

Development of Polyimide Nanofiltration Membranes by Phase Inversion Technique for Processing Dairy Industrial Effluent

Boya Venkata Swamy¹, Ashok Kumar Kusuma², G B Radhika³, G. Sridevi⁴,

¹*Department of Chemistry, B.V. Raju Institute of Technology, Narsapur, Medak – 502313, Telangana., India*

²*Department of Physics, B.V. Raju Institute of Technology, Narsapur, Medak – 502313, Telangana., India*

³*Department of Chemical Engineering, B.V. Raju Institute of Technology, Narsapur, Medak – 502313, Telangana., India*

⁴*Department of Civil Engineering, B.V. Raju Institute of Technology, Narsapur, Medak – 502313, Telangana., India*

Abstract

Nanofiltration (NF) membranes have exhibited potential to efficiently remove trace contaminants from water compared to conventional methods. In the present investigation, polyimide (P 84) and cellulose acetate (CA) membranes were synthesized by phase inversion using mixed solvent system for the treatment of dairy effluent by NF. These indigenous membranes were characterized by fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscope (SEM) to elucidate intermolecular interactions, crystallinity, thermal stability, surface and cross sectional morphologies of the membranes, respectively. The influence of various parameters such as flux and rejection of total dissolved solids (TDS), chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were studied. Performance of P 84 membranes was compared to CA for recovery of reusable water. Flux values of 17 L m⁻²h⁻¹ for P 84 and 14.8 L m⁻² h⁻¹ for CA were observed at a constant feed pressure of 20 bar. TDS, COD and BOD rejections were found to be 50%, 70.6% and 44% for P 84 and in case of CA membranes 81.33%, 75.6% and 72%, respectively. Separation performance proved to be strongly influenced by the choice of solvent systems used in membrane casting. The membranes were found to be highly efficient in treating dairy industrial effluent with substantial potential for scale-up due to the phase inversion technique of casting that was adopted.

Keywords: Dairy industrial effluent, Nanofiltration, Phase-inversion, Membrane characterization.

Introduction

In dairy industries, water is the key processing medium. It has high consumption throughout all the steps of dairy industry including cleaning, sanitization, heating, cooling, floor washing and rinsing of different plant units, thus contributing to effluent production ("white waters", first rinse water, etc.) from 0.2 to 10 L per litre of processed milk [1,2]. Moreover, this processed effluent contains diluted fractions of the dairy products, which significantly contribute to the non accidental losses of milk and to the total waste-water production. Dairy effluent is distinguished by the high BOD and COD contents, high levels of dissolved or suspended solids including fats, oils and grease, nutrients such as ammonia or minerals and phosphates and therefore require proper attention before disposal[3, 4]. This effluent results in water eutrophication and is hazardous to aquatic life and soils, causing significant environmental problems when it is discarded without treatment.

Many technologies developed to treat dairy effluent, such as coagulation [5], ecological treatment system [6], anaerobic or/and aerobic reactors [7] and membrane separation [8]. Among these, membrane technology has edge over others in removal of a high degree of dissolved, colloidal and particulate matter and selectivity in size of pollutants to be removed thus providing the possibility of developing very compact treatment plants. Research dedicated to the treatment of dairy streams using nanofiltration (NF) and reverse osmosis (RO) revealed convenient operations for achieving the set targets [9, 10] such as to concentrate and to elevate value to the milk constituents in non food applications as well as, simultaneously produce treated water that can be reused in the dairy factory mainly due to the separation characteristic of NF as it operates at the intermediate range between ultrafiltration (UF) and reverse osmosis (RO). In addition, NF membranes have molecular-scale pores throughout their selective layer and yield a relatively high permeate flux at low operating pressure [11].

The practical applications for NF membranes have ranged from their use in the dairy industry for recovering small organic molecules such as fat, sugars, proteins, and peptides [12, 13] to their wide use in the treatment of industrial effluents contaminated with organics. To cope with the demand from industries, today most membrane manufacturers worldwide produce NF membranes [14]. Commercial membranes are made mostly from polymers such as aromatic polyamide, polysulfone, and poly (ethersulfone) etc. Cellulose acetate (CA) [15] and polyimide [16] are common polymers used for NF and RO membranes. Some are already commercially available since the 1970s [17]. However, there are some existing challenges, even still present nowadays, such as the need of an improved chemical stability and a high rejection of organic compounds combined with high water fluxes. On the other hand, membrane performance depends on several parameters involved in membrane synthesis [18]. For the preparation of

NF and RO membranes, several methods have been employed, such as using phase inversion, interfacial polymerization and solvent resistant method [19]. The final performance, however, directly linked to the structure, depends on multiple factors, including the composition of the polymeric solution (solvents, polymer concentration, additives) and non-compositional parameters at the level of the membrane synthesis process and post-treatment (evaporation time, temperature, annealing time, etc) [20, 21].

In response to the challenge of developing new membrane materials, we have synthesized the P 84 and CA based NF membranes by phase inversion using mixed solvent system and applied for removal of salts and micro pollutants from dairy effluent. These indigenous membranes were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermo gravimetric analysis (TGA) and scanning electron microscopic (SEM) studies to elucidate the structural, crystallinity, thermal stability, surface and cross sectional morphologies of the membranes, respectively. The influence of color, TDS, conductivity, turbidity, COD and BOD content in the feed, permeate and reject samples were analyzed. The flux and% rejection at various operating conditions were evaluated.

