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# The removal of phenol from synthetic wastewater using calix [4] resorcinarene derivative based polymer inclusion membrane

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## ABSTRACT

***Abstract:*** *In the present study, the removal of phenol from synthetic wastewater across polymer inclusion membrane (PIM) containing calix[4]resorcinarene derivative used as a carrier were investigated. Phenol removal showing high efficiency when transported through PIMs prepared from cellulose triacetate (CTA) as a polymeric support material and 2-NPOE as a plasticizer. The effects of membrane composition, type of plasticizer, carrier content, pH phase's solution, and membrane stability, were examined in the facilitated transport experiments of phenol across PIM. A PIM containing 0.1 g CTA, 0.15g/g CTA of carrier and 1.5 g/g CTA of NPOE, provided the highest percentage of phenol over 5 days of transport, the feed solution in these transport experiments was at pH 2, while the stripping solution contained 0.25M NaOH. The prepared PIM were characterized by using Fourier transform Infra Red (FTIR), XRD and Thermo gravimetric analysis (TGA) techniques.*

## I. Introduction

Phenol contaminant are found in wastewaters of various industries such as petroleum refining, coal conversion, plastics, textiles, iron and steel manufacturing as well as pulp and paper manufacturing. All Industries use specific chemicals or the other raw materials to produce their last products, each process can produce hazardous wastes. A waste is considered a hazardous if it is reactive, ignitable, corrosive or toxic. Ninety five chemicals have been defined as toxic including phenol on the basis of production volume, exposure, and biological effects. Wastewaters are usually classified as industrial wastewater or municipal wastewater. Industrial wastewater with characteristics compatible with municipal wastewater is often discharged to the municipal sewers [1]. Typical phenol concentrations in these wastewaters range from 100 to 1000 mg/L. The majority of phenols are toxic substances, some have been classified as hazardous wastes and some are known or suspected carcinogens [2].

Current treatment technologies are available to remove phenol from wastewaters. Both physicochemical and biological treatment techniques are successful in full scale industrial use, and high efficiencies of phenol removal can be obtained. Conventional processes for removal of phenols from industrial wastewaters include extraction, adsorption on activated carbon, bacterial and chemical oxidation, electrochemical techniques, etc. [3-7]. All of these methods suffer from serious shortcomings such as high costs, the incompleteness of purification, the formation of hazardous by-products, low efficiency and applicability to a limited concentration range.

Membrane technology, which promises interesting alternatives to the conventional methods for phenol removal, has received significant attention. Membrane technology is favorable due to its selectivity, flexibility, and enrichment properties associated with traditional separation techniques, like solvent extraction [8-10]. Polymer inclusion membranes (PIMs) have emerged in recent years as an attractive alternative to supported liquid membranes (SLMs) due to their better stability. PIMs are composed of base polymer usually cellulosic derivatives and polyvinylchloride (PVC) that provides mechanical strength a carrier, which is responsible for the extraction and transport of the target chemical species through the membrane PIM, and a plasticizer, in general, 2-Nitro phenyl octyl ether (NPOE), which provides elasticity to the membrane and increases the solubility of the extracted species in the membrane liquid phase [11]. Recently, several studies concerning the preparation, characterizations and applications of new polymer inclusion membranes (PIMs) for the extractive removal of phenol from aqueous solution were published [12,13], but no researches have focused on the removal of phenol using calix[4]resorcinarene derivatives as carrier in PIM. This work is a part of our investigation on the extractive properties of calix[4]resorcinarene toward toxic phenol, in the present study, we have developed different PIMs for the extraction and transport of phenol from synthetic wastewater. The optimization of the parameter influencing the transfer of phenol was determined and discussed. The membrane was characterized with, Fourier transform infrared (FTIR), X-Ray diffraction (XRD), and thermogravimetric analysis (TGA) to obtain information regarding its composition.

