EXTENDING THE LIFE TIME OF POLYMER INCLUSION MEMBRANE CONTAINING COPOLY(EUGENOL-DVB) AS CARRIER FOR PHENOL TRANSPORT

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Received June 28, 2013; Accepted August 29, 2013

ABSTRACT

A study of phenol transport was conducted in correlation to the evaluation of copoly(eugenol-divinylbenzene, DVB) as carrier using polymer inclusion membrane (PIM) method. The performance of copoly(eugenol-DVB) was observed based on the parameters of Membrane Liquid (ML) loss. Some variations, including the effect of plasticizer concentration, stirring speed, and measurement of lifetime of the membrane, were studied. Related to the lifetime, the effect of the concentration of $NaNO_3$ salt was also studied. The tensile strength of membrane before and after the transport was measured and their morphology was characterized using SEM (Scanning Electron Microscope). Results of the study indicate that the value of the tensile strength of the membrane after the transport was lower than that before the transport. The lifetime of the membrane was not only depending on the capacity of the membrane in restraining ML loss, but also on the concentration of salt that was added to the solution of source phase. In addition, the lifetime of the membrane had correlation to the number of ML loss, i.e. the addition of salt lead to lower amount of ML loss and gave longer lifetime. With the addition of 0.1 M $NaNO_3$, the lifetime of the membrane extended to 62 days, which is longer than the lifetime without the addition of NaO_3 which was only 7 days.

***Keywords**: crosslinked; polymer; polymer inclusion membranes; membrane carrier; DVB*

ABSTRAK

Telah dilakukan penelitian tentang transpor fenol yang berkaitan dengan evaluasi kopoly(eugenol-divinilbenzena, DVB) sebagai senyawa pembawa (carrier) menggunakan metode polymer inclusion membrane (PIM). Pada tulisan ini kopoly(eugenol-DVB) 12% diobservasi berdasarkan pada parameter membrane liquid (ML) loss. Beberapa variasi, termasuk pengaruh konsentrasi plasticizer, kecepatan pengadukan, dan pengukuran waktu hidup (lifetime) membran telah diteliti. Berkaitan dengan waktu hidup, juga telah dipelajari pengaruh konsentrasi garam $NaNO_3$. Tensile strength (kuat tarik) membran sebelum dan sesudah transpor diukur dan dikarakterisasi menggunakan SEM (Scanning Electron Microscope). Hasil penelitian menunjukkan bahwa nilai tensile strength membran setelah transpor lebih kecil dibandingkan sebelum transpor. Waktu hidup membran, tidak hanya tergantung pada kemampuan membran dalam menahan ML loss, tetapi juga tergantung pada konsentrasi garam yang ditambahkan pada larutan fasa sumber. Hasil penelitian menunjukkan bahwa waktu hidup membran berkaitan dengan jumlah ML loss, dengan penambahan konsentrasi garam menghasilkan jumlah ML loss yang rendah dan waktu hidup yang tinggi. Pada penambahan konsentrasi garam 0,1 M, membran mempunyai waktu hidup sampai 62 hari lebih lama dibandingkan tanpa penambahan garam yang memiliki waktu hidup hanya 7 hari.

***Kata Kunci**: sambung silang; polimer; polymer inclusion membranes; senyawa pembawa; DVB*

INTRODUCTION

Liquid membranes have attracted a large number of the attention for the separation of various chemical species, such as small organic compounds, cationic dye, metal ions, and inorganic anions, in both industrial processes and in chemical analysis [1-4]. More specifically, application of the membranes on the recovery and concentration of phenol from wastewater is of major interest in environment.

In separation techniques using liquid membranes, chemical species are extracted on the basis of the

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mechanisms similar to those in conventional liquid-liquid extraction; however large amounts of organic diluents, which are often volatile, flammable, and harmful, are not required. The extraction chemistry is basically the same as that found in solvent extraction, but the transport process is governed by kinetic rather than equilibrium parameters, that is, under non-equilibrium conditions during liquid membrane transport.

