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Removal of heavy metal chromium from tannery effluent using ultrafiltration membrane

P. Angelin Vinodhini and P. N. Sudha*

Abstract

The present study was aimed to fabricate a novel ultrafiltration membrane using cellulose acetate, nanochitosan, and polyethylene glycol of ratio 1:2:2 by phase inversion method. Analytical techniques such as Fourier transform infrared spectroscopy (FTIR), X-ray diffractometer (XRD), and scanning electron microscopy (SEM) have been employed to characterize the prepared membrane. FTIR and XRD results revealed the formation of blended membrane with increased amorphous nature. SEM studies exhibited the rough surface with numerous pores. The prepared membrane was also characterized for its ultrafiltration performance by membrane compaction, pure water flux, water content, and porosity. The results showed that the membrane obtained a pure water flux of 25.32 l/m² h. The water content was found to be 24 % and a high porosity of 83 % was obtained which showed the membrane's high hydrophilicity and more porous nature. The main focus of the present study was toxic hexavalent chromium removal from tannery effluent using the prepared hydrophilic membrane, which causes various adverse effects. The effect of pH of the solution (viz., pH 5, 7, and 9), membrane thickness (0.1 and 0.2 mm), and the applied pressure (50 and 100 kPa) were studied which are the key factors in determining the efficiency of the prepared membrane in remediation of tannery effluent. The results showed high percentage removal of chromium at pH 7 using 0.2 mm thickness at 100 kPa. The physicochemical parameters of the tannery effluent were also found to be reduced.

Keywords: Cellulose acetate, Nanochitosan, Polyethylene glycol, Ultrafiltration membrane, Remediation of tannery effluent

Background

The one and only substance that is found on earth's crust for the survival of living things is water which regulates the earth's temperature as well as the temperature of the human body. The most valued water is now get polluted by the anthropogenic activities by the emission of domestic or urban sewage, agricultural waste, pollutants, and industrial effluents. There are numerous data and statistics which claim that the earth's water resources are being depleted, polluted, and rendered unpotable at an alarming rate (Malik et al. 2014). Thus, the whole world is under stress for the want of pure water. The main source of water pollution is industrial effluents which consist of acids, alkalis, toxic heavy metals, oil, grease, dyes, pesticides, and even radioactive materials.

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Heavy metals which are the natural constituents of the earth crust are persistent environmental contaminants because they cannot be degraded or destroyed (Duruibe et al. 2007). Heavy metals such as mercury, lead, cadmium, copper, and chromium are toxic even in small amounts (Pang et al. 2015). The health hazards associated with exposure to chromium are dependent on its oxidation state. The hexavalent form, Cr(VI), is toxic and has adverse effects on the skin like ulcerations, dermatitis, and allergic skin reactions. It is also proved to be carcinogenic (Barbooti 2015). The chromium removal techniques available are precipitation, adsorption, and solvent extraction (Moosa et al. 2015) among which membrane techniques have been proven to be one of the respective methods. It is simple and economical for the removal of heavy metal ions from aqueous solution.

A wide range of polymeric materials have been used to prepare various membrane types. The choices of polymer



taken for the current study are the biopolymer chitosan in its nanosize, a porogen polyethylene glycol, and membrane matrix material cellulose acetate. Each polymer has their unique properties constituting for the performance of the membrane prepared. The second most abundantly available chitin is deacetylated to get chitosan (Sudha 2010) which is further converted into its nanoform by suitable crosslinking agents. Owing to its invaluable applications, chitosan (CS) has become very vital in various fields like pharmaceutical (Kato et al. 2003; Kumar et al. 2004), biomedical (Suh and Matthew 2000; Tucci and Rocotti 2003; Ng and Swami 2005), water treatment (Northcott et al. 2005; Crini 2005), cosmetics (Rinoudo 2006; Sun et al. 2006), agriculture (Boonlertniruni et al. 2008; El Hadrami et al. 2010), and food industry (Ham-Pichavant et al. 2005; De Lima et al. 2010). The properties of chitosan are found to be more enhanced when used in its nanoscale. Thus, the ever increasing field of nanotechnology has also been implemented in the present study.

Cellulose acetate (CA), the most important cellulose ester was one of the first membrane polymer used for aqueous-based separations and used both as reverse osmosis and UF membrane material (Kuttowy and Sourirajan 1975). Its convincing properties such as good toughness, high biocompatibility, good desalting, high flux, and relatively low cost (Idris and Yet 2006) makes it versatile for use as membrane matrix. Another important additive for membrane is the pore forming agent which is very essential for the formation of pores in the membrane. The synthetic polyether polyethylene glycol (PEG) was employed as porogen which is inexpensive, non-toxic, and also soluble in many organic solvents like toluene, ethanol, acetone, and chlorinated hydrocarbons. However, it is insoluble in ethers, aliphatic hydrocarbons, fats, and mineral oil (Rowe et al. 2003). So far, there is no literature found for using nanochitosan in membrane technology which emphasizes the novelty of the present work.

Thus, the main objective of the present work is to prepare a novel ultrafiltration membrane of nanochitosan, cellulose acetate, and polyethylene glycol using popular phase inversion process, to characterize for its formation and suitability using Fourier transform infrared spectroscopy (FTIR), X-ray diffractometer (XRD), scanning electron microscopy (SEM), membrane compaction, pure water flux, water content, and porosity and to find the efficiency of the prepared membrane for the removal of chromium from tannery effluent and the analysis of the results to achieve the most favorable conditions.

Methods

Materials

Commercial grade cellulose acetate and sodium lauryl sulfate (SLS) were obtained from ChenChems, India.

Chitosan was purchased from India Sea Foods, Cochin, Kerala, which is 92 % deacetylated. Polyethylene glycol and acetic acid were procured from Sisco Research Laboratories Pvt. Ltd., Mumbai, India. *N,N'*-dimethylformamide was procured from Thermo Fisher Scientific India Pvt. Ltd., Mumbai. Sodium tripolyphosphate (TPP) was procured from Finar Chemicals Limited, Ahmedabad, India. Deionized and distilled water was employed for the preparation of nanochitosan and gelation bath.

