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BULLETIN OF SCIENTIFIC RESEARCH

Multilayer Polymeric Nano composite Membrane for Oxygen Separation

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Abstract: Air separation is a process of separating primary components from the atmospheric air. Development of membrane technologies plays a key role in air separation. Multi-layer polymeric nanocomposite membranes have been developed by a novel technique using Polyacrylonitrile (PAN) and cellulose acetate (CA) along with nano silica particles (SiO2) to obtain a higher oxygen selectivity and permeability. For the construction of the multilayer membrane, the Box-Behnken design has been used by employing three independent variables namely PAN Electro spinning time, the SiO2 percentage in the PAN polymer and CA/PEG polymer concentration. The developed membranes have been characterized for its surface morphology and physical properties. Along with the analysis of compound desirability, the results were also subject to statistical analysis in order to form regression equations. The electro spun fiber diameter increases along with the concentration of SiO2 nanoparticles and the range is from 50 nm to 400 nm. Moreover, the maximum pore size on the surface of the membrane lies between 200 to 400 nm whereas the maximum percentage of oxygen purity obtained is 48 with the permeate flux of 5.45 cm3/cm2/min.

Keywords: Air separation, membrane, permeability, electrospinning, box-behnken.

1. Introduction

Air separation plays a major role in industries by enhancing its process performance. Two major types of primary components are present in the atmospheric air which is nitrogen and oxygen and an oxy-rich air is needed for many industrial applications [1]. Pure oxygen is required for the metal production process [2], medical processes, air humidification, combustion processes [3-7] and bioprocesses [8] including food packing industry [9]. The two major types of air separation processes are cryogenic distillation and pressure swing adsorption and are considered as traditional methods for air separation. A high amount of energy is required for separation process through cryogenic distillation [10] to freeze the atmospheric air up to -200^{o}C and it yields a purity range of 99 to 99.9% of O_2. Oxygen and nitrogen separation can also be conducted by employing pressure swing adsorption and vacuum pressure swing adsorption and it will result in a purity level of 90-95% for O_2/N_2 separation [7]. Membranes are pervasively being considered in separation processes due to simple methodology, low energy consumption [11] and low cost for of development [12-13]. In the development of membranes, polymers are widely used based

on their oxygen selectivity [14]. Nonporous polymeric membranes are mostly suitable for gas separation. However, membranes with pore size of 5 to 10 nm have also been used for gas separation in recent times. The mechanisms involved in the transportation of gas through the membrane can be classified based on the pore size such as Knudsen-diffusion, molecular sieving, and solution diffusion [15]. The solution-diffusion mechanism [16, 17] contains three steps namely sorption, diffusion, and desorption of gas species [18]. The quantity and quality of separated air species are governed by two main parameters which are permeability and selectivity [19]. Three types of membrane are used in air separation such as hollow fiber [20], spiral wound and flat sheet membranes [21]. However, disadvantages such as low purity level and poor mechanical strength of membranes exist leading to initiation of innovation and research in the area of the polymeric membrane so as to obtain higher purity and quantity of the selectively targeted gas. Polymers such as cellulose acetate, polysulfone, ethyl acetate, PTMSP [22] Polydimethylsiloxane (PDMS), Polyvinylchloride, Polyacrylonitrile (PAN), Polyaramid are used to construct the membranes for filtration and separation [23]. Initially, pure polymeric membranes were developed for air separation but it has some shortcomings such as less purity, chemical degradation, low mechanical strength and thermal stability [24].Mixed matrix membranes were also developed to attain higher quantity (permeability) of target gas species with improved mechanical properties by incorporation of nano metal oxides and fillers[24-28]. Despite the developments, difficulties in separation of binary gas species from the atmospheric air (for example O_2/Ar, H_2/N_2, and CO_2/O_2) by mixed matrix membrane continue to exist. The maximum possible O_2/N_2 separation factor for the commercially available membrane is 6-8 and the purity level of O_2 achieved was ~40%. [15]. Hence there is a strong need to construct a polymeric membrane with facile fabrication method, low cost, and high-level purity separation.

