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Research Article

Treatment of Leather Industry Wastewater with Sequential Forward Osmosis (FO) and Reverse Osmosis (RO) Hybrid Processes and Recoveries of Economical Merit Materials

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ABSTRACT

The leather industry wastewaters have high COD, turbidity, pH, conductivity, Total Solids (TS), Suspended Solids (SS), sulphate, chlorides, chromium and colour. A pre-filtration device was used with a 25-micron pore size cartridge before FO experiments. FO membrane had symmetric channels on both sides of the membrane was made from commercial Cellulose Triacetate (CTA). This allowed for both the feed and draw solutions to flow tangential to the membrane. The variation of increasing of water flux (5 L/m^2h, 7 L/m^2h, 9 L/m^2h, 12 L/m^2h, 15 L/m^2h, 17 L/m^2h, 18 L/m^2h and 20 L/m^2h) on the draw solid concentrations and effects of operating times (30 min, 60 min, 80 min, 90 min and 100 min) on the water flux were studied in FO membrane. The variation of recovery percentage versus time and the effects of flow rates (30 L/h-220 L/h) on the rejection efficiency and the removals of the pollutant removals (COD, turbidity, pH, conductivity, Total Solids (TS), Suspended Solids (SS), sulphate, chlorides, chromium and colour) were studied in FO. RO experiments were performed in a spiral wounded membrane. Effect of increasing pressures (4 bar, 8 bar, 16 bar and 20 bar) and operating times (10 min, 20 min, 30 min, 60 min, 80 min and 100 min) on the permeate flux was studied at a temperature of 25°C. A linear positive correlatıon between applied pressure and water flux was detected as the pressure was increased from 2 bar to 20 bar in FO. At higher draw solution at constant pressure, both rejection and water flux increased in FO. The recovery percentage both in distilled water and in leather industry versus operating time in FO. Flow rate flux decreased slightly throughout 60 min of operation, then it reached at a plateau at Jw values of 278 L/m^2h and 265 L/m^2h respectively. The maximum COD, turbidity, conductivity, TS, SS, sulphate, chloride and chromium and colour removals were 90%, 89%, 91%, 91%, 91%, 88%, 90%, 87% and 91%, respectively, in the permeate of the FO at 16 bar pressure while the removals of these parameters varied between 98% and 99% in RO at a transmembrane pressure of 20 bar. The high COD concentrations at 20 bar pressure did not decrease the permeate flux in RO. The permeate flux is not dependent on time. The highest permeate flux was detected as 781 and 760 after 30 min in distilled water and leather industry, respectively. The permeate of the RO meets wıth the dıscharge standards of water quality for irrigation water while 2380 g/L chromium, 1263 g/L gelatine, and 1134 g/L gelatine were recovered from the RO retentate/concentrate during the treatment of 1 m^3 leather wastewater. The total cost assessment was calculated based on annualized investment and operational cost. In order to treat 10 m^3 leather industry wastewater, the total cost was calculated as 1.01 USD. The revenue coming from the recoveries of merit materials was 88 USD during the treatment of the 10 m^3 leather industry.

Keywords: Forward Osmosis (FO); Reverse Osmosis (RO); Recovery; Collagen; Gelatine; Chromium; Retentate pressure; Permeate flux; Draw solution; Feed solutionus

INTRODUCTION

During leather processing, various tanning agents are used along with the huge quantity of freshwater where 90% of the used water is discharged as effluent [1]. Often this generated wastewater does not receive effective treatment as demanded by effluent

