

## REMOVAL OF CU (II) AND FE (II) IONS THROUGH THIN FILM COMPOSITE (TFC) WITH HYBRID MEMBRANE

NURUL AIDA SULAIMAN, NORIN ZAMIAH KASSIM SHAARI\*,  
NORAZAH ABDUL RAHMAN

Faculty of Chemical Engineering, Universiti Teknologi MARA (UITM),  
40450 Shah Alam, Selangor Darul Ehsan, Malaysia

\*Corresponding Author: norinzamiah@salam.uitm.edu.my

### Abstract

In recent years, there has been rising concern about environmental issues and specifically about the presence of heavy metal in water. Therefore, the removal of heavy metal ions from wastewater is very important with respect to the ecological health and public health. This paper presents the possibility of removing metal ions by using a hybrid membrane through thin film composite (TFC) membrane which represents an integrated polymer complexation method. The hybrid membrane was formulated from blended poly(vinyl alcohol) (PVA) and chitosan which was cross linked with various concentration of tetraethyl orthosilicate (TEOS) such as 1%, 3% w/w and 5%w/w through using sol-gel technique under acidic condition. The hybrid membrane was coated on polysulfone membrane as the porous support. The separation process was conducted on the different heavy metal solutions containing Cu (II) and Fe (II) ions at various concentrations (50,100,150,200,250 ppm).The properties of the thin film composite (TFC) membranes were characterized by using Fourier Transform Infrared (FTIR) spectroscopy and Thermogravimetric Analysis (TGA). The influence of TEOS concentration and Cu (II) and Fe (II) ion concentration was investigated with the aim to identify on the removal percentage efficiency of Cu (II) and Fe (II) ions. Result showed that the fabricated thin film composites with higher concentrations of TEOS were able to remove higher percentage Cu (II) and Fe (II) from the feed solution.

Keywords: Hybrid membrane, Polyvinyl Alcohol (PVA), Chitosan, Tetraethyl orthosilicate (TEOS), Thin Film Composite.

### 1. Introduction

In the last decades, high content of heavy metal from liquid waste industries has become a major environmental concern [1]. The heavy metal need to be separated before being discharged to surface waters or the sewage system. Heavy metals are generally toxic and dangerous to the human being. Particularly, metal such as copper (Cu) and ferum (Fe) usually show the tendency to accumulate in living organism [2].

### **Nomenclatures**

PPM      Parts Per Million  
wt%      Weight percent

### **Abbreviations**

AAS      Atomic Absorption Spectroscopy  
CS      Chitosan  
Cu      Copper  
Fe      Ferum  
FTIR      Fourier Transform Infrared  
HCl      Hydrochloric Acid  
NMP      1-methyl-2-pyrrolidone  
PVA      Polyvinyl Alcohol  
TEOS      Tetraethyl orthosilicate  
TFC      Thin Film Composite  
TGA      Thermogravimetric Analysis

Copper (Cu), is an important metal used in various engineering processes [3]. Cu is used in production of wires for various industries such as electrical industries, automotive, and electronic appliances [3]. It is one of the toxic metals, which can cause many health hazards and dangerous effects on living beings. Too much intake of copper through air, water and food can cause diseases such as liver damage, Wilson's disease and insomnia [2, 3]. The main sources of copper pollution in water are from metal industries such as mines industries, effluents from water treatment plant, electro-refining plant, and acid spillage from water sulphuric acid plant [3, 4].

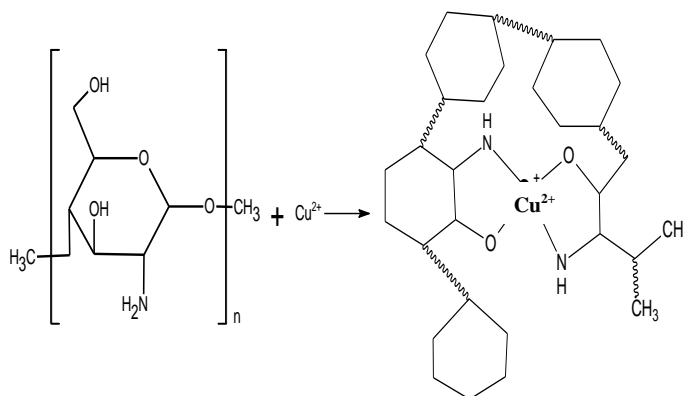
Ferum (Fe) or iron is one of the most abundant minerals in the Earth's crust, and it is very common to be found in groundwater [5]. Iron can give water an unpleasant taste, odour and colour. It can cause reddish – brown marks on laundry, glassware, sinks, and concrete. Besides that, these particles of iron may come from corroded pipes or from water supply itself. These particles form from oxidation process in the plumbing system and it will precipitate the iron. Although iron in a household water supply is not hazardous to health, but they can be a nuisance and damage for the laundry and other items [5].

