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Modeling and Simulation for Pervaporation Process: An Alternative for Removing Phenol from Wastewater

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A simulator named PERVAP was developed applying the mathematical model, that is essentially predictive, to simulate the pervaporation process. In the present work, the separation of phenol/water mixture was studied in polyurethane (PU) membrane, which is highly hydrophobic, indicating that it is useful for recovery of volatile organic compounds from water. Thus, in order to validate the model, experimental data were used, showing a good agreement. The good performance of the model, also, allows its application for the study of the effect of the process variables, as for example, the downstream pressure and the feed composition on the separation.

1. Introduction

Phenolic compounds are present in many industry wastewaters from manufacturing phenols to related chemicals. Because of environmental reasons, phenol needs to be removed from wastewater. The environment legislation, concerning the harmless level of 0.5 ppm for phenol, makes more difficult to find out chemical and biological separation processes able to attend this restriction. Indeed, alternatives to the conventional biological treatment are important, since, increasing the phenol concentration, the biological treatment becomes more difficult.

Pervaporation, a term derived from two major operations involved in the separation process, namely, permeation and evaporation, is defined as a separation process in which a liquid feed mixture is separated by means of selective diffusion-vaporization through a nonporous membrane. This is potentially an effective process for separating azeotropic mixtures. The solution–diffusion mechanism is adopted to describe pervaporative transport through dense membranes and this has become the accepted pattern for this process. According to this mechanism, the transport occurs in three steps: (a) selective sorption of the components on the membrane surface; (b) diffusion of the components through the membrane; (c) desorption on the permeate side. Pervaporation - based process holds a large potential for utilization by the traditional chemical industry and by emerging areas such as environmental and biochemical engineering, using dense membranes to separate different types of mixtures and it represents an alternative unit operation for replacing conventional separation processes usually applied to remove volatile organic compounds from water, and for recovering

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key aroma compounds. From the stand point of performance, this membrane technology is considered as a reliable separation process compared to conventional processes.
In this study, a simulator named PERVAP based on a predictive pervaporation modeling was applied (Alvarez *et al.*, 2008).

2. Pervaporation Process Modeling

According to the solution-diffusion mechanism, the mass transport of the permeant components through the membrane can be described according to Alvarez *et al.* (2008) as:

2.1 Transport in the boundary layer

Considering at steady state, according to the first Fick's law, the solution of the general equation of the molar flux of solute *i* through the boundary layer is expressed as (Alvarez et *al.*, 2008):

$$J_i = \frac{D_{i,f}}{\delta_{bl}}\left(C_{i,f} - C_{i,1}^{m}\right) \tag{1}$$

where the concentration of component *i* in the feed phase ($C_{i,f}$) can be solved expressing the driving force in terms of activities.

2.2 Transport in the membrane

At steady state, the diffusive flux of each component, considering the interfaces of the membrane with the feed phase and with the permeate phase, is defined as:

$$J_i = \frac{D_i^m}{\ell}\left(C_{i,1}^{m} - C_{i,2}^{m}\right) \tag{2}$$

where D_i^m is the diffusivity coefficient of the component *i* in the membrane. In the permeation process, the permeants define a concentration profile through the membrane, from the feed phase up to the permeate phase. Taking into account the permeation process, the concentration of permeants *i* and *j* in the membrane in the downstream is described by the following equations:

$$C_{i,2}^{m} = \frac{x_{i,f}\,\alpha\, p}{\bar{\gamma}_i^m\left[1+(\alpha-1)x_{i,f}\right]} \quad \text{and} \quad C_{j,2}^{m} = \frac{(1-x_{i,f})\,p\,P_i^{sat}}{\bar{\gamma}_j^m\left[1+(\alpha-1)x_{i,f}\right]P_j^{sat}} \tag{3}$$

where: $p=P_2/P_i^{sat}$ is the partial pressure, P_2 is the downstream pressure (kPa), P_i^{sat} is the saturated vapour pressure (kPa), α is the selectivity, $x_{i,f}$ is the feed mole fraction of component *i*, $\bar{\gamma}_i^m$ and $\bar{\gamma}_j^m$ are the activity coefficient in the membrane for component *i* and *j*, respectively. Replacing Eq. 3 for component "*i*" in Eq. 2, comes the Eq. 4:

$$J_i = \frac{D_i^m}{\ell \bar{\gamma}_i^m}\left(x_{i,f}\gamma_{i,f} - \frac{x_{i,f}\ \alpha\ p}{1+(\alpha-1)x_{i,f}} \right) \tag{4}$$

where, the diffusion coefficient of component *i* in the membrane, D_i^m, can be predicted by the free-volume theory described by the following equation (Eq. 5) (Vrentas and Duda, 1977, 1979):

$$D_i^m = D_0(1-\phi_1)^2(1-2\chi\phi_1)\exp\left(\frac{-E}{RT}\right)\exp\left(-\frac{\omega_1\hat{V}_1^* + \xi\omega_2\hat{V}_2^*}{\frac{K_{11}}{\gamma}\omega_1(K_{21}-T_{g1}+T)+\frac{K_{12}}{\gamma}\omega_2(K_{22}-T_{g2}+T)} \right) \tag{5}$$

