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Selection of membrane separation processes for treatment of tannery effluent

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Abstract

Effluents from four units of a tannery, namely, soaking, liming, deliming-bating and dyeing were tested using molecular weight cut-off membranes in separation processes using a stirred cell in continuous mode. A suitable membrane was selected and the effluent was treated with the selected membrane, in a continuous cross flow cell. Various properties, namely, chemical oxygen demand (COD), biological oxygen demand (BOD), total solids, conductivity, etc, of the treated effluent were used to evaluate the efficiency of the treatment process.

Keywords: Tannery effluents, membrane separation processes, molecular weight cut-off, stirred batch cell, cross flow cell.

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Introduction

A typical tannery consists of several unit operations, namely, soaking, liming, deliming-bating, pickling, tanning, dyeing, etc. Each of these processes results in huge amount of effluent, which contains appreciable organic materials (mainly dissolved fats, flesh, keratin, bones, etc) and inorganic chemicals (various salts like sodium chloride, sodium sulfate, sodium sulfide, calcium hydroxide, etc) with high COD and BOD content. With increasing awareness of environmental conservation, government policy is increasingly stricter and proper treatment of industrial wastewater (including tannery effluents) has become an important social issue. Membrane based separation processes can have a key role in this regard and treatment of tannery wastewater using membrane separation is a field of active research in past few years. In recent years, membrane technologies have been developing rapidly and their cost is continuing to reduce while the application possibilities are ever extending [1, 2].

Research utilizing membrane separation technologies for tannery effluent have followed two distinct trends. First, effluents from different steps (except chrome tanning) are combined and subjected to membrane separations preceded by an adequate pre-treatment protocol. Thereafter, the common effluent is subjected to gravity settling, coagulation, and nanofiltration, followed by reverse osmosis to produce effluent having BOD and COD levels much lower than the permissible level [3, 4]. Sludge coming out of the coagulation step can be used as high quality fertilizer. Effluent from chrome tanning step containing toxic chromium to the level of 2000 to 4000 mg/l is treated separately to recover and reuse chromium and the treated effluent can either be discharged or reused. With tanning effluent being the most toxic in nature, research efforts have focused on methods to reduce its toxic load. These efforts have resulted in the availability of a plethora of membrane-based processes for the treatment of tannery effluent [5-12]. The second trend of research emphasizes that since each of the tannery steps results in the consumption of high levels of chemicals and the generation of large quantities of wastewater, effluent from each step should be treated separately using hybrid membrane separation processes, with an appropriate pretreatment method. In such cases, generated organic sludge can be used as fertilizer with the treated water being used in one of two applications. A chemical rich application can be recycled, thereby improving operating efficiency. The second application makes use of the low BOD and COD content with recycling to process water. This idea was first conceptualized by Cassano et al. [13] and has since appeared in multiple reports on research aimed at treatment of specific effluent. Das et al. [14] developed an integrated process including nanofiltration (NF) followed by reverse osmosis (RO) for treating

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soaking effluent. Further, several applications have been reported that include the use of ultrafiltration (UF) and RO for treating degreasing effluent [15, 16], UF and NF for treating effluent from liming and deliming-bating steps [17-19], and UF for colour removing leather dyeing effluent [20]. However, this latter application does not provide complete treatment of the dyeing effluent as the treated water contains high BOD and COD levels, although the use of NF followed by RO is a suitable application for removing dye, as well as COD and BOD [21].

Selection of membrane with an appropriate molecular weight cut-off (MWCO) is the heart of a membrane separation unit, with permeate flux and quality being important aspects in this regard. A high permeate flux is necessary for filtration to be economically feasible, and product quality should at least meet, or exceed, the level obtained by other standard treatment techniques. Permeate flux during filtration depends on operating condition (transmembrane pressure, temperature and turbulence), nature of membrane, molecular weight cut off, and the nature of the feed solution. Keeping the other factors constant, water flux increases with MWCO because the membrane permeability is proportional to the square of the pore radius [22].

