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: 07 January 2010

To cite this Article Prabhavathy, C. and De, Sirshendu(2010) 'Estimation of Transport Parameters during Ultrafiltration of Pickling Effluent from a Tannery', Separation Science and Technology, 45: 1, 11 — 20
To link to this Article: DOI: 10.1080/01496390903401788
URL: http://dx.doi.org/10.1080/01496390903401788

Separation Science and Technology, 45: 11–20, 2010

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390903401788

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Estimation of Transport Parameters during Ultrafiltration of Pickling Effluent from a Tannery

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Pickling effluent, being an industrial one, contains a large number of components with unknown transport coefficients. A combined model based on osmotic pressure and the Kedem-Katchalsky mechanism is used to predict these coefficients relevant to this process, e.g., effective osmotic coefficient, solute diffusivity, solute permeability, and reflection coefficient. These coefficients are evaluated utilizing the model and a large number of experimental data generated during ultrafiltration of pretreated pickling effluent. The performance criteria are evaluated in terms of the chemical oxygen demand (COD), the total dissolved solids (TDS), the total solids (TS), pH, and the conductivity of the permeate. The experiments also reveal that the proposed scheme is successfully reducing the COD to well below the prescribed limits and underscore the importance of transmembrane pressure drop and cross flow velocity on the permeate flux and quality.

Keywords diffusivity; Kedem-Katchalsky model; osmotic coefficient; pickling effluent; total solids

INTRODUCTION

Treatment of tannery effluent is a complex process where wastewater is stripped of harmful contents and rendered safe, so that it can be returned to the environment. Due to water scarcity, it is important to recycle the wastewater discharged from process industries to reusable grade water. The tannery processes can be characterized by high consumption of water and chemicals, most of which are found in the final wastewater (1). These effluents contain suspended solids, organic matter, chemicals, etc. Sodium chloride, sodium sulfide, lime, chromium, protein, fats, etc. are the major constituents (1). The effluent has a high chemical oxygen demand (COD).

Pickling acidification is the final step in preparing the hides for the tanning process (2). This is usually done in presence of salt. The hides are placed in a solution composed of water, sulfuric acid, and salt. The pH of the pickled effluent is about 1.5. Low pH prepares the hide to accept the tanning materials and the salt controls the swelling of the hide. The pickling process is also a preserving process, allowing the hides to be transported and stored for long periods without any deterioration. Pickling prevents deeper penetration of the tanning agent in the chrome tanning process.

Membrane based technology is gradually emerging as a technically significant and commercially viable "cleaner technology" for the treatment of wastewater from textile industries, tanneries, petrochemicals, paint industries, paper, and pulp industries (4–8). The main advantage of a membrane based process is that concentration and separation are achieved without a change of state and without use of chemicals or thermal energy, thus making the process energy-efficient and ideally suited for recycling of primary resources and recovery applications (9). Cross-flow filtration reduces the concentration polarization and is widely used in water and wastewater treatment (10). The performance criteria are evaluated in terms of chemical oxygen demand (COD), total dissolved solids (TDS), total solids (TS), pH, and the conductivity of the permeate. Cassano et al. presented a detailed conceptual possibility of various applications of the membrane based processes, e.g., microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) on different effluent streams of the beam house (11). It is reported that reverse osmosis could be employed for treatment of exhausted liquor coming from pickling unit, after an appropriate pretreatment, to recover the salt component in the retentate (11). The permeate solution could be employed for the preparation of soaking baths or as washing water. Ahmed et.al. studied the behavior of membrane with respect to the composition of the solution at various stages and reported on tanning and liming bath by employing nanofiltration solution (12). Galiana-Aleixandre et al. (13) has used nanofiltration for the pickling effluent and the feasibility of the process is evaluated. In these works, energy intensive reverse osmosis and nanofiltration process were used. The present work demonstrates that less energy intensive ultrafiltration, preceded by a suitable pretreatment method, can lead to permeate having qualities within the permissible

Received 21 November 2008; accepted 31 August 2009.
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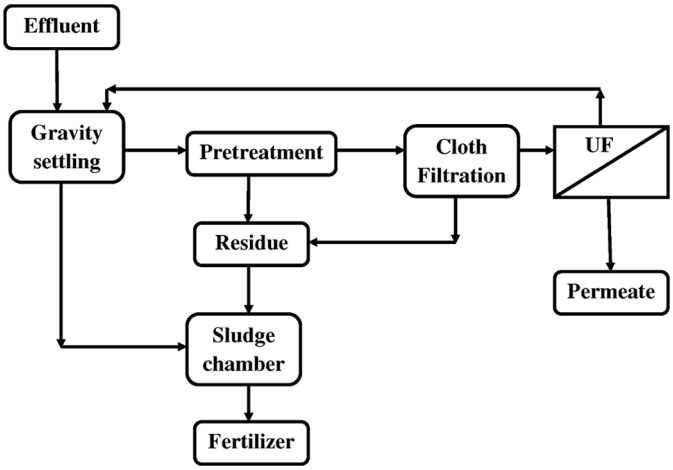

FIG. 1. Proposed schematic of pickling effluent treatment.

limits. The proposed schematic for the pickling effluent is presented in Fig. 1. The retentate of the membrane process can be recycled to the gravity settling chamber for further processing and the final permeate of UF can be recycled to the "beam house" for makeup water and chemicals (13).

