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Evaluation of activated composite membranes for the facilitated transport of phenol

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Abstract: In this work the results on the first use of an activated composite membrane (ACM) containing Cyanex 923 for the extraction and transport of phenol are presented. A new dense layer-ACM configuration constituted by piperazine showed better stability than that prepared with 1,3-phenylenediamine. The effects of several parameters on the transport of phenol such as feed phase pH, carrier concentration and stripping phase composition were evaluated. The performance of the membrane was also evaluated during continuous additions of phenol and for a long period of time, observing the same rate of extraction and reextraction. Moreover, phenol transport was evaluated starting from synthetic wastewater of resin production plants type. The results exhibit the potential use of ACMs in the elimination and transport of organic species, even when analyte is initially found in complex solutions.

Keywords: activated composite membrane; Cyanex 923; phenol; resin manufacturing wastewater; transport.

1 Introduction

Phenol is a highly toxic compound, which can be found in various concentrations in wastewater. Phenolic compounds are present in different industrial processes, such as in the production of phenolic resins, colorants

or pesticides, etc. (1). Due to its toxicity, the EPA has set a limit of 2 mg l⁻¹ phenol in water (2), while the Mexican government establishes a maximum level of 0.001 mg l⁻¹ in water for human consumption (3).

Phenol removal from water comprises several strategies (1, 4), some of them destructive. Among these, total oxidation stands out due the great variety of modalities it covers. Thus, oxygen or air has been used for phenol oxidation in the presence or absence of catalysts as noble metals or transition metal cations, frequently supported on alumina or carbon. Additionally oxidation with ozone, hydrogen peroxide and chlorine has been reported as well the electrochemical phenol direct oxidation or indirect, including electro-Fenton (5). However, in these cases, an adequate oxidant dosage and appropriated physical and chemical conditions are necessary in order to avoid the appearance of intermediates and to assure the diminishing of phenolic compounds (6).

An example of a non-destructive phenol recovery technique is liquid-liquid extraction with various extractants such as cumene, TBP, hexane, 2-octanol or kerosene with recovery percentages from 70 to 99%. Distillation, which has the advantage of recovering several compounds at a time, is a strategy designed for samples with concentrations higher than 3000 mg l⁻¹ (4).

Other non-destructive methods are based on the sorption of phenol in various materials such as activated carbon or chitosan. Others are based on the use of polymeric adsorbent materials made of styrene and divinylbenzene with a hydrophobic structure, different particle size, surface area and degree of cross-linking (7). Solvent impregnated resins (SIRs) have also been used due to the interaction between the extractant agent and phenol (8–10); thus, Amberlite XAD-16 resin impregnated with Cyanex 923 was used in order to improve the extraction rate. However, in both cases it is necessary to desorb the phenol after its extraction for a later process.

Considering the above, membrane technology offers the possibility to extract and release an analyte by means of a simple and continuous procedure. A kind of membrane that gathers the selectivity of liquid membranes and stability of asymmetric membranes is the activated composite membrane (ACM) (11). The ACM consists of a

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dense layer that contains an extractant, all supported in a porous polymeric support. The ACMs have been used for the removal of metal ions with excellent results in extraction percentage (>95%) and short removal and separation times (<2 h) (12–16). However, the application of this type of membrane for removal and transport of organic compounds is scarce, so the present work is an important contribution in the field of membrane separation.

2 Experimental

2.1 Materials

All commercial reagents were ACS grade and purchased from Aldrich (St. Louis, MO, USA). The Cyanex 923 extractant was kindly supplied by Cytec Industries Inc. (Hermosillo, Mexico); this compound has shown affinity for phenolics compounds in previous reports (17–20).

