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NaA Nano zeolite incorporated polystyrene mixed matrix membrane for separation of hydrazine and water using pervaporation

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Abstract--The composite polystyrene (PS) membranes were prepared in toluene solvent system for pervaporation of hydrazine/water mixtures. Hydrophilic NaA zeolite was incorporated to the extent of 10 - 40% of polymer weight to enhance separation properties. The nanofillers were incorporated into the polymer to reduce degree of swelling and improve selective nature with respect to water. Sorption studies were carried out in water, hydrazine hydrate binary mixture of varying compositions to establish membrane–liquid interactions. Membranes were characterized by FTIR, XRD and SEM to study formation of functional groups and intermolecular interactions, degree of crystallinity and d-spacing, besides surface morphologies of the composite films, respectively. Effect of feed composition, temperature, membrane thickness and downstream pressure on the membrane performance was evaluated using the optimum 40% zeolite-loaded membrane. For a feed mixture containing 36wt% water, a selectivity of 124.89 at a reasonable flux of 32.45 g/m^{2}h was observed. PS membrane appears to have considerable potential to dewater highly alkaline solvents owing to its ability to separate hydrazine hydrate. The composite nature of the membrane makes it feasible to fabricate modular configurations for scale-up.

Keywords :- Polystyrene, NaA zeolite, Hydrazine hydrate, Pervaporation, Membrane.

1.INTRODUCTION

Hydrazine hydrate ($N_2H_4 \cdot H_2O$) is an important inorganic chemical with high heats of combustion and hence becomes highly useful as rocket fuel. The other main applications of hydrazine hydrate include de-oxygenation of boiler feed water, fuel cells and production of blowing agents. As of the year 2000, approximately 120,000 tons of hydrazine hydrate (corresponding to a 64% solution of hydrazine in water by weight) was manufactured worldwide per year. However, production of hydrazine hydrate using various reaction routes still poses problems with regard to its yield and purity. Ordinary distillation provides hydrazine in the form of hydrate (64 wt. % of hydrazine). This form of hydrazine finds wide applications; whereas, use of hydrazine in rocket propulsion requires anhydrous hydrazine. Therefore, the removal of water from hydrate state to produce anhydrous hydrazine is essential to make it suitable for such purposes. However, conventional separation techniques for the removal of water experience difficulty as hydrazine forms an azeotrope with water at 71.5 wt. % of hydrazine. Further, hydrazine and water are highly polar by nature and there is strong hydrogen bonding between them. The explosive nature of hydrazine and the high energy consumption during distillation process pave the path to search for alternative technologies to produce anhydrous hydrazine. Application of membrane technology is one such attempt to address the stated problems. Pervaporation process, in particular, is considered because of its potential to separate azeotropic mixtures [1].

The membrane-based pervaporation (PV) technique is cost effective compared to conventional processes for specific separations involving azeotropic and close boiling mixtures owing to its high separation factor and flux rates. Moreover, PV is a safe and environmentally clean process. Membranes with high resistance to alkaline solutions can be synthesized. The technique was previously applied for separation of azeotropic mixtures and commercialized globally for the dehydration of alcohols [3].

Fabrication of economically viable membranes yielding high permeability and selectivity is the key to the economical success of these processes. In the case of solvent dehydration, it is believed that water transport in the membrane proceeds in a special manner due to the presence of hydrophilic polar groups which act as fixed carriers to aid mass transfer through the barrier. Since most polymer membranes suffer from the inherent drawback of trade-off between permeability and selectivity, many physical and chemical methods have been introduced to modify the existing polymer materials in an attempt to overcome the trade-off hurdle and meet the practical application requirements [2]. The chemical modification techniques include crosslinking, grafting, plasma treatment. Physical treatment includes thermal treatment, blending. Blending synergistically combines the advantages of individual components to overcome individual deficiencies.

Membrane performance can also be modified by using a porous substrate, which provides mechanical strength, feasibility of scale-up and long life. The presence of the ultra porous substrate could help in reducing the thickness of the uppermost active membrane layer to a minimum to achieve maximum throughput. Furthermore membrane can be modified by embedding nano-size selective fillers (as zeolites, silicates or activated carbon) in the polymer matrix.

Zeolites are microporous, crystalline alumino silicates with well defined structures that can reinforce polymer membranes due to their stability, physicochemical property as well as nanoporous morphology. Zeolites preferentially adsorb water molecules when the pore size of zeolite is almost equal to the size of the water molecules. When a membrane is filled with hydrophilic zeolite it gives higher water flux and selectivity over the pristine polymeric membrane [4]. They possess superior thermal and mechanical stability; they exhibit greater selectivity and flux.

