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Preparation and characterization of xanthated cotton fiber modified cellulose triacetate ultrafiltration membrane

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ABSTRACT

Cellulose triacetate (CTA)/xanthated cotton fiber (XCF) blend ultrafiltration (UF) membranes were prepared via phase inversion in the absence and presence of 2.5 wt.% additive, namely polyethylene glycol 6000 (PEG 6000). The XCF which can adsorb heavy metal ions was chosen as the modifier. The prepared membranes were characterized using pure water flux, contact angle, rejection of the metal ion solution, flux recovery ratio, and mechanical analysis techniques to investigate the influence of XCF and PEG 6000 on the final properties of the membranes. Membrane cross-sectional structures and surface morphology were characterized by scanning electron microscopy and atomic force microscopy, respectively. The results showed that the permeability, ion adsorption, surface hydrophilicity, and mechanical properties of the ultrafiltration membranes were enhanced greatly. According to molecular weight, the interception rate of heavy metal ions followed this order: Cu(II) > Zn (II) > Ni(II) > Cd(II). Compared with the membranes prepared from pure CTA, the CTA/XCF blend UF membranes possessed better performances.

Keywords: Ultrafiltration membrane; Cellulose triacetate; Xanthated cotton fiber; Heavy metal ions

1. Introduction

In recent years, more and more attention has been paid to the removal of toxic heavy metal ions from the industrial effluents due to the increasing requirement for the high-purity products and the increasing attention to the environmental protection [1,2]. Effective removal of the heavy metal ions from aqueous solution is important for the protection of the environment. Conventional physical and chemical treatment methods used to remove the heavy metal ions include chemical precipitation–neutralization [3], solvent extraction, ion exchange [4], adsorption [5], biosorption [6], and coagulation [7]. However, these techniques have some disadvantages, for example, the cost is high and the operational procedure is complicated [8–10]. Currently, the membrane separation technology has become an effective method to treat wastewater and groundwater containing toxic metal ions, since it is easy to operate and compatible with existing equipment and technology [11–14].

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In view of the demand for improving the properties of membranes, such as mechanical properties, thermal stability, and chemical stability, the research of membrane material has become one of the most important factors restricting the development of the membrane. Cellulose triacetate (CTA) is one of the most common cellulose derivatives, which is a suitable material for ultrafiltration membranes because of its excellent film-forming property, moderate flux, high salt rejection property, cost effectiveness, relatively easy processibility, renewability non-toxicity of raw material [15]. Recently, it has been widely used in the new high-technology application fields, such as chiral separation, medical membranes, and optical films with highly controlled optical property [16,17]. However, the thermal and chemical stability of CTA is low. In order to improve its properties, some other high-performance polymers, such as poly(ether-ether-sulfone) [18] and TEMPO-oxidized cellulose nanofibrils [19] are usually used to blend with it.

The xanthated cotton fiber (XCF) was chosen as the modifier due to it can adsorb heavy metal ions. Heavy metals, such as Cu, Ni, Zn, and Cd could be separated and concentrated by the water-soluble macromolecular compounds through binding and subsequent ultrafiltrated from the unbound components. Thus, the toxic heavy metals could be removed from the waste streams, while the precious metals could be reserved [20,21]. Due to the presence of sulfur atom, which has a very strong affinity with most of the heavy metals and stability of their metal sulfur complex in basic medium, the xanthate group was chosen in this study. Moreover, because of its simple preparation, big adsorption quantity, cheap, effective trace heavy metal ion separation, and enrichment of reagents, XCF has been used in many industries such as food and beverage industry, environmental protection, health, mineral processing, and many other industries. It is well-known that blending two different polymers can provide a feasible and cheap way for developing novel materials with designed properties, which is less complicated than designing new polymers. Therefore, other researchers have studied the effect of operating parameters on the selective separation of heavy metals from binary mixtures via polymer-enhanced ultrafiltration [22–25]. Over the past few years, many modifiers have been reported in membrane processes were found to be successful. Baharuddin et al. prepared polysulfone hollow fiber, using unmodified starch as additives. They found that unmodified starch showed better retention for zinc ions than polyethyleneimine, whereas polyethyleneimine retention for lead ions was higher [26]. Valle et al. [27] prepared ultrafiltration (UF) membranes used poly (N-vinylpyrrolidone-co-2-acrylamido-2-methylpropane sulfonate sodium), poly(VP-co-AMPS) as additives. They reported that the copolymer and homopolymers exhibited different retention properties for the metal ions. Pereira et al. [28] prepared Polysulfone/PANI TiO_2 (polyaniline titania) nanocomposites UF membranes by the phase inversion method and observed that PANI TiO_2 nanocomposite membranes showed better hydrophilicity, improved permeability, enhanced porosity, water uptake, and good antifouling ability when compared with neat polysulfone membranes. However, the bad compatibility between organic polymer and inorganic additives restricted their application in UF. And yet, an extensive literature survey reveals that there is no published document about the exploitation of XCF in the modification of CTA membranes.

In this work, ultrafiltration membranes were prepared by blending CTA with XCF as additives. The objective of this work was to study the influence of the XCF addition on the membrane structure and membrane properties including morphology, permeation performance, antifouling property, surface hydrophilicity, and mechanical properties, especially the separation of toxic heavy metal ions, such as Cu (II), Ni(II), Zn(II), and Cd(II).

