Studies on the performance of pervaporation for the separation of aqueous-organic mixtures

Synopsis of the thesis to be submitted in the partial fulfilment of the award of the degree of

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Abstract

Pervaporation of model and actual wastewater consisting of acetic acid (HAc), ethylene glycol (EG), and vinegar was extensively investigated using commercial, modified and synthesized polymeric composite membranes, for a wide range of operating conditions. Effect of several physico-chemical parameters such as feed concentration, feed temperature and feed flow rate on the pervaporation flux, separation factor, selectivity, permeance and intrinsic membrane permeability was critically analyzed with respect to existing theories. The membranes used in the study were characterized by FTIR, FESEM, AFM, XRD, TGA, DSC, contact angle measurement and by evaluating the mechanical properties. A mathematical model following Flory-Huggins equations were used to determine the binary interaction parameters for EG-water system to study the sorption behavior of solvent transport through the polymeric membranes. The predicted sorption data were computed using MATLAB (version 2017 in a symbolic mathematics tool box) and compared with the experimental results. Findings of this work may provide useful insights to pervaporation fundamentals, system design and scale up for the acetic acid and ethylene glycol dehydration. The process allowed the production of permeate stream with great reutilization possibilities and developed a set of performance parameters. Based on this, further treatment of wastewater may be investigated for the recovery of water as well as valuable organic compounds. The study has focused on improving the pervaporation performance based on membrane modifications and identifying suitable physico-chemical parameters.

Brief description on the state of art of the research topic

Dehydration of organic solvents plays an important role in the downstream separation processes in chemical, petrochemicals, food and beverage, pharmaceutical, and allied industries. Pervaporation is a membrane-based process for separating binary or multi-component mixtures of miscellaneous organic solvents like aromatics, alcohols, ketones, ethers, acetic acid, acetone, dioxane, ethylene glycol and so on (Smitha et al., 2004). It is much touted as an efficient and environmentally benign separation process both as a stand-alone unit and a supplementary to the distillation. Pervaporative dehydration of aqueous HAc, one of the top fifty organic intermediates in the chemical industry, has been reported by several researchers, however with different membranes (Aminabhavi and Naik, 2003; Durmaz-Hilmioglu et al., 2001; Jullok et al., 2011; Kuila et al., 2011). Polyvinyl alcohol (PVA)-based membranes are claimed to be suitable for the dehydration of acetic acid with no limitation (Chapman et al., 2008). Ethylene glycol (EG) is also a widely used precursor in organic chemical industries for the manufacturing of unsaturated polyester resins,
polyacetate fibers, plasticizers antifreezing agents. EG dehydration by traditional multistage evaporation and distillation is highly energy intensive, requiring high pressure steam for reboiler. As an alternative, pervaporation dehydration of EG has been explored in a number of several recent studies using an assortment of polymeric or ceramic membranes (Wu et al., 2015; Rao et al., 2007; Sun et al., 2015). Surface modification by grafting hydrophilic copolymers onto the PVA chains during cross-linking allowed the improvement of the separation factor. PVA was modified by cross-linking with glutaraldehyde (Aminabhavi et al., 2003; Durmaz-Hilmioglu et al., 2001). Modified PVA and casting sodium alginate onto a microporous polypropylene membranes have also been used (Kuila and Ray 2011; Zhang et al., 2014). Physico-chemical modification of a PVA can also be made by incorporating graphene oxide (GO) to improve its chemical tunability and mechanical strength. The hybrid membranes are observed to exhibit higher water flux and better fouling resistance (Wang et al., 2012; Lee et al., 2013). For PVA membrane amount of cross linking agent can counter the inherent swelling susceptibility and minimize compaction. Imparting hydrophilicity on the surface of the support layer (Belfar et al., 2000; Huang et al., 2000), incorporation of a coupling agents or surfactants (Jonsson and Jonsson, 1991) are some of the ways in order to reap the benefit of trans-layer interfacial interaction.

**Definition of the problem**

A volatile organic compound even at low concentrations renders the water unfit for reuse or discharge, thus warranting its effective reclamation. Dehydration by traditional multistage evaporation and distillation is highly energy intensive, requiring high pressure steam for reboiler. Increased cost as well as the formation of azeotropes limits the separation efficiencies of the distillation process. This necessitates the importance of pervaporation as an alternative dehydration protocol for aqueous-organic mixture, which is the premise of the present work. Pervaporation can be evaluated in terms of several indices such as permeation flux, selectivity, separation factor and long-term membrane performance. All the factors above should be addressed in order for the process to be used commercially. Considering that the recovery of valuable compounds from aqueous solutions by pervaporation is very promising, this thesis draws attention to such recovery process as its general topic with special emphasis on the selective separation of acetic acid, vinegar and ethylene glycol.

