Papermaking effluent treatment: a new cellulose nanocrystalline/polysulfone composite membrane

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Abstract

Membrane technique is more and more used in the papermaking effluent treatment because of the advantages of environmental, high efficient and low energy consumption. In this work, a new cellulose nanocrystalline (CNC)/polysulfone (PSF) composite membrane was prepared with L-S phase invasion and was used to separate papermaking effluent. The composite membranes were coagulated in methanol/water coagulation bath with different concentration. The properties of the membrane which was used to treat the papermaking effluent were characterized. The cross section of the membrane was characterized by a scanning electron microscopy (SEM). The tensile strength was measured. Flux and rejection rate were studied. Moreover, the properties of the effluent which separated with membrane were characterized. Results showed that the membrane structure differed as the methanol concentration changed. With the increase of the CNC content, the tensile strength increase first and then decrease. The new composite membrane has a relative high flux during the treatment of papermaking effluent. At the same time, the lignin content, suspended solids (SS) and chemical oxygen demand in the papermaking effluent all decreases obviously.

Keywords: cellulose nanocrystalline (CNC); methanol; papermaking effluent

1. Introduction

In recent years, environmental pollution and pollution control has become a global hotspot issues. Papermaking effluent emissions increase year by year with the rapid development of paper industry which is a direct threat to human health.
According to statistics, in 2010, the chemical oxygen demand (COD\textsubscript{Cr}) emissions in China are 719 thousand tons which accounts for 20.3% of the national industrial emissions. The pollutant of paper-mill black liquor accounts for 90% of the total pollutants. Moreover, lignin and its degradations are the composition that polluted most. If the black liquor can't get effective treatment and emission directly, the environment will be polluted and resources will be wasted. So, the key to solve the papermaking effluent is to treat the black liquor completely and effectively [1].

There are many methods to deal with the papermaking effluent, such as flocculation, alkali recovery, acidulation precipitation, concentrate treatment, biological method, oxidation and membrane separation [2-4]. Membrane separation was widely used as the advantages of high efficiency, energy conservation, environmental and convenient. In paper industry, ultrafiltration is the membrane technology that most widely used. Gonder, ZB et al. [5] used ultrafiltration membranes to treat pulp and paper mill wastewater. They applied Taguchi method to find the optimum conditions, namely, pH 10, temperature 25\textdegree C, transmembrane pressure 6 bar, and volume reduction factor 3. Membrane filtration process was also used by Yong Zhang et al. [6] to concentrate the effluent from alkaline peroxide mechanical pulping plants. In the experiment, they obtained the optimal filtration conditions and reach a good concentrate result. Simonic, M [7] compared the coagulation and UF treatment of pulp and paper mill wastewater. The multi-channel membrane with an active surface removed the turbidity and TSS at above 99%. In this study, a new ultrafiltration membrane was used to treat the papermaking effluent.

For the good properties of chemical stability, heat-resisting and pressure resistance, we use PSF as the main material to prepare the membrane. Different concentration of methanol solution was used as the coagulation bath. CNC was used to improve the properties of the composite membrane. The papermaking effluent was treated by the composite membrane. Lignin content and the suspended solids (SS) in the papermaking effluent and filtrated solution were evaluated.

2. Experimental Materials and Methods

2.1. Materials

PSF was supplied by Polysulfone plastics limited company (Dalian, China). The pellet form PSF was dried at 50 \textdegree C for 24 h. Polyethylene glycol (PEG) was used as porogen, which was obtained from Beijing chemical reagent company (Beijing, China). CNC was self-made. The width and length of the fibre are all in nanoscale. Methanol was purchased from Beijing chemical reagent company (Beijing, China). N,N-dimethylacetamide (DMAC) was used as the solvent, which was supplied by Beijing Chemical Plant (Beijing, China).

2.2. Membrane Preparation

Firstly, added 3g of PEG (3%) and a certain amount of CNC into a triangular flask. DMAC was used to dissolve PEG and disperse CNC homogeneously. Then, added 18 g of PSF (18%) into the mixture and swayed the flask in table concentrator for 8 h at 60 \textdegree C. The homogeneous casting solution was vacuumized to degas. After that, the membrane was prepared with L-S phase inversion and the coagulation bath was used methanol/ water with different concentration (10%, 30% and 50%). All membranes were kept in a water container before characterizations.