When a membrane is filled with hydrophilic zeolite it gives higher water flux and selectivity over the pristine polymeric membrane. Fig 1.1 shows hydrophilic zeolite 4A with pore size of 0.4 nm that is marginally larger than the water molecule (0.26 nm).

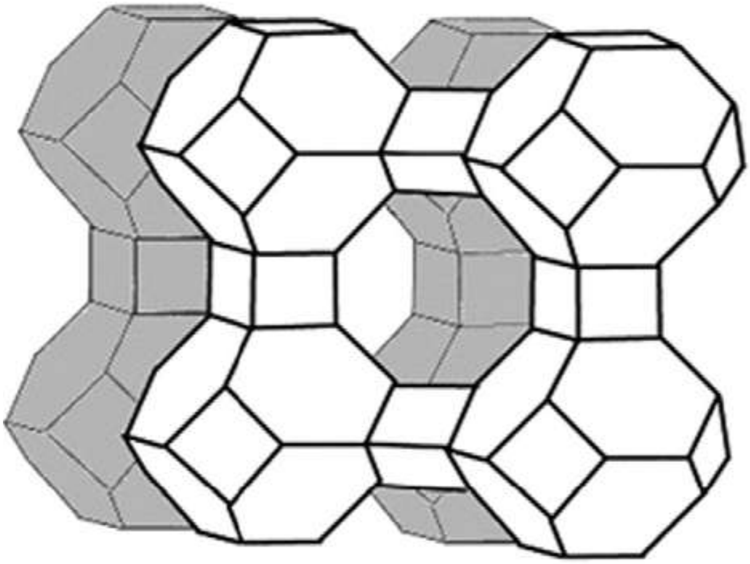


Fig 1.1: Structure of 4A zeolite

The present study involves synthesis of NaA (4A) zeolites particles and mixed matrix membranes by incorporating the synthesized nano particles into hydrophobic Polystyrene (PS) polymer for the dehydration of hydrazine hydrate. This is an attempt to attain both hydrophilic and hydrophobic characteristics to the membrane to overcome the trade-off between selectivity and flux. Further, hydrazine being highly alkaline (pH≥12) in nature, both NaA zeolite and PS polymer were reported to be chemically and mechanically stable in hydrazine hydrate so they were chosen for the dehydration studies.

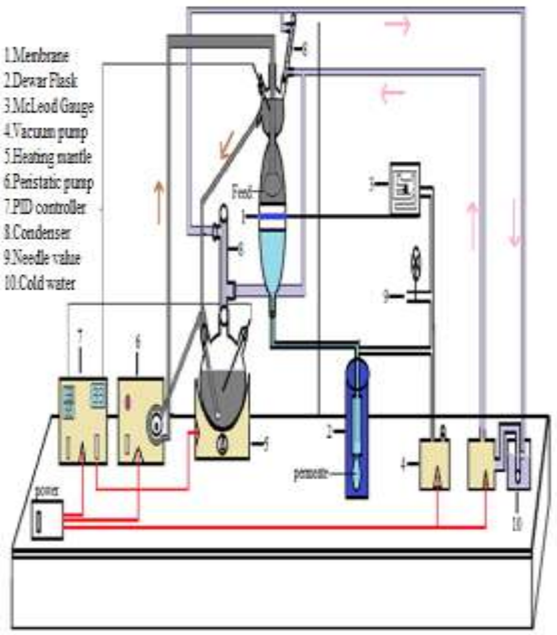
2.MATERIALS AND METHODS

2.1 Materials

Polystyrene (PS) was supplied by Sigma Aldrich (USA), Sodium Aluminate (Al-E Merck, 99%), Sodium Hydroxide Pellets (NaOH - BDH, 97.5%), Sodium Metasilicate (Na_2O_3Si - Loba, 99%), Hydrazine hydrate (99%) and Toluene rectified LR (99.01%) by Sigma Aldrich pvt.ltd, Bangalore, India. All solvents and chemicals were used as received.

2.2 Experimental setup

The experimental setup designed and fabricated to estimate the membrane performance by carrying out pervaporation studies is as shown in Fig (2.1). The pervaporation test cell is made of glass and it consists of flanges to secure the membrane. The membrane was kept on a highly porous stainless steel support facing the feed solution. Initially, a fixed volume of feed component was taken in the feed chamber. The membrane upstream side was kept at the atmospheric pressure, and a partial vacuum was maintained at the downstream side by a vacuum pump (VacuuTech, Bangalore, India). The downstream side pressure was regulated with an air inlet using a valve. Here the pervaporation experiment was conducted with zeolite incorporated membrane having effective area of 38.465 cm^2. Permeate was collected in liquid nitrogen trap and allowed to warm up at ambient temperature for analysis. The membrane performance was determined by calculating component flux and selectivity that was obtained by determining the weight of the permeate obtained using sensitive weighing balance of 0.1 mg accuracy.



