Pak. J. Biotechnol. Vol. 15 (2) 357-364 (2018) ISSN Print: 1812-1837
www.pjbt.org ISSN Online: 2312-7791

# SURFACE IMPROVEMENT AND MODIFICATION OF PDMS.$SiO_2$/PES MEMBRANE FOR ETHANOL/WATER SEPARATION IN MEMBRANE BIOREACTOR

Amirhossein Farahi, Ghasem D. Najafpour*, Aliasghar Ghoreyshi

Biotechnology Research Laboratory, Faculty of Chemical Engineering, Noushirvani University of Technology, Babol, Iran.

Article received 2.4.2018, Revised 19.5.2018, Accepted 27.5.2018

## ABSTRACT

An ethanol selective composite membrane consists of dense and hydrophobic polydimethylsiloxane (PDMS) as active layer on polyethersulfone (PES) as support layer was successfully fabricated. In order to improve membrane's ethanol selectivity, $SiO_2$ was coated on the surface of composite membrane. For $SiO_2$ coating, the composite PDMS surface was modified by corona treatment at corona time of 6 min and corona input power of 360 W. As a result, the ethanol separation factor has significantly increased (from 6.9 to 10.5 for total flux of 510 g/$m^2$.h). The ethanol separation factor using PDMS/PES modified surface membrane was improved by 52%. In the next step, the performance of the fabricated PDMS.$SiO_2$/PES membrane was examined in membrane bioreactor (MBR). Based on obtained data, bioethanol concentration in conventional fermentation was 18.9 g/l while bioethanol concentration in broth of MBR and cold trap were 23.54 and 195.4 g/l, respectively. In addition, the cell concentration at conventional fermentation was 12.3 g/l. The cell concentration in MBR using the PDMS fabricated membrane has reached to 16.1 g/l. Therefore, the modified fabricated composite PDMS.$SiO_2$/PES membrane was quite effective for ethanol separation. The fabricated composite PDMS membrane was much superior than the commercial PDMS membrane.

**Keywords**: Bioethanol; Membrane bioreactor; Composite membrane; Surface modification

## 1. INTRODUCTION

World's energy demand is substantially depending on fossil fuel. As fossil fuel resources are gradually depleted; renewable energy sources should be considered as the most desire alternative for fossil fuel. Combustion of fossil fuel causes environmental pollution and climate changes; while, renewable energy sources such as bioethanol and biodiesel are not considered as environmental threat. Bioethanol as an alternative resource is one of the most useful renewable fuel (Shafigh k *et al.*, 2004; Peng *et al.*, 2010; El-Sebaii and Shalaby, 2012; Hamidreza Ghafouri Taleghani *et al.*, 2014; Rezakazemi *et al.*, 2015; Adnan Hasan *et al.*, 2016). Bioethanol is produced from waste, lignocelluloses materials and agricultural products such as corn, wheat, sugarcane and sweet sorghum (Nasidi *et al.*, 2016).

Fermentation of carbohydrates derived from agro-sources to ethanol resulted in a mixture of ethanol and water solution; that should be separated. Recently researches are focused on integrated systems; since conventional processes such as distillation operation that is often used for the separation of ethanol and water are energy intensive (Ikegami *et al.*, 2002). Use of membrane bioreactor (MBR) in ethanol production is an integrated system along with application of membrane pervaporation processes. In MBR, bioethanol is produced through fermentation process; separated in pervaporation process using ethanol selective membrane (Trifunović and Trägårdh, 2005; El-Sebaii and Shalaby, 2012). Pervaporation technology, compared to traditional separation technology such as distillation has high separation efficiency, low energy consumption, simple operation and low utility costs (Chen *et al.*, 2008). In pervaporation, separation mechanism is based on ability of nonporous membranes to be selective to transporting components from the feed to the permeate side (Trifunović and Trägårdh, 2005). One of the best ethanol selective membranes for separation of ethanol in membrane bioreactor is PDMS membrane (Peng *et al.*, 2010; Rezakazemi *et al.*, 2015; Fu *et al.*, 2016). High ethanol selectivity of PDMS membrane is due to free rotation of Si-O bonds (El-Sebaii and Shalaby, 2012).

