

SEPARATION OF LANDFILL LEACHATE WITH POLYMERIC ULTRAFILTRATION MEMBRANES

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Summary

The use of ultrafiltration for treatment of landfill leachate was evaluated. A high-strength industrial landfill leachate that has undergone some pretreatment contains residual suspended solids. These solids have molecular diameters greater than 190 Å and diameters between 32 and 55 Å, and foul ultrafiltration membranes. The fouling layer is 99 percent inorganic and does not block the passage of organic carbon across the membrane. It acts simply to create a pressure drop that results in lower flux. This fouling layer can be minimized by increasing shear at the membrane surface (increased stirring rate) and/or lowering the strength of the leachate. Membranes cast from an aromatic polymer exhibit the highest flux when used with leachate.

Introduction

When water comes into contact with liquid or solid wastes, soluble portions of the wastes dissolve in the water to produce a heavily polluted liquid leachate. Slater et al. conducted extensive research aimed at finding a suitable process or series of processes to treat industrial wastewaters and landfill leachates [1]. They found that 80 to 85 percent of the organic matter present in a particular industrial landfill leachate permeated an ultrafiltration membrane with a low molecular weight cutoff of 500. Leachate had been pretreated to remove suspended matter. On the basis of this finding, ultrafiltration (UF) was eliminated as a primary means of treating landfill leachate. However, it was suggested that UF might prove to be effective as a pretreatment process for reverse osmosis (RO). UF can be used to remove the larger molecular weight components of leachate that tend to foul reverse osmosis membranes.

UF membranes are extremely thin polymer films (4–200 millionths of an inch) supported by a thicker (2–5 mils) layer of open-celled sponge. The thin polymer film is anisotropic with pore diameters, depending on membrane selection, between 10 and 200 Å. The membrane acts as a molecular screen with rejection properties based on the size, shape, and chemical structure of solute and solvent molecules. Unlike classical filters, the UF mem-

brane functions as the sole solute barrier. There should be no cake formation at the membrane surface. The anisotropic nature of the polymer film prevents plugging of the micropores. A particle of solute that is small enough to fit into a micropore will pass easily through the entire film and the spongy support layer beneath the film.

One of the important variables associated with UF is the rate at which solute and solvent permeate the membrane. In general, flux through the membrane is a function of solute concentration, solute diffusivity, solution viscosity, solution temperature and the hydrodynamic conditions in the fluid in contact with the membrane. The flux, $J(t)$, can be expressed as

$$J(t) = \frac{\Delta P}{\phi [R_m, R_i, R_f]} \quad (1)$$

where the R terms are resistances to flow through the membrane. The membrane resistance to flow, R_m , is the resistance that the membrane offers in the absence of concentration polarization, surface fouling, and membrane solute interaction. For water-based landfill leachate, R_m is determined by measuring the flux of deionized water through a specific membrane at a given temperature and pressure. The membrane-solute interaction, R_i , is the resistance to flow through the membrane that results from physical adsorption of solute onto the membrane. R_i is a function of concentration and temperature.

The film resistance, R_f , results from the formation of a gel fouling layer on the membrane surface. When solutions of high molecular weight solutes, or solutions containing a large percentage of suspended solids are passed through an UF unit, the concentration of solute or suspended solids is greatest at the membrane surface at which separation occurs. Should this concentration exceed the gel point of the particular solute, a gel layer forms. This gel is permeable to solvent but creates a pressure drop that lowers the net pressure available to drive solvent through the ultrafiltration membrane. The magnitude of R_f depends on the type and concentration of solute, solute gel compressibility, transmembrane pressure, and operating conditions.

Operating conditions are extremely important to minimizing R_f . Fouling layer resistance will increase as long as the convective transport of solute toward the membrane is greater than the convective and diffusive flux away from the membrane. Therefore, operating conditions must be selected such that convective and diffusive fluxes away from the membranes are maximized. Once a gel layer forms, flux is no longer pressure-dependent, and increase in pressure results in the formation of a deeper fouling layer that produces a greater pressure drop while the flux remains unchanged. In this case, flux is a function of only the mass transfer characteristics of the unit.

