

Interlayer-Free Hybrid Organo-Silica Membranes  
Based Teos and Tevs For Water Desalination

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**ABSTRACT**

This work investigates hybrid silica membranes by mixing tetraethyl orthosilicate (TEOS) and triethoxy vinyl silane (TEVS) by employing  $K_2S_2O_8$  (KPS) as initiator. KPS aims to provide radical polymerization to create C - C bonds linkage as a secondary network and then generates more spaces in silica network. Then free radical polymerization formed by KPS affects the oriented growth of particles. In order to avoid the decomposition of C - C groups within the silica matrices, it was found that the calcination temperature of xerogels recommends up to 350°C. Densification was formed when TEVS composition ratio is greater than TEOS composition. Therefore, the TEVS:TEOS molar ratio was set as 10:90 whilst microporosity was attained. This indicates that pure TEVS is not suitable to produce amorphous silica due to the functional groups formed block pores. The water fluxes found ( $< 2 \text{ kg m}^{-2} \text{ h}^{-1}$ ), however, the water fluxes for the hybrid organo-silica membranes reduced slightly only as a function of the salt content in the saline water, contrary to pure silica. This strongly suggests that the salt concentration polarisation was greatly reduced by having carbon moieties embedded into silica matrices. The water fluxes increased significantly from 4 to 21-24  $\text{kg m}^{-2} \text{ h}^{-1}$  as the temperature was raised from 40 to 60 °C whilst maintaining salt rejections in excess of 99%. This was mainly attributed to the linear organic C-C chains embedded in the silica matrices. In conclusion, the incorporation between organic-inorganic network enhance the hydrophobic properties of silica matrices.

**Key Words:** *Interlayer-free membranes, Hybrid Organo-Silica Membranes, TEOS, TEVS*

## 1. INTRODUCTION

Organo silica matrices have been using for many application of industrial and biomedical applications, such as catalysis, dye removal, gas sensing, biomolecule and polymer conjugation (Bringley et al., 2008, Marcon et al., 2008, Sharma et al., 2004). The strategy about organosilica membranes have also been described (Elma et al., 2012). A new concept of a combination between organic-inorganic hybrid silica based membranes is trying to be applied in order to obtain a better performance as well as the stability of robust silica membranes. Therefore, it is aimed to prevent siloxane groups surrounded by silanol groups in silica matrices, which easily react (mobile and actively interact) with water and then replaced by functional groups to become less hydrophilic (Castricum et al., 2008, Castricum et al., 2011, Wahab et al., 2004, Wei et al., 2008).

A few strategies have been similarly reported to this work, that is the incorporation of methyl ( $\text{CH}_3$ ) ligand groups such as in methyl triethoxy silane (MTES) (Duke et al., 2007) and or organo silane bridges ( $\text{H}_2\text{CH}_2\text{C}$ ) of 1,2-bis(triethoxysilyl) ethane (BTESE) (Xu et al., 2011). Our recent work also shows a great improvement of non-ligand organic templated silica membranes for water desalination (Elma et al., 2015).

Wahab et al., (Wahab et al., 2004) successfully prepared hydrophobic microporous silica membranes (mixtures of TEOS and TEVS) that resistance to humid atmosphere using acid ( $\text{HNO}_3$ ) as catalyst. So far, there was no membrane performance reported in gas separation as well as desalination using this precursor. The incorporation between organic-inorganic silica network is excellent way to minimise the hydrophilicity of silica matrices due to the double bond of TEVS may hydrolysed and polymerized to form C-C single bond in order to fill more space in the porous structure (Kleitz, 2008).

In addition, potassium persulfate (KPS) is applied to promote the crosslinking of the vinyl groups. It also aims to generate free radicals responsible for the initiation of the vinyl polymerization on the TEVS precursor. The polymerization mechanism can be generally expressed by four sequential steps involving initiation, propagation, chain-transfer and termination steps which have all been summarized in detail elsewhere (Nguyen et al., 2002, Huang and Lee, 1985, Davis et al., 1999, Maxwell et al., 1993, Tonge et al., 1998, Yamada et al., 1999). In the case of the simultaneous co-condensation and copolymerization between the TEVS and TEOS precursors in forming the copolymers, Figure 1 shows the general reaction between the sol-gel and free radical reactions.

