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Preliminary evaluation of a hydrophilic microfiltration membrane in treating high strength wastewater

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ABSTRACT

In this study, two types of flat sheet membranes were produced and tested in the laboratory. These types of membranes are hydrophilic and hydrophobic flat sheet membranes. The membranes were prepared using a phase-inversion technique. Three synthetic based polymers were used to produce the membrane. These polymers are polysulfone (PSF), polyethylene glycol (PEG), and N-methyl-2-pyrrolidone (NMP). Fourteen polymer solutions were formulated by Response Surface Method and the polymers concentrations used were 15 wt % for PSF, 30–40 wt % for PEG and 45–55 wt % for NMP. The produced membranes were physically characterized by scanning electron microscope (SEM) measurements of their top surface and cross-section images. The produced membranes are used to test the flux value for pure water, synthetic wastewater and raw wastewater using a bench scale unit. Meanwhile, the rejection performance is evaluated using synthetic wastewater and raw wastewater. The pure water flux for the hydrophobic membrane ranges from 78.45 L/m^{2}h to 88.05 L/m^{2}h, while pure water flux for the hydrophilic membrane ranges from 41.92 L/m^{2}h to 52.25 L/m^{2}h. Meanwhile, the COD rejection rate from raw wastewater was greater for the hydrophilic membrane (58%) compared to the hydrophobic membrane (42%). Results obtained from the bench scale unit show a gradual increase in the percentage removal of COD, BOB and TOC with time and it increased from 0 to 75% from the 1st day to the 8th day while only a 20% increment was observed from the 8th day up to the end of the test. But, the percentage removal obtained form hydrophilic membrane is slightly higher than the percentage removal of the hydrophobic membrane.

Keywords: Membrane; Hydrophilic; Hydrophobic; Production; Testing

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1. Introduction

The last two decades witnessed the introduction of advanced treatment processes including the membrane bioreactor (MBR). The utilization of MBR has begun to be considered as an alternative to conventional treatment. This is because MBR provides many advantages compared with conventional treatment such as relatively smaller footprint, complete removal of solids and the ability to achieve higher effluent quality. The disadvantage of the MBR is flux decline, due to membrane fouling. Visvanathan et al. [1] classified the membrane types.

Flat sheet membrane is a microporous plastic film with specific pore size ratings which can retain any particles larger than their pore size primarily by surface capture. A hydrophobic flat sheet membrane has higher strength

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than a hydrophilic flat sheet membrane but the water will not easily permeate through a hydrophobic membrane and it adsorbs high molecular weight components and its rate of fouling is very high compared to the hydrophilic membrane. A hydrophilic polymer can be added to a hydrophobic membrane to form a higher permeability than that of the hydrophilic membrane. Membranes have the ability to remove organic and inorganic substances, micro-pollutants such as pathogens, bacteria, and some harmful chemicals which cannot be removed by conventional water and wastewater treatment systems. The flexibility of membrane usage in treating wastewater was highlighted by Chang and Fane [2] and Altinkaya [3].

Cho and Lee [4] highlighted that fouling is the main problem which limits the usage of membranes in microfiltration particularly if the membrane is manufactured from hydrophobic polymers. Microfiltration is a term used to describe the removal of particulates from a feed stream [5]. Then the aim of microfiltration is primarily to separate the particles from liquids. The cut-offs of the porous membranes used for this purpose are normally between 0.1 and 10 μm [6]. However, membranes with cut-offs between 0.02 and 20 μm are also referred to in microfiltration, depending on the kind of solid matters to be separated and the aim of the membrane process. The main processes that cause membrane fouling are adsorption, adhesion, scaling, and polymerisation. Fouling occurs due to a combination of chemical and physical interactions. Membrane fouling is complex and it is not possible to localize and define it clearly because of the multiple interactions of various fouling constituents found in the feed and between the constituents and the membrane surface [7]. Al-Malack [8] studied the impact of HRT on membrane performance.

In this study, the production and testing methods of high hydrophilicity asymmetry microporous membranes are discussed. The production method used is called the phase inversion technique and it is the most world widely used technique. Before testing, the characteristics of the produced membranes were determined using scanning electron microscope (SEM). This served the purpose of examining the pore size and pore size distribution of the produced membranes (hydrophilic and hydrophobic). Based on the flux (mainly COD, BOD and TOS) test using synthetic wastewater, the most optimum composition of membranes are decided. Also, the produced membranes are tested to determine their efficiency in treating actual wastewater.

