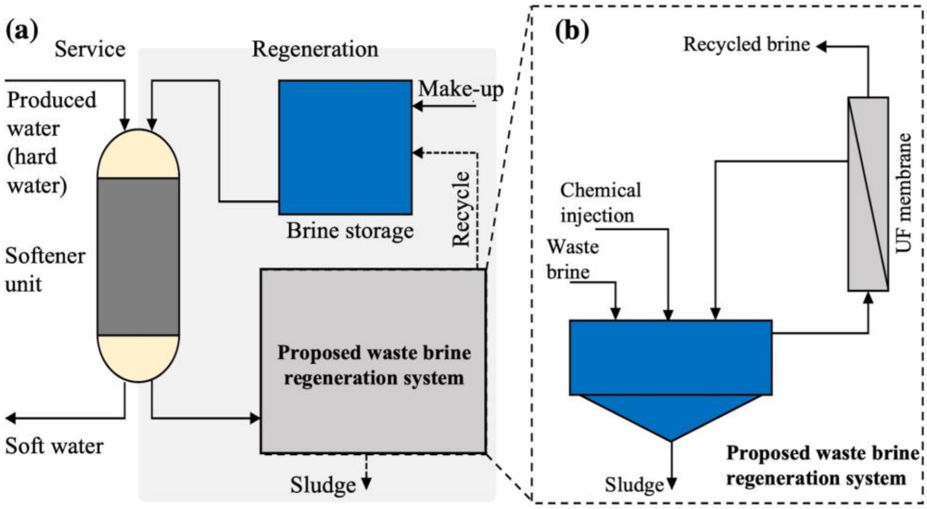

Figure 1 Schematic illustration of (a) the proposed waste brine regeneration process and (b) the combined chemical precipitation-ultrafiltration process.

A chemical precipitation-UF technique (Figure 1(b)) is proposed here to regenerate the waste brine. The chemical precipitation is used to remove the hardness by injecting a mixture of sodium hydroxide and sodium carbonate solution into the waste brine. The chemical injection produces sludge needs a clarifier for precipitation of the sludge. Then, a UF membrane is employed to improve the removal of the remaining sludge and to produce a high-quality brine. The permeate of UF is recycled to the brine storage while the concentrate is recirculated to the clarifier or chemical precipitation unit. The sludge is removed from the bottom part of the clarifier.

2.3 Combined Chemical Precipitation-UF System

A schematic of the experimental set-up and photographs of the system are shown in Figures 2(a) and (b). The system comprised a feed water tank, a membrane module, a chemical injection module, a stabilizer tank, and a chemical-in-place (CIP) unit. The system was designed for a capacity of 500 L/day. A polypropylene (PP) UF membrane with a nominal pore size of 50 nm was purchased from GDP Filter, Indonesia. The membrane was treated by the manufacturer to improve its hydrophilicity.

The membrane module had an effective surface area of 5.4 m^2 (module diameter = 4 inch; membrane effective length = 0.4 m; fiber outside diameter = 0.4 mm). Technical grade NaOH and Na_2CO_3 were used for chemical injection and citric acid was used for chemically enhanced backwash. These chemicals were purchased from a local supplier (Brataco, Indonesia). Demineralized water was used for the preparation of the chemical solutions. During operation, the waste brine from the feed tank was transferred to the stabilizer tank using a feed pump. The waste brine was then injected by chemical solutions supplied from the chemical injection system. The mol ratio of NaOH to Na2CO3 was 2:1.