Experimental

Materials

P 84 having an average molecular weight of 75000 (Fig. 1a) and CA with an average molecular weight of 37,000 (39.8 wt% acetyl) were purchased from Sigma-Aldrich, Mumbai, India. Analytical grade solvents such as acetone, 1, 4-Dioxane, *N, N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were procured from sd fine Chemicals, Hyderabad, India. The chemical and physical structures of P 84 are shown in Fig. 1 (a) and (b), respectively. The configuration of flat sheet membranes with an effective area of 0.015 m², for NF flat sheet membranes was synthesized indigenously in the laboratory. Automatic film coater and non-woven fabric supports were obtained from Permionics Membranes Pvt. Ltd., Vadodara, India. The dairy industrial effluent was obtained from AP Dairy Development Co-Operative Federation Ltd, IDA Nacharam, Hyderabad, India. The feed characteristics of dairy industrial effluent are depicted in Table 1. Potassium dichromate, ferrous ammonium sulfate, mercuric sulfate, sulfuric acid, ferroin indicator for COD analysis, sodium thiosulfate, Winkler's reagent, MnSO₄, potassium iodide, starch indicator for BOD analysis, citric acid, HCl, EDTA, NaOH and sodium metabisulphite (SMBS) for washing and storing of the membranes were purchased from sd fine Chemicals, Hyderabad, India. BOD incubator (RCI-S.NO-313 India), COD analyzer (DRB 200 COD Reactor, Germany) and Colorimeter (Hach-DR-890) procured from M/s Hach, Bangalore, India. Conductivity meter (DCM-900) and pH meter (DPH-504) were purchased from Global Electronics, Hyderabad, India.

Membrane synthesis and post-treatment

Polyamide (P 84) and cellulose acetate (CA) nonporous membranes for NF were prepared by phase inversion method using mixed solvent systems. The P 84 polymer solution was prepared by dissolving 25 % w/v of P 84 in 60 % DMF and 15 % THF solvent mixtures, whereas for CA membrane the polymer solution consist of 10 % w/v CA dissolved in 18 % acetone and 72 % dioxane. A 200 µm thick film of the homogeneous bubble free polymeric solution was deposited on top of a polyester non woven support by using a custom-build blade knife and an automatic film coater at a low casting speed (0.67 m/min). The nascent film was immersed in a coagulation bath (distilled water at 4 °C) to induce the polymer precipitation and was kept there for 15-20 min. The membrane was stored in distilled water at room temperature until use. The photographs of indigenously synthesized membranes of P 84 and CA are provided in Fig. 2 (a) and (b), respectively.

Description of NF systems

The schematic representation of pilot scale NF system is shown in Fig. 3. A feed tank of 100 L capacity made of stainless steel was provided for storage and supply of effluent to the system. An inexpensive micron rope cartridge made of hydrophobic polypropylene (PP), having contact angle of 110° and 5 µm pore size, was installed upstream of the spiral wound membrane module as a prefilter. The cartridge is used to prevent the entry of suspended solid particles which could damage the membrane while its porous nature ensures a very small pressure drop. The cartridge can be replaced once it gets fouled and can be recycled a couple of times by treating with dilute acid. A high pressure pump (Hironisha, Japan) capable of maintaining a pressure up to 300 psi was installed for transporting the feed throughout the system. The pump 2 HP single phase motor (Crompton, India) was operated in this process. A restricting needle valve was provided at the concentrate outlet of the membrane pressure vessel, to pressurize the feed to the desired value installed upstream of the valve-indicated by a pressure gauge. The feed tank had a provision for recycle of the reject which passed through heat exchanger for maintaining constant temperature (28-30 °C). Heat exchanger consists of a large glass column, which is circulated with ice-cooled water. The product coming out of the heat exchanger is then fed back to the feed tank, called as concentrate. Permeate and concentrate flow rates were measured using flow rotameters.

Experimental procedure

Before starting the experiment, the NF flat sheet membrane was fixed in system cell and was cleaned and wetted using distilled water until the permeate conductivity reached to 0.01 mScm⁻¹. The experiments were carried out with de-ionized water to study the effect of pressure on flux. Deionized water was taken in feed tank and transported through the flat sheet NF membrane module using high pressure pump (Fig. 4). The concentrate tube was left to flow outside into a bucket instead of feed tank in order to maintain the constant feed concentration. The system pressure was varied by restricting the needle valve on the concentrate lane. The flow rates of permeate and concentrate were measured at each pressure.

Initially, the stainless steel feed tank was filled with 30 L of dairy effluent and the system was initially run to remove 2.2 L of distilled water that was present in the system, which is known as dead volume. A sample of initial feed was collected for analysis.

The experiment was performed at 75% solvent recovery, optimum pressure of 21 bar, with recycle of the concentrate to study the effect of feed concentration on flux and % rejection. The flow rates of permeate and concentrate were measured in regular time intervals to note any declination in flux. After a particular water recovery was attained, the initial feed, final concentrate and average permeate samples were analyzed for TDS, COD, BOD and turbidity. Finally, the system was cleaned and washed with distilled water to remove solutes from the membrane surface and pores.

Fouling and its prevention

In general, fouling of membranes is caused by suspended solids, microbes and organic materials present in the feed water that accumulate either on the membrane surface or within the pores [22]. An aqueous solution of citric acid or HCl (1% w/v) was run through the system for about 10 to 15 min for removal of mineral salt scales. Tetra sodium EDTA concentration of 1% w/v and trisodiumphosphate/sodium hydroxide was used to remove organic and inorganic scales. Finally, sodium lauryl sulfate was used for polishing the membrane surface by generating a soapy lather.

Membrane Characterization

Fourier transform infrared (FTIR)

The NF membranes of P 84 and CA have been characterized for their intermolecular behavior. The membranes were scanned in the range 400–4000 cm^{-1} wave numbers using Thermo Nicolet Nexus 670 spectrometer (résolution 4 cm^{-1}).

X-Ray Diffraction (XRD) analysis

A Siemens D 5000 powder X-ray diffractometer was used to assess the solid-state morphology of both P 84 and CA NF membranes. X-rays of 1.54 Å wavelengths were generated by a CuK source.

Thermo Gravimetric Analysis (TGA)

Thermal stability of P 84 and CA membranes was examined (Seiko 220TG/DTA analyzer) in the temperature range of 25–800°C at a heating rate of 10°C min^{-1} with continuous flushing using pure nitrogen gas at 200 ml min^{-1} to determine the thermal stability and decomposition characteristics.

Scanning Electron Microscopy (SEM)

The surface and cross sectional morphologies of the P 84 and CA were studied by SEM Model JEOL JSM – 6380, LA, USA. In preparing the specimens, the fracture surface of the cross-section of the NF two layered membrane inclusive of non-woven fabric polyester support and nano-porous substrate were obtained by cutting the membrane in liquid nitrogen to ensure smooth morphology.

