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Separation of Pyridine/Water Solutions Using Pervaporation

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ABSTRACT

Studies were performed on the separation of pyridine/water solutions using pervaporation. Organic permeation experiments were performed using a 'silicalite'-filled silicone composite membrane. Effects of feed concentration, feed temperature, and permeate side pressure were examined. Benchmark conditions of 5.0 wt% pyridine, 50°C, and 2 torr were chosen. At the benchmark conditions, an organic selectivity of 34 and a permeate flux of 0.428 kg/m^2·h was achieved. An increase in feed concentration caused an increase in both the permeate concentration and flux, but caused a decrease in the selectivity. Also, permeate compositions far exceeded standard vapor–liquid equilibrium. Temperature had an Arrhenius-type relationship with regard to flux, but had no effect on the selectivity. Increasing the permeate pressure caused a steady decrease in permeate flux and also decreased the permeate composition and selectivity.

INTRODUCTION

The separation of pyridine/water solutions using pervaporation (PV) has been examined, with a focus on organic permeation. Low concentrations of pyridine in a feed stream can be concentrated to high concentrations in the permeate (for possible reuse) while purifying the water stream. Wastewater streams containing pyridine can be successfully purified to meet environmental standards by use of pervaporation. Pyridine could

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also be recycled for further use, thus helping to reduce the total amount of waste generated. Pyridine is listed as a commonly recycled solvent in the pharmaceutical industry (1). Pyridine is a frequently used chemical for pharmaceutical production, for waterproofing chemicals, and for rubber accelerators. It is commonly used as an intermediate in chemical synthesis. Many pyridine derivatives are useful chemicals.

The primary environmental focus placed on organic permeation is for removal of trace volatile organic compounds (VOCs) from water. This is for final processing before allowing the stream to exit the plant. These very dilute concentrations usually have less than 1% organic. Often the chemicals in question are not very soluble in water, such as benzene or chloroform. In this area, pervaporation has been found to be very economical. A great benefit is the fact that a pervaporation unit can easily be attached to an existing system. Another environmental use of organic permeation is in solvent recycling. This application involves recovering by-product and solvent waste streams used in various steps in a chemical process. Concentrations in these streams can range from very dilute to up to 10 wt% organic. Here pervaporation has a greater challenge in processing, as it must stand up against more traditional separation techniques.

Pervaporation is a membrane process involving the use of a nonporous membrane to affect a separation. A liquid feed stream is passed across the membrane at atmospheric pressure, while a low vapor pressure is maintained on the permeate side of the membrane. The transported components come off the membrane on the permeate side in the vapor phase. The low vapor pressure is maintained either by use of a vacuum pump or by use of a sweep gas. The permeate side pressure must be kept below the saturation pressure of the transported components to desorb the components from the membrane (2). Pervaporation is unique as a membrane process in that a phase change occurs with separation.

The pervaporation process is generally regarded as a three-step mechanism:

1. Selective sorption into the membrane on the feed side
2. Selective diffusion through the membrane
3. Desorption into a vapor phase on the permeate side

Transport in pervaporation is generally described using a solution–diffusion mechanism. The selectivity of the membrane is determined by the selective sorption and/or the selective diffusion through the polymer. The desorption step is considered insignificant as a resistance to transport (2).

The driving force for the separation is a difference in chemical potential, $\Delta\mu$, across the membrane. The flux for any transported component can be described by

$$J_i = L_i \frac{\Delta \mu_i}{l} \qquad (1)$$

where L_i is the phenomenological coefficient, which is a function of both the solubility and the diffusivity of the transporting component, and l is the membrane thickness. Other more detailed expressions describing pervaporative transport can be found in the literature (2–5). The flux is easily calculated from lab data by weighing the collected permeate, and dividing it by the time it took to collect and the total membrane area. This gives the total flux, which is an important measure of the system productivity.

