

FORMULATION OF HYBRID MEMBRANE LAYER BY USING PVA/CHITOSAN BLENDED POLYMERS ON POROUS POLYSULFONE SUPPORT, AND THE APPLICATION ON COPPER ION REMOVAL

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Nurul Aida Sulaiman, Norin Zamiah Kassim Shaari*, Norazah Abd Rahman, Mohammad Hafizh Abd Fathel, Aqila Zulaikha Nazreen Elangko

*Corresponding author
norinzamiah@salam.uitm.edu.my

Department of Chemical and Process Engineering, Faculty of Chemical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

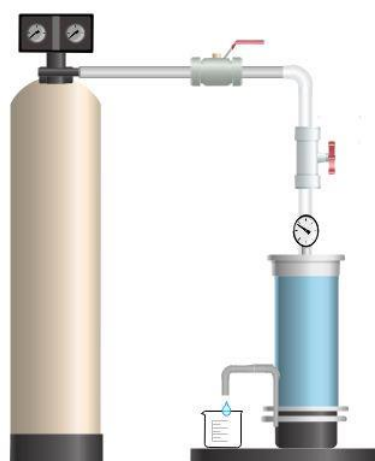


Figure 1 Dead End filtration equipment for performance testing of the membrane

Abstract

In this study, a thin film composite membrane was fabricated by using hybrid membrane as the barrier layer and polysulfone membrane as base membrane. During the formulation of hybrid membrane, a polymer blend of polyvinyl alcohol with chitosan was chosen as organic polymer and it was cross-linked with tetraethylorthosilicate (TEOS), where sol gel method is used to prepare the hybrid membrane. Phase inversion method is used to prepare the base membrane. The aim of this study is to determine the optimum concentration of the polymer for porous support membrane as well as the concentration of chitosan and TEOS in the fabrication of the thin film composite. Four concentrations of polysulfone (PSF) solution was prepared (13wt%, 14wt%, 15wt% and 17wt %) and the optimum concentration was determined. For the hybrid membrane, concentration of chitosan solution was varied at 1wt%, 2wt% and 3wt% with fixed concentration of polyvinyl alcohol (PVA) solution (10wt %). Results showed that 2wt% chitosan and 13 wt% PSF is sufficient to remove acceptable percentage of copper ion. For this purpose of identifying optimum amount of TEOS, pH of the feed copper ion solution was adjusted to three conditions (pH 3, 7, 10). Although, the percentage removal is highest at pH 10 but when dealing with natural integrated complexation method, pH 7 is found to be the optimum pH for the removal of copper ion. Besides that, 3 wt% TEOS in hybrid membrane has found to give a remarkable percentage removal of copper ion. Overall, a new formulation of thin film composite membrane show a great potential to compete with those commercial membrane in thin film composite membrane application especially separation process.

Keywords: Thin film composite membrane, hybrid membrane, polysulfone membrane, tetraethylorthosilicate, chitosan, integrated complexation method

Abstrak

Dalam kajian ini, selaput nipis komposit telah dibangunkan dengan menggunakan selaput hibrid sebagai lapisan halangan dan selaput *polysulfone* sebagai selaput asas. Semasa pembentukan selaput hibrid, campuran polimer *polyvinyl alcohol* dengan *chitosan* dipilih sebagai polimer organik dan ia telah bersambung silang dengan *tetraethylorthosilicate (TEOS)*, di mana kaedah sol – gel telah digunakan untuk menyediakan selaput hibrid. kaedah penyongsangan fasa digunakan untuk menyediakan selaput asas. Tujuan kajian ini adalah untuk menentukan kepekatan optimum polimer selaput asas serta kepekatan *chitosan* dan *TEOS* dalam pembuatan selaput nipis komposit. Empat kepekatan *polysulfone (PSF)* telah digunakan (13wt%, 14wt%, 15wt% dan 17wt%) dan kepekatan optimum ditentukan. Untuk selaput hibrid, kepekatan larutan *chitosan* telah disediakan pada 1wt% 2wt% dan 3wt% berat dengan kepekatan tetap *polyvinyl alcohol (PVA)* sebanyak (10wt%). Hasil kajian menunjukkan bahawa 2wt% *chitosan* dan 13% kepekatan *PSF* cukup untuk menyingkirkan peratusan ion tembaga yang dikehendaki. Untuk mengenal pasti jumlah optimum *TEOS*, larutan ion tembaga telah diselaraskan kepada tiga larutan berbeza pH (pH 3, 7, 10). Walaupun, penyingkiran peratusan adalah paling tinggi pada pH 10 tetapi apabila berurusan dengan kaedah kompleks bersepadu. Jadi, pH 7 didapati pH optimum untuk penyingkiran ion tembaga. Selain itu, 3% berat *TEOS* dalam selaput hibrid telah didapati dapat menyingkirkan peratusan yang luar biasa daripada ion tembaga. Secara keseluruhan, rekaan selaput nipis komposit yang baru menunjukkan potensi yang besar untuk bersaing dengan selaput nipis komposit yang sedia ada terutama dalam proses penapisan tembaga ion.