2.2 Preparation of activated composite membrane

The activated composite membrane was prepared according Benavente et al. (21). First the porous layer is prepared by dissolving polysulfone in *N,N'*-dimethylformamide (15% w/v) and then depositing it on a nonwoven paper support (Hollytex 3329, Talas Co., NY, USA). The porous membrane is then formed by phase inversion, submerging it in a water bath. On the top of the previous porous layer, a dense layer containing the carrier agent (Cyanex 923) was formed by interfacial polymerization due to the interaction of two different phases: one of them, the diamine aqueous solution (2% w/v) (1,3-phenylenediamine or piperazine), and the other, a kerosene organic solution containing 1,3,5-benzenetricarbonyl chloride (0.1% w/v) and the organic Cyanex 923 ligand. The prepared ACM was washed with deionized water and dried in an oven for 30 min at 60°C. An inactivated composite membrane (ICM) was prepared similarly to an ACM without including the Cyanex organic ligand.

2.3 ACM characterization

ACM was analyzed by Raman spectroscopy using a Perkin-Elmer Spectrum GX system (Waltham, MA, USA) in a spectral window of 400–3400 cm⁻¹. Energy dispersive X-ray spectroscopy was done using a JEOL JSM-6300 (Peabody, MA, USA) to determine the percentage of phosphorous

encapsulated in the ACM, which is correlated to the extractant (500×, 3 membranes prepared separately were analyzed).

2.4 Batch studies

Batch phenol removal experiments were carried out by immersion of 4 cm² of ACM prepared as described in 30 ml of a solution containing different concentrations of phenol. After the extraction, the remaining phenol in the aqueous solution was quantified in a capillary electrophoresis equipment (P/ACE system, MDQ Beckman Coulter, Brea, CA, USA) with UV detector (214 nm) as described by Bonoli et al. (22). Phenol extraction percentage (% E_{ph}) was calculated according Eq. [1], where C_{initial} and C_{final} are the phenol concentration in the aqueous phase before and after the extraction process, respectively.

$$\%E_{\text{ph}} = 1 - \frac{C_{\text{final}}}{C_{\text{initial}}} \times 100 \quad [1]$$

Experiments carried out with the ICM do not show changes in the initial aqueous phenol concentration. For each value, the relative standard deviation in percentage (%RSD) was calculated.

2.5 Transport studies

The cell used for the transport of phenol through the ACM consists of two compartments: one containing 200 ml of phenol as the feed phase and the other with 200 ml of NaOH at different concentrations as the stripping phase. In the center both compartments are connected through a hole (11.34 cm²) in which the ACM is placed.

All transport experiments were performed in duplicate at room temperature for 7 h under constant agitation. Samples from both compartments were analyzed every hour in order to measure the phenol concentration in both, feed and stripping phases. Phenol quantification was carried out in a UV/Vis Lambda 40 spectrophotometer (Perkin-Elmer, Waltham, MA, USA) at 510 nm, as described by Woolard and Irvine (23). The percentage of phenol recovery (%R_{ph}) was calculated according Eq. [2], where C_{feed,initial} is the phenol concentration at the beginning of the experiment in feed phase, and C_{stripping,end} is the phenol concentration in the stripping solution after the transport process.

$$\%R_{\text{ph}} = \frac{C_{\text{stripping,end}}}{C_{\text{feed,initial}}} \times 100 \quad [2]$$

For each value, the relative standard deviation in percentage (%RSD) was calculated.

3 Results and discussion

3.1 ACM characterization

The ACM characterization was performed by Raman spectroscopy (Figure 1), obtaining information from each membrane layer. From the spectrum obtained for the polysulfone porous layer (Figure 1A); the vibrations corresponding to the C-H bond can be observed at 3080 cm^{-1} as well as a double band at 1720 and 1613 cm^{-1} due to in-plane benzene ring deformation. At 1272 cm^{-1} the asymmetric C-O-C stretching band is recognized, while the symmetric stretching mode occurs at 1149 cm^{-1} . The band at 856 cm^{-1} is the result of asymmetric C-S-C stretching bond (24).

For ICM (ACM without extractant) (Figure 1B) the C-H stretching bands of piperazine appear at 3077 , 2955 and 2757 cm^{-1} . Frequencies 1629 and 1723 cm^{-1} are assigned to an in-plane benzene ring vibration corresponding to terephthaloyl chloride attached to piperazine molecules. The symmetric C-N stretching vibration appears in the region 1090 – 1145 cm^{-1} , while a weak intensity band at 628 cm^{-1} is assigned to C-C-N deformation vibration (25).