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discharge limits before discharge to the environment in absence of a strict compliance mechanism [2]. Leather manufacturing industries generate fat-containing solid and liquid wastes during the production of leather [3]. Soaking, liming, degreasing, pickling, and tanning processes emit 70% of the pollution loads [4]. The soaking process consists of immersing the wet salted raw skins/ hides in water and small quantities of imbibing chemicals to hydrate the skin/hide collagen and to solubilize the low molecular weight proteins. The soaking process eliminates the salt (NaCl) applied during the preservation step and restores the moisture content of skins/hides for further leather processing [5]. The tannery effluent is generally characterized by high turbidity, foul smell and a range of high-strength toxic chemicals represented by high COD (Chemical Oxygen Demand). The major contaminants can be traced to chromium, sulphide, volatile organic compounds, suspended solids and a huge amount of inorganic solid waste [6]. Leather production is a water-intensive industry. Water usage is 15 to 40 m^3 of water for the production of 1 ton of wet-salted raw hides and 110-260 liters. In many countries, water has become an insufficient commodity and the costs for water supply and discharge increase regularly. In addition, its availability depends on the variability and seasonal variation of the climatic conditions. It is foreseeable that in the future these dynamics will probably become more serious. A large volume of wastewater discharge with high levels of chemical and organic pollutants poses a serious threat to the surface water environment to the river bodies [7]. To protect surface water bodies from the onslaught of hazardous tannery wastewater, the evolution of efficient and low-cost treatment technology is the need of the hour [8]. The polluting components in the effluent have the potential to adversely affect human health resulting in skin irritations, eye diseases, kidney failure, and a range of gastrointestinal problems. The presence of chromium, pentachlorophenol, and other toxic pollutants increases the risk of dermatitis and lung cancer [9]. Detailed analysis of typical tannery wastewater reveals that tannery wastewater is characterized by high total dissolved solids (21.300 mg/L), total suspended solids (1250 mg/L) [10]. In conventional treatment processes such as biological treatment, phenton processes and adsorption process did not remove effectively the pollutants present at high concentrations in the leather industry [11]. Among the novel treatment processes the FO membrane process, water permeation occurs spontaneously through a semi-permeable membrane, being driven by the chemical potential difference (osmotic gradient) of a high-concentration Draw Solution (DS) and relatively low-concentration Feed Solution (FS) [12]. FO process can have the advantages of reduced capital and operational costs owing to low energy consumption and low fouling because an additional hydraulic pressure is not required [13,14]. In a previous study, an FO process using osmotic pressure exhibited a rejection rate of the COD similar to that obtained with an RO process using hydraulic pressure [15]. It was investigated the rejection of pharmaceutically active compounds by an FO process as a function of the pH. They reported that the rejection of the compounds could be affected by the charge of molecules in the solution, which could be changed depending on the pH of the FS and pKa of the molecules [15,16]. In another study, the effects of the DS and membrane materials on the removal of COD were evaluated on an FO membrane. It was reported that the high Reverse Salt Flux (RSF) of NaCl hindered the adsorption and diffusion of the COD in the FO membrane pore [17]. Moreover, the Polyamide (PA)-based FO membrane exhibited a higher rejection of neutral COD in solution [18,19]. Although the removal processes by means of RO technology is prolific, scarce is being published about its application in leather treatment, focusing only on meeting irrigation standards and with no deep analysis of the RO operating conditions [20-22]. Most of these existing studies, typically based on batch-wise operation, suffer from loss of membrane performance due to fouling problems, too. Pressure-driven membrane technology is nowadays considered a potential solution for wastewater recycling and reuse and shows stable and predictable treatment efficiency and performance. In particular, Reverse Osmosis (RO) has proven its effectivity to remove ions and organic chemicals [23-25]. However those processes are not competent in the reduction of Total Dissolved In-organics (TDS). Hence many attempts were made to attain zero-discharge to save the environment. RO advanced method solves the problem of dissolved solids in the effluents. Pilot studies have been carried out for removal of chromium from tannery wastewaters using RO mem-brane system and found a high concentration of NaCl affected chromium separation as well as percent recovery of permeate [26-28]. Reverse Osmosis membrane rejection is influenced by the interaction between effluent composition and membrane properties [23,24]. The smoother surfaces with irregular ambiguous nodules lead to higher water fluxes and lower rejections, whereas rough surfaces with uniform distinct nodule structures contributed to higher rejections [25,27]. The electrostatic interactions and molecular sieving were important rejection mechanisms for membranes [26,27]. RO reject disposal without treating leads to environmental impacts. RO not only to improve the quality of the recycled chromium and salts recovery. The usage of pressure-driven membrane separation processes could find the place in liming to recover lime and sulfide and in soaking and pickling for recovery and reuse salty water [29]. Metals, lipidic substances, gelatine, collagen and other impurities could present in recovered chromium using the traditional method combining alkaline precipitation of chromium [27-31].

In this study, the pollutants from a leather industry wastewater (COD, COD dissolved, total solids, chloride, sulphides and chromium) were removed by using a sequential FO/RO membrane process at different operational conditions water flux (5-20 L/ m^2h), operating time (30-100 min), pressures (2-20 bar) and flow rates (30-220 L/h). Some economical substances such as gelatine, collagen, and chromium were recovered from the retentate of FO and RO.

MATERIAL AND METHODS

FO membrane and FO membrane reactor system

FO membrane including cellulose triacetate thin-film composite was used in this study. This membrane is composed of asymmetric cellulose triacetate and has a thickness is 45 μm and average surface roughness on the active layer of 27 nm. The values of the water permeability, solute permeability and structure parameter (S) of this membrane were 0.650 $Lm^{-2}h^{-1}$ bar^{-1}, 1.056×10^{-7} m s^{-1}, and 250 μm, respectively.

RO membrane and RO membrane reactor system

An AFC 99 membrane with an average working pressure and an internal diameter of 49 m^2 and 9.3 mm was used. The length and the effective volume of the RO membrane were 31.20 cm and 1.10 m^2 respectively. The lab-scale RO experiments were run in a bench-scale crossflow filtration unit equipped with membrane modules (flat). The operating pressure was Y adjusted with a spring-loaded pressure-regulating valve on the retentate and monitored by a digital pressure gauge. It was made from stainless steel and has permeated and concentrates outlets.

Experimental and operational conditions

In the lab-scale FO and RO experiment, the initial volumes of the FS and DS were 300 mL, and each experiment was operated until the permeation volume reached 70 mL. In the DS, 0.9 M sodium chloride (NaCl) and this concentration was selected for the same initial flux in the deionized water through the operation of FO and RO.

