

Polysulfone/nanocomposites mixed matrix ultrafiltration membrane for the recovery of Maillard reaction products

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(Received February 3, 2016, Revised June 15, 2017, Accepted July 17, 2017)

Abstract. Maillard reaction products like melanoidins present in industrial fermentation wastewaters are complex compounds with various functional properties. In this work, novel ultrafiltration (UF) mixed matrix membrane (MMM) composed of polysulfone (PSF) and nanocomposites was prepared through a phase inversion process for the recovery of melanoidins. Nanocomposites were prepared with acid functionalized multiwalled carbon nanotubes (MWCNTs) as the reinforcing filler for chitosan-thermoplastic starch blend. Higher nanocomposites content in the PSF matrix reduced the membrane permeability and melanoidins retention indicating tighter membrane with surface defects. The membrane surface defects could be sealed with dilute polyvinyl alcohol (PVA) solution. The best performing membrane (1% nanocomposites in 18% PSF membrane sealed with 0.25% PVA coating) resulted in uniform melanoidins retention of 98% and permeability of 3.6 L/m² h bar over a period of 8h. This demonstrates a low fouling PSF membrane for high melanoidins recovery.

Keywords: maillard reaction products; melanoidins; ultrafiltration; nanocomposites; mixed matrix membrane

1. Introduction

Industrial fermentation processes employing molasses, such as alcohol and bakers yeast production, generate large volumes of wastewater containing melanoidins and phenolics. Melanoidins are complex compounds produced through Maillard reaction between amino and carbonyl groups of organic matter. Both melanoidins and phenolics possess antioxidant and antimicrobial activity (Guimaraes *et al.* 2007), which deter the biological treatment of molasses fermentation wastewater.

Further, anticarcinogenic, antimutagenic, antiallergenic and antiaging activities have been identified with such antioxidants (Guimaraes *et al.* 2007). These functional properties are of considerable interest in the food, cosmetic and pharmaceutical industries for preservation and to avoid degradation of feed stocks. With a growing global interest in natural plant based antioxidants, various raw materials have been screened. These include agro-industrial residues such as sugarcane molasses, potato peel waste, olive mill waste water, grape seeds and peels, citrus seeds and peels,

green-vegetable byproducts, and cocoa byproducts (Moure 2001, Llorach 2004). Molasses fermentation wastewater is yet another readily available source of antioxidants.

Various approaches have been investigated for melanoidins separation from fermentation wastewater. These include adsorption using activated carbon and chitin nanofibers (Figaro *et al.* 2006, Dolphen 2011), ion-exchange using acrylic or styrenic resins (Serpen 2007, www.purolite.com) and membrane filtration with nanofiltration (NF) and reverse osmosis (RO). (Nataraj 2006), NF and RO are promising for melanoidins concentration but energy consumption due to high pressure operation (up to 70 bar) is a concern. Thus, there is an interest in developing suitable low pressure membranes for this application.

Polysulfone (PSF) membranes are widely used in microfiltration (MF) and ultrafiltration (UF) applications due to low cost, superior film forming ability, good mechanical and anti-compaction properties, strong chemical and thermal stabilities and acid/alkaline resistance (Ma 2012). In recent years, mixed matrix membranes (MMMs) involving dispersion of inorganic particles in a polymer matrix have been prepared with polysulfone by phase inversion technique. Various inorganic materials used to prepare PSF MMMs include TiO₂, SiO₂, ZrO₂, Fe₃O₄, silica, carbon nanotubes, clay and Ag-nanoparticles (Ma 2012, Yang *et al.* 2007, Ahmad 2011, Yang 1996, Huang *et al.* 2010, Qiu *et al.* 2009, Choi 2006, Zodrow *et al.* 2009, Mierzwa *et al.* 2013). Addition of these materials improves the overall and surface porosity. MMMs containing metal organic frameworks (MOFs), carbon nanotubes, zeolites etc. have been widely studied for gas separations (Basu *et al.* 2011, Zornoza *et al.* 2011, Khan *et al.* 2012) and few applications on liquid separations (Basu *et al.* 2009, 2017).

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Resource recovery from food wastes (cheese whey, winery sludge, oat mill waste) using ultrafiltration membrane process has been reported (Galanakis *et al.* 2014, Galanakis *et al.* 2013, Patsioura *et al.* 2011).

Chitosan and multi walled carbon nanotubes (MWCNT) are being extensively investigated as adsorbents in water treatment. Chitosan derivatives were successfully utilized for removal of anions (nitrate) and specific organic pollutants from industrial wastewater (Patil 2013). Chitin nanofibres prepared from shrimp shell waste was found promising for adsorption of melanoidins (Dolphen 2011). Carbon nanotubes have been similarly tested for removal of aromatic hydrocarbons. Hence nanocomposites were prepared using acid functionalized MWCNTs as the reinforcing filler for chitosan-thermoplastic starch blend (Deepthi *et al.* 2014).

This study reports the incorporation of nanocomposite in PSF membrane for the preparation of MMMs, and its application for melanoidins recovery from wastewater. Incorporating MWCNTs into membranes is reported to reduce membrane fouling (Lin 2008, Vatanpoura *et al.* 2011, Ajmani *et al.* 2012). The focus is on development of nanocomposites/PSF MMMs that operate at lower pressure (1-2 bar) with high melanoidins retention. Such a membrane is expected to have significant application in fermentation wastewater treatment.

