

Deep eutectic solvent functionalized mesoporous silica SBA-15 based mixed matrix polymeric membranes for mitigation of CO₂ (Extended Version)

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ABSTRACT

The carbon dioxide (CO₂) separation can be enhanced by using modified materials like a deep eutectic solvent (DES) modified mesoporous silica SBA-15 in polymeric support i.e polysulfone via mixed matrix membranes (MMMs). The pure SBA-15 and DES are potential candidates for the CO₂ capturing and their combination has not been reported yet. In this work, a fresh DES was synthesized by combining equal concentrations of Decanoic acid and choline chloride by mass. MMMs were fabricated by DES functionalized SBA-15 (DES-SBA) filler. The DES-SBA-based polymeric MMMs of different compositions, from 5% to 20% with the difference of five

each, were developed and subjected to the gas permeation analysis to evaluate relative selectivities and permeabilities of membranes. The DES-SBA-based MMMs were characterized by SEM and FTIR to obtain distribution analysis of filler in the polymer matrix as well as the cross-sectional and surface morphology and the structural analysis of membranes, respectively. The gas permeation evaluations have been utilized to mixed and pure gas samples and the findings of selectivities for CO₂/N₂ and CO₂/CH₄ and permeabilities of synthesized MMMs are being reported. The performance of the MMMs has been enhanced via functionalization of SBA-15 by DES as compared to the neat polysulfone (PSF) based simple membrane.

Keywords: Deep eutectic solvent; Selectivity; Permeability; Carbon dioxide; Mesoporous Silica SBA-15

1. INTRODUCTION

Human activity played a significant role in the release of CO₂ gas into the atmosphere, which is the primary source of air pollution and global warming [1]. The fossil fuels combustion, streams of natural gas, coal gasification products and anaerobic digestion causing biogas formation are all common sources of CO₂ [2]. The consequences of CO₂ presence in the atmosphere results in defrosting icy masses, rising ocean levels, loss of the fertility of earth, heavy rain fall expanded global temperature, developing long seasons, and relentless cyclones [3, 4]. Hereafter, It has proven to be a significant difficulty for mankind to spare CO₂ from the biosphere [5]. The removal of deleterious gas or impurities from a combination of many gases is a big task on an industrial scale. [6]. The cryogenic separation, chemical absorption using a reactive solvent and pressure swing adsorption are the most often used industrial procedures for this purpose [7]. Furthermore, these approaches have a high initial investment, require complex equipment, and use a lot of energy [2].

Now-a-days, the demand of using environmental friendly, cost effective, and energy efficient conventional technology for removal of CO₂ is increasing gradually and has colossal marketplace from industrial point of view such as purification of H₂, treatment of petroleum gas, CO₂ capture, and expulsion of CO₂ from flue gas [8, 9]. The most effective technology used today is membrane-based gas separation innovation [10]. However, membranes made of polymeric materials experience perm-selectivity exchange off limitation [11]. So as to overlap

this confinement, mixed matrix membranes (MMMs) are now developed [12-14]. In general, two or more diverse materials having discrete properties are utilized to make MMMs. One material called polymer, constitute a continuous phase and other one named filler or additive constitute the dispersed phase of membrane. This combination impart distinctive transport properties to the membrane system [10].

The polymer ought to have high selectivity and high permeability of CO₂ to achieve separation. For the case of CO₂/N₂ or CO₂/CH₄ separation, as reported in literature that kinetic diameter of N₂ or CH₄ molecule is more than that of CO₂ molecule, the polymer had diffusivity-selectivity >1. For the case of CO₂/H₂ separation, diffusivity selectivity <1 as the kinetic diameter of H₂ is smaller than CO₂. In order to encounter high selectivity for separation of CO₂, the polymer ought to have high reactivity selectivity or solubility selectivity. Consequently, the functional groups should be adhered to the polymer, which just have high affinity for CO₂ molecules. Moreover, the polymer ought to have high mechanical stability as sources of CO₂, temperature, content %, and pressure fluctuate widely. The CO₂ gas feeds from industries encompass numerous amount of other contaminant gas such as NO_x, H₂S, SO_x, etc., so chemical strength of polymer is important too [15]. The another technique to attain better perm-selectivity results is the functionalization of the additive or filler. The studies are being carried out to incorporate functionalized or modified filler into membranes to enhance the proficiency of gaseous separation [16]. However, only hinderance in the execution of widespread variety of polymeric materials lies in intrinsic perm-selectivity tradeoff, which is clarified by Robeson in the upper bound curve [17].

The polysulfone is used as polymeric support materials in membranes due to its better strength, high thermal stability, non-corrosiveness and easy process ability [18-20]. The efficiency of MMMs depends upon the filler attribute as its agglomeration among each other [21] and its attraction with the polymer are the main concerns [22]. The filler distribution on the whole membrane is also depends upon pore properties, shape and particle size of filler as the gas separation effected by these factors [2, 23]. The mesoporous silica SBA-15 is a potential candidate for CO₂ separation via MMMs as it has large pore size and surface area and high thermal stability. The pore size of SBA-15 can be tuned by synthetic conditions and it has neat columnar hexagonal pore structure. The Hydrolysis-condensation hydrothermal reaction is generally used to synthesize SBA-15, in which Pluronic P₁₂₃ (EO₂₀PO₇₀EO₂₀) is used as template

to grow SBA-15 crystals [24]. The condensation process controls the SBA-15 morphology [25]. The use of mesoporous silica SBA-15 as filler in MMM has already been reported [26]. In the current study, for the sake of functionalization of SBA-15, DES is formed by combining decanoic acid and choline chloride. As the decanoic acid has carboxyl group and choline chloride has amine group so this combination has been made to attract CO₂. In the MMMs, the polymeric support matrix is polysulfone (PSF) and DES-SBA is filler which is a hybrid material made up of inorganic and organic compounds. The various compositions are used to develop MMMs, the membranes are analyzed by different characterizations and the performance of membranes is estimated by gas permeation testing machine. The DES-SBA based membranes has been proved better membranes for the separation of CO₂ from the mixture of gases like CO₂/N₂ and CO₂/CH₄.