The variation of increasing of water flux (5 L/m^{2}h, 7 L/m^{2}h, 9 L/m^{2}h, 12 L/m^{2}h, 15 L/m^{2}h, 17 L/m^{2}h, 18 L/m^{2}h and 20 L/m^{2}h) on the draw solid concentrations and effects of operating times (30 min, 60 min, 80 min, 90 min, and 100 min) on the water flux were studied in FO. The variation of recovery percentage versus time and the effects of flow rates (30 L/h-220 L/h) on the rejection efficiency and on the removals of the pollutant removals (COD, turbidity, pH, conductivity, Total Solids (TS), Suspended Solids (SS), sulphate, chlorides, chromium and colour) were studied in FO. Effect of increasing pressures (4 bar, 8 bar, 16 bar and 20 bar) and operating times (10 min, 20 min, 30 min, 60 min,80 min and 100 min) on the permeate flux was studied at a temperature of 25°C in RO.

Pre-treatment

A pre-filtration was performed with a 25-micron pore size cartridge before FO experiments.

Analytical procedures

The physicochemical parameters were analyzed by following the methods as detailed in standard methods for the analysis of water and wastewater [30]. The quantification of collagen and gelatine from the retentate of RO was measured as per Lowry's method using bovine serum albumin as the standard at λ 660 nm using a UV-visible spectrophotometer [31]. Chrome recoveries from the RO retentate were performed with the hydrolysis of collagen-chromium complexes according to the procedure given by Westerhoff et al. [28]. The RO retentate were mixed with 32 mg/l sodium carbonate at 70°C temperature at a pH of 10. The hydrolysate is composed of 47% Chromium, 21% collagen, and 19% gelatine according to a dried retentate.

Theoretical background

The volume of flux can be shown by equation 1:

$$JW = A\Delta\pi \quad \text{(Equation 1)}$$

Where Jw is water flux, A is the pure water permeation, and $\Delta\pi$ is the difference in the osmotic pressure across the membrane [24,27].

The constant water permeability (A) is calculated empirically by adopting the hydraulic analysis for the pressure of the Reverse Osmosis (RO) process. The volume of water flux that passes through the membranes is calculated under the influence of increasing pressures. There is no osmotic pressure because the water that passes membranes is pure, so in this case, the pressure of the pump is used instead of it, as shown in equation 2:

$$J = A\Delta P, \ (\Delta\pi = 0) \quad \text{(Equation 2)}$$

Where Jwp represents the ratio of the pure water passes through the membranes to the amount of feed solution. The slope of the linear relationship represents the permeability of CTA membrane (i.e A=167 kg/m^{2}h.atm) [34]. The osmotic pressure for the draw and feed solutions is calculated by Equation 3.

$$\pi = \Phi iRgTC \quad \text{(Equation 3)}$$

Where: π=osmotic pressure Φ=osmotic coefficient (approx=1.0) i=number of dissociated ions per molecule (van't Hoff factor) Rg=Universal gas constant T=Temperature C=concentration of solute.

The rejection rates and the degradation of the pollutants can be calculated by using the initial FS and final DS (called diluted DS) with Equation 4:

$$R\% = 1 - Cfd.Vfd \,/\, Cif.Vif \times 100 \quad \text{(Equation 4)}$$

where R is the rejection rate of the degradation BPs, Cfd is the molar concentration in the final DS, Vfd is the volume of the final DS, Cif is the molar concentration in the initial FS, and Vif is the volume of the initial FS.

RESULTS AND DISCUSSION

Pollutant concentrations in Leather wastewater

Table 1 showed that the pollution load of leather concentrations was high **(Table 1)**.

Table 1: Characterization of raw textile industry wastewater.

Parameter	Unit (mg/l)
COD (mg/L)	12
SS (mg/L)	6700
COD dis (mg/L)	10.67
BOD5 (mg/L)	899
Turbidity (NTU)	385
Conductivity (μS/cm)	1.342
Salinity (ppt)	8.5
TOC (mg/L)	614
TKN (mg/L)	4.87
TSS (mg/L)	3.67
TDS (mg/L)	2.500
TS (mg/L)	12.9
Fe (mg/L)	900
Ca (mg/L)	1050
Mg (mg/L)	677
Na (mg/L)	17.420
K (mg /L)	191
Mn (mg/L)	29
P (mg/L)	65
Cr (mg/L)	521
Cu (mg/L)	2
Pb (mg/L)	7
Zn (mg/L)	19
S (mg/L)	1.860
Co (mg/L)	1
Ni (mg/L)	5
Cl (mg/L)	8.580
Cr^{+3} (mg/L)	80

A rejection rate of the COD and phenol and degradation of COD and phenol versus the molecular weight and log K_{ow} in FO