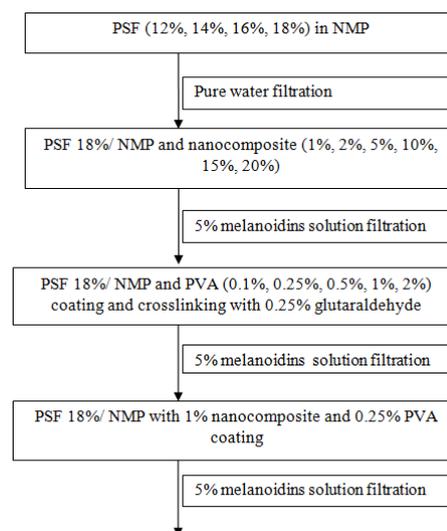
2. Experimental

2.1 Materials

Polysulfone (PSF) Udel[®] P-3500 was purchased from Solvay Specialty Polymers, India, and non-woven polypropylene/polyethylene fabric Novatexx 2471 from Freudenberg, Germany. D-glucose, glycine, and N-Methyl-2-Pyrrolidone (NMP) were obtained from Sigma Aldrich, India, and glutaraldehyde (GA) solution (25% aqueous) from Merck, India. Polyvinyl alcohol LR (MW 125000) and dibutyl maleate (DBM) were procured from S.D. Fine Chemicals, Bangalore, India. Chitosan was obtained from Marine Chemicals, Cochin, India with 85% deacetylation. Tapioca starch was obtained from Natsyn Catalysts, Bangalore, India. MWCNTs with diameter ranging from 50-70 nm and lengths ranging from 1-2 μm were purchased from I-Can Nano, Kolkata, India. All other reagents were analytical grade and purchased locally.

2.2 Melanoidins synthesis

Melanoidins were synthesized in the laboratory by mixing 1M D-glucose, 1M glycine and 0.5 M sodium carbonate in 1L distilled water. The solution was autoclaved at 121°C for 20 min, cooled to room temperature ($28 \pm 2^\circ\text{C}$) and the pH adjusted to 7 using 1N NaOH. Chemical oxygen demand (COD) of the solution was 30,000 mg/L and it was dark brown in colour. The resulting stock solution was dialyzed for 72 h in distilled water using cellulose dialysis tube (Sigma Aldrich, USA) that retains molecules ≥ 12 kDa. The dialysate (distilled water) was replaced every 24 h. The dialyzed fraction was stored at 4°C and was used in all further experiments.



Scheme 1 Flow diagram of preparing the PVA coated PSF-nanocomposite membrane

2.3 Synthesis of nanocomposites

A detailed description on the preparation of nanocomposites and their characterization has been mentioned in our earlier study (Deepthi *et al.* 2014). MWCNTs were functionalized with an acid mixture ($\text{H}_2\text{SO}_4/\text{HNO}_3$) by sonication followed by heating at 50°C in microwave reactor. It was then washed with deionized water and oven dried at 100°C, to obtain acid functionalized multiwalled carbon nanotubes (f-MWCNTs). Chitosan was cross-linked with glutaraldehyde (25% v/v) and filtered, followed by oven drying at 50°C. The product was referred as X-CTS. Thermoplastic starch (X-TPS) was prepared using a mixture of starch, glycerol and water. The mixture was cross-linked with glutaraldehyde. The nanocomposites were prepared by mixing equal amount of X-CTS and X-TPS along with 4% f-MWCNTs. The mixture was mixed in a kitchen mixer and sonicated using ultrasonicator (Branson, Model 2510 E/DTH) for 30 min. DBM (10% v/v) was then added in the mixture as coupling agent in order to improve the interfacial interaction of blend composites with f-MWCNTs. The final mixture was again mixed for 10 min in a kitchen mixer (12000-18000 rpm at $28 \pm 2^\circ\text{C}$). The nanocomposites powder stored at room temperature for further use.

2.4 Membrane preparation

PSF membranes of different concentrations (12%, 14%, 16%, and 18%) with NMP were prepared by phase inversion method using an automatic film applicator (A J Carsten Co. Ltd., Canada). The mixtures were stirred for 24 h in a mechanical stirrer followed by overnight degassing at room temperature. PSF films of controlled thickness (250 μm) were cast on non-woven polypropylene support and coagulated by immersion in a water bath at room temperature. After 10 min, the membranes were immersed in a fresh water bath for an hour and finally preserved in water at 4°C. Similarly, MMMs were prepared by adding different amounts of nanocomposites (1%, 2%, 5%, 10%,

15%, and 20%) in the PSF (18 wt%)/NMP (82 wt%) mixture. The nanocomposites were dispersed in NMP for 24 h before adding the required PSF in the mixture. The PSF and MMMs were cast at 77 mm/s, under relative humidity of 42-48% and temperature 22-24°C. PVA layer of different concentrations (0.1%, 0.25%, 0.5%, 1%, and 2%) on top of MMMs was applied by dip coating at different time intervals (1h-4 h). PVA was dissolved in a hot aqueous solution (90°C) under stirring for 8 h and the solution was cooled to room temperature before coating. Membranes were attached on a glass plate and the ensemble was dipped in the PVA solution for a specified time (1 h-4 h). Excess PVA solution was drained by holding the ensemble vertically. This was followed by crosslinking with glutaraldehyde (2.5% v/v). The membranes were dried at room temperature for 24 h and stored in water at 4°C. The preparation of MMM and PVA coating has been shown in scheme 1 as a flow diagram.

