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Evaluation of Phenol Transport Using Polymer Inclusion Membrane (PIM) with Polyeugenol as a Carrier

Evaluasi Transpor Fenol menggunakan Polymer Inclusion Membrane (PIM) dengan Polieugenol sebagai Karir

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Abstract

A recovery study of phenol with Polymer Inclusion Membranes (PIMs) needs to be evaluated to determine values of transport kinetic parameter, level of stability, and selectivity of the membrane. This paper describes results of the evaluation of phenol transport using PIMs with polyeugenol as a carrier. PIMs were made by mixing polyeugenol, dibenzylether, and polyvinylchloride in a solvent (tetrahydrofuran) then printed in a container with diameter 4.5 cm and allowed to vaporize for 72 hours. Further evaluation studies are conducted at pH 4.5 with various parameters, among of them are various times that were taken to identify parameters of the transport kinetics of phenol, membrane stability, characterization, and testing of membrane selectivity by comparing transport of phenol with another compound, in this study chromium is used. This study results in calculation of values of transport kinetics of membrane permeability obtained at 8.8 x 10^{-5} m/s, flux value of 9.512 x 10^{-4} g/m^2s, and diffusion coefficient of 3.826 x 10^{-11} m^2/s. Repeating use over three times, 48 hours, indicates reduction in power of phenol transport by 70.81%. While selectivity test indicates that membrane is used more selectively against phenol than chromium metal. Based on study results, phenol transport effectiveness using PIM with polyeugenol as carrier is 91.4% in optimum condition.

Keywords: membrane, phenol, polyeugenol, polymer inclusion membrane

Abstrak

Studi recovery fenol menggunakan Polymer Inclusion Membran (PIM) perlu dievaluasi untuk menentukan nilai parameter kinetika, kestabilan, dan selektifitas membran. Artikel ini mendiskripsikan hasil evaluasi transport fenol dengan metode PIM dengan polieugenol sebagai membrane karir. PIM dibuat dengan mencampurkan polieugenol, dibenzileter, dan polivinilklorida ke dalam pelarut tetrahidrofuran kemudian dicetak dengan cetakan berdiameter 4,5 cm dan diuapkan selama 72 jam. Studi evaluasi dilakukan pada pH 4,5 dengan beberapa variasi parameter, yaitu kinetika transport, stabilitas membran, karakterisasi, dan uji selektifitas membran dengan membandingkan transport fenol dengan senyawa lain berupa logam, dalam penelitian ini digunakan kromium. Dari hasil studi kinetika transport didapatkan nilai permeabilitas membran 8,8 x 10^{-5} m/s, nilai fluks 9,512 x 10^{-4} g/m^2s, koefisien difusi 3,826 x 10^{-11} m^2/s. Pada penggunaan membran yang berulang sebanyak tiga kali selama 48 jam, didapatkan kemampuan transport fenol sebesar 70,81%. Uji selektifitas menunjukkan bahwa membran lebih selektif terhadap fenol dibandingkan kromium. Berdasarkan hasil studi, recovery fenol melalui PIM dengan polieugenol sebagai karir memiliki efisiensi sebesar 91,4% pada kondisi optimum.

Kata Kunci: membran, fenol, polieugenol, *polymer inclusion membrane*

1. Introduction

Phenol is one of organic compounds that can be contaminant when exposed to the environment. In particular, the concentration of these compounds can give bad effect on humans, which include liver and kidney damage, decreased blood pressure, heart rate weakening, until death. Therefore, a reduction of phenol is necessary in order to prevent its effect on health and environment (Yu *et al*., 2012). Concentration of phenol in drinking water that is allowed according to WHO standard is 0.2 mg/l (Nwaici *and Warigbani,* 2013).
Based on the latest advance, reduced levels of phenol in wastewater can be done with separation or destruction technology, which

includes biodegradation (Busca *et al*., 2008), adsorption (Djebbar *et al*., 2012), electro-chemical oxidation (Zhang *et al*, 2011), hollow-fiber membrane (Shen *et al*., 2012), and others.