Preparation of nanochitosan

Nanochitosan was prepared by sol-gel method using TPP. Ten grams of chitosan was dissolved in 2000 ml of 2 % (ν/ν) acetic acid. The above solution was stirred well for 45 min. Then, 100 ml of 0.75 mg/ml TPP was dropped into the beaker. A milky emulsion was obtained. The nanochitosan was washed several times in deionized water. This solution was then allowed to settle for 24 h. The supernatant solution was then decanted (Sivakami et al. 2013). Particle size of the prepared nanochitosan was investigated by using a dynamic light scattering (DLS) device (zeta plus from Brookhaven), and the average particle size of nanochitosan was found to be 100 nm.

Fabrication of membranes Solution blending of polymers

Membrane was prepared using CA, NCS, and PEG in 1:2:2 ratio with a polar solvent dimethylformamide (DMF) under constant mechanical stirring for 1 h at room temperature. The homogeneous polymer solution obtained was allowed to stand for 10 min in an airtight condition to get rid of air bubbles.

Casting of membranes

The membrane was prepared by phase inversion process (Witte et al. 1996; Loeb and Sourirajan 1963; Arthanareeswaran et al. 2007; Nath 2008; Velu et al. 2011) which is a well-known technique to prepare asymmetric membranes. The deaerated polymeric solution was casted on a glass plate, and the thickness of the membrane was maintained about 0.2 mm approximately. After allowing the solvent to evaporate, the glass plate was immersed in the gelation bath for final precipitation.

Prior to membrane casting, 2 l gelation bath consisting of 2.5 % (ν/ν) DMF and 0.2 wt.% SLS in distilled water (non-solvent) was prepared and cooled to 15 ± 2 °C (Arthanareeswaran et al. 2004). After gelation process, the membrane was removed from it and washed thoroughly with demineralized water and subsequently stored in 0.1 % formalin solution to prevent microbial growth.

Membrane characterization

FTIE

A thermo nicolet AVATAR 330 IR spectrophotometer was used to record the IR spectra within the range of 4000–400 cm⁻¹. The IR spectra were recorded in a solid state using a KBr pellet method.

XRD

The molecular packing of the blend membranes were analyzed with X-ray powder diffractometer (XRD-SHIMADZU XD-D1) using a Ni-filtered Cu K α X-ray radiation source. Percentage of crystallinity X_c % was measured as a ratio of crystalline area to the total area of the peaks using the formula given by Nara and Komiya (1983).

SEM

The surface and cross-sectional morphology of the prepared blend membranes were viewed and photographed using scanning electron microscopy. For the analysis, the blend membranes were cut into pieces of various sizes and wiped with filter paper. The membranes were coated with a thin gold-palladium layer by a sputter coater unit (VG-Microtech, UCK field, UK), and the cross section topography was analyzed with a Cambridge stereoscan 440 scanning electron microscope (SEM, Leica, Cambridge, UK) operated at an acceleration voltage of 20 kV.

Ultrafiltration characterization

Membrane compaction

The prepared membranes were thoroughly washed and cut into desired size and loaded in the UF test cell of 38.5 cm² area and initially pressurized with distilled water at 240 kPa. The water flux was measured at every 10 min. The flux generally declines initially and attained steady state after 90 min of compaction. The prepressurized membranes were used in subsequent ultrafiltration experiments at 100 kPa (Kuttowy and Sourirajan 1975).

Pure water flux

Membranes after compaction were subjected to pure water flux estimation at a transmembrane pressure of 100 kPa. The flux was measured under steady state flow. The pure water flux was determined (Osada and Nakagawa 1992) using the expression,

$$J_{\rm w} = \frac{Q}{\Delta t \times A}$$

where $J_{\rm w}$ is the pure water flux (l m⁻² h⁻¹), Q is the amount of permeates collected (l), Δt is the sampling time (h), and A is the membrane area (m²).

Water content

Water content of the membranes were obtained after soaking membranes in water for 24 h and the membranes were weighed followed by mopping it with blotting paper. These wet membranes were placed in vacuum drier at 75 °C for 48 h and cooled it to room temperature in a dessicator, and the dry weights of the membranes were determined. The percent water content was calculated (Tamura et al. 1981) by using the following equation:

% water content =
$$\frac{\text{wet sample weight - dry sample weight}}{\text{wet sample weight}} \times 100$$

Porosity

The overall porosity (ε) was determined by gravimetric method, as defined in the following equation (Li et al. 2009):

$$\varepsilon = \frac{w_1 - w_2}{A \times l \times d_{\rm w}}$$

where w_1 is the weight of the wet membrane, w_2 is the weight of the dry membrane, A is the membrane effective area (m²), d_w is the water density (0.998 g/cm³), and l is the membrane thickness (m).

Collection of tannery effluent from Ranipet, Vellore District, Tamilnadu

The effluent sample for the current study was collected from the final discharge point wherein effluent from all the stages of processing were treated and released together from a leather tanning unit in Ranipet, Vellore district, Tamilnadu, India, to the water stream. Polythene containers of 5 l capacity was used for the collection of effluent samples and immediately transported to the laboratory with due care and stored at 4 °C in refrigerator until further analysis.

The color of the tannery effluent was observed visually and recorded, and the odor was detected by smelling. pH was measured using Elico pH meter on the site. Other physicochemical parameters such as pH, electrical conductivity (EC), dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), total solids (TS), total hardness (TH), salinity, turbidity, and sodium were analyzed in the laboratory following standard methods (APHA 1993; Trivedy and Goel 1986).

