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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Online publication date: 24 February 2003

To cite this Article Chakraborty, S. , Bag, B. C. , Gupta, S. Das , De, S. and Basu, J. K.(2003) 'Separation and Fractionation of Dye Solution by Nanofiltration', Separation Science and Technology, 38: 1, 219 — 235

To link to this Article: DOI: 10.1081/SS-120016707

URL: http://dx.doi.org/10.1081/SS-120016707

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SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 1, pp. 219–235, 2003

Separation and Fractionation of Dye Solution by Nanofiltration

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ABSTRACT

A membrane-based separation process (nanofiltration) is used to separate dyes from aqueous solution. The selected dyes are crystal violet (molecular weight 408) and methylene blue (molecular weight 373), respectively. An organic membrane with molecular weight cutoff of 400 is used for the experiments. The experiments are conducted in an unstirred batch cell and a rectangular cross-flow cell for single as well as binary dye mixtures. It has been observed that for cross-flow cell, the system reaches steady-state quickly. Separation up to 95% for the single component is achieved. For mixtures, separations up to 60% and 35% of the two dyes are obtained respectively. The separation and fractionation of the dye(s) are studied as functions of operating parameters, e.g., transmembrane pressure, dye concentration in the feed, and cross-flow velocity.

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DOI: 10.1081/SS-120016707 0149-6395 (Print); 1520-5754 (Online)

www.dekker.com

Key Words: Nanofiltration; Dye; Batch cell; Cross-flow cell; Fractionation.

INTRODUCTION

Dyes are widely used in different process industries like textile, pulp and paper, dyeing, paint, ink, etc. Often the effluents from such industries, which are rich in color, are discharged into the atmosphere without proper treatment. This causes extensive environmental pollution. The ingestion of the dye-containing wastewater causes severe headaches, skin irritation, and ulceration of the skin and mucous membranes.[1] Therefore, treatment of these effluents is essential. Separation and reuse of the costly dyes from the effluent mixtures can be an added advantage.

The existing processes for removal of color from wastewater are chemical coagulation, flotation, chemical oxidation, and adsorption.[1] Adsorption is the most common technique, but is a slow process and its performance is limited by the equilibrium. Membrane-based separation process may be an attractive alternative in this regard. In fact membrane separation processes are gradually emerging as a technically significant and commercially viable process in the treatment of wastewater. Reverse osmosis has been widely used to treat the textile dyehouse effluent.[2–6] In these works, wastewater from different washing and rinsing steps is treated by reverse osmosis. Permeate is reused as washwater and the retentate is either reused or discarded. Brandon et al.[2] and Porter and Goodman[3] used dynamically formed Zirconium Oxide–polyacrylate membrane in tubular form to treat textile dye-house effluent. More than 95% of dye recovery was observed. Similar results were obtained using spiral-wound modules.[4] El Nasher[5] studied economic feasibility of reverse osmosis to treat dye-containing effluent. Nowak et al.[7] studied cross-flow ultrafiltration of an actual textile dye bath in a tubular membrane and reported up to 97% dye removal (of molecular weight greater than 780). Yazhen et al.[8] had used nanofiltration for the treatment of textile dye plant effluent. Experimental runs with pure dye solutions as well as an industrial dye solution confirmed the process potential. Schrig and Widmer[9] undertook nanofiltration of a mixture of dye salt and sodium chloride in a spiral wound module. Yu et al.[10] applied nanofiltration for the desalting and concentrating of aqueous dye at a dye-producing plant. The developed process using nanofiltration was continuous, was not labor intensive, and produced a high purity product of consistent quality. Dhale and Mahajani[11] reported a combined process of nanofiltration and wet oxidation to treat dye bath waste stream. Rejections up to 99% of color were reported in nanofiltration and retentate was treated by wet oxidation process. In the work of Van der Bruggen et al.[12] different samples from the wastewater treatment sequence of a textile factory were filtrated with different nanofiltration membranes. It had been observed that flux decline due to adsorption of organic material on the membrane decreased the membrane capacity by up to 73%, but the process water flux, which is largely concentration dependent, reached a stable value in all experiments. It was concluded that membrane based separation processes are technically and economically feasible treatment process for dye-containing effluent.