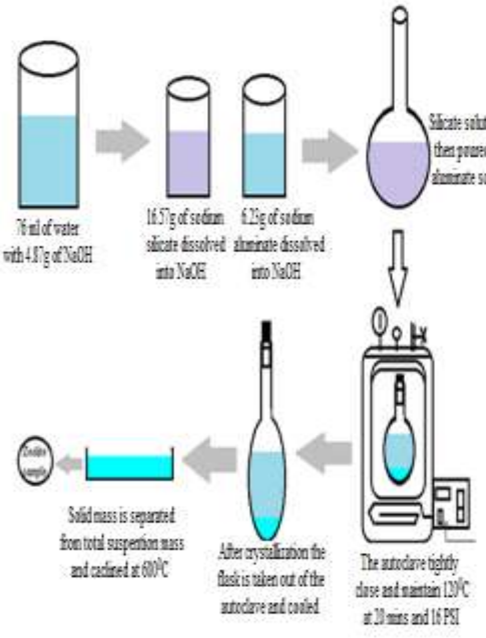


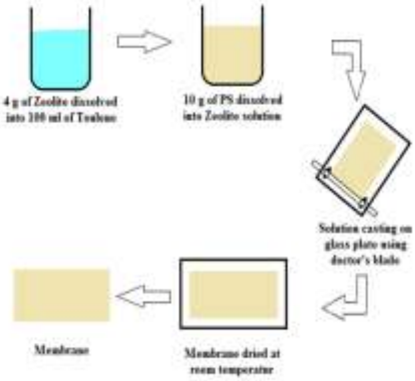
Fig 2.1: Schematic of laboratory pervaporation manifold.   Fig 2.2: Step-wise procedure of zeolite preparation.

2.3 Synthesis of zeolite

NaA zeolite solution was prepared by mixing sodium aluminate and sodium silicate solutions. NaOH (4.87 g) was dissolved in 76 ml of distilled water. The solution was divided into two equal volumes and kept in polypropylene bottles. Aluminate solution was prepared by adding 6.23 g sodium aluminate to one part of the NaOH solution until it dissolves. Silicate solution was prepared by adding 16.57 g sodium silicate to another part of the NaOH solution. Silicate solution was then poured into aluminate solution and mixed until a thick homogenized gel was formed. The typical pH value of the gel is 12, which was measured with pH meter. The homogeneous solution was transferred into a 250ml conical flask and closed. The flask was then placed in an autoclave maintained at 120 ^{0}C and 16 PSI for 20 minutes. After crystallization, the autoclave was cooled. The flask was then taken out from the autoclave; the solid mass was separated from total suspension mass in flask. The solid mass was kept in hot air oven at 60-70 ^{o} C for drying, later the solid sample was kept in muffle furnace for calcination at 600 ^{0} C for 1 hr. After calcination the sample was collected into a sample vial.

2.4 Membrane Preparation

In this study a conventional procedure was adopted for membrane preparation. The above synthesized NaA zeolite was initially added to toluene and sonicated for 3 hours. A known weight of zeolite i.e. 10, 20, 30 and 40% of polymer weight was added to the toluene solvent which was sonicated for about 3 h for complete dispersion of the inorganic filler. To this zeolite medium, 10 wt% PS polymer was added and stirred vigorously for 2–3 h to obtain a homogenous solution. To prepare a free-standing film this hot bubble-free polymer solution was cast on a clean glass plate and allowed to dry at room temperature for 24 hours to evaporate solvent completely after which the membranes were peeled off from the glass plate. The thickness of the prepared membrane was measured using a screw gauge. The obtained membranes were tested for dehydration of hydrazine hydrate by PV studies and compared with pristine PS membrane reported in literature [1].



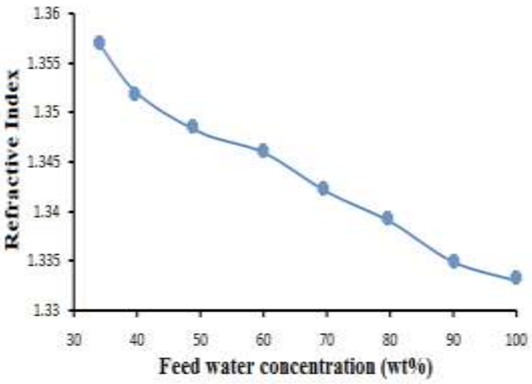


Fig 2.3: Step-wise procedure of membrane preparation.   Fig 2.4: Standard RI curve of hydrazine/water system.