Remediation of tannery effluent using prepared blend membrane by studying the effect of pH of the solution, membrane thickness, and applied pressure

The effluent that has already undergone primary and secondary treatment process in industry itself and that which is let out to the water streams was collected and subjected to subsequent ultrafiltration process. The UF cell was fixed with the prepared membrane and was filled with the tannery effluent solution, and filtration was started. The permeate was collected periodically in the stoppered bottles, and the physicochemical factors were analyzed after each period of remediation as per the methods of APHA (1993) and Trivedy and Goel (1986). The heavy metal chromium was analyzed using Atomic absorption spectrometer (Varian 4AA Atomic Absorption Spectrometer).

The percentage chromium rejection was calculated from the concentration of chromium in the feed and permeates using the equation given below.

% Cr rejection =
$$\left[1-\left(C_{\rm p}/C_{\rm f}\right)\right] \times 100$$

where C_p is the concentration of chromium in permeate and C_f is the concentration of chromium in feed.

The extent of remediation of the effluents was investigated by changing the pH of the solution, membrane thickness, and applied pressure. The physicochemical parameters of the effluent before and after treatment were measured as mean of three individual observations. The physical and chemical characteristics of the raw effluent were analyzed and given in Table 1 along with the accepted limit given by ISI standards for disposal of industrial wastewater of inland surface water.

Table 1 Physicochemical analysis of tannery effluent

Parameters	Raw effluent	Accepted limits ^a
Physical parameters		
Color	Blackish color	Colorless
Odor	Disagreeable smell	Odorless
рН	7.43	6.5-8.5
Chemical parameters		
Electrical conductivity (EC) (mS/cm)	27.3	0.288
Dissolved oxygen (DO) mg/l	0.2	4–6
Biochemical oxygen demand (BOD) mg/l	2556	30
Chemical oxygen demand (COD) mg/l	6419	250
Total dissolved solids (TDS) mg/l	15,900	2100
Total solids (TS) mg/l	31,740	2200
Total hardness (TH) mg/l	923	300
Salinity (mg/l)	16,200	Not mentioned
Turbidity (NTU)	453	10
Sodium (mg/l)	5000	1000-1500
Chromium (Cr) (mg/l)	1055	2.0

Values expressed as mean of six individual values

Effect of pH

pH is the most important of all the factors affecting the removal of heavy metals. pH adjustment is extremely important as well since it can be used as a means to selectively separate heavy metals from multicomponent mixtures and the removal rate to separate heavy metals differs when pH is carefully adjusted (Zeng et al. 2009). The effect of pH on the filtration of tannery effluent by the membrane was carried out at room temperature and at three different pH values.

Effect of membrane thickness

Thickness is a key parameter in membrane processes since it influences both the membrane selectivity and the membrane resistance against flux (Abdelrasoul et al. 2015). It also plays an important role in the amount of conductive heat loss though the membrane. The filtration study was conducted using two different membrane thicknesses, viz., 0.1 and 0.2 mm.

Effect of applied pressure

The transmembrane pressure is the driving force for the pressure-driven membrane process (Gökşen 2005). Applied pressure is considered as one of the most critical aspects in the membrane performance and operation. The UF experiment was carried out at two different pressures namely 50 and 100 kPa.

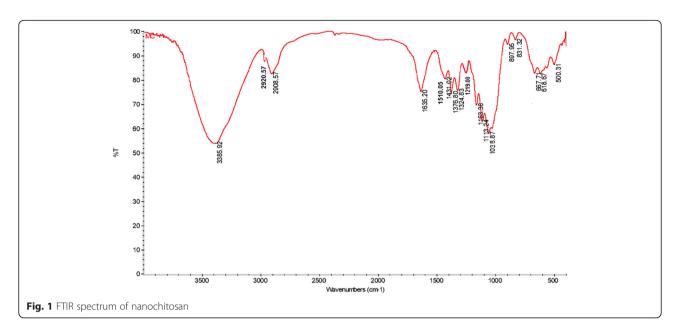
Results and discussion Membrane characterization

FTIR

IR spectroscopy is an excellent method and has been extensively used for the qualitative analysis in which specific absorption peaks can be identified for particular groups (Qu et al. 2010). The interactions between the functional groups in a polymer blend can be obtained directly and gross structural details can be investigated. The chemical nature of a substance including chemical bonds, molecular orientations, molecular energy levels, and molecular interactions (Gorey and Escobar 2011) can be assessed using this technique. Thus, the prepared blend has been analyzed using FTIR, and the possible interactions that had taken place were studied.

The FTIR spectral details of the prepared NCS are shown in Fig. 1. A prominent broad peak at 3385.92 cm⁻¹ indicates the presence of O–H and N–H stretching vibration (Vimal et al. 2013). Peak at 1324.83 cm⁻¹ is assigned to P=O stretching vibration whereas at 1038.87 cm⁻¹ is assigned to P–O stretching vibration. The N–H bending vibration corresponds to the peak at 1510.05 cm⁻¹ which was proved by Mohammadpour Dounighi et al. (2010) who obtained peak at 1540 cm⁻¹ in CS/TPP nanoparticles. The deformation vibrations of C–H and O–H groups were observed at 1431.02 and 1376.80 cm⁻¹. A peak for

^aISI standards for disposal of industrial wastewater of inland surface water

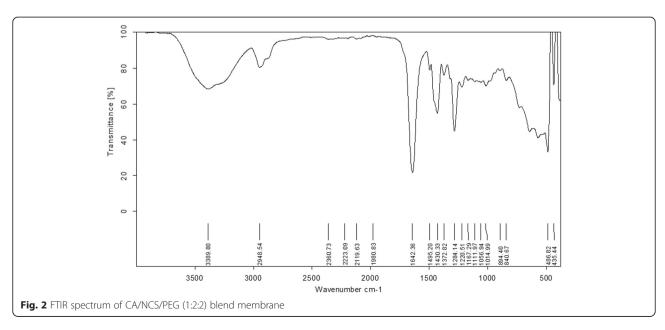


C=O stretching vibration is observed at 1635.20 cm⁻¹. Peaks at 1219.00, 1163.38, and 1113.24 cm⁻¹ were due to C-N stretching, C-O stretching, and C-O-C ether linkages, respectively.