Analytical methods

The feed and permeate samples were analyzed for TDS, COD, BOD and color (platinum–cobalt procedure) according to APHA methods [23]. The conductivity of above samples was determined using the digital conductivity meter. The feed and permeate samples were treated with mercuric sulphate (HgSO_4), which converts the chlorides into insoluble mercuric chloride (HgCl_2) precipitate and gets removed from the titration medium.

Results and discussion

Membranes characterization

FTIR

Fig. 5 shows FTIR spectra of CA and P 84 membranes. From Fig. 5 (a), the imide group is characterized by bands at around 1785 cm^{-1} and 1744 cm^{-1} were attributed to the asymmetrical and symmetrical stretching vibration of C=O in the imide group, respectively. The peak at 1430 cm^{-1} represents the stretch of C – N in the imide group [24]. From Fig. 5 (b), besides the carbonyl stretching mode at 1786 cm^{-1} , the peak at 1183 cm^{-1} could be assigned to the asymmetric stretching of the C–O–C linkage of the acetyl substituent. The broad peak appeared at 3488 cm^{-1} represents the hydroxyl (–OH) group of CA.

XRD Analysis

X-ray diffraction studies not only indicate the nature of the compounds but also enable to identify the space between the clusters of the polymer chains. It is a well-known fact that the *d*-spacing (*d*) value gives an indication of cluster space existing in the polymer [25]. The X-ray diffractograms of P 84 and CA NF membranes are shown in Fig. 6. The XRD pattern of P 84 membrane appears to be amorphous in nature (Curve 6 (b)), whereas the XRD pattern of CA membrane appears to be semi crystalline in nature with little sharp peaks at 15°, 26° and 30° of 2θ (Curve 6 (a)), with inter-segmental spacing values between polymer chains (*d*-spacing) of 4.38 Å, 3.29 Å and 1.75 Å, respectively, which might have imparted better separation factor to the membrane.

TGA Studies

Thermal stability of CA and P 84 membranes is shown in Fig. 7 (a and b). TGA curve of CA (Fig. 7 (a)) shows the beginning of weight loss at 340 °C, followed by final decomposition around 400 °C. The TGA curve of P 84 membrane (Fig. 7 (b)) found to be stable upto 500 °C and later there was a gradual decrease in weight of the membrane and final decomposition of the membrane occurring at 600 °C. From these observations it is concluded that P 84 is high thermal stability than CA. Hence the membranes can be used even at high temperatures.

SEM Analysis

Fig. 8 shows the surface and cross-sectional views of CA and P 84 membranes. The surface morphology of CA and P 84 (Fig. 8 (a) and (b)), it can be seen that the membrane appears to be nanoporous in nature and these pores are distributed unevenly on the surface. The cross-sectional view of CA and P 84 membranes (Fig. 8 (c) and (d)) showed the formation of two different layers, in which the top layer indicate the nanoporous CA and P 84 layer and the bottom layer is non-woven polyester fabric support with adequate interpenetration of the top layer. No agglomerations or cluster formation of any of the polymers were observed.

Effect of pressure on flux

The effect of pure water pressure on flux, % rejection and conductivity for CA and P 84 using NF processes is represented in Fig. 9 (a) and (b), respectively. As expected, a raise in pure water pressure results in an increase of flux and rejection for CA and P 84 (Fig. 9 (a)) membranes, when compared with CA the flux enhanced in P 84. In addition to that the conductivities of pure water proportionate increase of pressure for both CA and P 84 (Fig. 9 (b)) membranes were noticed. Since the driving force of the process increases it results in enhancement of flux due to increased affinity between H₂O molecules and the imide groups of P 84 membrane or -OH functional groups in CA. The flux was zero at applied pressure less than 5 bar, due to high osmotic pressure arising from substantial concentration of dissolved solids in the effluent feed. Additionally, the conductivities of permeate decrease with cumulative time for both CA and P 84 (Fig. 9 (b)) membranes during NF process.

Effect of time on flux, % rejection and conductivity for dairy effluent

Effect of time on flux, % rejection and conductivity for dairy effluent using CA and P 84 membranes by NF process is graphically illustrated in Fig. 10 (a) and (b), respectively. The declination of flux is found to be 18.54 % for CA and 17.09 % for P 84 (Fig. 10 (a)), which is due to increasing concentration polarization near the membrane surface and retention of salts into the feed. On other hand, the % rejection of salts was decreased from 85.18 to 74.35 % in CA and from 66 to 50% for P 84 with the cumulative time was shown in Fig. 10 (a) and (b), respectively. Moreover, the conductivities of permeate gradually increases for both P 84 and CA membranes, whereas the conductivity of reject steadily decreases for CA and increases for P 84 (Fig. 10 (b)) with cumulative time.

Separation of TDS, conductivity, turbidity, COD and BOD

Table 2 depicts the TDS, conductivity, turbidity, COD and BOD values present in feed, average permeate and final reject for both CA and P 84 by NF processes. The percentage recovery of P 84 and CA membranes was obtained 66 and 70 %, respectively. From experimental observations it can be concluded that CA reduces the TDS, conductivity, turbidity, COD and BOD present in the feed effluent to a greater extent than P 84 membrane. The permeate obtained during the process was analyzed as per the APHA standards which can be safely disposed into environment or recycled for utilization in agricultural activities or industrial cooling towers [23].

Conclusions

The study revealed that indigenously synthesized cellulose acetate and polyimide membranes can be effectively used for separation of dairy effluent by nanofiltration. These indigenous membranes were characterized by fourier transform infrared spectroscopy, x-ray diffraction, thermogravimetric analysis and scanning electron microscope for structural, nature, thermal, surface and cross sectional morphology studies. The flux, rejection and conductivities for a given pure water and effluent was evaluated under various operating conditions. Polyimide and cellulose acetate membranes are effectively removed total dissolved solids, turbidity, chemical oxygen demand and biochemical oxygen demand from dairy effluent. Polyimide is a solvent resistant membrane whose application can be extended to solvent recovery and treatment of wastewater containing large concentrations of strong organic liquids. From experimental results it can be concluded that, using these indigenous membranes for nanofiltration process is more economical, consume less energy, eco friendly, ease of operation and maintenance over commercial membranes, with negligible efficiency in separation. Moreover, these membranes exhibited considerably high pure water permeability, good stability, excellent anti-fouling ability and which clearly offer vast potential for application in treatment of effluents coming from dairy, pharmaceutical, biochemical and food industries.