**Objectives and Scope of work**

1. To study the surface modification and characterization of selected pervaporation membranes by multifunctional cross linking agents.
2. To evaluate the comparative swelling characteristics of various composite membranes cross linked with different cross- linkers.

3. Study of the pervaporation of different combinations of acetic acid-water, vinegar-water and ethylene glycol-water binary solution in various proportions in a pilot plant.

4. To investigate the effect of physico-chemical parameters such as feed temperature, feed concentration and feed flow rate on the pervaporation flux and separation factor.

5. To study the intrinsic membrane properties like permeability, permeance, membrane selectivity and mechanical properties of membranes.

6. To study the diffusion behavior and mechanism of solute/solvent transport through polymeric membranes in pervaporation.

7. To develop mathematical model for the study of sorption behavior of solvent transport through the polymeric membrane.

Original contribution by the thesis

The present research would act as a benchmark to explore the amenability of pervaporation to be used commercially either as stand-alone system or as a supplement to the traditional equilibrium separation such as distillation in particular, for the recovery of industrially important volatile organic compounds from aqueous-organic mixture. In this work, pervaporation performance of the studied membranes was evaluated on the basis of experimental results in combination with mathematical modeling of sorption behavior. This dissertation offers an innovative analytical and methodological approach for synthesis of a number of cross-linked composite membranes by using three different cross-linking agents and two different support matrix for pervaporation dehydration of acetic acid, vinegar and ethylene glycol aqueous mixture with a wide range of concentrations. The applicability of the Flory-Huggins model for PVA-PES membrane in ethylene glycol-water systems was assessed after comparing the predicted and experimental equilibrium data. The study presents and corroborates some fundamental and applied aspects of pervaporation, which could be useful for large scale operation.

Methodology of research

(i) Chemicals and membranes used

Various chemicals (AR grade) such as polyvinyl alcohol (PVA), graphene oxide (GO), dimethyl sulfoxide (DMSO), glutaraldehyde, formaldehyde, borax, sodium sulphate, sulfuric acid and others used in the present study were purchased/procured from M/s
Loba Chem and M/s S D. Fine-Chem, Mumbai, India and were used as received without 
additional processing. Preparation of stock solutions was carried out with deionized water, 
having a conductivity of 20 µS/cm, produced from a reverse osmosis system. All other 
chemicals were of reagent grade and were used without additional processing. Polyether 
sulfone (PES) support membrane was kindly provided by M/s Permionics Membrane Pvt. 
Ltd, Baroda, India. The details of the commercial, modified and prepared asymmetric flat 
sheet PVA composite membranes used in the present study are shown in Table 1.

**Table 1 Membranes with different cross-linking agents used in the present PV study**

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Cross-linking agent</th>
<th>Feed mixture for pervaporation study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial (PVA-PES)</td>
<td>Glutaraldehyde</td>
<td>Acetic acid -Water</td>
</tr>
<tr>
<td>(PVA-PES)</td>
<td>5 vol% Formaldehyde</td>
<td>Vinegar-water</td>
</tr>
<tr>
<td>(PVA)</td>
<td>5 vol% Glutaraldehyde</td>
<td>Vinegar-water</td>
</tr>
<tr>
<td>(PVA-GO)</td>
<td>5 vol% Glutaraldehyde</td>
<td>Vinegar-water</td>
</tr>
<tr>
<td>(PVA-GO)_{2}</td>
<td>5 vol% Glutaraldehyde</td>
<td>Vinegar-water</td>
</tr>
<tr>
<td>(PVA-PES, 0.2% Borax)</td>
<td>0.2 wt% borax</td>
<td>Ethylene glycol-Water</td>
</tr>
<tr>
<td>(PVA-PES, 0.5% Borax)</td>
<td>0.5 wt% borax</td>
<td>Ethylene glycol-Water</td>
</tr>
<tr>
<td>(PVA-PES, Uncross-linked)</td>
<td>--</td>
<td>Ethylene glycol-Water</td>
</tr>
</tbody>
</table>

(ii) **Swelling behaviour of membrane**

Degrees of swelling (DS) of the prepared membranes were estimated by immersing the 
membrane samples into the binary feed mixture for 24 to 48 h to guarantee equilibrium. 
Samples were taken out and weighed immediately. Percentage degree of swelling was 
determined as (Richau et al., 1996) Eq (1)

\[
\% DS = \left( \frac{W_{wet} - W_{dry}}{W_{dry}} \right) \times 100
\]  

where \(W_{dry}\) and \(W_{wet}\) are the weight of dry and swollen membrane, respectively.

