MINISTRY OF EDUCATION AND TRAINING

VIETNAM ACADEMY OF SCIENCES AND TECHNOLOGY

GRADUATE UNIVERSITY OF SCIENCES AND TECHNOLOGY

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INVESTIGATE ON POTENTIAL DRAW SOLUTIONS TO BE USED IN FORWARD OSMOSIS TECHNOLOGY FOR THE DESALINATION TREATMENT OF SALINE AND BRACKISH WATER

SUMMARY FOR DOCTORAL THESIS
IN ENVIRONMENTAL ENGINEERING

Code: 9 52 03 20

Ha Noi - 2025

The thesis was done at: Graduate University of Sciences and Technology, Vietnam Academy of Sciences and Technology

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The thesis was defended before the Doctoral Thesis Evaluation Council organized by Graduate University of Sciences and Technology, Vietnam Academy of Sciences and Technology at .... : .... , ... / .... / 2025

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INTRODUCTION

1. The urgency of the thesis

Since ancient times, freshwater has always been considered an extremely important resource, because it plays an essential role in maintaining life and the normal development of both humans and other lifeforms. However, in recent years, under the combined impact of many objective and subjective factors, the world in general and Vietnam in particular are experiencing a shortage of freshwater to serve the needs of people, especially during the dry season.

Faced with this practical situation, developing new desalination technologies to produce freshwater is becoming an inevitable development trend in the world, and Vietnam is no exception. However, the desalination technologies that are commonly used today (including evaporation-condensation technology and reverse osmosis technology) all have certain disadvantages, requiring the development of new desalination technologies that are more effective and environmentally friendly [1,2]. One of such potential solutions proposed is the forward osmosis technology, because compared to other traditional desalination technologies, this technology has the advantage of lower energy consumption and allows more stable operation, while still maintaining the quality of the output water source to ensure strict technical requirements for domestic uses [3–5].

The most important factor in a forward osmosis system is the draw solution - because the main driving force for the mass transfer of water from the feed stream through the semipermeable membrane to the draw solution is the difference in natural osmotic pressure between the feed stream and the draw solution. Therefore, choosing the appropriate draw solution (or more specifically, the appropriate draw solute) is a very important task, determining the overall operating efficiency of desalination systems producing freshwater utilizing the forward osmosis technology [6,7]. In general, an ideal draw solute or draw solution for a desalination system producing freshwater utilizing the forward osmosis technology must meet the following three basic requirements: (1) possessing a high natural osmotic pressure; (2) causing negligible reverse draw solute flux through the membrane, and (3) being easy to regenerate. In addition, since the reverse draw solute flux phenomenon is inevitable, an ideal draw solution must also be relatively safe for human health in particular, and for the entire ecosystem and environment in general [8].

Therefore, it can be affirmed that the study in this thesis *"Investigate on potential draw solutions to be used in forward osmosis technology for the desalination treatment of saline and brackish water"* is a promising approach, satisfying the practical needs of society while also catching up with general research trends around the globe. Specifically, the study focused on the investigation of potential draw solutions with high water flux capacity, the most notable of which is the novel draw solution containing a mixture of trisodium α-DL-alanine diacetate and citric acid. In addition, the study also investigated the effects of some operating conditions and extended operating duration on the performance of forward osmosis systems using these potential draw solutions, thereby obtaining a general and comprehensive view on their possible application in producing freshwater from saline and brackish water sources..

2. Research objectives

Selecting some potential novel draw solutions to be used in forward osmosis technology for the desalination treatment of saline and brackish water, and determining the influence of operating conditions and extended operating duration on the performance of these potential draw solutions in laboratory scale.

3. Research content

- Investigate the basic performance of some selected potential draw solutions.
- Investigate the influence of some operating conditions (including: inlet flow rate, inlet pressure difference, and inlet temperature) on the performance of selected potential draw solutions, and optimize these operating conditions to obtain the best forward osmosis efficiency.
- Investigate the influence of the long-term operation on the performance and fouling characteristics of semipermeable membrane when utilizing the selected potential draw solutions, and the membrane cleansing efficiency of the conventional direct washing method.
- Investigate the freshwater production capability of forward osmosis systems utilizing the selected potential draw solutions.
- Investigate the forward osmosis performance of selected potential draw solutions against actual saline/brackish water samples.

