CHAPTER 4
RESULTS AND DISCUSSIONS

In this study, the result obtained from the jar test experiments of the mixing liquid in MBR tank was used to determine the flocculant and the dosage for the subsequent in-line flocculation MBR system. The jar test was also applied to raw septic tank effluent to make an efficiency comparison of three different flocculants. The purpose of the jar test was to provide a quick evaluation of flocculants and to determine their effective dosages. The flocculants employed in this study were PAM with different kind of charges, which include cationic-PAM (C-PAM), anionic-PAM (A-PAM) and nonionic-PAM (Non-PAM). The efficiencies of these three flocculants were evaluated with respect to turbidity removal, TCOD removal and SCOD removal. It should be noted that the appropriate flocculant used for in-line flocculation MBR system was identified as that one which corresponded to high efficiency removal in jar test experiment.

4.1 Preliminary Flocculation Test

4.1.1 Effects of PAMs on MBR mixing liquid

In order to clearly illustrate the effect of various PAMs, the effects were divided into three main categories: turbidity removal, TCOD removal and SCOD removal. The results obtained from jar test experiment for turbidity removal of PAMs are shown in Figure 4.1. The result showed that the percentage of turbidity removal of C-PAM is seen to increase with the PAM dosage. The efficiency of the C-PAM in the removal of turbidity is 34% for the dosage of 0.1 mg/L and up to 90% for 10 mg/L. In case of A-PAM and Non-PAM, it can be observed that the trends of the turbidity removal efficiency of both A-PAM and Non-PAM are different from that obtained from the result of C-PAM. The reduction trends of turbidity with A-PAM and Non-PAM are almost similar and the differences are not significant. It is clear that the flocculation using A-PAM and Non-PAM can improve the turbidity reduction especially at low doses as can be seen that the turbidity was 70% reduced at 1.0 mg/L of A-PAM and 65% reduced at 1.5 mg/L of Non-PAM. Nevertheless, increasing the dosage beyond 1 mg/L of A-PAM and 1.5 mg/L of Non-PAM did not significantly improve the efficiency. This behavior suggests that floc breakup might occurred due to the charge reversal and restabilization when there was excessive or overdosing of flocculant (Boerlage *et al.,* 2003).

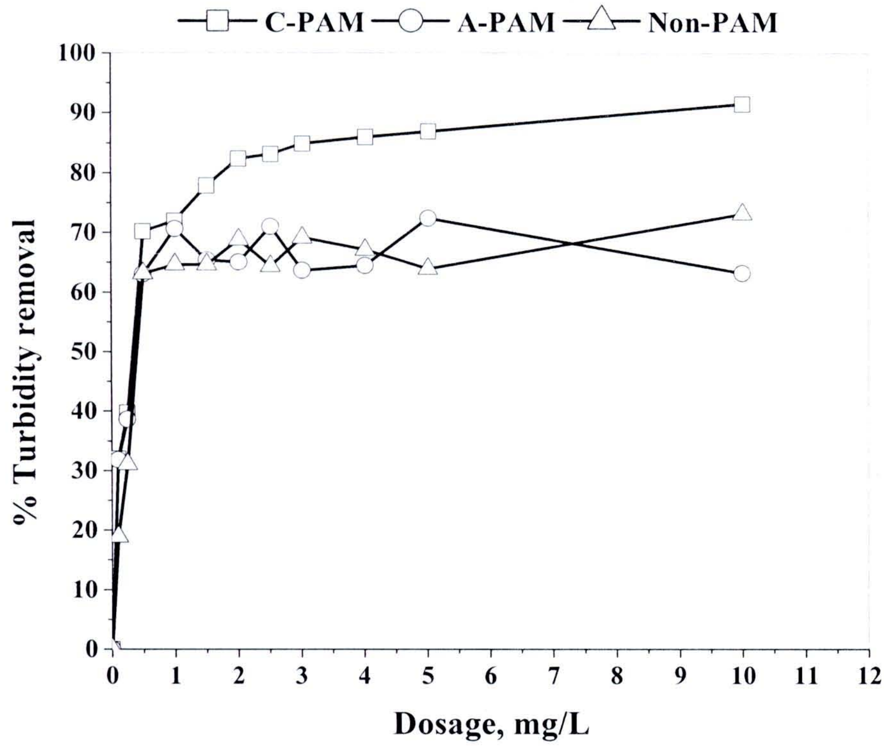

Figure 4.1 The effect of PAMs on turbidity reduction of MBR mxing liquid.

The effect of various PAMs with different dosages on the removal of TCOD and SCOD are shown in Figures 4.2 and 4.3, respectively. It is clear that the removals of TCOD and SCOD increased with PAM dosage, when the C-PAM was used as flocculant. In case of A-PAM and Non-PAM, the removal trends of the TCOD and SCOD are also similar to the turbidity removal, the efficiency did not increase when the PAM dosage increased. These results indicate that the TCOD removal and SCOD removal efficiency were not influenced by A-PAM and Non-PAM. However, the percentage removal of SCOD with A-PAM and Non-PAM were more significant than the removal of TCOD even at the low dosage. It can be seen that the percentage of SCOD removal were more than 60% at 0.5 mg/L for both A-PAM and Non-PAM.

From the results obtained in this study, it could be anticipated that there would be a decrease in fouling potential using PAMs since it reduced the dissolved organic matter, which is known as an important foulant. In addition, it was expected that there would be less fouling in MBR system using C-PAM than using A-PAM and Non-PAM.

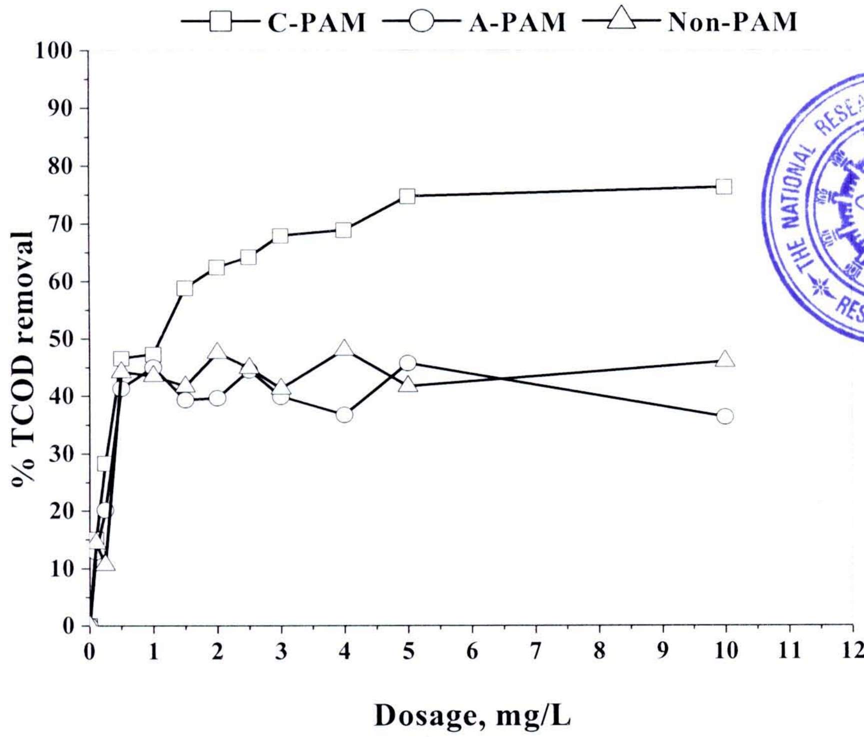

Figure 4.2 The effect of PAMs on TCOD removal of MBR mxing liquid.

