CHAPTER IV

RESULT AND DISCUSSION

4.0 Introduction

In this study, nanofiltration-surfactant (NFS) membranes were prepared through dry/wet phase inversion process. Combination of polymer/solvent/non-solvent/additive/surfactant was the new formulation of polymer solution. Polymer concentration and types of surfactant were used as the parameters investigated throughout the experiment. Sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) were chosen as anionic and cationic surfactant, respectively. In this study, twelve formulation of polymer with different concentrations had been prepared ranging from 17wt% to 21wt% with addition of 5% additive and 2% surfactants. From the prepared formulation, the high membrane performance was determined.

4.1 Effects of Polymer Concentration on Performance of NFS Membrane

4.1.1 Pure Water Permeation (PWP)

Pure water permeation (PWP) and salt rejection are considered to be the key specification factors for any membrane performance characterization. PWP and salt

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4.1 Effects of Polymer Concentration on Performance of NFS Membrane

4.1.1 Pure Water Permeation (PWP)

Pure water permeation (PWP) and salt rejection are considered to be the key specification factors for any membrane performance characterization. PWP and salt rejection have direct relationships with the number of pores and the pore size on the membrane surface.

FIGURE 29: Effect of Polymer Concentration on Pure Water Permeation

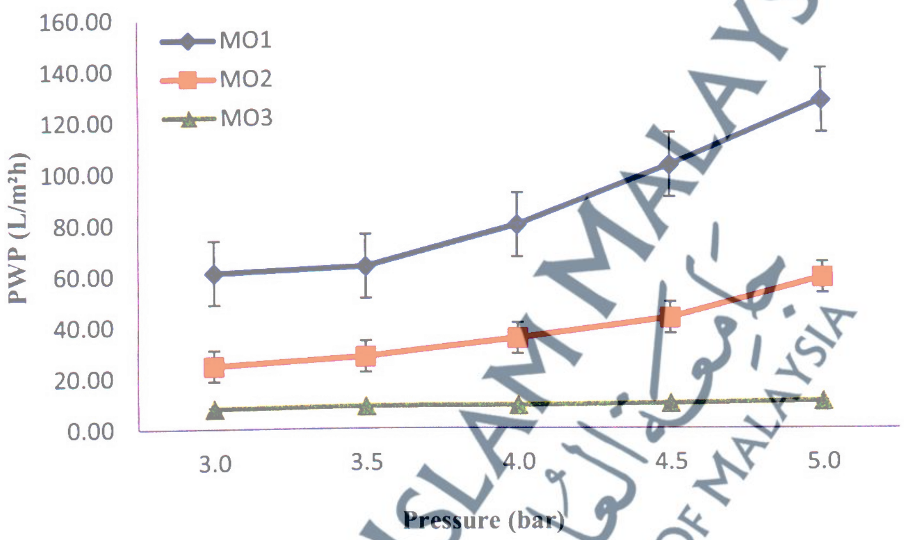


Figure 29 shows pure water permeation (PWP) vs P at different polymer concentration. From MO1 to MO3, the flux increased gradually as operating pressure increased. MO1 showed higher water flux of about 127.36 L/m^{2}h at 5 bar operating pressure while MO3 had the least water flux of about 10.60 L/m^{2}h at the same operating pressure. According to Ismail and Hassan (2006), as a polymer concentration increased, the water flux was decreased result during preparation of the dope formulation where turbidimetric titration method was used to find the equilibrium state of the polymer and commonly used technique to measure the good formulation of dope solution. Thus, membrane preparation was depending on the thermodynamically based on non-solvent during turbidimetric titration method (Ismail & Hassan, 2006).

4.1.2 Salt Rejection

I. NaCl

FIGURE 30: Effect of Polymer Concentration on NaCl Permeation Flux and Rejection

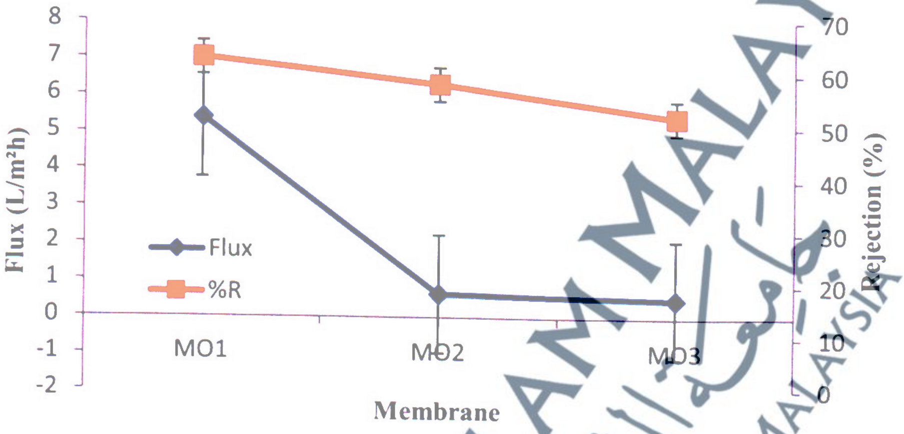


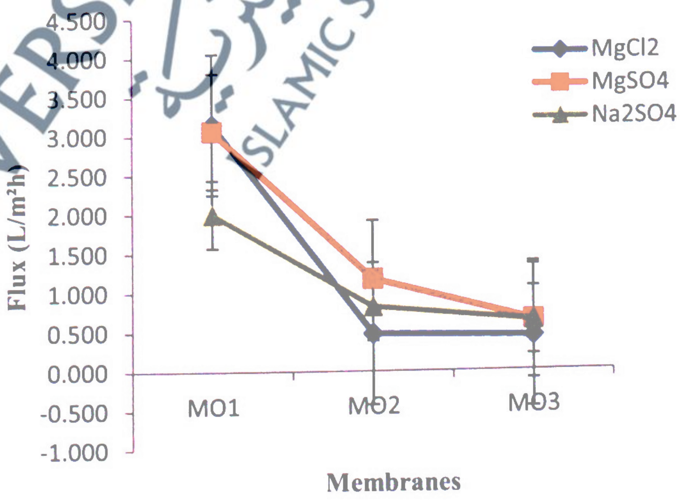
Figure 30 shows as polymer concentration increase, the permeation flux will decrease as well as rejection of NaCl. At 5.3792 L/m²h, MO1 shows the highest flux and give rejection of about 63%. MO3 with the highest polymer concentration gives permeation flux of about 0.5082 L/m²h and rejection of NaCl only up to 52%. NaCl permeation flux decreases when polymer concentration increases due to the lower in concentration polarization where NaCl molecules were retained on the membrane surface.

Moreover, higher polymer concentration will produce thicker membrane surface than lower polymer concentration that the permeation flux of NaCl decreased. Feed pressure, cross flow velocity and feed composition would become the key factors that affect the value of permeation flux and it is important parameters to determine the permeation flux for membrane performances (Koyuncu and Topacik, 2003). Besides, study has been made to prove that decreasing of NaCl rejection by the membrane might influence by electrostatic interaction of ions in aqueous solution and the charge of the membrane (He et al., 2009).

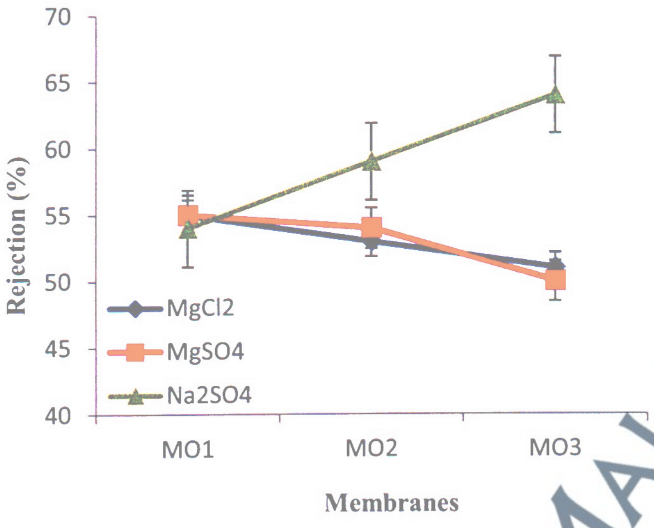
II. Multivalent Salt Rejection

This subtopic highlights on permeation flux and rejection of three types multivalent salt solutions. For each salt, 0.01M concentration had been used for testing with different polymer concentrations. Figure 31 (a) and (b) shows the plot of flux and rejection versus polymer concentration of three types of multivalent salt solutions. MO1 at 3.145 L/m²h, $MgCl_2$ with the lowest polymer concentration possess the highest rejection of about 55%. Mohammad et al. (2007) in their research found that divalent positive cation such as Mg^{2+} was estimated to have lower rejection against negatively charged membrane, which is in good agreement with the present study (Mohammad et al., 2007).

FIGURE 31: (a) Permeation Flux of Multivalent Salt; (b) Rejection of Multivalent Salt Solutions



(a)



(b)

$MgCl_2$ permeate flux and rejection also showed that as polymer concentration increase, both permeate flux and rejection would decrease. The lowest $MgCl_2$ rejection of about 51% was achieved for the highest polymer concentration. Besides, the data revealed promising results in terms of permeation flux that for membrane without additive and surfactant where $MgSO_4$ gives 55% of rejection at 3.057 L/m²h of permeate flux. The similar trend was obtained when polymer concentration was increased, permeate flux and rejection of $MgSO_4$ would decrease. Whereas, Na_2SO_4 showed different results where it gives higher rejection of about 64% when polymer concentration was increased.

There is researcher studied on the behaviour of the negatively charged nanofiltration membrane, the rejection of Na_2SO_4 should increase due to the content of monovalent ions (Na^+) and divalent co-ions (SO_4^{2-}) that would affect the permeate flux and rejection of salt solutions (Mohammad et al., 2007). Na_2SO_4 shows that rejection increases up to 64% while permeate flux decreases from 1.999 L/m²h to 0.628 L/m²h when polymer concentration increases.

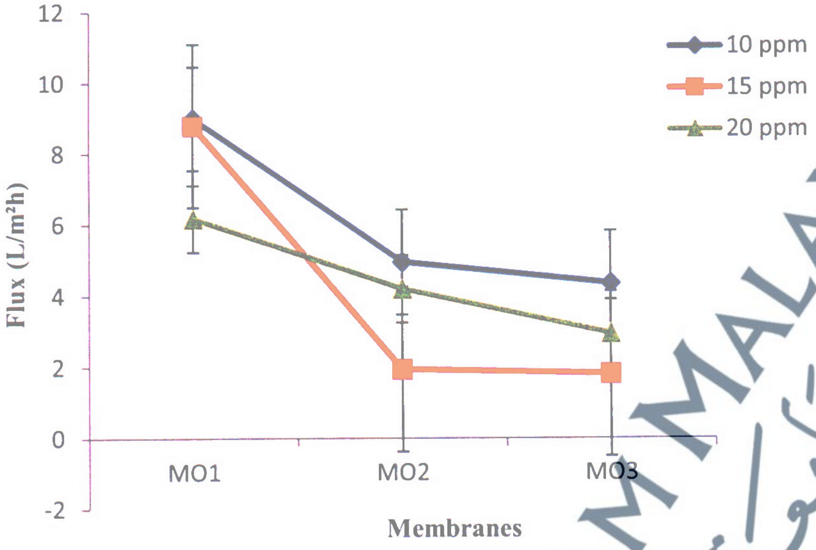
4.1.3 Dyes

(A) Methyl Violet Dye

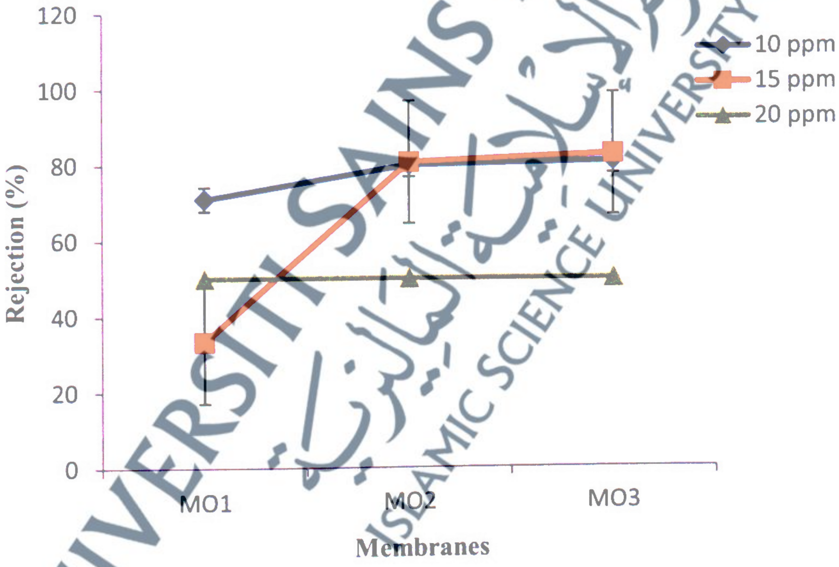
Figure 36 shows the effect of polymer concentration on permeate flux and rejection of methyl violet at three different dye concentrations. Dye solution of 10ppm shows highest flux among other concentrations. However, the permeate flux decreased from 8.9901 L/m²h to 4.3245 L/m²h as polymer concentration increase. The rejection of 10ppm methyl violet shows that as polymer concentration increase, the rejection will also increase from 71% to 81%.

At 8.7864 L/m²h, MO1 can reject only 33.3% of dye pigment for 15ppm of methyl violet. Since polymer concentration also plays an important role in this study, the color rejection of methyl violet increase sharply to 82.9%. As dye concentration increase, the permeate flux decreased to 2.9318 L/m²h. However, at 20ppm of Methyl violet, MO1 to MO3 resulted on the same rejection of about 50%. This finding provides evidence that in nanofilration membrane process, concentration of polymer plays an important role to determine the performance of the prepared membranes. Research has proven that, higher concentration of feed lead to the higher osmotic pressure and lower the permeate flux (Akbari et al., 2002). As can be seen in Figure 32, permeate flux is always higher at lower polymer concentration and decreased gradually when polymer concentration as well as methyl violet concentration were increased.

FIGURE 32: (a) Permeation Flux; (b) Percentage of Rejection of Methyl Violet Dye



(a)



(b)

(B) Methyl Blue Dye

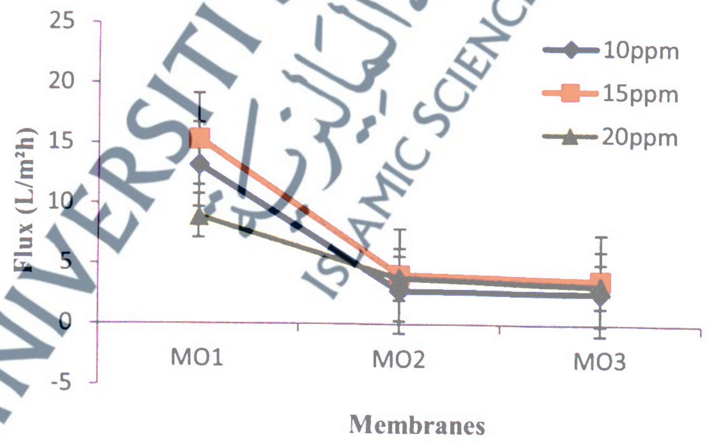
Besides Methyl violet, another dye which is methyl blue was used tested under 4 bar operating pressure. Figure 33 shows experimental data of permeate flux and removal of methyl blue using nanofiltration membrane at different polymer concentration. The highest permeate flux were obtained from the lowest polymer concentration at the lowest dye concentration. At 13.1886 L/m^{2}h, MO1 can remove dye of about 98.3% at 10ppm of methyl blue concentration. The results shows that the permeate flux gradually decrease as polymer concentration increase until 2.5969 L/m^{2}h for MO3 and increase the rejection up to 98.7% for the same dye concentration.

Research has been made to show that concentration of feed solutions is other parameter that affects the membrane performance (Akbari et al., 2002). At 15ppm of dye concentration, the permeate flux shows the same results where the flux decrease when polymer concentration increase from 15.3193 L/m^{2}h to 3.6984 L/m^{2}h. Other than that, the rejection on 15ppm dye concentration increasing up to 99.1% for MO3. This finding indicates that, efficiency of nanofiltration membrane was proven to remove dye effectively. Membrane performance in terms of permeation flux and rejection of 20ppm dye that affects the membrane performance.

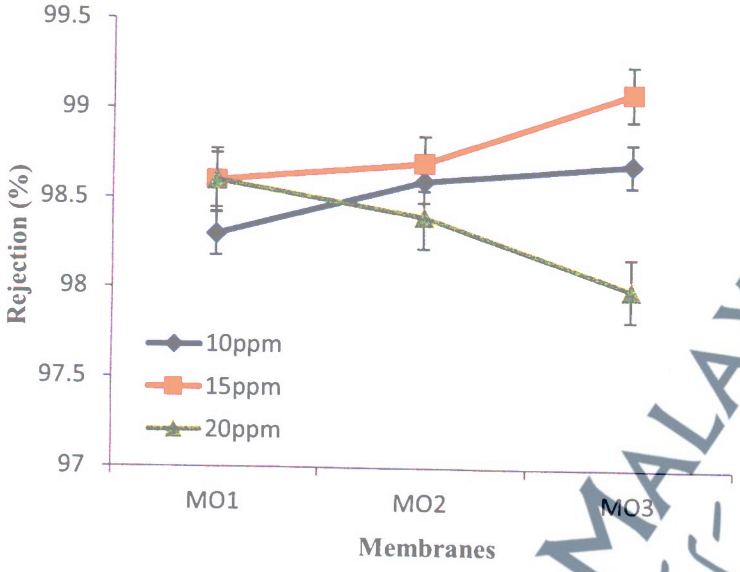
At 15ppm of dye concentration, the permeate flux shows the same results where the flux decrease when polymer concentration increase from 15.3193 L/m^{2}h to 3.6984 L/m^{2}h. Other than that, the rejection on 15ppm dye concentration increasing up to 99.1% for MO3. This finding indicates that, efficiency of nanofiltration membrane was proven remove dye effectively. Membrane performance in terms of permeation flux and rejection of 20ppm dye concentration keep decreasing. MO3 with highest polymer concentration in the formulation shows 3.1958 L/m²h of permeation flux and 98% rejection.

Mo and co-workers in their research found that separation of dyes through membrane process using commercial membranes gives rejection of dyes almost 100% where the complete separation of dyes from dye solution occurred. However, different kind of dyes will give different results on permeates flux, depending on chemical and physical properties of dye used. Moreover, they also found the critical factors that affecting the flux of the membrane which are the molecular size and the shape of the dyes considering the properties of the dyes (Mo et al., 2008). Since the experimental gives rejection up to 99.1%, indicate that, the experimental data on dye rejection using tailor-made membrane was comparable with commercial membrane.

FIGURE 33: (a) Permeation Flux; (b) Percentage Rejection of Methyl Blue Dye



(a)



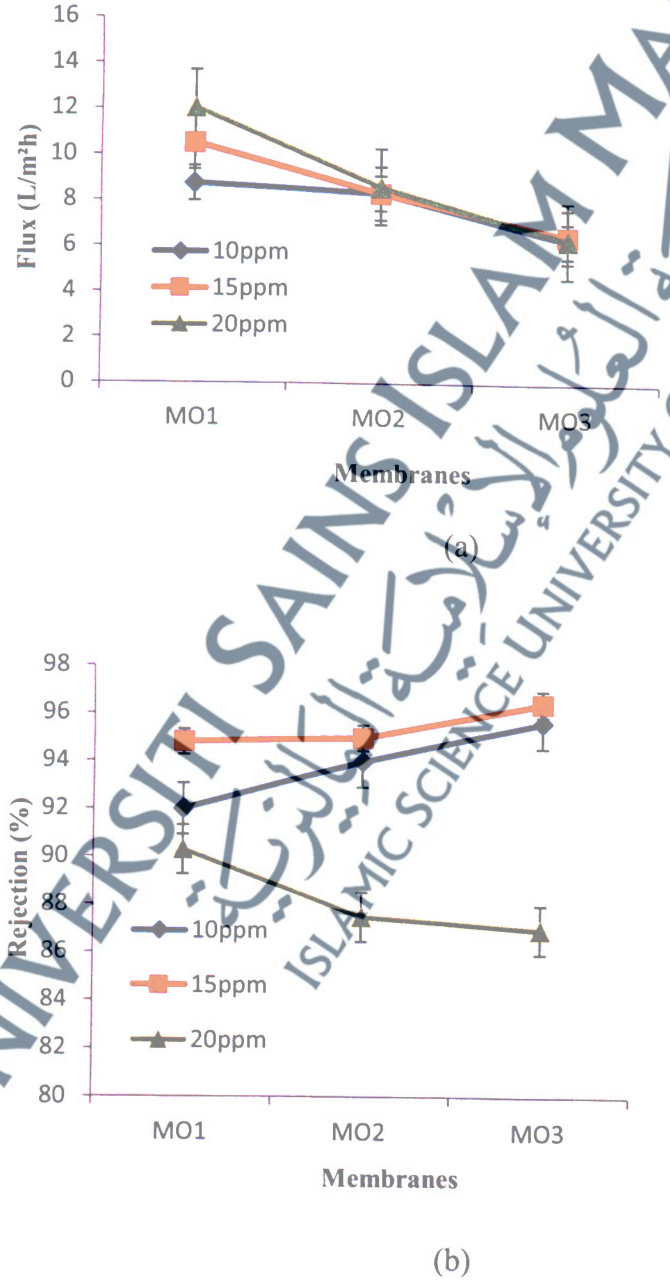
(b)

(C) Acid Orange Dye

In order to complete the experimental data, Acid orange was tested to see the further membrane performance and operates under 4 bar operating pressure. Figure 38 presents the results of permeation flux and percentage rejection of Acid orange respectively. For 10ppm dye concentration, at 8.7539 L/m^{2}h, MO1 gives rejection of about 92%. As polymer concentration increase, the permeation fluxes keep decreasing to 6.2924 L/m^{2}h and rejection increasing up to 95.7%. The same trending happens with 15ppm of dye concentration, where the highest polymer concentration, MO3 gives the lowest permeation flux of about 6.4873 L/m^{2}h and gives rejection of 96.5%.

At 20ppm of dye concentration, the permeation fluxes keep decreasing as polymer concentration increase from 12.0452 L/m^{2}h to 6.3077 L/m^{2}h. However, the rejection is decreasing as polymer concentration increase. At high polymer concentration, MO3 gives only 87% of dye rejection. This indicates that the high concentration of acid orange will decrease the percentage of rejection due to the denser polymer. Other than that, membrane performances properties also will be affected by structure of the prepared membranes itself by changed of number of pores, substructure layer and finger-like channel.

