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Dehydration of industrial isopropanol wastewater by pervaporation using carboxy methyl cellulose and graphene oxide hybrid membranes

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Isopropanol (IPA) is widely used as an industrial solvent, cleaning agent, and in producing chemicals, fuels and medical products. Many applications require anhydrous IPA without water. IPA-containing wastewaters are generated from its production and uses. Dewatering and recycling IPA from these waste streams is important for both economic and environmental reasons. IPA and water form an azeotropic mixture, making conventional dehydration methods like distillation and extraction challenging. Membrane-based processes such as pervaporation offer advantages over these processes, as it can break azeotropes while requiring lower energy and having a smaller footprint. In this study, hybrid membrane was used to dehydration of industrial isopropanol wastewater by pervaporation. The study focused on preparing hybrid membranes for pervaporation dehydration by incorporating graphene oxide into a carboxy methyl cellulose matrix. This integration of graphene oxide led to an enhancement in the dehydration separation performance of the hybrid membranes. Additionally, the research systematically characterized and evaluated the impact of graphene oxide concentration, operation temperature, and feed IPA concentration on various properties such as hydrophilicity, swelling, and dehydration. These analyses aimed to understand the influence of these factors on the overall performance and properties of the hybrid membranes. Optimum process conditions have been determined and under these conditions, water flux 4.7 kg/m^{2}h and separation factor value of 128 were obtained. The study's findings pave the way for the future development of carboxy methyl cellulose (CMC) based hybrid membranes for implementation in pervaporative dehydration processes.

Keywords: Dehydration; Isopropanol; Membrane; Pervaporation; Wastewater

INTRODUCTION

Understanding the challenges in recovering isopropyl alcohol (IPA) from pharmaceutical industry wastewater is crucial due to the complexity of the components involved. The presence of solvents, inorganic salts, and organic compounds makes the separation process intricate. IPA, being a common solvent in drug synthesis, forms azeotropic mixtures with water, especially at around 13 wt% water under ambient pressure, leading to challenges in separation. Additionally, mixtures with close boiling points further complicate the recovery process. Dehydration is a critical step in the recovery of IPA from such wastewater streams as it helps in separating IPA from water and other components effectively. By leveraging dehydration techniques, such as distillation or molecular sieves, it is possible to overcome the challenges posed by the presence of water and the formation of azeotropic mixtures during the recovery process. Implementing a well-designed separation strategy that includes dehydration steps can facilitate the efficient recovery of IPA from pharmaceutical industry wastewater [1-3].

Traditional separation methods for IPA/water mixtures, such as azeotropic distillation and extraction distillation, are known for their high energy consumption and waste generation. Azeotropic distillation typically requires the addition of di-isopropyl-ether or cyclohexane, and extractive distillation uses ethylene glycol as a separating agent. However, these methods are costly due to the high energy consumption and the use of additional chemicals [1-3]. Pervaporation (PV) stands out as an alternative separation process to these traditional methods, known for its energy efficiency, environmental friendliness, and ease of operation. PV is a membrane-assisted separation process that is considered advantageous due to its lower energy requirements and minimal environmental impact [4-8]. It is commonly employed for the dehydration of alcohols and offers a promising solution for the separation of IPA/water mixtures [9].

Pervaporation is a membrane-based separation process that finds significant utility in effectively separating liquid azeotropes.

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Unlike traditional separation methods reliant on the vapor-liquid equilibrium, pervaporation separation is unique in that the transport resistance is determined by the mobility of the components across the membrane and the sorption equilibrium. The application of pervaporation in separating IPA/water mixtures is particularly intriguing due to the challenges posed by the formation of azeotropic mixtures during conventional distillation processes. Notably, there have been reports indicating the installation of 16 industrial pervaporation units specifically dedicated to the dehydration of IPA, highlighting the practical importance and successful implementation of this technology in the pharmaceutical industry. By leveraging the advantages offered by pervaporation, such as its independence from vapour-liquid equilibrium and its efficient separation capabilities, industries can achieve enhanced separation efficiency and cost-effective recovery of valuable solvents like IPA from complex mixtures in processes like drug synthesis and pharmaceutical wastewater treatment.