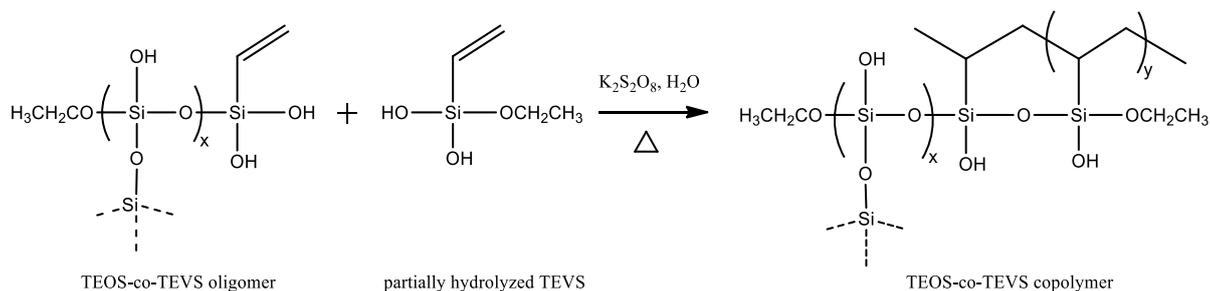


Figure 1. Free radical polymerization of the vinyl functionalized oligomers and TEVS monomers.

In this study, co-condensation method has been chosen to minimise the mobility of silanol groups on silica matrices through incorporation of hydrophobic functional groups of TEVS. A series of TEOS-TEVS copolymeric hybrid organosilica xerogels are synthesised and systematically characterised and investigated as potential materials for membrane preparation. Subsequently, optimised TEOS-TEVS synthesis is chosen for the preparation of membranes.

## 5. EXPERIMENT

### 2.1. Sol Preparation Procedure

A two-step sol-gel process using acid and base catalyst was carried out to prepare organo silica sol. This sol preparation procedure is similar to our previous work (Elma et al., 2014, Elma et al., 2015). The molar ratios between TEOS and TEVS precursors 10:90 and 2.5 for KPS. In addition,  $\text{K}_2\text{S}_2\text{O}_8$  (KPS) as solid granules was added into the combined sol and stirred for 1 h.

### 2.2. Xerogel Characterization and Membrane Fabrication via Dip-Coating

Xerogel characterization procedure as well as the hybrid organic silica membranes were prepared by using no intermediate layer, known as interlayer-free method. The procedure of membrane fabrication also can be seen in our publication recently (Elma et al., 2014, Elma et al., 2015).

## 6. RESULTS AND DISCUSSION

### Xerogel Characterisation of TEVS:TEOS hybrids

Prior to the sol-gel processing of the TEVS:TEOS composites, the chemical properties of the two silane precursors were studied by FTIR technique to determine the relevant absorption bands of interest relating to the various vinyl vibrations. Figure 2 shows the FTIR spectra of the TEVS and TEOS precursors.

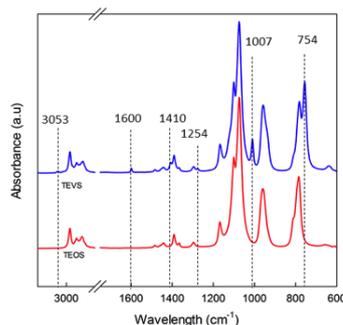


Figure 2. FTIR-ATR spectra of the TEVS and TEOS precursors.

Since the vinyl group on the TEVS is the discerning difference between itself and the TEOS, it is straight forward that any additional peaks observed in the TEVS IR spectra would be directly related to the vinyl vibrations as well as the Si-C vibrations. In Figure 2, the most intense peak is mainly due to the Si-O stretch in the region  $1100\text{--}1200\text{ cm}^{-1}$ . The C-H stretching and bending vibrations near  $2900$  and  $1400\text{ cm}^{-1}$  respectively, as well as  $\text{CH}_2$  rocking at  $950\text{ cm}^{-1}$ , are all due to the ethoxy groups. The differential peaks between the spectra are  $3053$ ,  $1600$ ,  $1410$ ,  $1254$ ,  $1007$  and  $754\text{ cm}^{-1}$  of which only  $1254$  and  $754\text{ cm}^{-1}$  are due to the Si-C vibrational bands (Wang et al., 2011, Eon et al., 2004, Eon et al., 2006, Sulca et al., 2009, Sharma et al., 2004) and the rest are due to the various vinyl vibrational modes (De et al., 1993). These peaks of interest will be paid a closer attention in the IR spectra of as-synthesized and calcined TEVS:TEOS composite xerogels. In addition, Figure 3 (a) also shows that at about  $300\text{ }^\circ\text{C}$  there is a change in slope, which tends to increase the mass loss until  $400\text{ }^\circ\text{C}$ . These results are associated with the loss of carbon, as the ongoing mass loss associated with silica condensations reactions should be slight only. Hence, based on these results and the FTIR results in Figure 3 (b), the calcination temperature for membrane preparations will be limited to  $350\text{ }^\circ\text{C}$  in order to ensure that C-C moieties are kept embedded into the silica matrices.