Kata kunci: selaput nipis komposit, selaput hibrid, selaput *polysulfone*, *tetraethylorthosilicate*, *chitosan*, kaedah kompleks bersepadu

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1.0 INTRODUCTION

The use of heavy metals for industrial purpose has been of great concern because of their increased discharge, toxic nature and other adverse effects on receiving waters. The copper metal is one of the heavy metal usually used in metal cleaning and plating baths, pulp, paper and paper board mills, wood pulp production, and the fertilizer industry. Industrial effluents from these industries have high probability to contain harmful metals that can endanger human life as well as aquatic life. The customary method used for heavy metal removal from wastewater such as electrodialysis, chemical precipitation, ion exchange, and solvent extraction had been proven inefficient because they are unable to reduce the concentration to the required levels and always incur large operational and capital cost. Also, some techniques have been found to produce significant quantity of secondary wastes such as sludge created from precipitation process which will eventually pose treatment difficulties.

Therefore, This study develops an integrated complexation method to remove heavy metal ions especially Copper ions by fabricating a thin film composite, which consists of a hybrid membrane as the barrier layer and polysulfone membrane as porous support membrane. The complexation will occur on the hybrid membrane layer that consists of chitosan blended with Polyvinylalcohol (PVA) and

cross- linked with Tetraethylorthosilicate (TEOS) as silica nano precursor.

Polysulfone membrane is prepared using phase inversion method. The polymer concentration during casting plays an important role towards the performance of thin film composite membrane. However, polysulfone is hydrophobic which makes it easy to foul. A suitable polysulfone concentration needs to be used to have high flux rate and rejection towards copper ion [1].

Chitosan is widely used in many industries such as food, pharmaceutical, biotechnology and water treatment industries. [2]. Chitosan is a good complexation material where it can separate and adsorb a wide range of pollutants including heavy metals [3]. Chitosans has functional groups, which allows metal ions to be bind at its active sites which is then removed. The amine group in chitosan provides an active site for adsorption of metal ions. These sites will form a complex with the metal ions so that its size will be bigger than the pore size. This will hinder the macromolecules from passing through and allows small water molecules to permeate. Other than that, chitosan's biological properties, high selectivity, biodegradability, bioactivity and biocompatibility are the reasons why chitosan makes a good material for membrane technology [2].

The aim of this paper is to identify the optimum concentration for polysulfone support membrane for the thin film composite. The hybrid membrane in this

study was prepared from polymer blending PVA with chitosan and cross - linked with TEOS. These hybrid membranes were coated as thin film layer onto polysulfone (PSF) membrane to form a thin film composite membrane. Polyvinyl alcohol (PVA) is used for this study because of its hydrophilic in nature and contains pendant hydroxyl groups. High hydrophilicity is needed for membrane separation due to minimise the membrane fouling by organic matter [4]. The hydroxyl groups in the repeating units of the polymer are expected to produce strong secondary interactions with the residual silanol groups generated from acid catalyzed hydrolysis and polycondensations of TEOS[5]. Therefore the present work aims are not only investigating the porous support membrane, but for the best condition of feed solution and the performance of TFC membrane by varying chitosan and the TEOS concentrations.

