

Removal of Phenol from Aqueous Solutions by Polymer Inclusion Membranes (PIMs): Modeling of the Extraction Process

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Abstract. The aim of the present paper was to study the results of two series of membranes based on poly(vinyl-alcohol) (PVA) with various composition of β -cyclodextrin (β -CD) as extractant prepared by using or not a cross-linking agent. The obtained membranes were characterized with conventional methods: scanning electron microscopy (SEM), X-ray diffraction (XRD) and water swelling test. In this study, the combined effects of various experimental parameters on the phenol extraction yield by polymer inclusion membrane are investigated in a batch system using a 2³ full factorial design. An empirical relationship between phenol extraction yield and independent variables (initial phenol concentration, pH and agitation speed) was obtained. Statistical analysis showed that the initial phenol concentration was the most effective parameter. An extraction yield of about 33% was obtained after an equilibrium period of 50 min.

Keywords: Polymer inclusion membrane (PIM), cyclodextrin, extraction, phenol, design of experiment, statistical analysis.

1. Introduction

Phenols (Phenol and Phenolic compounds) are considered to be hazardous wastes; which are released into the aquatic environment by industries such as oil refineries, coal gasification sites, petrochemical units ... etc. The content of phenolic compounds in industrial wastewater (about 200 - 2000 mg/L) is usually higher than the standard limits (mostly less than 0.5 mg/L) established for their release into aquatic environment. These compounds are toxic, even at low concentrations and a previous treatment is indispensable before their discharge in to the environment. Several methods were proposed for treating phenolic effluents: chemical degradation, biological oxidation, adsorption, solvent extraction, membrane technology and combined methods. Indeed, Membrane technology promises interesting alternatives to the conventional methods for phenol removal and recovery. Currently, one of approaches used is based on the concept of molecular recognition [1]. Membrane showing facilitated transport properties, which involve specific carriers from supramolecular chemistry such as crown-ethers, calixarenes or cyclodextrins. Cyclodextrins (CDs), water-soluble oligosaccharides consisting of 6, 7 and 8 glucose units corresponding to α -, β - and γ -CD respectively, are extensively used in separation due to their remarkable property to accommodate hydrophobic molecules in their cavity [2]. The inclusion complexation between CD and organic compounds with low polarity have been studied for several decades and much past research has indicated that the process of inclusion complexation between CD and guest is driven by electrostatic forces, Van Der Waals forces, hydrophobic interactions and hydrogen bonding [3]. However, the excellent water-solubility of CDs limits the use in heterogeneous solution. A useful method is to graft CDs on polymer supports in order to easily reproduce and complexing the substrat [4]. Various applications of PVA/CD membrane have been reported in the literature [1], [2], [5]-[7].

The aim of the present paper is both to test the efficiency of PVA / β -CD membrane in the removal of phenol from aqueous solution and to predict the phenol removal process using the experimental design of methodology. Although statistical design of experiments is largely employed in the optimization of industrial process; it is rarely applied in the membrane processes [8], [9]. In this study, a 2^3 factorial design at two levels is used to define the percentage removal of phenol by polymer inclusion membrane according to the initial phenol concentration of the solution, pH of the solution and agitation speed.

2. Experimental

2.1. Materials

Polyvinyl alcohols (PVA) with degree of hydrolysis of 95 %, and Dimethyl sulfoxide (DMSO) were purchased from BIOCHEM. Hexamethylene, 1, 6- diisocyanate (HMDI) and β -Cyclodextrin (β -CD) were purchased from Alfa Aesar.

2.2. PVA / β -CD membranes preparation

The immobilization of cyclodextrin onto PVA was carried out according to the procedure previously reported by Miyata and al. [4]. PVA was dissolved in DMSO at 50 °C and magnetically stirred for 24h. The obtained solution was mixed with various amount of CD (weight ratio β -CD to PVA was of 2% to 20 wt-%) and stirred for 30 minutes until a homogeneous and transparent solution is obtained. The solution was poured into Petri dishes and dried during 4 days at 60 °C.

