Tạp chí phân tích Hóa, Lý và Sinh học - Tập 30, số 03/2024

INVESTIGATING MEMBRANE FOULING CHARACTERISTICS AND CLEANSING STRATEGIES IN FORWARD OSMOSIS DESALINATION USING POLYVINYLPYRROLIDONE K17

Đến tòa soạn 20-06-2024

Hoang Minh Tao * [1,2], **Nguyen Quang Trung** [1], **Nguyen Ngoc Tung**[1],
Bui Quang Minh [1], **Trinh Tuan Hung** [1], **Nguyen Thị Hoai Thu** [1], **Hoang Thi Thoa** [1]

[1] *Center for High Technology Research and Development, Vietnam Academy of Science and Technology*

[2] *Graduate University of Science and Technology, Vietnam Academy of Science and Technology*

** Email: htm1205@gmail.com*

TÓM TẮT

NGHIÊN CỨU ĐẶC TRƯNG NHIỄM BẨN MÀNG VÀ CÁC GIẢI PHÁP LÀM SẠCH TRONG HỆ THỐNG KHỬ MẶN THẨM THẤU XUÔI SỬ DỤNG CHẤT LÔI CUỐN POLYVINYLPYRROLIDONE K17

Công trình này khảo sát các đặc trưng của hiện tượng nhiễm bẩn màng lên hiệu quả hoạt động của hệ thống khử mặn trên cơ sở công nghệ lọc thẩm thấu xuôi sử dụng chất lôi cuốn Polyvinylpyrrolidone K17, thông qua đánh giá sự thay đổi của giá trị thông lượng nước thẩm thấu qua màng và giá trị thông lượng chất lôi cuốn thẩm thấu ngược qua màng, cũng như ảnh chụp kính hiển vi điện tử quét (SEM). Kết quả khảo sát cho thấy, tồn tại những khác biệt đáng kể giữa tác nhân gây nhiễm bẩn tại phía bề mặt màng bán thấm tiếp xúc với dung dịch cần xử lý và tác nhân gây nhiễm bẩn tại phía bề mặt màng bán thấm tiếp xúc với dung dịch lôi cuốn. Bên cạnh đó, kết quả so sánh hiệu quả làm sạch giữa phương pháp rửa xuôi và phương pháp rửa ngược cũng giúp chứng minh sự tồn tại của tình trạng nhiễm bẩn xảy ra trong cấu trúc màng bán thấm. Điều này nhấn mạnh sự cần thiết của việc phải xác định được những phương pháp làm sạch mới nhằm cải thiện khả năng vận hành lâu dài và ổn định cho các hệ thống khử mặn trên cơ sở công nghệ lọc thẩm thấu xuôi sử dụng chất lôi cuốn Polyvinylpyrrolidone K17.

Keywords: *thẩm thấu xuôi, Polyvinylpyrrolidone K17, SEM, nhiễm bẩn, làm sạch*

1. INTRODUCTION

In recent years, due to a variety of factors, freshwater scarcity has become increasingly severe worldwide, including in Vietnam [1]. Particularly, the Mekong Delta region is experiencing a growing trend of saltwater intrusion, threatening agricultural activities in one of the nation's primary rice-producing areas [2].

To address this issue, numerous solutions have been proposed, with desalination technologies for producing freshwater from brackish sources, or even directly from seawater, being the most prominent among all. Currently, thermal distillation and reverse osmosis are the most widely applied technologies in industrial-scale desalination plants. However, there exists notable drawbacks in these methods, primarily the significant energy requirements needed to drive the desalination process, which is not fully aligned with green development and environmental protection trends [3,4].

Forward osmosis technology is emerging as a promising new answer to the question of desalination. Unlike reverse osmosis, the driving force for the mass transfer of water in forward osmosis systems is the difference in natural osmotic pressure on either side of a semi-permeable membrane. Therefore, forward osmosis systems typically require much less energy for operation, while also offering significant improvement in solute rejection efficiency [5].