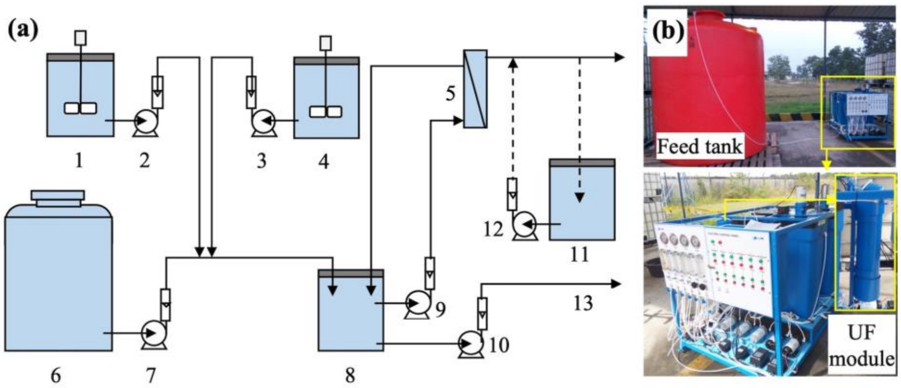

Figure 2 Schematic illustration of the combined chemical precipitation-ultrafiltration process: (a) process flow diagram and (b) photograph of the bench scale combined chemical precipitation-ultrafiltration system (1 – NaOH tank; 2 – dosing pump; 3 – dosing pump; 4 – Na_2CO_3 tank; 5 – UF module; 6 – feed tank; 7 – feed pump; 8 – stabilizer tank; 9 – UF pump; 10 – discharge pump; 11 – CIP tank; 12 – CIP pump; 13 – sludge discharge).

The chemical dosing was varied during the field test to obtain maximum hardness removal. The solution in the stabilizer tank was filtered by using the UF membrane in crossflow filtration mode. The concentrate stream from the UF membrane was recirculated back into the stabilizer tank. The UF membrane was operated at trans-membrane pressures of 0.02 to 0.14 MPa with a constant permeate flow of 60 L/h. The sludge formed in the stabilizer tank was disposed to a sludge collecting tank (not shown in the schematic diagram) by using a sludge disposal pump.

3 Results and Discussions

3.1 Removal of Ca and Mg

Figures 3(a) and (b) show the Ca and Mg concentrations in the feed and the UF permeate during the field test. Meanwhile, the chemical dosage and photographs of the UF permeate, waste brine, and sludge are shown in Figures 3(c) and (d), respectively. At the beginning of the operation, the total removal of Ca and Mg was less than 80%. This was due to the low mol ratio of chemical to total Ca and Mg (chemical/hardness = 0.4-1.0/1 (mol/mol)), except for the first day of trial (see Figure 3(c)).

On the first day, there was a problem in the piping system so the mixing of the chemical and the waste brine in the stabilizer tank was disturbed. Consequently, the removal of the hardness was very low. The removal increased from day 6 to 9 when the chemical dosage was increased to 1.3 to 1.6 (mol/mol). The removal of Ca was 97.0 ± 3.4 to 100.0 ± 0.1 while the Mg removal was 95.4 ± 3.4 to 99.6 ± 0.3. It is obvious that the increase in chemical dosage improved the hardness removal. On the 10th day of operation, the removal of Ca and Mg decreased again due to the decrease in chemical injection from 1.6 to 1.1 (mol/mol).

The high chemical injection dosage needed for obtaining almost complete removal of hardness may be associated with the low efficiency of the chemical precipitation reaction due to a low mixing rate [24]. As can be seen in Figure 2(a), the mixing of the chemical and the waste brine only relies on the solution recirculation (UF concentration). As a consequence, a relatively high chemical injection was needed. Actually, on the first day, the system was equipped with a static mixer before the stabilizer tank. However, precipitation occurred in the mixer, leading to plugging of the piping and the static mixer. Therefore, the static mixer was removed and replaced by solution recirculation.