2.3. Inclusion complex characterization

The inclusion complex of phenol and β -CD was confirmed by UV-vis spectrum shown in Fig. 1, where the phenol intensity peak increased in presence of β -CD (Fig. 1). This result is comforted by Chen et al. (2006) who have characterized the inclusion complex of nitrobenzene and β -CD by UV-vis spectroscopy. The formation of the inclusion complex can be described as follows: $H + G \Leftrightarrow H - G$

Where: H represents the host, β -CD, G the guest, Phenol, and H-G the inclusion complex.

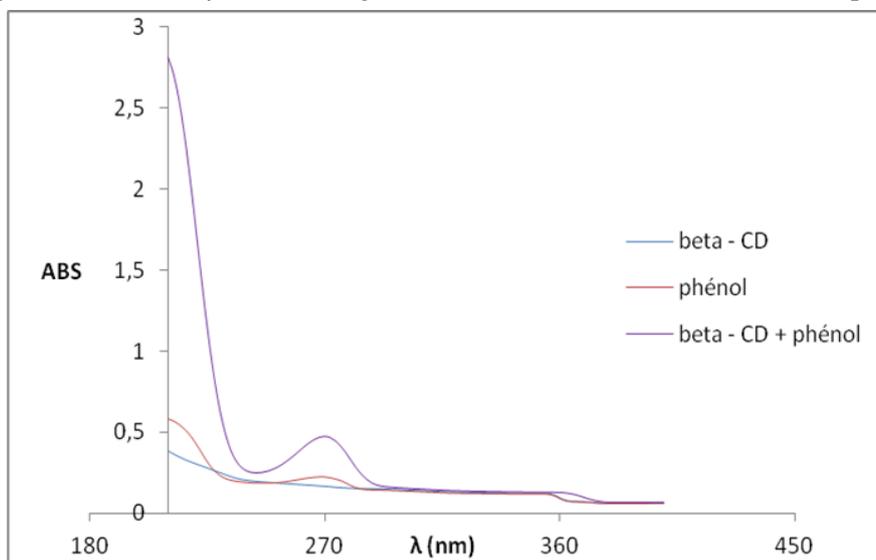


Fig. 1: UV-vis spectra of phenol and β -CD-phenol complex

2.4. Phenol's liquid-solid extraction

The kinetic study of the phenol liquid-solid extraction was carried out considering the following parameters: contact time, the cross-linker content, and the percentage of β -CD in the membranes. The Fig. 2 shows the effect of addition of cross-linker on the phenol extraction yield. As it can be seen, the extraction is not affected by the addition of a cross-linker agent.

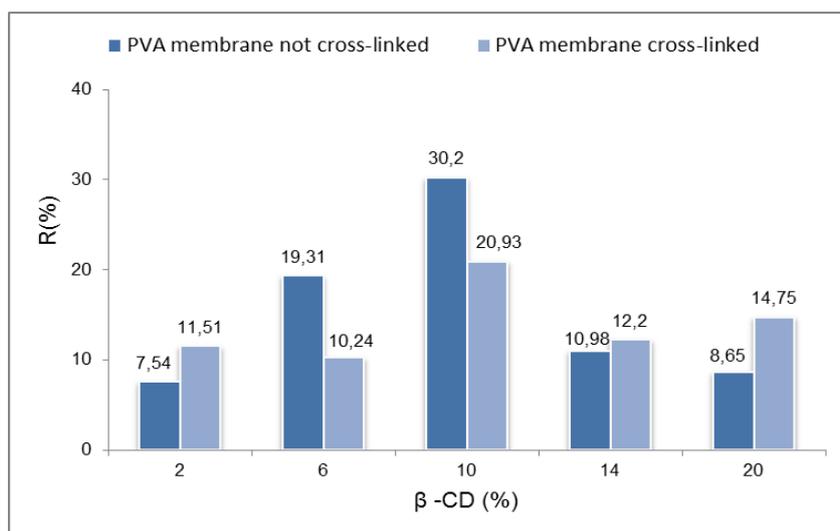


Fig. 2: Effect of the amount of β -CD (%) on the phenol extraction yield

2.5. Extraction's mechanism

The phenol extraction mechanism by PVA/ β -CD membrane can be described by the theory of “free volume” as proposed by Peng et al. (2006). β -CD can be regarded as fixed carriers: first, phenol molecules are adsorbed on the PVA/ β -CD membrane and then, are transported through the membrane by jumping from one CD to another and diffusing through the polymer network (Fig. 3).

