INTRODUCTION

Several chemical compounds are widely used as basic ingredients to produce a product in the pharmaceutical field. In addition to the pharmaceutical sector, the use of these chemical compounds has now significantly increased in the industrial sector. Phenolic compounds are the examples of chemical widely used for different purposes (Kiswando et al. 2012). Phenol is used in the home as a disinfectant, cleaning agent, and deodorizer. Phenol is also used in laboratories to synthesize C-methyl-4,10,16,22-tetramethoxycalix(4) arene with BF₃-methanol as a catalyst (Kiswando 2016), while on an industrial scale phenol is used for the manufacture of phenolic resins such as phenol-formaldehyde resins (Dakhil 2013; Strecková et al. 2012).

Inadequate handling of liquid waste containing phenolic compounds and their derivatives from industry, hospitals, laboratories or domestic liquid waste can cause problems for the environment and human health (Li 2020). Another impact caused by the lack of handling of liquid waste containing phenolic compounds is the increase in water pollution (Liu et al. 2013).
increase in the level of water pollution by phenolic waste is due to inadequate waste management, reflecting the need for more effective treatment technology (Villegas et al. 2016; Saratale et al. 2015). The development of phenol recovery methods from wastewater is currently the concern of many researchers, in order to find solutions for phenol waste management (Ariesmayana, 2018; Sun et al. 2017). Phenol waste treatment needs to be carried out with methods that are more practical, inexpensive, and fast (Othman et al. 2015). One of the renewable methods that can be used to perform the separation and recovery of phenol is liquid membrane method (Refinel et al. 2019; Kiswandono 2016; Yang et al. 2015).

Because it has a broad separation spectrum, is selective, and is simple to use, liquid membrane-based separation technology is presently generating an increasing amount of interest (Rosly et al. 2018). These benefits result from the fact that liquid membrane separation doesn’t require any extra chemical substances and that it uses very little energy and is therefore technically, economically, and energetically advantageous (Pavón et al. 2020; Kazemi et al. 2014).

One of the developments of a liquid membrane method that has better stability among other liquid membrane methods in an effort to separate and purify phenol compounds from wastewater is Polymer Inclusion Membrane (PIM) method (Kiswandono et al. 2022; Saka et al. 2020; Kiswandono et al. 2019; Benosmane et al. 2018; Kiswandono et al. 2013; Kiswandono et al. 2012). The PIM method is considered capable of increasing stability for two reasons. The first is associated with the presence of a basic polymer (polyvinyl chloride-PVC) which is expected to overcome the loss of carrier (Cho et al. 2018; O’Bryan et al. 2017; Suah 2017; Wang et al. 2017; Febrisasari et al. 2016; Kaya et al. 2016). Secondly, PIM membranes also contain plasticizers that function to improve the stability of the membrane (Sellami et al. 2019; Chaouqi et al. 2019; Croft et al. 2018; Ling et al. 2017; Turgut et al. 2017).

Eugenol is the natural compound-based carrier that can be used to carry phenol (Djunaïdi 2019). Eugenol can be used as a starting material for polymer synthesis because it has three functional groups, namely allyl, ether and hydroxy groups (Djunaïdi et al. 2018; Hikmah et al. 2018; Silva et al. 2018). The availability of hydroxy groups allows interactions with phenols that have the same group to pass through the membrane (Kiswandono et al. 2019). The requirement for polymers that can be used as carrier in the membrane phase is the membrane must have a structure that allows interaction with the compound to be transported and has a high molecular weight (Saka et al. 2020).

One alternative to increase the active site in a membrane is by copolymerization (Kiswandono et al. 2020). Ethylene Glycol Dimethacrylate (EGDMA) can be used as an initial raw material for chemical synthesis to form homopolymers and copolymers (Kiswandono et al. 2017). The copolymer resulting from this polymerization has increased molecular weight, so it is expected to increase the ability of the membrane to interact with phenolic compounds, thereby increasing the efficiency in transporting phenol.

