Effect of Filtration Type on BSAFouling with PVBHollow Fiber Membrane

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***Abstract*—Hydrophilic poly (vinyl butyral) (PVB) hollow fiber membranes prepared via thermally induced phase separation(TIPS) were used for the filtration of bovine serum albumin (BSA)suspension, and the effect of filtration type on the BSA fouling of the membrane was studied. The results show that compared inside-out filtration with outside-in filtration, therelative fluxof the former is a little smaller than that of the latter for the same concentration of BSA suspension. Therelative flux is the smallest at isoelectric point (IEP), and the greater relative flux is obtainedat higherpH.The SEM results show that the inner surface and the pore channels of the inside-outfiltration membraneare accumulated withBSA particles for 30 min of filtration, while little aggregated BSA particles are shown on the outer surface of the outside-in filtration membrane.**

Keywords-membrane fouling;ultrafiltrationtypes;poly (vinylbutyral) hollow fiber membrane;bovine serum albumin

I. INTRODUCTION

Membrane filtration is increasingly used in the separation and purification of protein-containing suspensions, such as receive therapeutic products from mammalian, recover extracellular proteins produced via fermentation [1].One of the critical issues in the filtration is the flux declination caused by membrane fouling, which is usually induced by pore blocking or plugging inside the membrane pores and cake layer formation on the membrane surface due to the protein adsorption, aggregation and deposition [2 , 3]. It is commonly considered that thehydrophilicity, morphologies and charge of membrane surface have great relationship with membrane fouling [4,5].S. Boributh et al. [6] proved that the membranes modified with hydrophilic material exhibited good anti-fouling properties.

As poly (vinyl butyral)(PVB)can endure the low temperature, bacteria, microorganism, alkali and diluent acid,and some hydrophilicity,it seems to be an attractive material for preparing the membrane [7 , 8]. The hydrophilic PVB hollow fiber membranes were prepared via thermally induced phase separation [7], and the BSA fouling behavior of PVB hollow fiber membranes were investigated for the first time by different operation types.

II. EXPERIMENTAL

A. Materials

PVB hollow fiber membranes were preparedvia thermally induced phase separation (TIPS) [7], the molecular weight cut off (MWCO) of dextran was 20kDa, the inner diameter and outside diameter were 0.868mm and 1.170 mm, respectively. Two membrane moduleswere assembled by30 hollow fiberswith the effective length of 28.0 cm, one for inside-out ultrafiltration (UF) and another for outside-in.BSAwith a molecular weight of 67kDa was purchased from Sinopharm Chemical Reagent Co., Ltd (China).0.1M of NaOH and HClsolution were used to regulate the pH of BSA suspension.

B. Filtration experiment

Cross-flow filtration was used forbothinside-out and outside-in filtration. The BSA suspensionwas stirred for 1 h by a magnetic stirrer (DF-101S) and the feed temperature waskept at 25^{o}C, and then pumped into themembrane module by a peristaltic pump (YZ1515).The flow rateof the BSA suspension was adjusted by the inlet and outlet valves, and the mean flow velocity through the membrane was about 0.26 m/s.The mass of the filtrate was weighted by anelectronic balance (PB203-E) and the BSA concentration was determined by Coomassie brilliant blue method [9]. The pH value of BSA suspension was measured by pH meter (PHS-3C).

C. Cleaning of the fouled membrane

After the experiment, the membrane was cleaned withreverse osmosis (RO) water for 15min, and then was cleaned with 0.1M NaOHand 0.1M NaOClsolution for 30 min, respectively, the initial flux could be restored by the above effective chemical cleaning.

D. SEM observation

The virgin and fouled PVB hollow fiber membranes werefractured in liquid nitrogen and sprayed with Au. The cross-sections, inner and outer surfaces of hollow fiber membranes were observed using a scanning electron microscope (SEM) (FEI Quanta-200) with an accelerating voltage of 20 kV.

