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Composite Multi Wall Carbon Nano Tube Polydimethylsiloxane Membrane Bioreactor for Enhanced Bioethanol Production from Broomcorn Seeds

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A B S T R A C T

Broomcorn seed (*Sorghum vulgare*) was used as raw material for bioethanol production. Optimum conditions were obtained from response surface method. Broomcorn seed flour (45 g/l) was treated by alkaline treatment and dual enzymatic hydrolysis (0.7 g/l of α- amylase and 0.42 g/l of amyloglucosidase). The hydrolyzed total sugar of 25.5 g/L was used in conventional bioethanol production (8.1 g/l) using *Saccharomyces cerevisiae*. Enhanced bioethanol production was performed in membrane bioreactor (MBR) in integrated batch fermentation and membrane pervaporation process. Application of commercial polydimethylsiloxane/polyethyleneterephthalate/polyimide (PDMS/PET/PI) membrane in MBR resulted in ethanol concentration of 10.15 g/l in broth and 70.2 g/l in cold trap of MBR. Cell concentration in broth was increased from 7.2 in conventional fermentation to 9.05 g/l in MBR. In addition, ethanol production in MBR using fabricated membrane having ethanol separation factor of 8.7; ethanol concentration in broth and cold trap were 11.1 and 88.5 g/ l, respectively. Also the cell concentration of 10.2 g/l was obtained in MBR with fabricated membrane. In MBR, surface modified multi wall carbon nano tube (MWCNT) coated on membrane having ethanol separation factor of 10.2, resulted ethanol concentration of 11.9 and 110 g/l in broth and cold trap, respectively. Finally, for MBR using modified membrane the cell concentration of 11.01 g/l was obtained. Based on a comparison study, maximum ethanol separation and yield were obtained for modified membrane having MWCNT and the surface was modified by corona treatment.

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1. INTRODUCTION

In 2016, daily gasoline consumption has been reported as 73 million liters by Iranian financial tribune. Since Iranian transportation sectors have very high fuel demands, use of fossil fuels generated tremendous amount of air pollution and anxious gas emission due to heavy fuel consumption. High global energy demand and depletion of fossil oil resources caused great environmental concerns. Generally for resolving air pollution, alternative and renewable energy sources should replace fossil sources. Application of bioenergy as renewable source has the potential to reduce air pollution [1-4].

Bioethanol as a renewable resource, among alternative fuels, is one of the most useful fuels [5]. Also, bioethanol known as a clean and renewable fuel are derived from all kinds of agro waste and biomass materials. Biomass such as grains (corn, wheat), tubers (cassava, potato), stalk (sugarcane and sweet sorghum) and lignocelluloses materials are important feedstock sources for bioethanol production [6]. *Sorghum vulgare* (broomcorn) is a type of sorghum plant that is used for various brooms [7]. Unlike other types of sorghum, such as sweet sorghum, this kind of sorghum was not in target of studies for production of ethanol [8-10]. Broomcorn has bunch of seeds rich in starch, protein, moisture fiber, lipid and ash with weight percentages of 59.62, 13.37, 10.06, 9.04, 3.64 and 4.27%, respectively [7]. Therefore, the rich content of starch in the broomcorn seed makes it a suitable biomass for bioethanol production**.** The starch consists of amylose and amylopectin. Hydrolysis of natural polysaccharides may take place in a two step process; at first step, amylose and amylopectin are

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broken into trisaccharide, disaccharide and α-dextrin units using α-amylase in starch liquefaction process. In the next step, the produced maltose, maltotriose and α-dextrin units are broken down to glucose units using amyloglucosidase in starch saccharification [11]. Finally, monomeric sugar of hexosan is produced by enzymatic hydrolysis of broomcorn seeds; the obtained sugar is fermentable for bioethanol fermentation process.

According to the IUPAC definition, membrane reactor is a device capable of performing a chemical reaction and separation in the same unit [12]. Using membrane bioreactor (MBR) in ethanol production is an integrated fermentation and membrane pervaporation process. In MBR, bioethanol is produced via fermentation process followed by pervaporation process using selective membrane. Pervaporation is an energy-saving separation method compared to conventional separation process such as distillation. The separation mechanism of pervaporation is based on ability of nonporous membranes to be selective for transporting components from the feed to the permeate side [3, 13]. One of the suitable membranes in membrane bioreactor for ethanol separation in pervaporaton process is PDMS that is highly ethanol selective [14].

In this study, a new source for bioethanol production was investigated. For this purpose, scarification of broomcorn seeds (*Sorghum vulgare*) solution was pretreated by NaOH; then, hydrolyzed by dual enzymes (α-amylase and amyloglucosidase). The hydrolizate sugar solution was prepared for *Saccharomyces cerevisiae* fermentation. Finally, ethanol was produced by fermentation process. Ethanol production conditions were optimized via Design Expert software. The optimum conditions for ethanol production were obtained. Then, at optimum conditions ethanol production in membrane bioreactor using commercial and two types of fabricated composite membrane were performed.