The purpose of the present study was to identify optimal conditions for membrane separation processes used for the treatment of four tannery effluents, namely, soaking, liming, deliming-bating and dyeing. Performance of the selected membranes was evaluated by permeate flux, i.e. productivity of the process and permeate quality in terms of COD, BOD, total solids, conductivity, etc.

Materials and Methods

Effluents

Soaking, liming and deliming-bating effluents were collected from M/s, Alison Tannery, Kolkata, India, whereas dyeing effluent was collected from M/s, N. A. Trading, Bantala Leather Complex, Kolkata, India.

Membranes

Membranes of five MWCOs, namely, 1, 5, 10, 15 or 20 kDa were used, for UF. These membranes were supplied by, M/s, Permionics Membranes Pvt. Ltd., Gorwa, Vadodara, India. NF membrane with a MWCO 400 Da was supplied by M/s, Genesis Membrane Sepratech Pvt. Ltd., Mumbai, India. RO-TFC membranes with a MWCO of either 400 Da or 5kDa were procured from M/s, Permionics Membranes Pvt. Ltd., Gorwa, Vadodara, India. The composition and pure water permeability of the membranes employed in this study are provided in Table 1.

Table 1. Specifications of membranes used during filtration.

MWCO	Lp $\times 10^{11}$ (m/Pas)	Membrane material
20 kDa	5.85	Poly ether sulfone (PES)
15 kDa	5.1	Poly amide (PA)
10 kDa	4.20	Poly ether sulfone (PES)
5 kDa	3.91	Thin film composite (TFC)
1 kDa	3.35	Poly amide (PA)
400 Da	2.60	Thin film composite (TFC)

Chemicals

Commercial potassium-alum was used for coagulation. Chemicals required for COD and BOD determination were purchased from Merck Limited, India and Loba Chemie, India and were of analytical grade. All reagents were used without further treatment.

Stirred cell and operating conditions

Stirred experiments were conducted in a 650 ml capacity filtration cell in continuous mode. A 5-liter capacity feed tank was connected to a single cylinder-reciprocating pump that discharged to the cell. The stirrer speed was set using a variac (variable A.C. transformer for smooth control of voltage and thereby stirring speed) and was measured by a hand-held digital tachometer (Agronic, India). Inside the cell, a circular membrane was placed over a base support. The membrane diameter was 6.7 cm and the effective membrane area was 35.26 cm^2. Permeate was collected from the bottom outlet of the cell. A schematic of the experimental set up is shown in Figure. 1. The operating pressure used during experiment was fixed at 414 kPa and 828 kPa for UF and NF, respectively, with a stirring speed of 1000 rpm. The duration of each experiment was 45 minutes. All the experiments were conducted at a room temperature of 30 ± 2 ^oC.

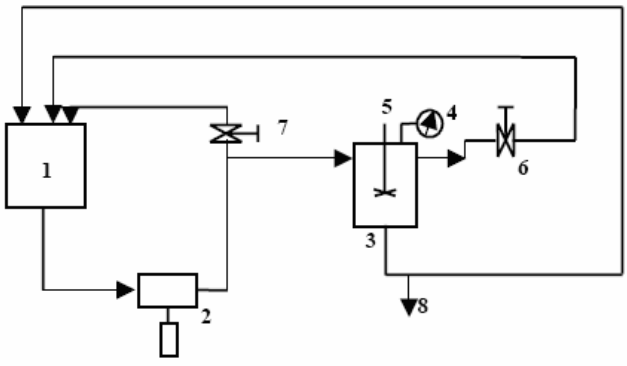

Figure 1. Schematic of the experimental setup: (1) Feed tank; (2) Pump; (3) Filtration cell; (4) Pressure gauge; (5) Stirrer; (6) Retentate valve; (7) Bypass valve; (8) Permeate sampling.