However, membrane separation processes are influenced by several operating parameters and thus it is difficult to predict the membrane performance in different applications. One of the most important drawbacks of the membrane separation process is the decline in flux due to concentration polarization and membrane fouling during the operation.[13–15] Concentration polarization refers to the buildup of solute species within a thin boundary layer adjacent to the membrane surface. The accumulation of species at the membrane surface adversely affects the membrane performance. Due to the limitations imposed by concentration polarization and membrane fouling, there is a need of detailed study of the effects of the controlling parameters in the process.

The present work is a part of a larger study in the combined use of adsorption complimented by membrane separation. It is envisaged that the bulk removal of the dye will take place in an adsorption unit, whereas removal of remaining amount (10–30 ppm) will be treated in the nanofiltration unit. A representative concentration of the dyes in industrial effluent is of the order of 150–200 ppm. If this is used directly in a nanofiltration unit, it may result in severe concentration polarization, membrane fouling, and hence a substantial decrease of the permeate flux, i.e., the throughput of the process. This will invariably lead to a deterioration of permeate quality as well. On the other hand, the adsorption process, being an equilibrium governed process, is inherently a slow one. The concentration difference between the bulk and the solid phase governs the adsorption process. Thus adsorption may be more effective for higher ranges of concentration.

One of the objectives of the present study is to probe the possibility of fractionation of dye-mixture using nanofiltration. The two dyes selected for this study are crystal violet (molecular weight 408) and methylene blue (molecular weight 373). Thus a 400 molecular weight cutoff membrane is chosen for the present study. It needs to be pointed out here that even with a 400 molecular weight cutoff membrane the retention of crystal violet is up to 94% in a cross-flow cell. An extensive study has been carried out to observe the effects of different parameters and also to identify a set of favorable conditions in the separation as well as fractionation of dye mixtures from aqueous solution. Two process configurations are selected, unstirred batch and cross flow. Several experiments are conducted with aqueous solution of crystal violet, methylene blue, and aqueous mixture of the two dyes at different operating conditions.

MATERIALS AND METHODS

Crystal violet, molecular weight 408 (hexamethyl pararosaniline chloride) and methylene blue, molecular weight 373 (methyl thionine chloride, 3,7-bis [Dimethyl amino] phenazothionium chloride) are the two dyes used in the experiments. The systems used for detailed study are (i) aqueous solution of crystal violet, (ii) aqueous solution of methylene blue, (iii) aqueous mixture of crystal violet and methylene blue.

Unstirred Batch Cell

Figure 1 represents the flow diagram of the batch cell operation. The feed solution from the feed tank is pumped to the batch cell. Inside the cell a circular membrane is placed over a metallic support. The diameter of the membrane is 65 mm. The permeate is collected from the bottom of the cell.

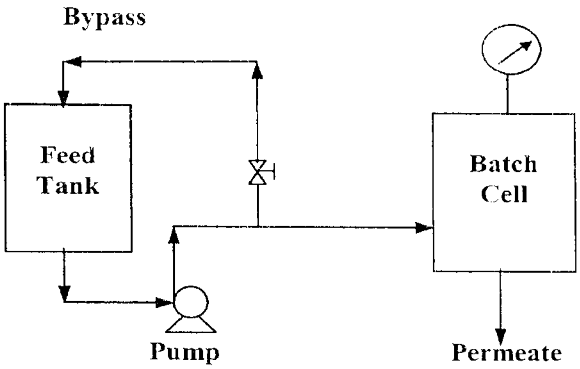

Figure 1. Schematic of the batch nanofiltration cell.

Cross-Flow Cell

Figure 2 represents the flow diagram of the continuous cross-flow nanofiltration unit. From the feed tank, the feed solution is pumped to the cell, where it passes through a channel. The membrane on a metal support forms one side of the channel. The width of the membrane is 4.5 cm, length 26 cm, and the channel height is 1.65 mm. The retentate solution is recycled to the feed tank. In the retentate line of the cell, a rotameter is placed to measure the flow rate. The pressure inside the cell is maintained by operating the two valves manually. Permeate samples are collected from the bottom of the cell.