CHAPTER 1: LITERATURE OVERVIEW

1.1. Desalination technologies for freshwater production

1.1.1. Freshwater and the importance of freshwater

1.1.2. The current situation of freshwater resource in Vietnam

1.1.3. Desalination technologies for the purpose of freshwater production

1.2. Forward osmosis technology

1.2.1. Osmosis processes and the classification of osmosis processes

1.2.2. Review on research trends in Vietnam and around the globe

1.3. Factors influencing the performance of forward osmosis systems

1.3.1. Semipermeable membrane

1.3.2. Draw solution

1.3.3. The phenomenon of concentration polarization

1.3.4. Operational parameters

1.4. Membrane fouling, methods to control and mitigate membrane fouling

1.4.1. Membrane fouling

1.4.2. Methods to control membrane fouling

1.4.3. Methods to mitigate membrane fouling

1.5. Research direction of the thesis

CHAPTER 2: RESEARCH SUBJECT AND METHODOLOGY

2.1. Research subjects

- **Feed stream**: deionized water, simulated brackish water made from refined NaCl salt with salinity of 5‰ – 25‰, and actual brackish water samples pretreated to remove insoluble solids with size ≥ 5 µm.

- **Draw solution**: MGDA solution, MAL solution, and PVP solution. This thesis focused on studying some important forward osmosis of the draw solutions, and the influence of some factors (including operating conditions and extended operating duration) on the forward osmosis efficiency of the draw solutions.

- **Hệ thống thử nghiệm**: Experiments in this thesis were carried out on Forward Osmosis CF042 Cell Assembly modules, which is an experimental platform for laboratory-scale research on FO membrane processes with an effective membrane area of 42 cm^2 and a body mainly made of acetal copolymer plastic material to minimize its potential influence on relevant properties of both the feed stream and the draw solution..

2.2. Research methodologies

2.2.1. Reagents and materials

2.2.2. Equipment and instruments

2.2.3. General experimental procedures

2.2.4. Specific experimental procedures for each research content

2.2.5. Results processing methods

The forward osmosis efficiency of the draw solution was evaluated based on three main criteria, including water flux (Jw), reverse draw solute flux (Js), and draw solute loss coefficient (Rds). Their value were calculated based on actual results conducted on a laboratory-scale experimental system, specifically as follows:

$$Jw = \frac{m0 - mt}{A \times t \times \rho} \quad \textbf{(Equation 1)}$$

$$Js = \frac{Ct \times (V0 - Jw \times t \times A)}{t \times A} \quad \textbf{(Equation 2)}$$

$$Rds = \frac{Js}{Jw} \quad \textbf{(Equation 3)}$$

Experiments with short operating durations were performed in repeat for at least five times, with the results being reviewed through Analysis of Variance (ANOVA) on the Microsoft Excel 2016 software to ensure their overall reliability (≥ 95%). In case of abnormal results detection, the experiment would again be performed in batches of triplicates and abnormal results being gradually eliminated, so that the final results could achieve an overall reliability of no less than 95%.

In contrast, experiments with extended operating durations were performed only once without repetition, with results being processed on the Microsoft Excel 2016 and Design Expert 12 softwares to determine the changes over time of various forward osmosis parameters.

In addition, the response surface method (RSM) in combination with the 3-level Box–Behnken experimental design was also used to optimize the operating conditions for the forward osmosis systems utilizing the selected draw solution. Elements of the design environment were determined based on results from previous experiments, which were to be presented in the relevant sections of Chapter 3. Results and discussion. Specific details of experiment design and result processing were performed automatically on the Design Expert 12 software.

2.2.6. Semipermeable membrane analysis

In addition to the experimental method as presented, the effect of long-term operation on the semipermeable membrane was also evaluated through scanning electron microscopy (SEM) analysis. First, the semipermeable membrane was removed from the forward osmosis system immediately after the experiment was completed, then quickly rinsed with deionized water to eliminate any remaining traces of either the draw solution or the feed solution while avoiding the removal of foulants developed on the surface of the membrane. Afterward, the membrane was dried by gently blotting filter paper, then its surfaces were plated with a layer of gold-palladium alloy using a sputter deposition device. SEM images of the membrane surfaces were taken utilizing a Jeol SM-6510LV scanning electron microscope (Jeol, Japan) at an acceleration voltage of 8 - 12 kV and a magnification level of 500 - 2,000 times.

