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PREPARATION AND PERFORMANCE STUDIES ON POLYETHERSULFONE ULTRAFILTRATION MEMBRANES MODIFIED WITH GELATIN FOR TREATMENT OF TANNERY AND DISTILLERY WASTEWATER

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Abstract - In this study polyethersulfone ultrafiltration membrane were prepared with the modifier gelatin at 0, 5, 10, 15 and 20 wt % using DMF as solvent by phase inversion process. Morphologies and characteristics of the membranes were investigated through the methods of SEM, XRD, contact angle measurements. The performance of the modified membrane for the treatment of leather and distillery wastewater through a deadend ultrafiltration process was studied. Morphological investigation showed that the 10% gelatin content in 90% PES results in a two layer structure with a porous top and homogeneous sub-layer with uniform number of pores on the surface. The pure water flux of the modified membrane increases with gelatin concentration, which results in better permeation for both leather and distillery wastewater. In addition to 80-90% reduction in BOD and COD, all modified PES UF membranes showed moderate removal of total suspended and dissolved solids, chlorides, sulphate, oil and grease, potassium, sodium and ammonical nitrogen, apart from color removal.

Keywords: Polyethersulfone; Gelatin; Ultrafiltration; Tannery and distillery effluents.

INTRODUCTION

Waste stream generated from water-based effluent from leather and distillery industries can be effectively recycled and reused using ultrafiltration processes through which large quantity of water can be saved. Recent developments in membrane technology have enabled industries to implement various treatment strategies for successful remediation of wastewater. Through membranes, excellent separation can be achieved without adding substance mass, heat or energy to the system. Development of high

performance polymeric membranes is essential for specific processes like treatment, recycle and reuse of waste water from textile, tanning, distilleries and similar industries (Causserand *et al.*, 2002; Sternberg, 1987). These membrane separation processes offer a wide range of advantages over conventional separation processes such as low operating cost because they are less energy intensive and ease of operation under ambient temperature (no phase change is involved). Ultrafiltration a membrane-based separation, is a fractionation technique that can simultaneously concentrate macromolecules or colloidal sub-

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stances in process streams. Its separation capability covers from the upper side of the ionic range well into the macromolecular range, i.e., from 0.001 to 0.02 µm. The applicability of these systems can be further widened with the development of new membrane materials (Zhao et al., 2013; Tai-Ping et al., 1991) with specific applications. The use of ceramic membranes in liquid pollution treatment is actually limited due to the price and low permeability of ceramic membrane; nevertheless, these membranes are more resistant to solvent, pH and oxidation. To obtain membranes with special properties, additives can be dissolved in the casting solution. The role of these additives is to create a spongy membrane structure, but prevent the formation of macrovoids, enhance pore formation, improve pore interconnectivity and/or introduce hydrophilicity. Reduced quantities of additives can supplement or improve the membrane characteristics, but an excess may lead to degradation and product failure.

Generally hydrophilic structures are obtained by the addition of polyvinylpyrrolidone (PVP). Other additives are: polyvinylpyrrolidone (PVP), glycerol, alcohols, dialcohols, polyethylene glycols (PEG), polyethylene oxide (PEO), anhydrous lithium chloride, (LiCl), lithium chloride (LiCl.H₂O) and ZnCl₂.

The current investigation involves the development of polyethersulfone gelatin blended ultrafiltration membranes by the phase inversion method; characterizing them and studying their performance for typical effluents from tannery and distillery units. A number of research works have been reported to implement membrane technology, which has potential for the treatment of leather and distillery wastewater from different production streams to reduce pollution in fresh water and discharge of waste water (Jitsuhara and Kimura, 2004). Nanofiltration membranes performed 90% color removal, turbidity, TDS and COD when compared with microfiltration (MF) for leather and distillery effluents (Brinck et al., 2000). The cellulose acetate membranes for treatment of leather effluent showed a permeate flux of 33–42.0 Lm⁻² h⁻¹along with separation of suspended and dissolved solids, chlorides, sulphate, oil and grease, ammonical nitrogen, potassium and sodium by more than 80% (Jarvis and Wagener, 1995; Mahendran et al., 2000). PES UF flat membranes on the industrial scale are considered to be technically and economical feasible for treatment of leather and distillery effluents (Huang et al., 1994). Ultrafiltration has wide application in the recovery of milk solids (Briao and Tavares, 2012) and disposal of effluents from dairy waste water (Namvar Mahboub and Pakizeh, 2012). Therefore, polymers are the