2.0 METHODOLOGY

2.1 Materials for Preparation of Thin Film Composite Membrane

In the preparation of thin film composite membrane, the materials that was used were polyvinyl alcohol (PVA) with a hydrolysis degree of 87-89% (MW : 85,000 – 124,000) pellets, polysulfone resin pellets (MW: 44,000 – 53,000), commercial chitosan (deacetylation degree 84.8 ± 1.2 %), tetraethylorthosilicate (TEOS) with 99% purity, hydrochloric acid with 37% purity as catalyst, acetic acid and copper (II) chloride dehydrate powder. N-methyl-2-pyrrolidone with purity of 99% was obtained from Merck, Malaysia. Deionized water was also as coagulation medium. All this material was employed without further purification.

2.2 Preparation of Hybrid Membrane

For the preparation of hybrid membrane, polyvinyl alcohol (PVA) was blended with chitosan (Cs) to produce a hybrid membrane. PVA solution and chitosan solution was prepared separately. First, to produce chitosan solution, 3g of chitosan was dissolved in 2wt% of acetic acid at room temperature with vigorous stirring [2], [6]. Next, 10 g of PVA pellets was dissolved in 90 mL of distilled water with 9:1 ratio which produced 10 wt% PVA solution [2], [6]. Then, the solution was heated at 90°C for 6 hours. The solution was stirred continuously until PVA pellets completely dissolved in distilled water. The chitosan solution was mixed with PVA solution to produce a blend mixture. The mixture was heated at 60°C for 4 hours to produce a homogeneous solution. Then, the mixture was left to cool at room temperature. Next, 3wt% of TEOS as a nano precursor was added to the mixture by sol-gel method [7], [6]. Then, 1 ml of hydrochloric acid at 37 wt% which acts

as a catalyst was added to the mixture solution. Then, the solution was heated at 30°C under continuous mixing for 10 hours[6]. The same method was used to prepare hybrid membrane solution at different chitosan concentration 1%, 2% and 3wt% polymer

2.3 Preparation of a Polysulfone Support Membrane

For the preparation of polysulfone (PSF) support membrane, phase inversion technique was used. 13 g of polysulfone beads was dissolved in 87 g of N-methyl-2-pyrrolidone (NMP) to produce polysulfone polymer solution with 13wt% of polymer concentration. The solution was stirred continuously for approximately 4 to 6 hours at 60°C until it turn homogeneous. The solution was left for several hours at room temperature to remove air bubbles. A casting machine was used to cast the polysulfone solution onto a glass plate with adjusted thickness. The film was immersed in water as a coagulation medium for 1 hour. The film was left in a large amount of water for 24 hour. The film was cured in an oven for 1 hour. The same method was used to prepare polysulfone polymer solution at concentration 14 %, 15% and 17 wt% polymer [7], [6].

2.4 Preparation of Thin Film Composites

The thin film composite membrane consists of hybrid membrane as the barrier layer and polysulfone membrane as the support layer. A thin layer was formed by coating hybrid membrane with 2 wt% concentration of chitosan in 10 wt% PVA solution onto polysulfone support membrane using a glass rod. The membrane produced was left for 24 hour at room temperature and was cured in an oven for 1 hour at 45°C [7], [6].

Table 1 Membranes with different dope solution (PSF) on support membrane and different chitosan concentration on hybrid membrane

Sample	PSF (wt%)	NMP (wt%)	PVA (wt%)	Cs (wt%)	TEOS (wt%)
PSF13%	13	87	-	-	-
PSF14%	14	86	-	-	-
PSF15%	15	85	-	-	-
PSF17%	17	83	-	-	-
HM2%Cs	13	87	10	2	3
HM3%Cs	13	87	10	3	3

*HM : Hybrid Membrane, wt% : weight percent

2.5 Characterization of Thin Film Composite Membrane

The surface morphologies of cross sectional area on the polysulfone support layer were analyzed using SEM Images. The membrane was coated with a 10-

nm-thick layer of gold using a sputter coater before the analysis [8].