CHAPTER 3: RESULTS AND DISCUSSIONS

3.1. Forward osmosis characteristics of the semipermeable membrane

Overall, there was no significant difference between experimental results achieved from this Thesis and other experimental results achieved from previous studies implemented by the PhD. candidate [46]. This indicated that the TFC membrane used in this research was highly stable, allowing the comparison of experimental results obtained from this study with relevant experimental results obtained from other similar previously published works..

Specifically, when the forward osmosis system was operated continuously for up to 150 minutes, the volume of water permeating through the semipermeable membrane increased steadily over time at all concentrations of the NaCl draw solution. This demonstrated that the experimental system was designed appropriately, allowing stable operation for up to 150 minutes and/or 154 mL of water permeation without significantly affecting the forward osmosis efficiency of the draw solution. In other words, dilution of the draw solution caused by the permeation of water through the semipermeable membrane did not significantly affect the results of experiments conducted within the operating duration limit of less than 150 minutes and/or the volume of water permeation limit of less than 54 mL.

More notably, there appeared to be a “stall” in the forward osmosis efficiency when the concentration of the NaCl draw solution was in the range of 20–30 ‰. This observation can be explained on the basis of certain phenomena such as internal concentration polarization (ICP) and external concentration polarization (ECP). Specifically, when the forward osmosis capability of the draw solution exceeds a certain threshold, the local concentration polarization phenomenon would become particularly severe, leading to an increase in osmotic resistance that is roughly in balance with the respective increase in osmotic pressure difference. As such, the overall forward osmosis efficiency of the draw solution would exhibit somewhat negligible increases [58].

However, since the feed solution in these experiments was deionized water, the concentration polarization (CP) phenomenon would mainly occur only in the draw solution side. At the same time, the ability of the CP phenomenon to create osmotic resistance also depends largely on the mass transfer efficiency of water within the bulk of the draw solution. Therefore, once the concentration of the draw increased beyond the threshold of 30‰, the increase in osmotic resistance caused by the CP phenomenon could not maintain equilibrium with the increase in osmotic pressure, leading to a significant increase in water flux similar to when the concentration of the NaCl draw solution was less than 20‰.

However, it should also be noted that even with the same concentration of the NaCl draw solute, the water flux at specific sample acquiring points (more specifically, after every 15 minutes) was not entirely stable, but fluctuating around an average value corresponding to near linear lines in the water permeation - operation duration plot. There are many different factors that can lead to such behaviour, but it can be mainly attributed to the continuous changes in the concentration of the draw solution the throughout the length of operation, and the changes in the flow regime of solutions inside the forward osmosis module caused by the design of the inlet and the operating mode of the pumps.

Overall, the TFC semipermeable membrane used in this study was determined to possess relatively consistent forward osmosis properties as disclosed by the manufacturer, with the difference in average water flux at equivalent draw solution concentrations (60‰ NaCl solution, equivalent to 1 mol/L) of only about 2.2%.

3.2. Forward osmosis efficiency of the investigated draw solutions

In order to evaluate forward osmosis characteristics of the investigated draw solutions (PVP solutions, MAL solutions, and MGDA solutions), a number of forward osmosis experiments combined with nanofiltration regeneration were performed with the concentration of draw solutions being adjusted in the range of 5 – 30 % and the concentration of feed solutions being adjusted in the range of 5 – 25 ‰.

In general, for all three types of investigated draw solutions, the water flux value only increased significantly when the draw solution concentration increased up to a certain threshold, after which the increase in water flux became largely negligible. Such a trend was especially obvious with the feed stream being simulated salt solutions, and can be explained through the fact that after a certain concentration threshold, the CP phenomenon could become significantly more severe, leading to prominent increases in water permeation resistance which would negatively impact the supposedly improvement in water flux .

In addition, with the increase in salinity of the feed stream, water flux value also decreased, mostly due to the reduction in osmotic pressure difference between the draw solution and the feed solution. Particularly, when the salinity of the feed stream increased to 15 - 20 ‰, the water flux would decrease very low (below 5 LMH) at all concentrations of the draw solution, indicating that the investigated draw solutions are not effective in desalination applications for brackish water sources with too high salinity (initial salinity of the feed stream being higher than 10‰).

In order to obtain a more comprehensive view of the draw solutions currently being studied within the framework of this Thesis, the PhD. candidate also conducted some additional experiments on forward osmosis efficiency of these draw solutions against a series of feed streams with salinity below 10‰.