Based on the information provided above, this investigation examined phenol transport by the PIM method using a membrane prepared from a 10% copolymer of eugenol and ethylene glycol (Co-EEGDMA) as a carrier. The pH of the source phase, the concentration of the receiving phase, and the transport duration were some of the variables that were assessed as potential phenol transport efficacy determinants. Additionally, different conditions such as plasticizer concentrations, salt concentrations, and membrane lifetimes were investigated in order to determine the stability and capability of the PIM membrane with 10% Co-EEGDMA as a carrier. It is anticipated that this PIM membrane will effectively transport phenol, and that it will do so with excellent stability.

MATERIALS AND METHODS

The instruments used in this study include a digital analytical balance (Mettler Toledo AB54-S), pH scale (Thermo ScientificTM Orion StarTM A211 Benchtop pH Meter, Ottawa, ON, Canada), while the analysis and characterization in this study used UV-Vis 772 Spectrophotometer (Shanghai, China), Cary 630 Fourier Transform Infrared (FTIR), (Agilent Technology, Santa Clara, CA, USA), and JSM-6360LA Scanning Electron Microscope (Tokyo, Japan). Two cylindrical compartments and a PIM membrane make up the transport apparatus. The chamber has a diameter of 5 centimeters, and its functional diameter (which is in direct contact with the phenol solution of 3.5 cm), and 50 mL volume (Figure 1).
The materials used in this study were masking tape, aluminum foil, tissue, distilled water, aquabidest, copoly-eugenol ethylene glycol dimethacrylate (co-EEGDMA) 10%, in addition to the pro-analyst quality (pa) chemicals produced by Merck, including polyvinyl chloride (PVC), dibenzyl ether (DBE), phenol (C₆H₅OH), chloroform (CHCl₃), sodium hydroxide (NaOH), hydrochloric acid (HCl), 4-aminoantipyrine (C₁₁H₁₃N₃O), potassium ferricyanide [K₄Fe(CN)₆], ammonium hydroxide (NH₄OH), sodium sulfate (Na₂SO₄), dipotassium phosphate (K₂HPO₄), sodium nitrate (NaNO₃), sodium chloride (NaCl), potassium chloride (KCl) and potassium nitrate (KNO₃), these chemicals were used as received.

50 mL of NaOH is used as the reception phase in one chamber tube, and 50 mL of 60 ppm phenol is used as the source phase in the other chamber tube. The 4-aminoantipyrine technique was then used to determine the amount of phenol present in the source phase and receiving phase using a UV-Vis spectrophotometer with a maximum wavelength of 456 nm (Kiswandono et al. 2022). The steps were as follows: The end volume was 10 mL after the addition of 5 mL each of the source phase, receiving phase, and standard phenol solution in a range of concentrations. While the pH of the recipient phase was adjusted with 0.5 M HCl, 1 mL of 2% 4-aminoantipyrine and 8% potassium ferricyanide were added after the pH of the source phase and the standard phenol solution was adjusted with 1 M NH₄OH, phosphate buffer. Until the hue of the solution turned pink, the solution was left to stand.

After the solution’s color changed, 5 mL of chloroform was added and it was moved into a separating funnel. The organic layer, or chloroform layer (bottom), was separated after the separating funnel was shaken and left to stand for a while until separation happened. A UV-Vis spectrophotometer was used to measure the absorbance of the chloroform extract at a wavelength (λ) of 456 nm. The calibration curve was used to determine the levels of phenol in the source phase and the receiving phase.

Setting up the PIM

The 10% co-EEGDMA as a carrier, the PVC as the base polymer, and the DBE as the plasticizer made up the three primary components of the PIM membrane, in the weight ratio of 10:32:58. Once the raw ingredients were transferred into a mold with a magnetic stirrer, 10 mL of tetrahydrofuran (THF) was added to homogenize the mixture. The mixture was then left to stand for three days to let the solvent naturally drain. As illustrated in Figure 1, the produced PIM membrane was put on the transport chamber and used for phenol transport experiments.