Due to the high amount of toxicity and polluting metal in industrial wastewater, there are several methods that had been applied to remove heavy metal from wastewater, which include chemical precipitation, membrane separation, electrodialysis, ion – exchange flotation and adsorption [6]. However, all these methods have some limitations and inherent disadvantages such as ineffective and costly especially in removing heavy metal ions from dilute solutions [7, 8]. Among all these methods, adsorptions of ion-exchange membrane separation have been extensively utilized in the removal heavy metal. Membrane separation also has received extensively attention recently regarding the wastewater treatment due to its capability in removing suspended solid, organic compound and inorganic contaminant such as heavy metal ion [2].

In the past decades, a wide variety of achievements in thin film composite (TFC) membrane has been reported around the world [9]. The thin film composite

membrane is consists of a porous support layer with a thin layer coated on top of it. The main advantages of the TFC membrane is that the coated of hybrid layer on TFC membrane and the porous support of TFC membrane can be optimised individually with respect to the structure, stability, and performance [10]. Besides that, TFC membrane can minimise the cost of membrane by reducing the quantity of performance material used [9]. In this study, the top layer material of TFC membrane is made up with hybrid membrane. During the formation of hybrid membrane, polymer blending, pva and chitosan was selected. These polymer blending membranes have been studied regularly since hydroxyl groups of pva form strong interactions with water through hydrogen bonding [11]. Polymer blending is one of the suitable ways to have a new material that has unique properties and can be commercial it. This was determined by the realization that new molecules are not always required to meet the need for new materials because polymer blending usually can be implemented more rapidly and economically than the development of new materials. The material of the membrane has been improved by the interactions between blended chitosan and pva through hydrophobic side chain combination and intramolecular and intermolecular hydrogen bonds [12].

Therefore, in this study, chitosan was selected as adsorbent due to their ability to chelate five or six greater concentration of metals than other adsorbent [13]. Chitosan is biodegradable polymer usually exists in nature as chitin. Chitosan is formed when some acetyls are removed from chitin [14]. Usually, chitosan can be dissolved in acid and have over 60% deacetylation degree of chitin [14, 15]. It consists of linear copolymer of 2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose joined by  $\beta$  (1, 4) glycosidic bonds. Besides that, it has unique behaviour like cationic behavior, polycationic structure and chelation properties [16]. Chitosan has an amino on C2 and a hydroxyl on C3, it is also has flat bonds so that they can chelate more transition metal ions as shown in Fig. 1. Chelating can be recognized from the presence of a large number of functional groups like acetamido, primary amino, and hydroxyl groups.

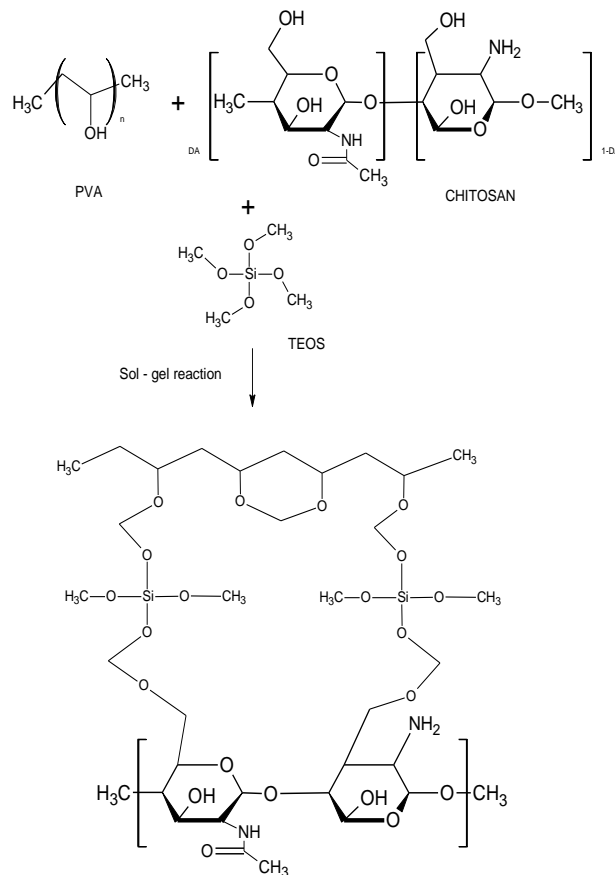


**Fig. 1. Formation of chitosan chelates with  $\text{Cu}^{2+}$  ion.**

In this study, The cross linking reaction on the polymer blending of pva/chitosan is needed in order to increase the rigidity structure of the membrane, improved the thermal properties, and inhibits the swelling of the membrane [17]. Addition of TEOS through chemical reaction as cross linking agent by sol –gel method in this study can give a stable membrane with good mechanical strength and higher

selective permeability towards water. The adjustment of concentration and amount of TEOS for preparation of hybrid membrane must be conducted in order to get the best performance of the hybrid membrane [17] and to avoid excessive crosslinking that will increase the brittle structure in the dimensional stability. Thus, making it unsuitable for pervaporation and separation application [9].