Acknowledgements We are thankful to B V Raju Institute of Technology, Narsapur, Medak for giving opportunity to the first author for doing research.

Table 1 Feed characteristics of dairy industrial effluent

Feed Characteristics	
TDS (ppm)	765
Conductivity (mS/cm)	0.88
Turbidity (FAU)	200
Color (Pt-Co)	40
pH	6-6.5
BOD (ppm)	8.09
COD (ppm)	360

Table 2 TDS, Conductivity, Turbidity, BOD and COD using CA and P84 membranes

Membrane Type	TDS (ppm)	Conductivity (mS/cm)	Turbidity (FAU)	BOD (ppm)	COD (ppm)
CA -Permeate	108.16	0.169	0	8.09	88
P84- Permeate	258.4	0.56	8	10.21	150
CA - Reject	1200	1.14	200	30.00	660
P84- Reject	1156	0.95	156	36.00	700

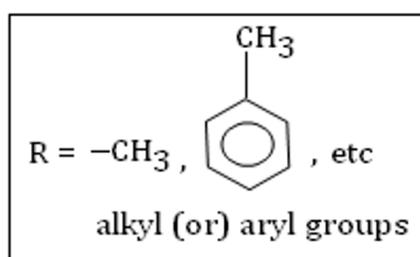
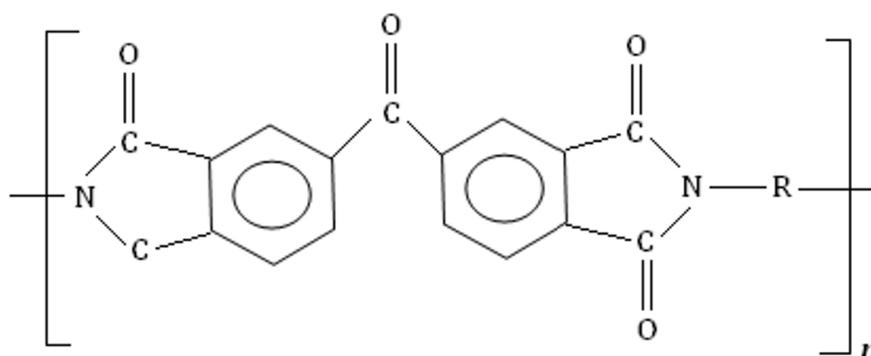