The facilitated transport using SLM (Supported Liquid Membrane) has reached a significant importance for use in various purification and separations processes, whereas their lack of stability, which might prevent upscale applications, has also been reported [5]. Recently facilitated transport of metal ions through polymeric inclusion membrane (PIM) carrier membranes resulted good selectivity in ion separations with real improvement of the membrane stability as compared to liquid membrane [6-7]. Polymer inclusion membranes (PIMs) are becoming of great interest for the separation of chemical species [8-15]. PIMs are thin and flexible films that are easily prepared by casting an organic solution containing a base-polymer, such as poly(vinyl chloride) (PVC) or cellulose triacetate (CTA), an extractant as a carrier, and often a plasticizer or modifier. PIMs have better stability compared to other types of liquid membranes such as bulk liquid membranes, emulsion liquid membranes, and supported liquid membranes, because the rate of loss of the membrane liquid phase to the aqueous phase that the membrane is in contact with is small [8].

The key to successful of PIMs is to achieve extended membrane lifetime. Some research has been carried out to investigate the stability of PIMs. This paper is aimed at the evaluation of polymer inclusion membrane for transport phenol using the copoly(eugenol-DVB) 12% as carrier, plasticizer and polyvinyl chloride of (PVC) as a matrix polymer furthermore to increase lifetime with copoly(eugenol-DVB) 12% as carrier. The stability of the membrane based on copoly(eugenol-DVB) as carrier was observed using the parameters of membrane liquid (ML) loss. Many factors that influence on the stability of the membrane, such as, the plasticizer concentration, stirring, stability of PIM, lifetime and $NaNO_3$ concentration have been studied. The effect of salt concentration was also investigated in relation to membrane lifetime.

EXPERIMENTAL SECTION

The standard condition was set as Kiswandono et al. [15], including the transport equipment, the membrane composition, the preparation of membrane and the procedure of the transport of phenol.

Materials

All reagents were analytical grade and were used without further purification. Poly(vinylchloride) (PVC), tetrahydrofurane (THF), divinylbenzene (DVB), dibenzyl ether (DBE), NaOH, 4-aminoantipyrine are products of Merck. All the organic chemicals were used as received. The pH of the source and of the stripping phase was adjusted using HCl and NH_4OH.

Instrumentation

The PIM cell consists of two cylindrical chambers that are separated by membrane. The effective volume of each chamber was 50 mL and the effective diameter of the membrane was 2.5 cm.

The membrane before and after used in the transport experiments were characterized by Scanning Electron Microscope (Shimadzu U8000) to evaluate its morphological change during the transport experiment and Universal Testing Machine, UTM (Zwick/Z0,5) to evaluate its tensile strength. The Analytical balance, UV-spectrophotometer (772-Spectrophotometer) and pH meter (HM-30R) were used for measurements of sample.

Procedure

Preparation of PIM

PIM were prepared by mixing copoly(eugenol-DVB) as carrier (0.027 g), PVC as matrix polymer (0.0864 g) and DBE as plasticizer (0.1566 g). THF was added to homogenize the mixtures using magnetic stirrers, and then leave to evaporate the solvent slowly.

Transport of phenol using polymer synthesis

The standard condition was set as Kiswandono et al. [15]. The aqueous feed solution was prepared by dissolving phenol in deionized water at various concentrations. NaOH solution was used as the stripping phase. Transport process was done by placing 50 mL of phenol solution (60 ppm) into the source phase chamber and 50 mL of NaOH (0.25 M) into the stripping phase chamber, and stirred at room temperature. The concentrations of phenol present in the source and stripping phases were analyzed using 4-aminoantipyrine method [16-17] and the absorbance was measured with UV-visible spectrometer at wavelength of 450 nm.

