

# Novel Silica Functionalized Monosodium Glutamate/PVA Cross-linked Membranes for Alkali Recovery by Diffusion Dialysis

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## Research Article

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# **Novel silica functionalized monosodium glutamate/PVA cross-linked membranes for alkali recovery by diffusion dialysis**

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## **Abstract**

In this work, two types of silica functionalized monosodium glutamate (GMSG and VMSG)/poly(vinyl alcohol) (PVA) were cross-linked by sol-gel process to prepare novel hybrid cation exchange membranes (CEMs). The prepared membranes were systematically characterized by FTIR, ion exchange capacity (IEC), TGA, water uptake, water swelling, mechanical strength and diffusion dialysis (DD) performance for alkali separation using NaOH/Na<sub>2</sub>WO<sub>4</sub> solution. The FTIR peaks around 1260-1350 cm<sup>-1</sup> confirmed the secondary C–N linkages. The cross-linking between GMSG/VMSG and PVA was verified by the presence of stretching peaks of Si–O–C, Si–O–Si, C–O–C, and –C(=O)–O–C groups between 1080-1120 cm<sup>-1</sup>. TGA results indicated that GMSG membranes showed relatively high thermal stability as compared to VMSG membranes. Water uptake and degree of swelling decreased while IEC values increased with the increase of GMSG/VMSG content in membrane matrix. The mechanical properties of the membranes improved up to 40% GMSG/VMSG content. The NaOH dialysis coefficient (U<sub>OH</sub>) values improved while values of separation factor (S) declined with the increase of GMSG/VMSG content. Finally, the effect of temperature was studied and it was found that increase in temperature from 25 to 45 °C resulted in increase of diffusion coefficient and decrease of separation factor for both GMSG/VMSG crossed-linked with PVA membranes.

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**Keywords:** Silica functionalized; monosodium glutamate; PVA; diffusion dialysis

## 1. Introduction

It is a bitter fact that huge quantity of alkaline water is being produced from several industrial wastes like printing, paper, metal ores and leather industries which results in serious environment pollution [1-3]. The discharge of alkaline water without treatment process not only wastes useful substances but also disturbs the water pH of rivers which causes severe damage to aquatic life [4]. The traditional methods which have been applied for the treatment of alkaline waste are (a) neutralization of alkali substances with acids (b) lowering the concentration of alkali substances by diluting them and (c) directly burning these substances like in paper and pulp industry. These traditional processes are either energy extensive/require a large amount of commercial acids or a large amount of sludge is produced which poses disposal problems [5, 6]. In recent years, membrane-based alkali separation technology has been developed which includes nano-filtration, reverse osmosis, electro-dialysis, ultra-filtration and diffusion dialysis (DD) [3, 7]. DD is the most dominant process among all as it is environment friendly, requires less energy and has less installation cost as well. Other advantages include absence of pollution, simple construction of apparatus, recoverable alkali and continuous operation [6, 8]. The most important advantage of this process is that it does not require any external driving force as it is spontaneous separation process which relies on simple technique of ion diffusion (movement of ions from high to low concentration) [9]. The alkali separation properties of DD process are remarkably affected by cation exchange membranes (CEM). Recently, a lot of work on CEMs has been done which focuses on various properties of these membranes like NaOH permeability, alkaline resistance, salt rejection, thermo-mechanical stability and selectivity [10]. A lot of polymeric materials have been used, for the development of cation exchange membranes for alkaline recovery, which include poly(vinylidene fluoride), polysulfone, polystyrene, polyetheretherketone, poly(ethylene oxide) and poly(vinyl alcohol) [11-14]. The most critical issues of CEMs having high IEC capacities are their low stability, high degree of swelling and permeability issues in alkaline conditions due to the lack of enough cross-linking [15]. By combining the properties of both inorganic and organic polymer materials, hybrid membranes can be prepared in which inorganic material is dispersed into the organic polymer matrix in order to obtain the required mechanical strength and separation properties [16]. These modifications have made most PVA based hybrid membranes [17, 18]. PVA has several advantages like high water solubility, low cost and excellent film forming properties [19]. PVA also possesses  $\text{-OH}$

groups in abundant which can facilitate extraordinary reaction with  $-\text{Si}-\text{O}-\text{CH}_3$  group through sol-gel process. However, due to absence of cation exchange groups in PVA matrix, mixing with other materials having cation exchange group is required to obtain ion exchange capacities [20, 21]. Hao et al. studied the effect of carboxyl ( $-\text{COOH}$ ) group content on PVA/ $\text{SiO}_2$  membranes prepared by sol-gel process for alkali recovery and found that separation factor was increased up to 36.2 [22]. Wu et al. prepared PVA hybrid membrane containing maleic anhydride for NaOH separation performance through DD process and observed noticeable increase in  $\text{Na}^+$  transport, permeability and IEC values with the addition of maleic anhydride containing  $-\text{COOH}$  groups [23]. Wang et al. studied the influence of mesoporous silica functionalized phosphotungstic acid on PVA membranes for alkali recovery and observed improved thermo-mechanical properties along with improved values of IEC between 0.015 to 0.030 mmol/g [24]. Tong et al. studied separation properties of NaOH/ $\text{Na}_2\text{WO}_4$  solution using un-charged PVA-silica hybrid membranes prepared by sol-gel process and found that alkoxysilanes significantly enhanced both mechanical properties and selectivity [2]. Gu et al. studied DD performance of NaOH/ $\text{Na}_2\text{WO}_4$  solution using multisilicon copolymer/PVA hybrid membranes. The results indicated that the addition of  $\text{Si}-\text{OH}$  groups significantly improved the permeation of  $\text{OH}^-$  ions [10]. Mondal et al. prepared silica functionalized aminoisophthalic acid cross-linked PVA membranes through sol-gel process for the recovery of alkaline solution through DD process. The resulting membranes demonstrated high performance parameters like IEC values within 0.48–0.93 mmol/g, dialysis coefficient values between 0.0068–0.0097 m/h and separation factor reached to 31.79 [25]. Hence, PVA based hybrid membranes have been developed with different cross-linkers and cation exchange groups to improve the DD performance for alkali recovery [17]. The  $-\text{Si}-\text{OCH}_3$  cross-linked PVA based hybrid cation exchange membranes have been used in many DD applications for alkaline separation [26]. Monosodium glutamate (MSG) is environmental friendly, easily available and cheap food additive having extremely hydrophilic nature due to the presence of  $-\text{COOH}$  group [27]. The  $-\text{COOH}$  or  $-\text{COONa}$  groups (cation exchange component) via ion exchange process can transfer  $\text{Na}^+$  ions, while  $\text{OH}^-$  ions may be transferred through membrane via weak interactions such as hydrogen bonding with the hydroxyl ( $-\text{OH}$ ) groups of PVA and also  $-\text{Si}-\text{OH}$  groups, presents in the membrane [11, 28].

In this work, two series of novel silica functionalized monosodium glutamate (GMSG, VMSG) cross-linked PVA hybrid cation exchange membranes have been synthesized which has never been synthesized and studied before for alkaline recovery, according to the best of our literature survey. Moreover, Fourier transform infrared spectroscopy (FTIR), IEC, water uptake, swelling degree, thermo gravimetric analysis (TGA) and mechanical strength of the prepared membranes have been analysed. Finally DD performance properties in term of  $U_{OH}$  and selectivity were evaluated via DD test at two different temperatures using NaOH/Na<sub>2</sub>WO<sub>4</sub> solution as a model for alkali waste feed solution.

## **2. Experimental**

### **2.1. Materials**

Polyvinyl alcohol (Hydrolyzed 90%,  $M_w = 30,000\text{--}70,000$  g/mol), 3-glycidoxypropyltrimethoxysilane, vinyltrimethoxysilane and sodium tungstate (Na<sub>2</sub>WO<sub>4</sub>) were purchased from Sigma Aldrich, USA. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Merck, Germany. Monosodium glutamate was purchased from Ajinomoto, China. Deionized water utilized as a solvent was prepared in our laboratory.

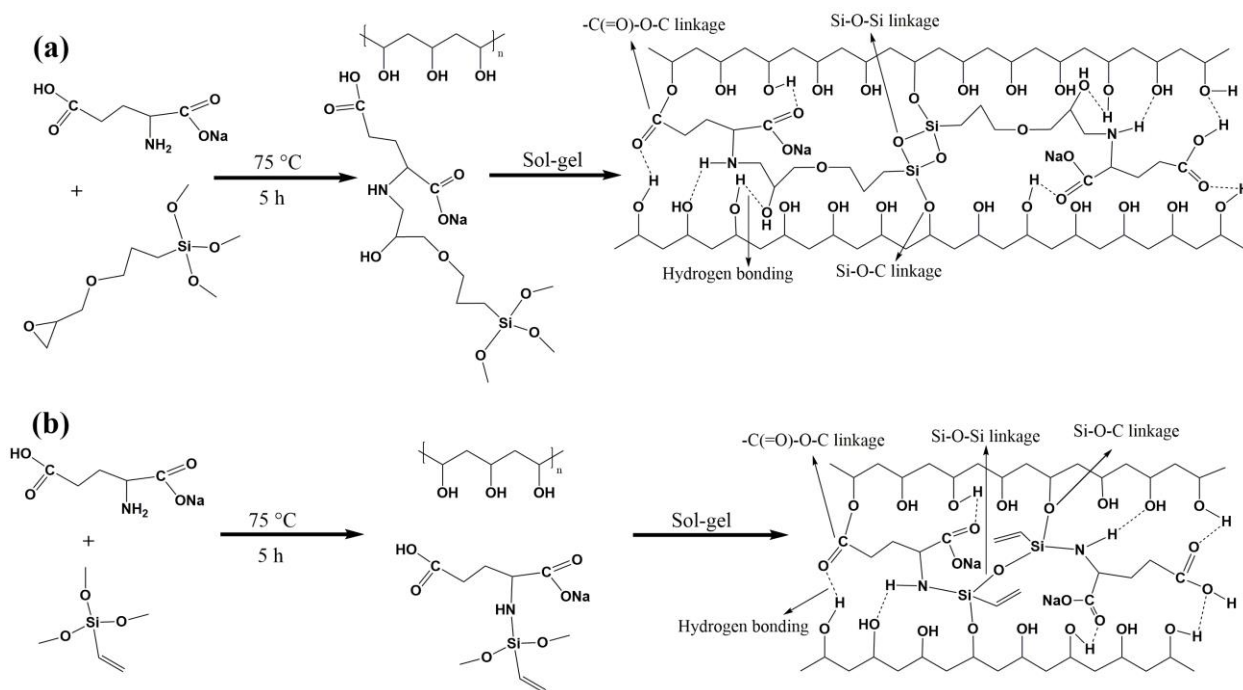
### **2.2. Synthesis of silica functionalized monosodium glutamate (GMSG, VMSG)**

Two types of silica functionalized monosodium glutamate (GMSG, VMSG) were separately prepared by the reaction of monosodium glutamate with 3-glycidoxypropyltrimethoxysilane and vinyltrimethoxysilane, respectively. First, 1 g (5.9 mmol) of monosodium glutamate was added to 10 mL of deionized water with continuous stirring at 75 °C for 30 min in a 50 mL round bottom flask and then calculated amount of 3-glycidoxypropyltrimethoxysilane (1.39 g/ 5.9 mmol) was added to this mixture and stirring was continued on a hot plate for 5 h at 75 °C in order to complete the reaction and obtain viscous solution of GMSG. Similarly, 1 g (5.9 mmol) of monosodium glutamate and 0.87 g (5.9 mmol) of vinyltrimethoxysilane were processed to obtain viscous solution of VMSG.