Cross flow cell and operating conditions

The cross flow cell consisted of two rectangular flanges with a grooved bottom flange and a polished mirror top flange. The membrane was placed on a porous stainless steel support in the bottom flange. The channel thickness was determined by thickness of a rectangular silicon rubber gasket (after tightening). The effective length of the channel was 26.1 cm, with a width of 4.9 cm. The height of the flow channel was 3.4 mm. The effective membrane area was 127.89 cm^2. The schematic of this cross flow cell has previously been reported [23]. The operating pressure was 414 kPa for all the UF experiments and 828 kPa for NF experiments. A pressure of 1725 kPa and 1655 kPa was used for soaking effluent and dyeing effluent, respectively, during RO experiments. A cross flow rate of 90 l/h was used in all the experiments.

Experimental procedure

The membrane was compacted first at a pressure higher than the highest operating pressure for 4 hours. During compaction of the membrane, water flux was measured continuously until a constant flux was achieved. Water flux was measured at different operating pressures. The membrane permeability was determined from the slope of the flux versus pressure curve. Next, the feed tank was filled with pretreated effluent and was pumped into the cell. Permeate from the bottom of the cell was collected in a beaker (50 ml capacity), where its cumulative weight was measured with the help of an electronic balance. The density of the permeate stream was measured, and the cumulative weights were converted to cumulative volumes. From the slope of the cumulative volume versus time curve, the permeate flux was obtained as a function of operating time. After each run, the feed cell and the membrane were washed thoroughly using distilled water. After treatment of soaking, liming, deliming-bating effluent, the membranes were dipped in 0.12 (N) HCl solution for three hours. After treatment of dyeing effluent, the membrane was dipped in 1% sodium dodecyl sulphate solution for 3 hours. Next, the membrane was carefully washed with distilled water to remove traces of acid or surfactant. The stirred continuous cell was reassembled and the membrane permeability was again measured using distilled water. It was observed that the membrane permeability remained almost constant between successive runs.

Analysis

Feed and permeate were analyzed for total solids (TS), total dissolved solids (TDS), conductivity, pH, chloride ion concentration, calcium ion concentration, dye concentration. Feed and permeate calcium and chloride were estimated by Orion Aplus™ Benchtop Ion Meter (supplied by M/s, Thermo Electron Corporation, Beverly, MA, U.S.A.) using ion specific electrodes. COD and BOD values of each stream were measured by standard techniques [24]. Dye concentrations in various streams of dyeing effluent were measured by UV Spectophotometer (make: Thermo Spectronic, USA; model: GENESYS 2). The wavelength at which maximum absorption occurred was 460 nm. The conductivities and TDS of all the streams were measured by an auto ranging conductivity meter (Chemito 130 manufactured by Toshniwal Instruments, India). pH of the samples was measured by a pH meter, supplied by Toshniwal Instruments, India. Total solids (TS) of all the samples were measured by standard technique.

Pretreatment

Characterization of effluent emerging from soaking unit was presented in Table 2. It was observed that the organic and inorganic content of this effluent was quite high. Therefore, direct treatment of effluent to the membrane unit caused clogging of membrane. To avoid this, a pretreatment was carried out. Supernatant from gravity settled effluent was subjected to coagulation by alum. Coagulation study using commercial potassium-alum was carried out with optimum alum dose of 2% (wt/vol) [14]. The clarified liquor was poured over a fine polypropylene cloth and then subjected to membrane filtration. This helped in retaining some of the larger coagulated particles still suspended in the clarified liquor.

Table 2. Characterization of soaking effluent.

	pH	Cond. (mS/cm)	TS (g/l)	TDS (g/l)	COD (mg/l)	BOD (mg/l)
Feed	10.5	53.8	56.8	35.1	9280	3569
After alum dose	7.25	48.5	43.1	32.3	4120	1585

The optimum alum dose for the treatment of both liming and deliming-bating effluent was found to be 2% (wt/vol) [17,19]. Various properties of liming and deliming-bating effluent were presented in Table 3 and 4, respectively.