## II. Materials and methods

### II.1. Chemicals

The structure and abbreviation of the carrier and plasticizers used in the present study are shown in Fig. 1. The carrier, (C-octyl) calix[4]resorcinarene, abbreviated as RC8, and 2-nitrophenyloctanoate (2-NPOT) were synthesized in our laboratory [14,15]. Phenol, resorcinol, aldehydes, ethanol, hydrochloric acid, potassium hydroxide, salts, dichloromethane, cellulose acetate (CA) and cellulose triacetate (CTA), 2-nitrophenyl-octylether(2-NPOE), 2-nitrophenylpentylether (2-NPPE) were analytical grade reagents purchased from Fluka. Aqueous solutions were prepared by dissolving the respective analytical grade reagent in deionized water with a resistivity no less than 18.2 MΩ cm obtained with a Milli-Q Plus system. The pH adjustment was done by addition of dilute hydrochloric acid (0.01M) or sodium hydroxide (0.25M) to prepare the desired pH solution.

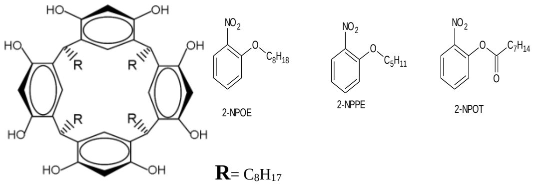


***Figure1.*** *Chemical structure of Calix [4] resorcinarene (RC8) and Plasticizers.*

### II.2. Membrane Preparation

PIMs were prepared according to the procedure reported by Sigiura [16], the amount of each constituent was a function of the series of experiments to be performed. Thus, for CTA and/or CA membrane 10 ml of a polymer solution (0.1g of polymer in dichloromethane), calix[4]resorcinarene (0−0.06g/g CTA), and plasticizer (0−3g of plasticizer/g CTA) were placed into a Petri dish of 9.0 cm diameter. This solution was allowed to evaporate overnight at room temperature (25 ± 1°C). The film was then carefully peeled out of the bottom of the Petri dish and stored in deionized water for 24h [17,18].

### II.3. Membrane Characterizations

In order to characterize the PIM and obtain information regarding its composition and the nature of the interaction between component: polymeric support, plasticizer, and carrier, it was used FTIR, XRD and TGA techniques, the FTIR spectrums were acquired using FTIR spectrophotometer Jasco FT/IR-4100 measurement were taken in the wave number range from 400 to 4000 cm$^{-1}$. The degrees of crystallinity of the CTA-CA membranes, pure carriers and CA/CTA Membrane-carriers were evaluated using Philips, model X-Pert X-ray diffractometer (XRD) operating at 40 kV, using Cu as radiation source, the scans were obtained using a scan step size of 0.03◦ with a scan step time of 0.25 s. The thermogravimetric analyses (TGA) were achieved using a SETARAM TG 96, thermal analysis instrument. A sample of 3mg of membranes was dried at 100 °C to remove moisture for 30 min, and then programmed from room temperature to 750 °C at rate of 10 °C/min under the nitrogen atmosphere.

### II.4. Transport Experiments

A typical laboratory scale device was used for phenol transport experiments through the PIM. It consisted of two compartments made of Teflon with a maximum capacity of 400 ml separated by the PIM. Of interest, the film side exposed to air during solvent evaporation faced the feed compartment and the PIM area exposed to the aqueous phase were 12.56 cm$^2$. In order to minimize the boundary layer thickness, both the source and stripping compartments were provided with a mechanical stirrer adjusted to 600 rpm [18]. One of them contained $10^{-3}$ M of phenol as the feed phase, and the other, the stripping phase, contained NaOH in different concentrations. The Transport can take place by diffusion. All transport experiments were carried out at 25±1°C. All transport experiments were carried out in duplicate keeping the aforementioned cell at room temperature. The feed solution and the stripping phase were put into their respective compartments. In all figures, the reported error bars represent the standard deviation of the data.

### II.5. Phenol Analyses

The influence of the studied parameters on the transport of Phenol was analyzed during 5 days. Samples of 4 ml were manually extracted with a pipette from both half-cells each day, and the phenol quantification in the transport experiments was carried out using a UV/vis spectrophotometer **Jenway-Serie 6800** at 210 nm, the effect of pH on the shape and emplacement of the band absorption of phenol is done in the Fig. 2. The study shows that the pH influences the movement and intensity of the absorption band at 210 nm, for that correction to the absorbance is made when calculating the concentration of phenol in stripping phase.

