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REDUCTION OF COD FROM SIMULATED WASTEWATER BY FABRICATED HYDROPHOBIC MEMBRANE

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ABSTRACT:

Hydrophobic membrane was fabricated using 15% of Polysulfone (PSF) as a polymer and 85% of dimethylformamide (DMF) as a solvent by phase inversion method. Distilled water was used to test water flux and membrane permeation. Scanning electron microscope was used to study the structural changes on the membrane surface. Synthetic wastewater was used to test the efficiency of the hydrophobic membrane. Membrane efficiency examined by chemical oxygen demand (COD) percentage removal. The results showed that the pure water flux dropped from 85 L/m^2.hr to 75 L/m^2.hr. for the first run and from 86 L/m^2.hr to 82 L/m^2.hr for the second and third runs. For synthetic wastewater the flux dropped from 75 to 38 L/m^2.hr, 75 L/m^2.hr to 52 L/m^2.hr and 75 to 45 L/m2.hr for the first, second and third runs, respectively. Removal efficiency of COD was 90% after 10 days, then it dropped down to 70 %, after cleaning the membrane, the removing increased up to 90% after 8 days.

KEYWORDS: COD, Membrane, Hydrophobic, wastewater

ازالة المتطلب الكيمياوي للاوكسجين من مياه عادمة مصنعة باستخدام غشاء مصنع نافر للماء

نداء عادل جاسم

الخلاصة

تم تصنيع غشاء من النوع النافر من الماء باستخدام 15% كنسبة وزنية من البوليسلفون كمادة بوليميرية اساسية و85% من الدايمثيلفورماميد كمادة مذيبة بطريقة المادة الغاطسة. تم استخدام الماء المقطر لفحص كمية الدفق للماء خلال الغشاء. تم استخدام المجهر الالكترونى الماسح لدراسة هيكلية الغشاء. تم تصنيع مياه عادمة ملوثة من خلط عدة مواد كيمياوية وذلك لغرض فحص كفاءة الغشاء بعد القيام بفحص نسبة المتطلب الكيمياوي للاوكسجين قبل وبعد استعمال الغشاء. اظهرت النتائج نسبة تغير الدفق للمياه خلال الغشاء من 85لتر/مترمربع.ساعة الى 75 لتر /متر مربع.ساعة. ومن 86لتر/مترمربع.ساعة الى 82 لتر /مترمربع .ساعة لاكثر من تجربة. اما المياه العادمة فكان التغير بالدفق من 75لتر/مترمربع.ساعة الى 38 لتر/مترمربع.ساعة ومن 75لتر/مترمربع.ساعة الى 52 لتر /متر مربع.ساعة ومن 75 الى 45 لتر /متر مربع .ساعة لاكثر من تجربة. اما نسبة ازالة المتطلب الكيمياوي للاوكسجين فقد انخفض من 90% الى 70% بعد عشر ايام، وبعد تنظيف الغشاء نسبة الازالة ارتفع الى 90% بعد ثمانية ايام.

1. LIST OF ABBREVIATIONS

BOD: Biological Oxigyne Demand

COD: Chemical Oxigyne Demand

DMF: Dimethylformamide

NMP: N-Methylene-2-Pyrrolidone

PEG: Polythyleneglycol

PSF: Polysulfone

PVP: Polyvinylpyrollidone

TOC: Total Organic Carbon

TSS: Total Suspended Solids

2. INTRODUCTION

The urban growth leads to an accumulation of a large volume of wastewater that is disposed of into the environment. So, the surface and ground water is polluted with contaminants in all worldwide (Metcalf and Eddy, 2003). In the last five decades, the membrane technology is used in many kinds of water and wastewater treatment, such as, potable water, industrial wastewater, sewage, desalination and others. This become as important process.