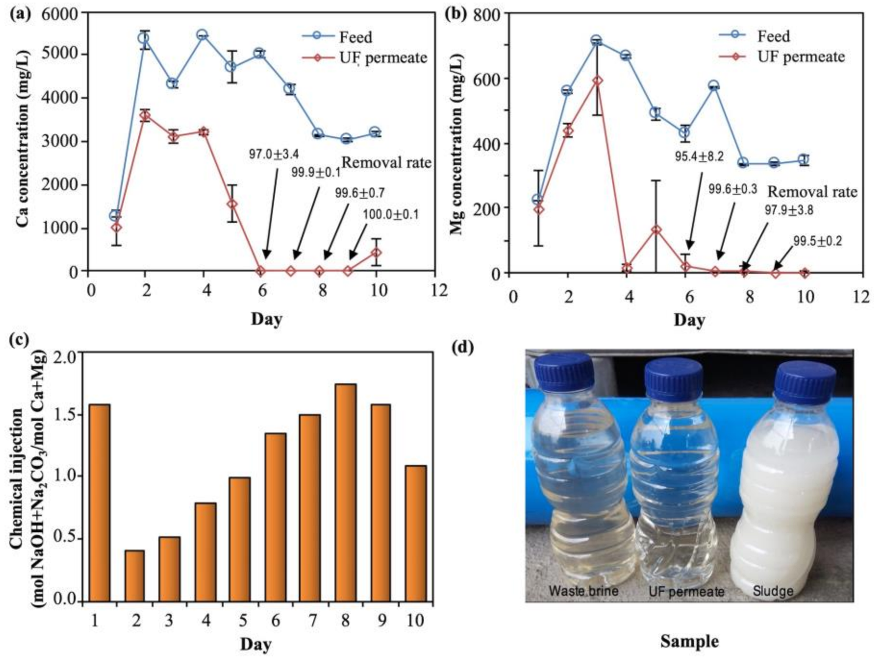

Figure 3 (a) Ca concentration and (b) Mg concentration of the feed and the UF permeate, (c) chemical dosage, and (d) photographs of the waste brine, the UF permeate and the sludge from the chemical precipitation-UF system.

3.2 Oil Content, Turbidity, and TSS

The oil content of the waste brine and the UF permeate are shown in Figure 4(a). As can be seen from the figure, the oil content of the treated brine was also reduced. Almost complete removal of the oil content was observed on the 8th day of operation. The reduction of the oil content may be attributed to the precipitation of the oil in a high pH environment [25]. Even though the system showed a relatively low oil removal, the treated waste brine met the requirement of oil content (<1 mg/L).

The turbidity and TSS of the feed waste brine and the UF permeate are shown in Figure 4(b). As can be seen in the figure, the UF permeate showed lower turbidity and TSS values than the feed. This is the main purpose of UF usage in the system. It is well known that the chemical precipitation method can be used to effectively remove hardness. However, it needs a large clarifier to provide sufficient retention time for the precipitate to settle (see Figure 4(c)). This problem can be addressed by using a UF membrane. Since the UF membrane was operated in crossflow filtration mode, continuous filtration was possible. It can be observed from Figure 4(b) that the reduction of turbidity and TSS from the waste brine seemed to be very low. Actually, the UF removed turbidity and TSS from the stabilizer tank. In the tank, the turbidity and TSS of the chemically injected waste brine were increased due to the formation of sludge. For instance, on the 8th day, the turbidity and TSS of the solution in the stabilizer tank were up to 226 and 190 times higher, respectively, than in the waste brine. In this period, the removals of turbidity and TSS from the solution in the stabilizer tank by UF were 99.9 ± 0.1 and 100.0 ± 0.0, respectively.

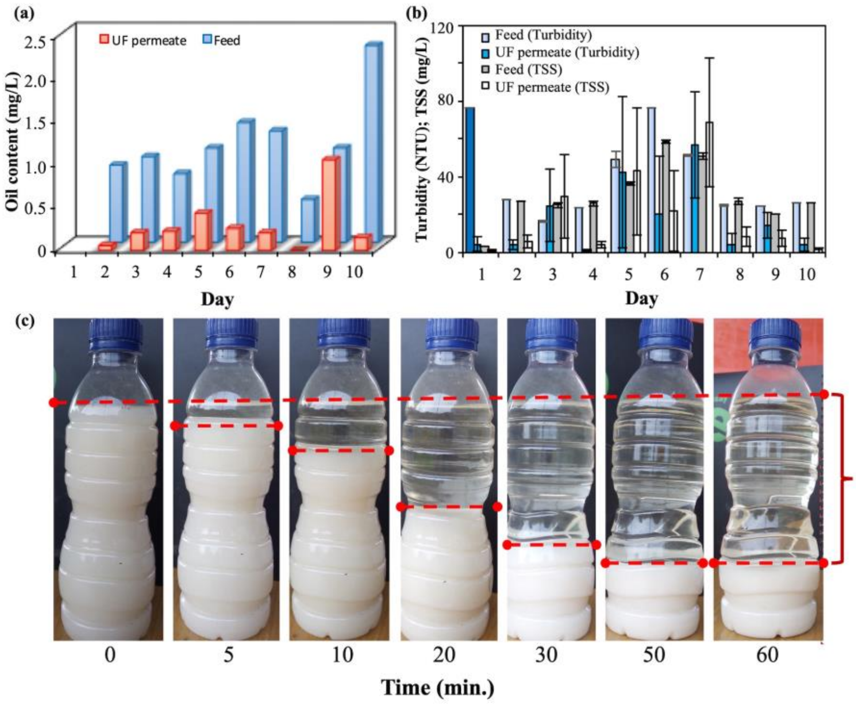

Figure 4 (a) Average oil content, (b) turbidity and TSS, and (c) photograph of the sludge at various times.