However, as the effluent is a mixture of a vast number of components, any attempt to understand the basic physics of the process poses a significant challenge. This in turn, complicates the development of design equations for easy scale-up. The unknown yet relevant transport parameters need to be estimated from a series of experiments covering a wide range of operating conditions. These experiments include flow in the laminar and turbulent zones, as well as turbulent promoter assisted cases. To further analyze the data, a typical combination model involving the concepts of osmotic pressure and Kedem-Katchalsky mechanism is used and the unknown parameters are evaluated by optimization. The consistencies of these parameters are verified as well. As Sherwood number relations for turbulence promoter assisted cases are not known explicitly, these coefficients along with experimental data are used to evaluate the unknown constants of a proposed Sherwood number relation. The evaluated relation is physically consistent and accurately explains the experimental data.

THEORY

Theoretical modeling is carried out to predict the system performance in terms of permeate flux and permeate concentration. The model includes the mass transfer within the concentration boundary layer (outside the membrane surface) and osmotic pressure and Kedem-Katchalsky model to include solvent and solute flux within the porous membrane matrix. It is clear that the feed contains both organic and inorganic components and in each category there are large numbers of species, whose identification and exact concentration are difficult to determine. Therefore, for simplification, it is assumed total solids in the pretreated pickling effluent as a pseudo single component.

According to film theory, the permeate flux (J) is expressed in terms of mass transfer coefficient (k) as (14),

$$J = k \ln\left[\frac{(c_m - c_p)}{(c_0 - c_p)}\right] \tag{1}$$

Solvent flow through the membrane is quantified by Darcy's law for flow through a porous medium (14).

$$J = L_P(\Delta P - \sigma\Delta\pi) \tag{2}$$

where, L_p is the membrane permeability and σ is the reflection coefficient.

The osmotic pressure difference ($\Delta\pi$) across the membrane is given as,

$$\Delta\pi = \pi_m - \pi_p \tag{3}$$

where, π_m is the osmotic pressure at the membrane surface and π_p is that in the permeate stream. Osmotic pressure which is a function of solute concentration (expressed in terms of total solids) can be related through van Hoff's relationship,

$$\pi = ac \tag{4}$$

where, the osmotic coefficient 'a' is given as $a = RT/M$. Using Eqs. (2) to (4), the permeate flux is described as,

$$J = L_p[\Delta P - a\sigma(c_m - c_p)] \tag{5}$$

From Eq. (1), the membrane surface concentration (c_m), can be related to the permeate concentration (c_p) in terms of total solids as,

$$c_m = c_p + (c_0 - c_p)\exp^{\left[\frac{J}{k}\right]} \tag{6}$$

On combining Eq. (5) and Eq. (6), the permeate flux can be expressed as

$$J = L_p[\Delta P - a\sigma((c_0 - c_p)\exp^{\left[\frac{J}{k}\right]})] \tag{7}$$

According to the Kedem-Katchalsky model the solute flux is a sum of convective and diffusive transport, (15,16).

$$Jc_p = B(c_m - c_p) + \frac{(1-\sigma)(c_{avg})J}{\ln\left[\frac{c_m}{c_p}\right]} \tag{8}$$

where, c_{avg} is the average solute concentration in the pore. One way of representation of c_{avg} is log mean concentration difference (17), given as $c_{avg} = \frac{(c_m - c_p)}{\ln[\frac{c_m}{c_p}]}$

The first term on the right hand side of Eq. (8) is the diffusive flux and the second term is the convective flux. Combine Eqs. (1), (7), (8), and after algebraic simplification, the following nonlinear algebraic equation is obtained,

$$c_p = \frac{B}{J}((c_0 - c_p)\exp^{\left[\frac{J}{k}\right]}) + \frac{(1-\sigma)((c_0 - c_p)\exp^{\left[\frac{J}{k}\right]})}{\ln\left[1 + \frac{(c_0 - c_p)\exp^{\left[\frac{J}{k}\right]}}{c_p}\right]} \quad (9)$$

The mass transfer coefficient under laminar flow conditions is given by Leveque's equation (18),

$$\mathrm{Sh} = \frac{\mathrm{kd_e}}{\mathrm{D}} = 1.86\left(\mathrm{Re}\,\mathrm{Sc}\frac{\mathrm{d_e}}{\mathrm{L}}\right)^{\frac{1}{3}} \quad (10)$$

and that for turbulent flow is given as (18),

$$\mathrm{Sh} = \frac{\mathrm{kd_e}}{\mathrm{D}} = 0.023(\mathrm{Re})^{0.8}(\mathrm{Sc})^{0.33} \quad (11)$$

where, d_e is the hydraulic diameter of the flow channel. For a thin rectangular channel, the value of d_e is $4h$, where, h is the half height of the channel. With the knowledge of four transport parameters, namely, diffusivity (D), osmotic coefficient (a), solute permeability through the membrane (B), and reflection coefficient (σ), Eq. (9) can be solved iteratively to obtain the value of c_p, c_m and permeate flux. These four parameters are estimated using the procedure presented in the next section.