The integrated use of many kinds of treatment like biological, chemical and physical treatment by biodegradation, organic and inorganic removing and infiltrating with membrane technique, ensuring the effective removing of contaminant from water and wastewater (Cicek et al., 1998). The facilities of water reuse is studied with the facilities of membrane bioreactor (Arevalo et al., 2012). Among many kinds of membrane, a ceramic membrane was used in industrial wastewater treatment. It is the most commercial membrane that was used in many wastewater treatment applications. However, nowadays, the most significant membrane is made from submerged organic membrane; it is suitable for sewage waste treatment (Rahman and Al-Malack, 2006). The hydrophobic membrane is used for water and wastewater treatment, such as, ultrafiltration and microfiltration membrane. Polysulfone (PSF) material is widely used to produce a hydrophobic membrane because of its low cost, excellent membrane ability, high hydrophobicit, membrane fouling fast, good mechanical and anti-compression properties, high chemical and thermal stabilities, non-solvent (coagulant) used for coagulation and good oil removing (Masuelli (2013); Aminudina, et al. (2013)). The hydrophobic membrane can also made of, Poly (vinylidene fluoride) (PVDF) because of its high chemical and thermal stability, good mechanical strength and easy production for hollow fiber membrane (Chenggui et al. (2009); Zularisam,et al. (2007)). Polyethylene glycol (PEG) material was used via polysulphone (PSF) and N-methylene-2-pyrrolidone (NMP), with a certain amount to fabricate nanofiltration membrane to remove metal ions from water (Homayoonfal et al., 2010). The changing in membrane materials and there amount impact the membrane characteristics and performance, like, pore size, water flux, fouling rate and COD and TOC removing percentage (Jae-Hoon and How, 2008). Water flux and solute rejection can evaluate the membrane performance, when flux increase solute rejection will decrease and the contaminant removing rate decrease too (Aminudina et al., (2013); Aryanti et al., (2013)). But, for high flux and porosity, many polymers are mixed in certain concentration like polysulfone (PS), polyvinylpyrollidone (PVP) and N, N-dimethylformamide (DMF) (Singh et al., 2012). Hydrophobic membrane has an efficiency to remove contaminant from surface water and COD, BOD, TOC and TSS from sewage and industrial wastewater using different polymers (Praneeth, 2014). Fouling can caused in hydrophobic membrane by adsorption of solvents on the membrane lead to cake formation (Shen et al., 2010). However, fouling can removed by backwashing or by chemical cleaning (Hua et al., 2008). The aim of this study is to fabricate a hydrophobic membrane using Polysulfone (PSF) as a polymer and dimethylformamide (DMF) as a solvent, with finding the rate of pure water and synthetic wastewater flux and computing COD removing percentage from a synthetic wastewater.

3. METHODOLOGY

3.1. Materials and Method

Two materials were used in the production of the hydrophobic membrane. Dimethylformamide (DMF) and Polysulfone (PSF) were purchased from Selangor market in Malaysia. Polysulfone has been present for quite some time. It has become classical material for polymeric membrane preparation, distilled water was used given its high non-solvent strength. Fig. 1 shows the chemical structures for DMF and PSF (Fred et al, 1984), synthetic wastewater was used to test the membrane efficiency in terms of water flux.

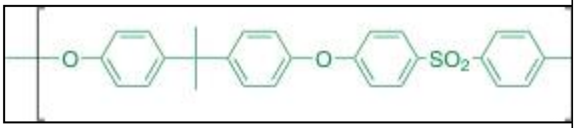
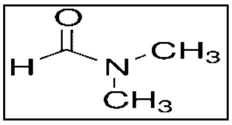
polymer	(PSF) Polysulfone	(DMF) Dimethylformamide
Chemical structure		

Fig. 1.Chemical structures for DMF and PSF

3.2. Equipments

The magnetic stirrer, KMC-130 SH which was used for mixing the materials. Casting knife and steel-supporting plate used in the experiment to spread the casting solution on a glass plate in 500 µm thin Fig. 2. They are manufactured using mild steel and were designed and fabricated by Rising Sun Sdn. Bhd. situated in Ulu Kelang, Selangor. The samples' pore size and their distribution as well as top and cross-section of the produced membranes were facilitated using scanning electron microscope SEM Model LEO 1455 VP.