3.3 Na, Cl, and pH

Figure 5 shows the Na and Cl concentration and the pH of the waste brine and the UF permeate. It can be seen that the concentration of NaCl was relatively high, about 2 to 3% wt. The aim of the waste brine regeneration process is to recover this brine. The chemical injection results in an increase in Na concentration of the UF permeate. It is expected that the brine can be reused for the proceeding regeneration process after being added by fresh brine. Reusing the regenerated waste brine may reduce the fresh brine make-up and eliminate the disposal of brine into a disposal well. This is beneficial to reduce the operational cost and to solve associated waste brine problems.

However, the pH value of the UF permeate was still relatively high due to the chemical injection. The maximum pH value of the treated waste brine should be 8. Combining the treated waste brine, which has a high pH value, with fresh brine can cause a problem in the softening process. Therefore, chemical neutralization is needed. For the neutralization process, hydrochloric acid may be used. Besides neutralization, HCl provides additional Cl, which is useful for waste brine recovery.

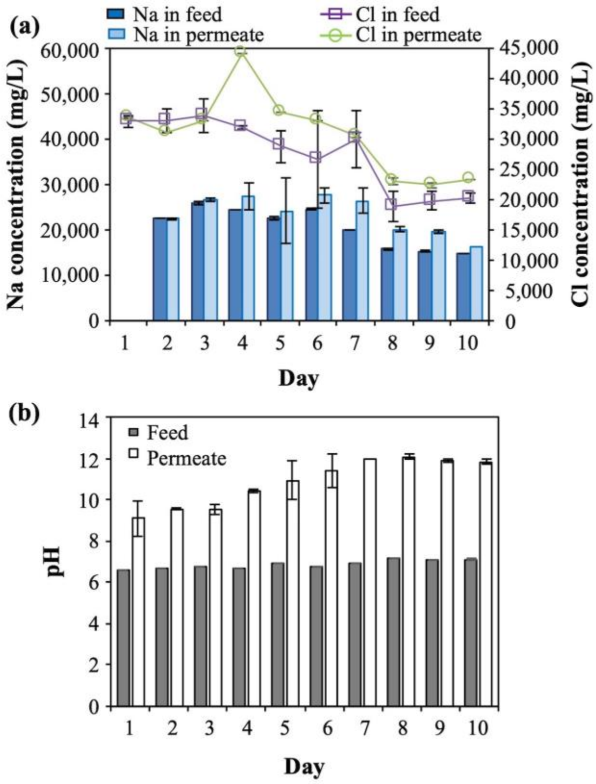

Figure 5 (a) Na and Cl concentration and (b) pH of the waste brine and the UF permeate.

3.4 Long-Term Performance of UF Plant

Figure 6 shows the permeability of the UF membrane during the filtration of waste brine after chemical injection, on the 8th day of operation. Rapid permeability declines were observed due to the high turbidity and TSS values of the solution. On this day, the turbidity of the solution in the stabilizer tank was 2,400 to 5,680 mg/L, while the TSS was 2,520 to 4,950 mg/L. A periodic backwash was then conducted with the feed pressure increased from 0.05 MPa to 0.15 MPa. As can be seen in Figure 6, backwashing using UF product can be used to recover UF permeability. However, after the shut-down period, the permeability was not effectively recovered, even though chemically enhanced backwash was used. The backwash and chemically enhanced backwash showed better permeability recovery in a continuous process. More effective permeability recovery was exhibited by chemically enhanced backwash using an acid solution, i.e. citric acid, which may be associated with the dissolution of the precipitate from the membrane surface [26,27].

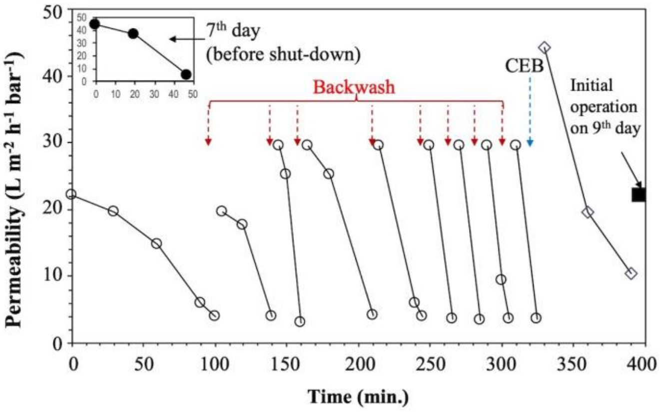

Figure 6 The permeability of the UF membrane at various operation times (on the 8th day of operation; CEB – chemically enhanced backwash).