Operating Conditions

Single Component

Four feed concentrations of 5, 10, 15, and 20 ppm, operating pressures of 276, 415, 550, and 690 kPa are chosen for experiments with crystal violet in the batch cell. For methylene blue, two feed concentrations of 15 and 20 ppm are selected and operating pressures of 276 and 415 kPa are used. For cross-flow cell, three feed concentrations of 10, 15, and 20 ppm, operating pressures of 276, 415, and 550 kPa and cross-flow velocities 14, 21, and 28 cm/sec are used.

Multicomponent System

For batch cell, two feed concentrations of 20 ppm (10 each) and 40 ppm (20 each of crystal violet & methylene blue), operating pressures of 276 and 415 kPa are used. In case of cross-flow cell, two feed concentrations of 20 ppm (10 each) and 32 ppm (16 each) are selected. The operating pressures are 276 and 415 kPa and three cross-flow velocities are 14, 28, and 42 cm/s.

Membrane

An organic membrane (PPN) of molecular weight cutoff 400, supplied by M/s Permionics, Baroda is used in the experiments.

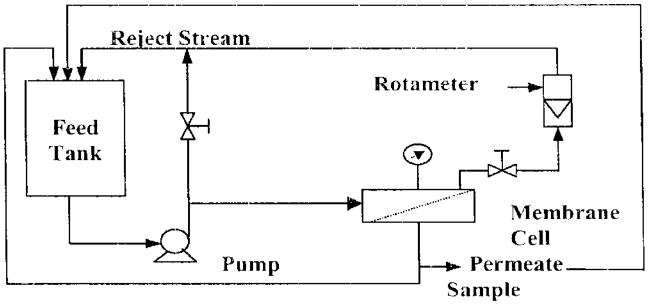

Figure 2. Schematic of the continuous cross-flow nanofiltration cell.

EXPERIMENTAL PROCEDURE

The experimental process involves the following steps:

(i) Compaction of membranes: Before using a fresh membrane, it is compacted at a pressure of 690 kPa for 3 h using distilled water.
(ii) Preparation of feed solution: All feed solutions are prepared using distilled water.
(iii) Determination of membrane permeability: Membrane permeability is determined using pure distilled water. Flux values of distilled water at different operating pressures are measured. The slope of this curve gives the membrane permeability.
(iv) Conduction of experiments: Experimental runs are conducted in the two cells. The operating parameters are feed concentration and transmembrane pressure difference for unstirred batch system and cross-flow velocity, feed concentration and pressure difference for cross-flow system. During each experiment, cumulative volumes of permeate are collected. The permeate flux values are obtained from the slope of the plot of the cumulative permeate volume versus time. Permeate samples are collected at different time to find out the permeate concentration. In the batch cell, the duration of each experiment is 50–60 minutes and in cross-flow cell 45 minutes.
(v) Determination of the new membrane permeability: After thoroughly cleaning the system several times by distilled water, the membrane permeability is reevaluated. It is observed that the membrane permeability remains almost constant between successive runs.

(vi) Analysis of the samples: Permeate samples are analyzed by UV-2100 spectrophotometer, supplied by Shimadzu Corporation, Japan (at wavelengths of 584 and 664 nm, for crystal violet and methylene blue, respectively) to measure the permeate concentration. For the dye mixture, the standard method by Vogel,[16] is used for the concentration of each species.

The following general observations regarding the experiments may be noted:

(i) The effect of pH is found to be marginal for the concentration levels (achieved after adsorption) used in this study. Therefore, pH variation is not taken to be a process variable in this study.

(ii) The increase in bulk concentration in the batch cell is marginal over the duration of experimentation (1 h). For example, for an operating pressure difference of 550 kPa and initial bulk concentration of 19.87 ppm, the bulk concentration increases to 21.32 ppm at the end of the experiment.