### **2.3. Fabrication of GMSG and VMSG cross-linked PVA hybrid membranes**

GMSG and VMSG cross-linked PVA hybrid cation exchange membranes were synthesized through sol-gel process without using any hazardous chemical and organic solvent. For this

purpose, 10 g of PVA was dissolved in 90 mL of deionized water with continuous stirring for 4 h at 90 °C till clear solution was obtained which was then cooled down to 65 °C. To prepare GMSG/VMSG cross-linked PVA hybrid membranes, the calculated amount of GMSG/VMSG solutions were added carefully to the PVA solutions. A little amount of 1 M HCl solution was then added to this mixture and the solution was stirred at 65 °C for 24 h to complete the cross-linking reaction as per proposed reaction scheme as shown in Scheme I. As per the suggested reaction scheme, hydrolysed silanol (Si-OH) undergo sol-gel reaction to form Si-O-Si linkages, Si-OH react with PVA through cross-linking reaction to form Si-O-C linkages and self-condensation of the -C-OH groups of PVA to form C-O-C linkages. The development of -C(=O)-O-C linkage is the result of reaction between -COOH groups present in GMSG/VMSG and -OH groups of PVA.



**Scheme I.** Proposed Reaction scheme for (a) Synthesis of silica functionalized monosodium glutamate (GMSG) and GMSG cross-linked PVA matrix. (b) Synthesis of silica functionalized monosodium glutamate (VMSG) and VMSG cross-linked PVA matrix.

The resulting gel mixtures were casted on petri dishes and dried at room temperature for about four days. The obtained membranes were carefully peeled off from the petri dishes with the help of knife blade. The membranes were then processed for thermal treatment in a vacuum oven for

5 h at 120 °C to ensure the complete reaction conversion into the hybrid membranes [29]. The obtained membranes were labelled as GMSG20, GMSG40, GMSG60 and VMSG20, VMSG40, VMSG60 series with different wt. % content of GMSG and VMSG inside the membrane matrix, which were 20, 40 and 60 wt. % of PVA as shown in Table 1. The thickness of the membranes was maintained to around 120 to 150  $\mu\text{m}$ .

## **2.4. Membrane characterization**

### **2.4.1. Fourier transform infrared (FTIR) spectroscopy**

FTIR spectroscopic analysis of the PVA hybrid membrane was performed using IR Shimadzu, Prestige-21 (Japan) spectrometer equipped with Horizontal Attenuated Total Reflectance (HATR) accessory. The experiment was performed in the wave number range of 4000–400  $\text{cm}^{-1}$  and 100 scans were collected per spectrum at the resolution of 4  $\text{cm}^{-1}$  with air as its background.

### **2.4.2. Ion exchange capacity (IEC)**

Membrane IEC value was calculated to investigate the content of interchangeable ionic ( $-\text{COOH}$  or  $-\text{COONa}$ ) group in membrane using acid base titration method. The dried sample was weighed ( $W_{\text{dry}}$ ) and soaked in 1.0 M HCl solution for two days at room temperature to convert the ion exchange groups into  $\text{H}^+$  form. Afterwards, the sample was washed with plenty of deionized water to ensure the complete removal of acid residues and immersed in 0.05 M solution of NaOH for 48 h. This NaOH solution was titrated against 0.05 M HCl solution with phenolphthalein as an indicator to determine the decreased amount of NaOH. The IEC (mmol/g) was measured by the amount of HCl per dry weight of membrane by equation 1 [30, 31].

$$\text{IEC} = \frac{C_{\text{HCl}} \times V_{\text{HCl}}}{W_{\text{dry}}} \quad (1)$$

Where, IEC is the Ion exchange capacity (mmol/g),  $C_{\text{HCl}}$ ,  $V_{\text{HCl}}$  and  $W_{\text{dry}}$  represent the molar concentration of HCl solution, volume of HCl consumed and dry membrane weight (g), respectively.

#### 2.4.3. Thermal gravimetric analysis (TGA)

TGA was performed using Mettler Toledo analyser at a heating rate of 10 °C/min and over a temperature range from room temperature to 800 °C. Nitrogen gas at a flow rate of 15 mL/min was supplied to obtain the inert atmosphere.

#### 2.4.4. Mechanical properties

Mechanical properties like tensile strength and elongation at break of the hybrid membranes were determined using U-CAN Dynatex, tensile tester (UT-2080, Taiwan) having crosshead speed of 100 mm/min. The experiment was performed at  $25 \pm 2\%$  relative humidity and 25 °C using dumbbell shaped sample having 25 mm length and 5 mm width.

#### 2.4.5. Water uptake and swelling degree

Water uptake was measured to investigate the hydrophilicity of membrane. Small pieces of membranes were dried in a vacuum oven at 75 °C for 24 h. The dried pieces of membranes were weighed and soaked in deionized water at room temperature for 72 h. Afterwards, the pieces were withdrawn, wiped out with blotting paper to remove extra water and weighed again. The Water uptake (%) was determined [32] using equation 2.

$$\text{water uptake (\%)} = \frac{W_2 - W_1}{W_1} \times 100 \quad (2)$$

Where,  $W_1$  and  $W_2$  represent dried membranes weight and wet membrane weight respectively. Swelling degree is used to investigate the stability of membrane in hot water. Degree of swelling of the membrane was determined using water immersion method, by membrane swelling behaviour in water. The weight gain of the dry membrane was measured for a certain time after immersed in water at 65 °C [33]. Pre-weighed dry membrane pieces ( $W_1$ ) was dipped in water at 65 °C and then taken out after 72 h. As a final point, the extra surface water from the membrane was wiped dry quickly with blotting paper and then wet piece of membrane was weighed ( $W_3$ ). Swelling degree (%) was measured using the following equation

$$\text{Swelling degree (\%)} = \frac{W_3 - W_1}{W_1} \times 100 \quad (3)$$



### 2.3.6. Diffusion dialysis

To investigate the potential application of the membrane for alkali recovery, DD experiment was performed using NaOH/Na<sub>2</sub>WO<sub>4</sub> aqueous solution [34] in a cell of two compartments separated by the prepared membrane having an effective area of about 6.2 cm<sup>2</sup> as shown schematically in Sch. II. The feed side of the dialysis cell was filled with 100 mL of 1M NaOH and 0.1M Na<sub>2</sub>WO<sub>4</sub> aqueous solution as model aqueous waste feed solution and permeate side was filled with 100 mL of deionized water as dialysate. The membrane was immersed in the feed solution for 1 h before the test. Both sides of the dialysis cell were stirred continuously with the help of magnetic stirrer at equal speed to avoid concentration polarization. The experiment was performed at 25 °C or 45 °C for 1 h and then from both compartments of the cell, feed and permeate solutions were removed. The concentration of OH<sup>-</sup> ions in feed and permeate sides were measured by titration method using 0.1M HCl solution, while ultraviolet spectrophotometry method was used to measure the WO<sub>4</sub><sup>2-</sup> concentration.

The dialysis coefficient (U) was calculated using equation 4 [31, 35].

$$U = \frac{M}{At\Delta C} \quad (4)$$

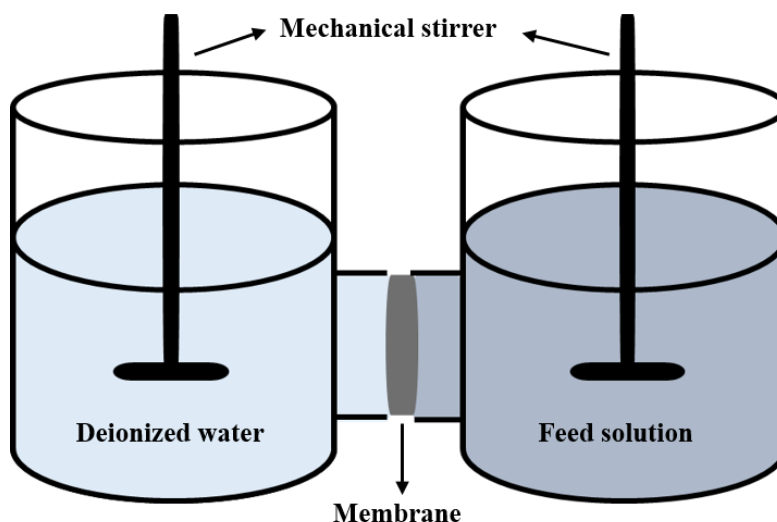
Where, M, represents the amount of substance transported in moles, A is the effective area of membrane (m<sup>2</sup>), t stands for time in h and  $\Delta C$  is the logarithm average concentration difference (mol/m<sup>3</sup>) between the two compartments which was calculated using equation 5 [13, 36].

$$\Delta C = \frac{C_f^0 - (C_f^t - C_d^t)}{\ln[C_f^0 / (C_f^t - C_d^t)]} \quad (5)$$

Where C<sub>f</sub><sup>0</sup> and C<sub>f</sub><sup>t</sup> are the concentrations of feed solutions at time 0 and t, respectively and concentration of dialysate at t time is C<sub>d</sub><sup>t</sup>.