Background

Bhattacharyya reported that during the UF of concentrated laundry wastes using a tubular UF unit, the membrane became severely fouled [2]. By

maintaining a high channel or feed velocity (154 cm/sec), it was possible to minimize the fouling problem. In the UF of TNT-manufacturing wastes [3], the reported solution to the fouling problem was similar to that employed for laundry waste; channel velocity was increased to 200 cm/sec and fouling was minimized. During the UF of an oil-water-detergent system, Bhattacharyya minimized fouling by increasing the operating temperature of the unit to reduce the viscosity of the solution and minimize gel formation [4]. In all cases, increasing the convective transport of solute away from the membrane surface minimized fouling and improved flux.

Pearson found that flux can be restored by recycling retentate past the membrane, under zero applied pressure, and flushing the membrane with a cleaning solution [5]. While this procedure yields good results, it fails to stop the formation of fouling layers. Instead, it eliminates the fouling layer after it has formed. This results in process downtime. Gillespie reported that the fouling layer formed during the UF of macromolecular solutions was degraded by hydrolytic immobilized enzymes [6]. Over a ten-day period, average flux was increased to twice the control value.

Experimental

Experiments were carried out with an Amicon 2 liter, Model 2000 UF cell (Amicon Corp., Danvers, Mass.) with a variable speed stirrer. Pressure was created by cylinder nitrogen with an adjustable pressure regulator. For these experiments, this system was sufficient; it was easily adjusted and taken apart when variables and membranes were changed. Membranes, obtained from Amicon, ranged in molecular weight cutoff from 500 to 300,000. Table 1 presents some of the characteristics of the membranes. Table 2 is a summary of key leachate properties.

TABLE 1

Membrane properties

Membrane type	Membrane pore size (Å)	Membrane composition	Range of clean water flow rates ^a (ml cm ⁻² min ⁻¹)
XM-300	190	substituted olefin	0.8-2.0
XM-100	55	substituted olefin	0.5-2.0
XM-50	32	substituted olefin	1.0-1.8
PM-30	23	aromatic polymer	5.0-10.0
PM-10	19	aromatic polymer	2.5-4.0
UM-10	14	polyelectrolyte complex	—
UM-2	12	polyelectrolyte complex	—
UM-6	10.5	polyelectrolyte complex	—
YM-10	—	cellulose acetate	0.1-0.2

^aRef. [7].

TABLE 2

Leachate characteristics (EPA-07)

Parameter	Leachates included in study aqueous phase
TOC	14,000—17,000
pH	variable (adjusted to 7.0 for purpose of feed)
TKN	1,300—1,500
TDS	16,500—20,000
Phosphorus	12—16
Ammonia	1,100—1,300
Color	amber
Na	1,700—17,000
Ca	1,700—17,000
Mn	170—17,000
Ni	17—1,700

All values in mg/l unless otherwise noted. TOC = total organic carbon; TDS = total dissolved solids.

New membranes were washed in distilled water for a minimum of one hour before use. This removed the protective coating applied to the membranes by the supplier. After the protective coating was removed, membranes were tested with distilled water to compare the flux to the acceptable range published in the Amicon Systems Catalog [7]. Membranes were stored in a solution of 10 percent ethanol in distilled water. Distilled water flux through the membrane is a reliable means of determining membrane condition. However, this method requires stopping the process. A promising method of verifying that the membrane is undamaged utilizes polymeric dyes. Poly R 478 (40,000—60,000 MW) is an intensely colored purple dye; when added to leachate, it turns the solution a deep purple. Under normal operating conditions, all but a few of the very high molecular weight membranes rejected the polymeric dye and yielded permeate free of color. However, when a defect appeared in the membrane, permeate turned light purple indicating the polymer dye had not been rejected and the membrane was no longer selective.

It was necessary to determine which membranes could be used with leachate. Each of the four membrane types PM, YM, UM and XM were tested by soaking in leachate, at zero applied pressure, for six hours. Membranes were cleaned to remove adsorbed material, by running distilled water through the membranes, and water flux was measured. This flux was compared to water flux prior to leachate immersion. Water flux through the PM, YM, and XM membranes did not change, to within 2 percent. However, water flux through the UM membrane increased 64.5 percent. To confirm that type UM membranes were unsuitable for use with leachate, an UM 05 membrane was used to filter a raffinose solution (MW 504) of known concentration.

Raffinose rejection decreased 4.3 percent after immersion in leachate. The increase in flux and the decrease in rejection indicated the UM type membrane was not suitable for use with leachate.