2.3 Selectivity

The selectivity, for the pervaporation process, can be obtained from flux equations for the components *i* and *j*, which can be expressed by Eq. 6:

$$\alpha_{i,j} = \frac{D_i^m \bar{\gamma}_j^m\left(\gamma_{i,f}x_{i,f} + \frac{x_{i,f}\,\alpha_{i,j}\,p}{1+(\alpha_{i,j}-1)x_{i,f}} \right)(1-x_{i,f})}{D_j^m \bar{\gamma}_i^m\left(\gamma_{j,f}x_{j,f} - \frac{(1-x_{i,f})pP_i^{sat}}{P_j^{sat}\left[1+(\alpha_{i,j}-1)x_{i,f}\right]} \right)x_{i,f}} \tag{6}$$

Using this modelling, the PERVAP simulator was developed in order to carry out simulations for existing and new processes.

3. Results and Discussion

Polyurethane membrane was used for the separation of the binary mixture (phenol/water) by pervaporation. This membrane was chosen due to the fact that the literature also provides experimental data of pervaporation involving this mixture, enabling the application of the software PERVAP. It is necessary the knowledge of the structural formula of the polymer, which allows the application of the free-volume theory for the prediction of the free-volume parameters of the polymer and, consequently, the diffusion coefficient of water and phenol in the membrane.

The simulation was done using the software PERVAP, based on solution-diffusion model. The diffusion coefficient is predicted by the free-volume theory of Vrentas and Duda (1977). The experimental data of pervaporation used in the begin of the simulation are necessary to estimate the activity coefficients of the species (feed) in the membrane, as Alvarez *et al.* (2008). This was necessary because of the lack of interaction parameters data of a thermodynamic model involving the pairs water-PU and phenol-PU in literature at the operating temperature.

The pervaporation experimental data of the phenol-water mixture in PU were taken from Hoshi *et al.* (1997). The free-volume parameters for phenol were estimated from

viscosity data of the pure component, as Viswanath and Natarajan (1989). The free-volume parameters for water were extracted from Hong (1995). The process data considered in pervaporation were: average thickness of the membrane: 8.0 μm: pressure in the feed side: 101.325 kPa; operating temperature: 333.15 K and pressure in the permeate side: 0.33 kPa.

Table 1 shows the free-volume parameters of the polymer. Table 2 shows the free-volume parameters used by the software PERVAP.

The calculation of the activity coefficient of the mixture components in the feed was made through the UNIFAC group contribution method and the vapor pressure was calculated as the Antoine model.

Table 1 Free-volume parameters of the polymer

Polymer	V_2^*	K_{12}/γ	$K_{22} - T_{g2}$	T_{G2}
PU	0.75546	2.89 x 10^{-4}	-163	231

Table 2 Free-volume parameters used in PERVAP simulator for predicting the activity coefficients

Components	V_1^*	K_{11}/γ	$K_{21} - T_{g1}$	D_0	χ	ε	E
Water	1.0710[§]	2.18×10^{-3}[§]	-152.29[§]	8.55×10^{-4}[§]	0.01858	0.2694	0
Phenol	0.7906	1.12×10^{-3}	-171.90	3.90×10^{-8}	0.00650	0.0550	0

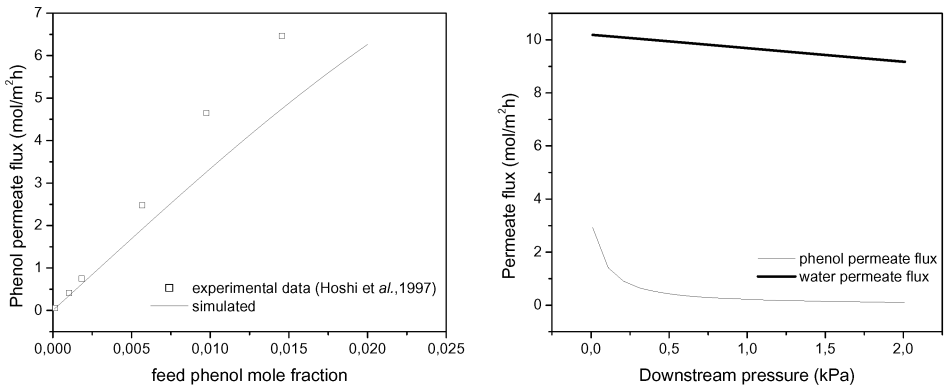
[§] from Hong (1995)

From Table 1 and Table 2, considering PU membrane, the activity coefficients for water and phenol were estimated and are 2.4881×10^{-7} and 7.1744×10^{-11}, respectively. The diffusion coefficients for water and phenol are 2.2377×10^{-10} and 6.6412×10^{-15}, respectively.

Once provided all the parameters for the simulator PERVAP, the results were generated and analysed. Experimental data available in Hoshi *et al*. (1997) were used. The obtained behavior for the permeate phenol flux *versus* the feed phenol mole fraction is shown in Figure 1(a). The results with phenol are close to the experimental data, following a similar tendency.