most important materials economically available to prepare membranes that can be prepared over a wide range of film-forming options and modified to achieve tailored properties. Polyethersulfone is a superior polymer available for membrane preparation; being more flexible, it has excellent mechanical. chemical, electrical and thermal properties (Tam et al., 1993, 1996). Blending with other polymers or compounds (Chen et al., 1996) also provides improvement in desired properties such as solvent resistance, improved processability, hydrophilicity, separation selectivity and high productivity. Gelatin is a protein-made material obtained by hydrolysis of collagen derived from the skin, white connective tissue, and bones of animal. Gelatin contains carboxyl groups on its chain backbones and has the potential to mix with chitosan due to its ability to form hydrogen bonding with chitosan (Kamizawa, 1978). Moreover, gelatin is also a biodegradable polymer with many attractive properties, such as excellent biocompatibility, non-antigenicity, plasticity and adhesiveness, and it is widely used in biomedical and pharmaceutical industries (Pieracci et al., 1999) Thus, gelatin was selected as a suitable candidate blended with polyethersulfone.

In this investigation, we created a series of PES / gelatin composite membranes by varying the ratio of components. The purpose of this work was to prepare soft and elastic membrane with biomaterial that can be used for ultrafiltration separation processes. Because of the good biological activity of gelatin, a combination of these two materials of polymer and biopolymer may also have beneficial effects on the UF characteristics of composite membranes. The major advantages of this approach are its simplicity, low cost and the potentially improved membrane properties and hydrophilicity. The work involved the investigation of not only elemental properties of the composite membranes by means of XRD and hydrophilicity, but also the membrane performance activity, including the permeability and selectivity (rejection). The data obtained in this research work suggest that the PES/gelatin composite membranes are a promising candidate biomaterial for membrane applications. Based on the above considerations, PES membranes blended with gelatin were prepared by the phase inversion method. The reduction of BOD, COD and color removal from aqueous solutions of tannery and distillery wastewater was studied. The effect of gelatin composition on their UF characteristics such as porosity, pure water permeability, hydrophilicity, XRD, and morphology was examined to achieve specific membrane morphology which enables the desired separation performances.

MATERIALS AND METHODS

Chemicals

Commercial grade polyethersulfone (PES) having molecular weight $\approx 3.1 \times 10^5$, and density 1.76×10^3 kg/m³ was obtained from Solvay chemicals Limited, India, and used without any further treatment. Gelatin of molecular weight $\approx 1.65 \times 10^5$, density = 1.07×10^3 kg/m^3 and N,N-dimethylformamide (DMF) were purchased from Sigma-Aldrich India Limited. Proteins such as bovine serum albumin (BSA), M_w = 69 kDa, trypsin M_w = 20 kDa and pepsin M_w = 35 kDa were purchased from Sisco Research Laboratories (SRL), India. Egg albumin (EA) $M_w = 45 \text{ kDa was}$ purchased from Central Drug House, India. Copper(II) sulfate (AR), nickel(II) sulfate (AR) and chromium(III) chloride(AR) procured from SRL, Fischer and CDH India Ltd, respectively. The source of the effluent was the discharge from leather industries at Ranipet and from distilleries at Vellore, Tamilnadu, India.

Preparation of PES/Gelatin Membrane

Polyethersulfone and gelatin at different compositions as given in Table 1, were dissolved in 82.5 wt % DMF under continuous agitation at 70 °C for 12 h. This casting dope was spread over a glass plate. A film of uniform thickness was obtained using a 250 micron film applicator. After 30s of evaporation time, the wet phase inversion was carried out by immersing the polymer solution film coated glass plate into a coagulation bath of non-solvent containing 0.3% SLS-water mixture at 30°C for 12h, where an exchange of solvent and non-solvent takes place and the membrane is formed. The resulted membrane was rinsed with pure water and preserved in 1% formalin solution to avoid drying and microbial growth on the membrane surface.