FIGURE 34: (a) Permeate Flux; (b) Percentage Rejection of Acid Orange Dye



4.2 Effect of Addition of PEG Additive on PES Membrane Performance

4.2.1 Pure Water Permeation

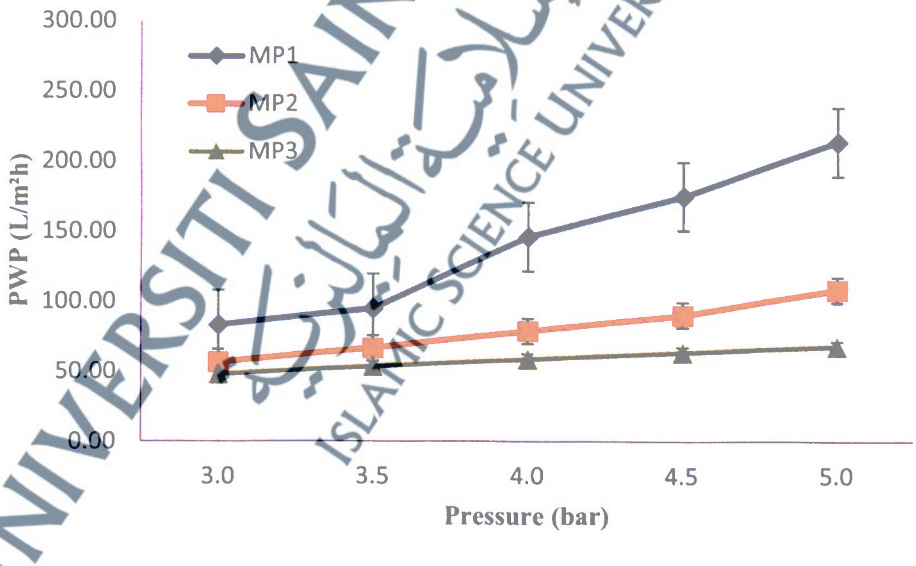
Figure 35 shows pure water permeation result for membrane with addition of PEG 600. In order to study the influence of additive on the nanofiltration performance, different polymer concentrations has been prepared and were tested at five operating pressures. Different pressure might give different performance of water flux for each polymer concentration.

In Figure 35, the graph illustrates the pure water permeation (PWP) of three different polymer concentration of nanofiltration containing PEG 600 as additive. The results show the increasing of PWP as pressure applied increase. However, an addition of PEG600 in high polymer concentration decreased the PWP. Highest PWP obtained by MP1 of about 214.72 L/m^{2}h at 5 bar operating pressure. While, the lowest PWP obtained is from MP3 of about 48.20 L/m^{2}h at the least operating pressure. Many researchers found that addition of additive in the polymer solution is one of the factors that influence the membrane performance. This might due to addition of additive would change the structures of the prepared membrane.

Besides, addition of PEG will influence the formation of pores in the membranes that leads to the permeability of the membrane (Chakrabarty et al., 2008). As polymer concentration increase from MP1 to MP3, the PWP gradually decrease from 214.72 L/m^{2}h to 68.19 L/m^{2}h at the highest operating pressure which is 5 bar. Unlike membrane without additives, PEG 600 has been proves as better pore former than other additives. Other than that, addition of PEG 600 in the polymer solution might increase the hydrophilicity and resulted to the changes of performance of nanofiltration membranes (Arthanareeswaran et al., 2010).

In this study, MP3 with higher polymer concentration shows the lowest PWP. However, PWP increase as pressure applied increase from 48.20 L/m^{2}h to 68.19 L/m^{2}h. According to Ahmad et al. (2005) in their research, they have studied different polymer concentration and obtained the average PWP decreased as polymer concentration increase and increasing the polymer concentration is said to lead to the increasing of polymer solution viscosity (Ahmad et al., 2005). Likewise, addition of PEG 600 in the polymer solution has improved the viscosity of the membrane and increases the membrane performances.

FIGURE 35: Water Flux of Polymer Concentration with PEG 600



4.2.2 Flux and Salt Rejection

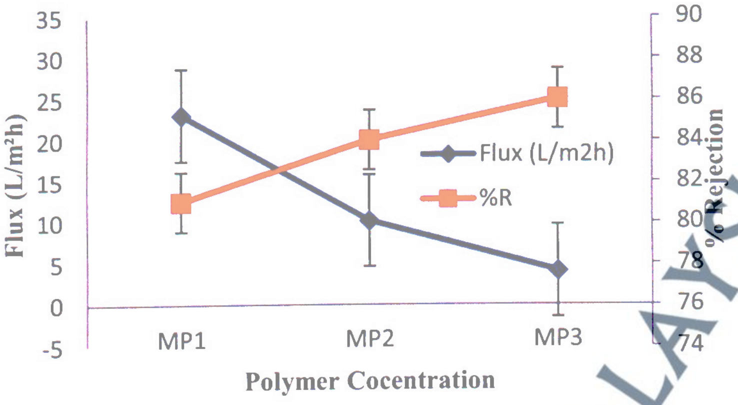
I. NaCl Rejection

Using a simple dead-end permeation cell, the membrane performance which is described in terms of flux and salt rejection was tested under operating pressure of 4 bars. The permeation experiment was performed using 0.01M NaCl solutions.

The experimental data based on Figure 36 shows the membrane flux decreased as polymer concentration increased with addition of PEG 600. The decreasing of membranes fluxes resulted in increasing of NaCl rejection. MP1 with the least polymer concentration shows high flux of 23.095 L/m^{2}h and gives high rejection of NaCl of about 81%. This indicates that, addition of PEG 600 to MP1 membrane is more porous in terms of number of pore.

Besides, study had been done shows that the addition of PEG 600 in the polymer solution ease the transportation with the solvent in the separation process that leads to homogenous skin layer and high rejection (Ma et al., 2011). Unlike MP1, MP3 with the highest polymer concentration shows different results where it has the lowest flux of 4.067 L/m^{2}h and have rejection almost 86%. This shows that MP3 with 21% of polymer concentration has a dense membrane surface layer although with the presence of PEG 600 as pore former. Furthermore, Ma et al. (2011) in their studies found that addition of PEG 600 has increase the polymer lean phase of the surface layer and leads to the membranes with more pores and high rejection (Ma et al., 2011).

FIGURE 36: Fluxes and Salt Rejection vs. Polymer Concentration



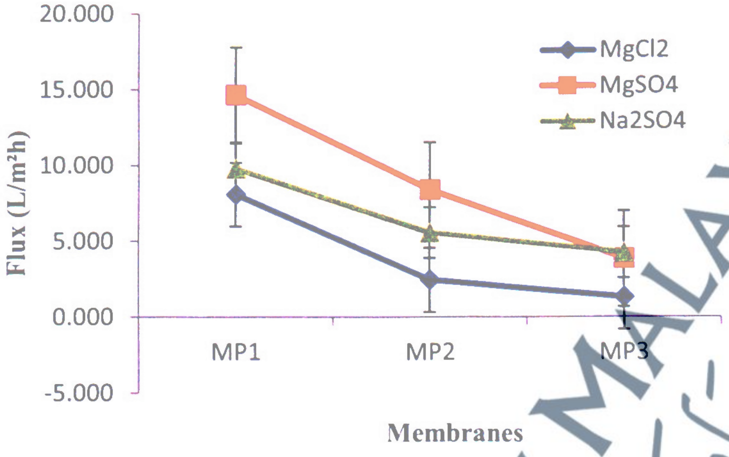
II. Multivalent Salts ($MgCl_2$, $MgSO_4$, Na_2SO_4)

Figure 37(a) shows the results from the permeation flux of each salts tested with different polymer concentration containing PEG 600 as additive. It has been said that, addition of PEG as additive in polymer solution will increased the permeation flux while decreased the solute rejection. However, experimental data for each multivalent salts faces decreasing of permeation flux as polymer concentration increase. At 8.094 L/m^2h, $MgCl_2$ gives rejection of about 58% for membrane MP1. The permeation fluxes decreased when polymer concentration increase to MP3 of about 1.298 L/m^2h and rejection increase sharply up to 92%. Chakrabarty et al. (2008) in their study proves that addition of PEG600 at higher polymer concentration influence the formation of pores on the membrane surface that affects the permeability of the membrane. Thus, membrane with addition of PEG600 had increased the $MgCl_2$ rejection.

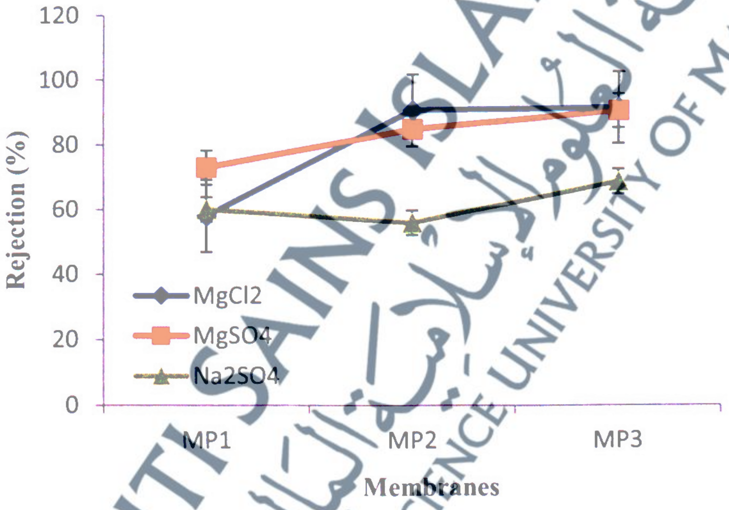
For $MgSO_4$, MP1 shows highest permeation flux of about 14.679 L/m^2h and rejection of about 73%. The same trending happens with $MgCl_2$ where the permeation fluxes of $MgSO_4$ decrease as polymer concentration increase and leads to increasing of salt rejection. High retention of $MgSO_4$ was obtained by high polymer concentration, MP3 of about 91%. Researcher found that positive cations like Mg^{2+} would expect to lower the salt rejection. However, with addition of small percentage PEG 600, it has been proven that the increasing of $MgSO_4$ rejections. Experimental data also shows that, the permeation flux of Na_2SO_4 decreased as polymer concentration increased.

At 9.786 L/m^2h, MP1 gives only 60% of salt rejection. The permeation flux of Na_2SO_4 decreased as polymer concentration increase to 4.225 L/m^2h and increases the rejection to 71%. This is in line with some studies that revealed the negatively charged nanofiltration membrane will make rejection of Na_2SO_4 increase due the interaction of ions on the membrane surface that affects the permeation flux as well as Na_2SO_4 rejections (Mohammad et al., 2007). Zhu et al. (2007) suggested in their study that, PEG will increased the hydrophilicity and lead to the changes in the performance of nanofiltration membrane and solute retention when it is entrapped by the membrane materials. Moreover, they also found that, addition of PEG600 in the polymer solution and were tested for few hour shows that the PWP decreased.

FIGURE 37: (a) Permeation Flux; (b) Percentage Rejection of Different Polymer Concentration



(a)



(b)

4.2.3 Flux and Dyes Rejection

(A) Methyl Violet Dye

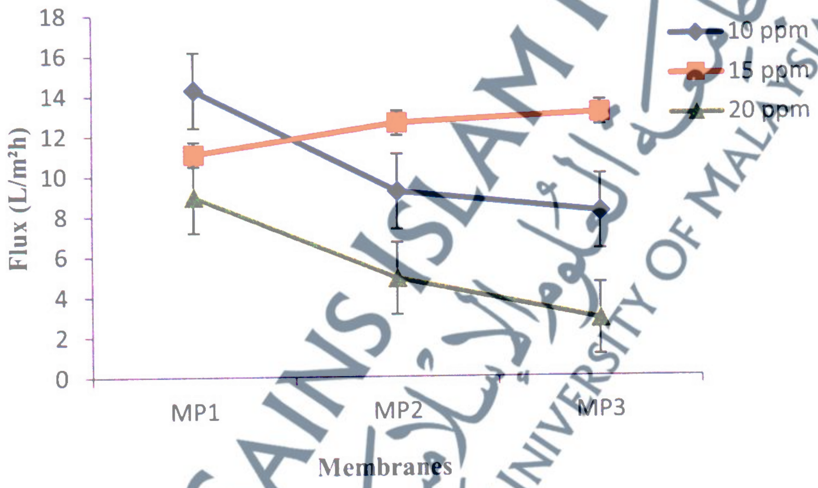
For further study on performance of nanofiltration membrane with addition of additives, methyl violet was used for tested. Using the simple dead-end permeation cell, three different dye concentrations was used. Figure 40 shows the permeation flux and percentage of rejection of methyl violet respectively. From the permeation flux results, we can see that the decreasing of flux for 10ppm and 20ppm dye concentration.

Since 10ppm methyl violet is the lowest dye concentration, it often shows results of higher permeation flux proportionate others dye concentrations of about 14.3149 L/m^{2}h at the lower polymer concentration. The rejection shows only 56% of methyl violet can reject by MP1. As polymer concentration increase, the permeation flux of 10ppm Methyl violet decrease to 8.2376 L/m^{2}h and rejection gradually increase until 70%. According to Jung et al. (2004) said that the thickness of top layer of the membrane also plays an important role in membrane filtration process. As polymer concentration increase, the thickness of membranes top layer might be increase. Thus, it will result to decreasing of permeation flux due to dependency on the top layer resistance during the transportation process (Jung et al., 2004).

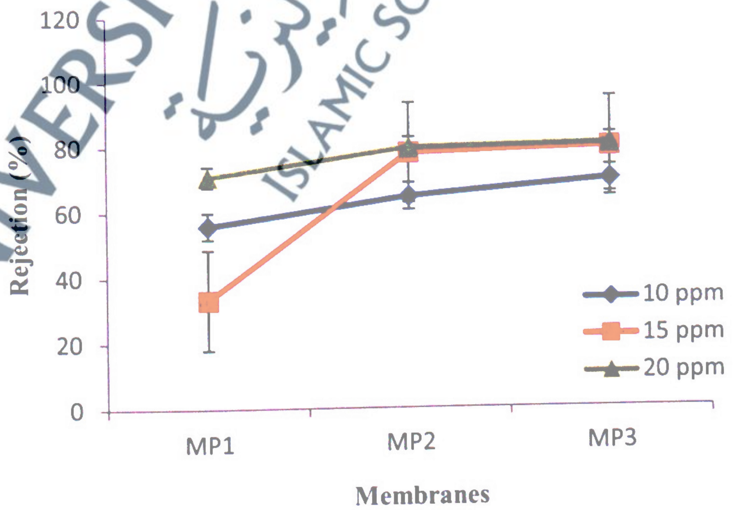
The result on methyl violet testing would be different for 15ppm dye concentration where the permeation flux increases as well as rejection. This is due to the changes on membrane structures that lead to the high permeation flux and high rejection of methyl violet. MP1 was observed to have 11.1223 L/m^{2}h of permeation flux and have low rejection of about 33.3%. Since the feed concentration was part of the parameters occur in this study, this could be concluded that, 15ppm dye concentration more concentrated than 10ppm. However, the rejection at 15ppm dye concentration increases sharply up to 80% when polymer concentration increases.

The same trending shows by 20ppm methyl violet concentration. When polymer concentration increase, the permeation flux of 20ppm methyl violet decrease from 8.9901 L/m^{2}h to 2.8852 L/m^{2}h and rejection was increase from 71% to 81%. Increasing of 10% in rejection of methyl might be significance from increasing of polymer concentration and addition of PEG 600 that has been said by many researchers to be as pore former (Ma et al., 2011; Arthanareeswaran et al., 2010).

FIGURE 38: (a) Permeation Flux; (b) Percentage Rejection of Methyl Violet Dye



(a)



(b)

(B) Methyl Blue Dye

Addition of PEG 600 as additive in polymer solution will be studied in terms of permeation flux as well as rejection of methyl blue. Three different dye concentrations have been used for three different polymer concentrations. This is because to observe the effects of both polymer concentration also dye concentration in removing Methyl blue effectively in presence of PEG 600. The results below presented the experimental data that have been done in terms of permeation flux and percentage rejection of methyl blue and methyl blue seems can reject almost 100% of dye content.

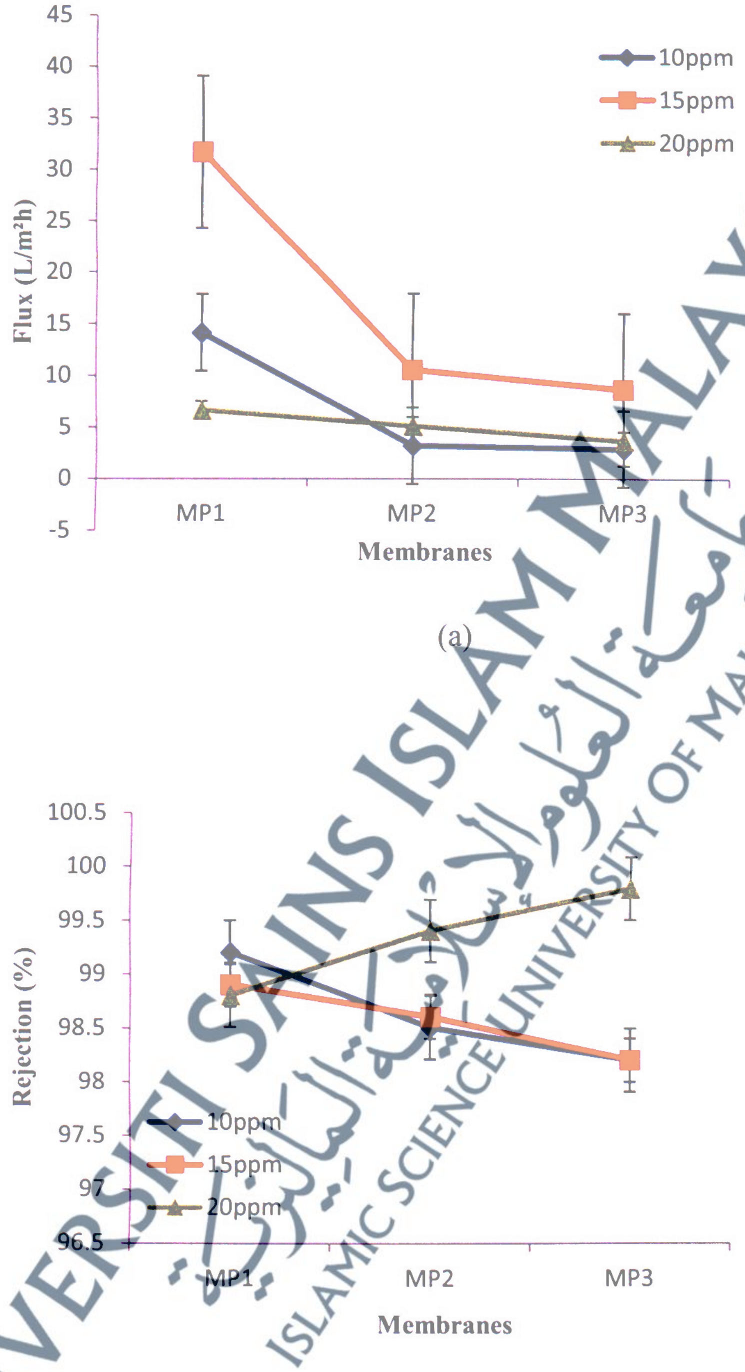
At 14.1820 L/m^{2}h, 10ppm of methyl blue rejects almost 99.2% of dye contents. MP1 shows the highest rejection of dye due to the role of lower dye concentration and polymer concentration. Addition of additive is said to be one of major factors to get an optimal membrane structures where improve the membrane performances. Number of pores and surface roughness also influence the membrane performances (Chakrabarty et al., 2008).

As dye concentration increase, permeation flux of MP1 drop to 6.6619 L/m^{2}h. However, there is no significance decreasing in rejection where 20ppm rejects almost 98.8%. Various research has been done conclude that trans-membrane pressure is factors that affects the decline of permeation flux and leads to increasing of rejection where pressure applied will influence the transportation of solute across membrane. Researcher also study that reducing of fluxes is due to the effect of concentration polarization that caused the retainers of solutes on the membrane surface. Due to this phenomenon, it causes the high rejection of methyl blue (Petrinić et al., 2007). And, addition of PEG 600 assists in transportation of solute through the membrane. Moreover, experimental also revealed that, as polymer concentration increase, the permeation flux will decrease.

As described in subtopic 4.1 where polymer concentration also important factors in this study which cause the thicker membrane surface. From MP1 to MP3, the permeation flux of 15ppm dye concentration decrease from 31.7234 L/m^{2}h to 8.6432 L/m^{2}h. Rejection of 15ppm dye concentration also showed a decrease about 0.7% from 98.9% to 98.2%. This shows that, when polymer concentration increases, the percentage rejection not much has changed. With addition of additive, MP2 shows increasing of permeation flux for 20ppm dye concentration from 3.791 L/m^{2}h to 5.114 L/m^{2}h. This revealed that, the efficiency of pore forming additives in changing the membrane properties. In addition, PEG 600 is well known as better pore former than other additives where it will increase the hydrophilicity and improve the membrane performances (Arthanareeswaran et al., 2010).

Furthermore, experimental data in Figure 39 shows that, at 20ppm dye concentration, the permeate flux was decreased to 3.6501 L/m^{2}h. Akbari and co-workers in their studies discover that concentration play an important aspects in nanofiltration membrane. Theoretically, when concentration is higher, it will increase the osmotic pressure resulting to decreasing of permeate flux and increase the rejection (Akbari et al., 2002). Likewise, at 20ppm dye concentration, rejection of Methyl blue keep increasing up to 99.8% which indicate the complete separation of dye compounds from dye solutions.

FIGURE 39: (a) Permeation Flux; (b) Percentage Rejection of Methyl Blue Dye



(a)

(b)

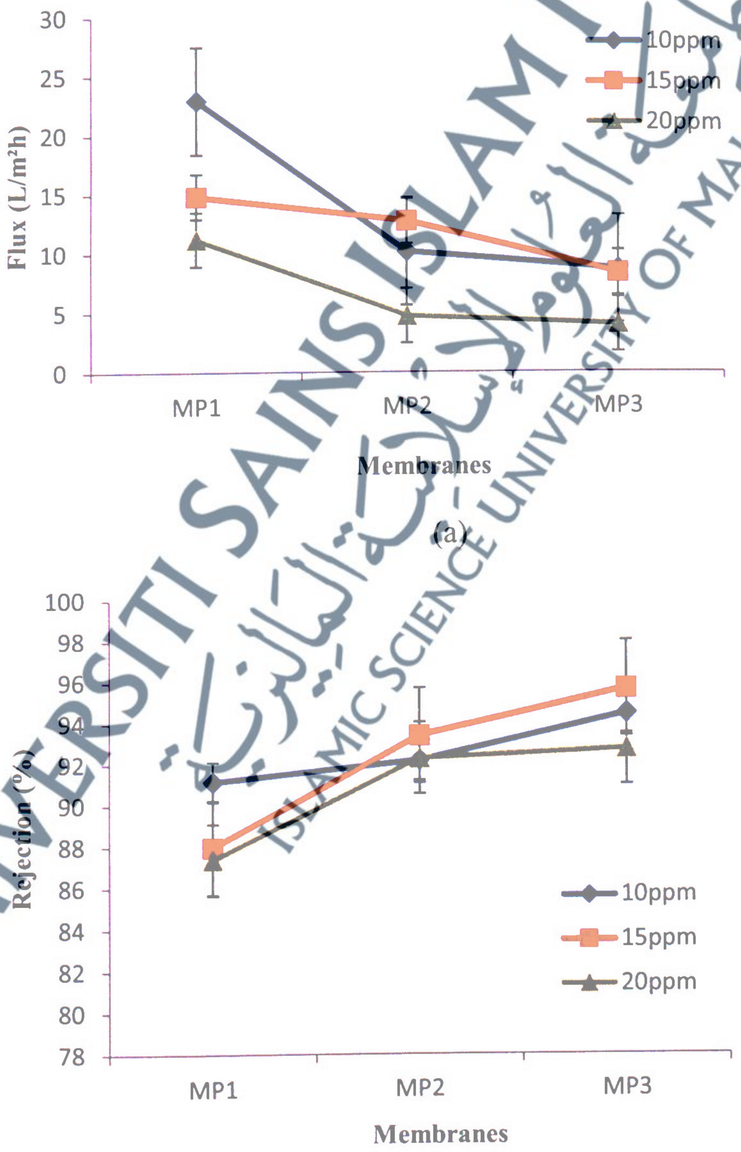
(C) Acid Orange Dye

According to Lopes et al. (2005), in filtration system, permeate flux is the most important parameters to evaluate the membrane performance. Other than that, author claims that permeate flux if part of fundamental factor for optimization process (Lopes et al., 2005). Figure 40 (a) and (b) illustrated the permeate flux and percentage rejection of acid orange respectively. From overall figure, we can see that the permeate flux of acid orange decrease while rejection increase as polymer concentration increase. At 22.9721 L/m^{2}h, MP1 at 10ppm dye concentration gives rejection of about 91.2%.