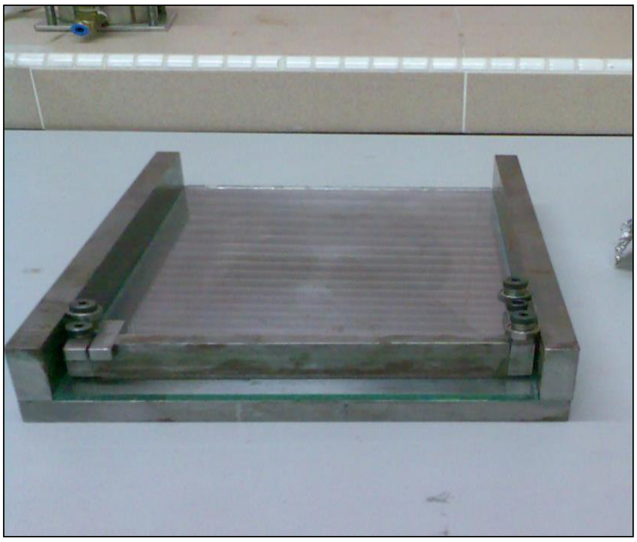


Fig. 2. Casting knife

Fig. 3 shows the stir cross-flow cell that was used to evaluate the membrane performance. The stir cross-flow cell was fabricated in a local factory located near University Putra Malaysia and it has three ports, a lower port was used for inflow, an upper port was used for collecting filtered outflow for testing and the remaining port was connected to a valve for pressure regulation. Peristaltic pump with a dimensions of 120 mm x 230 mm was used suck the flux from the membrane with flow of 27 ml/min. The speed of pump shaft is 90 rpm. The effective area of the tested membrane was 27.7 cm^2.

Fig. 3. Stir cross-flow cell

3.3. Hydrophobic membrane preparation

In this experiment, 15% wt of PSF and 85% wt of DMF ware used. PSF is a polymer material in a form of powder while DMF is a solvent that diluted PSF and convert it to liquid by mixing. Surface Response Method (SRM) is used to determine the percentage of weight for PSF and DMF in the mixture. The equivalent volume (in ml) to the percentage of weight was calculated for both materials. Fourteen runs were used in order to determine the best percentages of both PSF and DMF including the calculations of the equivalent volumes (in ml) in mixing process for each run. A 500 ml beaker was used for mixing PSF with DMF at a temperature of 100°C with continuous stirring to increase the dissolve rate of PSF. The process of adding PSF was done slowly until the whole allocated volume was completed and both PSF and DMF were converted to a liquid solution in the beaker. Then the solution in the beaker was covered and left to cool down at a room temperature for 12 hours. The cooling process is necessary to remove the gases produced after mixing and to prevent formation of small pebbles which affect the pore size distribution on the membrane surface. After that, casting process with a constant manual speed was carried out using a knife and casting plate. The polymer solution at 25ºC was poured into the casting plate and the knife was used to get a homogenous thickness of 500 μm and smooth surface. The casting process should be done within 10 seconds otherwise the thickness of membrane become not homogenous (with different thickness). Afterward, the casted membrane was opened to air for 12 seconds when resultant phase separation process was done. In order to complete phase separation, the membrane was immersed in water bath overnight at room temperature. A white color membrane was formed after it was separated from the casting plate and later the produced membrane was immersed in distilled water as shown in

Fig. 4. Finally the membrane was dried by placing the membrane on an aluminum foil in an oven for 12 hours at 65°C in order to remove the moisture completely (Chenggui et al., (2009); Nurul et al., (2013)).

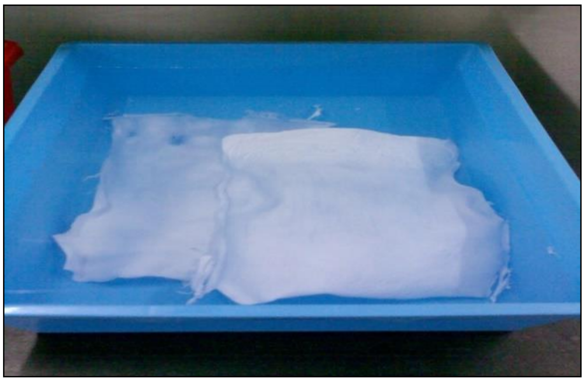


Fig. 4. The membrane is immersed in water

3.4. Pure Water Flux and Rejection Test

The membranes were tested by fitting them in a flat sheet membrane separation unit with 2.3*10-3 m^2 area, under 1.5 bar pressure, distilled water was feeding into the flat sheet membrane from a pressure reservoir (Fig. 5). The initial water flux was taken after flux become constant, with time interval 5 min and the water was collected in 50 ml beaker. The pure water flux was calculated using the equation (Cho and Lee, 1997):