2.6 Performance Testing of Thin Film Composite Membrane

The performances testing of Thin Film Composite membrane were carried out by using dead end filtration in laboratory scale apparatus shown at Figure 1. 3.82 g of Cu (II) nitrate trihydrate ((CuNO₃)₂·3H₂O) was funneled into 1000 ml volumetric flask. Then, the powder was diluted using distilled water up to the mark. The solution was shaken to produce a homogeneous solution. The resulting solution produced a copper solution of 1000 ppm. The 1000 ppm stock solution was diluted to produce 50, 150 and 250 ppm aqueous solution. Besides that, pH of the feed copper ion solution was adjusted to three conditions (pH 3, 7, 10).

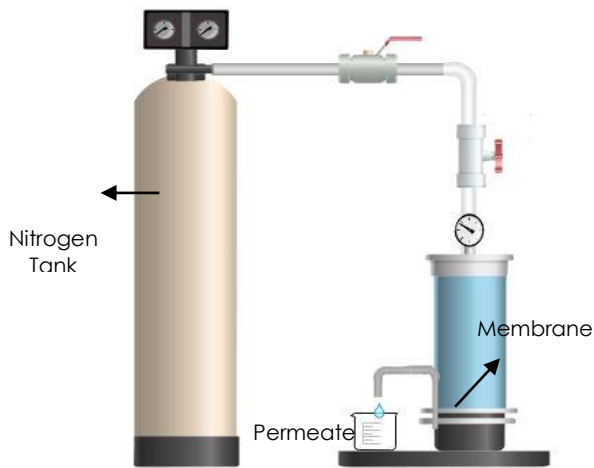


Figure 1 Dead End filtration equipment for performance testing of the fabricated TFC membrane

Sample from permeate solution were taken for metal analysis at the end of the experiment by using Atomic Absorption Spectroscopy AAS. The permeate flux, mL/cm².min⁻¹ was determined analytically from the total volume of permeate collected against time by using Eq. (1).

$$\text{Flux, } F = \Delta V / A \cdot \Delta t \quad (1)$$

where ΔV (mL) is the volume of the permeate sample, A is an effective membrane area in cm², and Δt is time permeate.

The rate of percentage removal of copper ions was calculated from the concentration of copper ions in the feed and permeates by using Eq. (2).

$$R\% = C_f - C_p / C_f \times 100 \quad (2)$$

where C_f is the concentration feed solution, C_p is the concentration of permeate copper ions solution.

3.0 RESULTS AND DISCUSSION

3.1 Effect of Polysulfone Concentration on Support Layer

Figure 2 shows the Cross section of membrane morphology of PSF membrane; (a) PSF 13w%, (b) PSF 14%, (c) PSF 15%, (d) PSF 17%. From Figure 2 we can see that the structure of PSF membrane with different PSF concentrations can be described in terms of presence or absence of connecting voids. Usually, an asymmetric structure is formed across the membrane since the solvent-non-solvent exchange probably will lead to different starting conditions for phase separation at layers far from the surface [9], [10].

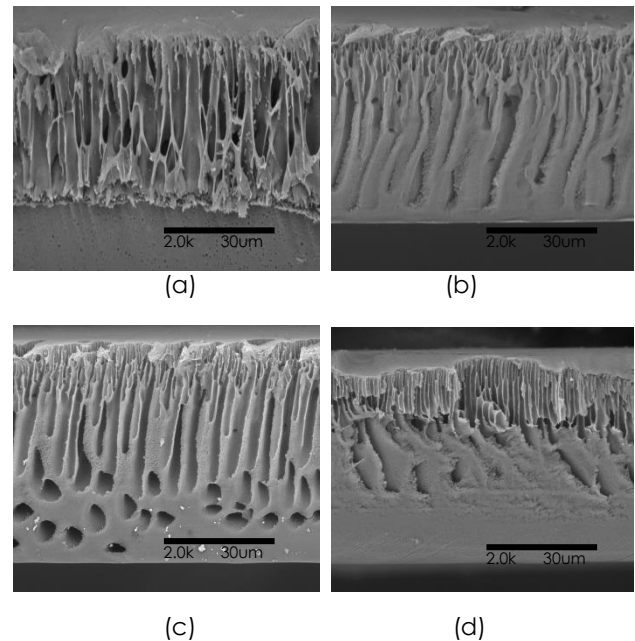


Figure 2 Cross section of membrane morphology of PSF membrane; (a) PSF 13% , (b) PSF 14%, (c) PSF 15%, (d) PSF 17%