Fig. 1 (a) Fig. 1 Structure of P 84 membrane (a) Chemical

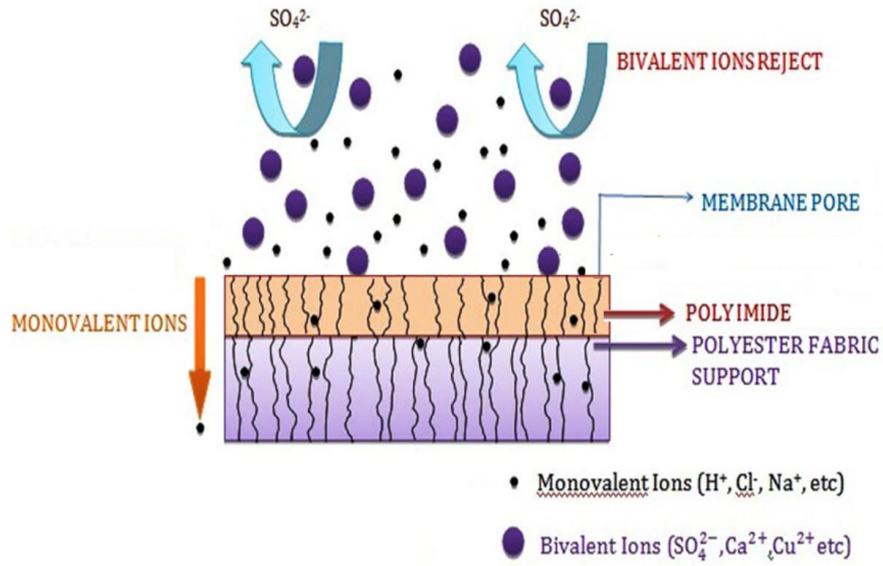


Fig. 1 (b) Fig. 1 Structure of P 84 membrane (b) Physical



Fig. 2 Photographs of (a) P 84



Fig. 2 Photographs of (b) CA

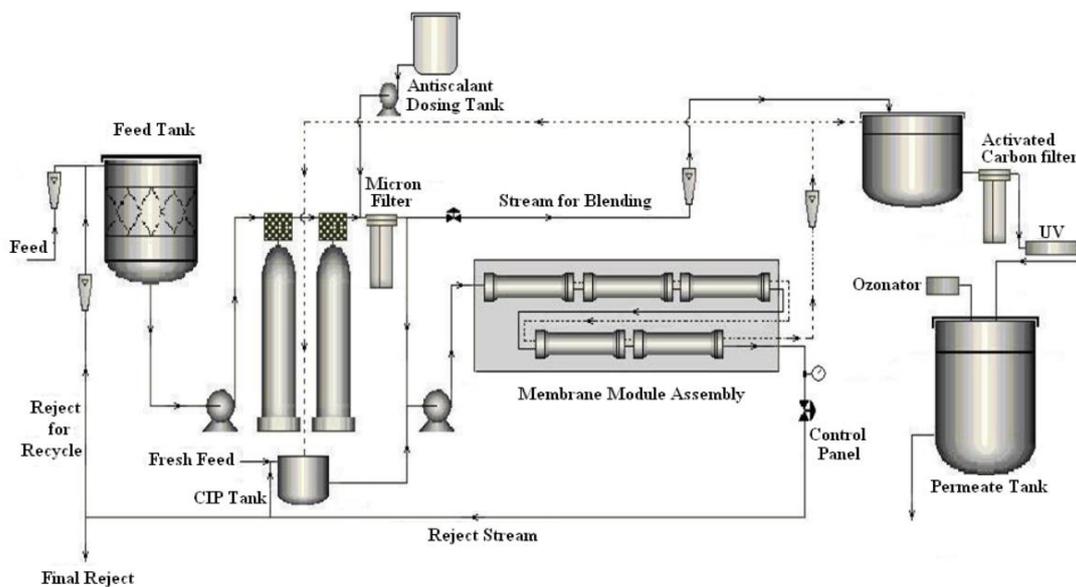


Fig. 3 Schematic representation of pilot- scale NF system

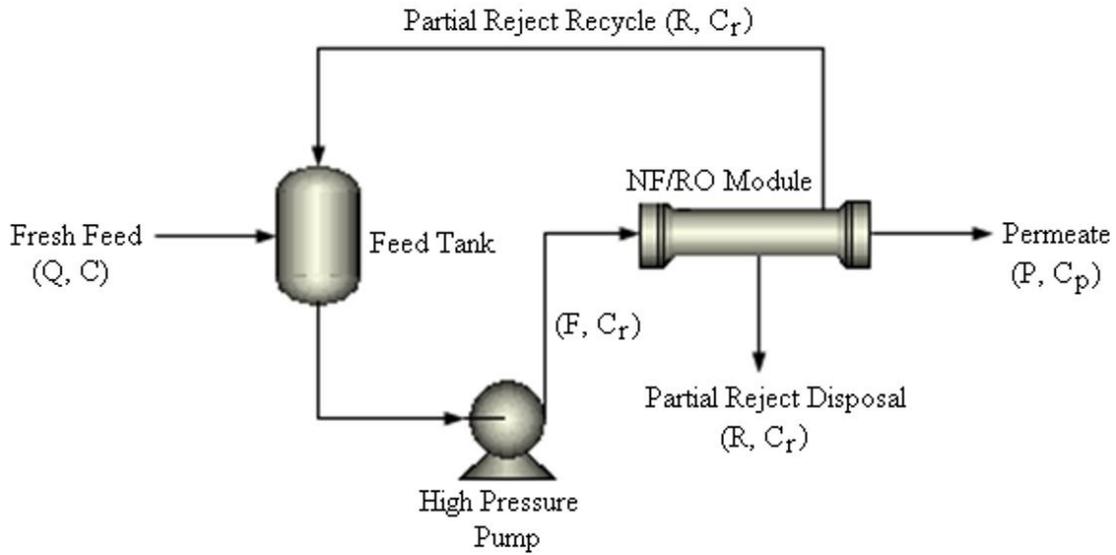


Fig. 4 Fig. 4 Process flow diagram of NF system