As polymer concentration increase, the rejection increase up to 94.5% while permeate flux decreased to 8.6461 L/m^{2}h. This might due to the increasing of polymer concentration that cause the polymer solution more viscous and make the membrane surface thicker. Although PEG 600 was said to be pore former, membrane surface also part of the important role that affects the membrane performance. Moreover, as dye concentration increases, acid orange showed a decrease of permeate flux as well as rejection. MP3 shows permeate flux of about 3.9776 L/m^{2}h and rejection of about 92.8%. This indicates that, more solutes were retains at the surface of the membrane since 20ppm is higher dye concentration. Besides, this phenomenon might due to the concentration polarization and osmotic pressure that leads to fouling on the membrane surface and cause the decreasing of permeate flux and increasing in dye rejection (Petrinić et al., 2007).

Aouni and co-workers has studied that the causes of decline permeate flux of dyes solution. Authors claim that dye molecule can be absorbed on the membrane surface and affects the permeate flux due to interaction of physicochemical between dye molecule and membrane surface. Other than that, they have studied several factors contribute to the decreasing of permeate flux of dye solutions such as type of solute and solute concentration (Aouni et al., 2012). Thus, the study proven that using high concentration of acid orange will resulted to decreasing of permeate flux and increase the rejection up to 95.7% .

FIGURE 40: (a) Permeate Flux; (b) Percentage Rejection of Acid Orange Dye



(a)

(b)

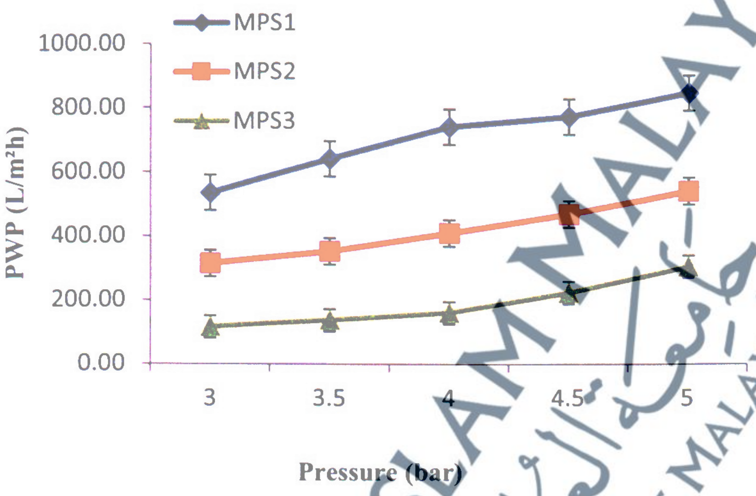
4.3 Effect of Anionic Surfactant on Membrane Performance

4.3.1 Pure Water Permeation

As can be seen on the result, the PWP increase gradually similar with other membrane that had been discussed before. Addition of SDS had enhanced more the PWP of nanofiltration membrane and improves the membrane performance. Other than that, addition of SDS was said to increase the porosity of the membrane. At 3 bar operating pressure, MPS1 gives PWP value of about 535.70 L/m^{2}h. And the value increase gradually as operating pressure increase up to 851.85 L/m^{2}h. Since MPS1 was the least polymer concentration, it happens to have high PWP than other polymer concentration. Least polymer concentration will give least membrane thickness and lead to high PWP (Ismail and Hassan, 2007). As polymer concentration increase, PWP will decrease.

As can be seen on the Figure 41, at the same operating MPS1 decreased from 535.70 L/m^{2}h to 116.51 L/m^{2}h. The same trending happens with another polymer concentration for each operating pressure where PWP decreased as polymer concentration increase. MPS3 with high polymer concentration has lowest PWP of about 309.30 L/m^{2}h at 5 bar operating pressure. Huang et al. (2014) in their studies stated that PWP will increase linearly as operating pressure increase. In their study also found that operating pressure becomes factor that affect the membrane performance. Authors found that operating pressure applied helps on effective driving force between membrane surfaces that overcome the resistance and lead to high PWP (Huang et al., 2014). Increasing of PWP value as pressure applied increase also might due to the increase on concentration polarization with helps from SDS as anionic surfactant that improve the membrane performance on PWP (Fernández et al., 2005).

FIGURE 41: Pure Water Permeation (PWP) of Membrane with Anionic Surfactant



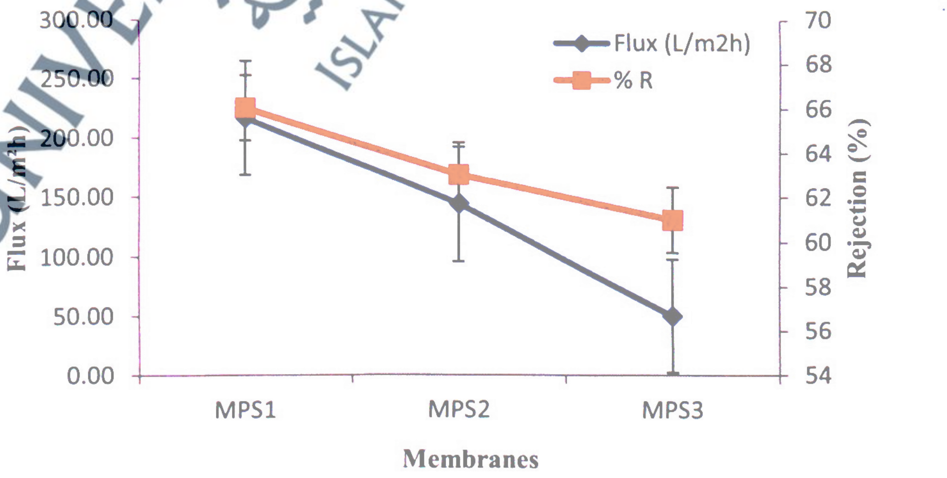
4.3.2 NaCl Salt Rejection

The performance of asymmetric nanofiltration membrane was characterized in terms of fluxes and percentage of rejection. For monovalent salt performance, 0.01M of NaCl was used as feed to apply on nanofiltration-surfactant (NFS) membrane using anionic surfactant. The results were showed that as polymer concentration increase, both permeate flux and rejection decreases.

Addition of SDS as anionic surfactant was found to increase the permeate flux of solutes. This revealed by MPS1 where it obtain high permeate flux of about 216.5127 L/m^{2}h and rejection of 66%. As polymer concentration increase to MPS3, the permeate flux of NaCl decrease to 50.4496 L/m^{2}h and rejection of about 61%. Researchers found when polymer concentration increases, it will increase the thickness of membrane surface that results increasing of salt rejection. Reducing on membrane pores also become the important parameters that increase the salt rejection. Other than that, addition of SDS shows to decrease the permeation flux as polymer concentration increase to MPS3. In this state, polymer concentration was found to be the important parameter where SDS influences the membrane structure (Ismail and Hassan, 2006).

However, in this study, SDS was used as the strongest anionic surfactant. Studies had been done revealed that addition of small amount of surfactant in polymer solution causes the changes in membrane morphology and structures. In addition, charges possess by surfactant either positive or negative charges might cause slightly changes on membrane surface (Rahimpour et al., 2007). As polymer concentration increase, it was observed that both permeation flux and rejection of NaCl decreases. This was explained that polymer concentration affects the membrane performance. Moreover, high polymer concentration will have high viscosity and changes the thickness of membrane surface as well as pore radius.

FIGURE 42: Flux vs. Rejection of Nanofiltration-Surfactant (NFS) Membrane



4.3.3 Multivalent Salt ($MgCl_2$, $MgSO_4$, Na_2SO_4) Rejection

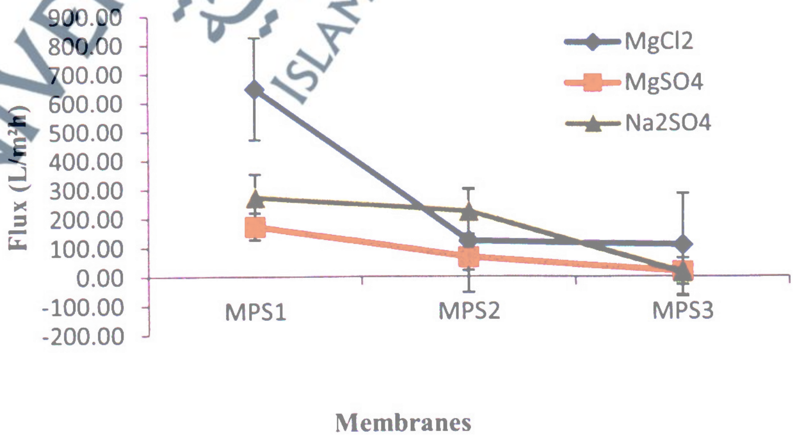
In membrane process, permeate flux was the important parameter in the design and economic analysis. This flux was affected by feed pressure, temperature and feed composition. In this subtopic, 0.01M of each multivalent salt solution was tested prior to membrane testing under 4 bar operating pressure.

$MgCl_2$ from MPS1 membrane gives the highest rejection among other salt solution of about 649.538 L/m^{2}h and rejection of 30%. However, the permeate flux decreased when polymer concentration increase to 110.560 L/m^{2}h for MPS3 and rejection increase gradually up to 68%. The result presented for $MgCl_2$ proves that, addition of SDS improve the membrane permeability by increasing the salt rejection while decrease the permeate flux. Ismail and Hassan (2006) found that increasing of salt rejection also resulted from the increasing of polymer concentration that lead to the increase of pore size fraction which smaller than electrolyte sized. Thus, it contributes to the increasing of salt rejection.

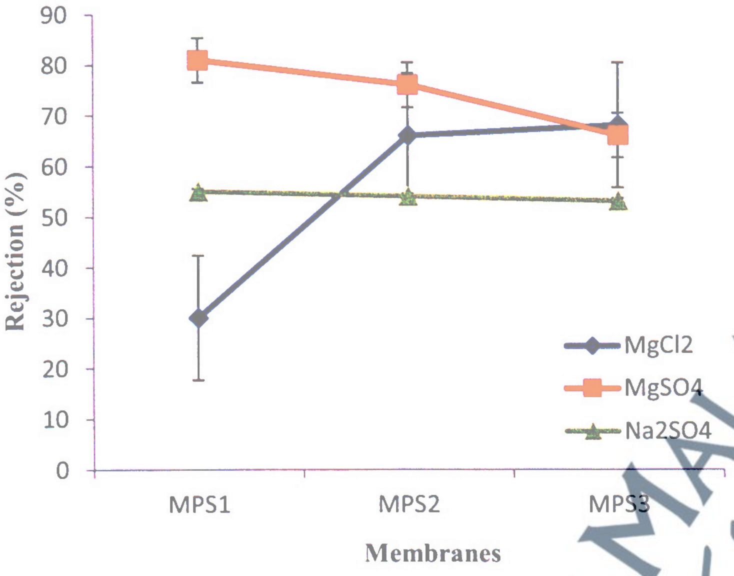
As presented on Figure 43, $MgSO_4$ shows the permeate flux decrease dramatically from 173.210 L/m^{2}h to 18.169 L/m^{2}h and gives decreasing of rejection as well from 81% to 66%. This result might be due to the positive charge of Mg^{2+} was expected to decrease the salt rejection since prepared NFS membrane possessed negative charges. At lower polymer concentration, MPS1 of Na_2SO_4 give permeate flux of about 225.926 L/m2h. The variation of membrane flux and rejection were according to polymer concentration as the main parameters in the study and addition of surfactant was said to improve the membrane performance. Increase in polymer concentration of prepared membranes results in membrane with lesser flux (Gohil and Ray, 2009). In addition, increasing the polymer concentration to MPS3, the permeate flux shows decreasing of about 16.188 L/m^{2}h. Increasing of polymer concentration has led to increasing of polymer solution viscosity and changes the thickness of membrane surface.

Ghaemi and co-workers found in their study that, addition of small amount SDS in the polymer solution produces thinner top-layer and more porous sub-layer. Thus, it will create a layer of SDS molecules on the membrane surface. Moreover, SDS was found to decrease the interaction between polymer chains when both of them form a complex of polymer-surfactant complex (Ghaemi et al., 2012). This evidence was in line with the experimental data where membrane with SDS has high permeation flux at lower polymer concentration. Besides, percentage rejection of Na_2SO_4 however decreased. This might due to the Na^{2+} molecules was smaller than the pore size of the membrane.

FIGURE 43: (a) Permeation Flux; (b) Percentage Rejection of Multivalent Salts Solution



(a)



(b)

4.3.4 Dyes Rejection

Further study has been done to show the effect of anionic surfactant in polymer solution. PWP results revealed that addition of anionic surfactant improves the membrane permeability by raising the PWP up to 851.85 L/m^{2}h at 5 bar operating pressure. In addition, NFS membrane shows decreasing of both permeate flux and rejection on NaCl salt solutions. This might due effect from increasing of polymer concentration. Multivalent salt solutions show the same result by using NFS membrane. In treating dyes wastewater, there was no exactly evidence the use of NFS membrane for removal of dyes. Thus, in study the effect of anionic surfactant on dyes removal, three types of colors was used with three different feed concentrations (10ppm, 15ppm, 20ppm). Prior to the testing, the same dead-end permeation cell was used at has been operated under 4 bar operating pressure.

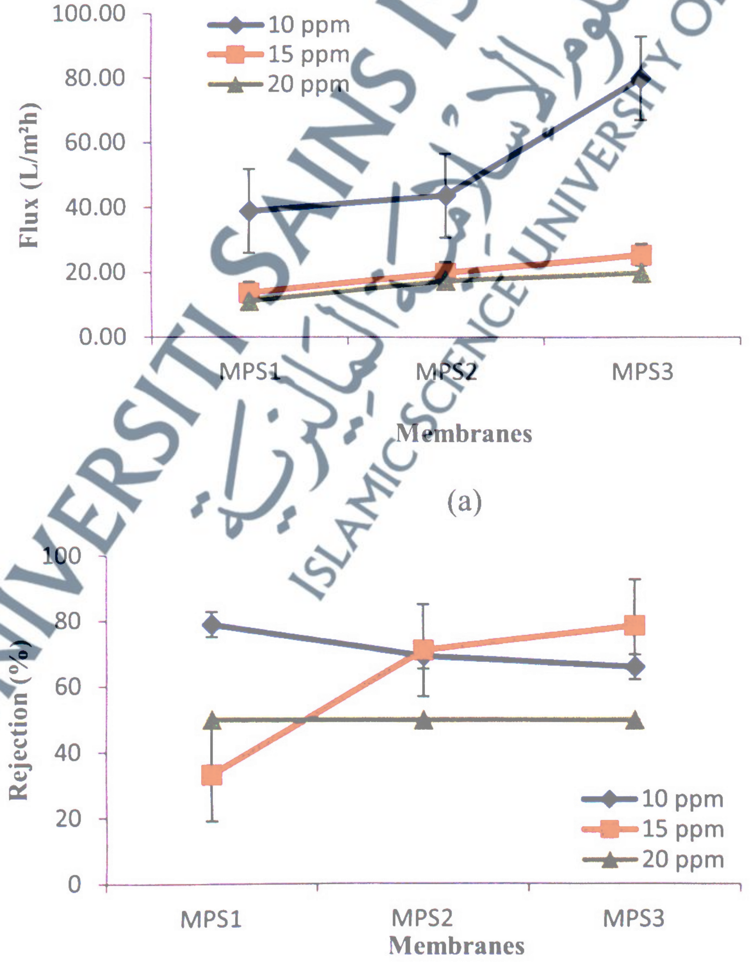
(A) Methyl Violet Dye

Figure 44 (a) and (b) shows permeation flux and percentage rejection of methyl violet that have molecular weight of 407.99 g/mol. Addition of SDS surfactant in polymer solution has increase the permeate flux of methyl violet up to 79.6979 L/m^{2}h for MPS3 and gives rejection of about 66.2% at 10ppm dye concentration. As dye concentration increase, the permeation flux seems to decrease to 19.8636 L/m^{2}h for MPS3 at 20ppm of dye concentration. Huang et al., (2014) study the effect of dye concentration on membrane performance. They observed that, feed concentration influence the membrane performance and become the parameters in experimental design.

The dye retention rate and permeate flux will change in the course of concentration and when feed dye concentration increases the permeate flux of MPS1will decreased from 38.8364 L/m^{2}h to 11.0843 L/m^{2}h. This is due to the increasing of osmotic pressure and amount of dye adsorption on membrane surface. Researcher also founds that increasing of feed dye concentration on membrane surface causes shielding effects to occur by the anions in the solution that lead increasing of permeate flux. Shielding effects cause due to the blocking of dye molecules on the membrane surface and different charges of both dye molecule and membrane itself (Yu et al., 2012). Other than that, experimental data also shows that when polymer concentration increase, the permeate flux also increase. At 15ppm dye concentration, permeate flux of methyl violet increase from 13.7760 L/m^{2}h to 25.3974 Lm^{2}h from MPS1 to MPS3 respectively. This might due to the increasing of polymer concentration will produce denser membrane and increase the membrane thickness.

Moreover, at the same dye concentration, the rejection of methyl violet increase from 33.3% to 79% as polymer concentration increases. This shows that, as polymer concentration increase, the membrane thickness will increase that causes in the high rejection. However, for 20ppm dye concentration, the membrane resultant of the same percentage rejection of about 50%. This might due to related with membrane structure and feed concentration since 20ppm is the higher dye concentration in the study. Other than that, 50% of rejection gives by MPS3 for three different concentrations might due to the composition of dyes itself which is almost 90% of methyl violet content.

FIGURE 44: (a) Permeation Flux; (b) Percentage Rejection of Methyl violet Dye



(a)

(b)

(B) Methyl Blue Dye

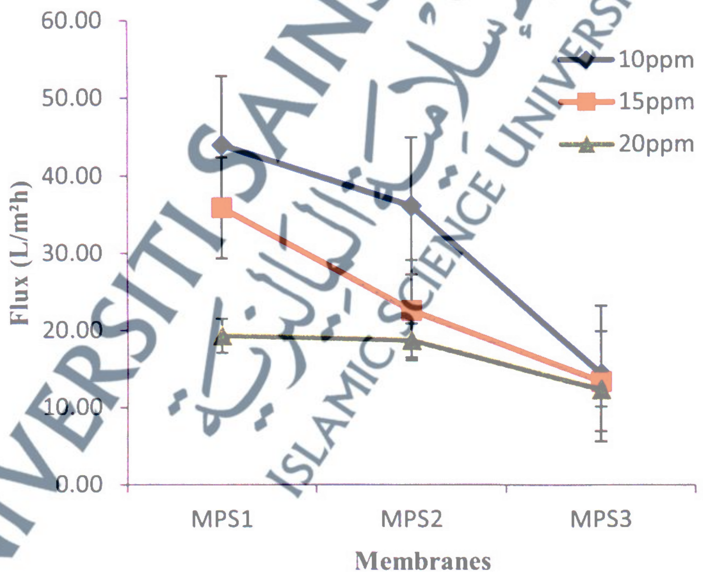
The permeation flux and percentage of rejection using anionic dyes (methyl blue) at three different feed concentrations were presented on Figure 45 as below. From Figure 49, the permeation flux of methyl blue decrease as polymer concentration increase as well as feed concentration increase. At 10ppm dye concentration, the permeation flux decreased from 43.9620 L/m^{2}h to 14.4905 L/m^{2}h from MPS1 to MPS3 respectively.

Experimental data also shows that, the percentage rejection of methyl blue for 10ppm dye concentration increase as polymer concentration increase from 98.3% to 99.2%. This can be explained by the effects of steric hindrance and electrostatic action that influence the rejection characteristic of the nanofiltration membrane charged to solute charged. Moreover, dye with high molecular weight or have high negative charge will be more capably rejected by the negatively charged membrane. In this study, methyl blue used as one of anionic dyes has molecular weight of 799.81g/mol.

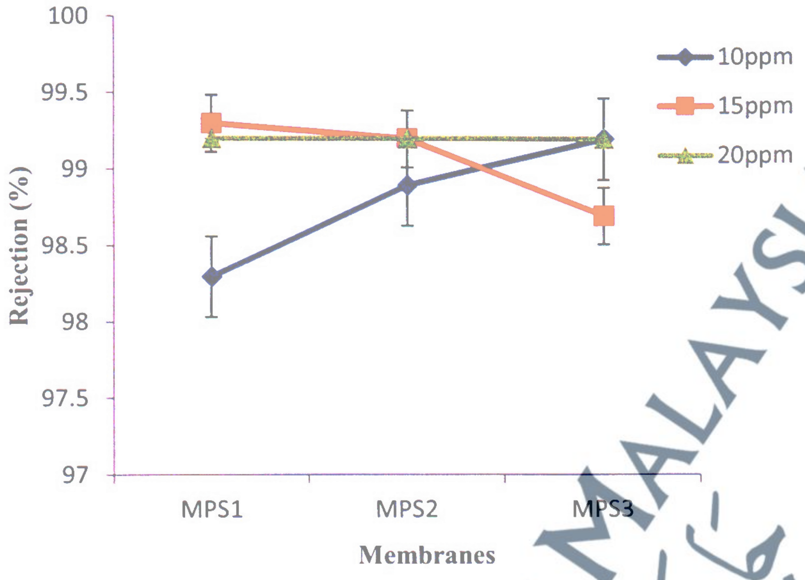
Some researchers investigated that, operating pressure also affects the membrane performance where, increasing of operating pressure will lead to increase of permeation flux (Yu et al. 2012). However, in this study, 4 bar was the optimum operating pressure for NFS membrane performance testing as NFS membrane could stand at low pressure and had been tested in PWP experiment. The same trending happens for 15ppm and 20ppm dye concentration where the permeation flux decreases as polymer concentration increase.

Moreover, MPS1 also shows decreasing of permeation flux from 43.9620 L/m^{2}h to 19.3603 L/m^{2}h when feed concentration increase. While, the rejection also increase from 10ppm to 20ppm of dye concentration. Decreasing of permeate flux of methyl blue might be due to involvement of organic and inorganic solutes that can be retained at the membrane surface and causing concentration polarization. Other than that, it can be said that dye molecules that adsorbed on the membrane surface will influence the permeate flux and physicochemical interactions between dyes molecule and membrane surface. Furthermore, the nature of membrane material itself, the type of solute, the solute concentration and cross flow velocity could be parameters to determine the adsorption of dye retention (Aouni et al., 2012).