The cross sections of fabricated polysulfone membranes from Figure 2 was viewed by SEM images which displayed generally finger - like structure for all types [1]. According Barth *et al.* (2003), finger-like pores can even be found in the lower parts of the PSF membranes [10]. Another statement of Barth *et al.* (2003) about finger - like pores is concerns with the effect of the thermodynamic particularities of the non-solvents [10]. Strong non-solvents lead to the formation of many finger-like pores, while solvents with lower coagulation potential produce more homogeneous sponge-like structures. For 13% polysulfone at Figure 2(a), it has finger like structure with highest macrovoids, which makes it less dense

than the other concentration of PSF membrane. Arthanareeswaran *et al.* (2010) defined that large macrovoids in the structure of membrane usually result in increased permeability, and therefore may be desirable in moderate-pressure ultrafiltration application [1], [11]. Thus 13% concentration of PSF membrane has the highest permeability coefficient compare to the other concentration based on their structure at Figure 2 where more water can pass through the membrane allowing the membrane to have the highest flux rate [1], [12], [11]. Polysulfone with 14% concentration has less finger-like macrovoids than polysulfone with 13% concentration. This shows that membrane with 14% concentration is less porous than 13%. Therefore, the flux rate of polysulfone 14% is smaller compared to 13%. Polysulfone with 15% concentration has even lesser finger-like macrovoids than of 14% thus the flux rate is smaller than 13% and 14%. Polysulfone with 17% concentration has sponge-like structure which shows that the membrane is denser than the rest. The 17% membrane should have smaller flux rate since it has less macrovoids compare to the others.

Based on Table 2, 13% PSF shows the highest flux rate while 17% PSF has the lowest flux rate at 30, 60 and 90 minutes respectively. This is due to the permeability coefficient. A membrane with higher permeability coefficient has higher flux rate. A denser membrane has lower flux rate because water is unable to permeate through it. For the instance, referring at Table 2, the highest value of flux rate is 0.245 at 13% PSF occur at the first 30 minutes permeation while the lowest flux rate value is at 17% PSF which is no permeation rate occur at first 30 and also occurred at 60 and 90 minutes permeation. This shows that polymer concentration is directly related to the flux. With increasing polymer concentration, the denser the membrane, the lower the flux rate value. The flux rate also decreases with increasing copper concentration. Table 2 also shows that higher flux rate is obtained from copper solution with 50 ppm while for 250 ppm of copper solution, the flux rate is the lowest. This is due to phenomena called concentration polarization. Concentration polarization occurs when the solute is being retained by the membrane. This causes the solute to accumulate and form a layer of high concentration solute to form at the interface of the membrane [13]. Thus, the membrane becomes less permeable causing the flux rate to be small. Higher solution concentration causes more solute to be retained which reduces the flux rate. Therefore, 13% PSF concentration had been selected to formulate porous support membrane. A suitable polysulfone concentration needs to be used to have high flux rate [1].

Table 2 Water flux of 13wt%, 14wt%, 15wt% and 17wt% of PSF at 50 ppm copper concentration

Concentration of PSF/ permeation time (min)	30	60	90
	Flux (ml/min.cm ²)		
13	0.245	0.183	0.123
14	0.189	0.153	0.112
15	0.132	0.122	0.101
17	0	0.01	0

3.2 Effect of Chitosan Concentration on Cu(II) Ions Removal

The uses of chitosan for membrane fabrication technology have become a great interest because it promises various remarkable advantages for heavy metal separation such as copper. Instead of other biopolymer, chitosan becomes the best alternative biopolymer due to its physic- chemical characteristic, chemical stability, high selectivity, excellent chelation behavior and high selectivity towards pollutants as well as heavy metals [14], [15], [16]. During the formation of hybrid membrane as barrier layer of TFC membrane, the optimum chitosan concentration was selected. Therefore, Figure 4 shows the percentage removal of Cu (II) ion by varying chitosan concentration. From Figure 4, it is clearly shown that chitosan has ability to chelate Cu(II) ions at higher concentration of copper solution while by increasing the concentration of from 1wt% to 3wt% resulted in a slight increase Cu(II) ions removal. There are no significant difference for Cu (II) ions removal from 2wt% and 3wt% of Chitosan concentration. Therefore, 2wt% of chitosan concentration is selected for the formulation of hybrid membrane. 2wt% of chitosan had been selected due to maximum adsorption capacity of copper ions. the amount of chitosan that able to adsorb more heavy metal ion is consistent with findings of past studies by M. Luisa Cervera *et al.* (2003) [17].