In this regard, we intend to develop multilayer polymeric nanocomposite membranes by a new methodology to attain higher purity of oxygen for commercial uses. In this research work, multilayer polymeric nanocomposites membranes have been developed using polyacrylonitrile (PAN) and cellulose acetate (CA) as polymers and nano silica particles (SiO_2) as a composite constituent. The properties of the obtained membrane were characterized for surface morphology, pore structure, oxygen separation efficiency and nature of particles. The data resulted from the filtration studies are reported and discussed in detail. Design of experiment was designed by Box-benhnken method for constructing membrane and the properties were analyzed.

Experimental

Materials

Polyacrylonitrile (PAN) $(C_3H_3N)_n$ [29] and cellulose acetate (CA) polymers are used for preparing the membrane by electro spinning and casting method respectively. N, N-Dimethylformamide (DMF) and acetone are used as solvents for dissolving PAN and CA polymer. In the membrane construction, polyethylene glycol (PEG 600) $(OH\ (C_2H_4O)_n\ H)$ was used as pore former to develop pores on the surface of the membrane [30-31].Silicon dioxide (SiO_2) has been synthesized by hydrothermal method [32] to mix in the polymer solution which makes the oxygen molecule to diffuse through the membrane during oxygen separation [33].

Mechanism of oxygen absorption by the membrane

Separation of oxygen from the mixture of various gaseous can be achieved by the membrane technology with the mechanism of

molecular sieving or solution diffusion. Oxygen separation mechanism was achieved based on the pore size of the membrane and by which permeates are transported from one part of a system to another by a concentration gradient as shown in figure 1. The quantity and quality of the selective gaseous component is determined by the selectivity of the polymer and the additives [11]. Solution-diffusion principle is generally applicable for polymeric membranes [34]. When the selective gas molecules are absorbed by the membrane surface, the molecules are randomly diffused to membrane and desorbed as permeate on the other side of the membrane. The rate of absorption and diffusion of oxygen is higher when compared to oxygen as the molecular size of the former (3.75Å) is lower than that of nitrogen (4.07Å).

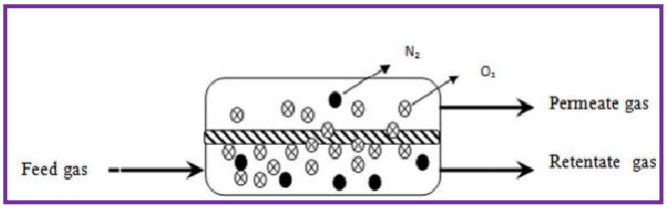


Figure 1. Schematic diagram of the principle of membrane gas separation process

Apart from the solution diffusion principle, the multilayer membrane performance has also been governed by the pore size and the tortuous nature of the pore path. In this research work, an attempt has been made to develop a multilayer membrane by combining the principle of molecular sieving and solution-diffusion mechanism.

SiO_2 incorporated electro spun web and its characterization

Silica nanoparticles have been synthesized by the hydrothermal method based on our previous work [32] and the synthesized silica particles were characterized by High-Resolution Transmission Electron Microscope (FEI Quanta FEG 200) and X-Ray Diffractometer (LabX XRD-6000). PAN polymer (8%) was dissolved in N, N-dimethylformamide and the different proportion of additives as SiO_2 (10%, 20%, and 30%) was added to the polymer solution as per the experimental plan (Table I). The solution was homogeneously mixed by ultrasonicator and then taken for electrospinning.

