UTILIZATION OF THE POLYMER INCLUSION MEMBRANE METHOD FOR PHENOL TRANSPORT USING CO-EDVB 8% AS A CARRIER

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ABSTRACT
To separate and purify organic contaminants, the employment of liquid membrane technology based on the Polymer Inclusion Membrane (PIM) technique is a major alternative. This technology has been extensively employed on an industrial, hospital, and academic laboratory scale. This work produced PIM membranes using dibenzyl ether, polyvinyl chloride, and copoly-eugenol divinyl benzene (Co-EDVB) 8%, respectively, as plasticizers, support polymers, and carriers. Also, the optimization test for phenol transport was conducted utilizing parameters for the impact of membrane thickness and transport duration. The plasticizer effect, different salt kinds, salt concentrations, repeated use, and longevity factors were used to assess the robustness and stability of the PIM membrane. The findings indicated that the type T_{54} membrane's thickness and a twenty-four hours transit period were the ideal conditions for phenol transport. The proportion of phenol concentration that was successfully delivered to the receiving phase under these ideal circumstances was 89.03 percent. Also, it was discovered that the PIM membrane's stability and durability were impacted by the use of plasticizers and salt. The membrane life was increased to up to thirty-four days by adding sodium nitrate salt to the source phase at a concentration of 0.01 M.

Keywords: Co-EDVB, Evaluation, Phenol, Optimization, PIM.

INTRODUCTION
Phenol is an organic pollutant that is toxic and carcinogenic. Phenol, heavy metal ions, and synthetic dyes pollution in the environment usually comes from wastewater from industrial-scale production processes, disposal of products containing these materials, and their utilization. Apart from being found in industrial waste, phenol is also present in hospital waste. The liquid waste containing phenolic compounds and their derivatives is disposed of directly into the environment without treatment or with inappropriate treatment. It can cause environmental pollution and threaten the health of humans in the vicinity. Therefore, efforts to deal with phenol waste and its derivatives need to be increased. Based on this research, an alternative technology for treating phenol wastewater is needed that is good, environmentally friendly, or green chemistry, simple, and easy to implement. One of the technologies that can be used is the liquid membrane technology with the Polymer Inclusion Membrane (PIM) method. In the field of analytical chemistry, the PIM method is an alternative method used for the separation and purification of the analyte, because the PIM method can increase the sensitivity and selectivity in the process of separating and purifying an analyte. The PIM method can be used for the separation and purification of other pollutants such as dyes such as malachite green and heavy metals present in aquatic environments. The advantages of using the PIM method in dealing with the problem of liquid waste are low energy requirements, economical (no use of many chemicals), selective in the separation process, and good stability.
The stability of the membrane in the PIM method is due to the presence of basic polymers and plasticizers in the membrane components, thereby reducing leakage during the separation or recovery process. Recovery of phenol from wastewater using liquid membrane technology based on the PIM method always involves carriers that have the same structure as phenols to allow interactions between phenols to be recovered from wastewater. In addition, the carrier that will be used must have a high molecular weight to increase the active site. Copolymerization using diene compounds, such as divinyl benzene, is one method that can be used to expand the active site of the carrier (DVB). The goal of diene compound polymerization is to produce a cross-linked structure as the final product. Eugenol includes three functional groups, including allyl, ether, and hydroxyl groups, making it a suitable starting material for the synthesis of polymers. It is anticipated that the produced polymer will have a high molecular weight and numerous active sites (–OH groups and benzene rings). It is hoped that by increasing the synthesized polymer's active site, the pace of transport will also rise, making the transport process quicker and more effective. The percentage of phenol that was effectively carried in an earlier study, which was concerned with maximizing the reduction of phenol concentrations in wastewater utilizing the Polymer Inclusion Membrane (PIM) technique with copoly-eugenol diallyl phthalate (Co-EDAF) 8% carrier, was 82.42%. Additionally, earlier research showed that the PIM approach with a 10% carrier of copoly-eugenol ethylene glycol dimethacrylate (Co-EEGDMA) successfully separated phenol from wastewater by 90.82%. The second research's separation factor was quite good, but the PIM membrane used in the optimization process was not further assessed for its durability and stability. As a result, the question of what the ideal conditions for phenol transport using the PIM method with Co-EDVB 8% carrier was investigated in this study, along with how the membrane's resistance and stability were assessed through testing the PIM membrane's performance in transporting phenol. Based on this research, phenol transport will be carried out using copoly (eugenol-divinyl benzene) or Co-EDVB carriers with the PIM method. The goal of the study was to carry out a phenol transport optimization test covering variables such as the phenol pH factor in the source phase, the concentration of sodium hydroxide as a stripping agent in the receiving phase, membrane thickness, and transport time that had an impact on the efficiency of phenol transport capabilities. In addition, stability and durability tests were carried out on the PIM membrane in several test variations, such as the amount of plasticizer, types of salt, salt concentrations, repeated use, and lifetime.