In this study, the loss of membrane liquid was determined by weighing method that is the sum of the loss of the carrier and membrane solvent. The amount of liquid membrane loss was obtained by weighing the membrane before transport on an analytical balance. After stopping the experiment at a certain time, the total

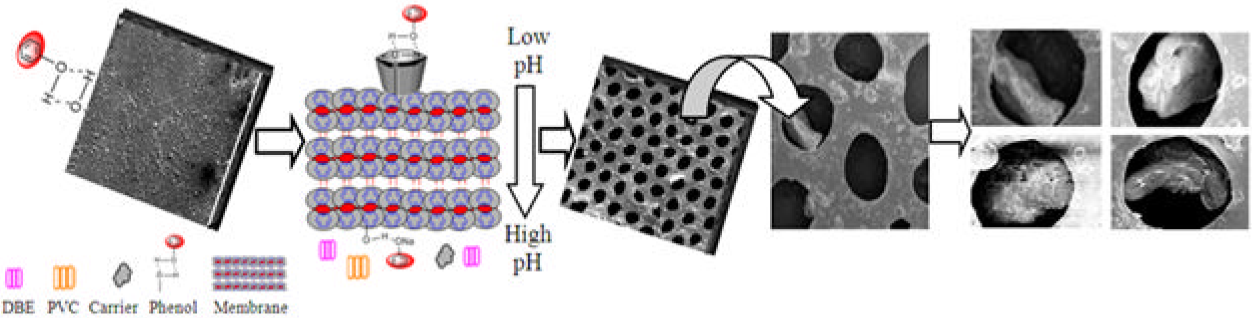

Fig 1. Illustration of the loss components of the membranes in phenol transport process

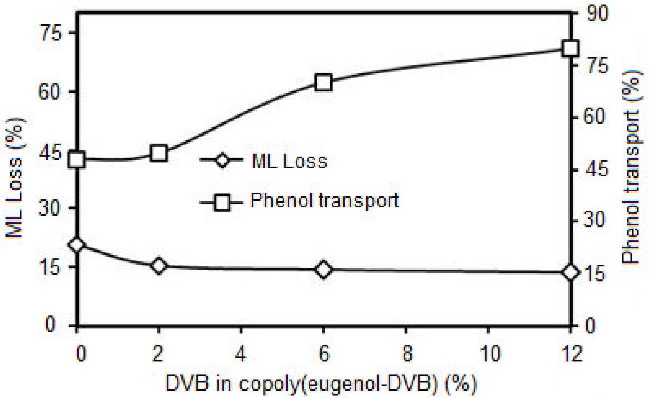

Fig 2. Membrane loss and phenol transport with different amount of crosslink agent

membrane was weighed again on an analytical balance. The amount of ML loss left within the membrane was determined from the weights of the decayed membrane and the dry membrane. Moreover, the loading of phenol into the membrane liquid and the possible water molecules associated with the carrier and phenol within the membrane pores might cause extra errors in the determination of ML loss. However this difference is much lower than the normal experimental error and therefore can be neglected. If any water molecules remained within the membrane pores, the loss of membrane liquid determined by the weighing method would tend to be lower than the actual loss [9,18]. Transport parameters evaluated were the concentration of plasticizer variation, stirring effect, $NaNO_3$ salt effect, and lifetime of the membrane.

RESULT AND DISCUSSION

Membrane Liquid (ML) Loss

In the liquid membrane technique, carrier compound as a facilitator plays an important function and is critical in the performance of separation from source phases. The phenol transport process begins with phenol diffusion through the boundary of layers in the source phases, and then the adsorption of phenol in source-membrane interface phase occurs. The phenol is transported in membrane phase and through the membrane phase, and desorption occurs in the interfacial phases of membrane-stripping, and the phenol eventually diffuses back to stripping phase.

The membranes used in the phenol transport process allow the leaching or loss of some components of membrane. According to the theory of Progressive Wetting Mechanisms [18], during the transport process with extended time, it will lower the interface and contact angle tension; it is due to the contamination of the membrane and aqueous solution interface, the decomposition of chelating agents, and other factors. When the interfacial tension decreases at a certain level, emulsification is suddenly formed. This has led to the loss on the component of the membrane adjacent to source or stripping phase solution. Under this mechanism, the liquid membrane leakage related to the composition of the membrane forming materials. The missing components of membrane can be derived from DBE, PVC or carrier compound.

