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Enhancement of ultrafiltration with a γ-Al_2O_3 ceramic membrane by an electrical field

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ABSTRACT

Membrane fouling and concentration polarization are two of the main barriers for the application of the membrane separation technique in food industry. In order to increase membrane separation efficiency caused by membrane fouling and concentration polarization, γ-Al_2O_3 membrane was employed to separate bovine serum albumin (BSA) solution in the presence of an electrical field. In this paper, the influences of electric field intensity, pH of bulk solution, and operating time on membrane performance were investigated. It was found that the influence of an external electric field on the membrane process depends on the charged properties of bulk solution. For negatively charged BSA in the solution of pH 6.8, an external electric field can improve both the flux and rejection of membrane. What is more, separation process can be maintained at a quite high flux for 60 min without significant decrease in this method, and the increase of electric field intensity can improve the membrane separation efficiency. By analyzing transport resistance coefficient of membrane process, it was showed that application of electric field can sharply reduce boundary layer resistance R_{b1}, membrane fouling resistance R_f, and total resistance R_t. These results indicated that an electric field can decrease the concentration polarization and membrane fouling on the membrane surface, which contribute to the improvement of membrane separation efficiency.

Keywords: γ-Al_2O_3 ceramic membrane; Electric field; Bovine serum albumin; Concentration polarization; Membrane fouling

1. Introduction

In recent years, ultrafiltration has been applied to widely diversified fields such as the food industry, chemical engineering, and biomedicine. However, a significant flux decline over time due to concentration polarization and fouling is the main limitation on the efficient use of ultrafiltration. In order to overcome this limitation, various techniques have been developed to improve ultrafiltration by increasing the flux. These include cross-flow filtration, upward and inclined filtration, dynamic filtration with a rotating cylindrical membrane [1–4], and electrically enhanced filtration [5,6].

The electro-ultrafiltration technology can be defined as a cross-flow ultrafiltration process, during the process, the suspended charged particulates will move away from the surface of membrane with the action of an electric field and flow shears, and the boundary layer thickness of membrane surface decreases [7,8]. The electrophoresis increase the movement of charged particulates, and meanwhile the electro-osmosis effect can promote the velocity of

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solvent permeability across the membrane pores. Therefore, membrane pollution can be greatly declined [9]. Bovine serum albumin (BSA), shark cartilage polysaccharide, hyaluronic acid, and dextran sulfate are charged negatively in the water solution of pH 7 and can be used to examine the role of an electric field on enhancement of ultrafiltration [10–13]. However, most of these works focused on the organic membrane in the presence of an electric field and there are few reports on inorganic membrane [14–17]. And electro-ultrafiltration is suited to the separation of protein since its surface charge changes according to the solution pH. Because of this, there is a growing tendency to study on this topic, but they all study the effect of a positive electric field, while the effect of a negative electrical field has not been researched.

The purpose of this work is to determine the effect of both positive and negative electrical fields on the dynamic behaviors of ultrafiltration using a protein (BSA) in terms of electrical field strength and pH. And the influences of electric field strength, pH, and operating time on the process of the ultrafiltration of BSA ($M_w = 67{,}000$) solution in the presence of an electric field were studied. The mechanisms of electrical ultrafiltration to improve the separation performance were further analyzed.

2. Materials and methods

2.1. Materials and equipments

BSA ($M_w = 67{,}000\,g/mol$) was supplied by Shanghai Biotechnology Corporation of China. γ-alumina membranes ($M_w = 67{,}000\,g/mol$) and 4040 Mode Ultrafiltration apparatus with an DC electric field were made in Research Institute of Light Industry and Chemical Engineering, South China University of Technology, which are presented in our previous studies [18,19]. Deionized water obtained with a Milli Q system was used for all experiments. The other chemicals were of analytic reagents and supplied by Guangzhou Chemical Products Corporation.

The adjustive DC power from Guangdong Zhaoqing Apparatus Corporation was used to supply different electric strength. PC 2102 UV–vis spectrometer were purchased from Shanghai, China. And pH meter were obtained using a model 3C from Shanghai Hongyi Corporation.

2.2. Electro-ultrafiltration process

The electro-ultrafiltration was carried out in a plate filter with 100 cm^2 filter area. γ-Al_2O_3 membranes were conducted to test different electro-ultrafiltration for different electric strength, operating pressures and temperatures. When anode is fixed in upper chamber of membrane module and cathode is under ultrafiltration membrane, the direction of electric field is downward and as same as that of membrane flux. Whereas cathode is designed in the bottom chamber and anode is under the membrane, the direction of electric field is upward.