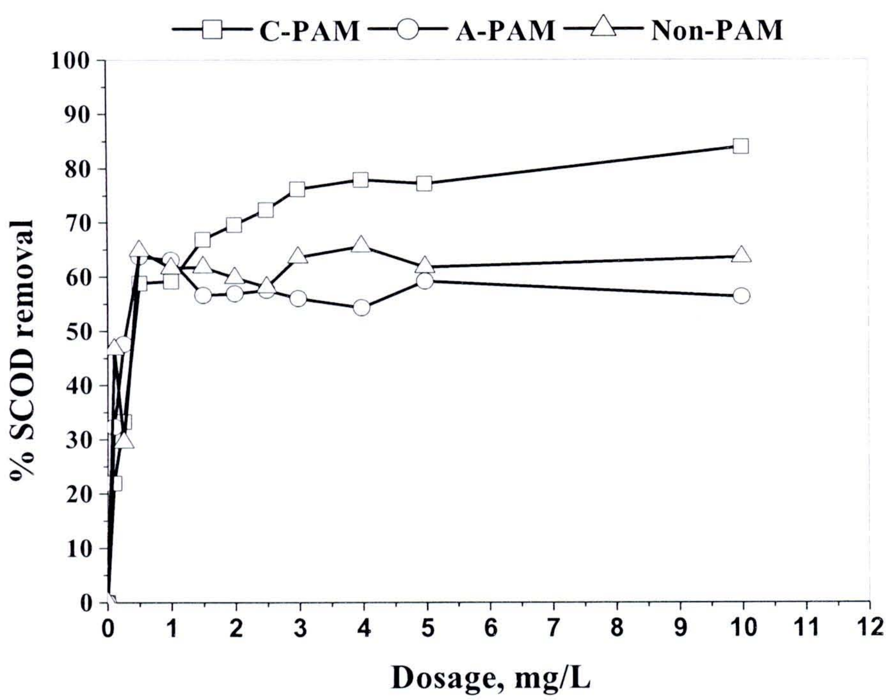

Figure 4.3 The effect of PAMs on SCOD removal of MBR mxing liquid.

4.1.2 Effects of PAMs on Septic tank Effluent

The effect of various PAMs on turbidity removal, TCOD removal and SCOD removal are shown in Figure 4.4, Figure 4.5 and Figure 4.6, respectively. In this case, jar tests were performed by using the septic tank effluent in order to study the effect of various PAMs on turbidity, TCOD and SCOD removal from the raw septic tank effluent. Another purpose was to decide for the kind of flocculant that would be added into the MBR system with the feed wastewater by in-line flocculation. These data were also used to assist in explaining the effect of flocculation on membrane performance. Hence, the effect of various PAMs on the feed wastewater of the in-line flocculation could be evaluated.

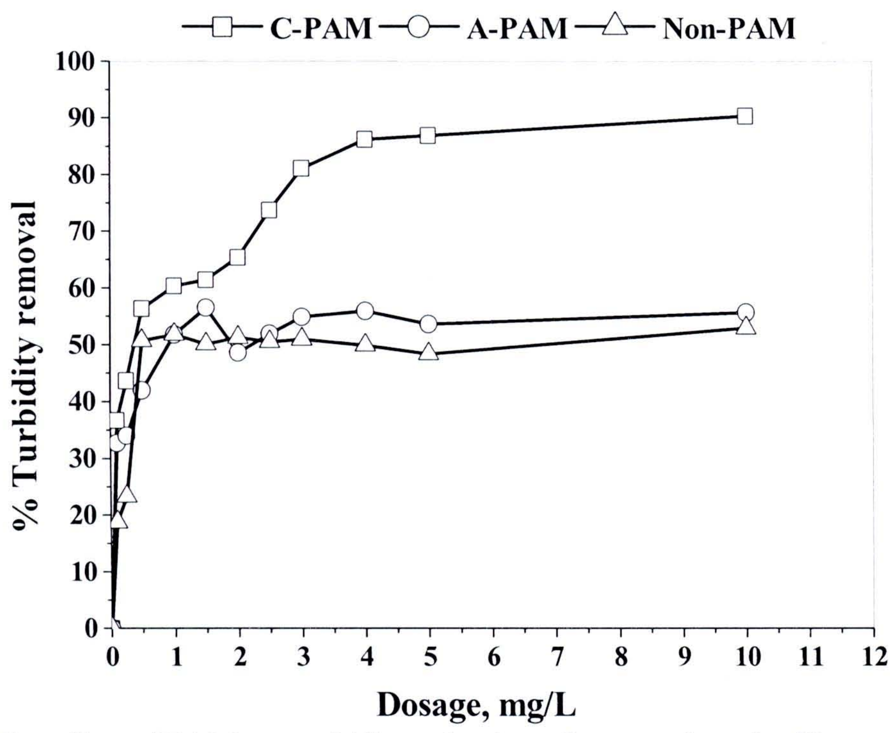

Figure 4.4 The effect of PAMs on turbidity reduction of raw septic tank effluent.

As shown in Figure 4.4, the effects of various PAMs on turbidity removal of raw septic tank effluent were similar to the results obtained from section 4.1.1. The result showed that the percentage of turbidity removal of C-PAM increased when the dosage of C-PAM was increased. It can be seen that the turbidity removal was 35% at 0.1 mg/L and up to 90% at 10 mg/L of C-PAM. In case of A-PAM and Non-PAM the removal efficiency were not as effective as C-PAM in the removal of turbidity. The highest removal of turbidity was only 55% at 1.5 mg/L of A-PAM and 50% at 0.5 mg/L of Non-PAM. In term of TCOD and SCOD removal, the results are shown in Figure 4.5 and Figure 4.6, respectively. It can be observed that the trends of the TCOD and SCOD removal efficiencies of C-PAM increased with dosage increased, although the removal efficiencies were almost steady at high dosage of flocculant. In case of A-PAM and Non-PAM, the removal efficiencies of both PAMs were increased with PAM dosages until 3 mg/L and 4 mg/L, respectively, and then decreased gradually in higher dosages. These results indicated that could affect determining the optimum dosage of these flocculant which could be observed at 3 mg/L for A-PAM and at 4 mg/L for Non-PAM.

As the results, it also indicated that the use of C-PAM showed higher removal efficiencies than A-PAM and Non-PAM. Therefore, C-PAM was chosen to use as a flocculant for subsequent experiments due to its high efficiencies in tubidity, TCOD and SCOD removals.

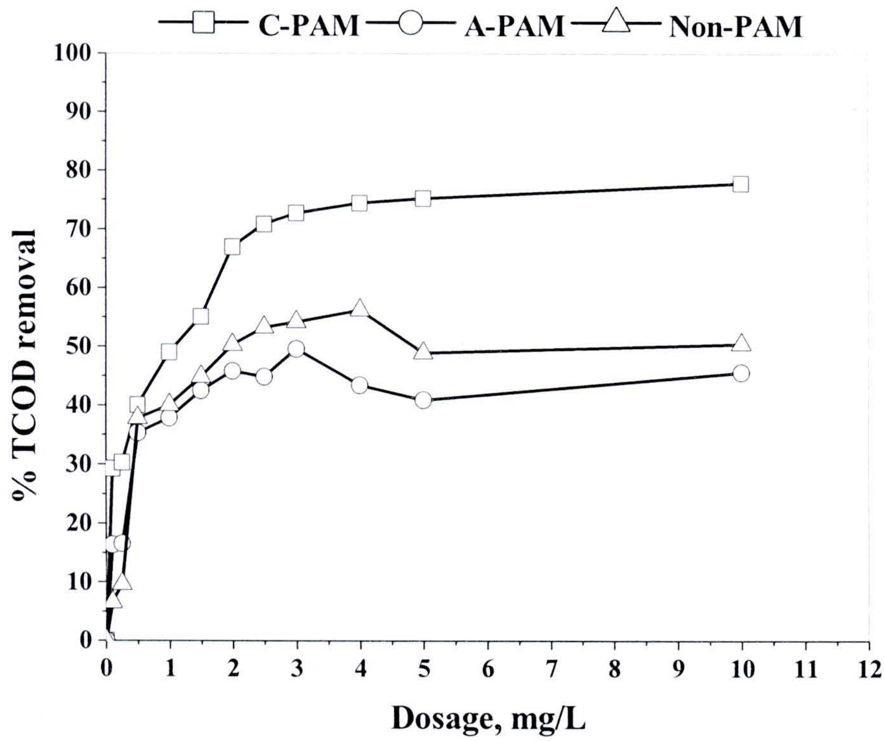

Figure 4.5 The effect of PAMs on TCOD removal of raw septic tank effluent.