3.5 Techno-Economic Analysis

It was found that the combined chemical precipitation-UF technique can be used for waste brine regeneration by removing the hardness components. Waste brine regeneration may provide several benefits for the softening system of a steam flooding plant, including brine disposal elimination and brine make-up reduction. Even though chemical injection is required, the addition of sodium hydroxide and sodium carbonate will increase the sodium concentration, which is beneficial for softener regeneration. At the CPI steam flooding plant, about 1,576,800 m^3/year of waste brine is produced. It was analyzed that the average NaCl concentration of the waste brine was 2.5% wt. Accordingly, 39,420 ton/year NaCl can be reused. Assuming that the NaCl price is 100 \$/ton, the NaCl cost saving is about 3,942,000 \$/year. In addition, if the operation and maintenance cost of the deep-well injection will be 0.86 \$/m^3 [28], the cost saving for brine disposal will be 1,348,579 \$/year.

4 Conclusion

In this study, the performance of a pilot-scale chemical precipitation-UF unit was investigated for waste brine regeneration in a CPI steam flooding plant. It was found that the combined process can be used to regenerate the waste brine by removing up to 100% (±0.1) of Ca and up to 99.6% (±0.3) of Mg. High hardness removal was achieved when the chemical dosage was 1.3 to 1.7 (mol $NaOH+Na_2CO_3$/mol Ca+Mg). Rapid flux declines were observed in the UF membrane due to the high turbidity and TSS values of the chemically treated waste brine. Backwash with an acid solution could effectively recover UF membrane permeability. Even though the process can effectively regenerate waste brine, pH adjustment is needed due to the high pH value of the UF permeate.

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References

[1] Fakhru'l-Razi, A., Pendashteh, A., Abdullah, L.C., Biak, D.R.A., Madaeni, S.S. & Abidin, Z.Z., *Review of Technologies for Oil and Gas Produced Water Treatment*, Journal of Hazardous Materials, **170**, pp. 530-551, 2009.

[2] Michaud, C.F., *'Zero D' A Method of Reducing Industrial Softener Discharge*, Water Conditioning & Purification Magazine, April, pp. 1-4, 2010.

[3] Michaud, C.F., *Zero Discharge Softener Regeneration*, Water Conditioning & Purification Magazine, **39**, pp. 40-45, 1994.

[4] Drioli, E., Stankiewicz, A.I. & Macedonio, F., *Membrane Engineering in Process Intensification-An Overview*, Journal of Membrane Science, **380**, pp. 1-8, 2011.

[5] Sianipar, M., Kim, S.H., Khoiruddin, K., Iskandar, F. & Wenten, I.G., *Functionalized Carbon Nanotube (CNT) Membrane: Progress and Challenges*, The Royal Society of Chemistry, RSC Advances, **7**, pp. 51175-51198, 2017.

[6] Aryanti, P.T.P., Sianipar, M., Zunita, M. & Wenten, I.G., *Modified Membrane with Antibacterial Properties*, Membrane Water Treatment, **8**, pp. 463-481, 2017.

[7] Wenten, I.G., Khoiruddin, K., Aryanti, P.T.P. & Hakim, A.N., *Scale-up Strategies for Membrane-Based Desalination Processes: A Review*, Journal of Membrane Science and Research, **2**, pp. 42-58, 2016.

[8] Song, Y., Qin, W., Li, T., Hu, Q. & Gao, C., *The Role of Nanofiltration Membrane Surface Charge on the Scale-Prone Ions Concentration Polarization for Low or Medium Saline Water Softening*, Desalination, **432**, pp. 81-88, 2018.

[9] Labban, O., Liu, C., Chong, T.H. & Lienhard V.J.H., *Fundamentals of Low-Pressure Nanofiltration: Membrane Characterization, Modeling, and Understanding the Multi-Ionic Interactions in Water Softening*, Journal of Membrane Science, **521**, pp. 18-32, 2017.