Fig. 1 illustrates membrane components to be separated from the membrane pores or membrane pores leaving. The missing membrane components are evidenced by the difference in weight of the membrane before and after the transport. The loss of membrane components is called membrane liquid (ML) loss.

Percentage of ML loss is used as a guide for endurance, strength and lifetime of the membrane. Resilience and strength of the membrane can be explained by the ability of membrane to be used repeatedly, and the resultant tensile strength value of the membrane.

Some researchers have reported that the loss of membrane constituent components is one of the main reasons of instability in the transport process using liquid membrane [18-20]. The influence of loss of membrane constituent components on the stability of the PIM in this research is shown in Fig. 2. Fig. 2 shows ML loss in variation of the number of crosslink agents of 2%, 6% and 12%. ML loss decreased from 2% to 12% by the increasing the amount of crosslinking agents but the percentage of transport phenol is

Table 1. Tensile strength of copoly(eugenol-DVB)

No	Type of copoly(eugenol-DVB)	Tensile strength (MPa)	
		Before transport	After transport (24 h)
1.	Copoly(eugenol-DVB) 0%	11.3	6.0
2.	Copoly(eugenol-DVB) 2%	11.9	7.5
3.	Copoly(eugenol-DVB) 6%	12.9	9.7
4.	Copoly(eugenol-DVB) 12%	13.8	10.7

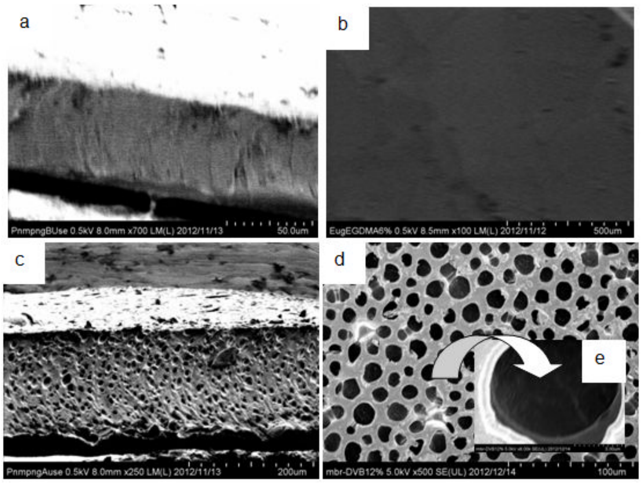

Fig 3. SEM of copoly(eugenol-DVB) 12%. Before transport (a) cross section, 700x (b) surface section 100x. After transport (c) Cross section 250x (d) Surface section 500x and (e) Surface section 8000x

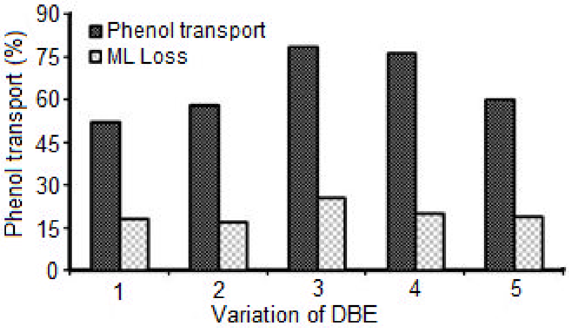

Fig 4. Membrane loss and phenol transport with different number of plasticizer. (1) [DBE] = 0.1466 g (56.4%), (2) [DBE] = 0.1500 g (56.9%), (3) [DBE] = 1566 g (58.0%), (4) [DBE] = 0.1600 g (58.5%), and (5) [DBE] = 0.1666 g (59.5%)

increasing. This suggests that the membrane composed of the copoly(eugenol-DVB) as carrier of 12% is the most stable membranes. Small ML suggests that the membrane has a high and stable endurance. Similar results were obtained in previous works [21-22] in which it was reported that not only the physical parameters but also both chemical composition and physical parameters of the support affected the chemical species transport efficiency through a LM system. This stability is also related to the value of tensile strength of the membrane.