Sol – gel method have been the most suitable method for hybrid membrane preparation due to its simplicity and easy to handle [18]. The key advantages of the sol- gel process for material blending are it can produce high purity homogenous hybrid materials. Also, it stands as the new method for inorganic – organic hybrid materials [19]. Sol – gel method consists of hydrolysis and condensations process which led to the membranes matrix modification. The silanol group (Si-OH) formed is converted into siloxane (Si-O-C) crosslinks due to dehydration reaction with other silanol groups during membrane drying. The silanol groups of siloxane and the groups of CS/PVA formed hydrogen and covalent bonds. This is the crosslinking effect in the reaction [19]. The reaction between polymer blending of PVA /chitosan and inorganic polymer, TEOS by the sol – gel method to form hybrid membrane are shown in Fig. 2.



**Fig. 2. Interaction between polymers blending of PVA /chitosan and cross linked with inorganic polymer, TEOS by the sole – gel method to form a hybrid membrane.**

Besides that, the performance of thin – film composite (TFC) membrane was related to the preparation of porous support membrane. Therefore, in this study, phase inversion method was used to prepare a polysulfone membrane that act as the porous support layers. The phase inversion method is a process which polymer in the liquid phase is transformed to a solid phase. The porous support membrane use in the making of TFC membrane was classified as asymmetric membrane [20].

## **2. Materials and Methods**

### **2.1. Materials**

In the preparation of thin film composite membrane, the material required were polyvinyl alcohol with a hydrolysis degree of 87-89% (MW : 85,000 – 124,000), polysulfone resin pellet (MW: 44,000 – 53,000), tetraorthosilicate (TEOS) with 99% purity and hydrochloric acid with 37% purity as catalyst and commercial chitosan (deacetylation degree  $84.8 \pm 1.2$  %). These chemicals were obtained from Sigma Aldrich, Malaysia. 1-methyl-2-pyrrolidone (NMP) with purity of 99% was obtained from Merck, Malaysia. Deionized water was also used as solvent. All this material was employed without further purification.

### **2.3. Methods**

#### **2.3.1. Preparation of hybrid membrane**

Chitosan solution was synthesized by dissolving 3 g of chitosan flakes in 2 wt. % of acetic acid solution to produce 2 wt. % of chitosan solution. The solution was stirred vigorously for six hours. For the time being, PVA solution was prepared by dissolving 10 g of PVA pellet in 90 ml of distilled water and stirred at 90°C for 6 hours. The solution also was stirred vigorously for six hours until it homogenous. Then, the chitosan solution (1wt. %) and PVA solution (10wt. %) from the earlier were mixed and stirred for four hours under 40°C conditions to form a homogenous solution. Next, the mixture was left for cooling process at room temperature. TEOS with 1, 3 and 5 wt. % concentrations were added into the solution as a nano precursor. This method was known as a sol-gel method. 1 ml of hydrochloric acid (37% w/w) was added into the solution as a catalyst. The solution was stirred continuously for 10 hours under temperature of 30°C.

#### **2.3.2. Preparation of porous support membrane**

The phase inversion technique was applied in order to prepare the porous support membrane. Polysulfone consisting of 13 wt % was prepared by dissolving 13g of polysulfone pellet into the solvent of 1-methyl-2-pyrrolidone. The mixture was stirred continuously at 60°C for 5 hours until a homogenous mixture was formed. Then, the mixture was left at room temperature to remove air bubbles. The polysulfone solution was cast onto a glass plate by using casting machine and by adjusting the thickness of 40 - 60  $\mu\text{m}$ . The polysulfone membrane formed was left overnight in the coagulation bath at room temperature.

#### **2.3.3. Preparation of thin film composite membrane**

The polysulfone membrane was placed on a glass plate. Then, a hybrid membrane solution was cast on the polysulfone as a thin layer to form a thin film composite membrane. Glass rod was used for the casting process. The composite membrane

was left for 24 hours at room temperature and then, it was heated at 45°C in an oven for 1 hour.

## 2.4. Characterisation methodology of hybrid membrane

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

FTIR was performed on a Perkin – Elmer Spectrum 2000 FTIR instrument. These instruments were measure the functional structure of a hybrid membrane sample. The wavelength of hybrid membrane sample will be evaluate in the range 400 cm-1 to 4000 cm-1[21].

### 2.4.2. Thermogravimetry analysis (TGA)

The thermal stability of hybrid membrane also can be evaluated by using Thermogravimetry analysis, but it is more focused on temperature degradation and the weight residue of the sample. The sample weight ranged from 5 to 10 mg in the powder form. The sample was heated from 0°C to 900°C at a heating rate of 10 °C/min [22].

## 2.5. Performance testing

The performance of the synthesized thin film composite membrane was performed by dead-end filtration of standard solutions of Copper (II) nitrate and Ferum (II) nitrate. Solutions of Copper (II) nitrate and Ferum (II) nitrate with different concentrations of (50, 100, 150, 200 and 250 ppm) were prepared. Membrane filtration rig features of a 300 ml bench stainless steel tangential flow stirred cell and pressurized with nitrogen, which was set at 6 bars. Fig. 3 shows the schematic diagram of the membrane filtration apparatus. The concentration of Cu and Fe after permeate was determined by using Atomic Absorption Spectroscopy (AAS).