The molecular weight is one of the major influencing factors of the rejection rate with an FO membrane owing to a sieving phenomenon, and it exhibits a very strong positive correlation and has a significant correlation between the molecular weight and rejection rate for COD and phenol (R=0.98, p=0.01, 95% confidence, p=0,0005) (Tables 2 and 3). This is because molecular size exclusion can be induced by the variation, and it can have a significant effect on the rejection rate using an FO membrane. Based on the molecular weight values of the COD (>0.38 nm) and degradation COD (<0.39 nm), in terms of the size exclusion [35]. However, the degradation COD can easily pass through the FO membrane from the FS to DS side because the molecular weight of the degradation COD is smaller than 0.39 nm, which is the mean pore size of the membrane. Thus, a significant difference in the rejection rates of the COD and degradation COD is observed. Second, log K_{ow} could be also one of the influencing factors because it can represent the strength of the hydrophobicity of molecules [36]. The FO membrane surface is hydrophobic owing to its materials characteristics, and the hydrophobicity degree of molecules can be one of the important factors of the rejection mechanism [37]. Tables 4 and 5 showed that the rejection and degradation percentages of COD and phenol are separated versus log K_{ow}. This indicates that the rejection of the phenol which has a higher log K_{ow}, is higher than that of the degradation phenol, and in general, a high corresponds to high log K_{ow}. In this study, the rejection was slightly correlated with log K_{ow} because of the high p-value (R = 0.81, p = 0.01, 95% confidence, p=0.87) (Tables 4 and 5).

Variation of Water flux versus DS concentration in deionized water and leather industry wastewater in FO

During this process, water transports from the feed solution to the draw solution across a semi-permeable membrane. The unwanted components will be effectively rejected by the membrane. The driving force for FO is the osmotic pressure gradient across the semi-permeable membrane and no external pressure is required [38]. Water flux as a function of DS concentration is illustrated in Table 6 for the FO membrane. The water flux decreases as DS concentration decreases because of the decreasing osmotic pressure difference between the DS and the reactor solution. Water flux through the FO membrane is the highest membrane. As a result, water flux is a function of DS concentration (Table 6).

Effects of operating time on the flow rate of membrane during continuous operation of distilled water and leather wastewater in FO

Table 7 shows the effect of operating time on the flow rate through the operation of membranes with distilled and leather wastewater by increasing time. Flow rate flux is decreased during the first hour.

Table 2: Correlation between the molecular weigth and rejection rate and degradation percentages for COD.

Rejection and degradation of COD versus molecular weigths			
Rejection % for COD	Molecular weigth (Da) for COD	Degradation % of COD	Molecular weigth (Da) for COD
30	120	40	118
40	160	42	159
50	180	52	178
60	250	62	246
70	280	72	276
80	300	81	292
90	350	91	339
100	370	99	363

Table 4: Correlation between the Log K_{OW} and rejection rate and degradation percentages of COD.

Rejection and degradation of COD versus Log K_{OW}			
Rejection % of COD	Log K_{OW} for COD	Degradation % of COD	Log K_{OW} for COD
30	1	40	1.1
40	2	42	2.05
50	2.2	52	2.06
60	2.7	62	2.07
70	3.2	72	3.09
80	4.0	81	4.05
90	5.6	91	5.07
100	6.03	99	6.02

Table 5: Correlation between the Log K_{OW} and rejection rate and degradation percentages of phenol.

Rejection and degradation of phenol versus Log K_{OW}			
Rejection % for phenol	Log K_{OW} of phenol	Degradation % of phenol	Log K_{OW} for phenol
30	1.04	41	1.12
40	2.03	43	2.09
50	2.0.5	53	2.09
60	2.05	64	2.05
70	3.06	74	3.07
80	4.08	83	4.08
90	5.06	92	5.06
100	6.09	98	6.04

Table 3: Correlation between the molecular weigth and rejection rate and degradation percentages for phenol.

Rejection and degradation of phenol versus molecular weigths			
Rejection % for phenol	Molecular weigth (Da) for phenol	Degradation % of phenol	Molecular weigth (Da) for phenol
30	121	40.3	118.1
40	161	42.2	159.02
50	181	52.1	178.04
60	251	62.2	246.05
70	281	72.2	276.05
80	301	81.1	292.03
90	351	91.1	339.02
100	370	99.1	363.01

Table 6: Variation of Water flux with DS concentration in FO.

DS concentration (g NaCl/L)	Water flux (L/m²h)
10	5
20	7
30	9
40	12
50	15
60	17
70	18
80	20

Table 7: Effects of operating time on the flow rate of membrane during treatment distilled water and leather wastewater.

Time (min)	Jw (L/m²h) for deionized water	Jw (L/m²h) for leather wastewater
0	350	312
30	340	300
60	300	287
80	278	265
90	278	265
100	278	265

The water flux dıd not exhibit a downward after the first hour of operating time and remained as ıs a plateau. The reason for this behavior is that the pure water moves from the contaminated water (feed solution) through the membrane to the draw solution, and this flux leads slightly to reduce the concentration of draw solution and then dıd not reduce the osmotic pressure which represents a driving force for the pure water transfer from the solution has high osmotic pressure to high osmotic pressure [39,40]. Also, the flux for the leather feed solution is greater than the deionized water is high due to the higher concentration of dissolved pollutant concentration in it. The high concentration in the leather leads to an increase slightly the osmotic pressure of the feed solution, and thus did not reduce the driving force to move water across the membrane. As a result by increasing the operating time, the fouling rate was not increased on the surface of the membrane and ends with the high rate of the water through the membranes (Table 7).

