

## Multilayer polymeric composite membrane for gas separation

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*Received 28 February 2024; accepted 15 July 2024*

Gas separation is the process of separating primary gaseous components from the composition of air. The separated primary gaseous components are essential for many industrial purposes such as chemical, medical, aeronautical, food processing industries. Oxygen enriched air plays a crucial role in the fuel combustion process and medical applications. Membrane technology emerges in the field of gas separation due to its inherent multidirectional characteristics. The multilayer composite polymeric membrane has been developed using electrospun web, nonwoven substrate and casting polymer solution to improve the permeability and selectivity of oxygen gas molecule from the gas mixture. This membrane also consists of polyethylene glycol (PEG) and SiO<sub>2</sub> nanoparticles which are used to improve the permeability and selectivity of oxygen molecules. Box- Behnken design has been wielded for the membrane construction by three independent variables such as volume of electrospinning solution (mL), Casting Solution (mL) and PEG concentration (%). Oxygen separation is carried out using the gas separation unit and it is constructed based on the principle of air separation. To analyze the performance of the developed membrane, the purity of oxygen from the composite membrane is estimated by a GC-MS. Mass per unit area and thickness of all membrane samples has been tested. From the results, the electrospun web thickness and casting solution concentration directly influence the oxygen purity and air separation rate. SiO<sub>2</sub> nanoparticles are added to the casting solution and the electrospun web. The presence of SiO<sub>2</sub> in the top and bottom layer of the membrane is used to attract the O<sub>2</sub> molecules. Maximum oxygen purity was obtained from the membrane which has an electrospun web with 6mL and 30% casting solution with 2% PEG. From this flat sheet composite membrane, the purity range of oxygen is 42.2% with moderate permeability flux.

**Keywords:** Casting solution, Gas separation, Nanoparticles, Polymeric membrane, Permeability

### Introduction

Air is a mixture of gas containing primary components like nitrogen (78%), oxygen (21%), argon (0.93%) and some other components. Gas separation process has an advantage in many fields due to its requirement in the present scenario. Gas separation states the information of selective segregation of gaseous components from its major volume. Large quantities of high-purity gas components are used in several industries such as the steel, chemical, semiconductor, aeronautical, refining, food processing and medical industries. Gas separation process is considered as a vital operation which is employed in chemical industries<sup>1,2</sup>. Oxygen enriched air is used for effective oxy-combustion process, coal fired boiler and feed stoke for gasifiers<sup>3,4,5</sup>. Selectivity and permeability are the important terminologies in the membrane-based gas separation process<sup>6</sup>. The selectivity tells about how fast specific gas species travels through the membrane compared to other gas molecules. It is determined by the ratio of the fast gas permeability to the slow gas

permeability. Permeability determines the membrane area which is needed to allow the separated target gas species through the membrane<sup>7</sup>.

The gas separation is done by various traditional methods like cryogenic distillation, pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) to improve the purity of particular components in air<sup>8,9</sup>. The production volume of cryogenic distillation has 100 tons of oxygen per day with an oxygen purity of more than 99%. Pressure swing adsorption has the ability to produce 20 to 100 tonnes of oxygen per day with a purity range of 90%. Cryogenic distillation and pressure swing adsorption method exhibits disadvantages like high energy consumption, high operation cost and high volume of vessels required for air separation. Membrane technology in gas separation is an emerging technique. Commercially available membrane gives oxygen purity of about 25 to 40%<sup>10</sup>. With respect to gas separation, a membrane is a perm selective interface between two phases which facilitates the separation of gas species based on the solution-diffusion mechanism. The development of a potential

polymeric membrane is the key area of research in membrane technology. Gas separations by a polymeric membrane have huge application in industry separation activity<sup>11</sup>. It has an application due to its inherent characteristics like low cost with high economical to operate, simplest process in terms of engineering design<sup>12</sup>, requires the least amount of equipment for startup<sup>13,14</sup> and less energy consumption<sup>15,16</sup>. In order to overcome the disadvantages in the conventional operation, membrane technology was exposed to the area of gas separation. A recent process which uses oxygen permeable membrane along with oxygen absorbent was created to produce pure oxygen from air<sup>17</sup>. Now a days, researchers heed towards the development of membrane, selection of polymers, process variable, additives to improve the gas separation performance. In the area of oxygen separation Mixed Ionic and Electronic Conducting (MIEC) ceramic membranes are used<sup>18</sup>. Asymmetric membranes are suitable for gas separation due to thin and dense skin layers supported by thick porous sub layers. Selectivity depends on the configuration of membrane, type of membrane construction and membrane material<sup>19</sup>. The permeability parameter of the polydimethylsiloxane (PDMS) membrane depends on the thickness<sup>20</sup>. Permeability and selectivity are the two key challenging parameters that estimate the membrane application and performance. PDMS and polyimide membrane have O<sub>2</sub> enrichment in the range of 35% and 57% respectively<sup>21</sup>.

Recent days the researchers are aiming to develop a membrane with mixed ionic-electronic conductors (MIEC) for oxygen separation. However, it is not cost effective. Ceramic based membranes are more attractive and it is called as oxygen transport membrane (OTM). The mechanism of oxygen separation for the OTM is surface diffusion and bulk diffusion. This gives more than 99% purity, however the rate of production is comparatively low.

Multilayer high performance composite membrane was developed to separate CO<sub>2</sub>/CH<sub>4</sub> from oilfield associated gas<sup>22</sup>. Mixed matrix membrane with zeolite imidazolate framework (ZIF-L) nanoflakes showed increased CO<sub>2</sub> permeability with CO<sub>2</sub>/N<sub>2</sub> selectivity<sup>23</sup>. In recent research, cellulose based membranes were developed for the application of gas separation and water purification<sup>24</sup>. Polysulfone (PSf) modified Cellulose Triacetate (CTA) blend membranes were fabricated to separate carbon dioxide (CO<sub>2</sub>) from methane (CH<sub>4</sub>). These membranes exhibit improved

CO<sub>2</sub>/CH<sub>4</sub> selectivity of 30.70 without compromising on the CO<sub>2</sub> permeability<sup>25</sup>. Fabrication of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles incorporated mixed matrix membranes were prepared to separate O<sub>2</sub>/N<sub>2</sub> gas from gas mixture<sup>26</sup>. Superior O<sub>2</sub> permeability of 240.3 Barrer with 16.3 O<sub>2</sub>/N<sub>2</sub> selectivity is obtained using the CeO<sub>2</sub>/carbon composite molecular sieving membranes (CMSMs)<sup>27</sup>.

