

# A Study on Anti – Fouling Behaviour and Mechanical Properties of PVA/Chitosan/TEOS Hybrid membrane in The Treatment of Copper Solution

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**Abstract.** In a wastewater treatment by using membrane filtration, fouling has been one of the major problems. In this study, the anti-fouling behaviour of the fabricated thin-film composite membrane were studied during the treatment of water containing copper ion. The membranes were prepared from a polymer blend of 2wt.% chitosan with 10 wt.% poly(vinyl alcohol) (PVA) and then it was cross – linked with tetraethylorthosilicate (TEOS) through sol-gel method. The membrane had been evaluated for its resistance against organic fouling where humic acid had been chosen as organic foulant model which represent the natural organic matter (NOM) in water or wastewater. The dead-end filtration experiments were carried out by using 50 ppm of copper solution with and without the presence of humic acid as feed solution, which was passed through two types of thin film composite membranes. The possible reversible fouling was evaluated by using relative flux decay (RFD) and relative flux recovery (RFR) calculations. The percentage of copper ion removal was evaluated by using Atomic Absorption Spectroscopy (AAS). Based on the results, with the presence of humic acid, the membrane incorporated with silica precursor (TEOS) showed lower flux decay (3%) and higher flux recovery (76%), which show that the formulated hybrid membrane possesses the anti fouling property. The same trend was observed in the mechanical properties of hybrid membrane, where the presence of TEOS has improved the tensile strength and flexibility of the membrane. Therefore, the fabricated thin film composite with the anti-fouling properties and good physical flexibility has potential to be used in the treatment of wastewater containing heavy metal as it could result in good saving in term of operational cost.

## 1.Introduction

Heavy metals are regularly assumed to be hazardous and highly toxic to human being. They have tendency to accumulate on human body and easily effect on human being indirectly [1][2]. Excess amount of heavy metal accumulate in living things, it can cause serious health syndromes such as kidney damage, liver damage and many else. Furthermore, heavy metals can easily enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater [2]. Therefore, many treatment technologies has been applied to overcome this problem such as chemical precipitation, ion – exchange and membrane separation. However, there is still some limitations of these processes such as production of high sludge and high operating cost. Fenglian Fu et. al (2011) [3][4] reported that membrane filtration are the most frequently studied for the treatment of heavy metal from industrial wastewater because of its higher efficiency of heavy metal removal. Membrane filtration is becoming a common method for heavy metal removal due to its simplicity, no solvent is consumed and the quality of removed particles



are maintained throughout the process [3][4]. However, there are limitations which affect the membrane performance that is fouling on membrane surface. Fouling can affect the separation performance of membrane and decreases the permeate flux [5][6]. Yan Hao et. al (2011) reported that higher membrane fouling phenomena occurs in the treatment of industrial wastewater because it contains of multiple substances especially metal ions. Thus, many researcher has developed new membranes that have high hydrophilicity to overcome the fouling problem [7]. In this study, a new thin-film composite membrane has been developed. Generally, the thin-film composite membrane has its own class compared to a normal membrane as it consists of more than one layers of membrane (top selective layer and bottom porous substrate). Each of the layers can be independently controlled and optimized to achieve desired selectivity and permeability while offering excellent mechanical strength and compression resistance [8]. One of the methods to enhance hydrophilicity of membrane is by incorporating hydrophilic polymer in membrane formulation [7].