(iii) **Pervaporation (PV) study**

Pervaporation experiments were conducted in a small pilot plant assembly, the basic 
schematic diagram of which is shown in Fig. 1, however experiments were also performed 
using three other modified experimental set-ups (not shown here). The permeation cell of 
the basic experimental set-up consisted of two detachable stainless steel parts which were 
provided with inlet and outlet openings for the flow of feed solution and withdrawal of 
permeated product respectively. The liquid feed-mixture is circulated in contact with the 
membrane using a peristaltic pump from a feed tank, equipped with an overhead condenser 
to prevent any loss of feed due to evaporation. The effective area of the membrane was 160 
cm\(^2\). The constant temperature of feed was maintained by using a thermostat bath. The
permeate compositions were analysed using Abbe Refractometer (Model-RSRT-1) or digital automatic Karl-Fischer titrator (Model-Veego/Matic-D).

![Diagram of experimental setup](image)

**Fig. 1** Schematic diagram of experimental set-up of pervaporation used in the present study

**(iv) Flux and separation factor**

The trans-membrane flux in pervaporation is generally expressed as mass flux or molar flux (Verhoef et al., 2008).

\[
P_i^G = \frac{J_i}{l} = \frac{J_i}{(\gamma_i x_i P_{i,\text{sat}} - \gamma_i P_p)}
\]

(2)

The membrane separation factor (\(\beta\)) can be defined as the ratio of the molar component concentrations in the fluids on either side of the membrane. Hence:

\[
\beta = \frac{y(1-x)}{x(1-y)}
\]

(3)

Where \(P_i\) is the membrane permeability, \(l\) is the membrane thickness and \(\gamma\) is the activity coefficient, which may be calculated using Van Laar equation. The mole fraction in the feed and permeate solution is denoted as \(x\) and \(y\), \(P_{i,\text{sat}}\) is the saturated vapor pressure and \(P_p\) is the permeate pressure obtained during the PV experiment.

**(v) Pervaporation separation index (PSI) and enrichment factor**

PSI is a measure of the separation ability of a membrane (Kariduraganavar et al., 2005) and can be determined as Eq. (4)

\[
PSI = J \times (\alpha - 1)
\]

(4)

where \(J\) is the permeation flux and \(\alpha\) is the membrane selectivity.

An enrichment factor (EF) is simply the ratio of concentrations of the preferentially pervaporating species in permeate and feed (Dutta et al., 1997) as calculated from eq (5)

\[
EF = \frac{C_{wp}}{C_{wf}}
\]

(5)
Where \( C_{wp} \) and \( C_{wf} \) are concentrations of water in the pervaporate and feed sides.

**(vi) Intrinsic membrane permeability, permeance and selectivity**

The membrane permeability, \( (P_i^G) \) is defined as the transport flux of the material through the membrane per unit driving force per unit membrane thickness (Baker et al., 2010). The membrane permeance \( (P_i^G/\bar{l}) \) is the ratio of membrane permeability to membrane thickness.

Membrane selectivity \( (\alpha_{mem}) \), defined as the ratio of the permeabilities or permeances of components i and j through the membrane is given by Eq. (6)

\[
\alpha_{mem} = \frac{P_i^G}{P_j^G}
\]

**(vii) Diffusion and partition coefficient**

Fick’s law is used to describe the binary diffusion, which can be expressed as

\[
J_i = -D_i \frac{dC}{dh}
\]

where \( J_i \) is the permeation flux of component \( i \) per unit area (kg/m\(^2\)h), \( D_i \) is the diffusion coefficient of component \( i \) (m\(^2\)/s), \( C \) is the concentration of permeant (kg/m\(^3\)) and \( h \) is the diffusion length (m). The concentration profile in this study is assumed to be linear as a result, Eq.(7) can be rewritten as (Kusumocahyo et al., 2000).

\[
D_i = \frac{J_i \delta}{C}
\]

Where \( \delta \) is the membrane thickness. Thus the partition coefficient \( (K) \) of species \( i \) between membrane and feed can be determined using Eq.(9)

\[
(P_i) = D_i K_i
\]

**(viii) Determination of activation energy**

Effect of temperature on pervaporation can be described by Arrhenius type relationship (Jullok et al., 2011).

\[
X = X_0 \exp\left(-\frac{E_X}{RT}\right)
\]

where \( X \) is the PV flux \( (J) \), \( X_0 \) is the pre-exponential factor, \( R \) is the universal gas constant (J/mol K), \( T \) is the temperature (K), and \( E_X \) is the activation energies of flux (kJ/mol).