2. Experimental

2.1. Materials

CTA was purchased from Acros Organics (DS = 2.96, Mw = 3.50×10^5). XCF and N-methyl pyrrolidone (NMP) were commercial products of laboratory grade (Beijing Chemical Works, China) and used as received. Copper (II) sulfate (AR), nickel (II) sulfate (AR), zinc (II) sulfate (AR), and cadmium (II) chloride (AR) were purchased from Beijing Chemical Works (Beijing, China). Polyethylene glycol 6000 (PEG 6000, Mw 6000Da) was purchased from Hengcheng Chemical Co. (Beijing, China).

2.2. Membrane preparation

The preparation method involved is the same as that of the phase inversion method employed as reported already by other researchers [20,29,30]. The homogeneous solutions were prepared by dissolving CTA and XCF in the presence and absence of PEG 6000 as the additive in NMP, under constant mechanical stirring in a round-bottom flask for 4 h at 40℃. After kept for 6 h at 40℃ to remove air bubbles, solution was casted on a glass plate substrate by a homemade casting knife. Then, the glass plate with casting film was gently immersed into the gelation bath. Thickness of the blend membrane was maintained at 0.22 ± 0.02 mm. After primarily phase separation and formation of membrane, it was stored in water for 12 h in order to complete phase separation. The membrane sheets were subsequently stored in distilled water, containing 0.1 wt.% formalin solution to prevent microbial growth. A series of polymer solutions were prepared by varying the composition of CTA and XCF with PEG 6000, as shown in Table 1.

2.3. Scanning electron microscopy

The cross-sectional images of the CTA and CTA/XCF blend membranes were observed by scanning electron microscope (scanning electron microscopy (SEM), PhilipsXL30E). The membranes were cut into pieces of various sizes and mopped with filter paper. These membranes pieces were frozen under liquid nitrogen for 60 s. Frozen bits of the membranes were broken and kept in a desiccator. These dry samples were coated with gold by sputtering for producing electric conductivity. The photographs were taken in very high vacuum conditions operating at 20 kV.

2.4. Atomic force microscopy analysis

The surface morphology and roughness of the prepared membranes were studied using atomic force microscope (SII Nanotechnology SPMSPI3800N). Small squares of the prepared membranes were cut and glued onto a glass substrate. The scanning area of the membrane was approximately 5 μm × 5 μm, and the surface roughness was measured by tapping mode. All the roughness parameters were calculated by the software.

2.5. Membrane performance characterization

2.5.1. Pure water flux

Firstly, each membrane was initially pressurized for 60 min at 0.2 MPa; then, each membrane was subjected to pure water flux (PWF) estimation at a transmembrane pressure of 0.1 MPa. The steady permeability was measured by Millipore 8200 ultrafiltration model with an effective membrane area of 28.7 cm^2. The PWF was determined as follows:

$$Ji = \frac{Q}{A(\Delta t)} \tag{1}$$

where Ji was water flux (l m^{-2} h^{-1}), Q was the quantity of permeate (l), Δt was the permeation time (h), and A was the effective membrane area (m^2).

2.5.2. Rejection of the metal ion solution

Since the pore size of the UF membranes were not suitable for separating heavy metal ions, water-soluble polymer polyethyleneimine (PEI) was used to bind the metals to form macromolecular complexes [21]. One thousand parts per million solutions of Cu(II), Ni(II), Zn(II), and Cd(II) in 1 wt.% aqueous solution of PEI in distilled water were prepared, and the pH of the solutions was adjusted to 6 ± 0.25 using 0.1 N HCl or 0.1 N NaOH solutions. Solutions containing PEI and individual metal ions were thoroughly mixed and left standing for 5 d to complete binding [31]. The percentage rejection of the metal ions was determined by analysis of the concentrations of the feed (C_f) and permeate (C_p) with anatomic absorption spectrophotometer (AAS, Perkin-Elmer 3110):

$$R(\%) = \left[1 - \frac{C_p}{C_f}\right] \times 100\% \tag{2}$$

where C_p and C_f were metal ion concentrations of permeate and feed solutions, respectively.

2.5.3. Flux recovery ratio

In order to evaluate the antifouling ability of the membranes, flux recovery ratio (FRR) was introduced [32] and calculated using the following expression:

Table 1
Composition and casting conditions of CTA/XCF blend membranes

Membrane	CTA (wt.%)	NMP (wt.%)	PEG 6000 (wt.%)	XCF (wt.%)
(a)	10	90	0	0
(b)	10	90	0	0.5
(c)	10	90	0	1.0
(d)	10	90	0	1.5
(e)	10	87.5	2.5	0
(f)	10	87.5	2.5	0.5
(g)	10	87.5	2.5	1.0
(h)	10	87.5	2.5	1.5

Note: Casting temperature = 40 ± 1˚C; casting relative humidity = 25 ± 2%; solvent evaporation time = 30 s.

$$\text{FRR}\ (\%) = \frac{Ji_2}{Ji_1} \times 100\% \tag{3}$$

where Ji_1 ($\mathrm{l\,m^{-2}\,h^{-1}}$) was first obtained at 0.1 MPa; Ji_2 ($\mathrm{l\,m^{-2}\,h^{-1}}$) was the PWF of the cleaned membranes and was measured at 0.1 MPa again.