2.5 Characterization of samples

The morphology of the nanocomposites, PSF membranes and PSF/ nanocomposites MMMs was determined by scanning electron microscope (SEM) (Zeiss-EVO/MA10 instrument). The membrane samples were prepared by freeze fracturing under liquid nitrogen. After chemical drying with hexamethyldisilazane, the samples were coated with palladium in an argon atmosphere using a vacuum evaporator and examined. The porosity and the pore size of the membranes were determined by gravimetric method and by filtration velocity method respectively. The BET surface area of the membrane was evaluated by using the Brunauer-Emmett-Teller theory using nitrogen gas as an adsorbate in Smart Instruments Co., Mumbai, India. The Fourier transform infrared spectroscopy (FTIR) spectra of nanocomposites and membranes were recorded between 400 and 4000 cm^{-1} using a Perkin-Elmer spectrum 1000 FTIR spectrometer, USA. Water was used as the probe liquid for determination of the hydrophilicity at the membrane surface following the sessile drop method at 25°C and a relative humidity of 65%. The static contact angle of water on the surface of a polymer membrane was measured by using a goniometer (Kruss DSA10, Germany). The drop images were stored by a video camera. Drops were formed using a 10 μL syringe. The average value of the contact angle on each membrane was calculated using at least five different locations.

2.6 Adsorption-desorption and filtration of melanoidins

All the experiments were carried out in triplicate with 5% melanoidins solution. Different amount of nanocomposites (0.5%, 1%, 2.5%, 5%, 10%, 15%, 20%, 25%) were added in 5% (v/v) melanoidins solution. Adsorption was carried out at room temperature in a 250 mL shake flask (Scigenics Biotech, India) at 120 rpm. Samples at different time intervals (1, 2, 3, 4 h) were analyzed after centrifugation (Thermo Fisher Scientific, India) at 7000 rpm for 20 min. The melanoidins retention percentage was calculated at 475 nm in Eq. (1)

$$\text{Retention (\%)} = [(C_i - C_f) / C_i] \times 100 \quad (1)$$

where C_i = Initial melanoidins concentration (mg/L) and C_f = Final melanoidins concentration (mg/L)

The melanoidins concentration was calculated at 475 nm as colour in Eq. (2)

$$\text{Colour (Co-Pt)} = (\text{Absorbance } 475 \text{ nm} \times 500 \times \text{dilution factor}) / 0.132 \quad (2)$$

The melanoidins adsorbed on to nanocomposite were recovered by desorption using different solvents (e.g. 25% pyridine, 5N HCl, 5N NaOH, hot water 90°C, acetone, 10% ethanol, NaCl). The reaction was carried out in shake flask (4g/L) at 120 rpm, 24h, at room temperature. The melanoidins recovered was calculated using Eq. (3)

$$\text{Desorption (\%)} = [(C_{ed} / (C_o - C_e))] \times 100 \quad (3)$$

where C_{ed} = Melanoidins concentration in the liquid phase after desorption (mg/L), C_o = Initial melanoidins concentration (mg/L) and C_e = Melanoidins concentration in the liquid phase after adsorption (mg/L).

Filtration was conducted using a dead-end filtration cell (Millipore, India) with 0.00152 m^2 active membrane area. The feed melanoidins solution (5%) was poured into the cell and pressurized with nitrogen to the desired pressure (1 bar for pure water filtration and 2 bar for melanoidins solution filtration) at room temperature (27°C). Permeate was collected under atmospheric pressure. Sampling was done after 1 h of filtration at constant pressure. The feed solution was stirred by a teflon lined magnetic stirrer at 700 rpm. Permeability was calculated using Eq. (4)

$$\text{Permeability (L/m}^2 \text{ hbar)} = V / (A \times \Delta P \times t) \quad (4)$$

where V = Permeate volume (L), A = Membrane filtration area (m^2), ΔP = Transmembrane pressure (bar), and t = Filtration time (h)

3. Results and discussion

3.1 Recovery of melanoidins

Fig. 1(a) shows the SEM image of the nanocomposites. The X-CTS/X-TPS/f-MWCNTs as nanocomposites appear as a mixture of particles of different shapes and sizes. Fig. S-1 (supplementary sheet) shows the FTIR spectra of f-MWCNTs, PSF and MMMs. f-MWCNTs exhibit absorptions spectrum at wavenumbers 1656 cm^{-1} and 1730 cm^{-1} attributing to carbonyl groups in ester and ring structure (C=O stretching), 3425 cm^{-1} (O-H stretching), 3650 cm^{-1} (-COO asymmetric stretching), respectively. PSF exhibits absorption spectrums at wavenumbers at 1013 cm^{-1} and 1295 cm^{-1} as C-O-C stretch and C-O stretch groups respectively, 1115 cm^{-1} and 1322 cm^{-1} represents presence of S=O vibration and 2930-3000 cm^{-1} is associated with aromatic C-H bond (Coates 2000). Fig. 1(b) shows the adsorption of melanoidins using nanocomposites. Different concentrations of nanocomposites (0.5% to 25%) were studied for different time intervals (1h to 4h). Melanoidins recovery (as retention) increases with increased concentration of the