After use with leachate, membranes were cleaned with a cleaning solution of 2.5 ml l^{-1} Embiozyme R08-1, an enzyme-based detergent. Cleaning was carried out in the ultrafiltration cell at zero applied pressure and a stirrer setting of three. Full flux restoration, as measured by distilled water flux, was obtained. However, flux fell rapidly when leachate was reapplied.

To measure permeate flux, during the course of an ultrafiltration experiment, a graduated cylinder was used to collect permeate over a specific time interval. To determine the effect of stirring rate on formation of a fouling layer, the initial concentration and temperature of the leachate solution were held constant and stirring rate was varied. The pressure at which a gel layer formed was measured, as a function of stirring rate, by noting the point at which an increase in pressure failed to produce an increase in flux. To determine the effect of temperature on the formation of a fouling layer, initial concentration and stirring rate were held constant and temperature was varied. The pressure at which a gel layer formed was measured as a function of temperature. To determine the effect of leachate solution concentration on the formation of a fouling layer, the initial temperature and stirring rate were held constant and concentration was varied. The pressure at which a gel layer formed was measured as a function of concentration.

Total organic carbon (TOC) assays were completed by wet chemical oxidation of all carbon present in the sample, followed by analysis with an Oceanography International Model 05-24B-HR Carbon Analyzer with a Horiba PIR-2000I infrared spectrophotometer. Total dissolved solids (TDS) were measured by evaporation, in an aluminum pan, of a known quantity of sample at 100°C and differential weighing.

Experiments were run in the batch mode of operation. There was no recycle; thus, feed composition at the membrane boundary did not vary. The transient variables of the experiment were the thickness and constitution of the layer formed by material exceeding the molecular weight cut-off. Organic matter was found to be only a small part of the "fouling" layer formed during runs. On the whole, flux variations were the primary transients and were a direct consequence of filtration of colloidal and microcolloidal complexes.

Results and discussion

Fouling ranges

A volume of pretreated leachate was ultrafiltered through a series of membranes with molecular weight cutoffs of 300,000, 100,000, 50,000, 30,000, 10,000 and 2,000. The permeate from a higher molecular weight membrane was used as the feed for the next membrane in the series. Figures 1 through 3 are typical plots of flux as a function of time. With the exception of the

300,000 and 50,000 molecular weight membranes, flux remained constant at the initial value. Flux through the 300,000 and 50,000 molecular weight membranes showed a sharp decrease during the first minutes of operation. This was followed by gradual leveling-off to a steady-state value. Replicates

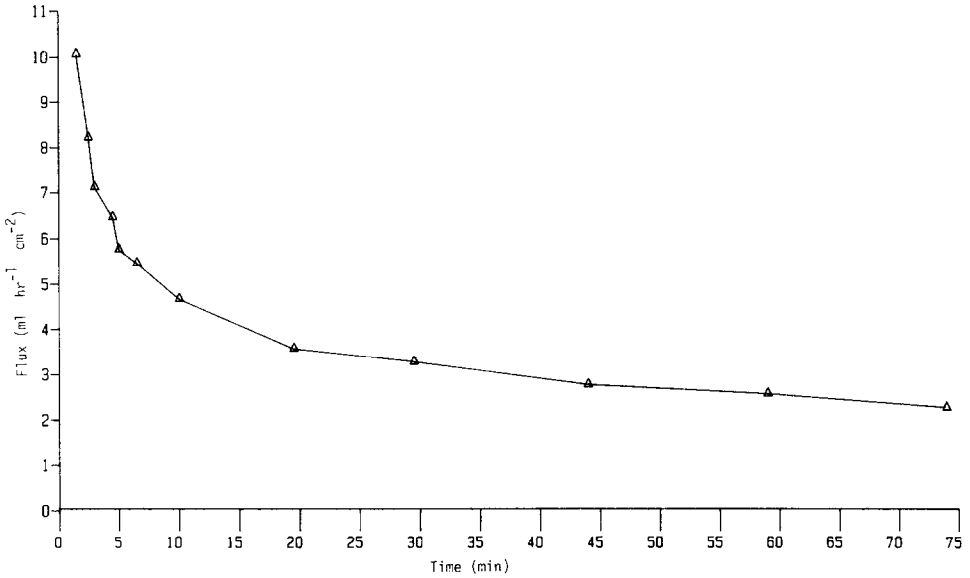


Fig. 1. Flux vs. time for XM-300. Feed — pretreated leachate; pressure — 60 psig; temperature — 23°C.