2. MATERIALS AND METHODOLOGY

2.1 Materials

The Choline chloride, Decanoic acid, Pluronic P123 and Polysulfone (M.W = 22,000) were purchased from Sigma-Aldrich, USA. The fisher scientific provided Tetrahydrofuran (THF). Furthermore, analytical grade reagents (like CTAB, ethanol, TEOS etc.) were used during experimentation. Deionized (DI) water was utilized for washing purpose.

2.2 Synthesis of SBA-15

According to already reported method [27], the SBA-15 was synthesized. Shortly, at 40 °C, the Pluronic P₁₂₃ taken 2 g and dissolved in 12 ml DI water, then it was stirred for 3 hrs after adding 2 M HCl (60 ml). At 100 °C, for 24 hrs, the reaction was taken place in the mixture when it was left in the air tight hydrothermal autoclave. The yield obtained from Teflon-lined hydrothermal autoclave was filtered and washed with DI water and dried. Finally, the SBA-15 was calcined at 600 °C for 6 hrs [28, 29].

2.3 Formation of DES

Deep eutectic solvent can be formed by combining safe and cheap components, minimum two or more than two. These components are categorized as acceptor and donor as shifting of hydrogen

bonds takes place between them so known as hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD). If a homogeneous mixture is formed by mixing HBD and HBA and the melting point (MP) of mixture becomes lower in comparison with the individual component, the mixture is said to be DES [30-32]. Hence, DES was produced via combining decanoic acid i.e HBD and choline chloride i.e HBA. The mixing was take place at 80 °C by magnetic stirrer adjusted at 100 rpms for 3 hrs in a round bottom flask. The homogeneous composition was formed using equal concentrations of the constituents by mass. The DES formed becomes solid below 80 °C that has a great difference from the MPs of the individual constituents which confirms the synthesis of DES [33, 34]. **Fig. 1** described the whole synthesis.

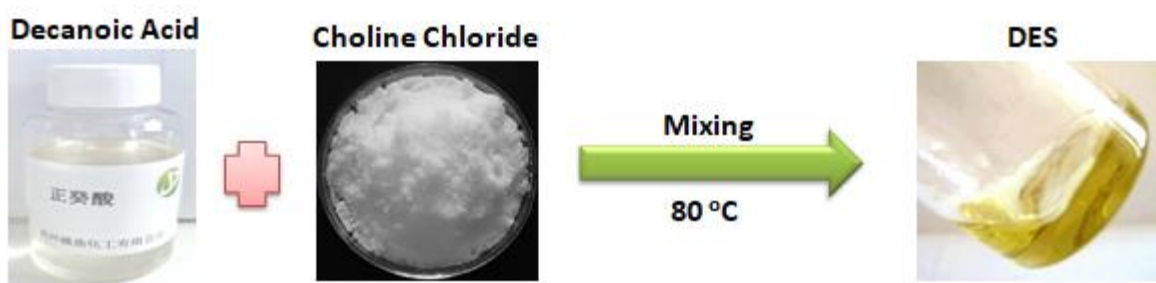


Figure 1: Synthesis of Deep Eutectic Solvent.

2.4 Surface tuning of SBA-15 by DES

Functionalization of SBA-15 using DES is shown in the **Fig.2**, in which SBA-15 was modified by DES with the help of a technique known as solvent evaporation. The SBA-15 and DES was combined in ethanol with eight parts of SBA-15 and one part of DES by mass and mixed vigorously for 6 hrs, then ethanol was evaporated from the mixture at room temperature by undercover placing for 24 hrs. The yield material was placed in an oven for 1 hr for further drying at 40 °C. The product in the form of dry powder was named as DES-SBA [35, 36].

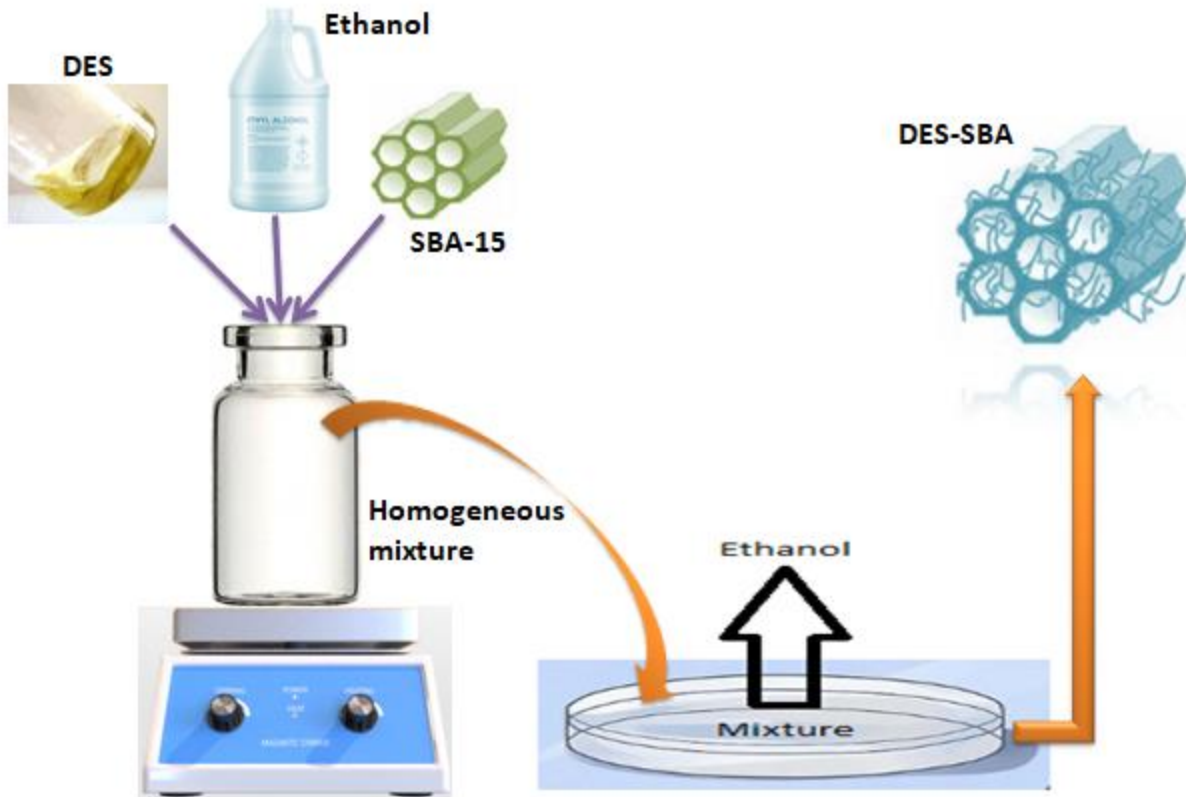


Figure 2: The process flow of Modification of SBA-15 by DES.