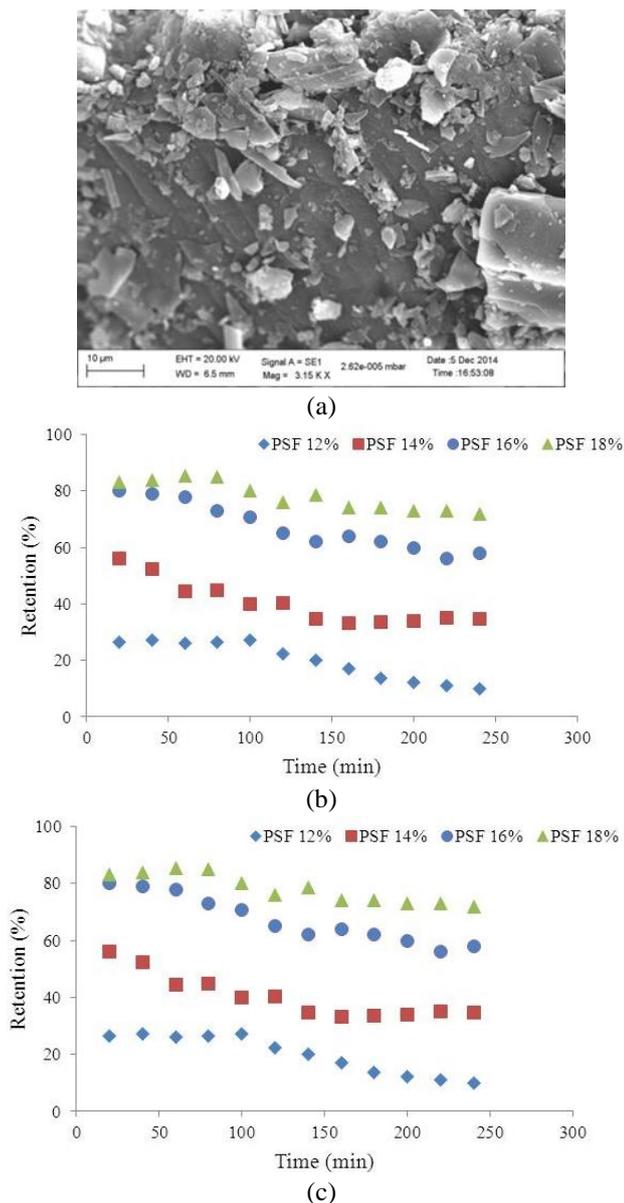


Fig. 1 (a) SEM image of nanocomposites. Melanoidins recovery by (b) nanocomposites adsorption, and (c) PSF membrane filtration at room temperature

Table 1 Porosity, pore radius and surface area of the membranes with or without nanocomposites

Material	Porosity (%)	Pore radius (μm)	Surface area (m ² /g)	Pure water permeability (L/m ² h bar)
Nanocomposites			300±10	
PSF	32.8±2	0.022±0.01	18.70±1	50±0.5
MMM 5%	46.9±2.1	0.022±0.01	19±0.5	48±0.5
MMM 10%	46.3±2	0.020±0.015	19.8±0.5	49±3
MMM 15%	69.5±2.3	0.018±0.012	20.8±0.25	46±0.5
MMM 20%	89.0±2.2	0.015±0.01	21±0.5	44±1

nanocomposites (0.5% to 25%) and contact time (1 h to 4 h). More than 95% adsorption was obtained with 5% nanocomposites and 4 h contact time. Enhancement in melanoidins adsorption was noticed at 1 h contact time with

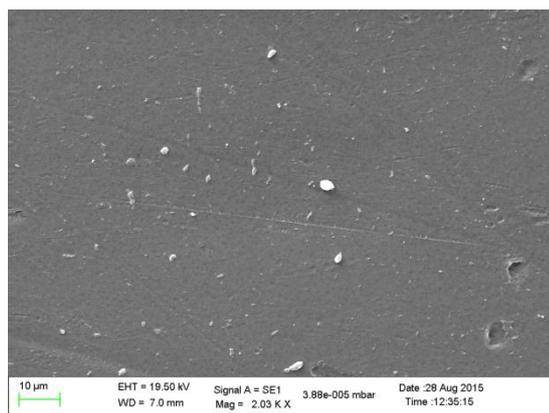
increased nanocomposites concentration from 10% to 25%. Such high and rapid adsorption is due to the high surface area of the nanocomposites. Similar adsorptions studies have been reported with chitin fiber and activated carbon, but no desorption studies have been reported in the literature (Figaro *et al.* 2006, Dolphen 2011). In the present work, 70-75% melanoidins was recovered using 25% pyridine as desorbent, but <5% was desorbed using rest of the solvents (acidic solution pH 2, basic solution pH 11, neutral solution pH 7, 0.5M NaCl, 1 N NaOH, acetone, ethanol, 5% NaOH+0.2% H₂O₂+ 25% ethanol).