Table1. Experimental plan of nano composite membrane construction

Independent Variables	Levels		
	-1	0	1
Con. of SiO_2 in electro spun solution own (X_1)	10	20	30
Electro spinning time, h (X_2)	1	2	3
CA/PEG concentration,% (X_3)	10 %	15 %	20 %

The PAN and SiO_2 blended solution was taken in the 5mL syringe and fitted with a micro controlled syringe pump. The flow rate of the polymer solution was set as 0.75 ml/h. A DC supply voltage of 18 kV (Gamma High Voltage Apparatus, USA) was applied between the needle tip and the collector covered with aluminum foil. The polymer coming out from the needle tip was split due to the repulsive force set at the needle [35-37]. During this process, the solvent was evaporated and polymeric fibers were deposited on the aluminum foil in the form of the nanofibrous mat. The diameter of the nanofiber was characterized by scanning electron microscope (HITACHI S-3400 SEM) at the voltage of 10-15 kV. The principle of electro spinning apparatus was shown in figure 2.

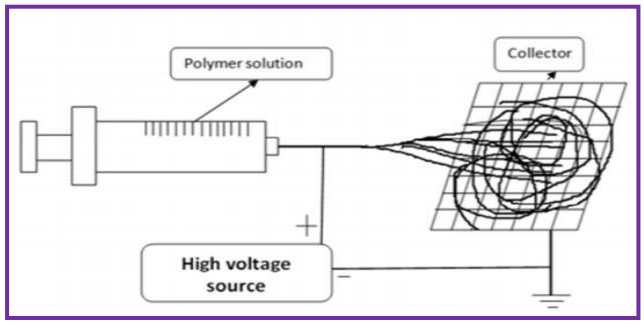


Figure 2. The principle of electrospinning apparatus

Non composite membrane construction

A polymeric solution of 10 ml was prepared with cellulose acetate polymer and polyethylene glycol (60:40) with the additive as SiO_2. The as-prepared solution was poured onto the surface of the electro spun web which was kept on the glass plate. The polymer solution was covered on both sides of the electro spun membrane and form s a multilayer membrane. After drying at room temperature, the prepared membrane was heat set at 80 °C. By various trials, the polymer/pore former proportion (cellulose acetate/PEG 600) was identified as 60:40 to get more uniform pores on the surface of the membrane with the additive (SiO_2) percentage of 30%. Further increase in additive nanocomposite resulted in the formation of multiple cracks on the membrane surfaces. The schematic diagram of the multilayer polymeric nanocomposite membrane and its cross section is given in figure 3 (a) and (b). To analyze the influence of various process variables on purity and permeability of oxygen, an experimental plan has been designed based on Box-Behnken method.

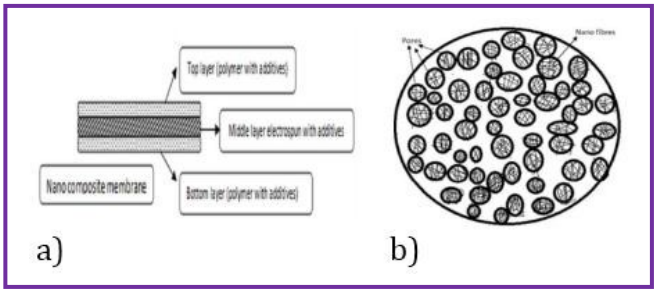


Figure 3. a) Principle of membrane construction b) cross section of the membrane

Table 2. Non composite membrane construction

S. No	X_1 SiO_2%	X_2 Time h	X_3 (CA & PEG) %	Thickness (mm)	GSM of Membrane	Permeate Flux ($cm^3/cm^2/m$)	O_2 %	Compound Desirability	Rank
1	10	1	15	0.288	206	7.71	30	0.68	8
2	30	1	15	0.401	187	6.07	37	0.68	7
3	10	3	15	0.431	210	5.83	35	0.75	3
4	30	3	15	0.436	214	5.45	48	0.87	1
5	10	2	10	0.418	133	7.24	31	0.00	-
6	30	2	10	0.463	136	7.74	33	0.74	4
7	10	2	20	0.558	270	7.47	36	0.71	5
8	30	2	20	0.448	253	9.89	28	0.68	6
9	20	1	10	0.423	151	6.29	27	0.43	13
10	20	3	10	0.427	154	2.39	35	0.00	-
11	20	1	20	0.432	210	2.44	32	0.46	12
12	20	3	20	0.531	274	4.78	40	0.75	2
13	20	2	15	0.368	202	7.80	28	0.54	9
14	20	2	15	0.331	188	8.24	29	0.54	10
15	20	2	15	0.301	191	8.85	31	0.54	11