2.5 Development of MMMs

The MMMs were formulated by unification of various concentrations (wt. %) of functionalized DES-SBA into the doped solution (PSF/THF) as shown in **Table 1**. First of all, polysulfone polymer was taken in THF solvent and allowed the resultant solution to stir for a period of 3 hrs at 35°C. When polysulfone dissolved and homogenous solution formed then different wt. % of DES-SBA filler was poured smoothly and mixed for next 24 hrs. The stirring process is stopped, and scotch bottle is kept static in previous position in order to remove trapped air bubbles, and then membrane solution was spread in the petri-dish ensuring its bottom was flat and left to dry with exterior of petri-dish covered by aluminium foil, having small holes on it, for a period of another 24 hrs [18-20, 35]. The schematic diagram of MMMs formulation is displayed by **Fig. 3**.

Table 1: The Composition of MMMs.

Membrane	Composition	PSF	DES-SBA	THF
DS-0	PSF	4.8	-	95.2
DS-1	DES-SBA 5%	4.8	0.238	94.962
DS-2	DES-SBA 10%	4.8	0.476	94.724
DS-3	DES-SBA 15%	4.8	0.714	94.486
DS-4	DES-SBA 20%	4.8	0.952	94.248

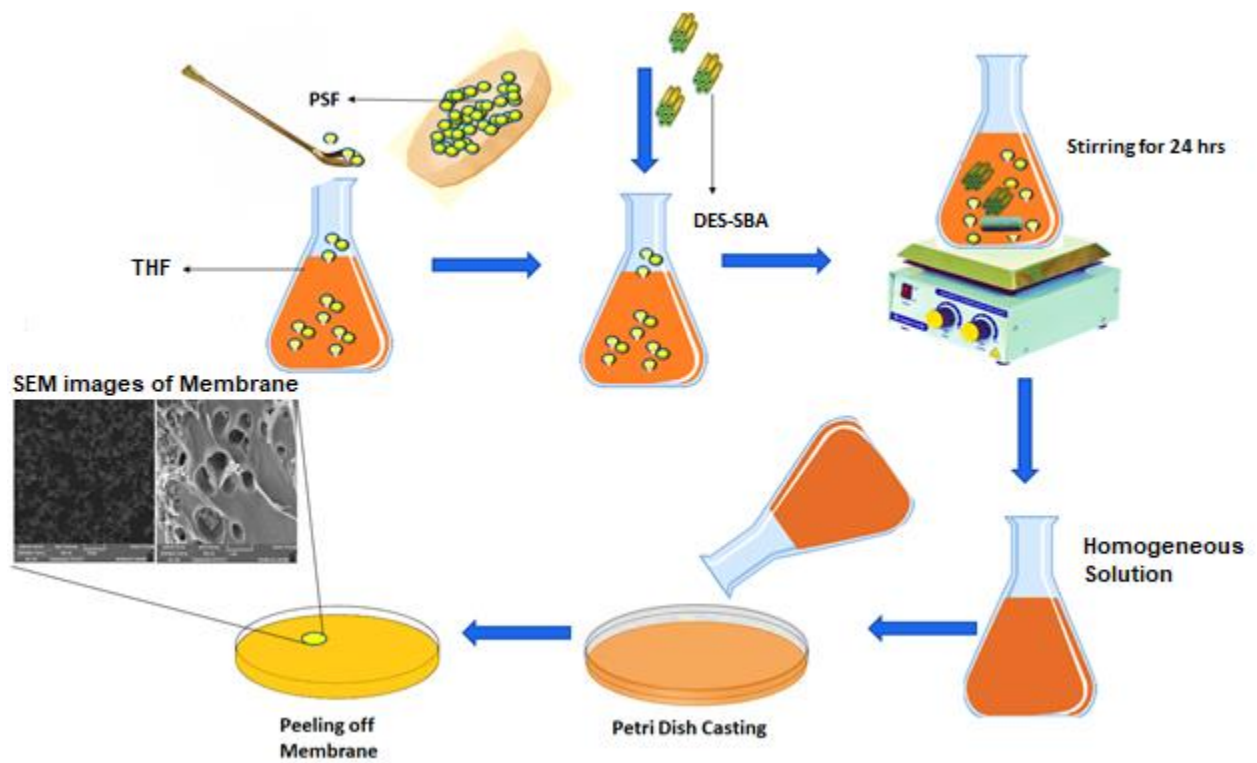


Figure 3: The complete process of membrane fabrication.

3. RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy (SEM)

The cross-sectional and surface morphology of all formulated membranes were characterized by SEM (Tescan Vega, LMU). To analyze cross-sectional analysis of formulated membranes, samples were prepared in liquid nitrogen and coated with layer of gold and scans are performed at 15KV voltage and various magnifications. **Fig. 4** shows the cross-sectional and surface of various compositions of MMMs. It is cleared from the morphology that membranes porosity is increasing when filler loading increased [37]. The surface images revealed the filler distribution in the polymer matrix and the cross-section images exhibits the clear pores in the MMMs of all compositions. The dispersion of filler and the pores in membranes are the significant factors for the passage of CO₂ [38].