Numerical Solution

Since pretreated tannery effluent contains various salts at different concentration levels as well as some smaller sized organic materials, the four parameters, namely, diffusivity (D), osmotic coefficient (a), solute permeability (B), and reflection coefficient (σ) are difficult to obtain. Hence, an optimization method is employed with an initial guess of these four parameters and minimizing the following error function to estimate the values of these parameters,

$$\mathrm{S} = \sum_{\mathrm{i}=1}^{\mathrm{n}}\left(\frac{\mathrm{J^{exp}} - \mathrm{J^{calc}}}{\mathrm{J^{exp}}}\right)^2 + \sum_{\mathrm{i}=1}^{\mathrm{n}}\left(\frac{\mathrm{c_p^{exp}} - \mathrm{c_p^{calc}}}{\mathrm{c_p^{exp}}}\right)^2 \quad (12)$$

BCPOL subroutine of IMSL library using unconstrained direct search algorithm is used for optimization. The permeate flux, the membrane surface concentration, and the permeate concentration are obtained by solving the model equations in an iterative manner following the algorithm presented in Fig. 2.

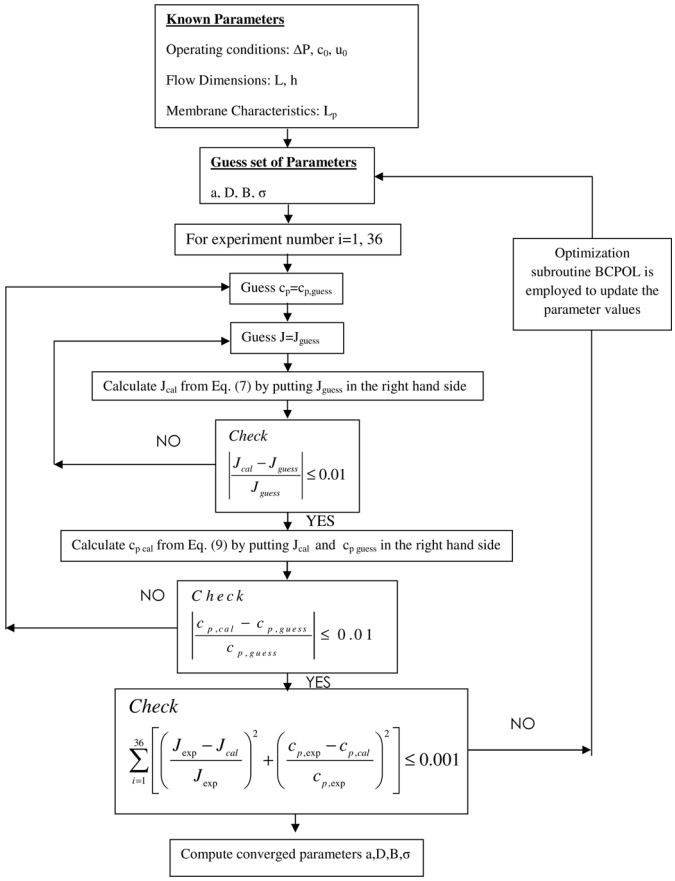

FIG. 2. Algorithm for the estimation of parameters.

EXPERIMENTAL

Membranes

Organic thin film composite (TFC) membranes of molecular weight cut off (MWCO) 5 kDa are used for UF. M/s, Permionics Membranes Pvt. Ltd., India, supplied ultrafiltration membranes. The effective length of the membrane is 14.6×10^{-2} m and width is 5.5×10^{-2} m. The permeability of the membrane is determined using distilled water and is found to be 4×10^{-11} m/Pa.s with a hydraulic membrane resistance of $25 \times 10^{12}\,\mathrm{m^{-1}}$.

Chemicals Used

Calcium oxide is used for coagulation and is procured from M/s, Qualigens, India. The chemicals required for determination of COD are procured from M/s, Loba Chemie, India. The chemicals are of analytical grade and are used without further treatment.

Ultrafiltration of the Effluent

Effluent

Effluent is collected from the pickling unit of N.A. Trading, Bantala Leather Complex, Kolkata, India. The

TABLE 1
Characterization of pickling effluent from tannery and effects of calcium oxide dosing

Properties	pH	Conductivity (S/m)	TDS (g/l)	COD (ppm)	TS (g/l)
Feed	1.4	6.8	44.9	1120	133.00
0.1% CaO	1.20	6.41	42.4	528	138.40
0.2% CaO	1.49	6.22	41.1	480	135.40
0.3% CaO	1.89	5.95	39.2	464	131.20
0.4% CaO	7.26	5.73	37.7	432	127.60
0.5% CaO	9.65	5.61	37.1	512	132.00
1.0% CaO	12.75	5.91	38.9	528	156.00

characterization of the effluent has been carried out and is presented in Table 1.

Pretreatment

The effluent is kept in six $\times$ 100 ml capacity cylinders. The optimum coagulant is determined by adding 0.1 to 0.5 g/l and 1.0 g/l calcium oxide to the effluent and measuring turbidity, BOD, COD, TS, and TDS after 30 minutes. Once the optimum coagulation dose is obtained, the supernatant of the gravity settled liquor is treated with the optimum calcium oxide dose. The gravity settlement is carried out in a 10 liter container. After coagulation, the sludge settles at the bottom and the supernatant is siphoned out. A fine nylon filter cloth is used for further clarification of the collected supernatant. The sludge produced is sun dried and pulverized to powder form and analyzed for its fertilizer value.

Membrane Filtration Cell

A rectangular cross-flow cell, made of stainless steel, was designed and fabricated. Two neoprene rubber gaskets are placed over the membrane forming the flow channel. The channel height after tightening the two flanges is found to be 3.4×10^{-3} m. The cell consists of two rectangular matching flanges. The inner surface of the top flange is mirror polished. The bottom flange is grooved, forming the channels for the permeate flow. A porous stainless steel plate is placed on the lower flange that provides mechanical support to the membrane. For experiments with turbulent promoters, 9 equispaced wires of diameter 1.66 mm are placed laterally (along the width of the channel) in between the two gaskets. The spacing between the turbulent promoters is 15.0 mm. Localized turbulence is created in the flow path due to the presence of these turbulent promoters. Two flanges are tightened to create a leak proof channel for conducting experiments in cross flow mode.