2.5 Sorption Studies

The sorption of pure liquids in polymer membranes is usually carried out to determine swelling of membrane. The synthesized membranes were cut into small pieces. These pieces were weighed and immersed in Hydrazine hydrate – water mixture of varying composition at room temperature for 24 hours. The membrane pieces were taken out carefully and immediately wiped with tissue to remove excess surface solvent. The soaked membrane pieces were then weighed by using an electronic balance (Citizen electronic balance, India).The sorption studies were carried out by finding out mass differences between swollen membrane and dry membrane as follows

$$D_s = \frac{M_s - M_d}{M_d} \qquad \text{----------------------------- (2.1)}$$

where M_s and M_d are mass of swollen and dry membranes.

2.6 Membrane Performance

The performance of the mixed matrix membranes prepared is estimated by carrying out the pervaporation experimental studies for the dehydration of hydrazine hydrate. The flux and selectivity are the basic parameters that determine the membrane performance.

The feed and permeate samples of hydrazine hydrate/water systems were analyzed using digital refractometer (Rudolph Research Analytical DSR-k with a display resolution of 0.0001 and an accuracy of 0.0001@20^{0}C, India). Composition of unknown permeate samples were determined from the calibration plots of standard refractive index (RI) curves of hydrazine/water systems as shown in Fig.2.4. The range of n_D for water was in the range 1.474 to 1.333. The membrane selectivity is calculated using above Standard RI curve of Hydrazine/Water system. When feed and permeate samples of hydrazine/water of RI values are compared to standard RI curve to find selectivity.

2.6.1 Flux

Flux is defined as the mass or molar flow of any species per unit area, per unit time. The permeate flux is calculated by using:

$$J = \frac{W}{A*T}\ (kg/\mathrm{m}^2 h) \qquad \text{----------------------- (2.2)}$$

Where W is mass of permeate (kg)
A is effective membrane area (m^2)
T is time in hours (h)

2.6.2 Selectivity

Membrane selectivity is used to compare the separating capacity of membrane for two or more species. The membrane selectivity is also known as perm selectivity.

Selectivity is calculated by using:

$$\alpha = \frac{X_o * Y_w}{X_w * Y_o} \qquad \text{-------------------------- (2.3)}$$

Where x, y denote weight fractions of feed and permeate and the subscripts o and w represent organic and water respectively.

3.RESULTS AND DISCUSSION

3.1 Membranes characterization

Membranes were characterized using different characterization techniques to confirm membrane modification post zeolite addition. Phase, crystal structure, average crystal size of zeolite filled PS membrane was investigated using XRD (WRD PAN Analytical "XPERT^{3}PRO" Germany). Membranes were studied using FTIR spectrometer (Nicolet-740, Perkin-Elmer 283B IR Spectrometer, Japan) to make a comparison between pristine and zeolite incorporated PS membranes. SEM characterization was done using digital scanning electron microscope (JEOL JSM 5410, Japan) to study the morphology before and after zeolite loading.

3.1.1 X-ray diffraction (XRD)

Using the XRD analysis, the lattice arrangement of the crystallites atoms and the size of crystals were obtained using Bragg's law and Debye-Scherrer Equation respectively. XRD patterns of PS (a), 4A zeolite (b) and 40 wt% 4A zeolite incorporated PS (c) membranes were obtained varying the angle of diffraction from 5^0 to 50^o as shown in Fig 3.1. The crystallanity of PS membrane increased with zeolite loading and the intensity of the zeolite filled PS peak enhanced when compared to pristine PS. The zeolite peaks are matching JCPDS FILE#97-002-4901[17] and average crystal size is 24.56 nm. This is attributed to an increase in concentration of inorganic compound within the membrane matrix. The effective d-spacing decreased in zeolite filled PS compared to pristine PS membrane. The effective d-spacing decreased from 7.42 to 6.97 at 10^o of 2θ and 4.92 to 4.58 at 20^o of 2θ for PS and zeolite filled PS membranes, respectively. This decrease in d-spacing allows selective permeation of the smaller water molecules with increased retention of the larger hydrazine molecules [18].