The selectivity is a measure of the ability of the membrane to separate two components. Two different selectivity parameters are commonly used. The more commonly used selectivity takes the form

$$\alpha_A = \frac{y_A/y_B}{x_A/x_B} \qquad (2)$$

where y_A = mass fraction of component A in the permeate
y_B = mass fraction of component B in the permeate
x_A = mass fraction of component A in the feed
x_B = mass fraction of component B in the feed

Another form the selectivity sometimes takes is

$$\beta_A = y_A/x_A \qquad (3)$$

where y_A and x_A are the same as above. This is also referred to as an enrichment factor.

Pervaporation separations can be broken into three major categories. The first type of separation is dehydration. Dehydration involves removing low concentrations of water from a mostly organic stream. Typical membranes for this application include poly(vinyl alcohol) and polyacrylonitrile, to name just two. One application for this type of separation is to purify alcohols (e.g., ethanol and isopropyl alcohol) above their azeotropic concentration. The second type of separation is organic permeation. Organic permeation deals with removing low quantities of organics from a water stream. Hydrophobic membranes, such as polydimethylsiloxane, are used for this type of separation. Wastewater purification, such as removal of VOCs from water, is a major application for this form of pervaporation (3). The third type of separation is an organic/organic separation. Membranes for this type of separation are chosen based on the compounds being separated. Less work has been done on this type of separation. One application for the third type is the separation of isomeric xylenes. The focus of this paper is on organic permeation.

The authors have previously investigated organic permeation of several solvents. The solvents successfully separated include ethanol, butanol isomers, acetone, ethyl acetate, and tetrahydrofuran (THF) (6–10). These solvents are all common to the pharmaceutical and speciality chemical industries, and are also used in other industries.

Very little work has been done using pervaporation for the separation of pyridine/water solutions. In our review of the literature, only three articles describing the separation of pyridine and water were found. Two of the papers are on dehydration (one is on a PVA membrane) and one involves testing a membrane (PDMS) for organic permeation.

Okamoto et al. (11) studied the effectiveness of a polydimethylsiloxane membrane in separating water from ethanol, pyridine, and dioxane. The effect of feed composition on permeate concentration was studied and compared to the standard vapor–liquid equilibrium (VLE) data. The runs were made at 25°C with a membrane 500–2000 μm thick. For a feed concentration of 5% pyridine, a permeate concentration of 83% pyridine was achieved. Due to the thickness of the membrane, a very low specific permeation rate and therefore a very low flux were achieved.

Kujawski et al. (12) described the effectiveness of several hydrophilic membranes for this separation, including PEAA (polyethylene grafted with acrylic acid), PESS (polystyrene and sulfonated polystyrene-*co*-divinylbenzene), PETS (polyethylene grafted with sulfonic acid), NAFION [poly(tetrafluoroethylene - *co* - perfluoro - 3,6 - dioxa - 4 - methyl - 7 - octensulfonic acid], RAIPORE [poly(tetrafluoroethylene-*co*-styrene sulfonic acid)], and GFT (multilayer supported polyvinyl alcohol). They also examined swelling of the different polymers. All of these membranes, with the exception of the GFT membrane, are ionic membranes. The PEAA membrane has a carboxylic group, and the PESS, PETS, NAFION, and RAIPORE membranes all have a sulfonic group. The paper compared the performance of these different membranes to each other. Table 1 gives some results to experiments performed on ion-exchange membranes. The authors went on to describe the effectiveness of the neutral membrane, a GFT membrane. For a feed concentration of 41.3% water, a permeate concentration of 95% water was achieved with a flux of approximately 0.32 kg/m^2·h.