EXPERIMENTAL

Materials and Methods
Along with Merck's pro-analyst (pa) quality chemicals like distilled water, aquabides, copoly(eugenol-divinyl benzene) or Co-EDVB 8%, polyvinyl chloride, dibenzyl ether, phenol, chloroform, sodium hydroxide, hydrochloric acid, 4-aminoantipyrine, ammonium hydroxide, sodium sulfate, dipotassium. In this investigation, analysis and characterization were carried out using the Fourier Transform Infrared Cary 630 from Agilent Technologies in Santa Clara, California, and the Scanning Electron Microscope JSM-6360LA from Tokyo, Japan. A digital analytical balance (ADB 200-4 Kern, Germany), a pH scale (Thermo Scientific TM Orion Star TM A211 Benchtop pH Meter, Ottawa, ON, Canada), a PIM membrane, a cylindrical chamber divided by a PIM membrane, and other tools are used. The chamber is in direct contact with the phenol solution and has an effective diameter of 3.5 cm, a capacity of 50 mL, and a diameter of 5 cm. 50 mL of phenol is used as the source phase in one chamber tube, while 50 mL of sodium hydroxide is used as the receiving phase in the other chamber tube. Then, using 4-aminoantifirin as the complex molecule, the concentration of phenol in the source phase and receiving phase was determined using a UV-Vis spectrophotometer with a maximum wavelength of 456 nm.

The Phenol Concentration was Measured using the Subsequent Procedures
Prepare a receiving phase solution comprising 5 mL of sodium hydroxide, 5 mL of phenol standard solution in concentrations of 10, 20, 30, 40, and 50 ppm, and a source phase solution containing 5 mL of phenol. The Indonesian National Standard (SNI 06-6989.21-2004), which explains how to test for phenol concentration using Spectrophotometry, lists these stages. Each of the previously made solutions was then given a 5 mL addition of aquabides to make a total of 10 mL. 1 mL of 4-aminoantipyrine 2% and potassium ferricyanide 8% were added after the pH of the source phase and phenol standard solution had
been brought down to 10.2, 10.2, and 10.2, respectively. This was carried out as hydrochloric acid, 0.5 M, was used to modify the pH of the receiving phase. The solution was allowed to settle until the color became pink. 5 mL of chloroform was added when the solution's color changed, and the mixture was then transferred to a separatory funnel. After the separatory funnel was gently agitated to aid in purification, the lowest organic layer, or chloroform layer, was separated. The absorbance of the chloroform extract was measured using a UV-Vis spectrophotometer at a wavelength (λ) of 456 nm. The levels of phenol in the source and receiving phases were calculated from the findings of the calibration curve.

The Preparation of the PIM
Carriers, fundamental polymers, and plasticizers made up the PIM membrane's three primary parts. The carrier was copoly(eugenol-divinyl benzene), the base polymer was polyvinyl chloride, and the plasticizer was dibenzyl ether. It was produced using a mold that featured a magnetic stirrer and a weight-to-size ratio of 10:32:58. In addition, the mixture was homogenized in a mold with 10 mL of tetrahydrofuran before being left for three days to allow the solvent to spontaneously evaporate. The transport device (chamber) that had been successfully created with the PIM membrane was then linked to it and used for all phenol transport procedures.