The FTIR spectral details of CA/NCS/PEG (1:2:2) blend membrane are given in Fig. 2. The O–H and N–H stretching vibration of the membrane is observed at 3389.80 cm⁻¹ which is wider. The O–H stretching is attributed to the enhanced intermolecular hydrogen bonding formed between the polymers (Yu et al. 1999). The peaks at 2948.54 cm⁻¹ and 1642.36 cm⁻¹ were due to the asymmetric C–H stretching and C=O stretching vibration, respectively. The peak at 1495.20 cm⁻¹ was assigned to the deformation vibration of N–H. A peak

for P=O stretching vibration was found at 1284.14 cm⁻¹ and for P=O stretching vibration at 1014.99 cm⁻¹ which showed a shift from 1038.87 cm⁻¹ characteristic of pure NCS (Vijayalakshmi et al. 2014). C=N stretching vibration and C=O=C ether linkage were observed at 1220.51 and 1056.94 cm⁻¹, respectively.

There is a shift in the OH and NH frequencies for the prepared membrane from NCS, i.e., the peak obtained at $3385.92~{\rm cm}^{-1}$ has been shifted to $3389.80~{\rm cm}^{-1}$. The C=O peak at $1635.20~{\rm cm}^{-1}$ for NCS has been found to be shifted to $1642.36~{\rm cm}^{-1}$. Peak at $1324.83~{\rm cm}^{-1}$ for P=O was observed to have a shift in the IR spectrum to $1284.14~{\rm cm}^{-1}$. This shows that there is strong intermolecular hydrogen bonding taking place which leads to



the membrane formation. Moreover, the P–O bond at 1038.87 cm⁻¹ for NCS has undergone a significant shift in the prepared membrane and observed at lower region of 1014.99 cm⁻¹. Thus, the FTIR spectra analysis reflects that the nanoparticles were binded with the CA matrix due to strong interactive forces.

XRD

The X-ray diffraction analysis is a non-destructive analytical technique that gives the information about the crystallographic structure, chemical composition, and physical properties of materials (Subbu et al. 2014). It has been routinely used for crystalline phase identification based on the diffraction peak position and pattern (Jayakrishnan and Ramesan 2016). The crystalline/amorphous ratio of the constituent polymer in a blend plays a vital role in understanding the development of membranes during gelation. Thus, X-ray diffraction patterns of the prepared membrane were measured to investigate the change in the crystalline nature.

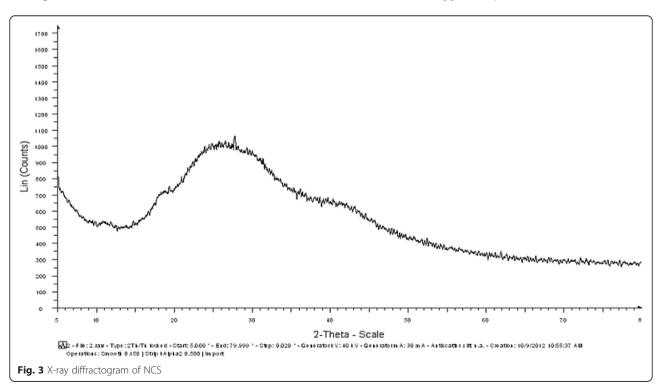
Figure 3 shows the X-ray diffractogram of NCS. The percentage of crystallinity was found to be 17 % which may be due to the certain orderliness in its structure which was retained even after the addition of the crosslinker TPP to chitosan. The 2θ value obtained at 26° was wider indicating the amorphous nature of the chitosan nanoparticles of size 100 nm. For the chitosan nanoparticles which were in the range of 5–180 nm, the 2θ value was found to be 20.4357 as reported by Vellingiri et al. (2013).

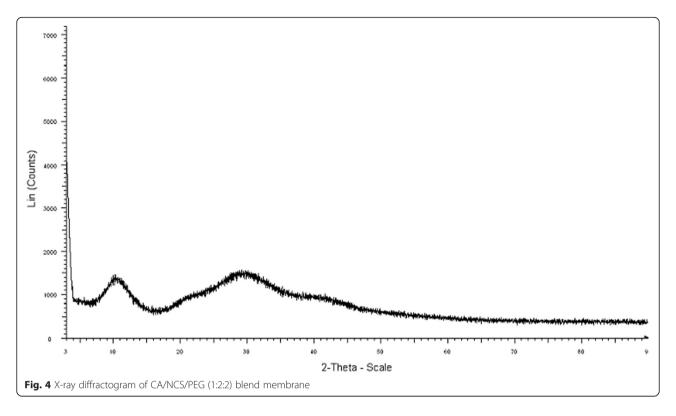
Figure 4 shows the X-ray diffractogram of CA/NCS/ PEG (1:2:2) blend membrane. The blend showed lesser percentage of crystallinity which is 6 % when compared to NCS whose value was 17 %. This revealed that the blend has become more amorphous which may be due to enhanced disruption of orderliness by the addition of nanochitosan and polyethylene glycol in greater amount. It was observed that nanochitosan was amorphous and showed diffraction peaks at 2θ values 15.19° and 23° (Karuppasamy et al. 2012). There was also a significant shift in the 2θ values to 10.5° and 29.5° which were fairly broad. It was also observed that the intensity of the crystalline peaks was decreased and broadened upon the addition of nanochitosan. This disorderliness may be attributed to the formation of intermolecular hydrogen bonding formed between CA, NCS, and PEG, thus favoring the filtration process.

Scanning electron microscopy

The scanning electron microscope is an extremely useful tool to characterize the surface morphology of the membrane (Zeng et al. 2016) and to investigate the structure of polymeric integrally skinned membrane (Kesting 1985).

