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Treatment of fatliquoring effluent from a tannery using membrane separation process: Experimental and modeling

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ABSTRACT

Treatment of fatliquoring effluent generated from a tannery, using a hybrid separation process involving gravity settling, two step coagulation, nanofiltration and reverse osmosis is presented in this study. The optimum dose of coagulation, i.e., 0.5% (w/v) of ferrous sulfate followed by 0.15% (w/v) calcium oxide resulted in reduction of chemical oxygen demand from 13688 to 4921 mg/l. Low pressure nanofiltration of the supernatant was carried out in the range of 828–1242 kPa. Chemical oxygen demand of the nanofiltration permeate varied from about 1300–2700 mg/l depending upon the operating conditions. To bring the chemical oxygen demand value less than the allowable permissible limit in India (250 mg/l), nanofiltration permeate was subjected to reverse osmosis (operating pressure range from 1313 to 1724 kPa). The final treated effluent, i.e., reverse osmosis permeate had chemical oxygen demand values in the range of 117–174 mg/l. The membrane filtration experiments included flow in laminar, laminar with turbulent promoter and turbulent flow regimes. Using a combination of osmotic pressure and solution diffusion model for both nanofiltration and reverse osmosis, three transport coefficients, namely, the effective osmotic coefficient, solute diffusivity and solute permeability through the membrane were obtained by comparing the permeate flux and permeate concentrations using the model calculated values and the experimental data. The calculated data agreed closely with the experimental values.

1. Introduction

Pollution prevention and waste minimization has become an essential component of study owing to environmental significance regarding treatment of complex effluent generated from tanneries. Leather industry has always been considered one of the most polluting industries characterized by low technological level of its operations. Stringent rules have been imposed on tanneries concerning the disposal of wastewater within permissible standards. It is noted that tannery effluent is the most polluting one among all the industrial wastes [1]. Leather industries generate large volume of liquid effluent from each processing steps. It is reported that approximately 50% of the chemicals in these processes become wastewater or sludge [2]. When these effluents are discharged to surrounding environment without prior treatment, they create severe environmental problems [3,4]. The amount of complex effluent discharged from a leather complex for producing 1 kg of leather varies from 30 to 40 l per day, depending upon the quantity of leather produced and various operations involved [5]. Each tannery operation, e.g., soaking, liming, deliming, bating, pickling, degreasing, tanning, neutralization, dyeing, fatliquoring, etc., produces huge polluting effluent.

Leathers must be lubricated in order to re-establish the fat content lost in the previous procedures like tanning where the natural fats are cleaned from the skin and hide and thereby, making the leather hard and rough. Fatliquoring, a post tanning operation involves the process of incorporating fat, grease and oils into the skin of the leather before the leather is dried. Fatliquoring is usually performed in large containers using an oil emulsion at temperature of about 60–65 °C for 30–40 min [5]. Fatliquors are oils which are added to the leather making the final product softer. Oils are applied to the leather in the form of emulsion. Oils and other fatty acid substances present in the fatliquor replace the natural oils lost in the beamhouse and tanyard processes and give leather, the enviable softness. Fatliquoring improves the physical properties such as tensile strength, waterproof, toughness, extensibility, wetting properties and resistance towards chemical actions [6]. The presence of fats, grease and oils in the effluent generated after fatliquoring cannot be discharged as such since they may clog sewage or pollute receiving streams leading to environmental pollution. It may be interesting to note, for a typical tannery processing 3500 kg raw hide per day, the volume of wastewater generated from the fatliquoring step is around 10,000 l per day [5].

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Nomenclature

a	osmotic pressure coefficient (Pa m^3/kg)
B	solute permeability through the membrane (m/s)
c	concentration (kg/m^3)
c_m	membrane surface concentration (kg/m^3)
$c_{p\,ss}$	steady state permeate concentration (kg/m^3)
$c_{p\,ss}^{exp}$	experimental permeate concentration (kg/m^3)
$c_{p\,ss}^{calc}$	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)
E	electrical energy (kWh/m^3)
h	channel half height (m)
k	mass transfer coefficient (m/s)
K	Potassium
L	channel length (m)
L_p	membrane permeability (m/Pa s)
M.D.	Mean deviation about mean
N	nitrogen
n	exponent in Eq. (13)
n_1	number of experiments
OC	Organic Carbon
P	phosphorous
Q	volumetric flow rate (m^3/s)
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_{ss}	steady state permeate flux (m^3/m^2 s)
J_w^0	pure water flux (m^3/m^2 s)
J_{ss}^{exp}	experimental permeate flux (m^3/m^2 s)
J_{ss}^{calc}	calculated permeate flux (m^3/m^2 s)
z_i	z_i = ith calculated variable – ith experimental variable
$\bar{z}$	arithmetic average of z_i

Greek letters

α	$\alpha = a/\Delta P$ in Eq. (6)
β	coefficient in Eq. (13)
β	$\beta = \beta/J_w^0$ in Eq. (8)
δ	concentration boundary layer thickness (m)
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	Standard deviation

The objective of wastewater treatment is to select the best available technology that will meet the quality standards. Literature study reveals that the conventional treatment of common effluent from tannery is not favorable in case of disposal for large volumes of effluent. Nowadays, membrane based separation technique, a cost effective clean and green technology finds application in wastewater processing of wide range of industries [7–13]. Membrane based operations are opted for processing of these effluents because of the affordable price of the membranes. Pressure driven membrane processes are quite suitable for removal of oily wastewater [14]. The present study focuses on membrane separation process for the pretreated fatliquoring effluent that reports a high amount of oil and grease (4000 mg/l).

In this work, rate governed separation processes, like reverse osmosis (RO) and nanofiltration (NF) are used, preceded by a suitable pretreatment method, that leads to permeate having qualities

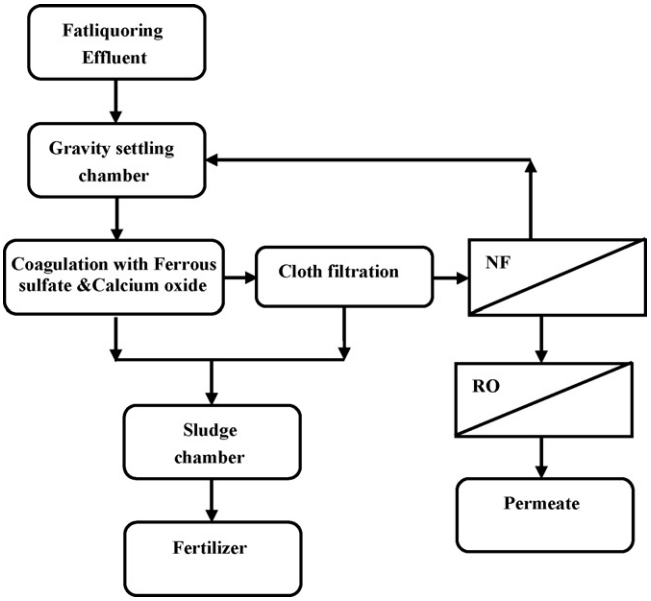

Fig. 1. Proposed schematic of fatliquoring effluent treatment.