Pervaporation is a separation process where a component in a liquid mixture selectively permeates through a dense membrane, facilitated by a chemical potential gradient. It offers economic and environmental advantages, being energy-efficient and eco-friendly [10-12]. In pervaporation, the liquid mixture encounters a dense, homogeneous membrane that separates the feed and the permeating stream. The components dissolve in the membrane, diffusing through it at varying speeds before evaporating downstream. The resulting vapor is condensed back into a liquid form. The efficiency of pervaporation hinges on the interaction between the components and the membrane material, with the membrane's chemical nature and structure playing a pivotal role in determining performance [13]. The mass transfer mechanism in pervaporation currently relies on the solution diffusion model. This model posits that species dissolve at the surface of the membrane with higher chemical potential, diffuse through the polymer's free volume in a sorbed state, and transition to the fluid phase downstream where the chemical potential is lower. The dense polymeric membrane actively participates in both the dissolution and diffusion processes, making it a crucial element in the efficiency and effectiveness of pervaporation for separating components in liquid mixtures [14-18].

The membrane is critical in pervaporation applications. Polymeric, inorganic and hybrid membranes have been widely used for pervaporative separation. However, polymer applications were limited by several issues, including low mechanical and biostability and low reject rates. Inorganic membranes have been limited by the high cost of manufacturing. The inclusion of inorganic components into polymeric membranes is expected to enhance the membranes' separation properties. The synergistic effects of combining polymers with inorganic fillers/particles is hypothesized to result in higher performing membranes for the separation. The key requirements of these hybrid membranes are that the polymer component confers chemical/ thermal stability, ease of processing and high hydrophilicity [4].

In this study, pervaporative recovery of isopropanol from pharmaceutical industry wastewater was investigated with GO/CMC hybrid membrane. The compatibility of the polymers used in the prepared hybrid membrane was visualized by SEM analysis. The chemical bond structure of the GO/CMC blend membrane was determined by FTIR. The effect of GO concentration, feed water concentration and temperature on the separation performance was investigated.

EXPERIMENTAL

Materials

In this study, the materials used for the membrane synthesis and experimental procedures were purchased from specific suppliers. Carboxymethyl cellulose (CMC) was supplied from Denkim Denizli Kimya Inc. Graphene oxide were acquired from Hazerfen Kimya A.Ş. Glutaraldehyde, acetone and hydrochloric acid were obtained from Sigma Aldrich.

- *Membrane preparation.* 5 wt.% of CMC is dissolved in deionized water to obtain a homogeneous polymeric membrane solution. A certain amount of GO particles (ranging from 0.5 wt.% to 4 wt.%) based on the mass of the polymer were added to the CMC solution. Solution casting method was used for the casting and drying of membrane. After drying, the membrane was crosslinked to improve its stability and mechanical properties. The dry membrane underwent a cross-linking process using a combination of glutaraldehyde (1% by weight), HCl (1% by weight), acetone (85% by weight), and water (15% by weight) [18]. Following the cross-linking procedure, the hybrid membrane was washed with distilled water and subsequently allowed to dry. This cross-linking treatment is essential to enhance the stability and performance of the membrane for its intended applications.
- *Membrane characterization.* In the study, the synthesized membranes underwent characterization using Fourier-transform infrared

spectroscopy (FTIR) and scanning electron microscopy (SEM). These characterization techniques are crucial for analyzing the chemical structure and structural morphology of the membranes.

FTIR analysis was conducted to assess alterations in the chemical structure of the carboxy methyl cellulose (CMC) membrane due to the incorporation of graphene oxide (GO). The FTIR analysis involved conducting 4 scans within the spectral range of 400-4000 cm^{-1}. This analysis helps in understanding the chemical interactions and structural changes resulting from the addition of graphene oxide in the membrane matrix.

The compatibility and miscibility between GO and CMC were evaluated through SEM analysis by capturing cross-sectional images of the membrane. This method allows for a visual examination of the interface between GO and cellulose acetate within the membrane, providing insights into their interaction, distribution, and compatibility at a microscale level.

Pervaporative recovery of isopropanol

Pervaporative recovery of isopropanol was carried out in a laboratory-scale pervaporation system.