Basically, fouling on membrane filtration largely depend on their interaction among membrane surface and types of foulant in water[7]. Natural organic matter (NOM) is a complex matrix of organic material that is frequently found in surface water with three major substances - hydrophobic (humic substances), hydrophilic and transphilic fraction [9]. The major fraction of natural organic matter (NOM) is humic acid (HA) which contributes to problems like odour, taste, colour and acidity to the water. Humic acid (HA) has high ability of metal complexation capacity and interactive properties with organic pollutants which has caused an increase in transport and distribution of inorganic and organic micro-pollutants [9]. Through an extensive research on organic fouling, it has been reported that membrane fouling is caused by the attachment of colloidal and soluble organic matter to the membrane [10]. Therefore, fouling should become worse when humid acid is combined with metal ions due to an increase in the ionic strength between the humic acid substance [6]. Therefore, in this study, thin-film composite membranes which were formulated from chitosan, PVA and TEOS as the thin layer and coated on polysulfone membrane were tested on the anti fouling behaviour by using humic acid as the foulant model. The anti-fouling behaviour was determined by using relative flux decay (RFD) and relative flux recovery (RFR) calculations.

## 2. Materials and Method

### 2.1 Chemicals.

Poly(vinyl alcohol) (PVA) with a hydrolysis degree of 87-89% (MW : 85,000 – 124,000), polysulfone (PSF) resin pellet (MW: 44,000 – 53,000), tetraethylorthosilicate (TEOS) with 99% purity and hydrochloric acid with 37% purity as catalyst and commercial chitosan (deacetylation degree  $84.8 \pm 1.2$  %), humic acid (CAS Number 1415-93-6) and copper nitrate  $[\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}]$  were used in this study. 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 a solvent.

### 2.2 Formulation of TFC Membrane

The method to prepare thin film composite membrane for heavy metal removal was according to Norin et. al (2012) with some modification [11][12][13]. The formulation consists of two important steps, preparation of polysulfone polymer solution for porous support membrane and formulation of hybrid membrane by using sol –gel method. The hybrid layer was coated on the polysulfone membrane. There were three types of membranes that were produced and the formulation was shown in Table 1. In this study, the membrane had an effective surface area of  $17.3494 \text{ cm}^2$  in a flat sheet configuration and the mode of filtration is according to dead-end filtration [13].

### 2.3 Fouling Performance of TFC Membrane

In this study, the anti-fouling performance testing is performed using the dead-end filtration rig at 8 bar. The anti-fouling performance of the fabricated thin film composite membrane was evaluated by using copper solution as the feed solution with and without the presence of humic acid. 13wt% polysulfone membrane and hybrid membrane with different concentration of TEOS were used in the experiment. Firstly, 1000 ppm of humic acid stock solution was prepared by dissolving 10 gram of humic acid powder in 10000 ppm of NaOH. The prepared stock of humid acid solution was stored in a volumetric flask at room temperature in a dark place [14]. Next, 0.5 grams of copper nitrate was

diluted with deionized water to prepare 1L of 500 ppm copper solution in a volumetric flask. For the membrane fouling performance, the membrane was evaluated through the filtration of copper stock solution with and without the presence of humic acid. A mixture of 50 mL of 50 ppm copper nitrate solution with 50 mL of each humic acid solution was prepared and used immediately. Each filtration process of the membrane was conducted in 3 stages. Firstly, pure water flux is recorded for 0.5 hour and the stabilized flux was denoted as  $J_o$ . Then, the membrane was tested with a copper-humic acid solution for 2 hours and the collection of permeate was made at every 30 minute interval and the volume collected was recorded. The stabilized flux is denoted as  $J_p$ . Then, the membrane was cleaned by back-wash method. The back-washing method is done by immersing the membrane in 50 mL of deionized water and being stirred in a shaker at 100 rpm for 30 minutes. Lastly, pure water flux was recorded again for 0.5 hour and the final flux was denoted as  $J_f$ . Relative flux Decay (RFD) and Relative Flux Recovery (RFR) were calculated by using equations (2) and (3) respectively [7]. Samples from permeate solution was analyzed for copper concentration by using Atomic Absorption Spectroscopy (AAS). The permeate flux,  $\text{mL}/\text{cm}^2\cdot\text{min}^{-1}$  was determined analytically from the total volume of permeate collected against time by using Eq. (1).