**(ix) Thermogravimetric analysis (TGA) and Differential scanning calorimetry**

The thermal degradation propensities of the as-prepared membranes were evaluated with a TGA 2050 Thermogravimetric Analyzer under nitrogen atmosphere. The glass transition temperature \( T_g \) was measured by means of DSC using an in-built data analysis software.
(x) **Fourier Transform Infrared Spectroscopy (FTIR)**
The presence of organic functional groups on the membrane surface was analyzed by the Fourier transform infrared spectroscopy (Perkin Elmer Spectrum GX) using a wave number range of 400 – 4000 cm\(^{-1}\) at a resolution of 4.0 cm\(^{-1}\) with an acquisition time of 1 min.

(xi) **AFM analysis**
Atomic force microscopy (AFM) was carried out using a NT-MDT NTEGRA Aura Autoprobe CP atomic force microscope. The surface roughness parameter in terms of root mean square (RMS) roughness was calculated.

(xii) **XRD analysis**
The crystal structures of the as-prepared composite polymer membranes were examined using X-Pert-MPD (Philips, Holland) X-ray diffractometer (XRD) with Cu K radiation of wavelength \(\lambda = 1.54056 \, \text{Å}\) in the range \(5^\circ \leq 2\theta \leq 50^\circ\). The X-ray generator was operated at an excitation voltage of 45 kV and a current of 40 mA.

(xiii) **FE-SEM analysis**
The cross-sectional and outer surface topologies of the prepared membranes were investigated via field emission scanning electron microscopy (FE-SEM) using JEOLFE-SEM (JSM-6701F) at 5kV under different magnifications.

(xiv) **Mechanical property of membrane**
Tensile strength, Elongation at break and Modulus of elasticity of the prepared membrane were measured using Universal Testing Machine (UTM) (Simadzu AG 100 KNG, Japan).

(xv) **Modeling of sorption behaviour**
Flory–Huggins equations are applied to commercial (PVA-PES) composite membrane cross-linked with glutaraldehyde for EG-water binary mixtures. Sorption of pure solvents and binary mixture was determined. Thermodynamic equations for the Gibbs free energy change can be expressed as Eq. (11) and (12) (Mulder et al., 1985; Yang and Lue, 2013).

\[
\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - \Delta S_{\text{mix}} \quad (11)
\]

\[
\frac{\Delta G_{\text{mix}}}{RT} = n_i \ln \phi_i + n_m \ln \phi_m + X_{\text{im}} n_i \phi_m \quad (12)
\]

where \(\Delta H_{\text{mix}}\) is the enthalpy change of mixing and \(\Delta S_{\text{mix}}\) is the entropy of mixing and \(X_{\text{im}}\) is the F-H interaction parameter, can be calculated as per Eq. (13) for pure solvent sorption.

\[
X_{\text{im}} = -\frac{\ln \phi_i + (1 - \phi_i)}{(1 - \phi_i)^2} \quad (13)
\]
The Gibbs free energy of mixing for a ternary system is expressed as Eq. (14) and the derivative of Eq. (14) can obtain the model equations (15), (16) in terms of activity of water and ethylene glycol (Flory 1953; Mulder et al., 1985).

$$\frac{\Delta G_{mix}}{RT} = n_w \ln \varphi_w + n_{EG} \ln \varphi_{EG} + n_m \ln \varphi_m + X_{w-EG} n_w \varphi_{EG} + X_{wm} n_m \varphi_m + X_{EGm} n_{EG} \varphi_m$$  \hspace{1cm} (14)$$

$$\ln a_w = \ln \varphi_w + \varphi_{EG} (1 - \frac{V_w}{V_{EG}}) + \varphi_m (1 - \frac{V_m}{V_{m}}) + (X_{w-EG} \varphi_{EG} + X_{wm} \varphi_m) (1 - \varphi_w) + \frac{\partial X_{w-EG}}{\partial \varphi_{EG}} - \varphi_w \varphi_m 2 \frac{\partial X_{wm}}{\partial \varphi_m} - \frac{V_w}{V_{EG}} \varphi_{EG} 2 \frac{\partial X_{EGm}}{\partial \varphi_m}$$