Modern membrane engineering is a vital and emerging route to execute the process intensification (PI) strategy by new membrane design, configuration and methodology development with less complexity in application, lower energy consumption and higher performance. The selection of methods to obtain air separation is very essential to obtain higher quantity and quality of target species of gas. The recent research work is being addressed to the investigation of new materials and to the development of new membrane structures that exhibit both higher selectivity and permeability to specific gases. To satisfy the above requirements multilayer membrane has been developed with new concepts.

## Experimental Section

### Materials

A multilayer composite membrane was prepared with various components in various forms. Polyacrylonitrile (C<sub>3</sub>H<sub>3</sub>N)<sub>n</sub>, Nylon 6 (C<sub>6</sub>H<sub>11</sub>NO)<sub>n</sub>, N,N-dimethylformamide, and polyethylene glycol (PEG, Mol.wt. 600) were used to prepare the membrane. The pores on the surface of the membrane were enhanced by polyethylene glycol<sup>28,29</sup>. SiO<sub>2</sub> nanoparticles was synthesized from rice husk<sup>30</sup> by chemical and thermal treatment which was added in the casting solution as well as in electrospinning solution. Polyester and polypropylene staple fibres of 38 mm were used to prepare the fibrous substrate using miniature carding machine and thermal bonding machine.

### Membrane preparation

#### Design of experiments

Response surface methodology (RSM) is a statistical technique for empirical model building, exploring the relationship between variables and optimizes the response. In RSM, Box-behnken design has been used to derive the experimental plan. In Box-Behnken experimental design, the level of one of the factors is fixed at the centre level while combinations of all levels of the other factors are applied. By Box Behnken method, 15 experiments have been formulated to

construct composite membrane and then the respective samples are derived. Each factor or independent variables is placed at one of three equally spaced values, usually coded -1, 0, and +1. These optimized samples are taken to develop composite membrane. The variables with respective particulars for design of experiments are given in Table 1.

#### Methodology to fabricate the membrane

In the development of multilayer membrane three independent steps are involved such as electro spinning of SiO<sub>2</sub> imparted PAN solution, preparation of PET/PP blended nonwoven web by miniature carding machine and preparation of casting solution such as polyamide solution with PEG and SiO<sub>2</sub> nanoparticles. To construct the membrane, design of experiments has been used with independent variables as volume of electrospinning solution which influences the fine pore size of the membrane, polyethylene glycol which causes various pore sizes on top and bottom surface of the membrane and

concentration of polyamide solution which influences the pore path and stability of the membrane.

The schematic diagram of the membrane is shown in Fig. 1. The mechanism behind the preparation of the membrane is the middle layer of electrospun web which has very fine fibrous material with embedded SiO<sub>2</sub> nanoparticles will absorb O<sub>2</sub> and transfer to the next layer. The porous space in the PET/PP substrate will help to transfer the O<sub>2</sub> to next layer which is nylon 6 polymer embedded with SiO<sub>2</sub> nanoparticles. The porous substrate between the electrospun web and nylon polymer layers will help to hold more quantity of O<sub>2</sub> molecules and that can transfer to the outer layer. The SiO<sub>2</sub> nanoparticles are embedded in electrospun web and nylon polymer which helps to absorb O<sub>2</sub> molecules sufficiently. The silica nanoparticles will improve the number of polar OH group which leads to the improvement of solubility parameter of gas molecules in membrane.

#### Electrospun web preparation with SiO<sub>2</sub>

SiO<sub>2</sub> nanoparticle of 3% on the weight of material is dispersed in 10% concentration of PAN polymer solution as per the experimental plan for electro spinning and DMF is used as the solvent. In the electro spinning process, 18 kVA of voltage is applied on the syringe tip as shown in Fig. 2. An electrically

Table 1 — Design of experiments by Box- Behnken method for membrane construction

S. No.	Independent variables	-1	0	+1
1.	Vol. of solution for electrospinning (mL)	2	4	6
2.	Concentration of polyamide (%)	20	25	30
3.	Polyethylene glycol (%)	1	2	3