$$\text{flux}, f : \frac{\Delta v}{A \cdot \Delta t} \quad (1)$$

$$\text{RFD} : \left[ \frac{(J_o - J_p)}{J_o} \right] \times 100 \quad (2)$$

$$\text{RFR} : \left( \frac{J_f}{J_p} \right) \times 100 \quad (3)$$

Where  $\Delta v$  (mL) is the volume of the permeate sample,  $A$  is an effective membrane area in  $\text{cm}^2$ , and  $\Delta t$  is time permeate. The rate of percentage removal ( $R\%$ ) of copper ions was calculated from the concentration of copper ions in the feed and permeates by using Eq. (4).

$$R\% : \left[ \frac{(C_f - C_p)}{C_f} \right] \times 100 \quad (4)$$

Where  $C_f$  is the concentration feed solution,  $C_p$  is the concentration of permeate copper ions solution

**Table 1.** Formulation of membranes.

Sample	Membrane name	PSF (wt%)	NMP	PVA	CS (wt%)	TEOS (wt%)
13wt% polysulfone (porous support)	M1	13	87	0	0	0
PVA/Chitosan/0wt%TEOS coated on PSF support membrane	M2	13	87	10	2	0
PVA/Chitosan/3wt%TEOS coated on PSF support membrane	M3	13	87	10	3	3

PSF: Polysulfone, NMP: N-methyl-2-pyrrolidone, PVA: Poly (vinyl alcohol), CS: chitosan, TEOS: tetraethylorthosilicate, wt%: weight percent

#### 2.4 Mechanical analysis

The samples were prepared in the dry states and the analysis was carried out using Instron Universal testing model. The hybrid membranes were cut into a rectangular shape of 100 mm length and 40 mm

width. The speed of the machine was 5mm/min and the gauge length was set at 25 mm according to the standard method ASTM D 882 for evaluation on tensile of thin film [17].