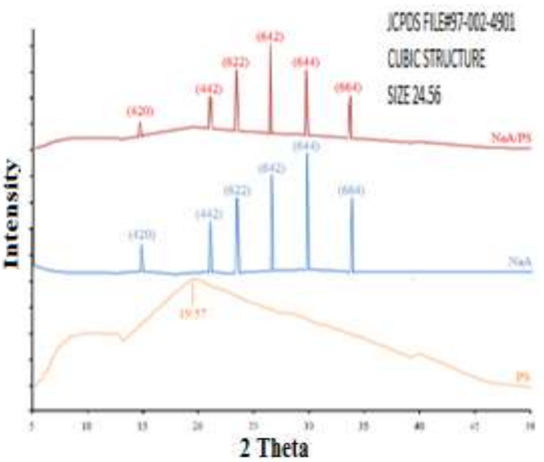


Fig 3.1: XRD patterns of PS and 4A zeolite and 40% 4A zeolite filled PS membranes.

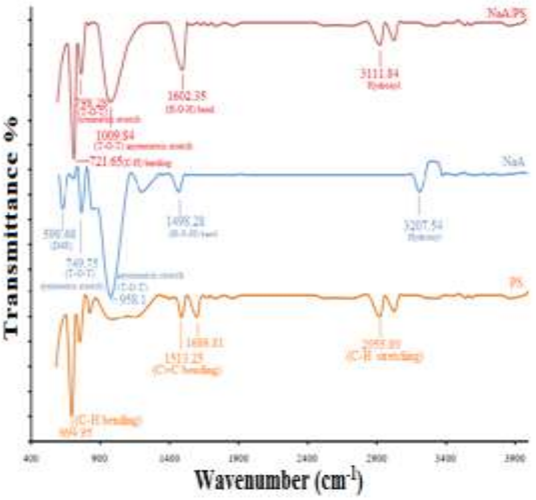


Fig 3.2: FTIR spectra of PS and 4A zeolite and 40% 4A zeolite filled membranes.

3.1.2 Fourier transform infrared radiation (FTIR)

This is one of the Infrared spectroscopy techniques, with the principle “molecular vibrational resonance”. Using this technique, the unique molecular vibrations, based upon the bonding structure of the functional groups, can be understood.

Fig 3.2 shows the FTIR spectra of PS (a) and 4A zeolite (b) and 40% 4A zeolite-loaded PS (c) membranes. The spectra of PS reveals a peak at 694.95 cm^{-1}, 1513.25 cm^{-1}, 2955.89 cm^{-1} corresponding to C-H bonding, C=C bending, C-H stretching. The spectra of 4A zeolite reveals a peak at 598.68 cm^{-1}, 749.75 cm^{-1}, 958.1 cm^{-1}, 1498.28 cm^{-1}, 3207.54 cm^{-1} corresponding to D4R, T-O-T symmetric stretching, T-O-T asymmetric stretching, H-O-H bend and hydroxyl group. 4A zeolite incorporated PS membrane revealed extra peaks that correspond to 4A zeolite peaks [17, 18].

3.1.3 Scanning electron microscopy (SEM)

Using SEM analysis, we can view and understand the topographic image of synthesized sample. Additionally we can measure the particle size range approximately using the scale given at the bottom of the image.

Fig 3.3 represents the surface morphologies of 4A zeolite and 4A zeolite incorporated PS membrane. Zeolite (40% loaded) filled PS membrane was very smooth dense in appearance thus indicating highly fine dispersion owing to sonication. Fig 3.3 shows 4A zeolite is cubic in structure and homogenous dispersion of zeolite in a systematic and uniform pattern in the polymer film can be observed.