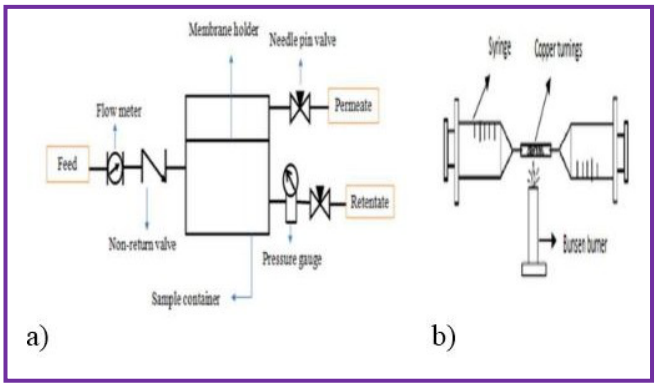


Figure 4 a) Schematic diagram of air separation equipment b) air quality evaluation equipment

The SiO_2 percentage in electro spinning solution, electro spinning time and polymer concentration (CA/PEG) were taken as independent variables to design the experimental plan as shown in Table I. Based on Box-Behnken design, fifteen different combinations of independent variables have been derived and given in Table II. Experiments were conducted and fifteen samples of the multilayer polymeric nanocomposite membrane have been obtained.

The as prepared membranes were characterized for thickness; permeate flux, oxygen purity and surface morphology. The principle diagram of air separation unit and oxygen quality evaluation unit are shown in figure 4 (a) and (b) respectively.

The prepared membrane is placed on the membrane holder and the fresh dry air is taken from a compressor. The air is fed to the container by air flow meter with the feed rate of 2 l/m. The retentive and permeate valve is kept at the open condition to minimize the pressure generation. The oxygen molecules are attracted by the membrane surface and it is permeated through the membrane by molecular sieving and solution-diffusion mechanism. The oxy-rich air is collected from the permeate valve. The permeate flux was calculated by Equation 1

$$J = \frac{Q_p}{A_s} \quad (1)$$

Where J = permeate flux ($cm^3/cm^2/min$)

Q_p = permeate flow (cm^3/min)

A_s= surface area of the membrane (cm^2)

The collected oxy-rich air was taken in 100 ml glass syringe and it was connected to the glass tube which contains extra pure copper turnings. The other end of the glass tube is connected to the opposite syringe. Bunsen burner was used to heat the copper turning. When heating the glass tube, the collected oxy-rich air is pushed from opposite syringe and vice-versa. Due to the application of heat, the copper is converted into cupric oxide and the color of the copper turning becomes black. The steady state volume of air in the syringe is observed after the reaction between oxygen and copper has been completed and finally, the amount of the residual air is noted.

Characterization and Properties

Characterization of SiO_2

The synthesized silica particles have been analyzed by TEM and its particle size was found to be in a various range from 30 to 67 nm as shown in figure 5.