III. RESULTS AND DISCUSSION

A. Effect of transmembranepressure on permeate flux

Effect of transmembrane pressure (TMP) on permeate flux at pH 7.36 is shown in Figure1, where J is the mean permeate fluxfrom 10 to 12 min.The permeate flux of inside-out UF increased linearly with TMP in the range of 20kPa to 100kPa, as shown in Figure 1(a).However, the permeate flux of outside-in UF increased linearly with TMP only in the range of 20kPa to 70kPa, and then increasedslowly with the increase of TMP, as shown in Figure1(b).The pure waterfluxwas much greater than that of the BSA suspension and the slope decreasedas the BSA concentration increased. This means that the membrane is more easily fouled with the increase of BSA concentration. The flux of outside-inUFis much smaller than that of inside-out, because the dense skin is the outer surface, the surface may shrink and the size of micro-pores on the outer surface may decrease duo to the pressure, furthermore, the flux of the outside-inUF is calculated on the basis of outer surface of the fibers, and that of the inside-outUF is on the basis of inner surface, the area of the latter is much smaller than the former.Both the rejections of outside-in UF and inside-out UF are over 96%.

B. The flux declination at various BSA concentrations

Figure2 shows the declination of permeate flux at various BSAconcentrations at TMP100kPa, pH7.36,where $J_0$is the pure water flux. The relative fluxes (J/J_0)for the filtration of BSA suspensiondeclined quicklyat the beginning of filtration for the first 5 min and gradually approached pseudo-steady values after 10 min. This indicates that the fouling occurs in the early filtration period, and the aggregate of BSA may occuron the membrane surface [10].

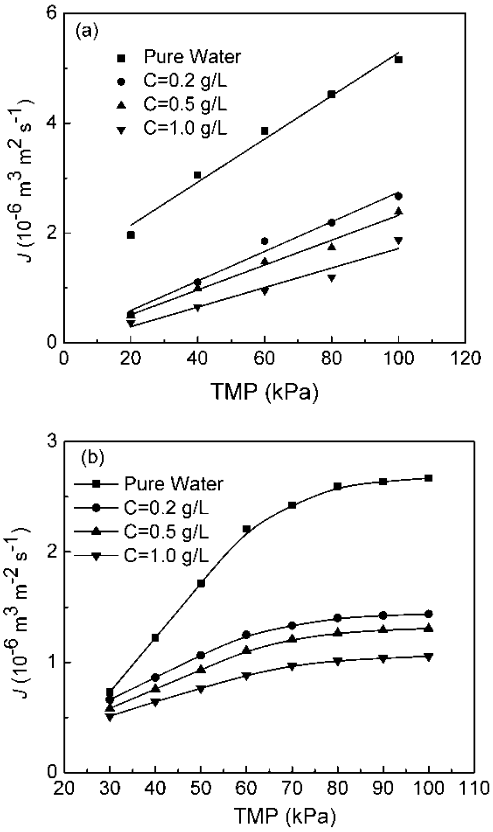


Figure 1. Effect of TMP on permeateflux at different BSA concentrations. (a) Inside-out. (b) Outside-in.

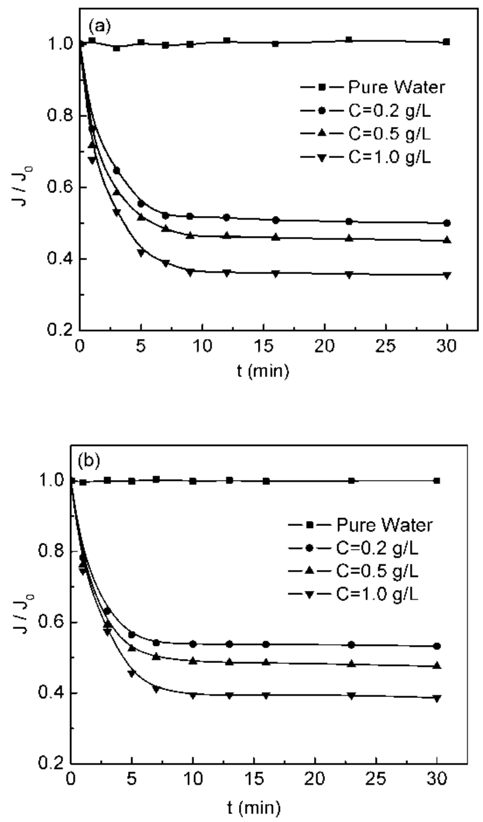


Figure 2. The permeate flux declination at various BSA concentrations. (a) Inside-out. (b) Outside-in.