2.6. Contact angle

Contact angle, which also is called wetting angle, is the angle when the liquid on the solid surface keeping perspective in the thermodynamic equilibrium. It is a sign of measuring the interfacial tension, but also the important parameter for determining the performance of hydrophilic and hydrophobic substances. The strong hydrophilicity of sample surface will lead small contact angle value [33].

The contact angle between the water and the membrane was directly measured using a contact angle measuring instrument (JC2000C1, Chenguang Co., Shanghai, China) for evaluation of their hydrophilicity. Distilled water was used as the probe liquid in all the measurements. Before carrying out the experiments, the frozen-dried membrane sample was washed thoroughly with water, and mopped with blotting paper, to remove the moisture present on the membrane surface. Then, 5 μl distilled water was dropped onto membrane surface. The contact angle of the droplet was calculated by the software of contact angle meter. To minimize the experimental errors, the contact angle was measured at five random locations for each sample and then the average value was reported.

2.7. Mechanical properties of the CTA/XCF

After removing water present in the membranes, tensile strength and elongation at break of blend membrane was performed at room temperature according to ASTM D882 using a Shimazu AG-10-TB Universal material-testing machine with a crosshead speed of 1 mm/min. The samples were cut to the standard shape of 10 mm wide and 30 mm gauge length. The measurement was performed at 48 ± 2% relative humidity. For each membrane, three samples were evaluated and the average values were reported for accuracy.

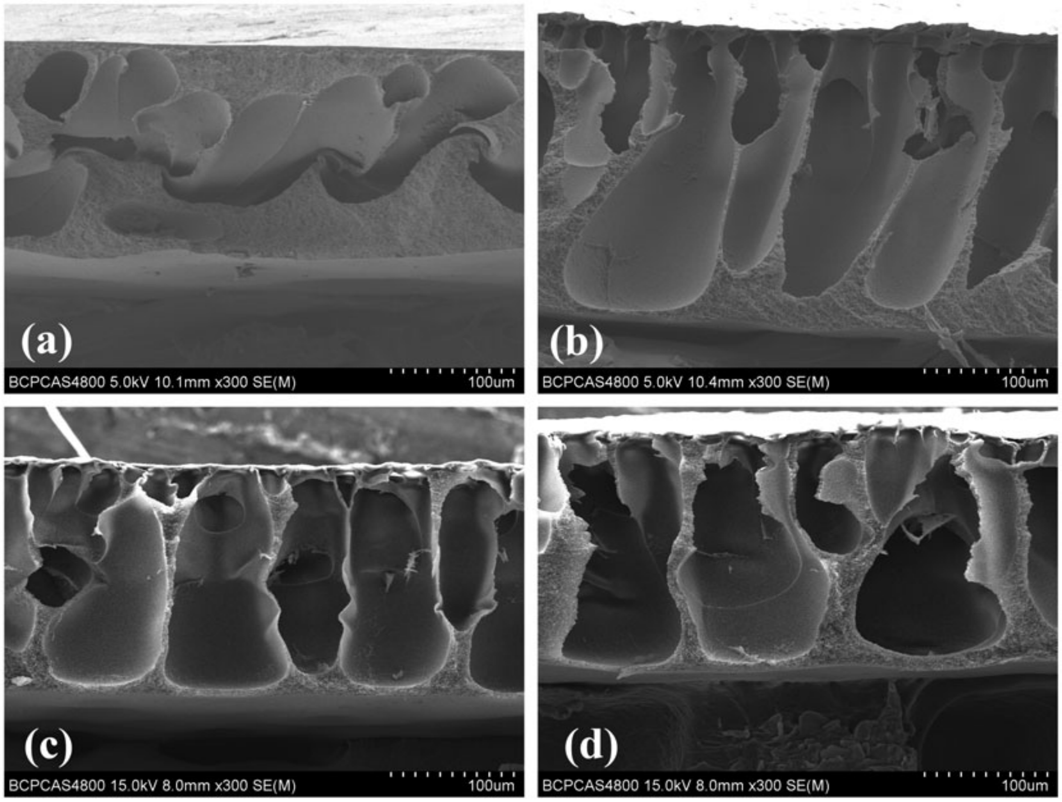

Fig. 1. SEM cross-sectional images of CTA/XCF blend membranes: (a) XCF-0%, 0 wt.% PEG 6000; (b) XCF-0%, 2.5 wt.% PEG 6000; (c) XCF-0.5%, 0 wt.% PEG 6000; (d) XCF-0.5%, 2.5 wt.% PEG 6000.

3. Results and discussion

3.1. Morphological studies

SEM images were taken to determine the effects of the XCF composition on the final CTA ultrafiltration membrane structure. The cross sections of membranes were taken. The dense skin layer (top layer) and porous sub layer (sub layer) of the ultrafiltration membranes play an important role in helping to identify the significance of membrane in the mechanism of selectivity and permeability. It is known that the top layer of membrane is responsible for the permeation or rejection, while the sub layer of the membrane acts as a mechanical support [34].

When the cast film was immersed in the distilled water bath, precipitation started because of the low miscibility between the polymer CTA and the nonsolvent (water). Simultaneously, the miscibility between the solvent NMP and the nonsolvent (water) caused diffusional flow of the solvent and nonsolvent (exchange of solvent and nonsolvent). Generally, the structure of the dense layer was determined by the ratio of nonsolvent inflow to the solvent out flow. In our preparation, different concentration of XCF was added into the casting solution. In the process of film forming, NMP diffused from the casting solution into the coagulation bath, forming a dense layer and supporting layer of the pore structure. The rate of the demixing process affected the morphology of the membranes [35–37].