2. Material and methods

2.1. Materials

Polysulfone (PSF) which was purchased from local suppliers is used in the membranes production. The selection of PSF as a proper polymeric material for membrane preparation (by wet phase separation) is based on its mechanical and thermal stability, chemical resistance in acidic and alkaline media, solubility with some water miscible solvents and also to its availability in the market. Polyethylene glycol (PEG) was used in the experiment as an additive polymer to enhance the hydrophilicity of the produced membrane. This will increase the penetration property of the membrane. Meanwhile, N-methyl-2-pyrrolidone (NMP) was used as a solvent because of its strong interaction with polymer and miscibility with water. Also, it is a good solvent for polysulfone without further purification. Both of these materials were purchased from local suppliers.

2.2. Hydrophilic membrane preparation

2.2.1. Mixing

By using a 500 ml beaker, the mixing process was carried out on the Vision Brand hot plate and was stirred by magnetic stirrer KMC-130 SH. The objective of heating and stirring was to increase the dissolution rate of PSF in NMP.

First of all, PSF and NMP were mixed first and it was heated to 100°C while continuously stirring. The full volume of NMP was added into the 500 ml beaker followed by a portion of the total PSF needed. This is because NMP which acts as a solvent effectively dissolves the solid PSF into liquid form for a better mixing process. Other than that, the density of PEG was higher, and it is very difficult to mix with PSF if it is still in a solid form. A phenomenon was observed where the PSF pellets began to stick together as soon as the PEG was introduced into the solution, in the situation where the three elements were mixed together simultaneously. Consequently, an unsmooth mixing process occurred because of the sticky PSF pellets blocking the stirring path of the stirrer in the beaker. After the PSF was fully dissolved in the form of liquid, the liquid was cooled down to 35°C. Then, the PEG was added to enhance the hydrophilicity of the solution. The solution was heated again for 30 min until a homogenous solution was obtained. It was found that the whole mixing process took between 5–6 h. By using the respond surface method of Design Expect Software, 14 combinations of PSF/PEG/NMP solution were prepared according to their range as shown in Table 1. Kaiser et al. [9] reported that morphology of the cross section of the PSF porous layers prepared from the PSF/DMA (N,N-dimethyl acetamide) solution with 25 wt% of polymer showed the macrovoid area and the area of the cellular structure.

2.2.2. Cooling

The cooling process was carried out by covering the upper open end of the beaker with aluminium foil, and letting the warm homogenous polymer solution fully degassed and cooled at room temperature for overnight.

Table 1
Composition for the 14 runs hydrophilic membrane

Run	PSF wt%	PEG wt%	NMP wt%	Run	PSF wt%	PEG wt%	NMP wt%
1	15.00	35.00	50.00	8	15.00	35.00	50.00
2	15.00	35.00	50.00	9	15.00	42.07	50.00
3	15.00	40.00	45.00	10	15.00	35.00	50.00
4	15.00	35.00	50.00	11	15.00	35.00	42.93
5	15.00	30.00	55.00	12	15.00	35.00	50.00
6	15.00	40.00	55.00	13	15.00	27.93	50.00
7	15.00	30.00	45.00	14	15.00	35.00	57.07

The phenomenon was observed where the surface of the solution experienced a phase-separation process when the aluminium foil was closed improperly. This could be due to water vapour which would enter the beaker and react with the surface of the solution.

2.2.3. Casting

The membrane casting process was carried out manually by pouring the completely homogenous polymer solution on a flat glass plate of the casting tool. Then, the tool casting knife was moved over the glass plate to get a thin film membrane. The casting duration wa fixed to 10 s and throughout this duration, the entire polymer solution was completely spread on the glass plate which was supported by a steel plate. After that, the produced thin film was exposed to air for 10 s.

2.2.4. Quenching

The glass plate was carefully and slowly immersed into a water bath with slanted orientation. As soon as it was immersed into the water bath, the phase-separation process started where NMP diffused out and water diffused into the thin film. In less than 2 min time, a white colour membrane was formed and it was detached from the glass plate automatically. By setting the temperature at 90°C, the newly produced membrane was kept in the water bath overnight to make sure that the phase-separation process was fully completed.

2.2.5. Immersing

As shown in Fig. 1, the membranes were immersed into a container filled with distilled water. The purpose was to flush away the possible NMP still left on the surfaces of the membranes. This process was carried out at room temperature. To ensure that the excessive NMP was completely removed, the membranes were kept in distilled water overnight. Note that the membranes had to be covered up to avoid small particles polluting the water.

Fig. 1. Immersing of membranes in distilled water.

2.2.6. Membrane drying

After a lengthy overnight immersion in distilled water, the membranes were lifted out. By setting the temperature to 60°C, the membranes were dried in an oven for overnight by placing them onto an aluminium foil as shown in Fig. 2. The purpose of drying was to remove excessive water content in the membranes before they were used and tested. The dried membranes were kept in a desiccator until further usage.