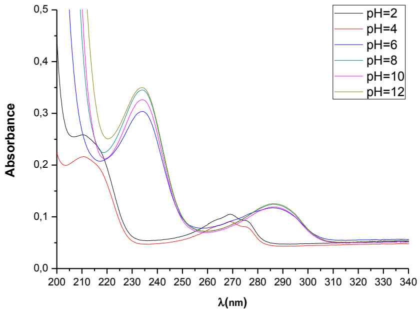


***Figure 2.*** *Effect of pH on absorption of phenol in water at the concentration of 3.10$^{-5}$M.*

## III. Results and discussion

### III.1. PIMs Characterizations

After the addition of carrier and plasticizer, a small shifting of bands was observed due to the vibration coupling of bands. After addition of NPOE and RC8, we observed that the wide band at the region 3559 $cm^{-1}$ in the blank membrane based on 100% CTA, characteristic of hydroxyl groups (OH) was shifted to 3511 $cm^{-1}$, and then the band at 2952 $cm^{-1}$ attributed to CH bonds in CTA was shifted to 2896 $cm^{-1}$ due to the aliphatic chain in RC8 and NPOE. In addition the band at 1641 $cm^{-1}$ attributed to carbonyl (C=O) was altered to 1613 $cm^{-1}$ This could be explained by a combination of factors such as hydrogen bonding between CTA and phenol –OH of RC8, hydrophobic interaction and steric match. The significant bands were interpreted which conforms the impregnation of carrier RC8 and NPOE onto the PIMs. According to the results of the FTIR spectra (Fig.3.), there was no formation of covalent bonds between the constituents of the membrane, and there were only weak interactions between the constituents, i.e. van der Waals and hydrogen bonds [20]. Consequently, the analysis and comparison of the obtained spectra revealed that all the membrane constituents remained as pure components inside the membrane [20].

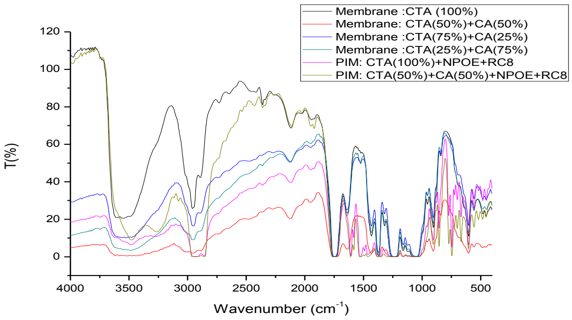


***Figure 3.*** *Spectrum of different membranes and PIMs.*

Fig.4, depicts the X-ray diffractograms of the Membrane, PIM, and RC8 membranes. Two unresolved bands of diffuse diffraction were observed between 10° and 20° for the CA and CTA membrane which confirmed an amorphous structure. When RC8 and plasticizer 2-NPOE was added to the polymeric support, a minor modification was observed (a slight increase of the broad peak around 20°). These findings allow us to ignore carrier crystallization within the membrane and suggest an amorphous state of the prepared PIMs [18]. This amorphous state confirms the presence of plasticizer in the membrane which acts as the solvent of the carrier.

Fig. 5, shows the TGA curves of the CTA, CA membrane with different composition, and PIMs at a heating rate of 10 °C/min in $N_2$. The thermograms show that the mixture of the two polymers CA and CTA acts as one block, indeed the interactions between the various components of the PIM are maintained together by hydrogen bonds interactions and Van der Waals; there are not new covalent bands between the carrier and polymer in the PIMs.