$$J_w = \frac{V}{\Delta t \, A} \quad (1)$$

Where Jw is the water flux (L/m2. h), V is the quantity of permeate (L), Δt is the sampling time (h) and A is the membrane area (m^2). The procedure was repeated with synthetic wastewater, the synthetic wastewater was prepared using the components illustrated in Table 1.

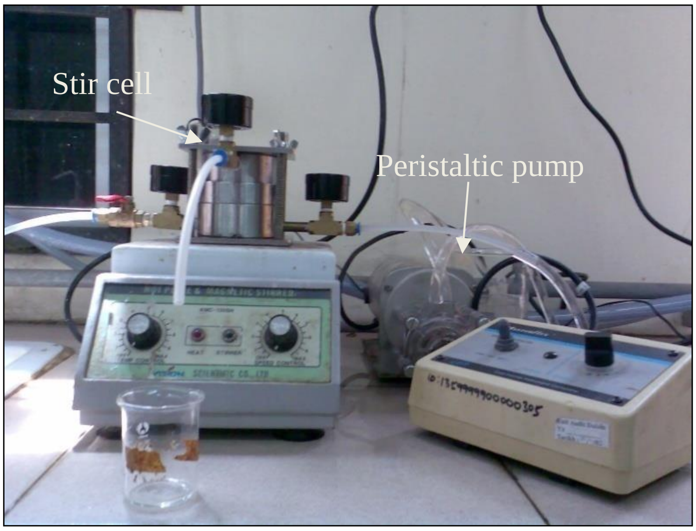


Fig. 5. Setup for water flux and rejection test using peristaltic pump.

Table 1. Chemicals used for preparation of synthetic wastewater.

	Chemical	Concentration, (mg/L)	g/10L
1	CH_3COONH_4	600	6
2	Glucose	5600	56
3	$NaHCO_3$	6600	66
4	$CaCl_2.2H_2O$	110	1.1
5	NH_4Cl	160	1.60
6	NaCl	150	1.50
7	$FeCl_3.6H_2O$	12	0.12
8	K_2HPO_4	350	3.5
9	Glutamic acid	2500	25
10	KH_2PO_4	250	2.5
11	$MgSO_4$.7H2O	165	1.65

3.5. COD Removal Test

After water flux test had been done, water collected, and weighted in order to prepare it for COD measuring. The COD of the samples was determined according to the dichromate digestion method approved by United Stated Environmental Protection Agency (U.S. EPA) for reporting wastewater analysis (HACH1992). Actually, COD was measured by the percentage removal with the following formula:

$$\%COD\ removal = \frac{COD_{\ 1} - COD_{\ 2}}{COD_{\ 1}} \times 100\% 2$$

Where:

COD_1: primary (feeding) COD

COD_2: final (filtrates) COD

4. RESULTS AND DISCUSSION

4.1. Membrane morphologies

The cross sectional morphology of the membranes was studied using scanning electron microscopy (SEM) after the samples were immersed into liquid nitrogen, and coated with gold. Figs. 6 and 7 show the surfaces and cross-section morphology respectively of PSf membrane prepared using DMF as solvent. The cross-section morphology of UF membranes can be easily studied by SEM due to the presence of large pores in the substructure of the asymmetric membranes. Obviously, the membrane is spongy dens structure and few separated closed end drop-like, for the cross section with large pore size because of using 15% PSF with 85% DMF without any additives and it can be seen the presence of fine pores and a few closed pores at the outer surface of the fiber. The formation of voids can be attributed to the penetration of bore fluid and external coagulant from surfaces of the membrane during the phase inversion process. However, the faster the exchange rate of solvent and non-solvent in the coagulation process, the larger pores. In contrast, the slower the exchange rate of solvent and non-solvent in the coagulation process, the smaller pores, more drop like pores and a spongy or non void structure is resulted, which finally alters the membrane permeability.