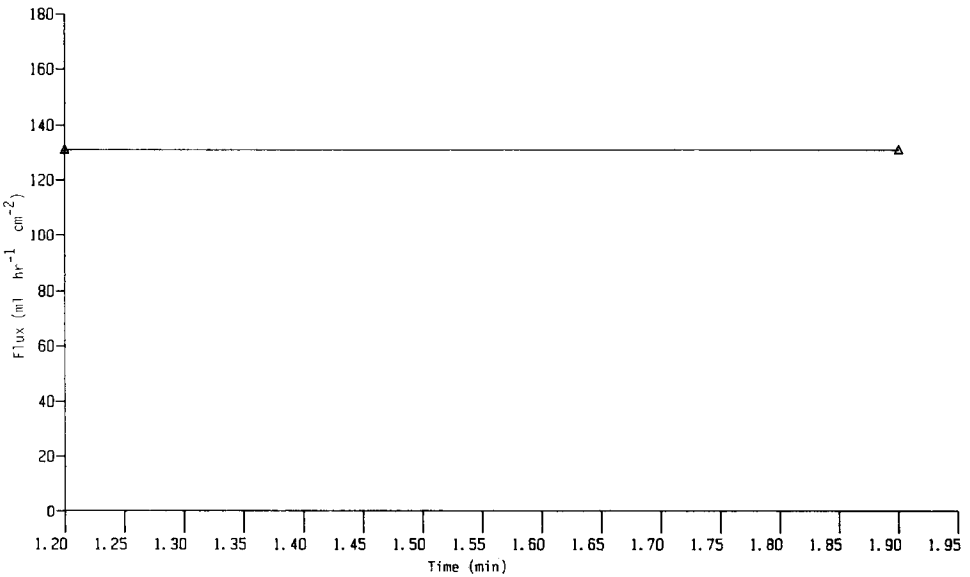


Fig. 2. Flux vs. time for XM-100. Feed — filtrate from XM-300; pressure — 60 psig; temperature — 23°C.

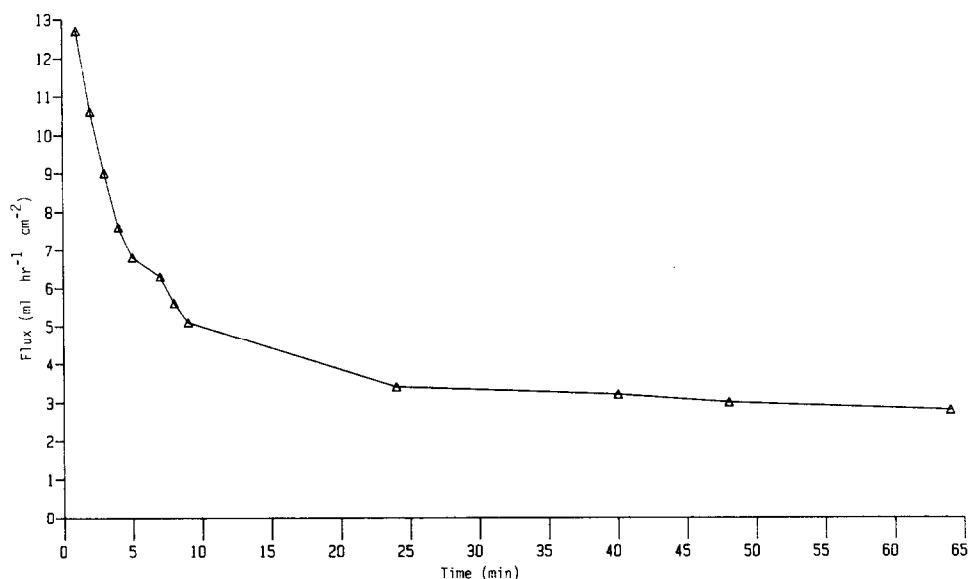


Fig. 3. Flux vs. time for XM-50. Feed — filtrate from XM-100; pressure — 60 psig; temperature — 23°C.

displayed similar behavior with less variability than suggested by Amicon water flux data.