within the permissible limits. The solvent and solutes can only be transported across the membrane by first dissolving in, and subsequently diffusing through, the membrane [15]. The proposed schematic is presented in Fig. 1. Conducting experiments under continuous cross-flow mode validates the separation scheme. A detailed parametric study for cross-flow experiments has been undertaken to observe the effects of the operating conditions, i.e., the transmembrane pressure drop and the cross-flow velocity on the permeate flux and quality. The performance of the separation schemes are evaluated in terms of chemical oxygen demand (COD), total dissolved solids (TDS), total solids (TS), pH and conductivity of the permeate. The COD values of the treated effluent are found to be well within the permissible limits. In case of NF as well as RO, an osmotic pressure model in combination with solution diffusion model is used to determine the transport parameters, namely, osmotic coefficient, solute diffusivity and solute permeability through the membrane.

2. Theory

To predict the system performance in terms of permeate flux and permeate concentration, a steady state model is developed for a two step membrane separation processes namely, nanofiltration followed by reverse osmosis for treatment of fatliquoring effluent collected from a tannery. Theoretical modeling includes a well-organized method for the determination of model parameters by fitting the calculated results of permeate flux and permeate concentration with the corresponding experimental data by combining film theory, Darcy's law and solution diffusion model.

Darcy's law quantifies solvent flow through the membrane for flow through a porous medium [16],

$$J_{ss} = L_p(\Delta P - \Delta\pi) \quad (1)$$

where, L_p is the membrane permeability. The osmotic pressure difference across the membrane is given as,

$$\Delta\pi = \pi_m - \pi_p \quad (2)$$

where, π_m is the osmotic pressure at the membrane surface and π_p is that in the permeate stream. Osmotic pressure can be related to the solute concentration through van't Hoff relationship,

$$\pi = ac \quad (3)$$

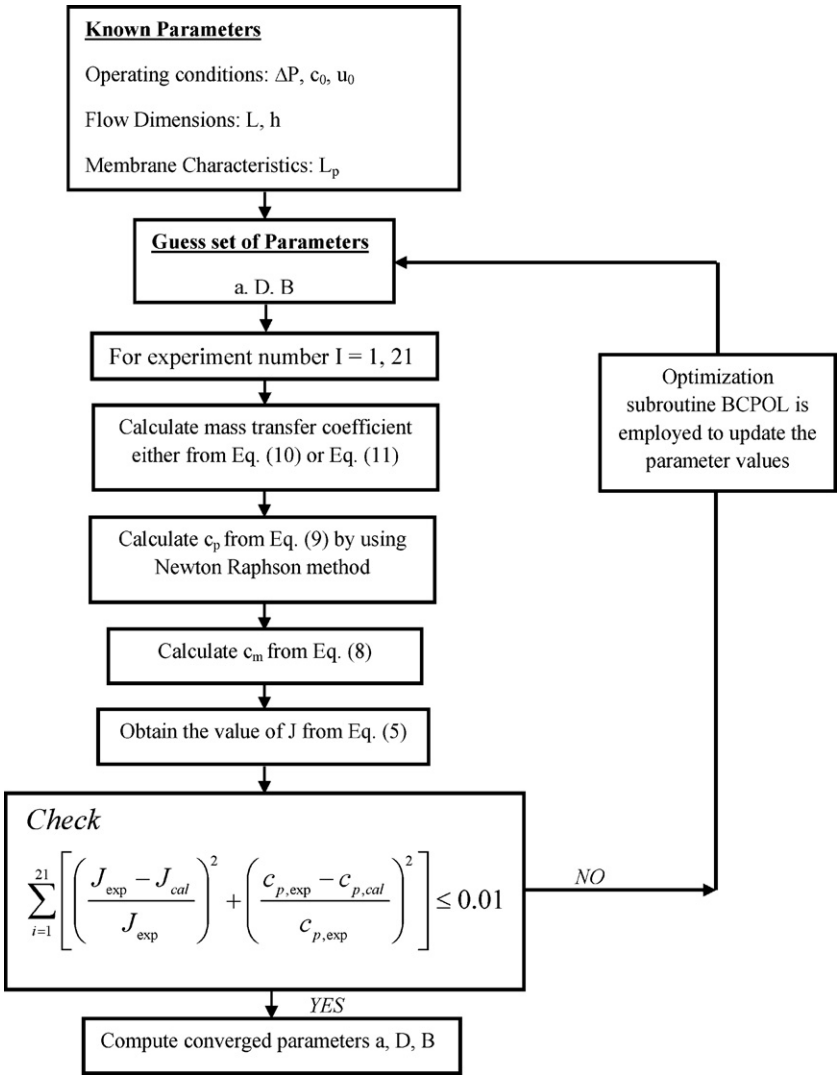

Fig. 2. Algorithm for estimation of parameters.

where, '*a*' is effective the osmotic coefficient. Using Eqs. (1)–(3), the permeate flux is described as,

$$J_{ss} = L_p[\Delta P - a(c_m - c_{p\,ss})] \quad (4)$$

According to stagnant film theory, the permeate flux is expressed in terms of mass transfer coefficient ($k = D/\delta$) as,

$$J_{ss} = k \ln\left(\frac{c_m - c_{p\,ss}}{c_0 - c_{p\,ss}}\right) \quad (5)$$

Combining Eqs. (4) and (5), the following expression is obtained,

$$J_w^0[1 - \alpha(c_m - c_{p\,ss})] = k \ln\left(\frac{c_m - c_{p\,ss}}{c_0 - c_{p\,ss}}\right) \quad (6)$$

where, $\alpha = a/\Delta P$ and $J_w^0 = L_p \Delta P$.

According to solution diffusion model, the solute flux through the membrane is proportional to concentration difference across the membrane surface. Therefore, the following equation is obtained,

$$J_{ss} c_{p\,ss} = B(c_m - c_{p\,ss}) \quad (7)$$

Combining Eqs. (1) and (7), and after algebraic simplification, the term c_m in terms of $c_{p\,ss}$ can be expressed as

$$c_m = c_{p\,ss} + \frac{c_{p\,ss}}{\alpha c_{p\,ss} + \beta} \quad (8)$$

Table 1
Characterization of fatliquoring effluent from tannery and effects of ferrous sulfate and calcium oxide dosing.

