Water Resources and Industry 3 (2013) 48–62

Contents lists available at ScienceDirect

Water Resources and Industry

journal homepage: www.elsevier.com/locate/wri

Combination technology of ceramic microfiltration and reverse osmosis for tannery wastewater recovery

Priyankari Bhattacharya [a], Arpan Roy [a], Subhendu Sarkar [a], Sourja Ghosh [a,*], Swachchha Majumdar [a], Sanjay Chakraborty [b], Samir Mandal [b], Aniruddha Mukhopadhyay [c], Sibdas Bandyopadhyay [d]

[a] *Ceramic Membrane Division, CSIR-Central Glass and Ceramic Research Institute, Kolkata-700 032, India*
[b] *Government College of Leather Technology, Salt Lake City, Kolkata-700 098, India*
[c] *Department of Environmental Science, University of Calcutta, 35 Ballygunge Circular Road, Kolkata-700 019, India*
[d] *Formerly of Ceramic Membrane Division, CSIR-Central Glass & Ceramic Research Institute, Kolkata-700 032, India*

ARTICLE INFO

Article history:
Received 3 July 2013
Received in revised form
2 September 2013
Accepted 12 September 2013

Keywords:
Tannery wastewater
Ceramic microfiltration
Reverse osmosis
Reuse
Leather

ABSTRACT

Treatment of highly contaminated composite tannery wastewater from common effluent treatment plant (CETP) was undertaken using indigenously developed ceramic microfiltration membranes. The effluent had a high load of organic and inorganic materials represented by about 5680 mg/L of chemical oxygen demand (COD), 759 mg/L of biochemical oxygen demand (BOD_5) etc. The current study proposed a dual stage treatment involving microfiltration (MF) followed by reverse osmosis (RO) compared to conventional process. The final water was fit for reuse in the tanning process. Organic loadings in terms of COD and BOD_5 values were below detection limit and turbidity was reduced to 0.025 NTU in the combined process. Reuse study was conducted using cow hide and leather properties were compared to that of control. Leather tanned with RO permeate had better tensile strength, stitch tear strength and grain crackness properties. Dye uptake was also more in case of leather tanned with RO permeate.

* Corresponding author. Tel.: +91 33 2473 3469/76; fax: +91 33 2473 0957.
E-mail addresses: sourja@cgcri.res.in, sourja.g@gmail.com (S. Ghosh).

2212-3717
http://dx.doi.org/10.1016/j.wri.2013.09.002

1. Introduction

Leather has many applications apart from leather goods such as for production of various cosmetics, fertilizers, etc. and is one of the most booming industries of today′s world. The raw material used consists of hide or skin of animals that undergoes various pre- and post tanning operations involving use of many chemicals. Conversion of leather takes place in aqueous medium containing acids, alkalis, chromium salts, tanning agents, oils, fats and salts, etc. As such, large amount of toxic effluent is produced having huge chemical oxygen demand and biochemical oxygen demand, suspended and dissolved solids, chromium, surfactants etc. [1,2]. Various treatment technologies have been proposed by the researchers worldwide to treat the toxic effluent. Raw vegetable tannery wastewater was treated following coagulation- flocculation method with poly aluminum chloride in alone and in combination with a coagulant [3]. The study resulted in successful removal of total suspended solids (TSS), COD and colour. In another study bittern was used as coagulant, ozone for oxidation and activated carbon for adsorption [1]. The combined process resulted in reduction of suspended solids, colour, turbidity, chromium, nitrogen, etc. Apart from these methods conventional activated sludge process has been studied for tannery wastewater treatment with significant removal of BOD_5 and COD alone [4] or, in combination with several physicochemical methods [5].

To overcome the drawbacks associated with conventional treatment processes scientists are constantly trying to reach for newer and cleaner technologies. Membrane processes gain importance in this regard. Successful treatment of tannery wastewater collected from beam house units was achieved with nanofiltration (NF) and RO [6]. Treatment and reuse of tannery wastewater produced in retanning process was studied by researchers [7]. Different steps including biological pretreatment, physico-chemical process using a polymeric coagulant and finally reverse osmosis with plane membrane was employed. The combination method resulted in satisfactory removal suitable for wastewater recovery and reuse. In another study, a combination process of filtration using a microfilter, ultrafiltration and reverse osmosis was used for treatment of a physico-chemically treated tannery wastewater [8]. Attempt was undertaken by scientists to treat tannery effluent from secondary clarifier containing huge amount of total dissolved solids and other impurities. Pre-treated effluent was subjected to pilot scale membrane system consisting of nanofiltration and reverse osmosis. About 98% removal of total dissolved solids was obtained while permeate recovery was about 78%. The treated water was used in wet finishing process of tanning [9]. Most of these studies are based on different organic membranes. However, the commonly used polymeric membranes have the drawbacks like lower thermal and acid–alkali resistance [10]. CSIR- Central Glass and Ceramic Research Institute have indigenously developed ceramic membranes from cost effective composition of clay and alumina. Ceramic membrane can operate at wide range of temperature and are stable at harsh environment of acid and alkali. They have narrow and well defined pore size distribution and excellent chemical resistance against strong cleaning agents which ensures stability of membrane performance for longer time [11]. Ceramic membranes have been effectively used for treatment of industrial and domestic wastewater [12,13].

In the present study an attempt was undertaken to treat, reuse and recycle the composite tannery wastewater with high organic loading. The work presented in this paper is aimed at reducing the various steps involved in conventional common effluent treatment plant to two steps and at the same time recycling the treated water for leather processing. In an earlier study, treatment and reuse of tannery wastewater was performed using polymeric ultrafiltration and reverse osmosis process [14]. In the present work the composite tannery wastewater which includes combined effluents collected from different units of pre- and post-tanning operations was treated using ceramic microfiltration process. The permeate produced from MF was subjected to RO as second step of treatment. Pretreatment is essential for RO process since fouling occurs in RO membrane due to hard scales and soft amorphous complexes present in wastewater. Scaling occurs due to super-saturation of RO brine with respect to salts having low solubility. Concentrations of total dissolved solids, crystallization of specific compounds etc. may result in formation of scales that develops at the back end of RO system where concentration is low and moves towards higher concentration in the front. Wastewater contains very fine suspended solids which can cause blocking of pores of the membrane which might be difficult to clean causing irreversible fouling. To prevent such fouling feed water of RO must have turbidity below 1 NTU. Hence pre-treatment is a necessity in RO process [8,15,16]. Low pressure membranes are one of the most viable, safe and cost effective means of pre-treatment to RO [17]. These membranes often reduce the process steps involved in conventional pre-treatment like coagulation, flocculation, sedimentation, etc. [18]. Quality of RO feed produced by using these membranes is far superior to conventional process. MF/UF polymeric membranes have been successfully used as RO pre-treatment of secondary clarifier effluent [19]. Ceramic membranes are widely used for treatment of food products, wastewater, industrial applications, etc. The ceramic MF membranes have high porosity and their pore structure is suitable for separation of turbid and colloidal contaminants from higher loading wastewater. As a result, the process produces permeate which are generally free from suspended solids and are suitable to be used as feed to the next stage RO process. Ceramic membranes have long shelf life, resistance to harsh chemicals, high working temperature and can be sterilized. Due to these reasons, instead of other physicochemical treatments the ceramic membrane based MF process was selected for pretreatment of raw tannery effluent [20,21].