The results suggested that when the salinity of the feed stream increased from 0‰ to 10‰, the water flux achieved by all three selected draw solutions would decrease in a near linear manner. In particular, compared to water fluxes obtained at 0‰ of the feed stream salinity, the water fluxes obtained at 10‰ of the feed stream salinity decreased by about 37 – 48%, with the largest decrease belonging to the 20% MAL draw solution.

More specifically, when the salinity of the feed stream increased from 0‰ to 10‰, the water flux of the 20% MAL draw solution decreased from 10.61 LMH to 5.51 LMH, equivalent to a reduction of about 48%. This result can be explained by certain physical-chemical interactions between the 20% MAL draw solution and feed solution, causing the forward osmosis capability of the draw solution to decrease rapidly with the increase of the salinity of the feed solution. The same phenomenon also occurred when the draw solution was a 60‰ NaCl salt solution (control draw solution), with the water flux value decreasing from 16.19 LMH to 7.62 LMH – equivalent to a reduction of about 53%. In contrast, both the 20% PVP draw solution and the 25% MGDA draw solution showed relatively more stable forward osmosis efficiency when the salinity of the feed stream increased from 0‰ to 10‰, with water flux reductions being approximately 42% and 37%, respectively.

In addition, the reverse draw solute diffusion of the MGDA draw solution was particularly severe, evidenced by its significantly higher reverse draw solute flux and draw solute loss coefficient compared to the 60‰ NaCl control draw solution. This phenomenon can be explained by certain physical-chemical interactions between the solute components in the MGDA draw solution (MGDA-3Na salt, citric acid, and their respective dissociated ions) and the material components that make up the semipermeable membrane, causing the osmotic selectivity of the membrane for these solute components to become worse than the osmotic selectivity of the membrane for NaCl salt and its respective dissociated ions. Therefore, the solute components in the MGDA draw solution would move through the semipermeable membrane more easily than NaCl salt and its respective dissociated ions, even though these dissociated ions are quite small. In addition, it should be noted that the 60‰ NaCl draw solution had a much lower actual draw solute concentration compared to the 25% MGDA draw solution.

In contrast, the reverse draw solute flux and draw solute loss coefficient of both the MAL draw solution and the PVP draw solution were relatively low. This phenomenon can be explained by the fact that both polyvinylpyrrolidone and maltodextrin are polymeric compounds with relatively large molecular sizes and do not dissociate in their aqueous solutions, therefore their diffusion rate through the semipermeable membrane would often be worse than those with relatively smaller molecular sizes themselves or those that could dissociate into much smaller ions (for example, MGDA-3Na salt or citric acid). In particular, the 20% PVP draw solution exhibited a draw solute loss coefficient about 50% less than that of the 20% MAL draw solution, demonstrating its superior stability and safety when being used forward osmosis applications.

3.3. Influence of operational parameters on the forward osmosis characteristics of the investigated draw solutions

Experimental results indicated that when the inlet pressure difference between the feed stream and the draw solution stream increased, water flux would also increase. Conversely, when the pressure on the draw solution side was higher than that on the feed stream side, water flux appeared to decrease sharply. Since the inlet flows on both sides were maintained within a suitable range, the above phenomenon can be determined to be due to the influence of the change in the pressure difference between the feed stream and the draw solution stream.

The driving force of most membrane filtration processes – including forward osmosis processes – is the pressure difference between the two sides of the semipermeable membrane. Particularly, in forward osmosis processes, this driving force is a combination of the natural osmotic pressure difference and the hydraulic pressure difference between the feed stream and the draw solution stream [36]. These two types of pressure differences can create either a synergistic effect (acting in the same direction) or a contrariety effect (acting in the opposite direction and cancel each other out), thereby influencing the resulting water flux. However, increasing the pressure on the side of the feed stream might also cause NaCl molecular and its dissociated ions to be pushed into the microporous structure of the semipermeable membrane, leading to membrane fouling and the ICP phenomenon – both of which would hinder the mass transfer of water through the membrane.

Conversely, the increase in pressure difference between the feed stream and the draw solution stream led to significant reductions in reverse draw solute flux, which was mostly due to the mass transfer of reverse draw solute flux being in the complete opposite direction of the increase in hydraulic pressure difference, therefore being more hindered when hydraulic pressure difference increased. In addition, the relationship between inlet pressure difference and operating efficiency parameters was similar among various feed stream salinity (deionized water and 10‰ NaCl solution) and draw solution (20% PVP solution, 20% MAL solution, and 25% MGDA solution), lending reliability to the obtained experimental results.