Phenol transport

The source phase’s pH has an impact

Experiments were carried out at different pH values of 3.5, 4.5, 5.5, 6.5, and 7.5 while maintaining a constant 0.5 M concentration of NaOH as the receiving phase in order to assess the impact of source phase pH. After that, a magnetic stirrer was used to agitate the solution in the source phase and the receiving phase in the chamber for nine hours at room temperature. The source phase’s ideal pH was determined from these trials and subsequently used in additional experiments.
**NaOH concentration has an impact**

A series of tests were carried out at various NaOH concentrations of 0.05, 0.1, 0.15, 0.25, and 0.5 M to assess the influence of NaOH concentration in the receiving phase, while the pH of phenol in the source phase was maintained at the ideal pH found in the preceding method. For nine hours, a magnetic stirrer was used to agitate the two solutions in the chamber at room temperature. The ideal NaOH concentration was discovered through these experiments and used throughout the remainder of the research.

**Effect of time**

A series of tests were conducted at the ideal source phase pH and NaOH content, and the solution was stirred at various intervals of 4, 9, 15, 24, 39, 48, and 62 hours to examine the influence of time. Form these experiments, the optimum time was obtained.

**Assessment of PIM capability and resistance**

**A plasticizer’s load’s impact**

PIM membranes were prepared with the use of plastizer with varied masses of 0.3032; 0.3100; 0.3132; 0.3200; 0.3232 g. Based on the procedures in the literature (Kiswandono et al., 2022), In this work, the amount of plasticizer employed was modified to create a membrane that is neither overly greasy nor rigid. The membrane was then moved between two tube chambers containing the source phase and the receiving phase after being weighed beforehand. Thereafter, 50 mL of 60 ppm phenol with the ideal pH and NaOH with the ideal concentration were added to the source phase and receiving phase, respectively. For 48 hours, the phenol solution was stirred at room temperature and out of the sun. The same treatment was applied during the study at room temperature and was not exposed to sunlight in accordance with the chemical data sheet’s recommendation that safe storage conditions are in a cool environment. Using a UV-Vis spectrophotometer and the 4-aminoantiphyrin technique, the concentration of phenol in both phases was determined (Kiswandono et al. 2022).

**Effect of salt concentration**

For this aim, phenol transport tests were conducted using a source phase filled with 50 mL of salt solution in 60 ppm phenol with pH values of 5.5, 0.001, 0.01, 0.1, and 1.00 M, and a receiving phase filled with 50 mL of 0.5 M NaOH solution. Each phase received a small magnetic bar, and the chamber was sealed. It was agitated for 24 hours at ambient temperature without being exposed to sunlight. Using a UV-Vis spectrophotometer with a 456 nm wavelength, the phenol concentrations present in the source and receiving phases were examined after 24 hours.

**Lifetime of PIM membrane**

Two sets of experiments were used to test the phenol transport process, each with a source phase containing 50 mL of a 60 ppm phenol solution with a pH of 5.5 and a receiving phase containing 50 mL of 0.5 M NaOH. The first experiment had no salt addition, while the second experiment included salt addition with an ideal concentration of 0.01 M. Each phase was given a tiny magnetic bar and agitated at ambient temperature before the chamber was sealed. Periodically measuring the pH of the source and receiving phases was done until the source phase’s pH reached ±9.00.

**RESULT AND DISCUSSION**

**Phenol transport**

**The source phase’s pH has an impact**

The first step of this investigation was carried out to evaluate the influence of pH by carrying out the experiment at various pH of 3.5, 4.5, 5.5, 6.5, and 7.5 for phenol transport. Benosmane et al. (2018) claim that the pH in the source phase affects phenol transport.

According to the transport process’s findings, phenol was delivered at a pH of 5.5 and had 34.07% of its total content in the receiving phase (% Cp). It was hypothesized that this transport is connected to hydrogen bonding since phenol and the carrier (10% co-EEGDMA) interacted negatively on the membrane surface (Kiswandono et al. 2022).

