Doctoral Dissertation
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Technical Feasibility Study of the Treatment of Liquid Waste from the Oil & Gas Industry with Membrane-based Techniques

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I hereby declare that the contents and organisation of this dissertation constitute my own original work and does not compromise in any way the rights of third parties, including those relating to the security of personal data.

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Summary

Environmental challenges related to the management of complex aqueous liquids related to the various phase of hydrocarbon-based energy production are many and diverse. Compared to traditional treatment methods, membrane processes may offer an environmentally friendly alternative under some circumstances, due to their high selectivity, scalability, and cost efficiency. This dissertation investigates the application of membrane technology in the context of oil and gas aqueous by-product treatment and ULO recovery.

The dissertation is divided into 3 chapters. Chapter 1 investigates the potential utilization of a forward osmosis-based system combined with nanofiltration to concentrate produced water and extract freshwater. High recovery experiments are discussed, followed by nanofiltration applied on the diluted draw solution to regenerate it and achieve a final freshwater product. Chapter 2 examines instead forward osmosis for a different application, namely, for amine water volume reduction (dewatering). In this case, the process does not aim at extracting freshwater but to concentrate the amine water as much as possible, without necessarily recover the draw agent. Chapter 3 studies the purification of used lubricant oil (ULO) obtained from oil & gas industry with porous ultrafiltration ceramic membranes. Using real ULO samples, different native and grafted membranes are investigated to understand the effect of pore size, membrane surface modification, and different test conditions (e.g., pressure, temperature, and crossflow).

Improper liquid waste treatment and disposal from oil & gas industry can have both environmental and economic detrimental effects. This study focused on the use of membrane technology for the treatment of produced water, amine water, and used lubricant oils. Synthetic produced water and amine water were

experimented using forward osmosis. Ultrafiltration was the method of choice for experimenting on the treatment and recovery of used lubricant oils. Overall, these methods provided viable treatment solutions to waste liquids from the oil & gas industry, with each method having its own merits. It is crucial, however, to also highlight the challenges for each method used, and the viable solutions and/or further studies that can overcome those challenges.

The process of forward osmosis followed by nanofiltration for the treatment of synthetic produced water and the regeneration of the draw solution is only partly technically viable. $MgCl_2$ was tested as draw agent at various osmotic pressures and draw-to-feed ratios in order to determine the ideal parameters to achieve the highest recovery, with modelling to validate the data and to explore different conditions. The combination of FO followed by NF achieved up to 73% water recovery for the specific feed solution investigated, but with important loss of draw agent, which suggests the need to replenish the draw agent continuously. Also, the results suggest the potential need of using reverse osmosis membranes instead of NF membranes for the draw agent recovery. Further improvements to this study may include the use of real produced water samples and economic calculations to gain insight into the economic viability of the most promising configurations.

Concentration of amine water (a byproduct of gas sweetening processes) was experimented using forward osmosis. The most suitable draw solution (NaCl) was used for high recovery experiments. Varying osmotic pressure and draw-to-feed volume ratios, experimental and simulated results were combined to estimate achievable recovery rate under a broad range of operating conditions, once again supported by modelling by deploying the analytical FO equations. High osmotic pressure combined with larger initial DS-to-FS volume ratio yielded higher recovery rates, with the highest recovery achieved being 55%. Counter-current configuration proved as superior to co-current configuration in terms of system efficiency. Nevertheless, it is important to note that higher osmotic pressures would ultimately result in increased operational costs and possible complications in managing or discharging the effluent draw solution. The membrane mostly succeeded in preventing reverse flux, with high retention rate of TOC and TN observed. Overall, FO demonstrated medium to high potential in dewatering amine water; however, challenges, such as membrane fouling (which requires constant cleaning and/or membrane changeout depending on operating conditions) still stand. Overall, the practical application of this method would require careful study of the system objectives, costs, and legal limitations.

Finally, several lab scale tests were performed for the recovery of ULO using UF membranes with different pore sizes (10 nm, 30 nm, and 5 nm). The obtained results showed that suitable purity, yield, and viscosity retention were achieved using the 10 nm ceramic UF membranes. This was further examined using not only native ceramic membranes, but also grafted ceramic membranes. In addition, different feed oils were tested; clean lube oil, base oil, ULO after a first pre-treatment (using a distillation column), ULO after a second pre-treatment (using a second distillation column), and crude ULO. Tests performed using clean lube oil as a feed showed a stable flux with time, with no observable influence of membrane pore size or grafting chemistry. In addition, up to 100% removal of several metals, such as Ca, Mg, and Mo was observed, while other elements, such as P, Zn, and Fe, were partially removed. High declining fluxes were obtained when testing base oil as the feed stream with native membranes. Moreover, fluxes were pore size dependent. Finally, testing different ULO with different pre-treatment as feed streams using native 10 nm membrane resulted in a stable flux that was independent from the feed type. High removal of metals, such as Ca, Mg, and Mo was observed, while other elements, such as P, S, Zn, Si, were retained at a lower rate by the membrane, similar to the results obtained for the clean lube oil.

Based on the conducted literature review and experimental results of this study, membrane technology demonstrates technical promise in treatment of different liquid streams and from the oil & gas industry. While the experimental results highlight the positive outcomes, it is vital to consider economic and legal limitations in managing the effluent solutions that may require further treatment before safely discharging into the environment.