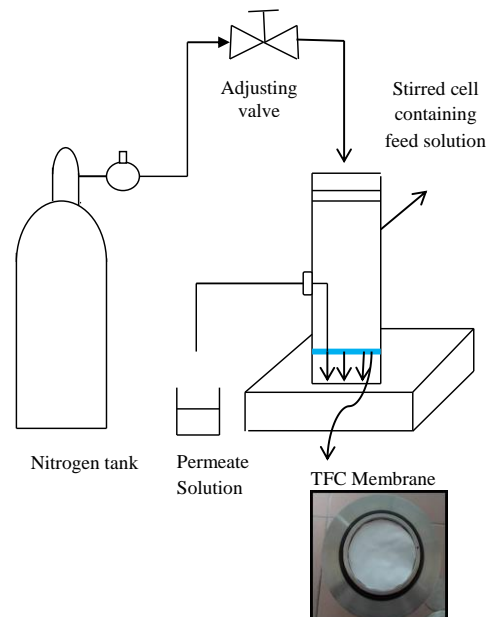


Fig. 3. Schematic diagram of the membrane filtration apparatus.

### 3. Results and Discussion

#### 3.1. Performance testing

##### 3.1.1. Effect of TEOS concentration on percentage removal of Cu and Fe

The performance testing was conducted at room temperature and at fixed pressure 6 bar. Figure 4 shows the results from performance testing of thin film composite of various concentrations of TEOS (1%, 3% and 5%) on percentage removal of Fe and Cu at various feed solution concentrations (50,100,150, 200, 250) ppm. Overall, it was found that the highest percentage removal was obtained at highest TEOS content for both Cu and Fe ions. From the results, it shows that the highest percentage removal of Cu is 66.25% at membrane consisted 5% TEOS as shown in Fig. 4c. For Ferum ions, the highest percentages removal was shown in Fig. 4b at membrane consisted 5% TEOS, where the removal is 53.74%.

The membranes that have TEOS contain hydrophilic hydroxyl group. Thus, Increase in hydroxyl group will make increasing in electrostatic interaction between the hydrophilicity negatively group with counter metal ions [23]. It is clearly reported by Neama et al. (2013) [24] and Zulfikar et al. (2006) [23] for the membrane containing TEOS stand as crosslinking agent. Besides that, metal adsorption can be attributed to the strong acidity and hydrophilic nature of the membrane [24]. At higher concentration of TEOS, there is repulsion amongst the negatively charged OH groups, and hence the network structure increases [23]. As a result, the structure of the membrane will be more compact. Besides, the compact structure of silanol groups of TEOS with –OH groups in chitosan-PVA make more metal ions uptake [25]. Thus, it controlled Fe (II) ions and Cu (II) from pass through the membrane and this resulted on high percentage removal at high concentration of TEOS.

##### 3.1.2. Effect of permeation time

For the effect of permeation time, Fig. 4 also shows the effects of TEOS content with the duration of permeation time. From figure 4a, it shows a big differences between the percentage removal of Cu and Fe ions from membrane consisted 1% and 3% TEOS. However, the percentage removal for membrane consisted 3 and 5 % TEOS is no much differences. From figure 4c at 120 minutes of permeation time, it can be clearly seen that the percentage removal of Cu from membrane consisted 3% and 5% TEOS no differences at all. By referring on Zulfikar et al. [23], the more interaction with silano group such as TEOS will cause the structure of membrane become denser. The much dense membrane structure will decrease the water absorption. Thus, the results from Fig. 4c shows the maximum TEOS contents incorporated with organic compound is 3% TEOS due to its similar performance with membrane consisted 5% TEOS.

##### 3.1.3. Comparison between Cu(II) and Fe(II) on percentage removal

Based on Figs. 4a), b) and c) also clearly shows the comparison with the variation in TEOS concentration and permeation time. In comparison, the

percentage removal of copper is higher than ferum. This may due to the adsorption ability of the chitosan. The binding attraction of chitosan for transition metal ions has been widely studied. The result was proven by literature studies of Krajewska et. al (2001) [26], studying the absorptivity coefficients of 15 metal ions through chitosan membranes. From its literature studies showed that the selected affinity series of the coefficients ( $\text{Hg} > \text{Cu}^{2+} > \text{Fe}^{2+} > \text{Ni}^{2+} > \text{Ag}^+ > \text{Cd}^{2+} > \text{Pb}^{2+} > \text{Co}^{2+} > \text{Cr}^{2+}$ ) corresponds to the metal ion–polymer binding attraction sequence, approving chelation of these ions by chitosan [26]. Therefore, the result in this studies showed that copper ion has high attraction ability to the biopolymer chitosan as compared to the ferum ions.