Properties	pH	Conductivity (S/m)	TDS (g/l)	COD (mg/l)	TS (g/l)	TSS (g/l)
Feed	4.15	1.18	7.8	13688	21.5	13.7
After ferrous sulfate dose (5 mg/ml)	3.79	0.85	5.9	8954	17.4	11.5
After CaO dose (1.5 mg/ml)	8	0.64	4.3	4921	15.7	11.4

The amount of oil and grease present in the fatliquoring effluent feed = 4000 mg/l.
The amount of oil and grease present in the fatliquoring effluent after two step coagulation = 12 mg/ml.

On substituting Eq. (8) in Eq. (6), the following nonlinear algebraic equation of c_p is obtained,

$$\frac{\beta J_w^0}{\alpha c_{p\,ss} + \beta} - k \ln\left[\frac{c_{p\,ss}}{(\alpha c_{p\,ss} + \beta)(c_0 - c_{p\,ss})}\right] = 0 \quad (9)$$

where, $\beta = B/J_w^0$.

The mass transfer coefficient under laminar flow conditions is given by Leveque's equation [16],

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

and that for turbulent flow is given by [16],

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

where, d_e is the equivalent diameter of the flow channel. For a thin channel, the value of d_e is $4h$, where, h is the half height of the channel. With a knowledge of the parameter values, i.e., D, a and B, Eq. (8) can be solved iteratively to obtain the value of c_p, c_m and permeate flux.

2.1. Numerical solution

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

$$S = \sum_{i=1}^{N}\left(\frac{J_{ss}^{exp} - J_{ss}^{calc}}{J_{ss}^{exp}}\right)^2 + \sum_{i=1}^{N}\left(\frac{c_{p\,ss}^{exp} - c_{p\,ss}^{calc}}{c_{p\,ss}^{exp}}\right)^2 \quad (12)$$

BCPOL subroutine of IMSL (International Mathematics and Statistics Library) library using unconstrained direct search algorithm is used for optimization and Newton–Raphson algorithm is employed for solution of Eq. (8). The algorithm for calculation is presented in Fig. 2.

3. Experimental

3.1. Membranes

Organic thin film composite (TFC) membranes consisting of a thin film polyamide skin over a polysulfone support with molecular weight cut off (MWCO) 400 is used for nanofiltration and reverse osmosis. All membranes are procured from M/s, Genesis Membrane Sepratech Pvt. Ltd., Mumbai, India. The permeability of the membrane is determined using distilled water and is found to be 2.84×10^{-11} m/Pa s for nanofiltration and 2.01×10^{-12} m/Pa s for reverse osmosis membranes.

3.2. Chemicals used

Commercial grade ferrous sulfate and calcium oxide is used for coagulation. The standard quality chemicals required for determination of COD are used without further treatment.

3.3. Effluent

The wastewater (effluent) used in this study was collected from the fatliquoring unit of M/s Alison Tannery, Kolkata, India. The characterization of the effluent has been carried out and is presented in Table 1.

3.4. Pretreatment

Pretreatment of the effluent is carried out with different dose of ferrous sulfate followed by calcium oxide. Gravity settling is allowed for one day. The optimum coagulant dose is determined by adding various amounts of coagulant and then measuring COD, TS, conductivity and TDS. The gravity settling is carried out in a 10 l 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.

3.5. 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 effective length of the membrane is 14.6×10^{-2} m and width is 5.5×10^{-2} m. 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, nine 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, TDS, conductivity and pH. The membrane module assembly is available elsewhere [17].

3.6. Operating conditions

The operating pressures for NF are 828, 966, 1104 and 1242 kPa and those for RO are 1313, 1448, 1586, 1724 kPa. The cross-flow rates are 60 (Reynolds number (Re) = 606), 90 (Re = 909), 120 (Re = 1212) and 150 l/h (Re = 1515). These cross-flow rates correspond to the cross-flow velocities as 0.1, 0.15, 0.2 and 0.25 m/s, respectively in laminar regime both with and without promoters and 0.7 (Re = 4242), 0.8 (Re = 4848), 0.9 (Re = 5454) and 1.0 m/s (Re = 6060) are used in turbulent regime.

3.7. Experimental procedure

A fresh membrane is compacted at a pressure higher than the maximum operating pressure for 3 h using distilled water and then its permeability is measured. The effluent is placed in a stainless steel feed tank of 2 l capacity. A high pressure reciprocating 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 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 cumulative volume versus time plot. The precision of flux measurement is ±5%. Duration of the cross-flow experiment is 1 h.

Once an experimental run is over, the membrane is thoroughly washed, in situ, with distilled water for 15 min at a pressure of 200 kPa. The cross-flow channel is then dismantled and the membrane is dipped in dilute acid solution for 3 h. Then, it is washed carefully with distilled water to remove traces of acid. 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 are conducted at a temperature of 32 ± 2 °C.

3.8. Analysis

The conductivity, total dissolved solids and 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 of all the samples are measured by taking a known volume of sample in a petridish and keeping in an oven maintained at 105 ± 2 °C till complete drying of the sample. Oil and grease present in water can be extracted in petroleum ether, which is immiscible in water and can be separated by using a separator funnel. The residue after evaporation of this petroleum ether will yield the oil and grease (4000 mg/l). COD values are determined using standard techniques [18]. Chemical analysis for fatliquoring effluent sludge is determined using standard methods [19]. Walkley and Black rapid titration method had been used for Organic Carbon measurements [19].

4. Results and discussion

4.1. Pretreatment

A major constituent of fatliquoring effluent contains wastewater emulsion, which includes fats, oils and grease. These emulsions result in fouling the membrane surface during cross-flow membrane filtration. The amount of oil and grease present in the fatliquoring effluent is found to be 4000 mg/l. Stringent rules are imposed on the treatment of this effluent due to presence of such high content of oils. Various chemical conditioning agents are tested and two coagulants are identified, optimum coagulant dosages are added one by one for treatment of this effluent. The pH of the fatliquoring effluent is 4.15. First an optimum dose of 0.5% (w/v) ferrous sulfate is added to the emulsified wastewater, which breaks the emulsion, and pH is slightly reduced to 3.8. Lowering the pH makes coagulation more effective but neutralization is necessary to make the effluent suitable for membrane separation process. So after acidification, calcium oxide of 0.15% (w/v) is added to raise the pH to 8. Addition of optimum coagulant dosage reduces the COD (64% reduction) significantly. The values of COD, TS and TDS obtained after sludge separation are 4921 mg/l, 15.7 g/l, and 4.3 g/l, respectively. The amount of oil and grease present in the pretreated fatliquoring effluent is found to be 12 mg/l. A noticeable improvement in color is observed after pretreatment. The properties of fatliquoring effluent (feed) from tannery and effects of ferrous sulfate and calcium oxide dosing are presented in Table 1. The sludge produced is dried, pulverized and analyzed for its fertilizer value. The amount of sludge generated is 47 g/l, which can be used as an organic fertilizer after drying. The results of chemical analysis of fatliquoring effluent sludge are given in Table 2. The supernatant liquor after a coarse filtration by a fine cloth is subjected to membrane filtration. The cloth filtered liquor is first subjected to nanofiltration and permeate thus obtained is subjected to reverse osmosis in the cross-flow mode. Similar pretreatment of soaking, liming, deliming-bating effluent using commercial alum prior to membrane filtration is already reported [20–22].