PIM Membrane Thickness Variation
PIM membranes were made with three variations in the total weight of the constituent components. Variations in the total weight of the making-up components of the membrane would produce membranes with different thicknesses. Placed in the middle of the transport pipe are polymer membranes with varying thicknesses of $T_{27}$, $T_{54}$, and $T_{108}$ that had been printed and contained carriers. Following that, 50 mL of sodium hydroxide and 50 mL of phenol were added, the latter at an optimum concentration of 60 ppm on the source phase and 50 mL on the receiving phase, respectively. The chamber was stirred with a magnetic stirrer at room temperature for nine hours with plastic wrap on it.

Variation in Transport Time
In the center of the transport pipe (chamber), the PIM membrane containing the carrier with the ideal membrane thickness was placed. Next, 50 mL of phenol at a concentration of 60 ppm was added as the source phase with the ideal pH, and 50 mL of sodium hydroxide was added as the receiving phase with the ideal concentration. The chamber was covered in plastic and agitated at room temperature for 4, 9, 12, 18, 24, 28, 32, and 48 hours with varying transit times.

Evaluation of PIMs' Capability and Resistance
Variations in Types of Salt
The PIM membrane was positioned in the center of the transport pipe (chamber), containing the carrier with the ideal membrane thickness. Additionally, 50 mL of a 60 ppm phenol solution that contained salt and the optimum pH was added to the source phase. The salts in the source phase included sodium sulfate, sodium chloride, sodium nitrate, potassium nitrate, and potassium chloride, each at a concentration of 0.01 M. During the receiving phase, 50 mL of sodium hydroxide was supplied at the appropriate concentration. The chamber was agitated with a magnetic stirrer at room temperature and wrapped in plastic for optimal travel time.

Variation in Salt Concentration
The PIM membrane was positioned in the center of the transport pipe (chamber), containing the carrier with the ideal membrane thickness. Furthermore, the source phase with the ideal pH and ideal salt type received 50 mL of a 60 ppm phenol solution combination. The source phase's salt content was adjusted from 0 to 0.001, 0.01 to 0.1, and 1 M. The ideal concentration of sodium hydroxide was applied to 50 mL of the receiving phase. For the best transit time, a magnetic stirrer was used to agitate the chamber at room temperature.

Lifetime
Without any time restrictions, the phenol transport procedure was carried out under ideal circumstances. The transport pipe is magnetically agitated and sealed on both the receiving phase and the source phase.
Lifetime is determined by the pH of the source phase. A rise in pH in the source phase indicates the PIM membrane is beginning to leak. Periodically, the source phase's pH was monitored up to a pH of 9.0, at which point the transport process was halted. The PIM membrane's stability with or without salt will be evaluated by the lifespan measurement. The PIM membrane's stability was evaluated in two different scenarios: without salt and with optimal salt content.

RESULTS AND DISCUSSION

Phenol Transport Optimization
In this study, the transfer of phenol from the source phase to the receiving phase was investigated using a membrane phase containing a copoly(eugenol-divinylbenzene) 8% carrier. A 50 mL solution of aqueous sodium hydroxide is used in the receiving phase, whereas a 50 mL solution of phenolic solution at a 60 ppm concentration was used in the source phase. By converting the phenol in the source phase into phenolic ions in the receiving phase, the sodium hydroxide solution acts as a stripping agent, preventing phenol from diffusing back into the membrane phase.

PIM Membrane Thickness Variation
The thickness and total weight of the PIM membrane could be varied by varying the weight of the components making up the membrane. The efficiency of phenol transport could be affected by the thickness and total weight of the PIM membrane used during the transport process. Based on differences in the thickness and overall weight of the PIM membrane, Fig.-1 depicted the fluctuation in the percentage of phenol concentration in the receiving phase (%Cp).

![Graph Depicting Changes in the PIM Membrane's Thickness and Overall, Weight in Relation to the Amount of Transferred Phenol](image)

**Information**

- %Cs: the proportion of phenol in the source phase.
- %Cp: the proportion of phenol in the receiving phase.