[10] Tang, S.C.N., Birnhack, L., Cohen, Y. & Lahav, O., *Selective Separation of Divalent Ions from Seawater Using an Integrated Ion-Exchange/Nanofiltration Approach*, Chemical Engineering and Processing-Process Intensification, **126**, pp. 8-15, 2018.

[11] Yildiz, E., Nuhoglu, A., Keskinler, B., Akay, G. & Farizoglu, B., *Water Softening in a Crossflow Membrane Reactor*, Desalination, **159**, pp. 139-152, 2003.

[12] Juang, R.S. & Chiou, C.H., *Feasibility of the Use of Polymer-Assisted Membrane Filtration for Brackish Water Softening*, Journal of Membrane Science, **187**, pp. 119-127, 2001.

[13] Brastad, K.S. & He, Z., *Water Softening Using Microbial Desalination Cell Technology*, Desalination, **309**, pp. 32-37, 2013.

[14] Salehi, F., Razavi, S.M.A. & Elahi, M., *Purifying Anion Exchange Resin Regeneration Effluent Using Polyamide Nanofiltration Membrane*, Desalination, **278**, pp. 31-35, 2011.

[15] Rawson, J.R.Y. & Ayala, R.E., *System for the Purification and Reuse of Spent Brine in a Water Softener*, U.S. Patent No 7, 132,052, 2006.

[16] Lien, L.A., Spent Brine Reclamation, US Patent No. 6, 004,464, 1999.

[17] Brigano, F.A., Soucie, W.J. & Rak, S.F., *Reclaiming of Spent Brine*, U.S. Patent No. 5, 254,257, 1993.

[18] Sanmartino, J.A., Khayet, M., García-Payo, M.C., El-Bakouri, H. & Riaza, A., *Treatment of Reverse Osmosis Brine by Direct Contact Membrane Distillation: Chemical Pretreatment Approach*, Desalination, **420**, pp. 79-90, 2017.

[19] Gryta, M., Karakulski, K., Tomaszewska, M. & Morawski, A., *Treatment of Effluents from the Regeneration of Ion Exchangers Using the MD Process*, Desalination, **180**, pp. 173-180, 2005.

[20] Yan, K.K., Jiao, L., Lin, S., Ji, X., Lu, Y. & Zhang, L., *Superhydrophobic Electrospun Nanofiber Membrane Coated by Carbon Nanotubes Network for Membrane Distillation*, Desalination, **437**, pp. 26-33, 2018.

[21] Susanto, H., *Towards Practical Implementations of Membrane Distillation*, Chemical Engineering and Processing: Process Intensification, **50**, pp. 139-150, 2011.

[22] Himma, N.F., Prasetya, N., Anisah, S. & Wenten, I.G., *Superhydrophobic Membrane: Progress in Preparation and Its Separation Properties*, Reviews in Chemical Engineering, **35**, pp. 211-238, 2019.

[23] Aguinaldo, J.T., *Application of Integrated Chemical Precipitation and Ultrafiltration as Pre-Treatment in Seawater Desalination*, Desalination and Water Treatment, **2**, pp. 115-127, 2009.

[24] Nason, J.A. & Lawler, D.F., *Particle Size Distribution Dynamics during Precipitative Softening: Declining Solution Composition*, Water Research, **43**, pp. 303-312, 2009.
[25] Rajaković-Ognjanović, V., Aleksić, G. & Rajaković, L., *Governing Factors for Motor Oil Removal from Water with Different Sorption Materials*, Journal of Hazardous Materials, **154**, pp. 558-563, 2008.
[26] Shi, X., Tal, G., Hankins, N.P. & Gitis, V., *Fouling and Cleaning of Ultrafiltration Membranes: A Review*, Journal of Water Process Engineering, **1**, pp. 121-138, 2014.
[27] Julian, H., Ye, Y., Li, H. & Chen, V., *Scaling Mitigation in Submerged Vacuum Membrane Distillation and Crystallization (VMDC) with Periodic Air-Backwash*, Journal of Membrane Science, **547**, pp. 19-33, 2018.
[28] Foldager, R.A., *Economics of Desalination Concentrate Disposal Methods in Inland Regions: Deep-Well Injection, Evaporation Ponds, and Salinity Gradient Solar Ponds*, New Mexico State University Honors Program Thesis in Environmental Science, 2003.