FIGURE 45: (a) Permeation Flux; (b) % Rejection of Methyl Blue Dye



(a)



(b)

(C) Acid Orange Dye

Simple dead-end filtration cell was set up. Tested with three dyes concentration, NFS membrane will undergo the permeation test that conducted under 4 bar operating pressure. Figure 46 shows permeation flux and rejection of acid orange respectively. It clearly shows that, for MPS3, when the dye concentration increase from 10ppm to 20ppm, the permeation flux decrease from 16.54874 L/m^{2}h to 12.93901 L/m^{2}h and rejection also decreased from 93.9 % to 91%. This can be explaining due to the blockage of the membrane pores and occurring of membrane fouling on the membrane surface.

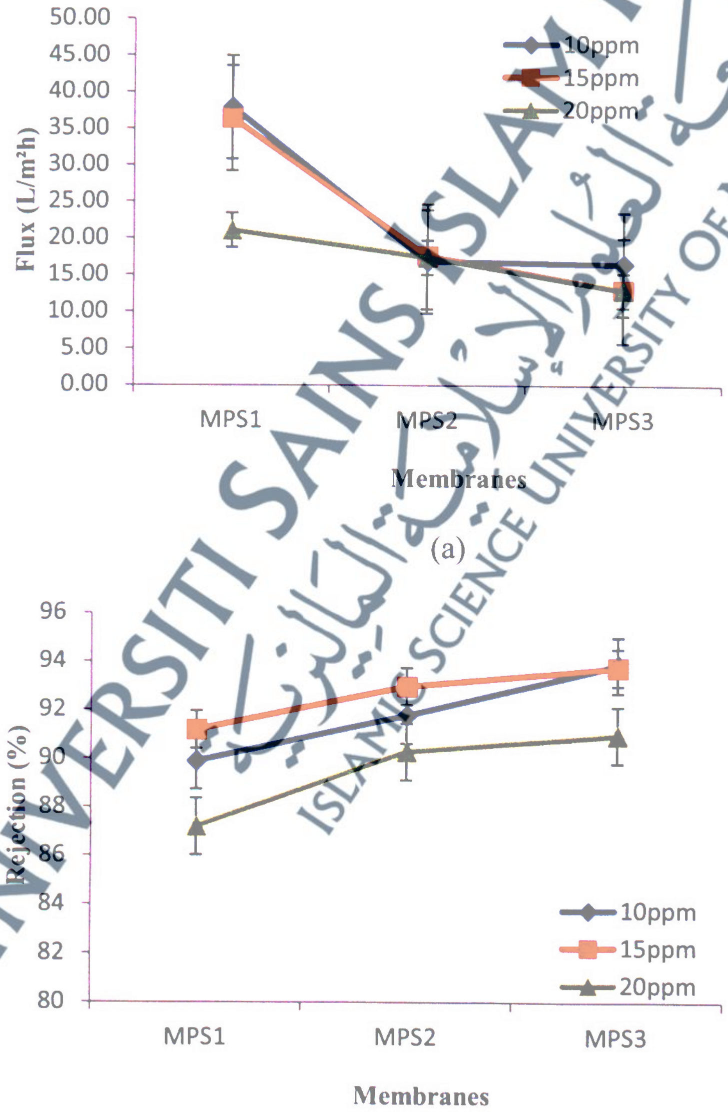
At 10ppm dye concentration, the permeation flux also decreases from 37.92923 L/m^{2}h to 16.54874 L/m^{2}h as polymer concentration increase. In this state, polymer concentration also plays important parameters that affect the permeation flux performance of NFS membrane. This is due to the increasing of polymer concentration would produces membrane with thicker surface with average of less pores formed on the surface. Increasing of dye concentration will lead to more adsorption of dye molecules on the membrane surface.

Besides, concentration polarization has become the factors for decreasing of permeation fluxes where the dyes molecules were retained on the membrane surface and formed the accumulation of particles on the membrane surface (Petrinić et al., 2007).

In nanofiltration membrane separation, concentration plays a significant role where higher concentration will causes high osmotic pressure and consequently lower the permeate flux (Akbari et al., 2002). As can be seen in Figure 50, at 15ppm dye concentration, permeation flux of acid orange greatly decreased from 36.4397 L/m^{2}h to 12.9326 L/m^{2}h and the highest permeate flux always shows by lower concentration which is 10ppm of about 37.9292 L/m^{2}h for MPS1 polymer concentration. For 15ppm dye concentration shows increasing of color rejection up to 93.8% as polymer concentration increase. One interesting point found by Mo et al. in their research that the separation of dyes by the membrane is almost 100%, indicating the complete separation of dye compounds from dye solution. In their research using NF PA composite membrane, they achieved the rejection almost 99.5%. This shows that, tailor-made NFS membrane could give the comparable result with NF PA composite membrane used by the researcher (Mo et al., 2008). Thus, it can be conclude that, addition of SDS as anionic surfactant in polymer concentration has increase the membrane performance.

Moreover, solute rejections also can be influenced by several parameters for example, membrane pore size, the size of the solute and the solute-membrane charge interactions (Wei et al., 2013). Although SDS is cheap and readily available, it will produce more porous of membrane substructure that sometimes leads to the less operational membrane because anionic surfactant gives less interaction between dyes molecule and NFS membrane surface.

FIGURE 46: (a) Permeation Flux; (b) % Rejection of Acid Orange Dye



(a)

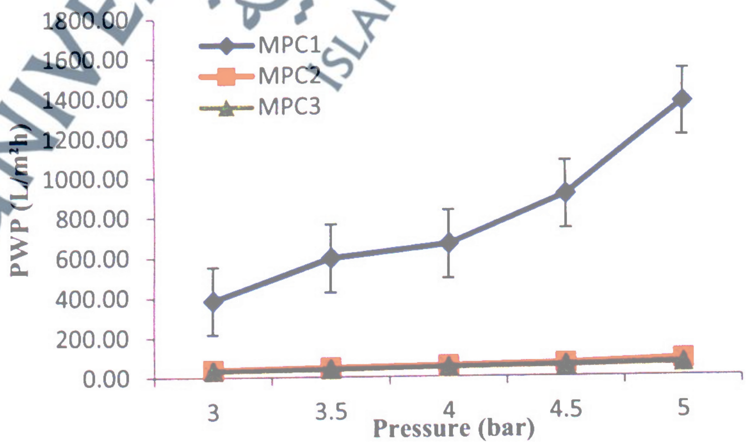
(b)

4.4 Effect of Cationic Surfactant on Nanofiltration Membrane Performance

4.4.1 Pure Water Permeation (PWP)

Figure 47 illustrate that the addition of small amount CTAB in the casting solution increased the PWP as pressure increase. This was observed that CTAB will increase the porosity of membrane support layer and results in higher PWP. Other researcher also stated that the addition of CTAB in the casting solution result in an increase in the PWP. Some researcher also reported that CTAB will increase the membrane porosity on the membrane support layer resulted in higher PWP (Rahimpour et al., 2007; Mulijani et al., 2010). Moreover, the experimental result also shows that MPC1 always give higher PWP as pressure applied increase. However, as polymer concentration increase to MPC3, PWP shows greatly decreased. This is due to the fact that, increasing the polymer concentration in the casting solution resultant to high polymer concentration on the membrane surface. Thus, the volume fraction of polymer will increase and give impacts to lower membrane porosity (Tsai et al., 2000).

FIGURE 47: Pure Water Permeation (PWP) of NFS Membrane with CTAB



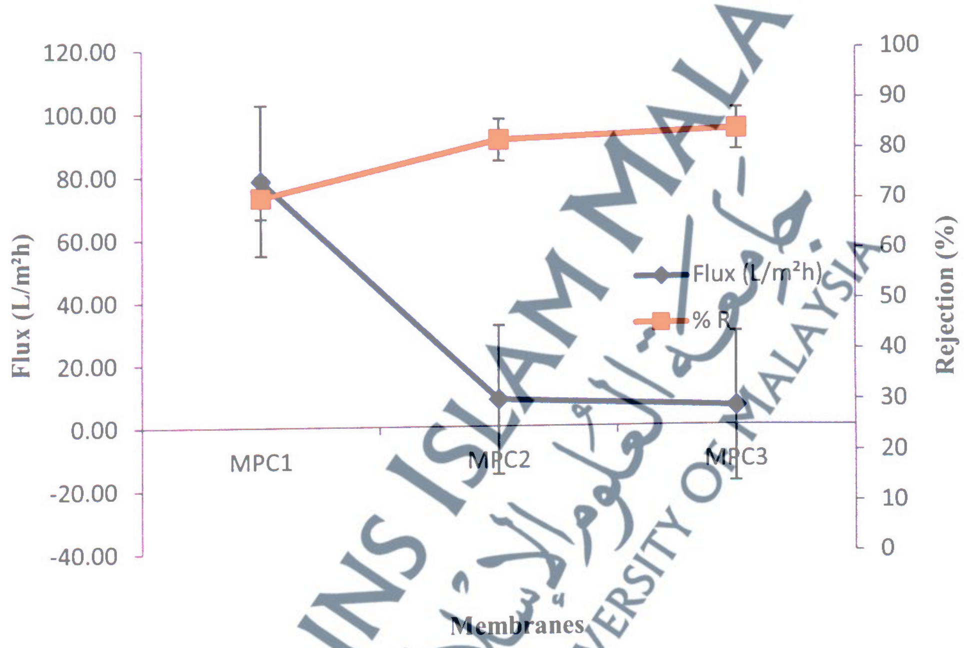
4.4.2 NaCl Salt Rejection

The results show permeation flux decline sharply as polymer concentration increase from 78.7319 L/m^{2}h to 5.9728 L/m^{2}h from MPC1 to MPC3 respectively. This indicates that MPC1 with low polymer concentration produces less dense top layer of membrane so that the transportation is efficiently occur. Ismail and Hassan has stated in their study that as a polymer concentration increase the flux was decreased and resultant the increasing of salt rejection.

Furthermore, when polymer concentration increases, the membrane thickness also increased which causes the increasing of salt rejection. This was in line with experimental data shows increasing of NaCl rejection from 71% to 84% as polymer concentration increase from MPC1 to MPC3. Addition of CTAB in polymer solution indicates that the NFS membrane could retain the NaCl salt solutions up to 84%. Increasing of polymer solution was found to cause the reduction of membrane pores that increase the salt rejection (Ismail and Hassan, 2006). Mansourpanah et al., observed that decline of permeation flux in salt solution is due to the complex formation between polymer and surfactant with opposite ionic charges.

In addition, authors also found that the interaction between surfactant and polymers influence the permeation flux as well as rejection of salt solutions (Mansourpanah et al., 2009). MPC3 show the lowest permeation flux and highest NaCl rejection of about 5.9728 L/m^{2}h and 84% respectively. Normally, in nanofiltration the retention of the ionic species leads to presence of osmotic pressure across the membrane. It can be said that, when polymer concentration increase, the osmotic pressure could be increase. Research has been done to show that presence of osmotic pressure causes permeation flux decline due to reducing of driving force across the membrane (Petrinić et al., 2007).

FIGURE 48: Permeation vs Rejection of NaCl Salt Solution



4.4.3 Multivalent Salt Solution Testing

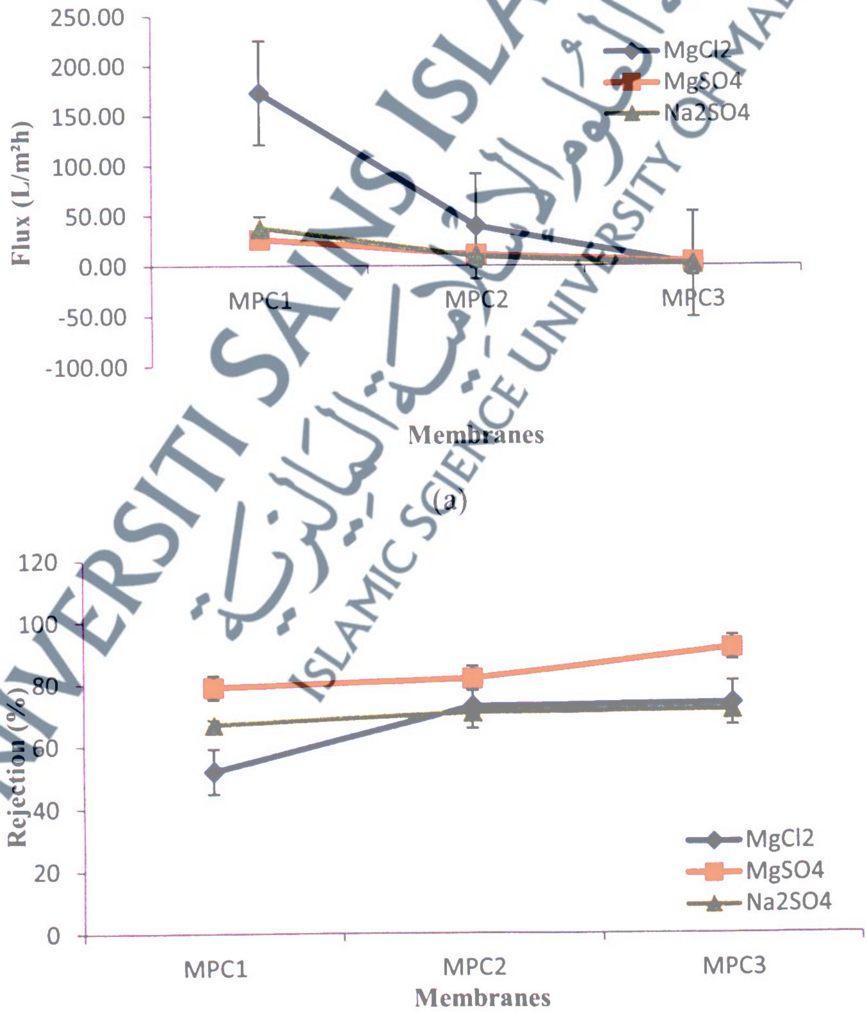
Study has been done shows that addition of CTAB in casting solution will increase the salty solution rejection. Based on the Figure 49, all three types of multivalent salt shows increasing in rejection as polymer concentration from MPC1 to MPC3. Highest permeation flux occurs at MPC1 for $MgCl_2$ of about 173.210 L/m^{2}h. However, the permeation flux shows greatly decrease to 0.967 L/m^{2}h from MPC1 to MPC3. This shows that, polymer concentration give greatly impacts on NFS membrane performance. Increasing of polymer solution would produce denser membrane top layer and changes the membrane support layer. Effect of polymer concentration on membrane performance has been study by Ismail and Hassan where in their study observed that polymer concentration become the important part in study the membrane performance.

Authors in their study found that, increasing of polymer concentration will affects the increasing of pore size which is smaller than the electrolyte size. This situation leads to increase in percentage of rejection which was in good agreement with the results of the present day (Ismail and Hassan, 2006). Increasing in rejection of $MgCl_2$ as polymer concentration increased revealed that addition of cationic surfactant with the presence of PEG 600 in polymer solution influence the formation of pores in the membrane support layer that affects the permeability which are related to pores on the membrane surface (Chakrabarty et al., 2008).

Addition of small amount of cationic surfactant was believed to enhance the $MgCl_2$ salt solution due to the slight decrease in permeation flux of the membrane (Mansourpanah et al., 2009). The same trending shows by $MgSO_4$ and Na_2SO_4 salt solutions where the permeation flux decrease as polymer concentration increase from 14.679 L/m^2h to 3.815 L/m^2h and from 9.786 L/m^2h to 4.225 L/m^2h respectively. The rejection of $MgSO_4$ and Na_2SO_4 also shows same trend of increasing in rejection as polymer concentration increase. The highest rejection was found from $MgSO_4$ for MPC3 of about 92%. This can be explained that MPC3 has less pores on the membrane surface so that it could retain high number of $MgSO_4$ molecules on the membrane surface. Researcher found that positive cations like Mg^{2+} would expect to lower the salt rejection.

However, with addition of small percentage CTAB and helps of PEG 600, it has been proven that the increasing of $MgSO_4$ rejections (Mohammad et al., 2007). The present finding also supported researcher study which concluded that transport mechanism in polymeric membrane is well known as critical factor to ensure that the membrane is practically use in the separation processes (Ismail and Hassan, 2006). Other than that, researcher also stated that the concept of nanofiltration process in separation of ionic species that result to osmotic pressure which cause the permeation flux decrease thereby increasing the salt rejection (Petrinić et al., 2007).

FIGURE 49: (a) Permeation Flux; (b) % Rejection of Multivalent Salt Solution



(a)

(b)

4.4.4 Dyes Rejection

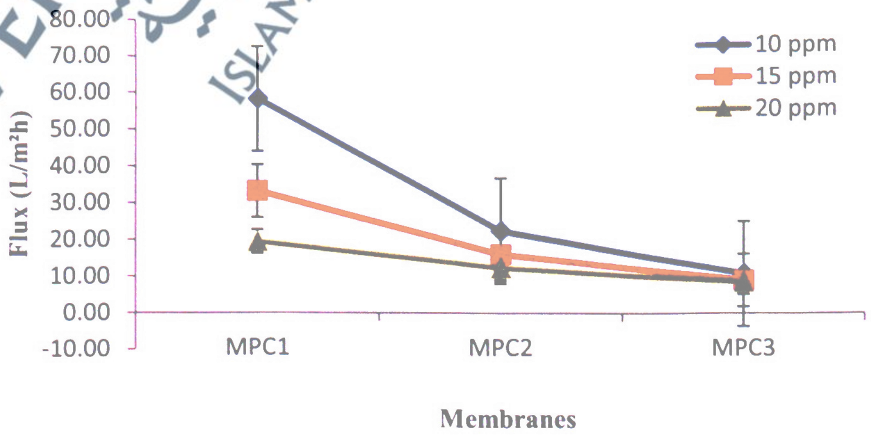
(A) Methyl Violet Dye

As we can see, the permeation flux decreases as polymer concentration increase from MPC1 to MPC3. At 10ppm of dye concentration, the flux decrease from 58.3854 L/m^{2}h to 10.7718 L/m^{2}h. Decreasing of permeation flux as polymer concentration increase indicates the membrane surface formed was denser and thicker. The same trending happen when feed concentration increase where permeation flux decreases. for MPC2, when dye concentration increase from 10ppm to 20ppm, the permeation flux keep decreasing from 22.4365 L/m^{2}h to 12.2902 L/m^{2}h. Decreasing of permeation flux when dye concentration increase can be explained due to the shielding effects on the membrane surface due to high concentration of ionic solutions (Yu et al., 2012). Permeation flux decrease when dye concentration increase also indicates that dye concentration also plays a significant role on the permeate flux. This was due to the amount of dye molecules deposited on the membrane surface which leads to concentration polarization and a higher probability of fouling (Wei et al., 2013).

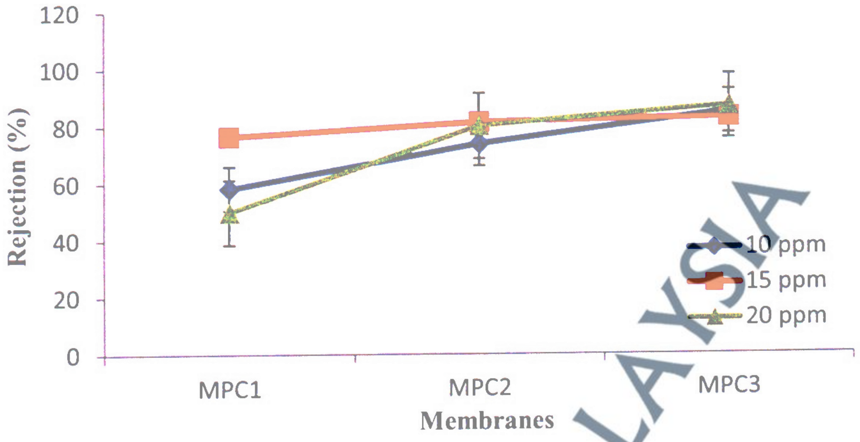
Theoretically, when permeation fluxes decrease, the rejection should be increase. Our finding revealed that for MPC membrane, the rejection increase as polymer concentration increases. The greatest increasing of rejection occurs at 20ppm of dye concentration of about from 50% to 87% for MPC1 and MPC3 membranes. Increasing of methyl violet rejection might be due to the fact that an increase in the initial polymer concentration in the casting solution leads to a much higher polymer concentration on the membrane surface. The thicker membrane could retain more dye molecules on the membrane surface. In addition, addition of surfactant in the casting solution might influence the formation process of macrovoids that give significant effects on membrane performance (Tsai et al., 2000). The same trending observed for 10ppm and 15ppm dye concentration where rejection of methyl violet increase as polymer concentration increases.

At 10ppm dye concentration, there was great increase of methyl violet rejection from MPC1 to MPC3 of about 58.4% to 85%. Previous research has shown that increasing of dye rejection is due to the adsorption of dye molecule on the membrane surface where first effects the permeation flux and increases the solution rejection. The adsorption occur was the affects from the physicochemical interactions or due to charges between dye solution and membrane surface (Aouni et al., 2012). This can be concluded that, addition of cationic surfactant in polymer solution will gives great impact by producing membrane with high performance and experimental data shows that higher rejection was due to the adsorption of molecules on the membrane surface.

FIGURE 50: (a) Permeation Flux; (b) % Rejection of Methyl Violet Dye



(a)



(b)

(B) Methyl Blue Dye

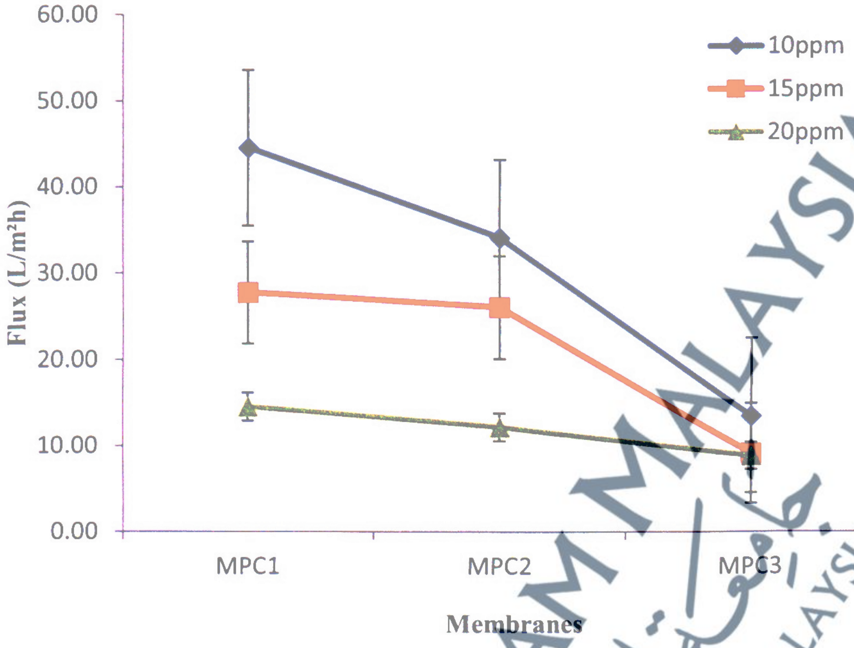
Aqueous solution of the methyl blue dyes (10ppm, 15ppm, 20ppm) prepared by dissolving them in distilled water were used for the membrane separation study. Figure 51 shows the membrane performance as the three different dye concentrations were treated with the MPC membrane. From the study, it was found that the separation of dyes by MPC membrane is that the rejection of dyes is almost 100%, indicates the complete separation of dye compounds from the dye solutions. Besides, methyl blue permeation test illustrate decreasing of permeation flux as polymer concentration increase from 44.5652 L/m^{2}h to 13.6817 L/m^{2}h for MPC1 to MPC3 at 10ppm dye concentration.