Among these methods, the membrane method is a method that is quite a concern in recent years. Kiswandono, et al. (2012) conducted a phenol recovery with Bulk Liquid Membrane method with polyeugenol as a membrane carrier. Furthermore, Kiswandono, et al. (2012) recovers phenol with Polymer Inclusion Membrane (PIM) using Copoly (eugenol-DVB) as a carrier membrane with rejection percentage of 75.6%. This is less than transport using polyeugenol.

PIM, which is part of the SLM (Supported Liquid Membrane) method, is effective in separating desired substance in a liquid waste. PIM consists of basic polymers, plasticizers, and carrier compounds that are selective for purified substance. The ingredients are mixed in a solvent which is then evaporated at room temperature until dry (Gherasim *and Bourceanu*, 2013). Specific advantages of PIMs are immobilizing the effective membrane carrier, preparation is easy, flexible, stable, better mechanical properties, and its stability is higher than other SLM methods (Saf *et al*., 2011). In addition, the main advantage of PIMs is the level of its selectivity compared to solvent extraction method or the others (Guo *et al*., 2011).

Polyeugenol as a carrier in the PIM is expected to be an effective compound to transport phenol in wastewater because of similarity of functional groups. This study evaluates the effectiveness of PIM use with polyeugenol as a carrier for phenol transport. Evaluation is based on several parameters including determination of kinetic parameters based on various times of transport, membrane use repeatation, and selectivity of phenol transport with another compound. This study uses chromium as a comparison in the selectivity test to prove that polyeugenol is a suitable carrier for phenol recovery.

2. Methodology

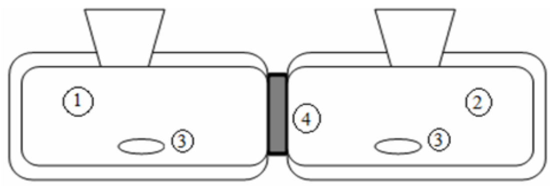
Materials used in this study are Polyeugenol and Polyvinylchloride. Chemicals are pure products of analytical quality, i.e., $CHCl_3$, NaOH, HCl, 4-aminoantipirin, $K_4Fe(CN)_6$, NH_4OH, Na_2SO_4 anhydrous, tetrahydrofuran, dibenzylether (DBE), and $CrCl_3$. The tools used in this study are pH meter, a series of tools such as chamber of phenol transport, magnetic stir bar, separating funnel, supporting tools such as tools and plastic cups, analytical balance (Mettler Toledo AB54-S), shaker, UV-Vis spectrophotometer (772 Spectrophotometer), infrared spectro-photometer (Shimadzu FTIR 8201PC), Analytical Scanning Electron Microscope (JSM-6360LA).

2.1. Preparation of Polymer Inclusion Membranes

PIMs are made by mixing polyeugenol as a carrier, polyvinylchloride (PVC) as a based polymer, and dibenzylether (DBE) as a plasticizer. PIMs are prepared by dissolving polyeugenol, PVC, and DBE in tetra-hydrofuran (THF) solvent by poly-eugenol/PVC/DBE ratio of 10: 32: 58 in THF solvent as much as ± 10 mL.Total weight of PIM is 270 mg. After all, ingredients are homogeneously mixed, PIMs are printed by using a glass mold with diameter 4.5 cm and allowed to stand for 72 hours to dry.

2.2. Transport of Phenol through PIM-Polyeugenol

PIM with a diameter of 4.5 mounted on the membrane column barrier transports phenol between the source and the strip phase, then hand of strip phase column is filled by 40 ml of NaOH with pH 11, and the source phase is filled by 40 mL of 100 ppm phenol solution with pH 4.5 (Figure 1).