Tensile Strength

The plasticizer used in these membranes plays the dual role of : (1) plasticizing the matrix forming polymer, thereby increasing the softness, flexibility and mechanical strength of the membrane and (2) solvent for the extractant in the membrane matrix [23]. The characterization of tensile strength of the membrane before and after transport was tested by a Universal Testing Machine. The characterization was done to provide information on membrane strength. In the tensile test, the specimen was loaded by tensile force vertically that continuously increases and the observation was simultaneously done on the extension of specimen. The results showed that the tensile strength of the membrane after transport were smaller than that of before transport.

Table 1 shows a comparison of the tensile strength of membrane before and after transport. Table 1 showed that the tensile strength of membrane after transport was smaller than before transport. This is because the membranes used for phenol transport from source phase to stripping phase possibly contains the components of membrane involved in the leaching into stripping phase. The leaching components can be derived from DBE as compounds that make the membranes become strong and elastic. The decreasing amount of DBE in the membrane after the phenol transport process causes the reduced strength of membrane and the tensile strength become weak and easily broken.

The reduced tensile strength of the membrane can be attributed to the loss of the components of the membrane during the transport process takes place. The membranes used in this study were porous liquid membranes. The pores in the membranes were covered by plasticizer as liquid media. The use of membranes for transport enables the components of the membranes leaching. The leaching components of membrane will result in porous PIM membrane surface [24]. It is also supported by the result of scanning electron microscope of the membrane (Fig. 3). This figure showed that almost all of the surface and cross-section of membrane were porous. This means that in the transport process, there are lost or leaching, so the cross-section and the surface of the membranes are porous after transport.

Table 2. Tensile strength of the membrane before transport with different number of DBE (using 0.0864 g PVC and 0.027 g copoly(eugenol-DVB) 12%)

Number of DBE in the copoly(eugenol-DVB) 12% (g)	Percentage of DBE in the copoly(eugenol-DVB) 12% (%)	Tensile strength (Mpa)
0.1466	56.4	12.6
0.1500	56.9	14.8
0.1566	58.0	13.8
0.1600	58.5	14.7
0.1666	59.5	17.8

ML is not completely insoluble in aqueous solutions and a certain degree of solubility exists between the interface of ML and the aqueous solution so that no membrane pores that is not visible clearly.

The Effect of Plasticizer

The plasticizers are known to neutralize the strong van der Waals forces between the polymer chains imparting softness and flexibility in the PIM [8,23]. The choice of a suitable PIM composition should be based not only on the interactions between the different membrane components but also on their effect on the extraction and transport of the species of interest [12].

Plasticizer is the component of membrane that affects the stability of the membrane and has a role for condensing or solidifying the membrane. Low plasticizer concentrations are not expected because they can cause the membranes become rigid and brittle. Minimum plasticizer concentration depends on a comparison of the plasticizer and base polymer, *i.e.* PVC and copoly(eugenol-DVB) as a carrier. Plasticizer concentrations suitable for the use in the membrane were between 65-70% w/w and the base polymer concentrations were 30-35% w/w. Variation in plasticizer affects the difference in the coverage the membrane pores.

It was expected that the addition of a plasticizer to the membrane would lead to a further improvement in the transport rate and might be expected to increase the diffusivity of species through the membrane [25]. The addition of plasticizer will increase the elasticity of the membrane, but the addition of excess plasticizer concentration will add obstacles for the phenol transport. It has been reported by Nghiem [8], that the excessive plasticizer concentration make plasticizers to exclude to the membrane/aqueous interface and form a film on the surface of the membrane, so that it becomes a barrier to the transport across the membrane. In this study, dibenzyl ether (DBE) that was used as plasticizer would cover the membrane pores to leach to the membrane surface and blocking the interaction between phenol and copoly(eugenol-DVB). Furthermore, Nghiem [8] explained that the excess of plasticizer can significantly reduce the mechanical strength of the membrane.