The system consists of a membrane cell containing the membrane and feed mixture, a mechanical mixer for homogenization of the mixture, a vacuum pump to ensure low pressure in the underflow and cooling traps where the flow through the membrane is collected. The membrane is placed in the membrane cell. The feed mixture was fed into the membrane cell through a feed pump and the mixture was mixed with the help of a mechanical mixer. Due to the use of hydrophilic membranes, the water in the mixture passed through the membrane and the purification process was carried out. IPA could not pass through the membrane and remained in the feed mixture. In the pervaporation process, one side of the membrane is in contact with the liquid while the other side is vacuum. Water passed through the membrane perfectly and evaporated at low pressure on the passing stream side. Then the water obtained as vapor in cooling traps was condensed with liquid nitrogen and obtained in liquid phase. The separation performance of the membrane was determined by flux and selectivity. Flux and separation were calculated using Equations 1 and 2, respectively.

$$J = \frac{m}{A.t} \tag{1}$$

m is the amount of sample collected in the passing stream, A is the membrane area and t is the time.

$$\alpha = \frac{y_{su} / y_{IPA}}{x_{su} / x_{IPA}} \tag{2}$$

y is the percentage by weight in the passing stream and x is the percentage by weight in the feed. Isopropanol concentration was determined by refractometer.

RESULTS AND DISCUSSION

Characterization results

- *FTIR analysis.* The FTIR spectra of GO/CMC hybrid membranes are given in Fig. 1.

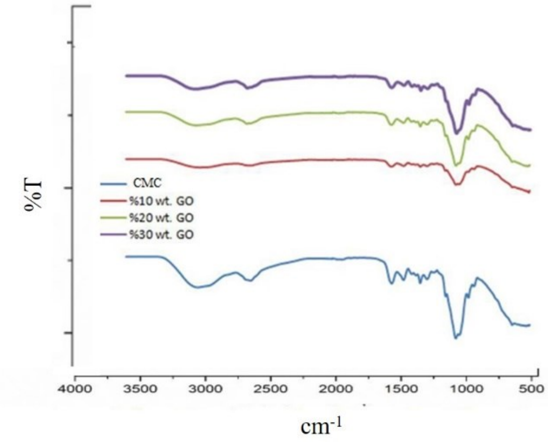

Fig. 1. FTIR spectra of the membranes

The strong absorption band at 3450 cm^{-1} is due to O-H stretching vibrations of surface hydroxyl groups and adsorbed water. The peak at 2926 cm^{-1} is the C-H vibration peak of the CMC polymer. The peaks at 1720 cm^{-1} and 1651 cm^{-1} belong to the COO- group of CMC. The multiple peaks of GO in the range 1000-1700 cm^{-1} correspond to oxygen-containing functional groups [19, 20].

- *SEM analysis.* SEM analysis was performed with samples taken from GO/CMC hybrid membrane. Fig.c2 shows the cross-sectional image of GO/CMC hybrid membrane.

SEM images showed that the polymer and additive were well mixed, no phase separation was observed and exhibited coherent polymeric behavior. All these are the result of molecular interaction between the polymers. A certain number of hydroxyl groups are required for CMC to be miscible with GO. Therefore, there is an intermolecular interaction involving hydroxyl groups. Strong interpolymer interaction occurred between CMC and GO and thus no phase separation occurred. As a result, homogeneous hybrid films were obtained [25].