Finally, in ACM spectrum (Figure 1C) a band at 1415 cm^{-1} is observed due to P=O bond (in addition to the bands observed for the porous and dense layers) indicating the presence of Cyanex 923 encapsulated in the membrane.

3.2 Batch studies

The evaluation of the polyamide layer composition is important since this layer contains the immobilized extractant agent which makes the extraction process possible. In order to select the most suitable dense layer for phenol extraction, ACM characterization as well as the phenol batch extraction experiments and the accuracy of the readings obtained during 7 h of experimentation were taken into account. EDS analysis shows a higher percentage of phosphorus for piperazine-ACM (4% of phosphorous atoms, 6.5% of RSD) which may be associated with a greater amount of encapsulated Cyanex 923. As a consequence, a higher amount of extracted phenol is reached (43.08%). This may be due to the fact that an aromatic amine such as *m*-phenylenediamine forms denser layers than alicyclic amines because of their more rigid structure (26). Thus, the denser is the layer, the less Cyanex 923 can be retained (3% of phosphorous atoms, 8.9% of RSD) and the phenol extraction decreases (35.39%). Additionally, in the three experiments performed for each membrane

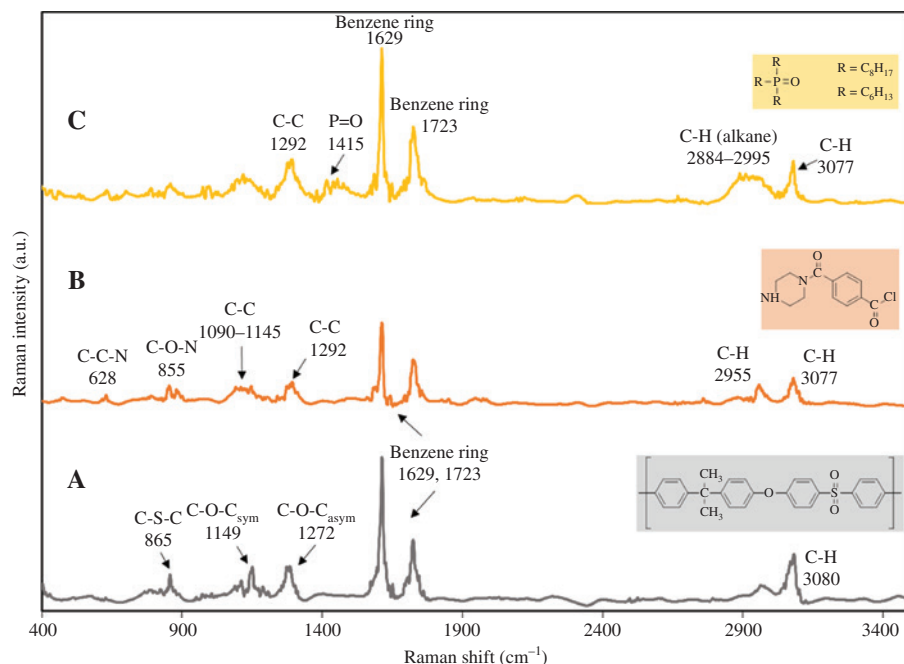


Figure 1: Verification of the presence of Cyanex in the activated composite membrane. Raman spectra for (A) Polysulfone porous layer, (B) ICM prepared with piperazine, and (C) ACM prepared with piperazine as dense layer and 2 mol l^{-1} of Cyanex in casting solution.

type, the sampling was performed over 7 h yielded readings with relative standard deviation (in percentage) ranging from 7 to 50% for 1,3-phenylenediamine while for piperazine they were no more than 7%.