## 3.2. Characterisation of hybrid membrane

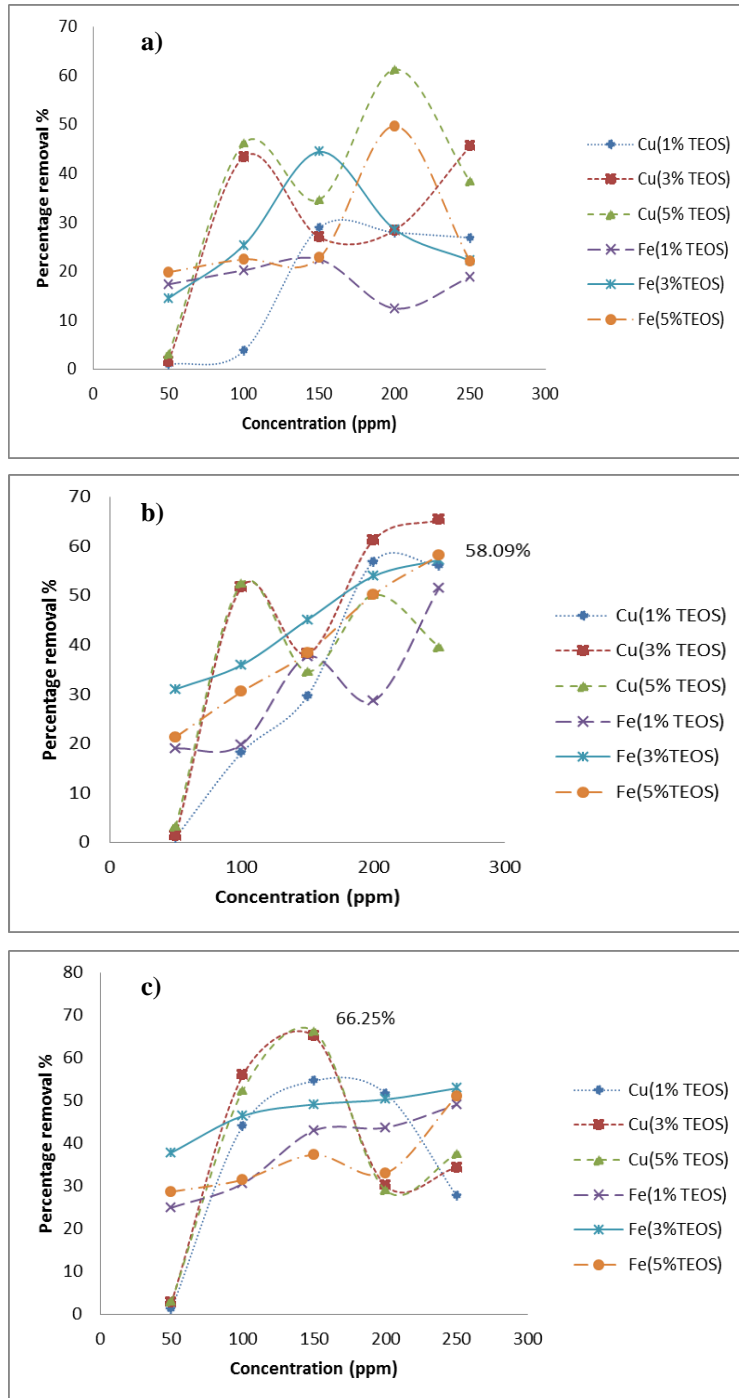
### 3.2.1. FTIR

The FTIR spectra of the hybrid membranes shown in Fig. 5 are mostly similar. Spectrum (a) represents the raw hybrid membrane (chitosan/PVA). It shows the very strong absorption peak at 3269.71  $\text{cm}^{-1}$ , which is assigned to the hydroxyl group (-OH) of pure PVA. A medium peak at spectra (a) is visible at 1638.79  $\text{cm}^{-1}$ . This peak goes to the carboxyl stretching (C=O) of the secondary amide band (amide I) of pure chitosan. Besides that, there is a small peak appears between 1210  $\text{cm}^{-1}$  and 1320  $\text{cm}^{-1}$  from spectrum (a) which attributed to -C-O stretching of carboxylic acid.