### 3. Results and Discussions

#### 3.1. Interaction of humid acid with $\text{Cu}^{2+}$ ions during performance testing

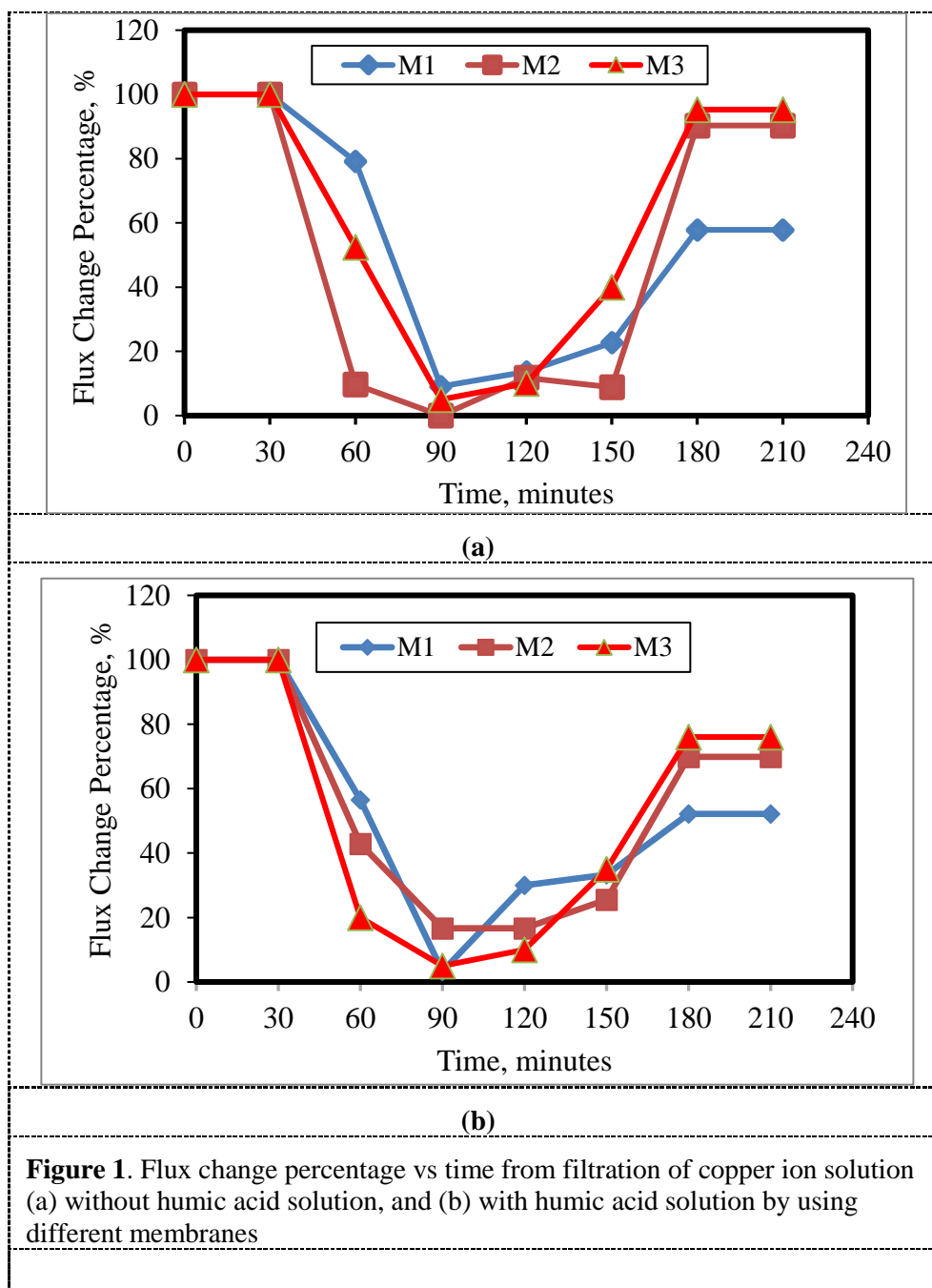
In this study, heavy metal solution was mixed with the organic foulant (humic acid) to examine the membrane fouling performance. Humic acid was chosen as organic pollutant in the heavy metal solution to simulate the actual environment of the feed solution [15][7][16][4]. Figure 1 (a) (b) show the permeate fluxes, ( $J$ ) of the PSF membrane and TFC membrane with and without addition of nano-silica, tetraethylorthosilicate (TEOS) during the filtration of humid acid solution and without humid acid solution towards copper ion solution. Correspondingly, the data of the prepared membrane from the experiment are summarized in Table 2. As shown in Figure 1 and Table 2, for feed solution without humic acid, membrane M3 that incorporated with silica precursor (3wt% TEOS) had the lowest initial permeate flux due to an increase of selective interaction of between water molecules and hydroxyl groups of the hybrid membranes [13]. However, it has higher flux recovery as compared to M1 and M2 where 33% of flux drop after the 2 hours filtration and a 95% flux recovery after the membrane cleaning. This result indicates that the membrane containing TEOS exhibited almost fully recoverable to its initial flux. For the feed solution with humic acid, interaction of humid acid (HA) with copper solution has caused all membranes have lower flux recovery as compared to that without the presence of humic acid. These results show natural organic matter (NOM) represented by humic acid has really caused the organic fouling towards the membranes.

**Table 2.** Relative flux decay (RFD) and relative flux recovery (RFR) of the TFC membranes towards filtration of copper ion solution with and without humic acid.