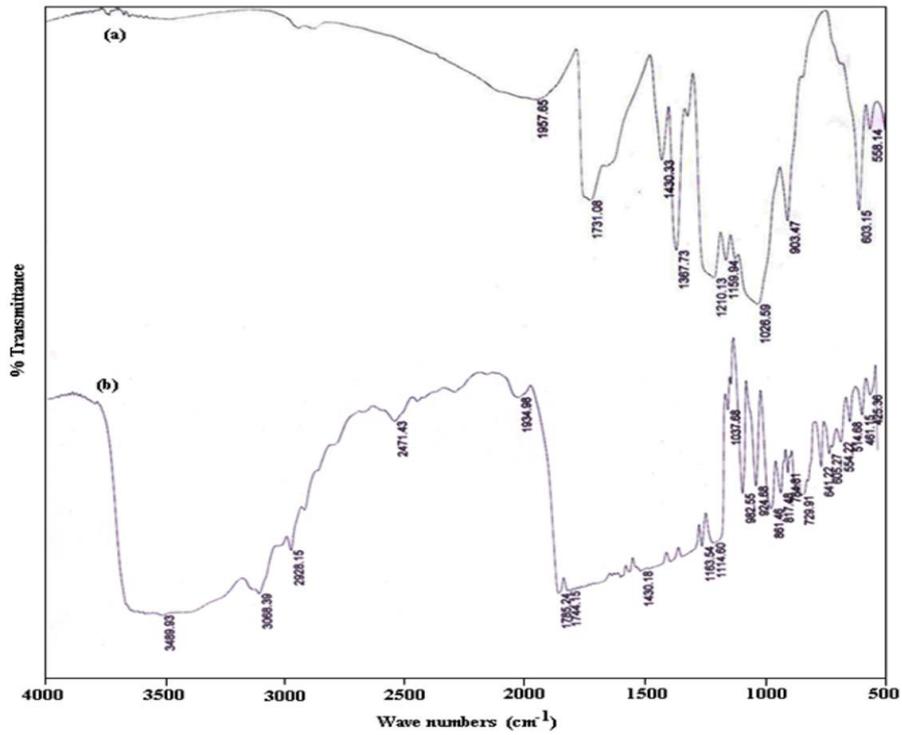


Fig. 5 Fig. 5 FTIR spectra of (a) P84 and (b) CA membranes

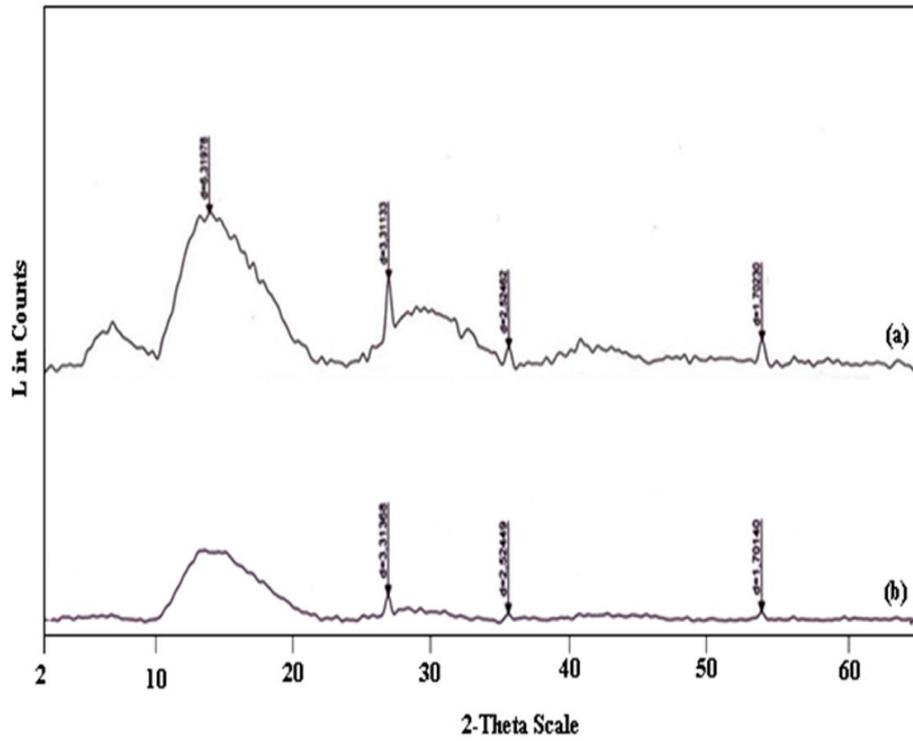


Fig. 6 Fig. 6 XRD spectra of (a) CA and (b) P84 membranes

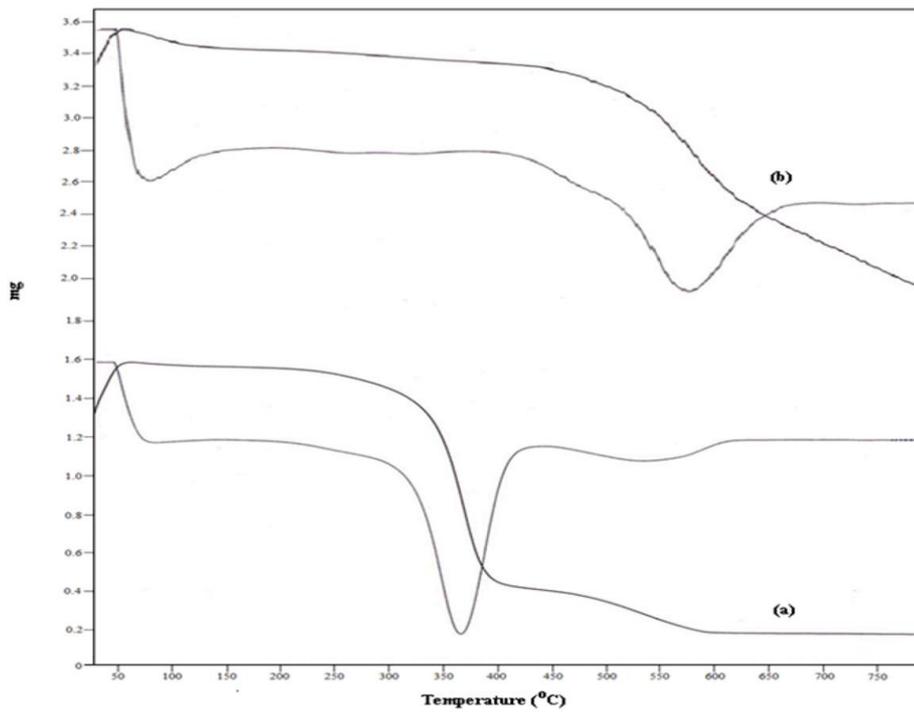


Fig. 7 Fig. 7 TGA curves of (a) CA and (b) P84 membranes

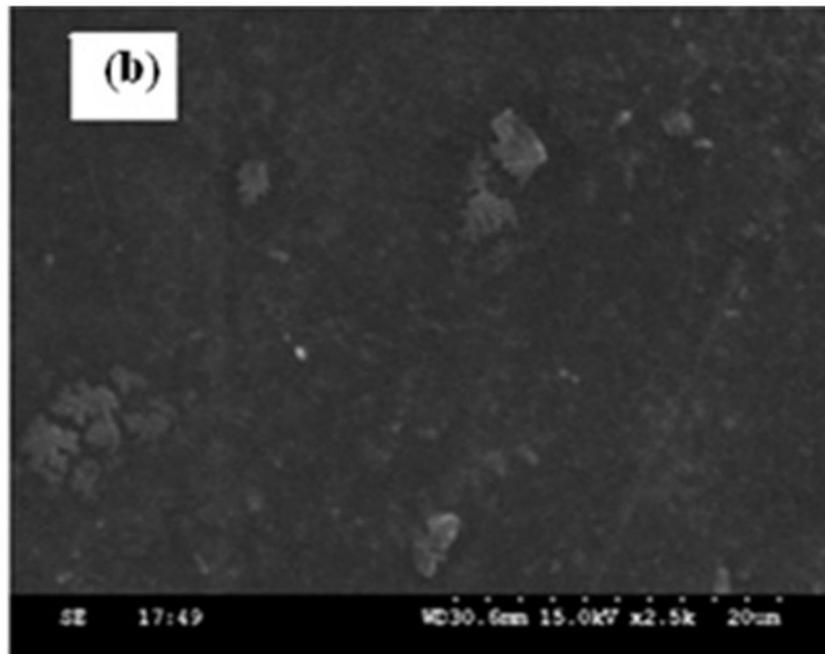
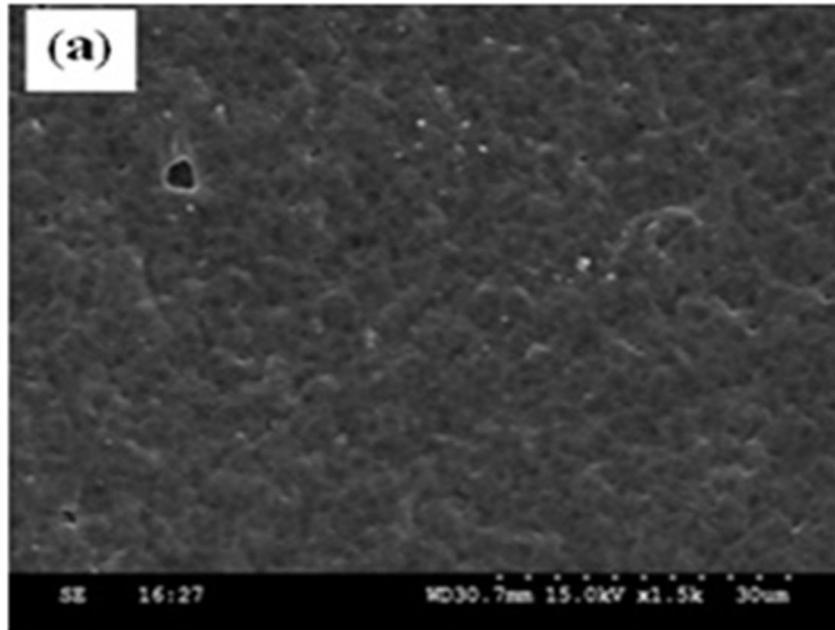