Table 1: Hydrophilicity of PES/gelatin membranes.

	mpositions 5wt%)	Solvent DMF (wt %)	Mean contact Angle (°)	
PES (%)	Gelatin (%)			
100	0	82.5	86.5	
95	5	82.5	75.4	
90	10	82.5	69.4	
85	15	82.5	57.5	
80	20	82.5	51.2	

Membrane Characterization

The XRD diffraction patterns of pure PES membrane and PES/gelatin composite membranes were studied using XRD (model 6000x diffractometer Japan using Nickle filter). The morphological structure of the membranes was studied using SEM (model HITACHI S-3000H) from Hitachi, Tokyo, Japan. The top surface of the membrane was ion sputtered to avoid charging during scanning of the membrane surface. The contact angles of PES-Gelatin membranes were measured by the sessile drop method by using Rame-Hart Instruments (Model 250-F1), Munich, Germany. Contact angles were measured to evaluate the effects of gelatin content on hydrophilicity and surface properties of the membranes. Water was dispensed from a needle attached to a Gilmont microliter syringe filled with ultra pure water. Water droplets, 12 µL in size, were placed on the membrane surface. The contact angle was measured at four different positions of each membrane sample; the average contact angle value is reported.

Membrane samples were cut into the desired size and soaked in water for 24 h and weighed immediately after blotting to remove the free surface water. Wet membranes were dried for 24 h at 75 ± 5 °C in a vacuum oven and weighed. The percent water uptake was calculated using:

% Water uptake =
$$\frac{W_1 - W_2}{W_1} \times 100$$
 (1)

Porosity of the PES-Gelatin membrane was determined by analysis of its weight in the wet and dry state, Membrane porosity was calculated from Equa-

% Porosity =
$$\frac{W_1 - W_2}{\rho_w V_T} \times 100$$

where $V_T = \frac{W_1 - W_2}{\rho_w} + \frac{W_2}{\rho_{md}}$ (2)

where W_1 and W_2 are the weight of membrane samples in the wet and dry state, (g); ρ_w density of water, (g/cm³); V_T membrane volume in the wet state, (cm³) and ρ_{md} is the density of the membrane in dry state (g/cm^3) .

UF Experimental Setup and Performance Analysis

Experiments were performed in a dead-end standard ultrafiltration stirred cell (model Cell-XFUF076) from Millipore, USA with effective filtration area of 38 cm². The cell was operated at 4 atm transmembrane pressure using a nitrogen gas cylinder. Prepared membranes were thoroughly washed

and cut into samples of 75 mm diameter for performance studies. This membrane was placed in the 5L stirred cell and supported with a stainless steel disc. The membrane permeate during the first 10 min was collected and termed the initial water flux (J_{wi}) . The water flux was measured every 30 minutes until it reached the steady state condition. The membranes were compacted at the steady state for 4 h and then permeate was measured for 10 min and considered as the steady state flux (J_{ws}) . Water permeability flux was calculated over measured time intervals using Equation (3):

$$Flux(J) = \frac{Q}{A \Delta t} \tag{3}$$

where, J_{wi} is the initial water flux and J_{ws} is the steady state water flux (Lm⁻²h⁻¹); Q, quantity of water permeate (L); A, effective membrane area (m²); Δt , sampling time (h).

Permeate water fluxes were calculated using Equation (3) every half an hour. The rejection can be evaluated by using Equation (4):

$$Rejection (\%) = \left(1 - \frac{C_f}{C_p}\right) x \, 100 \tag{4}$$

where C_f and C_p are the feed and permeate concentration of the effluent solution. The BOD, COD and other properties of the effluent before and after treatment were analyzed and reported in Table 2 and Table 3.

Table 2: Analytical determinations of partially treated tannery effluent from PES/Gelatin membranes, A refers to 100% PES; B - 95/05 PES/Gelatin; C-90/10 PES/Gelatin; D- 85/15 PES/Gelatin; and E- 80/20 PES/Gelatin.