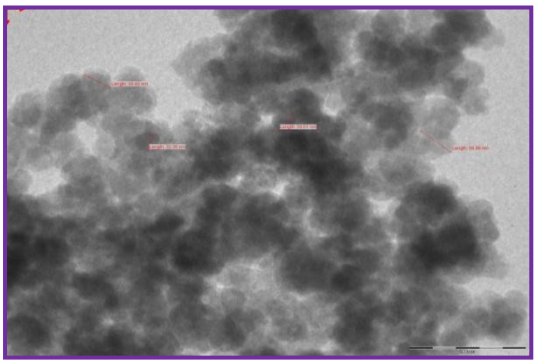


Figure 5. TEM image of silica nano particles

The morphology of the particles is found to 3-dimensional with amorphous nature. Further, in order to ascertain the nature of obtained silica, X-ray diffractogram was performed. Figure 6 shows that the resulted silica exhibits only a broad reflection in at 2θ = 22°, which leads to an inference that the particles are in amorphous nature [30]. The

obtained results are in good agreement with that of TEM.

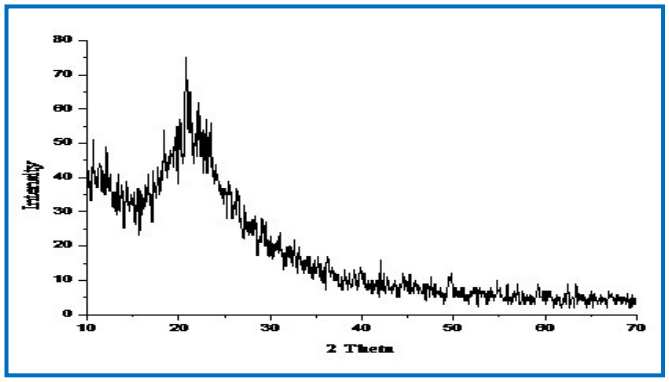


Figure 6. XRD pattern of silica nano particles

Characterization of electro spun web

The Polyacrylonitrile (PAN) was spun with different concentrations of additive SiO_2 (10%, 20%, and 30%) to form an electro spun web and the scanning electron microscope images of the same were shown in figure 7. At lower concentration of SiO_2 (10%), the formation of beads was less and uniform fibers were observed, whereas at higher concentration (30%) the formation of beads was more. The average fiber diameter is 128 nm for 10% SiO_2 added PAN nanofibres, 156 nm for 20% SiO_2 added PAN fibers and 181 nm for 30% SiO_2 added PAN nanofibres.

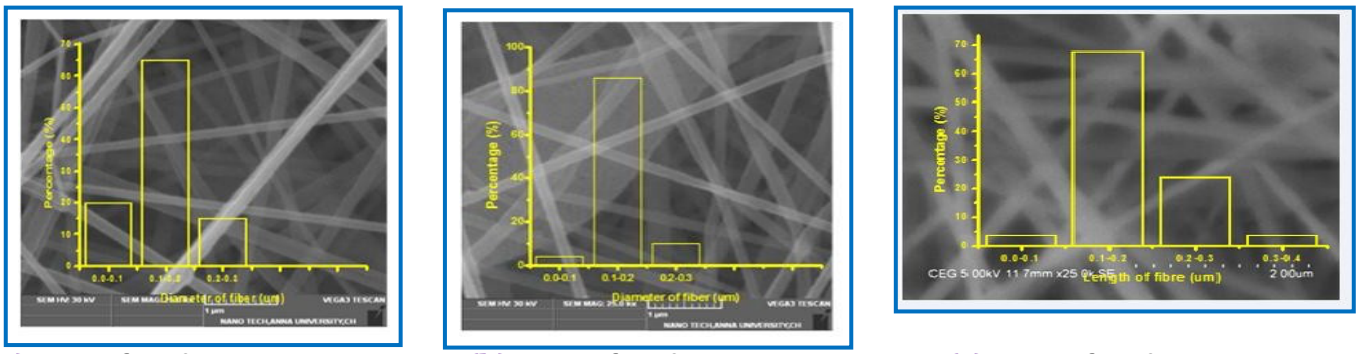
Characterization of polymeric nanocomposite membrane