2.3. Determination of membrane flux (J)

The flux, the basic permeation property of membranes, was tested in a self-made ultrafiltration unit (effective area = 50.3 cm^2) fed with pure water at 0.2 MPa. The flux at 25°C ($kg/(m^2\,h)$) was calculated by the following equation:

$$J = \frac{V}{S \times t \times \Delta P} \tag{1}$$

where J is the flux, $L/(m^2\,h)$; V is the volume of permeation solution, L; S is the membrane area, m^2; t is the operating time, h; and ΔP is the transmembrane pressure, MPa.

2.4. Determination of membrane rejection (R)

The same unit was fed with BSA at 0.2 MPa of 30 min in order to obtain the membrane rejection. The BSA concentration of permeation solution and bulk solution were tested by a spectrophotometer. The rejection (%) was obtained by:

$$R = 1 - \frac{A_p}{A_f} \tag{2}$$

where A_p and A_f represent the BSA concentration of permeation solution and bulk solution, respectively.

2.5. Recovery rate of flux after rinse

The recovery rate of flux after rinse was calculated by the following formula:

$$\mathrm{Re} = \frac{J_0'}{J_0} \times 100\% \tag{3}$$

where Re is the recovery rate of flux after rinse; J_0 is the membrane flux before rinse; and J_0' is the membrane flux after cleaning.

3. Results and discussion

3.1. The effect of electric fields on BSA ultrafiltration process

The relation of the permeate flux to the electric field strength is presented in Fig. 1. Based on it, the variation in the average permeate flux with electric field strength were obtained and presented in Fig. 2. It can be seen that a positive electric field is efficient for the enhancement of flux and that the increase of electric field strength increases the permeate flux for the BSA (pH = 6.8). Indeed, the average permeate flux increased by 21, 66, 109, and 167% when the electric field strength was $E = 8$, 12, 16, and 20 V/cm, respectively. Moreover, when ultrafiltration was undertaken without an electric field, the permeate flux declined by 29.7% after 20 min, while in the presence of a positive electric field, the permeate flux reached a steady-state high value after approximately 20 min and no decrease was seen during 60 min. However, the negative electric field decreased the permeate flux. A decrease of about 43.2% of the permeate flux was seen with the highest negative electric field ($E = -20$ V/cm) than the current was UF ($E = 0$ V/m).

As shown in Fig. 3, the rejection of BSA solution can be increased under a positive field with an upward direction. When electric field intensity is higher than +12 V/cm, the membrane retention increases slowly. But rejection of BSA has not always been reducing under negative electric fields. It is because that isoelectric point of BSA is 4.7 and, dissociation of acidic groups is enhanced in BSA below pH 6.8, the negatively charged proteins move to cathode in the DC electric fields. The positive electric fields make BSA molecules move off the surface of membrane, reduce the thickness of membrane surface boundary layer and the surface concentration polarization. Positive electric fields can also strengthen membrane penetration and increase water flux.

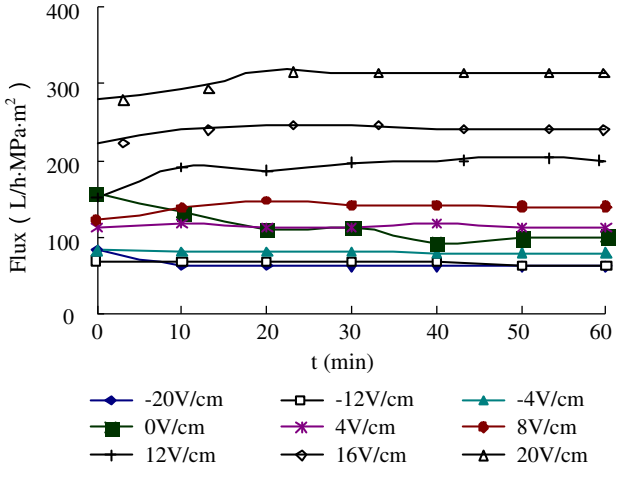

Fig. 1. The membrane flux of BSA under electric fields (0.2% BSA).

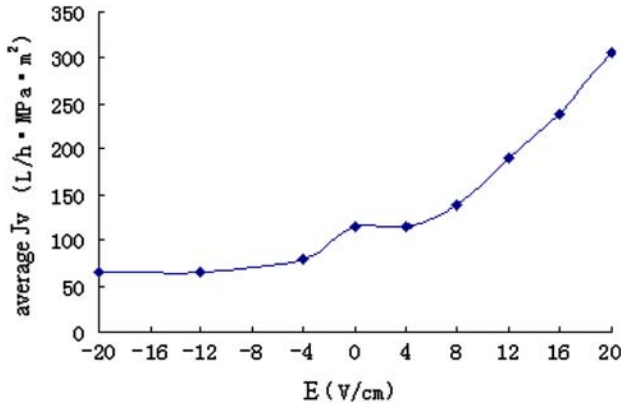

Fig. 2. Effects of electric field strength on permeate flux.