The surface morphology of nanochitosan and the blend membrane were observed using SEM and are shown in Figs. 5 and 6. The surface of the membrane helps to identify the significance of membrane in the mechanism of selectivity and permeability. The top layer of membrane is responsible for the permeation whereas the sublayer acts as a mechanical support (Rajesh et al. 2011). The surface

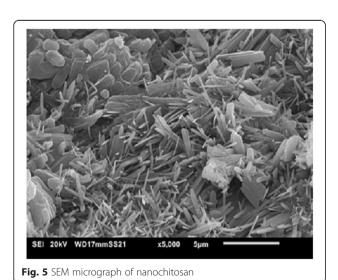




of the prepared membrane clearly shows their asymmetric nature and roughness. The membrane has uniform pores exhibiting more porous structure.

The shape and structure were related to the concentration and composition of additive in the casting solution (Sivakumar et al. 2000). Thus, the prepared membrane was found to be more porous with more PEG content showing small multiple uniform voids when compared with NCS. This is supported by the study done by Saljoughi et al. (2009) that increasing PEG concentration causes formation of greater macrovoids and more porous structures due to

the intensification of thermodynamic instability of the casting solution by PEG. Moreover, the number of pores and pore sizes depends upon the pore forming agent PEG, which leaches out of the membrane in gelation bath during phase separation process (Ananth et al. 2012). However, the pore size of membrane was reduced with increased PEG content in the blend solution (Khulbe et al. 1995) due to the reduced leachability of PEG during gelation in view of strong interactions of PEG with CA and NCS. Hence, the membrane can facilitate the filtration process efficiently.



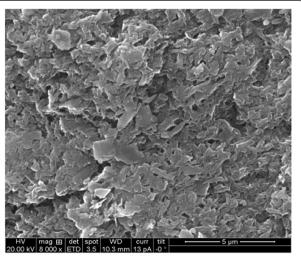


Fig. 6 SEM micrographs of CA/NCS/PEG (1:2:2) blend membrane

Ultrafiltration characterization of the membrane

The efficiency of the prepared membrane was found out using various ultrafiltration characterization techniques such as membrane compaction, pure water flux, water content and porosity.

Membrane compaction

Compaction occurs when membranes are subjected to high pressures. The significance of compaction varies with membrane formulation and operating pressure (Pusch and Mossa 1978). Before using a fresh membrane, it was compacted to make membrane with rigid pore structure and size. When compacted with deionized water for 2 h at a transmembrane pressure of 240 kPa which is higher than the maximum operating pressure used for the present study, there may be reorganization of the polymeric chains (Maheswari et al. 2013). The limitation of the transmembrane pressure was <300 kPa.

The water flux was calculated from the experimental permeate flow rate measured at every 10 min interval. During compaction, initially, the pure water flux was found to be high and declines gradually and reaches a steady state after 90 min. This constant value indicates the completion of compaction. This may be due to the fact that the walls of the pores become closer, denser, and uniform resulting in reduction in pore size as well as the flux during compaction (Eren et al. 2015). Furthermore, the polymeric chains reorganize under hydraulic pressure during compaction leading to change in the structure with a lowered volume of porosity.

Pure water flux

The key requirement of any membrane is pure water flux (PWF), and it was determined for the prepared blend membrane at 100 kPa pressure after completion of compaction. Pure water flux is one of the key components that explain the pore size and pore distribution of the membranes (Shi et al. 2012). It is an essential

parameter for the membranes, which is useful for any industrial process. The value of pure water flux of the prepared membrane was found to be 25.32 l/m^2 h.

Water content

The percentage water content represents the fraction of water molecules occupied in the pores of the membrane. This is considered to be an important parameter for membrane characterization (Tamura et al. 1981), since PWF can be predicted based on these results also. The percent water content was calculated for the prepared membrane, and the value obtained was 24 %. This shows that the prepared membrane has become more porous due to the leachability of water-soluble additive, PEG, leading to the formation of more number of pores. This shows the membrane's hydrophilicity since water content of the membrane is related to hydrophilicity of the membrane (Sivakumar et al. 2006).

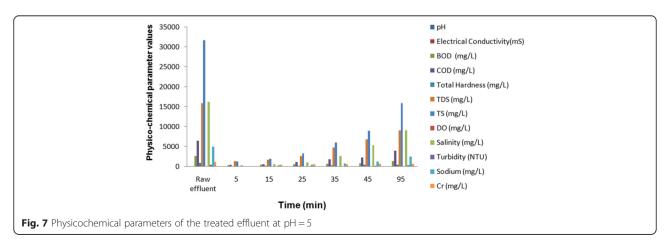
Porosity

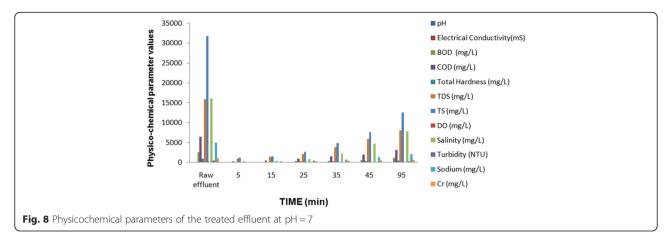
Porosity, ε , is the void fraction of the membrane. The membrane porosity is related to the pore formation during the process of membrane formation by immersion precipitation (Wienk et al. 1996). A highest percentage of porosity of 83 % was obtained indicating the more porous nature, and it is attributed to the leachability of PEG present in higher concentration.

Remediation of tannery effluent using prepared blend membrane by studying the effect of pH of the solution, membrane thickness, and applied pressure Effect of pH

The effect of pH on the filtration of tannery effluent by the membrane was carried out at room temperature and at three different pH values, and the results obtained are shown in Figs. 7, 8, and 9.