In composite PDMS membrane, for different purposes such as improvement of surface roughness, hydrophobicity and ethanol selectivity, the fillers such as nanosilica, zeolite, carbon black, graphene and carbon nano tubes were incorporated into polymer (Novak, 1993; Herrera-Herrera *et al.*, 2012; Nour *et al.*, 2013; Romasanta *et al.*, 2013; Sun *et al.*, 2013). For coating nanoparticles on the surface of membrane, surface treatment of membrane is applied by corona treatment of modified surface membrane (Moghimifar *et al.*, 2014). Implementation of corona treatment for surface modification leads to enhancement of ethanol separation

Corresponding author E. mail: *najafpour8@gmail.com

factor using $SiO_2$ surface coated membrane. Corona treatment generated physical effect on the membrane surface which leads to coating nanoparticles on the membrane surface at optimum condition in this work (corona time of 6 min and corona input power of 360 W). For input power greater than 360 W, serious surface damage was observed. Therefore, the dense active layer of composite membrane did not damage at optimal conditions of corona treatment. Furthermore, creation of extra chemical bonds may change the chemical nature of the membrane. The corona treatment performs by generating a visible electrical discharge from an electrode over the polymeric surface at low voltage (10-40 kV) and high frequency (1-4 kHz). The corona discharge causes partial ionization of the surrounding atmosphere and produces excited species (free radicals, ions or electrons). These chemical species are able to react and oxidize the molecule exposed to the outer surface of polymer (Ozdemir *et al.*, 1999; Pal *et al.*, 2008; Sadeghi *et al.*, 2013; Rocca-Smith *et al.*, 2016).

In this study, phase inversion method was used for the fabrication of membranes. Immersion precipitation phase inversion was used for fabrication of PES membrane as support layer because the PES as support membrane must be porous to increase total flux. Then, a dense and nonporous layer of PDMS as active layer was established on the support layer by solvent evaporation method used in pervaporation process. In next step, surface modification by corona treatment and $SiO_2$ coating on the surface of composite membrane were performed. Ethanol selectivity and flux of the fabricated composite membrane in a pervaporation process were experimentally examined. AFM and FESEM were carried out for the characterization of the fabricated membrane. Finally, ethanol was produced via fermentation of glucose (concentration of 50 g/l) in membrane bioreactor using the novel fabricated membrane ($SiO_2$ coated on PDMS/PES composite membrane). The obtained results were compared to conventional fermentation.

## 2. MATERIALS AND METHODS

**2.1. Materials:** $SiO_2$ with molecular weight of 60.084 g/mol and density of 2.634 g/cm$^3$ was supplied by Merck (Darmstadt, Germany). PES Ultrason E6020 with molecular weight of 58000 Da was supplied (BASF, Germany). Dimethyl acetamide (DMAc), dibutyltin dilaurate, tetraethyl orthosilicate (TEOS) and n-heptane were purchased (Merck Germany). Analytical grade PDMS having viscosity of 150 cSt was supplied (Aldrich, USA).

**2.2. Composite PDMS/PES membrane preparation:** Asymmetric layer of PES was prepared as support layer via phase inversion technique. Homogeneous solutions including PES (16 wt%) and DMAc (84 wt%) as solvents were prepared. The blended solutions were casted on a glass plate at room temperature. For membrane fabrication, an automatic casting machine was used to spread out uniformly the polymeric solution for high accurate membrane thickness and repeatability. The thickensses of all the support layers were set at 100 μm. The glass plate was immediately immersed in the coagulation bath. The casted layer was stored in distilled water for 48 h. Finally, the film was washed out with distilled water and then dried and kept at room temperature for duration of 48 h. For preparation of the active layer on support layer, PDMS was dissolved in n-heptane solution. Then, the weight ratio of PDMS, TEOS as cross-linking agent and dibutyltin dilaurate as catalyst were 10: 1:0.2. The solution was stirred for 2 h at room temperature. The support layer was pasted on a glass plate and the PDMS solution was uniformly distributed on the surface. For duration of 24 h, the active layers were partially cross linked at room temperature. In order to complete the cross linkage, the composite membrane was heat treated at 70 °C for 4 h (Shahrabi *et al.*, 2012).