The final portion of the paper (12) described the use of pervaporation in combination with distillation to give highly pure pyridine (99.9%). The process used a distillation column followed by a dehydration pervaporation unit, which was followed by another distillation column, and then a

TABLE 1
Comparison of Membranes at a Feed Concentration of 41.3 wt% Water and a Temperature of 40°C (12)

Membrane	Permeate (wt% H_2O)	Flux ($kg/m^2 \cdot h$) Total	Flux ($kg/m^2 \cdot h$) Water	Thickness (μm)
PETS	98.0%	0.52	0.51	315
RAIPORE	85.7%	3.85	3.30	50
PESS	81.0%	0.93	0.75	180
NAFION	72.2%	0.68	0.49	170

final dehydration pervaporation unit. The first column was used to bring the pyridine/water solution to its azeotropic concentration. A high flux membrane could then be used to raise the pyridine concentration above its azeotropic concentration. This enriched stream was sent to the second distillation column. In the second column, the bottoms stream was around 95% pyridine. Finally, the last pervaporation unit increased the final stream to above 99% pure. All the streams except the first were recycled to maximize efficiency. The bottoms stream from the first distillation column was drawn off (mostly water).

Dehydration of amines and diamines by pervaporation with ionomer and PVA-based membranes was studied by Xie et al. (13). Their study is similar to the previous one (12); it analyzes the ability of different membranes to separate water and pyridine. The membranes studied included PEA, PESS, NAFION, a GFT membrane, a treated GFT membrane (GFT over-crosslinked with hydrocarbon chains), and an RAI 1010 membrane (RAIPORE from the previous paper).

EXPERIMENTAL METHODS

The experimental system used in these studies employed a flat sheet membrane cell as shown in Fig. 1. The feed solution is constantly pumped to the membrane cell, flows across the membrane, and is then removed through the retentate port. The membrane area for separation is 28.74 cm^2. The vaporous permeate is collected in two condensers placed in series and immersed in liquid nitrogen. Due to the small area of the membrane and low single-pass recovery, the retentate concentration is fairly close to that of the feed concentration. The feed temperature was easily measured and kept constant in a water bath. The permeate pressure was measured using a mercury manometer and was controlled by the vacuum

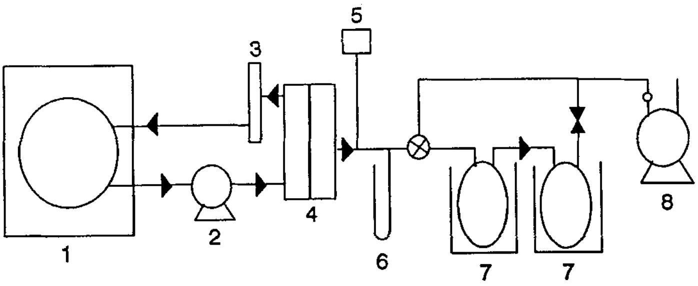

FIG. 1 Membrane pervaporation system process diagram. System components: temperature controlled feed tank (1), feed pump (2), flowmeter (3), membrane cell (4), pressure meter (5), pressure manometer (6), permeate condensers (7), vacuum pump and pressure regulator (8).

pump. The flow rate was controlled using a micropump and was kept fairly constant at 1500 mL/min.

The membrane used for all of the runs performed was an organophilic membrane. The membrane utilized was a silicone composite membrane (designation: Pervap 1170) obtained from the GFT Division of Carbone of America Corp. The membrane is PDMS with a zeolite filling.

For measuring concentrations, the refractive index was measured using a refractometer (Reichert-Jung, Auto Abbe Automatic). The refractive index of pyridine/water solutions was found to be linear with concentration. Pyridine has a very high refractive index and is quite distinct from water, so this was found to be a very accurate measure of concentration.

RESULTS AND DISCUSSION

The first series of tests was performed to evaluate the effect of feed concentration on pervaporative performance. All runs performed varying the feed concentration were kept at a constant feed temperature of 50°C and a permeate side pressure of 2 torr. Figure 2 shows the effect of feed concentration on permeate concentration. Also indicated on this figure is the VLE line of the pyridine/water solution. It can clearly be seen that the permeate concentration from pervaporation far exceeds the VLE. Also, the azeotrope was successfully broken. The azeotrope occurs at 58.7 wt% pyridine (for 50°C and 1 atm), and the permeate goes above 60 wt% at a feed concentration above 3 wt% pyridine. This clearly demonstrates the effectiveness of pervaporation for this separation.