Table 1 shows the porosity, pore radius and surface area of the nanocomposites, PSF, and MMMs with different content of nanocomposites (5%, 10%, 15%, and 20%). The surface area of nanocomposites was 300±10 m²/g. Addition of nanocomposites in the PSF matrix improves the surface area of the PSF membrane from 18.70±1 m²/g to 21±0.5 m²/g. This improves the adsorption properties of the membrane. The porosity of the membrane increases with increase in the nanocomposites content in the PSF membrane. The pore radius of the membrane decreases with increasing nanocomposites content in the membrane which indicates the formation of a tighter membrane with the addition of nanocomposites. The pore size is in the ultrafiltration range and porosity decreases with increasing PSF concentration. The pure water flux through the membrane decreases with increasing nanocomposites content in the membrane, which correlate with the decrease in the pore radius of the membrane.

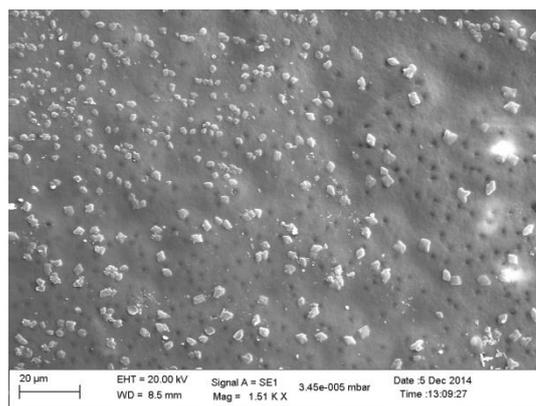
Fig. 1(c) shows the filtration performance of these membranes over duration of 4h. Melanoidins retention increased with increasing membrane PSF content. However, for all membranes, retention decreased with increasing filtration time, possibly due to swelling of the membranes. Melanoidins retention increased with increasing membrane PSF content. However, for all membranes, retention decreased with increasing filtration time, possibly due to swelling of the membrane. This is due to an increase in the average pore size of the membrane, in which melanoidins as colloidal particles passes easily through the interconnected pores of the membrane structure (Lifang 2015). PSF16% and PSF18% membranes showed comparatively higher retention (80% over 30 min), with PSF16% being marginally higher than PSF18%. Thus, PSF16% and PSF18% were selected for preparing MMMs. However, below 18% the polymer matrix could not hold the nanocomposites in suspension. So, further studies were done with PSF18%.

3.2 Filtration performance of MMMs

Fig. 2 shows the distribution of nanocomposites on the PSF polymer matrix. The nanocomposites are well dispersed and uniformly distributed in the PSF matrix of MMMs (Fig. 2(b)-2(e)). No aggregation was observed. This indicates that the nanocomposites and the PSF are compatible to each other. The MMM sample with 20% nanocomposites (Fig. 2(e)) shows some pitted marks on the surface. These are due to the loss of the nanocomposites during freeze-fracturing of the samples for SEM analysis. The SEM cross-section images of MMMs with different nanocomposite content in PSF, also shows that the

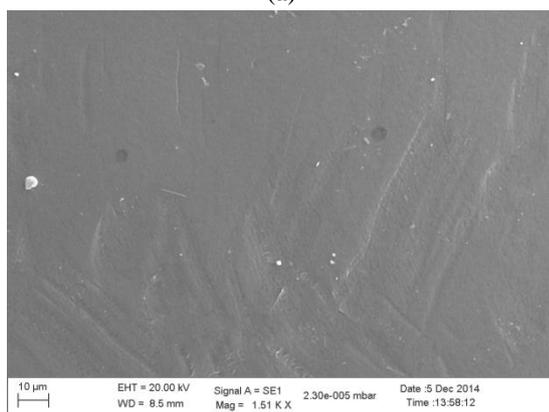


(a)

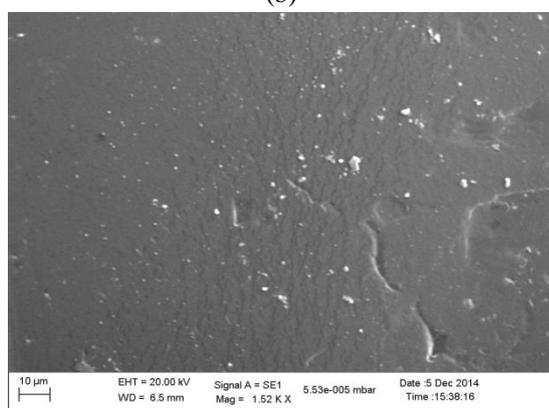


(e)

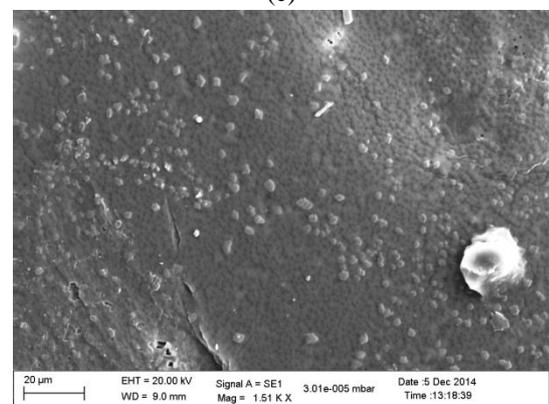
Fig. 2 Continued



(b)