Table 2
Result of chemical analysis for fatliquoring effluent sludge.

Effluent	pH	OC (wt%)	N (wt%)	P (wt%)	K (wt%)
Fatliquoring sludge	7	20.1	0.26	0.17	0.25

4.2. Filtration in the cross-flow mode

Membrane processes operates by permeation. The objective of cross-flow or tangential flow filtration is to maintain a high velocity across the membrane surface to minimize particle deposition and membrane fouling. Here a portion of the concentrate stream is recycled to the system inlet and mixed with the incoming feed stream. The filtration experiments of the fatliquoring effluent are performed by modifying the most important operating variables like transmembrane pressure and tangential velocity.

4.3. Nanofiltration

Nanofiltration is a process that finds increased application in wastewater treatment processes. The experiments are conducted in three different flow regimes: laminar, laminar with promoter and purely turbulent. The flux decline behaviors of the effluent at 1242 kPa and different Reynolds number reveal that the time required to reach steady state decreases with an increase in Reynolds number. Flux decline is lower at high cross-flow velocities. Steady state is achieved faster for turbulent promoter compared to laminar flow. For example, the steady state is attained in about 253 s for Re = 1212 and 1242 kPa pressure, whereas at the same pressure and Reynolds number, the steady state is attained within 222 s in turbulent promoter assisted cases. Turbulent promoters create local turbulence and hence reduce the concentration polarization at the membrane surface. Similarly in turbulent region steady state is attained in about 180 s for Re = 5454 and 1242 kPa pressure.

The variation of steady state permeate flux with the transmembrane pressure drop is presented in Fig. 3. It may be observed from the figure, that permeate flux varies almost linearly with the operating pressure. As presented in Eq. (3), the variation of osmotic pressure is linear with concentration. As has been discussed in the

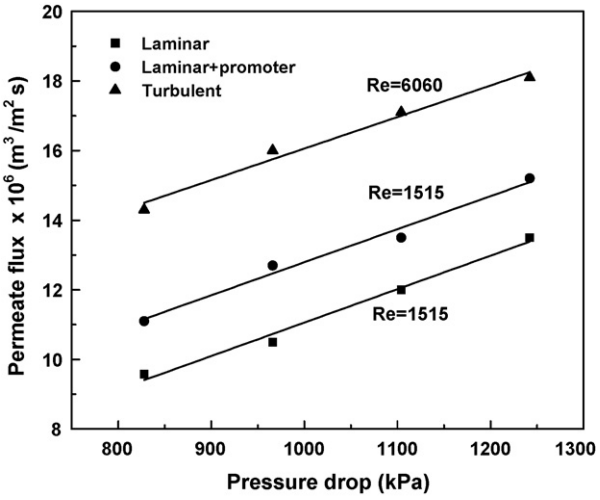

Fig. 3. Variation of permeate flux with operating pressure in NF.

Table 3
Permeate analysis after nanofiltration.

Serial no.	Pressure (kPa)	Reynolds no.	TDS (g/l)	TS (g/l)	TSS (g/l)	COD (mg/l)	Conductivity (S/m)
Turbulent regime							
1	828	6060	3.1	6.6	3.5	1353	0.55
2	966	6060	3.1	6.8	3.7	1315	0.6
3	1104	6060	3.1	7.1	4	1256	0.63
4	1242	4242	2.9	8.7	5.8	1403	0.53
5	1242	4848	2.9	8.2	5.3	1376	0.49
6	1242	5454	2.8	8.1	5.3	1214	0.47
7	1242	6060	2.7	7.8	5.1	1190	0.47
Laminar regime							
1	828	1515	4.3	8.4	4.1	2754	0.66
2	966	1515	4.2	8.7	4.5	2688	0.65
3	1104	1515	4.2	9.1	4.9	2593	0.63
4	1242	606	4.1	10.8	6.7	2937	0.62
5	1242	909	4.0	10.5	6.5	2871	0.61
6	1242	1212	3.8	9.7	5.9	2520	0.58
7	1242	1515	3.5	9.3	5.8	2406	0.53
With turbulent promoter							
1	828	1515	3.6	7.7	4.1	2316	0.64
2	966	1515	3.5	7. 8	4.1	2258	0.6
3	1104	1515	3.4	8.3	4.9	2229	0.54
4	1242	606	3.4	9.4	6	2400	0.6
5	1242	909	3.3	9.3	6	2368	0.56
6	1242	1212	3.2	9.2	6	2204	0.51
7	1242	1515	3.2	8.5	5.3	2134	0.48

later part of the manuscript, the concentration difference across the membrane ($c_m - c_p$) varies almost linearly with the operating pressure, the permeate flux exhibits a linear variation with the transmembrane pressure drop. Higher flux is achieved at higher pressure due to enhanced driving force. It can be observed that use of promoters leads to a significant flux enhancement compared to purely laminar flow regime. The permeate flux increases with increase in operating pressure and Reynolds number. The values of flux obtained in the turbulent regime is higher compared to laminar and turbulent promoter assisted cases due to the result of higher turbulence caused at high Reynolds numbers. For laminar flow regime, permeate flux varies in the range of $9.6–13.5 \times 10^{-6}$ m^3/m^2 s. The variation in laminar flow in presence of turbulent promoters and purely turbulent flow regime are $11.1–15.2 \times 10^{-6}$ and $14.3–18.1 \times 10^{-6}$ m^3/m^2 s, respectively. The use of turbulent promoters in laminar region results in substantial increase in flux of around 12–21% for NF. For example, at $Re = 1515$ the flux enhancement is 16% and 21% at 828 and 966 kPa pressures, respectively. For purely turbulent flow, flux enhancement is still higher compared to laminar flow. At $Re = 6060$ and 828 kPa, the percentage flux enhancement for purely turbulent case is about 51%. Similar steady state flux data have been obtained during nanofiltration of pretreated soaking, dyeing and tanning effluent. In the same range of operating pressure and flow regimes, permeate flux varies in between 2 and 10×10^{-6} m^3/m^2 s for soaking effluent [20]; $1–4 \times 10^{-6}$ m^3/m^2 s for tanning effluent [23] using the same membrane. The flux enhancement achieved compared to pure laminar flow regime is 25–40% for soaking effluent [20]; 30–57% for tanning effluent [23]. Cassano et al. [24] reported a flux decline from 5.6 to 1.4×10^{-6} m^3/m^2 s over a period of 30 min at 5–5.75 bar transmembrane pressure difference under recycle mode for nanofiltration of vegetable tanning effluent.