Decrease in flux indicated that a fouling layer had formed; visual inspection of the membrane surface at the conclusion of the experiment confirmed the presence of gel. The sharp initial decrease in flux was caused by the rapid accumulation of material on the surface of the membrane, causing a pressure drop that reduced the pressure available to drive solvent through the membrane. The flux stopped decreasing and the fouling layer reached a constant thickness once the transport of fouling material away from the surface equalled the rate at which fouling material was transported to the surface. The fact that fouling only occurred at the 300,000 and 50,000 molecular weight cutoff levels indicates that material in the pretreated landfill leachate, capable of fouling ultrafiltration membranes, lies within these two levels. Cutoffs correspond to a molecular diameter greater than 190 Å and molecular diameters between 32 and 55 Å. Pretreatment may not have been sufficient to remove all high molecular weight suspended and colloidal matter.

Fouling layer characteristics

Fouling of the 300,000 and 50,000 molecular weight membranes was caused primarily by the separation of suspended and dissolved solids from the leachate solution at the membrane surface. Passing pretreated leachate through the 300,000 molecular weight membrane resulted in nine percent reduction of total dissolved solids. Passing doubly filtered leachate (300,000 and 100,000) through the 50,000 molecular weight membrane yielded ap-

proximately 40 mg of suspended solids from 1 liter of leachate solution. There was no reduction in TDS for the solutions that did not foul the other UF membranes.

Total organic carbon experiments on both fouling layers revealed that both were comprised of material that was 99 percent inorganic. Possibly the calcium used in lime treatment stage was not removed totally by recarbonation and plated out on the membrane. It is also possible that some metal complexes were not removed completely during pretreatment.

Fouling layer effects

Formation of a fouling layer during UF of leachate causes a substantial reduction of flux. However, the fouling layer is permeable to organic carbon present in the leachate. The TOC of permeate of the YM-30 membrane remained constant, despite the presence of a fouling layer, see Figs. 4 and 5. Complete volumetric recovery of feed as filtrate was obtained in all cases. TOC recovery was dictated by molecular weight cutoff; mass balances on TOC were accurate to within ± 5 percent. TDS exhibited no change, except for the losses due to fouling layer formation on the 300,000 and 50,000 molecular weight membranes.

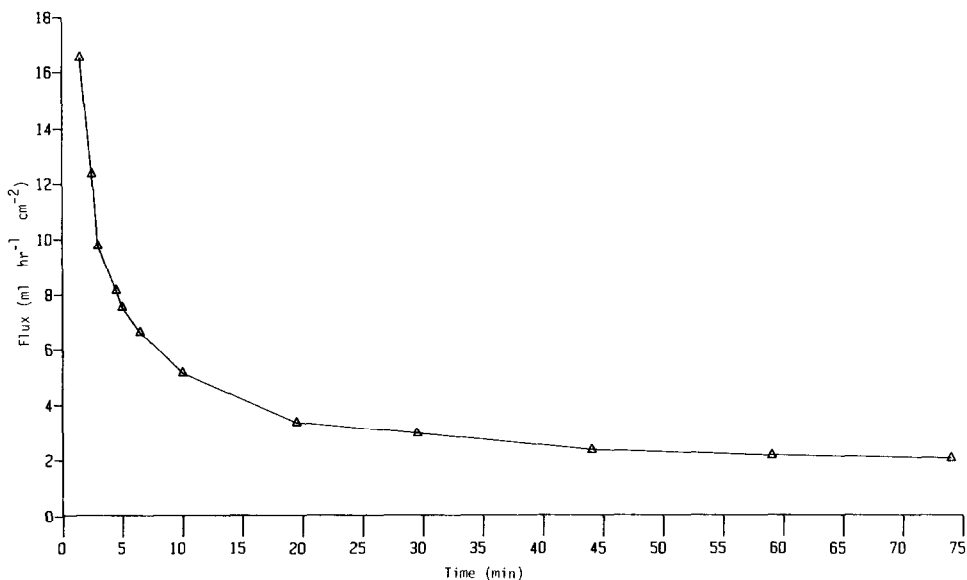


Fig. 4. Flux vs. time for YM-30. Feed — pretreated leachate; pressure — 60 psig; temperature — 23°C.