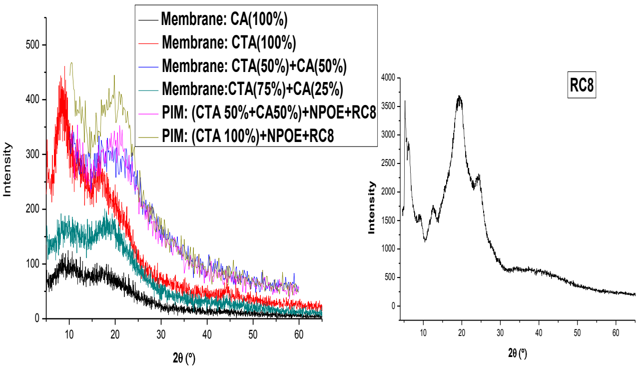


***Figure.* 4** *X-ray diffractograms of the Membranes, PIMs, and RC8.*

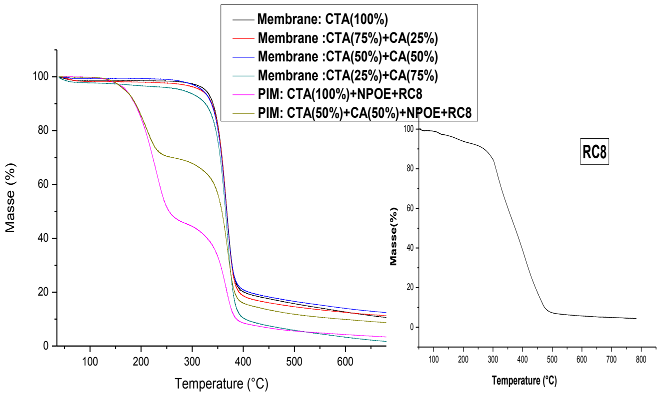


***Figure 5.*** *Thermograms of the Membranes, PIMs, and RC8.*

## III.2 Optimization of parameters influencing removal efficiency of phenol using PIMs

### III.2.1 Effect of support nature for PIM preparation on the transport of phenol

The influence of the nature of base polymer on the rate removal of phenol was investigated. It can be observed in Table-1, when the PIM is prepared with 100% of CTA the removal of phenol is the maximum and reach 93,27%, but in the case of PIM with CA the removal decrease, probably due to the hydrophilic character of cellulose acetate, in addition, the CTA has the higher acetyl groups participating in dipole−dipole interactions allowing a better immobilization of the extractant and then better complexation.

***Table 1****. Effect of support nature for PIM preparation on the transport of phenol*

| **(Base polymers)+NPOE+RC8** | **Phenol transported (%)** |
|---|---|
| **CA** | 45,00 (3,22) |
| **CTA** | 93,27 (6,87) |
| **CTA (50%)-CA(50%)** | 59,00 (4,78) |
| **CTA (75%)-CA(25%)** | 72,75 (5,76) |
| **CTA (25%)-CA(75%)** | 54,00 (4,34) |

Feed phase: phenol $10^{-3}$ M, pH 2. Stripping phase: NaOH 0.25 M. Membrane: 12.60 $cm^2$ of surface area, Calix[4]resorcinarene 0.15 g/g CTA, 1.5 2-NPOE/g base polymer. Values obtained after 5 days of experimentation. %RSD in parentheses

### III.2.2 Effect of the chemical nature of plasticizer on the transport of phenol

In this work three plasticizers with different chemical structure properties, 2-Nitrophenyloctylether (2-NPOE), 2-Nitrophenyl octanoate (2-NPOT) and 2-Nitrophenyl pentyl ether (2-NPPE) have been evaluated for the preparation of PIMs useful for the removal of phenol. The Table-2 summarizes the results.

NPOE has been the most common plasticizer used for cellulosic derivatives membrane, a higher removal of phenol was observed with NPOE with 93,27%. This is due to the fact that this plasticizer prefers neutral molecules [12] indeed phenol is uncharged at pH 2, which is favorable for the formation of phenol-calix[4]resorcinarene complex.

***Table 2.*** *Effect of the chemical nature of plasticizer on the transport of phenol*

| **Plasticizer** | **Phenol transported (%)** |
|---|---|
| **2-NPOE** | 93,27 (6,87) |
| **2-NPPE** | 70,00 (5,23) |
| **2-NPOT** | 60,00 (5,32) |

Feed phase: phenol $10^{-3}$ M, pH 2. Stripping phase: NaOH 0.25 M. Membrane: 12.60 $cm^2$ of surface area, Calix[4]resorcinarene 0.15g/g CTA, 1.5 plasticizer/g CTA. Values obtained after 5 days of experimentation. %RSD in parentheses

### III.2.3. Effect of plasticizer content on the transport of phenol

The effect of the quantity of the plasticizer added in the membrane on the removal of phenol was studied by preparing PIMs at fixed quantity of calix[4]resorcinarene (0.15 g/g CTA), the results of these experiments are presented in Fig. 6.