The carrier content in the membrane has a significant effect on the analyte extraction; in order to find the better preparation conditions concerning on Cyanex 923 content, several membranes were prepared from casting solutions at different extractant concentrations (0.5–2 mol l⁻¹). The effects of the Cyanex 923 content of the ACM on the phenol extraction are shown in Table 1. It becomes clear that phenol extraction becomes higher just when Cyanex 923 concentration reaches a 2 mol l⁻¹ value in the casting solution. It is important to note that was not possible to evaluate higher concentrations of Cyanex 923 due to the low solubility of acid chloride in organic media at the uppermost extractant amount. For this reason, 2 mol l⁻¹ concentration was used for the following experiments.

Once it was proved the feasibility of phenol extraction with ACM-Cyanex 923, the piperazine prepared membranes were used in transport experiments.

3.3 Transport studies

According to the literature the stripping phase is one of the key factors for effective transport; for this reason different concentrations of a strong base (NaOH) were evaluated as stripping solutions in order to obtain the best re-extracting conditions for phenol transport. The use of this strong base would allow the membrane-extracted-phenol to be released from the ACM due to the formation of sodium phenolate in the stripping phase (27).

Figure 2 shows that increasing the NaOH concentration increases the phenol transport. Nevertheless, with a NaOH concentration of 2.5 mol l⁻¹, the recovery of phenol decreases because of the swelling of dense membrane due

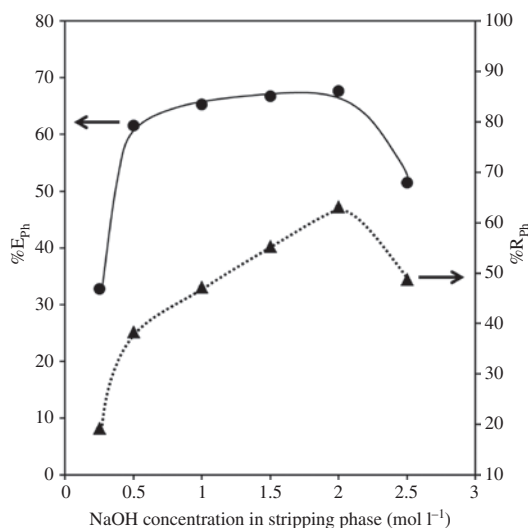


Figure 2: Effect of variation of the stripping phase NaOH concentration on phenol transport.

Experimental conditions: 25 mg l⁻¹ of phenol in the feed phase (pH = 2); ACM prepared with piperazine as a dense layer and 2 mol l⁻¹ of Cyanex in the casting solution, 11.34 cm² of membrane surface area. Values were obtained after 7 h counted from the start of the experiment. 0.28 < %RSD < 11.90.

to the extreme alkaline medium and the eventual extractant loss. This allowed choosing 2 mol l⁻¹ as the optimal concentration of NaOH for subsequent phenol recovery experiments.

In order to evaluate the influence of pH value of feed solution on phenol transport, several values of pH (2, 3, 5, 7, 9 and 11) were imposed by using NaOH or HCl solutions (25 mg l⁻¹ phenol in the feed phase). As a result, a decrease of the extraction percentage at higher pH values was observed: an 87.41% (%RSD = 3.34) of extraction percentage at pH 2, and a 25.18% (%RSD = 3.98) at pH 11. This can be explained because phenolate (charged species) is the predominant species at pH 11 and cannot be extracted by Cyanex 923, a non-polar compound. Also, as a consequence of the high extraction percentages in acidic conditions, more phenol is transferred to the ACM and as a result more phenol could be re-extracted to the stripping phase: 63.13% (%RSD = 3.56) of phenol transported to the stripping phase when pH in the feed phase was 2, and 37.80% (%RSD = 9.04) of the phenol transported to the stripping phase when pH in the feed solution was 11. For this, the pH value in the feed solution that favors the extraction is 2 and this value was imposed in subsequent experiments.