2. MATERIALS AND METHODS

2. 1. Broomcorn Seed and Microorganism Broomcorn seeds **(***Sorghum vulgare*) were supplied by the Agricultural Organization of Mazandaran, Sari, Iran. The seeds were ground to flour. The flour was washed to remove the seed shells. Then, the flour was kept in oven at 105°C and stored in desiccators at room temperature for the next stage of experiments. The live hydrated organism of *Saccharomyces cerevisiae* 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 °C 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 agitated at 200rpm and 30 °C for 24 h [15].

2. 2. Pretreatment and Enzymatic Hydrolysis Alkaline pretreatment was performed for deproteinization and plant cell disruption. In alkaline treatment of the broomcorn seed, a defined concentration (based on RSM design) of broomcorn seed flour was dissolved in 450 ml of 0.1 M NaOH solution and stirred at 60°C for 1h. Then, the alkaline pretreated solution was mixed with 550 ml of potassium hydrogen phthalate buffer (0.1 M); the final pH was set at 6.1. The mixture was heated and boiled at 105°C, where the gelatinization started and the viscosity of the solution increased. After cooling to 95°C, a defined concentration (based on RSM design) of heat-resistant α-amylase (Serva, 30 Unit/mg) was added to the solution for the liquefaction process; the solution was kept at that temperature for 2 h. In the next step, the pH of the solution was reduced to 4.5 using phosphoric acid. In the following step, a defined amount (based on RSM design) of amyloglucosidase (Serva, 120 Unit/mg) was added to the liquefied starch solution at 60°C and stirred at 120 rpm for 48 h.

2. 3. Optimization of Ethanol Production In order to optimize the ethanol production from broomcorn seed conditions, response surface method (RSM) was applied to design necessary experiment [16]. Therefore, Design-Expert 7.0 (Stat-ease Inc., USA) was used to perform the regression and statistical and graphical analysis. Three independent variables including substrate concentration (A) in the range of 15-75 g/l of broomcorn seed, α-amylase concentration (B) in the range of 0-1.2 g/l and amyloglucosidase concentration (C) in the range of 0-0.8 g/l were selected as experimental parameters. The effect of these parameters on concentration of ethanol as the response was studied. Central composite design (CCD) of RSM is one of the most popular tools used in optimization process condition. CCD method essentially includes a full or fractional factorial design with center points that are augmented with a group of axial points that allow estimation of the curvature in the resulting model [16, 17]. In this study, a 5- level 3 factors central composite design (CCD) was employed. According to the CCD, a 5 level 3 factors design was employed and total numbers of 20 experiments were performed in this case. The results were fitted to the following second order polynomial equation to predict the optimum ethanol production conditions:

$$Y = \beta_O + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^{\,2} + \sum_{i-1} \sum_{j=i+1} \beta_{ij} X_i X_j + \varepsilon \qquad (1)$$

where, Y represents the response variable, β_0 is the intercept; β_i and β_{ii} are the first and second order quadratic model coefficients for the variables,

respectively. Also, β_{ij} is the linear model coefficient for the interactions between i and j; while X_i and X_j are recoded independent process variables and ε is the random error [18].

At optimum conditions, the medium by optimum concentration of broomcorn seed as substrate, 3 g/l of yeast extract and 5 g/l of NH_4Cl were prepared. The pH value was set at 5.2 provided by buffer solution of potassium hydrogen phthalate (0.1 M) and sodium hydroxide (0.1 M). Fermentation was carried out at 32°C and agitation rate of 200rpm. Ethanol fermentation was performed in conventional process and via batch fermentation in designed membrane bioreactor (MBR) [15, 19].

2. 4. Membrane Preparation

2. 4. 1. Commercial Membrane Polydimethylsiloxane (PDMS) as a nonporous membrane was selected for separation and concentrating bioethanol via pervaporation process in MBR. The membrane with an effective thickness of 3-5 μm PDMS as hydrophobic active layer on support layers consisted of polyethylene terephthalate (PET) with thickness of 100 μm and polyimid (PI) with thickness of 150 μm was provided by Pervatech Company (Netherland).