Fig. 8 SEM images of (a) CA surface (b) P84 surface

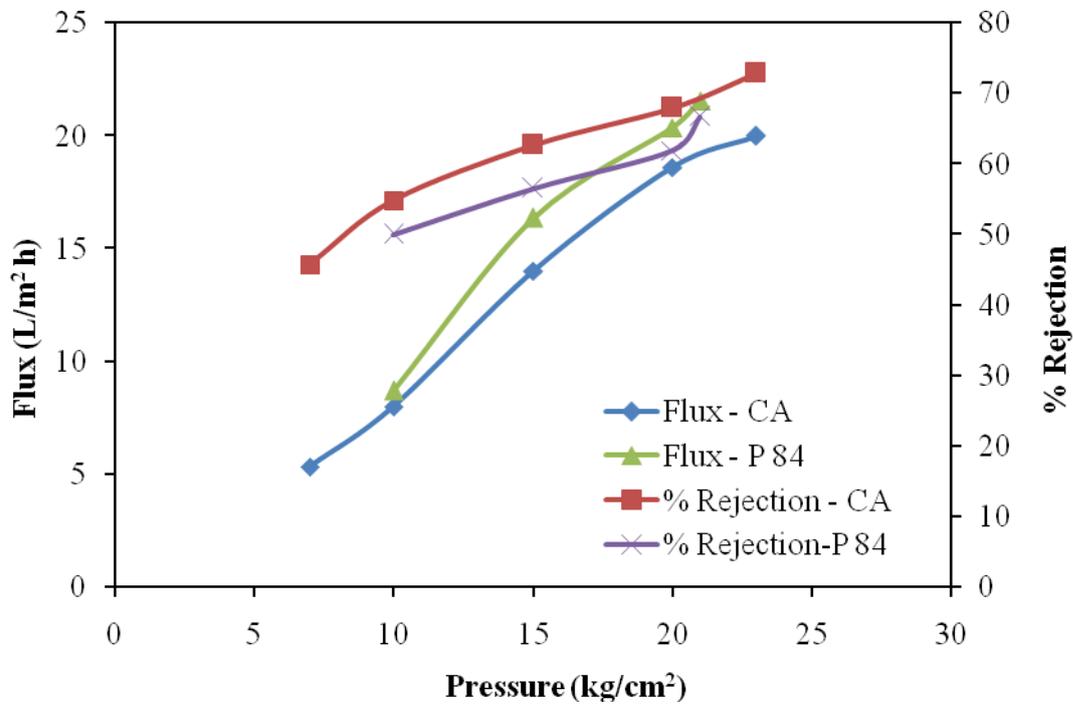


Fig. 9 (a) Effect of pure water (a) pressure on flux and percentage rejection

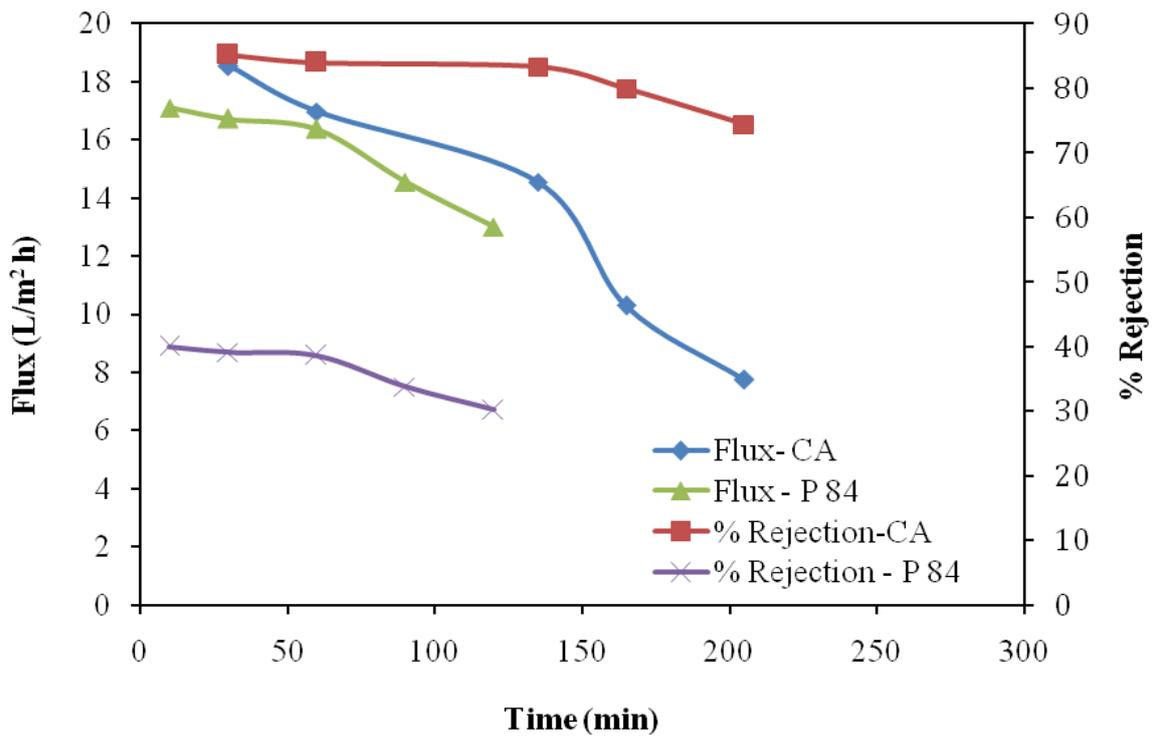


Fig. 9 (b) Effect of pure water (b) pressure on conductivity of permeate and reject of CA and P84 membranes