**2.3 Surface modification by corona treatment for $SiO_2$ coating:** In corona treatment, membranes with dimension of 10×10 cm were placed on the silicon roller. Corona treatment of membrane using a commercial device (Naaj Corona, Rangin Plast Co., Amol, Iran) was applied in the air at atmospheric pressure. The distance between aluminum electrode and backing roll was adjusted to 2 mm. The corona unit was operated with the air gap between the electrode and backing roll. Corona surface treatment was applied at desired condition which is included corona input power of 360W and the corona time of 6 min (Sadeghi *et al.*, 2013; Moghimifar *et al.*, 2014). After corona treatment, the treated membrane was placed in the $SiO_2$ solution (concentration 1000 ppm) for 30 min. Finally, treated membranes were kept in oven for 15 min.

**2.4. Microorganism:** *Saccharomyces cerevisiae* PTCC 24860 was supplied by Iranian Research Organization for Science and Technology (IROST). The medium for seed culture contained 10 g/l of glucose, 0.45 g/l of $NH_4Cl$ and 1 g/l of yeast extract. The medium was autoclaved at 121 $^oC$ and 15 psig for 20 min. The sterilized medium was inoculated with 5% of pure seed culture of the microorganism and then the culture was cultivated in an incubator-shaker at 30 $^oC$ and agitated 200 rpm for 24 h (Esfahanian *et al.*, 2012).

**2.5. Pervaporation process in membrane bioreactor:** The fabricated membrane was applied in

membrane bioreactor. Ethanol was produced in MBR integrated with pervaporation process from glucose solution at concentration of 50 g/l as substrate. The temperature of broth was sat at 32ºC and the pH of solution was 5.2. The working volume of the fermentation broth was 1260 ml. In fact, the MBR had a working volume of 1260 ml fermentation broth on the top and a pervaporation cell having 50.24 $cm^2$ effective permeation areas for the membrane at the bottom of fermentation vessel. Vacuum condition on the permeate side was maintained by a vacuum pump (Edwards, England). Two cold traps of liquid nitrogen were arranged in parallel allowed to collect permeate. Then, the collected sample was weighed and analyzed by high performance liquid chromatography (HPLC) (Smartline, Knauer, Germany). The HPLC column was Eurokat H (Knauer, Germany). The oven temperature was 75°C. The sample size, elluent and flow rate were 20µl, $H_2SO_4$ (0.01 N) and 0.5 ml/min, respectively.

**2.6. Membrane characterization:** The fabricated membranes were fractured in liquid nitrogen and then coated by a thin layer of gold with a sputtering system under vacuum. To observe the top surface and cross-sectional structures, membranes were characterized by Field Emission Scanning Electron Microscopy (FESEM) using Hitachi FESEM model S-4160 (Hitachi, Japan,). The membrane surfaces were characterized using Atomic Force Microscopy (AFM). The AFM analyzes were performed under AFM microscope (Nanosurf easy scan2 flex, Switzerland).

**2.7. MBR Experimental set up:** Schematic diagram for ethanol fermentation using MBR fabricated PDMS membrane in pervaporation system is shown in Fig. 1. Fermentation was performed at constant temperature 32 ºC. The bioreactor working volume was 1260 ml at atmospheric pressure. The other side of the membrane was evacuated by vacuum pump (E2M2–Edwards). Vapor-side pressure was kept at lower than 2 mmHg. Permeate vapor was trapped in a liquid nitrogen trap at -196 ºC.