Sl.	Sl. Parameters		Feed	Permeate qualities				
No				A	В	C	D	E
1	рН		6.3	6.9	6.8	7.1	6.3	6.4
2	Total suspended solids	mg/L	88	55	38	32	40	46
3	Total dissolved solids	mg/L	5560	4560	4619	1952	2567	3451
4	Chloride (as Cl)	mg/L	2669	1763	1983	835	942	1562
5	Sulphate (as SO ₄)	mg/L	1020	459	469	201	210	365
6	B.O.D 3 days at 27 °C	mg/L	322	87	76	35	68	76
7	C.O.D	mg/L	1136	567	671	233	287	234
8	Oil & Grease	mg/L	8	4	3.92	3.8	4.8	6
9	Sulfides	mg/L	30	18	12.4	9.6	11.5	17
10	Ammonical Nitrogen	mg/L	52	19	23	19	21	26
11	Potassium	mg/L	1.6	0.8	0.36	0.25	0.26	1.4
12	Hexavalent chromium	mg/L	4.2	2.8	3.01	1.12	2.8	4
13	Total chromium	mg/L	5.25	2.8	2.5	1.51	2.01	3.2
14	Sodium	%	53.35	51	51	46	51.5	52

Table 3: Analytical determinations of partially treated distillery effluent from PES/gelatin membranes (A-E as in Table 2).

Sl.	Parameters	Feed	Permeate Qualities					
No				Α	В	C	D	E
1	рН		6.3	6.8	7.1	6.7	6.8	6.3
2	Total suspended solids	mg/L	36	22	24	21	29	32
3	Total dissolved solids	mg/L	4000	2250	2541	2200	3456	3689
4	Chloride	mg/L	950	826	835	765	869	892
5	Sulphate	mg/L	2470	405	478	376	561	791
6	BOD, 3 days at 27 °C	mg/L	189	72	88	70	114	125
7	COD	mg/L	1010	728	802	710	889	973
8	Oil & Grease	mg/L	4	3.4	3.6	3.2	3.79	3.85
9	Sulphides	mg/L	42	12	14	11	21	25
10	Ammonical Nitrogen	mg/L	35	28	30	26	31	32
11	Potassium	mg/L	48	26	28	23	33	38
12	Sodium	%	77	56	59	55	69	73

Treatment of Leather Effluent

The leather and distillery effluents were collected from nearby common effluent treatment plants (CETP). The synthesized PES membrane and PES/ Gelatin blend membranes were used in the ultrafiltration setup to carry out treatment of a typical tannery effluent collected from CETP, industrial region of Ranipet, Tamilnadu. The effluent was pretreated by adding chlorine so that the build up of organic materials on the surface of membrane would not lead to immediate fouling. The chlorinated effluent was further filtered in a conventional filter to remove the macro impurities (if any) in the range of mm. Partially treated tannery effluent was treated in the ultrafiltration equipment provided with PES/gelatin membranes of different composition at normal temperature and an operating pressure of 414 kPa.

Physico-chemical characteristics such as colour. total dissolved solids, total suspended solids, pH, chloride, sulphate, BOD, COD, ammonical nitrogen, sodium, total potassium, and total chromium were analysed. The final results of PES- Gelatin blend membranes on performance of tannery effluent separation are given in Table 2; A refers to 100% PES; B - 95/05 PES/Gelatin; C-90/10 PES/Gelatin; D- 85/15 PES/Gelatin; and E-80/20 PES/Gelatin, respectively.

Treatment of Distillery Effluent

Surface water is the source of the raw water supply for distillery industries. Each liter of alcohol produced in India generates about 15 liters of spent wash. Even though wastewater is generated at various stages of alcohol production, wastewater from the fermented sludge, spent wash and spent lees are the main contributors to pollution. The physicochemical characteristics of the distillery spent-wash from the primary treatment unit that was used for this study are reported in Table 3. PES/Gelatin blend membranes were used in the Ultrafiltration setup to carry out treatment of a distillery effluent. The ultrafiltration unit was operated at an applied pressure difference of 414 kPa. The performance of PES -Gelatin blend membranes in the treatment of distillery effluent is shown in Table 3.