However, similar to other membrane filtration methods, membrane fouling is a phenomenon that can negatively impact the operational efficiency of forward osmosis desalination systems. Membrane fouling is defined as the deposition of suspended particles, colloids, organic macromolecules, insoluble inorganic compounds, microbial biomass, or a combination of these foulants, on the surface or within the porous structure of the semipermeable membrane. Fouling not only leads to reductions in water flux and output water quality, but also increases the operational costs of forward osmosis systems and shortens membrane lifespan [6].

According to Mi and Elimelech, the mechanisms of membrane fouling are relatively complex, involving chemical interactions between solute components in the feed solution and the draw solution, hydrodynamic factors within the membrane module, and specific characteristics of the semipermeable membrane itself [7]. Therefore, when researching potential novel draw solutes to be used in forward osmosis systems, it is essential to examine membrane fouling characteristics to comprehensively evaluate the efficiency of those draw solutes under real-world operational conditions.

This study investigates the fouling characteristics of a forward osmosis system using Polyvinylpyrrolidone K17 (hereby abbreviated as PVP K17) as the draw solute, and evaluates the effectiveness of common membrane cleaning methods in alleviating the impacts of fouling on desalination performance of the forward osmosis system. In particular, desalination performance was evaluated through water flux and reverse solute flux, while the characteristics of foulants were analyzed using scanning electron microscopy (SEM) images. Similarly, the effectiveness of membrane cleaning methods was determined by comparing the changes in desalination performance of the semipermeable membrane at the beginning, after extended operations, and after being cleansed post-extended operation.

2. METHODOLOGY

2.1. Materials and Equipment

Aqueous solvent: Deionized water (salinity ≤ 5 ppm) was produced using the Direct-Q® 5 UV Remote Water Purification System (Merck, Germany) at the Center for High Technology Research and Development, Vietnam Academy of Science and Technology.

Draw solute: Polyvinylpyrrolidone K17 (analytical grade) was supplied by Sigma-Aldrich (USA).

Salt solute: Refined sea salt was supplied by Long Hai (Vietnam).

Semipermeable membrane: HFFO membranes were supplied by Aquaporin (Denmark). These were thin-film composite (TFC) flat sheet membranes with dimensions of 56 × 115 mm, and an effective filtration area of 42 cm².

Testing module: Forward Osmosis CF042 Cell Assembly module was supplied by Sterlitech (USA). This module was a laboratory-scale forward osmosis filtration module specifically designed for testing and evaluating the performance of forward osmosis membranes in a controlled laboratory environment.

Flow pumps: HF-8377 flow pumps were acquired from Haedon (Taiwan), capable of providing output flow in the range of 0 – 1,200 $\mathrm{mL \cdot min^{-1}}$.

Digital scale: GeeLeaf GL05 digital scale was acquired from GeeLeaf (China), with maximum weighing capacity of 5 kg and an accuracy of 1 g.

Salinity meters: Ezdo 7021 handheld conductivity/TDS/salinity meters were acquired from GonDo (Taiwan), with an accuracy of 1 ppm (for 0 – 1,000 ppm scale) or 0.01 ppt (for 1.00 – 12.00 ppt scale).

Other auxiliary equipment and tools: Water containers, water pipes, control valves, pressure gauges...

2.2. Experimental Method

In general, experiments were conducted using the setup described in the published work by Nguyen Quang Trung et al. [8]. Specifically, after performing system cleaning steps, 1,000 mL of the feed solution (deionized water or 10‰ salt solution) and 1,000 mL of 20% Polyvinylpyrrolidone K17 draw solution (hereby abbreviated as PVP 20% solution) were loaded into the respective containers. Experiments were then commenced by simultaneously starting the feed solution pump and the draw solution pump, and continued for a total duration of non-continuous 700 hours (equivalent to roughly 30 days of continuous operation). Through this duration, after every 120 minutes, experiments were either temporarily stopped until the next day, or both the feed solution and the draw solution were replaced by 1,000 mL of respective fresh solutions. The weight of the draw solution and the salinity of the feed solution were periodically recorded to monitor the changes in these parameters over time.

In particular, base-line operational parameters for experiments in this study were established as following:

Feed solution: 10‰ salt solution (for JW determination) or deionized water (for JD determination).

Draw solution: PVP 20% solution.