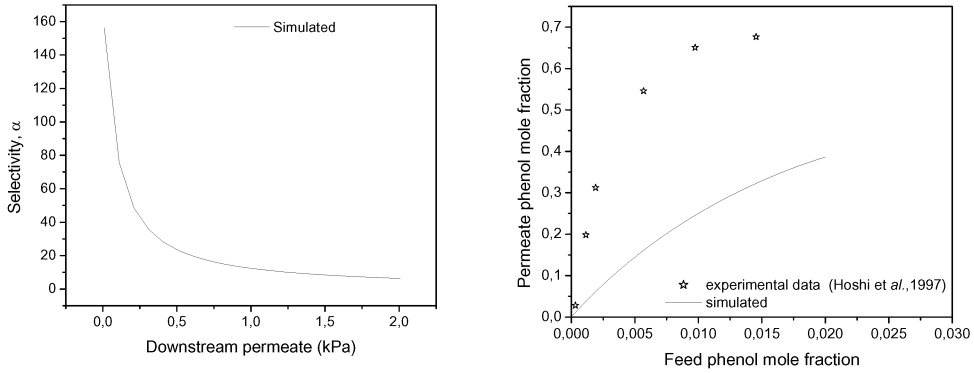
Figure 1(b) shows the behavior of water and phenol permeate flux with the downstream pressure. It was observed that the water flux is not affected with the change of pressure, while the phenol flux decreases dramatically increasing the pressure to approximately 0.5 kPa. After this value, the phenol flux remains constant. This may be due to the membrane and its polymeric structure has a greater resistance to the fluxes, requiring a lower pressure on the downstream to have a greater permeation of phenol.

Figure 2(a) presents the evaluation of the downstream pressure on the selectivity. In this case, it is noted that lower is the pressure, greater is the selectivity, favoring the permeation of the feed components. When the selectivity is high, there is a better separation, preferably of the desired component, in this case phenol.



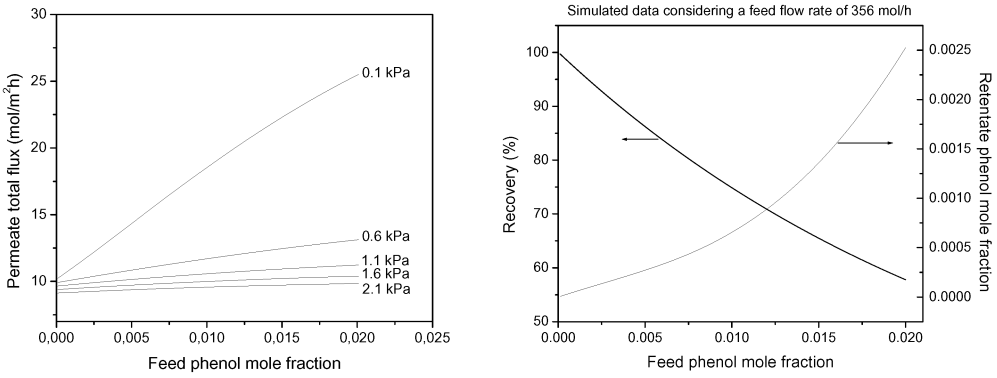
(a) (b)

Figure 1. (a) Permeate phenol flux versus the feed phenol mole fraction. (b) Water and phenol permeate fluxes with the downstream pressure



(a) (b)

Figure 2. (a) Downstream pressure effect in the selectivity; (b) Permeate phenol mole fraction versus feed phenol mole fraction



(a) (b)

Figure 3. (a) Permeate total flux versus feed phenol mole fraction; (b) Recovery and retentate phenol mole fraction versus feed phenol mole fraction

Figure 2(b) shows that higher is the phenol concentration in the feed, greater is the phenol concentration obtained in the permeate. It is possible to verify that the phenol may be concentrated in the permeate when the feed mixture is composed by diluted mixtures of phenol.

Analysing Figure 3(a), there is a possible advantage to operate with lower vacuum pressure, because lower is the pressure, the permeate fluxes will be favored and greater will be the selectivity, which is characteristic of the pervaporation process.

Figure 3(b), the results obtained for the analysis of the phenol concentration in the permeate are related to the recovery percentages in function of the concentration of this component in the feed. It was observed that with the increase in the phenol concentration in the feed, keeping the variables pressure and temperature in the permeate constant, there is a reduction in the recovery and, hence, an increase in the phenol concentration in the retentate, which could require a second stage of pervaporation for treating this retentate. However, it is possible to verify that lower is the phenol concentration in the feed, lower is the loss of phenol in the retentate, which indicates that the pervaporation process is excellent for the treatment of dilute solutions of phenol.

4. Conclusions

For the simulation of the system phenol-water in a polyurethane membrane, the obtained results showed that a better separation of phenol occurs when greater is the driving force, i.e., a lower pressure in downstream side and diluted concentrations of phenol in the feed. It is possible to see through the simulations, even, that the model represents the experimental data adequately.

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