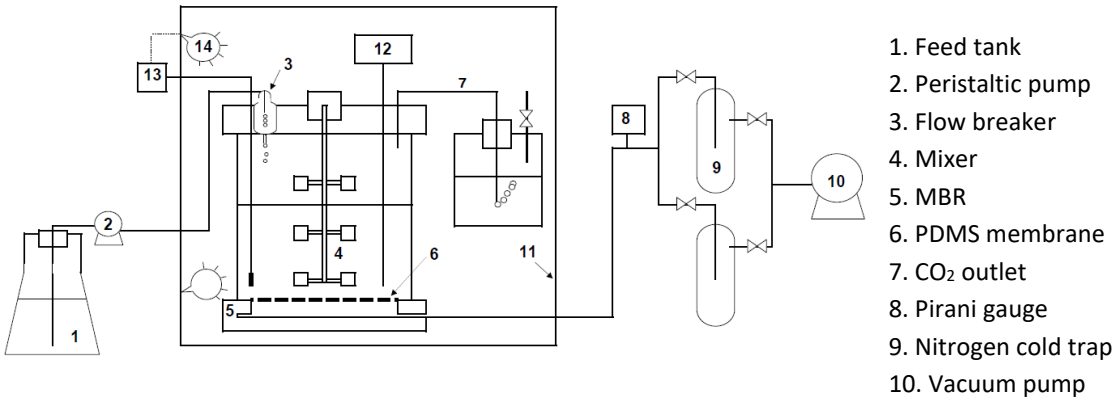


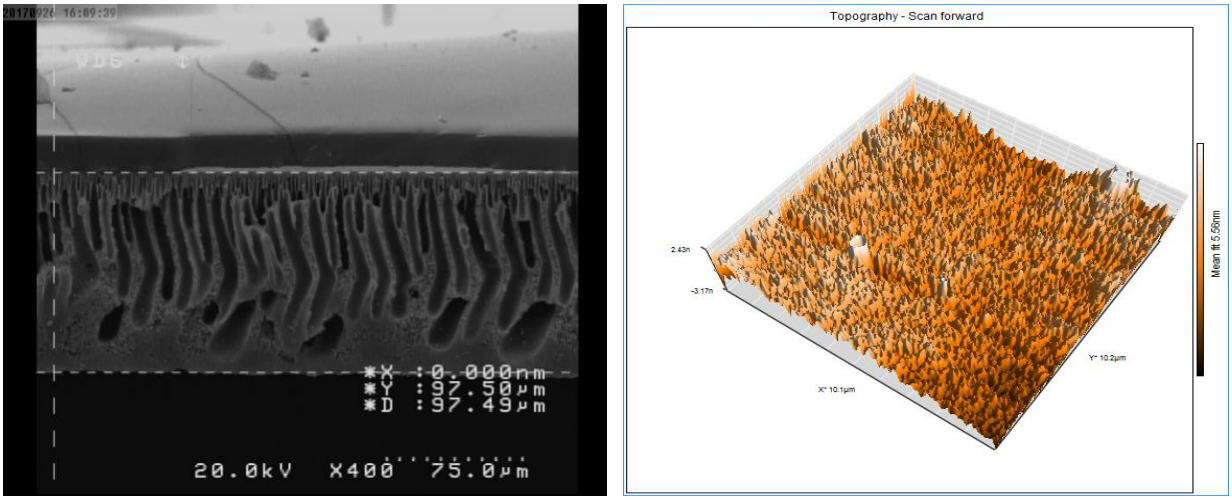

**Fig. 1. Schematic diagrams of MBR pervaporation system for fermentation (Najafpour, 2015)**

## 3. RESULTS AND DISCUSSION

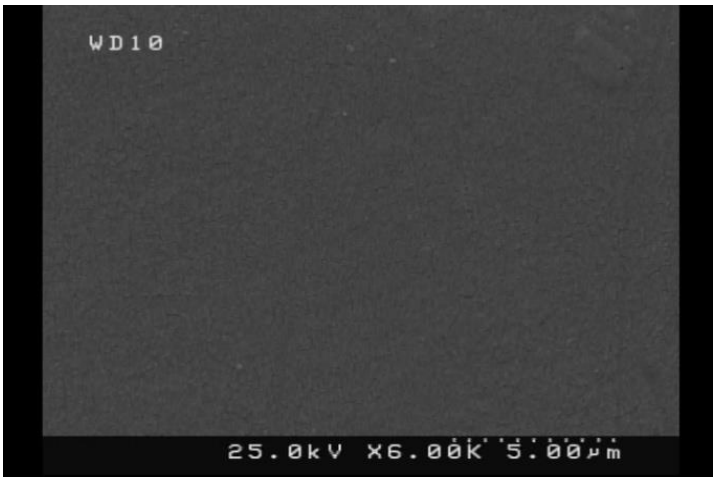
At first, composite PDMS/PES membrane was successfully fabricated. Then, $SiO_2$ was coated on the surface of corona treated membrane. Finally, the performance of fabricated membrane was investigated in membrane bioreactor for ethanol production.

**3.1. Preparation of composite PDMS/PES membranes:** Cross sectional FESEM of fabricated composite PDMS/PES membrane is shown in Fig. 2a. The polydimethylsiloxane as hydrophobic active layer was successfully established. The active layer had thickness of 20 µm ±5 on the support layer which havd thickness of 100 µm ±5. As shown in this figure, PES as membrane support has a finger-like structure. Fig. 2b depicts AFM surface image of the composite PDMS/PES membrane. The surface roughness ($R_a$) of the PDMS/PES composite membrane was determined to be 0.621nm. Fig.2c shows the top surface of FESEM image of the composite PDMS/PES membrane without any surface treatment. As shown in the composite PDMS/PES membrane have smooth surface; that was due to formation of dense PDMS layer on the support layer.