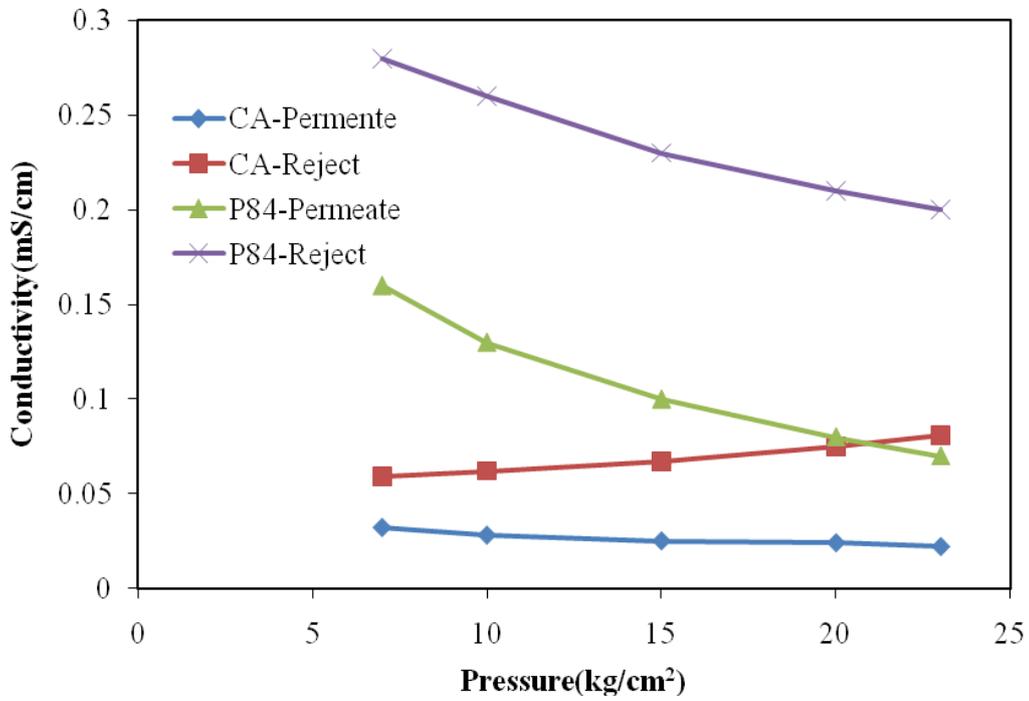


Fig. 10 (a) Influence of dairy effluent on performance of CA and P84 membranes (a) time Vs flux and percentage rejection

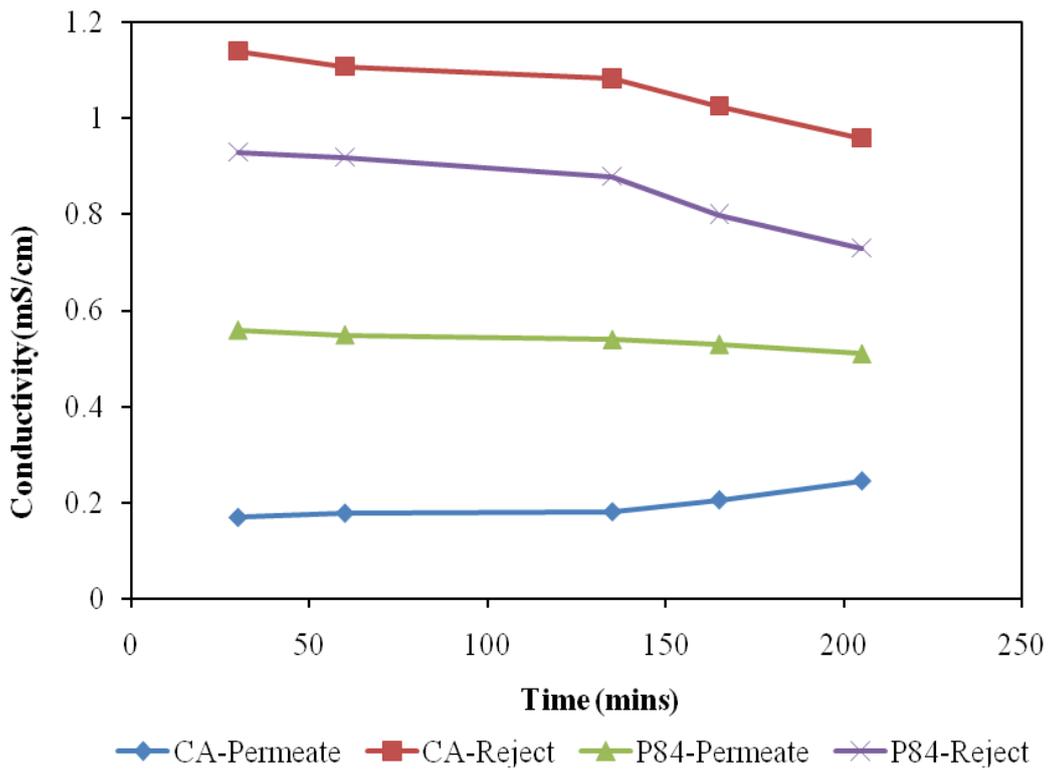


Fig. 10 (b) Influence of dairy effluent on performance of CA and P84 membranes (b) time Vs conductivity at 20 bar

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