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Solute Separations from Water by Dialysis. II. Separation of Phenol by Downstream Conjugation

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Abstract

The dialysis of phenol through a permselective hydrophobic membrane into a solution sink of caustic (as a conjugating base) was evaluated as a method of extracting dilute contaminants from industrial effluent streams. A series of membranes for this service was characterized in a small rotating batch dialyzer and these results were used to evaluate a process configuration for handling a continuous feed of a prototype industrial effluent.

INTRODUCTION

This study on the extraction of phenol from dilute aqueous solutions parallels an earlier treatment of the separation by dialysis of dilute aniline concentrations in water (*1*). The process utilizes a membrane which is permeable to nonionic organic species (aniline or phenol respectively), but which is substantially impermeable both to their ionic forms (anilinium or phenolate ions) and to water. Some six polymeric formulations were examined as potential membrane materials which would allow reasonably good transport rates and still possess the requisite selectivities.

In practical applications of dialysis to the extraction of contaminants from dilute streams, the driving force across the membrane must be maintained by means other than simple downstream dilution which would, in effect, only aggravate the source problem. In the case of aniline contaminants, a high acid concentration can be maintained on the dialysate side of the permselective membrane (rapidly converting permeant aniline to the nonpermeating anilinium ion). In the case studied here, un-ionized phenol crossing the permselective membrane reacts with excess NaOH to form the nonpermeant phenolate ion.

Membrane parameters have been obtained in the present work with a small rotating batch dialyzer of the sort reported by Regan et al. (*2*). These permitted the projection to a continuous flow configuration suitable for in-plant use.

The membrane permeabilities P for various membrane formulations were obtained from transient experiments in the batch dialyzer through the following expression (derived earlier in Ref. *1*):

$$P = \frac{V_A}{At} \frac{(1 + K_{eq}c_2^B)}{(1 + V_A/V_B + K_{eq}c_2^B)} \ln \frac{(c_1^A)^0}{(c_1^A - c_1^B)} \tag{1}$$

where transmembrane flux $= P(c_1^A - c_1^B)$, V_A is the charge volume, V_B is the receiver volume, $(c_1^A)^0$ is the initial concentration of phenol in compartment A, and

$$K_{eq} = \frac{c_3^B}{c_1^B c_2^B}$$

Subscripts 1, 2, and 3 refer to the phenol, NaOH, and phenolate ion, respectively.

The membrane permeability data are sufficient to permit consideration of the continuous configuration sketched in Fig. 1 if one ignores mass

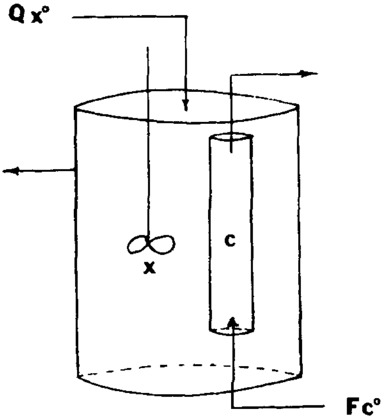

FIG. 1. Continuous process for removing phenol trace compositions through facilitated dialysis into caustic.

transfer limitations in the bulk fluid phases. A continuous caustic purge is to be supplied to a well-mixed sink maintained at concentration x_2. The feed stream containing phenol is fed through a tubular unit (possibly in a hollow fiber configuration). This situation is described mathematically in terms of the following equations:

Nomenclature

ψ is the transmembrane flux $[= P(c_1 - x_1)]$, c is the concentrations in the phenol source stream, x is the concentration in the caustic sink, F is the flow rate of the source stream, Q is the flow rate of caustic stream, A is the membrane area, and L is the membrane length. The subscripts are as defined above, and the superscript 0 is the inlet concentration.

Describing Equations

(1) A phenol balance on the source stream:

$$\frac{d(Fc_1)}{dz} + \psi A = 0 \tag{2}$$

(2) Prescription of equilibrium in the sink between phenol–phenolate–caustic:

$$x_3/(x_1 + x_2) = K \tag{3}$$

(3) A phenol balance on the sink:

$$Q\{(x_1 - x_1^0) + (x_3 - x_3^0)\} = AP\int_0^L (c_1 - x_1)\,dz \tag{4}$$

(4) A caustic balance in the sink:

$$Q(x_2^0 - x_2) = Q(x_3) \tag{5}$$

Since Eq. (2)–(5) represent a linear system (albeit of integrodifferential equations), they may be solved through the straightforward application of operational calculus (see Appendix) leading to the equation set given below.

Case I: For Sufficiently High Caustic Concentrations (Such that $x_2 = x_2^0$*)*

$$x_1 = \frac{Fc_1^0[\exp(-\alpha L) - 1]}{Q(1 + \beta) + F(\exp(-\alpha L) - 1)} \tag{6}$$

$$c_1/(c_1^0) = \frac{F[\exp(-\alpha L) - 1] + Q(1 + \beta)\exp(-\alpha L)}{F[\exp(-\alpha L) - 1] + Q(1 + \beta)} \tag{7}$$

where

$$\alpha = PA/F \tag{8}$$

$$\beta = Kx_2^0/(1 + Kx_1^0) \tag{9}$$

Case II: For Process Dependent Caustic Concentrations

Here the equation set must be solved in a trial and error calculation around x_1.