1. Feed solution phase
2. Stripping solution phase
3. Magnetic stirrer
4. Membrane PIM

Figure 1. Design of experimental set up of PIM (Kiswandono *et al*., 2012)

Phenol transporting column is closed and then each phase is stirred with a various times, i.e. 1, 6, 12, 24, 48, and 72 hours at room temperature. In addition, the evaluation test is also conducted repeatedly including selectivity of PIM against phenol by comparing phenol transport and chromium transport.

Detection Method:
Characterization of PIM surface is done by using Scanning Electron Microscope (SEM) and Fourier Transform Infra Red (FTIR). Detection method on phenol transport, the concentration of phenols contained in the source phase and strip phase is analyzed by using a UV-Vis spectrophotometer at a maximum wavelength 455 nm. Each variation is repeated three times.

2.3. Determination of Transport Kinetic Parameters

Transport kinetic parameters of phenol through PIM-Polyeugenol are calculated in this study, i.e. permeability, flux, and the diffusion coefficient of transport. The calculation refers to the Kusumocahyo (2006), in which the determination of the permeability of transport is calculated from first-order equation.

$$\ln\left(\frac{C_s}{C_s^0}\right) = -\left(\frac{A}{V_s}\right) P_s t \qquad (1)$$

The equation is valid for the first order kinetics where C_s is concentration of phenol in phase after source of transport at time t (based on a variation of 1, 6, 12, 24, 48, and 72 hours), while C_s^o is initial concentration of phenol in source phase, A is surface area of the membrane, V_s is volume of phenol in the source phase, and Ps is permeability of transport which is calculated from curve of the relationship between $\ln\left(\frac{C_s}{C_s^0}\right)$ and t.

Determination of the flux transport is calculated by the following formula.

$$J_s = P_s C_s \qquad (2)$$

J_s is flux transport of phenol in the source phase. After obtained the value of the permeability and flux transport, diffusion coefficients can then be obtained from the following formula.

$$P = \left(\frac{D}{d}\right) K_p \qquad (3)$$

Here, *d* is thickness of the membrane, *D* is diffusion coefficient to be searched, and K_p is partition coefficient which results from division of the concentration of analyte-carrier complex and analyte concentration in source phase.

3. Results and Discussion

3.1. PIM Characterizations

PIM is made of polyeugenol, PVC, and DBE. Polyeugenol serves as a carrier that carries active phenols in the system. PVC serves as a base polymer that supports immobilized polyeugenol, and DBE serves as a plasticizer which makes the PIM becomes more elastic and not brittle. This step results in PIM sheet with diameter of ± 4.5 cm and thickness of 0.04 µm. Thickness of PIM is controlled by mass and volume of the membrane components, and diameter of the glass mold. PIM surface characterization using the scanning electron microscope is indicated in Figure 2.

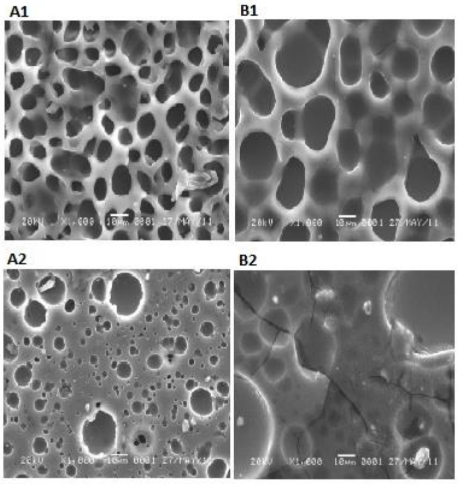


Figure 2. PIM surface morphology imaged by SEM (1000 X). A1: PVC-DBE top surface; A2: PVC-DBE bottom surface; B1: PVC-DBE-polyeugenol top surface; B2: PVC-DBE-polyeugenol bottom surface.