PIMs that using the plasticizers was transparent with uniform thickness. Table 2 showed that the strength of the membrane increases with the increasing amount of plasticizer. It indicates that the addition of plasticizer supports the physical properties of the membrane.

At the low DBE concentration, the composition of the membrane would be dominated by the matrix membrane of PVC, so that the phenol transported to stripping phase was low (Fig. 4). Raut et al. [13] studied the Cs recovery from acidic feeds at a time period of 24 h in PIM containing calix(4)-bis-2,3-naptho-crown-6 that was without plasticizer resulted in no Cs(I) transport while acid transport was also very low (~5%). In the third variation, *i.e.* the amount of DBE 0.1566 g (58%, w/w), the percentage of phenol transport to stripping phase got optimal results due to the presence of a sufficient active group without covered by plasticizer and the basic membranes of PVC. Variation in the amount of DBE gave higher transport up to 79% (Fig. 4) which might be due to the favorable plasticization effect beyond which a decrease in transport was seen which was attributed to intermolecular interactions resulting in lower mass transfer.

The percentage of transport phenol decreases with the increasing viscosity, *i.e.* by the addition of plasticizer. In an early investigation, Sugiura [26] observed that the lanthanide ion flux through a CTA membrane increased to an optimum value then decreased as the plasticizer concentration increased from 0 to 2 M. Fig. 4 showed that the greater the addition of plasticizers, the lower the phenols transported. This is because the plasticizers migrate into the membrane as explained previously.

The largest percentage of ML loss occurred when the percentage of phenol transported to stripping phase was optimum. It indicated that the components of the membrane underwent leaching plasticizer, *i.e.* DBE. After reaching the largest percentage of ML loss, the large number of DBE will cause smaller ML loss. It is because the large number of DBE will lead to stronger membrane because DBE binds PVC and copoly(eugenol-DVB) as carrier, so the strength of the membrane was larger (Table 2) and made the membranes more stable.

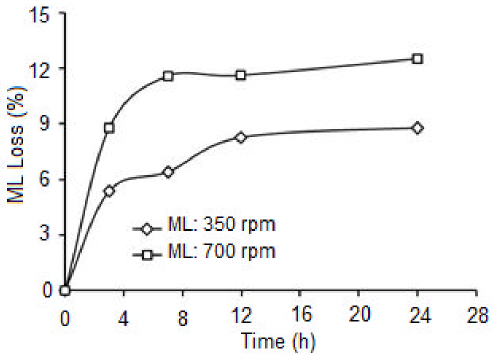

Fig 5. The effect of stirring speed (stirrer) of ML loss

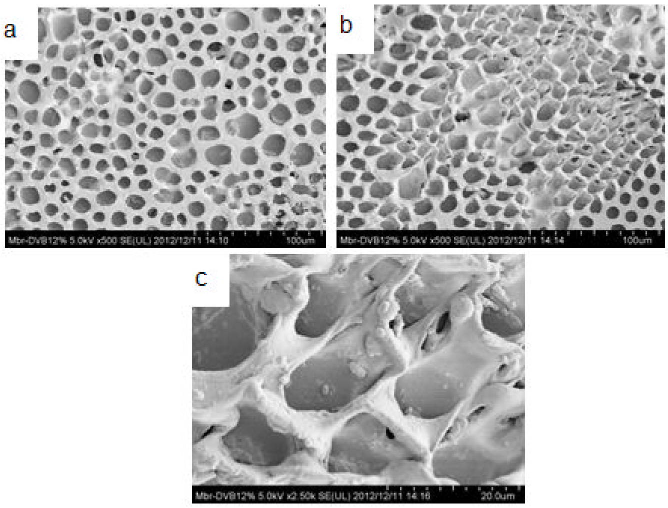

Fig 6. SEM of surface copoly(eugenol-DVB) 12% of membrane after transport (a) stirrer 350 rpm, 500x (b) Stirrer 700 rpm, 500x and (c) Stirrer 700 rpm 2500x