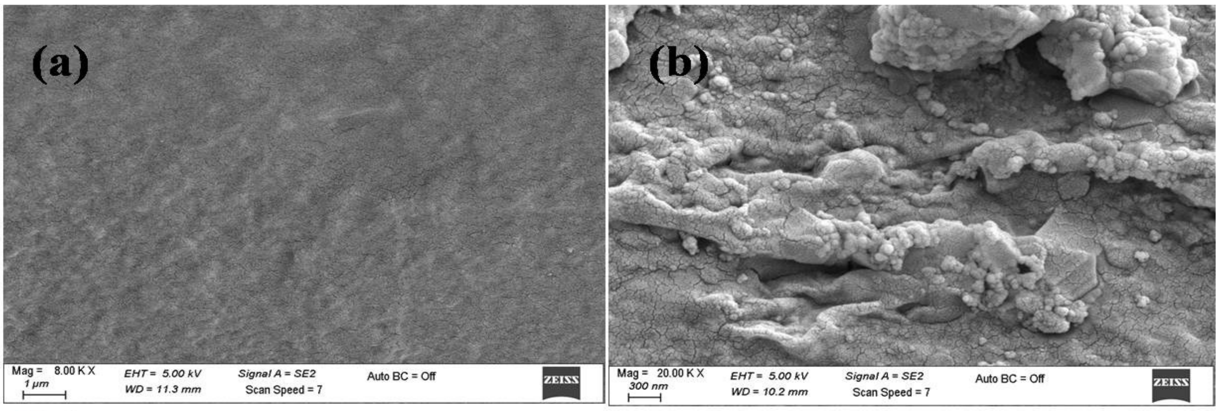

Fig. 2. Sectional image of GO/CMC hybrid membrane

Pervaporation results

- *Effect of GO concentration.* Membranes with four different GO loading rates (0.5%, 1% 2% and 4%) were used in the experimental study for pervaporative recovery of isopropanol. The experiments were carried out using isopropanol-water mixture containing 13% water at room temperature. The effect of the amount of GO on the separation performance of the membrane is given in Fig. 3.

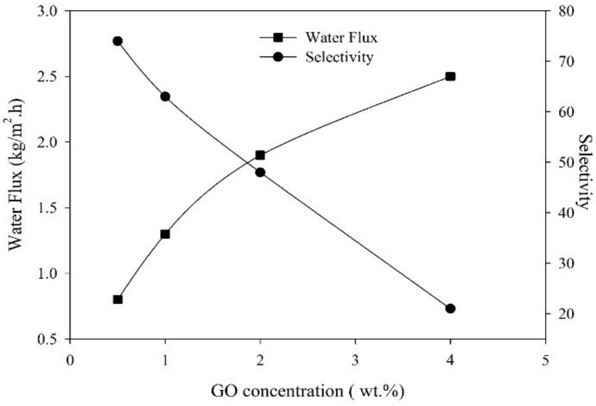

Fig. 3. Effect of GO concentration on flux and selectivity

The hydrophilic nature of CMC causes high water permeation. GO also increases water passage due to its hydrophilic nature. As the amount of GO increases, flux increases and selectivity decreases. As the amount of GO increases, the hydrophilicity of the membrane increases and the selectivity value decreases [26-28].

- *Effect of feed concentration.* The results of pervaporative recovery of isopropanol tested at room temperature using a GO/CMC hybrid membrane containing 0.5 wt.% GO are shown in Fig. 4. Isopropanol-water mixture is known to exhibit azeotropic mixing at 13 wt% water content. The effect of feed water concentration was investigated for isopropanol-water blends containing 6, 13, 20 and 27 wt% water. As expected, with increasing water concentration, the total flux increases due to the so-called ‘plasticizing effect’ of water, which leads to an increase in the free volume of the membrane allowing molecules to more easily pass through the membrane. Furthermore, more hydrogen bonds can be formed between the hydrophilic polar groups of the membrane and the water in the feed mixture at higher water concentrations, resulting in higher flux and correspondingly lower separation factor.

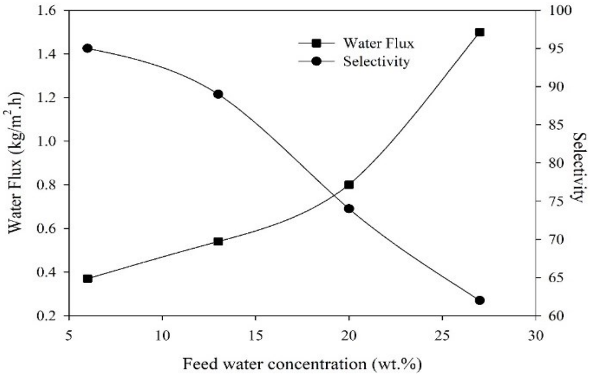

Fig. 4. Effect of feed water concentration on flux and selectivity

The plasticizing and swelling effects of water had a negative effect on the separation factor of the membrane; since the polymer chains can move quickly and easily, the resulting free volume results in a lower separation factor in low concentration IPA mixtures. As the water concentration in the feed mixture increased from 6% to 27%, the total flux increased from 0.37 kg/m^2.h to 1.5 kg/m^2.h, while the selectivity decreased from 95 to 62 [24, 20-32].

- *Effect of temperature.* The effect of temperature on the separation performance of GO/CMC hybrid membrane is shown in Fig. 5. As the operating temperature increases, the thermal mobility of the chains of the GO/CMC polymer intensifies, the free volume increases.