Similarly, inlet temperature also had some significant influences on the operating efficiency of the forward osmosis desalination system. Specifically, for all three draw solutions being investigated, when inlet temperature increased from $10^{o}C$ to $30^{o}C$, both water flux and reverse draw solute flux tended to increase gradually, causing the value of draw solute loss coefficient to remain almost unchanged. However, once inlet temperature continued to increase from $30^{o}C$ to $40^{o}C$, both water flux and reverse draw solute flux of all three investigated draw solutions exhibited substantial reductions.

This phenomenon can be explained by the influences of temperature on both natural osmotic pressure of aqueous solutions and osmotic properties of the semipermeable membrane itself [105-107]. More specifically, the influence of temperature osmotic properties of the semipermeable membrane was determined to significantly contribute to the changes in forward osmosis performance of draw solutions when the inlet temperature increases from $30^{o}C$ to $40^{o}C$, since such results were markedly difference from reports in relevant literatures: both water flux and reverse draw solute flux decreased with the increase of inlet temperature, which completely contradicted most existing publications.

The reason for this phenomenon could be due to certain alterations in osmotic properties of the semipermeable membrane caused by changes in ambient temperature. Specifically, when the temperature increases beyond 30oC, physical and chemical properties of the membrane could undergo some transformation that negatively impacts its capability to facilitate mass transfer of both water and other solute molecules, leading to the observed reductions in both water flux and reverse draw solute flux. This result emphasized the importance of examining related properties of semipermeable membranes prior to large-scale operation, so that the highest efficiency of desalination systems utilizing forward osmosis technology could be ensured.

Finally, experimental results also showed that there would be some significant reductions in water flux when the inlet flow was too low (below 200 mL/min) or too high (above 500 mL/min). This was because flow rate is an important factor determining fluid dynamics, thereby affecting the diffusion efficiency of solutes in both the draw solution and the feed solution. Specifically, due to the mass transfer of water through the semipermeable membrane, the concentrations of the draw solution and the feed solution in the area near the membrane surface would be lower or higher than their respective value at the inlet, leading to substantial reductions in forward osmosis efficiency. To limit this phenomenon, the fluids moving within the forward osmosis system would need to create a suitable stirring effect, promoting the diffusion of solute components between the area near the membrane surface and the bulk of those solutions.

At lower inlet flow rates, there are no turbulences perpendicular to the flow direction which limits the horizontal mixing between adjacent layers of the fluid system (laminar flow regime). This phenomenon can lead to local concentration polarization near the surface and within the structure of the semipermeable membrane, significantly hindering the mass transfer of water. Conversely, higher inlet flow rates would lead to turbulent flow regime, which encourages horizontal mixing between adjacent layers of the fluid system. However, excessive turbulence caused by elevated inlet flow rate might lead to unstable operation conditions, encouraging the formation of abnormally high or low hydraulic pressure regions, thereby negatively affecting the mass transfer of water through the semipermeable membrane and reducing the obtained water flux [141].

Such a phenomenon could also be used to explain the change in reverse draw solute flux. Specifically, when inlet flow rate of the feed stream increased from 100 mL/min to 300 mL/min, reverse draw solute flux of both the 20% PVP draw solution and the 20% MAL draw solution also tended to increase gradually. However, when inlet flow rate of the feed stream continued to increase from 300 mL/min to 650 mL/min, these values reduced gradually. In combination with the changes in water flux, these would lead to negenible fluctuations in the value of draw solute loss coefficient for both those draw solutions.

Similar changes in draw solute loss coefficient were also observed for the 25% MGDA draw solution, although its reverse draw solute flux varied in a not very clear pattern within the investigated range of inlet flow rate.

3.4. Optimizing operating conditions of the forward osmosis system

Based on the results presented in the previous section, the PhD. candidate performed an optimization of forward osmosis operating conditions using the 3-level Box–Behnken experimental design method on the Design Expert 12 software.

Overall, through Sequential model sum of squares and Model summary statistics tests, it can be determined that for all three selected draw solutions, the quadratic model is the most suitable to describe the relationship between the investigated input variables (operating conditions of the forward osmosis system) and the evaluation results (water flux and draw solute loss coefficient). In addition, the analysis of variance (ANOVA) results also confirmed the quadratic model's capability to predict and optimize the influence of input variables on evaluation results within the determined Box–Behnken experimental design framework.