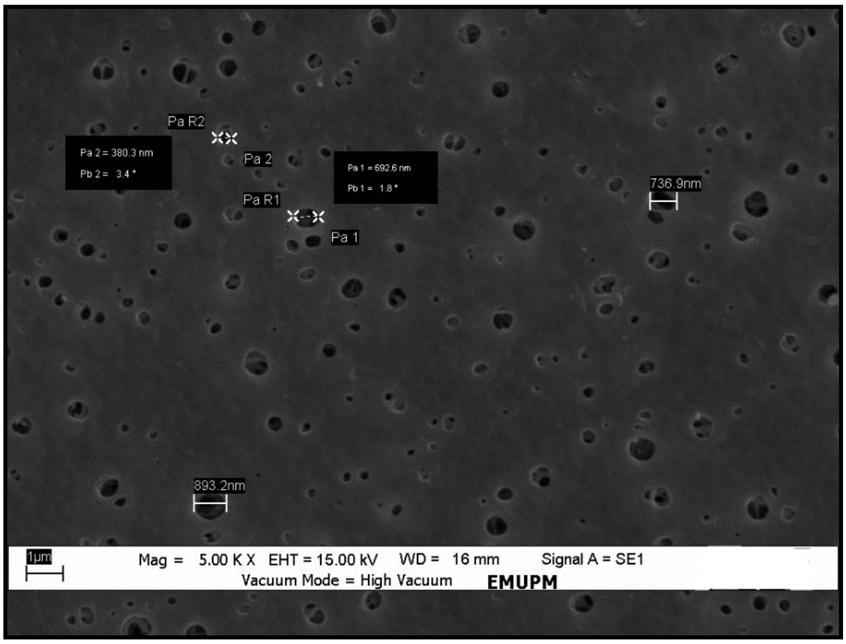


Fig. 6. SEM images for membrane top surface.

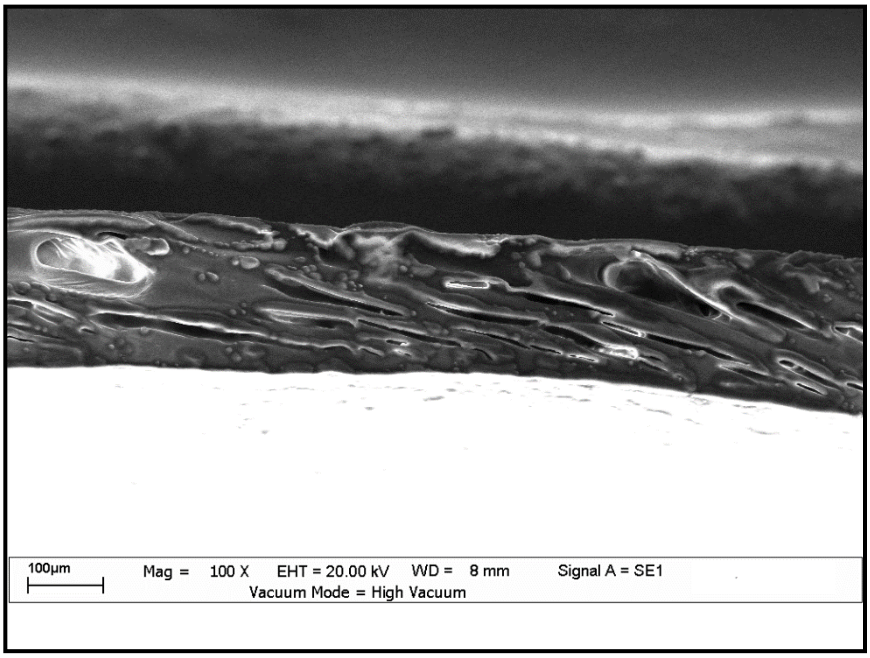


Fig. 7. SEM image for membrane cross section.