The transport test demonstrates that phenol removal increase when the content 1.5 (gNPOE/gCTA) of plasticized is reached. But, at higher plasticizer quantity the transport decreases and the PIM become brittle, Nghiem [11] reports that an excessive plasticizer concentration is unfavorable because it could retarget to the membrane /aqueous interface and form a layer on the membrane surface which would create an additional barrier to the removal of phenol through the PIM.

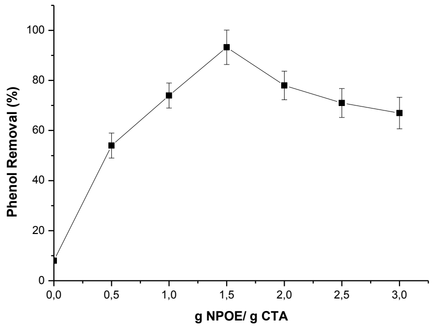


***Figure 6.** Effect of plasticizer content on the transport of phenol.*

Feed phase: phenol $10^{-3}$ M, pH 2. Stripping phase: NaOH 0.25 M. Membrane: 12.60 $cm^2$ of surface area, Calix[4]resorcinarene 0.15 g/g CTA, (0-3g NPOE/g CTA). Values obtained after 5 days of experimentation.

### III.2.4. Effect of carrier contents on the transport of phenol

The effect of carrier calix[4]resorcinarene content in PIMs on the transport of phenol was studied according to the operating condition on the legend of Fig. 7. As shown in Fig. 7. Membrane without carriers exhibits basal transport of phenol from feed to strip phase compared to PIMs, which indicates that the facilitated transport ability of PIMs is caused by the presence of a carrier in membrane system.

The removal of phenol is enhanced with the increase of carrier content in PIMs and reaches the maximum when calix[4]resorcinarene content is equal to (0,15g /g CTA), after this quantity the removal of phenol begin to decrease when the content increase to (0,25g /g CTA). This may be explained by the membrane viscosity, the membrane viscosity also increases with the increase of the carrier concentration. The high viscosity in the membrane thus limits the diffusion of phenol-carrier complex into the membrane liquid phase [19].

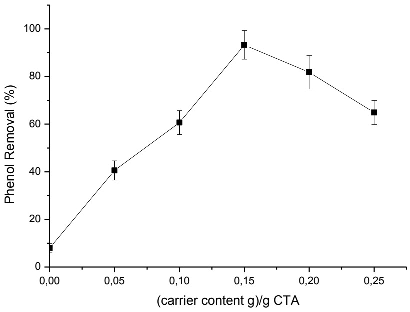


***Figure 7.** Effect of carrier contents on the transport of phenol.*

Feed phase: phenol $10^{-3}$ M, pH 2. Stripping phase: NaOH 0.25 M. Membrane: 12.60 $cm^2$ of surface area, Calix[4]resorcinarene (0- 0.25 g/g CTA), 1.5 2-NPOE/g CTA. Values obtained after 5 days of experimentation.

### III.2.5. Effect of pH solution of feed phase on the removal of phenol

In this study, the effect of feed phase pH on the transport of phenol was investigated. It can be observed in Fig. 8. When the feed solution pH is equal to 2, the removal efficiency of phenol reach the maximum 93,27%, this result is in agrement with those obtained by Pérez-Silva et al. [12], the phenol-calix[4]resorcianarene complex was formed by hydrogen bond (scheme), in addition the degree of ionization of phenol was comparatively stronger at the higher pH (pH>3). Which decrease the complexation rate between calix[4]resorcianrene and phenol. Since the formation rate of phenol-calix[4]resorcinarene complex was influenced strongly by pH of feed phase.