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 nanofiltration under various operating conditions are presented in Table 3 for laminar, laminar with turbulent promoters and turbulent cases. It can be observed from Table 3 that the TS values in the permeate decrease with Reynolds number and operating pressure in all the three flow regimes. With increase in Reynolds number, the membrane surface concentration becomes less due to forced convection, resulting in lower permeation of solutes (less TS) through the membrane. For example, in turbulent regime at an operating pressure of 1242 kPa, as the Reynolds number increases from 4242 to 6060 TS reduces from 8.7 to 7.8 g/l and TSS reduces from 5.8 to 5.1 g/l, respectively. Similar trend is also observed in case of laminar regime and laminar regime with turbulent promoters. It may be noted that at operating pressure 1242 kPa and $Re = 6060$, the permeate flux is found to be maximum and values of TS and TDS are the lowest. Therefore, at these operating conditions 10 l of permeate is collected from NF as a feed to RO.

The COD of the permeate remains comparatively very high in case of NF. The effect of transmembrane pressure and Reynolds number on permeate quality in terms of COD is presented in Table 3 for laminar, laminar with turbulent promoters and turbulent cases. It is observed that with an increase in transmembrane pressure and Reynolds number, the permeate quality improves. For example, at $Re = 1515$, COD value decreases from 2754 to 2406 mg/l for operating pressure 828 to 1242 kPa in the laminar region. The COD of the NF permeate is very high and therefore, an RO step is suggested to improve the quality of the final permeate.

The paper discusses the values of the parameters in terms of the composition of the effluent that help to scale up the system. Combination of osmotic pressure and solution diffusion model is used to calculate steady state permeate flux and permeate concentration values. The effective osmotic coefficient (a), solute diffusivity (D) and solute permeability (B) through the membrane are calculated by optimizing experimental flux and permeate TS values both for laminar and turbulent flow regimes as described in Section 2. The sum of error function, s (in Eq. (13)) is 0.25. The optimized values are: $a = (1.5 \pm 0.50) \times 10^4$ Pa m^3/kg, $D = (4.19 \pm 0.002) \times 10^{-10}$ m^2/s and $B = (2.73 \pm 0.30) \times 10^{-6}$ m/s. The feed to NF after pretreatment contains large amount of organic as well as inorganic solutes. Thus, the effective osmotic coefficient 'a' is less than that of salt, i.e., sodium chloride (about 8.5×10^4 Pa m^3/kg). This fact is supported by the diffusivity value as well. For sodium chloride, the diffusivity is 1.5×10^{-9} m^2/s whereas, the effective diffusivity obtained is one order of magnitude lower than that of sodium chloride. Since, the parameters a, D, B for the feed solution to NF, obtained by this method are independent of the flow regime, calculations are done

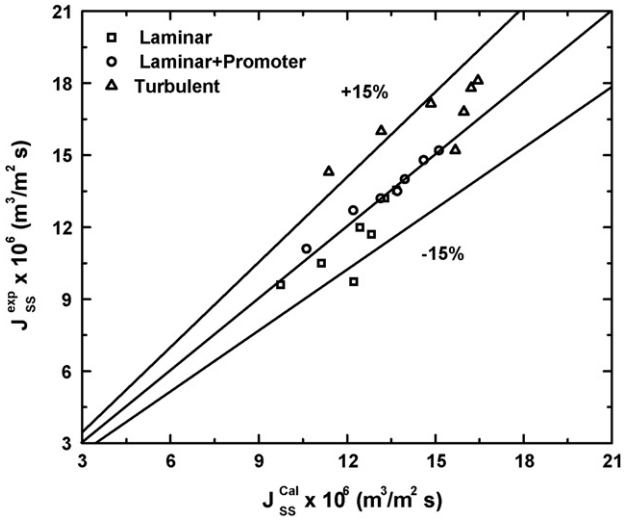

Fig. 4. Comparison between the experimental and calculated flux for different operating conditions in NF.

using these values of the parameters in case of laminar flow with promoters. But the expression of Sherwood number is not known in this case. Hence, the following expression of Sherwood number is considered,

$$Sh = \alpha_0 (Re)^n (Sc)^{1/3} \tag{13}$$

For all the seven experimental runs with turbulent promoters, optimization is carried out to evaluate the values of α_0 and n, which are found to be (1.19 ± 0.005) and (0.39 ± 0.07), respectively. From Eqs. (9) and (10), α_0 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. At these optimized parameter combinations, the comparison between experimental and calculated permeate flux and permeate concentrations are presented in Figs. 4 and 5 for all the flow regimes. It is observed from Fig. 4 that the calculated permeate flux values are within ±15% of the experimental data. The standard deviation between the calculated and experimental flux values is computed using the formula

$$\sigma = \sqrt{\frac{\sum (z_i - \bar{z})^2}{n_1}} \tag{14}$$

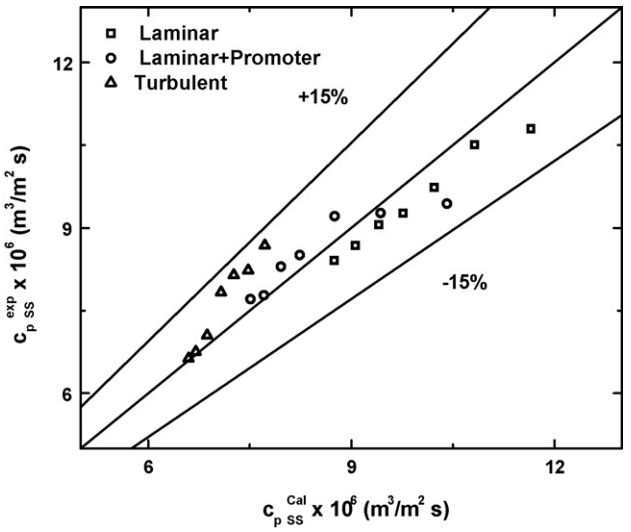

Fig. 5. Comparison between the experimental and calculated permeate (TS) concentration for different operating condition in NF.