The separation factor (S) determined by the ratio of (two dialysis coefficients) U<sub>OH</sub> and U<sub>WO<sub>4</sub><sup>2-</sup></sub> in the solution and was calculated using equation 6 [37].

$$S = \frac{U_{OH}}{U_{WO_4^{2-}}} \quad (6)$$

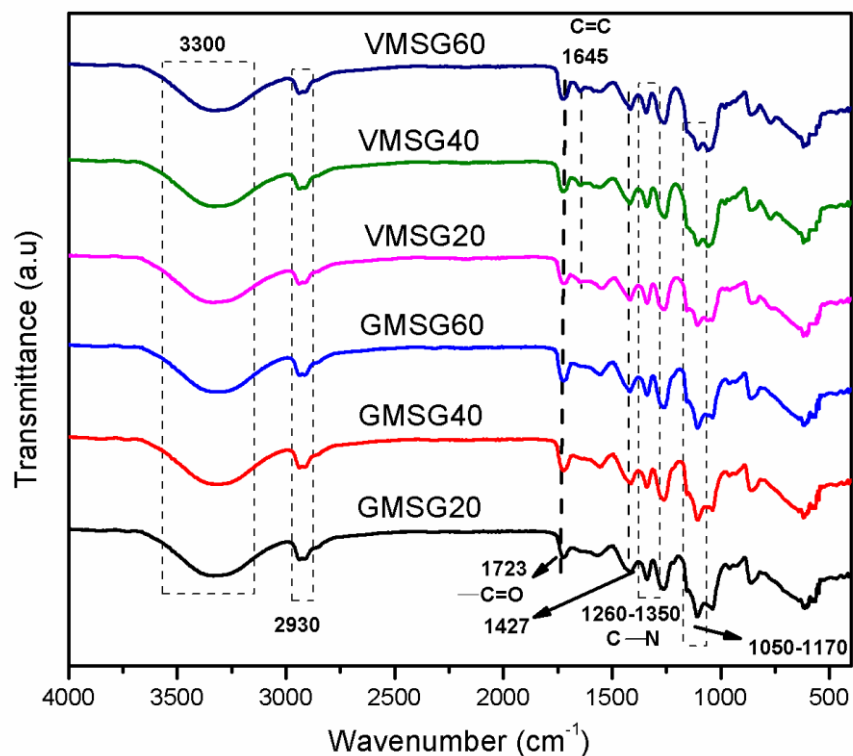


**Scheme II.** Schematic diagram for two compartment dialysis cell

### 3. Results and discussions

#### 3.1. FTIR spectra analysis

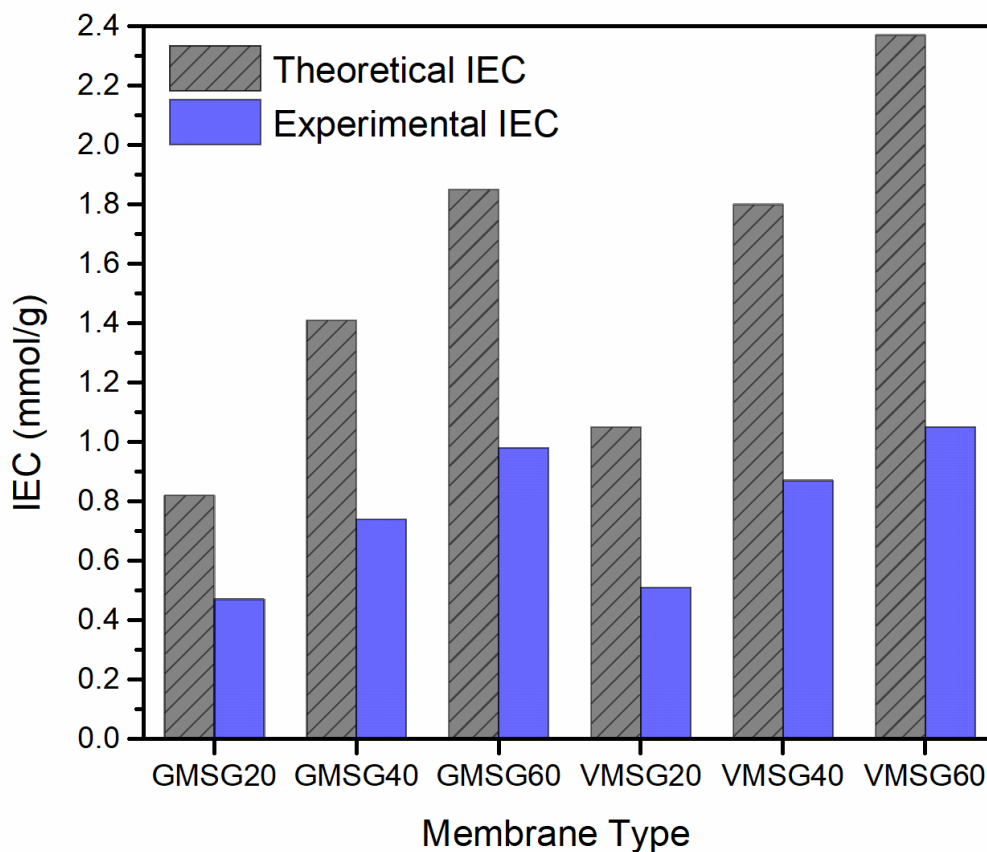
The FTIR spectra of GMSG and VMSG cross-linked PVA hybrid membranes are demonstrated in Fig. 1. Absorption band between  $1260\text{--}1350\text{ cm}^{-1}$  represents the stretching vibration of secondary C–N group [25, 38] which confirms the formation of GMSG/VMSG (Scheme 1 a). The broad band around  $3300\text{ cm}^{-1}$  is assigned to stretching vibration of –OH group of PVA and cross-linker [39]. The peaks appearing at  $2930\text{ cm}^{-1}$  and  $1427\text{ cm}^{-1}$  represent –CH stretching and bending vibrations, respectively [40–45]. The characteristic sharp peak at  $1723\text{ cm}^{-1}$  is attributed to stretching vibration of carbonyl (–C=O) group from GMSG/VMSG [46, 47], the intensity of which increases with the increase of GMSG/VMSG contents in the membrane matrix. The small peak at  $1645\text{ cm}^{-1}$  is attributed to the stretching vibration of C=C [48], which becomes gradually stronger by increasing content of VMSG. The stretching peaks of Si–O–C, Si–O–Si, ether linkages (C–O–C), and ester linkages (–C(=O)–O–C) are observed between  $1050\text{--}1170\text{ cm}^{-1}$  which confirm the cross-linking reactions [33, 49–51].



**Fig.1.** FTIR spectra of (GMSG/VMSG)/PVA cross-linked membranes

### 3.2. Ion exchange capacity (IEC)

The IEC value was measured using the titration method to confirm the charged nature of the CEMs and results are shown in Fig. 2. The IEC was mainly contributed from the  $-\text{COOH}/-\text{COONa}$  groups (Scheme 1 a, b) present inside membrane matrix. By increasing GMSG and VMSG amount, the  $-\text{COOH}/-\text{COONa}$  content increases which results in gradual increase of both theoretical and experimental IEC values as shown in Table 1. Hence, GMSG, VMSG can be applied as new types of cross-linking agents for the synthesis of hybrid cation exchange membranes.



**Fig.2.** Theoretical and experimental IEC values of (GMSG/VMSG)/PVA cross-linked membranes

The experimental IEC values increase from 0.47 mmol/g to 1.05 mmol/g, which is slightly higher than the reported hybrid PVA/poly(AA-co- $\gamma$ -MPS) membrane having IEC value 0.76 mmol/g to 0.90 mmol/g [11]. The higher experimental IEC values of membranes are due to having  $-\text{COOH}$  and  $-\text{COONa}$  groups present in GMSG/VMSG cross-linked membranes. It is also interesting to note that  $-\text{COONa}/-\text{COOH}$  groups remain stable during the sol-gel reaction and only  $-\text{Si-O-CH}_3$  groups react with  $-\text{OH}$  groups of PVA [52]. The experimental IEC values depend upon the amount of fixed charge groups in membranes so it can also be claimed that increasing the amount of GMSG, VMSG in the membranes results in an increase of IEC values.

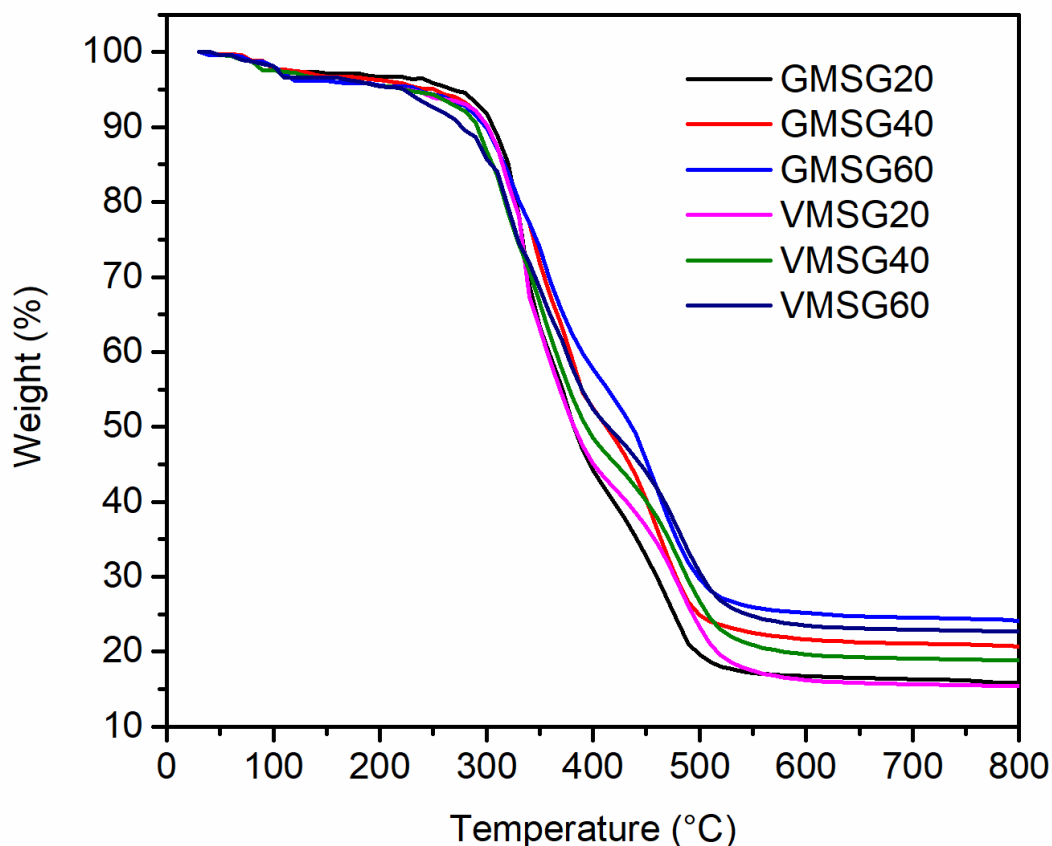
**Table 1**

Composition and ion exchange capacity (IEC) values of (GMSG/VMSG)/PVA cross-linked membranes

Membrane	GMSG (wt. %)	VMSG (wt. %)	Theoretical IEC (mmol/g)	Experimental IEC (mmol/g)
GMSG20	20%	—	0.82	0.47
GMSG40	40%	—	1.41	0.74
GMSG60	60%	—	1.85	0.98
VMSG20	—	20%	1.05	0.51
VMSG40	—	40%	1.80	0.87
VMSG60	—	60%	2.37	1.05

### 3.3. TGA analysis

The thermal stability of the prepared membranes was determined using TGA and the results are reported in the form of thermograms as shown in Fig. 3. Each thermogram shows following degradation steps. The first step, in the temperature range of 30–190 °C is attributed to dehydration and removal of bounded and unbounded water molecules from membrane [41]. The second step from 190 to 370 °C is due to the degradation of the –COOH and –COONa groups [53]. The next step from 370 to 490 °C is attributed to the elimination of –OH groups from the PVA [54]. Final degradation stage occurring from 490 to 800 °C is due to the carbonization of degraded product into ash residue by the degradation of main polymer backbones [55]. It has been observed that by increasing GMSG/VMSG content in the membrane, the weight loss keeps on increasing due to increase of cross-linked and compact structure owing as a result of abundance of –COOH/–COONa groups concentration inside the membrane matrix.