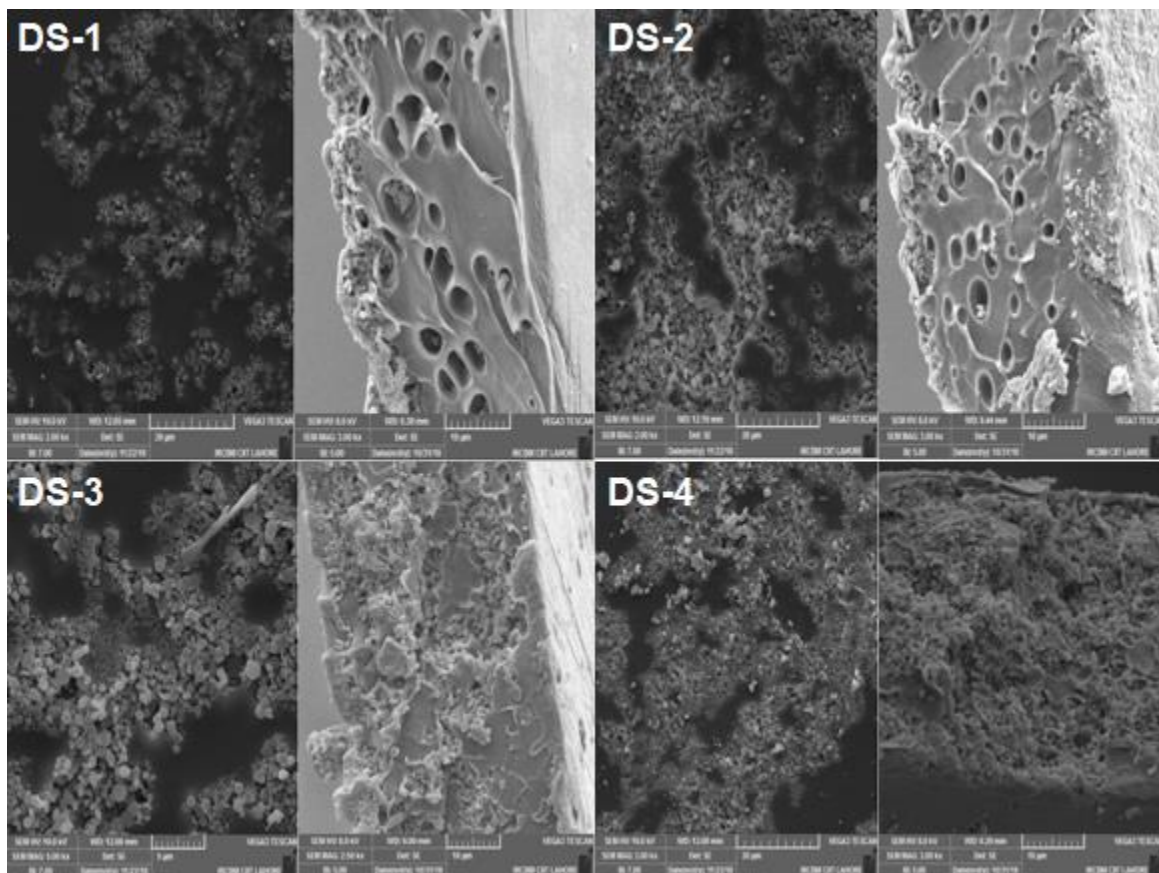


Figure 4: Surface and Cross-sectional morphology of synthesized MMMs

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Bonding chemistry of MMMs was analyzed by FTIR (Nicolet 6700, USA) at spectral range 650-1700 cm^{-1} . The resolution taken was 8 cm^{-1} and the MMMs were scanned 128 times. **Fig. 5** exhibits spectra of FTIR for silica, functionalized silica, polymer and MMMs. In figure, polysulfone peaks are depressed by increasing amount of filler. This depression describes the interaction of filler with polymer i.e PSF. And the characteristic peaks of the mesoporous silica have also been overwrite among these peaks. It can be seen that the characteristic peaks of the components of the filler cannot be seen clearly the reason is that the modifying material is used in such a small quantity that cannot be observed in these cases. The characteristic peaks of the PSF and the other materials used in the filler are given the following **Table 2**.

Table 2. The characteristic wave number of different bonds stretches

Spectral assignment	Wave number, cm^{-1}
C_6H_6 ring stretch	1488-1587
$\text{CH}_3\text{-C-CH}_3$ Symmetric stretch	1410,1364
C-O asymmetric stretch	1244,1014
S=O Symmetric	1308,1150
C-SO ₂ -C asymmetric stretch	1322
Si-O-Si stretch	1100

In simple polysulfone membrane, all the characteristic peaks of polysulfone can be seen in the spectra. For example the peak of benzene ring can be seen at 1490 cm^{-1} , the symmetric $\text{CH}_3\text{-C-CH}_3$ stretching can be seen at 1410 cm^{-1} , the peaks of symmetric S=O and asymmetric C-SO₂-C are in range of 1300-1350 cm^{-1} . The sharpness of the two peaks in the 900-1200 cm^{-1} is diminishing for the membranes that means the interaction between the PSF and DES-SBA [39, 40].