2. 4. 2. Fabricated PDMS/PES.PVP Membrane Coated with MWCNT Composite PDMS as active layer with a thickness of 20 μm was fabricated on polyethersolfune (PES) having polyvinylpyrrolidone (PVP) as support layer, thickness of 100 μm. For preparation and casting of active layer on PES as support layer, PDMS with 30% (wt) was dissolved in n-heptane solution. Then, PDMS, cross linking agent, tetraethyl ortho-silicate and dibutyltin dilaurate as catalyst, were dissolved in the above solution (n-heptane) having weight ratio of 10:1:0.2. In order to improve ethanol separation factor and also to enhance ethanol selectivity in the fabricated composite membrane, MWCNT with defined weight percentages were deposited on PDMS matrix as an active layer of the PDMS/ PES composite membrane. In addition, for the novel membrane, corona surface treatment was applied for corona time of 6 min and corona input power of 360W for MWCNT coating on the surface of PDMS/PES membranes.

Therefore, application of these novel fabricated composite membranes for ethanol production and ethanol separation in membrane bioreactor were investigated. Figure 1 shows FESESM of fabricated composite membranes. Fig. 1a displays composite PDMS/PES.PVP membranes with blended MWCNT in active layer matrix. In this figure, MWCNT has been dispersed uniformly in active layer matrix of PDMS that has probably resulted in high separation factor. Fig. 1b depicts composite PDMS/PES.PVP membranes with coated MWCNT on the surface of membrane. The surface was modified by corona treatment that also has probably results in improved separation factor. Due to using corona the surface is not uniformly modified.

2. 5. Analysis Starch content in the solution of enzymatic hydrolysis was determined by means of resorcinol reagent [20]. The concentration of reducing sugars was measured via colorimetric method using dinitrosalicylic acid (DNS) at the wavelength of 540 nm by spectrophotometer (Unico, USA). The optical density (OD) was determined at the wave length of 620 nm. The cell dry weight was obtained based on OD absorbance defined by calibration curve. The concentration of ethanol and glucose were measured using Smartline high performance liquid chromatography (Knauer, Germany) by Eurokat H (Knauer, Germany) column. The oven temperature, sample size, elluent and flow rate were 75°C, 20μl, H_2SO_4 (0.01 N) and 0.5 ml/min, respectively.

Pervaporation performances in all experiments were evaluated by flux (J) and separation factor (α) [13].

$$\alpha = \frac{y_{alcohol}/(1-y_{alcohol})}{x_{alcohol}/(1-x_{alcohol})} \quad (2)$$

$$J = \frac{Wi}{(\Delta t \times A)} \quad (3)$$

where, Δt is the process time, A refers to the effective area of membrane and Wi represents the weight of ethanol in permeate.

3. RESULTS AND DISCUSSIONS

3. 1. Standard Calibration Curve Prior to discussing ethanol production from broomcorn seed

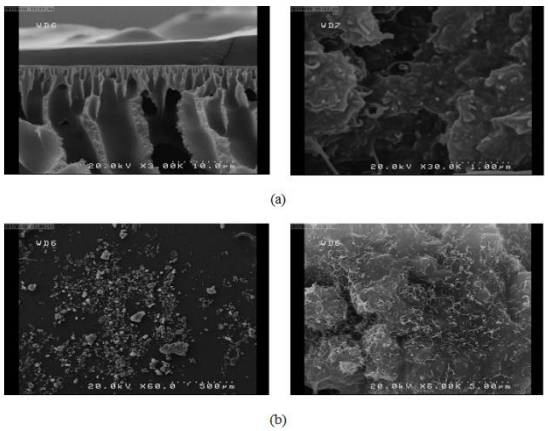

Figure 1. Fabricated composite MWCNT.PDMS/PES.PVP membrane; (a) MWCNT blended in PDMS active layer of composite membrane by two magnification, (b) MWCNT coated on the surface of composite membrane by two magnification

having high starch content through conventional and membrane bioreactor processes, it is necessary to determine the reducing sugar, starch and cell density based on related calibration curves. The calibration curve for reducing sugar is based on colorimetric method using DNS reagent and absorbance at wave length 540 nm. The calibration curve for cell concentration based on optical density is defined according to absorbance at wave length 620 nm. Finally, for calibration curve of starch concentration using resorcinol reagent is determined by absorbance at wave length 420 nm.

3. 2. Optimization for Ethanol Production from Broomcorn Seeds In this study, for optimization conditions, according to the CCD design for 5 levels and 3 factors, total number of 20 experiments were designed and performed. The obtained results based on the experimental design ethanol production of broomcorn seed flour are summarized in Table 1. The ethanol fermentation was carried out at 32 ºC and the pH value was set at 5.2.

The results of regression and analysis of variance (ANOVA) for bioethanol production from broomcorn seed were studied. The experimental design and results were analyzed by selecting the appropriate model either linear, quadratic and so polynomials.