Fig. 1(a) depicts that the membrane prepared from pure CTA exhibited a finger-like cavities and all small pores were not fully developed in the sub layer. Further, the number of pores was less in pure CTA (Fig. 1(a)) when compared with CTA membrane prepared in the presence of 0.5 wt.% XCF (Fig. 1(c)). According to the SEM cross-sectional images, an initial increase in the XCF concentration (from 0 to 0.5 wt.%) caused a greater formation of porous structures in the sub layer of the membranes (Fig. 1(a)–(c)). The changes in the morphologies could be attributed to the changes in the blend composition by the addition of XCF. In this study, the presence of XCF as a hydrophilic composition might intensify thermodynamic instability of the cast film solution and this resulted in intensive increase of mutual diffusivities between the nonsolvent (water) and the solvent NMP in the system during solidification of the casting solution [38]. Similar observations were reported by other researchers [39]. Thus, using more XCF, the precipitation rate could be accelerated in the coagulation bath and consequently caused instantaneous demixing in the coagulation bath [40].

A comparison of Fig. 1((b) and (d)) clearly shows that when PEG 6000 content increased from 0 to 2.5 wt.%, the sub layer seemed to have finger-like cavities as well as greater macrovoids. These SEM results confirmed the effect of additive on PWF and pore size of CTA/XCF blend membranes. The hydrophilic additive PEG 6000 increased thermodynamic instability of the cast film and promoted the instantaneous demixing in the coagulation bath. Hence, adding PEG 6000 to the casting solution would increase the macroporous and finger-like cavity of the ultrafiltration membrane.

3.2. Atomic force microscopy analysis

The atomic force microscopy (AFM) technique was also employed to evaluate changes in surface morphology and roughness of the CTA/XCF blend membranes. The images and roughness parameters are illustrated in Figs. 2 and 3 and Table 2. In these images, the brightest area presents the highest point of the membrane surface and the dark regions illustrates valley or membrane pores. The surface morphology of the membrane was changed after addition of XCF and PEG 6000 into the CTA casting solution. It was observed from Fig. 2(a) and Table 2 that the surface roughness of the membranes decreased with an increase in concentration of XCF in the casting solution. This was due to the high viscosity of the CTA casting solution and its highly crystalline structure. The decrease of mean distance between the highest peaks and lowest valleys indicated the decrease in mean pore size in the membrane surface. But in the case of XCF blend at 1.5 wt.% composition, the surface roughness of the membrane was bigger than that of the pure CTA membrane. This was due to the segmental gap formed between the components in the blend system because of its incompatibility. From Fig. 3, it was observed that the surface roughness increased with incorporating PEG 6000 into membranes. This result may be attributed to the addition of hydrophilic additives PEG 6000, which increased thermodynamic instability of the cast film and promoted instantaneous demixing process in the coagulation bath. The increasing pore number of the membranes was conformed to the SEM images.

3.3. PWF analysis

The PWF is an important characteristic of membrane for any industrial application. The PWF of all membranes is shown in Fig. 4. The low PWF value