RESULTS AND DISCUSSION

The membrane permeability is found to be nearly constant between the different experimental runs.

Unstirred Batch Cell

Figure 3 shows the variation of permeate flux with time for different feed concentrations of crystal violet at different pressures. It is evident from the figure that the permeate flux decreases with time of operation. This is due to the concentration polarization phenomenon. Therefore, during the experimental run, the membrane surface concentration increases. This leads to an increase in osmotic pressure near the membrane-solution interface and thereby, a decrease in the available driving force (i.e., transmembrane pressure). This results in a reduction in permeate flux. It may be observed from the figure that decline in flux at the end of the operation is about 15% from its initial value for the feed concentration of 19.87 ppm and 550 kPa pressure. At higher feed concentration, the solute buildup on the membrane–surface is more resulting in an increase in osmotic pressure and subsequent reduction in

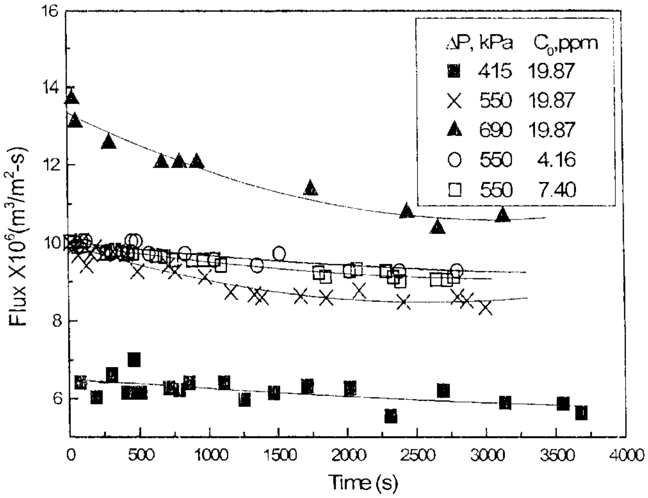

Figure 3. Variation of permeate flux of crystal violet with time at different feed concentrations and operating pressure differences in the batch cell.

permeate flux. This trend is evident from the figure at different feed concentration levels and at constant operation pressure of 550 kPa. For a fixed-feed concentration of 19.87 ppm, the increase in flux with operating pressures 415, 550, and 690 kPa are clearly observed in Fig. 3.

Figure 4 shows the variation in permeate concentration and observed retention of crystal violet with pressure difference at a fixed-feed concentration. It may be observed from the figure that with increase in operating pressure difference for a fixed-feed concentration, the permeate concentration increases at any point of time of operation. Increase in the operating pressure facilitates the convective flux through the membrane. As a result, the permeate concentration increases with pressure. The observed retention ($R_0 = 1 - C_p/C_0$) of crystal violet at different pressure difference is also shown in Fig. 4. At higher pressure, permeate concentration increases leading to a decline in observed retention. At higher pressures, membrane surface concentration increases, thereby increasing the convection of solute through the membrane. Thus permeate concentration increases resulting in a reduction in observed retention. It may be noted that for a feed concentration of 17.6 ppm, retention is about 95% for crystal violet at 415 kPa pressure at the end of operation. As pressure increases to 690 kPa, retention decreases to about 40% (at the end of the run). Therefore, a lower operating pressure results in a higher retention of crystal violet, but at the cost of the flux.

Figure 5 shows the variation of observed retention of methylene blue with time at different feed concentrations at an operating pressure of 415 kPa. It is clear that the retention of methylene blue decreases with time for a fixed pressure and concentration. The retention is more for lower feed concentration. This trend is similar to the experimental results with crystal violet. Interestingly, it may be observed that at the end of operation, methylene blue retention $[(1 - C_p/C_0)]$ is 20% (for 14.31 ppm feed concentration) and 15% for (23.5 ppm) whereas for crystal violet, the maximum observed retention (for $C_0 = 17.6$ ppm) is about 92% at the same pressure of 415 kPa (Fig. 4). Therefore, the present membrane retains more crystal violet compared with methylene blue.