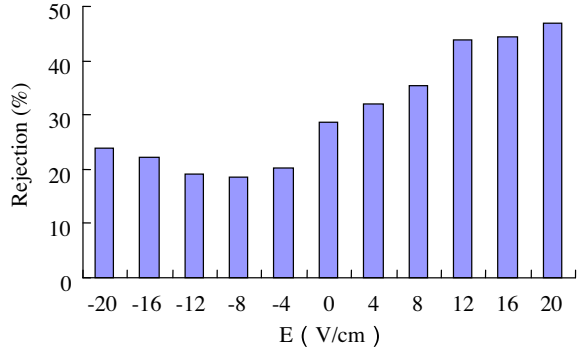

Fig. 3. The membrane rejection of BSA under electric fields (25°C, 0.2 MPa).

Negative DC electric fields can aggravate the BSA molecules to aggregate on the membrane surface and increase thickness of the boundary layer, thereby enhance the membrane surface "gel" effect and the membrane resistance. However, when the gel layer accumulated to a certain degree, the gel layer controlled membrane separation process, membrane flux cannot reduce if we improve the negative electric field strengths.

3.2. The effect of pH on BSA ultrafiltration under electric fields

Figs. 4 and 5 present the separation performance of the membranes with different condition of pH values and electric fields strength. As shown in Fig. 4, the separation of BSA at pH 3 is completely different,

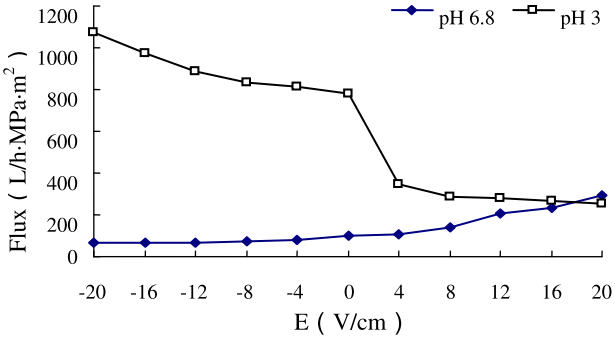

Fig. 4. The membrane flux of BSA in different pH (25℃, 0.2 MPa).

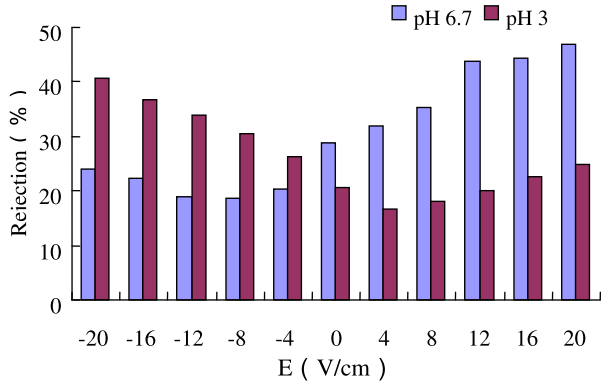

Fig. 5. The membrane rejection of BSA in different pH (25℃, 0.2 MPa).

comparing with that at pH 6.8. When electric field strength is 0, membrane flux of 781.32 L/h m^2 at pH 3 is eight times as that at pH 6.8. Negative DC current can improve membrane flux and the rejection. The flux reaches 1,074 L/h m^2 at pH 6.8 with an electric strength of −20 V/cm, which is 37.5% higher than that without an electric field. And rejection increases from 20.5 to 40.8% as shown in Fig. 5.

When the pH is less than 4.7 (BSA isoelectric point), the BSA is positively charged and the applied negative electric fields can make BSA move off the membrane surface as result of electrophoresis of BSA. The boundary layer thickness and ultrafiltration resistance are decreased. Meanwhile, electrophoresis and electro-osmosis when pH is greater than 4.7, BSA is of negative charge and an electric field has an opposite effect on ultrafiltration process.

The pH of feed solution is contributed to the BSA charges, particles shapes and forces between particles and membrane materials, which are several important factors of separation. Therefore, basis on membrane material and solution properties, we can improve the membrane flux and rejection of targeted substances by controlling pH and electric fields strength.

3.3. Flux renewing under an electric field

As shown in Fig. 6, ultrafiltration flux decreases under an electric field of −20 V/cm for 20 min and then it quickly increases under an electric field of +20 V/cm. A positive and a negative electric field were used to treat ultrafiltration of BSA solution for three times, ultrafiltration membranes flux were restored to the original value of 105.5, 98.6, and 95.6% and complete the "electric self-cleaning" effect. "Electric self-cleaning" is due to the effect of external electric field, membrane materials, and BSA concentration. An electric field can destroy the boundary layer formed by concentration polarization.