**Fig.3.** TGA thermograms of (GMSG/VMSG)/PVA cross-linked membranes

The experimental data indicated that the temperature at which degradation initiated ( $T_d$ ) values were 242–257 °C and temperature at 10% weight loss ( $T_{10\%}$ ) values of membrane were 286–306 °C. The  $T_d$  and  $T_{10\%}$  values gradually decreased by increasing the (GMSG/VMSG) content from 20 to 60 wt. % in membrane as indicated in Table 2. This is due to the increasing amount of –COOH/–COONa function groups which starts to degrade at relatively lower temperature. It was also noted that temperature at 50% weight loss ( $T_{50\%}$ ) was 382, 437, 383 and 417°C for GMSG20, GMSG60, VMSG40, and VMSG60 membranes, respectively. The enhancement in  $T_{50\%}$  by increasing the amount of GMSG and VMSG loading is due to increase of silica linkages which offer resistance to degradation.

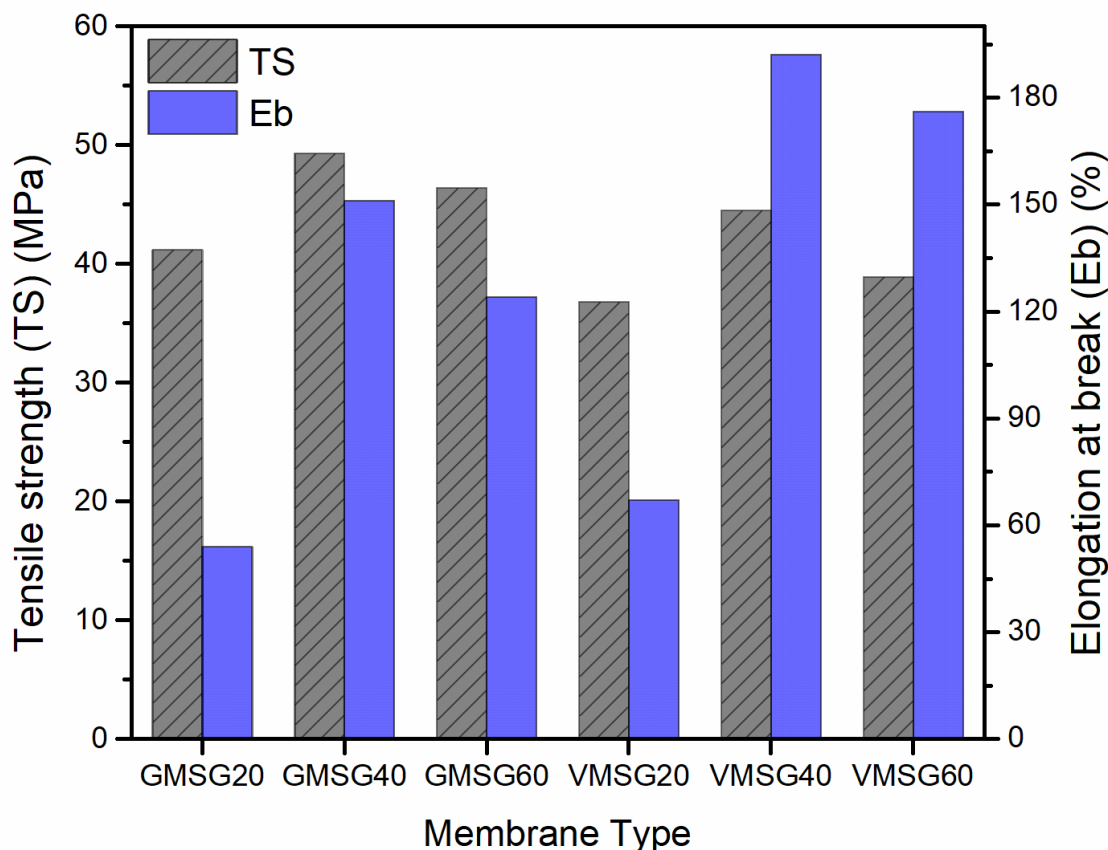
**Table 2**

Thermal stability of (GMSG/VMSG)/PVA cross-linked membranes

Membrane type	T <sub>d</sub> (°C)	T <sub>10%</sub> (°C)	T <sub>50%</sub> (°C)	Residue at end (%)
GMSG20	257	306	382	15.8
GMSG40	254	299	413	20.6
GMSG60	251	297	437	23.1
VMSG20	246	300	383	15.4
VMSG40	243	293	394	18.6
VMSG60	242	286	417	22.6

### 3.4. Mechanical strength

Mechanical properties of membranes such as tensile strength (TS) and elongation at break (Eb) were determined and obtained results are shown in Table 3 and exhibited in Fig. 4. The TS values of the cation exchange membranes are in the range of 36.8–49.3 MPa, whereas the Eb values are in the range of 54–192%. These values are much higher than those of PVDF based hybrid membranes (TS: 7.5–13 MPa, Eb: 47–123%) [56] and PVA/multi-alkoxy silicon copolymer membranes (17.4–44.4 MPa, 33.4–114.0%) [57] which proves the superior mechanical properties of our membranes as compared to other similar membranes as reported in the literature. It was found that addition of the GMSG and VMSG up to 40 wt. % results in improvement of both TS and Eb values and further addition results in decrease of these properties. The increase in the mechanical properties with the addition of GMSG, VMSG is due to cross-linking of GMSG/VMSG with PVA through sol-gel reaction resulting in the formation of covalent bonding, hydrogen bonding and homogeneous dispersion of silica throughout the polymer matrix causing superior mechanical properties. However, at higher GMSG and VMSG content (60 wt.%), the high amount of silica disturbs the homogeneity of the membrane [58] and results in the decline of mechanical strength.



**Fig.4.** Mechanical properties of (GMSG/VMSG)/PVA cross-linked membranes

It can also be observed from Fig. 4 that membranes cross-linked with GMSG show higher strength than the corresponding VMSG cross-linked membranes; whereas, membranes cross-linked with VMSG show higher flexibility as compared to corresponding GMSG membranes. The increased strength of GMSG membrane is due to the formation of Si–O–C linkages (Scheme I a) as a result of cross-linking reaction of hydrolyzed Si–OH groups of GMSG and –OH groups of PVA; as well as hydrogen bonding interaction between –OH groups of GMSG and –OH groups of PVA. The increased flexibility of VMSG cross-linked membranes is due to the unreacted C=C groups (Scheme I b) which provide extra flexibility to the membranes.



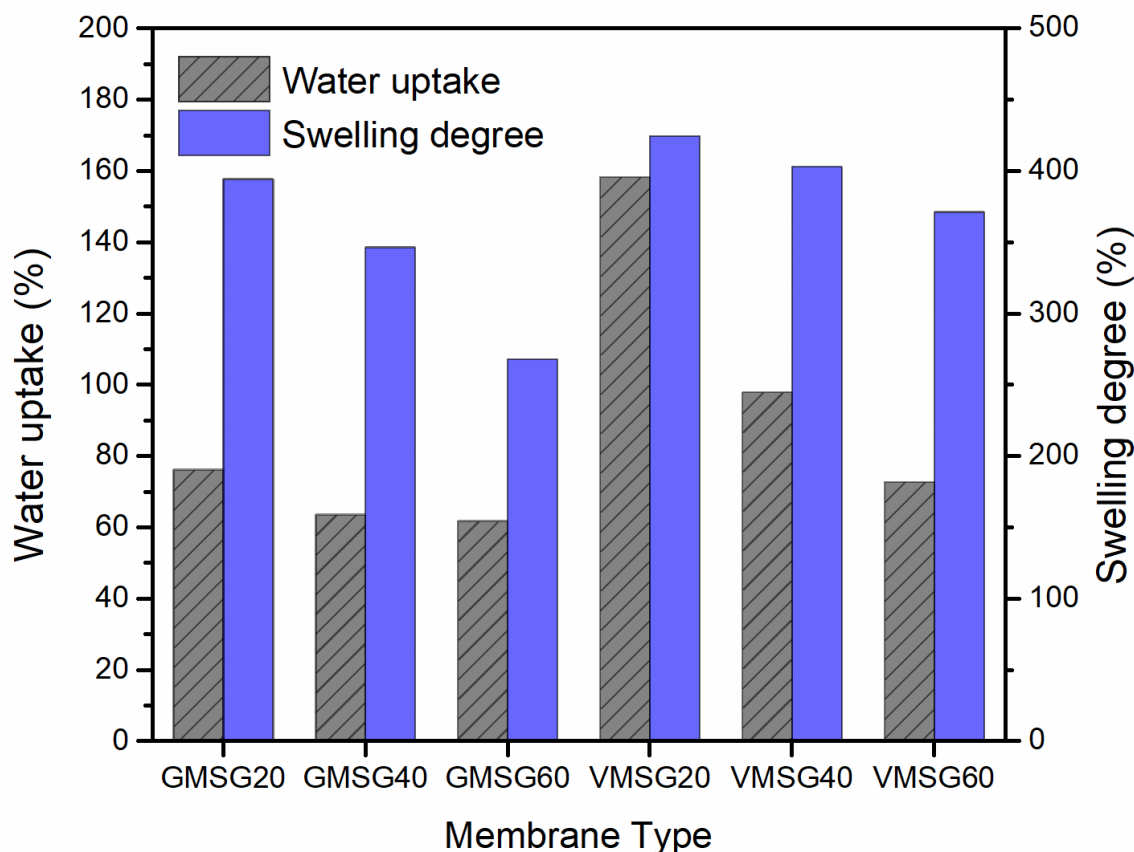
**Table 3**

Mechanical properties, water uptake and swelling degree of (GMSG/VMSG)/PVA cross-linked membranes

Membrane	TS (MPa)	Eb (%)	Swelling degree (%)	Water uptake (%)
GMSG20	41.2	54	394.2	76.1
GMSG40	49.3	151	346.3	63.5
GMSG60	46.4	124	267.9	61.7
VMSG20	36.8	67	424.2	158.3
VMSG40	44.5	192	402.7	97.8
VMSG60	38.9	176	371.1	72.7

**3.5. Water uptake and swelling degree**

The water uptake and swelling degree values of the prepared membranes are shown in Table 3 and shown in Fig. 5. Water uptake values of prepared membranes were in the range of 61.7–158.3%. Moreover, the results show that the water uptake values of prepared membranes decreased by increasing the contents of GMSG/VMSG in PVA blend matrix. This could be due to the extensive cross-linking nature of GMSG/VMSG which causes the reduction of water uptake. The cross-linking of GMSG/VMSG with PVA leads to the formation of Si–O–Si groups and ester linkages which results in enhanced compact structure [20, 25, 41] as shown in Scheme 1. The compact membrane structure ultimately reduces the free spaces between the polymer chain molecules which can accommodate the water molecules [59, 60]. It is interesting to note that VMSG-based membranes demonstrate higher water uptake values as compared to GMSG based cross-linked membranes (Fig. 5) due to the presence of polar hydrophilic (–COOH) groups character in of in higher content as compared to that in GMSG based membranes. It can be seen from Fig. 5 that by increasing the concentration of GMSG and VMSG from 20 to 60 wt. %, the swelling degree was decreased from 394.2 to 267.9% and 424.2 to 371.1%, respectively. The decrease in swelling degree with increase of GMSG/VMSG loading is due to presence of –COOH and Si–OCH<sub>3</sub> groups in GMSG/VMSG.