Multicomponent System

The selective permeation rate through the membrane of the two dyes as discussed earlier necessitates the study of the fractionation of the dye mixture. The concentration level achieved after the fractionation in nanofiltration process is indeed very low, and an economic recovery for reuse may not be possible for the dyes selected herein. But the study is general in nature and the fractionation concept probed herein ensures its applicability for a variety of operational setups involving costly dyes for which the economics of reuse may be favorable.

The effect of pressure on dye fractionation in terms of observed retention is shown in Fig. 6, with feed concentration 10 ppm each. At 415 kPa, average retention for methylene blue is 30% and that of crystal violet is 53%. At 276 kPa pressure, R_0 for crystal violet is 60% and that of methylene blue is 40%. These observations corroborate the fact that the observed retention of a species decreases with increase in pressure. It is apparent that the permeate stream is richer (compared to feed) in methylene blue.

The comparison between the experimental flux profiles at 415 kPa of single component as well as the mixture at the same overall feed concentration level is presented in Fig. 7. It is clear from the figure that in between two single component systems, the permeate flux for methylene blue is higher than that for crystal violet. The mixture of crystal violet and methylene blue (10 ppm each) is also presented in the figure. The flux profile for the mixture lies in between the flux profiles of methylene blue and crystal violet.

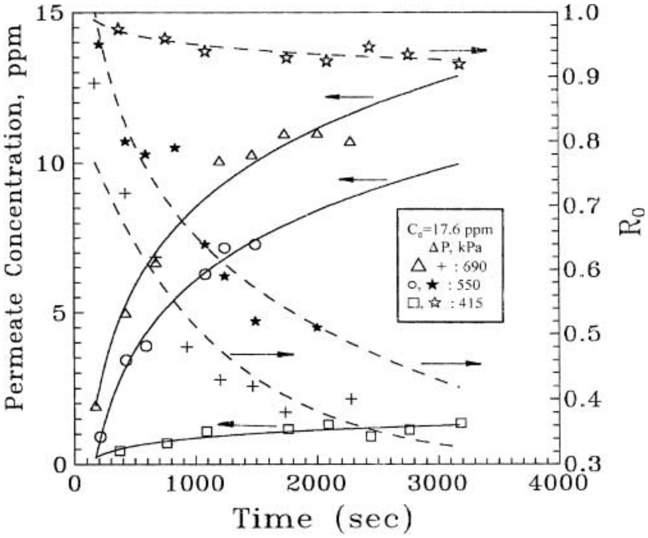

Figure 4. Variation of both permeate concentration and observed retention with time of crystal violet at a fixed-feed concentration (17.6 ppm) and different operating pressures in the batch cell.

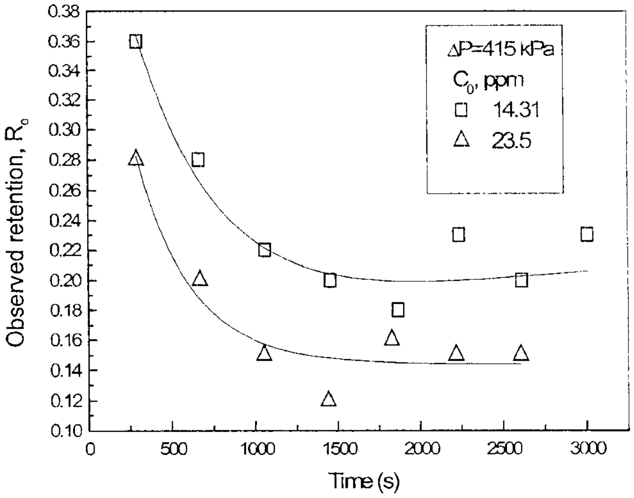

Figure 5. Variation of observed retention of methylene blue with time at a fixed pressure of 415 kPa in batch cell.