Additionally, experiments were performed to study the effect of the initial phenol concentration in the feed phase (5, 10, 25 and 50 mg l⁻¹) on its extraction and transport percentage. A 99.91% of the extraction percentage

Table 1: Phenol extraction percentages obtained with ACM prepared at different Cyanex 923 concentration in the casting organic solution.^a

Cyanex 923 concentration in casting organic solution (mol l ⁻¹)	% E _{ph}	% RSD
0.5	31.83	2.77
1.0	40.24	1.28
1.5	40.67	3.74
2.0	44.17	5.90

^aExperimental conditions: membrane surface area, 4 cm²; 25 mg l⁻¹ phenol in feed phase (pH = 2); ACM prepared with piperazine. Values were obtained after 7 h counted from the start of the experiment.

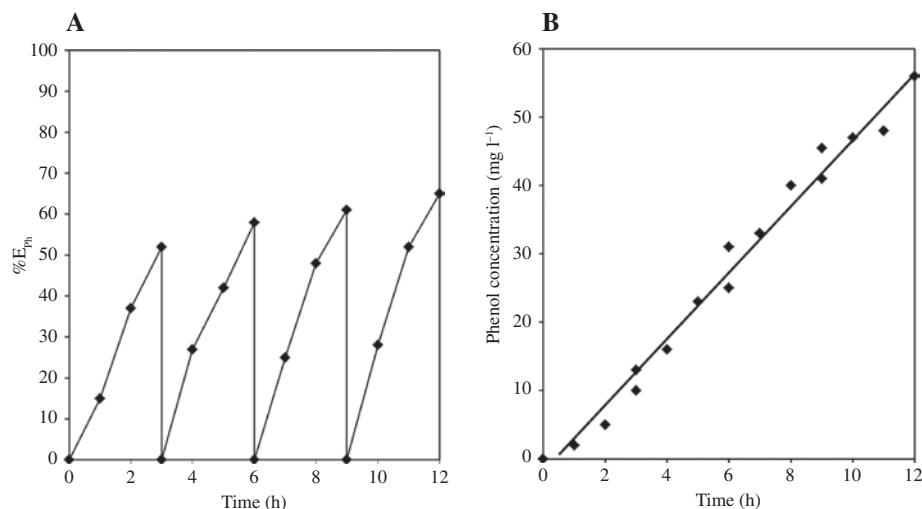


Figure 3: Continuous extraction through ACM.

(A) Phenol extracted from the feed phase to ACM; (B) phenol concentration observed in the stripping phase. Experimental conditions: initial 25 mg l⁻¹ phenol in the feed phase (pH=2); ACM prepared with piperazine as the dense layer and 2 mol l⁻¹ of Cyanex in the casting solution, 11.32 cm² of the membrane surface area; NaOH 2 mol l⁻¹ in the stripping phase; 12 h of analysis time.

towards the membrane was obtained with an initial concentration of phenol of 10 mg l⁻¹ (%RSD = 14.04). However, it was observed that there is a decrease in the percentage of phenol extraction at the lowest (5 mg l⁻¹; 85.99% phenol extracted with 9.19 of %RSD) and highest values (50 mg l⁻¹; 55.47% phenol extracted with 8.86 of %RSD)

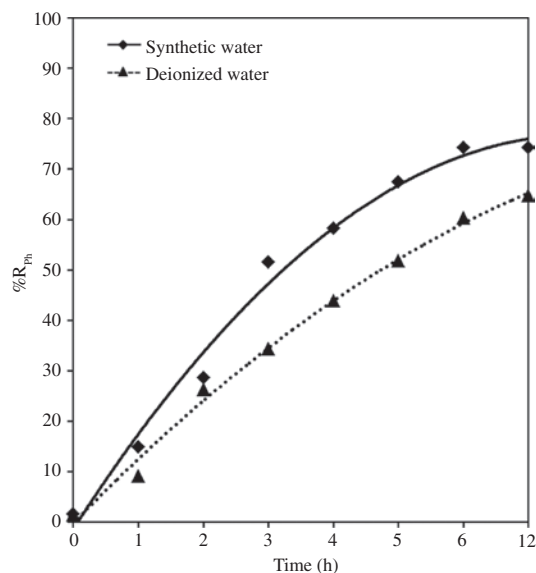


Figure 4: Comparative study of phenol transport between deionized water and synthetic wastewater.