Compared inside-out UF with outside-in, therelative flux declination of inside-out UF was greater than that of outside-in. Because the outer surface is the dense skin, and the inner surface is porous, and the latter is easily suffered with BSA foulant forthe rough surface can supply moresites to contact with BSA.

C. The flux declination at various pH

Figure 3 shows the permeate flux declination for the ultrafiltration of 0.2 g/L concentration of BSA suspension at TMP 100kPa. The flux at pH 9.72 was much greater than that at pH 4.70 both for outside-in UF and inside-out UF. Because the performance of protein molecular can be changed with pH for its acidand alkali duality,protein is positive while the pH is lower than its isoelectric point (IEP) and negative as pH is higher than IEP. The IEP of BSA is about 4.7, at which the solubilityof BSA is minimum and the protein becomes more easily aggregated due to lack of repulsion. At higher pH,both

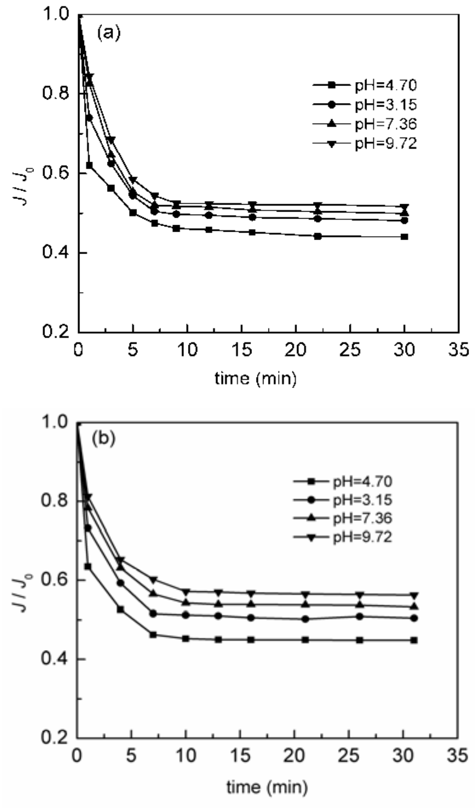


Figure 3. The flux declination with pH. (a)Inside-out.(b) Outside-in.

BSA and PVB membranes are negatively charged[11], the electrostatic repulsion may take effective action on keeping BSA from themembrane surface. In addition, higher pH can suppressor hinder the aggregationof protein molecules due to the repulsion between protein molecules [12].Similarly, therelative flux (J/J_0) for outside-in UF was a little greater than that of inside-out for the same concentration of BSA suspension at the same pH.