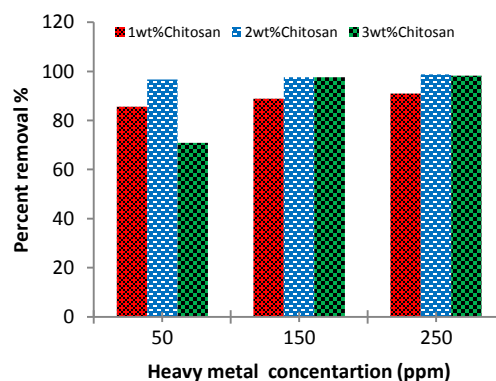


Figure 4 Percent removal of Cu(II) ions with different chitosan concentration 1%,2% and 3% Chitosan with different copper concentration at fixed pressure 6 bar

3.3 The Impact on Copper Ions Removal with Influence of TEOS Concentration and pH at Feed Solution

After successfully determined the optimum amount of polysulfone and chitosan in the previous section, this section will focus on varying the cross linker (TEOS) content in the blended polymer of PVA and Chitosan. Generally, the addition of cross linker is needed in order to increase the rigidity structure of the membrane, and improved the thermal and mechanical properties of hybrid membrane [4], [6], [18].

Figure 5 shows the trend of copper removal by varying the cross linker (TEOS) content during the performance testing of TFC membrane. The membrane was tested at three different pH feed solution of Cu (II) ions (i.e acidic, neutral and alkaline) with three different Cu(II) ions concentration (50, 150, 250 ppm). In the absence of TEOS, the percentage removal of copper is not too high especially in acid condition. In fact, without cross – linker TEOS, it is not recognized as hybrid membrane but it can still able to remove the Cu(II) ion with presence of blended PVA and chitosan. However, with the presence of TEOS, their percentage of removal is about to be the same which is more than 60% removal at acid condition of feed solution. It show that TEOS cross linker not only good to form membrane that have high thermal and mechanical properties but also it able to form rigid structure of blended PVA/Chitosan that assist the membrane to trap more heavy metal ion.

At pH 7 and pH 10, there is an increase of the percentage removal, where it has achieved more than 90%. Wan Ngah *et al.* [19] also found the similar behavior in their research. This could be explained by the fact that at higher pH values, less inhibitory effect of H^+ exists to protonate with amine group from chitosan, which could reduce the number of binding sites for Cu^{2+} adsorption. Plus, the lone pair electrons present in the amine ($-NH_2$) groups and lone pairs of electrons of hydroxyl ($-OH$) groups can establish bonds with transition metal ions. Although adsorption is increases at pH above than that, but there is a formation of Cu(II) hydroxide in a form of precipitate which might affect the adsorption. Furthermore, they have found that the combination of chitosan/PVA results the amine group present in PVA is protonated especially in acidic media; and the addition of TEOS helps to improve adsorption capacity of metal ion due to the agglomeration ability that promotes surface of adsorption [20], [21].

In Figure 5, it was also observed that the permeation flux decreased for all the TFC membranes with increasing of copper solution concentration in the feed. This is due to an increase of selective interaction of between water molecules and hydroxyl groups of hybrid membranes and concentration polarization of the membrane. As state earlier, concentration polarization occurs when the solute is being retained by the membrane. This

causes the solute to accumulate and form a layer of high concentration solute to form at the interface of the membrane [13].

As can be seen, the removal of metal ions increases on increasing the pH of copper ion solution. So, pH 7 and pH 10 of the feed solution is found to be the optimum pH for the removal of copper ion using TFC membrane because it's have the same performance on percent removal of Cu(II). However, in order to avoid the effect of hydroxide precipitation [17], pH 7 was selected, at which Cu(II) was almost fully removed at 90% above.