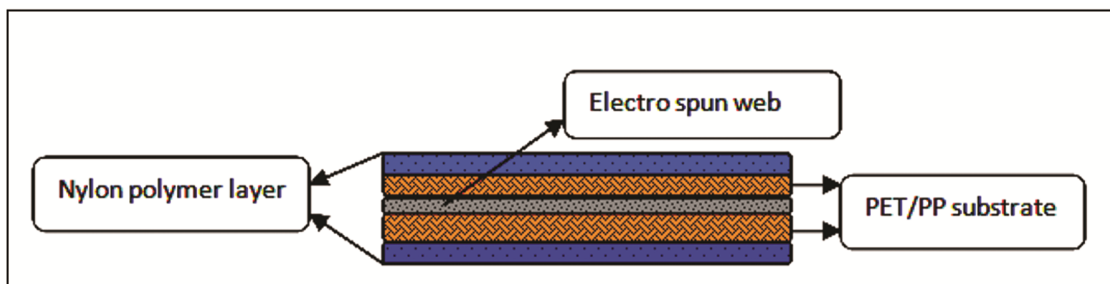


Fig. 1 — Schematic representation of multilayer membrane

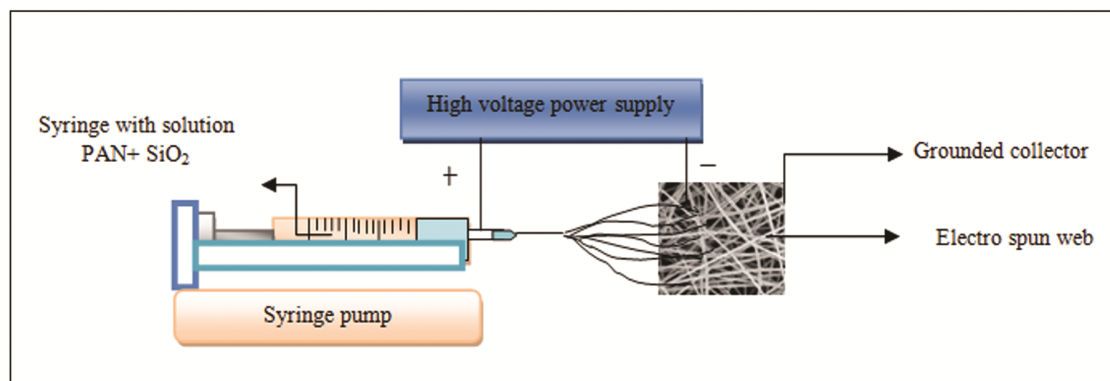


Fig. 2 — Principle diagram of electrospinning

charged jet of polymer solution was induced and the polymers solution is splitted into fibres and collected by the stationary collector. The distance between the syringe tip and the collector is maintained as 15 cm. The whipping instability of the polymer leads to stretching the polymer as fibres in nano dimensions<sup>31,32,33</sup>. Silica nano particles are taken as additives to enhance the membrane for adsorption of oxygen molecules. The silica nanoparticles will improve the number of polar OH group which leads to the improvement of solubility parameter of gas molecules in membrane<sup>34</sup>. Polysulfone mixed matrix membrane with silica nanoparticles results four times higher O<sub>2</sub> permeability and five times greater CH<sub>4</sub> permeability than in membrane which was made of pure Polysulfone (PSf)<sup>35</sup>. Silica nanoparticles are added to improve the stability of the membrane too. Incorporation of nanoparticles in membranes reduces interfacial defects and improve the compatibility between fillers and polymer matrix which enhances the overall mechanical stability, thermal stability and gas separation performance<sup>36</sup>.

#### Preparation of PET/PP Substrate

The substrate is incorporated into the membrane so as to create air passage with low pressure and to improve the mechanical strength. The substrate is made of polyester and polypropylene fibres in the ratio of 80:20. The fibers were thoroughly opened and fed to the miniature carding machine. The collected web from the carding machine is then bonded using the thermal bonding machine at the temperature of 140°C. It has given the consolidated web substrate which was used as a layer above and below the

electrospun web and it also imparts efficient air passage with low pressure. The schematic representation of the preparation of PET/PP substrate is shown in Fig. 3.

#### Preparation of nylon casting solution

Nylon polymer chips are dissolved in formic acid and 5% on the weight of polymer of SiO<sub>2</sub> is dispersed in the polymer solution. The concentration of nylon polymer varies between 20 to 30% and the concentration of polyethylene glycol is in the range of 1 to 3% are taken as per the experimental plan which is given in Table 1. As prepared polymer solution is poured over the already prepared sandwich of electrospun nano web and substrate. The schematic representation of the preparation of composite membrane is given in Figs 4 and 5. 'A' represents the preparation of nylon polymer solution, 'B' represents the preparation of nonwoven substrate with PET and PP and 'C' represents the electrospinning of PAN polymer. The solvent is removed by drying to create a solid layer of nylon on top and bottom of the membrane. The thickness of the cast film was approximately in the range of 100 to 200 µm.

#### Composite membrane construction

The membrane construction for separation was done by combining five layers membrane to obtain required characteristics like permeability, selectivity, mechanical stability with other properties. The Nylon polymeric solution with silica and pore former (PEG) are optimized to obtain an exact membrane with all required properties for gas separation. While evaporating the solvents, the PEG (pore former) also