Experimental conditions: 25 mg l⁻¹ phenol in feed phase (pH=2); ACM prepared with piperazine as dense layer and 2 mol l⁻¹ of Cyanex in casting solution, 11.34 cm² of membrane surface area; NaOH 2 mol l⁻¹ in stripping phase.

tested. The latter case because the membrane capacity is exceeded, while at low concentrations there is a diffusional negative effect during the phenol extraction process. As far as transport is concerned, the differences were smaller, so it can be inferred that the determining step in the process is the extraction of the phenol to the membrane. Additionally it is interesting to appreciate that even at low phenol concentration, a facilitated transport is still carried out.

3.4 Continuous extractions

Concerning the study of phenol extraction during a continuous process, a volume of phenol solution was added to the feed phase every 3 h (three additions) so that the initial volume and concentration was restored to the initial values (200 ml and 25 mg l⁻¹, respectively). The system was monitored observing that a percentage of the phenol extraction did not show significant changes during the four cycles (Figure 3A). Regarding the stripping phase (Figure 3B), there is a linear behavior indicating a transport mechanism that works with the same efficiency even after 12 h of continuous operation.

3.5 Studies with synthetic wastewater

The extraction and recovery of phenol with ACM from synthetic wastewater were conducted by doping water from an industrial park in Hidalgo state (México) with phenol

Table 2: COD values for feed and stripping solutions in the phenol transport experiment.^a

System	COD _{initial} (mg _{oxygen} l ⁻¹)		COD _{final} (mg _{oxygen} l ⁻¹)	
	Feed phase	Stripping phase	Feed phase	Stripping phase
Deionized water	68.29	3.85	20.76	40.97
Synthetic wastewater	673.71	1.14	564.51	68.63

^aExperimental conditions: initial 25 mg l⁻¹ phenol in the feed phase (pH = 2); ACM prepared with piperazine as the dense layer and 2 mol l⁻¹ of Cyanex in the casting solution, 11.32 cm² of the membrane surface area; NaOH 2 mol l⁻¹ in the stripping phase. 7 h of analysis time.

(25 mg l⁻¹), urea (0.5 mg l⁻¹), KH₂PO₄ (0.3 mg l⁻¹) and formaldehyde (23 mg l⁻¹), with the aim of simulating wastewater from resin production plants (28). Figure 4 shows that the percentage of phenol recovery in the stripping phase is higher when using synthetic water due to the components in the feed phase increasing the ionic strength, improving the phenol transport.

To evaluate the selectivity of ACM in the phenol extraction and transport, a chemical oxygen demand (COD) analysis was performed for both phases (feed and stripping phase) (Table 2). Results show a change attributable mainly to the amount of phenol transported as only 3% of the other components present in the simulated wastewater was transported to the discharge phase. Therefore it can be concluded that the process shows a high preference for the analyte of interest.

4 Conclusions

In this study, the facilitated transport of phenol through a novel ACM containing Cyanex 923 was investigated. According to the results, it was possible to develop a new configuration of the ACM with a dense piperazine layer that facilitates the transport of phenol and is less rigid than the conventional ACM prepared from 1,3-phenylenediamine.

In the transport experiments, sodium hydroxide concentration in the stripping phase plays an important role as at higher NaOH concentration, phenol transport is facilitated. However, an excess of this causes a loss of the extractant agent thus affecting the transport process. The pH value in the feed phase also has a great influence in the ACM extraction due to the acid-base phenol properties and the mechanism of extraction that requires phenol in its neutral form, that is, protonated.

It is important to mention that the extraction and transport of phenol is favorably affected when the feed phase has a high ionic strength. This is an advantage when using real solutions, generally complex in their composition and with a high ion concentration. Concurrently,

the same ACM can be reused up to three cycles without presenting important changes in the amount of phenol transported, which makes this a feasible method for the recovery of phenol.

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