(c)



(d)

Fig. 2 SEM image (top view) of (a) PSF, and MMMs with nanocomposites content of (b) 5%, (c) 10%, (d) 15% and (e) 20% (magnification 1.5KX)

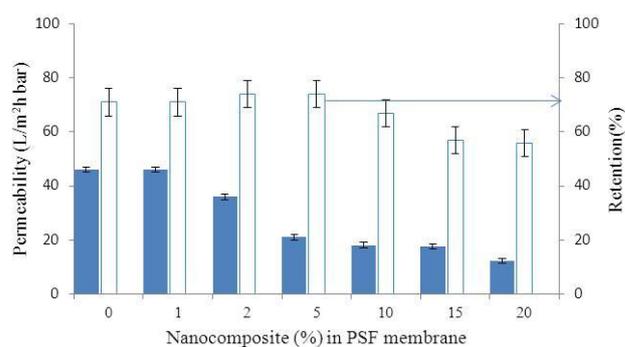


Fig. 3 Melanoidins permeability and retention in MMMs with varying nanocomposites content

nanocomposites are well distributed in the polymer matrix. The presences of nanocomposites are clearly visible at 20% nanocomposite PSF MMMs (Fig. S-2).

Fig. 3 shows the filtration performance of MMMs containing 1% to 20% nanocomposites in PSF18%. PSF18% with 1% nanocomposites shows a permeability of 45 L/m²hbar which is similar to the value for the control (PSF18% with 0% nanocomposite). However, further increase in nanocomposites content reduced the permeability. The decrease in the permeability with increased nanocomposites in the polymer matrix could be due to the increase in the density of the mixture resulting into a tighter membrane. The average melanoidins retention for PSF membrane is 71% which increased to 74% with the addition of 2% to 5% nanocomposites. Further increase in nanocomposite content in the MMM reduced the melanoidins retention to 67% (10% content), and 57% (15% and 20% content). The decrease in melanoidins retention indicates the possibility of interfacial voids between the polymer and the nanocomposites at higher concentrations. The presence of such voids results in non-selective of the solute from the solvent, as a result of which the efficiency of the membrane decreases. Thus, for further improvement of the MMM properties, 5% nanocomposites in PSF18% was selected.

3.3 Modification of MMMs

Fig. 4 shows the optimization of PVA coating conditions

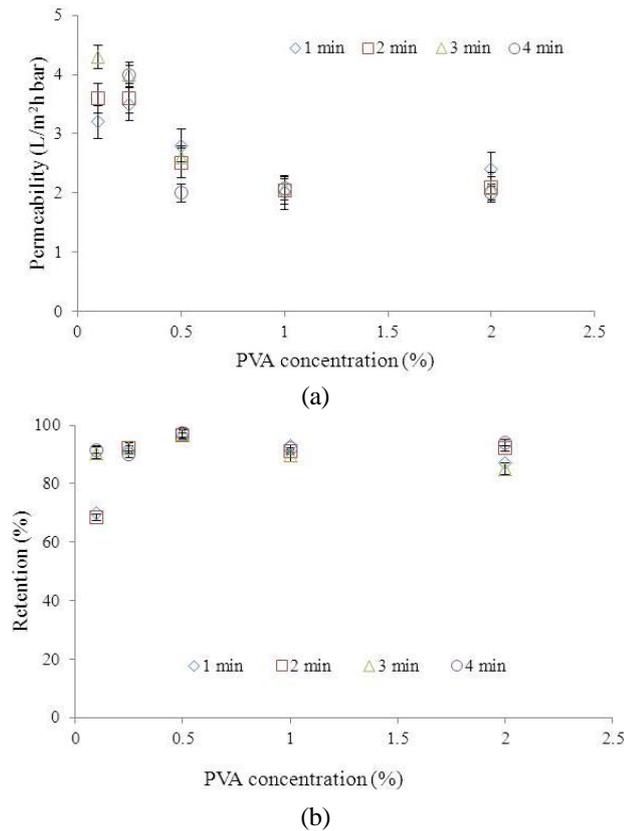


Fig. 4 Optimization of PVA coating time and concentrations on PSF 18% membrane wrt (a) permeability and (b) retention

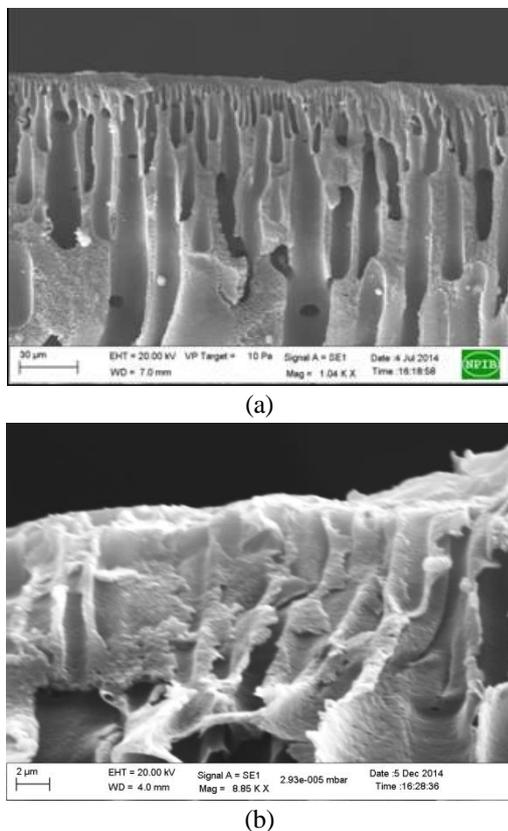


Fig. 5 SEM images of (a) PSF membrane and (b) PSF/1% nanocomposite-PVA coated membrane