The ethanol separation factor and flux of the fabricated PDMS/PES composite membrane were 6.9 and 440 $g/m^2.h$, respectively.




**(a)** **(b)**

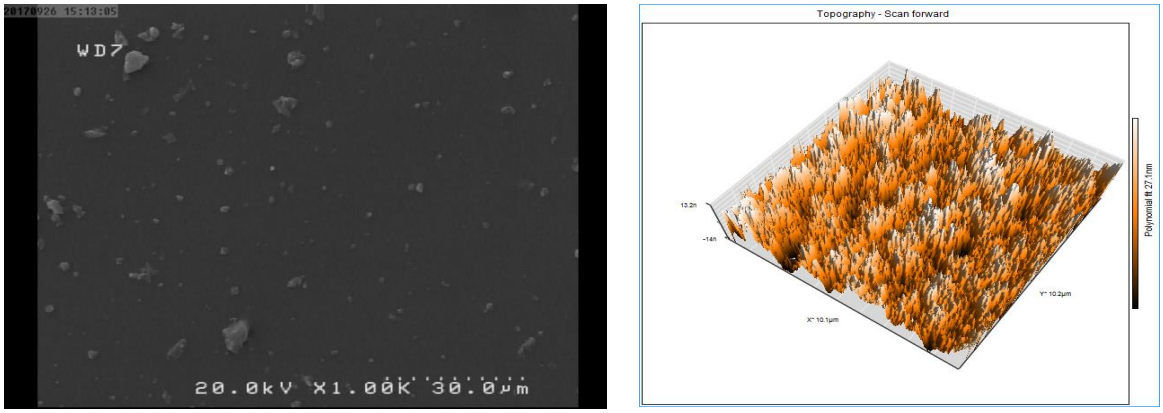



**(c)**

**Fig. 2: Characteristics of PDMS/PES composite membrane: (a) Cross sectional FESEM image, (b) Surface AFM image and (c) top FESEM image**

**3.2. $SiO_2$ Coating on corona surface modified membrane:** Corona treatment was performed to modify the surface of composite PDMS/PES membrane. After treatment, $SiO_2$ was coated on the surface of composite layer. As shown in Fig. 3a, the $SiO_2$ was successfully coated on the surface of composite PDMS/PES membrane after corona surface treatment. The AFM image of corona treated membrane and $SiO_2$coated membrane is shown in Fig. 3b. Corona treatment leads to more surface roughness that is due to high coating of $SiO_2$ on the surface of membranes. Based on obtained results, for corona time of 6 min and corona input power of 360 W, the average roughness ($R_a$) of treated membranes were 45.5 nm. The $SiO_2$ coating on the corona treated composite membrane resulted in more surface roughness and also more membrane hydrophobicity. In fact, increase in membrane hydrophobic surface leads to increase in the surface roughness; therefore, the contact angle has to increase; that is due to improvement of hydrophobicity of the membrane (Hobæk *et al.*, 2011). The ethanol separation factor and flux of surface modified PDMS.$SiO_2$/PES membrane were 10.5 and 510 g/$m^2$.h, respectively. Therefore, corona treatment and $SiO_2$coating have significantly improved etha-nol the membrane selectivity; while increasing hydrophobicity of the membrane. Also, the fabricated corona surface modified $SiO_2$ coated on PDMS /PES membrane has improved separation factor by 50% in compared to the commercial PDMS membrane. For commercial composite membrane that examined in membrane bioreactor for fermentation of glucose at concentration of 50g/l by effective thickness of 5 µm PDMS top layer (Pervatech Company. Netherland), at the same conditions, the

ethanol separation factor and total flux has been reported 7 and 460 g/m$^2$.h, respectively (Esfahanian *et al.*, 2012). Therefore, the fabricated $SiO_2$ coated on PDMS/PES membrane was premiere than the commercial PDMS membrane.