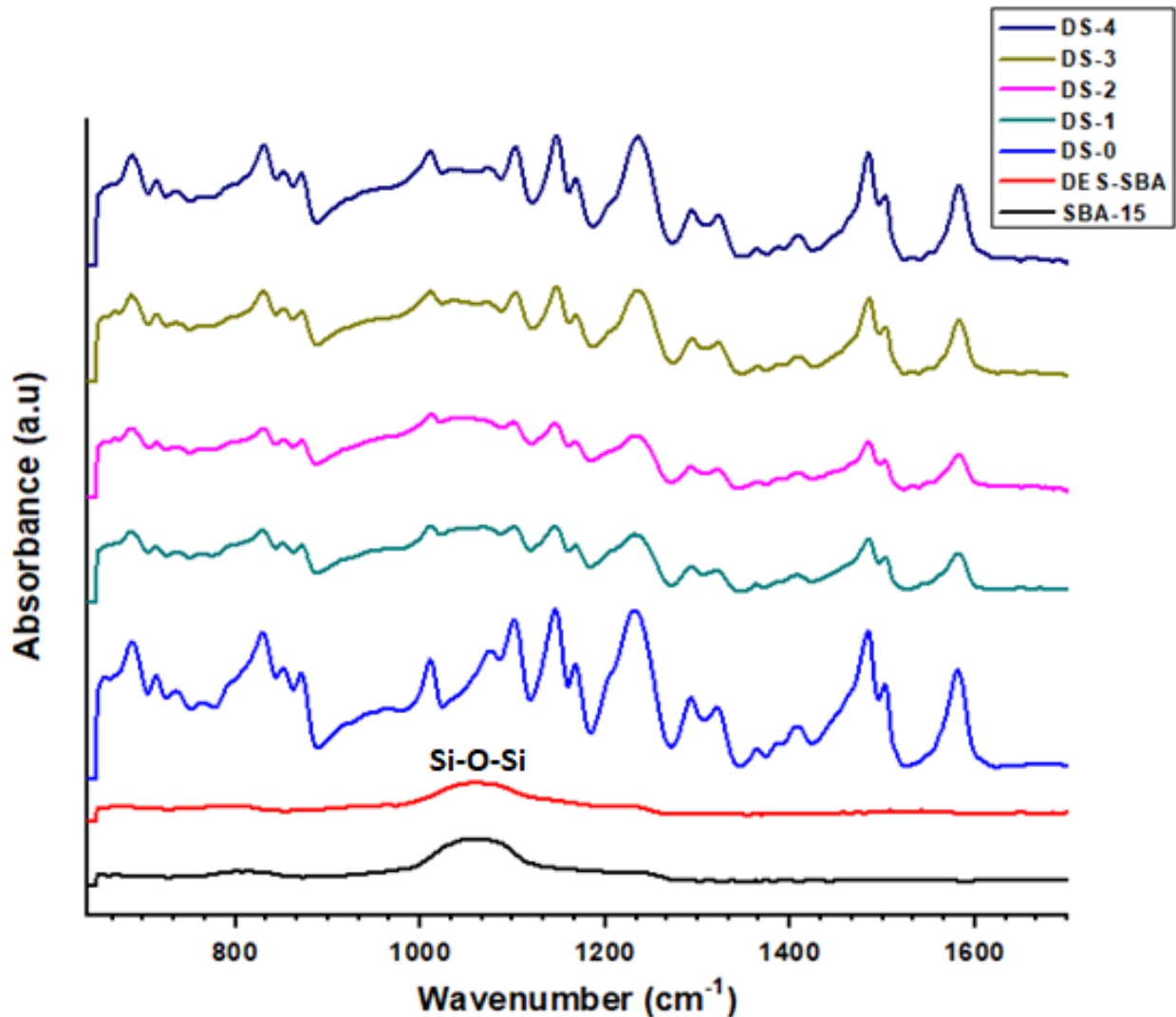


Figure 5: FTIR Spectra of SBA-15, DES-SBA and the synthesized MMMs

3.3 Analysis of Gas Permeation

The selectivities and permeability of CO₂ were evaluated at 10 bar pressure and room temperature and the results can be seen in the **Fig. 6(a & b)**. Permeability of pure PSF membrane DS-0 was 6.06 barrers and increased upto 22.3 barrers by using 20% filler in DS-4 membrane. The permeability of CO₂ has been gradually raised by enhancing loading of DES-SBA which indicates the elementary characteristic of the filler, which refers to the specific pores to give route for the selective gas. The selectivity of mixed gas pairs CO₂/CH₄ and CO₂/N₂ was also increasing by increasing filler loadings and a very large difference was reported in comparison

with the pure PSF membrane DS-0. In CO₂/CH₄ case, the selectivity of DS-0 was 23.31 and it increased upto 57.18 for DS-4 gradually and in CO₂/N₂ case the selectivity of DS-0 was 25.44 and it was increased upto 59.9 for DS-4 gradually. This rise in selectivities of MMMs refers to sturdy interface between the polymer and DES-SBA filler. The increasing concentration of DES-SBA filler in polymeric complex allowed the molecules of gas to diffuse into the pores of MMMs following the mesoporous channel and resulted in the high performance of CO₂ mitigation from mixed gases. Hence, permeation analysis is highly supporting hypothesis of the study.