Although several runs were performed at concentrations above 15 wt% pyridine, operation above this concentration is not recommended because

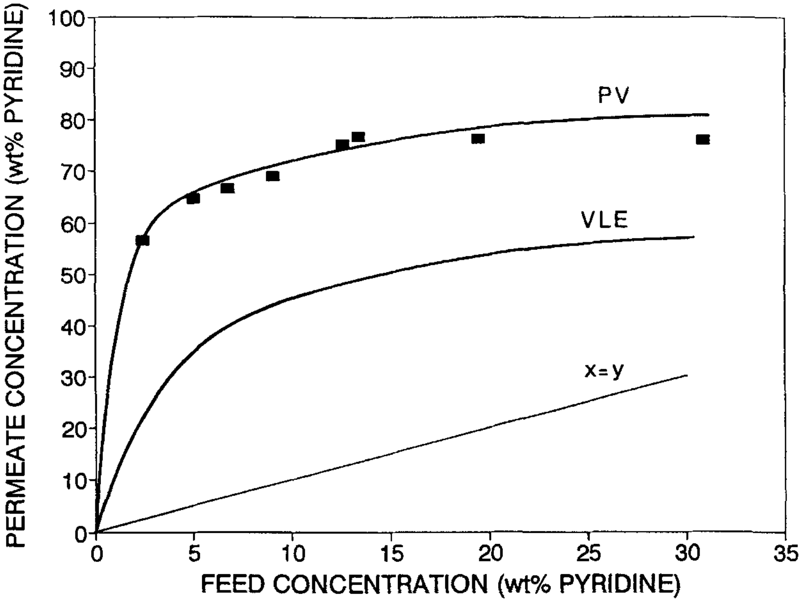

FIG. 2 Permeate concentration vs feed concentration at 2 torr permeate side pressure and 50°C. Comparison to vapor–liquid equilibria at 50°C.

the separation ability of the membrane begins to deteriorate. The result is poor selectivity through the membrane. Specifications for the membrane are that it should not be operated above a temperature of 80°C or above a feed concentration between 10 and 40 wt% organic, depending on the organic (14). The operating organic limit for pyridine using the Pervap 1170 membrane is 15 wt%. The temperature limit was not reached. No difficulties were encountered when the system was operated at 75°C.

The effect of feed concentration on flux was also examined. As seen in Fig. 3, an exponential relationship was observed for the total and pyridine fluxes. A linear regression was performed on the natural log of flux versus the reciprocal of feed concentration to give expressions for the total and the organic fluxes:

$$J_{\text{tot}} = 0.6357e^{-1.796/x} \tag{4}$$

$$J_{\text{pyr}} = 0.4837e^{-2.540/x} \tag{5}$$

where x is the weight percent of pyridine in the feed. This equation is good for feed concentrations from 0 to 15 wt% pyridine. It is important

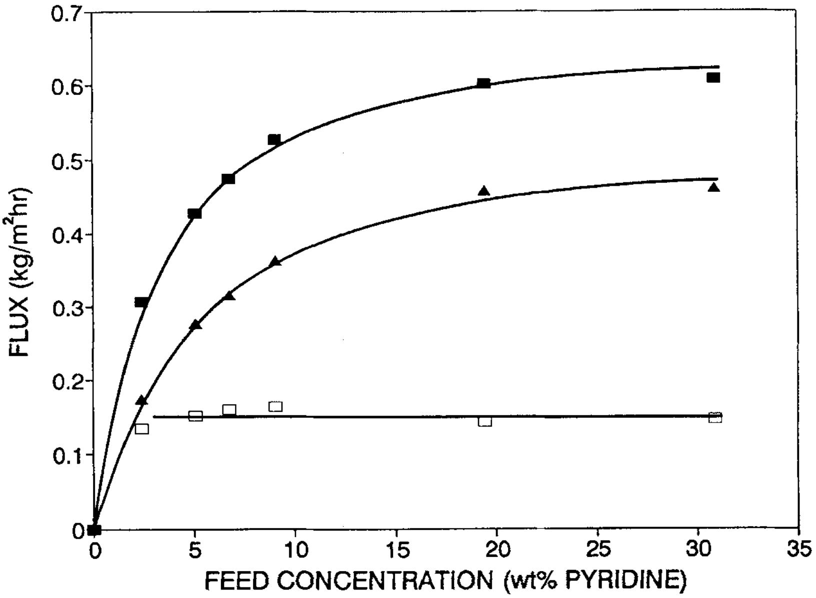

FIG. 3 Feed concentration vs total, pyridine, and water flux. Operated at 50°C and a permeate side pressure of 2 torr. Total flux (■), pyridine flux (▲), and water flux (□).