**(a)** **(b)**

**Fig. 3: Characteristics of surface coated by $SiO_2$ on PDMS/PES composite membrane: (a) top surface FESEM image, (b) Surface AFM image**

**3.3. Conventional ethanol production using glucose:** The fermentation broth contained glucose as substrate, $NH_4Cl$ and yeast extract having concentrations of 50, 5 and 3 g/l, respectively. The pH value was adjusted at 5.2 using buffer solution of potassium hydrogen phthalate (0.1 M) and sodium hydroxide (0.1 M) solution (Esfahanian *et al.*, 2012). In order to start fermentation, the sterilized medium was inoculated by the seed culture of *Saccharomyces cerevisiae*. The obtained results including produced ethanol concentration with respect to time in conventional fermentation and cell concentration in the course of fermentation is shown in Fig. 4. Maximum ethanol was produced after 16 hours of incubation with ethanol concentration of 18.9 g/l. At the stationary phase, the cell concentration was constant at 12.3 g/l.

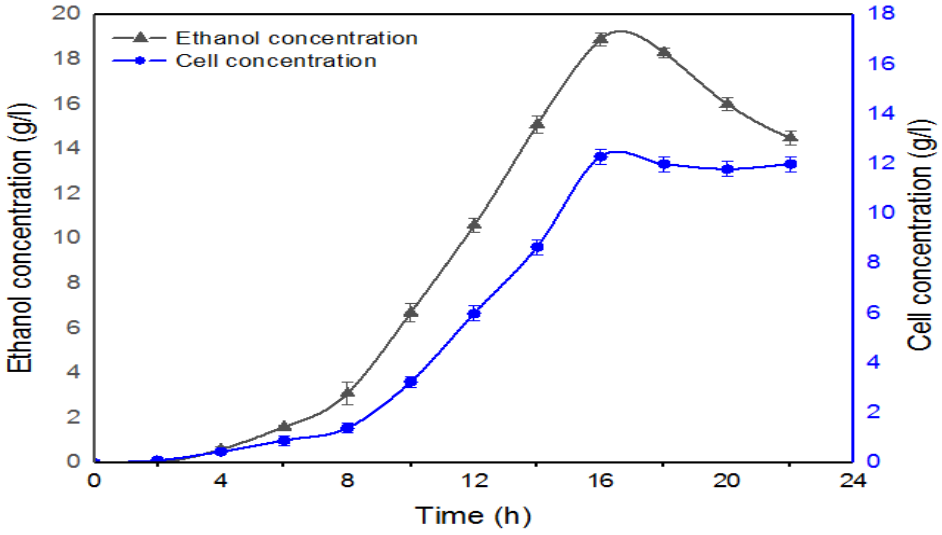



**Fig. 4. Conventional fermentation process for ethanol production**

**3.4. Ethanol production in membrane bioreactor by fabricated PDMS.$SiO_2$/PES membrane:** Integration of ethanol productions from glucose fermentation at initial glucose concentrate-ion of 50 g/l and ethanol separation unit using fabricated PDMS.$SiO_2$/PES membrane in membrane bioreactor was conducted in a special experimental set up discussed above. The glucose consumption, ethanol production in fermentation broth of MBR and the cold trap of MBR along with cell concentration with respect to time are depicted in Fig. 5. Glucose was completely consumed after 18 hours

of fermentation. In fact, after 16 hours of fermentation period, maximum ethanol was produced. The ethanol concentration was 23.54 g/l in the fermentation broth in MBR; while, ethanol concentration in the cold trap of MBR was 195.4 g/l. At the stationary phase of cell growth, the cell concentration in the MBR broth was 16.1 g/l; while the cell concentration in the conventional fermentation at the stationary phase was 12.3 g/l. Therefore, the cell concentration in the broth of MBR was 30% higher than conventional fermentation. In fact, that was due to ethanol removal from reactor using the fabricated ethanol selective membrane. The cell concentration in the broth of MBR has reached to higher level (16.1 g/l). Based on obtained results, the concentration of ethanol has significantly increased compared to conventional fermentation process that was due to ethanol permeation through membrane in the MBR. In fact, removal of ethanol in fermentation broth resulted in prevention of ethanol inhibition and increase in cell density.