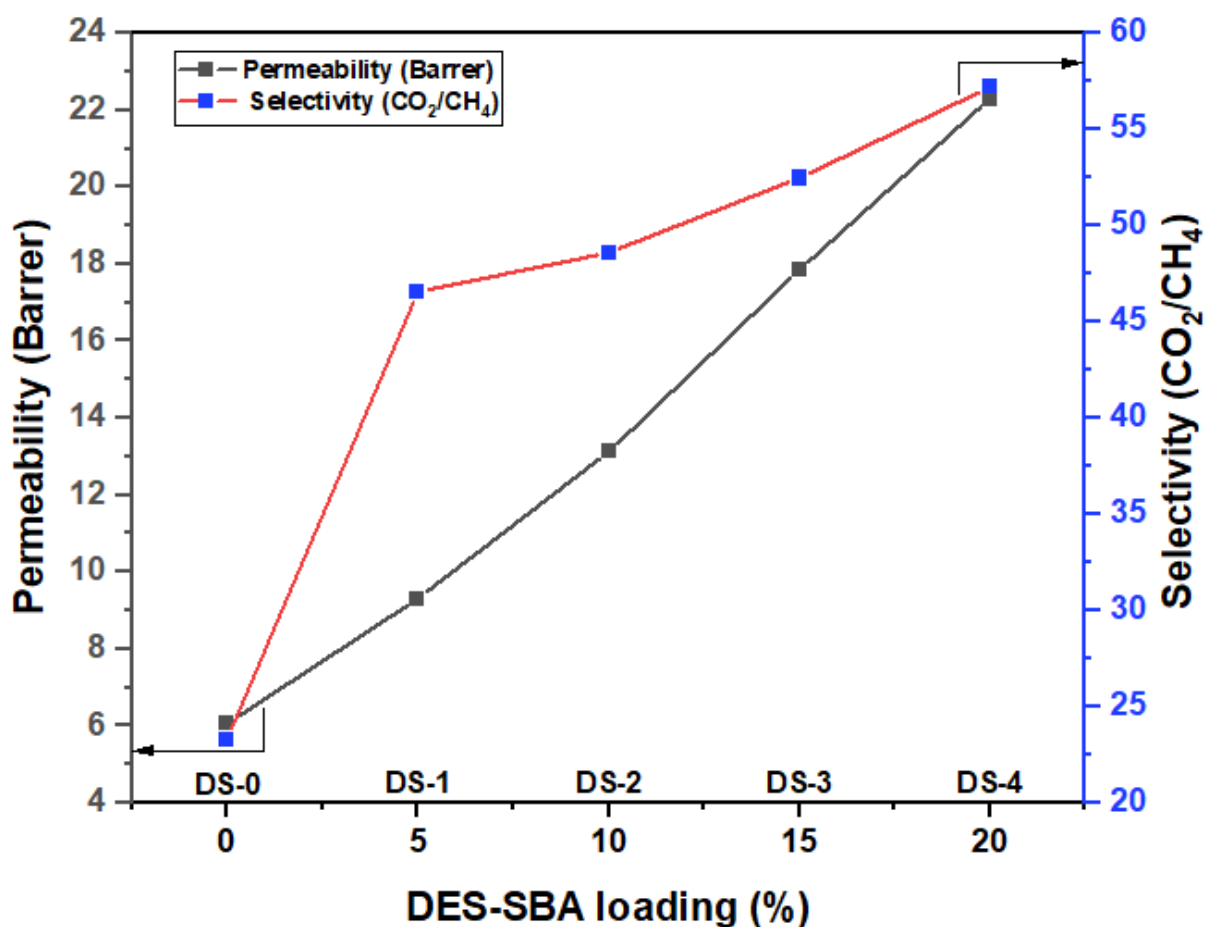


Figure 6(a): The permeabilities and the selectivities of Synthesized MMMs for CO₂/CH₄ gas mixture

The incorporation of functionalized SBA-15 with additional polar groups that are amine group from choline chloride and carboxyl group from decanoic acid in MMMs was applied to enhance the capability of MMMs to remove CO₂ from the mixed gases. The synthesized DS-1, DS-2, DS-

3 and DS-4 membranes exhibited higher selectivity and permeability of CO₂ in comparison with DS-0. The reason is that these functional groups has strong affinity for CO₂ and give a push towards the solubility of CO₂. Thus, a robust linkage between polymer and the filler is formed which give rise to the permeation of the selective gas with minimum loss of selectivity.

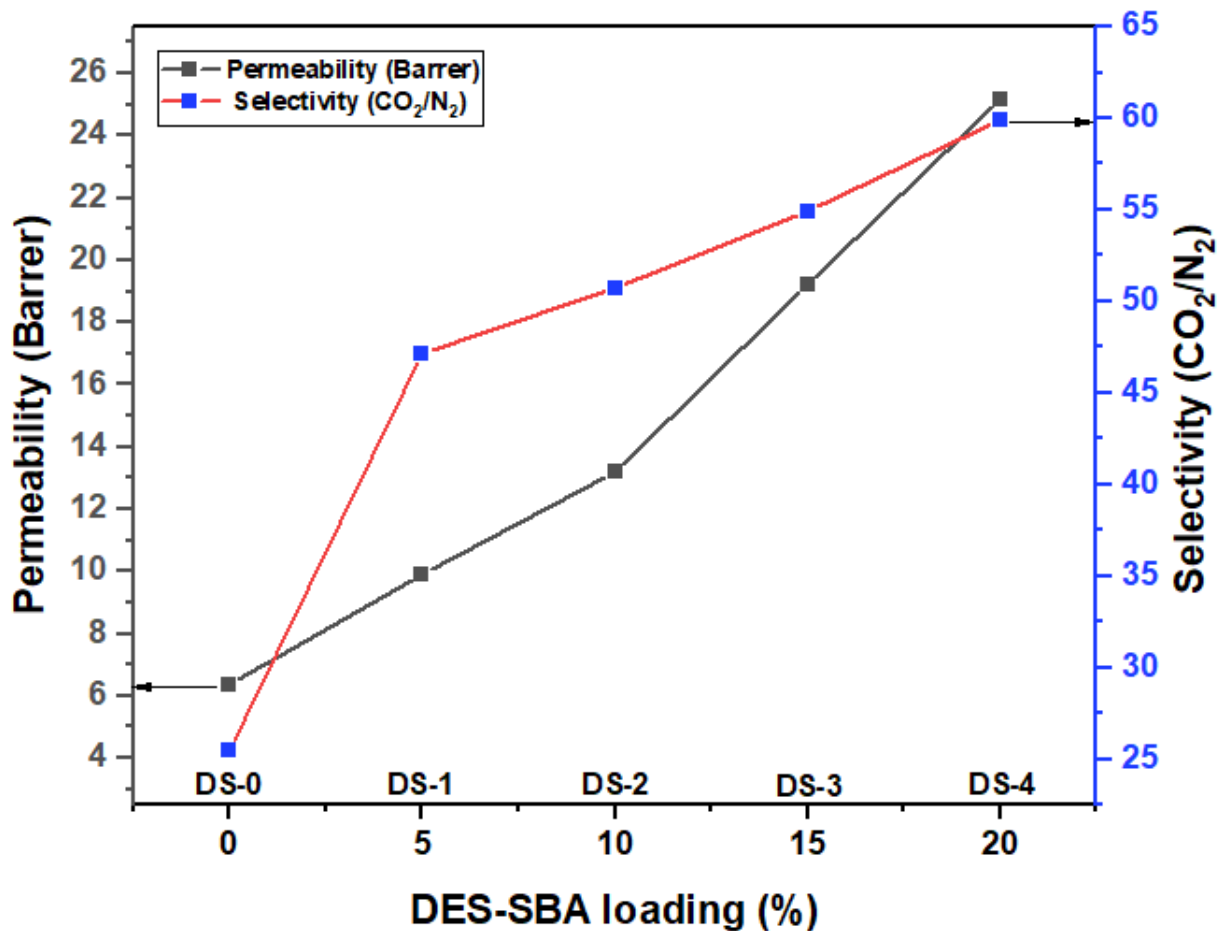


Figure 6(b): The permeabilities and the selectivities of Synthesized MMMs for CO₂/N₂ gas mixture