The treated water was reused for tanning operation and its characteristics were compared with that of fresh water for process optimization. The RO permeate was used in each step of tanning process in collaboration with a well known tannery industry located in Kolkata, the capital city of West Bengal in India. After tanning, the finished leather was subjected to various physical and chemical analyses to compare the finished product quality with that produced using fresh water.

2. Materials and methods

2.1. Characterization of wastewater

The composite tannery wastewater was collected from collection pit of common effluent treatment plant located at Kolkata. Immediately after collection, the wastewater was subjected to

Table 1
Characterization of untreated, MF and RO treated permeate.

Parameters	Raw composite effluent	MF permeate	MF retentate	RO permeate	RO retentate
pH	8.5	8.22	8.41	8.2	8.24
COD (mg/L)	5,680	520	780	BDL	200
BOD_5 (mg/L)	759	69	519	BDL	33
Turbidity (NTU)	285	0.785	308	0.025	45.2
Conductivity (μS/cm)	1,342	1188	1389	649	985
Salinity (ppt)	6.5	6.1	6.9	0.33	4.8
TOC (mg/L)	514	180	579	2.4	490
TKN (mg/L)	2.87	0.98	2.98	BDL	0.7
TSS (mg/L)	1,690	64	292	BDL	200
TDS (mg/L)	8,500	6224	7250	448	8015
TS (mg/L)	10,140	6090	7604	451	8110
Fe (mg/L)	150	11.0	9.4	ND	2.4
Ca (mg/L)	2,980	108.1	88.8	1.5	143.5
Mg (mg/L)	677	69.6	60.4	2.75	102.5
Na (mg/L)	17,420	2262.8	1947.7	354.02	2949.3
K (mg/L)	191	23.1	18.9	3.34	30.0
Mn (mg/L)	26	0.3	0.3	ND	0.1
P (mg/L)	165	53.4	5.6	0.09	4.5
Cr (mg/L)	521	0.7	1.6	0.09	1.6
Cu (mg/L)	2	0.4	0.7	0.01	0.8
Pb (mg/L)	7	0.6	0.3	0.03	0.7
Zn (mg/L)	19	17.4	1.0	0.06	1.7
S (mg/L)	2,860	207.4	106.3	14.37	464.8
Co (mg/L)	1	0.1	ND	ND	ND
Ni (mg/L)	5	0.3	0.4	0.04	0.7
Cl (mg/L)	6,580	5024	6475	1121	5250
Protein (mg/L)	3,520	562	957	21	72
Sulphide (mg/L)	185	ND	124	ND	22

characterization as shown in Table 1. All the analysis was performed as per standard methods of water and wastewater analysis APHA [22]. pH, turbidity, biochemical oxygen demand (BOD_5), salinity, conductivity and total dissolved solids were analyzed using instruments by HACH, USA. Chemical oxygen demand was performed in COD digester by Spectralab, India. Total organic carbon was analyzed in TOC analyzer, Shimadzu, Japan. Total kjeldahl nitrogen (TKN) was analyzed in Nitrogen analyzer by Pelican Instruments, India. Heavy metals were analyzed in atomic absorption spectrophotometer by Perkin Elmer, USA.

2.2. *The dual stage treatment process*

Crossflow microfiltration (MF) process based on indigenously developed ceramic membranes was selected as the first stage of treatment. The membrane was of tubular configuration. In each membrane element there were 19 numbers of circular channels of 4 mm inner diameter each. The study was conducted in bench scale set up with length of the ceramic tube being 200 mm and 35 mm outer diameter. The porosity of the ceramic element was 36% and filtration area of 0.0512 m^2. The ceramic membranes had high chemical and mechanical resistance. For the present microfiltration study about 8 L of feed was taken in 10 L capacity stainless steel tank. The ceramic membrane was encased in tubular stainless steel housing of 200 mm length and 60 mm outer diameter. The complete module was fitted horizontally in the set up. Feed was passed tangentially through the membrane at high flow rate. Permeate solution was collected through a small port at the bottom of the membrane module. The feed was circulated without pressure for about 30 min before membrane operation. The study was conducted in continuous mode where permeate produced was collected at regular intervals and new feed was added continuously. At the end of the experiment total volume of feed added and volume treated, was noted. Experiments were conducted at different transmembrane pressure (TMP) of 0.4–2.2 kg/cm^2 to observe the effect of operating pressure on the permeate flux with crossflow velocity of 1 m/s. After selecting 1.0 kg/cm^2 as optimized pressure, continuous study was conducted at this pressure. The study was continued for 8 h per day with total 15 days. After completion of experiment the system as well as the ceramic membrane was cleaned thoroughly with 0.1(N) acid and alkali solution, respectively, followed by washing with deionised water at high velocity and low pressure. The ceramic membrane surface was characterized by field emission scanning electron microscopy (FESEM) using an instrument of Jeol, Japan.

Permeate collected from the MF process was treated further using reverse osmosis. The spiral wound RO membrane was made of thin film composite polyamide material and was housed in stainless steel pressure vessel. The module had an effective area of 1.40 m^2. The feed was taken in 50 L feed tank made of high grade polymer. The RO reject was returned back to the feed tank of RO process for complete recycling of wastewater. Permeate was collected from one end of the module. The pump capacity was 36 LPM (liter per minute) at 40 kg/cm^2 pressure. The RO experiments were carried out at varying operating pressure of 1.75–14.0 kg/cm^2. Effect of time on permeate flux profile was observed at an operating pressure of 7 kg/cm^2. After completion of experiments the RO membrane was cleaned first by passing 2% citric acid solution (pH 4) for 1 h without pressure to remove the deposited particles. This was followed by washing the unit with deionised water and then by 0.1% EDTA solution at pH 11 for 1 h. A 0.1% NaOH solution was used for removal of biofoulants due to tannery wastewater. Finally the whole unit was washed by circulating deionised water for 1 h without any pressure.