TABLE 1. Experimental design and results for ethanol production from broomcorn seed

Run	A: Sorghum conc. (g/l)	B: α-amylase conc. (g/l)	C: Amyliglucosidase conc. (g/l)	Response: Ethanol conc. (g/l)
1	45	0.6	0.4	8
2	60	0.3	0.6	4.9
3	45	0.6	0.4	8.01
4	30	0.9	0.6	3.85
5	45	0.6	0.4	8.1
6	60	0.9	0.2	5
7	15	0.6	0.4	0.25
8	45	0	0.4	4.35
9	30	0.9	0.2	3.75
10	45	0.6	0.8	6.35
11	45	1.2	0.4	6.9
12	45	0.6	0.4	8
13	45	0.6	0	5.05
14	30	0.3	0.2	3.31
15	45	0.6	0.4	8.1
16	60	0.9	0.6	5.25
17	45	0.6	0.4	8.1
18	30	0.3	0.6	3.4
19	75	0.6	0.4	1.2
20	60	0.3	0.2	4.45

The statistical software suggested a second order quadratic regression surface model for predicting the optimum conditions for bioethanol production. The best fit models in terms of coded factors for the bioethanol obtained are given below:

$$\text{Ethanol Concentration (g/l)} = -16.92 + 0.78\,A + 10.62\,B + 13.56\,C + 2.77778E\text{-}004\,AB + 0.021\,AC - 0.3958\,BC - 8.45859E\text{-}003A^2 - 7.53B^2 - 16.48580C^2 \quad (4)$$

A, B and C are the coded types of broomcorn seed flour (*Sorghum vulgare*), α-amylase concentration and amyloglucosidase concentration, respectively. AB, AC and BC are the interaction terms. A^2, B^2 and C^2 are the squared terms of the independent variables. The ANOVA for the ethanol concentration model as a function of substrate, α-amylase and amyloglucosidase concentration are illustrated in Table 2. The regression value was found to be 0.97 indicating the suitability of the given model. Low error probability value [(Prob > F) < 0.0001] expressed that model can statistically be significant representing the observed experiment data. The validity of the models was demonstrated by the "Lack of Fit" of 4.27 imply the "Lack of Fit" is not significant and the models fit well to predicted values of bioethanol production. Based on P values results in Table 2, the model terms AB, BC, and AC model terms are not significant with P values more than 0.05. Therefore, these terms must be removed from fit model.

$$\text{Ethanol Concentration (g/l)} = -16.92 + 0.78\,A + 10.62\,B + 13.56\,C - 8.45859E\text{-}003A^2 - 7.53B^2 - 16.48580C^2 \quad (5)$$

Figure 2 displays the interaction relationship between independent variables on the response. Figure 2a shows the interaction and correlation of sorghum concentration

TABLE 2. Results of ANOVA for the developed model

Source	Degree of freedom	Sum of square	Coefficient estimate	F-value	P-value
Model	9	101.12	7.91	26.9	< 0.0001
A	1	3.23	0.45	7.5	0.0209
B	1	2.97	0.43	6.89	0.0254
C	1	0.76	0.22	1.77	0.02132
A^2	1	91.07	-1.9	211.51	≤ 0.0001
B^2	1	11.56	-0.68	26.86	0.0004
C^2	1	10.93	-0.66	25.39	0.0005
AB	1	0.0000125	0.00125	0.000029	0.9958
AC	1	0.033	0.064	0.076	0.7891
BC	1	0.00451	-0.024	0.01	0.9205

R-Squared=0.9692, C.V= 6.34, Standard deviation= 0.66, Lack of Fit=4.29

and α- amylase concentration as independent variables on ethanol production. Increase in sorghum flour concentration as the source of ethanol production, increased the concentration of produced ethanol. However, increasing beyond 50 g/l in the solution decreased the concentration of produced ethanol. Also increase in α- amylase concentration to above 0.7 g/l in enzymatic hydrolysis caused adversely affect on response. The simultaneous effect of sorghum flour and amyloglucosidase concentrations on ethanol production has illustrated in Figure 2b. The concentration of produced ethanol increased with increase of amyloglucosidase concentration to 0.4 g/l. Figure 2c also confirms the results of the two previous plots. As observed in this plot, the optimum concentrations of α-amylase and amyloglucosidase for production of ethanol from broomcorn seed were defined about 0.7 and 0.4 g/l, respectively.

The optimum condition of the experiment for production of ethanol, are summarized in Table 3. The experimental value of ethanol concentration (8.1g/l) was in a very good agreement with the predicted value (7.65 g/l). This implies the accuracy of model to predict the ethanol production from broomcorn seed.