Flux and membrane type

Separate portions of pretreated leachate were ultrafiltered through PM-30, YM-30, and XM-300 membranes. Consistent with eqn. (1) and values for the flow rate of deionized water given in Table 1, the PM-30 membrane had the

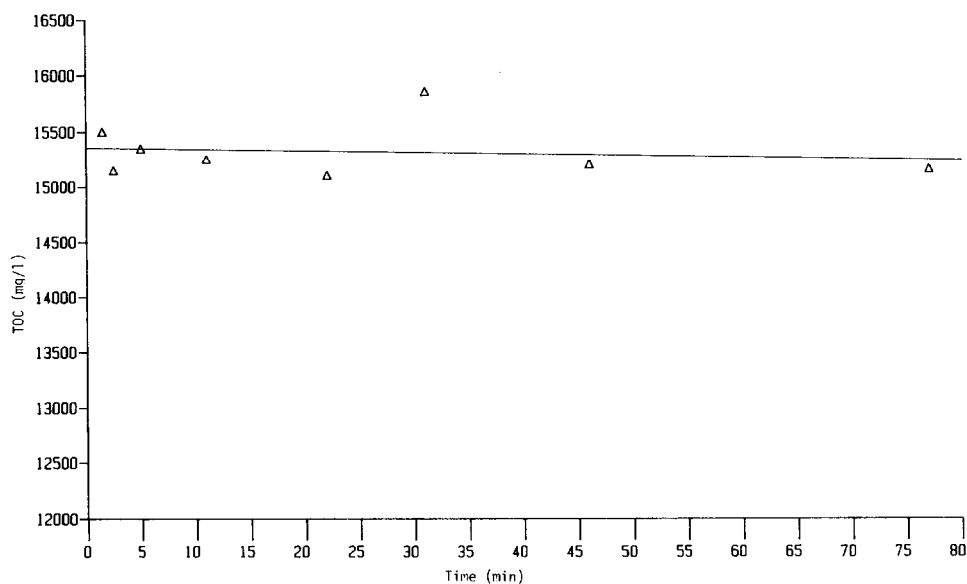


Fig. 5. Permeate TOC vs. time for YM-30. Feed — pretreated leachate; pressure — 60 psig; temperature — 23° C.

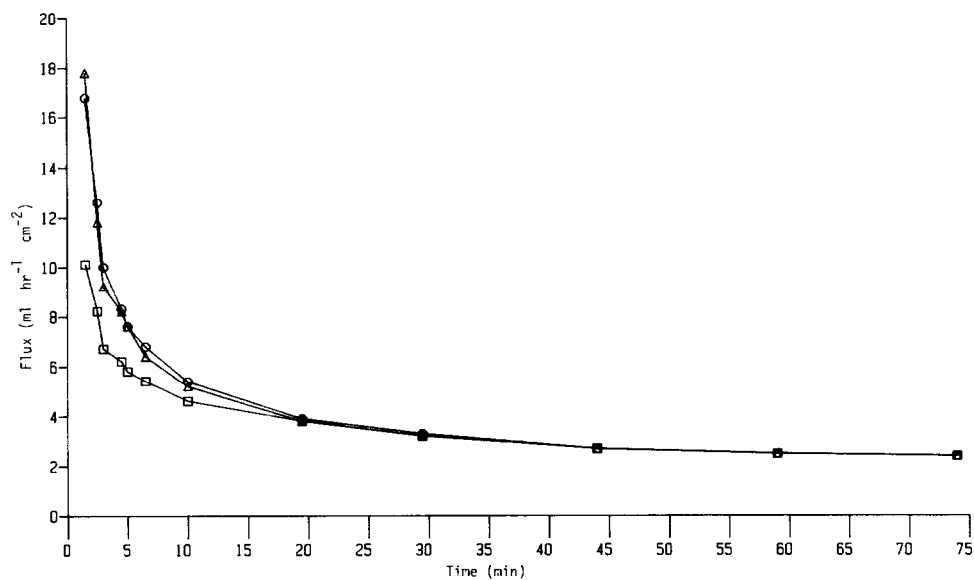


Fig. 6. Flux vs. time for XM-300, PM-30 and YM-30. Δ — PM-30; ○ — YM-30; □ — XM-300.

highest initial flux, see Fig. 6. However, as time passed the flux through the membrane approached the same steady-state value. This indicates that R_f is the dominant resistance, overshadowing differences in R_m among the three membranes.