$$\ln a_{EG} = \ln \varphi_{EG} + \varphi_w (1 - \frac{V_{EG}}{V_w}) + \varphi_m (1 - \frac{V_{m}}{V_{m}}) + (X_{w-EG} \varphi_{EG} + X_{EGm} \varphi_m) (1 - \varphi_{EG}) + \frac{V_{EG}}{V_w} \varphi_{EG} 2 \frac{\partial X_{w-EG}}{\partial \varphi_{EG}} - X_{wm} \frac{\partial X_{wm}}{\partial \varphi_m} + \frac{V_{EG}}{V_m} \varphi_{EG} 2 \frac{\partial X_{wm}}{\partial \varphi_m} - \frac{V_w}{V_{EG}} \varphi_w \varphi_m 2 \frac{\partial X_{EGm}}{\partial \varphi_m} - \varphi_w \varphi_m 2 \frac{\partial X_{EGm}}{\partial \varphi_m}$$

$$= \varphi_w + \varphi_{EG} + \varphi_m = 1$$  \hspace{1cm} (17)$$

where $X_{w-EG}$, $X_{wm}$ and $X_{EGm}$ are the F-H interaction parameter between water-EG, water-membrane and EG-membrane respectively. It can be considered as being concentration independent or dependent. The equations (15), (16) and (17) can be solved simultaneously using Matlab (Symbolic mathematics toolbox, version 2017) to predict the sorption behaviour.

**Results and discussion**

**Membrane swelling study**

Swelling of dense polymeric membrane plays a key role in the transport of molecules during pervaporation. The greater the affinity between solvent and polymer, the higher is the swelling. The data obtained for different membranes used in the present study indicates that the degree of swelling increased almost linearly with increasing water content in the feed mixture. Degree of swelling of 0.2 wt% borax cross linked PVA-PES composite membrane was less than that of 0.5 wt% borax cross linked membrane. This was probably due to the fact that addition of more cross-linker might have reduced membrane free volume resulting in restricted segmental motion (Qu et al., 2010). The analogous trend was observed for the PVA-GO composite membranes. However for the PVA-PES membrane cross-linked with glutaraldehyde, it was found that % degree of swelling decreased gradually with increase in water concentration at three different temperatures viz. 25, 45...
and 65°C. Also for the different composition of acetic acid-water mixture, % sorption was found to be increased with time upto nearly 28 h and thereafter it remains constant. This was probably due to the attainment of dynamic equilibrium between water and the membrane.

**Effect of feed concentration on flux and separation factor**

Individual and overall pervaporation flux with membrane separation factor was determined for all the synthesized membranes used in the present study. Fig. 2 reveals that overall flux of (PVA-GO) membrane decreased with increase in feed acetic acid concentration.

![Graph](image)

**Fig. 2** Overall pervaporation flux and separation factor in the simulated vinegar solution

Strong interaction between water and membrane makes it more swollen which results in facilitated water flux at higher water concentration (Durmaž et al., 2001). (PVA-GO)\textsubscript{2} has maximum flux of 0.24 m\textsuperscript{3}(STP)/m\textsuperscript{2}h and separation factor 62.2 at 2.5 vol% and 20 vol% of feed acetic acid concentration. Compare to acetic acid flux, the magnitude of water flux was observed to be higher for all feed acetic acid concentration. The analogous trends were also observed for the PV dehydration of acetic acid and ethylene glycol with different membranes.

**Effect of feed temperature on flux and separation factor**

Effect of the feed temperature on pervaporation performance over a temperature range from 50 to 90°C with a constant feed concentration of 50 vol% acetic acid with PVA-PES composite membrane cross-linked with glutaraldehyde are presented in Fig. 3. Figure indicates that molar fluxes of both water and acetic acid increased with increasing temperatures while the separation factor decreased. Effects of temperature on flux and separation factor shows the similar kind of results for the pervaporation study of vinegar-water and ethylene glycol-water mixture with the other prepared membranes.
Fig. 3 Molar flux and separation factor during PV study of acetic acid-water mixture.

**Apparent activation energy and flux**
Activation energies were calculated using Arrhenius type relationship. For water permeation it was significantly lower than those of acetic acid or ethylene glycol permeation, suggesting a higher permeation flux and separation efficiency of the prepared membranes used in the present pervaporation study.

**Pervaporation separation index and enrichment factor**
Pervaporation separation index and enrichment factor for water-acetic acid mixture through PVA-PES membrane cross-linked with glutaraldehyde are presented in Fig. 4. PSI was found to decrease with increasing feed concentration whereas enrichment factor increased. Similar observations were reported by Kuila and Ray (2011) for the dehydration of acetic acid by using a cross linked co-polymeric polyvinyl alcohol-acrylamide membrane.