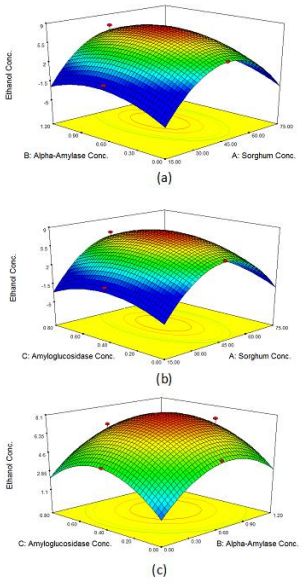

Figure 2. Response surface 3D plots for ethanol production process shows Interaction between: (a) sorghum concentration and α- amylase concentration, (b) sorghum concentration and amyloglucosidase concentration, (c) α-amylase concentration and amyloglucosidase concentration

TABLE 3. Optimum condition for the ethanol production

Sorghum conc. (g/l)	α- amylase conc. (g/l)	Amyloglucosidase conc. (g/l)	Produced ethanol conc.(g/l)
45	0.7	0.42	8.1

3. 3. Conventional Ethanol Production from Broomcorn Seeds The solution contained broomcorn seed flour by concentration of 45 g/l, after alkaline treatment was hydrolyzed using α-amylase at concentration of 0.7 g/l and amyloglucosidase at concentration of 0.42 g/l. Then 3 g/l of yeast extract and 5 g/l of NH_4Cl were added to the medium. The pH value was set at 5.2 using buffer solution of potassium hydrogen phthalate (0.1 M) and sodium hydroxide (0.1 M) solution. In order to start fermentation, the sterilized medium was inoculated by the seed culture of *Saccharomyces cerevisiae.* The result including produced ethanol concentration versus time in conventional fermentation and also cell concentration during fermentation is depicted in Figure 3. Maximum ethanol was produced after 16 hours of fermentation having ethanol concentration of 8.9 g/l. At the stationary phase of cell growth, ethanol and cell concentrations were approximately constant at 8.1 and 7.2 g/l, respectively.

3. 4. Ethanol Production in Membrane Bio Reactor by Commercial Membrane Integration of ethanol productions from hydrolyzed broomcorn seed via fermentation process and ethanol separation unit using an ethanol selective membrane in a single membrane bioreactor by commercial and novel fabricated membranes were performed. Fermentation process in broth was carried out at 32 °C. 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 on the permeate side was maintained by vacuum pump (Edwards, England). Two cold traps using liquid nitrogen were set in parallel allowing collecting ethanol permeated vapor [15].

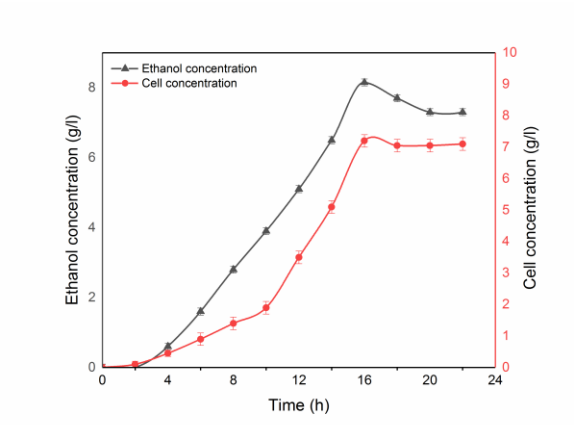

Figure 3. Results of fermentation in conventional process

The glucose consumption, ethanol production in broth of MBR and the cold trap of MBR along with cell concentration versus time are illustrated in Figure 4. The solution and conditions were similar to the conventional fermentation (at the best conditions presented by RSM). Glucose was consumed after 22 hours of fermentation. After 16 hours of fermentation, maximum ethanol concentration was 10.15 g/l in the broth of MBR, while ethanol concentration in the cold trap of MBR was 70.2 g/l. Therefore, the concentration of ethanol has significantly increased compared to conventional fermentation process. Such increase in ethanol concentration may be due to ethanol permanent exit in the fermenter and prevention of ethanol inhibition and also can increase the cell density.

Comparisons between cell concentrations in conventional ethanol production and in MBR ethanol production are shown in Figure 5. In the stationary phase of growth, the cell concentration in the broth of MBR was 9.05 g/l while the cell concentration in the conventional fermentation at the stationary phase or growth phase was 7.2 g/l. Therefore, the cell concentration in the broth of MBR was higher than conventional fermentation.