The total experimental work has been demonstrated in schematic diagram (Fig. 1).

2.3. *Reuse of treated water in leather processing*

To conduct the reuse study cow hides were taken and cut into two equal halves. One half was taken for reuse experiments and the other half as control. The hides of approximately equal weight was taken and subjected to tanning process in two separate drums. The treated water sample from RO process was used as experimental and fresh water was used as control. Both the samples were weighed equal to the weight of hides and 1.5% w/v oxalic acid was added for deliming of skin (pH 2.8). Tanning was carried out by treatment with various enzymes, syntans, fish oil, etc. to smoothen the

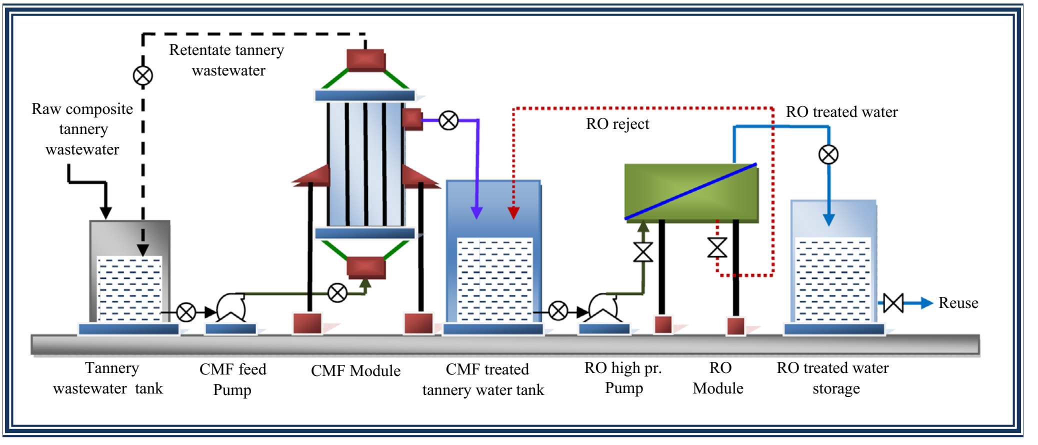

Fig. 1. Schematic representation of experimental work.

grain of leather a soft and flexible product. This operation was conducted for about two and half hours followed by neutralization to pH 4.5. Tanning is done to convert collagen protein of hide into stable material whereby it will not putrefy and be stable under conditions of heat and moisture. The next step was dyeing which is done to give the leather its colour. For making the leather soft and moisturized the hide skins were soaked in resin syntans and fats, etc. Dyes were selected according to the requirement of the industry. After dyeing process was completed the hide skins were preserved using preservative and formic acid. The wet leathers were then subjected to various steps like sammying where the hides are pressed to remove excess water. This was followed by setting and hanging overnight in vacuum for further drying. The leathers were then conditioned, stacked and buffered to cover up any imperfections that might have resulted. Pigment finish was applied to the crust to seal the colour and giving leather more protection and durability. The finished leathers were then tested for physical strength and chemical properties.

3. Results and discussions

3.1. Crossflow microfiltration study

The composite tannery effluent was first treated using ceramic membrane based microfiltration process. Experiments were performed with feed having 5 different initial COD values and the average data was represented in Table 1. From Table 1 it was observed that about 91% reduction in COD and BOD_5 was achieved. Turbidity of treated water reduced to below 1 NTU. Tannery effluent has high TKN value due to use of animal skin, hides etc. By MF process about 66% reduction of TKN was achieved. In the study of Majouli et al. [23], tubular microfiltration membrane made of cordierite/zirconia and alumina was used for treatment of beam house effluent. They obtained about 60–65% reduction of COD and 57–59% reduction of TKN.

Interestingly, complete removal of sulphide was achieved in the MF process itself. TOC reduction was about 65%. All the parameters when measured for retentate showed that maximum removal of organic and inorganic materials occurred in MF process which contributed to maximum retention. This also resulted in reversible fouling which was evident from the flux data. Fig. 2(a) suggested that in general, with increase in feed COD value, flux decreases. For a particular feed with COD value 5218 mg/L, after operation for about 7000 min at 1 kg/cm^2 transmembrane pressure, the permeate flux decreased from 47 kg/cm^2 to 34 kg/cm^2. To observe the effect of pressure on permeation flux, MF study was conducted at varying pressure (Fig. 2b) of 0.4–2.2 kg/cm^2. As expected, flux value increased with increasing pressure for feeds with different loadings. For feed COD of 5218 mg/L, at an operating

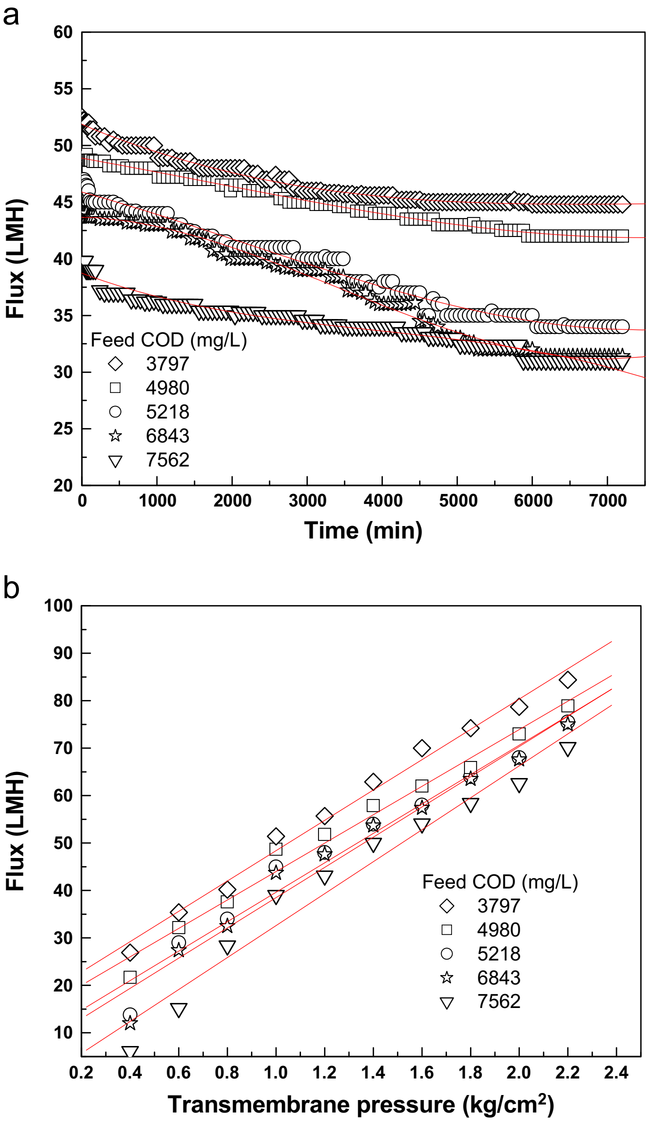

Fig. 2. (a) Effect of time on permeate flux of composite tannery effluent during crossflow microfiltration study (TMP: 1 kg/cm^2) and (b) effect of varying pressure on permeate flux of composite tannery effluent during crossflow microfiltration study with varying initial COD.