Table 3. Characterization of liming effluent.

	pH	Cond. (mS/cm)	TS (g/l)	TDS (g/l)	COD (mg/l)	BOD (mg/l)
Feed	13.14	44.0	60.9	29.48	15040	5784.6
After alum dose	6.8	28.7	47.2	19.0	3500	1346

Table 4. Characterization of deliming-bating effluent.

	pH	Cond. (mS/cm)	TS (g/l)	TDS (g/l)	COD (mg/l)	BOD (mg/l)
Feed	10.4	56.1	46.6	36.9	8120	3123
After alum dose	7.25	24.0	44.3	15.9	2732	1050.8

Results and Discussions

Treatment of soaking effluent

Performance testing of various membranes

Pretreated effluent is subjected to the stirred cell in continuous mode using various MWCO of membranes, starting from NF (MWCO 400 Da) to UF (MWCO ranging from 1 kDa to 20 kDa). Transient flux decline behavior using various membranes is shown in Figure 2.

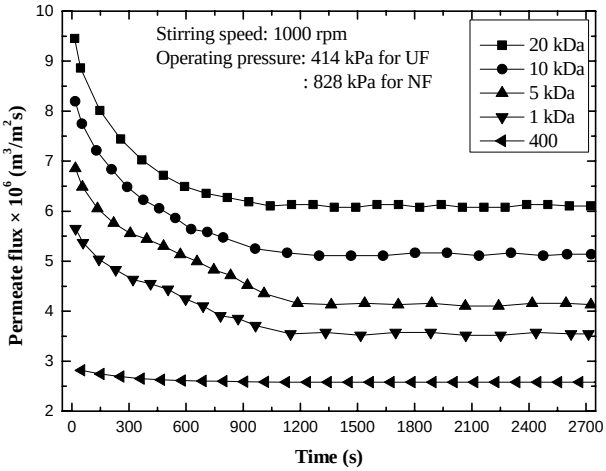

Figure 2. Flux decline of pretreated soaking effluent using various membranes.

In Fig. 2, operating pressure for all the UF membranes is 414 kPa and that for NF is 828 kPa. General trend for permeate flux profiles in Fig. 2 is that the flux decreases with the operating time. This is due to concentration polarization. As filtration progresses, solute particles deposit over the membrane surface, forming a polarized layer which grows in thickness. Some of the pores in the membrane are also clogged by the solutes. This is confirmed by observing the fact that pure water flux reduces when the same membrane is used without any chemical cleaning (cleaning by water only) just after the experiment. Combined effects of these phenomena lead to a decline in flux. It is observed that about 37% decline in flux occurs for 20 kDa MWCO membrane over the 20 minutes of operating time. This is about 37%, 40% and 37% for 10 kDa, 5 kDa and 1 kDa cut-off membranes. Interestingly, flux decline over the duration of the experiment for NF membrane is only about 9%. It may be pointed out that although the absolute flux increases from 1 kDa to 20 kDa cut-off membranes, the flux decreases steadily during the filtration time. On the other hand, for NF membrane, flux becomes almost constant beyond 10 minutes of operation. Since, the retentate and permeate streams are recycled to the feed chamber, both the feed volume and feed concentration remain unchanged and therefore, the value of steady state permeate flux remains same beyond 10 minutes as evident from Fig. 2. This indicates that the UF membranes having larger pore size (in the increasing order of 1 kDa to 20 kDa), they are more susceptible to pore clogging by the solute particles, resulting in steady decline in flux, although flux decline becomes gradual later on. For NF membrane, larger solute particles cannot enter the pores at all, leading to formation of a polarized layer over the membrane surface whose thickness remains constant by external stirring and hence almost a steady state flux is resulted beyond 10 minutes and flux decline is also minimum in this case. Suitability of a membrane separation process depends not only on its permeate flux, i.e., productivity but also on the permeate quality. It is observed from Table 5 that reduction in COD is only 1.2% in 20 kDa, 16% for 10 kDa, 24% for 5 kDa, 33% for 1 kDa and 78% for NF membrane. Total solid concentration in all UF membranes is almost insignificant (about 40 g/l TS concentration with respect to 43 g/l in the alum treated feed). But NF membrane shows about 26% retention of total solids. As expected, the TDS retention (i.e. retention of inorganic solutes) by UF membrane is marginal (comparing Table 2 and 5), whereas 400 Da NF membrane shows about 20% retention of inorganic solutes in terms of TDS. Therefore, as far as the quality of the permeate is concerned, NF membrane shows the most promising performance. Therefore, alum treated soaking effluent is treated using 400 Da MWCO NF membrane in a cross flow cell. In a cross flow cell, feed is allowed to flow tangentially over the membrane surface and hence the growth of the polarized layer of solutes over the membrane surface is more effectively controlled compared to a stirred cell. Therefore, the permeate flux and permeate quality are also expected to be improved in case of cross flow nanofiltration experiments compared to stirred cell experiments. Results of cross flow nanofiltration experiments at a typical pressure of 828 kPa and flow rate of 90 l/h are presented in Table 5a. It is observed from Table 5a that the steady state permeate flux of cross flow nanofiltration is 2.82×10^{-6} m^3/m^2s, whereas that in stirred cell is about $2.58\times10^{-6} m^3/m^2s$, indicating about 9% increase in cross flow mode. COD reduction also increases to 81%. Reduction in concentration in TS and TDS also increases to 30% and 28% in cross flow mode. It may be noted here that the permeate quality after NF is still not adequate to discharge in the sewage (discharge limit for COD is 250 mg/l and for BOD is 30 mg/l). For this, the