Pores of PVC-DBE surface before the addition of polyeugenol is larger than PVC-DBE surface after polyeugenol addition. The polyeugenol covers part of the membrane pores. Nghiem *et al*. (2006) said that some FTIR studies revealed no signs of a covalent bond among carrier, plasticizer, and basic membrane skeleton; among of them seems bonded to one another by forming secondary bonds such as hydrophobic, van der Waals, or hydrogen bonds. This is evidenced by FTIR spectra in Figure 3.

The spectra indicate that no change in functional groups of PVC. Polyeugenol addition gives a OH uptake bending at 3510.45 cm^{-1}, but it does not eliminate the existence of absorption of C-Cl bond vibrations at wave number 694.37 cm^{-1}, and absorption of asymmetric bending of methylene vibrations at wave number of 2924.09 cm^{-1}.

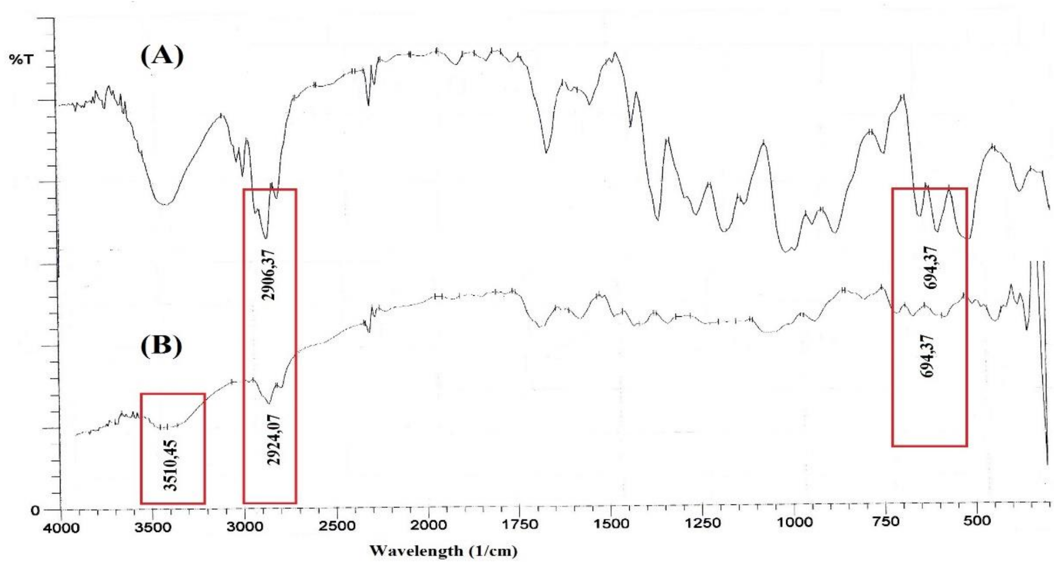


Figure 3. FTIR spectra of PIM. (A) Original PIM; (B) PIM with polyeugenol

3.2. Phenol Transport

Phenol transport through the membrane occurs by transport mechanism because of concentration gradient of phenol in the source phase gradient and strip phase. Polyeugenol acts as a carrier compound binding the phenol, so it can be transported to the strip phase. Back transport of phenol through the membrane phase is prevented by adding a stripping agent, NaOH, into the strip phase. Stripping agent works to convert phenol into phenol derivative compounds, namely sodium phenolics, and traps these compounds in strip phase so the phenol could not return to the membrane phase (Mortaheb *et al*., 2008).

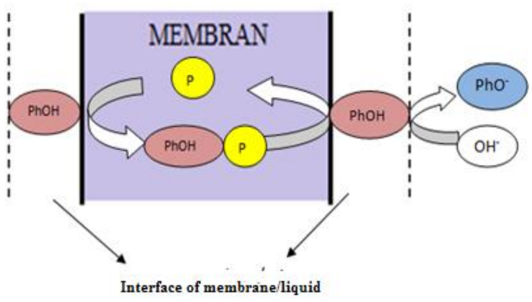


Figure 4. Schematic depicting the transport of phenol through PVC-based PIM with polyeugenol as a membrane carrier.