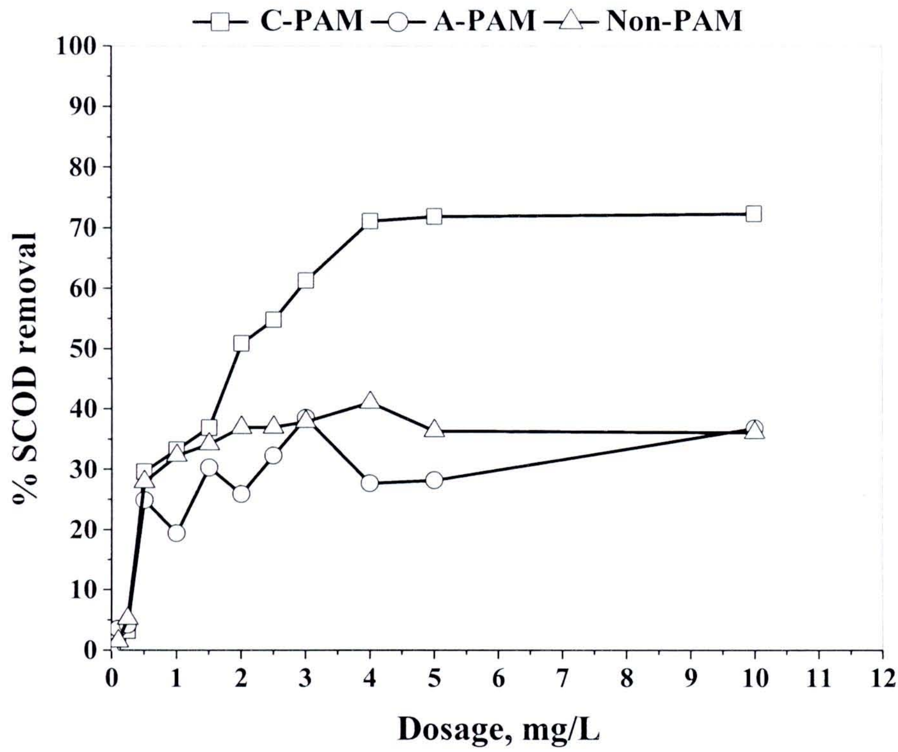

Figure 4.6 The effect of PAMs on SCOD removal of raw septic tank effluent.

4.1.3 The effect of C-PAM at Various Dosages on the MFI

In this section, the C-PAM was chosen to study the effect of flocculated mixing liquid of MBR tank on MFI fouling index. In each experiment, the mixing liquid from MBR tank was flocculated with C-APM at different dosages and then the sample was taken to study the MFI fouling index. The standard MFI were determined from the slope of *t/V* vs. *V* plot using the cake filtration (Equation (3.2)). The *t/V* vs. *V* curves of with and without flocculated of using 0.45 μm membrane test are shown in Figure 4.7 and the curves of using 0.1 μm membrane test are shown in Figure 4.8, respectively. The effect of C-PAM at various dosages on the value of $MFI_{0.45}$ and $MFI_{0.1}$ were studied and are shown in Figure 4.9.

An important observation from Figure 4.7 and 4.8 is the linearity in *t/V* vs. *V* plots for the mixing liquid flocculated with C-PAM of all dosages. A linear plot of *t/V* vs. *V* suggests that cake filtration was the dominant filtration mechanism during the filtration test. However, a wide range of particle sizes exist in mixed liquid, and therefore small particles which close to membrane pore size are expected to block/plug the membrane at the filtration period (complete and/or standard blocking) resulting in a sharp increase in the slope of *t/V* vs. *V* at the beginning of filtration. Eventually a cake is produced on the membrane surface and a linear increase in *t/V* vs. *V* is expected during the cake filtration period. However, no blocking filtration was observed in the *t/V* vs. *V* plots for flocculated mixing liquid induction. The absence of blocking filtration may be due to all particles in the flocculated mixing liquid were larger than 0.45 μm (membrane pore size of this study), and thus standard/complete blocking did not occur.

The effect of C-PAM at various dosages on the values of $MFI_{0.45}$ and $MFI_{0.1}$ are compared and shown in Figure 4.9. The results show that the MFI value decreased when C-PAM dosage increased for both cases. Normally the higher standard MFI value is obtained when the foulants of all sizes are deposited on the surface of the membrane where the large particles occupy a considerable membrane area and the small particles fill the void of the cake formed by larger particles, thereby resulting in a very compact cake with higher specific cake resistance (Javeed *et al.,* 2009). In this study, the flocculation process was used to aggregate colloids and suspended solids in mixing liquid from MBR system which could be affected to membrane pore plugging. In this section, particle size distribution analysis was carried out for the supernatant obtained from the flocculated solution. The results indicated the size of particles in supernatant is in a range of 0.1-10 μm, it is reasonable to suggest that all particles in flocculated solution are larger than 0.1 μm in size, the results as shown in Figure 4.10. When PAM adsorbed organics and small particles are filtered in the standard MFI test, they are not free to deposit on the membrane and hence results in a lower MFI value.

From Figure 4.9, the results show that the values of $MFI_{0.1}$ were lower than the values of $MFI_{0.45}$ except the values of without flocculation and flocculation with 10 mg/L of C-PAM, respectively. Theoretically, the $MFI_{0.1}$ should be higher than $MFI_{0.45}$ since the membrane 0.45 μm does not take into account the fouling effect of colloids (Cho *et al.,* 2002). On the other hand, the membrane pore size 0.1 μm is able to retain all the components responsible for fouling including small molecule (colloids and solutes) that are involved in membrane fouling. Therefore, the value of $MFI_{0.1}$ should be higher than the value of $MFI_{0.45}$. However, the opposite result was obtained from this study. The results suggested that the higher $MFI_{0.45}$ may be due to the size of particles in mixing liquid after flocculation were narrowed to the pore size of membrane used in this study, such particles are easier to be brought to the membrane surface and can plug to the membrane pore. Therefore, this effect resulted in flux decay and higher MFI values for 0.45 μm membrane. In case of the membrane pore size of 0.1 μm, particle sizes after flocculation were larger than the membrane pore size. Hence, the particles deposited on membrane surface could form a denser cake layer than particle plugging. Javeed *et al.* (2009) suggested that the cake on membrane surface acts as a second membrane for filtration. It is commonly accepted that particles smaller or larger than the pore size can be retained by membrane to form a cake layer on the surface. This would explain why filtration had continued for a sufficiently long period of time. In addition, these explanations can be confirmed by the results of particle size distribution retained in supernatant fractions of the flocculated mixing liquid after settling which shows in Figure 4.10 as mentioned as above. The results show that the mean particle size (Figure 4.11) was reduced with increased C-PAM dosages. As the results, it can be suggested that the particles and the size of particles formed by flocculant C-PAM could affect the performance of the filtration.

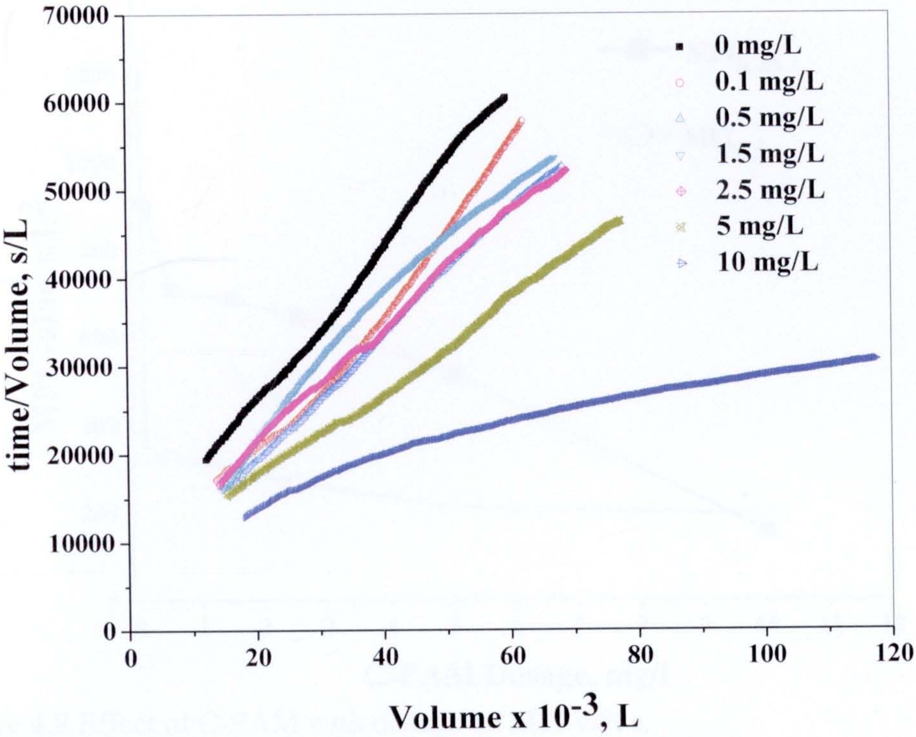

Figure 4.7 t/V vs. V of $MFI_{0.45}$ with different dosage of C-PAM.