These equations will be used in a representative applications situation later in this report.

MEMBRANE CHARACTERIZATION RESULTS FROM THE SMALL DIALYZER

Studies were performed in the small rotating batch dialyzer on polyethylene film (with and without plasticizer), Saran (polyvinylidene chloride), a styrene–butadiene block copolymer (Kraton-1101), a polymethylsilane–polycarbonate copolymer, and an ethyl cellulose polymer. Commercially available films of polyethylene were used as received. The Saran used was also the purchased wrapping film. The Kraton-1101 (styrene–butadiene block copolymer from Shell Chemical Co.) was cast from methyl isobutyl ketone solution onto clean glass plates. XD-7, the polymethylsilane–polycarbonate copolymer from General Electric, was prepared by casting from methylene chloride onto clean glass plates. The ethyl cellulose polymer was cast from methylene chloride solutions of Hercules T-50 (a formulation characterized as a 2.2 degree-of-substitution derivative, 50.8% ethoxyl with viscosity 50). Thorough removal of solvents was assured by drying the films for extended periods.

The characterization of the membranes was accomplished as in the earlier studies (*3*) by using the rotating batch dialyzer. Each compartment was analyzed at fixed time intervals through UV absorption at 271 nm (following adjustment to common pH and requisite aliquot dilution). In these tests the system was charged with 0.1 *M* phenol in Compartment A and 1.0 *M* NaOH in Compartment *B*. Based on the measured total transport of phenol into Compartment *B*, the equilibrium constant, and the excess NaOH concentration, the concentration of free phenol could be calculated. The ratio of phenolate to phenol was always greater than 10^4 so that the value of c_1^B was negligible. Analyses were performed on both compartments to obtain the consistency check of an overall material balance.

Table 1 presents derived permeabilities *P* and apparent membrane distribution coefficients K_D (defined as membrane concentration in g/cc/

TABLE 1

Phenol Permeability Through Selected Membranes

Polymer	Thickness (μ)	Effective diffusion coefficient D (cm^2/sec)	Distribution coefficient K_D
Polyethylene, Handy Wrap	14.1	0.11×10^{-7}	0.01
Polyethylene, nonplasticized	10.0	0.05×10^{-7}	0.01
Saran Wrap	10.0	0.06×10^{-7}	0.68
Kraton-1101	41.0	0.71×10^{-7}	0.51
XD-7 (Silane)	68.6	2.06×10^{-7}	0.51
Ethyl cellulose	35.2	0.96×10^{-7}	17.5

ambient phase concentration). The polysilane exhibited the highest transport rates of all materials examined. Surprisingly, the relatively stiff, crystalline ethyl cellulose showed higher permeability than the butadiene copolymer Kraton-1101. Since the permeability values obtained were in effect average values over the concentration range from 0.1 *M* to infinite dilution, it is possible that the ethyl cellulose was being plasticized by the phenol and that its morphology was affected accordingly. Alternatively, the 1.0 *M* sodium hydroxide (an effective swelling agent for native cellulose) might well be decreasing ethyl cellulose crystallinity, thus leading to the more permeable structure.

The transport rates through the two polyethylene samples follow the expected pattern: the less crystalline low-density material allows better transport than the denser, more crystalline membrane. Saran is apparently unaffected by phenol, exhibiting characteristically low permeability.

APPLICATION

Utilization of this process for the concentration of trace contaminants from plant waste streams (for more effective disposal in concentrated form) will understandably involve the use of continuous processing. The derivation leading to Eq. (6) and (7) provides a basis for a feasibility evaluation of this technology.

Consider a hollow fiber unit which is 1-m long and which consists of some 40 bundles, each containing 20,000 fibers. The fibers might be considered to be 200 μ in diameter (with a 25-μ wall thickness) offering some 0.0628 cm^2/cm of length in surface area for transport. An aggregate surface area for the unit described would then be some 0.52×10^7 cm^2.

For a membrane whose diffusion coefficient D ($= P \times$ thickness) is 2.06×10^{-7} cm^2/sec (the polycarbonate silane), the permeability constant is

$$P = D/(\text{thickness}) = 8.24 \times 10^{-5} \text{ cm/sec}$$

One may now consider a modest plant stream application involving continuous processing of a 10 gpm stream with inlet concentration $c_1{}^0$ of 0.1 M. Then $F = 667$ cc/sec and

$$\alpha L = PAL/F = 0.643 \tag{10}$$

Assume also that caustic is supplied at 1.0 M ($x_2{}^0$) concentration and at 1 gpm or 66.7 cc/sec.