Inlet flow rate – Feed solution: 200 $\mathrm{mL \cdot min^{-1}}$.

Inlet flow rate – Draw solution: Adjusted to maintain a difference in hydraulic pressure of 0.2 bar between the feed solution side and the draw solution side.

Inlet temperature – Both solutions: 30 °C.

Relative flow direction of the draw solution stream and feed solution stream: Counter-current.

After the 700-hours experimental period, the semipermeable membrane was cleansed either by surface flushing (replacing both the feed solution and draw solution with clean water, then operating the system under the same operational parameters as described for 30 minutes), or by membrane backwashing (replacing the feed solution with saturated salt solution and the draw solution with clean water, then operating the system under the same operational parameters as described for 30 minutes). Subsequently, the cleansed membranes were used for subsequent cycles of experiments, or sampled for scanning electron microscopy (SEM) imaging.

2.3. Methods for Result Calculation

Performance of the forward osmosis filtration system was evaluated based on two main parameters: water flux (JW), and reverse solute flux (JD). In particular, these parameters were calculated from experimental results as follows:

$$JW = (mt - m0) / (t \times A \times \rho)$$

$$JD = Ct \times (V0 - JW \times t \times A) / (t \times A)$$

where:

- **JW** was Water flux (unit: $L \cdot m^{-2} \cdot h^{-1}$, or LMH)

- **JD** was Reverse solute flux (unit: $g \cdot m^{-2} \cdot h^{-1}$, or GMH)

- **A** was the active filtration area of the semi-permeable membrane, which was 0.00042 m^2

- **ρ** was the specific density of water, which was 0.001 $g \cdot L^{-1}$

- **t** was the total operational duration of experimental system at the particular sampling point (unit: h)

- **m0** was the initial weight of the draw solution and its container (unit: g)

- **mt** was the weight of the draw solution and its container at the particular sampling point (unit: g)

- **Ct** was the concentration of dissolved solids in the feed solution at the particular sampling point (unit: $g \cdot L^{-1}$)

- **V0** was the initial volume of the feed solution, which was 1 L

2.4. Analytical Method

Changes in surface structure of the semipermeable membrane before and after 700-hours forward osmosis experiments were analyzed using images of various magnifications obtained from a HITACHI Miniscope TM-1000 under vacuum conditions with an accelerating voltage of 5 kV.

Membrane samples were prepared by quickly rinsing the membrane surface with deionized water, then gently blotting it dry with filter paper, before coating its surface with a gold-palladium alloy using a sputter deposition device.

3. RESULTS AND DISCUSSION

3.1. Membrane Fouling Characteristics

Experimental results (as shown in **Figure 1** and **Figure 2**) indicated that forward osmosis performance of the PVP 20% solution exhibited reductions over extended periods of operation.

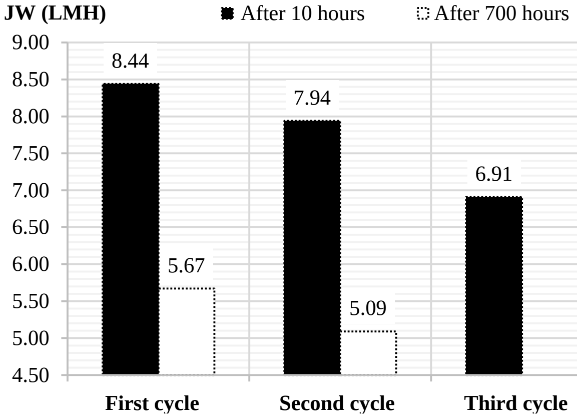

Figure 1 *Impact of surface flushing cleasing method on water flux (JW)*

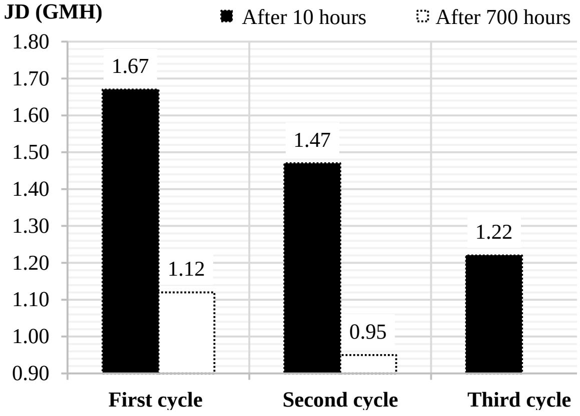

Figure 2 *Impact of surface flushing cleasing method on reverse solute flux (JD)*