On the basis of obtained results as discussed above, the relation between selectivity and the permeability was compared with well-known Robeson's plots as shown in the **Fig. 7(a & b)** as the researcher's tries to move closer to the Robeson upper bound limit [11, 41, 42]. The Robeson plot is basically designed to check the trade-off of permeability and selectivity of membrane because when permeability increases, selectivity decreases and vice versa. It is very much clear

that the synthesized membranes are overcoming the trade-off between permeabilities and the selectivities with respect to the increase in DES-BSA filler loadings from 5% to 20%, and the membrane DS-4 of 20% filler loading is touching the Robeson plot of 1991 in CO₂/CH₄ case [Fig. 7(a)] and surpassing the line in CO₂/N₂ case [Fig. 7(b)], which is a positive improvement, in the performance of the synthesized MMMs. The trends of the results are similar to the already reported works [43-46]. Therefore, with the help of above discussion, it is clear that the results of perm-selectivity are lying in the technologically attractive region.

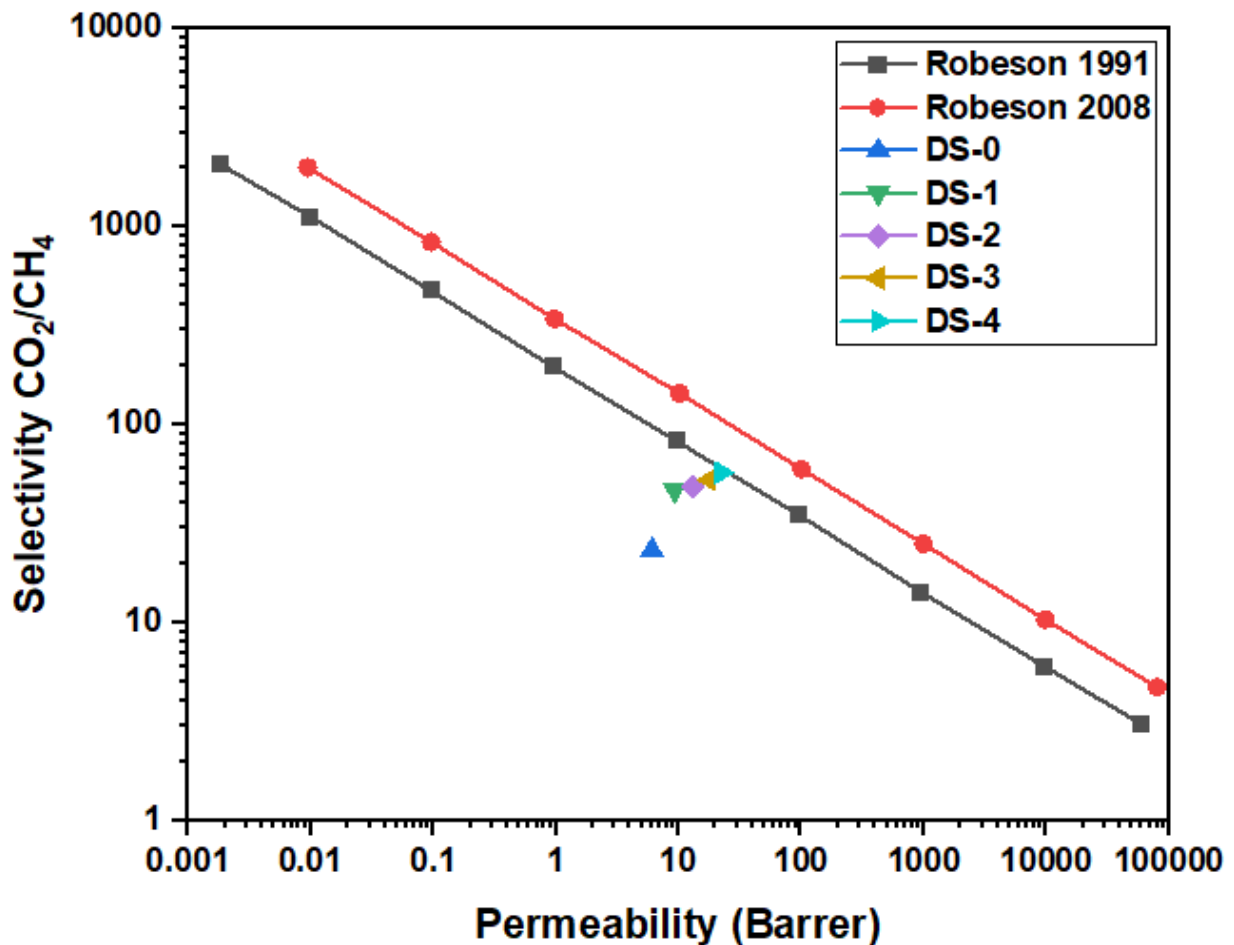


Figure 7(a): The Robeson plot of synthesized MMMs for CO₂/CH₄ gas mixture

In comparison with the other reported membranes for CO₂ separation, Farashi et al. [42] reported alumina based CO₂ capture membranes and reported selectivity of 24.73. Hasebe et al. [47] synthesized silica nanoparticle based polymeric CO₂ separation membranes and reported the CO₂/N₂ selectivity of 23. Ilyas et al. [48] fabricated ionic liquid functionalized zeolite based

MMMs and report the selectivities of 37 and 32 for CO_2/N_2 and CO_2/CH_4 and the permeability of 23.8 barrer. Khan et al. [49] synthesized sulfonated PEEK based gas separation membranes and reported maximum permeability of 10.4 barrer and selectivities of 28.1 (CO_2/N_2) and 12.8 (CO_2/CH_4). Khan et al. [50] fabricated fluorinated PEEK based CO_2 separation membranes and reported the selectivities of 47.4 (CO_2/CH_4) and 51.1 (CO_2/N_2). Waheed et al. [51] synthesized rice husk extracted silica based MMMs and reported the maximum permeability of 8.46 barrer and selectivities of 33.31 (CO_2/CH_4) and 32.79 (CO_2/N_2). Weng et al. [52] synthesized carbon molecule sized poly(phenylene oxide)/SBA-15 based MMMs for gas separation and reported the selectivity CO_2/CH_4 of 50.9. Hence, the DES-SBA based membranes exhibited better results as compared to all these reported studies. It is confirmed that these membranes are the potential candidates for the higher permeability and selectivity than pure PSF based membrane without any defect in the polymer matrix.