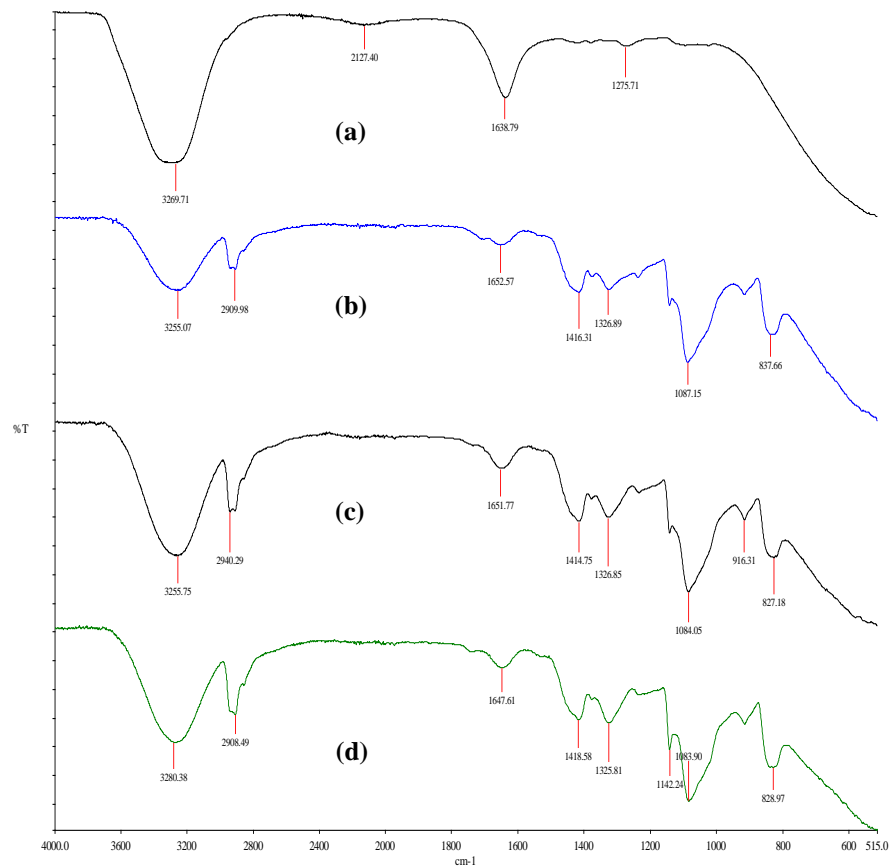
These results indicated the presence of hydrogen bonding within the molecular chain in chitosan. There is very small intensity appear between 1550  $\text{cm}^{-1}$  and 1570  $\text{cm}^{-1}$  assigned to the acetate group of the PVA [27]. For spectrum (b), (c) and (d) represent the spectrum of chitosan/PVA hybrid membrane with 1 % 3% and 5% of TEOS content respectively. In spectrum (b), (c) and (d) , the new peak exists in regions of 1110  $\text{cm}^{-1}$  to 1000  $\text{cm}^{-1}$  and 810  $\text{cm}^{-1}$  to 950  $\text{cm}^{-1}$ . It shows inorganic phase in TEOS content silica. These peaks are assigned respectively to Si-O-C stretching and Si-OH stretching.

From the peaks (b), (c) and (d), it shown the absorption peak in region 1110  $\text{cm}^{-1}$  to 1000  $\text{cm}^{-1}$  increase with amount of TEOS content increase [28]. The hydroxyl stretching of chitosan/PVA occurs at 3255.07  $\text{cm}^{-1}$ . The stretching also overlaps with amine band, C-H stretching at 2909.98  $\text{cm}^{-1}$ . These peaks relatively show a decrease in intensity compared to the spectrum (a) due to the hydrolysis reaction of the alkoxyl group [28]. At 1650 to 1670  $\text{cm}^{-1}$ , -C=O stretching also appears. This peak showed a decrease in intensity compared to spectrum (a). Peak appearing between 1416.31  $\text{cm}^{-1}$  and 1326.89  $\text{cm}^{-1}$  is assigned to C-H bending and C-N stretching of chitosan/PVA blended respectively. The intensity of the interaction of hydrogen bonding between Si-O on silica and functional groups on chitosan/PVA causes decrease in the C=O region in chitosan/PVA-silica hybrid membranes. The band of chitosan/PVA blended-TEOS hybrid membrane appears between 2910  $\text{cm}^{-1}$  and 2950  $\text{cm}^{-1}$  is due to the presence of C-H of hybrid material.





**Fig. 4.** Effects of the TEOS content and permeation time  
 a) percentage removal of Fe(II) and Cu (II) at 60 min permeate,  
 b) percentage removal of Fe(II) and Cu (II) at 90 min permeate,  
 c) percentage removal of Fe(II) and Cu (II) at 120 min permeate.



**Fig. 5. FTIR spectra of membranes (a) blended PVA/chitosan, (b) blended PVA/chitosan with 5% TEOS, (c) blended PVA/chitosan with 3% TEOS, (d) Blended PVA/chitosan with 1% TEOS.**

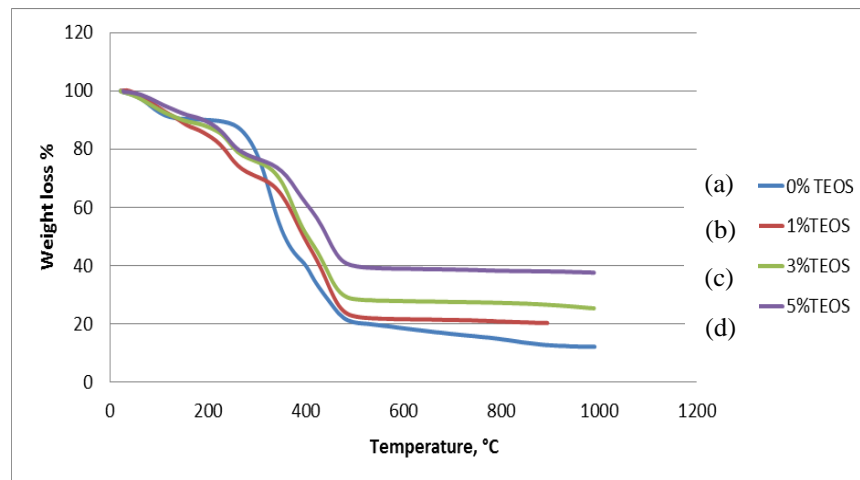
### 3.2.2. TGA

The purpose of TGA analysis in this study is to examine the thermal degradation and stability of the effect of TEOS content in the hybrid membrane. The thermal stability of hybrid membrane with different amount of TEOS was determined by TGA curve shown in Fig. 6. From Fig. 6, it shown the trends in weight loss is similar and the weight change within the membrane steps can be clearly found. The TGA curve showed three main steps of weight lost. The first weight lost that occurred at a temperature below 150°C is the removal of the residual water from the sample [28], due to the exposure of the sample to air during preparation.