**Fig.5.** Water uptake and swelling degree of (GMSG/VMSG)/PVA cross-linked membranes

As per proposed reaction scheme,  $\text{-COOH}$  groups react with  $\text{-OH}$  group of PVA by esterification reaction (formation of ester  $\text{-C(=O)-O-C}$  group), while  $\text{Si-OCH}_3$  groups react with  $\text{-OH}$  group of PVA via sol-gel reaction (formation of  $\text{Si-O-Si}$  and  $\text{Si-O-C}$  linkages) which can significantly improve the membrane stability [11, 22]. Hence, increased linkages provide strength to resist the swelling degree. GMSG (20–60) membranes exhibit lesser degree of swelling as compared to that of the VMSG (20–60) membranes, which is due to the low content of ( $\text{-COOH/-COONa}$ ) of ion exchange groups and greater cross-linking ability of GMSG. The favourable swelling resistance in the GMSG membrane is attributed to the advantages of GMSG over VMSG.

### 3.6. Diffusion dialysis (DD) analysis

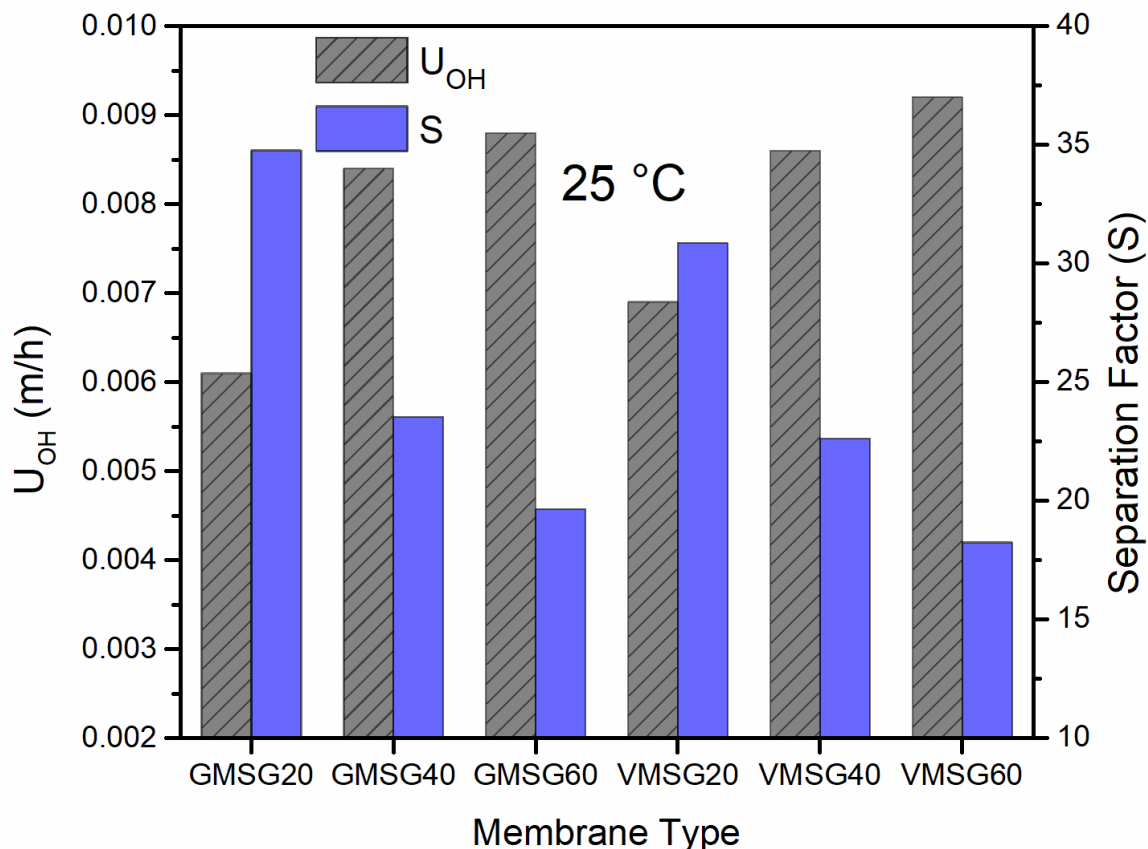
#### 3.6.1. DD performance at 25 °C

The prepared membranes were employed to separate NaOH/Na<sub>2</sub>WO<sub>4</sub> aqueous solution (1M NaOH/0.1M Na<sub>2</sub>WO<sub>4</sub>) as model aqueous waste feed for analyzing the DD performance and their potential use for application in alkali recovery. The dialysis coefficient of NaOH ( $U_{OH}$ ) and separation factor ( $S$ ) results at 25 °C for membranes having different wt.% of GMSG or VMSG in PVA matrix are shown in Fig. 6.

It has been observed that  $U_{OH}$  values increase gradually by increasing GMSG/VMSG amount, which is attributed to –COOH/–COONa groups in membrane matrix which are necessary for the DD process as they are able to migrate Na<sup>+</sup> ions through membrane to dialysate, therefore the available OH<sup>–</sup> ions also transfer through membrane from feed side to dialysate side in order to keep the solution electrically neutral. The  $U_{OH}$  values obtained are in the range of 0.0061–0.0092 m/h, which are greater than that of SPPO-based hybrid cation exchange membrane having  $U_{OH}$  value 0.0022 m/h at 25 °C [34]. It has been found that the membranes having 60 wt. % of GMSG/VMSG exhibit  $U_{OH}$  values of 0.0088 m/h and 0.0092 m/h, respectively which exceeds the  $U_{OH}$  value of SPPO-DSBPB based membranes (0.0081 m/h at 25 °C) [37] and PVA/SiO<sub>2</sub> hybrid membrane [61].

The GMSG and VMSG-based PVA hybrid membranes possess –COOH/–COONa functional groups which act as ion exchange sites to facilitate the migration of Na<sup>+</sup> ions. The transfer of OH<sup>–</sup> ions through the membrane takes place due to hydrogen bonding between hydroxyl groups of solution and –OH groups of PVA chain/ Si–OH group/ –COOH group present in the membrane. The existence of hydrogen bonding is beneficial for the migration of OH<sup>–</sup> ions through the membrane matrix [62]. The transport mechanism of OH<sup>–</sup> ions through the PVA membrane can be better explained by adsorption-desorption mechanism. This mechanism involves three steps: adsorption of OH<sup>–</sup> ions into the membrane by making the hydrogen bond with the –OH groups presents in the membrane, breaking the hydrogen bond and desorption of OH<sup>–</sup> ions from the membrane [25]. The complementary effect of –OH group of PVA and –COOH group from GMSG, VMSG form a network of hydrogen bonding with the OH<sup>–</sup> ion, enhance the permeability of OH<sup>–</sup> ions. The VMSG membrane series showed higher  $U_{OH}$  values

(due to its higher swelling) as compared to corresponding GMSG cross-linked membrane series as indicated in Fig. 6. These results were in agreement with low cross-linking and high IEC values which are beneficial to transport  $\text{OH}^-$  ions. Furthermore, ion exchange capacity of membranes highly influences on  $U_{\text{OH}}$  values.



**Fig.6.** Alkali dialysis coefficients ( $U_{\text{OH}}$ ) and separation factors (S) of (GMSG/VMSG)/PVA cross-linked membranes at 25 °C.

The separation factor (S) is the ratio of  $U_{\text{OH}}$  and  $U_{\text{WO}_4^{2-}}$  values. The separation factor values obtained are in the range of 18.24–34.76 at 25 °C and these values are higher than the reported value of PVA cross-linked silicon copolymer cation exchange membranes (16.9–18.5) at 25 °C [10] and are also comparable with other PVA hybrid membranes (11.6–20.2) at 25 °C [63]. The higher separation factor values are credited to the amplified selective interaction between the  $\text{OH}^-$  ions and the membranes matrix.

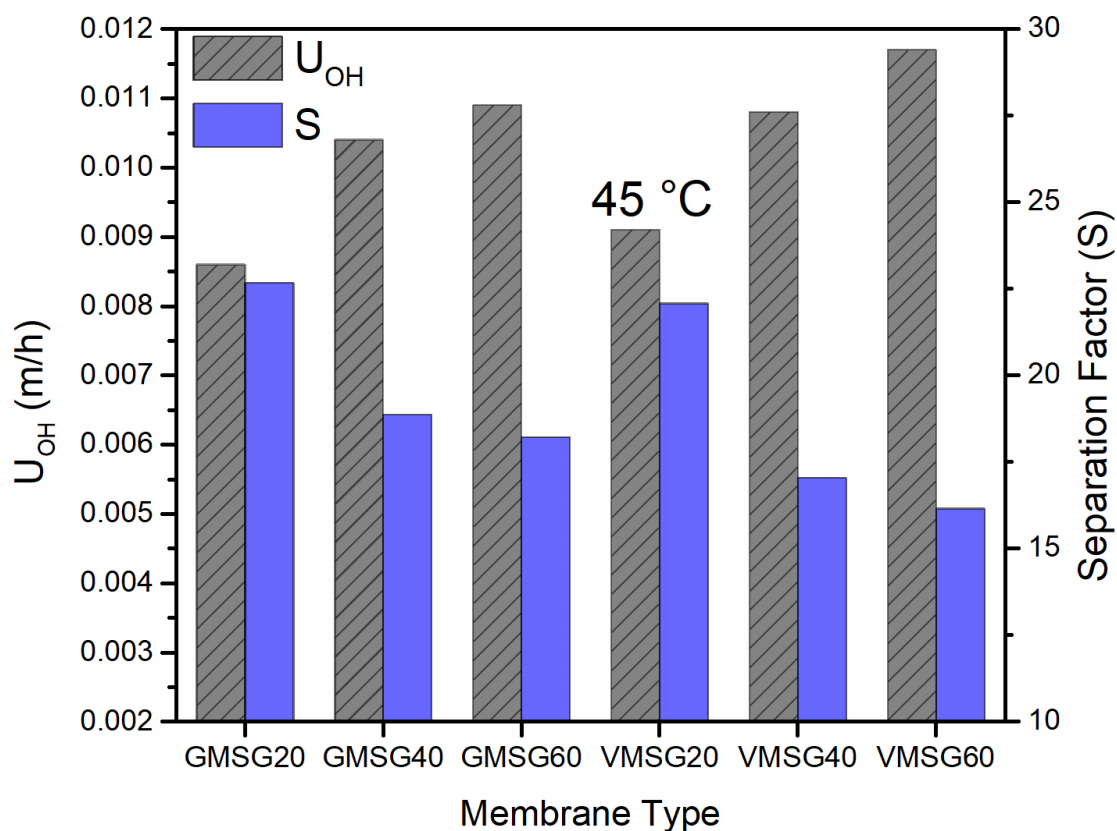
The S values were found to have decreasing trend by increasing the amount of GMSG/VMSG in the membranes. This decrease is mainly due to increase of phase separation at higher GMSG/VMSG content resulting in the transport of  $\text{WO}_4^{2-}$  ions through phase separation area of the membrane without much resistance. The free transport of  $\text{WO}_4^{2-}$  ions to dialysate is not favourable for membrane selectivity. It is also interesting to note that GMSG cross-linked membranes exhibit higher values of separation factor than that of VMSG membranes due to higher cross-linking degree and formation of more compact structure. A clear trade-off relation between  $U_{\text{OH}}$  and selectivity can be observed. For example, GMSG20 membrane exhibits maximum S value of 34.76, while it exhibits minimum  $U_{\text{OH}}$  value of 0.0061 m/h while VMSG60 exhibit lowest S value (18.24) and highest  $U_{\text{OH}}$  values (0.0092) .