Results from response surface analysis showed that for all three investigated draw solutions, inlet temperature was the most influential factor on both water flux and draw solute loss coefficient. In contrast, inlet pressure difference had a relatively small effect on both water flux and draw solute loss coefficient, especially when inlet flow rate was to be held constant and only inlet temperature was varied. Similarly, inlet flow rate only exerted a significant influence on water flux and draw solute loss coefficient when inlet pressure difference was held constant and only inlet temperature was varied.

With the aim of maximizing water flux and minimizing draw solute loss coefficient, some optimization calculations were automatically conducted on the Design Expert 12 software, which gave the results for the most optimal operating condition parameters as follows:

- For the 20% MAL draw solution: inlet pressure difference = 0.17 bar (on the feed stream side), inlet temperature = 27.5^{o}C, and inlet flow rate = 260 mL/min. The predicted values of water flux and draw solute loss coefficient for when the forward osmosis system operation would operate under these parameters were calculated to be 10.86 LMH and 0.238 g/L, respectively. Five confirmation experiments were conducted at the calculated optimal operating parameters to validate those predictions, with the actual values of water flux and draw solute loss coefficient obtained being 10.,858 ± 0.137 LMH and 0.2372 ± 0.0029 g/L, respectively.

- For the 20% PVP draw solution: inlet pressure difference = 0.40 bar (on the feed stream side), inlet temperature = 26.0^{o}C, and inlet flow rate = 270 mL/min. The predicted values of water flux and draw solute loss coefficient for when the forward osmosis system operation would operate under these parameters were calculated to be 14.78 LMH and 0.124 g/L, respectively. Five confirmation experiments were conducted at the calculated optimal operating parameters to validate those predictions, with the actual values of water flux and draw solute loss coefficient obtained being 14.816 ± 0.121 LMH and 0.1244 ± 0.0012 g/L, respectively.

- For the 25% MGDA draw solution: inlet pressure difference = 0.40 bar (on the feed stream side), inlet temperature = 30.0ºC, and inlet flow rate = 250 mL/min. The predicted values of water flux and draw solute loss coefficient for when the forward osmosis system operation would operate under these parameters were calculated to be 9.97 LMH and 0.359 g/L, respectively. Five confirmation experiments were conducted at the calculated optimal operating parameters to validate those predictions, with the actual values of water flux and draw solute loss coefficient obtained being 9.996 ± 0.192 LMH and 0.3580 ± 0.0020 g/L, respectively.

However, it should be noted that the above optimal operation parameters were only reliable within the specific scopes of the study in this Thesis, and therefore need to be re-verified if applied outside of such scopes. In addition, based on previous experimental results, there was a scientific basis to believe that the optimization results obtained with the feed stream of deionized water can also be completely applied to other cases where the feed stream is brackish water with salinity of up to 10‰.

3.5. Impacts of extended operating duration on forward osmosis characteristics of draw solutions and the efficiency of membrane cleansing methods

Experimental results suggested that there existed a decreasing trend in forward osmosis efficiency of all three investigated draw solutions when they were subjected to extended operation durations. Specifically, after 700 hours of quasi-continuous operation, the water flux generated by these draw solutions changed as follows: from 5.97 LMH to 4.87 LMH (equivalent to about 18% reduction) for the 25% MGDA draw solution, from 8.16 LMH to 5.49 LMH (equivalent to about 33% reduction) for the 20% PVP draw solution, and from 5.64 LMH to 3.16 LMH (equivalent to about 44% reduction) for the 20% MAL draw solution. This can be due to during extended operations, the phenomenon of fouling occurred on the surface and inside the porous structure of the semipermeable membrane, leading to a reduction in its effective area of mass transfer and its capability to facilitate the mass transfer of water [147].

In order to more accurately assess membrane fouling characteristics of the investigated draw solutions, some analysis were conducted on SEM images of semipermeable membrane surfaces after 700 hours of quasi-continuous operation, which is equivalent to about one month of actual continuous operation.

Specifically, for the 20% PVP draw solution, the main membrane fouling mechanism was found to be the deposition of otherwise dissolvable solids on the side of the semipermeable membrane that was in direct contact with the draw solution. These deposited particles had a relatively large size (about 10 μm or more) and rather complex structures. The formation of these depositions could be due to certain interactions between polyvinylpyrrolidone molecules and NaCl molecules (and/or their respective dissociated ions), leading to the reduction in solubility of the draw solute in the area around the surface and within the porous structure of the semipermeable membrane [198,199]. Conversely, on the side that was in direct contact with the feed solution, the main mechanism of membrane fouling was determined to be the growth of microorganisms, with a significant area of the membrane surface being covered by spherical structures with dimensions of approximately over 2 μm. According to Tang et al., such spherical structures often correspond to membrane contamination caused by the growth of microorganisms. The existence of this “biofilm” layer significantly affects the mass transfer capability of the membrane, hindering the transmembrane movements of both water and other solutes [157].