In particular, after the first 700 hours of operation, water flux of the forward osmosis system decreased from 8.44 LMH to 5.67 LMH, while reverse solute flux decreased from 1.67 GMH to 1.12 GMH (approximately 33% reduction in both cases). The cause of this phenomenon can be attributed to fouling occurring on the surface and within the porous structure of the semipermeable membrane after extended forward osmosis operation leading to significant reduction in effective membrane area, hindering the mass transfer of both water and other solutes [6].

These observations were corroborated by SEM images of the membrane surface, as presented in **Figure 3**. In particular, SEM image of fouled membrane sample indicated significant deposition of draw solute particles on the surface of the semipermeable membrane. Due to inherent properties of PVP K17, the deposited particles were relatively large in size (approximately over 10 µm) and complex in structure. This phenomenon can be due to specific interactions between PVP K17 molecules and NaCl molecules (specially, Na+ and/or Cl– ions), which led to reductions in the solubility of PVP K17 in the areas around the membrane surface [9].

Conversely, on the feed solution side, the primary fouling mechanism was determined to be the growth of microorganisms. In particular, SEM image of the fouled membrane sample revealed that a significant portion of the membrane surface was covered by spherical structures approximately 2 µm in size, corresponding to the average size range of numerous bacterias. The presence of this biofilm formed by bacterias would significantly impact the mass transfer efficiency of both water and draw solute [10].

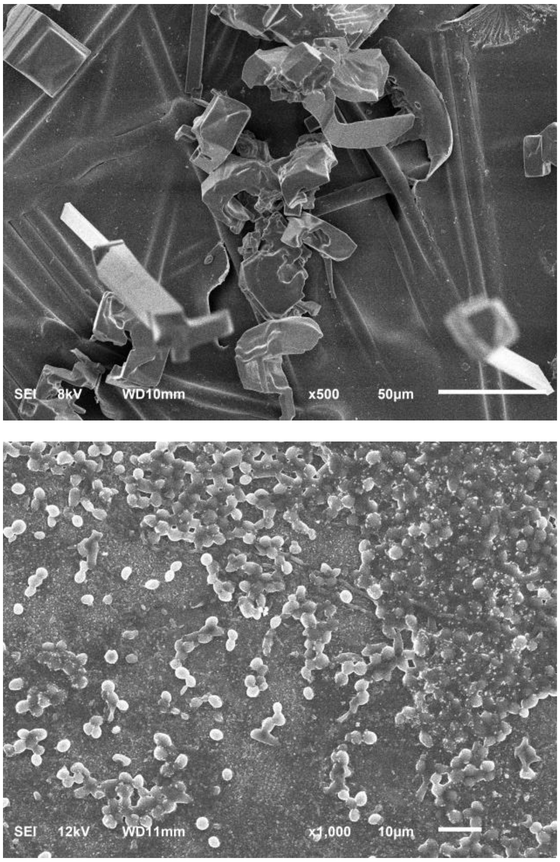

Figure 3 *SEM images of the membrane surface on the draw solution side (top) and the feed solution side (bottom)*

3.2. Efficiency of Surface Flushing on Foulants Removal and Membrane Cleansing

Experimental results (as shown in **Figure 1** and **Figure 2**) indicated that the surface flushing cleansing method can rather effectively alleviate the negative impacts of membrane fouling on water flux and draw solute flux. In particular, for the first 700-hours operational cycle, surface flushing can restore up to 82% of the reduction in water flux caused by fouling. However, for the second 700-hours operational cycle, this cleansing method can only offer up to 64% in water flux restoration.