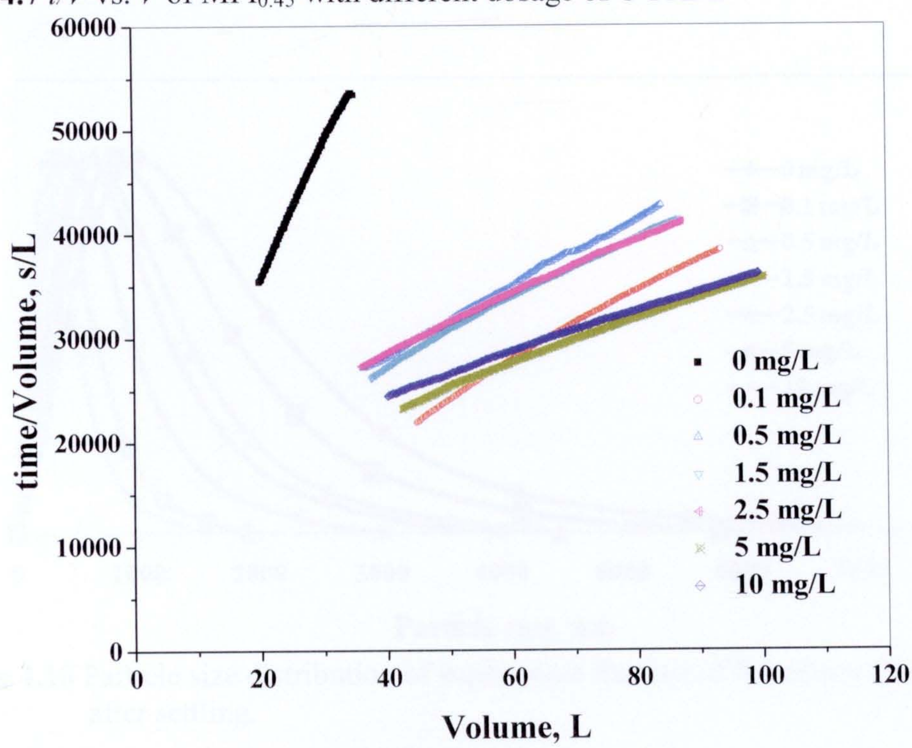

Figure 4.8 t/V vs. V of $MFI_{0.1}$ with different dosage of C-PAM.

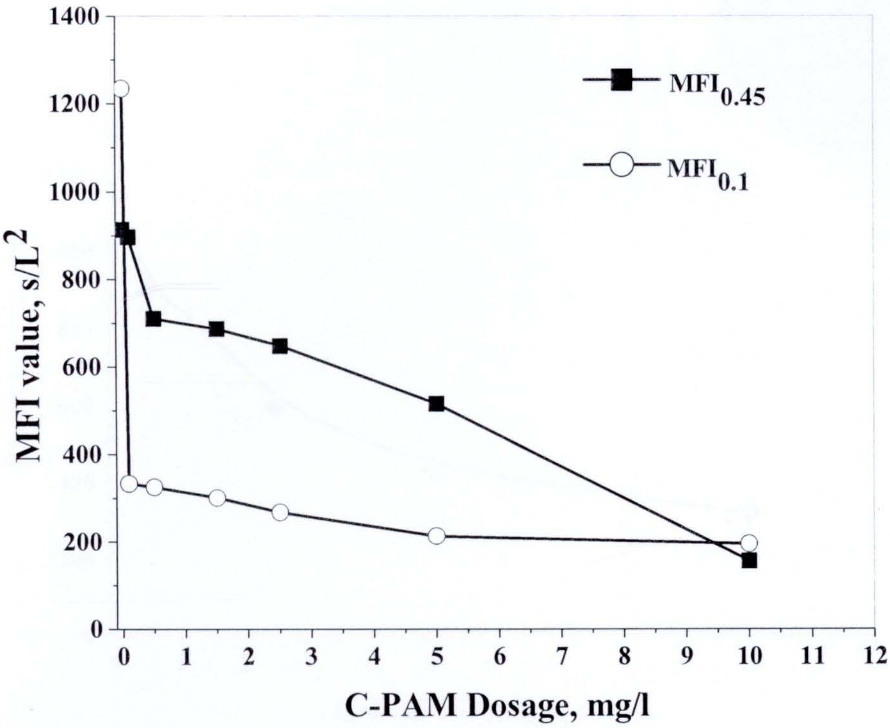

Figure 4.9 Effect of C-PAM with dosage on MFI value.

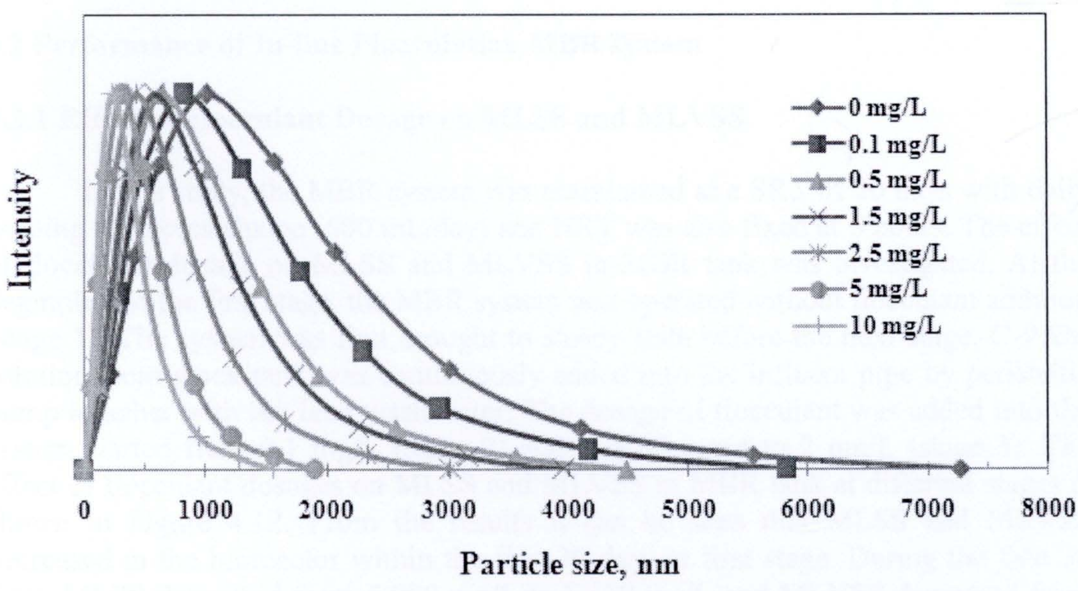

Figure 4.10 Particle size distribution of supernatant fraction of flocculated sludge after settling.

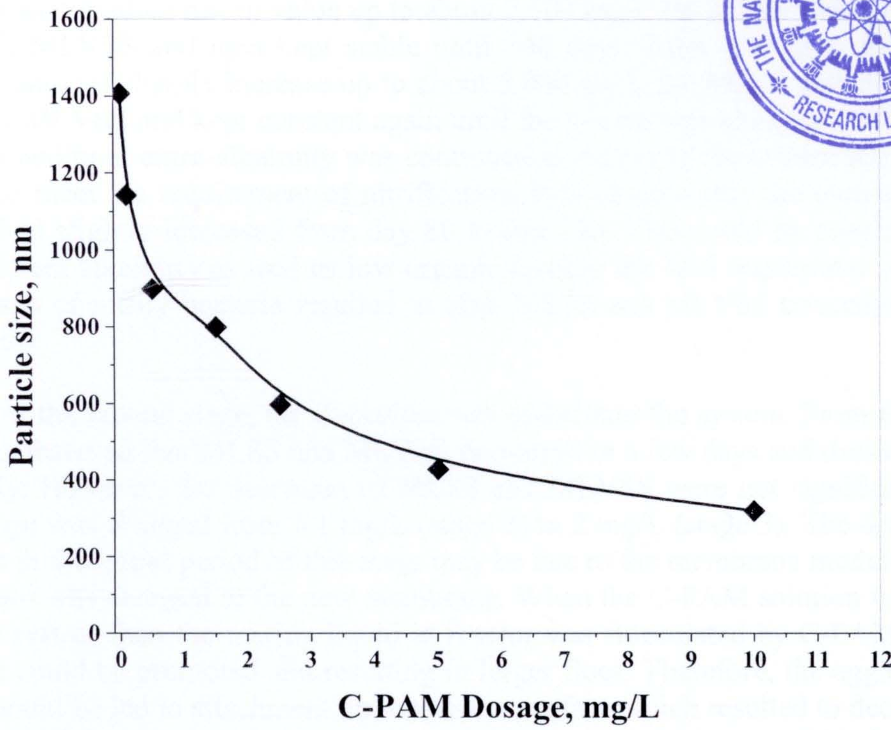

Figure 4.11 The mean of particle size retain in supernatant fraction of flocculated sludge after settling.