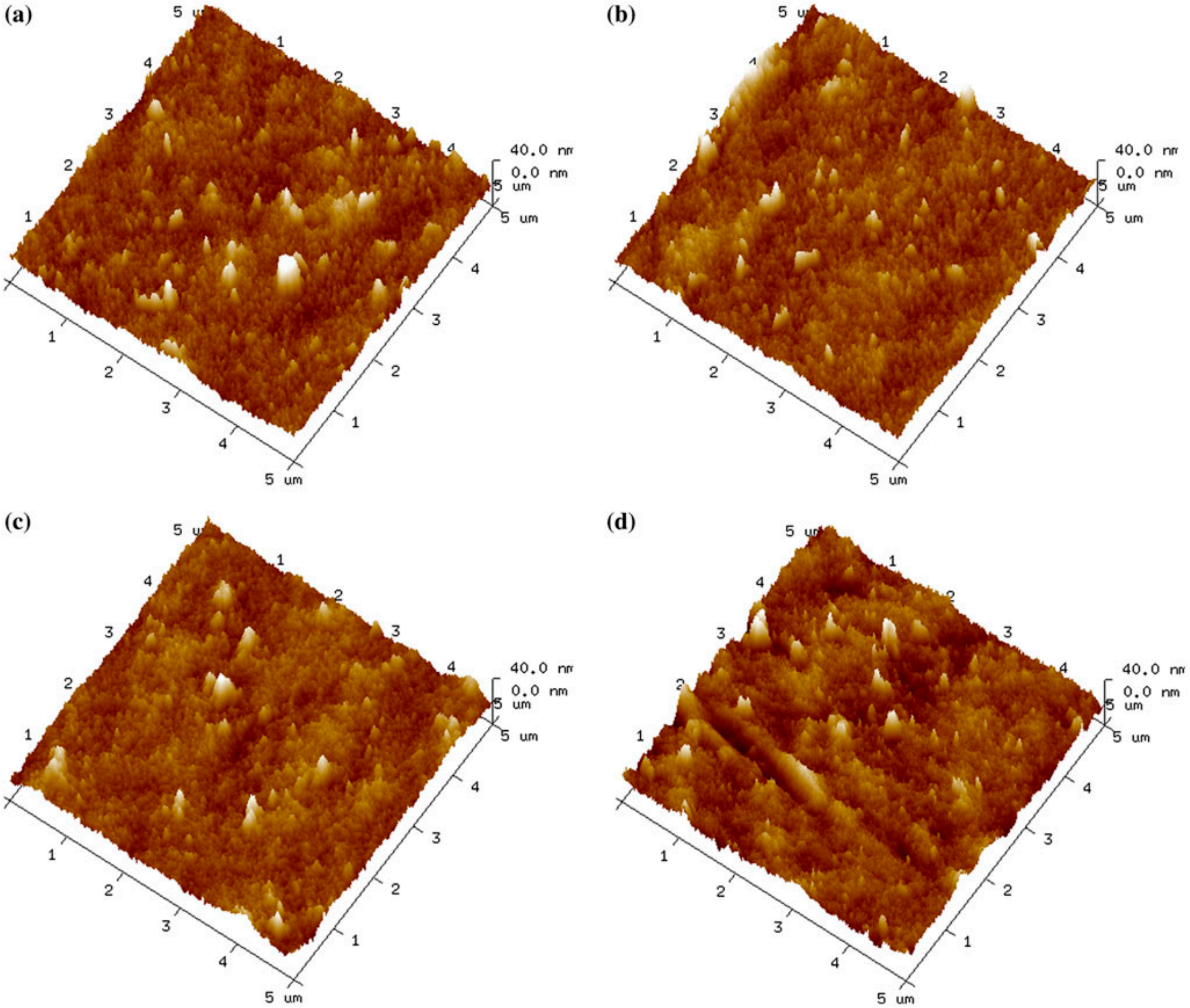

Fig. 2. AFM three-dimensional images of CTA/XCF blend membranes without additive: (a) XCF-0%; (b) XCF-0.5%; (c) XCF-1.0%; (d) XCF-1.5%.

of 90.57 L m^{-2} h^{-1} was obtained for pure CTA membrane, as shown in Fig. 4. This was due to the tight structure of pure CTA membrane and pores did not open up properly in the downstream side of the membranes [21]. From Fig. 4, it was clear that the PWF of CTA/XCF blend membranes was higher than that of pure CTA membrane. The PWF of membrane has increased from 90.57 to 123.69 Lm^{-2} h^{-1} with the XCF concentration increasing from 0 to 1.5 wt.% without additive. The linear increase in flux with XCF content in the absence of PEG 6000 due to the macrophase separation of blend membrane which in turn enhanced the pore size of membrane. This linear trend could be attributed to the higher porosity and more hydrophilic surface (Section 3.6). The membrane prepared in the presence of PEG 6000 yielded enhanced flux values. This trend indicated the leach ability of PEG 6000 in the gelation process, which leaded to the formation of higher and larger numbers of pores in the membranes. When the concentrations of both XCF and PEG 6000 increased simultaneously, the repulsive forces between polymer segments along with leach ability of PEG 6000 was enhanced and this favored the formation of macrovoids due to occurrence of more large size pores.