The T54 membrane or PIM membrane with a total weight of 0.54 g experienced the best phenol transport, with a phenol concentration in the receiving phase (%Cp) of 60.35%. Based on the graph above, it could be seen that variations in the thickness and total weight of the PIM membrane could affect the efficiency of phenol transport as evidenced by the different %Cp results depending on the type of thickness and total weight of the PIM membrane. PIM membranes with type T54 have a shape that was not too thick and thin, besides that membranes with type T54 are believed to have the maximum number of phenol molecules that interact with carriers, to increase the efficiency of the phenol transport process. The comparison of the components of the T54 membrane was very good, because the carriers, basic polymers, and plasticizers used are not too much or too little.

Variation of Transport Time
Another factor that affected the performance of phenol transport was the length of contact time. Time is an important factor that needs to be considered in phenol transport because the longer the transport time, the proportion of phenol concentration in the receiving phase might rise as a result of the significant increase in the interaction between phenol and carriers on the membrane. Good membrane performance was evaluated by the percentage of phenol concentration that was successfully conveyed to the receiving phase during the short transit duration. Figure-2 was a time variation graph of phenol transport. Based on the data as it had been shown in Fig.-2 above, it was known that the phenol transport with the highest percentage of phenol concentration was in the receiving phase (%Cp), namely during the 24-hour...
transport time with the %Cp of 89.03%. However, the phenol transport time above 24 hours experienced a decrease in the percentage of phenolic concentration in the receiving phase, because the sodium hydroxide solution in the receiving phase was unable to create any more sodium phenolic ions, this was made feasible. In addition, the longer transport time could also lead to a reduction in the components that make up the PIM membrane (leaching) which results in reduced active sites on the PIM membrane.\textsuperscript{33}

![Graph of Time Variation on the Concentration of Transported Phenol](image)

**Fig.-2.** Graph of Time Variation on the Concentration of Transported Phenol

### Evaluation of PIM Membrane Capability and Stability in Transporting Phenol

#### Variations in Types of Salt

This form of salt variation was accomplished by introducing several types of salt to the source phase, each at a concentration of 0.01 M. The PIM membrane used to transport the phenol can leach less when salt is present in the source phase, making the PIM membrane more stable as compared to when salt is not present.\textsuperscript{34} Figure-3 showed that the addition of the type of salt affects the efficiency of phenol transport.

![Graph of Variation of Salt Types on the Concentration of Transported Phenol](image)

**Fig.-3:** Graph of Variation of Salt Types on the Concentration of Transported Phenol

The addition of NaNO\textsubscript{3} salt in the source phase showed that phenol concentration was effectively transferred to the receiving phase in a larger proportion than when other types of salt were added, with an a%Cp of 68.62%. Compared to other varieties of salt, this type of salt has lower quantities of NaNO\textsubscript{3}. The quantity of cations in the phenol solution increases with the amount of cations present in the kind of salt present in the source phase. The number of ions in the source phase may hinder the transport of phenol, resulting in a decreased percentage of phenol concentration delivered to the receiving phase.\textsuperscript{35}

### Variation in Salt Concentration

To determine how much of the phenol concentration was effectively transmitted to the receiving phase (%Cp), salt was added to the source phase at various salt concentrations. Figure-4 demonstrates how the outcomes were changed by varying the concentration of the NaNO\textsubscript{3} salt in the source phase. The sodium nitrate concentration of 81.58% in the 0.001 M salt solution produced the highest percentage of phenol concentration that was effectively transferred to the receiving phase (%Cp). As a result of the lower percentage of phenol concentration delivered to the receiving phase due to the higher sodium nitrate salt concentration, the carrier's active side might be reduced.\textsuperscript{36} Because the ionic strength in the source phase is lower than that in the receiving phase, phenol transfer in conditions with no addition of salt or with the addition of low salt concentrations will result in an emulsion that forms readily. The membrane's longevity (life) may be shortened by the emulsion that has developed on the PIM membrane, which can also make the membrane unstable.\textsuperscript{24}
Lifetime
A leak in the PIM membrane used has occurred if the source phase's pH hits 9, which may be determined by continuously executing phenol transfer while keeping track of the source phase's pH. The PIM membrane's stability was examined under two different settings, namely with and without the addition of 0.01 M sodium nitrate salt, the results could be seen in Fig.-5.