4.2 Performance of In-line Flocculation MBR system

4.2.1 Effect of Flocculant Dosage on MLSS and MLVSS

In this study, the MBR system was maintained at a SRT of 20 days with daily wasting of excess sludge (600 mL/day) and HRT was also fixed at 6 hours. The effect of flocculant dosage on MLSS and MLVSS in MBR tank was investigated. At the beginning of the first stage, the MBR system was operated without flocculant addition (stage 1). The system was first brought to steady state before the next stage. C-PAM solution from stock tank was continuously added into the influent pipe by peristaltic pump together with the feed wastewater. The dosage of flocculant was added into the system started from 0.1 mg/L (stage 2) and then changed to 2 mg/L (stage 3). The effect of flocculant dosages on MLSS and MLVSS in MBR tank at different stages is shown in Figure 4.12. From the results it can be seen that MLSS and MLVSS decreased in the bioreactor within the first 30 days at first stage. During the first 30 days, MLSS decreased from 5,000 mg/L to 1,500 mg/L and MLVSS decreased from 4,000 mg/L to 1,200 mg/L. As a phenomenon, it could be from low COD in the feed wastewater during the period. The results of TCOD and SCOD of the feed wastewater are shown in Figure 4.13. It can be seen that the both of TCOD and SCOD of the feed wastewater were between 50 to 150 mg/L and 30 to 120 mg/L, respectively. Hence, it was possibly due to insufficient of carbon source for heterotrophic microbial at the start up of the system and then resulted to decrease in biomass. However, after 30 days MLSS and MLVSS kept at a relative constant until 70 days and then both of them showed gradual rise in value up to about 2,500 mg/L for MLSS and about 2,000 mg/L for MLVSS and then kept stable until 140 days. After 140 days, MLSS and MLVSS showed sharply increase up to about 5,000 mg/L for MLSS and about 4,000 mg/L for MLVSS and kept constant again until the system was changed to the second stage. In addition, extra-alkalinity was continued to supply to the system started from day 50 to meet the requirement of nitrification. It is obvious that the biomass in the reactor had slightly increased from day 80 to day 150. This could be concluded that the sufficient alkalinity as well as low organic level in the feed wastewater can faster the growth of nitrify bacteria resulted in high MLSS and MLVSS concentrations in the reactor.

At the second stage, the flocculant was added into the system. From the result, it can be observed that MLSS and MLVSS decreased in a few days and then increased gradually. However, the decreases of MLSS and MLVSS were not significant when the dosage was changed from 0.1 mg/L (stage 2) to 2 mg/L (stage 3). The decrease of biomass in the initial period of this stage may be due to the membrane module used in the system was changed to the new membrane. When the C-PAM solution was added into the system then the mixing liquid in reactor was flocculated by C-PAM and the biomass could be promoted and resulting in larger flocs. Therefore, the agglomerated sludge could be led to attachment on membrane surface which resulted to decreases of MLSS and MLVSS in mixing liquid. Another suggestion it possibly due to the released chemical (C-PAM) cause some cell to die, but then grew faster in the following days. The faster growth was at least partly because the new membrane allowed for high permeation flux during initial period, which provide more influent nutrients for faster cell growth.

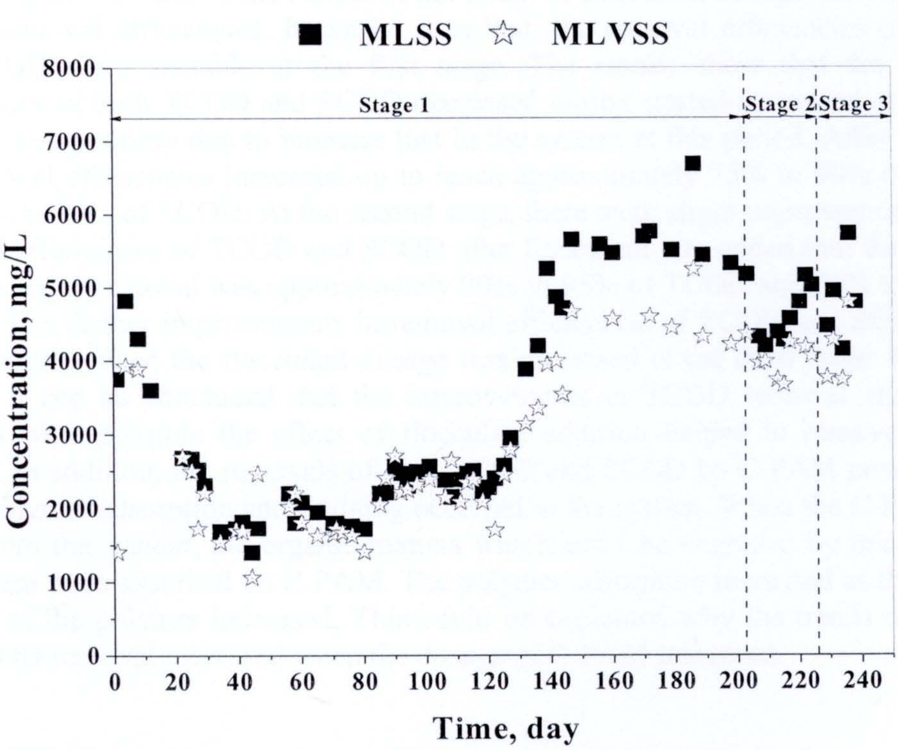

Figure 4.12 The effect of dosages on MLSS and MLVSS in MBR tank.

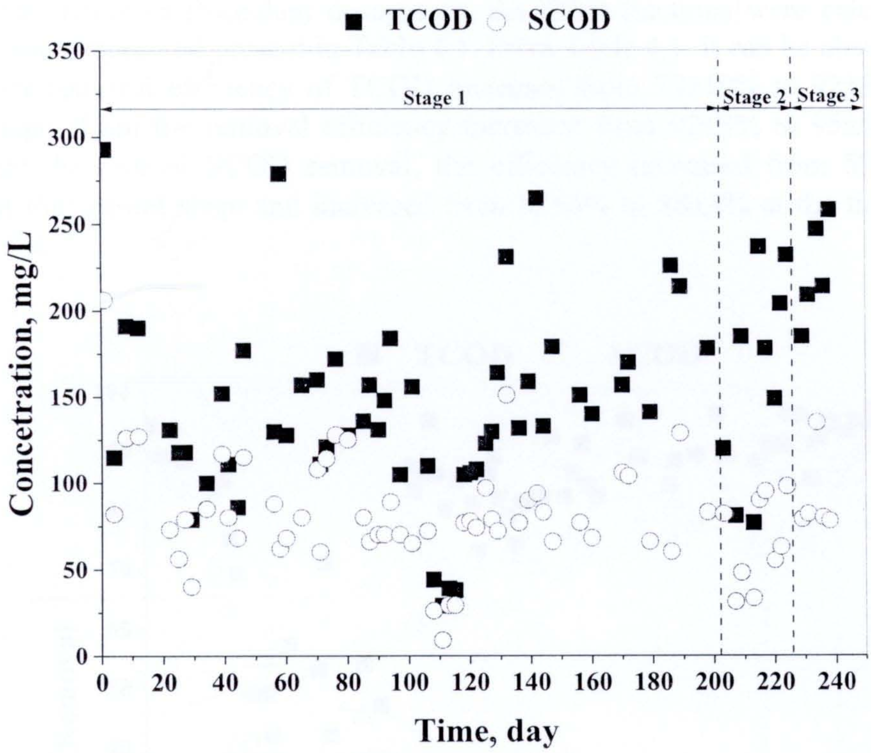

Figure 4.13 TCOD and SCOD of the feed wastewater.

4.2.2 Effect of flocculant dosage on COD removal

Figure 4.14 shows the results of the effect of flocculant dosages on TCOD and SCOD removal efficiencies. It can be seen that, the removal efficiencies of TCOD and SCOD were unstable at the first stage. The results show that the removal efficiencies of both TCOD and SCOD decreased during started-up period at the first stage. It was possibly due to biomass lost in the system at this period. After 80 days, the removal efficiencies increased up to reach approximately 75% to 90% of TCOD and 50% to 90% of SCOD. At the second stage, there were slight improvements in the removal efficiencies of TCOD and SCOD after flocculant was added into the system. The efficiency removal was approximately 90% to 95% of TCOD and 70% to 90% of SCOD. The further improvements in removal efficiencies of TCOD and SCOD were also observed when the flocculant dosage was increased at the third stage. From the results, it can be concluded that the improvements in TCOD removal and SCOD removal were possible the effect of flocculant addition helped to remove organic matters. In addition, the removals of both TCOD and SCOD by C-PAM possibly due to the polymer adsorption and bridging occurred in the system. When the C-PAM was added into the system, the organic matters which can't be degraded by microbial in the system were adsorbed on C-PAM. The polymer adsorption increased as the charge density of the polymer increased. This could be explained why the trends of TCOD and SCOD removal increased when the dosage of C-PAM increased.