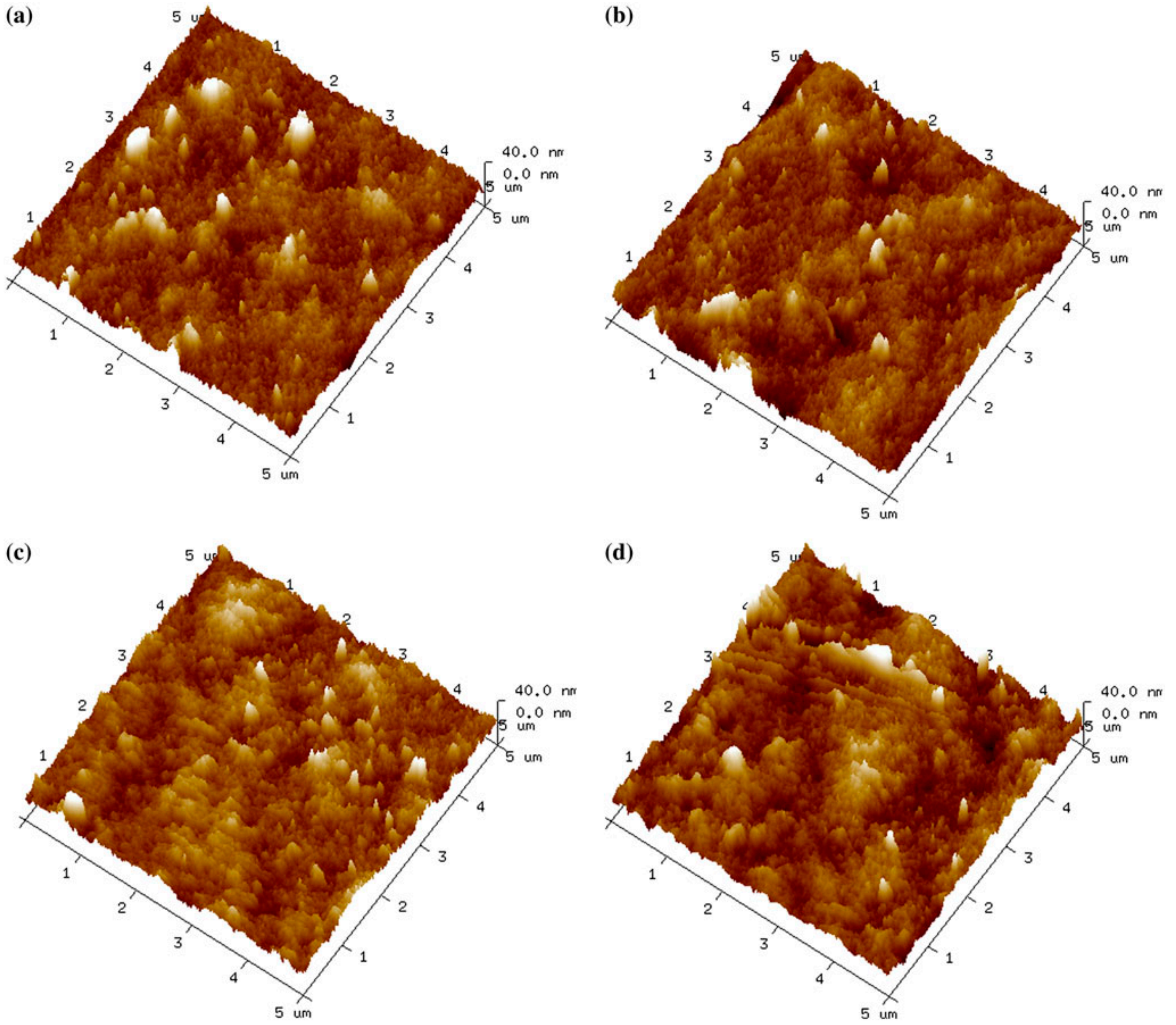

Fig. 3. AFM three-dimensional images of CTA/XCF blend membranes with additive: (a) XCF-0%, 2.5 wt.% PEG 6000; (b) XCF-0.5%, 2.5 wt.% PEG 6000; (c) XCF-1.0%, 2.5 wt.% PEG 6000; (d) XCF-1.5%, 2.5 wt.% PEG 6000.

3.4. Metal ion rejection studies

In drinking water purification, using polymer modified ultrafiltration membrane is considered to be an effective method to remove heavy metal ions. For the sake of reproducibility of the metal ion rejections, simultaneous permeate flux measurements were repeated at least three times and the average values were reported.

The pure CTA and CTA/XCF blend membranes were subjected to the rejection of metal-chelated ions and the results are given in Table 3. From the results, it would be seen that the rejection of a particular metal ion showed an upward and then downward tendency. As XCF concentration was less than 1.0 wt.%, the rejection of a particular metal ion increased significantly by adding XCF into CTA, which might be caused by the smaller pore size of the membrane surface. In AFM analysis, the pore size of the membrane surfaces decreased with the addition of XCF evidenced by the surface roughness analysis data. However, these values at 1.5 wt.% blend membranes were lower than that of pure CTA membranes due to the heterogeneity arising as a result of the higher XCF content creating gaps between the polymer chains.

Table 2
Surface roughness parameters of the CTA/XCF blend membranes

		Roughness parameters	
XCF (wt.%)	PEG 6000 (wt.%)	Ra (nm)	Rq (nm)
0.0	0.0	4.10	5.92
0.5	0.0	4.03	5.64
1.0	0.0	4.02	5.48
1.5	0.0	5.07	6.76
0.0	2.5	5.16	7.23
0.5	2.5	5.14	6.94
1.0	2.5	4.96	6.84
1.5	2.5	5.80	7.54

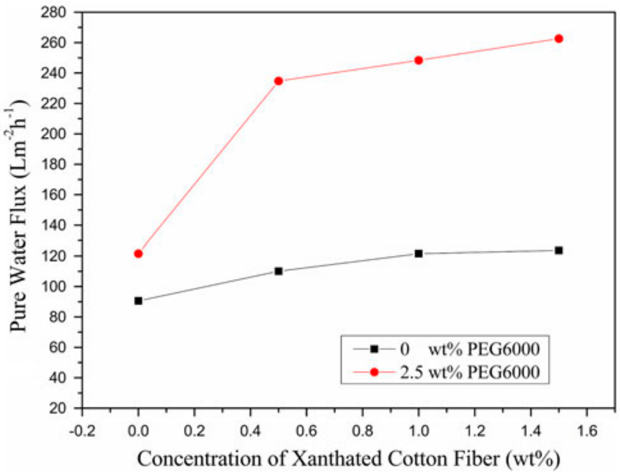

Fig. 4. The PWF of the CTA/XCF blend membranes at various compositions in the absence and presence of 2.5 wt.% additive.

The rejection studies mentioned above show that the binding capacity of Cu^{2+} with XCF was stronger than that of the other metal ions and the order was: Cu(II) > Ni(II) > Zn(II) > Cd(II). Further, the complexing capacity depends on the number of functional groups in the macromolecular complex and the atomic size of the metal [41]. The highest separation of Cu^{2+} might have been because of the formation of stronger complexes with stable short bonds.

The additive PEG 6000 played a key role in the membrane performance. When the additive concentration has increased from 0 to 2.5 wt.%, the rejection decreased linearly. This can be explained by the fact that the higher amount of nonsolvent additive leaded to rapid formation of larger and bigger pores during gelation because of the thermodynamically instability and lower free energy of the system. The decrease in rejection in the presence of additive might be attributed to the rapid leaching out of pore former creating larger pores.