HA (ppm)	Type of membrane	Membrane name	$J_0$ (mL/min.m <sup>2</sup> )	$J_p$ (mL/min.m <sup>2</sup> )	$J_t$ (mL/min.m <sup>2</sup> )	RFD	RFR	% copper ions removal
0	13wt% PSF	M1	0.04054	0.00845	0.02344	56.5166	30.8057	93.67
	0wt% TEOS	M2	0.00596	0.00653	0.00538	29.0323	90.3226	98.56
	3wt% TEOS	M3	0.00404	0.00192	0.003843	33.9286	95.2381	99.7
1000	13wt% PSF	M1	0.02651	0.01153	0.013833	38.7681	52.1739	93.26
	0wt% TEOS	M2	0.00605	0.003458	0.004227	26.2698	69.8444	99.6
	3wt% TEOS	M3	0.00480	0.003843	0.003650	3.00000	76.0000	92.72

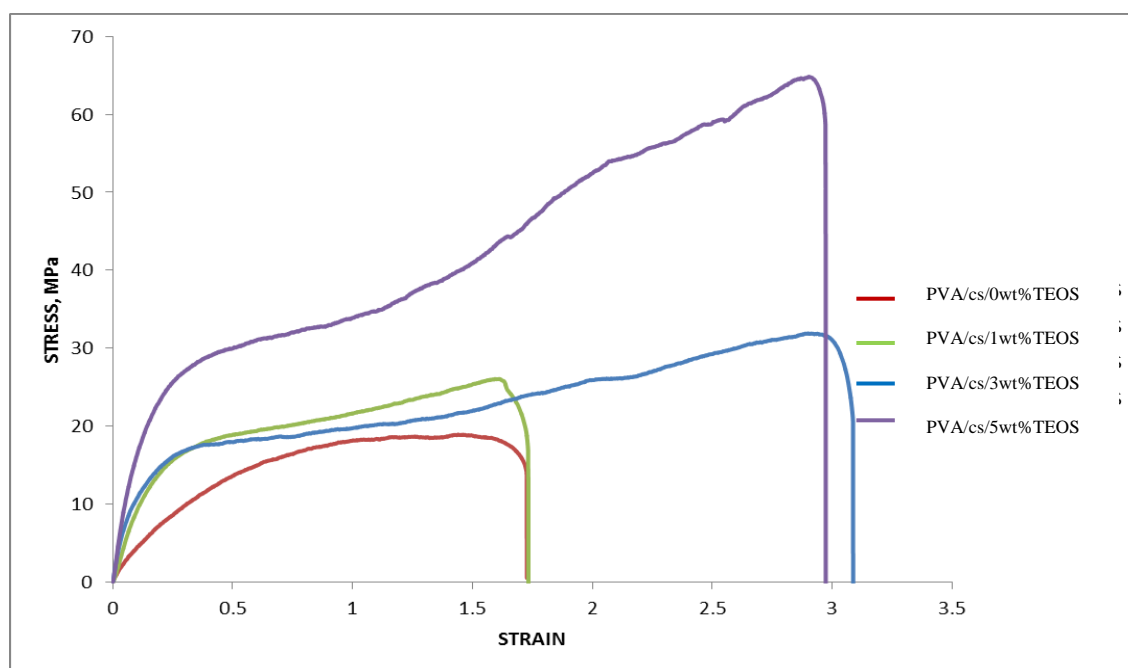
From Table 2, with the presence of humic acid, the membrane incorporated with TEOS (M3) had much lower flux decays (3%) as well as higher flux recovery (76%) as compared to M1 and M2. According to Jio Na et. al (2012), at first stage of filtration, concentration polarization phenomenon is significant as it plays a major role and then gradually it is replaced by the membrane pore blockage resistance and gel resistance. After that, the fouling resistance of membrane will continue to grow higher. Humic acid has properties that can adsorb strongly onto polysulfone (PSF) ultrafiltration membrane surface. This is because humic acid has a high active surface and the hydrophilicity of -COOH and -OH functional groups. Besides that another characteristics of humid acid is the hydrophobicity of central aromatic and fat molecules groups [4][5][15][16]. In a solution, humic acid exists in the shape of loose micellar aggregates which show the characteristics of colloidal particles. Since humic acid can be easily absorbed onto membrane surface and into membrane pores, the hydrophobicity of polysulfone membrane made the interaction of membrane and humic acid increases, resulting in a heavy absorption and flux decline significantly [4]. This will cause the membrane fouling resistances continued to grow higher by turns. Thus, it is proven from the results based on