2.3. Papermaking Effluent Treatment
The papermaking effluent was supplied by pulp and paper laboratory of Beijing Forestry University. It was separated directly by the composite membrane. Work pressure is 0.1 MPa.

2.4. Characterization

2.4.1. SEM

The cross section morphology of the membrane was observed by SEM (S-3000n, Hitachi, Japan). The membrane was fractured in liquid nitrogen and then coated with gold before test. SEM micrographs of ×500 and ×10000 magnifications were used.

2.4.2. Mechanical Properties

Tensile testing instrument (DCP-KZ300, Sichuan, China) was used to test the tensile strength of the composite membranes. All dry membranes were cut into 15mm in width and 100mm in length before test. The clipping distance was 50 mm and the testing speed was 20 mm/min.

2.4.3. Retention Rate

The retention rate of the bovine serum albumin (BSA) solution (1 g/L) was tested. Working pressure was 0.1 MPa, and the absorbance of the filtered solution was measured at 279 nm with ultraviolet (UV) spectrophotometer (UV-1801, Shanghai, China). The absorbance - concentration standard curve of BSA was made to calculate the concentration of the solution. The retention rate was calculated with the following equation:

$$R = \frac{(1-C_1/C) \times 100\%}{(1)}$$

Where R is the retention rate (%), C₁ and C are the concentration of the filtered and initial solutions, respectively.

2.4.4. Water Flux

The volume of filtered water V (m³) was obtained with a working pressure of 0.1 MPa and a working time [t (h)]. The pure water flux [J (L/m²h)] was calculated with the following equation:

$$J = \frac{V}{At}$$

(2)

Where V is the volume of filtered water (m³), A is the membrane area (m²) and t is the working time (h).

2.4.5. UV

Take a certain amount of the initial and filtered solution, and then dilute the solutions to constant volume. The absorbance reduction of the effluent was analyzed with an ultraviolet spectrophotometer. The entire range of effluents was recorded. COD_{Cz} and SS were measured according to GB 11914-89 and GB 11901-89, respectively. Lignin content was also measured.

3. Results and Discussion

3.1. Morphology of the membrane

Figure 1 showed the SEM micrographs of the membrane cross section and top layer. It can be seen from the picture that all the structure present finger-like pores, sponge-like pores, and macrovoids, despite the difference in pore size. Through the comparison for the three pictures of cross section, the finger-like pores change from long and thin into short and thick with the increasing of the methanol concentration of the coagulation bath. At the same time, the macrovoids in the top layer become small and less. It can be seen obviously from the growing sponge-like pore size of the top layer that the sponge-like pore size grows with the increase of the coagulant concentration.
It is generally known that external coagulant plays an important role in membrane formation process. Also, the top layer structure depends on the ratio of nonsolvent inflow and solvent outflow [8]. The increase of methanol concentration increases the diffusion rate between solvent and nonsolvent which leads to the growing sponge-like pore size. Moreover, when the top layer structure is porous, much nonsolvent diffuse into the sublayer to induce many nuclei at the same time which makes less macrovoids. Instead, the less porous in top layer will makes more macrovoids. Meanwhile, the increasing diffusion rate makes the finger-like pore more short and thick.

3.2. Mechanical properties of the composite membrane

Figure 2 presents the effect of CNC content and methanol concentration on the membrane tensile strength. As we can see from the picture, as the increasing of methanol concentration, the tensile strength of the composite membrane increases. Moreover, the tensile strength showed an escalating trend along with an increase in CNC content. When the CNC content still increased, the tensile strength decreased gradually.
With reference to figure 1, the sponge-like pore structure changes from dense to loose with the increasing of the methanol concentration. The loose structure has less macrovoids which makes fewer defects in the membrane, and the elongation is higher than the dense structure. Hence, the tensile strength increases with the methanol concentration. CNC has large surface areas and lots of hydrogen bonds which can improve the interfacial bonding strength between CNC and the membrane. And the high interfacial bonding strength enhanced the mechanical properties of the composite membrane. When CNC was added excessively, many pore defects were induced to the membrane which causes the decrease of the tensile strength. So, the methanol content in coagulation bath and the CNC content both have a positive effect on the mechanical properties within a proper range.