permeate from cross flow nanofiltration is subjected to RO (at 1725 kPa and 90 l/h cross flow rate). The quality of the permeate after RO is tabulated in Table 5a. It is observed from this table that after RO, COD and BOD values become 92 mg/l and 28.5 mg/l, respectively and both are within the permissible limit. Reduction in TS and TDS are about 85% and 81% with respect to original feed. Therefore, 400 Da MWCO NF membrane followed by RO should be the selected membrane process for the treatment of pretreated soaking effluent.

Table 5. Permeate properties of soaking effluent.

MWCO	COD (mg/l)	TS (g/l)	TDS (g/l)
20 kDa	4072	42.9	32.3
10 kDa	3451	42.5	31.2
5 kDa	3120	40.0	30.2
1 kDa	2744	38.6	30.0
400 Da	897	31.7	25.9

Table 5a. Properties of soaking effluent after membrane operations in cross flow cell.

	Pressure (kPa)	Flow rate (l/h)	Flux×10^6 (m^3/m^2s)	pH	Cond. (mS/cm)	TS (g/l)	TDS (g/l)	COD (mg/l)
NF	828	90	2.82	7.71	37.2	30.2	23.4	776
RO	1725	90	1.87	7.08	10.3	6.3	6.03	92.3

Treatment of liming effluent

Performance testing of various membranes

Pretreated liming effluent is subjected to various UF membranes and 400 Da MWCO NF membrane in a stirred cell. The profiles of permeate flux are shown in Fig.3. It is observed from the figure that the flux decline is due to concentration polarization and beyond about 5 minutes of operation, flux becomes steady state in all the cases. Attainment of steady state flux indicates that the pore blocking is completed quickly unlike the soaking effluent. Flux decline is 15% for 20 kDa, 13% for 10 kDa, 11% for 5 kDa, 9% for both 1 kDa and 400 Da MWCO NF membranes. Therefore, as far as flux decline is concerned, performance of 5 kDa, 1 kDa and 400 Da MWCO NF membranes is almost same. Regarding absolute flux value, 5 kDa UF membrane exhibits 60% more flux compared to NF membrane and 14% more flux compared to 1 kDa UF membrane. Quality of the permeate from various types of membrane is presented in Table 6. Reduction in COD is 1.1 % for 20 kDa, 32% for 10 kDa, 74% for 5 kDa, 75% for 1 kDa and 77% for 400 Da MWCO NF membrane. Therefore, as far as COD reduction is concerned, 5 kDa UF membrane shows almost same performance compared to 1 kDa UF and 400 Da MWCO NF membrane. 20 and 10 kDa UF membranes show almost no reduction in concentration of total solids. Whereas, 23% reduction in TS is observed in 5 kDa membrane. This value is 26% for 1 kDa UF and 30% for 400 Da MWCO NF membrane. Reduction in concentration of TDS is marginal for 20 kDa and 10 kDa UF membrane. This value is 25% for 5 kDa, 29% for 1 kDa and 36% for 400 Da MWCO NF membrane. Therefore, from the point of permeate quality, performance of 5 kDa UF membrane is almost equivalent to 1 kDa and NF membrane. Moreover, permeate flux is significantly more in case of 5 kDa UF membrane compared to 1 kDa UF membrane and 400 Da MWCO NF membrane. Therefore, 5 kDa UF membrane is selected as the possible membrane among the studied ones for treatment of liming effluent. Once this membrane is selected, using this membrane, a cross flow UF experiment is conducted (at 414 kPa and 90 l/h cross flow rate).