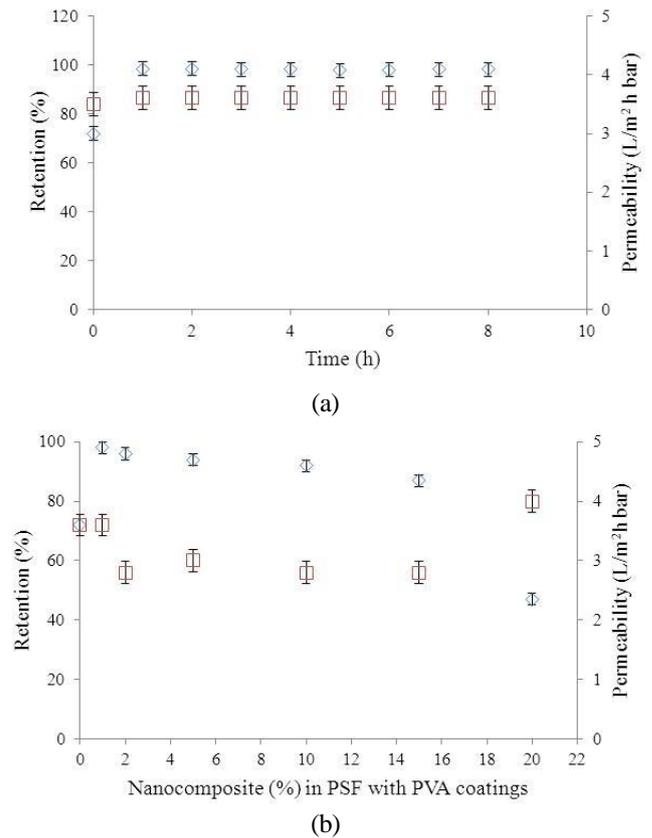


Fig. 6 Retention and permeability of (a) PVA coated MMMs and (b) long term performance of MMMs

on the MMM surface. Different concentrations of PVA (0.1% to 2%) were coated for different times (1 min to 4 min). The optimum condition was selected based on the permeability and retention of melanoidins. Fig. 4(a) shows the permeability trends. At lower PVA concentrations (0.1% and 0.25%), the permeability increased on the increasing coating time while the reverse was observed at higher PVA concentration ($\geq 0.5\%$). For any particular coating time, the permeability decreased with increasing PVA concentration. Higher PVA concentration and coating time results in the formation of thick and dense sealing over the asymmetric MMMs. Fig. 4(b) shows the retention of melanoidins. At lower PVA concentration (0.1%), retention increased from 70% to 91% with increasing the coating time from 2 min to 4 min. However, at other concentrations of PVA (0.25%, 0.5%, 1%) the melanoidins retention was almost similar for all the coating time interval. The melanoidins retention was more than 90%. At 2% PVA, the melanoidins retention improves with increased coating time from 1 min (80%) to 4 min (92%). Based on the permeability and retention trends, 0.25% PVA concentration and 2 min coating time was selected for further studies. Under these conditions, the melanoidins permeability was $3.5 L/m^2 h \text{ bar}$ and retention was 92%. The contact angle measurement of the membranes shows reduction in the angle from 78° (PSF) to 50° (PSF/1% nanocomposite). Further, PVA coating reduces the contact angle to 27° . The decrease in the contact angle indicates improvement in the wettability of the membranes, making it more hydrophilic.

Fig. 5(a) shows the SEM image of the PSF membrane, which is asymmetric with a thin separation layer at the top of a porous support. Addition of PVA coating forms another layer on top of the separation layer and thereby seals the probable membrane defects formed on addition of the nanocomposites in the PSF matrix (Fig. 5(b)).

3.4 Long-term filtration study of MMMs

Fig. 6(a) shows melanoidins retention and permeability for different nanocomposites content in PSF18% matrix with 0.25% PVA coated for 2 min. 98% melanoidins retention was obtained for 1% and 2%, 95% for 5% and 10%, and 90% for 15% of nanocomposites content in the MMMs. Further increase in nanocomposites content reduces the melanoidins retention with poor retention (40%) at 20% content. There is a sharp increase in permeability at 20% nanocomposites content indicating that surface defects resulting from high nanocomposites content in the PSF matrix are not completely sealed by the 0.25% PVA coating. Based on these results, PSF18% with 1% nanocomposite content and 0.25% PVA coating was examined further for the fouling tendency of the membranes. Fig. 6(b) shows the filtration over a period of 8h. Interestingly, the permeability was almost constant throughout this period maintaining 98% melanoidins retention.