### 3.6.2. DD performance at 45 °C

DD performances of GMSG/VMSG membranes were also studied at 45 °C and results are shown in Fig. 10. The obtained  $U_{\text{OH}}$  values are between 0.0086 -0.01117 m/h at 45 °C, which are around 30% greater than the  $U_{\text{OH}}$  values at 25 °C. This indicates that the permeability of  $\text{OH}^-$  ions increases significantly by increasing temperature proving that the membranes are thermo sensitive. With the increase of temperature, the polymer chain mobility increases which causes in increase of free volume [19, 64]. This results, in increased activity of ions in the solution for enhanced permeation of  $\text{OH}^-$  ion through the membranes and causes increase in  $U_{\text{OH}}$  values.

It is also interesting to that with the increase in temperature to 45 °C; S values obtained are lower than the values obtained at 25 °C. The decrease in S values is due to the different diffusion mechanism of  $\text{OH}^-$  and  $\text{WO}_4^{2-}$  ions at high temperature. The diffusivity of  $\text{WO}_4^{2-}$  ion is very low at normal temperature for its large size and higher valence. However, increase in temperature can accelerate the diffusion of both  $\text{OH}^-$  and  $\text{WO}_4^{2-}$  ions. The increase in diffusivity of  $\text{WO}_4^{2-}$  ions with temperature is more significant than  $\text{OH}^-$  ions [11, 34] resulting in decrease of membrane selectivity at high temperature.

Finally, the comparison of our work was done with other similar membranes reported in the literature for alkali separation. From the comparison, it can be easily seen that our membranes perform better than many other membranes and can be potential candidates for alkali separation applications in the industry.



**Fig.7.** Alkali dialysis coefficients ( $U_{OH}$ ) and separation factors (S) of (GMSG/VMSG)/PVA cross-linked membranes at 45 °C.

**Table 4** Comparison of our work with other literature membranes

Membrane Type	$U_{OH}$ (m/h)	S	Ref.
SPPO/DSBPB	0.0048-0.0081	12.61-36.88	[36]
PVA/SPPO/SiO <sub>2</sub>	0.007-0.013	12.5-181	[57]
PVA/SiO <sub>2</sub> (contain -COOH)	0.0068-0.0097	17.86-31.79	[24]
SPPO	0.0014	36	[33]
PVA/SiO <sub>2</sub> (contain -SO <sub>3</sub> Na)	0.011-0.022	11.6-20.2	[58]
PVA/SiO <sub>2</sub> (contain -SO <sub>3</sub> Na)	0.010-0.011	16.9-18.5	[10]
PVA/SiO <sub>2</sub> (Contain -COOH/-COONa)	0.0061-0.0092	18.24-34.76	This Work

## Conclusions

Novel and high performance hybrid cation exchange membranes were synthesized by cross-linking two types of silica functionalized mono sodium glutamate (GMSG/VMSG) with PVA by varying the GMSG/VMSG content from 20 to 60 wt. % . The FTIR spectra confirm successful crosslinking of GMSG/VMSG with PVA through covalent bonding via sol-gel reaction. The prepared membranes demonstrated good thermo-mechanical properties. The obtained tensile strength values were in the range of 36.8 MPa to 49.3 MPa and flexibility observed was 54 to 192%. Water uptake (61.7–158.3%) and water swelling degree (267.9–424.2%) decreased while IEC increased (0.47- 1.05 mmol/g) with the increase of GMSG, VMSG content in membrane matrix. The obtained  $U_{OH}$  values (0.0061–0.0092 m/h) increased while S values (18.24–34.76) decreased with the increase of GMSG, VMSG content. Finally, the influence of temperature on the DD process was also evaluated. It was observed that NaOH dialysis coefficient ( $U_{OH}$ ) values enhanced and selectivity reduced with the increase in temperature from 25 °C to 45 °C. The GMSG series of membranes demonstrated relatively lower permeability and higher selectivity values as compared to VMSG series. Hence, (GMSG/VMSG) cross-linked PVA membranes demonstrated excellent permeability and selectivity along with high thermo-mechanical properties, indicating their great potential for industrial applications particularly for recovery of alkali from waste water by diffusion dialysis.

## Declarations

## Funding

There is no special funding for this project.