Figure 1 (a) and (b) that the membrane with absence of humic acid as foulant model had low flux decay towards copper ion solution as well as higher flux recovery rate. However, their recovery rate decreases with interaction of humic acid on membranes but still higher as compared with flux decay. Besides that, the composite membrane (M3) exhibits better anti fouling performance than other membranes even with the presence of humic acid in feed solution. These results can be attributed to the hydrophilicity and long term stability of the membrane. These indicates that the improvement of TFC membrane can effectively counter back the fouling caused by NOM, especially in the case towards copper ion solution. According to Yan Hao et. al (2011), the flux will reduce drastically in the presence of metal ions due to intermolecular bonds production between organic compound and carboxylic acid group from humic acid. Therefore, it is the possible reason for the increase in fouling with the combination of copper ion and humic acid. Although the fouling has been enhanced in this experiment, the rejection copper ion through the membranes is high ( $> 90\%$ ). It was found that the copper ion removal efficiency of the M1, M2 and M3 were not significantly different where more than 90% removal was achieved.



### 3.2. Mechanical Strength of TFC Membrane

The composite membrane should be tough enough to withstand pressure during filtration. Therefore, mechanical properties is an important parameter to identify their stability of the pressure driven membrane [7].



**Figure 2. Stress vs Strain of hybrid membrane with different amount of TEOS Concentration**

As shown in Figure 2, the tensile strength and its elastic modulus increased with the increase in TEOS concentration. In general, TEOS content will improve the mechanical properties of hybrid membrane [18], where more TEOS content in membrane made the membrane becomes more rigid. Thus, it needs more strength to fracture. From the tensile strength result, it also showed that silica nano precursor such as TEOS can disperse uniformly throughout the polymer matrix and it interacts with polymer chain through hydrogen bonding. Thus, the polymer matrix becomes trapped between silica precipitates [19]. The increasing of tensile strength with increasing TEOS content is resulted from the interaction of the hydrogen bond or other bond formed between PVA/CS and TEOS after the sol-gel process. As reported by Xiojuan Lu et. al (2008), the tensile strength of the membrane increases with increasing of TEOS content but excess amount of TEOS content will cause hybrid homogeneity decreases, thus the flexibility or tensile strain will decrease. Based on Figure 2, the tensile strain increases at higher TEOS content from 1wt.% TEOS to 3wt.% TEOS but at 5wt.% TEOS, the strain starts to decrease. This is due to hybrid membrane that has too much TEOS content can cause the film become more rigid and show a decrease in flexibility [17]. Generally, TEOS network restricts the movement of the polymer molecules, which weaken the flexibility of the membrane. As the conclusions, from this study, TFC membrane with hybrid membrane consists of 3wt.% TEOS is sufficient to deal with high pressure during filtration and has good stability. In addition, membrane incorporated with 3wt.% TEOS also strong enough to withstand the transmembrane pressure during filtration and it is no easily broken during the cleaning or backwashing of the membrane.

### 4. Conclusion

The fabricated TFC membrane consists of chitosan/PVA/TEOS as the hybrid layer and polysulfone as the support membrane has the anti-fouling properties even when humic acid is used as a foulant model. It is exhibited through high RFR value which reaches up to 76% while RFD value is as low as 3%, with high percentage removal of copper ion (> 90%). Furthermore, the thin film composites possess good physical flexibility, which makes it potentially being used in the treatment of wastewater containing heavy metal as it could result in good saving in term of operational cost.



## Acknowledgments

The author would like to thank to Ministry of Higher Education (MOHE) and Universiti Teknologi MARA (UiTM) for awarding research grant, RMI/FRGS 5/3 (92/2014) for the financial support to conduct this research.

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