As per the experimental plan, fifteen different multilayer nanocomposite membranes have been prepared with 10 ml of the blended polymer solution as casting polymer solution. A blend of cellulose acetate and PEG forms a layer with pores on the surface and 30% SiO_2 particles are also homogeneously dispersed in the polymer solution to attract oxygen molecule. The pores on the surface of the membrane have been influenced by the quantity of PEG taken in each concentration of cellulose acetate polymer solution. The thickness of the multilayer nanocomposite membrane depends on the time taken to spin the PAN electro spun layer and the concentration of the cellulose acetate/ PEG solution. The surface morphology of the membrane is depicted in figure 8. Rougher surface with randomly distributed pores on the surface has been observed. The pore range of the membranes was characterized as 20 to 300 nm and it plays an essential role in penetration of the air molecules with oxygen to the electro spun fibrous layer. The cross section of the scanning electron microscope image of the membrane is shown in figure 9 and it shows that the random arrangement of fibers with the tortuous path in its structure.

Results and Discussion

Effect of process variables on permeate flux and oxygen purity

The effects of process variables on permeate flux and the oxygen purity are explained graphically in figure 10 and 11 respectively while nanofibres and the physical properties of the samples are given in Table II.



(a) 10% pf SiO^2 in PAN **(b)** 10% pf SiO^2 in PAN **(c)** 30% pf SiO^2 in PAN

Figure 7. Percentage of SiO2 in PAN

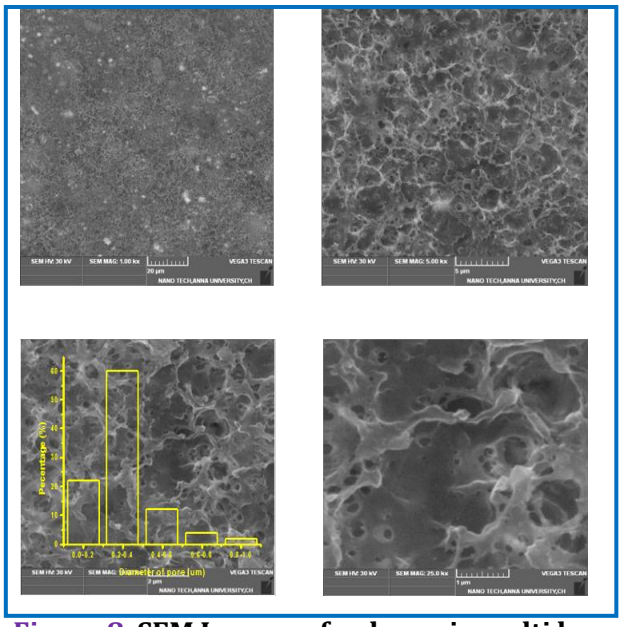


Figure 8. SEM Images of polymeric multi layer nanocomposite membrane

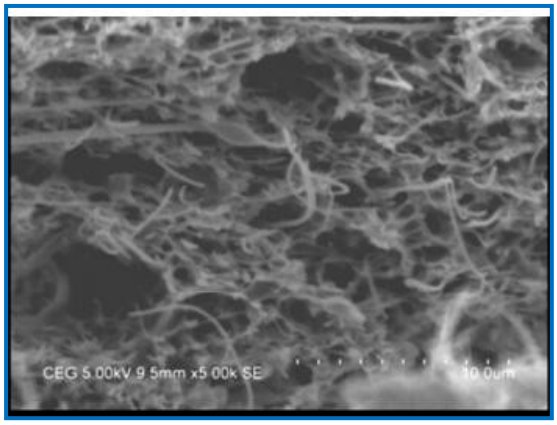


Figure 9. SEM image of the cross section of the polymeric multi layer nano composite membrane