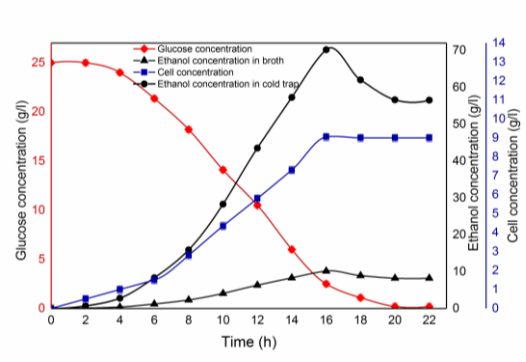

Figure 4. Results of membrane bioreactor using commercial membrane

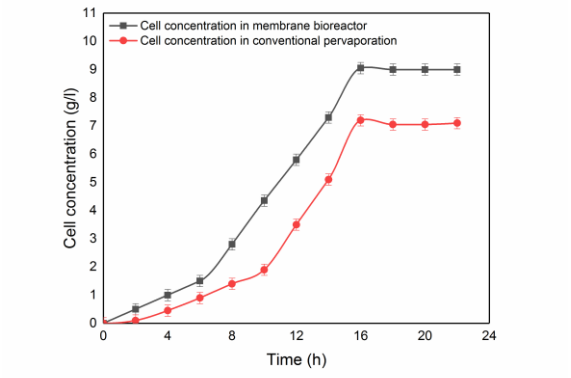

Figure 5. Cell concentrations in conventional and in MBR fermentation processes

In fact, due to ethanol removal from reactor using ethanol selective membrane, in the stationary phase of growth curve, the cell concentration in the broth of MBR has reached 9.05 g/l.

3. 5. Ethanol Production in Membrane Bioreactor Using MWCNT.PDMS/PES.PVP Membrane Figure 6 shows results of fermentation process having ethanol production in broth and cold trap of MBR, cell dry weight and glucose consumption versus time in MBR using fabricated MWCNT.PDMS/PES.PVP membrane. Glucose was totally consumed after 20 hours of fermentation. The produced ethanol in the broth and cold trap has reached to concentration of 11.1 and 88.5 g/l, respectively. Increasing ethanol production in this case was due to the use of membrane for additional ethanol selectivity in membrane bioreactor. The ethanol separation factor for MWCNT.PDMS/PES .PVP was determined to be 8.7 while ethanol separation factor for commercial PDMS/PET/PI was 7.4. In addition, due to continuous ethanol removal from the bioreactor using ethanol selective membrane, at the stationary phase of growth, the cell concentration in the broth of MBR reached 10.2 g/l.

3. 6. Ethanol Production in Membrane Bioreactor by Surface Modified MWCNT Coated on PDMS/PES.PVP Membrane Based on results in previous sections, the use of a specific membrane in MBR having high ethanol selectivity had a great impact on fermentation process. Therefore, in order to increase the ethanol selectivity, the composite PDMS/PES.PVP surface was modified by corona treatment and the surface was coated by multi-walled carbon nano tube (MWCNT). The ethanol production in broth and cold trap of MBR, cell dry weight and glucose consumption versus time in MBR with fabricated MWCNT coated on PDMS/PES.PVP membrane are shown in Figure 7. Glucose consumption was accelerated in the fermentation process. Therefore, glucose was totally consumed after 16 hours of fermentation.

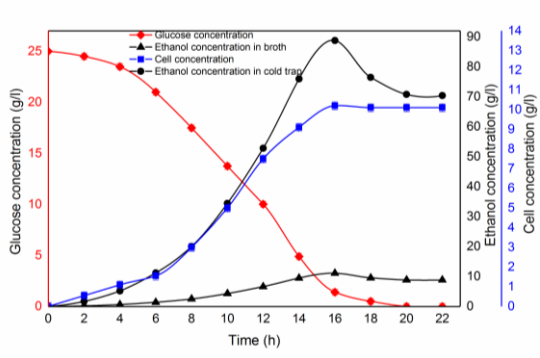

Figure 6. Results of membrane bioreactor with fabricated CNT.PDMS/ PES.PVP membrane

High glucose consumption was due to increase cell growth. In the stationary phase, the cell concentration in the broth of MBR has reached 11.01 g/l. As expected, the produced ethanol in the broth and cold trap has reached to concentration of 11.9 and 110 g/l, respectively. The ethanol separation factor for surface modified MWCNT coated on PDMS/PES membrane was determined as 10.2; that is high ethanol selectivity of the membrane has resulted in high ethanol production and increasing trend of cell growth in the membrane bioreactor.

The results of all experiments with different membranes and at different fermentation processes are summarized in Table 4. As data in the table shows, the use of a membrane bioreactor improves ethanol production and the use of fabricated membranes with high ethanol selectivity has increased cell growth and ethanol production.