pressure of 0.4 kg/cm^2 permeate flux was about 15 LMH (liter per meter square-hour, L/m^2/h) which increased to about 80 LMH corresponding to an increased operating pressure of 2.2 kg/cm^2. Water recovery was about 80–85% in MF process.

3.2. Characterization of the ceramic surface before and after MF study

Fig. 3(a) represented ceramic membrane surface before membrane filtration which indicated presence of clear and open pores on the surface. In Fig. 3(b) the membrane surface after filtration with tannery effluent was shown which reflected smooth surface compared to the initial rough structure,

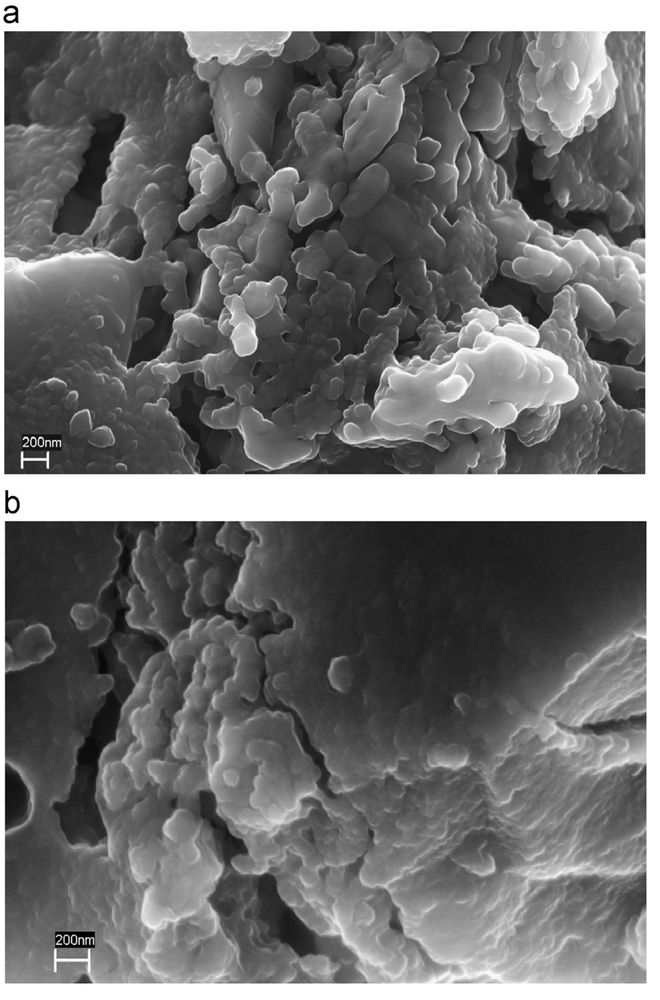

Fig. 3. (a) FESEM image of ceramic membrane surface before MF study and (b) after MF study with composite tannery effluent.

including many of the pores closed. This was obvious since composite tannery effluent had a high organic load in addition to the suspended and dissolved solid materials. Adsorption of the solid matter could take place on the membrane surface with blocking of the pores which could be explained by the decline in permeate flux during the MF study. For a better understanding, energy dispersive X-ray spectroscopy (EDX) analysis of this membrane surface was obtained (Fig. 4) which indicated presence of toxic heavy metals like chromium as well as, other inorganic constituents like sulfide, chloride, and iron in greater amount. These results explained the possible removal of chromium and other inorganic salts from wastewater by microfiltration membrane i.e. the cake formed on membrane surface acted as adsorbent that retained the organic and inorganic constituents and the resultant permeate was free from these toxicants.

3.3. Reverse osmosis study

RO process was incorporated with MF in order to ensure a complete treatment and to obtain a treated water quality suitable for water reuse with reduced concentration of dissolved salts and metallic components. The permeate produced from RO study (Table 1) had negligible concentration of

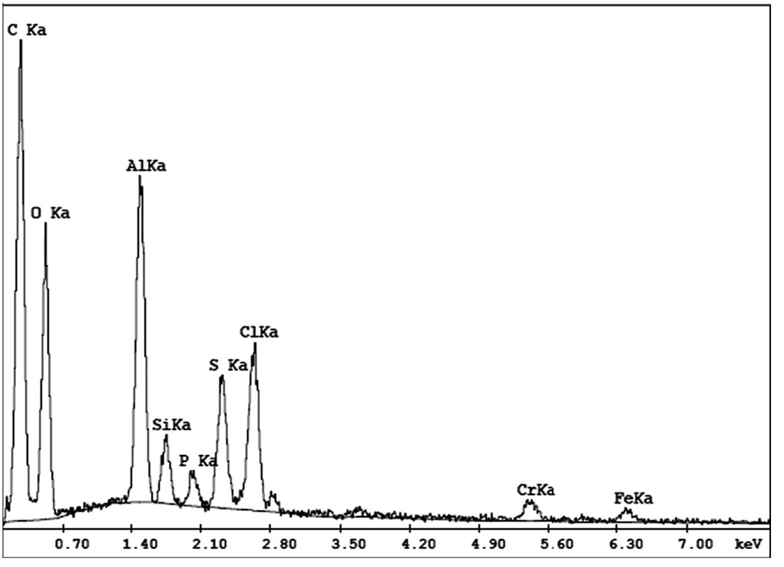

Fig. 4. EDX analysis of membrane surface after MF study with composite tannery effluent.

COD, BOD_5, TKN and TSS. Turbidity was about 0.025 NTU. About 99% reduction of TOC was obtained. Most of the metals like lead, copper, chromium, zinc and nickel, etc. were almost removed by RO process. There was reduced presence of sodium and chloride in RO permeate stream with about 95% reduction in the total dissolved solids. The retentate characteristics clearly revealed that maximum organic and inorganic substances were retained by RO membrane and as such, the permeate was free from those substances.