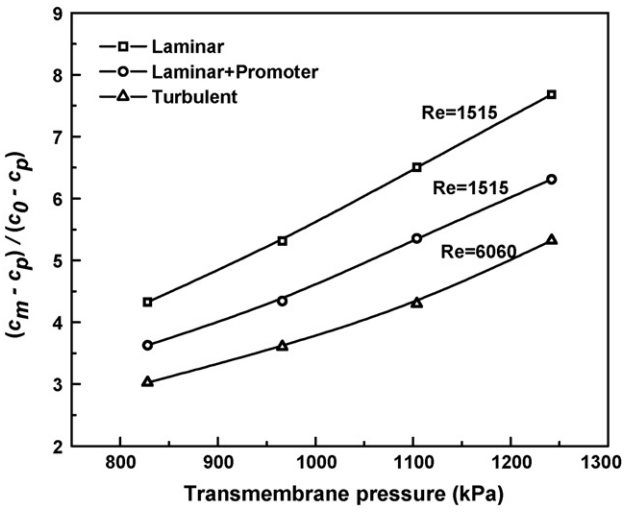

Fig. 6. Variation of polarization modulus with transmembrane pressure during NF.

where, z_i = ith calculated variable – ith experimental variable, n_1 = number of experiments. Variable refers to either permeate flux or permeate concentration. It is found to be 4.176×10^{-6} m^3/m^2 s. Between the experimental and calculated flux values the mean deviation about mean (M.D.) is computed using the formula

$$\text{M.D.} = \frac{1}{n_1} \sum \left| z_i - \bar{z} \right| \tag{15}$$

The mean deviation about mean value between the calculated and experimental flux values is found to be 8.1×10^{-7} m^3/m^2 s. Similarly, the standard deviation and mean deviation about mean value between the calculated and experimental permeate concentration values is found to be 0.41 and 0.25 g/l, respectively. The comparison between calculated and experimental permeate concentration (as total solids) is shown in Fig. 5. Here calculated permeate concentrations are within ±15% of the experimental data.

The separation of a solute by a membrane gives rise to an increased concentration of the solute at the membrane surface called concentration polarization. It has a negative influence on transmembrane flux. Polarization modulus is the extent of polarization on the membrane surface, which can be defined as $(c_m - c_p)/(c_0 - c_p)$. Concentration polarization cannot be completely avoided in any membrane based separation processes but its effects can be minimized. Variations of polarization modulus with transmembrane pressure are shown in Fig. 6. Polarization modulus increases with transmembrane pressure and decreases with channel Reynolds number for NF. On increasing turbulence using promoters or increased cross-flow velocity, membrane surface concentration as well as permeate concentration decreases leading to a decrease in polarization modulus. For example, at a pressure of 1104 kPa, the polarization modulus is 6.50 for laminar, 5.35 for flow with turbulent promoter and 4.29 for pure turbulent flow regime.

In case of NF, the variation of Sherwood number with Reynolds number for purely laminar, laminar with promoter and turbulent flow regimes are shown in Fig. 7. The Sherwood number for laminar region lies between 78.5 and 106.5 for *Re* between 606 and 1515. Similarly, the Sherwood number for turbulent region lies between 150.1 and 169 for *Re* between 4242 and 6060. Sherwood number relations are developed for the case of laminar flow with turbulent promoters. The Sherwood number for laminar with promoter case lies between 94.8 and 135.5 for overall *Re* lying between 606 and 1515. This indicates that using turbulent promoters, the mass transfer coefficient increases 1.2–1.27 times, compared to

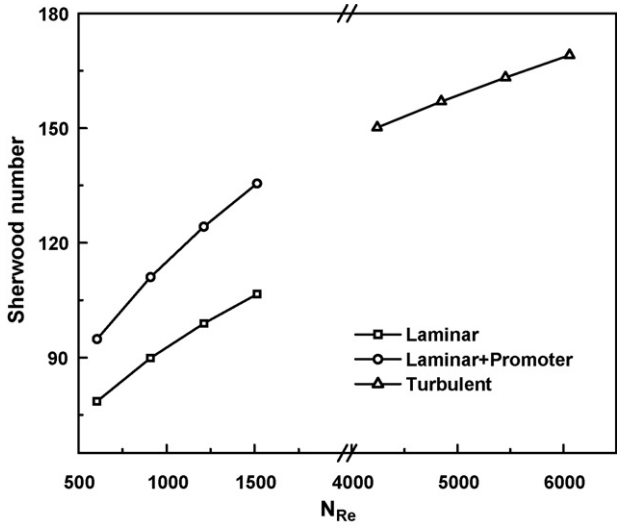

Fig. 7. Variation of Sherwood number with different flow regimes in NF.

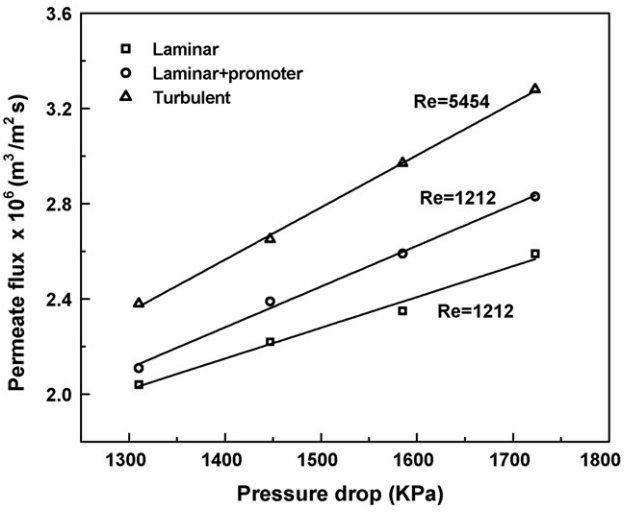

Fig. 8. Variation of permeate flux with operating pressure in RO.

entirely laminar flow. In pure turbulent flow, mass transfer coefficient increases 1.5–1.9 times, compared to laminar flow.

4.4. Reverse osmosis

Reverse osmosis is more useful and already recognized as an efficient technique for the separation of several inorganic and organic compounds, which find economic feasibility in industrial wastewater treatment process. The reverse osmosis membranes operate mainly by a solution diffusion mechanism. The flow of permeate through a reverse osmosis membrane depends on the applied pressure differential and the osmotic pressure drop across the membrane. Permeate from NF is collected and treated using RO in the cross-flow cell at different operating conditions. The nature of transient flux behavior is found to be identical to that of NF, i.e., the time required to reach steady state decreases with increase in cross-flow velocity. Similarly, the effects of applied pressure and Reynolds number are qualitatively the same as in NF, is presented in Fig. 8. For laminar flow regime, permeate flux varies in the range of 2–2.7 $\times 10^{-6}$ m^3/m^2 s. The variation in laminar flow in presence of turbulent promoters and purely turbulent flow regime are 2.1–2.9 $\times 10^{-6}$ m^3/m^2 s and 2.38–3.36 $\times 10^{-6}$ m^3/m^2 s, respectively. At *Re* = 5454 and 1586 kPa, the percentage flux enhancement is 26% with respect to laminar flow data. The treatment of nanofiltration permeate by reverse osmosis successfully retains the dissolved salts. Conductivity of permeate is very small suggesting that considerable amount of salt present in the feed has been retained by RO membrane. Similar steady state flux data have been obtained during reverse osmosis of nanofiltered soaking, dyeing and tanning effluent. In the same range of operating pressure and flow regimes, permeate flux varies in between 1 and 7 $\times 10^{-6}$ m^3/m^2 s for soaking effluent [20]; 0.5–4 $\times 10^{-6}$ m^3/m^2 s for tanning effluent [23] using similar membrane. The flux enhance-

Table 4
Permeate analysis after Reverse osmosis.