Fig. 4 PSI and enrichment factor during pervaporation study of acetic acid-water mixture.
Intrinsic membrane permeability, selectivity and feed concentration

Partial permeability of acetic acid and water with feed acetic acid concentration at a fixed temperature of 30°C are presented in Fig. 5. It indicates that with increase in feed concentration, both the partial permeability of acetic acid and water decreased and membrane selectivity is increased. Incorporation of GO into the PVA results in the enhanced water affinity towards the membrane which becomes more hydrophilic (Pezeshk et al., 2012). It was observed that (PVA-GO)$_2$ gives higher selectivity than (PVA-GO)$_1$ and (PVA)$_0$.

![Graph](image)

**Fig. 5** Partial permeabilities of acetic acid and water as a function of feed HAc concentration

The similar results were also obtained during the pervaporation separation of acetic acid-water and ethylene glycol-water with PVA-PES membranes.

Effect of feed temperature on membrane permeability

![Graph](image)

**Fig. 6** Water, acetic acid permeability and membrane selectivity as a function of feed temp
Intrinsic membrane selectivity and permeability of commercial (PVA-PES) membrane used for the pervaporation study of concentrated acetic acid-water mixture as a function of temperature is presented in Fig. 6, which shows that the permeabilities of both the component increases and membrane selectivity decreases. It was also noted that the magnitude of water permeability was always higher than that of acetic acid.

Membranes with their water permeability and selectivity

In general it was also observed that with increase in water concentration, the permeability of water increases for all the membranes. The reason for the increasing permeability may be attributed to the promotion of more turbulence at the membrane surface.

Table 2 Water permeability and selectivity of the prepared membranes during PV study

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Feed composition (vol%)</th>
<th>Feed temp (°C)</th>
<th>Max. water permeability (Barrer)</th>
<th>Membrane selectivity (α&lt;sub&gt;mem&lt;/sub&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial (PVA-PES)</td>
<td>50/50, HAc/W</td>
<td>90</td>
<td>35.76</td>
<td>4.76</td>
</tr>
<tr>
<td>(PVA-PES)</td>
<td>3/97, Vinegar/W</td>
<td>35</td>
<td>0.28</td>
<td>1.80</td>
</tr>
<tr>
<td>(PVA)</td>
<td>2.5/97.5, Vinegar/W</td>
<td>60</td>
<td>0.21</td>
<td>3.18</td>
</tr>
<tr>
<td>(PVA-GO&lt;sub&gt;1&lt;/sub&gt;)</td>
<td>2.5/97.5, Vinegar/W</td>
<td>60</td>
<td>0.36</td>
<td>4.00</td>
</tr>
<tr>
<td>(PVA-GO&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>2.5/97.5, Vinegar/W</td>
<td>60</td>
<td>0.51</td>
<td>4.25</td>
</tr>
<tr>
<td>(PVA-PES, 0.2% Borax)</td>
<td>80/20, EG/W</td>
<td>45</td>
<td>14.56</td>
<td>2.58</td>
</tr>
<tr>
<td>(PVA-PES, 0.5% Borax)</td>
<td>80/20, EG/W</td>
<td>45</td>
<td>10.02</td>
<td>1.10</td>
</tr>
<tr>
<td>(PVA-PES, Uncross-linked)</td>
<td>80/20, EG/W</td>
<td>45</td>
<td>11.12</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Table 2 indicates the maximum water permeability and selectivity determined during the PV performance of the different composite membranes used in the present study.

Effect of feed flow rate on diffusion coefficient

Water and EG diffusion coefficients of the borax cross-linked membrane evaluated at constant 45 °C for 80 vol% feed EG concentration are presented in Fig. 7.

![Fig. 7 Water and ethylene glycol diffusion coefficient in the PV study of EG-water mixture](image)
As shown in the figure both the EG and water diffusion coefficients increased with increasing feed flow rate. The diffusion coefficients of water decreased as borax content increased from 0.2 to 0.5% wt due to the reduction of membrane free volume resulting in restricted segmental motion of water diffusing molecule through membrane network (Qu et al., 2010). Effect of the feed concentration and temperature on diffusion and partition coefficient were also estimated with the other prepared membranes for vinegar-water mixture.

**Thermogravimetric and differential scanning calorimetry analysis**

TGA characterizations of the all prepared membrane are made to signify the heat resistance and thermal stability. Two stage weight losses were observed. The first weight loss is because of loss of water molecules and second weight loss may be due to the decomposition of polymeric backbone. All the PVA membrane shows considerable stability enhancement.