3. Results and discussion

3.1. Membrane morphologies

In order to observe the surface morphologies of the prepared membranes, samples from the membranes were observed by using a scanning electron microscopy (SEM) after gold coating. The top surfaces and cross-sections for the hydrophilic and hydrophobic membranes are shown in Fig. 3 and Fig. 4, respectively.

The pore sizes of the hydrophobic membrane were larger than that of the hydrophilic one. Since both types of membranes were produced using the same percentage

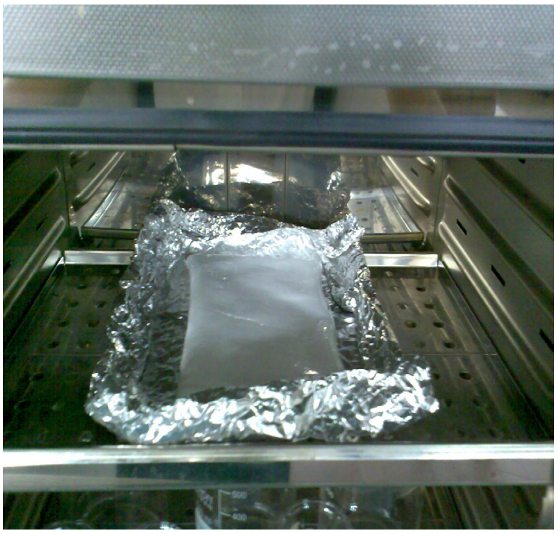

Fig. 2. Membrane placed on an aluminium foil in the oven.

of PSF (15%), the difference in pore sizes can be related to the action of the PEG additive which has been added during the preparation process of the hydrophilic membrane. This could be explained by the filling up of voids between PSF molecules by PEG molecules. On the other hand, the hydrophobic membrane was prepared only by PSF and DMF (solvent). It was found that the solution for the hydrophilic membrane was more turbid when compared to the hydrophobic membrane. So, the average pore size of the hydrophilic membrane was smaller. Other than that, it was found that the more PEG was added, the bigger the pore sizes would be. It was observed that the viscosity of the casting dope was higher if more PEG was added. The casting solution became thermodynamically less stable when more PEG was added, which suggests that PEG additive could play a major role in the membrane formation process as a macrovoid suppressor and giving the membrane a hydrophilic character [10], thus causing bigger pore sizes on the surface of the mem-

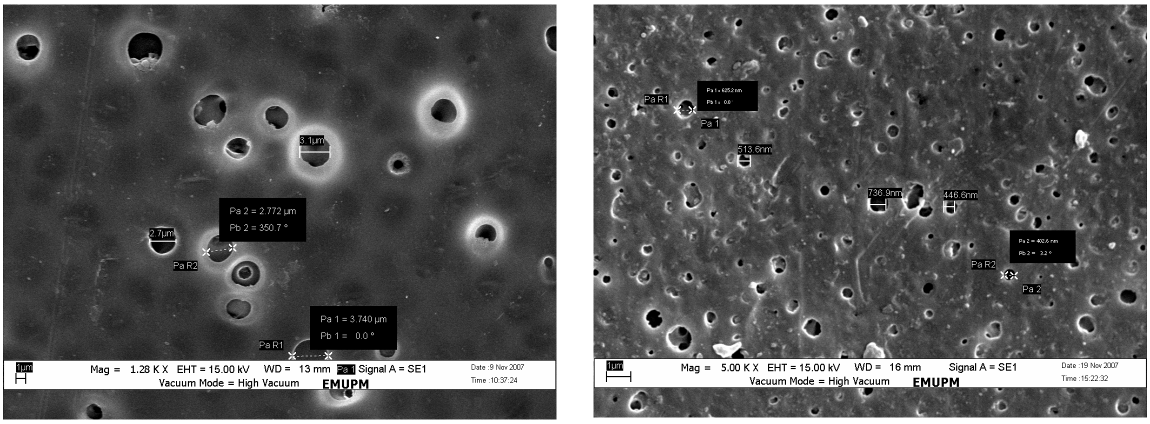

Fig. 3. SEM image for the top surface of the hydrophobic PSF membrane with the composition PSF/DMF = 15/85 wt% with 2000 magnification (left) and SEM image for the top surface of optimizing or Run 2 hydrophilic PSF and PEG membrane with the composition PSF/PEG/DMF = 15/35/50 wt% with 5000 magnification (right).