The pH of the tannery effluent was changed to acidic, and the filtration process was carried out. It was found that the physicochemical parameters were greatly reduced



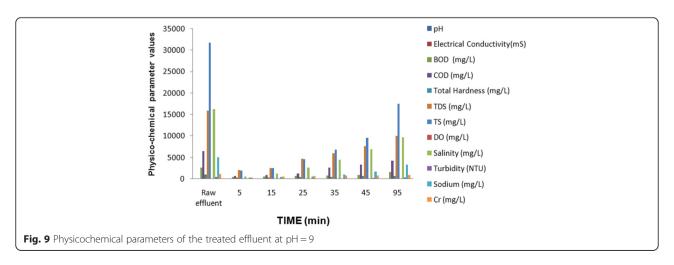


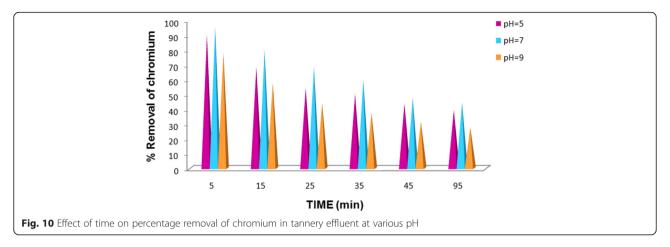
after 5 min. With the increase of time, these parameters were found to be increased which may be due to clogging of pores. The percentage removal of chromium at pH 5 was 90.142~% at 5 min and 39.242~% at 95 min.

The raw effluent itself in the pH of 7 and the maximum removal was found to take place at this pH. The high concentration of Cr discharged by leather industries was found to be 1055 mg/l. This was observed to be reduced to 46 mg/l after 5 min of filtration and to 586 mg/l at 95 min. Also, the other physicochemical parameters have found to be significantly reduced. Some even fell within the permissible limit of inland surface waters as given by ISI. The BOD and COD of the effluent were 2556 ml/l and 6419 mg/l, respectively, which were very high compared to the treated effluent. It was revealed from the results that even after 95 min, the membrane was able to reduce 56.22 % of BOD and 50.97 % of COD. The COD values were found to be hardly decreased as reported by Krishanamoorthi et al. (2009) which may be explained, as COD was mainly soluble consisting in hydrolyzed proteins of low molecular weights, but the effluent has other ionic materials like sodium and chromium.

In the basic medium, the percentage removal of chromium as well as the physicochemical parameters was not as high when compared with that of acidic and neutral medium. The percentage removal of chromium at pH 9 was only 77.915 % at 5 min which is very less when compared at pH 5 and 7, which are 90.142 and 95.640 %, respectively. This may be because the divalent chromium species ${\rm CrO_4^{2^-}}$ which is dominant at high pH would have formed metal complex with sodium present in the effluent and passed through the membrane (Chen et al. 2008).

Figure 10 indicates the percentage removal of chromium in tannery effluent at pH 5, pH 7, and pH 9 during various time intervals. The decrease in chromium rejection percentage with time for the studied pH at 5, 7, and 9 may be presumably due to the saturation of the membranes active sites with chromium ions (Habibi et al. 2015). On comparing the values obtained, it was clear that the removal of Cr was the highest in neutral medium than the acidic medium and was the least at basic medium. As stated by Arthanareeswaran et al. (2007), the rejection increases as the pH of the chromium solution increases and chosen an optimum pH of





6 for further rejection studies. The trend of results obtained for tannery effluent was found similar to that of the removal of Cr using synthetic wastewater which may be attributed to the formation of soluble hydroxides at high pH. Thus, it can be concluded that the membrane can withstand pH variations from acidic to basic. The maximum efficiencies for different parameters were found at neutral pH area, and they gradually reduced on both sides of the neutral pH (Chowdhury et al. 2013). Similar observation was made in the current study which may be accounted that the colloid substances in the leather industrial effluents usually carry negative electrical charges, whereas the membrane possesses a lot of positive charge due to the incorporation of chitosan nanoparticles in the polymer membrane matrix which has the capability of adsorbing particles leading to destabilization and thus also led to the assumption that the membrane acts as a adsorptive membrane.

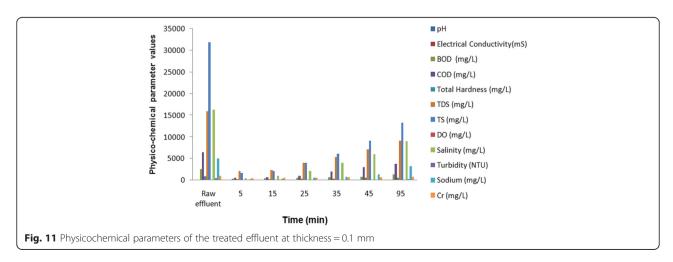
The effect of pH on chromium rejection plays an important role because the charges of both salt ions and membrane vary with pH (Verliefde et al. 2008). In a study done by Muthukrishnan and Guha (2008), it was found out that the rejection of chromium greatly increased when

pH rose from 2 to 7, as more bivalent ${\rm CrO_4^{2-}/Cr_2O_7^{2-}}$ ions were generated and the polyamide NF membrane was more negatively charged at higher pH. Similar findings were given by Yao et al. (2015) in which a quaternary ammonium-based UF membrane (QA membrane) was used to remove Cr(VI) ions in both acid and neutral pH more efficiently. Hence, removal of chromium from the membrane separation process is reliant on the pH of the solution.

Effect of membrane thickness

The membrane thickness places a crucial role in the removal process. Figure 11 shows the change in various physicochemical parameters at membrane thickness of 0.1 mm.

The EC, BOD, COD, TH, TDS, TS, DO, salinity, turbidity, Na, and Cr of the raw effluent were drastically high which were found to be reduced to a considerable extent. The EC value of 27.3 mS was observed to be reduced to 7.21 mS during the first 5 min of filtration which was almost 73 % of reduction. Similarly, the values of BOD, COD, TH, TDS, TS, salinity, turbidity, and Na which were 2556, 6419, 923, 15900, 31740,



16200, 453 and 5000 mg/l has been reduced to 312, 513, 223, 2095, 1654, 415, 42 and 218 mg/l, respectively. The percentage of chromium removal was 56.967 % at 5 min and even at 95 min; the membrane has the efficiency to remove about 30.237 % of chromium.