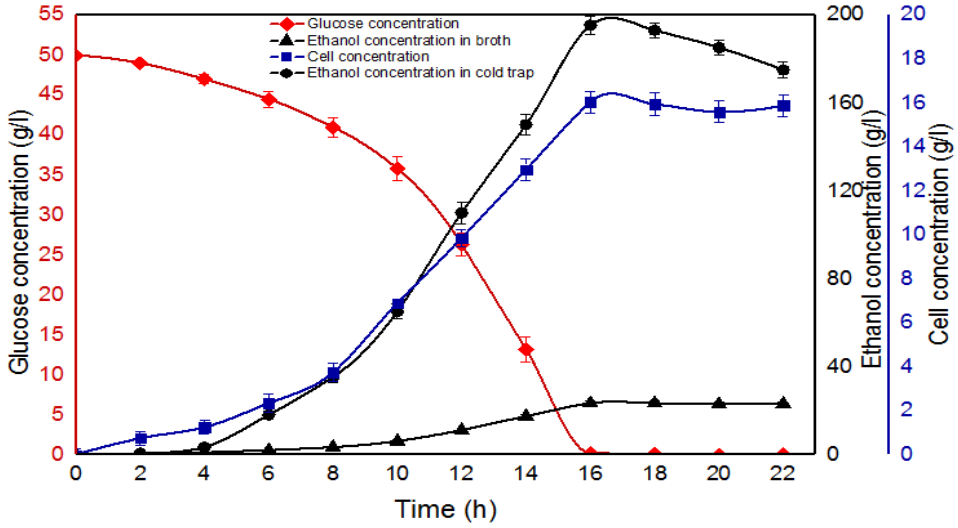



**Fig. 5:** Results of membrane bioreactor with fabricated corona surface modified $SiO_2$ coated on PDMS/ PES membrane

Comparative data for ethanol fermentation in conventional process and MBR fermentation process, the experimental results are summarized in Table 1. The membrane bioreactor using fabricated membrane had significant improvements in ethanol production.

**Table 1. The summarized results of fermentation**

| | Conventional process | MBR by fabricated membrane |
|---|---|---|
| **Glucose concentration (g/l)** | 50 | 50 |
| **Temperature (ºC)** | 32 | 32 |
| **pH** | 5.2 | 5.2 |
| **Ethanol Concentration** | | |
| **Broth (g/l)** | 18.9 | 23.54 |
| **Cold trap (g/l)** | - | 195.4 |
| **Cell density (g/l)** | 12.3 | 16.1 |

## 4. Conclusions

In present study, bioethanol production was performed by integration of batch fermentation and membrane pervaporation process in a membrane bioreactor (MBR). Based on obtained data, bioethanol production in MBR was significantly improved compared to conventional fermentation process. Based on ethanol selectivity and separation factor, the novel fabricated PDMS membrane preformed was much better than commercial PDSM membrane. The PDMS/PES fabricate membrane was suitable for ethanol separation. The surface of composite PDMS/PES membrane was successfully modified by corona treatment and $SiO_2$ coated. The surface modification of PDMS/PES membrane enhanced ethanol separation factor by 52%.

**Acknowledgements**

Authors gratefully acknowledge *Biotechnology Research Lab.*, Noshirvani University of Technology and the Rangin Plast Company for the facilities provided to conduct present research. Also, special thanks are extended to Nezhadgholi and Alizadeh Foundation, Babol, Iran for the financial support of present research through a research grant.

## REFERENCES


Adnan Hasan, Ambreen Aziz, Khalid Hassan, Imran Ali and S. Jabeen, Production of biodiesel from freshwater algae. Pak. J. Biotech, **13**: 267-274 (2016).

Chen, J., J. Li, R. Qi, H. Ye and C. Chen, Pervaporation performance of crosslinked polydimethylsiloxane membranes for deep desulfurization of fcc gasoline: Effect of different sulfur species. J. Membr. Sci, **322**: 113-121 (2008).

El-Sebaii, A. and S. Shalaby, Solar drying of agricultural products: A review. Renew. Sustain. Energ. Rev, **16**: 37-43 (2012).

Esfahanian, M., A. Ghorbanfarahi, A. Ghoreyshi, G. Najafpour, H. Younesi and A. Ahmad, Enhanced bioethanol production in batch fermentation by pervaporation using a pdms membrane bioreactor. Int. J. Engineering. Trans. B, **25**: 249-255 (2012).

Fu, C., D. Cai, S. Hu, Q. Miao, Y. Wang, P. Qin, Z. Wang and T. Tan, Ethanol fermentation integrated with pdms composite membrane: An effective process. Bioresource technology, **200**: 648-657 (2016).