![Graph of Variation of Salt Concentration to the Concentration of Transported Phenol](image1)

**Fig.-4:** Graph of Variation of Salt Concentration to the Concentration of Transported Phenol

![pH Variations of Phenol with Time in the Source Phase](image2)

**Fig.-5:** pH Variations of Phenol with Time in the Source Phase

Figure-5 shows that the PIM membrane with the source phase condition of no salt addition leaked on the 13th day with a pH of 9.1. The membrane was given PIM with the condition of the source phase adding sodium nitrate 0.01 M salt having a longer lifetime because leakage in the membrane occurred on the 34th day with a pH of 9.2 in the source phase. This showed that the PIM membrane with the addition of sodium nitrate 0.01 M salt is more stable than the PIM membrane without the addition of salt.

PIM Membrane Characterization Before and After Phenol Transport

**FT-IR (Fourier Transform-Infrared)**
FT-IR characterization will be used to ascertain the alterations in the wave numbers of the functional groups present in the PIM membrane before and after phenol transfer. The wave number of the hydrogen groups on the PIM membrane will change as a result of the interaction between phenol and carriers during the transport process. The difference in wave numbers could be seen in the FT-IR characterization results shown in Fig.-6.

![Comparison of the FT-IR Spectra of the PIM Membrane](image3)

**Fig.-6:** Comparison of the FT-IR Spectra of the PIM Membrane (a) Before Transport and (b) after Transport
The PIM membrane's characteristic FT-IR spectral peaks before and after phenol transfer were depicted in Fig.-6 above, some of the spectral peaks experienced a shift in wave number. The typical peaks are hydrogen bonding (-OH), stretching Csp²-H, aromatic rings (C=C), vinyl (CH₂=CH-), and aromatic rings (C-H). The specific absorption in both spectra indicated, the PIM membrane before and after transport has the same functional groups. The difference from these spectra is situated in the intensity (area) of the peaks and the shift in wave numbers. The two spectra were compared, and it was discovered that throughout the phenol transport process, there was contact between the -OH groups in the carriers and the -OH groups in the phenol, as evidenced by a shift to the right in wave number for hydrogen groups (-OH) absorption on the PIM membrane before and after phenol transport. Because the active site in the Co-EDVB 8% carrier present in the PIM membrane was partially destroyed or underwent leaching during the transport procedure, a shift in wave number in the -OH group could result. The outcomes of the PIM membrane characterization by SEM might also be used to demonstrate the loss of some of the active spots on the membrane following transport.

SEM (Scanning Emission Microscopy)

The PIM membrane's morphology will be seen through the characterization of the PIM membrane using SEM before and after phenol transfer. The findings of the SEM characterization of the membrane before and after phenol transfer were displayed in Fig.-7.

Figure-7 above shows that the PIM membrane after phenol transport had an uneven surface morphology and larger pore sizes compared to the PIM membrane before transport. This happened because, during the phenol transport process, the PIM membrane experienced leaching or lost some of the membrane components resulting in enlarged membrane pores. Partially, missing membrane components could come from carriers, basic polymers, or plasticizers. The findings of this investigation showed that the Co-EDVB 8% carrier and membrane utilized to transport phenol utilizing the Polymer Inclusion Membrane (PIM) technique had extremely excellent efficiency. However, this PIM membrane still has limitations in its use, which could only be used for 34 days (lifetime) and could be only used for up to 5 (five) repetitions.

CONCLUSION

It was determined from the study's findings and analysis that the PIM membrane's carrier copoly(eugenol-divinylbenzene) (Co-EDVB) 8% was effective, it was capable of transporting phenol at optimum conditions with the thickness of the PIM membrane which was not very thick and it was not very thin, and the length transport time was 24 hours. PIM membranes had good resistance and stability, they had been proven by their lifetime of 34 days and PIM membranes could be used up to 5 repetitions. However, the resistance and stability of the PIM membrane could be further increased by adding several influence parameters such as stirring speed and repeated use tests more than 5 times.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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