Small increasing of dye removal from 99.2% to 99.5% at the same concentration. It has been suggested that various fluxes obtain from different dye concentrations is depending on the chemical and physical properties of the dyes used. Mo et al., (2008) also added that the amount of solution penetrated through the membrane per unit time was changed according to the dye solution used. This can be said that the major factors affecting various fluxes of the membrane should be molecular size and shape of the dyes by considering the dyes properties (Mo et al., 2008). At 8.9715 L/m^{2}h, MPC3 obtain the highest color rejection of about 99.9% at 20ppm of dye concentration. This indicates that higher polymer concentration would retain almost 100% of dyes on the membrane surface. Thus, this could be the evidence that our homemade NFS membrane can produces the same value of color rejection as commercial membrane that available in industry. As the polymer concentration increase, the same trending possess by MPC membrane for 15ppm and 20ppm dye concentration.

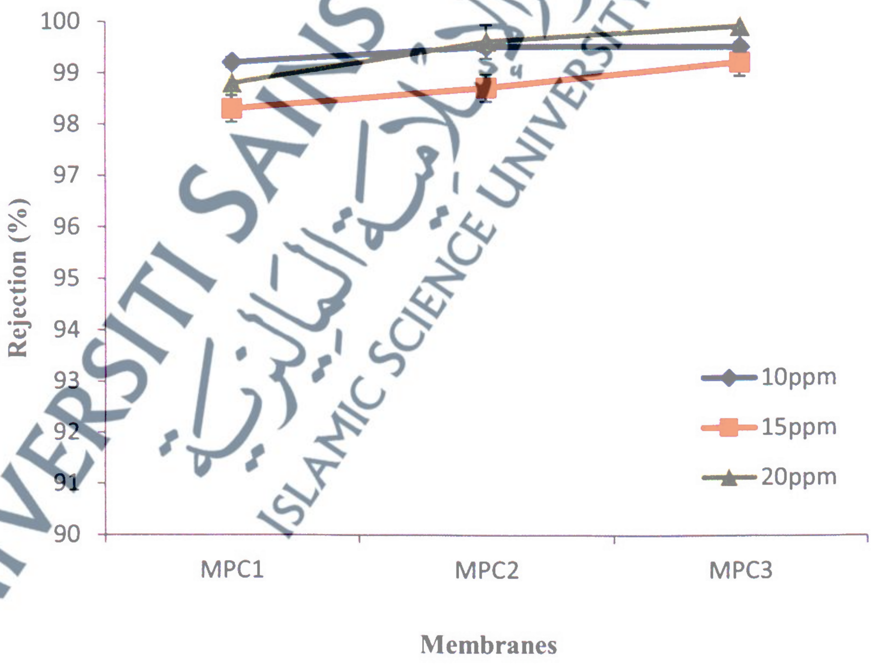
Previous study has reported that dye concentration also had significant effect on permeation flux values where flux will be decreased as dye concentration increase and the color removal will increase (Koyuncu and Topacik, 2002). Many researchers found that, addition of cationic surfactant in the casting solution can influence the formation process of macrovoids. This evidence could be explained by experimental data that shows increasing of dyes rejection as polymer concentration increase to shows that NFS membrane had the same membrane structure.

At 12.2554 L/m^{2}h, MPC2 gives rejection of about 99.6% at 20ppm dye concentration. This shows that, higher polymer concentration have thicker membrane surface that could retain high number of dye molecules on the membrane surface. Taking into account the presence of CTAB in polymer solution make the permeation flux of Methyl blue drop as dye concentration increase. Moreover, addition of CTAB has been said to decrease the membrane permeability while increase the dye rejection (Majewska-Nowak, 2009).

FIGURE 51: (a) Permeation Flux; (b) % Rejection of Methyl Blue Dye



(a)



(b)

(C) Acid Orange Dye

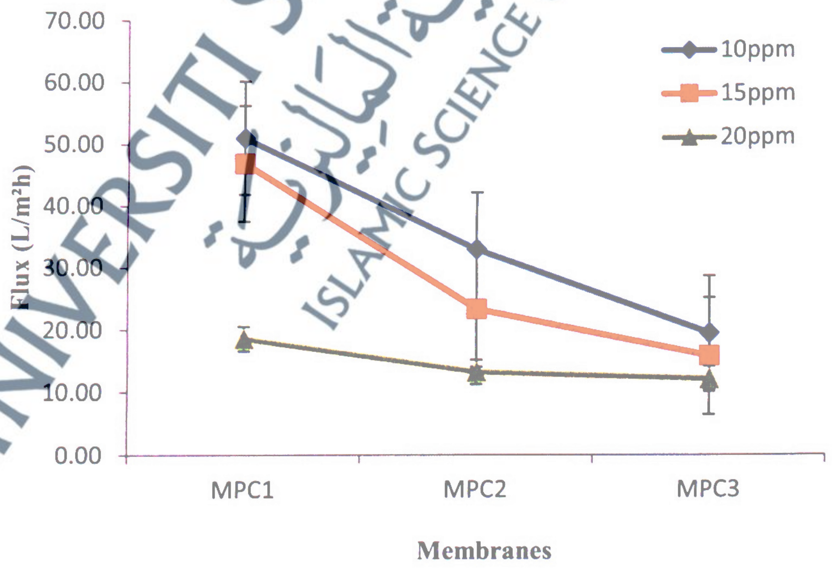
Figure 52(a) shows the permeation flux of acid orange dye tested using MPC membrane at three different polymer concentrations. The same trending happens for acid orange with other type of dyes. The permeation flux decreased when polymer concentration increase from 51.0443 L/m^{2}h to 19.5056 L/m^{2}h at 10ppm dye concentration. Permeation flux also shows decreasing order from 51.0443 L/m^{2}h to 18.5981 L/m^{2}h for MPC1 membrane as dye concentration increase. The results indicate that the polymer concentration and feed dye concentration has a significant effect on the permeate flux. This is because, high dye concentration will cause more dye molecules deposited on the membrane surface and leads to concentration polarization and high probability of fouling (Wei et al., 2013). Decreasing of permeation flux of acid orange dye has increase the percentage rejection of the dye.

At 10ppm dye concentration, dyes rejection increase from 90.7% up to 92.6%. Increasing of dye rejection as polymer concentration increase can be related to thicker membrane surface that could retain more dye molecules on the membrane surface. Therefore, less number of Acid orange dyes in the sample collected.

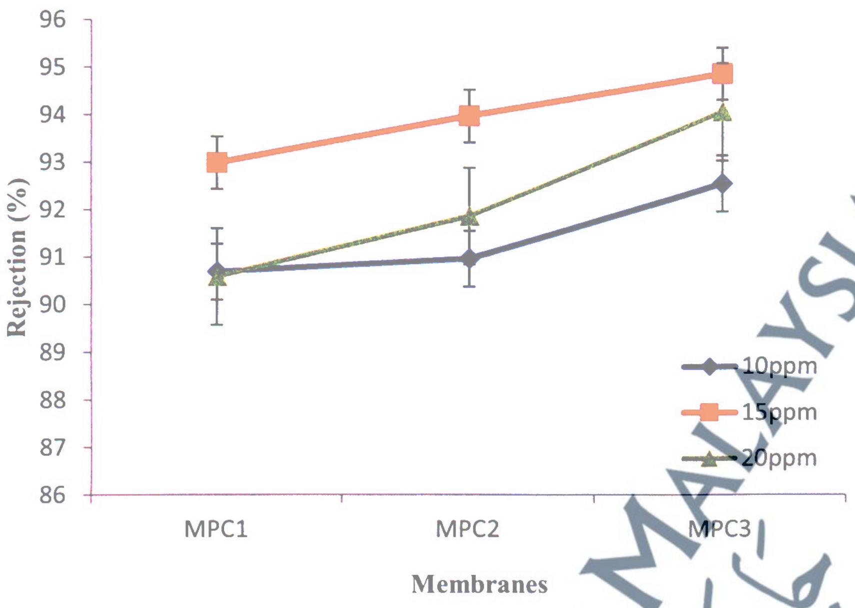
At 15.8714 L/m^{2}h, MPC3 with the higher polymer concentration obtained high percentage of rejection of about 94.9% for 15ppm dye concentration. As stated before, high dye rejection is due to the more dye molecule deposited on the membrane surface. Yu et al., (2012) discovered that concentration will give significant effects on the membrane performance for nanofiltration process. During the process, the number of dye molecule retained on the membrane surface will increase continuously, as a result, the dye permeation flux and rejection changes in course of concentration. Addition of CTAB in the polymer solution was said to increase the formation of macrovoid in the polymer solution. However, polymer concentration plays important role in this study also gives significant effect on the membrane performance.

Moreover, addition of CTAB in high polymer concentration always shows better performance of dye rejection. across the polymer concentration from MPC1 to MPC3, the permeation flux still show decreasing from 18.5981 L/m^{2}h to 12.1750 L/m^{2}h at 20ppm dye concentration. In addition, MPC3 shows better rejection of about 94.1%. This can be explained that MPC3 could retain high percentage of dye molecules on the membrane surface. With helps of PEG 600 as pore former, MPC membrane always become the best membrane in treating dyes solutions.

FIGURE 52: (a) Permeation Flux; (b) % Rejection of Acid Orange Dye



(a)



(b)

4.5 Molecular Orientation, Morphological and Thermal Study

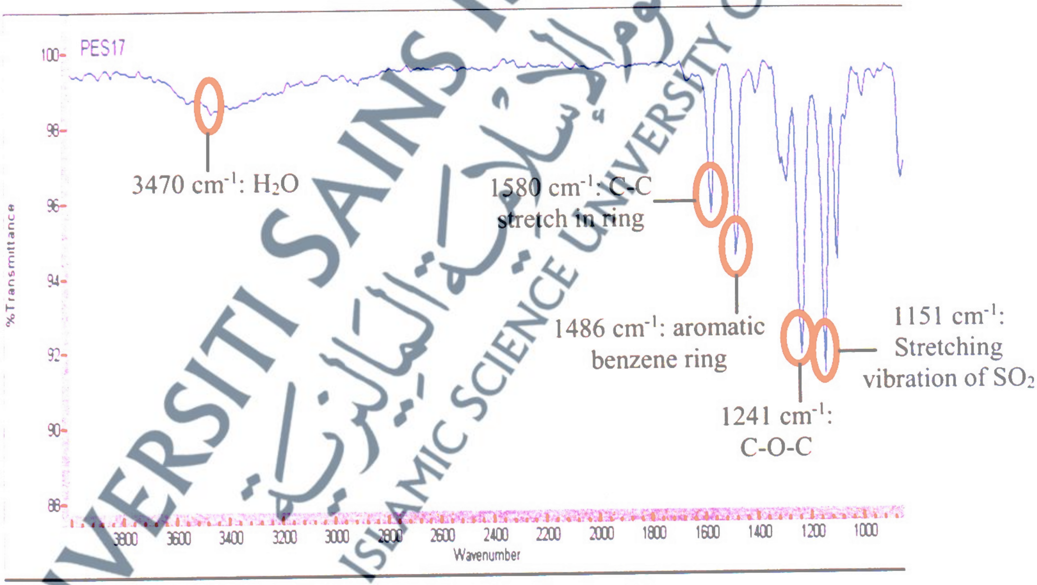
To be in line with experimental data with topic discussed above, membrane characterization had been done. Prepared membranes were study on molecular orientation, morphological study and thermal study. Molecular orientation is studied to confirm the functional group that presence in the polymer solution while morphological study is to observe the membrane structure that leads to the improvement of membrane performance.

Addition of different types of surfactant in the polymer solution also gives significant difference on membrane structure. Lastly, thermal study is to observe the mechanical strength of the membrane. During the testing, membrane would face several impacts that give high performance. Addition of additive and surfactant also would be factors that influence of the mechanical strength of the prepared membranes.

4.5.1 Molecular Orientation Study (FTIR)

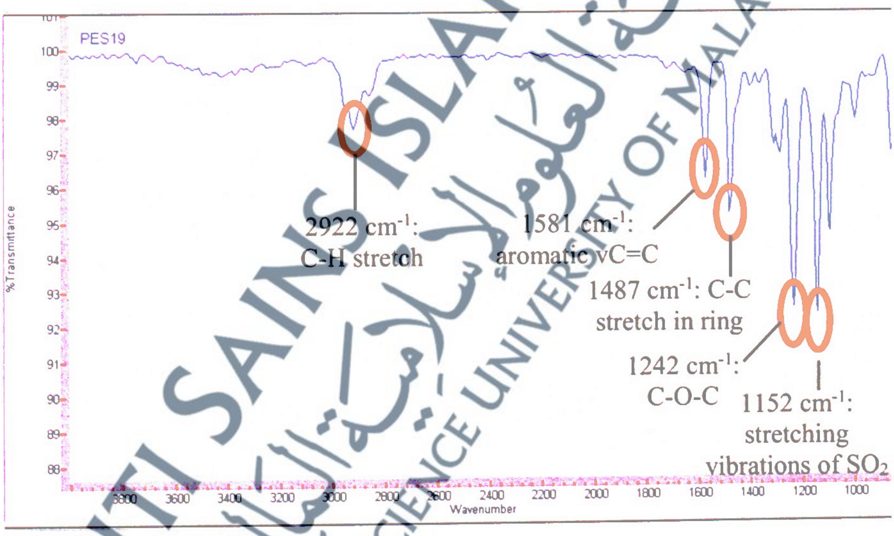
Based on the result, FTIR spectrum of MO1 shows water (H_2O) peak at 3470 cm^{-1} that shows water is presence in the polymer solution as non-solvent. For PES functional group, C-O-C stretch peak shows at 1241 cm^{-1} while stretching vibration of SO_2 was found at 1151 cm^{-1}. This was proved by Shaedi et al. (2012) where they found that SO_2 from PES showed FTIR peaks at 1114 cm^{-1} and 1280 cm^{-1}. Other than that, aromatic benzene ring of polymer was found at 1486 cm^{-1} where C-C stretching was shows peak of vibrations at 1580 cm^{-1}.

FIGURE 53: FTIR Spectrum of MO1 Membrane

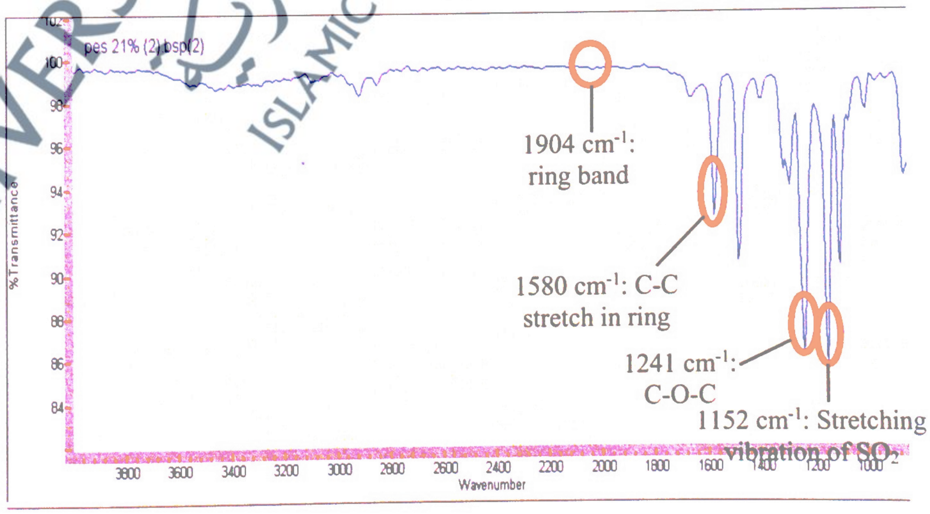


MO2 shows νC-O-C interaction at peak 1242 cm^{-1} from the polymer. As in the ring of hydrocarbon, C-H vibrations are presence at 2922 cm^{-1}. The same FTIR peak shows by S=O stretching vibrations presence at 1152 cm^{-1} of MO2 spectrum. Besides, increasing of polymer concentration up to 19wt% gives presence FTIR peak of aromatic *v*C=C in ring at 1487 cm^{-1}. To confirm that PES was used as polymer, C-C stretch (in-ring) shows peak at 1581.3 cm^{-1}. In MO3 spectrum shown by Figure 4.26(b), H_2O does not shows any significant peak. However, ring band of PES and C-C stretch in ring was shown at 1904 cm^{-1} and 1580 cm^{-1} respectively. As polymer concentration increase, the peak of C-O-C and stretching vibration of SO_2 has shown similar position at 1241 cm^{-1} and 1152 cm^{-1} respectively.

FIGURE 54: FTIR Spectrum of (a) MO2 and (b) MO3 Membranes



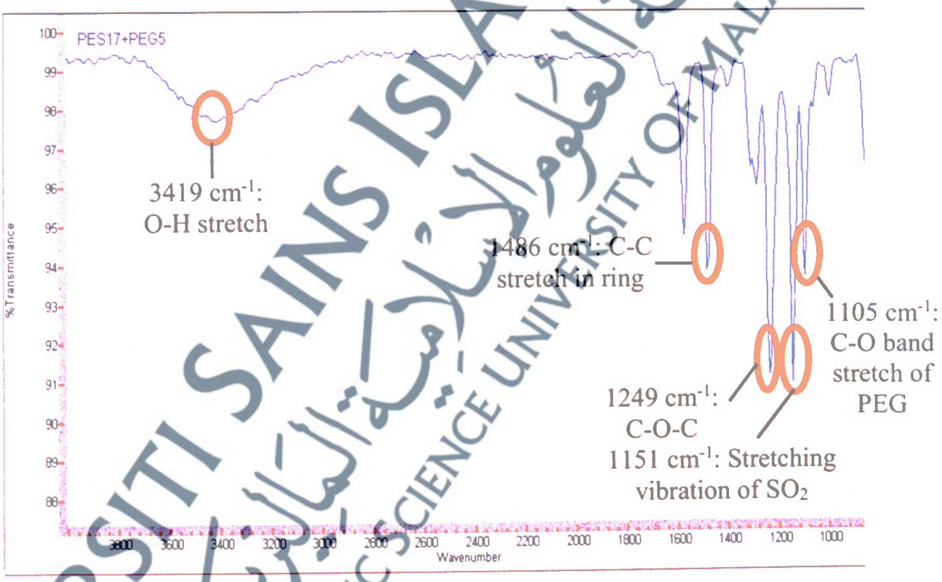
(a)



(b)

When the polymer solution is added with 5% of PEG as additive, OH stretching vibration was presence in the spectrum at peak 3419 cm^{-1} and peak 1105 cm^{-1} shows significant peak of C-O band stretch of PEG indicates the presence of PEG in the MP1 polymer solution shown by Figure 51 below. Vatsha et al. (2014) in their study found that new absorption peak in the infrared spectra shows that addition of additive in the polymer solution. Moreover, addition of PEG in MP1 membrane does not change the peak position of C-O-C and stretching vibration of SO_2 of PES at 1240 cm^{-1} and 1151 cm^{-1} respectively.

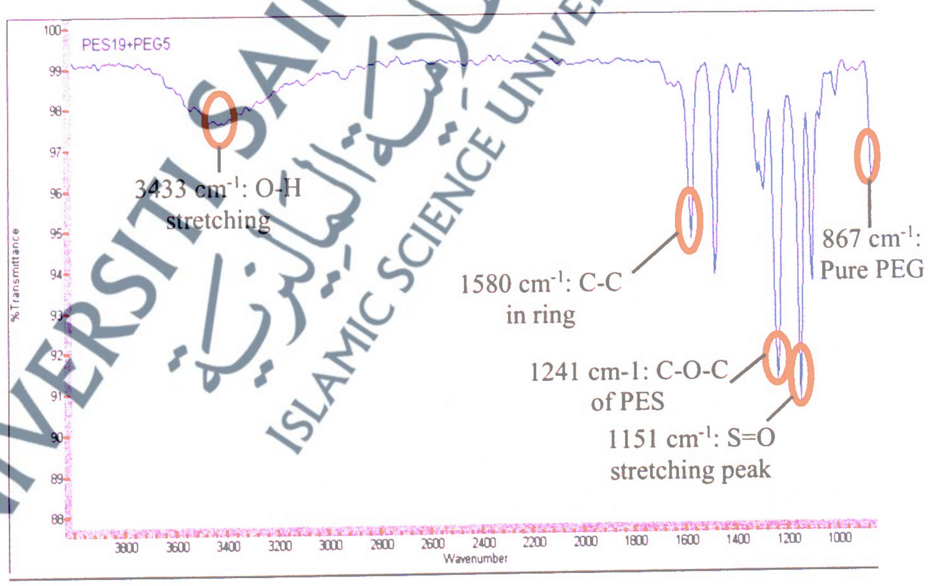
FIGURE 55: FTIR Spectrum of MP1 Membrane



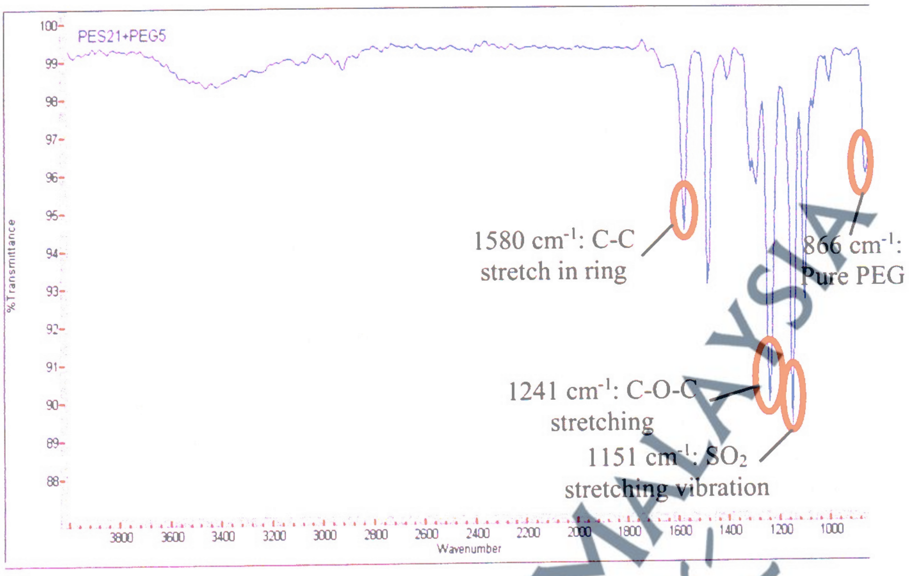
In MP2 with PEG 5% polymer solution, H_2O shows significant peak at 3433 cm^{-1} molecular orientation of O-H stretching to shows there was presence of water during preparation of polymer solution. S=O stretching vibrations of PES at 1151cm^{-1} and C-C stretch in ring was of polymer was shown up at 1868.2 cm^{-1}. Presence of PEG as additive in polymer solution was found at peak 867 cm^{-1} indicates the pure PEG contain in the polymer solutions. In this spectrum, PES as polymer material has shown preference where another functional group of PES showed up which is C-O-C from PES at peak 1241 cm^{-1}.