RESULT AND DISCUSSIONS

Ultrafiltration membranes prepared from Polyethersulfone blended with organic and inorganic materials have specific properties and can be used in high temperature applications, over a wide range of pH, in sterilized conditions for pharmaceutical applications, protein recovery, waste water treatment and other separation process. The results of the experimental work carried out are reported below.

Analytical Techniques: X-Ray Diffraction Pattern

The XRD diffraction patterns of PES membranes with added gelatin content ranging from 0 to 20% are shown in Figure 1. Pure PES membrane exhibits two crystalline peaks, increasing the content of gelatin brings out a weak broad profile, indicating that gelatin is an amorphous material. The X-ray diffraction patterns are expressed as simple mixed patterns of PES and gelatin, which have very good compatibility or otherwise each polymer would have its own crystalline region in the blends. However, the highest intensity of diffraction peaks occurs at 20 of 17.5° and 43.76° of the composite PES membrane. As the gelatin content increased to 20%, all the peaks became weaker and disappeared. The contact angle of PES membrane decreases to 17.2° for 20% gelatin and the intensity of the diffraction peak decreases with an increase in gelatin content, such that the peak is either absent or gets merged with the broad amorphous peak. The degree of crystallinity decreased with increasing gelatin in the composite, and the PES-gelatin mixtures tend to become amorphous. The decreased crystallinity of the composite film is mainly attributed to the broken hydrogen bonding of PES molecules.

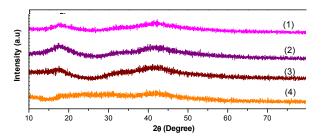


Figure 1: XRD pattern of PES/gelatin (1) 100% PES: (2) 95/5% PES/gelatin; (3) 90/10%, PES/gelatin; (4) 80/20%, PES/gelatin.

Hydrophilicity of PES/Gelatin Membranes

Hydrophilicity and wetability of membrane surfaces was evaluated by measuring water contact angle. A higher contact angle corresponds to a hydrophobic surface, whereas a small water contact angle means a hydrophilic surface. A number of researchers have reported that enhancing hydrophilicity of membrane surfaces could effectively reduce membrane fouling and result in an increase in the flux. Contact angles were measured at six different positions on each membrane surface, and the average is reported in Table 1. The hydrophilicity of PES membranes increases with an increase in gelatin content. The PES content was decreased to maintain the total weight percentage as 17.5% and 82.5wt% DMF. The contact angle of the PES membrane decreases to 51.2° for 20% gelatin, indicating the higher hydrophilicity. Therefore, we infer that the introduction of gelatin biomaterials on the membrane surfaces could effectively enhance the hydrophilicity of ultrafiltration membranes.

Effect of Gelatin on Thermal Stability

The Thermo-Gravimetric Analyses of PES, Gelatin and PES/gelatin blend membranes are shown in Figure 2.

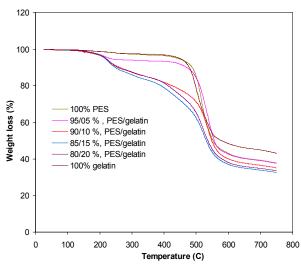


Figure 2: The TGA curves of 100% PES, 100% gelatin, and PES/gelatin blend membranes.

The curves of pure gelatin (100%) showed two zones of weight loss. The first weight loss in approximately the range 160 – 180 °C is due to the loss of water; the second weight loss starting at about 280 °C reveals the thermal degradation of gelatin protein. Kaminska and Sionkowska (1978) stated that this might be possible after the breaking-up of inter- and intra-molecular hydrogen bonds, which are responsible for the maintenance of the polymeric chain order (alpha-helix, beta-sheet structure) in protein films. On the other hand, PES shows a single step of weight loss between 450–500 °C. TGA curves of all blend polymers show the greatest weight loss in the temperature range of 250–400 °C, which are believed to

be due to the disintegration of intermolecular bonds and partial breaking of the molecular structure. As shown in Figure 2, it is understood that the incorporation of gelatin to the PES decrease the thermal stability of the blend film, but the miscibility of both polymer and biomaterials was confirmed from the thermal analysis.