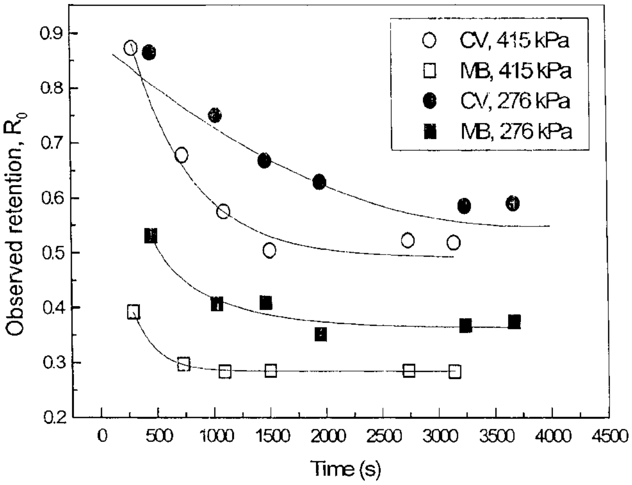

Figure 6. Variation of observed retention of crystal violet and methylene blue with time from a mixture of 10 ppm each in the batch cell.

Cross-Flow Cell

As discussed earlier, it may be noted that the decline in permeate flux and increase of permeate concentration is rapid in an unstirred batch cell. This is because of the unrestricted growth of the concentration boundary layer over the membrane surface. This limitation may be overcome in a continuous cross-flow system, where the growth of the concentration boundary layer is limited by the cross-flow velocity. Therefore, a number of experiments are carried out in the cross-flow system and are reported herein.

It has been observed during the experiments that the steady state in the cross-flow system is attained within 2–3 minutes from the start of the operation. Therefore, the steady-state values of the permeate flux and concentration are reported for the cross-flow nanofiltration experiments.

The variations of observed retention of crystal violet with operating pressure at different cross-flow velocities are presented in Fig. 8. It may be observed that the observed retention increases with cross-flow velocities due to minimization of concentration polarization. Interestingly, it may be noted that even for $C_0 = 20$ ppm, the observed retention for crystal violet is more than 90% for all operating pressures and cross-flow velocities, which is a marked improvement over the batch cell experiments (Fig. 4).

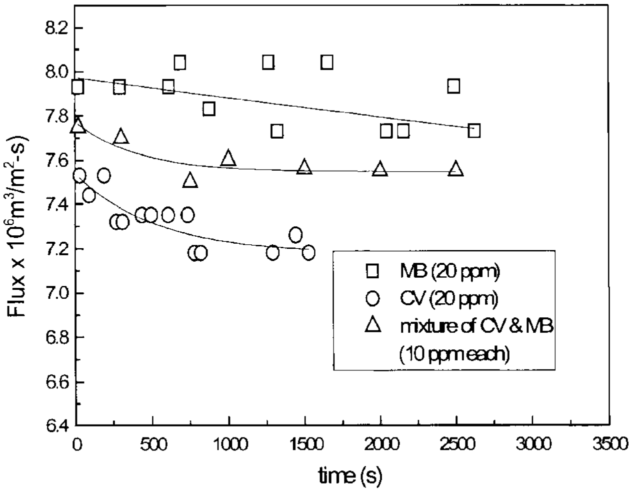

Figure 7. Comparison between the experimental values of permeate flux at a pressure of 415 kPa in batch cell.

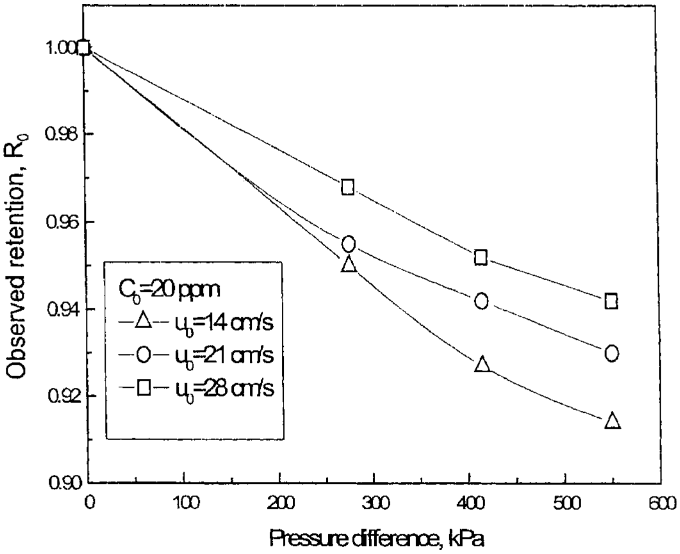

Figure 8. Variation of observed retention of crystal violet with pressure difference at different bulk velocity in the cross-flow cell.