MP3 shows various functional groups in the spectrum. C-O-C band stretch was found at 1241cm^{-1} to indicate the functional group presence in PES as polymer material. As PEG was added in the polymer solution, the peak of pure PEG was shown at 866 cm^{-1}. Another characteristic peak shown in Figure 56(b) was found belongs to PES as polymer materials which are 1241 cm^{-1} and 1151 cm^{-1} referred to C-O-C stretching and SO_2 stretch vibrations of PES. This can be concluding that, polymer material was the most important factors that give significant spectrum of prepared membrane.

FIGURE 56: FTIR Spectrum of (a) MP2 and (b) MP3 Membranes



(a)



(b)

S=O stretching vibration of SO_4 from SDS shows at 1409 cm^{-1} when 2% SDS is added as surfactant to the MPS1 solution. PEG was indicated by the presence of C-O band stretch at 1106 cm^{-1}. Besides, the important materials in the polymer solution making which is PES was shown by the presence of stretching vibration of SO_2 from PES at peak 1151 cm^{-1}. In the membrane fabrication especially polymer solution making, water has been used as non-solvent in order for the thermodynamically factors. Thus, OH stretching was found at peak 3363 cm^{-1} to indicate the presence of water in the prepared membrane.

FIGURE 57: FTIR Spectrum of MPS1 Membrane

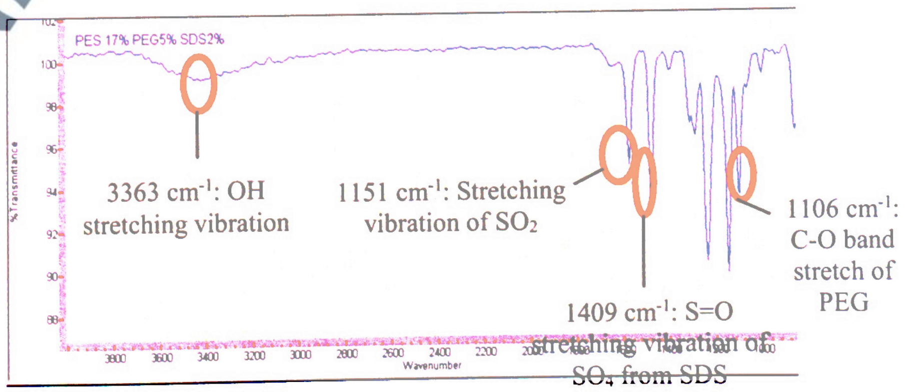
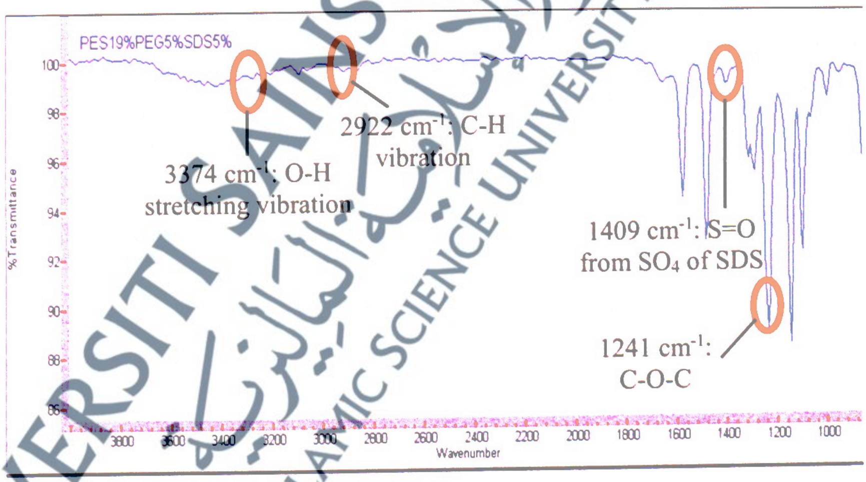


Figure 58 shows infrared spectrum of MPS2 membrane which found to has additional functional group that appears in the spectrum. Increasing polymer concentration was said to the affecting factors on membrane performance as well as molecular interaction between materials of the prepared polymer solutions.

In MPS2 of polymer concentration, S=O stretching vibrations of SO_4 and C-O-C stretch were found at peak 1409 cm^{-1} and 1241 cm^{-1} respectively to indicate the presence of SDS in the solution. Figure 4.30 also shows C-H vibrations from SDS at peak 2922 cm^{-1}. Moreover, O-H stretching vibration was found at 3374 cm^{-1} indicates the presence of water during the polymer solution making.

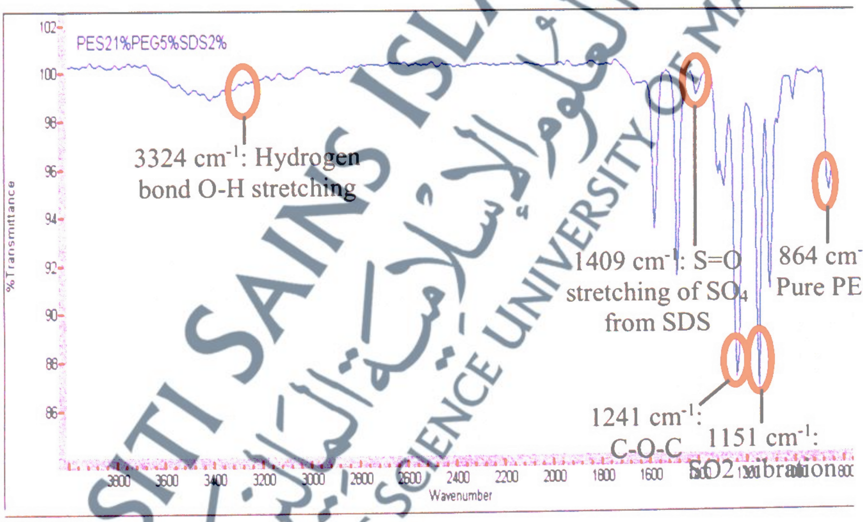
FIGURE 58: FTIR Spectrum of MPS2 Membrane



Increasing polymer solution up to MPS3 does not shows any changes as SDS were added in the polymer solution. However, the spectrum still shows the molecular orientation of surfactant and polymer to indicate the interaction both materials. Figure 63 shows infrared spectrum of MPS3 with highest polymer concentration.

In Figure 59 shows that hydrogen bond O-H stretching appears at peak 3324 cm^{-1} indicates the presence of OH functional group from water molecule. Addition of SDS in the polymer solutions gives molecular orientation of S=O stretching vibration from SO4 in SDS molecule at peak 1409 cm^{-1}. The same spectrum of SDS shown by three different polymer concentrations. Appearance of C-O-C and stretching vibration of SO_2 is appears at peak 1241 cm^{-1} and 1151 cm^{-1} from PES as polymer concentration. As PEG was added as additive in the polymer solution, pure PEG was found to be at 864 cm^{-1} in the spectrum.

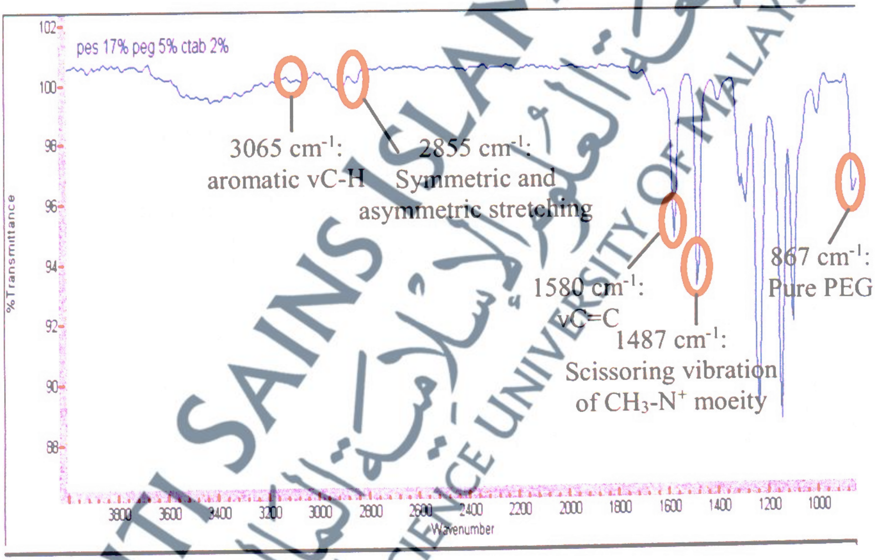
FIGURE 59: FTIR Spectrum of MPS3 Membrane



In this study, two types of surfactant were used which are anionic surfactant (SDS) and cationic surfactant (CTAB) in order to determine the effectiveness of nanofiltration-surfactant (NFS) membrane. Based on the experimental data discuss above, different surfactant types will give different membrane performance-properties. Figure 64 shows infrared spectrum of MPC1 which has CTAB as cationic surfactant added in the polymer solution.

From FTIR spectrum of MPC1, 1487 cm^{-1} and 2855 cm^{-1} peak show scissoring vibrations of CH_3-N^+ moiety and symmetric and asymmetric stretching CH_2 vibration of alkyl chain. Both peaks represented the presence of CTAB as cationic surfactant added to the polymer solution. Besides, aromatic *v*C=C appears at peak of 1580 cm^{-1} indicates the aromatic structure in PES molecule. Pure PEG has shown the molecular orientation at 867 cm^{-1} in the spectrum. This can be said that, PEG as additive also plays an important interaction between molecules in the polymer solution.

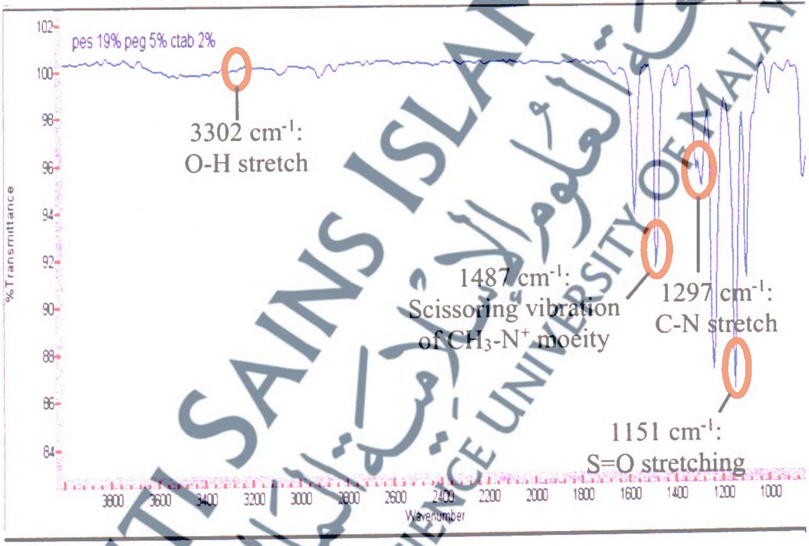
FIGURE 60: FTIR Spectrum of MPC1 Membrane



Based on the experimental data, increasing polymer concentration will increase membrane performance-properties. Increasing polymer concentration up to 19wt%, MPC2 gives different performance on the testing and interaction between molecules also has been studied. Figure 4.33 shows FTIR spectrum of MPC2 membrane with 19wt% of polymer concentration.

In MPC2 membrane, several new peaks was found indicate the addition of CTAB as cationic surfactant in the polymer solution. Scissoring vibration of CH_3-N^+ and C-N stretch was found to be at peaks 1487 cm^{-1} and 1297 cm^{-1} respectively. PES still shows very long band in each spectrum shows that stretching vibration of S=O of about 1151 cm^{-1}. According to Qu et al., S=O of PES was found to be at 1151cm^{-1} and 1105 cm^{-1} and prepared membrane shows the right spectrum of S=O location in the orientation (Qu et al., 2010).

FIGURE 61: FTIR Spectrum of MPC2 Membrane



3302 cm^{-1}: O-H stretch

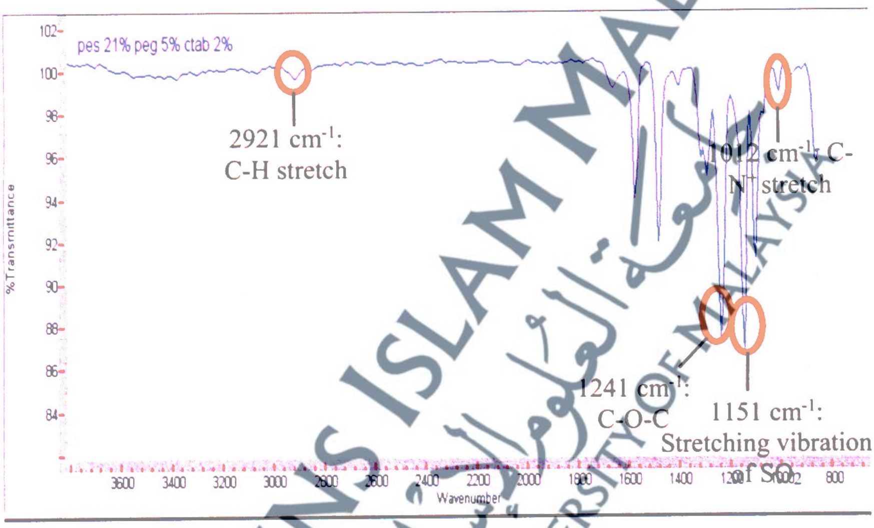
1487 cm^{-1}: Scissoring vibration of CH_3-N^+ moeity

1297 cm^{-1}: C-N stretch

1151 cm^{-1}: S=O stretching

MPC3 membrane always shows promising result during the experimental study. With low permeation flux, MPC3 was found to achieve almost complete removal efficacy. Interaction between surfactant molecule and increasing of polymer concentration also has been studied by infrared spectrum. MPC3 membrane in Figure 66 shows that, appearance of C-H stretch found to be lower at 2921 cm^{-1}. C-O-C interaction of PES polymer shows at 1241 cm^{-1} and stretching vibration of SO_2 also from polymer. In MPC3 spectrum, C-N$^+$ stretch were found higher at 1012 cm^{-1} than other polymer concentration. However, pure PEG does not show any peaks in MPC3 membrane spectrum. This indicates that, high polymer concentration gives lower interaction between additive and polymer molecule.

FIGURE 62: FTIR Spectrum of MPC3 Membrane



4.5.2 Morphological Study

In this study, MO1 has the least polymer concentration. As presented in the figure above, prepared membranes have asymmetric structure consisting of finger-like pores, substructure and thick bottom layer. In addition, some researchers have observed that, membrane that were prepared by PES/NMP solution will leads to the formation of big finger-like pores in the membranes. Besides, lower polymer concentration will produces more finger-like structures than membrane with high polymer concentration. Formation of big finger-like pore of PES membrane was affected by molecular weight structure of polymer.

Moreover, Barth et al., (2000) also stated that PES has polar materials which allow a faster and deeper diffusion of the polar non-solvent water into the membrane. Formation of thick support layer also shows that PES as polymer materials makes the membrane structure more stable. This structure was in line with membrane performance in terms of water fluxes, fluxes and rejection where lower polymer concentration always shows high PWP as pressure increase and shows high permeation flux as well as for the rejection. As can be seen in Figure 63, thicker bottom layer of the membrane was formed with spongy structure that helps on the separation of the solution. Lower polymer concentration also will produce membrane with thinner membrane surface that allow the separation occurs easily. Increasing on water flux, solution permeation fluxes as well as rejection also contributed by the membrane surface where it plays an important role for the separation process to occur.

FIGURE 63: Cross-sectional Structures of MO1 Membrane

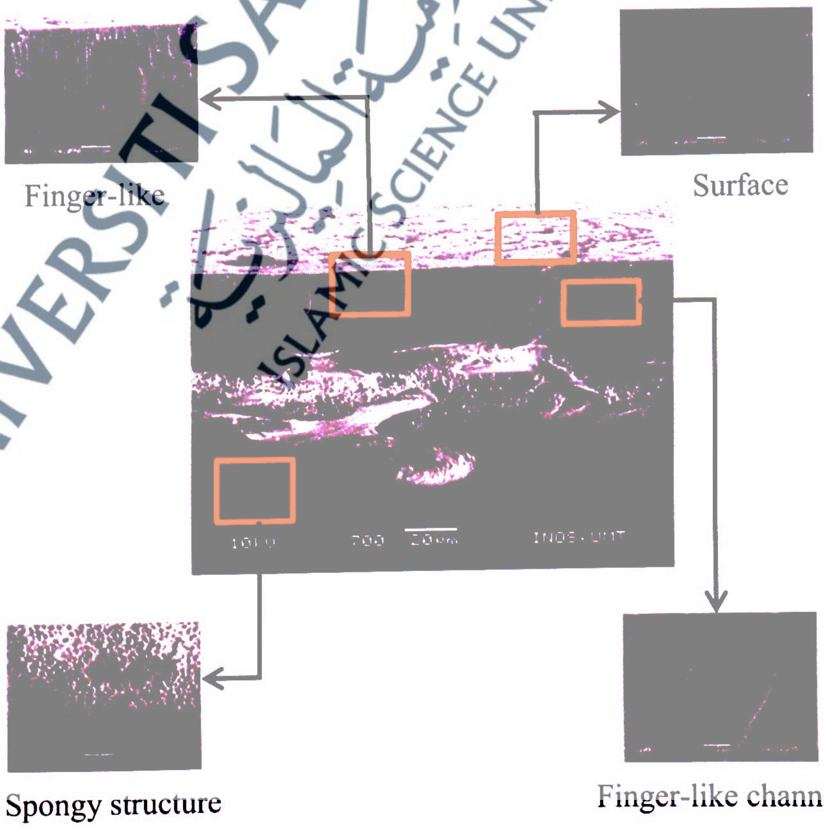
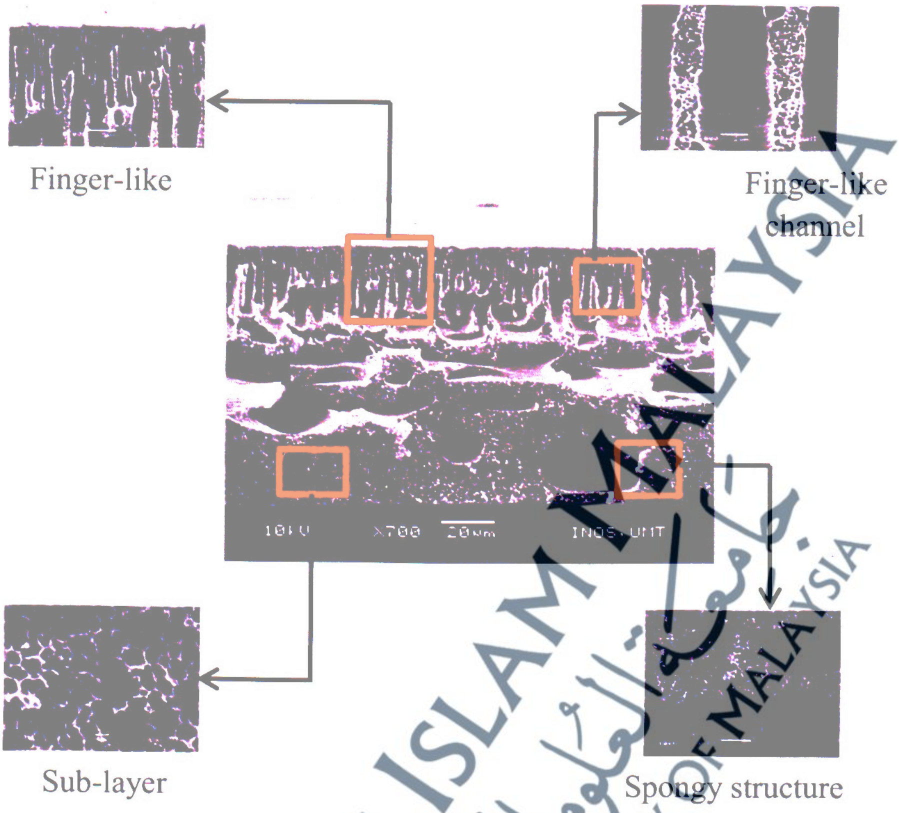


Figure 64 exhibits an asymmetric features consisting of dense top layer, finger-like structure and membrane sub-structure. Increasing of PES concentration up to 19wt% shows increasing of finger-like structure on the membrane sub-layer. Moreover, macrovoids also seems to be increased. As we can see in the figure above, medium polymer concentration forms unorganized finger-like structure on the membrane sub-layer. The same form of membrane support layer also exist where PES will form thick membrane support layer where this is makes the membrane more stable.

As discussed above, PES represents the more polar materials that allow a faster and diffusion of the polar non-solvent water into the membrane (Barth et al., 2000). Exchanges between molecules makes the membrane produces more pores as polymer concentration increase. Increasing the number of macrovoids shown that the membrane performance more effective with the stable support layer formed.

Other than that, the support layer was formed in nodular structure that helps the separation process occurs effectively. According to Ismail et al., (2011) addition of polymer in polymer solution will increase the active skin layer thickness where this active skin layer is important for membrane undergo a separation process. Author also observed that, increasing of polymer concentration will form transition layer that exist due to the redissolution steps during the drying process. Thus, it shows that, 19wt% of PES polymer solution also shows better in membrane performance of water flux, permeate fluxes as well as rejections.

FIGURE 64: Cross-sectional Structures of MO2 Membrane

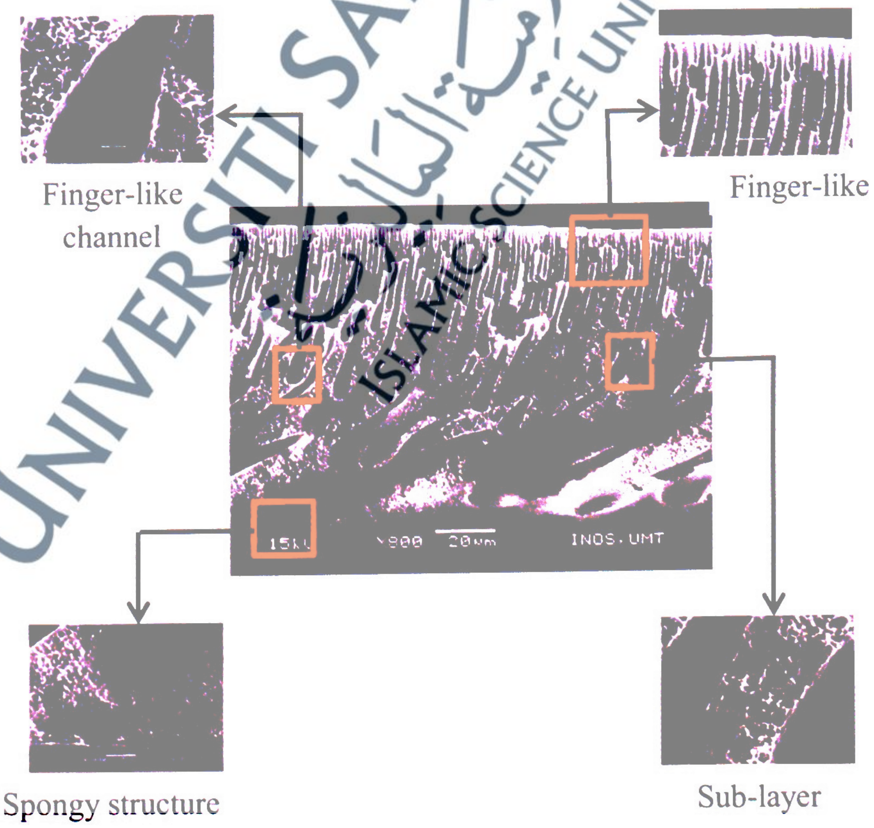


As the polymer concentration increase, the membrane thickness was said to increase as well. The membrane thickness resulted to increasing of membrane performances. This was in line with the membrane morphology as illustrated in Figure 65. Moreover, researchers also observed that increasing of membrane performance is due to the reduction of membrane pore radius on the membrane surface (Ismail & Hassan, 2006). The highest polymer concentration in this study was formulated at 21wt% of PES polymer concentration.