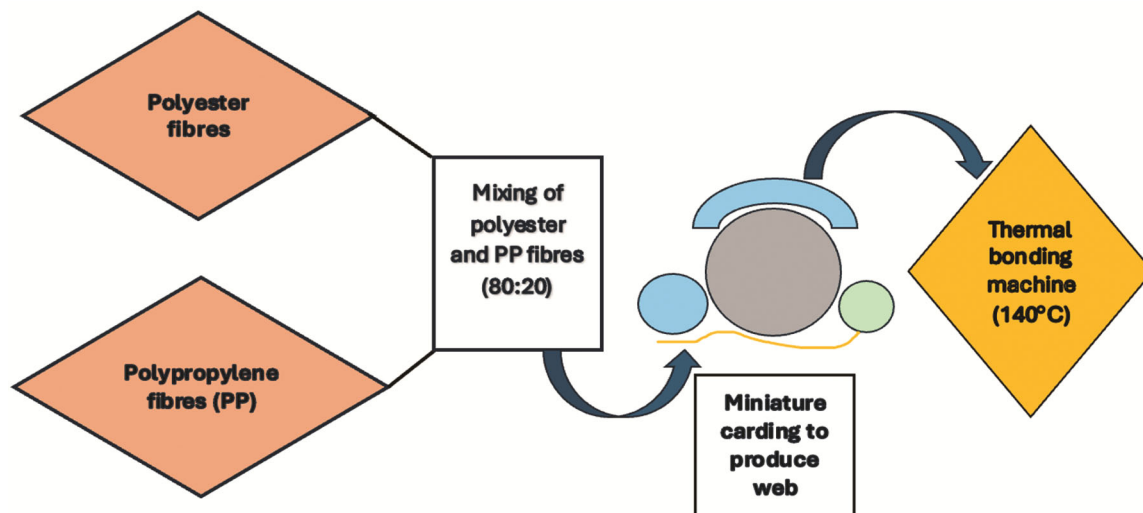


Fig. 3 — Schematic representation of preparation of PET/PP Substrate

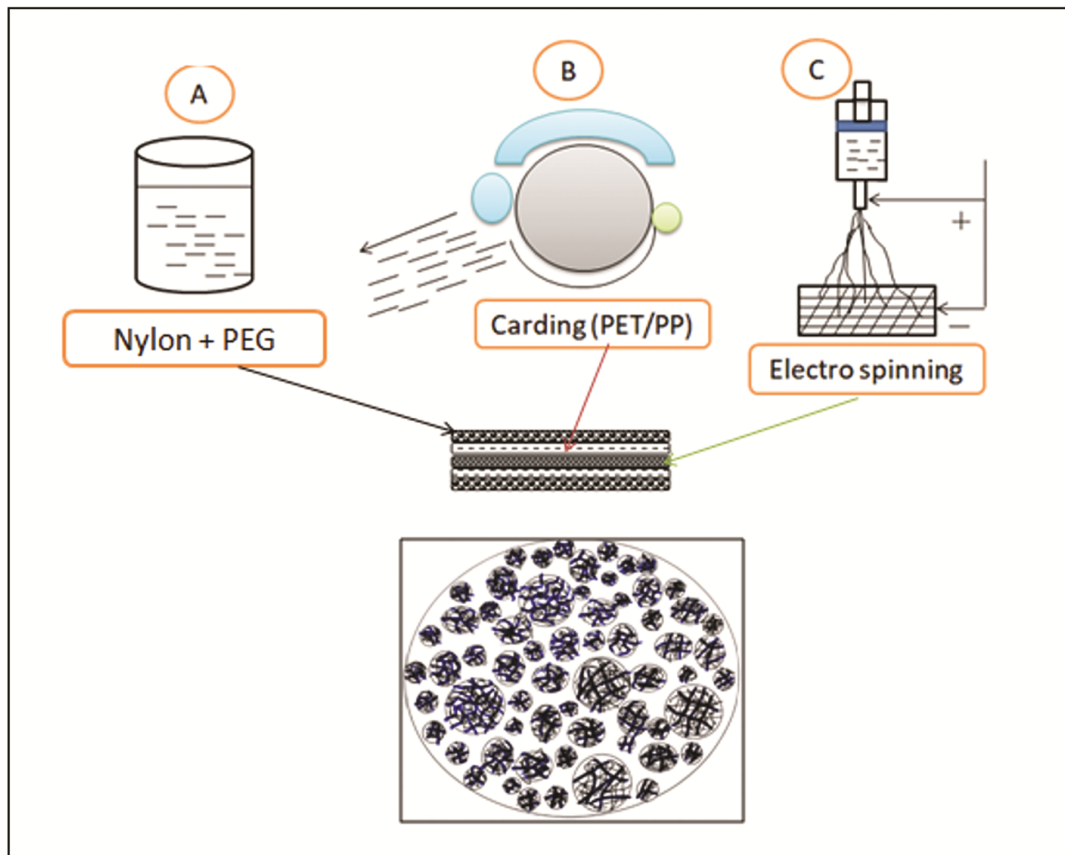


Fig. 4 — Schematic representation of the preparation of composite membrane



Substrate

Casting

Membrane

Fig. 5 — Construction of membrane

evaporates from the solution which form pores in the membrane structure. The nature of the construction of membrane by this method has bigger pores on its surface and it is helpful to access the subsequent layers of the membrane. The poured nylon polymer solution forms a thin top and bottom layer and penetrates through the substrate to fill the gaps and touches the middle electrospun layer. This membrane is expected to give high order of separation especially selectivity to obtain the gaseous components with lower pressure level.

#### Regression analysis

From the response surface methodology, Box-Behnken design was used to design the experiment, the advantage of the three factorial experimental designs is to be rotatable, which means the fitted model evaluates the response with equal precision at all points in the factor space that are equidistant from the center. The polynomial regression equation coefficient shows the relationship between proper response and factors affecting the response, which is given in Eq. (1).

$$Y = b_0 + b_i X_i + b_{ij} X_{ij} + \dots + b_{ij} X_i X_j \quad \dots(1)$$

Where  $b_0$ ,  $b_i$ , and  $b_{ij}$  are the regression equation coefficients,  $i$  and  $j$  are the independent variables and  $Y$  is the response of the independent variable.

#### Characterization

The synthesized silica nanoparticles and electrospun nanofibres are characterized by scanning electron microscope for its surface morphology and diameter; the nature of the silica nanoparticles such as amorphous/crystalline has been evaluated by XRD (PANalytical). The surface morphology of the constructed membrane was analyzed by an optical microscope with the resolution of 10 X. The as prepared PET/PP nonwoven fabric was tested for its tensile properties as per ASTM 5034-21. The mass per unit area of the constructed membrane was tested as per ASTM D3776 / D3776M-09a. FTIR analysis has been carried out for the prepared membrane. The oxygen purity level obtained through the membrane is tested by GC-MS.

#### Principle and instrument construction for oxygen separation

The design of gas separation unit is achieved based on the principle of separation mechanism and it is

given in Fig. 6<sup>(Ref.37,38)</sup>. The construction of an air separation unit comprises air regulator, pressure gauge, flow meter, non return valves and container which should withstand pressure and is shown in Fig. 7.

The sample is placed in the air separation unit and the compressed air is used for the separation of oxygen. The compressed air is passed through the airflow meter at the rate of 10 lpm and maintained as constant air flow. The permeate valve is opened to collect the separated air. The time taken to collect 10 g of air is recorded.

## Results and Discussion

#### Properties of silica nano particles

The XRD pattern of the nano silica powder obtained from rice husk is shown in Fig. 8. XRD pattern is used to determine the crystallographic planes and phase purity of silica. The characteristics peaks at  $2\theta$  of  $22^\circ$  indicate the formation of amorphous silica whereas crystalline quartz phase of silica generally shows broad peaks at  $2\theta$  of  $20.9^\circ$ ,  $26.6^\circ$ ,  $36.5^\circ$ <sup>(Ref.39)</sup>. Further from Fig. 8, the XRD pattern ensures the absence of any ordered crystalline structure.