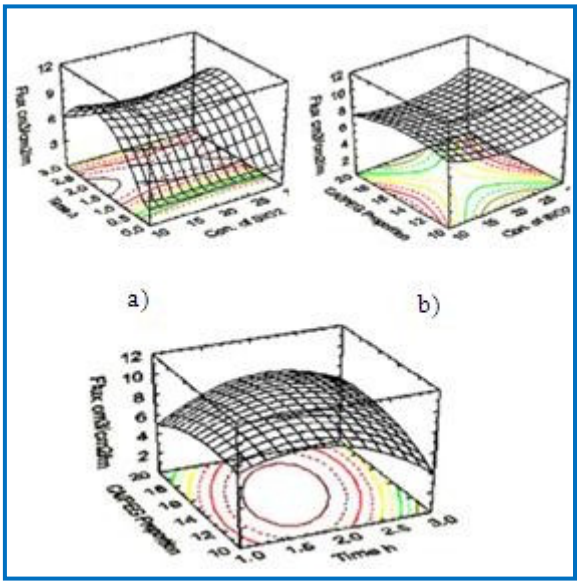


Figure 10 (a), (b) & (c) Effect of process variable on permeate flux

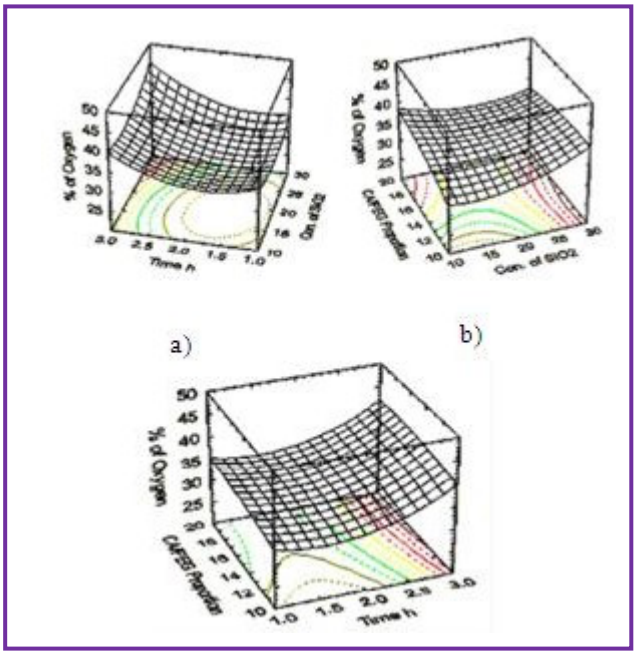


Figure 11 (a), (b) & (c) Effect of process variable on oxygen purity

Table2. Regression equations

Property	Regression Equation	R^2	F
Oxygen quality	$31.75-0.70\ X_1-18.33\ X_2 + 2.05X_3 + 0.03X_1^2 + 4.83\ X_2^2 - 0.02\ X_3^2 + 0.15\ X_1X_2 - 0.05\ X_1X_3$	86.1	1.77
Permeate flux	$2.85 - 0.61\ X_1 + 6.46\ X_2 + 0.70\ X_3 + 0.01\ X_1^2 - 3.07\ X_2^2 - 0.05\ X_3^2 + 0.03\ X_1X_2 + 0.009\ X_1X_3 + 0.31\ X_2X_3$	91.4	5.87

The process variables have a significant effect on different properties of the membrane. The proportions of CA/PEG and electro spinning time affects permeate flux because the random distribution of PEG in the polymer solution and the quantity of the PEG in each concentration influences the pore formation and pore depth on the surface of the membrane.