Mechanism of phenol transport from the source to the strip phase can be explained schematically in Figure 4. In Figure 4, PhOH is phenol molecules, P is the membrane carrier polyeugenol, and an ion phenolic PhO^-. Transport of phenol in optimum time (48 hours) with pH 4.5 indicates rejection percentage of 91.4%.

The area of the membrane contact with phenol is 4.90 cm^2. Characterization of the PIMs after the transport of phenol in the membrane is also done using SEM with results indicated in Figure 5.

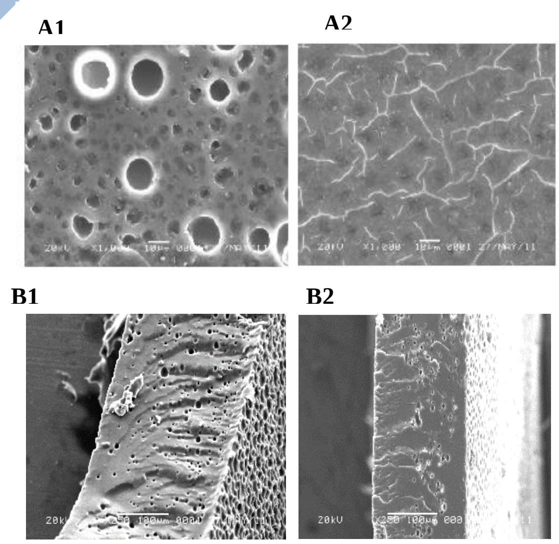


Figure 5. Morphology of of PIM imaged by SEM. A1: top surface after phenol transport (source phase); A2: bottom surface after phenol transport (strip phase); B1: Cross-section before phenol transport; B2: Cross-section after phenol transport.

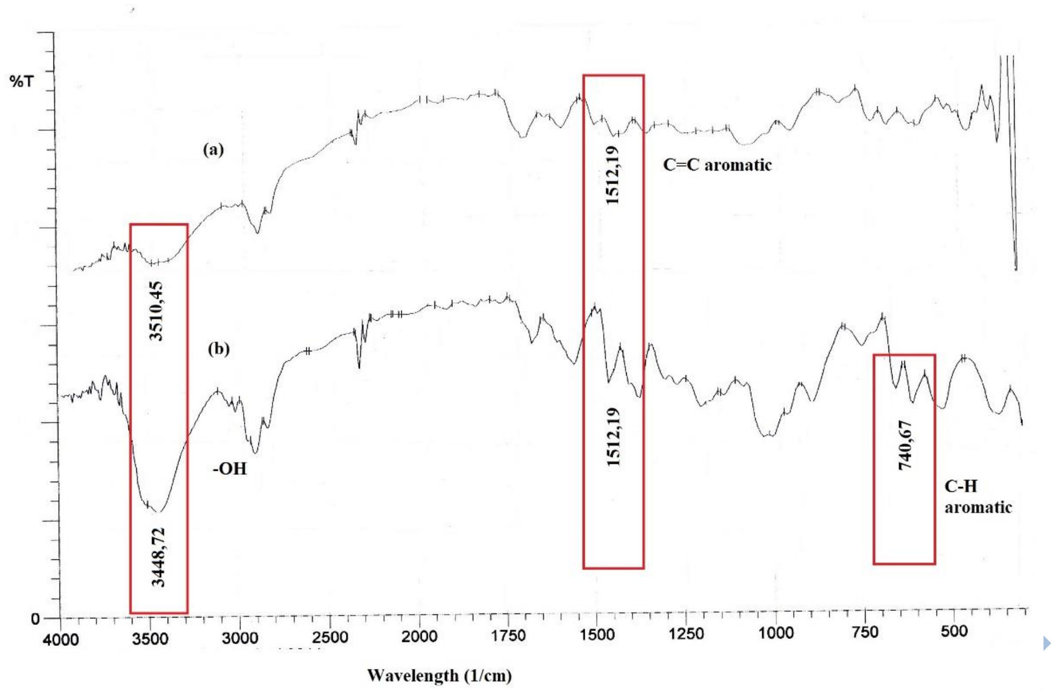


Figure 6. FTIR spectra of (a) PIM before contact with phenol and (b) PIM after contact with phenol