Similar results were obtained by Scholz et al. [24] who used a combined treatment of MBR and RO resulting into 90–100% reduction of COD, BOD and ammonia for mixed tannery effluent. Salt content was reduced to 97.1%. Reuse of tannery wastewater was studied by Ranganathan and Kabadgi [25]. In this study conventional treatment methods like neutralization, clari-flocculation and biological processes were used as pre-treatment before RO process. About 93–98%, 92–99% and 91–96% removal of TDS, sodium and chloride, respectively, were achieved for 5 different tanneries. 70–85% of water could be recovered and recycled. Krishnamoorthi and Saravanan [26] obtained 96% removal of COD and 97% of ammonia and nitrate by combined process of conventional activated sludge and RO. Considering these results, it may be concluded that the present two-step membrane filtration approach has substantial potential in treatment of higher loading tannery wastewater for its subsequent reuse.

The permeate flux profile of five different feed (MF permeate) with varying initial COD values was shown in Fig. 5(a) obtained after operation of membrane for 2500 min. Similar to MF process, higher COD value of feed resulted in lower permeation flux due to increased feed concentration. The figure indicated a decline of about 8% from an initial flux of 10 LMH for a feed with initial COD value of 472 mg/L at 7 kg/cm^2 (100 psi). Pressure variation between 1.75–14.0 kg/cm^2 showed an increase in flux with increasing pressure (Fig. 5b). The permeate produced was found suitable for reuse in leather tanning operations. The overall water recovery from RO process was about 65–75% with respect to the feed volume and volume of treated water produced.

3.4. Statistical data analysis

Data obtained from experiments conducted were analyzed statistically describing the effect of time and transmembrane pressure on permeate flux using computer programmes Statistica for Origin 8.5. Effect of time on permeate flux (Fig. 2a) for MF after 7200 min (120 h) of operation followed third

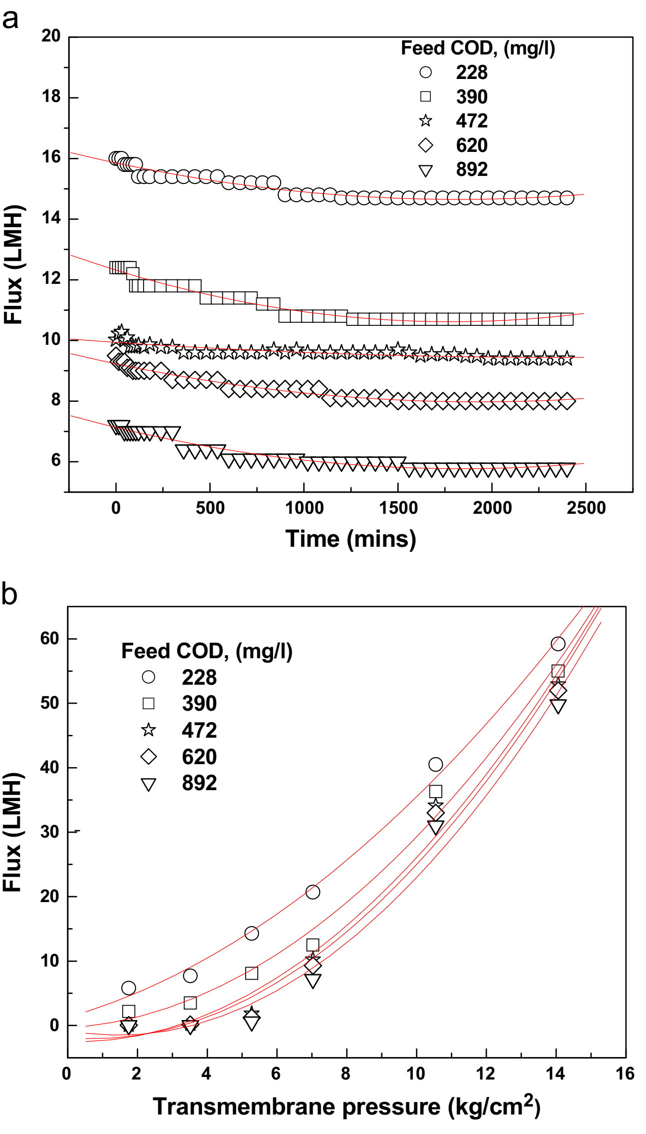

Fig. 5. (a) Effect of time on permeate flux during reverse osmosis study using MF permeate as feed (TMP: 7 kg/cm^2) and (b) effect of varying pressure on permeate flux during reverse osmosis study using MF permeate as feed with varying initial COD.

order polynomial as best fit for all COD values. Fig. 2(b) depicted that flux increased linearly with increasing pressure. In case of RO, effects of time on permeate flux showed polynomial second order behavior (Fig. 5a) after 40 h of operation. The effect of transmembrane pressure on flux showed best fit with second order polynomial behavior (Fig. 5b). Different parameters along with the correlation coefficient and standard error values were represented in Tables 4–7.

From the *t*-value (Table 4) it was observed that the quadratic effect of time was most significant on the MF process for initial COD value of 3797 mg/L whereas cubic effect was most significant for other COD values. From Table 5, *t*-value suggested that effect of pressure on flux was linear. In case of RO process the *t*-value (Table 6) represented that the time had significant quadratic effect on flux for

Table 2
Physical results of leather produced by conventional method and RO permeate.

Leather	Tensile strength (kg/cm^2)	Stitch tear strength (kg/cm)	Grain crackness (kg/cm)		Percent elongation (%)	Extension at grain crack (%)	Dye uptake (λ_{360})
			Just crack	Full crack			
Conventional method	558	135	279	845	31.8	12.6	2.807
RO permeate	691	217	384	918	38	13.9	2.839

Table 3
Comparative cost analysis of proposed treatment with conventional effluent treatment process.

Mode of operation		Capital cost (USD) (approx.)[a]	Operation and maintenance (USD)[b]	Cost per liter of water per day (USD)
Proposed scheme	Laboratory scale (Batch mode) MF+RO	6,251	2.4	0.04
	Pilot scale MF+RO	58,622	5.3	0.01
Industrial scale (conventional) [30][c]		1167,592	–	0.07

[a] Calculations are based on 3000 L of influent volume.
[b] Including manpower, electricity, chemical cleaning.
[c] Varies from industry to industry depending on area and type of effluent.

Table 4
Results of fitting the experimental values of permeate flux with varying time in MF process: $Y=A+B_1X+B_2X^2+B_3X^3$.