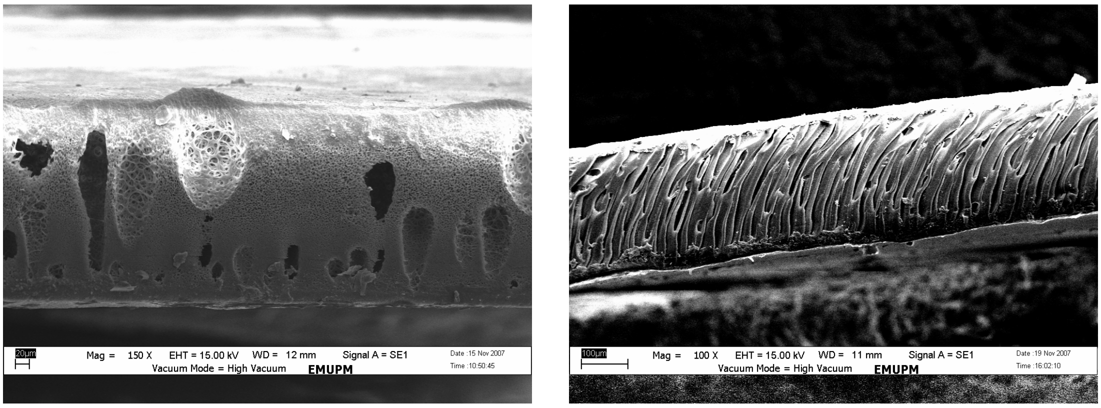

Fig. 4. SEM image shows the spongy dense structure in the cross section of the hydrophobic PSF membrane with the composition PSF/DMF = 15/ 85 wt% with 2000 magnification (left) and SEM image shows the finger like structure in the cross section of the optimizing hydrophilic PSF and PEG membrane with the composition PSF/PEG/DMF = 15/35/50 wt% with 5000 magnification (right).

brane. Meanwhile, it was found that higher addition of NMP resulted in larger pore sizes of the membrane. As mentioned earlier, NMP is a strong solvent for PSF. More NMP would decrease the viscosity of the casting dope, thus increasing the diffusion rate of water in and NMP out from the casting thin film, leading to lower polymer concentration at the water-casting film contact surface. Therefore, higher porosity of the membrane was obtained if more NMP was added.

3.2. Flux and hydraulic retention time

The produced membranes were tested first using distilled water with a pressure of 1.5 bar. The system was run as cross-flow filtration. The time interval was set at 5 min, when water was continuously collected using a 50 ml beaker. Fig. 5 shows the variation of the flux with the time.

Also, the membranes were tested using synthetic wastewater and the variation of the flux is shown in Fig. 6. A drop in the flux of synthetic wastewater was observed, while such a drop was not observed with the flux of distilled water. This could be related to the fact that synthetic wastewater carried larger particles compared with the size of particles for distilled water. Thus, particles which were bigger than the membrane pore size would cause clogging of the membrane surface and result in decreasing of flux with time.

The results show that the flux for synthetic wastewater tends to decrease at a faster rate, particularly at the beginning of the test. This is attributed to the fact that the clogging of membrane pores was faster at the beginning of the test. This phenomenon continued to occur until the pores of the second layer started to clog. At this level, there were not many changes in the flux rate.

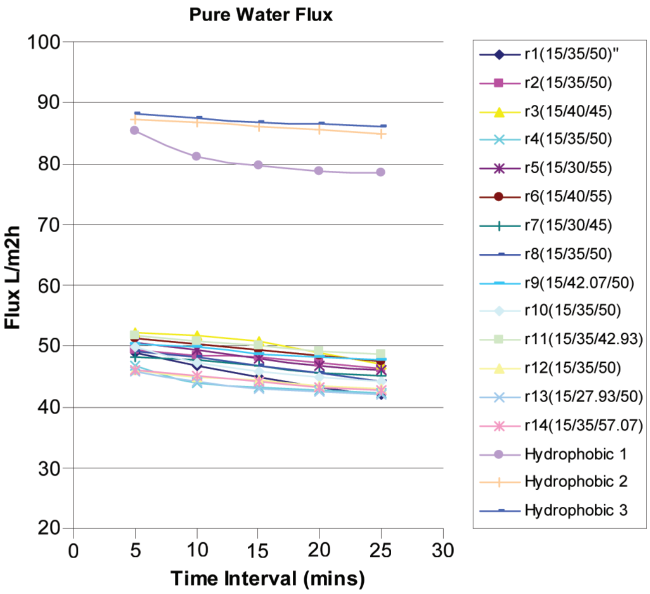

Fig. 5. Variation of the flux for distilled water with time.