The clarified effluent is pumped by a high pressure reciprocating pump from the stainless steel feed tank to the cross flow cell with a rectangular channel. The retentate stream is recycled to the feed tank routed through a rotameter. The pressure and the cross flow rate inside the membrane channel are independently set by operating the valves in the bypass line and that at the outlet of the membrane cell. Permeate samples are collected from the bottom of the cell and are analyzed for COD, TS (total solids), TDS (total dissolved solids), conductivity, and pH. The membrane module assembly is available elsewhere (19).

Operating Conditions

The operating pressures for UF are 276, 414, 552 and 690 kPa. The cross flow rates are 60 (Re = 606), 90 (Re = 909) and 120 l/h (Re = 1212). These cross flow rates correspond to the cross flow velocities as 0.1, 0.15 and 0.2 m/s, respectively.

Procedure

A fresh membrane is compacted at a pressure higher than the maximum operating pressure for 3 hours using distilled water and then its permeability is measured (4×10^{-11} m/Pa · s). The effluent is placed in a stainless steel feed tank of 2 liter capacity. A high pressure plunger pump is used to feed the effluent into the cross-flow membrane cell. Cumulative volumes of permeate are collected during the experiment. The permeate stream after collecting the required amount of sample is recycled to the feed tank to maintain a constant concentration in the feed tank. Permeate samples are collected at different time intervals for analysis. A bypass line is provided from the pump delivery to the feed tank. Retentate and bypass control valves are used to vary the pressure and flow rate accordingly. Values of permeate flux are determined from the slopes of the cumulative volume versus the time plot. The precision of flux measurement is in the order of $\pm 5\%$. The duration of the cross-flow experiment is one hour.

Once an experimental run is over, the membrane is thoroughly washed, in situ, with distilled water for 15 minutes at a pressure of 200 kPa. The cross-flow channel is then dismantled and the membrane is dipped in 0.1 (N) sodium dodecyl sulfate (SDS) solution for three hours.

Then, it is washed carefully with distilled water to remove traces of SDS. The cross-flow cell is reassembled and the membrane permeability is again measured. It is observed that the membrane permeability remains almost constant between successive runs. All the experiments have been conducted at a room temperature of $32 \pm 2°C$.

Analysis

The conductivity, total dissolved solids, turbidity, and the pH of all samples (feed, permeate, and retentate streams) are measured at room temperature using a water and soil analysis kit, model no 191E, manufactured by M/s, Toshniwal Instruments Ltd, India. Total solids (TS) of all the samples are measured by taking a known volume of sample in a petridish and keeping in an oven maintained at $105 \pm 2°C$ till complete drying of the sample. COD values are determined using standard techniques (20).

RESULTS AND DISCUSSION

Pretreatment of the Effluent

The pH of the pickling solution is 1.4 and hence the feed cannot be treated directly by membranes. Pretreatment with calcium oxide is therefore necessary for chemical conditioning. The properties of the calcium oxide treated effluent are tabulated in Table 1. It is clear from Table 1 that COD, the turbidity, and TS decrease sharply with an increase in calcium oxide dose till 0.4% calcium oxide. The pH of the feed gradually increases with calcium oxide concentration. At 0.1%, the pH is acidic and it is alkaline at 1.0%. The table shows that the pH is nearly neutral at 0.4% calcium oxide. It is clear that COD decreases initially and reaches a minimum value at 0.4% calcium oxide and then increases as the dosage is gradually increased to 0.5% to 1.0%. The properties such as TDS, conductivity, and TS show similar results around 0.4% calcium oxide dosing. From these observations, 0.4% of calcium oxide is selected as optimum concentration for coagulation.

Pretreatment results in a COD of 432 mg/l. TS and TDS are 127.6 and 37.7 g/l, respectively, after the sludge separation. The amount of sludge generated is 1.6 kg/100 liters, which can be used after drying as a fertilizer. The dried and pulverized sludge is analyzed for its fertilizer value. The results of chemical analysis of sludge from pickling effluent are given in Table 2. The supernatant after calcium oxide treatment is subjected to membrane filtration after a coarse filtration by a fine cloth.

TABLE 2
Results of chemical analysis for pickling effluent

Effluent	pH	OC (wt %)	N (wt %)	P (wt %)	K (wt %)
Pickling	6.8	1.23	0.23	0.136	0.56
Vermi-compost	7.1–7.8	9.97–10.62	1.80	0.90	0.40

Ultrafiltration in the Cross Flow Mode

The pretreated pickling effluent is subjected to membrane separation process with a 5 kDa ultrafiltration membrane. The experiments are conducted in three different flow regimes: laminar, laminar with promoter, and purely turbulent. Figure 3 represents the variation of permeate flux behavior with time at laminar regime with and without promoters at 276 kPa and 690 kPa pressures. It indicates that the time required to reach steady state is decreased with increase in Reynolds number. For example, it can be observed from Fig. 3 that the steady state is attained in about 1123 seconds for $Re = 606$ and 276 kPa pressure, whereas at the same pressure but $Re = 1212$, the steady state is attained within 1087 seconds. Similarly, the steady state is attained in 223 seconds for $Re = 606$ and 690 kPa pressure, whereas at the same pressure but $Re = 1212$, the steady state is attained within 193 seconds for laminar with promoter condition. It is also found that the steady state is achieved faster using turbulent promoters compared to laminar flow. The turbulence generated due to increased velocity and due to the presence of promoters reduces the concentration polarization at the membrane surface. The growth of polarized layer is controlled which establishes steady state faster compared to purely laminar condition. Figure 4 represents similar trends in turbulent regime at 276 kPa and $Re = 4242$, 5454. Steady state is attained at 1107 and 766 seconds, respectively.