COD (mg/L)	Parameters											
	A			B_1			B_2			B_3		
	Values	S.E	t-Value	Values	S.E	t-Value	Values	S.E	t-Value	Values	S.E	t-Value
3797, $R^2=0.9885$	51.86	0.07	785.1	−0.003	8.83e-5	−31.7	3.61e-7	3.03	11.94	−1.51e-11	2.85e-12	−5.30
4980, $R^2=0.9944$	48.88	0.05	1042.5	−0.0012	6.27e-8	−18.82	−6.37	2.15e-8	−2.97	1.28	2.02e-12	6.33
5218, $R^2=0.9815$	45.88	0.15	307.76	−0.002	1.99e-4	−9.23	−1.67e-7	6.83e-8	−2.44	2.61e-11	6.43e-12	4.07
6843, $R^2=0.9897$	43.69	0.12	352.69	−1.83e-4	1.65e-4	−1.10	−7.23e-7	5.68e-8	−12.73	7.04e-11	5.34e-12	13.18
7562, $R^2=0.9614$	38.92	0.16	239.78	−0.003	2.17e-4	−14.33	8.02e-7	7.44e-8	10.78	−8.51e-11	6.99e-12	12.16

initial feed COD value of 228 mg/L, 390 mg/L, 620 mg/L and 892 mg/L whereas for COD value of 472 mg/L, time had linear effect on flux. In case of pressure study the t-value (Table 7) depicted that quadratic effect of transmembrane pressure was most significant on flux in the RO process.

3.5. Physical and chemical properties of finished leather and produced effluent

The physical properties of leather includes measurement of tensile strength, stitch tear strength, percent of elongation, grain crackness etc. Among this tensile strength is the most important

Table 5
Results of fitting the experimental values of permeate flux with varying pressure in MF process: $Y=A+BX$.

COD (mg/L)	Variables					
	A			*B*		
	Value	S.E	*t*-Value	Value	S.E	*t*-Value
3797, $R^2=0.9882$	16.47	1.65	9.97	31.93	1.16	27.46
4980, $R^2=0.9797$	14.05	2.04	6.89	29.94	1.43	20.89
5218, $R^2=0.9649$	8.62	2.79	3.08	31.01	1.97	15.77
6843, $R^2=0.9646$	6.65	2.88	2.31	31.83	2.03	15.68
7562, $R^2=0.9548$	−1.05	3.46	−0.30	33.66	2.43	13.83

Table 6
Results of fitting the experimental values of permeate flux with varying time in RO process: $Y=A+B_1X+B_2X^2$.

COD (mg/L)	Variables								
	A			B_1			B_2		
	Value	S.E	*t*-Value	Value	S.E	*t*-Value	Value	S.E	*t*-Value
228, $R^2=0.9405$	15.85	0.34	466.85	−0.001	7.65e-5	−40.80	3.61e-7	3.32e-8	10.87
390, $R^2=0.9572$	12.32	0.04	306.32	−0.002	9.06e-5	−21.09	5.37e-7	3.93e-8	13.64
472, $R^2=0.7153$	9.94	0.03	284.55	−4.21e-4	7.77e-5	5.42	8.92e-7	3.37e-8	2.64
620, $R^2=0.9656$	9.23	0.03	345.32	−0.001	6.02e-5	−21.6	3.38e-7	2.61e-8	12.91
892, $R^2=0.9480$	7.13	0.03	199.21	−0.001	8.06e-5	−18.35	4.05e-7	3.50e-8	11.55

Table 7
Results of fitting the experimental values of permeate flux with varying pressure in RO process: $Y=A+B_1X+B_2X^2$.

COD (mg/L)	Variables								
	A			B_1			B_2		
	Value	S.E	*t*-Value	Value	S.E	*t*-Value	Value	S.E	*t*-Value
228, $R^2=0.9933$	1.27	2.52	0.50	1.55	0.77	2.06	0.187	0.047	3.96
390, $R^2=0.9818$	−0.35	4.23	−0.08	0.311	1.29	0.24	0.26	0.08	3.36
472, $R^2=0.9713$	−2.47	5.48	−0.45	−0.16	1.67	−0.09	0.30	0.10	2.95
620, $R^2=0.9712$	−1.85	5.40	−4.56	−0.48	1.65	−0.29	0.32	0.10	3.13
892, $R^2=0.9698$	−0.79	5.33	−0.15	−0.97	1.62	−0.59	0.33	0.09	3.36

mechanical property of leather. Tensile strength is measured to obtain the maximum tensile stress a material can resist unless fracture takes place [27–29]. Elongation of leather is measured to obtain the ability of the material to stretch or elongate when stress is applied. It is expressed as percentage and indicates the extent to which stress could be applied before fracture. The physical parameters of the leather sample prepared using tannery effluent treated by the combined process were shown in Table 2 where a comparison was made with that of fresh water. Tensile strength, percent of elongation and stitch tear strength was measured in Digital Dynamometer, IG/DES, Giuliani, Italy. Thickness of leather sample was measured in Thickness tester, IG/MS, Giuliani, Italy. Grain crackness was measured in Lastometer, IG/LAST, Giuliani, Italy. Carbon, Hydrogen and Nitrogen analysis of leather was done by CHNS/O elemental analyzer, 2400 series II, Perkin Elmer, USA. It was observed that the leather being processed with the treated effluent was of better quality compared to that of control in terms of physical properties. Dye uptake by leather was more in case of sample prepared with the treated effluent (Fig. 6). Tensile strength of this leather was about 19% more than that of leather tanned using

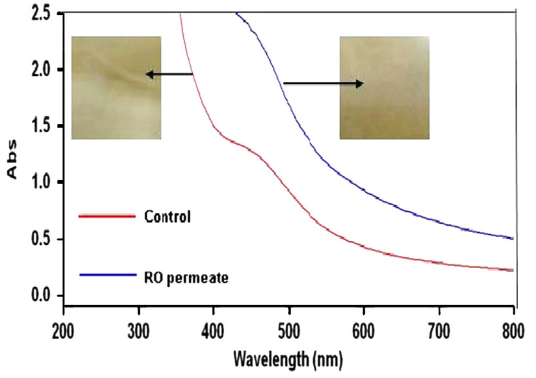

Fig. 6. Spectrophotometric determination of effluent after tanning for control and RO permeate.