The variations of permeate flux of crystal violet with operating pressure for different combinations of feed concentration and cross-flow velocities are presented in Fig. 9. As expected, the permeate flux increases with pressure for any combination of feed concentration and cross-flow velocity. Also, the permeate flux follows the expected trends with feed concentration at a fixed operating pressure, i.e., flux decreases with feed concentration. At a fixed-feed concentration, flux increases with cross-flow velocity due to reduction in concentration polarization, although the difference is marginal as observed from the figure, due to low osmotic pressures encountered for the concentration levels used in this study.

It may be observed from Fig. 8 that the observed retention of crystal violet can go up to 96% for $\Delta P = 276\,\text{kPa}$, $u_0 = 28\,\text{cm/s}$, and $C_0 = 20\,\text{ppm}$. The batch cell studies also indicate that there can be substantial difference in the retention values between crystal violet and methylene blue. Therefore, dye fractionation studies were conducted in the cross-flow system. Fig. 10 represents the variation of selectivity of methylene blue (between the two dyes) with cross-flow velocity at two different operating pressure levels,

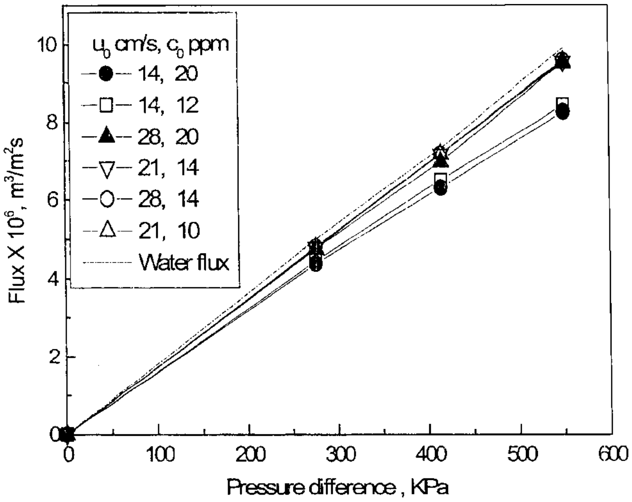

Figure 9. Variation of permeate flux with pressure at different feed concentrations and bulk velocities.

namely, 276 and 415 kPa. The selectivity (S) is defined as

$$S = \frac{\left[c_p/c_o\right]_{methylene\ \ blue}}{\left[c_p/c_o\right]_{crystal\ \ violet}}.$$

The figure reveals two trends. First, the selectivity of methylene blue increases with cross-flow velocity at any pressure, and second, for a fixed cross-flow velocity, selectivity increases with the operating pressure difference. The first trend can be explained by the fact that the membrane surface concentration decreases with cross-flow velocity and therefore more of methylene blue permeate through the membrane whereas the crystal violet is retained by the membrane due to size exclusion (crystal violet has molecular weight 408 whereas the membrane is a sharp 400 molecular weight cutoff). Thus it can be said that the effect of increase in the cross-flow velocity will be more on the permeate concentration of methylene blue compared to that of crystal violet. This would result in a relative increase of the permeation of methylene blue resulting in an increase in its selectivity. Similarly increase in pressure at a fixed cross-flow velocity results in relative increase in the permeation of methylene blue compared with crystal violet and a subsequent increase in selectivity results. The selectivity can be as high as 6.0 for ΔP = 415 kPa, for a cross-flow velocity of 42 cm/s. Therefore, with a suitable selection of