## Competing Interests

The authors declare that they have no competing interests

## Availability of data and materials

Not applicable

## Code Availability

Not applicable

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## Figures

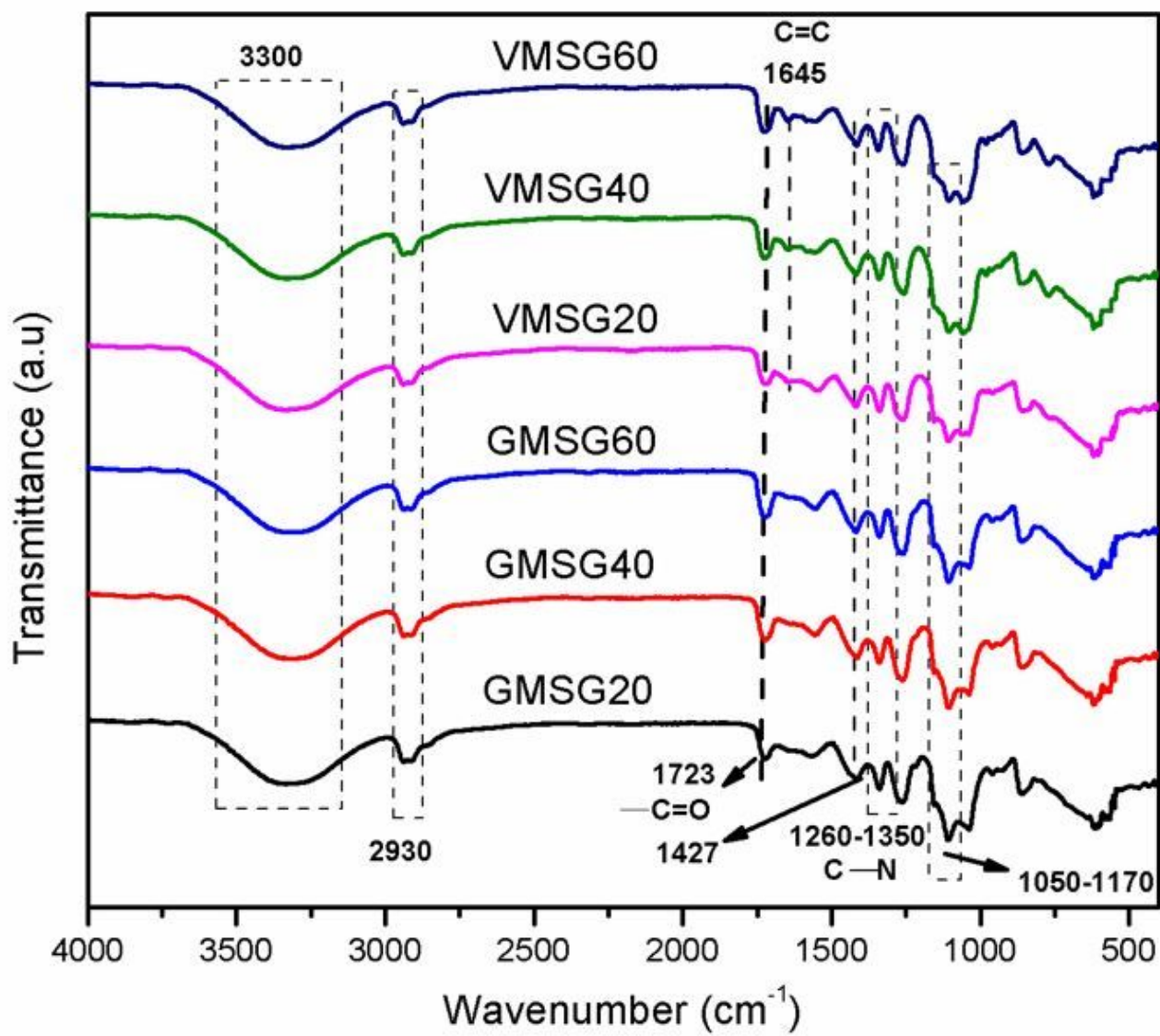


Figure 1

FTIR spectra of (GMSG/VMSG)/PVA cross-linked membranes

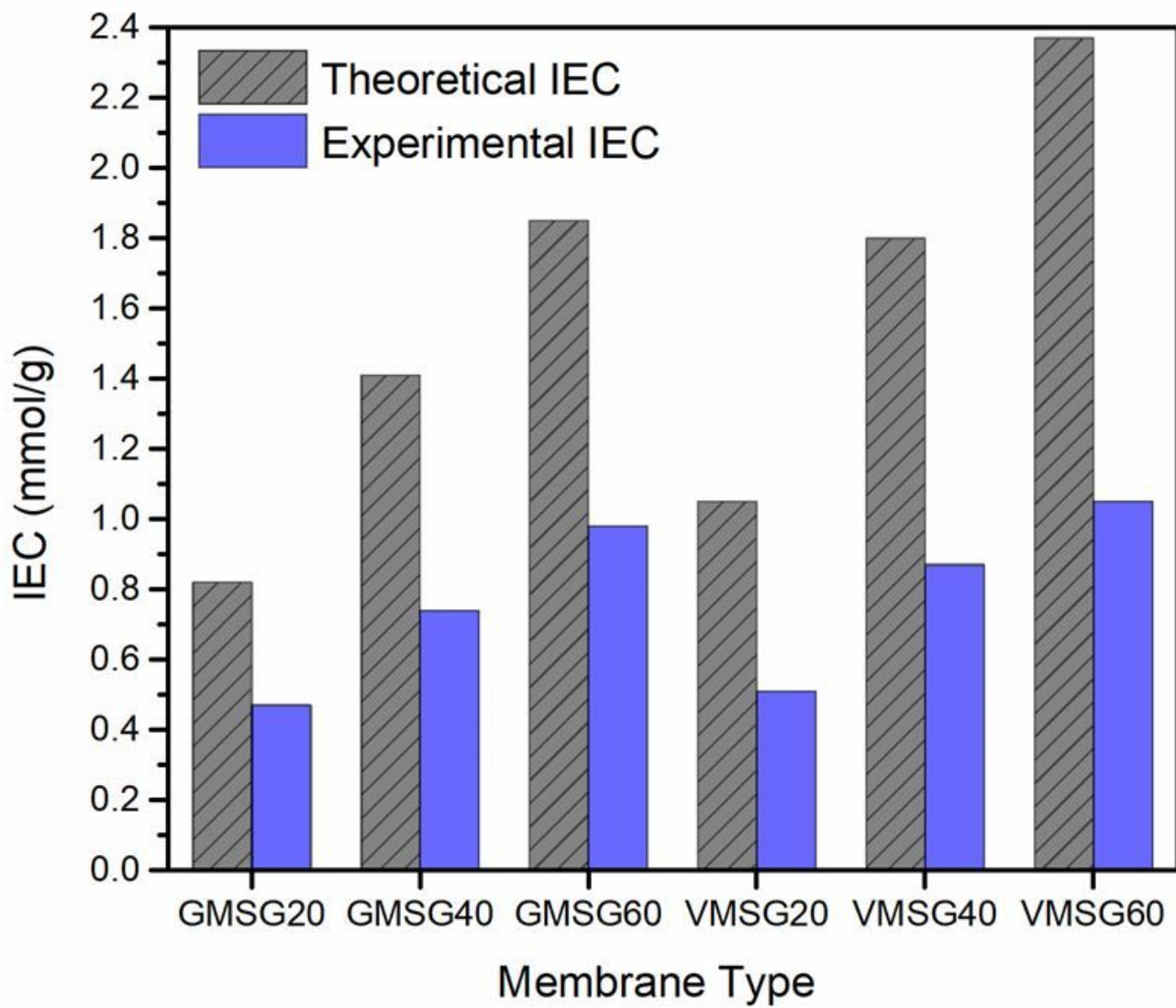


Figure 2

Theoretical and experimental IEC values of (GMSG/VMSG)/PVA cross-linked membranes

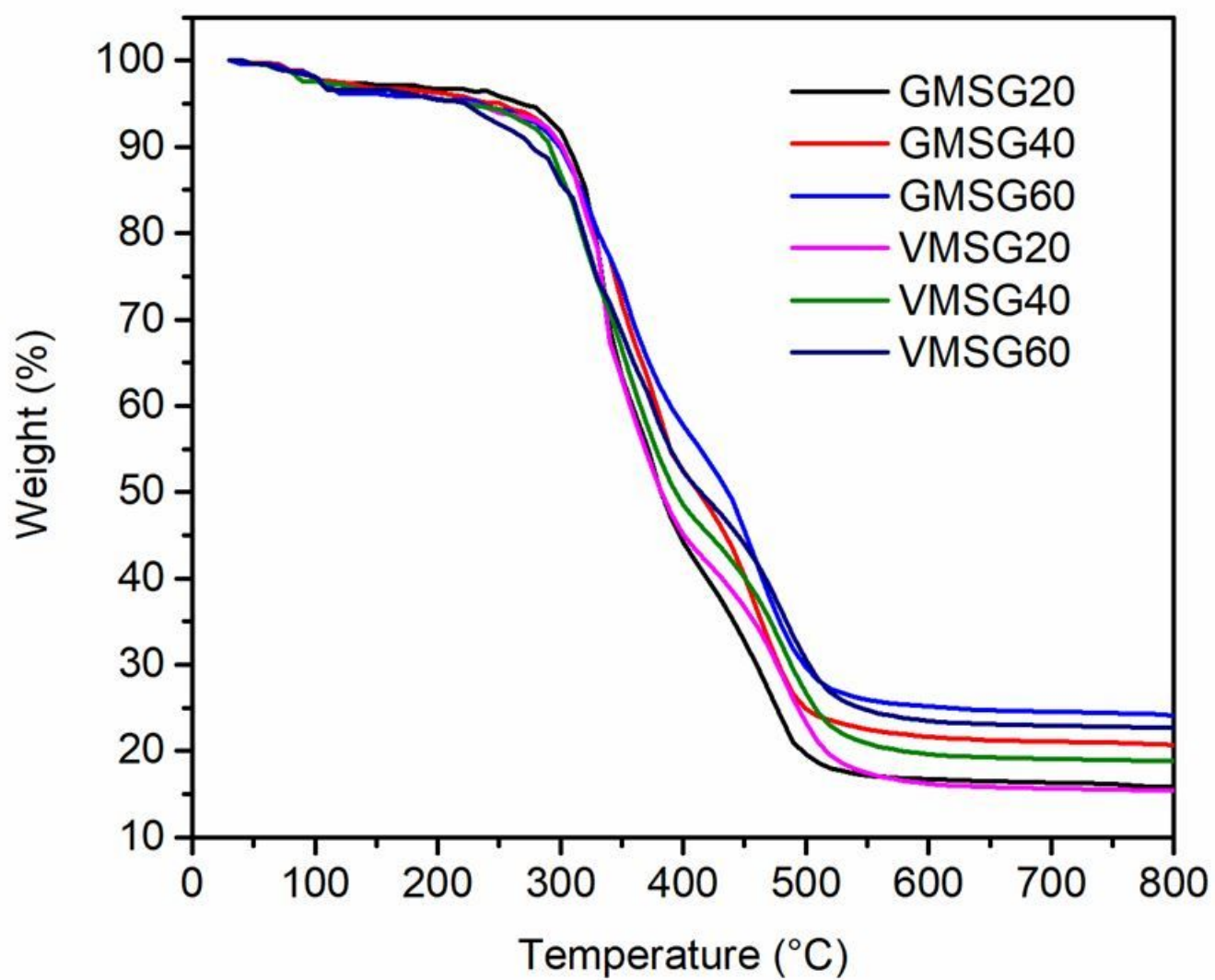


Figure 3

TGA thermograms of (GMSG/VMSG)/PVA cross-linked membranes

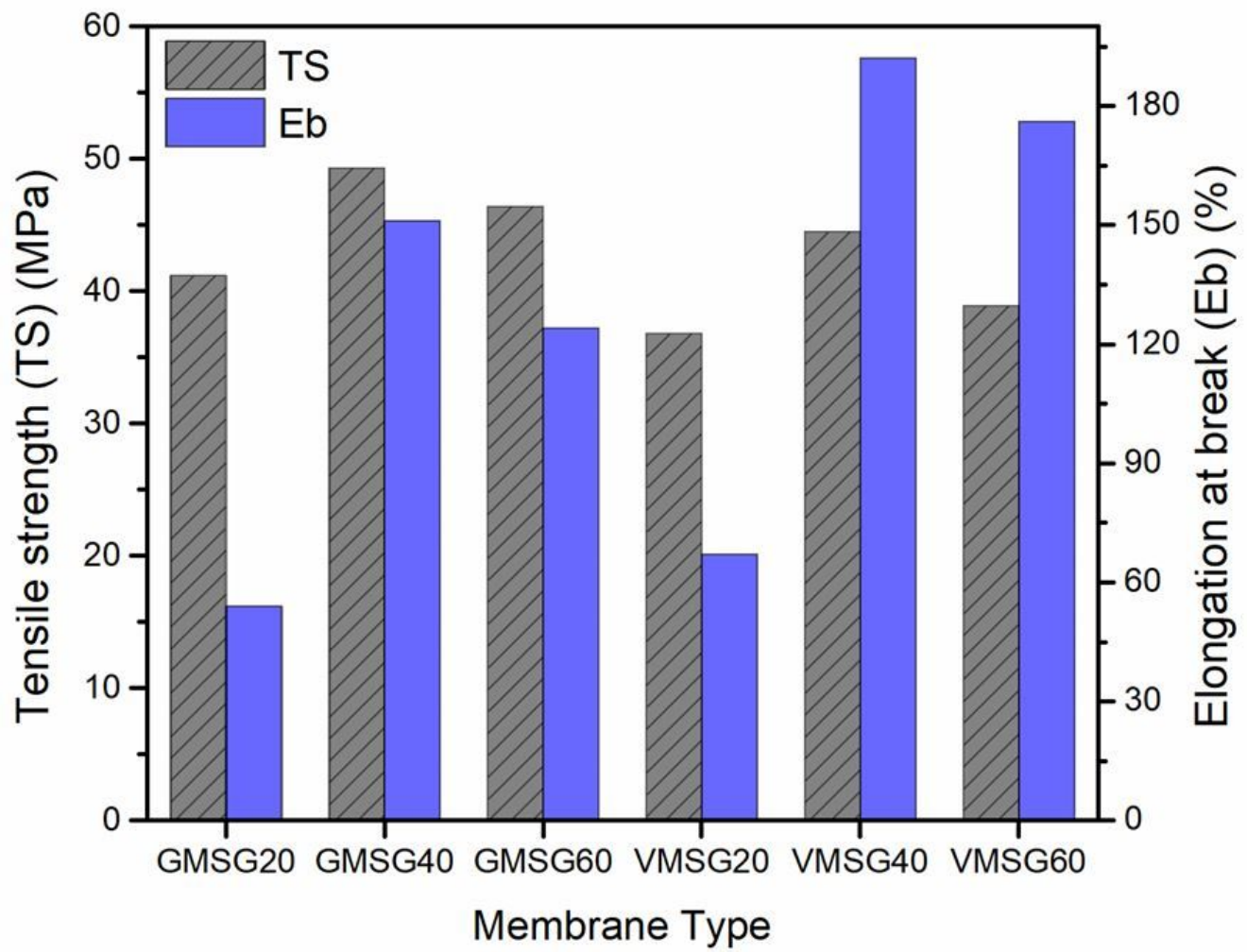
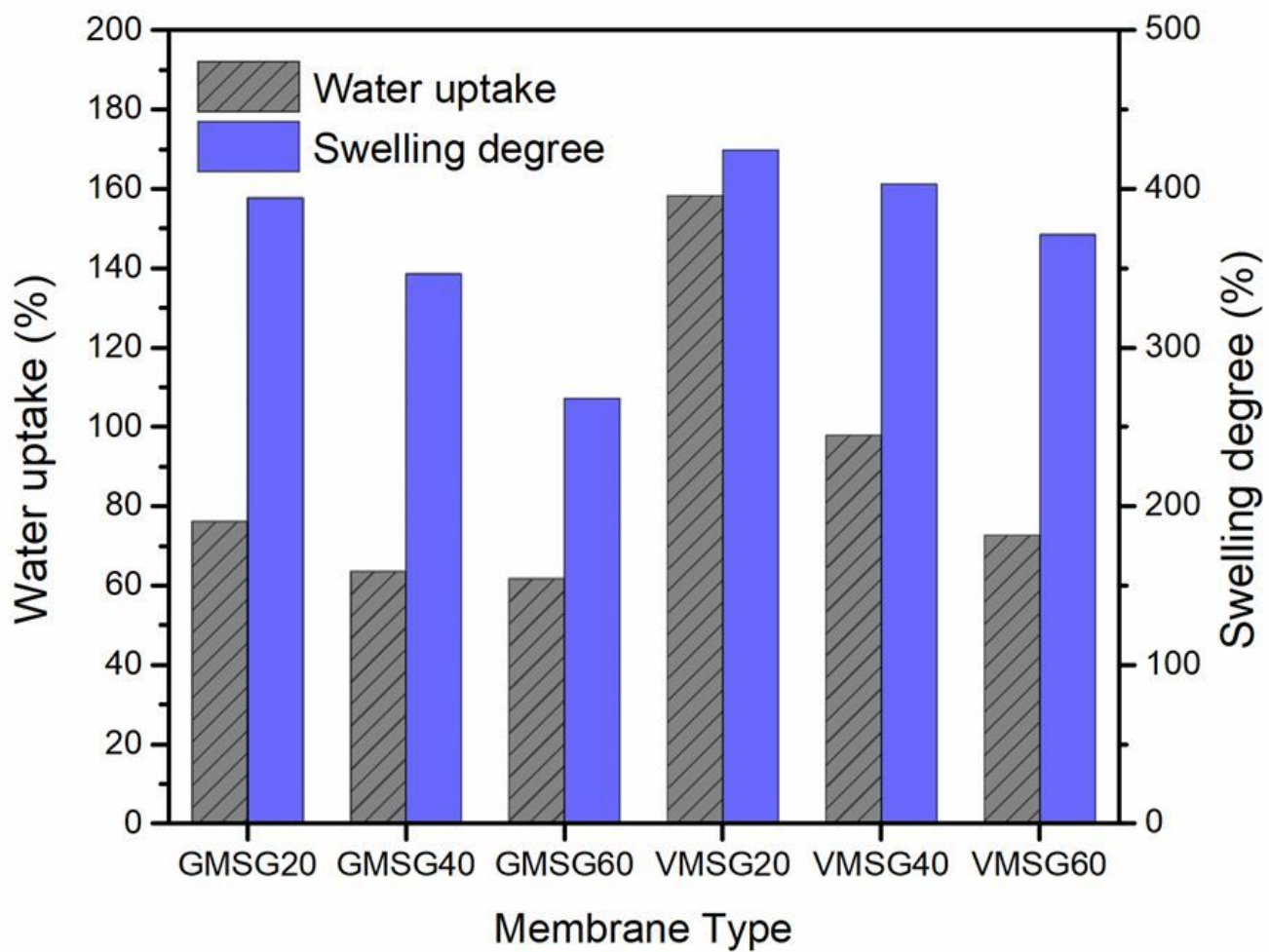