Serial no.	Pressure (kPa)	Reynolds no.	TDS (g/l)	TS (g/l)	COD (mg/l)	Conductivity (S/m)
Turbulent regime						
1	1313	5454	0.92	1.1	150	0.138
2	1448	5454	0.88	1	141	0.133
3	1586	5454	0.85	0.9	135	0.130
4	1724	4242	0.82	0.9	157	0.124
5	1724	4848	0.77	0.8	145	0.117
6	1724	5454	0.76	0.8	122	0.115
7	1724	6060	0.7	0.75	114	0.107
Laminar regime						
1	1313	1212	1.17	1.33	160	0.203
2	1448	1212	1.18	1.29	163	0.199
3	1586	1212	1.19	1.21	158	0.183
4	1724	606	1.25	1.3	210	0.197
5	1724	909	1.21	1.25	175	0.182
6	1724	1212	1.19	1.2	153	0.172
7	1724	1515	1.15	1.16	125	0.167
With turbulent promoter						
1	1313	1212	1.07	1.5	159	0.145
2	1448	1212	1.04	1.4	154	0.138
3	1586	1212	1.03	1.4	149	0.133
4	1724	606	1.01	1.2	174	0.130
5	1724	909	0.96	1.1	159	0.123
6	1724	1212	0.89	1.0	137	0.120
7	1724	1515	0.86	0.9	117	0.114

The amount of oil and grease present in the final treated fatliquoring effluent (i.e., after NF + RO) = 4–6 mg/l.
TSS in case of reverse osmosis is negligible.

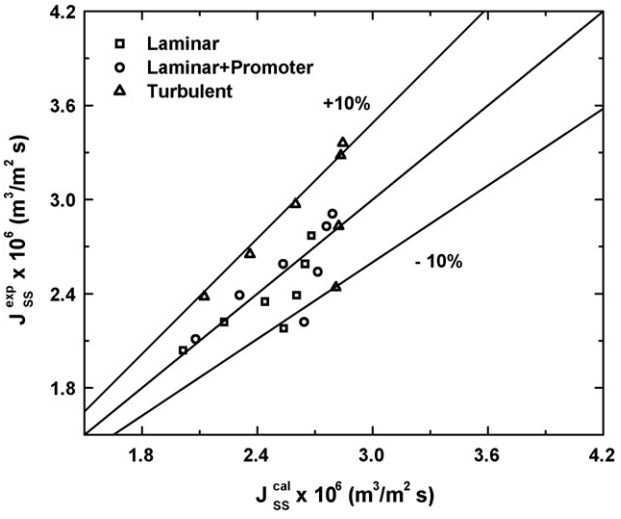

Fig. 9. Comparison between the experimental and calculated flux for different operating conditions in RO.

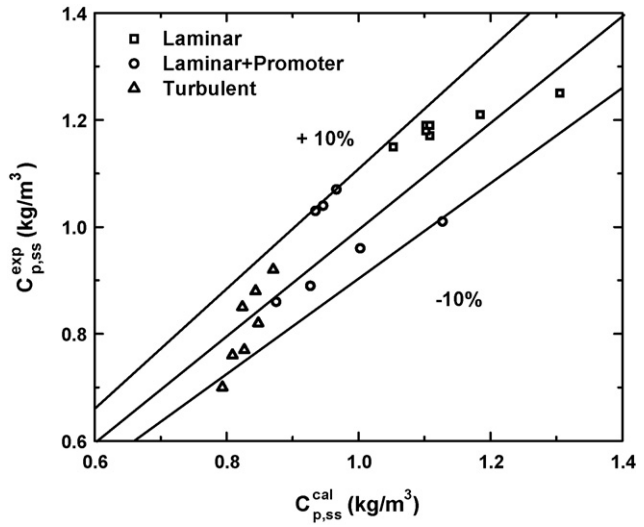

Fig. 10. Comparison between the experimental and calculated permeate concentration (TDS) for different operating condition in RO.

ment achieved compared to pure laminar flow regime is 30–40% for soaking effluent [20]; around 45% for tanning effluent [23].

In case of RO, variations of permeate COD, TS, TDS, and conductivity with transmembrane pressure at the operating Reynolds numbers in turbulent, laminar and laminar with turbulent promoter are shown in Table 4. The COD values reduce significantly with increase in Reynolds number. On increasing pressure more solvent passes through the membrane together with a fixed amount of the solute thereby permeate becomes purer increasing the permeate quality. The values of COD under different operating conditions are well within the discharge limit (250 mg/l) [18]. At 1724 kPa pressure and $Re = 1515$, the COD value is minimum (COD value is 125 mg/l for laminar and 117 mg/l for laminar with turbulent promoter case) with high permeate flux. However, at 1724 kPa pressure and $Re = 6060$ (under turbulent flow condition), COD value attains a minimum of 114 mg/l. At these operating conditions, the values of TS and TDS are found to be minimum.

Steady state permeate concentration is expressed in terms of TDS in case of reverse osmosis. Using all the experimental data in laminar and turbulent flow regime, the three parameters a, D and B are optimized as described in Section 2. The sum of error function, s (in Eq. (13)) is 0.196. The optimized values of these parameters are, $a = (6.19 \pm 0.021) \times 10^4$ Pa m^3/kg, $D = (1.00 \pm 0.0013) \times 10^{-10}$ m^2/s and $B = (4.54 \pm 0.10) \times 10^{-7}$ m/s. From these values, it may be observed that the osmotic coefficient is very close to that of pure sodium chloride (which is about 8.5×10^4 Pa m^3/kg). For Sherwood number correlation using promoters, the optimized value of α_0 is 0.91 ± 0.004 and that of n is equal to 0.41 ± 0.030. It is clear that these values of α_0 and n lie between the values correspond to pure laminar and pure turbulent flow regime. It may be noted that the values of α_0 and n are almost close in both NF and RO with turbulent promoter. Variation of calculated and experimental flux and permeate concentration for different operating conditions in RO are plotted in Figs. 9 and 10, respectively. It is observed from the figure that the calculated flux and permeate concentration values are within ±10% of the experimental data. The standard deviation and mean deviation about mean (M.D.) between the calculated and experimental flux values is computed using the formulas (14) and (15) and it is found to be 3.45×10^{-6} and 7.23×10^{-7} m^3/m^2 s. Similarly, the standard deviation and mean deviation about mean value between the calculated and experimental permeate concentration values is found to be 0.004 and 0.025 g/l, respectively.