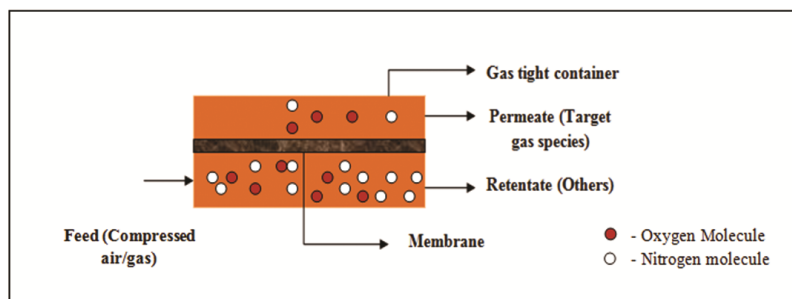


Fig. 6 — Principle of membrane gas separation unit

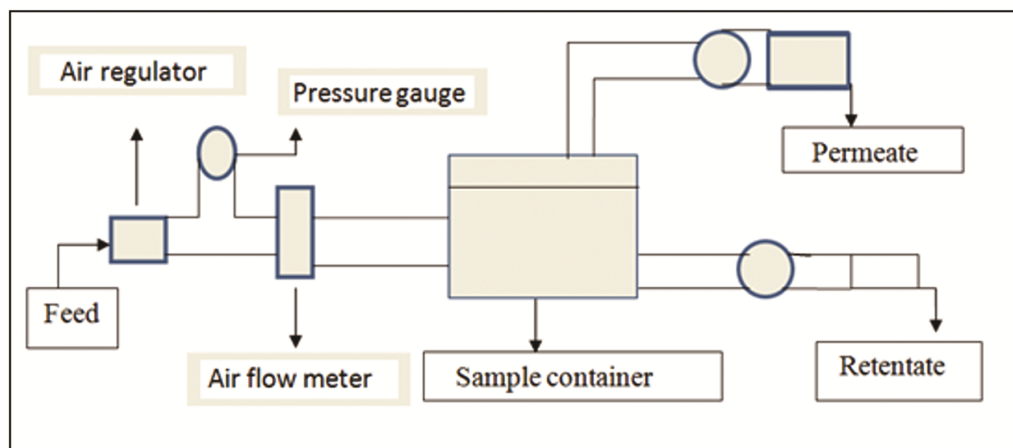


Fig. 7 — Design of air separation unit

### Surface morphology of nano fibres

Scanning Electron Microscope images of PAN/SiO<sub>2</sub> nano fibre is given in Fig. 9 and it shows more uniform fibre formation. SEM image exhibits the dispersion of nanoparticles, formation of nanofibers and morphology of the electrospun web<sup>40</sup>. The formation of beads can be visualized in the SEM image which is a key indicator to show how well nanoparticles are incorporated into the nano fibres. The presence of bead formation in the electrospun

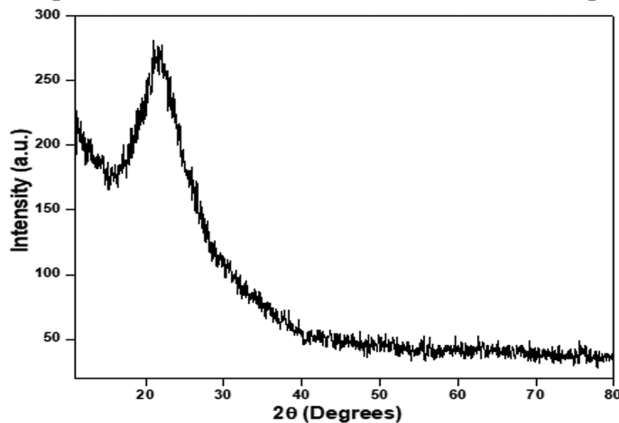


Fig. 8 — XRD plot of silica nanoparticles

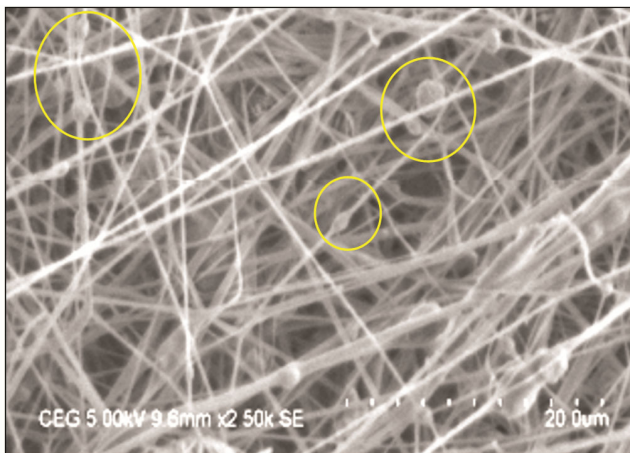


Fig. 9 — SEM image of PAN/SiO<sub>2</sub> nano fibre

web indicates the existence and distribution of nanoparticles in the web<sup>41</sup>. From the SEM image, it is evident that the nanoparticles are embedded within the fibres.

Nylon plays a crucial role in the casting solution for membrane fabrication. It provides a structural matrix of the membrane which influence the mechanical strength, rigidity and durability of the membrane. Nylon polymer plays a key role in membrane formation due to their properties such as structural integrity, chemical resistance and thermal stability. Nylon is a suitable material for robust membranes. The morphology of the membrane depends on the molecular weight and concentration of the polymer taken for the casting solution. When PEG is added to the nylon casting solution, it induces phase separation to form pores in the membrane which is crucial to create pathways for the gas molecules to diffuse. The interaction of the nylon polymer in the casting solution with the PEG (Pore former) is crucial for controlling size of the pore and its distribution. The optical microscope images of the prepared membrane were given in Fig. 10. It shows smooth membrane surface with less defects and it shows that 1% PEG gives non uniform pores and the distribution of pores increased in 2% PEG. 3% PEG gives more uniform pores, and it is well distributed. Higher concentration of PEG in membrane fabrication results in reduced pores due to the hinderance in phase inversion process and increased viscosity of the casting solution which leads to dense membrane structure<sup>42</sup>.

### Tensile strength of the substrate

The tensile strength of the PET/PP substrate influences the stability of the membrane and the average breaking load is around 2.8 Mpa. The stress-strain graph of the PET/PP substrate is given in Fig. 11.