Theoretically, an electric field can always remove the charged particle deposition of membrane surface and restore flux. But in practice, the BSA particles may adsorb on internal surface of the membrane pore and cause irreversible fouling. An external electric field did not fully recover all the flux.

3.4. Resistance of mass transfer of ultrafiltration process under an electric field

Several models have been proposed [20] to explain polarization and gel layer formation. The hydraulic resistance in-series model was obtained by modifying the Karman and Kozeny equation to describe membrane processes [21–23]. According to the Darcy's law [24], the resistance of mass transfer (J_v) was defined as follow:

$$J_v = \frac{\Delta P}{\mu[R_m + R_{b1} + R_f]} = \frac{\Delta P}{\mu \cdot R_t} \quad (4)$$

where ΔP is the pressure, MPa; μ is the solution viscosity; R_m is the membrane resistance; R_{b1} is the

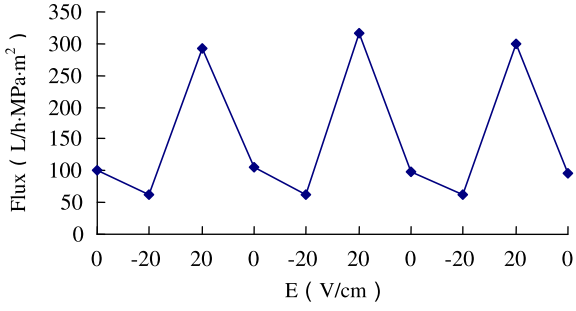

Fig. 6. The recoveries of membrane flux of BSA in electric field.

boundary layer resistance; R_f is the membrane fouling resistance; and R_t is the total resistance.

The steps of membrane resistance coefficient methods were used as follows:

(1) When detecting the incipient pure water flux of the membrane, $R_{b1} = R_f = 0$, according to Darcy's law

$$J_0 = \frac{\Delta P}{\mu R_m} \tag{5}$$

(2) When the membrane was polluted:

$$J_1 = \frac{\Delta P}{\mu[R_m + R_{b1} + R_f]} \tag{6}$$

(3) When detecting the incipient pure water flux of the membrane again after cleaning the polluted membrane:

$$J_2 = \frac{\Delta P}{\mu[R_m + R_f]} \tag{7}$$

Ultrafiltration experiments were conducted using BSA (pH 6.8) under different electric field strengths at a pressure of 0.2 MPa and 25°C. The initial membrane water flux $J_{0,}$ the membrane flux after running pollution J_1, and the membrane water flux after cleaning J_2 were measured and presented in Table 1, the values of R_m, R_{b1}, and R_f were calculated according to equations mentioned above and the results were reported in Table 2. It can be seen that the positive electric field (+20 V/cm) can decrease R_{b1}, R_f, and R_t to 69.2, 80.5, and 60.8%, comparing to those without electric fields. It showed that an electric field can decrease concentration polarization and membrane fouling on the membrane surface, which is contribute to the improvement of separation efficiency. While under a negative electric field, the negative particles would deposit to the membrane surface, which cause the increases of R_{b1} and R_f and the decline of separation efficiency.

Table 1
Decrease and recovery coefficient of flux under electric fields

E (V/cm)	J_0 (mL/(cm^2 h))	J_1 (mL/(cm^2 h))	J_2 (mL/(cm^2 h))	Re (%)
+20	71	28	57	79.7
0	71	11	31	43.5
−20	71	7	24	33.3

Table 2
Transport resistance of ultrafiltration of BSA under electric field

E (V/cm)	R_m (MPa h/cm)	R_{b1} (MPa h/cm)	R_f (MPa h/cm)	R_t (MPa h/cm)
+20	2.25×10^6	2.94×10^6	0.57×10^6	5.76×10^6
0	2.25×10^6	9.53×10^6	2.92×10^6	1.47×10^7
−20	2.25×10^6	1.54×10^7	4.50×10^6	2.21×10^7

4. Conclusions

(1) A positive electric field can enhance ultrafiltration of BSA (pH = 6.8) with Al_2O_3 membrane. With the increase of electric field, flux, and the retention rate can increase. Effects of a negative electric field on ultrafiltration of BSA (pH = 6.8) are opposite.
(2) The pH value of solution has great impact on the ultrafiltration of BSA. The flux is 781.32 L/h MPa m^2 at pH 3, as 7.8 times as that under neutral environment. Negative electric field can improve membrane flux and the rejection at pH 3 and flux increased 37.5%, rejection increases from 20.5 to 40.8% under an electric field of −20 V/cm.
(3) Using an external electric field, fouling Al_2O_3 membrane can restore the original membrane flux of more than 95% in a short time. After repeated treatment of an electric field, ideal flux recovery is obtained and it showed that an electric field is a simple and effective "self-cleaning" technology.

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