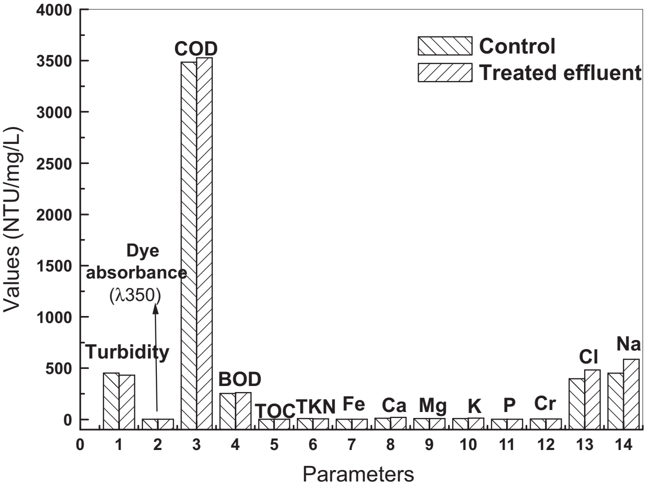

Fig. 7. Comparative characteristics of effluent produced after tanning process involving use of treated effluent and fresh water (control).

fresh water. Full crack in conventional leather occurred at 845 kg/cm but for treated effluent tanned leather, the crack took place at 918 kg/cm.

The effluent discharged at various steps of tanning were collected and subjected to characterization in terms of COD, TOC, TKN and chemical analysis for comparison with that of control. In addition, the final effluent that was discharged after the reusability study of tanning operation was also characterized. The water is discharged as effluent in several steps i.e. after pH adjustment, after neutralization, and after addition of preservatives. When compared with control mostly all the parameters in each step were comparable. Characteristics of the final effluent were shown in Fig. 7. It was observed that sodium and chloride ions were present in the effluent after reuse which could be due to the presence of these ions in the original treated effluent i.e. the RO permeate. Also TOC, COD and BOD_5 values were in the comparable range. Elements like cadmium, zinc, lead, cobalt etc. were negligible for both control and the RO treated water.

3.6. Cost analysis of the proposed process

A cost analysis of the proposed combined process of ceramic microfiltration followed by reverse osmosis process was made. The fixed cost included the cost of the ceramic MF setup and that of RO setup including the cost of membranes. Cost of the pilot scale setup of MF unit was about 2011 USD including 7 numbers of 19 channel ceramic membrane element. The elements were indigenously developed having an outer diameter of 34 mm and length of 1 m each costing about 27 USD. The cost of the polymeric RO membrane unit was about 5460 USD including two numbers of RO membrane modules of spirally wound configuration. From the laboratory scale studies, the operating cost of the MF process was found as 0.02 USD/L of water. Operating cost of the RO membrane was observed as 0.017 USD/L involving the electricity cost for running the recirculation pump. The maintenance cost would depend on the individual feed water quality, the chemical consumptions, cleaning and man power involvement. For plant operation and maintenance, generally 2–3 persons (manpower) are required. For the ceramic membranes, cleaning with low cost, dilute acid solution is required in 1 month while thorough cleaning is required after 6 months of operation or if flux decreases drastically. In case of RO process, if flux decline exceeds 15%, cleaning is required using the process as described in the materials and methods section. Overall, the total operating cost to produce 1 L of treated water from highly contaminated composite tannery effluent was approx. 0.03–0.04 USD/L. If the study is conducted in pilot scale, the combined process would cost about 0.01–0.015 USD/L of water/day. The costing is described in Table 3 including a comparison with that of conventional effluent treatment plant [30]. It might be observed that the overall costing for production of 1 L of treated water in the proposed approach is relatively lower than that of conventional treatment. Apart from low sludge production, the proposed process yields a higher water recovery. This reduces the pollution load on environment, as well as, minimizes the pollution tax. The installation cost is one time. While the ceramic microfiltration membranes have an operating life of 10–12 years, the RO membranes need to be replaced every 2–3 years or more with proper maintenance. According to Ranganathan and Kabadgi [25], the installation and commissioning cost of conventional tannery effluent treatment plant including RO costs about 2.33 lakh USD and the cost of treated water is about 1.56 USD/L. For further optimization more experiments are required which are currently under trail.

The ecofriendly approach of proposed treatment process reduces the pollution load to a considerable extent compared to the conventional effluent treatment process where the water is directly discharged which affects land and aquatic organisms and eventually human beings are getting affected. In common effluent treatment plant different types of chemicals are used as part of treatment which generates toxic sludge. Compared to this, the proposed process is environment friendly and the toxicity of sludge does not increase further [30–33]. This sludge after compacting could be used as land filling.

4. Conclusions

The study presented the efficiency of combined technology of ceramic membrane based microfiltration and reverse osmosis by polymeric membrane in successful treatment and reuse of composite tannery effluent. About 91% reduction in COD and BOD_5, 62% reduction in TOC and complete removal of sulphide was obtained in the direct microfiltration process while turbidity reduced to below 1 NTU. The RO process resulted in about 99% reduction of TOC and 82% reduction of sodium while turbidity value was about 0.025 NTU. Compared to the several stages in the conventional effluent treatment, the proposed two-stage process was able to successfully reduce toxic loading in terms of COD, BOD_5, heavy metals, etc. present in higher loading tannery effluent and also minimized fresh water consumption. The water was found suitable for reuse in leather tanning. Comparison between the fresh water and the treated water data strengthened the fact which indicated that the water produced by the combined technology resulted in leather of high quality having tensile strength of about 19% higher than that of the control. Even elongation was about 38% compared to the control having 31.8%.

The proposed process reduces the cost of treatment compared to that of conventional treatment. The process may be up-scaled further for proper implementation in industries. This technology would be of great help to reduce fresh water consumption that is used in huge amount i.e. about 100,000 t and wasted in large amount as well (about 80,000 t) in tannery industry.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgment

This study was conducted as a part of the Network Project (NWP 0044) funded by the Council of Scientific and Industrial Research, Govt. of India under the 11th Five Year Plan. The authors are thankful to M/s Weblec Industries, Kolkata for allowing us to conduct the reuse study.