The removal of PEG in the membrane by evaporation results in the formation of pores and a larger number of nanopores with fewer submicron pores formed on the surface of the

membrane. This combined porous nature of the membrane results from higher permeates flux with purity without any external pressure. The concentration of SiO_2 and electrospinning time affects the oxygen purity due to its attraction of oxygen molecule. The density of OH polar group in the polymer matrix was enhanced by incorporation of silica nanoparticles and it establishes the polar spaces at the intersection of the particles and polymer. The presence of polar space increases the solubility coefficient of condensable gases. Solubility nature of gases is decided by their condensability. The permeability of oxygen increases due to the presence of free spaces at the interface of the polymer-silica in the membrane structure. This leads to enhancement of oxygen solubility [33]. Further increase in electro spinning time leads to increase in thickness of the membrane which affects the diffusion rate of the oxygen molecules through the membrane, and it also increases the oxygen purity due to increased exposure of the active sites of the SiO_2 molecules on the surface of the nanofibres.

From figure 10 (a), (b) and (c), it was observed that higher and lower electro spinning time decreases the permeate flux due to the quantity of fibers produced. The extreme values of polymer concentrations were shown as restricted flow of air through the membrane, more layers of electro spun fibres are delivered. When the time was higher, resulted from restriction of flow of air and lowers the electro spinning time with same quantity of the casting polymer, leads to blocking of pores of electro spun web and reduces flow of air. Higher permeate flux has been achieved with electro spinning time of 2 h and 15% concentration of polymer (CA/PEG).

From the figure 11 (a), (b) and (c), it was observed that higher concentration of SiO_2 (30%) with electrospun time (3 h) gave rise to high oxygen purity due to its effect on attraction and diffusion of oxygen molecule through the membrane.

Regression analysis and compound desirability analysis

Regression equations for oxygen purity and permeate flux was given in Table III. Compound desirability function has been used to identify the best sample for oxygen purity and permeate flux and the compound desirability values of all samples are given in Table II. The weightage of the property was given as 80: 20 for oxygen purity and permeate flux respectively for compound desirability analysis. As per the rank, variables such as 30 % SiO_2, 3 hours of electro spinning time and 15 % concentration of blended polymer with CA/PEG of 60:40 proportion gave rise to highest oxygen purity with optimum flux. The absorption of oxygen is facilitated by the addition of SiO_2. The electro spun web and the casting polymeric solution also contain SiO_2 nanoparticles. Hence, the polymeric solution covered the electro spun web on both sides with incorporated 30 % SiO_2 nanoparticles and also attracted oxygen molecules.

CA/PEG proportion plays a crucial role in oxygen permeability and pore formation. Oxygen molecule along with air penetrates through the nonporous of the membrane which is formed by the addition of PEG. The highest concentration of CA/PEG that is 20% (60:40) gives lesser oxygen purity and a permeate flux value because the high CA/PEG proportion may have blocked the pores in the electro spun web.

The medium polymer concentration of CA/PEG proportion (15%) of 60:40 has resulted in higher oxygen purity and permeate flux value due to the formation of fewer microspores on the surface and the passing off through the membrane with a consistent rate. 3 h of electro spun time produces a higher amount of fibers which is directly proportional to the thickness of the fibrous web. The Higher thickness of the membrane restricted the air flow and increased the selectivity of oxygen molecules; hence higher separation of oxygen from the feedair is attained. By varying the process variables, permeate flux values ranging

from 2.39 to 9.89 $cm^3/cm^2/min$ and oxygen purity in the range of 27% to 48% can be attained.

Conclusion

Separation of oxygen is an important process for commercial application and the performance of oxygen separation membrane varies depending on the process variables. A novel multi-layer polymeric nanocomposite membrane has been developed to extract oxy-rich air from the atmospheric air without any external pressure application. The electro spun fiber with porous polymeric layers has been developed by combined mechanism of molecular sieving and solution diffusion for separation of air. By varying the process variables, the maximum purity of oxygen was achieved as 48% and this can be attributed to the SiO_2 incorporated surface layer and electro spun core. The synthesis of SiO_2 is a cost-effective method and the yield of SiO_2 is very high when compared to other SiO_2 synthesis methods. The selective oxygen purity and permeate flux can be derived from the regression equations. By the compound desirability function, the optimum best sample has been identified with respect to permeate flux and oxygen purity.

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