Figure 12 shows the change in the physicochemical parameters when used 0.2 mm of the thickness of membrane. It was evident that there was a vital increase in the removal efficiency of the membrane when its thickness was increased from 0.1 to 0.2 mm. The values of BOD, COD, TH, TDS, TS, salinity, turbidity, and Na which were 312, 513, 223, 2095, 1654, 415, 42 and 218 mg/l, respectively, when used 0.1 mm of membrane were found to be still reduced to 113, 237, 93, 944, 1162, 210, 22 and 112 mg/l, respectively. This enhancement in the removal efficiency may be attributed to thin skin layer and porous sublayer of the asymmetric membrane containing more number of voids. The EC was also retarded from 7.21 to 3.22 mS. In addition, the DO was found to be increased from 0.2 to 4.2 mg/l which favors the life of the aquatic ecosystem since the accepted limit given by ISI was 4-6 mg/l.

Figure 13 shows the effect of time on the percentage removal of chromium using 0.1 and 0.2 mm thickness of the membrane. It can be seen that the percentage removal of chromium with 0.1 mm thickness was 56.967 % which was less when compared with 0.2 mm thickness which gives removal percentage of 95.640. With the increase of time, the removal efficiency was retarded due to pore blocking. This was evidenced by a study conducted by Jyothi et al. (2014) in which the percentage rejection of chromium decreases as time increases. The same trend was observed till the 95 min, i.e., 30.237 % for 0.1 mm and 44.455 % for 0.2 mm thickness. It was obvious that as the membrane thickness increased, the percentage removal of chromium was also increased. An increase in membrane thickness correlates to a decrease in permeation flux and

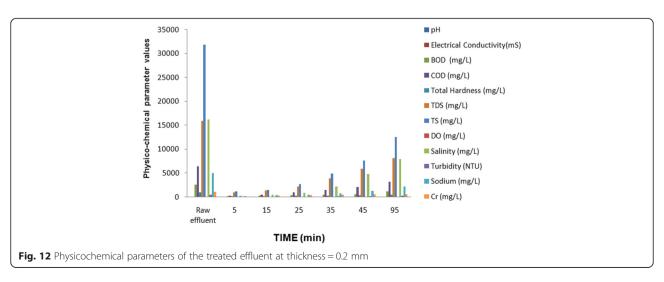
better retention of solute. This could be attributed that membranes had larger pores with increasing thickness (Abdelrasoul et al. 2015). Due to practical difficulties, using of 0.3 mm thickness has been avoided. Moreover, better removal of Cr and other physicochemical parameters has been obtained using 0.2 mm membrane thickness itself.

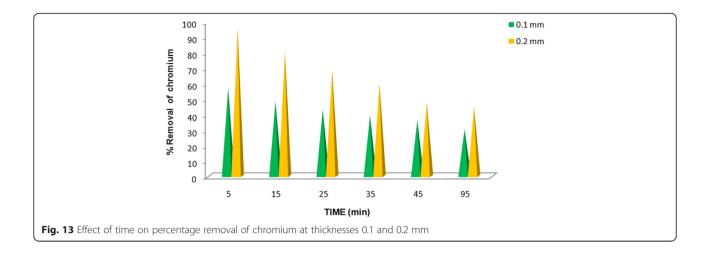
From the results, it was clear that the membrane thickness was a function of permeation characteristics and it was proved by Gotoh et al. (1993) that the flux for aqueous solution of dextran sodium sulfate decreased with an increase in membrane thickness, while the rejection for dextran sodium sulfate increased slightly. In another study by Barakat (2008), the metal ions rejection efficiency values were increased with pH increase, reaching maxima values at pH = 7, i.e., 97.6, 99.1, and 99.5 %, for Cu(II), Ni(II), and Cr(III) ions, respectively. Moreover, the percentage of TDS retention was only 86.8 % for 0.1 mm thickness whereas it was 94 % for 0.2 mm thickness which showed a closer value obtained by Kowalik-Klimczak and Gierycz (2014) which is 99.6 % of retention by UF.

Effect of applied pressure

Ultrafiltration process itself is a pressure-driven process except that it needs only minimum pressure for the filtration process to take place. In the porous UF membrane, the transport of solvent is directly proportional to the applied pressure (Trivunac and Stevanovic 2006). Two different pressures namely 50 and 100 kPa have been employed in this study and analyzed the changes that have taken place before and after filtration.

Figure 14 shows the effect of pressure on the removal of various physicochemical parameters at 50 kPa. The EC was found to be reduced from 27.3 to 7.22, 8.42, 9.31, 9.88, 10.74 and 13.5 mS at 5, 15, 25, 35, 45 and 95 min, respectively. The BOD and COD were found to be 2556 and 6419 mg/l which were reduced to 315, 411, 599, 628, 781 and 1301 mg/l for BOD and 525, 731,



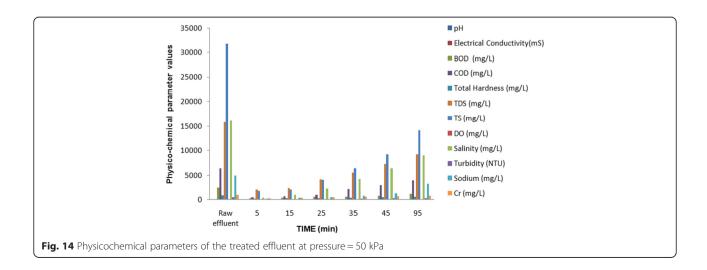


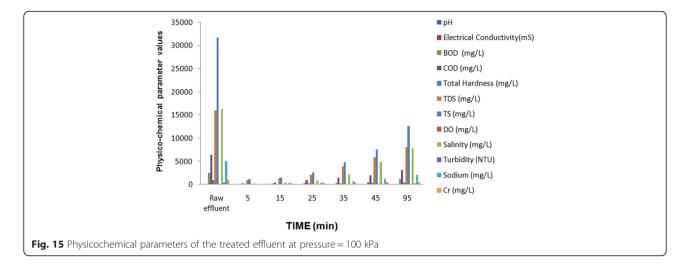
1066, 2216, 3022 and 3984 mg/l for COD at 5, 15, 25, 35, 45 and 95 min, respectively. Other parameters were also found to be reduced to a considerable amount. The heavy metal chromium was also reduced to a greater extent namely from 1055 to 333, 389, 473, 593, 684 and 749 mg/l.