to note these equations are specific for a temperature of 50°C and a permeate side pressure of 2 torr.

The selectivity shows a concave decrease with increasing feed concentration. The feed concentration has a greater effect on permeate concentration when the feed concentration is low. As feed concentration gets higher, it has less of an effect on permeate concentration. This can be seen in Fig. 2 where the permeate concentration begins to level out above 5 wt% pyridine in the feed. This change can also be seen in Fig. 4 where the selectivity begins to level off above 5.0 wt% pyridine in the feed.

The next set of runs involved examining the effect of temperature on pervaporative performance. These runs were conducted at a constant feed concentration of 5.0 wt% pyridine and a constant permeate side pressure of 2 torr. The temperature was varied in 10° increments between 30 and 70°C. A substantial increase in flux occurs over the range of temperatures examined, as seen in Fig. 5. The total flux increases from 0.178 kg/m^2·h at 30°C to 0.700 kg/m^2·h at 70°C. Although the flux increases, the permeate concentration remains relatively constant, ~65%, over the range of temperatures examined. The flux of both pyridine and water appears to rise proportionally, causing the permeate concentration to remain constant.

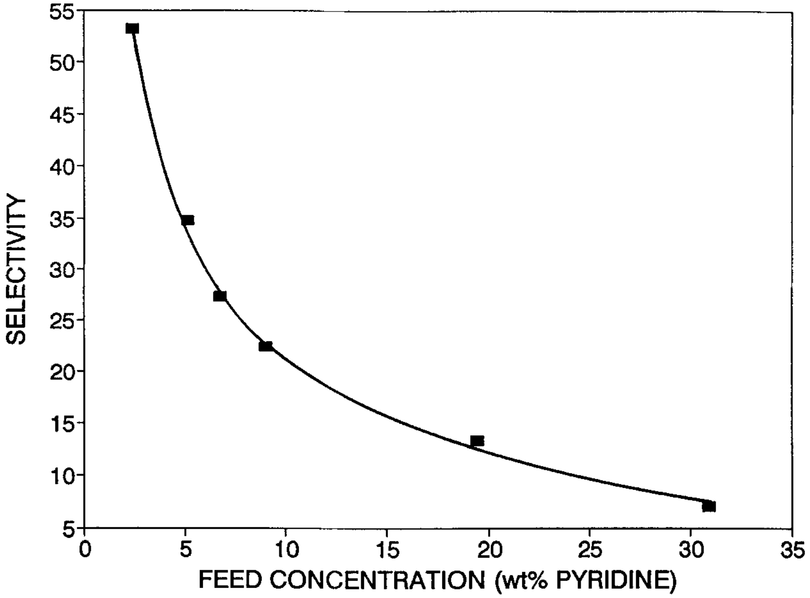

FIG. 4 Feed concentration vs selectivity at 50°C and 2 torr permeate side pressure.