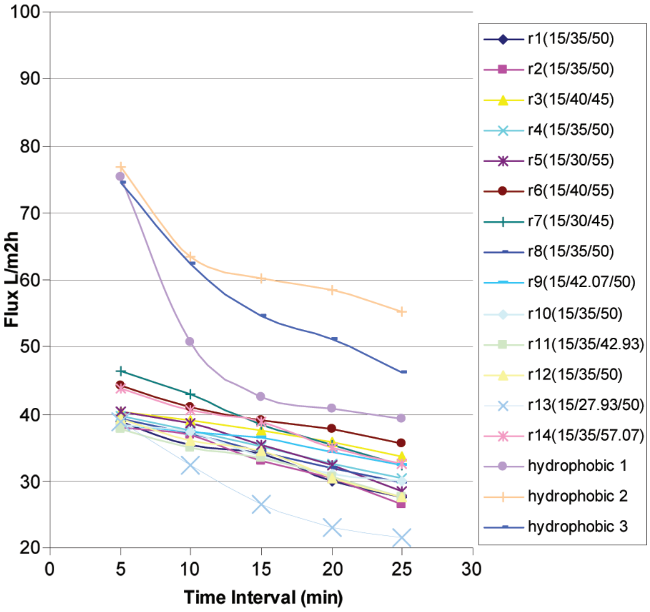

Fig. 6. Plotting of synthetic wastewater flux value for different membranes.

Natural wastewater which was classified as domestic industrial wastewater was also tested. Fig. 7 shows a generally higher flux for the hydrophobic membrane. However, the decreasing flux trend of the hydrophobic membrane was greater, especially during the beginning period. Meanwhile, there was a steady and constant decrease of flux for the hydrophilic membrane. This is attributed to the clogging which occurred on the surface of the hydrophobic membrane. In other words, particles were easier to attach on the surface of the hydrophobic membrane. Fig. 8 shows the comparison between the flux of distilled water and that of wastewater.

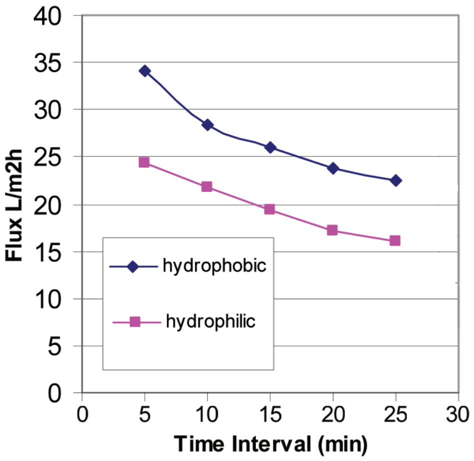

Fig. 7. Natural wastewater flux for hydrophobic and hydrophilic membranes.

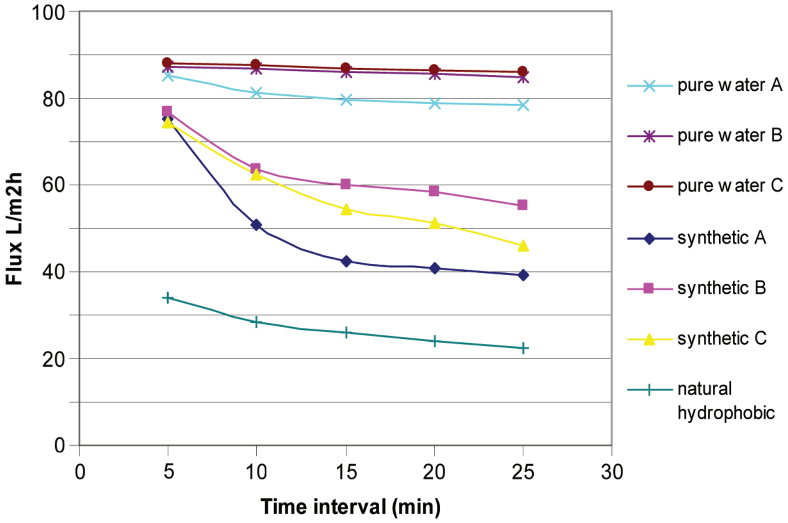

Fig. 8. Comparison of different testing solutions on fluxes of hydrophobic membranes.