The second weight loss is around 200°C to 400°C corresponds to the removal of hydroxyl group on PVA and chitosan [29]. However, the curves are not clearly shown. The final weight loss is after 500°C was related to the degradation of the polymer backbones in the hybrid membrane [29]. Table 1 showed the weight residue of the thermal degradation for hybrid membrane samples on the effect of TEOS content. The weight residue gradually increases around 400°C as the TEOS content increased. Therefore, the incorporation of inorganic polymer, TEOS into the polymer blending of PVA/chitosan significantly stabilized the thermal

degradation of the membranes [29]. Besides that, it also found that the interaction of the hydrogen bond or other bonds between the TEOS inorganic network was formed after the sol-gel process. It was believed that the polymeric chains formed from the interaction can controlled the thermal action and increasing the rigidity of the membrane.

In overall comparison, higher residual mass was achieved by chitosan/ PVA at 5% TEOS sample as compared to the other three membranes. The thermal degradation of the polymer occurs at higher temperature due to the higher presence of silica in TEOS. It requires more reaction activation energy and possesses higher order as higher content of TEOS provide strong incorporation of the silica with the polymer matrix of chitosan/PVA blended. Thus, a more thermal resistance and rigid structure of polymer are formed. Therefore, an increase in silica content contributes to higher weight residue when subjected to an increasing temperature and time [30].



**Fig. 6. TGA curves of the hybrid membrane sample, hybrid membrane with 0% TEOS, b) hybrid membrane with 1% TEOS, c) hybrid membrane with 3% TEOS, d) hybrid membrane with 5% TEOS**

**Table 1. Thermal analysis data of samples in TGA curves.**

Sample	The residual weight at temperature 500°C
(a)	20.3
(b)	22.6
(c)	28.4
(d)	39.75

#### 4. Conclusions

The organic-inorganic PVA/Chitosan/TEOS hybrid membranes, which reflect the integrated complexation process has been prepared. The performance and thermal stability of hybrid membrane are improved apparently by an appropriate choice of TEOS concentration. An increase of TEOS content, results to the increasing of

percentage removal of Copper and Ferum ions. Based on performance testing, the maximum TEOS contents incorporated in the hybrid membrane formulation is 3 wt% due to its similar performance with membrane consisted 5% TEOS. This fabricated membrane was found to remove higher of Cu ions compared to Ferum ions due to their high ability to absorb more in chitosan. Finally, the cross- linking of TEOS in polymeric chain formed rigid structure and high thermal resistances due to the increasing of silica contents.

## References

1. Crini, G.; Morin-Crini, N.; Fatin-Rouge, N.; Déon, S.; and Fievet, P. (2014). Metal removal from aqueous media by polymer-assisted ultrafiltration with chitosan. *Arabian Journal of Chemistry*, In press.
2. Barakat, M.A.; and Schmidt, E. (2010). Polymer-enhanced ultrafiltration process for heavy metals removal from industrial wastewater. *Desalination*, 256, 90–93, 2010.
3. Shrivastava, A.K. (2009). A review on copper pollution and its removal from water bodies by pollution control technologies. *Indian Journal of Environmental Protection*, 29, 552–560, 2009.
4. Bhatia, S.C. (2002). *Handbook of Industrial Pollution Control in Chemical Process and Allied Industries*. New Delhi: C.B.S Publisher.
5. Dvorak, B.I. (2014). *Drinking Water: Iron and Manganese*. NebGuide, University of Nebraska, USA.
6. Irani, M.; Keshtkar, A.; and Mousavian, M. (2012). Preparation of poly (vinyl alcohol)/tetraethyl orthosilicate hybrid membranes modified with TMPTMS by sol-gel method for removal of lead from aqueous solutions. *Korean Journal of Chemical Engineering*, 29, 1459–1465.
7. Jaros, K.; Kamiński, W.; Albińska, J.; and Nowak, U. (2005). Removal of heavy metal ions: copper, zinc and chromium from water on chitosan beads. *Environment Protection Engineering*, 31, 153-162.
8. Li, N.; and Bai, R. (2004). *Novel chitosan-cellulose hydrogel adsorbents for lead adsorption*. Conference Proceedings, AIChE Annual Meeting.
9. Smitha, B.; Suhanya, D.; Sridhar, S.; and Ramakrishna, M. (2004). Separation of organic-organic mixtures by pervaporation - A review. *Journal of Membrane Science*, 241, 1–21.
10. Ding, C.; Yin, J.; and Deng, B.; (2014). Effects of polysulfone ( PSF ) support layer on the performance of thin-film composite (TFC) membranes. *Journal of Chemical and Process Engineering*, 1, 1-8.
11. Ariyaskul, A.S.; Huang, R.Y.M.; Douglas, P.L.; Pal, R.; Feng, X.; Chen, P.; and Liu, L. (2006). Blended chitosan and polyvinyl alcohol membranes for the pervaporation dehydration of isopropanol. *Journal of Membrane Science*, 280, 815–823.
12. Bahrami, S.B.; Kordestani, S.S.; Mirzadeh, H.; and Mansoori, P. (2002). Poly (vinyl alcohol)- chitosan blends: Preparation, mechanical and physical properties. *Iranian Polymer Journal*, 12 (2), 139-146.
13. Aderonke, A.O.; Abimbola, B.A.; Ifeanyi, E.; Omotayo, S.A.; Oluwagbemiga, S.A.; and Oladotun, W.M. (2014). Adsorption of heavy