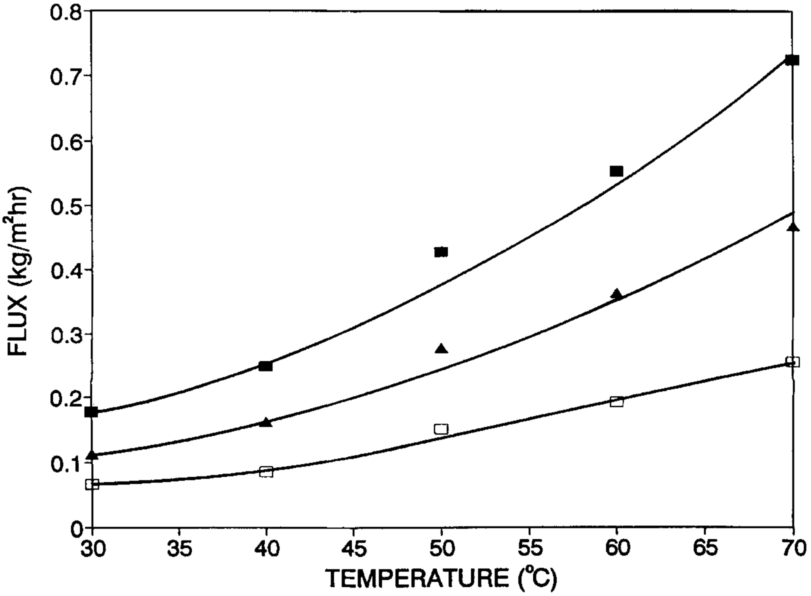

FIG. 5 Temperature vs total, pyridine, and water flux. Operated at a feed concentration of 5 wt% pyridine and a permeate side pressure of 2 torr. Total flux (■), pyridine flux (▲), and water flux (□).

An equation was developed to quantify the effect of temperature on total and pyridine flux. Figure 6, a graph of the inverse of the absolute temperature versus the natural log of flux, shows that a definite Arrhenius relationship exists. The equations for the fluxes was developed from this, and they take the form

$$J_{\text{tot}} = 43806e^{-3762/T} \tag{6}$$

$$J_{\text{pyr}} = 34063e^{-3821/T} \tag{7}$$

where T is the absolute temperature in degrees Kelvin. Once again, it is important to note that these equations were developed for a feed concentration of 5 wt% pyridine and a permeate side pressure of 2 torr. Also, these equations would change if a different type of membrane were used for the separation. Many different solvents previously studied by the Manhattan College group have been found to follow an Arrhenius relationship (6–10).

The final tests were performed to determine the effect of permeate side pressure on the separation. These runs were performed at a temperature

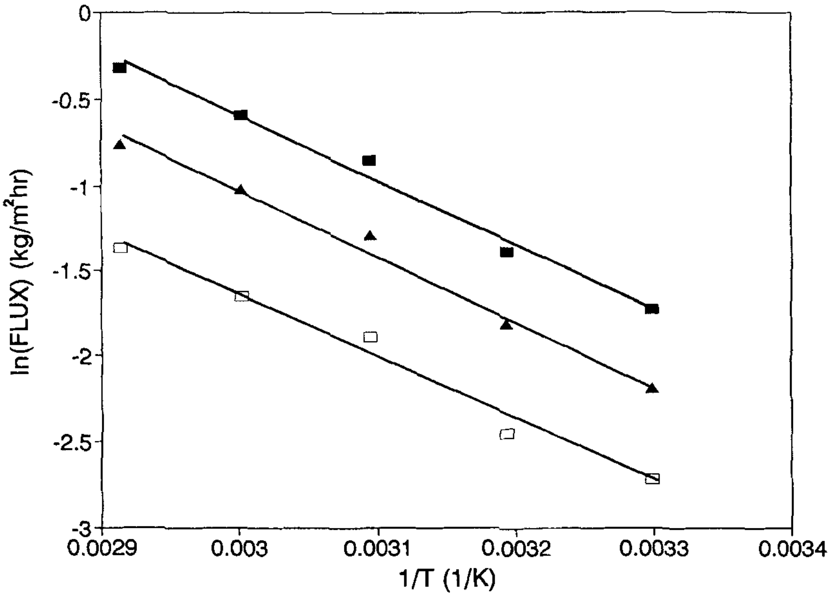

FIG. 6 Arrhenius plot of ln(total, pyridine, and water flux) vs inverse of temperature. Operated at a feed concentration of 5 wt% pyridine and a permeate side pressure of 2 torr. Total flux (■), pyridine flux (▲), and water flux (□).

of 50°C and a feed concentration of 5 wt% pyridine. The permeate side pressure was varied between 2 and 50 torr. The pressure had to be kept below ~75 torr, which is the vapor pressure of pyridine at 50°C. Above this pressure, pyridine will no longer desorb from the membrane.