Model Parameters

As discussed earlier, the effective osmotic pressure coefficient (a), solute diffusivity (D), solute permeability (B), and reflection coefficient (σ) through the membrane are

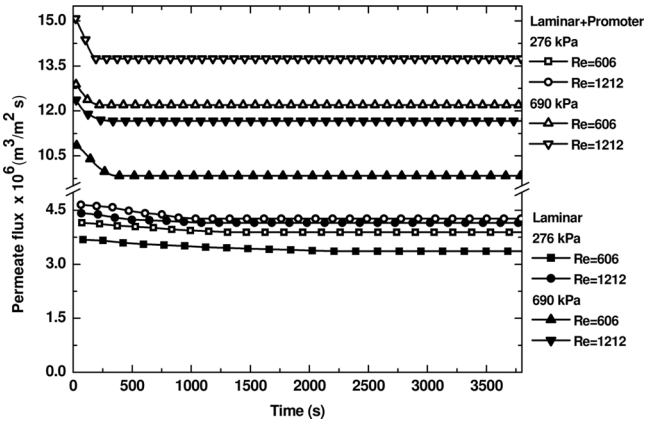

FIG. 3. Variation of permeate flux with time in both laminar and laminar + promoter flow regimes.

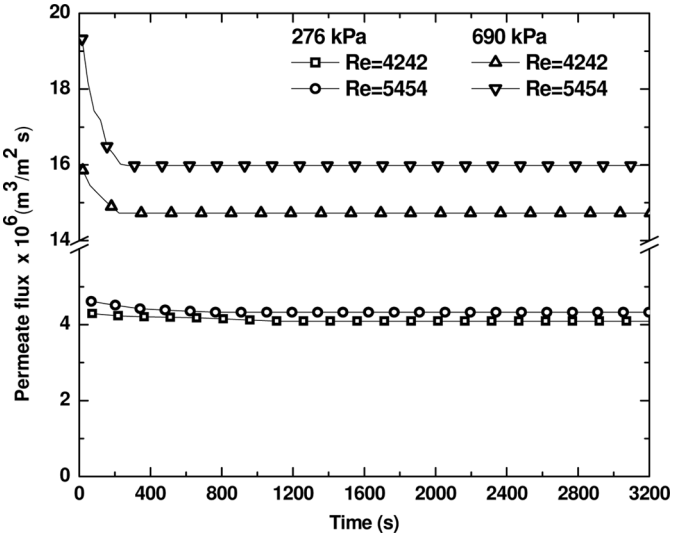

FIG. 4. Variation of permeate flux with time in turbulent flow regime.

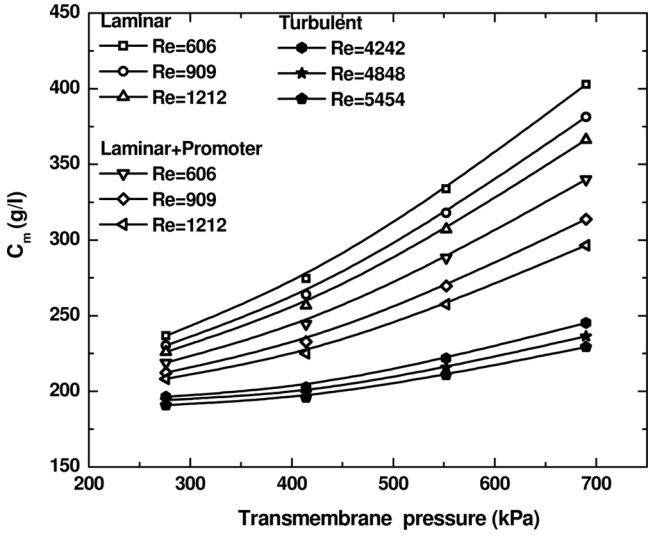

FIG. 5. Variation of membrane surface concentration with transmembrane pressure during UF.

calculated by comparing experimental flux and permeate TS values both for laminar and turbulent flow regimes with the calculated values. The estimated values are: $a = (5.625 \pm 0.50) \times 10^3\,\mathrm{Pa.m^3/kg}$, $D = (1.25 \pm 0.10) \times 10^{-9}\,\mathrm{m^2/s}$, $B = (7.03 \pm 0.02) \times 10^{-7}\,\mathrm{m/s}$ and $\sigma = 0.23 \pm 0.002$. The feed to UF after pretreatment contains a large amount of inorganic and some amount of organic solutes. Thus, the effective osmotic pressure coefficient '*a*' is less than that of salt, i.e., sodium chloride (about $8.5 \times 10^4\,\mathrm{Pa.m^3/kg}$). This fact is supported by the diffusivity value as well. For sodium chloride, the diffusivity is $1.5 \times 10^{-9}\,\mathrm{m^2/s}$ whereas the effective diffusivity obtained is of the same order as that of sodium chloride but with a slightly less absolute value. The value of the reflection coefficient indicates that there is significant contribution of convection compared to diffusive flux of solute through the membrane. Since, the parameters *a, D, B*, σ obtained by this method are independent of the flow regime, calculations are done using these values of the parameters in case of laminar flow with promoters. But the expression of the Sherwood number is not known in this case. Hence, the following expression of the Sherwood number is considered,