Influence of Stirring Speed

Variation in stirring speed greatly affects the endurance and strength of the membrane. The variation in the stirring speed is conducted to test the endurance and stability of the membranes from the effect of stirring. It is important to optimize the rate of stirring of the extraction solution in order to minimize the thickness of the stagnant liquid layers at the two membrane/solution interfaces. The increase in stirring speed can increase turbulence in the solution. In addition, the increase in stirring speed increases physical disorders such as friction between the interfacial phases of source-membrane and membrane-stripping [6,18]. The percentage of ML loss is an indicator of how much the lost components of the membrane and can be used as a parameter of how durable and stable the PIM membrane from physical disorders due to the effect of stirring. The variations in stirring speed used in this study were 350 rpm and 700 rpm.

Fig. 5 showed that the increase in the stirring speed produced the high percentage of ML loss. The same thing was also obtained in a study of Nosrati et al. [27] and Zheng et al. [19]. The stirring serves to accelerate and evenly distribute the equilibrium of reaction, but the condition of the membrane could be physically disturbed by the stirring itself. It is because the increase in the stirring speed could increase the physical contact between the membrane and the solution in the source phase and the stripping phase, so increasing the ML loss and causing the endurance of PIM membrane decreasing. However, PIM techniques in this study produced a smaller ML loss (<15%) compared to the ML loss that has been done by Zha et al. with SLM technique, which was above 30% [18].

Fig. 6 showed the results of SEM membrane after the transport with the stirring speeds of 350 rpm and 700 rpm. The increase in the stirring speed could increase physical disorder such as friction between the interfacial phases of source/membrane and membrane/stripping, so this disorder affects the surface of membrane. The surface of membrane with a stirring speed of 700 rpm looks bigger and wider than that with a stirring speed of 350 rpm. In addition, the surface of membrane with a stirring speed of 700 rpm looks like drawn out, so the stirring speed of 700 rpm causes many components of the membrane leaching, resulting ML loss at the stirring speed of 700 rpm greater than 350 rpm.

Lifetime

To study the long-term stability of the membrane, phenol transport efficiency for the period in the run mode continuously with optimum conditions. Observations on membrane stability through experiments by comparing the condition of the membrane lifetime [28]. The lifetime of PIM was determined in a similar way to the measurement of ML loss. A pH probe was inserted in the feed chamber and the pH of the feed solution was recorded. Since the pH value in the strip did not change significantly, it was only checked periodically. A PIMs was considered “failed” or leak when the pH the source phase has reached pH 9 then the process were stopped and the operating time was taken as the lifetime of the PIMs.

Fig. 7 showed the lifetime of the membranes with different variations in the addition of $NaNO_3$ concentration in the source phase with the constant conditions of stripping phase (0.25 M NaOH). The results showed that the increasing salt concentration in source phase will increase the lifetime of the membrane. Membrane leakage at the source phase