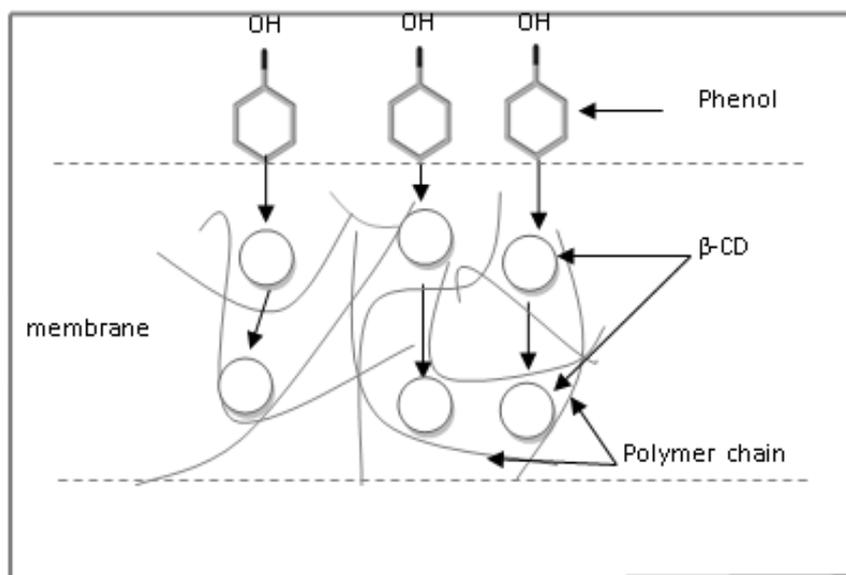


Fig. 3: Phenol diffusion mechanism through the PVA/ β -CD membrane

3. Experimental design methodology

3.1. Elaboration of the model

In order to evaluate the effect and interaction of the initial phenol concentration (Z_1), pH (Z_2) and agitation speed of the solution (Z_3) on the phenol extraction yield, a two level factorial design 2^3 was used. The original values of each factor and their corresponding levels are presented in Table 1.

Table 1: Values of Operating Factors of 2^3 full factorial at Two Levels

Operating parameters	level -1	level +1
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Z_1 : initial phenol concentration (ppm)	18	42
Z_2 : pH of the solution	4.6	9.4
Z_3 : Agitation speed (tr/min)	325	820

The correlation of independent variables and the response were estimated by a first-order polynomial equation 1 as shown below [10]:

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{23} x_2 x_3 + b_{123} x_1 x_2 x_3 + \varepsilon$$

Where: y is the phenol adsorption yield, b_0 is the average value of the response at the center point of the design, $b_1, b_2, b_3, b_{12}, b_{13}, b_{23}, b_{123}$, are the linear and interaction terms, respectively. ε is the random error component which is approximately normally and independently distributed with mean zero and constant variance.

For any factor Z_j , the transformation from natural to coded values x_j has been performed [11].

3.2. Statistical analysis

The application of the statistical test of Student [12]-[14] for the determined coefficients, allowed us to estimate their significance and eliminate those whose influence is not significant. After eliminating insignificant coefficients, the model equation becomes (2):

$$\hat{y} = 21.84 + 3.85 x_1 - 4.62 x_2 - x_3 - 2.32 x_1 x_3 + 0.94 x_2 x_3 - 1.36 x_{123}$$

The test of reliability for the predicting equation has been carried out by the Fisher's test [14], [15], it compared the residual variance with the replication variance. Table 2 gives the results of the variance analysis.

Table 2: Analysis of Variance for the first-Order Model

source of variations	SS	f	MS	F-value
residual error	9,977	4	2,494	7,717
experimental error	0.646	2	0.323	

SS represents the sum of squares; f is the degrees of freedom, and MS the mean squares.