Hamidreza Ghafouri Taleghani, Ghasem D. Najafpour and A.A. Ghoreyshi, Batch and continouse production of lactic acid using *lactobacillus bulgaricus* (atcc 8001). Pak. J. Biotech, **11**: 1-12 (2014).

Herrera-Herrera, A.V., M.Á. González-Curbelo, J. Hernández-Borges and M.Á. Rodríguez-Delgado, Carbon nanotubes applications in separation science: A review. Anal. Chim. Acta, **734**: 1-30 (2012).

Hobæk, T.C., K.G. Leinan, H.P. Leinaas and C. Thaulow, Surface nanoengineering inspired by evolution. BioNano Sci, **1**: 63-68 (2011).

Ikegami, T., H. Yanagishita, D. Kitamoto, H. Negishi, K. Haraya and T. Sano, Concentration of fermented ethanol by pervaporation using silicalite membranes coated with silicone rubber. Desalination, **149**: 49-54 (2002).

Moghimifar, V., A. Raisi and A. Aroujalian, Surface modification of polyethersulfone ultrafiltration membranes by corona plasma-assisted coating tio2 nanoparticles. J. Membr. Sci, **461**: 69-80 (2014).

Najafpour G., Biochemical engineering and biotechnology, Elsevier publication, First ed: 55-80 (2012).

Nasidi, M., R. Agu, Y. Deeni and G. Walker, Utilization of whole sorghum crop residues for bioethanol production. J. Institute Brewing, **122**: 268-277 (2016).

Nour, M., K. Berean, S. Balendhran, J.Z. Ou, J. Du Plessis, C. McSweeney, M. Bhaskaran, S. Sriram and K. Kalantar-zadeh, Cnt/pdms composite membranes for $H_2$ and $CH_4$ gas separation. Int. J. Hydrogen Energy, **38**: 10494-10501 (2013).

Novak, B.M., Hybrid nanocomposite materials between inorganic glasses and organic polymers. Adv. Mater, **5**: 422-433 (1993).

Ozdemir, M., C.U. Yurteri and H. Sadikoglu, Physical polymer surface modification methods and applications in food packaging polymers. Crit. Rev. Food Sci. Nutr, **39**: 457-477 (1999).

Pal, S., S.K. Ghatak, S. De and S. DasGupta, Characterization of co2 plasma treated polymeric membranes and quantification of flux enhancement. J. Membr. Sci, **323**: 1-10 (2008).

Peng, P., B. Shi and Y. Lan, A review of membrane materials for ethanol recovery by pervaporation. Separ. Sci.Tech, **46**: 234-246 (2010).

Rezakazemi, M., K. Shahidi and T. Mohammadi, Synthetic pdms composite membranes for pervaporation dehydration of ethanol. Desalination Water Treat, **54**: 1542-1549 (2015).

Rocca-Smith, J.R., T. Karbowiak, E. Marcuzzo, A. Sensidoni, F. Piasente, D. Champion, O. Heinz, P. Vitry, E. Bourillot and E. Lesniewska, Impact of corona treatment on pla film properties. Polymer Degrad. Stabil, **132**: 109-116 (2016).

Romasanta, L., M. Lopez-Manchado and R. Verdejo, The role of carbon nanotubes in both physical and chemical liquid–solid transition of polydimethylsiloxane. Eur. Polymer J., **49**: 1373-1380 (2013).

Sadeghi, I., A. Aroujalian, A. Raisi, B. Dabir and M. Fathizadeh, Surface modification of polyethersulfone ultrafiltration membranes by corona air plasma for separation of oil/water emulsions. J. Membr. Sci, **430**: 24-36 (2013).

Shafigh k, S.Ali and Ikram-UL Haq, Kinetic analysis of nutritional strategies for nvertase production by *saccharomyces cerevisiae*. Pak. J. Biotechnol. **1**: 25-30 (2004).

Shahrabi, S.S., H. Mortaheb, J. Barzin and M. Ehsani, 2012. Pervaporative performance of a pdms/blended pes composite membrane for

removal of toluene from water. Desalination, **287**: 281-289 (2012).

Sun, D., B.-B. Li and Z.-L. Xu, Pervaporation of ethanol/water mixture by organophilic nano-silica filled pdms composite membranes. Desalination, **322**: 159-166 (2013).

Trifunović, O. and G. Trägårdh, The influence of support layer on mass transport of homologous series of alcohols and esters through composite pervaporation membranes. J. Membr. Sci, **259**: 122-134 (2005).