3.5. FRR analysis

Membrane fouling could reduce the permeation efficiency and restrict the wide application of ultrafiltration membrane. FRR value has been introduced to evaluate membrane antifouling property. FRR is closely related to the effectiveness of ultrafiltration and economy; therefore, after ultrafiltration trapped ion solution, we investigated the water flux recovery, and the results are shown in Table 3.

In the absence of PEG 6000, when the concentration of XCF increased, the FRR value has obviously increased. The result demonstrated that CAT/XCF membranes had better surface hydrophilicity, which can be proven by the results of surface roughness and water contact angle. This was due to the formation of a large amount of free water generated on the

Table 3
Metal ion rejection and FRR of the CTA/XCF blend membranes

		Metal ion rejection (%)				Flux recovery ratio (%)			
XCF (wt.%)	PEG 6000 (wt.%)	Cu(II)	Zn(II)	Ni(II)	Cd(II)	Cu(II)	Zn(II)	Ni(II)	Cd(II)
0	0	91.74	90.16	88.83	86.53	43.65	48.36	60.32	68.48
0.5	0	96.25	95.22	93.94	93.49	53.79	60.58	64.77	69.41
1.0	0	98.75	98.28	97.11	96.05	60.80	64.05	70.72	73.93
1.5	0	90.48	89.10	87.57	85.96	65.92	70.90	75.95	78.85
0	2.5	90.31	90.02	87.79	86.08	51.39	55.37	59.26	70.08
0.5	2.5	95.11	93.25	90.10	90.09	59.88	62.22	69.83	76.27
1.0	2.5	97.91	96.82	95.44	93.79	66.13	68.74	73.87	79.20
1.5	2.5	90.03	88.29	86.64	85.12	76.91	79.30	82.09	84.15

CTA/XCF membranes surface. These weaker ions trapped aggregation could be easily removed from the blend membranes by hydraulic cleaning, which resulted in high FRR. For different ions in solution, the water FRR was in the order: Cu(II) > Ni(II) > Zn (II) > Cd(II). With XCF in the cast membrane solution, the more easily eluted behavior was found as the bigger volume of aggregation formed with metal ions; thus, the water flux recovery rate was also greater.

Similar trend had also been observed for the blend membranes prepared from 0 to 1.5 wt.% XCF with CTA in the presence of additive, PEG 6000. The FRR also has increased, which might be owed to the change of the aperture size with the addition PEG 6000.

3.6. Contact angle analysis

The surface of CTA membrane can easily form hydrogen bond with water molecule which makes water-ordered state. The study of the wettability of the membranes is of great importance in industrial applications. In order to increase the separation efficiency of UF membranes, it is essential that the substrate has a hydrophilic nature. It is known that the smaller the contact angle, the greater the hydrophilicity.

In the present study, membranes were subjected to the static water contact angle experiment five times and the average values are showed in Fig. 5. It can be seen from Fig. 5 that the contact angle was 84.5° for pure CTA membrane, corresponding to the low hydrophilicity, while the contact angles decreased with the enhancement of XCF concentration in the modified membranes. This was mainly due to the hydrophilicity of XCF and the polar surface. In the case of CTA/XCF blend membranes, the presence of sulfone groups of XCF effectively competed with water by hydrogen bonding and van der Waals interactions and leaded to lower contact angle [18]. The red bar chart in Fig. 5 shows that the corresponding CTA membrane without PEG 6000 in the cast solution possessed bigger contact angle value (84.5°) than the pure CTA membrane with PEG 6000 (61.7°). This implies that the addition of PEG 6000 promoted membrane surface hydrophilicity, which might be ascribed to the hydrophilic group of −OH in PEG 6000 remained on the membrane surface. The residual presence of a certain amount of PEG 6000 molecules in the membrane matrix resulted in the improvement of their hydrophilicity. In the meantime, the surface porosity has an intense effect on the contact angle, since the water drop could penetrate into the pores gradually due to the capillary force, which decreased the contact angle compared to membrane without additive [40].

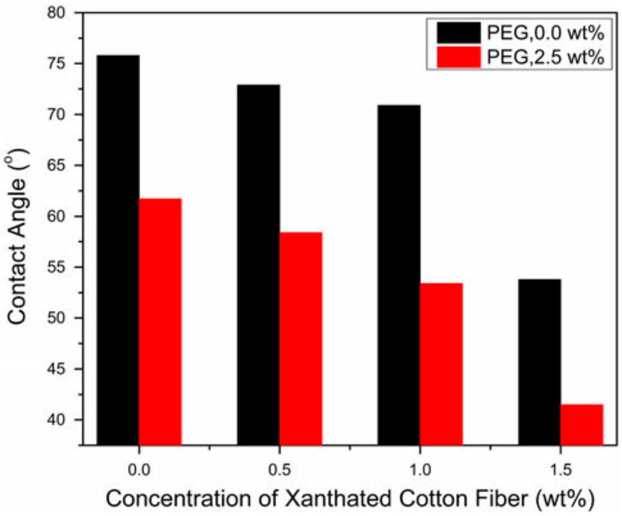

Fig. 5. The contact angle of the CTA/XCF blend membranes at various compositions in the absence and presence of 2.5 wt.% additive.