- metal ions onto chitosan grafted cocoa husk char. *African Journal of Pure and Applied Chemistry*, 8, 147–161.
14. Yao, Y.Y.K.; Lie, J.; and Yao, F. (2012). *Chitosan- Based Hydrogels, Function and Application*. United State of America: CRC Press.
  15. Velenje, K.P. (2000). Metal removal from aqueous solutions using chitosan-enhanced membrane filtration. *Journal of Membrane Science*, 165, 159–167.
  16. Reddy, D.H.K.; and Lee, S. (2013). Application of magnetic chitosan composites for the removal of toxic metal and dyes from aqueous solutions. *Advance in Colloid and Interface Science*, 201–202, 68–93.
  17. Xie, Z.; Hoang, M.; Duong, T.; Ng, D.; Dao, B.; and Gray, S. (2011). Sol – gel derived poly (vinyl alcohol)/maleic acid/silica hybrid membrane for desalination by pervaporation. *Journal of Membrane Science*, 383, 96–103.
  18. Spirk, S.; Findenig, G.; Doliska, A.; Reichel, V.E.; Swanson, N.L; Kargl, R.; Ribitsch, V.; and Stana-kleinschek, K. (2013). Chitosan – silane sol – gel hybrid thin films with controllable layer thickness and morphology. *Carbohydrate Polymers*, 93, 285–290.
  19. Milea, C.A.; and Bogatu, C. (2011). The influence of parameters in silica sol-gel process. *Bulletin of the Transilvania University of Brasov*, 4, 59–66.
  20. Yogesh, S.J.; Gupta, S.; Singh, K.; and Bhattacharya, A. (2008). Porometry studies of the polysulfone membranes on addition of poly(ethylene glycol) in gelation bath during preparation. *Journal of Mexican Chemical Society*, 52, 140–144.
  21. Xie, Z. (2012). *Hybrid organic-inorganic pervaporation membranes for desalination*. PhD thesis, Victoria University.
  22. Zamiah, N.; Shaari, K.; Rahman, N.A.; and Mara, U.T. (2012). Thin film composite membrane with hybrid membrane as the barrier layer: Preparation and characterization. Humanities, Science and Engineering (CHUSER), 2012 IEEE Colloquium, pp. 615–620.
  23. Zulfikar, M.A.; and Mohammad, A.W. (2006). Synthesis and characterization of poly(methyl methacrylate)/SiO<sub>2</sub> hybrid membranes: Effect of silica contents on membrane structure. *Jurnal Matematika & Sains*, 11, 134 – 139.
  24. Reiad, N.A.; Abdelsalam, O.E.; Abadir, E.F.; and Harraz, F.A. (2013). Preparation, characterization and application of chitosan/PEG film for removal iron from water. *Intenational Journal Sustainable Water and Environmental System*, 5, 43–49.
  25. Kittur, A.A.; Jeevankumar, B.K.; Kariduraganavar, M.Y.; and College, S.D.M. (2013). Pervaporation separation of water-dioxane mixtures poly (vinyl alcohol)-silicone based hybrid membranes. *International Journal of Current Engineering and Technology*, 148–156.
  26. Krajewska, B. (2001). Diffusion of metal ions through gel chitosan membranes. *Reactive and Functional Polymers*, 47, 37–47.
  27. Zhao, X.; Lv, I.; Pan, B.; Zhang, W.; Zhang, S.; and Zhang, Q. (2011). Polymer-supported nanocomposites for environmental application: A review. *Chemical Engineering Journal*, 170, 381–394.

28. Han, Y.H.; Taylor, A.; Mantle, M.D.; and Knowles, K.M. (2007). Sol–gel-derived organic–inorganic hybrid materials. *Journal of Non-Crystalline Solids*, 353, 313–320.
29. Xing, R.; and Ho, W.S.W. (2009). Synthesis and characterization of crosslinked polyvinylalcohol/polyethyleneglycol blend membranes for CO<sub>2</sub>/CH<sub>4</sub> separation. *Journal of the Taiwan Institute of Chemical Engineers*, 40, 654–662.
30. Varghese, J.G.; Karuppanan, R.S.; and Kariduraganavar, M.Y. (2010). Development of hybrid membranes using chitosan and silica precursors for pervaporation separation of water+isopropanol mixtures. *Journal of Chemical Engineering Data*, 55, 2084–2092.