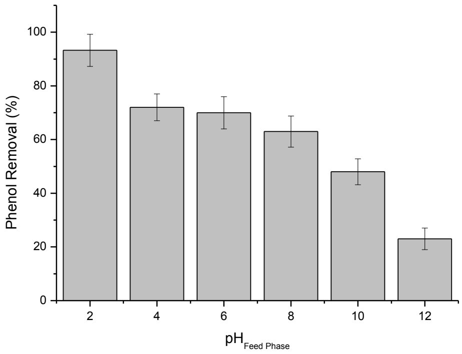
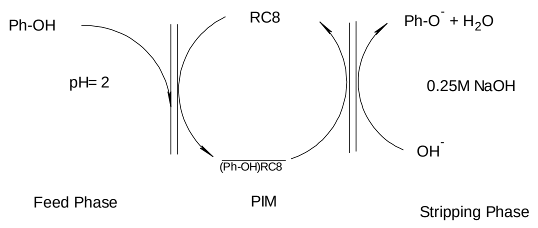


***Figure 8.** Effect of pH solution of feed phase on the removal of phenol.*

Feed phase: phenol $10^{-3}$ M, pH 2-12. Stripping phase: NaOH 0.25 M. Membrane: 12.60 $cm^2$ of surface area, Calix[4]resorcinarene 0.15 g/g CTA, 1.5 2-NPOE/g base polymer. Values obtained after 5 days of experimentation.



***Scheme:*** *mechanism scheme for the transport of phenol from acidic aqueous solution to alkaline stripping phase.*

### III.2.6. Effect of NaOH concentration in stripping phase on the transport of phenol

**Fig. 9.** Shows the influence of NaOH concentration in strip phase, on the removal efficiency of phenol, keeping the pH of feed phase constant at pH 2. From this figure it can be shown that the removal of phenol increases slightly with increasing the concentration of NaOH value from 0 to 0.25M, then, fast decreases up 0.25M concentration was observed. In general, the phenol uptake decreases at low and high pH values. At low pH values, the uptake of phenol is less due to the presence of H+ ions suppressing the ionization of phenol and hence its uptake on polar adsorbent is reduced. In the high pH range, phenol forms salts which are readily ionized leaving the negative charge on the phenolic group. At the same time, the presence OH- ions on the adsorbent prevents the uptake of phenolate ions. Similar behavior has been reported during the transport adsorption through PIM by Pérez-Silva et al. [12], and by Meng et al. [13].

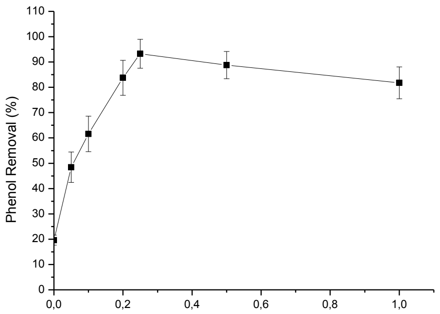


***Figure 9.*** *Effect of NaOH concentration in stripping phase on the transport of phenol.*

Feed phase: phenol $10^{-3}$ M, pH 2. Stripping phase: NaOH (0-0.25 M). Membrane: 12.60 cm$^2$ of surface area, Calix[4]resorcinarene 0.15 g/g CTA, 1.5 2-NPOE/g CTA. Values obtained after 5 days of experimentation.

### III.2.7. Effect of contact time

The effect of contact time on the percentage removal of phenol at optimum conditions of the others factor is the presented in Fig. 10. These figures show the removal of phenol increases with increasing mixing contact time. Highly increase of phenol removal efficiency during the first day was observed, indeed after 4 days the removal of phenol versus time curves are smooth and continue leading to saturation. These results indicated that the transport process can be considered very fast because of a large amount of phenol attached to the interface membrane within the first one dye of transport. The higher removal rate at initial period can be attributed to the increase of a number of vacant sites on the carrier available at the initial stage. This result is in agreement with those obtained by Pérez-Silva et al. [12], and by Meng et al. [13].

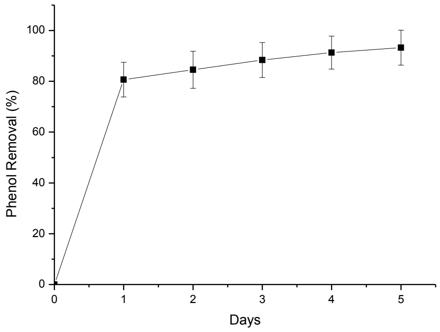


***Figure 10.*** *Effect of contact time on the removal of phenol.*

Feed phase: phenol $10^{-3}$ M, pH 2. Stripping phase: NaOH 0.25 M. Membrane: 12.60 cm$^2$ of surface area, Calix[4]resorcinarene 0.15 g/g CTA, 1.5 2-NPOE/g base polymer. Values obtained after 5 days of experimentation.