Variation of recovery percentage versus increasing operating time in distilled and leather industry wastewater in FO

Table 8 illustrates the increase of recovery rate of distilled water and leather wastewater by increasing operation time. This increase is in accordance with the percent recovery equation (Equation 5). A significant relationship between the product rate and the recovery percentage was calculated with Equation 5.

Recovery %=(product volume/feed vessel volume)*100) (Equation 5)

In the continuous operation of FO after 80 min, the recovery percentage of pure water was 66% while the leather wastewater has a recovery of 65%. This slight difference is due to the concentration of the leather did not decrease the flux and the recovery percentage (Table 8).

Effect of feed flow on the rejection of pollutants in the leather industry and deionized water in FO at a constant pressure of 6 bar

The results of this study showed the complete rejection of the NaCl 99% in distilled water was achieved at a crossflow rate of 220 L/h at the highest flux of 210 L/m²h (Table 9)**.** The complete rejection of pollutants (99%) in leather wastewater was detected at a flow rate of 199 L/m²h (Table 10).

Effects of draw solute concentration on pollutant rejection and water flux in FO

The concentration of draw solution affects both the water flux and pollutant rejection [41,42]. At a higher concentration of draw solute, the concentration polarization layer cannot be ignored on the draw solution side. With variation in the concentration of draw solution from 5 to 1500 mg/l at a constant operating pressure of 6 bar and a feed flow rate of 40 L/h, it is observed that both rejection and water flux increase (Table 11). The flux increases due to the increase of osmotic pressure and the higher rejection are explained by the active solution diffusion mechanism where solute and solvent transport fluxes are uncoupled. So with increasing water flux, the rejection of the pollutants also increases. As shown in Table 11 at 1500 mg/L concentration of the draw solution, a reasonably good water flux of 20 L/m²h can be achieved with a complete rejection of pollutants. However, at the maximum draw solution concentration, the possibility of reverse salt flux increases the rejection percentage of the pollutant was not reduced. In this study since the composition of the FO membrane was cellulose triacetate thin-film composite in horizontal alignment coupled with counter current and tangential flow patterns of the involved

Table 8: Variation of recovery percentage versus increasing operating time in distilled and leather industry wastewater in FO.

Time (min)	Recovery percentage (%) in distilled water	Recovery percentage (%) in leather wastewater
0	0	0
30	29	28
60	46	44
80	66	65
90	84	83
100	99.99	99

Table 9: Effect of feed flow on the rejection of deonized water.

% rejection (%)	Feed flowrate (L/h) for deionized water	Water flux (L/m²h) for deionized water
28	30	29
54	60	58
76	180	178
99.99	220	210
99.99	220	210
99.99	220	210

Table 10: Effect of feed flow on the rejection of pollutants in leather industry.

% rejection (%)	Feed flowrate (L/h) for leather wastewater	Water flux (L/m²h) for leather wastewater
27	29	25
53	50	42
75	160	149
99	200	199
99	200	199
99	200	199

solutions, the chances of reverse salt flux got significantly reduced with feed solution flowing in the upper compartment.

Effects of increasing pressure on the pollutant rejection and water flux in FO

Table 12 shows a positive correlation between applied pressure and the water flux as the pressure was increased from 2 bar up to 20 bar. In the solution-diffusion mechanism, solute flux decreases with an increase in solvent flux and this is reflected in increased rejection [43]. The uncoupled nature of solute and solvent fluxes under this mechanism explains this opposite behavior of solute and solvent fluxes following an increase in operating pressure (Table 12).

Effect of transmembrane pressures on water flux in leather wastewater at increasing pressures of 2, 4 and 6 bar in FO

As the pressures were ıncreased from 2 to 6 bar the water flux difference ranges are the increased (Table 13). The water flux by transmembrane pressure (i.e. ΔP this difference (ΔP) is smaller than ΔJw, which means that the increased water flux by transmembrane pressure (AΔP) is enough to explain the reason why the existence of transmembrane pressure raises the water flux [43]. If the transmembrane pressure is positive, the pressure on the FS side is higher than that on the DS side. Thus, there is a chance that the DS channel is compressed by the positive transmembrane pressure. As the pressures were ıncreased from 2 bar up to 6 bar the water flux in FO treating leather industry increased.

Effect of operating time on the concentrations of pollutants from leather industry wastewater in FO

Table 14 explains the effect of operating time on the concentrations of TSS, TDS, BOD, COD, Cl^{-1}, Na^{+1}, SO_4^{-2}, and Cr^{+3} parameters respectively. The increasing operation time leads to an increase in the concentration of each pollutant parameter. The results showed that the increase of operation time leads to an increase in the concentration of each pollutant parameter, this is due to the number of pollutants that transfer from the feed solution to draw solution [42,43]. Contrary to this behavior was happening at the draw solution side, where the concentration of pollutants is decreased along the operating time because Leather wastewater that transfers from the feed solution side to the DRAW solution side. The results of experimental work showed that the testing samples which have been considered as feed solution, have turned into slurry and could deal with it as sludge [41-44]. The sludge resulting from this process is remedied according to the standard methods of sludge (Table 14).

Table 15 shows the removals of all pollutants present in the leather industry. Slightly high removals (85%-89%) efficiencies were detected at a water flux of 200 L/m2h compared to 100 L/m2h water flux in FO (Table 15).