Moreover, the hybrid xerogels containing TEVS become microporous, as the isotherm reached saturation at very low relative pressures ( $p/p_0 < 0.05$ ). By mixing TEVS to the TEOS sol, the material adsorbed greatly reduced and this trend continues as a function of TEVS, leading to complete densification of the matrix for the 100TEVS (Figure 3 (c) and (d)). As densification of the matrix should be avoided at all costs, as this principally leads to non-permeable membranes, these results strongly indicate that only the 10TEVS can be used in the preparation of the membranes. Considering FTIR in this case cannot provide a clear understanding of the chemical structure of the composite xerogels, XPS analysis was employed. Figure 4 shows the XPS survey scan and their elemental concentrations of the 10TEVS with and without KPS, as well as pure TEVS for comparison.

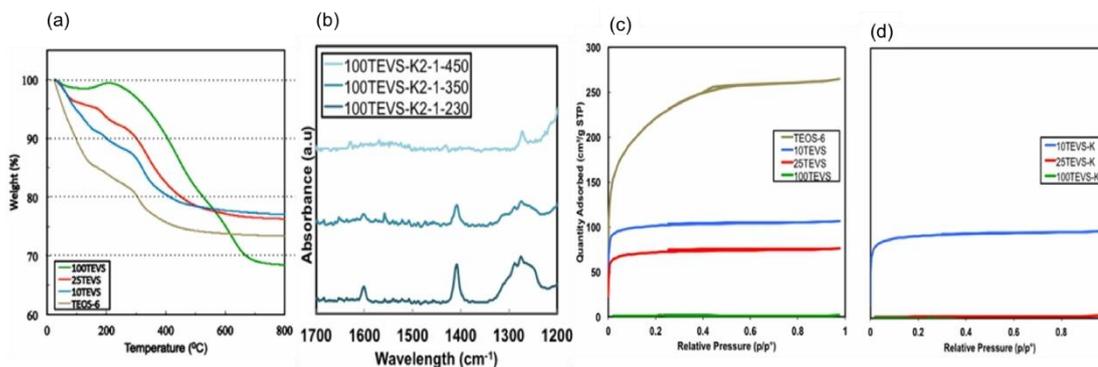


Figure 3. (a) TGA curves in air for TEVS/TEOS dried gels and (b) FTIR-ATR spectra of TEVS as a function of calcination temperature (c)  $N_2$  physisorption isotherms for the calcined TEVS:TEOS xerogels in  $N_2$  atmosphere at  $350\text{ }^\circ\text{C}$  without KPS and (d) with KPS

Figure 4 clearly confirms consistency the xerogels prepared with KPS are found to contain a higher concentration of the carbon compared to their counterparts. Perhaps due to vinyl polymerization that the C-C bonds may be more thermal resistant than the more reactive vinyl double bonds. However, the synthesis and chemical compositions of the organo-silica matrices is further confirmed by the XPS analysis and corroborate the previous results.

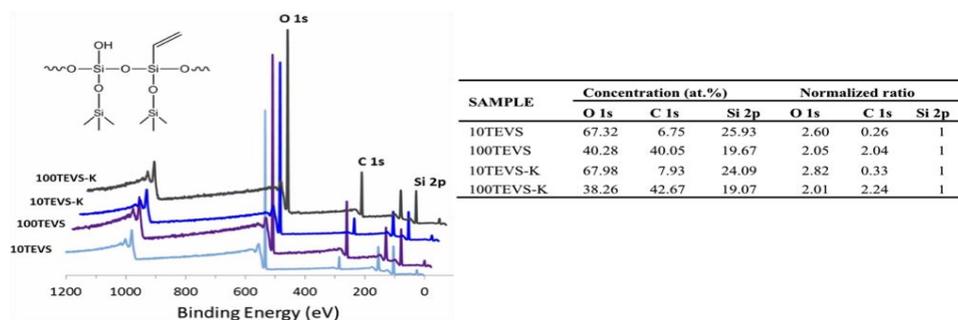


Figure 4. Typical XPS survey scan spectra of the 10TEVS and 100TEVS organosilica xerogels with and without KPS, and the chemical structure of the condensed copolymer network.