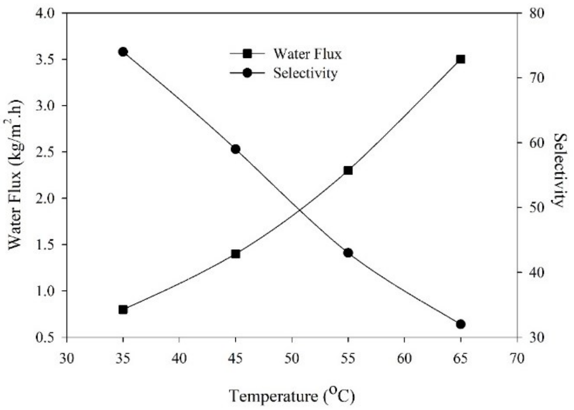

Fig. 5. Effect of temperature on flux and selectivity

The transfer of water is facilitated and an increase in water flux is observed as the temperature increases. Also, the vapor pressure of the feed increases as the temperature increases. This increase is to increase the driving force for mass transport through the membrane [33, 34]. This results in an increase in the flux value for both membranes. While 0.8 kg/m^{2}h flux was obtained at 35°C, the flux value increased to 3.5 kg/m^{2}h when the temperature increased to 65°C. The selectivity was 74 and 32 at 35°C and 65°C in the GO/CMC hybrid membrane.

CONCLUSION

The study introduces an innovative approach, the pervaporation process, for dehydrating isopropanol using a GO/CMC hybrid membrane. The research focused on understanding the impact of variables such as the concentration of graphene oxide (GO), feed water concentration, and temperature on the separation performance. It was observed that increasing the GO concentration led to enhanced membrane hydrophilicity and swelling, facilitating easier water passage through widened diffusion channels, thereby increasing flux. However, this also resulted in reduced diffusion selectivity, causing isopropanol to be carried along with water through the membrane, lowering the separation factor. Furthermore, elevating the water concentration in the feed solution increased the membrane's free volume by promoting greater contact between the membrane and water. This, in turn, increased flux but, as with the effect of GO concentration, decreased the separation factor. The experimental findings identified the optimal conditions for the process, which involved using a 0.5 wt.% GO loaded membrane at a feed water concentration of 13 wt% (azeotrope point) at 35°C. This configuration yielded the best separation performance, showcasing the efficiency of the pervaporation process for azeotropic mixtures of water and isopropanol at a 13% water concentration. Under these conditions, the obtained flux and selectivity values were recorded at 0.82 kg/m^2·h and 74, respectively. The study's results underscore the importance of fine-tuning key parameters such as membrane composition, feed water concentration, and temperature to optimize the pervaporation process for efficient dehydration of isopropanol, demonstrating the potential of this method in addressing challenges related to azeotropic mixtures in the pharmaceutical industry.