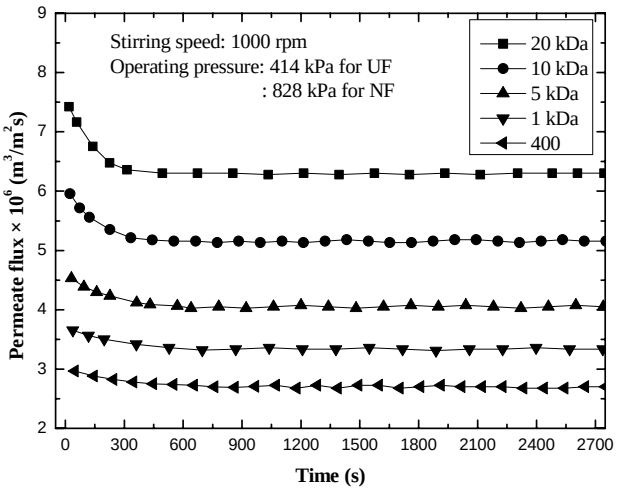

Figure 3. Flux decline of pretreated liming effluent using various membranes.

The results are shown in Table 6a. It is observed from this table that the steady state flux obtained is 4.71×10^{-6} m^3/m^2s which is 16 % more compared to that in the stirred cell (refer Fig. 3). 76% reduction in COD, 24% reduction in TS and 30% reduction in TDS is achieved. Therefore, the permeate quality as well as quantity are improved in cross flow ultrafiltration compared to stirred ultrafiltration. Still the COD (842 mg/l) and BOD (326 mg/l) values of the UF permeate are substantially higher than the permissible limit as mentioned earlier. Therefore, permeate from cross flow

ultrafiltration is collected and is subjected to NF using 400 Da MWCO NF membrane (at 828 kPa and 90 l/h cross flow rate). The permeate flux and quality are presented in Table 6a. It is observed that COD and BOD values are within the permissible limit. About 68% reduction in TS and 42% reduction in TDS are obtained in NF step compared to the feed to membrane separation processes. Thus, the pretreated liming effluent should be treated with 5 kDa UF membrane followed by 400 Da MWCO NF membrane.

Table 6. Permeate properties of liming effluent.

MWCO	COD (mg/l)	TS (g/l)	TDS (g/l)
20 kDa	3460	46.4	18.3
10 kDa	2390	46.3	18.1
5 kDa	921	36.2	14.2
1 kDa	860	35.1	13.4
400 Da	782	33.0	12.1

Table 6a. Properties of liming effluent after membrane operations in cross flow cell.

	Pressure (kPa)	Flow rate (l/h)	Flux×10^6 (m^3/m^2s)	pH	Cond. (mS/cm)	TS (g/l)	TDS (g/l)	COD (mg/l)
UF	414	90	4.71	7.44	20.2	35.8	13.3	842
NF	828	90	5.69	7.39	17.7	15.1	11.7	164