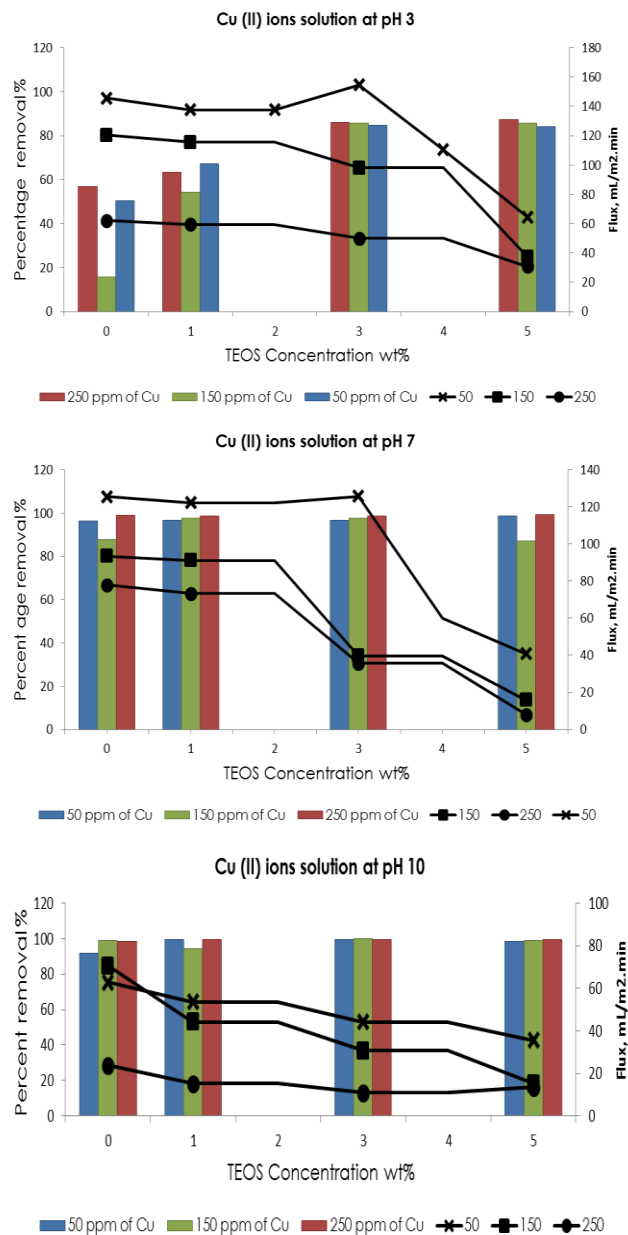


Figure 5 Percent removal of Cu(II) ions and permeate flux with different TEOS concentration 0%,1%, 3% and 5% with different pH and copper concentration at fixed pressure 6 bar

In other observation at Figure 5, 3 wt% and 5% TEOS in hybrid membrane has found to give a significant percentage removal of copper ion at any feed solution condition. At higher concentration of TEOS, there is repulsion amongst the negatively charged OH groups, and hence the network structure increases [22]. As a result, the structure of the membrane will be more compact. Therefore, the compact structure of silanol groups of TEOS with –OH groups in chitosan-PVA make more metal ions uptake. Thus, it controls Cu (II) ions from pass through the membrane and this has resulted on high percentage removal of the ions [6].

4.0 CONCLUSION

Based on the performance testing, polysulfone with 13% concentration was selected as the best concentration for the support layer of the thin film composite. For the hybrid membrane, 2wt% of chitosan concentration is sufficient to remove acceptable percentage of copper ion. Based on the result, the adsorption of metal ions is much more efficient in the feed solutions at high pH than in the low pH feed solutions. Finally, by selecting the optimum concentration of TEOS, the fabricated membrane could remove more than 90% of Cu (II) ions. Therefore, thin film composite from the PVA/Chitosan/TEOS hybrid membrane, which reflects the integrated complexation process during the removal of metal ions has been successfully prepared.

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