The flux is strongly effected by the change in permeate side pressure. The flux drops quickly between 2 and 30 torr, and then drops off more slowly after 30 torr. It can be seen from Fig. 7 that the pyridine flux drops off more quickly than that of the water. This is probably due to the fact that the vapor pressure of pyridine is lower than that of water (~91 torr at 50°C).

The permeate concentration is also effected by the permeate side pressure. The drop in pyridine flux relative to that of the water flux is reflected here. The permeate concentration drops to 49.9 wt% pyridine at a pressure of 50 torr. The results in Fig. 8 are not the same for every solvent. Some solvents, such as THF and acetone, actually have an increase in permeate concentration with an increase in permeate pressure (although the total flux still drops) (9, 10). This is probably due to the fact that their vapor pressures are higher than that of water at the same temperature.

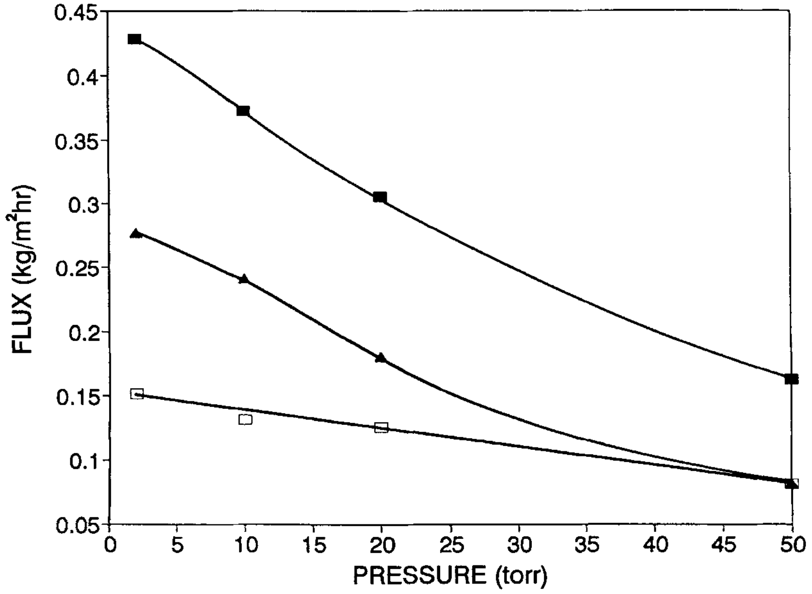

FIG. 7 Permeate side pressure vs total, pyridine, and water flux. Operated at a feed temperature of 50°C and a feed concentration of 5 wt% pyridine. Total flux (■), pyridine flux (▲), and water flux (□).