The cross section of PIM picture after phenol transport indicates that it is denser than PIM before phenol transport. The interaction between phenol and polyeugenol has been predicted as interaction that occurs because of hydrogen bonds between them. Phenol and polyeugenol are two compounds that have the same -OH, so it is possible that interactions occur because of the formation of hydrogen bonds between two OH groups so that all molecules of phenol and polyeugenol form a large number of hydrogen bonds (Vermerris and Nicholson, 2009).

The interaction of a compound with other compounds can be determined by qualitatively infrared spectra. Particular groups of atoms provide additional absorption at a certain density (Silverstein, 2015). Phenol interaction with membrane carrier in the PIM can be seen through characterization FTIR spectra shown in Figure 6. Absorbance of OH at the peak of 3448.72 cm^{-1} is more sharply demonstrated by addition of the phenol's OH group, and absorbance at wave number of 740.67 cm^{-1} indicates the presence of aromatic CH from phenol.

3.3. Kinetics of Transport

In order to determine parameters of transport kinetics, the relationship between transport phenol with various times is studied. This study uses various transport times of 1, 6, 12, 24, 48, and 72 hours. The curve obtained from the results of the various transport times can be seen at Figure 7.

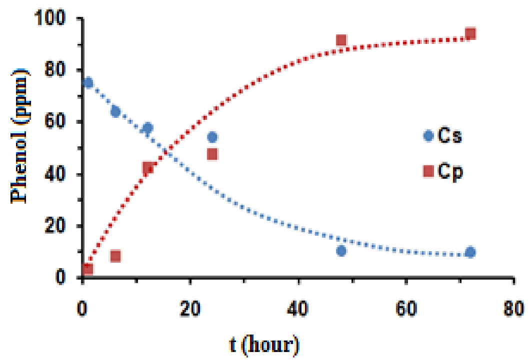


Figure 7. Curves of contact time between phenol concentration and membrane. Cs is the concentration of phenol in the source phase and Cp is the concentration of phenol in the strip phase.

Based on the mechanism in Figure 7, if the pH is acidic phenol-shaped molecule, the stoichiometry of the phenol transport in this study can be assumed as follows:

$$\log K_p = logK_{ex} + a \log[L]_{mem} \quad (4)$$

Equation of reaction between phenol and polyeugenolis as follows.

$$[\text{Fenol}]_{aq} + a[\text{polieugenol}]_{mem} \rightleftharpoons [\text{Fenol.Polieugenol}_a]_{mem} \quad (5)$$

It has been conducted to determine the order for mass transfer processes of phenol through membranes in this study. The closest R^2 value obtained indicates the first order curve, i.e. 0.911. While the second order curve is plotted to result in R^2 value of 0.837 and R^2 of third order value is 0.791. Thus, the most appropriate order to describe the transport kinetics of phenol in this study is the first order. Calculation by Equation (1) in this study results in permeability of the PIM in source phase (interface) i.e. 8.8 × 10^5 m/s. If equation is used to find value of the flux in the Equation (2), then the value of the flux in phase sources at the optimum time of 48 hours amounts to 9.512 × 10^{-4} g/m^{2}s. Partition coefficient between the phenol and the polyeugenol carrier is as follows.

$$K_p = \frac{[phenol-polyeugenol]_{PIM}}{[phenol]_{(s)}} \quad (6)$$

Then value of the diffusion coefficient can be determined by equation (3). The value of the diffusion coefficient is 3.826 × 10^{-11} m^2/s. Lamb and Nazarenko (1997) uses the same equation for the transport of Pb (II) with PIM-based CTA with TOPO compound as a carrier. The research finds value of coefficient diffusion of overall PbX2.TOPO (with X = I-, SCN-, Br, or NO 3) complex that approaches value of 10^{-12} m^2/s.