References

[1] M.A. George, H. Abeer, Al-Hindi Mahmoud, The impact of process sequences on pollutant removal efficiencies in tannery wastewater treatment, Water, Air, & Soil Pollution 224 (2013) 1–13.
[2] S. Aber, D. Salari, M.R. Parsa, Employing the Taguchi method to obtain the optimum conditions of coagulation–flocculation process in tannery wastewater treatment, Chemical Engineering Journal 162 (2010) 127–134.
[3] S.S. Borchate, G.S.S. Kulkarni, V.V. Kore, S. Kore, Application of coagulation–flocculation for vegetable tannery wastewater, International Journal of Engineering Science and Technology 4 (2012) 1944–1948.
[4] P.W. Ramteke, S. Awasthi, T. Srinath, B. Joseph, Efficiency assessment of common effluent treatment plant (CETP) treating tannery effluents, Environmental Monitoring and Assessment 169 (2010) 125–131.
[5] T. Mandal, S. Maity, D. Dasgupta, S. Datta, Advanced oxidation process and biotreatment: their roles in combined industrial wastewater treatment, Desalination 250 (2010) 87–94.
[6] M.K. Purkait, P.K. Bhattacharya, S. De, Membrane filtration of leather plant effluent: flux decline mechanism, Journal of Membrane Science 258 (2005) 85–96.
[7] S.D. Gisi, M. Galasso, G.D. Feo, Treatment of tannery wastewater through the combination of a conventional activated sludge process and reverse osmosis with a plane membrane, Desalination 241 (2009) 337–342.
[8] M. Fababuj-Roger, J.A. Mendoza-Roca, M.V. Galiana-Aleixandre, A. Bes-Pia, B. Cuartas-Uribe, A. Iborra-Clar, Reuse of tannery wastewaters by combination of ultrafiltration and reverse osmosis after a conventional physical–chemical treatment, Desalination 204 (2007) 219–226.
[9] R. Suthanthararajan, E. Ravindranath, K. Chits, B. Umamaheswari, T. Ramesh, S. Rajamam, Membrane application for recovery and reuse of water from treated tannery wastewater, Desalination 164 (2004) 151–156.
[10] R.J. Ciora Jr., P.K.T. Liu, Ceramic membranes for environmental related applications, Fluid/Particle Separation Journal 15 (2003) 51–60.
[11] S. Bandyopadhyay, D. Kundu, S.N. Roy, B.P. Ghosh, H.S. Maiti, Process for Preparing Water Having an Arsenic Level of Less than 10 PPB, US Patent 7014771. 2006.
[12] P. Bhattacharya, S. Dutta, S. Ghosh, S. Vedajnananda, S Bandyopadhyay, Crossflow microfiltration using ceramic membrane for treatment of sulphur black effluent from garment processing industry, Desalination 261 (2010) 67–72.
[13] P. Bhattacharya, S. Ghosh, S. Sarkar, S. Majumdar, S. Bandyopadhyay, Effectiveness of biosorption-assisted microfiltration process for treatment of domestic wastewater, Bioremediation Journal 15 (2011) 206–217.
[14] S. Krishanamoorthi, V. Sivakumar, V. Saravanan, T.V.Sriram Prabhu, Treatment and reuse of tannery waste water by embedded system, Modern Applied Science 3 (2009) 129–134.
[15] R.Y. Ning, P.T.L. Shen, Observations from analysis of reverse osmosis membrane Foulants, Ultrapure Water (1998) 37–40.
[16] R.Y. Ning, Sustaining the productivity of reverse osmosis plants, The Analyst Fall (2004) 1–5.
[17] R. Reardon, F. DiGiano, M. Aitken, S. Paranjabe, J.H. Kim, S.Y. Chan, Membrane Treatment of Secondary Effluent for Subsequent Reuse, Water Environment Research Foundation Report, IWA Publishing, 2005.
[18] Metcalf, Eddy, Wastewater Engineering Treatment and Reuse, McGraw Hill, New York, 2003.
[19] S. Paranjape, R. Reardon, X. Foussereau, Pretreatment technology for reverse osmosis membrane used in wastewater reclamation application past, present and future a literature review, in: Proceedings of the Water Environment Federation, 2003, pp. 459–486.
[20] J.W. Ryznar, A new index for determining amount of calcium carbonate scale formed by a water, Journal of the American Water Works Association 36 (1994) 472–486.
[21] S.R. Pandey, V. Jegatheesan, K. Baskaran, S. Muthukumaran, Ranking of pre-treatment technologies for reverse osmosis for water recovery, in: Derin Orhon et al. (Eds.), Proceeding of the Eighth International Symposium on Waste Management Problems in Agro-Industries (AGRO′2011) Çeşme, Izmir, Turkey, 2011 pp. 463–470.
[22] A.E. Greenberg, A.D. Eaton, L.S. Clesceri, E.W. Rice, Standard Methods for the Examination of Water and Wastewater, 21st ed., APHA, AWWA, WEF, USA, 2005.
[23] A. Majouli, S. Tahiri, S. Alami Younssi, H. Loukili, A. Albizane, Treatment of effluents coming from beamhouse section of tannery by microfiltration through cordierite/zirconia and alumina tubular ceramic membranes, Journal of Materials and Environmental Science 3 (2012) 808–815.
[24] W.G. Scholz, P. Rouge, A. Bodalo, U. Leitz, Desalination of mixed tannery effluent with membrane bioreactor and reverse osmosis treatment, Environmental Science & Technology 39 (2005) 8505–8511.
[25] K. Ranganathan, S. Kabadgi, Studies on feasibility of reverse osmosis (membrane) technology for treatment of tannery wastewater, Journal of Environmental Protection 2 (2011) 37–46.
[26] S. Krishnamoorthi, K. Saravanan, Tannery industry effluent treatment by combinations of activated sludge process and combined reverse osmosis system, Journal of Environmental Research and Development 5 (2011) 978–983.

[27] A.A. Raju, N.K. Chandrababu, N. Samivelu, C. Rose, N.M. Rao, Eco-friendly enzymatic dehairing using extracellular proteases from a *Bacillus* species isolate, Journal of the American Leather Chemists Association 91 (1996) 115–119.
[28] S. Pal, R. Banerjee, B.C. Bhattacharyya, R. Chakraborty, Application of a proteolytic enzyme in tanneries as a depilating agent, Journal of the American Leather Chemists Association 91 (1996) 59–63.
[29] C-K. Liu, N.P. Latona, J. Lee, P.H. Cooke, Microscopic observations of leather looseness and its effects on mechanical properties, Journal of the American Leather Chemists Association 104 (2009) 230–236.
[30] U. Sankar, Common Effluent Treatment Plants: an institutional arrangement for pollution control on small scale tanneries in India, in: Second International Conference on Environmental Development, Stockholm, 2000.
[31] S. Sinha, S. Sinha, Indian Leather Industry-the Challenge of Modernization, Oxford and IBH Publishing Co. Pvt. Ltd New Delhi 41.
[32] S. Mehta, S. Mundle, U. Sankar, Controlling Pollution: Incentives and Regulation, Sage Publications, New Delhi, 1997.
[33] A. Helble, C.H. Mobius, Current experience with the use of membrane bioreactor technology for the treatment of papermill effluent, in: PTS Water and Environmental Technology Symposim, Munich, 2009, pp. 1–27.