

## Recovery of PVA Using Polyethersulfone (PES) Hollow Fiber Ultrafiltration Membranes: Part II: Effect of Carboxymethyl Cellulose (CMC) Concentration

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### Abstract

Polyethersulfone (PES) hollow fiber ultrafiltration (UF) membrane with the molecular weight cut-off (MWCO) 20,000 was used for the recovery of polyvinyl alcohol (PVA) from the simulated wastewater. An attempt to study the effect of carboxymethyl cellulose as synthetic warp sizing agents on the PVA recovery was investigated in this case. Experimental results shown that PVA concentration in the retentate of PES hollow fiber membrane were lower with addition of carboxymethyl cellulose (CMC) in PVA solution. Besides, higher trans-membrane pressure from 1.0 to 2.1 bars, solution temperature 50-75 °C, and feed velocity 0.16-0.32 m/s, improved the PVA recovery in two different PVA solutions. PES hollow fiber ultrafiltration process was efficient for PVA recovery from the simulated wastewater using PVA solution with low carboxymethyl cellulose (CMC) concentration as synthetic warp sizing agents.

**Keywords:** Ultrafiltration membrane; hollow fiber; phase inversion method; polyethersulfone; alcohol additive.

### استرجاع الـ PVA باستخدام اغشية PES المجوفة نوع UF الجزء الثاني: تأثير مادة كاريوكسي مثيل سليولوز CMC

#### الخلاصة

اغشية بوليمرية مجوفة تم تحضيرها من مادة البولي ايثر سلفون (PES) (Ultra filtration) تمتلك (MWCO) (Molecular weight cut-off) بمقدار (20000MW) استخدمت لغرض استرجاع مادة البولي فينيل الكحول (PVA) من مخلفات المياه تم دراسة تأثير مادة كاريوكسيل مثيل سليولوز (CMC) كعامل غروي للخيوط المصنعة على استرجاع مادة البولي فينيل الكحول (PVA). النتائج العملية اظهرت بأن تركيز الـ (PVA) في الراجع المرفوض من قبل الاغشية المجوفة (PES) كان اقل مع اضافة مادة (CMC) الى محلول (PVA) بالاضافة الى ذلك ارتفاع الضغط من (1-2.1bar) ودرجة حرارة المحلول (50-75 C°) وسرعة المحلول الداخل (0.16-0.32 m/sec) يحسن من استرجاع (PVA) من المحلولين المختلفين لمادة (PVA) اغشية (PES) المجوفة كانت فعالة في استرجاع مادة (PVA) من مخلفات المياه التي تحتوي على تركيز واطئ من مادة (CMC).

### 1. Introduction

Ultrafiltration (UF) is currently used in very wide range of applications in the food processing, pharmaceutical, biomedical,

biotechnological, pulp and paper, and chemical industries. Membrane processes are also used extensively in the treatment of a variety of wastewater and effluent streams, both

industrial and municipal. Ultrafiltration (UF) separation method has been employed for recovering metals from waste effluents [1-9] and organic pollutants from aqueous solution [10-11]. Bodzek *et al.* [12] succeeded in recovering mineral oil by ultrafiltration (UF). Treatment of the oil/water emulsion systems using ultrafiltration (UF) was done by many workers [13-17].

For example, Pastof *et al.* [8] reported that ultrafiltration enhanced by the addition of polymers soluble in water. It is a technique for the recuperation of heavy metals in wastewater streams. An analysis is made of the influence of the molecular weight (inferior and superior to the molecular weight of the polymer) cut-off of the membrane and the quantity of the polymer on the permeate flux and the recovery of mercury. Their results show that with a membrane with a cut-off inferior to that of the combination metal polymer, the polymer concentration has no influence on the permeate flux, whereas for the membrane with a superior cut-off, there appears restrictions to the passing of water in accordance with the hydrodynamic model, and there is decreased efficiency in the recuperation of metal. The removal of single metal ions including  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cr}^{3+}$  from aqueous solutions (up to 200 mg/l) by ultrafiltration (UF) with the help of an anionic surfactant sodium dodecyl sulfate (SDS) was investigated by Juang *et al.* [9]. Their experiments were performed as a function of the membrane MWCO (1000–8000), material (polyamide, polyethersulfone), solution pH (2–12), and molar concentration ratio of the surfactant to metals (the S/M ratio, 0.5–27). There results show that