$$Sh = \alpha(\mathrm{Re})^n (Sc)^{1/3} \tag{13}$$

For all the twelve experimental runs with turbulent promoters, optimization is carried out to evaluate the values of α and *n,* which are found to be 0.44 ± 0.003 and 0.46 ± 0.002, respectively. As observed from Eqs. (10) and (11), α value should be in the range of 0.023 and 1.86 and value of *n* should be in the range of 0.33 and 0.8. The standard deviation of the above Sherwood number (in Eq. 13) is 0.027.

To clearly understand the amount of concentration polarization and the tendency of flux decline behavior, estimation of membrane surface concentration (c_m) is required. Variations of membrane surface concentration with transmembrane pressure are shown in Fig. 5. Membrane surface concentration increases with transmembrane pressure as the solute particles are convected at a higher rate towards the membrane surface. It decreases with channel Reynolds number due to the fact that the solutes are washed away at higher cross flow velocity by forced convection which leads to an increase in permeate flux. On increasing turbulence using promoters or increased cross flow velocity, membrane surface concentration as well as permeate concentration decreases leading to a decrease in membrane surface concentration. Membrane surface concentration is observed to be higher in case of the laminar flow regime with low cross flow velocity. For example, at a pressure of 690 kPa and $u_0 = 0.1$, 0.15 and 0.2 m/s, the membrane surface concentration is in the range of 366 to 403 g/l for laminar, 296 to 340 g/l for laminar flow with turbulent promoters. Similarly at a pressure of 690 kPa and $u_0 = 0.7$, 0.8 and 0.9 m/s, c_m varies from 229 to 245 g/l for a purely turbulent flow regime. Variations of c_m values lead to a flux enhancement in case of laminar flow with promoters in the range of 31% to 49%, compared to pure laminar flow regime.

Figure 6 shows the variation of the Sherwood number with the Reynolds number for purely laminar, laminar with promoter, and turbulent flow regimes. The Sherwood number for the laminar region lies between 47 and 60 for Re between 606 and 1212. Similarly, the Sherwood number for the turbulent region lies between 156 and 191 for Re between 4242 and 5454. The Sherwood number relations

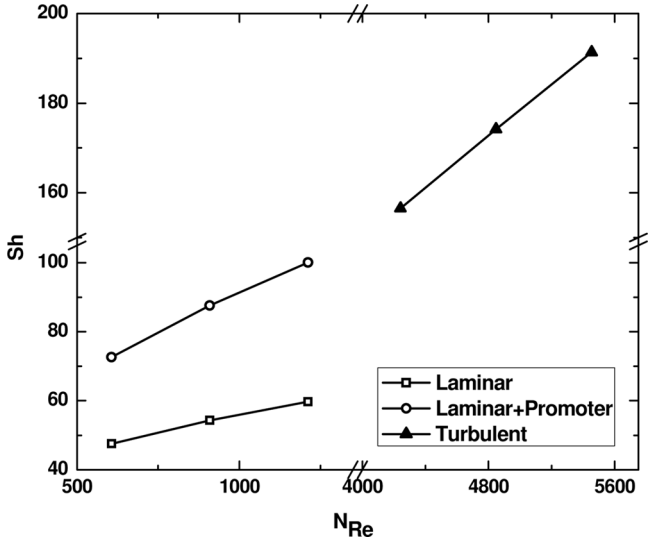

FIG. 6. Variation of Sherwood number with different flow regimes.

are developed for the case of laminar flow with turbulent promoters. The Sherwood number for laminar with promoter case lies between 73 and 100 for overall Re lying between 606 and 1212. This indicates that using turbulent promoters, the mass transfer coefficient increases 1.5 to 1.7 times, compared to pure laminar flow. In pure turbulent flow case, the mass transfer coefficient increases 3.2 to 3.3 times, compared to the laminar flow. Increase in mass transfer from membrane surface results in a decrease in concentration polarization and consequently, improvement in permeate flux as discussed earlier.

Variation in ratio of convective flux to diffusive flux with transmembrane pressure is shown in Fig. 7. At

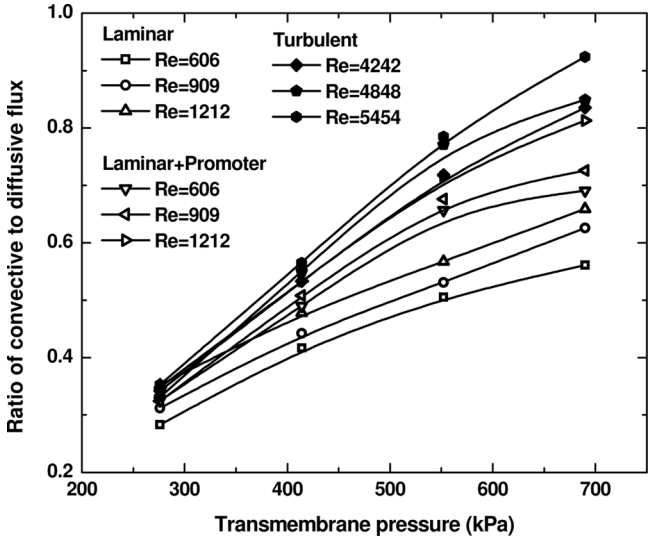

FIG. 7. Variation in ratio of convective to diffusive flux with operating conditions during UF.