Figure 15 shows the effect of pressure on the removal of various physicochemical parameters at 100 kPa. All the parameters were found to be greatly enhanced when the pressure was increased from 50 to 100 kPa. As can be seen, the EC values which were 7.22, 8.42, 9.31, 9.88, 10.74 and 13.5 mS using 50 kPa at 5, 15, 25, 35, 45 and 95 min were found to be reduced to 3.22, 5.41, 6.21, 8.16, 10.2 and 13.1 mS at 100 kPa, respectively. The BOD values at 5, 15, 25, 35, 45 and 95 min at 50 kPa were 315, 411, 599, 628, 781 and 1301 mg/l, respectively, which were further decreased to 113, 159, 295, 364, 545 and 1119 mg/l, respectively, at 100 kPa. In the same way, the COD values were also retarded. TH, TDS, TS, salinity, turbidity, and sodium values were all decreased, i.e., more

percentage removal was observed when the pressure has been increased from 50 to 100 kPa. In turn, the DO values have been increased for the survival of aquatic organisms.

Figure 16 shows the percentage removal of chromium at pressures 50 and 100 kPa during various time intervals. It was very much evident that the percentage removal of chromium which was only 68.436 % at 50 kPa was improved at 100 kPa whose removal percentage was found to be 95.640 %. Similar trend was observed as the time was increased. But there is a reduction in percentage removal of chromium with time which may be due to the applied pressure that the pollutants adsorbed in the pore of the membrane move slowly to the permeate during filtration. Thus, the permeate chromate concentration increased with the passage of time (Bade et al. 2008). Thus, the membrane was capable of removing 29.005 % of chromium at 50 kPa and 44.455 % of chromium at 100 kPa at 95 min. Hence, with an increase of the applied pressure, better rejection of the metal ions



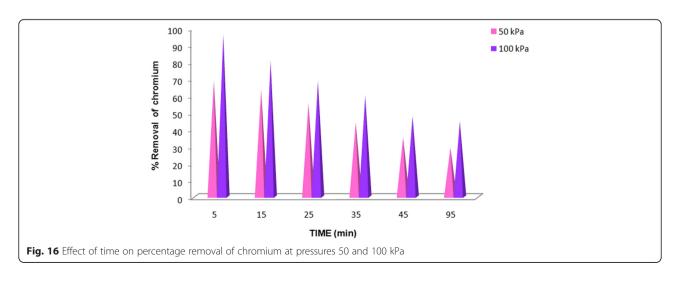


was obtained. Since high percentage chromium removal of 95.640 % was obtained at 100 kPa, further increase in applied pressure was not carried out in this study.

Also, in a study on the effect of applied pressure (0.4-1 MPa) on percentage solute rejection of chromium and copper ions by Boricha and Murthy (2010), it was found that the rejection increases with increase in feed pressure from 0.4 to 1 MPa for both the ions and the highest rejection was found to be 83.40 and 72.60 % for chromium and copper ions, respectively, at 1 MPa. In addition, the increase in the applied pressure increases the surfactant concentration polarization layer near the membrane surface on which the metal ions gets adsorbed (Kamble and Marathe 2005). Thus, when the charged species flows across a membrane, an unbalanced distribution of the electrical charges at the upstream and downstream interfaces of the membrane takes place. This consequently generates streaming potential, and as stated by Azoug et al. (1997), an increase of the transmembrane pressure may lead to a better rejection of the metal ions.

Conclusions

In this study, nanochitosan was prepared successfully with particle size of 100 nm. The membrane was prepared using phase inversion method and characterized using FTIR, XRD and SEM. Ultrafiltration characterization was done by membrane compaction, pure water flux, water content and porosity. FTIR result revealed that the polymers used have been blended well. XRD showed that the membrane is amorphous in nature and SEM exhibited rough surface and large number of pores. The results showed that the membrane obtained a pure water flux of 25.32 l/m² h. The water content was found to be 24 %, and a high porosity of 83 % was obtained which showed the membrane's high hydrophilicity and more porous nature. So the prepared membrane was used for the filtration of tannery effluent collected from Ranipet Industrial area. It can be concluded from this study that the membrane CA/NCS/PEG in 1:2:2 ratio was found to be suitable for reducing the physicochemical parameters such as EC, BOD, COD, TH, TDS, TS, salinity, turbidity and



sodium as well as the heavy metal chromium from tannery effluent in an effective and efficient way. The effect of pH, membrane thickness and the applied pressure was analyzed and found that maximum removal has taken place when the effluent was in neutral condition, at 0.2 mm membrane thickness and pressure 100 kPa. This membrane ratio could further be implemented at industrial level for the utmost benefit of mankind.

Competing interests

None of the authors have any competing interests including direct or indirect financial relations with any of the trademarks and company mentioned in this paper except that University Grants Commission (UGC), New Delhi, India, has funded this project.

Authors' contributions

PNS and PAV contributed to the conception and design of the study. PAV carried out the experiments, analyzed the data, and drafted the manuscript. PNS supervised the works. Both authors read and approved the final manuscript.

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