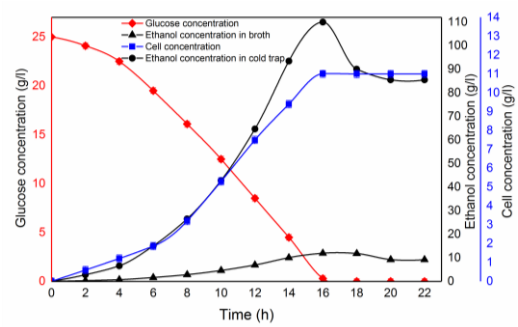

Figure 7. Results of membrane bioreactor with fabricated corona surface modified CNT coated on PDMS/ PES.PVP membrane

TABLE 4. The summarized results of fermentation

	Conventional process	MBR by commercial membrane	MBR by blended MWCNT	MBR by coated MWCNT
sorghum concentration (g/l)	45	45	45	45
Glucose utilization (g/l)	25.5	25.5	25.5	25.5
Temperature (°C)	32	32	32	32
pH	5.2	5.2	5.2	5.2
Ethanol concentration				
Broth (g/l)	8.1	10.15	11.1	11.9
Cold trap (g/l)	-	70.2	88.5	110
Cell density (g/l)	7.2	9.05	10.2	11.01
Separation factor	-	7.4	8.7	10.2

Based on this data, enhanced ethanol productivity in cold trap was 40% higher than that in similar work reported using commercial membrane [15].

4. CONCLUSION

In the present study, bioethanol production from broomcorn seeds (*Sorghum vulgare*) as a new source was investigated. By response surface method (RSM), the conditions of enzymatic hydrolysis and ethanol production was optimized. In optimum condition, the conventional fermentation was performed. Then, bioethanol production carried out by integration of batch fermentation and membrane pervaporation process in a membrane bioreactor (MBR). A commercial PDMS/PET/PI membrane was used in MBR. Membrane bioreactor in comparison with conventional process has significantly improved ethanol production. Afterwards, two fabricated high ethanol selective composite membranes were tested in MBR and it was observed that the use of membranes with high ethanol selectivity has increased cell growth and ethanol production.

5. ACKNOWLEDGEMENTS

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6.REFERENCES

1. CantÃº-Lozano, D. and Luna-Solano, G., "Bioethanol production process rheology", ***Industrial Crops and Products***, Vol., No., (2016).
2. El-Sebaii, A. and Shalaby, S., "Solar drying of agricultural products: A review", ***Renewable and Sustainable Energy Reviews***, Vol. 16, No. 1, (2012), 37-43.
3. Peng, P., Shi, B. and Lan, Y., "A review of membrane materials for ethanol recovery by pervaporation", ***Separation Science and Technology***, Vol. 46, No. 2, (2010), 234-246.
4. Wei, P., Cheng, L.-H., Zhang, L., Xu, X.-H., Chen, H.-l. and Gao, C.-j., "A review of membrane technology for bioethanol production", ***Renewable and Sustainable Energy Reviews***, Vol. 30, No., (2014), 388-400.
5. Rezakazemi, M., Shahidi, K. and Mohammadi, T., "Synthetic pdms composite membranes for pervaporation dehydration of ethanol", ***Desalination and Water Treatment***, Vol. 54, No. 6, (2015), 1542-1549.
6. Nasidi, M., Agu, R., Deeni, Y. and Walker, G., "Utilization of whole sorghum crop residues for bioethanol production", ***Journal of the Institute of Brewing***, Vol. 122, No. 2, (2016), 268-277.
7. Farahi, A., Najafpour, G., Ghoreyshi, A., Mohammadi, M. and Esfahanian, M., "Enzymatic production of reducing sugars from broomcorn seed (sorghum vulgare): Process optimization and

kinetic studies", ***World Applied Sciences Journal***, Vol. 18, No. 4, (2012), 568-574.