**Fourier Transform Infrared Spectroscopy of membrane**

FTIR spectra of PVA-PES membrane cross-linked with glutaraldehyde shows that there were few additional absorption peaks detected due to the absorption of $-O-H$ stretching and hydrogen bonds of water and acetic acid in the swollen membrane. In case of $(PVA-GO)_1$ and $(PVA-GO)_2$ due to hydrogen bonding interactions stretching vibration of hydroxyl groups are shifted to 3450 and 3434 cm$^{-1}$ in respectively. Borax crosslinked PVA-PES composite membrane with two different proportion of borax exhibited peaks in the range of 1324 – 1409 cm$^{-1}$, confirming crosslink formation.

**Atomic force microscopy**

AFM image of PVA-PES membrane cross-linked with formaldehyde are presented in Fig. 8.

![AFM images](image)

**Fig.8.** AFM images of pristine (a) and used (b) PVA-PES membrane for the pervaporation study of acetic acid-water mixture

Figure reveals that the ridges are not distinctly visible compared to the virgin membrane due to swelling for prolonged contact with different concentrations of acetic acid water.
mixture. AFM images of (PVA-GO) membrane shows higher swelling compare to pristine PVA membrane. AFM images was also recorded for PVA-PES composite membranes confirm that borax cross linking have imparted rougher surfaces.

**X-ray diffractometer analysis**

The X-ray diffraction measurement was carried out to observe the crystallinity of the composite polymer membrane. Compared to (PVA) \(_0\) the XRD peaks of (PVA-GO) \(_1\) and (PVA-GO) \(_2\) membranes were somewhat broadened by the incorporation of graphene oxide thereby indicating an enhanced amorphicity of the composite membranes. An overall decrease in relative crystallinity was observed in the case of PVA-PES composite membrane cross-linked with 0.2% wt borax as compared to that cross-linked with 0.5% wt borax.

**Field emission scanning electron microscopy of membrane**

The cross section and surface morphology of the as-prepared membranes used in the present study were examined by field emission scanning electron microcopy (FE-SEM). As shown in Fig. 9 that SEM result of (PVA) \(_0\) exhibits a compact and almost smooth surface while GO penetrated membrane have coarser topography with bumpy surfaces.

![Fig. 9 FE-SEM cross sections of (a) (PVA)\(_0\) (b) (PVA-GO)\(_1\) (c) (PVA-GO)\(_2\) membranes](image)

Also the SEM images of borax cross-linked PVA-PES membrane results that increasing the amount of cross-linker from 0.2% to 0.5 wt%, the structure became denser and uniform.

**Mechanical properties of the prepared membrane**

Tensile strength, Elongation at break and Modulus of elasticity of the newly prepared membranes used in the present pervaporation study are presented in Table 3. The values indicate that the modulus of elasticity of the borax cross-linked membrane is higher than (PVA-PES, Uncross-linked) membrane. The tensile strength and elongation at break of (PVA-GO)\(_1\) and (PVA-GO)\(_2\) is higher than (PVA)\(_0\) membrane. It was also observed that for the formaldehyde cross-linked (PVA-PES) membrane, tensile strength and modulus of elasticity are marginally reduced after immersion in water and acetic acid for one week.

**Table 3** Mechanical properties of the newly prepared membranes used in the present study
<table>
<thead>
<tr>
<th>Membrane</th>
<th>Max Tensile strength (MPa)</th>
<th>% Elongation at Max</th>
<th>Modulus of Elasticity (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PVA-PES)</td>
<td>27.23</td>
<td>16.18</td>
<td>155.2</td>
</tr>
<tr>
<td>(PVA)_0</td>
<td>24.5</td>
<td>14.6</td>
<td>145.4</td>
</tr>
<tr>
<td>(PVA-GO)_1</td>
<td>27.8</td>
<td>16.8</td>
<td>149.6</td>
</tr>
<tr>
<td>(PVA-GO)_2</td>
<td>27.2</td>
<td>16.4</td>
<td>147.7</td>
</tr>
<tr>
<td>(PVA-PES, 0.2%Borax)</td>
<td>2.15</td>
<td>8.84</td>
<td>17.56</td>
</tr>
<tr>
<td>(PVA-PES, 0.5%Borax)</td>
<td>2.29</td>
<td>10.67</td>
<td>21.46</td>
</tr>
<tr>
<td>(PVA-PES, Uncross-linked)</td>
<td>2.54</td>
<td>12.43</td>
<td>20.43</td>
</tr>
</tbody>
</table>