Variation of process variables to minimize the fouling layer

The effect of stirring on the formation of a fouling layer was studied at constant temperature and initial leachate concentration. Over a range of stirring rates, the pressure at which a fouling layer formed increased linearly with the rate. Since flux is proportional to the pressure, in the absence of a fouling layer, an increase in the stirring rate allows for an increase in pressure without fouling and, therefore, an increase in flux. Stirring creates greater shear at the membrane surface, increasing the convective transport of fouling material away from the surface, minimizing fouling.

The effect of leachate concentration on the formation of a fouling layer was studied at constant temperature and stirring rate. Over the leachate fractions of 0.75 to 1, achieved by dilution with distilled water, the pressure at which the fouling layer formed decreased with the logarithm of increasing leachate fraction, see Fig. 7. Therefore, at decreased leachate strength, operating pressures can be higher, without fouling, and greater flux can be realized. Decreased leachate concentration minimizes the rate at which fouling material reaches the surface of the membrane, helping to prevent fouling.

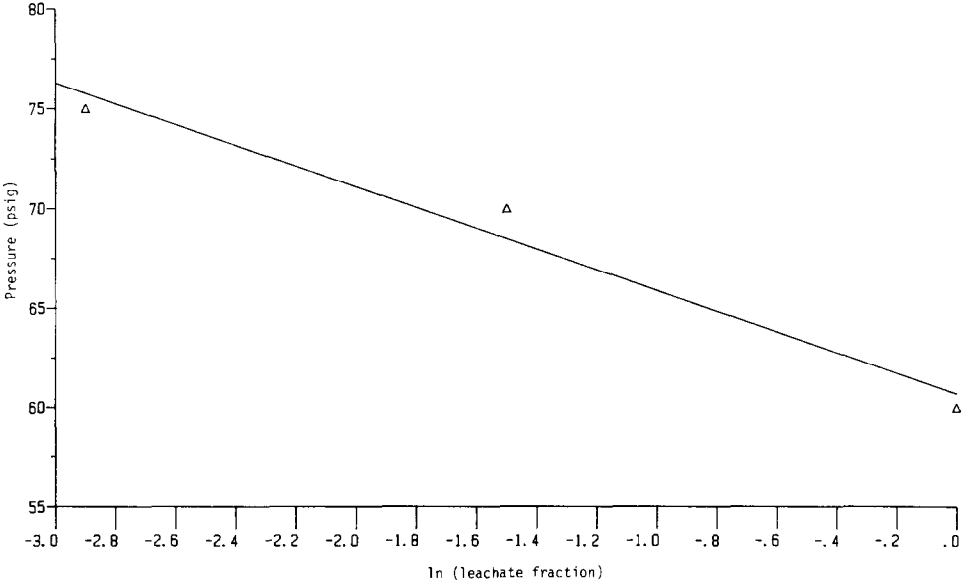


Fig. 7. Pressure at fouling. Feed — pretreated leachate; temperature — 23°C.

The effect of feed temperature on the formation of a fouling layer was studied at constant stirring rate and concentration over the temperature range of 24 to 42°C. The pressure at which a membrane fouled did not change with temperature. Diffusive transport of the fouling material away from the membrane surface is not the dominant means of transport; convective transport dominates. Increasing leachate temperature will not affect fouling.

Conclusion

UF can be included as a step in the overall treatment of landfill leachate, as added pretreatment before RO. Leachate that has been pretreated by physicochemical means may still contain suspended or dissolved solids with diameters greater than 190 Å and diameters between 32 and 55 Å. Variability in leachate feed leads to loss of uniformity of physicochemical treatment. This material fouled UF membranes with pore diameters greater than RO membranes, indicating RO membranes might be susceptible to fouling by this material, also. It is logical to remove this material by UF, under lower operating pressures, allowing for easier control of fouling than in RO at much higher operating pressures.

Fouling of the ultrafiltration membranes can be controlled by manipulation of operating variables, including pressure, leachate strength and shear rate at the membrane surface. Unfortunately, enzyme methods to degrade the fouling layer will not work because of the inorganic nature of the fouling layer. More complete physicochemical pretreatment will help to minimize membrane fouling.

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