The quantity of phenol transferred from the source phase to the receiving phase was determined by measurement using UV-Vis Spectroscopy, as shown in Figure 2. The amount of phenol removal that was effectively carried was 63.99%, and the receiving phase’s ideal phenol
percent recovery was 34.07%. Figure 2’s findings showed that less phenol was transferred to the receiving phase the more alkaline the source phase’s pH was.

**NaOH concentration has an impact**

Concentration as a substance that draws phenol from the membrane phase and transforms it into sodium phenolic compounds, NaOH solution is acknowledged to play a significant function in the receiving phase. Figure 3 displays the outcomes with various NaOH concentrations of 0.05, 0.1, 0.15, 0.25, and 0.5 M in the receiving phase.

According to the findings in Figure 3, the amount of NaOH present significantly affects the amount of phenol transferred during the reception phase. The optimal phenol transfer was achieved at pH 5.5 and 0.5 M NaOH concentration, as shown in Figure 3. Under this optimum condition, phenol removal was 72.83% and phenol recovery was 58.24% of the phenol transported in the receiving phase. This pattern is consistent with findings from other studies (Kiswandono et al. 2020).

**Effect of time**

Prior research by Kiswandono et al. (2020) looked at how time affected the phenol transport efficiency and the kinetics of poly-bisphenol A diglycidyl ether (poly-BADGE). In the current study, 10% copoly-EEGDMA was used as the carrier to assess the impact of transit duration on the transport efficiency of phenol (Kiswandono et al. 2020). By conducting studies at various times of 4, 9, 15, 24, 39, 48, and 62 hours, the impact of time on phenol transport was assessed. The results are displayed in Figure 4.

The results in Figure 4 show that the effect of transport time is rather evident, with the amount of phenol transported increasing as transport time increases and reaching the optimal level of 90.82% at transport time of 48 hours. This is due to the fact that as transit time grows, phenol in the membrane interacts more with the receiving phase. An rise in the number of unoccupied sites on carriers in PIM can be blamed for the early period’s increased deletion rate (Benosmane et al. 2018).
Assessment of PIM capability and resistance

A plasticizer’s load’s impact

Plasticizers are parts of PIM membranes that function as neutralizers of polar polymers with their own polar groups to diminish the intermolecular forces of attraction and shorten the distance between polymer molecules. Plasticizers are also present in PIM membrane components, which results in a membrane that is robust, elastic, more stable, and flexible. The impact of plasticizer concentrations added to the PIM membrane on phenol transport is seen in Figure 5. Figure 5 shows that the optimal amount of phenol transport (91.54%) was accomplished with 0.3132 g of plasticizer.

When plasticizers are added to the membrane, the rate of transport is accelerated and species diffusion is encouraged. Moreover, plasticizer boosts the membrane’s flexibility, but when the amount exceeds the permitted limit, it can also act as a barrier to the transfer of phenol to the receiving phase. According to reports, using more plasticizer than is necessary can reduce mass transfer and decrease transport due to intermolecular interactions between the target and plasticizer molecules (Benosmane et al. 2018).

Effect of salt concentration

The presence of salt in the membrane is an important factor associated with the stability of the membrane (Asrami 2019). In this study, the salt used was NaNO$_3$ and added with different concentrations into both the source phase and the receiving phase in order to evaluate the effect of salt concentrations on the transport yield. Figure 6 presents the experimental results obtained by adding salt to the source phase, demonstrating that higher salt concentrations resulted in a decrease in the percentage of phenol transferred to the receiving phase.

Figure 7 displays the experimental outcomes obtained by adding salt to the receiving phase. The pattern is similar to that seen when salt is added to the source phase (Figure 6), where the...
percentage of phenol transported decreases as salt concentration increases.

**Lifetime of PIM membrane**

Based on the membrane’s capacity to transport phenol at specific times, the stability and resiliency of the membrane were assessed. According to numerous studies, one of the primary causes of instability in the liquid membrane transport process is the loss of membrane components. By measuring the pH value, one may also estimate the membrane’s lifespan. It is well known that the PIM membrane is harmed when the pH of the source phase is raised. Also, the phenol transport mechanism was terminated when the pH reached 9, leading researchers to believe that the membrane had been harmed or had leaked. By conducting an experiment with and without the addition of 0.01 M NaNO$_3$ salt in the source phase, which contained 60 ppm phenol solution at pH 5.5, the PIM membrane lifetime was investigated.