REFERENCES

1. A. Urtiaga, E. Gorri and I. Ortiz, *Sep. Purif. Technol.*, **49**, 245 (2006).
2. J. Zuo, D. Hua, V. Maricar, Y. K. Ong, T.S. J. Chung, *Appl. Polym. Sci.*, **135**, 45086 (2017).
3. C. Y, Lai, Y. M. Sun, Y. L. Liu, *Journal of Membrane Science,* **685**, 121959 (2023).
4. X. W. Liu, Y. Cao, Y. X. Li, Z. L. Xu, Z. Li, M. Wang, X. H. Ma, *J. Membr. Sci.,* **576**, 26 (2019).
5. Q. Wang, N. Li, B. Bolto, M. Hoang, Z. Xie, *Desalination*, **387**, 46 (2016).
6. S. Assabumrungrat, J. Phongpatthanapanich, P. Praserthdam, T. Tagawa, S. Goto, *Chem. Eng. J.*, **95**, 57 (2003).
7. B. G. Park, T. T. Tsotsis*, Chem. Eng. Process.*, **43**, 1171 (2004).
8. D. Unlu, N. D. Hilmioglu, *J. Chem. Technol. Biotechnol.,* **91**, 122 (2016).
9. A. I. Kuzminova, M. E. Dmitrenko, D. Y. Poloneeva, A. A. Selyutin, A. S. Mazur, A. V. Emeline, V. Y. Mikhailovskii, N. D. Solovyev, S. S. Ermakov, A. A. Penkova, *J. Membr. Sci.,* **626**, 119194 (2021).
10. R. W. Baker, Membrane separation, in Encyclopedia of Separation Science, Academic Press, 2000, p. 205.
11. A. Basile, M. D. Marcello De Falco, G. Centi. G. Iaquaniello, Membrane Reactor Engineering: Applications for a Greener Process Industry. United Kingdom, Wiley, 2016.
12. P. Salehian, T. S. Chung, *J. Membr. Sci.*, **544**, 378 (2017).
13. A. Basile, A. Figoli, M. Khayet, Pervaporation, Vapour Permeation and Membrane Distillation: Principles and Applications. United Kingdom, Woodhead Publishing, 2015.
14. S. P. Dharupaneedi, R. V. Anjanapura, J. Han, T. M. Aminabhavi, *Ind. Eng. Chem. Res.* **53**, 14474 (2014).
15. J. K. Wu, M. J. Yin, W. Han, N. Wang, Q. F. An, *J. Mater .Sci.*, **55**, 2607 (2020).
16. D. P. Suhas, A. V. Raghu, H. M. Jeong, T. M. Aminabhavi, *RSC Adv.,* **3**, 17120 (2013).
17. R. Y. M. Huang, Pervaporation Membrane Separation Processes, Amsterdam, Elsevier Science Publishers BV, 1991.
18. H. E. A. Brüschke, N. P. Wynn, Membrane separations/pervaporation, in: I. D. Wilson, E. D. Adlard, M. Cooke, C. F. Poole (eds.), Encyclopedia of Separation Science, Academic Press, Germany, 2000, p. 1776.

19. Q. Zhao, J. Qian, Q. An, C. Gao, Z. Gui, H. Jin, *J. Membr. Sci*., **333,** 68 (2009).
20. M. Ozekmekci, D. Unlu, M. Copur, *Korean J. Chem. Eng*., **38**, 1859 (2021).
21. Y. M. Xu, N. L. Le, J. Zuo, T.S. Chung, *J. Membr. Sci*., **499**, 317 (2016).
22. D. Ünlü, *Gümüşhane Üniversitesi Fen Bilimleri Enstitüsü Dergisi*, **10**, 275 (2020).
23. H. Wu, X. Fang, X. Zhang, Z. Jiang, B. Li, X. Ma, *Sep. Purif. Technol*., **64**, 183 (2008).
24. X. H. Zhang, Q. L. Liu, Y. Xiong, A. M. Zhu, Y. Chen, Q. G. Zhang, *J. Membr. Sci*., **327**, 274 (2009).
25. Y. Miyashita, T. Suzuki, Y. Nishio, *Cellulose*, **9**, 215 (2002).
26. Z. Wang, H. Yu, J. Xia, F. Zhang, F. Li, Y. Xia, Y. Li, *Desalination*, **299**, 50 (2012).
27. W. Jang, J. Yun, K. Jeon, H. Byun, *RSC Adv.,* **5**, 46711 (2015).
28. J. Zhang, Z. Xu, W. Mai, C. Min, B. Zhou, M. Shan, X. Qian, *J. Mater. Chem. A.,* **1**, 3101 (2013).
29. J. Lu, Q. Nguyen, J. Zhou, Z.H. Ping, *J. Appl. Polym. Sci*., **89**, 2808 (2003).
30. K. Sunitha, Y. V. L. R. Kumar, S. Sridhar, *J. Mater. Sci*., **44**, 6280 (2009).
31. Z. Raeisi, A. Moheb, M. Sadeghi, A. Abdolmaleki, M. Alibouri, *Chem Eng Res Des*., **145**, 99 (2019).
32. T. Zhu, Y. Luo, Y. Lin, Q. Li, P. Yu, M. Zeng, *Sep. Purif. Technol.,* **74**, 242 (2010).
33. R. Castro-Muñoz, J. Buera-González, Ó. D. L Iglesia, F. Galiano, V. Fíla, M. Malankowska, C. Rubio, A. Figoli, C. Téllez, J. Coronas, *J. Membr. Sci.,* **582**, 423 (2019).
34. V. T. Magalad, G. S. Gokavi, K. V. S. N., Raju, T. M. Aminabhavi, *J. Membr. Sci*., **354**, 150, (2010).