4.2. Pure and wastewater flux

Flux from membrane can be calculated using eq. 1. Fig. 8 shows a comparison between pure water flux and wastewater flux. The flux of treated synthetic wastewater was decreased with time and this is because the small particles in the synthetic wastewater tend to clog the membrane surface pores after operation. Also, the performance of membrane is affected by the molecular size of the chemical components, because any molecular size greater than the membrane pore size will clog the pores (Wen Sun, et al., 2013). This is observed for all synthetic wastewaters (A, B and C). On contrary, the flux for all types of pure water (A, B and C) demonstrates almost a constant behavior. This is attributed to the fact that pure water does not contain impurities which clog the membrane surface pores. Shih et al., (2007) concluded that porous membrane surface is closed and the flux decreased after some time from the membrane operation. Same setup, equipment and method were used for treating various types of synthetic wastewater (A, B and C) but the flux obtained from the membrane for synthetic wastewater type C is higher than the other two (B and A). This is attributed to the fact that the size of impurities in the synthetic wastewater type C is smaller than the other two types (B and A).

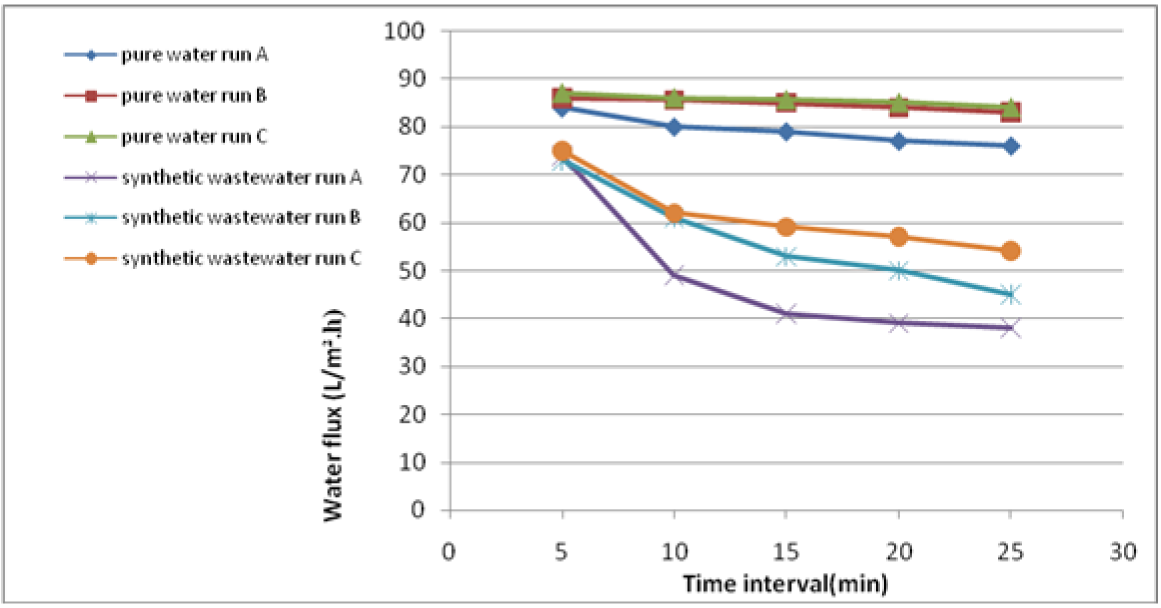


Fig. 8. Pure and synthetic versus water flux.

4.3. COD removal

COD removal was tested for both influent and effluent by using synthetic wastewater that was filtered through the membrane. The percentage of DMF used in the membrane casting has a direct effect on COD removal. This is because the pore size in the membrane surface is affected by the percentage of DMF used in the membrane casting. When the percentage of DMF increases, the size of pores are increase too and this will lead to increase water flux and decrease COD removal. According to Wang et al. (2012), when the percentage of DMF decrease, pores sizes decrease too. As a result, water flux decreased but the solute rejection and COD removal increased. COD removal values also can be affected by the characteristics of the wastewater, soluble COD causes small rejection for wastewater and less removal values (Claude, 2003). Fig. 9 shows COD percentage removal with the time. There is a gradual increase in COD percentage removal from the 1st day to the 8th day and this demonstrate that the membrane is working steadily and effectively. It is observed that the COD percentage removal is 5% on the 1st day and it was reached to 90% on the 10th day. The increase in COD removal was associated with the accumulation of particles on the membrane surface (Wen et al., 2013). After ten days from starting the operation and when the membrane is cleaned, COD percentage removal decreased suddenly down to 70% and it is gradually increased afterwards. This is because the particles are washed out during the membrane cleaning process and later they accumulated on the membrane surface again.