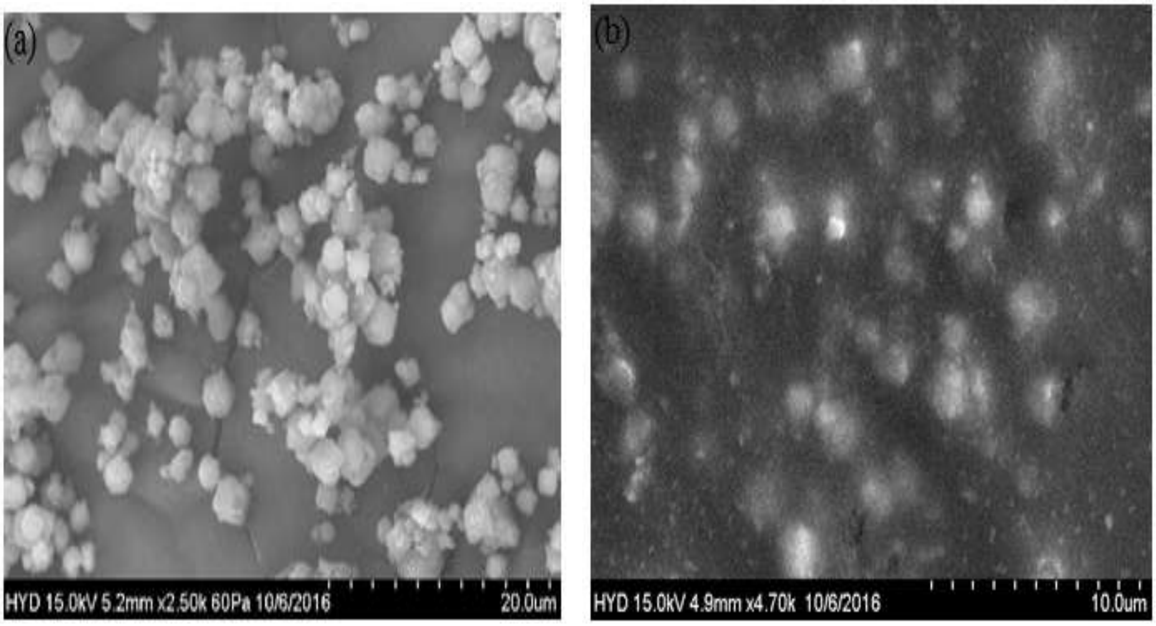


Fig 3.3: SEM images of (a) 4A zeolite surface and (b) 40% 4A zeolite of filled PS membranes surface.

3.1.4 Sorption behavior

The dependence of equilibrium swelling on composition of Hydrazine / water mixtures is shown in Fig 3.4. The equilibrium swelling ratio increased markedly with water concentration in the mixtures until a saturation point was reached. As the water concentration increased, the swelling also increased which motivated a faster entrance of water molecules inside the zeolite filled membranes. This phenomenon is quite important, since the PS membrane could mainly be employed for separating high concentrations of water from Hydrazine since the membrane swells excessively at higher feed water concentrations leading to reduced selectivity which can be observed in Fig 3.9.

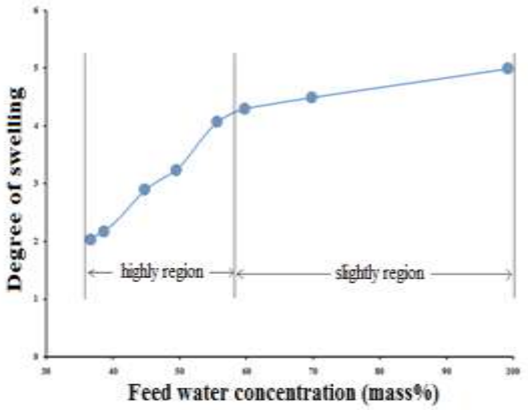


Fig 3.4: Effect of feed water concentration on membrane swelling.

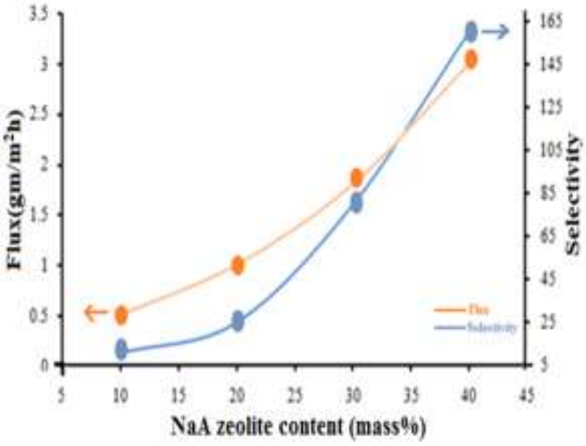


Fig 3.5: Effect of zeolite content on selectivity and fluxes.

3.2 Membrane performance

The effect of variation in % loading of zeolite on flux and selectivity was studied using the synthesized mixed matrix membranes. The performance of the synthesized membranes was also studied by varying different process parameters like, downstream side pressure, membrane thickness, temperature and feed water concentration.

3.2.1 Effect of zeolite content

Effect of zeolite 4A loading on PV performance was optimized to carry out further experiments with the most suitable membrane configuration. Zeolite loading in the polymer solution was varied from 10 to 40% of polymer weight for constant feed composition of 64 wt% hydrazine + 36 wt% water at 30 °C and 1 mmHg of downstream side pressure and membrane thickness (100µm). The results in Fig 3.5 indicate that both the flux and selectivity are high at 40% loading of zeolites compared to lower % of loading (10wt%, 20wt%, 30wt%). The increase in flux may be due to the increment in % loading of hydrophilic NaA nano fillers in the polymer matrix. The selectivity is increased as the fillers enhance the permeation of water molecules hindering the hydrazine molecules. So the experimental work and detailed studies were performed with 40% zeolite-filled polymer since it showed optimum PV performance for dehydrating hydrazine hydrate.