3.7. Mechanical properties analysis

In order to investigate the effect of XCF and PEG 6000 on mechanical properties, the tensile strength and elongation at break of the CTA/XCF blend membranes filled with different PEG 6000 content were measured as shown in Figs. 6 and 7, respectively. As evidenced from Fig. 6, with XCF content increasing, the tensile strength has been greatly improved and it decreased after increased firstly. When more XCF was added in the casting solution, the elongation at break decreased gradually, which was attributed to the film after drying has become more brittle.

The result indicates that the addition of XCF increased the tensile strength of CTA membranes to a higher value and further increase in XCF content would decrease the tensile strength. When the amount of XCF reached 1.0 wt.%, the mechanical tensile strength increased from the original 5.7–32.2 MPa. However, when the XCF content was above 1.0 wt.%, the larger pore size of the membrane reduced the tensile strength of the composite membrane.

Fig. 7 shows the stress–strain of membranes in the presence of PEG 6000. In the absence of PEG 6000, the mechanical properties of pure CTA and CTA/XCF blend membranes were higher than that of membranes with additive. The addition of PEG 6000

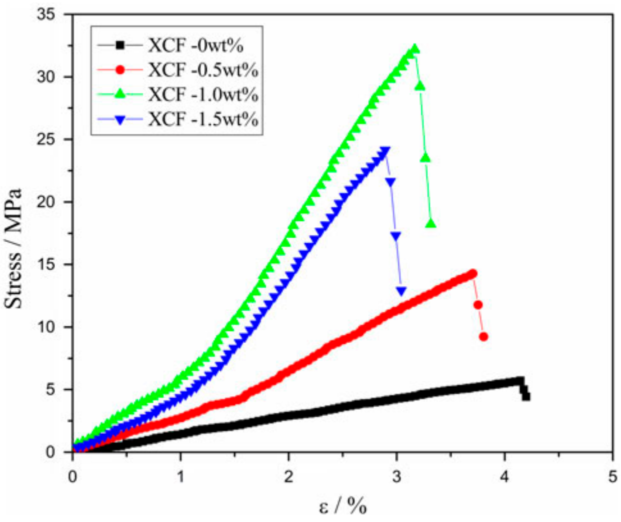

Fig. 6. Mechanical tensile (0 wt.% PEG 6000).

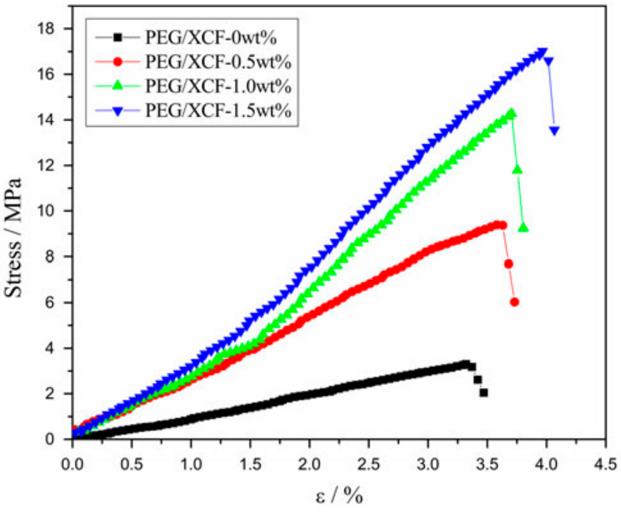

Fig. 7. Mechanical tensile (2.5 wt.% PEG 6000).

increased the porosity of the membranes, but it also caused undesirable changes in the mechanical properties. In addition, it can be seen from Fig. 6, with the addition of XCF, tensile strength and elongation at break significantly improved, and this is slightly different from that of Fig. 7. The fact might be that the addition of PEG 6000 would reduce the elongation at break of the film.

4. Conclusions

In this work, it has been demonstrated that CTA ultrafiltration membranes assisted by complexation is a promising separation technique applied to purification of effluents containing heavy metals. In the present investigation, CTA ultrafiltration membranes were prepared by phase inversion technique using XCF which can adsorb metal ions as the modification agent and polyethyleneglycol 6000 as the pore former. The effect of blend ratio on the morphology, permeation performance, antifouling property, surface hydrophilicity, and mechanical properties of the resultant membranes was evaluated.

The morphological studies were conducted using SEM. It was observed that the pore formation increased with the addition of XCF and PEG 6000 to the polymer membranes and morphological structure also changed. The prepared membranes were evaluated for the ultrafitration characteristic parameters such as PWF, contact angle, metal ion rejection, and FRR. The UF performance of CTA/XCF membranes illustrates that as the concentration of XCF in the casting solution was increased the PWF and FRR were increased, while the membrane contact angle was decreased. In the absence of PEG 6000, with the increase of the content of the XCF in coagulation bath, the permeability, ion selective of ultrafiltration membrane have greatly improved. At the same time, the mechanical properties of the composite film greatly improved, but with the increase of aperture, the tensile strength began to decline when the amount of XCF reached 1.0 wt.%. After adding PEG 6000, the permeability, ion selectivity of composite membrane presented the same variation. According to molecular weight, the interception rate of heavy metal ions followed this order: Cu(II) > Zn(II) > Ni(II) > Cd(II). Thus, the present study concludes that the XCF incorporated CTA membranes by the phase inversion method with the pore former PEG 6000 are promising candidates for efficient heavy metal ion removal from industrial waste water.

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