The application also requires a description of the phenolate equilibrium relationship, K of Eq. (3). For

$$\phi\text{OH} + \text{OH}^- \rightleftarrows \phi\text{O}^- + \text{H}_2\text{O}$$

$$K_{\text{eq}} = \frac{(C_{\phi\text{O}^-})(C_{\text{H}^+})(C_{\text{H}_2\text{O}})}{(C_{\phi\text{OH}})(C_{\text{H}^+})(C_{\text{OH}^-})} = \frac{K_{\phi\text{OH}}}{K_{\text{H}_2\text{O}}} \tag{11}$$

$$K_{\phi\text{OH}} = \frac{(C_{\phi\text{O}^-})(C_{\text{H}^+})}{(C_{\text{OH}^-})} = 1.28 \times 10^{-10}$$

(*Handbook of Chemistry and Physics*)

$$K_{\text{H}_2\text{O}} = \frac{(C_{\text{H}^+})(C_{\text{OH}^-})}{(C_{\text{H}_2\text{O}})} = \frac{1.0 \times 10^{-4}}{55.5} = 1.8 \times 10^{-16} \tag{12}$$

$$K_{\text{eq}} = \frac{K_{\phi\text{OH}}}{K_{\text{H}_2\text{O}}} = \frac{1.28 \times 10^{-10}}{1.8 \times 10^{-16}} = 71.0 \times 10^4 \tag{13}$$

K of Eq. (3) is given by $K_{\text{eq}}/C_{\text{H}_2\text{O}}$

$$K = \frac{71.0 \times 10^4}{(1000/18)} = 1.3 \times 10^4 \tag{14}$$

Equations (6), (7), and (9) can now be used with the data assembled in Eq. (10) and (14) to calculate the fraction of phenol remaining after treatment (C_1/C^0) and $x_3 = \beta x_1$, the phenolate loading of the caustic stream. These results are summarized for the base case and several larger devices in Table 2.

SUMMARY

It is possible to achieve 50% phenol removal from a 10-gpm 0.1 M stream with a dialysis unit using downstream conjugation. The sink effluent is concentrated phenolate at 0.476 M, and 40 bundles of 20,000

TABLE 2

Performance of Continuous Dialyzers[a]

Membrane provided	Fraction phenol removed $(1 - c_1/c_1^0)$	Phenolate loading to sink stream x_3
Base case: 40 bundles (1 m × 20,000 fibers)	0.475	0.476
100 bundles	0.798	0.800
200 bundles	0.932	0.795
400 bundles	0.96	0.98

[a] On a 10-gpm feed stream 0.1 *M* phenol and a 1-gpm sink of 1 *M* caustic.

each hollow fibers provide the requisite membrane area. With some 100 bundles, 80% removal is achieved and the sink concentrated to 0.8 *M*. While these results are not as economically attractive as might be hoped, they do represent a feasible removal and concentration process for phenol-loaded effluent streams.

APPENDIX

Solution to Continuous Dialyzer Set (Eqs. 2–5, text)

The equation set to be solved is the following. From Eq. (3):

$$x_3/(x_1x_2) = K$$

Combining this with Eq. (5), $(x_2^0 - x_2) = x_3$, one obtains:

$$x_2 = \frac{x_3}{Kx_3} = \frac{x_2^0}{1 + Kx_1} \tag{A-1}$$

For a phenol-free caustic purge feed ($x_3^0 = 0$; $x_1^0 = 0$), Eq. (4) provides:

$$Q(x_1 + Kx_1x_2) = AP\int_0^{L_0}(c_1 - x_1)\,dz = 0 \tag{A-2}$$

Finally, one may restate Eq. (3) and the flux definition:

$$\frac{d(Fc_1)}{dz} + \psi A = 0 \tag{A-3}$$

$$\psi = P(c_1 - x_1) \tag{A-4}$$

Transforming Eq. (A-3) yields:

$$F\bar{c}S - Fc^0 + PA(\bar{c} - \bar{x}) = 0$$

whence

$$c_1 = x_1 + (c_1{}^0 - x_1)e^{-\alpha z} \tag{A-5}$$

for $\alpha = PA/F$ and c_1 = phenol concentration in feed. It is now convenient to define

$$\beta = Kx_2{}^0/(1 + Kx_1)$$

and $x_2{}^0$ = caustic concentration if fresh dialyzing stream. Equation (A-2) then yields

$$x_1 = \frac{I}{Q(1 + \beta)}$$

and

$$\begin{aligned} Qx_1(1 + \beta) &= AP\int_0^L \{x_1 + (c_1{}^0 - x_1)e^{-\alpha z} - x_1\}\,dz \\ &= F(c_1{}^0 - x_1)(e^{-\alpha L} - 1) \end{aligned} \tag{A-6}$$

Solving Eq. (A-6) for x_1 gives the following expression (implicit in x_1 because of dependence of β on x_1):

$$x_1 = \frac{Fc_1{}^0(e^{-\alpha L} - 1)}{F(e^{-\alpha L} - 1) - Q(1 + \beta)} \tag{A-7}$$

Equation (A-5) then yields

$$c_1 = \frac{F(e^{-\alpha L} - 1) - Q(1 + \beta)e^{-\alpha L}}{F(e^{-\alpha L} - 1) - Q(1 + \beta)} \tag{A-8}$$

where again $\alpha = PA/F$.

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