3.2.2 Effect of downstream pressure

Effect of variation of downstream pressure on PV performance was studied and the results are shown in Fig 3.6 for constant feed composition of 64% hydrazine hydrate at 30°C, 40 wt% zeolite filled membrane, downstream pressure of 1mmHg and membrane thickness of 100µm.

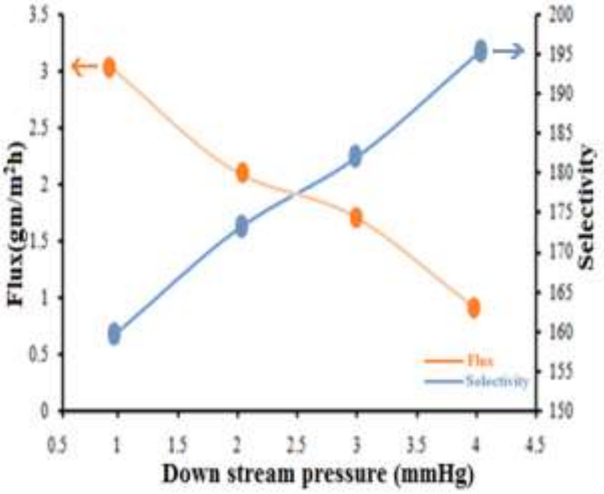


Fig 3.6: Effect of downstream pressure on selectivity and fluxes.

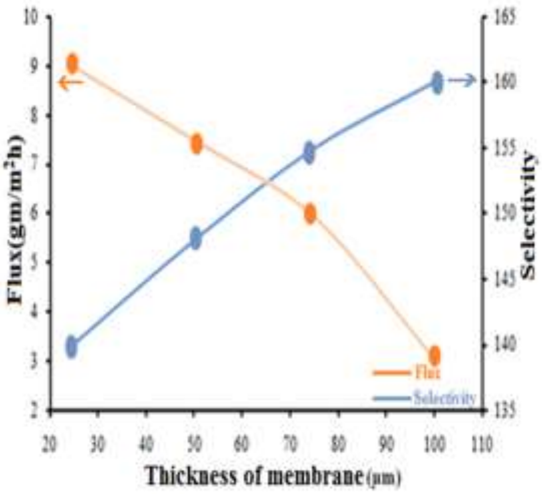


Fig 3.7: Effect of thickness of membrane on selectivity and fluxes.

Decreasing the downstream pressure decreased the flux but increasing the selectivity because the decrease in applied downstream energy decreased thus allowing only small water molecules to selectively permeate across the membrane.

3.2.3 Effect of thickness of membrane

Effect of membrane thickness(µm) on PV performance was studied and the results are shown in Fig 3.7 for constant feed composition of 64% Hydrazine hydrate, at 30°C temperature, 40 wt% zeolite filled membrane and downstream pressure 1mmHg.

When thickness of membrane decreased then flux increase and selectivity is decreased because thickness reduces the flow of molecules through the membrane.

3.2.4 Effect of feed temperature

Effect of feed temperature (°C) on PV separation was studied and the results are shown in Fig 3.8 for constant feed composition of 64% Hydrazine hydrate, 40 wt% zeolite filled membrane with a thickness of 25µm and downstream pressure of 1mmHg.

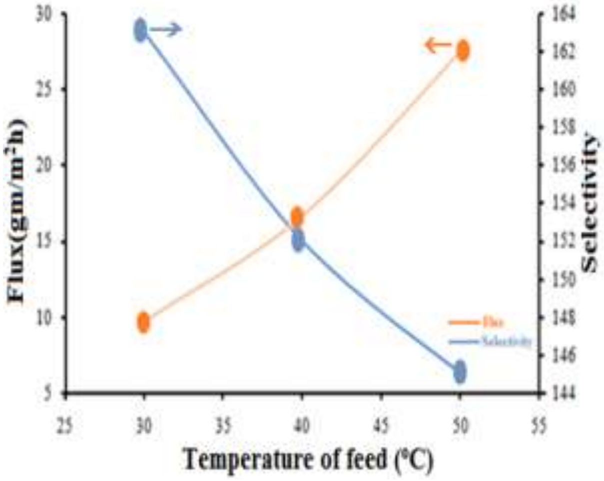


Fig 3.8: Effect of feed temperature on selectivity and flux.