different Reynolds number under different flow regimes, the ratio of convective to diffusive flux and operating pressure shows a trend that flux ratio increases almost linearly with operating pressure. At lower operating pressure, the diffusive flux is more dominant. As pressure increases the contribution of the convective flux also increases due to increase in driving force. At the same transmembrane pressure drop, the effect of convection is more dominant as the flow regime changes from laminar, laminar with promoter, and turbulent, in that order. This occurs due to the fact that as the turbulence increases the membrane surface concentration decreases leading to a decline of the concentration gradient across the membrane pores. These result into a reduction in diffusive contribution compared to the convective one.

A detailed parametric study is conducted to observe the effects of the operating conditions on the permeate flux and permeate quality. The results of permeate analysis after ultrafiltration under various operating conditions are presented in Table 3. It can be observed from Table 3 that the TS values in the permeate decrease when the Reynolds number or operating pressure increases. With increase in the Reynolds number, the membrane surface concentration becomes less due to forced convection, resulting in lower permeation of solutes (less TS) through the membrane. The conductivity of the permeate is the same as the feed, which signifies that almost all the salt present in the feed solution has permeated through the UF membrane.

Variations of permeate COD with transmembrane pressure at the operating Reynolds numbers in turbulent, laminar, and laminar with turbulent promoter are shown in Table 3. It is observed that with an increase in transmembrane pressure and the Reynolds number, the permeate quality improves. With increase in pressure, the solvent flux increases linearly, while the solute flux increases marginally. Thus with increasing pressure, more solvent passes through the membrane along with a fixed amount of the solute; and hence the permeate becomes purer and the permeate quality increases. It may be noted that all the values of COD under different operating conditions are well within the discharge limit (250 ppm). It may be calculated that at 276 kPa pressure and Reynolds number 4242, the retention of TDS, TS, and COD are 8%, 58%, and 58%, with respect to calcium oxide (0.4%) treated feed. At the same transmembrane pressure drop and Reynolds number 5454, these values become 8%, 60%, and 62%. This indicates that there is practically no change in TDS retention, because almost all inorganics permeate through the ultrafiltration membrane. TS and COD show a marginally higher retention within the range of cross flow rates, studied herein. At the same cross flow velocity and higher transmembrane pressure drop of 690 kPa, the retention values are 8%, 72%, and 73%. Therefore, the retention of salt does

TABLE 3
Permeate analysis after ultrafiltration

S.No.	Pressure, kPa	Reynolds No.	TDS, g/l	TS, g/l	COD, ppm	Conductivity, S/m
Turbulent regime						
1	276	4242	34.6	52.6	179	5.26
2	276	4848	34.8	51.5	171	5.28
3	276	5454	34.9	49.8	163	5.29
4	414	4242	34.9	48.9	161	5.29
5	414	4848	35.1	48.2	156	5.32
6	414	5454	35.1	47.4	150	5.32
7	552	4242	35.1	41.2	145	5.32
8	552	4848	35.1	40.1	131	5.33
9	552	5454	35.1	38.2	123	5.32
10	690	4242	35.1	35.4	116	5.32
11	690	4848	35.2	34.8	106	5.34
12	690	5454	35.2	34.4	87	5.34
Laminar regime						
1	276	606	38.5	63.2	198	5.83
2	276	909	38.7	62.6	182	5.87
3	276	1212	38.6	61.4	178	5.87
4	414	606	38.0	62.7	170	5.76
5	414	909	37.4	61.2	162	5.69
6	414	1212	37.7	59.0	157	5.71
7	552	606	38.4	60.0	149	5.83
8	552	909	38.5	58.4	138	5.83
9	552	1212	38.6	56.8	127	5.85
10	690	606	37.4	58.0	130	5.68
11	690	909	37.5	54.4	123	5.68
12	690	1212	36.9	52.0	101	5.60
With turbulent promoter						
1	276	606	36.1	57.8	183	5.49
2	276	909	36.5	55.0	178	5.53
3	276	1212	36.5	53.6	167	5.53
4	414	606	36.0	52.7	163	5.46
5	414	909	36.6	52.2	158	5.55
6	414	1212	36.5	51.3	153	5.53
7	552	606	36.5	52.3	147	5.53
8	552	909	36.0	50.0	136	5.46
9	552	1212	36.5	48.7	125	5.53
10	690	606	36.3	48.2	128	5.50
11	690	909	36.2	47.7	120	5.48
12	690	1212	36.1	45.7	98	5.48

not get affected by increase in pressure. On the other hand, the retention values of TS and COD increase significantly. The reasons of these variations are discussed already.

Using the estimated value of parameters, the comparison between experimental and calculated permeate flux and permeate concentrations are represented in Fig. 8 in all the flow regimes. It is observed from Fig. 8 that almost all the calculated permeate flux values are within ±15% of the experimental data. The comparison between the calculated and the experimental permeate concentration (expressed as total solids) is shown in Fig. 9. Almost all the calculated permeate concentrations are within ±15% of the experimental data.