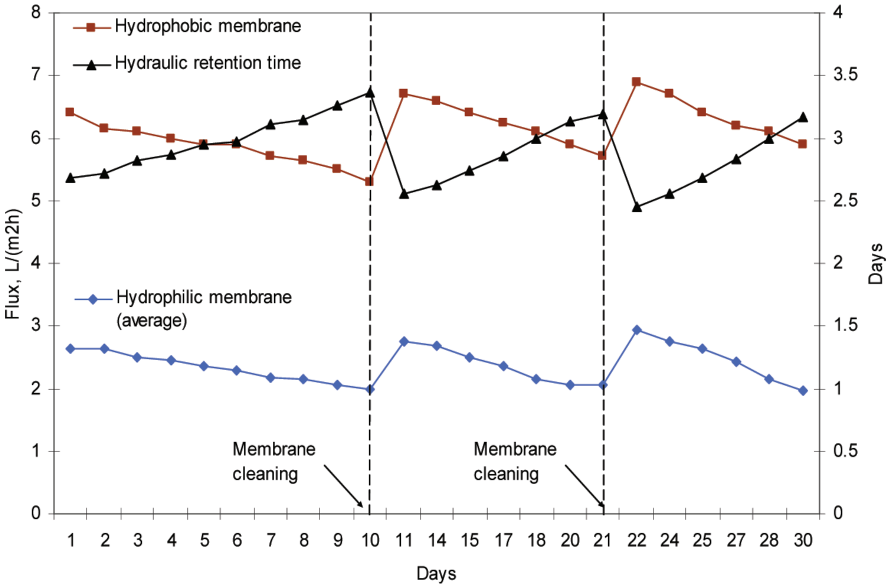

Fig. 9. Flux and hydraulic retention time for the tested membrane types.

Fig. 9 shows the flux for the hydrophobic and hydrophilic membranes and hydraulic retention time during the experiment period. For hydrophobic and hydrophilic membranes, the flux rates on the 1st day of the experiment were found to be 6.4 $Lm^{-2}h^{-1}$ and 2.625 $Lm^{-2}h^{-1}$ respectively.

This experiment revealed that the flux rate for the hydrophobic membrane was about 2.4 times higher than the flux rate obtained from the hydrophilic membrane. The difference in the flux rate can be attributed to the fact that the hydrophilic membrane has a smaller pore size compared to the hydrophobic membrane. It is observed that flux rates for both hydrophilic and hydrophobic membranes decreased with the time and this can be attributed to membrane fouling. After conducting a membrane cleaning process, the flux rates obtained from both types of membranes were found to be similar to the original rates. The decrease in the permeation volume gave a higher hydraulic retention time. The maximum hydraulic retention time was 3.36 d and the minimum was 2.45 d. The higher hydraulic retention time gave longer periods for the microorganisms to decompose the chemical solutes which led to the higher removal of the COD, BOD, TOC and vice versa.

3.3. COD removal

A bench scale unit was used to test the removal rate of the produced membrane (Fig. 10). The percentage removal of COD was studied using synthetic wastewater. Fig. 11 shows the distribution of the percentage removal for COD.

In this study, the ratio of PEG/NMP was used instead of concentration of PEG or concentration of NMP alone. This is because NMP was mixed with PSF first, then with PEG. Hence, the concentration of NMP would influence the effect of PEG which was added later in the process of membrane production. The increase of NMP or PEG concentrations would make the pore sizes of the produced membranes larger. This would reduce the rejection rate of COD. Liu [7] reported that increasing the ratio of PEG additive to NMP resulted in increasing water flux and decreasing solute rejection. This finding is in agreement with the results of the present study. In contrast, decreasing the ratio PEG/NMP results in decreasing water flux and increasing the solute rejection. Other than that, a higher concentration of PEG in the solution would enhance the hydrophilicity of the membrane and increase the flux of the membrane.

In the case of using actual wastewater, focus would be given on the possible difference in the removal efficiency of hydrophobic and hydrophilic membranes. It was found that the COD percentage removal from natural wastewater using the hydrophilic membrane is 58% and that using the hydrophobic membrane is 42%.

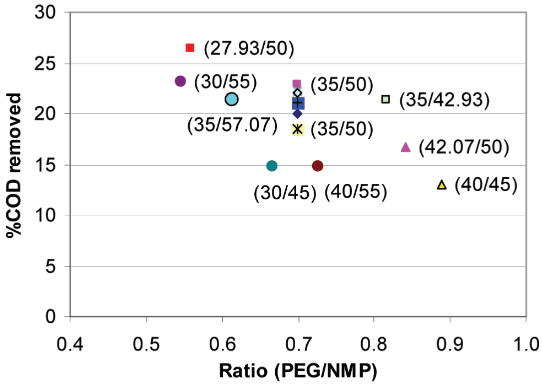

Fig. 11. Scattergram for percentage COD removal for hydrophilic membranes according to the ratio of PEG/NMP.

For both types of membranes, it was found that the percentage rejection of COD using natural wastewater is higher than the percentage rejection using synthetic wastewater. This can be attributed to the difference in the characteristics between actual wastewater and the synthetic wastewater. The actual wastewater used in the experiment was processed prior to use in order to obtain more soluble solution. However, it seems that many large chemical compounds were still present. The presence of the chemical compounds can be related to the industrial waste contributed by factories which are located near the sampling points.