The tabulated F value for the 5 % significance level and degrees of freedom f_1 and f_2 ($f_1 = N - p = 1$ and $f_2 = N_0 - 1 = 2$) is between 2.57 and 2.61. It was found that the estimated value of F is much less than this interval. The two variances are then statistically equal: the adjustment error between the real model and the postulated model is negligible in front of the experimental error. Hence, it can be concluded that the established predicting equation gives an excellent fit to the observed data.

The regression equation obtained (equation 2) shows that the phenol concentration of the solution has a positive effect on the extraction yield, since the corresponding coefficient ($b_1 = + 3.85$) is positive. Extraction capacity of phenol by β -cyclodextrin membrane is governed by a concentration gradient. The pH of the solution has a negative effect on extraction performance ($b_2 = - 4.62$). The negative sign of the coefficient indicates that the extraction rate decreases with increasing pH. Indeed, when the pH of the solution increases (basic pH) phenol molecules are transformed into ions phenolates and therefore their inclusion in the cavities of CDs becomes impossible (hydrophobic cavity). This results confirm that the extraction mechanism of phenol by β -CD is essentially the formation of an inclusion complex between cyclodextrin and phenol. An optimum pH of 2.0, has been suggested by Venkateswaran Palanivelu [16] in the transport of phenol through an MLS system using vegetable oils, such as liquid membrane.

The stirring speed factor ($b_3 = - 1$) does not have much influence in the chosen study domain, his effect is low and negative on the extraction yield. This little effect of the stirring rate on the phenol extraction by cyclodextrin membrane is also may be due to the swelling capacity of cyclodextrin membrane. The MEP has also demonstrated the existence of a strong interaction between the concentration and the stirring speed

of the solution (see Fig. 4). The effect of this interaction is negative (-2.32), it manifests in the treatment of high pH solutions.