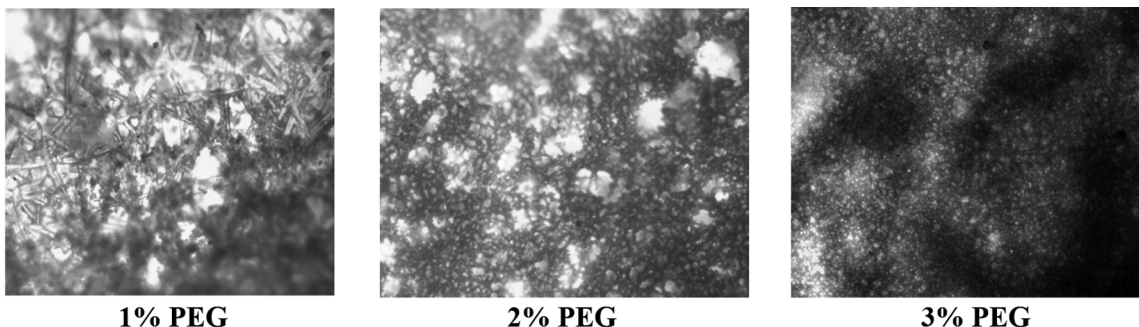


Fig. 10 — Optical microscope images of surface of the membrane

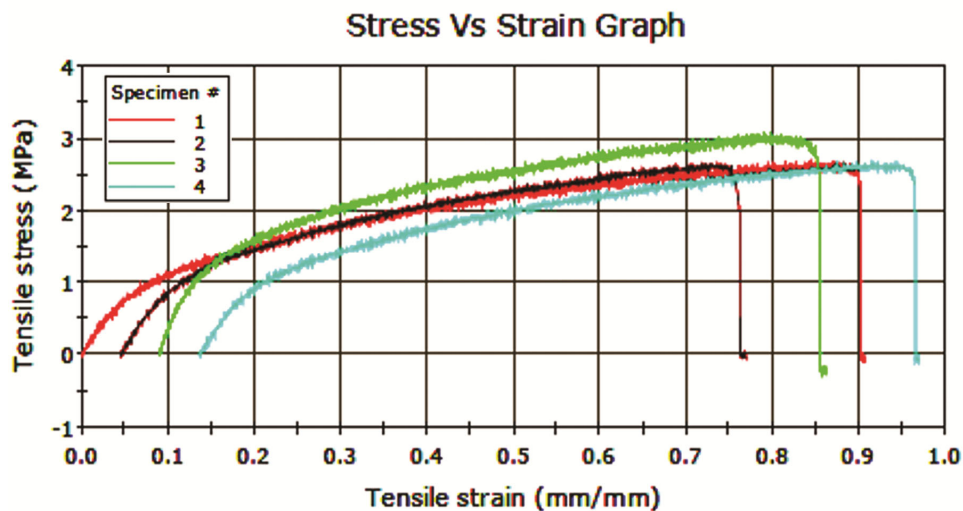


Fig. 11 — Stress/ Strain graph of the PET/PP substrate

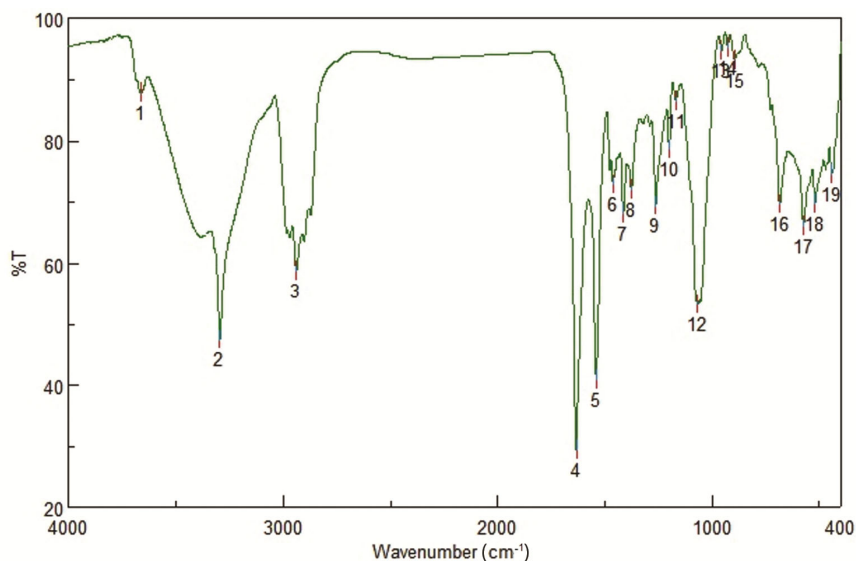


Fig. 12 — FTIR spectrum of the membrane

#### FTIR analysis of the membrane

The developed membrane of sample 4 which is giving high quantity of oxygen as 42.2% is tested for the functional elements present in the membrane by Fourier Transform Infra-Red (FTIR) analysis. The FTIR spectra of the membrane are given in Fig. 12. In case of polyacrylonitrile (PAN), it can be seen that the peaks located at 2938  $\text{cm}^{-1}$ , 1461  $\text{cm}^{-1}$ , 1376  $\text{cm}^{-1}$  and 1263  $\text{cm}^{-1}$  are corresponding to the vibrations of the aliphatic CH group (CH, CH<sub>2</sub>, and CH<sub>3</sub>). A weak peak located at 1633  $\text{cm}^{-1}$  was assigned to amide group.

FTIR transmittance spectrum (400 to 4000  $\text{cm}^{-1}$ ) confirms the presence of synthesized SiO<sub>2</sub> nanoparticles. The broad peak from 3000 to 3700  $\text{cm}^{-1}$

was assigned to the presence of O-H group. Similarly, a peak corresponding to vibration bending can be noticed at 1649  $\text{cm}^{-1}$ , which indicates the presence of O-H stretching bond. Moreover, the strong bands at 1069, 894 and 443  $\text{cm}^{-1}$  were associated to the asymmetric and symmetric Si-O-Si stretching vibration bonding. The nylon 6 has a medium band at peak 3294  $\text{cm}^{-1}$  that was attributed to the N-H stretch from amino groups. Following this, a C-H stretching vibration due to alkanes group was observed with a medium peak at 2938  $\text{cm}^{-1}$ . At peaks 1633  $\text{cm}^{-1}$  and 1539  $\text{cm}^{-1}$  two strong peaks were detected. The strong peaks formed at peaks range from 1500  $\text{cm}^{-1}$  to 1700  $\text{cm}^{-1}$ , due to amide I and II bands.