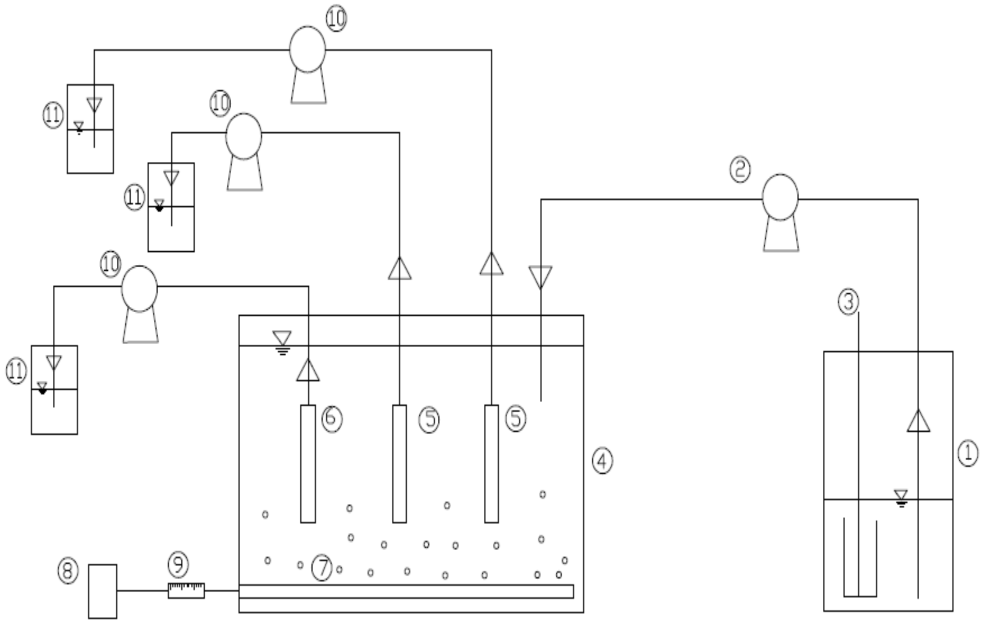

Fig. 10. Schematic diagram for the bench scale arrangements. 1 Influent tank, 2 Inlet pump, 3 Mechanical mixer, 4 Bioreactor tank, 5 Flat sheet membrane module (hydrophilic), 6 Flat sheet membrane module (hydrophobic), 7 Aeration pipe/air diffuser, 8 Air blower, 9 Air flow meter, 10 Suction pump, 11 Effluent tank.

3.4. COD, BOD and TOC removal and MLSS concentration

A gradual increase of the MLSS concentration was noticed, starting from the 2nd day of experiment and so on. In the beginning of the experiment, there was a small increment but from the 21st day of the experiment onwards a larger increment was observed. The larger increment indicated the rapid growth of the microorganisms from the decomposition of the chemical solutes in the bioreactor.

Figs. 12, 13 and 14 show a sharp increase in percentage removal of BOD and TOC (from 0% to 75%). This occurred from the 1st day to the 8th day of the experiment. But the same COD removal percentage occurred from the 1st day to the 5th day of the experiment. After this period, COD, BOD and TOC removal was found to be between 75–95%. The sharp increase in COD, BOD and TOC removal at the beginning of the experiment can be related to the effective filtration from membrane pores (for both hydrophobic and hydrophilic membranes). Decomposition process by microorganisms played a minor role because of the low MLSS concentration at the beginning of the experiment. After the 8th day, the biological process played a major role in the decomposition of the solutes which maintained

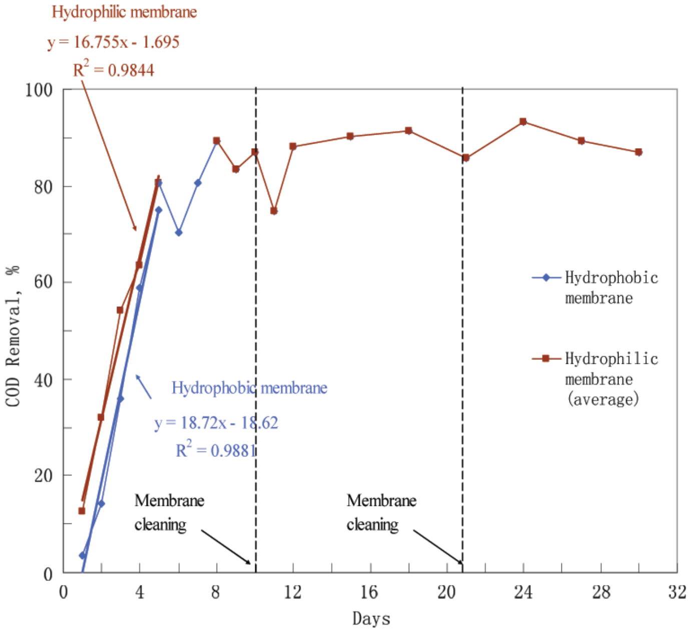

Fig. 12. COD removal results during the experiment period.