**Modeling of sorption behaviour during pervaporation**

It was observed from the sorption data that with increase in feed concentration of water, water uptake is increased and ethylene glycol uptake is decreased at 25°C. The maximum sorption selectivity was determined to be 4.21 at 80% vol water concentration. It was noted that the activity of water increased and ethylene glycol activity decreased with increased in feed water concentration. The Gibbs free energy was also decreased. F-H interaction parameter calculated from the pure water and ethylene glycol sorptions were 0.78 and 0.92 respectively which shows that the present membrane has more affinity towards water rather than ethylene glycol as the membrane is hydrophilic. The interaction parameters were also estimated by considering them as concentration independent or dependent with four different cases to predict the sorption model results. Fourth order polynomial expression was used to determine the adjustable parameters. In case of concentration dependent parameters, it was noted that with increase in water concentration, the value of \(X\)\(_wm\) was increased while value of \(X\)\(_w\)-\(EG\) was decreased. This may be due to the more interaction between the low molecular weight water and high molecular weight PVA. As the affinity between polymer and the solvent increased, the amount of liquid in the polymer increased and \(X\)\(_w\)-\(EG\) decreased (Chuang et al., 2000). The error between predicted and experimental data was decreased from around 60% to 10% when considering interaction parameter to be concentration dependent.

**Achievement with respect to objectives**

- Seven different polyvinyl alcohol (PVA) based composite membranes were synthesized and characterized through different analytical methods like FTIR, TGA, DSC, AFM, XRD and FESEM.
- Comparative swelling study of the as prepared membranes was carried out effectively using gravimetric method at different temperatures including room temperature.
The prepared membranes were successfully used in the pervaporation separation of acetic acid-water, vinegar-water and ethylene glycol-water binary feed solution in a wide range of feed concentrations.

Effect of various physico-chemical parameters such as feed temperature, feed concentration and feed flow rate on the permeate flux, separation factor, pervaporation separation index and enrichment factor were investigated.

Intrinsic properties like partial permeability, permeance and selectivity as well as the mechanical properties like tensile strength, elongation at break and modulus of elasticity of the newly prepared PVA composite membranes were evaluated and compared with pertinent literature.

Diffusion behavior during pervaporation transport through the prepared membranes was determined in terms of the diffusion and partition coefficient using Fick’s law.

Modeling of sorption behavior of ethylene glycol-water binary solution through commercial (PVA-PES) composite membrane cross-linked with glutaraldehyde was carried out using Flory-Huggins equations.

**Conclusion and future scope of study**

Seven different flat sheet hydrophilic PVA membranes cross-linked with glutaraldehyde, formaldehyde and borax were synthesized. The prepared membranes were thoroughly examined by using wide angle XRD, FTIR, TGA, DSC, FESEM and AFM analyses. TGA results indicate that GO incorporation could notably enhance the thermal stability of PVA-GO membrane. The overall decrease in relative crystalinity in the PVA-GO composites was observed from the XRD results. The PVA layers were successfully cross linked with two different concentrations e.g. 0.2 wt% and 0.5 wt% borax as cross linking agents although 0.2% borax cross-linked PVA-PES composite was found better in terms of flux, permeability and separation factor. The degree of swelling increased almost linearly with increasing water concentration. With increase in feed temperature degree of swelling decreased marginally. There was disproportionality between the flux and separation factor for all feed compositions and operating temperatures. The rate of increase of molar flux of water with temperature was found to be substantially higher than acetic acid. The apparent activation energy of water permeation was significantly lower. Incorporation of GO into the PVA results in the enhanced water permeability. PV flux and diffusion coefficients of both EG and water increased with increasing feed flow rate. Diffusion and partition coefficient for water and acid were also found to increase with temperature. Modeling results could produce satisfactory prediction of experimental sorption of ethylene glycol-water binary mixture. GO incorporated and borax cross-linked membrane exhibited higher
tensile strength and modulus of elasticity. However, further efforts for flux enhancement and tuning of the physico-chemical properties of the composite membranes are needed in the future. Active laboratory-scale pervaporation research should be complemented with more efforts in scaling up the process from laboratory to industry.

**Presentation and layout of the thesis**

The proposed thesis contains the following chapters with appropriate sections, subsections, references, appendices and the list of publications.

**Chapter 1**: Introduction

**Chapter 2**: Review of literature

**Chapter 3**: Materials and methods

**Chapter 4**: Theoretical consideration

**Chapter 5**: Results and discussions

**Chapter 6**: Summary and conclusion

**References**


**List of publications**

**Journal**


**Book Chapter**


**Conference proceeding**