The nanocomposites show high adsorption capacity for melanoidins. These materials when mixed in the polymer matrix, and on sealing the membrane defects using a diluted solution of PVA, the MMM resulted in almost complete retention of melanoidins maintaining a stable permeate flux under the study period. This indicates improvement in the fouling tendency of the PSF membranes. Thus, nanocomposites containing PSF membranes shows better retention of melanoidins, and PVA coating reduces the possibility of membrane fouling due to melanoidins. Similar results were obtained in many such PSF-based MMMs (Yang *et al.* 2007, Ahmad 2011, Huang *et al.* 2010, Zhang *et al.* 2008, Qiu *et al.* 2009, Zodrow *et al.* 2009, Mierzwa *et al.* 2013).

4. Conclusions

Flat sheet PSF/ nanocomposite membranes with different content of nanocomposites were prepared by phase-inversion method for the recovery of melanoidins. The study shows a very high retention of melanoidins with nanocomposites, but complete recovery is not possible. Incorporation of nanocomposites in PSF polymer matrix with 0.25% PVA coating as sealing is promising for melanoidins recovery and producing defect free MMMs. High melanoidins retention (98%) at constant permeability (3.6 L/m² h bar) could be obtained over a 8 h filtration period. The outcome would be of interest to molasses fermentation industries for the recovery of melanoidins with UF membrane.

Acknowledgements

The authors acknowledge the grant BT/IN/EU/06SPW/2012 from Department of

Biotechnology, Ministry of Science and Technology, Government of India for conducting this work. The authors thank Dr Ramamurthy, Indian Agricultural Research Institute (IARI), New Delhi for help with SEM analysis.

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Appendix

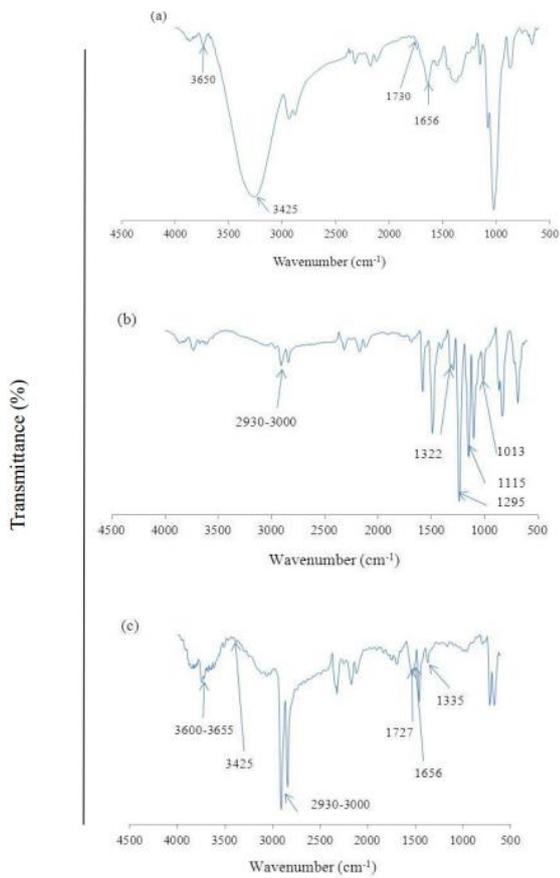
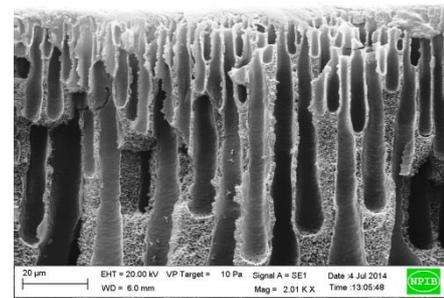
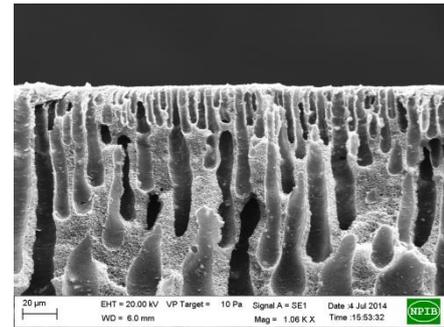


Fig. S-1 FTIR spectra of (a) f-MWCNTs, (b) PSF and (c) MMMs

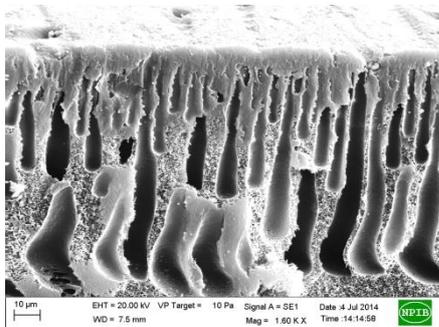


(c) 15%

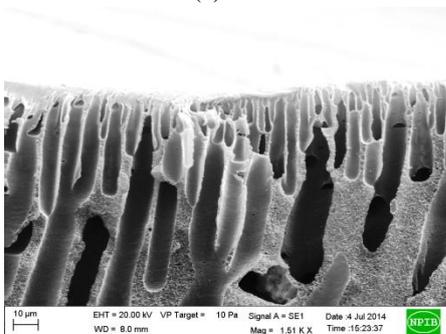


(d) 20%

Fig. S-2 Continued



(a) 5%



(b) 10%

Fig. S-2 SEM cross section images of MMMs with nanocomposite content in PSF of (a) 5%, (b) 10%, (c) 15% and (d) 20%