Table 2 — Experimental results of constructed membrane samples

S. No	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	Thickness (mm)	GSM (g/m <sup>2</sup> )	Oxygen Purity (%)	Air separation rate LPH
1	2	20	2	1.13	602	28.5	3.02
2	6	20	2	1.31	615	39.8	2.1
3	2	30	2	1.62	722	32.4	2.35
4	6	30	2	1.84	742	42.2	1.48
5	2	25	1	1.4	672	30.6	2.87
6	6	25	1	1.35	665	40.5	1.85
7	2	25	3	1.35	680	34.7	2.6
8	6	25	3	1.41	652	41.3	1.52
9	4	20	1	1.33	632	29.2	2.29
10	4	30	1	1.85	791	36.7	2.05
11	4	20	3	1.2	621	34.6	2.2
12	4	30	3	1.78	792	38.5	1.85
13	4	25	2	1.51	654	34.8	2.08
14	4	25	2	1.48	645	35.2	2.1
15	4	25	2	1.36	632	34.2	2.04

#### Analysis of oxygen purity and air separation rate

For the preparation of electrospun mat, the required volume of electro spinning solution was taken as per the experimental plan and the as prepared mat was converted to membrane by using polyamide and PEG. As per the experimental plan fifteen different types of membranes have been prepared, characterized, properties were analyzed and given in Table 2.

While constructing membrane, the volume of solution taken and concentration of the polymer obviously influence the thickness and mass per unit area of the membrane. The thickness of the membrane varies from 1.13 mm to 1.85 mm based on the influence of independent variables. The same trend has been followed for mass per unit area of the membrane and it was varied from 602 g/m<sup>2</sup> to 791 g/m<sup>2</sup>. The purity of oxygen varies from 28.5% to 42.2%. The rate of separation of air by membrane varies from 1.48 lph to 3.02 lph. The image evidence (Fig. 13) clearly shows the performance of the membrane.

#### Influence of independent variables on oxygen purity

The influence of independent variables on oxygen purity is shown in Fig. 13. The oxygen purity level increases gradually with respect to the volume of polymer solution used for electro spinning. This is due to the dense nano fibres and more active sites of SiO<sub>2</sub> on the fibres for absorbing O<sub>2</sub> molecules from the input air. However, the influence of concentration of polyamide polymer solution and the concentration of polyethylene glycol is lower while comparing the electrospun solution. Hence it proves that the dense layer of nano fibres and SiO<sub>2</sub> on the nano fibre and

polymer solution absorbs a greater amount of O<sub>2</sub> and it enhances the purity level. The polyamide polymer solution helps to produce compact membrane and polyethylene glycol helps to impart micro pores in the membrane to squeeze the absorbed O<sub>2</sub>. Incorporation of the SiO<sub>2</sub> nanoparticles leads to the higher surface area and introduction of free volumes within the membrane structure which leads to the increased oxygen permeability. The interaction between the silica nanoparticles incorporated membrane and oxygen molecules results in the adsorption and diffusion of the oxygen molecule through the membrane<sup>43</sup>. Silica nanoparticles within the polymer matrix also improves the selectivity of the membrane by reducing the segmental motion of the polymer chains which allows smaller gas molecules to pass through the membrane<sup>39</sup>. Increasing the volume of polymer solution improves the membrane structure and properties during the electrospinning process. Higher solution volumes result in uniform and dense fibre structure which leads to reduction in number of defects and irregularities in membrane, effective passage for oxygen molecules to diffuse and minimize the pathways for other gases thereby it enhances the selectivity of the oxygen molecules. In electrospinning process, fibre diameter and morphology can be controlled by increased volume of polymer solution<sup>44</sup>.

#### Influence of independent variables on air separation rate

The air separation through the membrane is based on the layer of nano fibres, concentration of casting polymer which covers the pores present in the nano fibrous web and substrate and concentration of

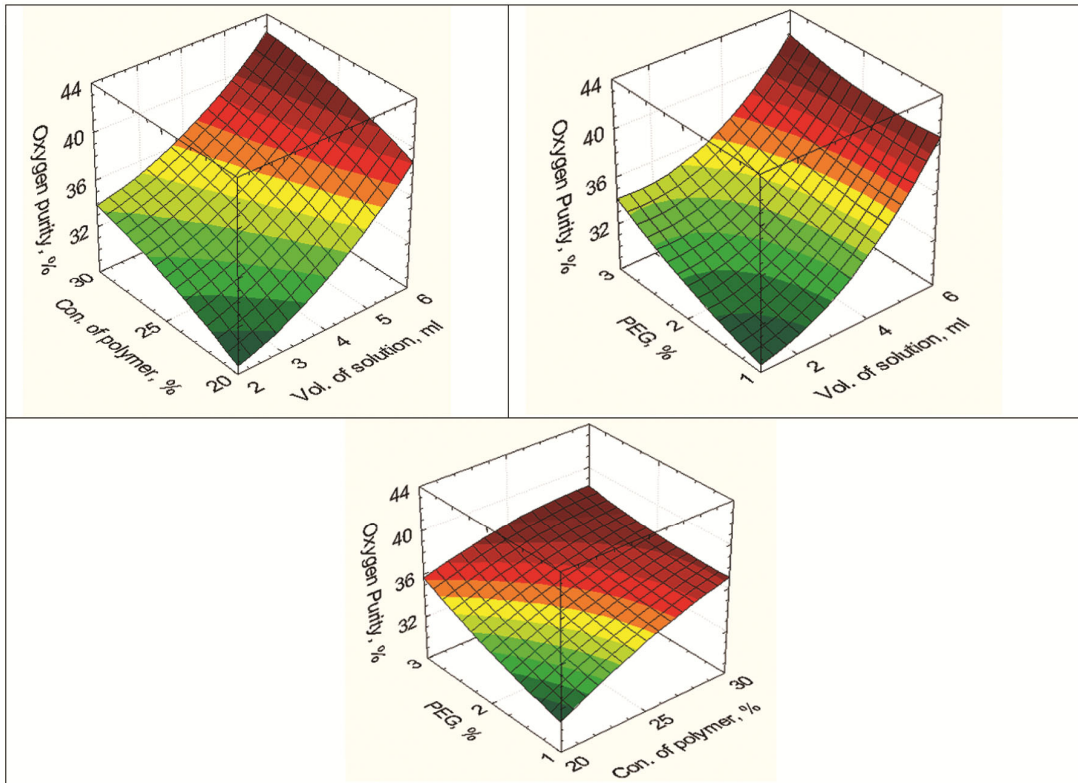


Fig. 13 — Graphical representation of Influence of independent variables on oxygen purity