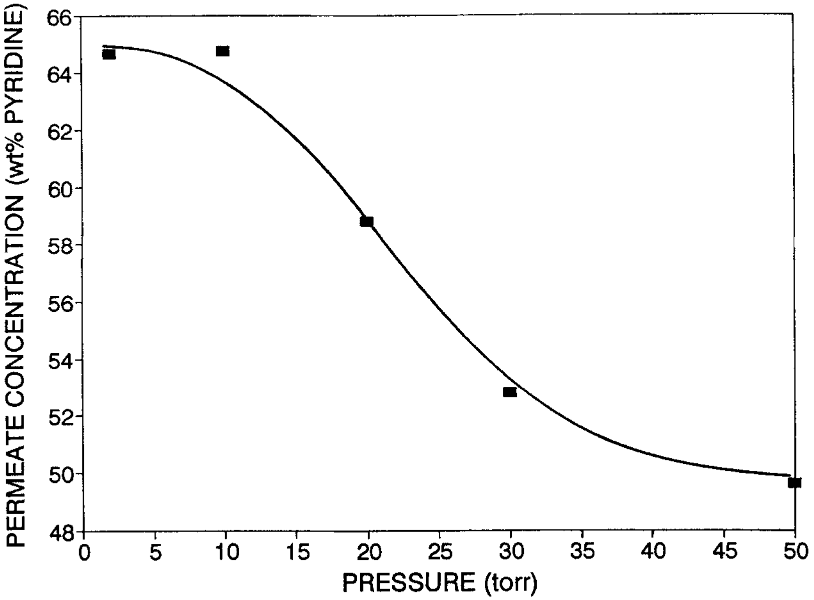

FIG. 8 Permeate side pressure vs permeate concentration, operated at a feed temperature of 50°C and a feed concentration of 5 wt% pyridine.

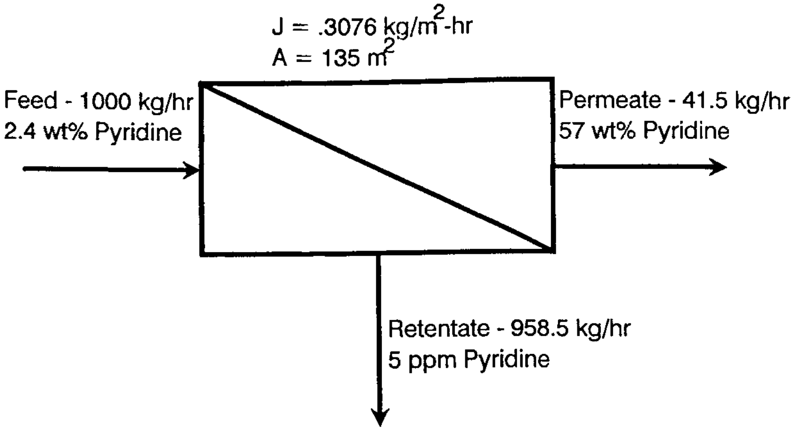

FIG. 9 Schematic representation of concentration and flow rates for the water purification example.

For industrial application, it is obviously desirable to determine the amount of membrane area required to complete a given task because membrane costs are a major expenditure in a pervaporation unit. In the given scenerio (Fig. 9), it is desirable to remove pyridine from a process stream where the initial concentration is 2.4 wt%. It is desired to lower the concentration to 5 ppm pyridine, as above this concentration the stream would be considered by the US EPA to be a hazardous waste (although some states have a stricter limit). A simple way to determine the membrane area is to do a mass balance around the membrane. Knowing the permeate flux and concentration at the feed concentration, it is easy to determine the required membrane area, ~135 m^2, as shown in Fig. 9. The major problem with this method is that it assumes the concentration at the membrane surface remains constant across the surface and no effects of concentration polarization or scale-up are included. This method will give a low estimation of the area requirements. Other, more accurate area equations do exist, and the reader is referred to those for more information (14–17).

CONCLUSIONS

Pervaporation has been proven to be an effective separation technique for pyridine/water solutions. Low concentrations of pyridine can be effectively removed from a wastewater stream using organic permeation. Using either dehydration or organic permeation, the water/pyridine azeotrope can effectively be broken.

The separation of pyridine/water solutions using an organophilic membrane was examined. The effect of feed temperature, feed concentration, and permeate side pressure were determined. Both the permeate composition and the permeate flux increase with feed concentration, rising sharply over low concentration while rising slowly at the higher compositions. Selectivity does the reverse, decreasing rapidly over the low feed concentration range while decreasing slowly at higher concentrations. The feed temperature caused an exponential increase in flux while having no effect on the permeate composition. Permeate side pressure caused a sigmoidal decrease in both the permeate concentration and the permeate flux. The pyridine flux decreased more rapidly than the water flux, causing a drop in permeate concentration. This was probably due to the higher vapor pressure of water as compared to pyridine.

Pervaporation is an effective separation technique for pyridine/water solutions. It can be used for removing low concentrations of pyridine in water streams. Also, it can be used to break the azeotrope which occurs in pyridine/water solutions.

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