This result can be attributed to severe fouling on both sides of the semipermeable membrane (as seen in Figure 3), therefore only allowing partial removal of foulants through surface flushing. According to Vrouwenvelder et al., biofilms formed by microbial growth typically exhibit high adhesion to the surface of semipermeable membrane, and are challenging to be removed completely with conventional surface flushing [11]. Similarly, surface flushing is also relatively ineffective in dealing with internal fouling caused by the deposition of particles within the membrane's porous structure, due to the inability to penetrate deep inside these clogged porous structures of the surface flushing stream [12].

Residual foulants still remaining within the porous structure and biofilm areas not entirely removed by surface flushing would continue to impede the mass transfer of water and other solutes through the semipermeable membrane, preventing water flux and reverse solute flux from being fully restored, while also exacerbating fouling in subsequent operational cycles.

3.3. Efficiency of Backwashing on Foulants Removal and Membrane Cleansing

Experimental results (as shown in **Figure 4** and **Figure 5**) demonstrated the improvements in foulants removal and membrane cleansing of the backwashing method, compared to those of the surface flushing method. In particular, for the first 700-hours operational cycle, backwashing can restore up to 95% of the reduction in water flux caused by fouling. For the second 700-hours operational cycle, its water flux restoration efficiency was lowered to 91%.

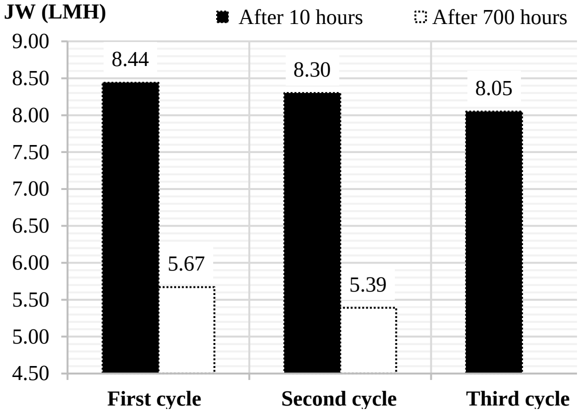

Figure 4 *Impact of backwashing cleasing method on water flux (JW)*

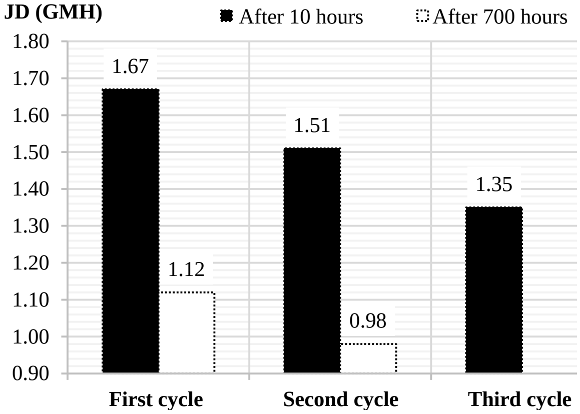

Figure 5 *Impact of backwashing cleasing method on reverse solute flux (JD)*

The differences in foulants removal and membrane cleansing efficiency between surface flushing method and backwashing method can be explained by two primary reasons. Firstly, the presence of saturated salt solution significantly disrupted the metabolic processes of microorganisms that caused membrane fouling, thereby destabilizing the biofilm and reducing its adhesion to the membrane surface [13]. Secondly, during backwashing, the water flux from the water side to the saturated salt solution side helped detaching parts of the biofilm from the membrane surface, thereby enhancing foulant removal efficiency of the flushing stream [14].

However, similar to surface flushing, backwashing was unable to entirely remove foulants deposited within porous structures of the semipermeable membrane, therefore unable to completely alleviate negative impacts caused by fouling. As such, this method can only restore approximately 95% of water flux after the first 700-hours operational cycle, and its cleansing efficiency would gradually decrease in subsequent 700-hours operational cycles.

4. CONCLUSIONS

This study successfully identified the impacts of membrane fouling on the performance of forward osmosis desalination systems, providing essential information to optimize membrane cleansing processes, which can help ensure stable and efficient operation of forward osmosis desalination systems. Specifically, this study discovered that membrane fouling occurred when using Polyvinylpyrrolidone K17 as the draw solute can lead to 33 – 36% reduction in water flux after the 700-hours operational cycles. This study also successfully determined that the fouling on membrane surface in contact with the draw solution was mainly caused by inorganic/organic dispositions, while the fouling on membrane surface in contact with the feed solution was mostly caused by the growth of microorganisms.