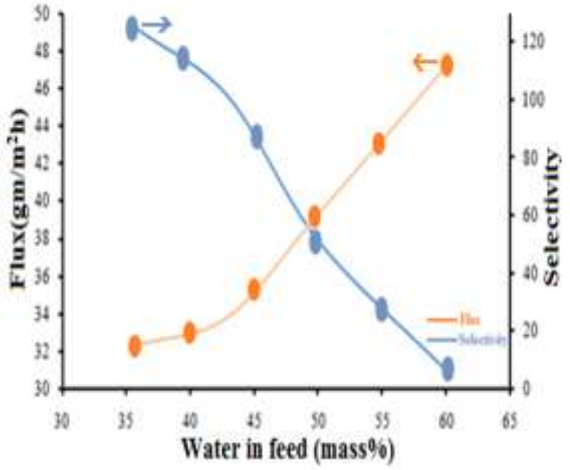


Fig 3.9: Effect of water in feed concentration on total selectivity and fluxes.

The increase in feed temperature increased the flux but decreased the selectivity. The increase in flux is attributed to the increase in the internal molecule interaction pressure that favors the easy passage of the molecules through the membrane because of the plasticization effect of the membrane at higher temperatures.

When feed temperature (^{0}C) is increased then flux increasing and selectivity is decreasing because in the feed internal molecule interaction pressure increasing and bonding energy also decreased between hydrazine and water molecules then molecules are crossing the membrane easily.

3.2.5 Effect of feed water concentration

Effect of feed water concentration on the membrane performance was studied with 40 wt% zeolite filled membrane with a thickness of 25µm at constant feed temperature of 50°C and downstream pressure (0.5mmHg) and the results are shown in Fig 3.9.

The increase in feed water concentration increased flux and decreased selectivity because membrane area is swelled in between the zeolite crystals.

S No	Membrane	Thickness of active layer (µm)	Flux (g/m²h)	Selectivity	Reference
1	PS with zeolite	25	32.45	124.89	Present Work
2	PEBAX-2533 on PPSU	10	51.95	107.109	(2)
3	BM80	60	1.622	10.647	
4	PERVAP 2200	2	122.4	1.09	
5	PERVAP 2201	2	4.0	3.58	
6	PERVAP 2202	2	31.4	1.93	
7	EC	58	96.5	1.72	
8	MEC4	75	81.8	3.23	
9	PS	56	1.02	5.45	
10	ABS	110	78.1	5.07	

Table-3.1: Comparison of pervaporation results for hydrazine hydrate with literature findings

The pristine PS membrane because of its strong hydrophobic nature exhibited very low flux and selectivity as reported in literature shown in table 3.1. One may, therefore, decrease its hydrophobicity by modifying the membrane, either by incorporating nanofillers or blending with hydrophilic polymer to obtain better flux and selectivity. In other words, the incorporation of nano fillers into the polymer matrix allows increment in mass transfer. The solution diffusion phenomenon ensures that the PS mixed matrix membrane, which has affinity for water, preferentially sorbs more water which also has higher mobility due to its smaller molecular size (MW 18) as compared to hydrazine (MW 32). The mixed matrix membrane consists of 4A zeolite which would have 0.4 nm pore size would be more permeable to water due to diffusivity considerations. Table 4.1 shows different membranes used in the literature for the separation of hydrazine-water mixtures and is compared with the PS mixed matrix membrane used in the present study which exhibited the highest selectivity amongst contemporary polymer membranes at a comparable flux.

4. CONCLUSIONS

Stable and composite mixed matrix membrane was synthesized by incorporating zeolite 4A for dehydration of hydrazine hydrate by pervaporation technique. This study shows that pervaporation is more suitable for dehydrating solvents which are volatile, such as hydrazine. The PS composite membrane demonstrated a better anti-swelling property and separation performance in PV dehydration of hydrazine along with high stable and chemical stability along with the NaA zeolite filling for this study. Mixed matrix membranes could become materials of the future since the presence of inorganic zeolite could enhance permselectivity of the organic polymers. Such membranes can also be scaled up due to their composite nature which gives added strength besides fine dispersion by sonication that enables uniform zeolite distribution during membrane casting on a large scale. The pervaporation could be employed where in large quantities of water and harsh organics concentrations could be separated easily onwards to achieve final flux 32.45 gm/m^{2}h and selectivity 124.89.

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