Effect of Gelatin Composition on Water Content

The water content of the PES membrane and PES/Gelatin blend membranes was measured at different compositions. The modifier gelatin was added in the casting solution of PES and its influence on water content of the membranes was studied. The water content of the membranes is an indirect indication of the hydrophilicity and flux behavior of membranes. Membranes were thoroughly washed with distilled water before the estimation of water content. The water content of the membrane decreases with increasing weight ratio of gelatin in the casting solution. The PES membrane in the absence of gelatin was found to have a water content of 75.8% due to the hydrophilic nature of the membrane. When the gelatin biomaterial content was increased to 10% the water content decreased to 69.8%.

Effect of Gelatin Composition on Hydraulic Resistance

Membrane resistance ($R_{\rm m}$), which denotes the intrinsic resistance of the membrane, is an indication of the tolerance towards hydraulic pressure and was measured with pure water as the feed. At the steady state, $R_{\rm m}$ was determined by measuring the pure water flux under various transmembrane pressures from 69 to 414 kPa for the PES/Gelatin membranes at various compositions, as illustrated in Figures 3. $R_{\rm m}$ was calculated from the inverse of the slope of the corresponding pressure Vs pure water flux plots. The presence of a biomaterial in the casting solution has a considerable effect on the membrane resistance.

From the experimental data it is evident that the pure PES membrane in the absence of gelatin exhibited a higher membrane resistance of 20.7 kPa L⁻¹.m⁻².h⁻¹ due to its low porosity. However, in the presence of gelatin from 5 to 20%, the hydraulic resistance decreased gradually from 12.3 to 5.3 kPa L⁻¹m⁻²h⁻¹. This may be explained by the fact that an increase in the composition of gelatin not only increases the shrinking of membranes, but also enhances the size of pores to a greater extent due to the extended segmental gap between the polymer chains, which leads to the decrease in the value of R_m (Kesting, 1985).

The decreased value of membrane hydraulic resistance may be due to the formation of macrovoids (Strathmann et al, 1975) on the membrane surfaces, thermodynamical instability, which enhances precipitation and a porous nature.

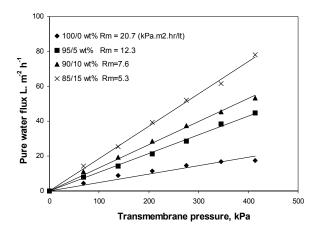


Figure 3: Effect of transmembrane pressure on pure water flux of PES/gelatin blend membrane, Rm-Membrane resistance, kPa.m².hr/L.

Pore Size Analysis

The protein rejection rate, molecular weight cutoff, average pore radius, porosity and number of pores has been estimated for the membranes at different weight ratios of PES/Gelatin by carrying out experiments in the ultrafiltration equipment. The results are reported in Table 4. The average pore radius of the membrane was indirectly determined using the model described by Sarbolouki (1982). It is evident from these results that the membrane prepared in the absence of additive has a relatively smaller pore size and porosity, as well as number of pores. The membranes without gelatin (100% PES) have the lowest pore size of 19.6 Å, the surface porosity and pore density are also lower than in the modified membranes, and further have a lower water flux and more

rejection. Addition of 5% gelatin into the casting solution induced the formation of a greater number of pores in the skin with relatively bigger pore size, leading to the increase in the permeate flux of the membrane. Further additions of gelatin resulted in the increase of the pore size and porosity, while the pores does not follow a uniform trend. The membranes with 20 and 15% of gelatin showed more number of pores with higher pore size. In other words, 20 and 15% of gelatin produced looser membranes. This is also supported by the membrane resistance shown in Figure 3.

Although bigger pore size will favor high permeate flux, the solute rejection will drastically fall. The membrane best suited for any application would be the one that has the most pores with the smallest size (Wang et al., 1994) because a smaller size of pores will favor better retention and a higher number of pores will favor high permeate flux. Hence, it seems that a gelatin concentration of 10 wt% in the casting solution would provide high permeate flux with high solute retention.