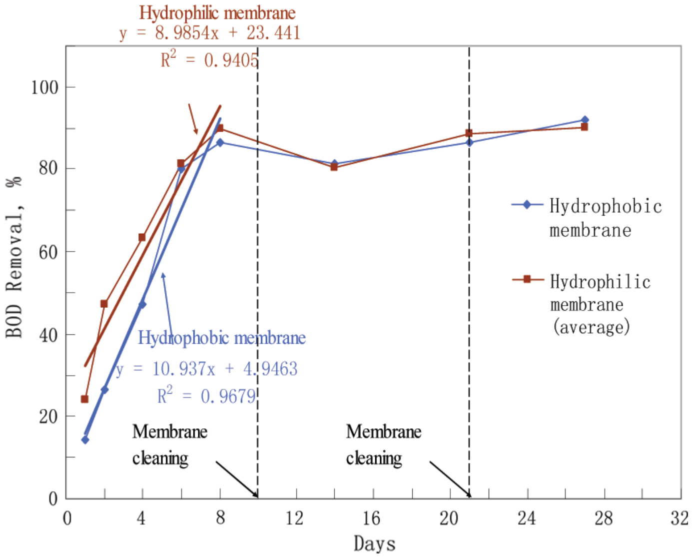

Fig. 13. BOD removal results during the experiment period.

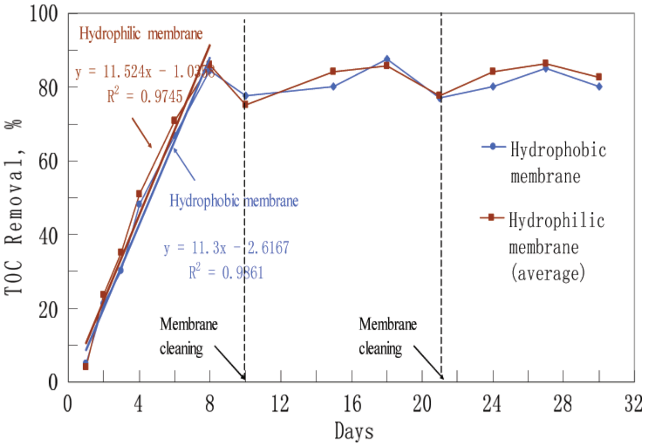

Fig. 14. TOC removal results during the experiment period.

COD, BOD and TOC removal between 75% and 95%, and this was indicated by the gradual increased in the MLSS concentration. An increase in the MLSS concentration usually corresponds with the increase in percentage removal of COD, BOD and TOC and vice versa. This is not applicable for the membrane after the cleaning process. A small drop in the concentration of MLSS from the 28th day to the 30th day was observed, which also showed a small decrease in the percentage removal of COD and TOC. Also, it was observed that the hydrophilic membrane had a slightly higher percentage removal of COD, BOB and TOC than the hydrophobic membrane for the period from the 1st to the 8th day of the experiment. This is attributed to the relatively smaller pores size of the hydrophilic membrane which retained much more solutes compared to the hydrophobic membrane. This justifies the higher percentage removal obtained from the use of the hydrophilic membrane compared with the hydrophobic one.

4. Conclusions

A phase inversion technique with three synthetic based polymers (polysulfone, polyethylene glycol, and N-methyl-2-pyrrolidone) was used to prepare hydrophilic microfiltration membranes in the laboratory. Polyethylene glycol was introduced to enhance the hydrophilicity of the produced membrane.

The use of PEG reduced the pore sizes of the membranes, thus decreasing the water flux, although, PEG introduction was to change the characteristics of the membrane from hydrophobic to hydrophilic. The distilled water flux obtained from the hydrophobic membrane ranges from 78.45 L/m^{2}h to 88.05 L/m^{2}h, while distilled water flux for the hydrophilic membrane ranges from 41.92 L/m^{2}h to 52.25 L/m^{2}h. The rate of flux decline for the hydrophobic membrane was faster than that of the hydrophilic membrane.

Membranes prepared with a higher ratio of PEG to NMP had higher pure water flux, but gave a lower rejection rate, in line with the increased pore sizes of the membranes. The COD percentage rejection rate using actual wastewater was greater for the hydrophilic membrane (58%) compared to the hydrophobic membrane (42%).

Results obtained from the bench scale unit show a gradual increase in the percentage removal of COD, BOB and TOC with time and it increased from 0 to 75 from the 1st to the 8th day while only 20% increment was observed from the 8th day up until the end of the test. But the percentage removal obtained from the hydrophilic membrane was slightly higher than the percentage removal of the hydrophobic membrane.

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