Treatment of deliming-bating effluent

Performance testing of various membranes

Pretreated deliming-bating effluent is subjected to UF of various cut-off membranes as well as NF with 400 Da MWCO membrane in a stirred cell. Profiles of permeate flux decline are presented in Figure 4. It is observed from Figure 4 that permeate flux declines over the duration of filtration and beyond five minutes of operation, flux attains a steady state. As discussed before, early attainment of steady state indicates early completion of pore blocking mechanism. Development of deposited (polarized) layer thickness is controlled by the external stirring. Decline in flux turns out to be 16% for 20 kDa, 14% for 10 kDa, 12% for 5 kDa, 10% for 1 kDa and 9% for NF membrane. Therefore, as far as flux decline is concerned, 5 kDa UF membrane shows slightly higher flux decline compared to 1 kDa UF and NF membrane. But with respect to absolute flux value, it delivers 22% more flux compared to1 kDa membrane and 61% more flux compared to NF membrane. Therefore, permeate quality of these three membranes have to be compared before final selection. Properties of the permeate of various membranes are listed in Table 7. It is observed from this table that reduction of COD is 6%, 17%, 77%, 78% and 80% for 20, 10, 5, 1 kDa UF and 400 Da MWCO NF membrane. Therefore, 5 kDa UF membrane shows almost equivalent performance in terms of percentage reduction of COD compared to 1 kDa and NF membrane. Reduction of total solids is insignificant for 20 and 10 kDa membranes. It is 44%, 49% and 52% for 5 kDa, 1 kDa and NF membrane. Reduction of total dissolved solids is 1.3%, 4.4%, 13.8%, 20.1% and 32.1% for 20, 10, 5, 1 kDa UF and NF membranes. Based on permeate quality and permeate flux, 5 kDa membrane is selected for treatment of deliming-bating effluent. The effluent is subjected to cross flow ultrafiltration using this membrane. The results are shown in Table 7a. It is observed from this table that flux and quality of permeate have been improved significantly when the cross flow system is used, compared to stirred ultrafiltration. But, COD and BOD values are still above the permissible level. To make the treated effluent disposable, ultrafiltered effluent is subjected to NF using 400 Da MWCO membrane (at 828 kPa and 90 l/h cross flow rate). The results are shown in Table 7a. It is observed from this table that the finally treated effluent is of dischargeable quality.

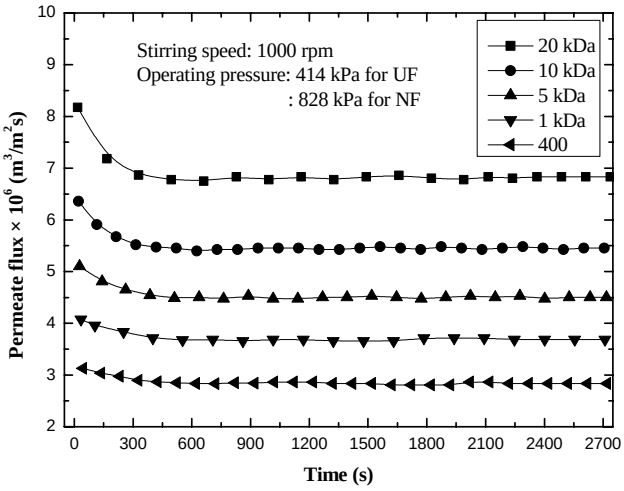

Figure 4. Flux decline of pretreated deliming-bating effluent using various membranes.

Table 7. Permeate properties of deliming-bating effluent.

MWCO	COD (mg/l)	TS (g/l)	TDS (g/l)
20 kDa	2564	42.1	15.7
10 kDa	2282	39.5	15.2
5 kDa	620	24.7	13.7
1 kDa	608	22.4	12.7
400 Da	540	21.2	10.8

Table 7a. Properties of deliming-bating effluent after membrane operations in cross flow cell.

	Pressure (kPa)	Flow rate (l/h)	Flux×10^6 (m^3/m^2s)	pH	Cond. (mS/cm)	TS (g/l)	TDS (g/l)	COD (mg/l)
UF	414	90	5.87	7.6	22.7	28.2	13.6	454
NF	828	90	6.09	7.87	13.4	17.7	8.74	92

Treatment of dyeing effluent

Effluent contains single dye with concentration 358 mg/l, with very high COD (14592 mg/l) and BOD (4169 mg/l) values. pH of the effluent is 5.83 and conductivity, TS, TDS, Cl^- concentration are 5.21 mS/cm, 29.2 g/l, 3.43 g/l, 4250 mg/l, respectively. Since, this effluent is generated after chrome tanning, it contains about 6 mg/l of toxic chromium. As dyeing is almost last step in a tannery, it does not contain huge amount of organic materials. High COD values are due to presence of chemicals and dye. Therefore, this effluent is not subjected to any pretreatment process and directly subjected to membrane filtration. Figure 5 presents the flux decline behavior of all the membranes.