Molecular Weight Cut-Off (MWCO)

The molecular weight cut-off of the membranes was investigated using percentage rejection of proteins of different size. Dextrins are commonly used because they are readily available in a variety of molecular weights and inexpensive. The percentage rejection of a membrane can range from 100 to 0%, where 100% means complete rejection while 0% implies no rejection. MWCO is a measure of the nominal pore size of the UF membranes, which is defined as the molecular weight above which a certain percentage of the solute in the feed solution is retained by the membrane. In this study, 80% rejection was chosen as the criterion for determining MWCO. However, the result shows that the % rejection for all the blend membranes is more than 80% for different molecular weights of dextrin's. The

Table 4: Protein rejection, molecular weight cut-off, average pore radius, surface porosity and number of pores of PES / gelatin blend membranes.

Polymer (17.5 wt %)		Rejection	MWCO	Average pore radius	Membrane porosity	Number of pores	
PES	gelatin	%	(kDa)	R (Å)	ε x 10 ⁵	n x 10 ⁻¹¹	
100	0	86.0	20	19.6	1.06	3.86	
95	05	84.3	35	37.6	2.72	6.12	
90	10	80.1	35	39.6	4.77	7.69	
85	15	87.2	69	47.5	4.98	10.04	
80	20	80.9	69	51.2	5.77	17.02	

MWCO of the PES membrane without gelatin is 20 kDa. When 20 wt% gelatin is blended with 80 wt % PES, the MWCO value increased to 69 kDa. It was expected that the incorporation of gelatin in place of PES would alter the MWCO of the resultant blend membranes. These results are in agreement with the permeability data of the derived membranes. Similar observations have been reported for Cellulose Acetate/Polyethersulfone (Sajitha *et al.*, 2003; Sivakumar *et al.*, 1999) and Cellulose Acetate/carboxylated Polysulfone (Thomas *et al.*, 1992).

Morphology of PES/Gelatin Blend Membranes

The formation of macrovoids can be suppressed during the immersion precipitation process by an increase of the polymer concentration in the casting solution and through coagulation by dissolved solvent instead of pure water. The SEM images of the top surfaces and cross sections of PES/gelatin blend ultrafiltration membrane for different blend compositions at 5000x and 250x magnifications are pictured in Figures 4 and 5, which reflect the effect of biomaterial blend composition on membrane morphology. The membrane had an asymmetric structure consisting of a dense skin layer and a porous sub-

layer that has cellular morphologies enclosed polymer matrix. The number of pores on the surface increased as the gelatin composition in the blend is increased, as shown in Figure 4c with 15% gelatin. This finding supports the analysis discussed earlier in this paper. Similarly (Smolders, 1992; Paillet et al 1993), the addition of PVP as additive to the polyethersulfone membrane was reported to suppress the formation of macrovoids in the sub-layer, while the top layer consisted of a closely packed layer of nodules. Pictorial studies shown in Figures 5a-d confirm that pores occurred in the top layer. The size of the pores increased with the increase in the amount of gelatin in the casting solution at lower percentage of gelatin. At higher concentration, more skin layers were formed. It should be noted that a small amount of gelatin was enough to initiate the formation of pores in the skin layer. Since the skin layer dictates the perm selectivity of a membrane, it is possible to have a strict control of the membrane performance. In addition, the permeation flux of modified PES membranes increases with the addition of gelatin in the casting solution. The results were consistent with qualitative observations of SEM, suggesting that the gelatin biomaterial played the role of pore former in the skin layer that increases the permeability of the PES membranes.

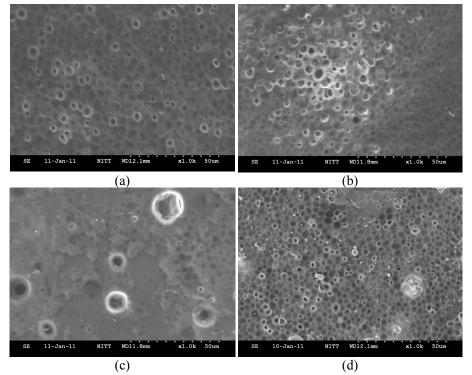


Figure 4: SEM Images of PES and gelatin membranes – Top Surface (a) 95/5 PES/gelatin; (b) 90/10 PES/gelatin; (c) 85/15 PES/gelatin; (d) 80/20 PES/gelatin.