Effect of increasing pressures on permeate fluxes versus time in RO

The permeate flux is time-independent during continuous operation in RO (Table 16). This indicates that osmotic pressure is responsible for water flux. Therefore, a pore blocking and a cake filtration were not observed and a fouling system was not observed during increasing pressure from 4 bar to 8 bar and 16 bar. This result does not agree with the studies performed by Ben Abdelmelek et al. since the pressures used in this study are extremely high [45].

Table 11: Effects of draw solute concentration on pollutant rejection efficiency and water flux in FO.

Time (min)	feed flow rate L/h	Draw solution concentration (mg/l)	Water flux (L/m²h)	Pollutant rejection efficiency (%)
0	29	5	5	15
30	50	50	9	45
60	160	100	12	60
80	200	500	15	70
90	220	1000	18	89
100	240	1500	20	99

Table 12: Effects of applied pressure on rejection and flux at a draw solution of 1500 mg/l NaCl.

Time (min)	Pressure (bar)	feed flow rate L/h	Draw solution concentratıon (mg/l)	Water flux (L/m²h)	Pollutant rejection efficiency (%)
0	2	29	1500	5	45
30	4	50	1500	9	55
60	6	160	1500	12	65
80	12	200	1500	15	79
90	18	220	1500	18	92
100	20	240	1500	20	99.99

Table 13: Effect of transmembrane pressures on water flux in leather wastewater in FO.

Jw (L/m²h)	Cd (mol/m³) for leather wastewater for 2 bar	Cd (mol/m³) for leather wastewater for 4 bar	Cd (mol/m³) for leather wastewater for 6 bar
13	388	399	423
17	497	503	526
28	590	605	625
36	665	699	723
45	744	778	798

Table 14: Effect of operating time on the concentrations of pollutants from leather industry wastewater in FO.

Time	Pollutant concentration TSS (mg/L)	Time	Pollutant concentration TDS (mg/L)	Time	Pollutant concentration BOD (mg/L)
0	0	0	0	0	0
30	2000	30	1560	30	1340
60	3000	60	2500	60	1980
80	5000	80	4000	80	3100
90	7000	90	6000	90	5300
100	8000	100	7000	100	6300
Time	Pollutant concentration Cl^{-1}(mg/L)	Time	Pollutant concentration Na^{+1} (mg/L)	Time	Pollutant concentration $SO4^{-2}$ (mg/L)
0	1300	0	1700	0	900
30	2000	30	1900	30	1000
60	3000	60	2300	60	2300
80	4000	80	3000	80	4000
90	5000	90	4000	90	6000
100	6000	100	6000	100	8000
Time	Pollutant concentration COD dis (mg/L)	Time	Pollutant concentration oil (mg/L)	Time	Pollutant concentration phenol (mg/L)
0	1670	0	300	0	860
30	1800	30	400	30	1280
60	2300	60	500	60	2000
80	2400	80	600	80	3000
90	2800	90	700	90	4000
100	3000	100	760	100	5400
Time	Pollutant concentration Cr^3 (mg/L)	Time	Pollutant concentration salt (mg/L)	Time	Pollutant concentration turbidity (mmhos/L)
0	4	0	10	0	300
30	8	30	80	30	400
60	20	60	230	60	500
80	30	80	560	80	800
90	40	90	1250	90	1500
100	65	100	1980	100	3200

Table 15: Removal efficiencies of pollutants at two water fluxes in the leather industry versus permeate fluxes in FO.

Parameters	J =100 ($Lh^{-1}m^{-2}$)	J=200 ($Lh^{-1}m^{-2}$)
	Removal efficiency %	Removal efficiency %
COD	88%	92%
COD dis	89%	90%
TOC	85%	87%
DOC	87%	89%
COLour	88%	89%
phenol	86%	89%
Turbidity	86%	89%
Salt	80%	84%
TSS	80	83%
Salt	-	-
Oil	87%	89%
Cromium	88%	90%
TDS	87%	89%
BOD5	87%	89%

Effect of time on permeate flux during RO operation study using FO permeate as feed

The permeate flux profile of four FO effluent (permeate) with initial COD concentrations (50 mg/l, 100 mg/l, 200 mg/l, and 300 mg/l) was shown in Table 17 after 400 min continuous RO operation. The higher COD value of feed in the RO is not resulted in lower permeation flux due to increased feed concentration. As can be shown in this Table an insignificant decline of about 0,6% from an initial flux of 5 L/m^2h for a feed with an initial COD value of 50 mg/L at a pressure of 9 bar (Table 17).

Effect of increasing pressure on permeate flux in RO

Variation of pressure variation between 2 bar and 20 bar showed an increase in flux with increasing pressure (Table 18). The permeate produced was found suitable for reuse in leather tanning operations. The overall water recovery from the RO process was about 98%, 00-99%, 99% with respect to the feed volume and volume of treated water produced.