According to Figure 65, MO3 form an asymmetric nanofiltration membrane structure with organized finger-like structure and seems to have more pores on the membrane surface. Increasing of polymer concentration up to 21wt% has reduced the number of macrovoids on the membrane support layer. MO3 also has long finger-like structure from the surface across the membrane sub-layer. This is due increasing of polymer concentration has increase the solution viscosity which exhibit formation of more finger-like structures and can be seen at the lower part of the PES membranes.

In addition, formation of finger-like pores because of strong solvent used in making PES membrane solution (Barth et al., 2000). As polymer concentration increase up to 21wt%, MO3 membrane shows thin support layer rather than MO1 and MO2 nanofiltration membrane. Organized finger-like structure, thin membrane support layer and long finger-like structure across the membrane shows that MO3 nanofiltration membrane performance was the best performance and occurred effectively. Nodular structure on the membrane support layer also helps in the membrane performance.

FIGURE 65: Cross-sectional Structures of MO3 Membrane

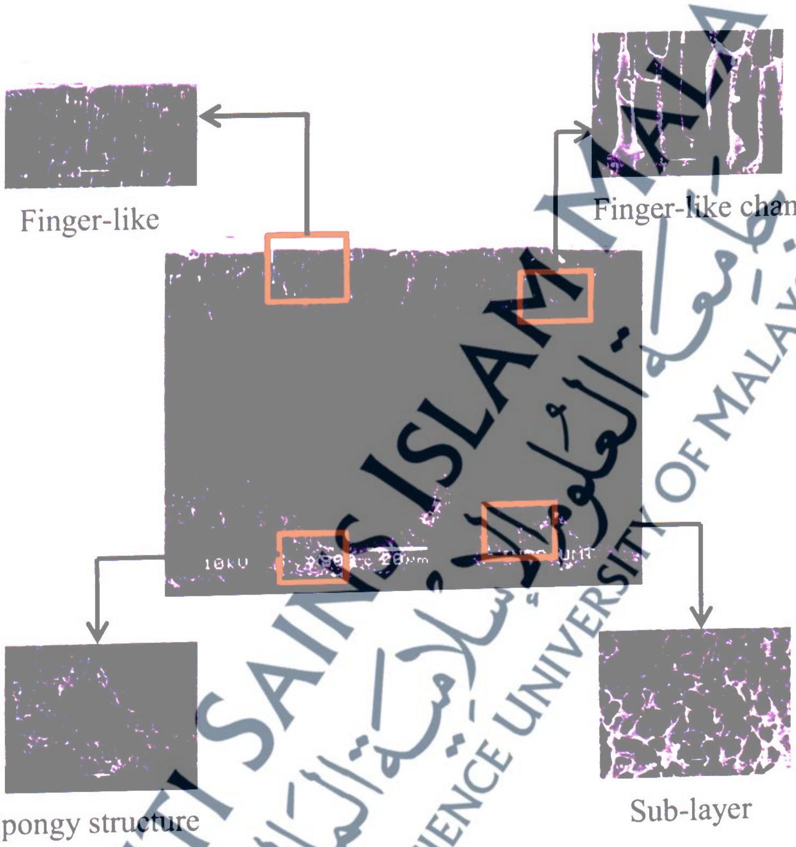


Membrane performance and properties was influenced by several factors for example, concentration of polymer solution, solvent and additives. An additive was to say became a pore forming agent in the polymer solution. The addition of some pore forming agent in the polymer solution was very effective in changing membrane properties. Previous study by Arthanareeswaran et al. (2010) found that PEG 600 is well known as a better pore former compared to others additives. They suggested that, addition of PEG in the polymer solution will increase the membrane hydrophilicity and resulted to important changes in the nanofiltration membrane performance (Arthanareeswaran et al., 2010).

Figure 66 shows that an asymmetric nanofiltration with addition of PEG 600 at the least polymer concentration (17wt%). Addition of PEG 600 gives membrane with more pores that lead to the high membrane performance. Formation of macrovoids also seen at the membrane sub-structure and spongy support layer as intermediary for the separation process takes place. Lower polymer concentration lead the produced membrane to be more fragile and brittle. In membrane performance testing, lower polymer concentration always shows high water flux, permeate flux as well as high in rejection.

Moreover, addition of PEG 600 in the polymer solution was studied to influence the pore formation in the immersion precipitation process because of strong hydration and large excluded volume in aqueous systems (Rahimpour et al., 2010). Lower polymer concentration and addition of additive also give short finger-like structure and formation of big cavity on the membrane sub-structure. According to Ma et al., addition of different molecular weight of PEG will cause the changes on the finger-like cavities in the sub-layer and large voids near the bottom surface (Ma et al., 2011). In this study, uses of PEG 600 as additive to ensure the fact that PEG with high molecular weight will form larger finger-like cavity on the membrane sub-layer.

FIGURE 66: Cross-sectional Structures of MP1 NF Membrane

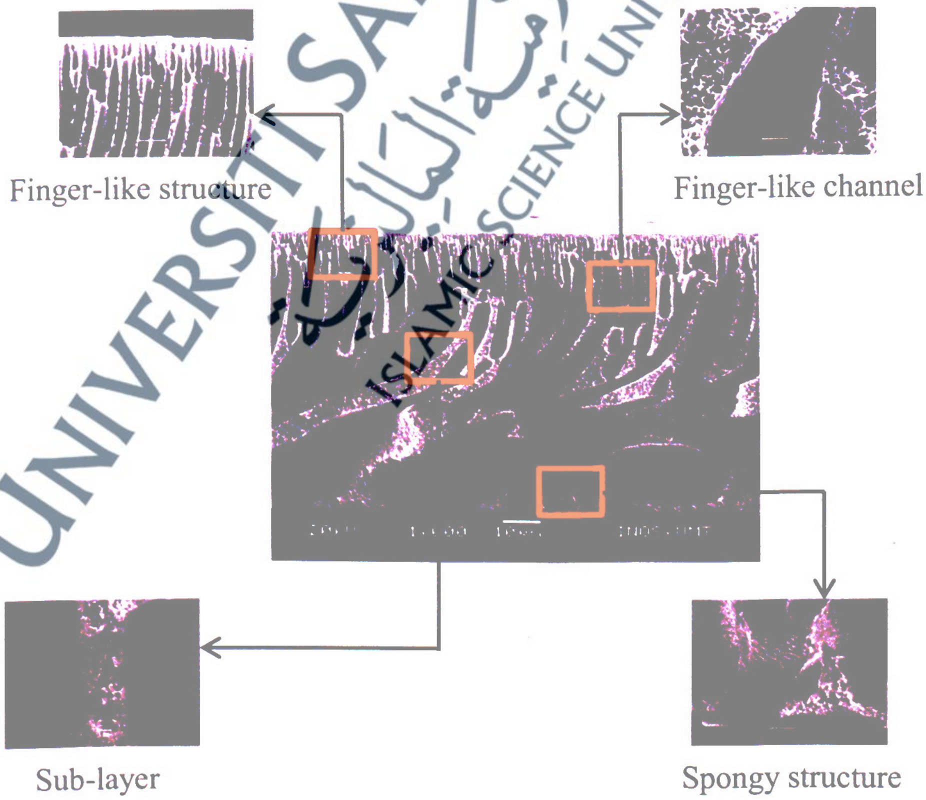


MP2 NF membrane has addition of PEG 600 as additive in 19wt% polymer solution. As has been discovered before, addition of PEG 600 forms membrane with finger-like structure that almost penetrate throughout the membrane cross-section. Other than that, it will improve the interconnectivity besides influencing the size and shape of macrovoids forms in the membrane (Idris et al., 2007). According to Ma et al., (2011), addition of PEG as additive in the casting solution will cause two effects which are dissolution of PEG consumes some of the solvents cause high in viscosity of membrane solution. Instead of that, polymer concentration also leads to the

increasing of polymer solution viscosity. Since PEG was hydrophilic in nature, the hydrophilicity of PEG in membrane dope will cause some exchange rate of solvent and non-solvent during the process. Thus, it will result to changes of morphological structure of the prepared membrane.

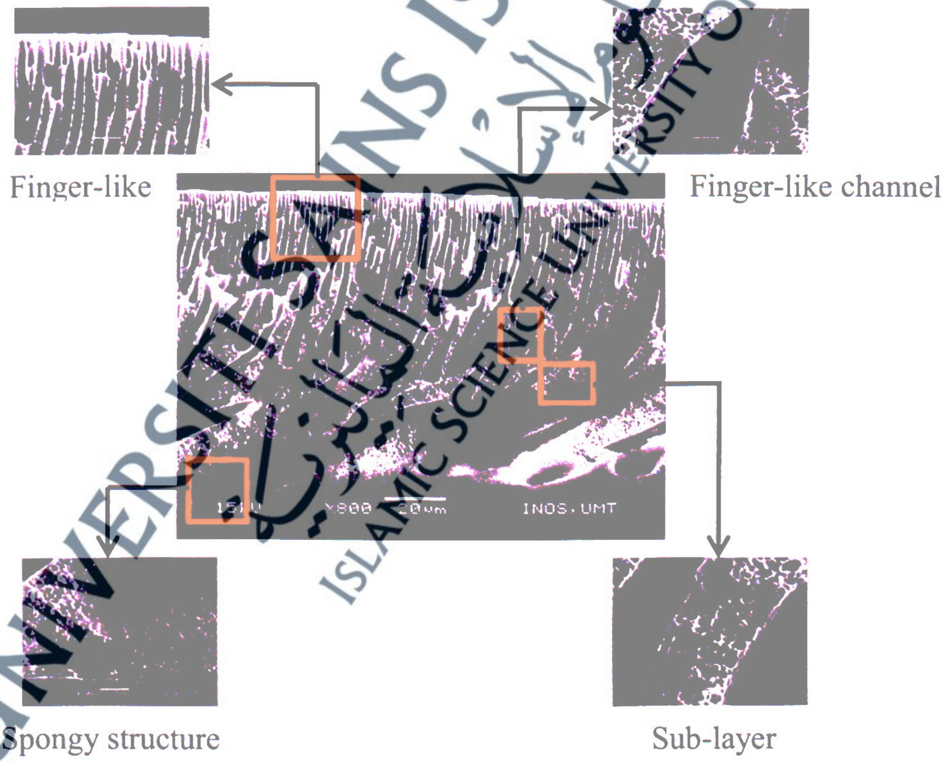
Some additive will have tendency to form macrovoids and others will supress it according to the additives properties (Chakrabarty et al., 2008). Based on Figure 67, addition of PEG 600 has increase the number pores on the membrane surface as PEG acts as pore former. Increasing of pores on the membrane surface will leads to the effectively of membrane performance. In addition, PEG 600 makes the finger-like structure longer across the membrane sub-layer where helps in efficacy of separation process throughout the membrane.

FIGURE 67: Cross-sectional Structures of MP2 NF Membrane



Increasing polymer concentration up to 21wt% shows that NF could be the best membrane for separation process. With high polymer concentration in the formulation, Figure 68 shows MP3 forms an asymmetric nanofiltration membrane with denser top layer and thick membrane surface. Increasing polymer concentration was said will increase the membrane surface thickness as well the polymer solution viscosity. Chakrabarty et al., (2008) in their study has stated that, addition of additive could be the one of the major factors influencing the membrane performance. Moreover, additive was used in order to have an optimal membrane structures that leads to membrane performance-properties.

FIGURE 68: Cross-sectional Structures of MP3 NF Membrane

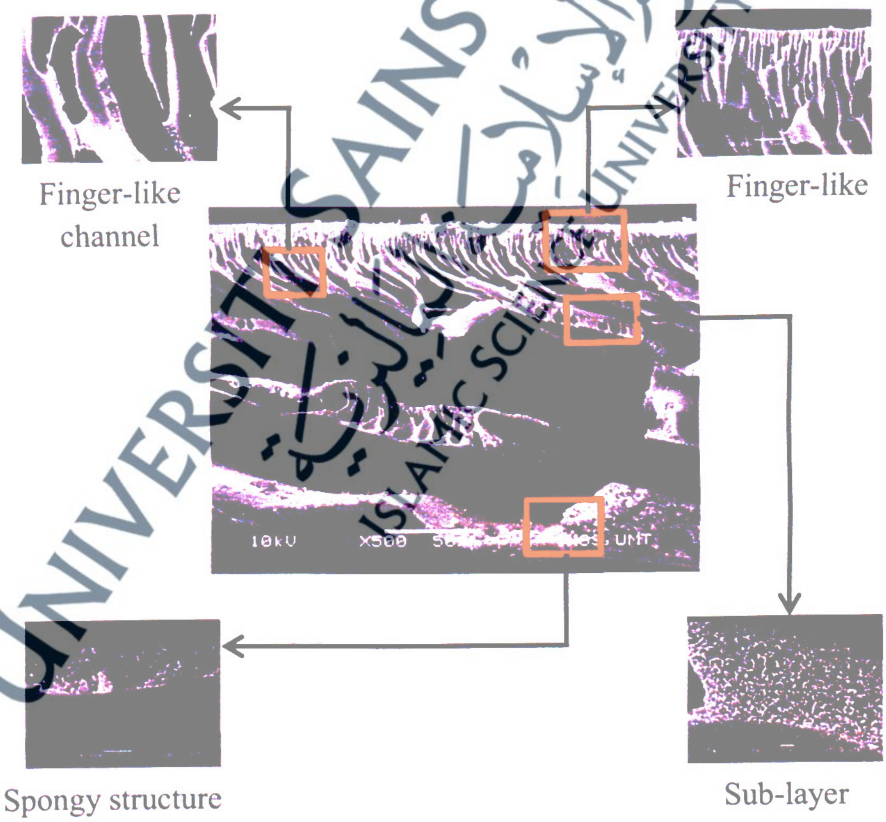


High polymer concentration also shows the least macrovoids formation. Other researchers found the similar structure in their study that, addition of PEG 600 as additive will form long finger-like structure throughout the membranes and improve the membrane pore interconnectivity. Idris et al., (2007) also observed that addition of PEG in the polymer solution will influence the shape and size of macrovoids in the membranes. 21wt% polymer concentration shows good membrane structure with spongy support layer that ease the separation process throughout the membrane. To study the effect of anionic surfactant in membrane performance properties, sodium dodecyl sulphate (SDS) was selected as strong anionic surfactant. Addition of SDS in the polymer solution always shows high water flux and permeates flux. However, SDS decreased the solution rejection.

Figure 69 illustrate the SEM image of nanofiltration membrane with addition of SDS as anionic surfactant. At least polymer concentration, MPS1 exhibit thin top layer, and the most striking results of more porous structure were formed. Based on the image of MPS1 membrane, there was huge cavity on the membrane sub-layer as the SDS was added into the polymer solution. Even though SDS influence the number of pores on the membrane surface, the cavity will make the membrane is not suitable for the continuous operation. Macrovoids also forms in the pore of the MPS1 membrane that shows the membranes is the most porous membrane. Other than that, polymer concentration also plays an important role in membrane structure. With the least polymer concentration, membrane contains SDS as surfactant produce more porous with brittle structures that is not suitable for the separation process.

According to Saedi et al. (2012), SDS was a hydrophilic surfactant that would affect the membrane morphology and porosity of sub-layer in three ways. Firstly, SDS will enhance the macrovoid formation and increase the membrane porosity by increasing the solvent-non-solvent mixing affinity. This can be explaining by the formation of huge cavity on the membrane support layer as well as formation of macrovoids. Moreover, SDS will increase the porosity and macrovoids via interaction of polymer-surfactant in the solution. Lastly, it will decrease the sub-layer porosity by decreasing demixing rate (Saedi et al., 2012). Other authors also found that addition of SDS in the casting solution will form PES-SDS interaction where SDS will corrupt the pores and leave defects in the membrane structure (Rahimpour et al., 2007).

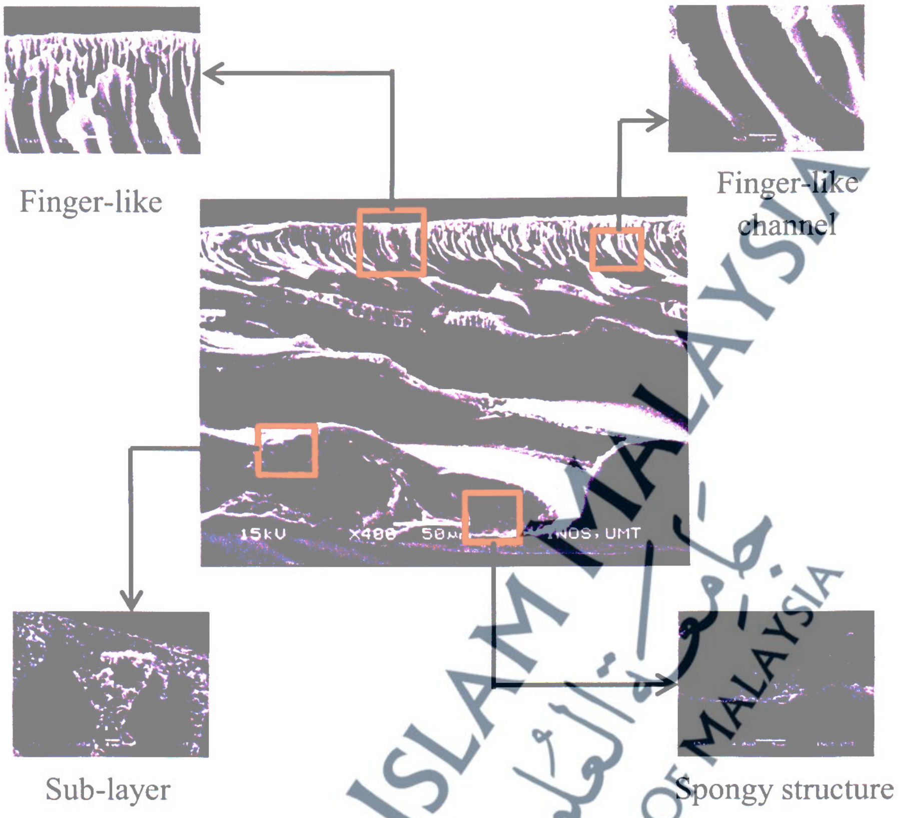
FIGURE 69: Cross-sectional Structures of MPS1 Membrane



Generally, researcher found that addition of surfactants in the polymer solution would affect the membrane morphology and structure besides effects of polymer concentration on the membrane performances. Researchers observed that addition of hydrophilic surfactant in the hydrophilic coagulant will be able to improve the formation of macrovoids and the hydrophilicity of membranes. On the other hand, charges of surfactants either negative or positive might give slightly changes on the membrane surface charge and alter the membrane performance (Rahimpour et al., 2007).

Figure 70 illustrate the cross-sectional image of MPS2 membrane with increasing polymer concentration up to 19wt%. Besides study the effect of surfactant type, polymer concentration always plays an important factor in order to determine the membrane performances. As discussing above, increasing of polymer concentration will lead to increase of polymer solution viscosity and makes the membrane top layer increase. However, addition of SDS in the polymer solution was resulted to formation of thinner top-layer and more porous sub-layer. According to Ghaemi et al. (2012), addition of SDS in the polymer solution lead to the formation of SDS layer on the membrane surface. Due to the lack of polymer-surfactant interaction, SDS changes the membrane structure with more porous substructure form. Thus, the membrane was lack of firmness in terms of membrane mechanical strength and membrane durability.

FIGURE 70: Cross-sectional Structures of MPS2 Membrane



Increasing of polymer concentration will increase the membrane thickness that caused increasing of rejection. When the thickness of membrane surface increase, the membrane pore was parameter that caused the increasing of rejection (Ismail & Hassan, 2006). Increasing polymer concentration up to 21% was the best polymer concentration in this formulation study. However, as has been mentioned by almost researchers, addition of SDS in the polymer solution will give membrane with higher porosity instead of increasing of finger-like structure.

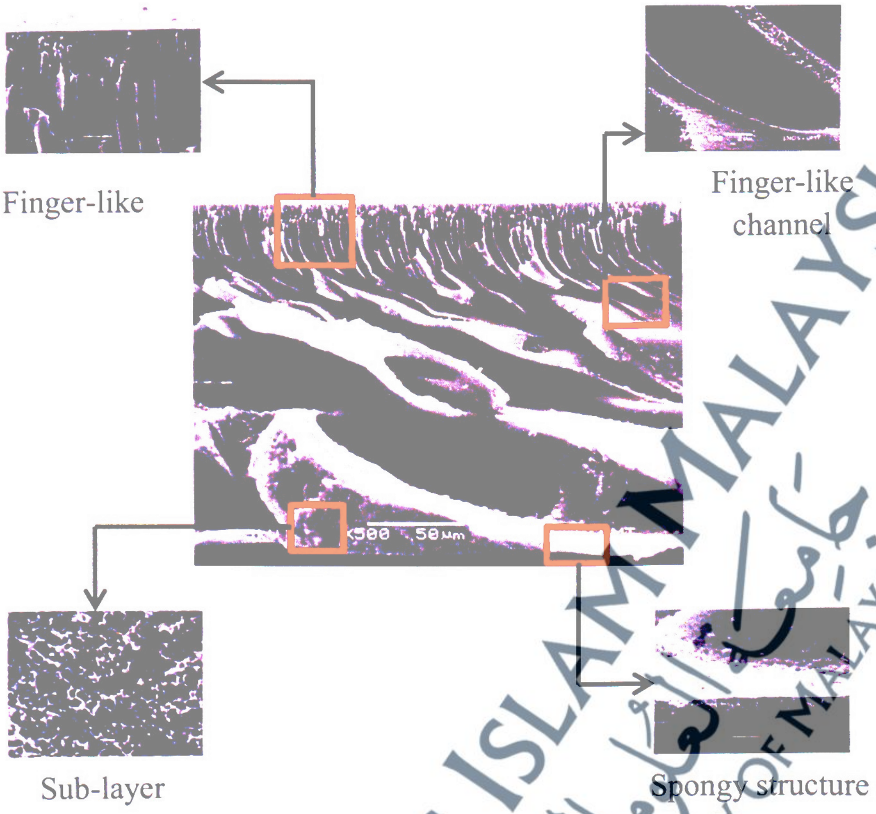
Tsai et al. (2000) in their study observed that, increase initial polymer concentration will increase the separation factor and decrease the permeation rate of polysulfone. This was in line with polyethersulfone as polymer concentration increase.