Similar observations could also be made for the 20% MAL draw solution, with the mechanism of membrane fouling that occurred on the draw solution side still being mainly due to the deposition of the maltodextrin draw solute itself (asymmetrical spherical form) [200,201], while the mechanism of membrane fouling that occurred on the feed solution side being predominantly due to the growth of microorganisms [157].

Notably, for the 25% MGDA draw solution, the side of the membrane surface that was in direct contact with the draw solution was relatively clean with almost no large-sized deposited particles or areas of special microbial growth. This might be due to MGDA-3Na salt being a cleaning agent, which can help prevent the attachment of both solid depositions and biological contaminations onto the membrane surface, thereby limiting the development of foulants. In addition, there also seemed to be no special interactions between both solutes of the MGDA draw solution (MGDA-3Na salt and citric acid) that could cause the decrease in solubility of these solutes which would lead to the deposition of solid particles. However, on the side of the membrane surface that was in direct contact with the feed solution, cubic crystalline structures with a size of about 10 μm could be observed. The formation of these crystalline salt crystals was most likely due to the elevated concentration of Na^+ ions near the surface of the semipermeable membrane, which was the direct result of MGDA-3Na draw solute reverse flux and the CP phenomenon.

Experiments on the foulant removal efficiency of the direct washing method showed that this membrane cleaning method helped to recover up to 98% of loss water flux caused by extended forward osmosis operations, with the specific recovering rate being 98%, 82%, and 78% in the case of 25% MGDA draw solution, 20% PVP draw solution, and 20% MAL draw solution, respectively. These results can be explained based on the nature of membrane fouling triggered by each draw solution.

Particularly, for the 25% MGDA draw solution, the main fouling mechanism was large salt crystal deposition on the surface of the semipermeable membrane. Since these salt crystals possessed the ability to easily dissolve back into aqueous mediums, the direct washing process managed to almost completely remove these crystallized salt crystals, thereby almost completely restoring the semipermeable membrane to its original state of permeability. On the contrary, for both the 20% MAL draw solution and the 20% PVP due solution, due to the relatively serious contamination on both sides of the semipermeable membrane, the direct washing method only allowed for a certain part of its original permeability to be restored. Both the deposition components existing inside the porous structure of the membrane and the "biofilm" layer on the surface of the membrane had not been completely cleansed and would continue to hindering the mass transfer of water through the membrane, making it impossible for water flux to be complete recovered while at the same time creating favorable conditions for the subsequent fouling processes to become even more severe.

3.6. Performance of the investigated draw solutions on actual brackish water samples

Experimental results showed that there was no significant difference in forward osmosis efficiency of the investigated draw solutions between when the feed solution being an actual pretreated brackish water sample and when the feed solution being simulated saline water with equivalent salinity (salinity calculated as NaCl concentration = 10‰).

Analysis on quality properties of clean water samples obtained after draw solution regeneration indicated that all three investigated draw solutions could be effectively regenerated by the nano filtration method, with the final products obtained meeting a number of key requirements as recommended in the National Technical Regulation QCVN 01-1:2018/BYT on the quality of clean water used for domestic purposes.

Bảng 3.1 Quality of clean water obtained after regenerating draw solutions, compared to requirements in National Technical Regulation QCVN 01-1:2018/BYT

Quality parameter		**Draw solutions**			**Requirement in QCVN 01-1:2018/BYT**
		20% MAL	**20% PVP**	**25% MGDA**	
pH	-	6.7	6.7	6.9	6.0 – 8.5
TDS	‰	373	291	436	< 1,000
Sodium	mg/L	10	10	120	< 200
Chloride	mg/L	0.4	0.4	0.4	0.2 – 1.0

CONCLUSIONS

The Thesis has completed the research contents as outlined, including:

- **Investigate the forward osmosis efficiency of some potential draw solution,** including the draw solution containing a combination of trisodium α-DL-alanine diacetate and citric acid (MGDA draw solution) with a mass ratio of 85/15, as well as two other potential draw solutions containing maltodextrin (MAL draw solution) and polyvinylpyrrolidone (PVP draw solution), which yielded promising results.