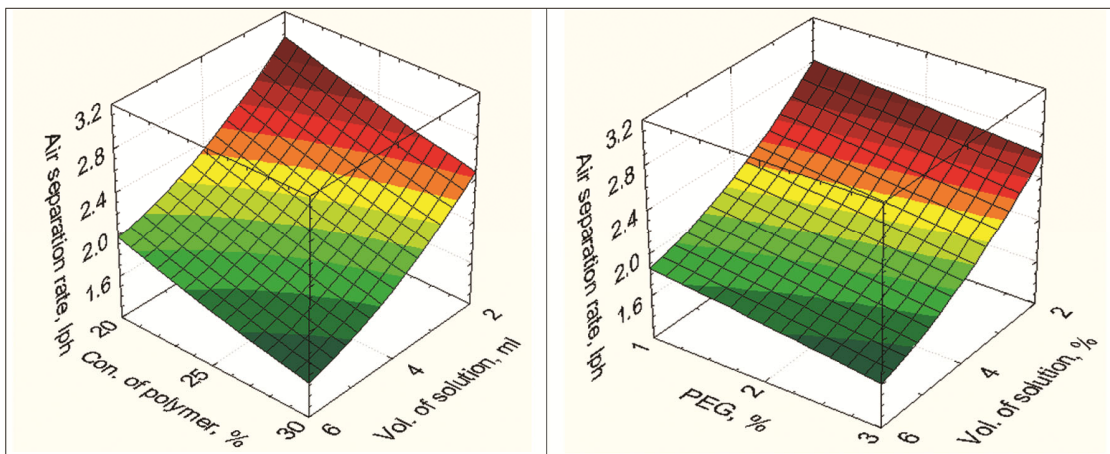


Fig. 14 — Graphical representation of Influence of independent variables on air separation rate

polyethylene glycol which act as a pore former. Influence of independent variables on air separation rate is shown in Fig. 14. It is observed from the figure, among the various independent variables, volume of polymer solution taken for electro spinning influences more on air separation, the impact of concentration of polymer solution and polyethylene glycol percentage is similar and it is next to the volume of polymer solution. Lower concentration of casting polymers leads to uneven and large pores

which increases the permeability of the gas molecules with reduced selectivity and also reduces the mechanical stability<sup>45,46</sup>. Higher concentration of the casting polymers leads to more uniform pores and reduced pore size which reduces permeability but increases the selectivity of gas molecules<sup>47,48</sup>. Therefore, an optimized polymer concentration is required to enhance the air separation rate by balancing permeability and selectivity<sup>49</sup>.

Table 3 — Regression equations for oxygen purity and air separation

Properties	Regression equation	R <sup>2</sup> value	F value
Oxygen purity	$-9.55+1.09X_1+1.98X_2+5.52X_3+0.377X_1^2-0.02 X_2^2+0.533X_3^2 - 0.037X_1X_2-0.4125X_1X_3 - 0.18 X_2X_3$	97.3	19.77
Rate of air separation	$5.42-0.536X_1-0.092X_2+0.062X_3+0.034X_1^2+0.001 X_2^2 - 0.001 X_3^2+0.0012X_1X_2-0.007X_1X_3 - 0.005 X_2X_3$	96.6	16.00

### Regression analysis

Regression analysis was carried out for the experimental results, based on the obtained coefficients. Regression equations are derived for the properties such as oxygen purity and air separation rate and these are given in Table 3. The R<sup>2</sup> value of both properties shows that the regression equation includes the impact of all the independent variables and its interactions. The independent variables significantly influence the oxygen purity and air separation rate. The F value shows that the coefficients significantly influence the output parameters of the process.

### Conclusion

Oxy-rich air separation is a tedious task from the atmospheric air and by membrane technology multilayer membrane is constructed with nano fibrous web as middle layer covered by substrate and top and bottom layer is covered with casting solution of polyamide. For the construction of membrane Box-Behnken experimental design is used and volume of polymer solution for electrospinning and concentration of casting polymer solution and concentration of polyethylene glycol are considered as independent variables. The PET/PP substrate offered support to the electrospun web which was kept above and at the bottom of it. SiO<sub>2</sub> nano particles are synthesized from rice husk by hydrothermal method, characterized and blended in electrospinning solution and casting polymer solution to enhance the selectivity of O<sub>2</sub> molecules from the atmospheric air. As per the experimental plan fifteen membrane samples were prepared and essential properties were measured. The electrospun web thickness and casting solution concentration directly influences the oxygen purity and air separation rate. Higher thickness of the membrane reduces the permeability and increases the selectivity parameters of target species.

Maximum oxygen purity was obtained from sample 4 which has electrospun web with 6 mL and 30% casting solution with 2% PEG. A higher range of gas flow rate was achieved from sample 1 which consists of Electrospun web using 2 mL and 20% casting solution with 2% PEG. It also gives

reasonable levels of oxygen purity. An appreciable scale of oxygen purity was obtained by the membrane which has fabricated electrospun web using 4 mL. It offered good separation efficiency due to the random arrangement of nanofibres, dense nature compared to 2 mL of nanofibrous web and high surface area contact with the gas species. A less dense electrospun web allows gas molecules to pass through the membrane easily. 2% PEG in the membrane imparts fewer uniform pores contrast to 3% PEG incorporated membrane which reduced the permeability rate to some extent. Hence the membrane with 2% PEG and 4 mL of electrospun web contributes to selectivity of oxygen gas molecules than permeability.

The membrane with 3% of PEG provides uniform pore distribution that depreciated the quality of the target gas separation but improves the air separation rate (LPH). While constructing 5 layered membranes (1 & 5 is casting layer, 2 & 4 is substrate and 3 is electrospun layer) SiO<sub>2</sub> present on the top, bottom and middle layer of the membrane helps to attract the O<sub>2</sub> molecules. The electrospun web which is present in the middle helps to attract and diffuse more quantity of O<sub>2</sub> molecule due to its high surface area to volume ratio and very smaller pore size. The surface porosity of the membrane and pore flow path was influenced by concentration of the PEG. Higher selectivity and reasonable permeability were acquired by the membrane structure that comprises 6 mL of electrospun web with 30% SiO<sub>2</sub>, 2% of PEG and 30% of casting solution.

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