3.3. Membrane permeability

The effect of CNC content and methanol concentration on the water flux and retention rate is shown in figure 3. The BSA retention rate varies from 96.73% to 98.88% which is a very high value. When the concentration of methanol is 10%, the membrane has a relative high retention rate compare to the concentration of 30% and 50%. The influence of the methanol concentration on retention rate of the pure membrane follows the sequence: methanol 10% > methanol 30% > methanol 50%. It can be seen that the BSA retention rate has decrease slightly when adding CNC gradually.
The water flux of the composite membrane improved significantly with an increase in the CNC content. Furthermore, coagulant also has a great influence on the water flux which we can see from the curve. When the methanol concentration is 10%, the curve has a sharp increase before CNC content reached 0.2%. Moreover, the water flux of methanol 30% is higher than methanol 10%, and water flux of methanol 50% is the lowest. At the same time, the BSA retention rate is all above 97%. When the CNC content is above 0.2%, the water flux of methanol 30% and 50% decreased. And the water flux of methanol 10% increases slightly.

This is all due to the various structure of the membrane. The increase of the methanol concentration in the coagulation bath makes the membrane structure changes from dense to loose which makes the membrane retention ability in the order of methanol 10%, methanol 30% and methanol 50%. The addition of CNC can increase the connection between finger-like pores and lead to the loose top layer which makes the BSA retention rate decrease gradually. Membrane which coagulated in methanol 10% presents a relatively high water flux but low tensile strength after the CNC content reached 0.2%. While the membrane which coagulated in methanol 30% has proper pore size and high tensile strength with the addition of 0.2% CNC, which also has a high water flux. From the above, we choose the membrane which CNC content is 0.2% and coagulation bath is methanol 30% to treat the paper effluent. It has a high water flux, high tensile strength and BSA retention rate.

3.4. Treatment of papermaking effluent

![UV spectrum of the papermaking effluent and the filtered solution.](image)

Figure 4 shows the UV spectrum of the papermaking effluent and the filtered solution. Lignin compounds absorb in the region 250-300 nm which are largely responsible for COD$_{Cr}$ to the effluent [9]. A reduction of absorbance in this region as shown in the curve indicates the retention ability of lignin and other impurities by the membrane. The absorption (215-290 nm) of phenol, lignin derived compounds, aromatic compounds which showed in the picture proves that there is a small part of lignin exist in the filtered solution. The initial and filtered effluent solution in Table 1 supports this observation. We can see from table 1 that the SS and lignin content reduced 89.1% and 92.8% respectively. The ultrafiltration flux of the effluent is 70.1 L/m$^2$h, which is a relatively high value. At the same time, the value of COD$_{Cr}$ reduced 65.9% and the pH has a slightly decrease. Figures showed that the membrane had a good property in the recovery of lignin, and it can also treat the paper effluent well in some extent. In order to get the filtered papermaking wastewater up to the standard demanded, methods (such as reverse osmosis, nanofiltration) can use together to deal with the waste.
Table 1. SS, Lignin content, pH of the papermaking effluent and filtered solution.

|                | SS (mg/L) | Lignin content (g/L) | pH  |
|----------------|-----------|----------------------|-----|
| Initial solution | 872.5     | 13.3                 | 11.4|
| Filtered solution | 95        | 0.955                | 10.7|

4. Conclusions

A new CNC/PSF composite membrane was prepared. With the increasing of the methanol concentration of the coagulation bath, the diffusion rate between the solvent and non-solvent increases. The finger-like pores change from long and thin into short and thick and the macrovoids in the top layer become small and less. Moreover, the sponge-like pore size in the top layer grows with the increase of the coagulant concentration. The tensile strength of the pure membrane increases with the methanol concentration. At the same time, appropriate amount of CNC can improve the tensile strength and water flux of the composite membrane. Furthermore, the composite membrane has a high retention rate.

The optimal filtration membrane conditions used in papermaking effluent treatment were: CNC content 0.2%, coagulation bath methanol 30%, working pressure 0.1MPa. The lignin content, SS and COD<sub>c</sub> in the filtrated solution reduced 89.1%, 92.8% and 65.9% respectively. The new composite membrane has a good property in lignin recovery and papermaking effluent treatment.

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