8. Ariyajaroenwong, P., Laopaiboon, P., Salakkam, A., Srinophakun, P. and Laopaiboon, L., "Kinetic models for batch and continuous ethanol fermentation from sweet sorghum juice by yeast immobilized on sweet sorghum stalks", ***Journal of the Taiwan Institute of Chemical Engineers***, Vol. 66, No., (2016), 210-216.
9. Castro, E., Nieves, I.U., Rondón, V., Sagues, W.J., Fernández-Sandoval, M.T., Yomano, L.P., York, S.W., Erickson, J. and Vermerris, W., "Potential for ethanol production from different sorghum cultivars", ***Industrial Crops and Products***, Vol. 109, No., (2017), 367-373.
10. Jafari, Y., Karimi, K. and Amiri, H., "Efficient bioconversion of whole sweet sorghum plant to acetone, butanol, and ethanol improved by acetone delignification", ***Journal of Cleaner Production***, Vol. 166, No., (2017), 1428-1437.
11. Singh, H. and Soni, S.K., "Production of starch-gel digesting amyloglucosidase by aspergillus oryzae hs-3 in solid state fermentation", ***Process Biochemistry***, Vol. 37, No. 5, (2001), 453-459.
12. Brunetti, A., Zito, P.F., Giorno, L., Drioli, E. and Barbieri, G., "Membrane reactors for low temperature applications: An overview", ***Chemical Engineering and Processing: Process Intensification***, Vol., No., (2017).
13. Trifunović, O. and Trägårdh, G., "The influence of support layer on mass transport of homologous series of alcohols and esters through composite pervaporation membranes", ***Journal of Membrane Science***, Vol. 259, No. 1, (2005), 122-134.
14. Fu, C., Cai, D., Hu, S., Miao, Q., Wang, Y., Qin, P., Wang, Z. and Tan, T., "Ethanol fermentation integrated with pdms composite membrane: An effective process", ***Bioresource Technology***, Vol. 200, No., (2016), 648-657.
15. Esfahanian, M., Ghorbanfarahi, A., Ghoreyshi, A., Najafpour, G., Younesi, H. and Ahmad, A., "Enhanced bioethanol production in batch fermentation by pervaporation using a pdms membrane bioreactor", ***International Journal of Engineering-Transactions B: Applications***, Vol. 25, No. 4, (2012), 249.
16. Tan, Y.H., Abdullah, M.O., Nolasco-Hipolito, C. and Zauzi, N.S.A., "Application of rsm and taguchi methods for optimizing the transesterification of waste cooking oil catalyzed by solid ostrich and chicken-eggshell derived cao", ***Renewable Energy***, Vol. 114, No., (2017), 437-447.
17. Verma, D., Thakur, P.S., Padhi, S., Khuroo, T., Talegaonkar, S. and Iqbal, Z., "Design expert assisted nanoformulation design for co-delivery of topotecan and thymoquinone: Optimization, in vitro characterization and stability assessment", ***Journal of Molecular Liquids***, Vol. 242, No., (2017), 382-394.
18. de Oliveira Faber, M. and Ferreira-Leitão, V.S., "Optimization of biohydrogen yield produced by bacterial consortia using residual glycerin from biodiesel production", ***Bioresource Technology***, Vol. 219, No., (2016), 365-370.
19. Esfahanian, M., Rad, A.S., Khoshhal, S., Najafpour, G. and Asghari, B., "Mathematical modeling of continuous ethanol fermentation in a membrane bioreactor by pervaporation compared to conventional system: Genetic algorithm", ***Bioresource Technology***, Vol. 212, No., (2016), 62-71.

Composite Multi Wall Carbon Nano Tube Polydimethylsiloxane Membrane Bioreactor for Enhanced Bioethanol Production from Broomcorn Seeds

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چکیده

دانه‌های جارو (سورگوم جارویی) به عنوان ماده اولیه در تولید بیواتانول استفاده شده است. در شرایط بهینه به دست آمده با استفاده از تکنیک پاسخ سطحی، مقدار 45 g/l از دانه‌های جاروی آرد شده مورد پیش تیمار قلیایی قرار گرفت و سپس با آنزیم‌های آلفاآمیلاز با غلظت 0/7 g/l و آمیلوگلوکوزیداز با غلظت 0/42 g/l هیدرولیز آنزیمی گردید. قند ساده حاصل که دارای غلظت g/l 25/5 بود، در روش سنتی با مخمر *Saccharomyces cerevisiae* تخمیر شد و 8/1 g/l اتانول به دست آمد. دربیوراکتورغشایی و با استفاده از ترکیب عملیات تخمیر و تکنولوژی غشایی تولید اتانول افزایش یافت. با استفاده از غشای تجاری پلی دی متیل سیلوکسان/ پلی اتیلن ترفتالات/ پلی ایمید (PDMS/PET/PI)، اتانول با غلظت 10/15 g/l در بیوراکتور و 70/2 g/l در کلدترپ بیوراکتورغشایی تولید شد. مقدار رشد سلولی از از 7/2 g/l در تولید سنتی به 9/05 g/l رسید. با استفاده از غشای ساخته شده با فاکتور جداسازی 8/7 مقدار اتانول تولیدی در بیوراکتور غشایی به 11/1g/l و در کلدترپ بیوراکتورغشایی به 88/5 g/l رسید. مقدار رشد سلولی در این حالت برابر 10/2g/l بوده است. همچنین با استفاده از غشای پلی دی متیل سیلوکسان ساخته شده و اصلاح سطح شده و پوشیده شده با نانولوله‌های کربنی چنددیواره با فاکتور جداسازی 10/2، به تولید اتانولی معادل g/l 11/9 و 110 g/l در بیوراکتور و کلدترپ بیوراکتورغشایی دست یافته شد. رشد سلولی در این حالت 11/01 g/l بود. بنابراین بیشترین اتانول تولید شده و جداسازی شده با استفاده از بیوراکتور غشایی و استفاده از غشای اصلاح سطح شده به وسیله کرونا و پوشیده شده با نانولوله‌های کربنی چنددیواره می‌باشد.

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