### TEVS:TEOS Hybrid Membranes

Figure 5 shows the temperature dependence of the water flux and salt rejection for 10TEVS-K (left side) and 10TEVS (right side) membranes. These results clearly show that the water fluxes are complying with Darcy's law ( $N = K \Delta P^\circ$ ) where the water flux ( $N$ ) is proportional to the water vapour pressure ( $\Delta P^\circ$ ) and coefficient  $K$ , which are in turn temperature dependent. In other words, the water flux through both membranes increased as a function of the feed temperature, which typically corresponds to an increase of the vapour pressure at the interface at the hybrid membranes and the bulk liquid. As the permeate temperature is

constant, the driving force for the diffusion of water from the feed to the permeate stream is enhanced. For instance, with an increase on feed temperature from 22 to 60 °C, water fluxes for the 10TEVS membranes increased approximately 22 fold at 0.3 wt% and 8 fold at 7.5 wt% while maintaining very high salt rejection (between 99.7 - 99.8% at 0.3 wt% and 99.7 - 99.9% at 7.5 wt% ). The combination of very high water fluxes (up to 23.9 kg m<sup>-2</sup> h<sup>-1</sup>) coupled with high salt rejections provides strong evidence of the good quality of both membranes.

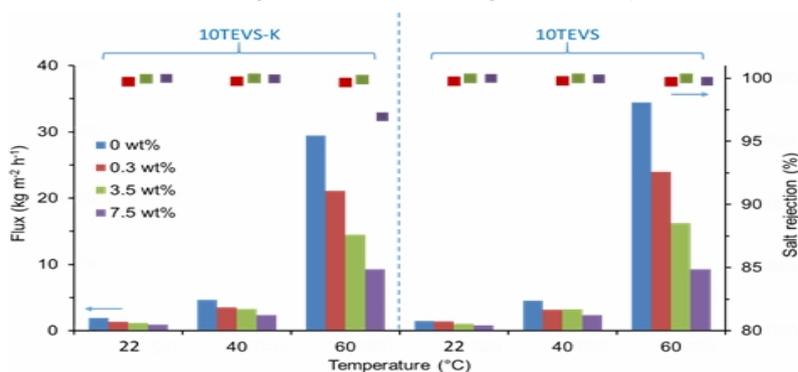


Figure 5. TEVS-K (left) TEVS (right) desalination performance as a function of the feed temperature.

In this work, only 10%TEVS was incorporated in a silica matrices. It is interesting to observe the very high water flux of 21 kg m<sup>-2</sup> h<sup>-1</sup> at 60 °C, which is 43% much higher than the results at 22 °C. A central consideration in this work was to keep the C-C chains embedded in the silica matrices. These ligand chains are not fixed such as siloxane bridges (Si-O-Si). As such C-C chains are linear and have the flexible ability to move within the constraints of the silica cage. Possibly this effect, coupled with carbon hydrophobicity and a high driving force associated high temperatures and water vapour pressure, provided ideal conditions for fast water diffusion through the TEVS derived membrane.

One interesting point here is that the 10TEVS-K membrane, in which the vinyl group was crosslinked with KPS, was able to revert its water fluxes to the original values at 22 °C. Hence, the higher water fluxes measured for the 10TEVS membrane at 60 °C could be associated with loss of structural integrity of the hybrid silica matrices, though salt rejections remained high (> 99%). In the case of the vinyl crosslinked 10TEVS-K membrane, the matrix was robust enough to oppose degradation. Possibly the vinyl crosslinking created a secondary linear C-C chain which may be constrained by the silica backbone.

## 7. CONCLUSIONS

A non conventional hybrid organosilica membranes TEOS and TEVS precursors membranes were successfully prepared and tested for water desalination. C-C

chains embedded in the silica matrices containing TEVS:TEOS observed at molar ratio 10:90 and calcined at 350 °C.

An important finding to this work is the suggestion that the hybrid silica containing carbon moieties was able to repel hydrated ions and avoid salt accumulation on the surface of the membranes. The much lower water fluxes of less than 2 kg m<sup>-2</sup> h<sup>-1</sup>. Nevertheless, the membranes had a very high salt rejection in excess of 99% for all salt concentration silane water tested.

A further important finding was the significant increase of water fluxes from 4 to 21-24 kg m<sup>-2</sup> h<sup>-1</sup> as the temperature rose from 40 to 60 °C, whilst salt rejections remained very high (> 99%). This was mainly attributed to the linear C-C chains for the hybrid organo-silica membranes constrained by the silica matrices.

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