The effects of flocculant dosages on the COD fractions were calculated as removal percentages and present in Table 4.1. From Table 4.1, it can be observed that the average removal efficiency of TCOD increased from 75±19% to 92±3% at the second stage. Then the removal efficiency increased from 92±3% to 95±1% at the third stage. In case of SCOD removal, the efficiency increased from 59±26% to 82±6% at the second stage and increased from 82±6% to 88±3% at the third stage, respectively.

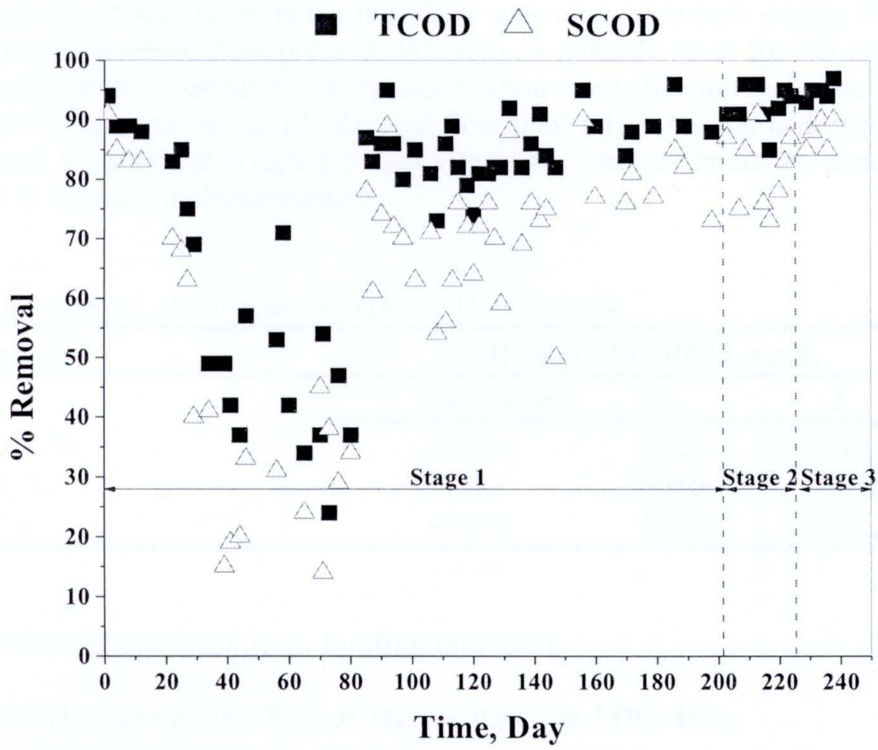

Figure 4.14 The effect of dosages on TCOD and SCOD removal efficiencies.

Table 4.1 Average of COD removal efficiencies at different C-PAM dosages

Dosage, mg/L	TCOD, %	SCOD, %
Non-dosed	75±19	59±26
0.1	92±3	82±6
2	95±1	88±3

4.2.3 Effect of Flocculant Dosage on Nitrogen Removal

Table 4.2 shows the removal efficiencies of NH_4-N, TKN and TN of the in-line flocculation MBR system. It can be seen that the average removal of NH_4-N was 95% at the first stage (without C-PAM) and up to 99% at the second stage and kept the same removal of 99% at the third stage. However, the effect of flocculant addition on TKN removal was not significant, all the removal efficiencies were higher than 99%. In case of TN removal, it can be seen that the removal efficiencies increased with dosage increased. The removal efficiency of TN at each stage was 46%, 59% and 75%, respectively. It should be noted that there was no anoxic tank design for this study to facilitate denitrification process. Normally, a possible route for TN removal can be through bacteria assimilation by nitrification-denitrification procedure. The improvement in the removal of TN through flocculant might be due to larger flocs were promoted by polymer bridging which allows for anoxic conditions inside the floc then led to increase in denitrification.

Table 4.2 The removal efficiencies of NH_4-N, TKN and TN

Parameter	Dosage of C-PAM, mg/L		
	Non-dosed	0.1	2
NH_4-N, %	95±12	99±1	99±1
TKN, %	99±2	99±0.1	99±0.3
TN, %	46±24	59±11	75±10

4.3 Effect of Flocculant Dosage on Fouling potential

4.3.1 Effect of Dosage on total EPS of Mixing liquid in MBR tank

In this study, the main components of EPS to be considered were protein and carbohydrate, and the results of EPS in the suspended biomass are presented in Figure 4.15. It can be seen that, for an in-line flocculation MBR operated at different flocculant dosages, the concentrations of total EPS components decreased with increased dosage. It seems that the total EPS reduction was mainly caused by the protein reduction, the carbohydrate content tended to slightly decrease. This statement implied that there was a protein related biological nitrogen removal in the MBR system. The principal mechanism for the nitrogen removal was assimilation and nitrification-denitrification. It was supposed that protein as organic nitrogen may convert to be inorganic nitrogen. This was known as a nitrification reaction. During the flocculant was added into the system, the large flocs had been promoted by polymer bridging. The agglomerated biomass could allow anoxic condition to happen to the inside of flocs which resulted in a denitrification. Thus, the protein content and EPS production were reduced. This suggestion is supported by increasing of TN removal.

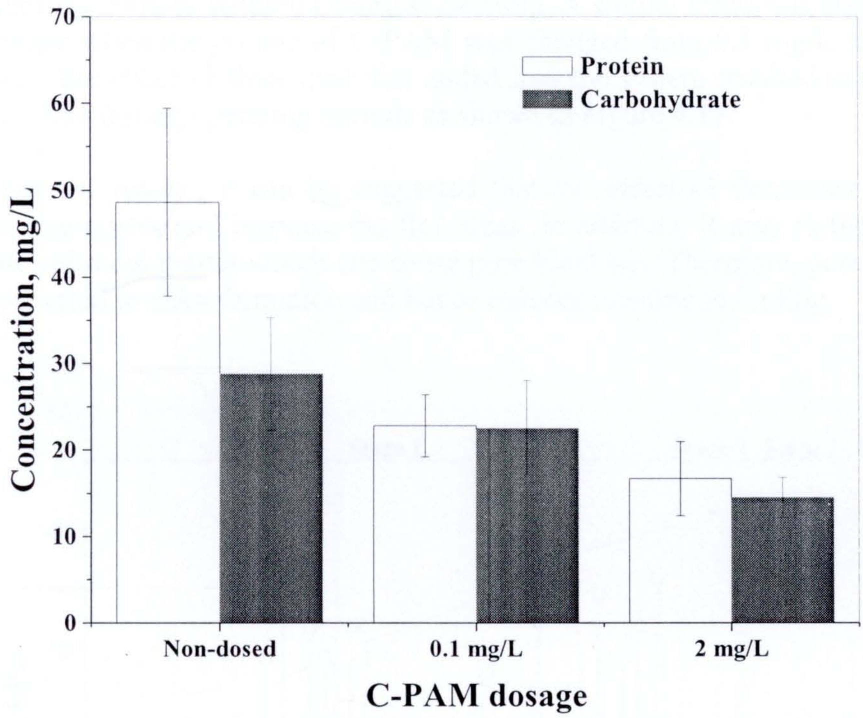

Figure 4.15 Total EPS content of sludge in MBR tank at different dosage of C-PAM.

4.3.2 Results of Transmembrane Pressure and Permeate Flux

In this study, an in-line flocculation MBR system was operated with a constant flux (16.7 L/m^2.h) to maintain a HRT of 6 hours throughout the study. TMP and permeate flux was monitored during the operation to know the effect of membrane fouling on MBR performance. In normal operation, the suction pump was stopped for one minute to allow membrane relaxation after each 5 minutes of filtration. TMP in kPa was registered from the pressure gauge which was connected to the permeate pipe from membrane modules. The permeate flux was consistently monitored to maintain it at desired flux. Figure 4.16 shows the TMP variation with time in different of flocculant dosage additions and the permeate flux is shown in Figure 4.17.