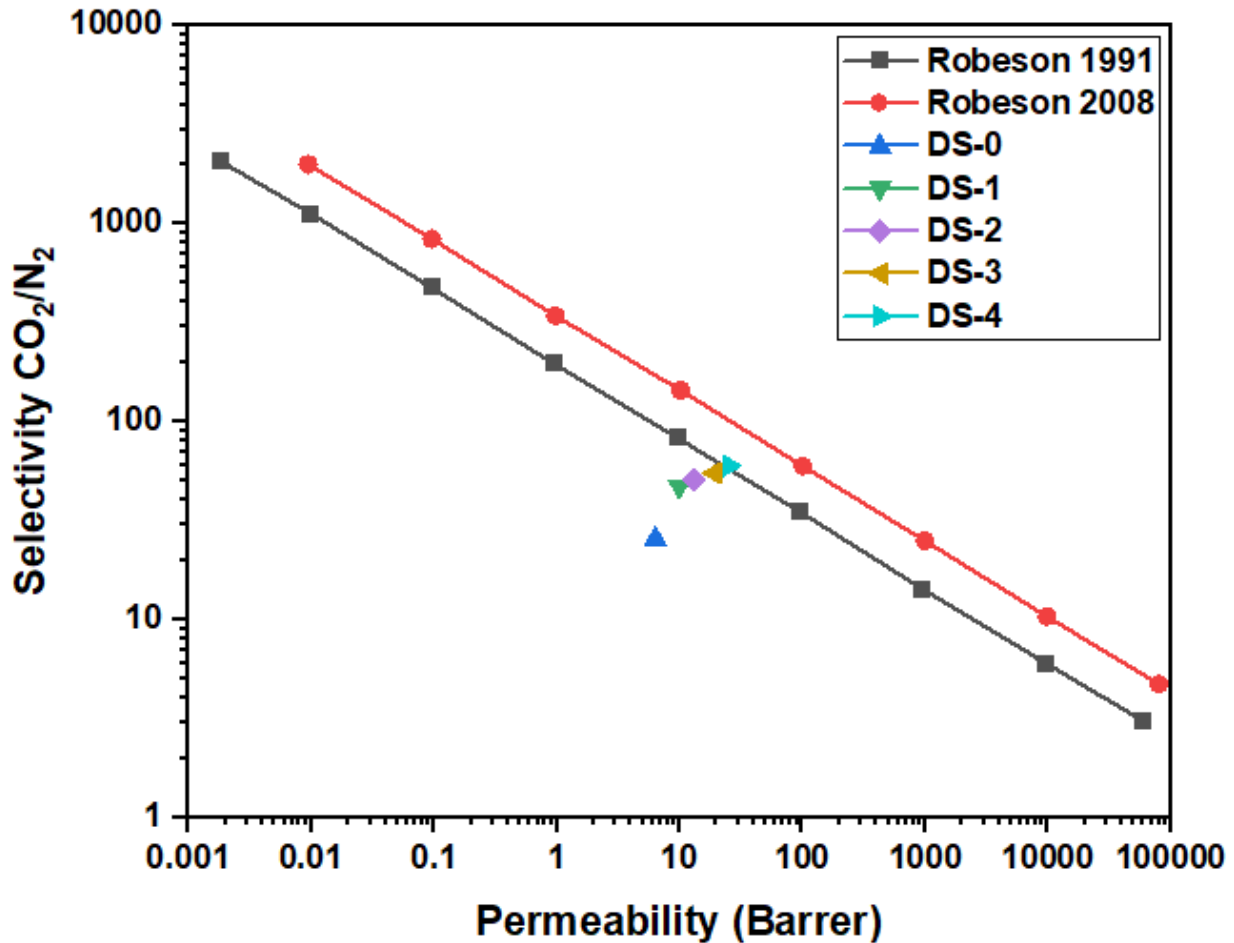


Figure 7(b): The Robeson plot of synthesized MMMs for CO₂/N₂ gas mixture

4. CONCLUSION

The study was focused on formation of decanoic acid/choline chloride based DES and the functionalization of SBA-15 by synthesized DES to utilized in the development of MMMs and the evaluation of the synthesized MMMs. DES was formed by combining 1:1 ratio (by mass) of decanoic acid and choline chloride at 80 °C. SBA-15 was modified by synthesized DES by solvent evaporation technique using ethanol as solvent. The MMMs of 5%, 10%, 15% and 20% was fabricated via casting solution technique. The MMMs was characterized by SEM and FTIR. The dispersion of filler in polymeric support and porosity of the MMMs was estimated via cross-sectional and surface morphology of membrane by micrographs. The combination study of the DES-SBA and the PSF polymer was estimated by characteristic peaks of the functional groups of the constituents involved. The study of permeation of gas was performed for estimating selectivity and permeability of the MMMs. In CO₂/CH₄ mixed gas case, the maximum CO₂

permeability for 20% filler loading was 22.3 barrer and the maximum selectivity of 57.18 and in CO₂/N₂ mixed gas case, the maximum permeability and the selectivity was 25.16 barrer and 59.9, respectively. Thus, the results showed the defect free mechanism of membrane synthesis and it is terminated that DES-SBA based membranes are prospective contenders for the reduction CO₂ from the gaseous mixtures.

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