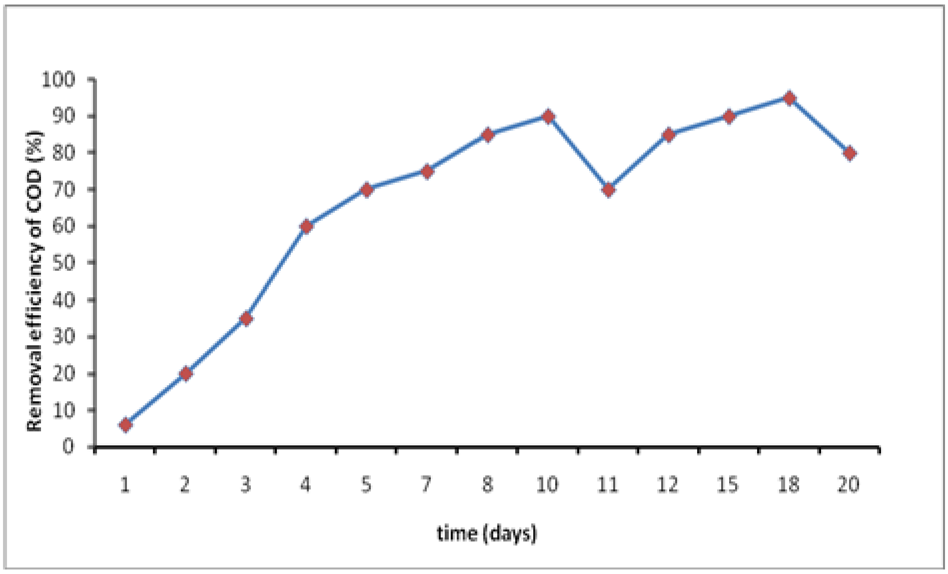


Fig. 9. Removal efficiency of COD (%) versus time.

5. CONCLUTION

A hydrophobic membranes was prepared by using Polysulfone (PSF) as a polymer and dimethylformamide (DFM) as a solvent amounts The SEM images of membranes indicated that addition DFM produce more smaller pores, more drop like pores and a spongy dense structure. The water flux through the membrane was tested with pure water and synthetic wastewater; there were decrease with water flux. The percentage removal for COD was tested and it increased gradually, but it decline suddenly after ten days, after the membrane was washed, the percentage removal increased again.

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7. REFERANCES

Aminudina. N. N., Basria, H., Harunb, Z. C., Yunosc M. Z., Goh Pei Seand, 2013, “Comparative Study on Effect of PEG and PVP as Additives on Polysulfone (PSF) Membrane Structure and Performance”, Jurnal Teknologi (Sciences & Engineering) vol. 65, no. 4, p.p. 47–51, eISSN 2180–3722

Arevalo, J., Ruiz L. M., Parada-Albarracin, J., Gonzalez-Perez, D. M., Perez, J., Moreno, B. & Gomez, M. A. 2012, “Wastewater reuse after treatment by MBR”. Microfiltration or Ultrafiltration, Desalination vol. 299, p.p. 22–27.

Aryanti, P. P. T., Khoiruddin, Wenten, I. G., 2013, “Influence of Additives on Polysulfone-Based Ultrafiltration Membrane Performance during Peat Water Filtration”, journal of water sustainability, vol.3, issu. 2, June, p.p. 85-96.

Chenggui Sun, 2009, “Poly (vinylidene fluoride) membranes: Preparation, modification, characterization and applications”, Waterloo, Ontario, Canada, master thesis presented to the University of Waterloo.

Cho. D. L., Lee. J. 1997, “Membrane Fouling in Microfiltration Process and its Control by Surface Modification of Membrane”, Polymer-Korea 21.