3.4. Endurance Test of Membrane

Membrane endurance test is conducted to determine stability of the membrane. In the endurance test result, the use of the membrane twice and three times leads to reduced phenol ltransport to strip phase. Figure 8 indicates comparison between results of phenol transport with the use of PIM once, twice, and three times that are performed at the optimum condition for 48 hours.

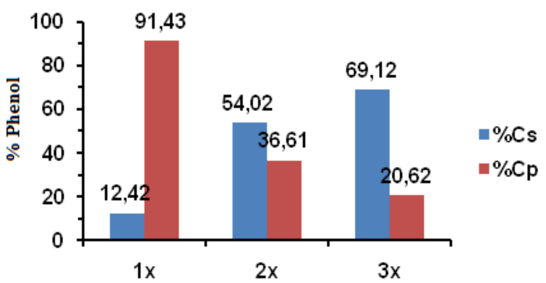


Figure 8. Relationship between phenol concentrations with repeated use of PIM. Cs: concentration of phenol in the source phase and Cp: concentration of phenol in the strip phase.

The concentration decreasing of phenol transport is expected because of the PIM use to the second and the third where phenol remaining in the membrane covers the membrane pore and blocks new phenol to enter the pore and blocks its interaction with active group of polyeugenol (based on fouling theory by Baker, 2004). Based on the graph, the use of membranes to three times causes the percentage of membrane transport reduced by 70.81%.

3.5. Selectivity of PIMs

Selectivity of PIMs is tested by doing phenol and chromium transport from artificial wastewater. Chromium represents a metal content in wastewater. Artificial wastewater is made by mixing a solution of phenol 100 ppm and 100 ppm Cr^{3+} with a total volume of 40 mL. This study is performed to determine selectivity of the membrane against phenol. Artificial waste transport is performed at pH 4.5 source, discharger 11, and the optimum time of 48 hours. Results of this study are indicated by the graph in Figure 9.

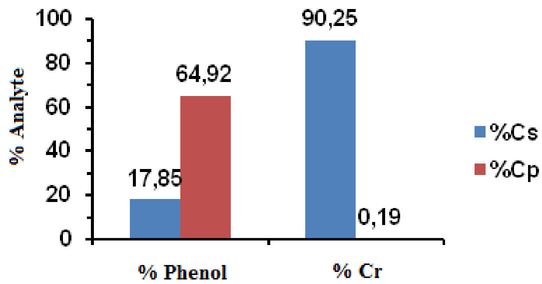


Figure 9. Comparison between the percentage of phenol and chromium (III) transport in the artificial wastewater using PIM. Cs: concentration of phenol in the source phase and Cp: concentration of phenol in the strip phase.

The graph illustrates that transport using PIM with polyeugenol as a carrier is a fairly selective method for phenol recovery in waste containing metals such as Cr^{3+}. One of this selectivity factors supporting is active group polyeugenol -OH which can interact selectively with phenol –OH, and also interaction between π bond in phenol and polyeugenol. It is possible that hydrogen bonds and π interaction are preferable than ionic bonds in the cation exchange process between protons belonging topolyeugenol with metal so that competition among metal will produce phenol with larger percentage of phenol transport than that of metal.

4. Conclusions

In the calculation of the transport kinetics, membrane permeability value is obtained at 8.8 x 10^{-5} m/s, the flux value of 9.512 x 10^{-4} g/m^2s, and the diffusion coefficient of 3.826 x 10^{-11} m^2/s. The repeated use over three times, 48 hours, indicates a reduction in power of phenol transport by 70.81%. While selectivity test indicates that the membrane used is more selective against phenol compared to chromium metal. Based on the study results in the optimum conditions, the phenol transport effectiveness by using PIM with polyeugenol as carrier is 91.4%.

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