- **Investigate the influence of some operational parameters on forward osmosis efficiency of some potential draw solutions.** The study determined that for all three draw solutions, operational parameters including inlet flow rate, inlet pressure difference, and inlet temperature significantly impacted forward osmosis performance, evidenced by the changes in water flux, reverse draw solute flux, and draw solute loss coefficient. The study also compared obtained results with relevant existing literature to reach meaningful observations.

- **Optimize operational parameters to obtain most efficient forward osmosis results for the three potential draw solutions.** Specifically, this study utilized the Box–Behnken experimental design method and the response surface method to further evaluate the influence of inlet flow rate, inlet pressure difference, and inlet temperature on forward osmosis efficiency of the three potential draw solutions, thereby establishing a suitable mathematical model to describe the relationship between the variable inputs and the evaluated results. In addition, this study also determined optimal operational parameters for the three potential draw solutions, and empirically verified the reliability of such optimization calculations.

- **Investigate the impact of extended operation on forward osmosis performance of the potential draw solutions and fouling characteristics of the semipermeable membrane**. Specifically, this study determined that with the 25% MGDA draw solution, the forward osmosis system could operate relatively stably for 700 hours in quasi-continuous conditions, resulting in a final water flux loss of approximately 18%. In contrast, after the same duration of quasi-continuous operation, the final water flux loss of the 20% MAL draw solution and the 20% PVP water solution reached approximately 44% and 33%, respectively.

This study also suggested that the direct washing method could allow particularly good membrane permeability recovery (98% of the initial value) when being applied on membranes fouled by extended operations using the 25% MGDA draw solution. In contrast, the same membrane cleaning method only achieved 78% and 82% recovery rate when being applied on membranes fouled by extended operations using the 20% MAL draw solution and 20% PVP draw solution, respectively.

- **Investigate the forward osmosis capacity of potential draw solutions against actual brackish water samples.** All three potential draw solutions exhibited equivalent forward osmosis capacity between when the feed solution being an actual brackish water sample and when the feed solution being simulated brackish water of the same salinity. These results demonstrated the potential for practical application of these draw solutions. In addition, the clean water obtained from the nanofiltration regeneration process of these three draw solutions were also determined to meet some key requirements outlined in the National Technical Regulation QCVN 01-1:2018/BYT on the quality of clean water used for domestic purposes.

LIST OF PUBLISHED WORKS RELATED TO THE THESIS

1. **Article on SCIE-indexed international journals**: Novel draw solution system based on trisodium dicarboxymethyl alaninate for water desalination applications, *International Journal of Environmental Science and Technology*, 22, 5327–5340, 2025 (journal with a WoS IF = 3.0 and in the SJR Q1 quartile). https://doi.org/10.1007/s13762-024-05984-z

2. **Book chapter by international publishers with ISBN**: Recent Trends in the Development of Draw Solutions for Forward Osmosis Based Desalination, *Advances in Water Quality Research (Volume 2)*, AkiNik Publications, New Delhi, 59–85, 2024. Book ISBN: 978-93-6135-266-9. https://doi.org/10.22271/ed.book.2808

3. **Article on national journals**: Investigating membrane fouling characteristics and cleansing strategies in forward osmosis desalination using polyvinylpyrrolidone K17, *Vietnam Journal of Analytical Sciences*, 30(3), 65–73, 2024 (journal in the list of recognized journal by the Vietnam State Council for Professorship).

4. **Article on national journals**: Influence of operational parameters on the efficiency of forward osmosis desalination systems using polyvinylpyrrolidone K17, *Vietnam Journal of Analytical Sciences*, 30(4), 77–84, 2024 (journal in the list of recognized journal by the Vietnam State Council for Professorship).

5. **Article on national conference proceedings**: The application of maltodextrin in forward osmosis desalination system: Membrane fouling characteristics and cleaning efficiency, *Conference Proceedings: Commercialization of Research Results - Opportunities and Solutions*, Publishing House of Natural Science and Technology, 336–342, 2025. Proceeding ISBN: 978-604-357-367-1.

6. **Article on SCIE-indexed international journals** (currently in the second round of peer-review): Potential application of the draw solution system based on trisodium α-DL-alanine diacetate in forward osmosis desalination systems, *Membrane and Water Treatment* (journal with a WoS IF = 0.8 and in the SJR Q3 quartile).