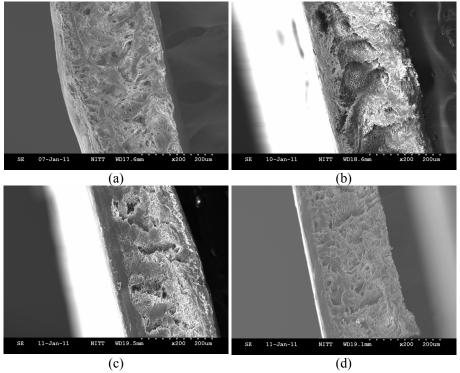


Figure 5: SEM images of PES and gelatin membranes; cross sectional view: (a) 95/5; PES/gelatin; (b) 90/10; PES/gelatin; (c) 85/15; PES/gelatin; (d) 80/20; PES/ gelatin.

Performance Evaluation of the PES/Gelatin System with Partially Treated Tannery Effluent

The leather and distillery effluents were passed through PES-Gelatin blend membranes of different compositions, 100% pure PES; PES and Gelatin as 5%, 10% and 15% respectively in a dead-end stirred ultrafiltration cell. The membrane developed with 10% of gelatin/90% PES showed overall better performance compared to the other membranes. Particularly, the value of sulfide removal for 10% gelatin had the very lowest value. The concentration of the permate is very low in sulfide and solubilized lime content and heavy metals are less, so that this dilute permeate stream can be recycled and reused in the pre-tannage step or in the tannage adjusting the tannin concentration to the desired value. The treated product for the 90-10% PES - Gelatin blend had properties closer to those of potable water to be used more readily for agriculture. Similarly, pure PES membranes without gelatin showed more than 50% reduction of the COD. However, 10% of gelatin added to pure PES membrane resulted in 80% reduction of COD with a significant decrease in the chromium level. About 50% of organic nitrogen was retained by the membrane, while the rejection for chromium was 28%. There is a strong reduction of suspended solid components and fat substances, with rejection of 84% for pure PES membrane and 98% for 10% gelatin with reference to initial feed. It was observed that there is reduction of hexavalent chromium from 4.2 mg/l to 2.8 mg/l for 100% PES membrane; by adding 10% gelatin the chromium content reduces to 1.12 mg/l.

Performance Evaluation of PES/Gelatin Membranes with Distillery Effluent

The pre-treated distillery wastewater, dark brown in color and free from suspended particles, was used as feed for the UF experiment operated at the optimal pressure of 414 kPa. The modified PES/gelatin membranes effectively removed the particles in the colloidal size range along with color removal. Permeate was dull white in color with reduction in TDS from 4000 to 2250 mg/L, sulphides from 2470 to 405 mg/L, and chloride from concentration 950 to 826 mg/L. The results indicate that a PES – gelatin blend membrane is comparatively superior in performance to a pure PES membrane in terms of all aspects of UF. From a closer analysis on the results, it could be concluded that, even within the PES – gelatin blends, the 90-10% PES – gelatin membrane has a better performance. Overall it was found that the membrane with

composition 90% PES and 10% gelatin produced permeate of desirable quantities when compared to similar membranes of other weight fractions under identical conditions. Furthermore, this combination provided higher flux rate results for handling a higher quantity of effluent.

CONCLUSION

The performance of modified PES/gelatin membranes for treating tannery and distillery waste water through ultrafiltration was investigated for different gelatin concentrations. The prepared membranes displayed asymmetric membrane morphology which varied with gelatin content. Water uptake and contact angle results confirmed that the hydrophilicity of PES/gelatin membranes is higher than that of neat PES membranes. The membrane surfaces incorporated with gelatin and the hydrophilic nature of gelatin segments further enhance the wettability, permeability and the antifouling ability of the modified PES membranes. Ultrafiltration performance characterization was done for all the developed membranes, which produced acceptable results as per standards. Blending of PES membranes with gelatin produced uniform pore sizes and uniformly distributed pores, which resulted in comparatively high permeate fluxes as compared with other blends of PES. A new type of polymeric blend membrane material based on PES/ gelatin has therefore been identified for treatment of industrial effluents. A PES/ gelatin blend of 90:10 weight percentage produced highly desirable results for the treated effluent.

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