Although polymer concentrations increase, addition of SDS as anionic surfactant also gives membrane with high porosity. This was illustrates in Figure 71.

Figure 71 shows the image of cross-sectional area of MPS3 membrane with higher polymer concentration. The image shows that, the finger-like structures were more organized than other two polymer concentration. The image also shows that, the formation of large macrovoids on the membrane sub-layer that caused the porosity of the membrane. With addition of small amount SDS in the polymer solution, high polymer concentration gives more organized structure without showing any brittleness on the membrane sub-layer. The spongy structure on the support layer helps increase the membrane performance by ease the transportation of the solute. Experimental data shows that, membrane with SDS shows high permeation flux with lower rejection. This can be proved from the membrane structure where increasing number of pores on the membrane surface. However, addition of SDS still gives porous structure towards the membrane.

Rahimpour et al. (2007) in their study found that addition of SDS will give effects towards membrane structure as well as membrane performance. First, it will decline the solvent evaporation rate and cause less interaction between polymer chains due to formation of polymer-surfactant complex.

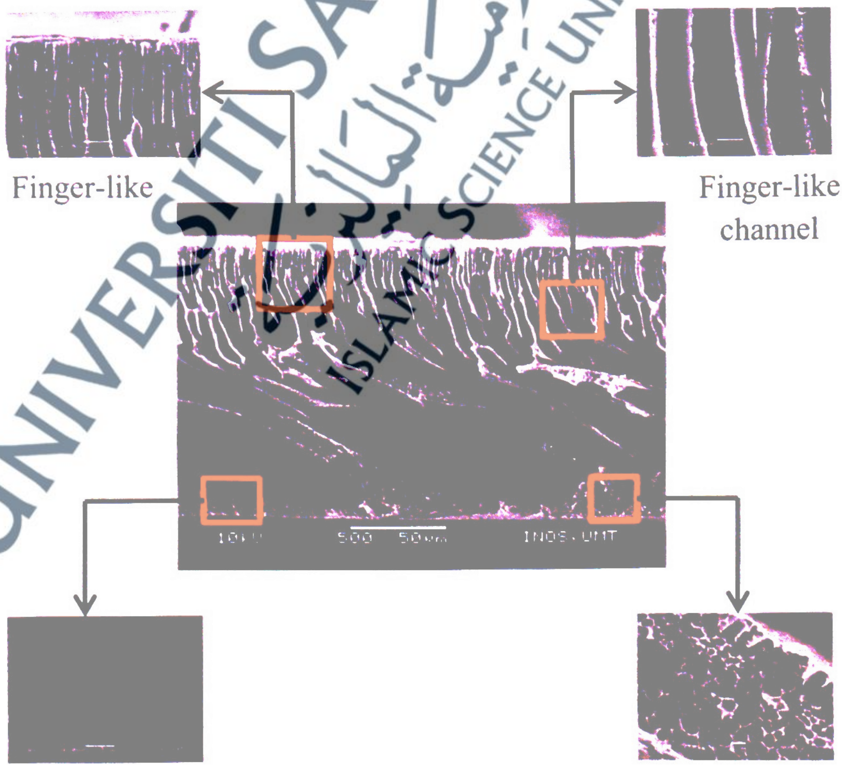
FIGURE 71: Cross-sectional Structures of MPS3 Membrane



There are important parts in surfactant that acts as surface active agents. They are consists of hydrophobic part and hydrophilic part. Surfactants were naming base on charges present in the hydrophilic portion of molecule. Ghaemi et al. (2012) observed that CTAB would give effects on the phase inversion process. Moreover, CTAB will increase the solution thermodynamic instability in the coagulation bath that helps in quick phase demixing and results in increasing of macrovoids formation. In Figure 76, lower polymer concentration has given membrane with thin surface and the pore structure was unorganized. Addition of CTAB in the polymer solution resulted towards formation of macrovoids in the membrane sub-structure. The image was in line with previous research that used CTAB as surfactant in their study. Saedi et al., (2012) found that, addition of an appropriate surfactant leads to induction or suppression of the macrovoids and finger-like pores in the sub-layer. In their study, they also observed their membrane structure consists of large finger-like pores and macrovoids on the membrane sub-layer when they used CTAB as surfactant.

Other than that, formation of microvoids also can be seen at the finger-like pores. Formation of micro-and macrovoids in the membrane structure helps the transportation of solute throughout the membrane. However, some researchers said that, formation micro-and macrovoids was not good in terms of membrane mechanical strength. Besides, lower polymer concentration also contributes in the membrane mechanical strength as well as membrane performance properties. Using PES as polymer materials shows that formation of spongy structure on membrane the sub-layer and at support layer. Other researchers also have found the same evidence where addition of appropriate surfactant will induced or suppressed the large finger-like pores and macrovoids on the membrane sub-layer (Rahimpour et al., 2007).

FIGURE 72: Cross-sectional Structures of MPC1



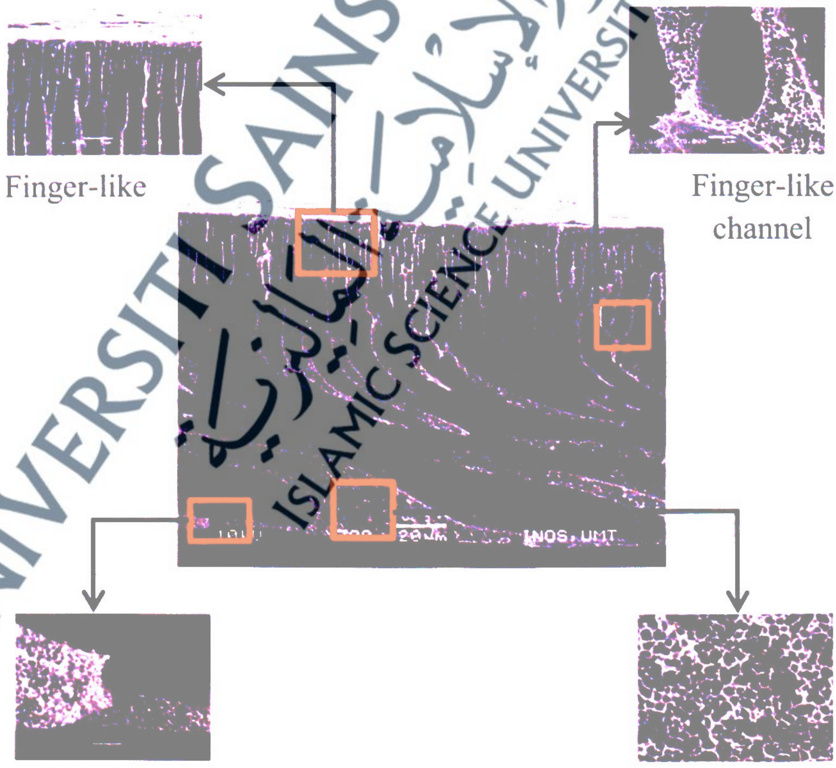
As discussed before, when polymer concentration increase, the PWP will decrease as well as permeation flux and will increase the solution rejection. This is because, increasing polymer concentration will increase the membrane surface and number of pores. Thicker membrane surface will leads to the more selective separation throughout the membrane. Moreover, addition of polymer in the solution also will increase the membrane viscosity that leads to the decreasing of PWP and solution permeation flux. Figure 73 shows the image of MPC2 with polymer concentration of 19wt%.

Asymmetric nanofiltration membranes were characterized in terms of fluxes and rejection. These parameters were aligned with membrane structures that leads to increase or decrease in fluxes and rejection. Experimental data shows, when polymer concentration increase, the flux was decrease and rejection will increase. Furthermore, as polymer concentration increased, the membrane thickness also increases and increases the solution rejection (Ismail & Hassan, 2007). Thus, in this study, polymer concentration always used as parameters for membrane characterization.

Increase polymer concentration up to 19wt% gives membrane with long finger-like structure across the membrane sub-layer. This helps the separation occurs effectively. Addition of CTAB as cationic surfactant in polymer solution gives membrane with large macrovoids on the membrane sub-layer. Increasing polymer concentration also will increase membrane pores on the membrane surface. Spongy sub-structure shows that membrane is more stable for separation process to occur. According to Mulijani et al., addition of CTAB in the polymer solution will increase membrane porosity where formation of macrovoids occurs (Mulijani et al., 2010).

In this study, besides CTAB, SDS was used as anionic surfactant added in the polymer solution. Addition of SDS in the polymer solution gives more porous structure with high brittleness where it is not suitable for continuous membrane process. Addition of CTAB in the polymer solution shows much improvement in the membrane performance as well as membrane structure. As can see on Figure 73, increasing polymer concentration will make the membrane more stable although the pores were not well organized. However, it is still better than addition of SDS in the polymer solution. According to Tsai et al., formation of macrovoids was due to the instantaneous demixing and spongy structure was formed due to delayed demixing (Tsai et al., 2000). This can be concluded that the size of macrovoids will decrease as polymer concentration increase.

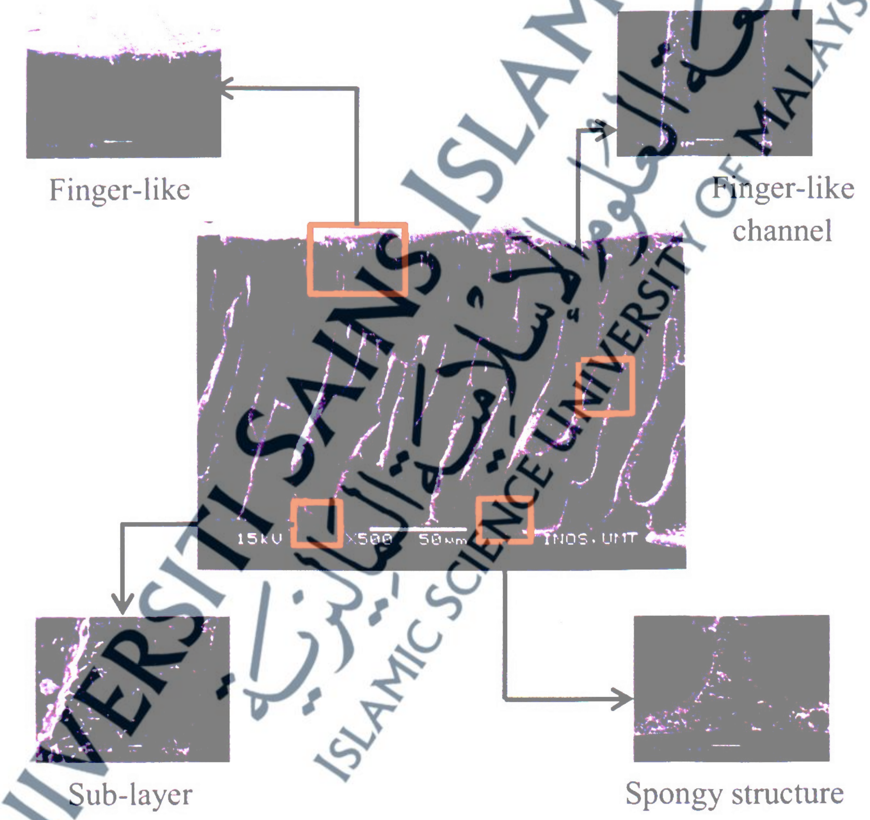
FIGURE 73: Cross-sectional Structures of MPC2 Membrane



Based on the experimental data of membrane performance, increasing polymer concentration up to 21wt% shows promising results in terms of water flux, permeation flux and rejection. 21wt% of polymer concentration shows most of dyes rejection increase up to 99.9%. To be in line with the experimental data, morphological structure of membrane with 21wt% polymer concentration already studied. From Figure 74, MPC3 membrane with polymer concentration 21wt% containing CTAB shows regular asymmetric nanofiltration membrane consists of finger-like pores, sub-layer and spongy support layer. Ghaemi et al., (2012) found that addition of CTAB have some effects on the phase inversion process. In addition, the complex between polymer and surfactant with opposite ionic charges may easily form that causes reduction on interaction between the polymer chains. This phenomena will resulted to delaying the polymer concentration rate and reduces the growth of top-layer thickness thus improved the formation of macrovoids on the membrane sub-layer. High polymer concentration of MPC3 with addition of CTAB causes the formation of long finger-like structure across the membrane sub-layer. This leads to the increasing of rejection using MPC3 membrane where long finger-like structure will facilitate the solution throughout the membrane. Based on the Figure 74 below, increasing polymer solution up to 21wt%, MPC3 possess less formation of macrovoids which membrane can stand for continuous operation. Besides, using PES as polymer material will makes the membrane has spongy structure.

Although some researchers said that addition of CTAB will have membrane with large finger-like pores in sub-layer of membranes, increasing of polymer concentration has shown that it will supress the macrovoids formation on the membrane sub-layer. However, addition of appropriate surfactant as well would affects the membrane structure either supress or induce the large finger-like structure on the membrane sub-layer (Saedi et al., 2012). Other than that, interaction between polymer and surfactant has been studied by several researchers. According to Mansourpanah et al., the complex structure between polymer and surfactant that have opposite ionic charges may be readily formed during the blending of the formulation. The interaction between surfactant and polymers can be understood as binding of the charged surfactant by the polymers (Mansourpanah et al., 2009). This phenomenon causes the significant changes on the membrane performance-properties.

FIGURE 74: Cross-sectional Structures of MPC3 Membrane

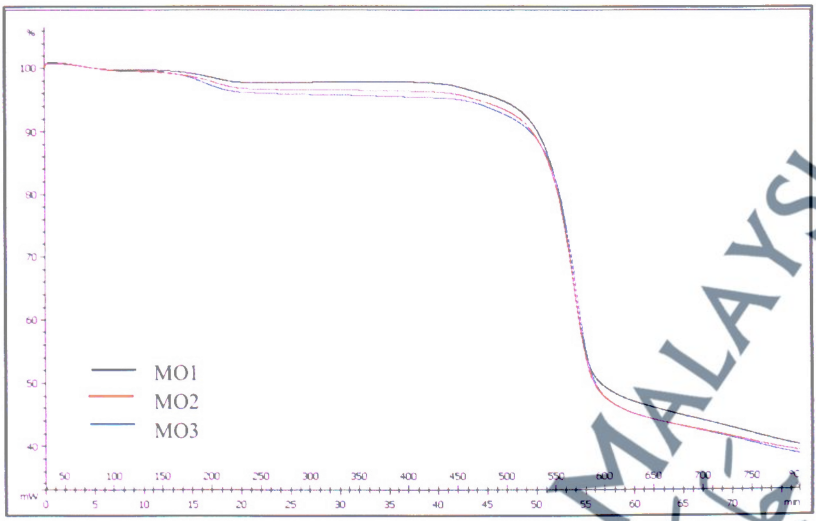


4.5.3 Thermal Analysis

The thermal decomposition behavior of the MO1, MO2 and MO3 membranes at different concentration was studied by TGA. Figure 4.47 shows thermal analysis of nanofiltration membrane at different polymer concentration ranging from 17wt% to 21wt%.

MO1 shows two stages of decomposition between 518.41°C to 558.24°C and 558.24°C to 598.79°C. According to Nasir et al. (2013) the first stage of decomposition from 518.41°C to 558.24°C shows that the amine from PES was decomposed. The weight percentage also decreased from 92.78% to 77.14% and second stage indicates that the decomposition process of PES where the weight percentage gradually decreased from 77.14% to 49.49%. The same trend were observed for MO2 and MO3 where it shows two steps of decomposition where MO2 from 519.37°C to 558.92°C and 558.92°C to 599.48°C due to the same decomposition process. All curves show almost 5% weight loss between 30°C to 500°C which due to loss of water absorbed. In the range of 500°C to 600°C there are almost 50% weight loss has been observed might due to the decomposition of the polymer.

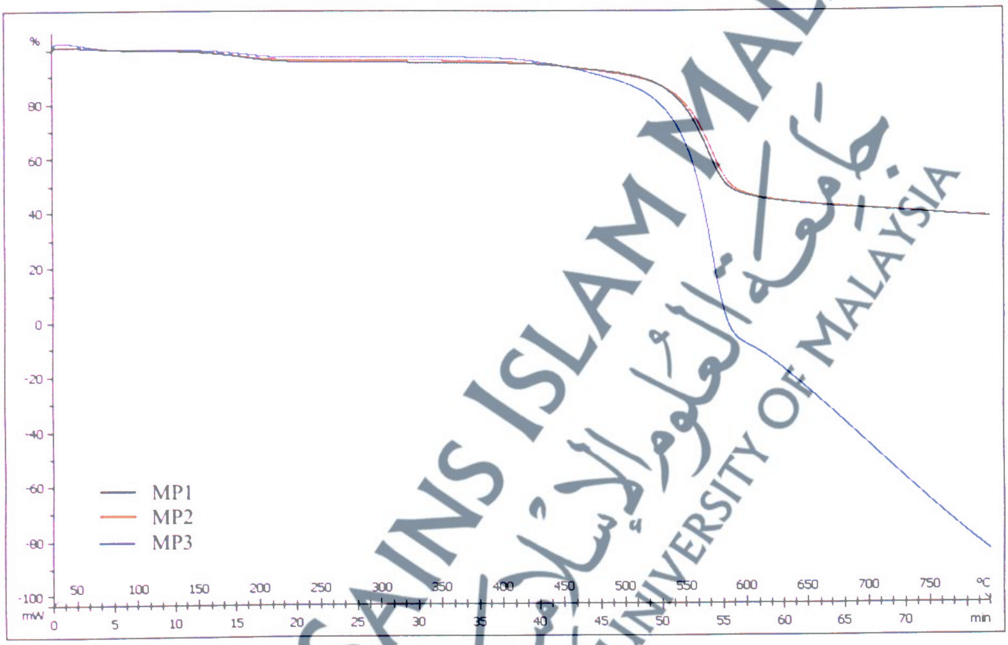
FIGURE 75: TGA Analysis of MO Membrane



Since PES was the polymer materials in this study, Figure 76 shows degradation of materials. Based on the figure above, all curves shows two stages of decomposition occurred during the process. The first stage of degradation shows the decomposition of pure PES at 550°C for all three different polymer concentrations. Decomposition of pure PES in this study was in line with previous experiment where pure PES shows the same range of decomposition. According to Qu et al. (2010) in their study shows that pure PES decomposed at temperature range of between 500°C to 600°C. Author also found in their study two stages of decomposition process occurred.

Figure 80 shows second stage of decomposition occurred due to the PEG as additive added in the polymer solution. Qu et al. (2010) stated that there was interaction between materials in the polymeric membrane during the blending. Decomposition process of PEG occurred at 600°C. MP3 shows significance decomposition process due to increasing of polymer concentration. At 558.96°C, 53.97% of weight loss from MP3 due to the decomposition of PEG. Moreover, MP3 shows significance changes between MP1 and MP2 indicates that the higher polymer concentration used.

FIGURE 76: TGA Analysis of MP Membrane

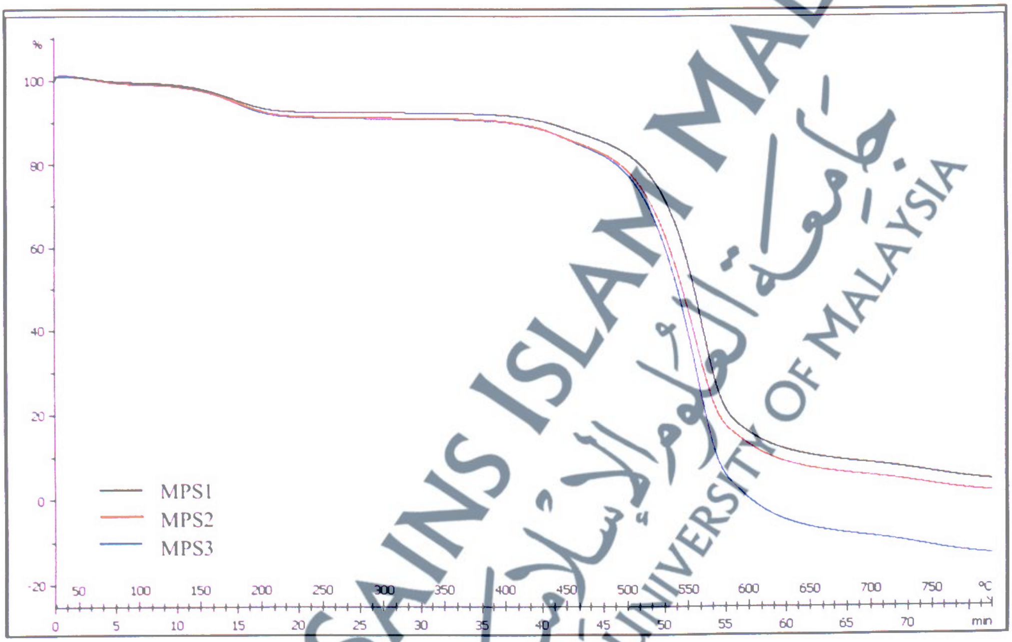


In order to study the effect of addition of surfactant in the polymer solution, TGA analysis has been done to determine the thermal decomposition of surfactant throughout the decomposition process. Figure 81 shows degradation curves of MPS membrane contains anionic surfactant.

All curves of MPS membrane in Figure 81 shows three stages of degradation. First stages occurred at 200°C shows 3-4% loss of water absorbed during the process. At 500°C, decomposition of pure PES process takes places according to the previous research by Qu et al., (2010) that shows that pure PES decomposed between 500°C to

600°C. Increasing of polymer concentration also shows significant effect on the thermal analysis study. Higher polymer concentration degraded less than other polymer concentration. As polymer concentration increase, the weight losses of PES decrease from 76.6% to 60.95% from MPS1 to MPS3 respectively.

FIGURE 77: TGA Analysis of MPS Membrane



Starting 550°C, third degradation occurred due to decomposition process of surfactant. According to Ramimoghadam et al. (2012) in their study shows that surfactant degradation occurs between 30-500°C. Author discussed that there are possibility of partial decomposition of surfactant where at the first stage, there were surfactant decomposed right after dehydration of water but incomplete, and in the last stage the residual surfactant decomposed completely between 500-600°C.

Between SDS and CTAB added as surfactant in the polymer solution, CTAB always shows promising result with high flux and high rejection. Morphological study also shows that, addition of CTAB in the polymer solution produces the best membrane structures. TGA analysis in Figure 82 shows decomposition of MPC membrane. As MPS membrane, MPC membranes also show three stages of degradation occurred during the decomposition process. The first stage occurs at 200-250°C that shows dehydration of water throughout the process. The same trending happen for all types of membranes where at 500°C shows degradation of PES during the process.

For MPS membrane, as polymer concentration increase, the degradation of SDS will decrease. However, for MPC membrane MPC3 shows the higher surfactant degradation of about 79.83% weight loss. Ramimoghadam et al. (2012) in their case also study the effect of CTAB in their research. They stated that there was possibility of partial decomposition of surfactant at the first stage. At 500-600°C which was the third stage shows that completely decomposition of the surfactant. High polymer concentration with CTAB gives promising results of thermal analysis of NFS membrane.

FIGURE 78: TGA Analysis of MPC Membrane