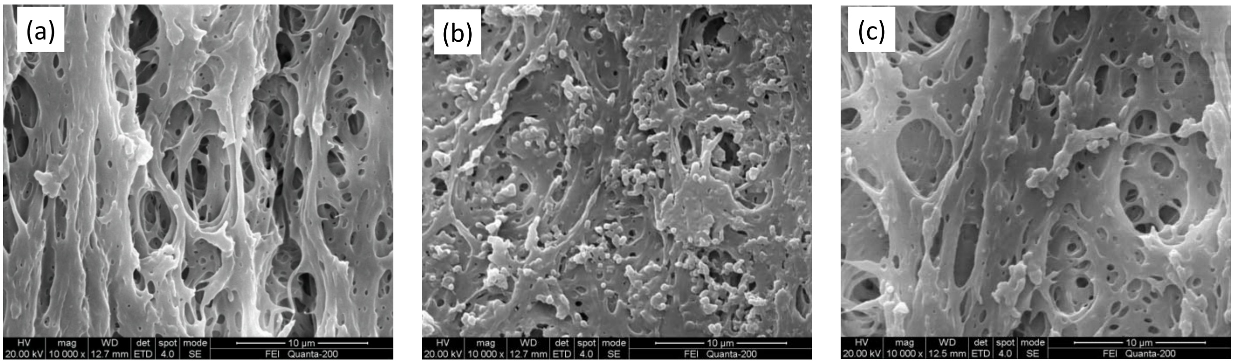
D. SEM analysis

The SEM morphologies of virgin and fouled PVB hollow fiber membranes are shown in Figures 4(a)-(f).The fouled membranes were used by 30 min UF of 0.2 g/L BSA suspension at pH 7.36. Figures4(a)-(c) were the images of inner-surfaces of virgin, the inside-out fouled membrane and outside-in fouled membrane, respectively. Figures 4(d)-(f) were the corresponding images of the outer-surfaces, respectively. Compared with the virgin membrane, the aggregated BSA particles wereoccurred on the inner surface for the inside-out UF membrane, as shown in Figures 4(b). This phenomenon confirmed that the BSA fouling was induced by the physical deposition of protein or protein aggregates within the membrane matrix. However, there were less aggregated BSA particles on the surface of outside-in UF membrane.

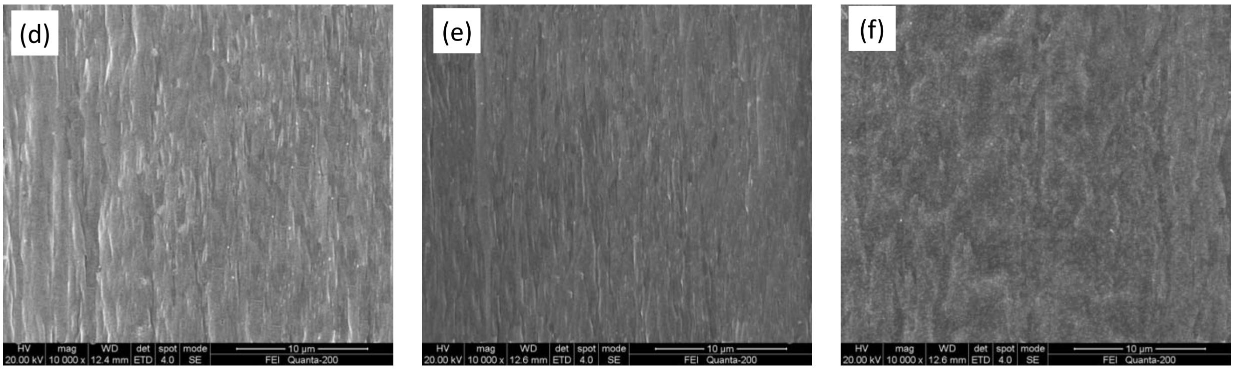
This difference between inside-out and outside-in UF is mainly due to the asymmetric structure of PVB membranes. The innersurface is porous while the outer surface is dense skin without detectable pores, and the porous structure can give sites for the aggregation of BSA molecules, causing the blockage of the pore channels. For the outside-in UF, as the outer surface is dense skin and the BSA particles from the bulk suspension is not so easy accumulate at cross-flow filtration.

IV. CONCLUSIONS

The effect of filtration type on BSA fouling has been studied using hydrophilic poly (vinyl butyral) (PVB) hollow fiber membranes with asymmetric structure as dense outer surface and porous inner surface.The permeate flux increases linearly with the increase of transmembrane pressure (TMP) in a certain range of TMP, the permeate fluxesof BSA suspension decline quicklyat the beginning of filtration for the first 5 min and gradually approach pseudo-steady values after 10 min. Compared inside-out filtration with outside-in, therelative fluxfor outside-in ultrafiltration (UF) is a little greater than that of inside-out for the same concentration of BSA at the same pH, and the inside-out UF membrane is more easily suffered with BSA fouling than that of outside-in. The fouling decreases with the increase of pH due to increase of repulsion of between protein molecules and the membrane. The SEM results show that the inner surface of the inside-out filtration membrane is accumulated with BSA particles while little BSA particles are shown on the outer surface of the outside-in filtration membrane.



Virgin Inside-out Outside-in



Virgin Inside-out Outside-in

Figure 4. SEM Images of PVB hollow fiber membranes. (a-c) inner-surface, (d-f) outer-surface

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