According to Table 1, adding salt to the source phase increases PIM’s stability in subsequent phases, which lowers membrane leakage. Table 1 shows that adding 0.01 M NaNO$_3$ to the source phase increased the membrane’s longevity compared to a membrane without salt addition.

**PIM membrane characterization**

Figs. 8 displays the functionality of the PIM membranes (prepared with the use of 0.3132 g plasticizer) before and after application for phenol transport, as seen by FT-IR. The FTIR spectra clearly show that the peak of the absorption band assigned to –OH stretching functional group

![Image](https://example.com/image1.png)

**Figure 6.** A Graph showing the effect of NaNO$_3$ concentrations added into the source phase on the percentage of transported phenol

![Image](https://example.com/image2.png)

**Figure 7.** A Graph showing the effect of NaNO$_3$ concentrations added into the receiving source on the percentage of transported phenol
experienced a shift in position from 3526 cm\(^{-1}\) to 3354 cm\(^{-1}\). There is also a shift change at 3391 cm\(^{-1}\). The phenol transport experiment resulted in a decrease in the relative intensity of the absorption band at 3526 cm\(^{-1}\) in the spectrum of the membrane, indicating that the membrane’s -OH group was leached into the receiving phase. Most likely, the interaction between the phenol and the carrier present in the PIM membrane through hydrogen interactions and \(\pi-\pi\) interactions caused this leaching.

Figure 9 shows the SEM micrographs of the PIM membrane before (Figure 9a) and after transport (Figure 9b), displaying a contrast surface morphology. The membrane’s micrograph after transport shows that it has undergone a leaching process or component release since there are pores and voids spanning the whole surface of the membrane. DBE and 10% co-EEGDMA carrier are two membrane components that dissolve in THF and fill the membrane pores formed by the polymer support (PVC). The visible pores of the membrane after transport indicate that there has been an interaction between phenol and the 10% co-EEGDMA carrier.

**CONCLUSION**

Under the ideal conditions of pH 5.5 of the phenol solution in the source phase, 0.5 M NaOH concentration, and 48 hours of phenol transport, a membrane made from PVC as a base polymer with 10% co-EEGDMA as a carrier and DBE as a plasticizer can be employed to transport phenol. The membrane’s resistance was only 24 days

<table>
<thead>
<tr>
<th>Without salt</th>
<th>Addition of NaNO(_3) 0.01M</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Day</strong></td>
<td><strong>pH</strong></td>
</tr>
<tr>
<td>0</td>
<td>5.5</td>
</tr>
<tr>
<td>1</td>
<td>5.6</td>
</tr>
<tr>
<td>4</td>
<td>6.2</td>
</tr>
<tr>
<td>6</td>
<td>6.3</td>
</tr>
<tr>
<td>12</td>
<td>7.2</td>
</tr>
<tr>
<td>14</td>
<td>7.8</td>
</tr>
<tr>
<td>18</td>
<td>8.3</td>
</tr>
<tr>
<td>22</td>
<td>8.6</td>
</tr>
<tr>
<td>24</td>
<td>9.26</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1. Lifetime of PIM membrane
without the addition of NaNO₃, but it rose to 108 days with the addition of 0.01 M NaNO₃. It is important to recognize that the loss of membrane elements throughout the transport process is a problem that necessitates additional research to increase the stability of the PIM membrane under investigation.

Acknowledgments

Acknowledgments to the Ministry of Research, Technology and Higher Education of the Republic of Indonesia (Kemenristekdikti RI) for funding this research (No. 027/E5/PG.02.00/PT/2022, 16th March 2022, No. 2143/UN26.21/PN/2022, 29th April 2022).

REFERENCES

ijc/article/view/21348/14053