Figure 4.16 shows that TMP increased rapidly with time in exponential manner at the first stage and ranged from 0 to 42 kPa. Behavior of such phenomenon has been recently observed and proposed by Cho and Fane (Cho *et al.,* 2002). They explained the phenomenon of rapid TMP to progressive pore blocking with colloid particles. This eventually leads to local flux increase in remaining open pores and exceed the critical flux of the feed solution resulting in a rapid TMP rise. Additionally, the membrane chemical cleaning (the cleaning procedure was explained in section 3.7) was required when TMP up to 30 kPa. From the result, it can be seen that at the first stage the membrane clogging was very fast in the first stage. The membrane module was cleaned due to frequent fouling within a short period of 7 days. It is interesting to observe that the TMP in the second stage after flocculant was added. The result shows that TMP was slightly increased during the second stage and the membrane can be used longer than 20 days without chemical cleaning. A similar trend was also found at the third stage when the dosage of C-PAM was changed from 0.1 mg/L to 2 mg/L. Furthermore, the effect of flocculant was added into the system resulted in the stable of permeate flux during operating periods as shown in Figure 4.17.

From the results, it can be suggested that the effect of flocculant could be forms fine aggregates and increase the floc sizes. In addition, it may further remove undesirable colloidal matter which can cause pore blockage. Therefore, pore blockage may be converted to cake formation and hence reduces membrane fouling.

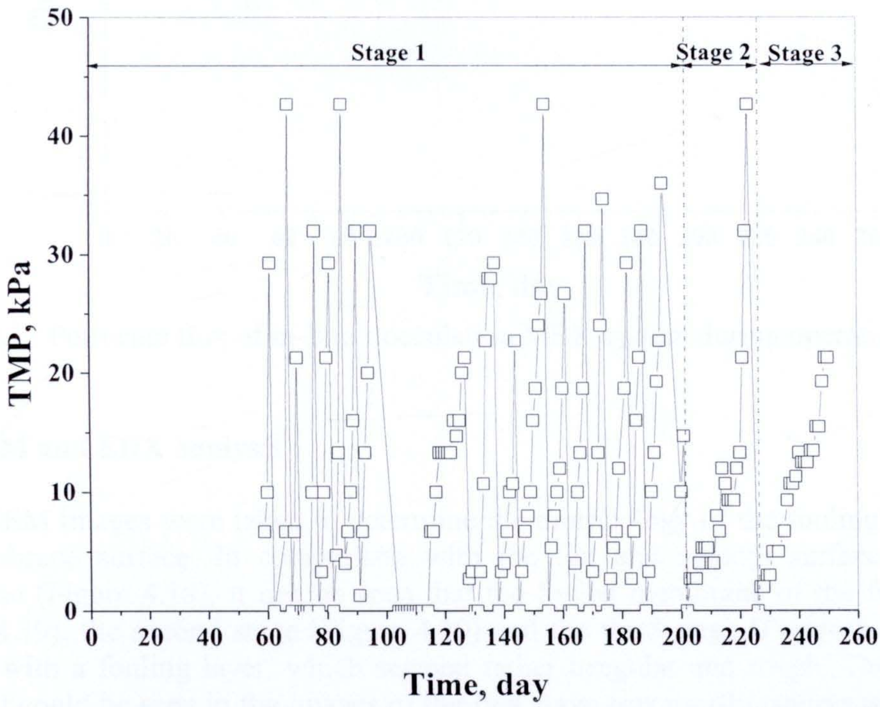

Figure 4.16 TMP variation of in-line flocculation MBR system at different dosage of C-PAM

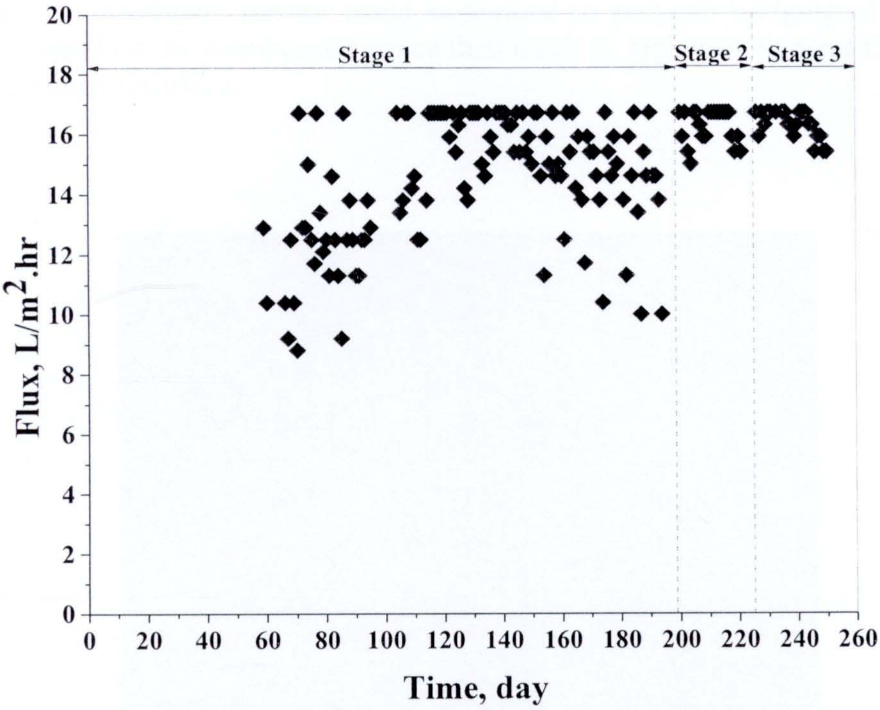

Figure 4.17 Permeate flux of in-line flocculation MBR system during operation.

4.3.3 SEM and EDX analysis

SEM images were taken to determine the morphology of the fouling layer on the membrane surface. In comparison with the flat and smooth surface of new membrane (Figure 4.18), it can be seen that the fouled membrane of the first stage (Figure 4.19), the second stage (Figure 4.20) and the third stage (Figure 4.21) were covered with a fouling layer, which seemed rather irregular and rough. The fouling layer that could be seen in the images of the first stage was mostly compressed of the cake layer. Such surface of fouled membrane it could be formed by deposition and pore blockage of complex materials present in the mixing liquid, which significantly decreased the permeate flux or increase the TMP. In case of the fouled membrane of the second stage and the third stage, it can be seen that the fouling layer on the membrane surface were seemed to be loosely. From the results it can be indicated that the loose layer could be affected by C-PAM addition, which can effectively flocculate or absorb small particles in mixing liquid by polymer bridging. Moreover, the flocculated particles can form a highly porous cake layer and prevent the deposition of particles on the membrane surface, which would enable a constant permeate flux.

The results of EDX spectra of fouled membrane surface at different conditions are shown in Figure 4.22, Figure 4.23, Figure 4.24 and Figure 4.25. The results show that the element of C and N on fouled membrane surface increased when the dosage of C-PAM increased. This may explain the increase of both elements on fouled membrane surface relative to the C-PAM addition. Since, the forms of C-PAM are usually co-polymer of acrylaminde which contains two primary function groups: an amide group ($NH_2C{=}O$) and the vinylic carbon double bond ($CH_2{=}CH$). Hence, the fouling layer on membrane surface could be formed by polymer bridging of the C-PAM and covered on the membrane surface then result in higher of element C and N on fouled membrane surface.

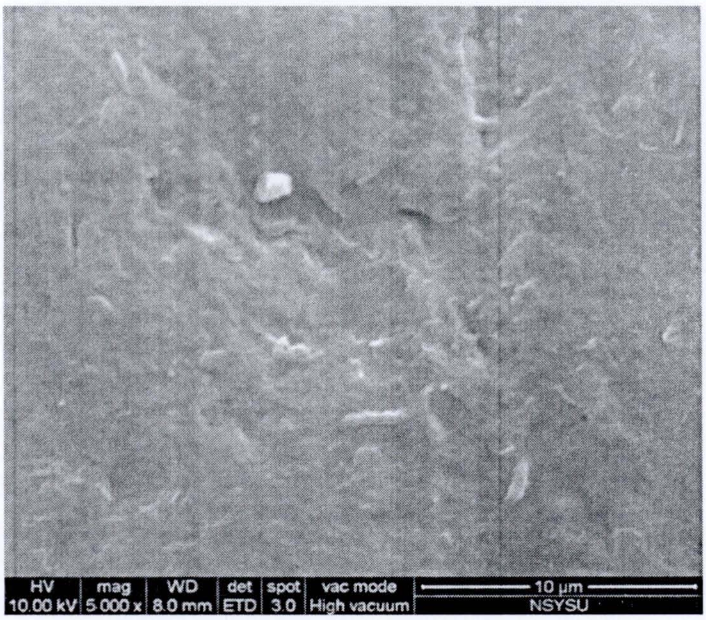

Figure 4.18 SEM photographs of membrane surface (New membrane).

Figure 4.19 SEM photographs of membrane surface at the first stage (Non-dosed).