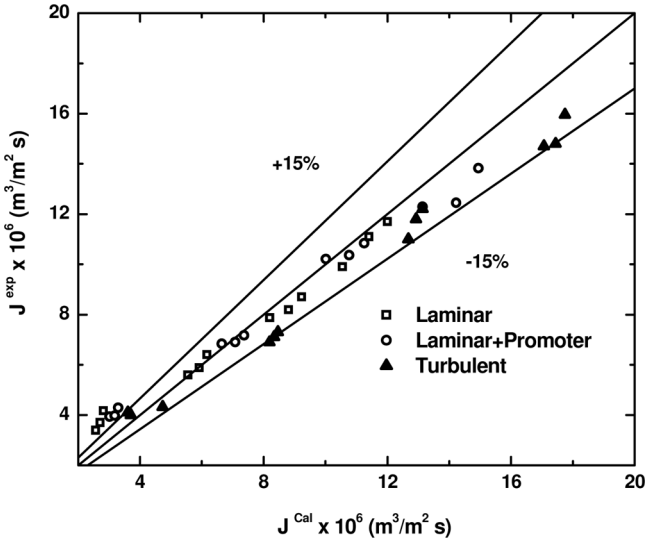

FIG. 8. Comparison between the experimental and calculated flux for different operating conditions in UF at steady state.

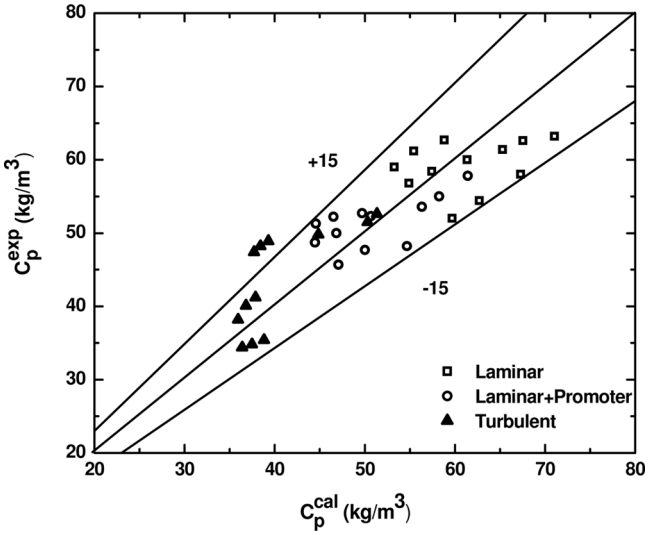

FIG. 9. Comparison between the experimental and calculated permeate (TS) concentration for different operating condition in UF at steady state.

CONCLUSION

A systematic study was carried out to treat effluent discharged from the pickling unit in a tannery using a combined process of coagulation with calcium oxide and ultrafiltration by using 5 kDa membranes. Effective osmotic pressure coefficient, the solute diffusivity, the solute permeability, and the reflection coefficient values through the membrane are estimated by using a combination of Kedem-Katchalsky and osmotic pressure model. The effective osmotic pressure coefficient and solute diffusivity reveals that the feed to UF contains mostly inorganic solutes. Relevant system parameters are obtained by comparing the calculated results with the experimental data. The estimated values of the parameters are as following: a (osmotic coefficient) $= (5.625 \pm 0.50) \times 10^3$ Pa.m^3/kg, D (Diffusivity) $= (1.25 \pm 0.10) \times 10^{-9}$ m^2/s, B (solute permeability through the membrane) $= (7.03 \pm 0.02) \times 10^{-7}$ m/s and σ (reflection coefficient) $= 0.23 \pm 0.002$. Once the model parameters are evaluated for laminar and turbulent flow conditions, the Sherwood number relations is also developed for the case of laminar flow with turbulent promoters. The calculated permeate flux and the permeate concentration values are within $\pm 15\%$ of the experimental data.

ACKNOWLEDGEMENT

This work is partially supported by a grant from the Department of Science and Technology, New Delhi, Government of India under the scheme no. DST/TSG/WM/2005/55. Any opinions, findings, and conclusions expressed in this paper are those of the authors and do not necessarily reflect the views of DST.

LIST OF SYMBOLS

a	osmotic pressure coefficient (Pa.m^3/kg)
B	Solute (TS) permeability through the membrane (m/s)
c	concentration (kg/m^3)
c_m	membrane surface concentration (kg/m^3)
c_p	permeate concentration (kg/m^3)
$c_p^{\exp}$	experimental permeate concentration (kg/m^3)
c_p^{calc}	calculated permeate concentration (kg/m^3)
c_0	feed concentration (kg/m^3)
d_e	hydraulic diameter (m)
D	effective solute diffusivity (m^2/s)
h	channel half height (m)
k	mass transfer coefficient (m/s)
K	Potassium
L	channel length (m)
L_p	membrane permeability (m/Pa.s)
N	Nitrogen
OC	Organic Carbon
P	Phosphorous
Re	Reynolds number ($\rho u_0 d_e/\mu$)
Sh	Sherwood number (kd_e/D)
Sc	Schmidt number ($\mu/\rho D$)
u_o	average velocity (m/s)
J	permeate flux (m^3/m^2.s)
J_w^0	pure water flux (m^3/m^2.s)
$J^{\exp}$	experimental permeate flux (m^3/m^2.s)
J^{calc}	calculated permeate flux (m^3/m^2.s)

Greek Symbols

ΔP	transmembrane pressure drop (Pa)
$\Delta\pi$	osmotic pressure difference (Pa)
π_m	osmotic pressure at the membrane surface (Pa)
π_p	osmotic pressure at the permeate side (Pa)
σ	reflection coefficient (−)

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