Cicek, N., Winnen, H., Suidan, M., Wrenn, B., Urbain, V. & Manem, J. 1998, “Effective of the membrane bioreactor in the biodegradation of high-molecular weight compounds”. WaterRes. Vol. 32, no. 5, p.p. 1553–1563

Claude M. M., Use of Polymeric Microfiltration Membrane to Remove Microorganisms and Organics Pollutants From Primary Sewage Effluent, 2003, Master thesis, Graduate faculty of the school of engineering, University of Southern of California

Fred W., Billmeyer, JR. 1984. “Textbook of polymer science”, 3rd edition, Rensselaer Polytechnic Institute, Troy, New York: J. Wiley.

Homayoonfal. M, Akbari.A 2010, “Preparation of Polysulfone Nano-Structured Membrane For Sulphate Ions Removal From Water”, Iran. J. Environ. Health. Sci. Eng., vol. 7, no. 5, p.p. 407-412.

Hua. H, Li. N, Wu. L, Zhong. H, Wu. G, Yuan. Z, Lin.X and Tang. L, 2008, “Anti-Fouling Ultrafiltration Membrane Pre- pared from Polysulfone-Graft-Methyl Acrylate Copoly- mers by UV-Induced Grafting Method” Journal of Envi- ronmental Sciences, Vol. 20, no. 5, p.p. 565-570.

Jae-Hoon C. and How Y. N., 2008, “Influence of Membrane Material on Performance of a Submerged Membrane Bioreactor”, Division of Environmental Science and Engineering, National University of Singapore, 9, Engineering Drive 1, Singapore 117576, Singapore.

Masuelli. M. A., 2013, “Synthesis Polysulfone-Acetylethanol Ultrafiltration Membranes. Application to Oily Wastewater Treatment”, Journal of Materials Physics and Chemistry, vol. 1, no. 3, p.p. 37-44.

Metcalf & Eddy 2003, Wastewater Engineering: Treatment and Reuse. McGraw-Hill, New York.

Nurul N. A., Hatijah B., Zawati H., Muhamad Z. Y., Goh P. S., 2013 Comparative Study on Effect of PEG and PVP as Additives on Polysulfone (PSF) Membrane Structure and Performance, Jurnal Teknologi (Sciences & Engineering), vol.65 iss.4, p.p. 47–51

Praneeth K., 2014, Synthesis and Characterization of Novel Polymeric Membranes for Water Purification and Effluents Treatment, A thesis of Doctor of Philosophy, School of Applied Sciences College of Science, Engineering and Health RMIT University, Australia.

Rahman, M. M. and Al-Malack, M. H. 2006, "Performance of a Crossflow Membrane Bioreactor (CFMBR) when Treating Refinery Wastewater". Desalination, vol 91, 1-3, p.p.16-26.

Shen. Y., Zhao. W., Xiao, K. and Huang. X., 2010, "A Systematic Insight into Fouling Propensity of Soluble Microbial Products in Membrane Bioreactors Based on Hydropho- bic Interaction and Size Exclusion" Journal of Mem- brane Science, Vol. 346, no. 1, p.p. 187-193.

Shih, Rey, Juin, Cheng 2007, "Effect of polarity of additional solvent on membrane formation" European Polymer Journal 43, p.p. 4004.

Singh. P. S., Parashuram, K., Maurya, S., Ray, P. and Reddy. A. V. R., 2012, "Structure-performance-fouling studies of polysulfone microfiltration hollow fibre membranes Bull. Mater". Sci., vol. 35, no. 5, October, p.p. 817–822. _c Indian Academy of Sciences.

Wang. Q., Wang, Z., Wu, Z., 2012, "Effects of solven compositions on physicochemical properties and anti-fouling ability of PVDF microfiltration membranes for wastewater treatment", Desalination 297, p.p. 79–86.

Wen, S., Junxia, L., Huaqiang, C., Bingzhi, D., 2013, "Pretreatment and Membrane Hydrophilic

Modification to Reduce Membrane Fouling", Membranes, vol. 3, p.p. 226-241

Zularisam, A. W., A.F. Ismail .A. F, M.R. Salim. M. R, Mimi Sakinah, Hiroaki. O., 2007,

"Fabrication, fouling and foulant analyses of asymmetric polysulfone (PSF) ultrafiltration membrane fouled with natural organic matter (NOM) source waters", Journal of Membrane Science vol 299, Issues 1–2, p.p. 97–113.