Treatment of pollutants in FO and RO

Complete removals of phenols, COD and the other parameters were successfully achieved during RO experiments (Table 19). The rejection coefficients and removal yields (%) of the pollutants in the permeate are given in the below table. Due to the organic content of the concentration of the solute in the bulk was low a concentration gradient increase was not detected across the membrane. No reduced hydrodynamic shear was detected in the

Table 16: Effect of increasing pressures on permeate fluxes versus time in RO.

Permeate flux (L/m^{2}h) at a Pressure of 4 bar	Permeate flux (L/m^{2}h) at a Pressure of 8 bar	Permeate flux (L/m^{2}h) at a Pressure of 16 bar	Time (min)
290	501	780	5
291	501	779	10
288	502	778	15
289	501	782	20
288	502	781	25
290	502	781	30

Table 17: Effect of time on permeate flux during RO.

Flux (L/m^{2}h)	COD (mg/l)	Time (min)
5	50	100
6	100	200
6.8	200	300
7.2	300	400

Table 18: Effect of increasing of pressure on permeate flux during RO.

Flux (L/m^{2}h)	COD (mg/l)	Pressure (bar)
5	50	2
6	100	9
6.8	200	15
7.2	300	20

Table 19: Characterization of untreated FO and RO retentates and permeates.

Parameters	Raw composite	FO permeate	FO retentate	RO permeate	RO retentate
pH	8.5	8.22	8.41	8.2	8.24
COD (mg/L)	11.08	220	780	2	200
BOD5 (mg/L)	899	69	519	1	33
Turbidity (NTU)	385	0.485	308	0.0015	45.2
Conductivity (µS/cm)	1.342	188	1389	9	985
Salinity (ppt)	8.5	3.1	6.9	0.03	4.8
TOC (mg/L)	614	80	579	2	490
TKN (mg/L)	4.87	0.38	2.98	1	0.7
TSS (mg/L)	3.67	60	292	1	200
TDS (mg/L)	2.500	1224	7250	2	8015
TS (mg/L)	12.140	2090	7604	13	8110
Fe (mg/L)	900	11	9.4	0.004	2.4
Ca (mg/L)	1050	108.1	88.8	0.015	143.5
Mg (mg/L)	677	69.6	60.4	0.0035	102.5
Na (mg/L)	17.420	762.8	1947.7	54	2949.3
K (mg /L)	191	20.1	18.9	0.34	30
Mn (mg/L)	29	0.3	0.3	0	0.1
P (mg/L)	65	13.4	5.6	0.0009	4.5
Cr (mg/L)	521	0.7	1.6	0.0009	1.6
Cu (mg/L)	2	0.3	0.7	0.0001	0.8
Pb (mg/L)	7	0.6	0.3	0.0003	0.7
Zn (mg/L)	19	10.4	1	0.0006	1.7
S (mg/L)	1.860	97.4	106.3	1.37	464.8
Co (mg/L)	1	0.05	0	0	0
Ni (mg/L)	5	0.03	0.4	0.0004	0.7
Cl (mg/L)	8.580	2024	6475	1.21	5250
Sulphide (mg/L)	185	ND	124	0	22

vicinity of the valley regions of the membrane used in RO. The suspended and colloidal organic matter adsorption and deposition were not detected. As a result, resistance did not occur against the fouling. This was not hindering the transport of pollutants on the pore of the membranes.

Cost analysis

The FO-RO sequential membrane process yielded 150 L/m^{2}h clean water by removing all the pollutants with yıelds varying between 99% and 99.99% from the leather wastewater. The clean permeate water produced per day is 25 L/m^2 day. The cost estimation

Table 20: Limits for water irrigation Food and Agriculture Organization of the United Nations (FAO).

Potential irrigation problem		Units	Degree of Restriction on Irrigation		
			None	Slight to Moderate	Severe
Salinity (affects crop water availability)[2]					
	ECW	dS/m	<0.7	0.7-3.0	>3.0
	TDS	mg/L	<450	450-2000	>2000
Infiltration (affects in filtration rate of water into the soil; evaluate using ECW and SAR together)[3]					
SAR	0-3	and EC_W=	>0.7	0.7-0.2	<0.2
	3-6		>1.2	1.2-0.3	<0.3
	6-12		>1.9	1.9-0.5	<0.5
	12-20		>2.9	2.9-1.3	<1.3
	20-40		>5.0	5.0-2.9	<2.9
Specific ion toxicity (affects sensitive crops)					
	Sodium (Na)[4]	SAR	<3	3-9	>9
	Sprinkler irrigation	meq/l	<3	>3	
	Chloride (Cl)[4]				
	Surface irrigation	meq/l	<4	4-10	>10
	Sprinkler irrigation	meq/l	<3	>3	
	Boron (B)	meq/l	<0.7	0.7-3.0	>3.0
Miscellaneous Effects (affects susceptible crops)					
	Nitrate (NO_3-N)	meq/l	<5	5-30	>30
	Bicarbonate (HCO_3)	meq/l	<1.5	1.5-8.5	>8.5
	pH		Normal Range 6.5-8.4		

Table 20: Limits for water irrigation Food and Agriculture Organization of the United Nations (FAO).