### III.2.8. Effect of the type of the counter-ion (anion) of Na$^+$ in stripping phase on the transport of phenol

To investigate the effect of the counter-ion of Na$^+$ on phenol removal, NaOH, NaNO$_3$, NaCl, and NaCO$_3$ was added into strip phase solution. The addition of different salts was done at concentration: 0.25M. From Table-3, high phenol removal was achieved up to 93 % at 0.25 M NaOH concentration. This phenomenon can be explained as follows: with the addition of NaOH, there is a reduction of the repulsive force between ions in the feed phase solution and the surface of the membrane. The attraction between the ions and membrane lead to the accelerated accumulation of phenol on the membrane surface and finally lead to the formation of a thick cake layer. The increase of NaOH concentration influenced the hydrophobicity character of the membrane [13]. When the concentration of NaOH increased, the hydrophobic character in the membrane also increased. The higher hydrophobic character meant that the membrane was more attracted to binding with particles than water.

***Table 3.*** *Effect of the type of the counter-ion (anion) of $Na^+$ in stripping phase on the transport of phenol*

| Anion type | % phenol transported |
|---|---|
| **$OH^-$** | 93,27 (6,87) |
| **$NO_3^-$** | 60,00 (5,45) |
| **$Cl^-$** | 44,50 (4,78) |
| **$CO_3^{-2}$** | 35,28 (4,69) |

Feed phase: phenol $10^{-3}$ M, pH 2. Stripping phase: NaOH, $NaNO_3$, NaCl, and $NaCO_3$ at 0.25 M. Membrane: 12.60 $cm^2$ of surface area, Calix[4]resorcinarene 0.15 g/g CTA, 1.5 2-NPOE/g base polymer. Values obtained after 5 days of experimentation. %RSD in parentheses

### III.2.8. Membrane stability

The stability of the PIM was evaluated under the same conditions where the feed and strip phases were renewed every 5 days (1 cycle) without changing the membrane, (Fig. 11.). A gradual decrease of the phenol removal efficiency was observed with the increase of number of cycle. This decrease appears to be linear. From the fourth cycle on, a remarkable decrease was observed, by approximately 26%, as shown in Fig. 11. The decrease in the stability of the membrane may have been caused by the partitioning of the carrier between the membrane and the aqueous solution. Moreover, the stability of the PIM was influenced by the properties and concentration of plasticizer used in the PIM [19].

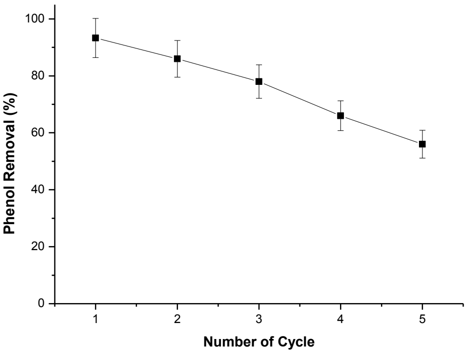


***Figure 11.*** *Membrane stability*

Feed phase: phenol $10^{-3}$ M, pH 2. Stripping phase: NaOH 0.25 M. Membrane: 12.60 $cm^2$ of surface area, Calix[4]resorcinarene 0.15 g/g CTA, 1.5 2-NPOE/g base polymer. 1 cycle: 5 days.

## IV. Conclusion

A new polymeric inclusion membrane system with calix[4]resorcinarene as carrier and mixture of CTA and CA as a base polymer was prepared by solvent evaporation and successfully applied in the facilitated transport of phenol from an synthetic wastewater, reaching up to 90% of the initial amount. The optimal composition includes 0.1 g CTA, 0.15g/g CTA of carrier, and 1.5g/g CTA of plasticizer. As expected, the transport efficiency of the PIM was found to be strongly dependent on pH phases, plasticizer nature and concentration, carrier, concentration. The characterizations of PIM demonstrate that there was no formation of covalent bonds between the constituents of the membrane, and there were only weak interactions between the constituents, i.e. van der Waals and hydrogen bonds.

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