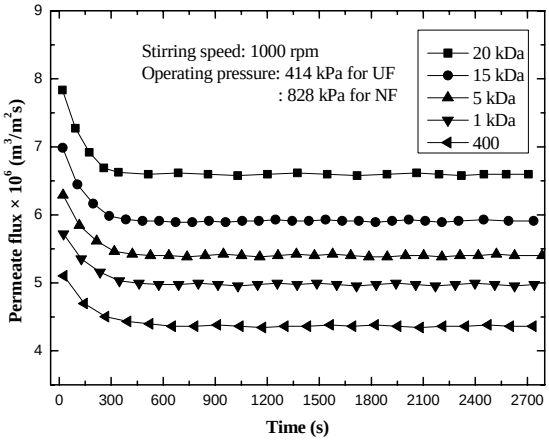

Figure 5. Flux decline of pretreated dyeing effluent using various membranes.

Flux becomes steady beyond five minutes of operation. As far as flux decline is concerned, all the membranes show a decline in permeate flux in the range of 13 to 16%. Therefore, a suitable membrane is to be selected based on the quality of the permeate. Permeate quality after various membrane systems is presented in Table 8. Percentage COD reduction is 3%, 7%, 12%, 17% and 89% for 20, 15, 5, 1 kDa UF membranes and NF membrane, respectively. Reductions in TS are 16%, 31%, 36%, 38% and 90% for these membranes. Retention of total dissolved solids is also maximum for NF membrane. Interestingly, NF membrane completely retains dye, whereas UF membranes show upto only 28% of dye retention (for 1 kDa membrane) as evident from Table 8. Chromium concentration is also zero in the permeate of NF membrane. Therefore, NF 400 Da MWCO membrane is selected for treatment of dyeing effluent. Results of the cross flow nanofiltration experiment with this membrane are presented in Table 8a. It shows improved flux (27.3%), less COD, TS and TDS with respect to stirred cell experiments. Although chromium and dye are completely removed by NF membrane, COD and BOD of the treated effluent are beyond the disposable limits. Hence, the NF treated effluent is subjected to cross flow RO and the permeate qualities are presented in Table 8a. It is clear from this table that RO treated water can safely be discharged. Therefore, 400 Da MWCO NF followed by RO should be the selected combination of membrane separation process for treatment of dyeing effluent.

Table 8. Permeate properties of dyeing effluent.

MWCO	COD (mg/l)	TS (g/l)	TDS (g/l)	Dye (mg/l)	Cr^{3+} (mg/l)
20 kDa	14216	24.6	3.2a	320	5.5
15 kDa	13520	20.1	3.0	295	5.2
5 kDa	12856	18.6	2.9	281	5
1 kDa	12160	18.0	2.8	256	4.7
400 Da	1657	3.0	2.3	0	0

Table 8a. Properties of dyeing effluent after membrane operations in cross flow cell.

	Pressure (kPa)	Flow rate (l/h)	Flux×10^6 (m^3/m^2s)	Dye conc. (mg/l)	pH	Cond. (mS/cm)	TS (g/l)	TDS (g/l)	COD (mg/l)	Cr^{3+} (mg/l)
NF	828	90	5.55	0	6.85	3.42	4.0	2.24	1272	0
RO	1655	90	6.13	0	7.6	0.27	0.3	0.18	32	0

Conclusions

A systematic study was carried out to select membrane based separation processes to treat the effluents discharged by four basic unit operations in a tannery. Pretreated soaking effluent can be treated by NF with 400 Da MWCO membrane followed by RO. Pretreated liming and deliming-bating effluents can be treated by UF with 5 kDa MWCO membrane followed by NF using 400 Da MWCO membrane. Dyeing plant effluent can be treated successfully by NF (400 Da MWCO) followed by RO.

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