In addition, this study also investigated the membrane cleansing efficiency of two popular physical cleansing methods, which were surface flushing and backwashing. Experimental results showed that backwashing with saturated salt solution can lead to 93 – 95% restoration of lost water flux caused by fouling, while the numbers for surface flushing were only 64 – 82%. Such divergence can be explained by the difference in the capability of surface flushing and backwashing in removing the biofilm which was attaching to the membrane surface.

Overall, these findings provided a theoretical basis for understanding the impacts of membrane fouling on the performance of forward osmosis desalination systems using Polyvinylpyrrolidone K17 as a draw solute. This study also highlighted the need for further in-depth evaluations of membrane fouling in order to determine appropriate cleansing approaches to effectively remove foulants caused by using Polyvinylpyrrolidone K17 as a draw solute in forward osmosis desalination systems.

Acknowledgements: The authors express their sincere gratitude to the Vietnam Academy of Science and Technology for their financial support of this research through project code: PC 0649.02/21-23.

REFERENCES

[1] Ngo TT, Le NT, Hoang TM, Luong DH, (2018). Water scarcity in Vietnam: A point of view on virtual water perspective. *Water Resources Management*, **32**, 3579.

[2] Duong TH, (2022). Studying the water scarcity in the downstream due to factors in the upstream — A case study. *Climate Change and Water Security: Select Proceedings of VCDRR 2021*, 325.

[3] Liu L, Wang M, Wang D, Gao C, (2009). Current patents of forward osmosis membrane process. *Recent Patents on Chemical Engineering*, **2**, 76.

[4] Cath TY, Childress AE, Elimelech M, (2006). Forward osmosis: Principles, applications, and recent developments. *Journal of Membrane Science*, **281**, 70.

[5] Aende A, Gardy J, Hassanpour A, (2020). Seawater desalination: A review of forward osmosis technique, its challenges, and future prospects. *Processes*, **8**, 901.

[6] Zhao S, Zou L, Tang CY, Mulcahy D, (2012). Recent developments in forward osmosis: Opportunities and challenges. *Journal of Membrane Science*, **396**, 1.

[7] Mi B, Elimelech M, (2008). Chemical and physical aspects of organic fouling of forward osmosis membranes. *Journal of Membrane Science*, **320**, 292.

[8] Nguyen QT, Hoang MT, Trinh TH, Nguyen NT, Le TG, (2022). Evaluation of polyvinylpyrrolidone as draw solute for desalination forward. *Water Supply*, **22**, 1652.

[9] Wang Y, Wicaksana F, Tang CY, Fane AG, (2010). Direct microscopic observation of forward osmosis membrane fouling. *Environmental Science and Technology*, **44**, 7102.

[10] Mitrouli S, Iantsios S, Arabelas AJ, Mitrakas M, llesdal MF, Jolseth PA, (2008). Pretreatment for desalination of seawater from an open intake by dual-media filtration:

Pilot testing and comparison of two different media. *Desalination*, **222**, 24.

[11] Vrouwenvelder JS, Manolarakis SA, Veenendaal HR, Van der Kooij D, (2000). Biofouling potential of chemicals used for scale control in RO and NF membranes. *Desalination*, **132**, 1.

[12] Arkhangelsky E, Wicaksana F, Chou S, Al-Rabiah AA, Al-Zahrani SM, Wang R, (2012). Effects of scaling and cleaning on the performance of forward osmosis hollow fiber membranes. *Journal of Membrane Science*, **415–416**, 101.

[13] Xu H, Liu Y, (2011). Control and cleaning of membrane biofouling by energy uncoupling and cellular communication. *Environmental Science and Technology*, **45**, 595.

[14] Le-Clech P, Chen V, Fane TAG, (2007). Fouling in membrane bioreactors used in wastewater treatment. *Journal of Membrane Science*, **284**, 17.