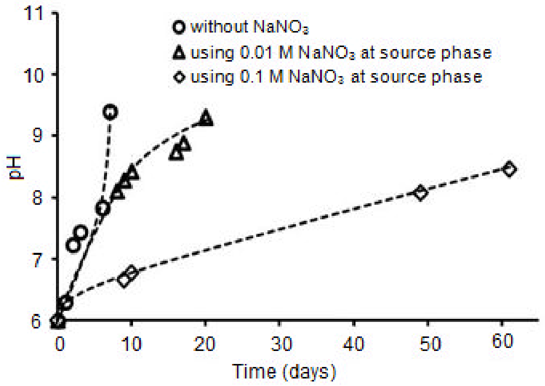

Fig 7. Effect of $NaNO_3$ addition in source phase on membrane lifetime

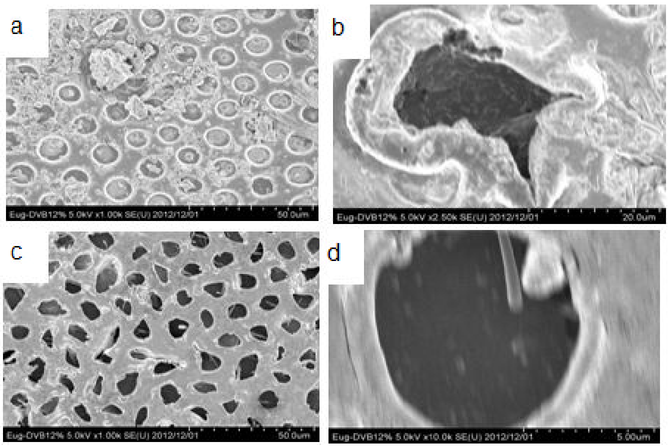

Fig 8. SEM of copoly(eugenol-DVB) 12% membrane for lifetime, using $NaNO_3$ (a) 1000x, and (b) 2500x, without $NaNO_3$ (c) 1000x and (d) 10000x

without the addition of $NaNO_3$ occurred on 7 days, while that with the addition of 0.01 M $NaNO_3$, the lifetime of the membrane increased to 20 days. Finally, an increase in the concentration of $NaNO_3$ to 0.1 M caused the increase of the lifetime of the membrane to 62 days. This is because the addition of $NaNO_3$ salt affected the ML loss in the membrane, *i.e.* the increasing concentration of salt will reduce the loss of organic phase of the membrane, so that the ML loss become small and the stability and lifetime of the membrane increased.

One cause of instability at LM is the kind of polymeric support and pore dimensions [28]. As shown clearly in Fig. 8a, b, the presence of $NaNO_3$ at source phase yielded deposition of particles on the surface of membrane. This deposition occurs due to the influence of salting out. Salting out is a purification method that utilizes the reduced solubility of certain molecules in solution which has a very high ionic strength. So that almost all the pores of the membrane were enclosed and the leakage of the membrane could be slowed down to increase the lifetime of the membranes. Meanwhile, with the absence of $NaNO_3$ at source phase (Fig. 8c, d), the surface of the membrane was clean from particle deposition and the pores were still clearly visible. These unblocked pores may cause higher leak and give rise to faster change of the acidity of the source phase to alkaline. The pores are also factors for the increasing leakage of the membrane, so that the lifetime of the membrane is getting shorter.

Deposition due to salting-out in this study occurred because of (1) the process competition between the salt and phenol to bind water. The addition of $NaNO_3$ will attract water molecules which are initially surrounding the phenol. This is caused by the fact that the salt ions have a greater charge density than phenol. Decreasing the amount of water bound to the phenol causes the phenol aggregation (increase hydrophobic interaction) so that phenol will precipitate out of the solution or (2) salting out effect can enhance the holding of DBE inside the membrane, resulting in the reduction of ML loss. The deposition may be the reprecipitation of DBE on the surface of membrane. As shown in Fig. 8a, b, the DBE was still stably maintained inside the membrane pores in the presence of $NaNO_3$.

CONCLUSION

The phenol transport using the membrane of copoly(eugenol-DVB) by the PIM technique resulted in the loss of some components of the membrane. The loss of components of the membrane was seen in the percentage of ML loss in each transport, so the pores of the membrane appear more clearly compared with those of the membrane before the transport. The increasingly large pores of membrane resulted in the decreased value of tensile strength of the membrane. The use of $NaNO_3$ salt when the transport occurred will blockade the pores of the membrane enhancing the lifetime of the membrane.

ACKNOWLEDGEMENT

I would like to express my sincere gratitude for the support by the Sandwich Program and Beasiswa Program Pasca Sarjana (BPPS) from Directorate General of Higher Education (DGHE) Republic of Indonesia for the funding of this research. Many thanks to all who helped in this study, especially Dr. Takeshi Hashimoto (Sophia University, Tokyo, Japan) and Latifun Jayanti (Department of Chemistry, Universitas Gadjah Mada, Sekip Utara, Yogyakarta, Indonesia,).

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