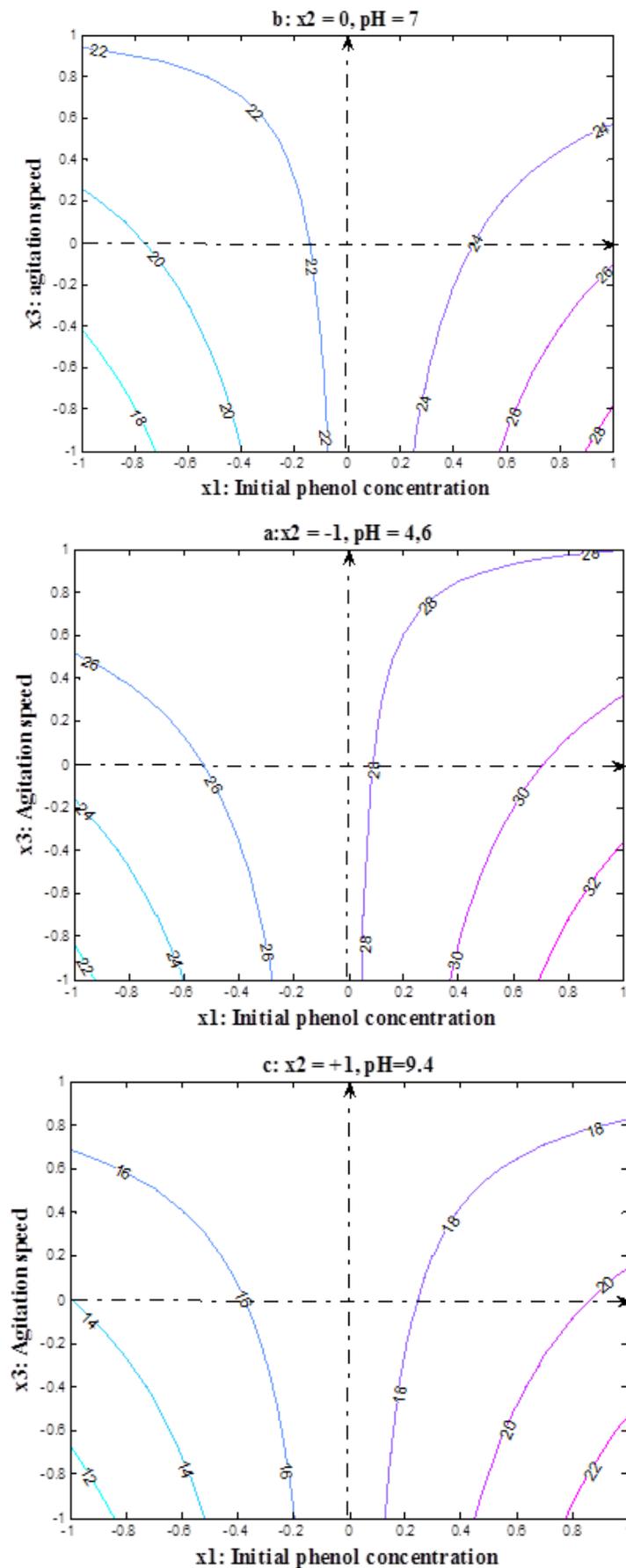


Fig. 4: Interaction contour plots for phenol extraction yield for different levels of pH

3.3. Residual analysis

The evaluation of the quality of the model is performed by an analysis of residues [15]. The values of the residues are plotted versus predicted responses (Fig. 5). This Fig. reveals that there is no apparent relation between the predicted and residues values, because points are randomly arranged.

All these results confirmed that the model obtained explains well the experimental results.

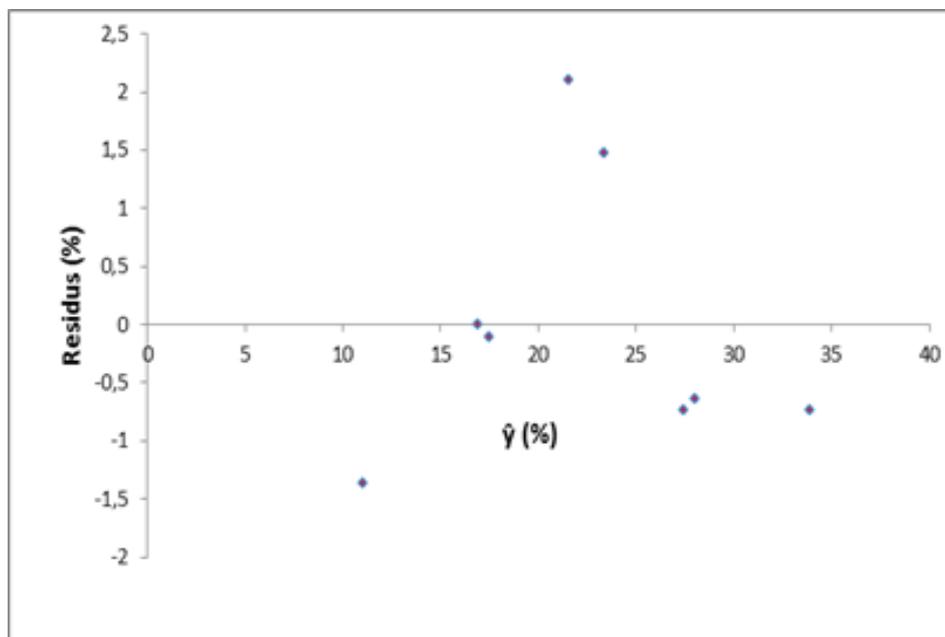


Fig. 5: Diagram of residues

4. Conclusion

The experimental designs methodology was used successfully for modelling the phenol extraction process by polymer inclusion membrane (PVA/ β -CD) in a batch system. An extraction yield of around 33% is obtained after an equilibrium time of 50 minutes. The model analysis has showed that the most important parameters are the initial concentration of phenol, with a positive effect ($b_1 = + 3.85$), the pH of the solution has a negative effect ($b_2 = - 4.62$). The stirring speed has a low and negative effect ($b_3 = -1$) on the phenol extraction yield, in the study domain chosen. The model revealed the existence of a strong interaction between the concentration of the solution and the stirring speed.

The kinetic study of liquid-solid extraction showed that the diffusion of phenol through PVA / β -CD membranes was governed by theory of “free volume” which states that phenol is transferred from amorphous zone to another by jumping from one CD site to another and diffusing through the polymer matrix.

5. References

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