The variation of polarization modulus with transmembrane pressure is plotted for RO in Fig. 11. Fouling causes resistance to flow through the membrane and eventual decline in overall flux. As in the case of NF, polarization modulus shows expected variation of increase with transmembrane pressure drop and decrease with Reynolds number. For example, at a pressure of 1724 kPa, the polarization modulus is 3.84 for laminar, 3.04 for flow with turbulent promoter and 2.2 for pure turbulent flow regime.

Sherwood number variations with Reynolds number in RO for purely laminar, laminar with turbulent promoter and turbulent flow regimes are shown in Fig. 12. The Sherwood number for laminar region lies between 126.5 and 171.6 for Re between 606 and 1515. Similarly, the Sherwood number for turbulent region lies between 241.7 and 272.2 for Re between 4242 and 6060. Sherwood number relations are developed for the case of laminar flow with turbulent promoters. The Sherwood number for laminar with promoter case lies between 155.8 and 226.18 for Re between 606 and 1515.

Once the pretreated effluent is treated with NF and RO, the resulting permeate stream can be reused as wash water or discharged safely to the environment. The amount of oil and grease present in the finally treated fatliquoring effluent is in the range of 4–6 mg/l which is within the permissible level, i.e., 10 mg/l [18].

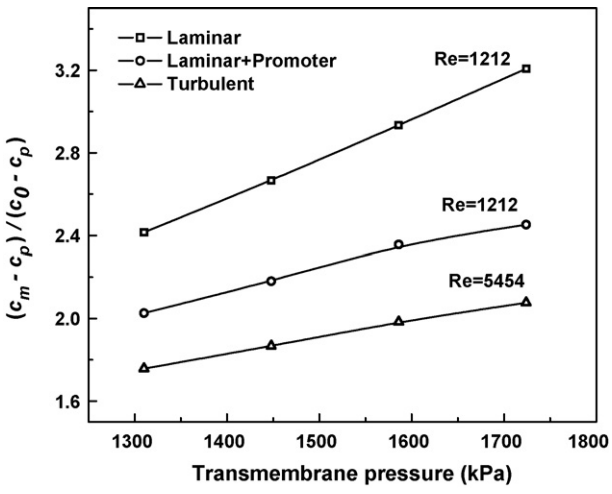

Fig. 11. Variation of polarization modulus with transmembrane pressure during RO.

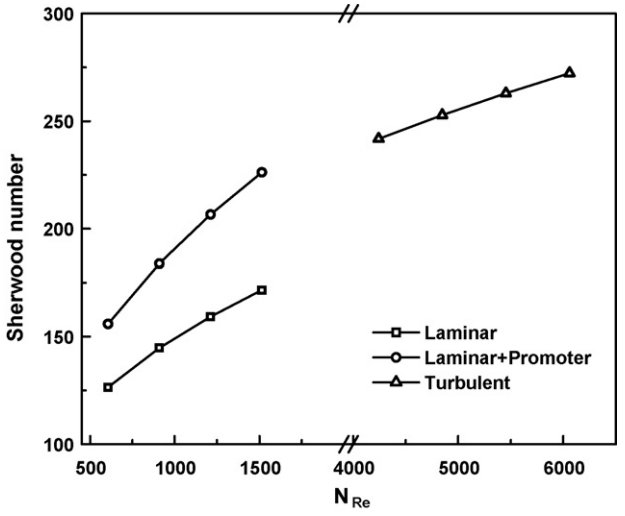

Fig. 12. Variation of Sherwood number with different flow regimes during RO.

The COD values of the permeate lies well within the permissible limit.

4.5. Estimation of operating cost

4.5.1. Cost of pretreatment per cubic meter of wastewater generated from fatliquoring effluent

As mentioned earlier, the optimum dosages of coagulant are 0.5% (w/v) of ferrous sulfate followed by 0.15% (w/v) calcium oxide. Commercial grade ferrous sulfate and calcium oxide are used for coagulation. The costs of ferrous sulfate and calcium oxide are 16 and 6 Rs/kg, respectively. Therefore, the cost for treatment of 1 m^3 of effluent is Rs. 90.

4.5.2. Cost of pumping during nanofiltration and reverse osmosis

The electrical energy per cubic meter of permeate during pumping into the membrane module can be calculated by Eq. (16).

$$E = \frac{Q\,\Delta P}{J_{ss} A \eta} \tag{16}$$

where, Q, ΔP, J_{ss}, A, η are the feed flow rate, pressure drop, steady state permeate flux, membrane area, efficiency of pump, respectively. Considering 70% pump efficiency, for nanofiltration operation the value of E ranges from 12 to 22 kWh/m^3 based on the operating conditions. Similarly, for reverse osmosis operation the value of E was in the range from 73 to 143 kWh/m^3. Based on the maximum value of E, electricity tariff for commercial purposes is Rs. 10 per kWh. For the maximum power requirement, i.e., 22 kWh/m^3 for nanofiltration and 143 kWh/m^3 for reverse osmosis total operating cost for membrane module is around Rs. 825.

5. Conclusion

The treatment scheme for the effluent exhausted from fatliquoring drain of a tannery includes a hybrid separation process involving gravity settling, coagulation, nanofiltration and reverse osmosis techniques. Treatment of NF permeate by RO successfully retains most of the dissolved salts. The transport coefficients namely the effective osmotic coefficient, solute diffusivity and solute permeability are estimated during nanofiltration as well as reverse osmosis of the pretreated fatliquoring effluent. The values are: $a = (1.5 \pm 0.50) \times 10^4$ Pa m^3/kg, $D = (4.19 \pm 0.002) \times 10^{-10}$ m^2/s and $B = (2.73 \pm 0.30) \times 10^{-6}$ m/s for NF case and $a = (6.19 \pm 0.021) \times 10^4$ Pa m^3/kg, $D = (1.00 \pm 0.0013) \times 10^{-10}$ m^2/s and $B = (4.54 \pm 0.10) \times 10^{-7}$ m/s for RO case. Combination of solution diffusion and osmotic pressure model are used to estimate the above transport coefficients. The solution methodology provides a basic calculation route to predict the system performance of a complex industrial effluent. For both NF and RO, the comparisons between the steady state experimental and calculated permeate fluxes demonstrate a close match (within ±15% for NF and ±10% for RO) between the two. The final permeate concentrations are well below the discharge limits.

Acknowledgement

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