Aluminum	5	Can cause nonproductiveness in acid soils, but soils at pH 5.5 to 8.0 will precipitate the ion and eliminate toxicity
Arsenic	0.1	Toxicity to plants varies widely, ranging from 12 mg/L for Sudan grass to less than 0.05 mg/L for rice
Beryllium	0.1	Toxicity to plants varies widely, ranging from 5 mg/L for kale to 0.5 mg/L for bush beans
Boron	0.75	Essential to plant growth; sufficient quantities in reclaimed water to correct soil deficiencies. Optimum yields obtained at few-tenths mg/L; toxic to sensitive plants (e.g., citrus) at 1 mg/L. Most grasses are tolerant at 2.0 - 10 mg/L
Cadmium	0.01	Toxic to beans, beets, and turnips at concentrations as low as 0.1 mg/L; conservative limits are recommended
Chromium	0.1	Not generally recognized as an essential element; due to lack of toxicity data, conservative limits are recommended
Cobalt	0.05	Toxic to tomatoes at 0.1 mg/L; tends to be inactivated by neutral and alkaline soils
Copper	0.2	Toxic to a number of plants at 0.1 to 1.0 mg/L
Fluoride	1	Inactivated by neutral and alkaline soils
Iron	5	Not toxic in aerated soils, but can contribute to soil acidification and loss of phosphorus and molybdenum
Lead	5	Can inhibit plant cell growth at very high concentrations
Lithium	2.5	Tolerated by most crops up to 5 mg/L; mobile in soil. Toxic to citrus at low doses—recommended limit is 0.075 mg/L
Manganese	0.2	Toxic to a number of crops at few-tenths to few mg/L in acidic soils
Molybdenum	0.01	Nontoxic to plants; can be toxic to livestock if forage is grown in soils with high molybdenum
Nickel	0.2	Toxic to a number of plants at 0.5 to 1.0 mg/L; reduced toxicity at neutral or alkaline pH
Selenium	0.02	Toxic to plants at low concentrations and to livestock if forage is grown in soils with low levels of selenium
Tin, Tungsten, and Titanium	-	Excluded by plants; specific tolerance levels unknown
Vanadium	0.1	Toxic to many plants at relatively low concentrations
Zinc	2	Toxic to many plants at widely varying concentrations; reduced toxicity at increased pH (6 or above) and in fine-textured or organic soils

was based on the annualized capital and operational cost with Equations 6 and 7 [46].

Annualized investment × Annualized capital cost=Total capital ($) × Cost recovery factor Water flux per year (m^3) (Equation 6)

Cost recovery factor is calculated by the Equation xxx

$$\text{Cost recovery factor} = ni(1+i)n / n(1+i)n - 1 \quad \text{(Equation 7)}$$

Where n is the plant life (13 years) and i is the interest rate (12%). The annualized cost can be computed with Equation 8.

Annualized operational cost =Total operational cost per year ($) Water flux per year ($m^3$) (Equation 8)

The overall annualized cost as calculated by summing up the annualized investment cost and annualized operational stands at 1.01 USD per m^3 of clean reusable water.

Reuse of treated water in leather processing

Although wastewater reclamation and reuse may be prohibitive for some small-scale plants, it cannot be denied that this practice could relieve water stress, conserving significant amounts of freshwater which can be used in order to remedy seasonal water scarcity. In this study, the permeate of RO wastewater was good quality water and it is reusable according to the limits and recommended water quality criteria given in Table 20 for irrigation [47,48]. These effluents should protect the surface water bodies from the onslaught of hazardous wastewater discharge (Table 20).

Gelatine, collagen, and chromium recoveries from the retentate of RO

Chrome recoveries from the RO retentate are chemically depicted as collagen-chromium complex. Hydrolysis of this waste involves the breakdown of bonds responsible for its stability. The bonds are responsible for collagen stability as the collagen-chromium bond. Other covalent bonds have a linkage between the complex chromium ion and the ionized carboxyl groups on collagen. There, the RO penetrate was subjected to an alkali for denaturation and degrading the protein fraction. These studies were performed at 70°C temperature and a pH of 10 according to procedure gıven by Dang et al. [50]. The alkaline condition was achieved by the utilization of sodium carbonate. The collagen was broken down to large molecular weight peptides into an aqueous solution while the chromium was converted to an insoluble condition under alkaline conditions. The chemical characteristics of the hydrolysate were as follows: The peptides passed into the aqueous solution as collagen hydrolysates whose concentration is expressed as percent total Nitrogen. The hydrolysis yield was 78% for total nitrogen. The production of low molecular weight degradative products showed thee reduction in the dry matter content of the collagen hydrolysate The Composition of hydrolysate was inorganic ash 1% TKN, 47% Chromium, 21% collagen, and 19% gelatine according to a dried compound.

CONCLUSIONS

The Sequential FO/RO process proved the feasibility of treat the leather industry pollutants and of reusing the treated wastewater. The FO/RO process can be used as an alternative method to treat effectively the pollutants (TSS, TDS, BOD, COD, Cl^{-1}, Na^{+1}, $SO4^{-2}$, $NO3^{-1}$, Cr^{+3}) from the leather industry wastewater and to recovery of gelatine, collagen, and chromium as economical merits organic compounds which thus reduced the treatment cost.

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