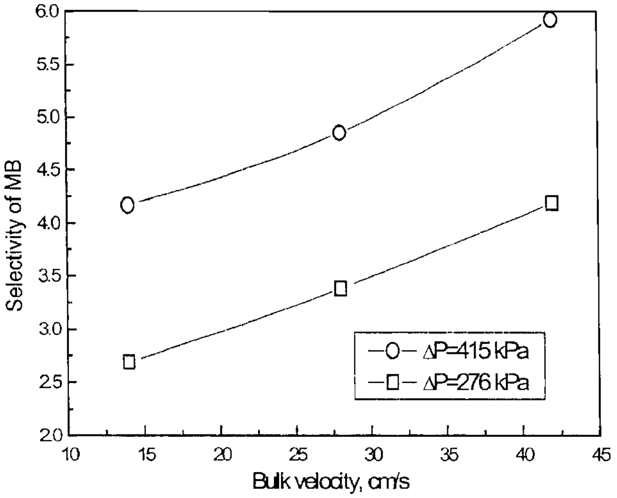

Figure 10. Variation of selectivity of methylene blue with bulk velocity in a mixture of crystal violet and methylene blue (16 ppm each) in the cross-flow cell.

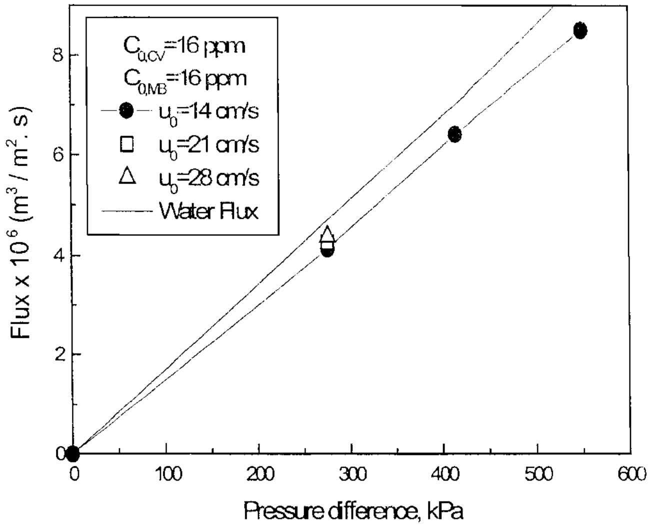

Figure 11. Variation of permeate flux with pressure and cross-flow velocity in the cross-flow cell in a 50:50 mixture of crystal violet and methylene blue.

membrane, operating pressure, and cross-flow velocity, fractionation of a specific dye from a dye mixture would be possible and may be used in practice.

The variation of permeate flux with pressure for a 50:50 mixture (16 ppm each) at cross-flow velocity of 14 cm/s is presented in Fig. 11. The effect of the cross-flow velocity at a particular pressure of 276 kPa has also been presented in the figure. The figure indicates an increase in permeate flux with pressure as expected. It may be noted that the permeate flux increases with cross-flow velocity due to reduction in concentration polarization. But the increase in flux values with cross-flow velocity is not much, as the osmotic pressure of the present dye solution is not significant.

CONCLUSIONS

Membrane separation process can be effectively used for the separation of dyes, e.g., crystal violet and methylene blue from the industrial effluents. The study indicates that nanofiltration is a viable process in this regard. It is also clear from this study that a mixture of crystal violet and methylene blue can be effectively fractionated using a suitable membrane.

The detailed parametric study on separation of dyes from aqueous solution and as well as on fractionation of dye mixtures will be useful for the selection of a set of operating conditions to obtain the optimum system performance and the design equations, in terms of permeate flux (throughput) and permeate concentration.

NOMENCLATURE

C_0	Feed concentration (ppm)
C_p	Permeate concentration (ppm)
R_0	Observed retention
S	Selectivity of methylene blue
u_0	Cross-flow velocity (cm/s)
Greek letters	
ΔP	Applied pressure difference

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Received October 2001
Revised April 2002