Figure 4

Mechanical properties of (GMSG/VMSG)/PVA cross-linked membranes





**Figure 5**

Water uptake and swelling degree of (GMSG/VMSG)/PVA cross-linked membranes



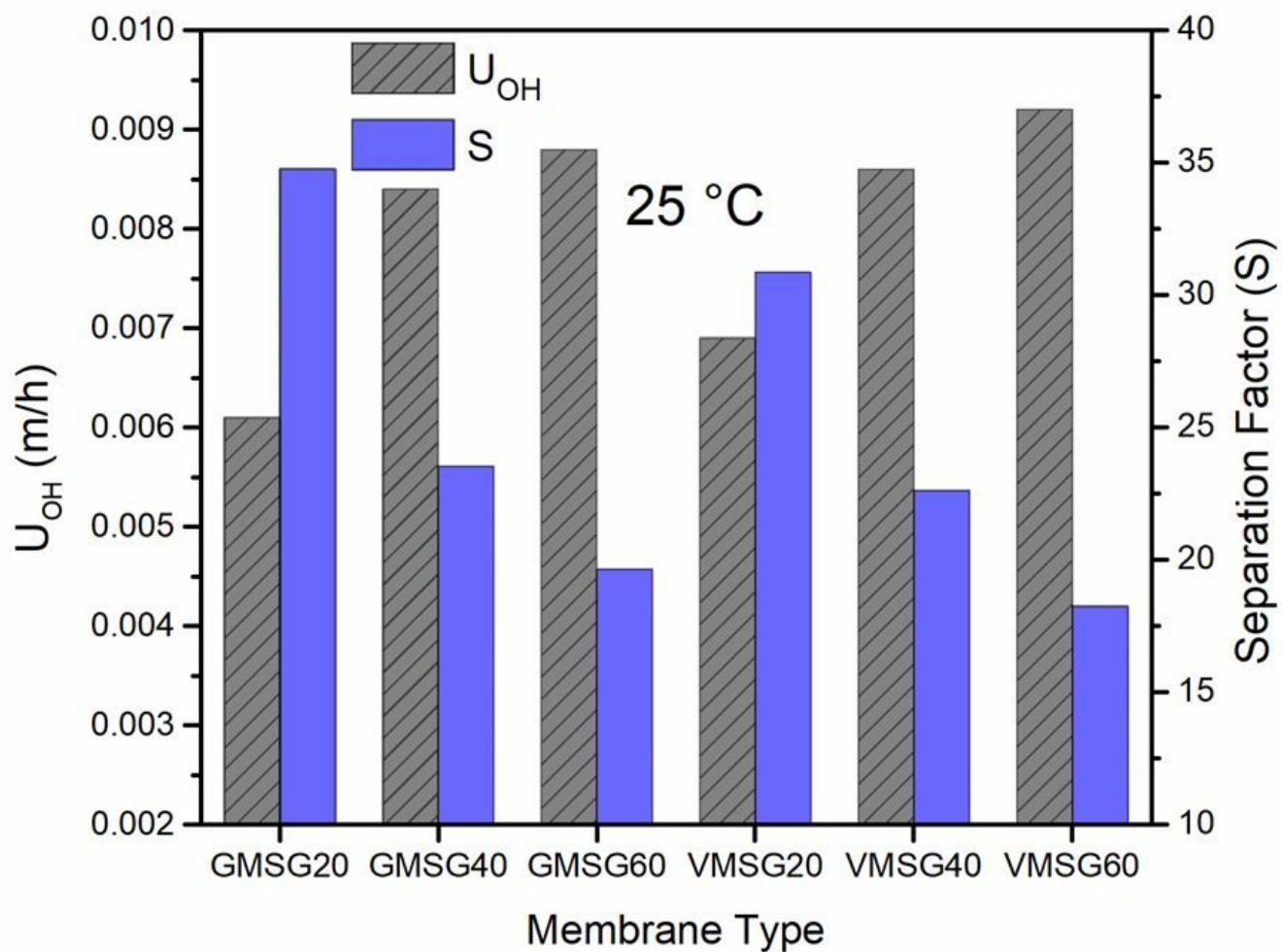
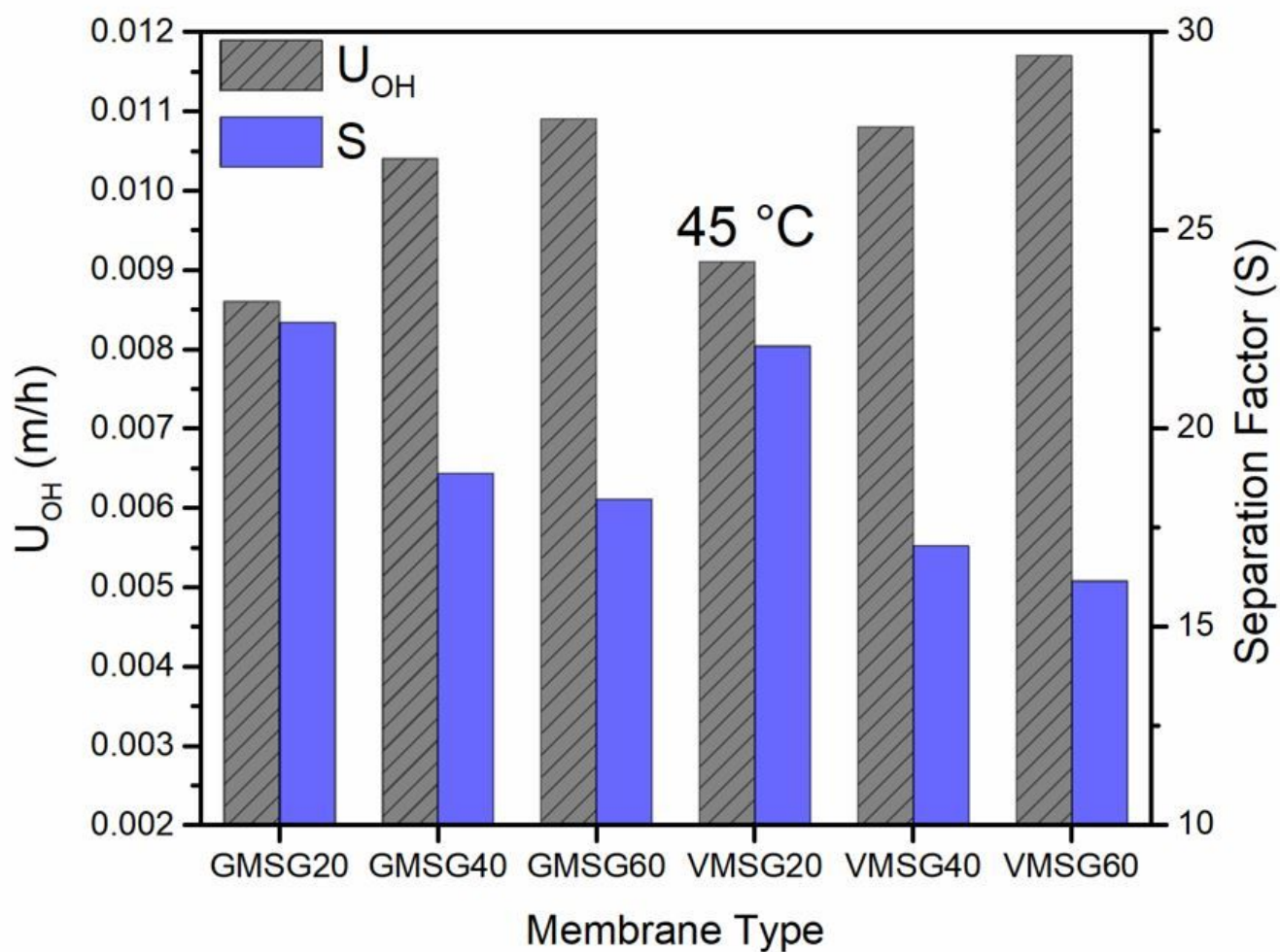


Figure 6

Alkali dialysis coefficients ( $U_{OH}$ ) and separation factors ( $S$ ) of (GMSG/VMSG)/PVA cross-linked membranes at 25 °C.



**Figure 7**

Alkali dialysis coefficients ( $U_{OH}$ ) and separation factors ( $S$ ) of (GMSG/VMSG)/PVA cross-linked membranes at 45 °C.

## Supplementary Files

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