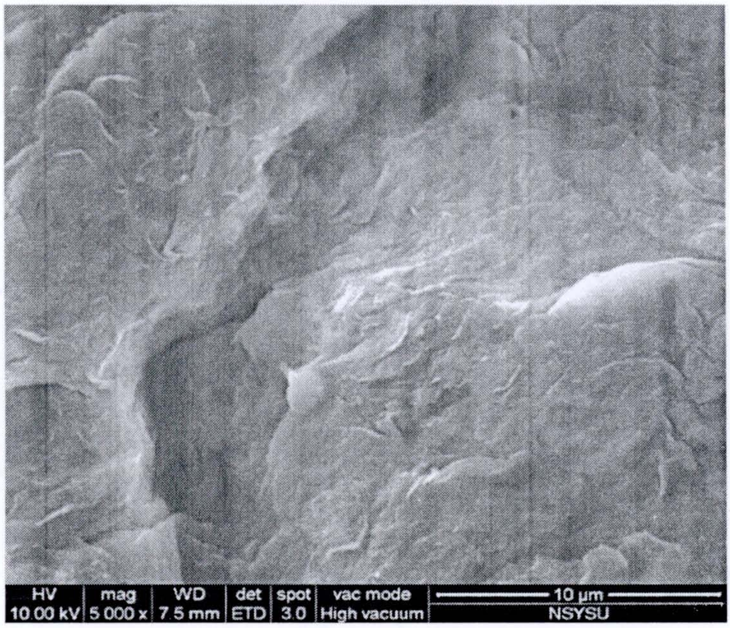

Figure 4.20 SEM photographs of membrane surface at the second stage (0.1 mg/L of C-PAM).

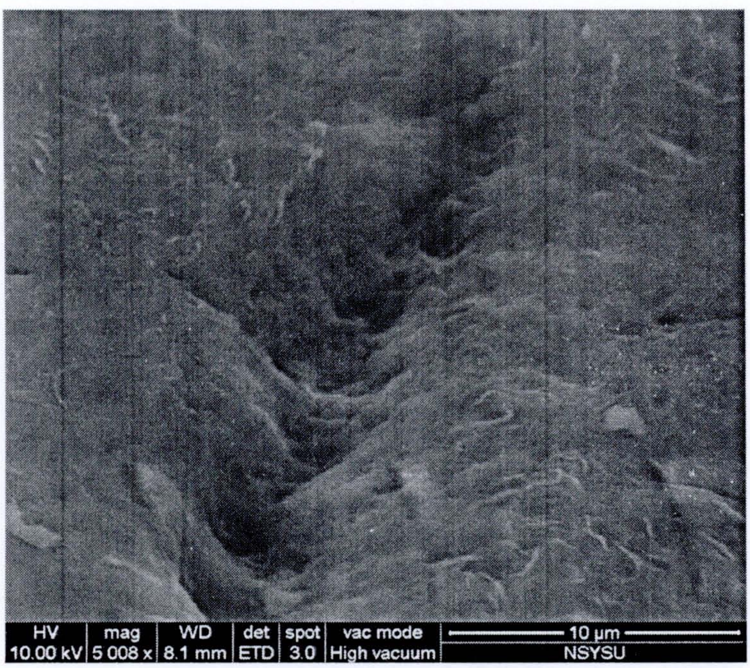

Figure 4.21 SEM photographs of membrane surface at the third stage (2 mg/L of C-PAM).

EDX Quantitative Results		
Element	Weight%	Atomic%
C	62.21	71.81
N	2.11	2.09
O	2.32	2.01
F	32.24	23.53
P	0.79	0.35
Na	0.32	0.20
Cl	0.00	0.00
Totals	100	100

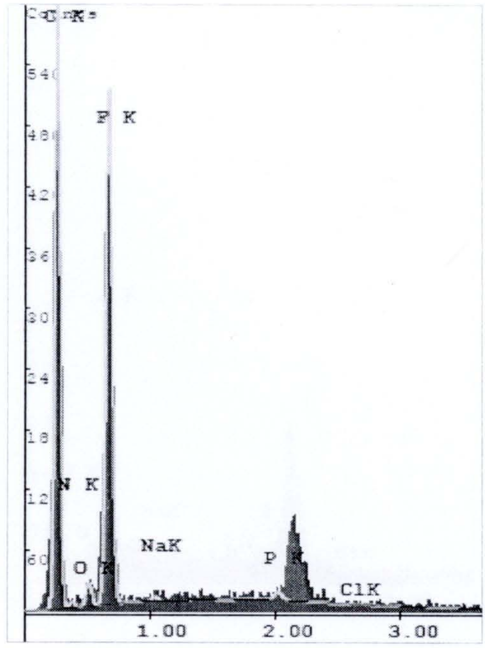

Figure 4.22 EDX of new membrane surface.

EDX Quantitative Results		
Element	Weight%	Atomic%
C	63.45	72.95
N	2.56	2.52
O	2.43	2.1
F	29.58	21.5
P	0.66	0.30
Na	0.61	0.37
Cl	0.71	0.28
Totals	100	100

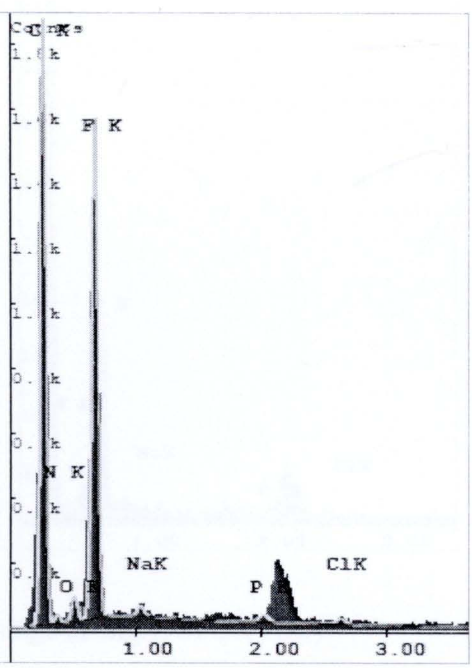

Figure 4.23 EDX of membrane surface at the first stage (Non-dosed).

EDX Quantitative Results		
Element	Weight%	Atomic%
C	66.71	74.81
N	6.22	5.98
O	3.71	3.12
F	21.58	15.3
P	1.78	0.78
Na	0.00	0.00
Cl	0.00	0.00
Totals	100	100

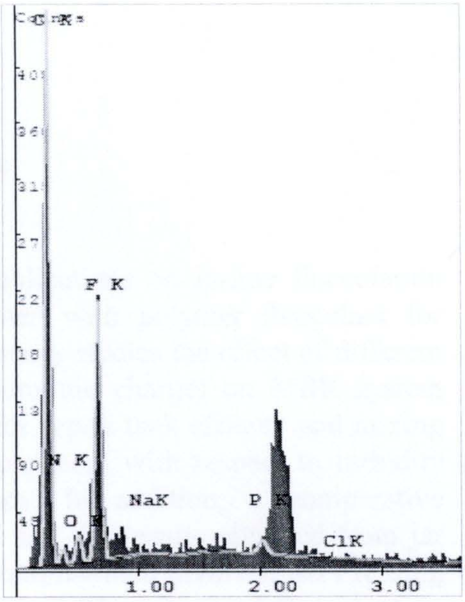

Figure 4.24 EDX of membrane surface at the second stage (0.1 mg/L of C-PAM).

EDX Quantitative Results		
Element	Weight%	Atomic%
C	70.60	77.94
N	4.64	4.39
O	4.69	3.89
F	19.24	13.43
P	0.83	0.35
Na	0.00	0.00
Cl	0.00	0.00
Totals	100	100

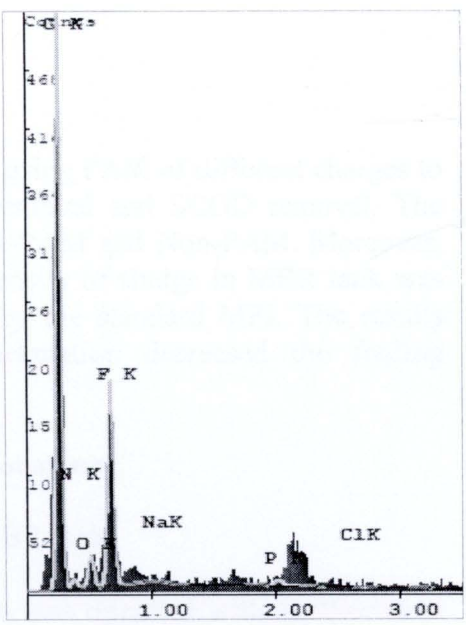

Figure 4.25 EDX of membrane surface at the third stage (2 mg/L of C-PAM).