complete removal of metal ions, except for monovalent  $\text{Cs}^+$ , could be achieved as long as the SDS micelles were formed. They examined effects of added electrolyte NaCl and the transmembrane pressure (TMP) on metal rejection. The potential of this UF process for the separation of binary metals involving  $\text{Sr}^{2+}$  or  $\text{Cr}^{3+}$  was particularly demonstrated using a low-MWCO membrane (1000) and at a relatively low S/M ratio (<5–10). Finally they studied the recovery and reuse of surfactant from the retentate.

The textile industry uses synthetic warp sizing agents such as polyvinyl alcohol (PVA), polyacrylate and carboxymethyl cellulose (CMC) in cotton blends, in place of starch and natural gums. After weaving, the size agents must be washed out, which requires large volumes of wash water. These sizing agents are, however, expensive and nonbiodegradable; thus, they pose challenging waste treatment and/or recovery problems [18]. Lin and Lan [19,20] investigated recovery of polyvinyl alcohol (PVA) by ultrafiltration (UF) from simulated desizing wastewater. Batch experiments using an UF cell were conducted to investigate the effects of operating pressure, temperature and mixer speed on the PVA retention, filtration rate and the rejection coefficient. In addition, observed that an operating pressure over 2 bars is sufficient for efficient operation of the PVA recovery process, and operating temperature lower than 80°C was significantly reduce the efficiency of PVA recovery. Similar effect was also found for the mixer operating at speed below 500 rpm. Besides, their batch experiments conducted to examine the performance characteristics of the UF membranes of the hydrophilic and hydrophobic types and of different pore sizes. Performances of those

membranes using several characteristic parameters of the ultrafiltration process were compared. It was indicated that the ultrafiltration performances of different membranes are not be easily judged by a single characteristic parameter alone. In the context of overall performances, it was found that the hydrophilic membranes to be superior to the hydrophobic types and the UF membrane of a lower molecular weight cut-off (MWCO) is definitely a better choice than that of a higher MWCO. In addition, they considered the reduction of the pollution strength of permeate in terms of chemical oxygen demand (COD).

Porter [21] reported the recovery polyvinyl alcohol from the textile process waste streams. Three filtration systems that are able to operate at 100°C or above were described. Two systems are tubular. One uses carbon tubes to support a zirconium oxide membrane and the other uses stainless steel tubes coated with a fused titanium dioxide layer to support a zirconium hydroxide membrane. The third system described is an asymmetric polyvinyl sulfone membrane in a spiral wound configuration. He described also the economics of the recovery process in addition to presented is the application of automated control to the PVA recovery process and to the recycle of bleaching rinse water to the scouring process. In this study, recovery of the polyvinyl alcohol (PVA) from the simulated desizing wastewater by polyethersulfone (PES) hollow fiber ultrafiltration (UF) membrane is investigated experimentally. In addition to, an attempt was done to study the effect carboxymethyl cellulose as additive on the PAV recovery.

## 2. Experimental Recovery of polyvinyl alcohol (PVA) from simulated desizing wastewater

The experimental system used for UF experiments to recover polyvinyl alcohol (PVA) from simulated desizing wastewater is shown in Figure 1. The system consists of a hollow fiber membrane module with length of 20 cm and has four polyethersulfone (PES) hollow fiber membranes. The PES hollow fiber membranes had an effective surface area of 30 cm<sup>2</sup> and a molecular weight cut-off (MWCO) of 20,000 and are able to use up to 125°C. An outside heating jacket used to keep the PVA solution temperature constant and in order to keep the temperature of the PVA solution in the membrane module constant. The initial PVA solution concentration was 2,000 mg/l, and carboxymethyl cellulose concentration was 200 mg/l and the ultrafiltration process started after heating 250 ml of the PVA solution to 75°C. The PVA concentration in permeate and retentate was measured by a UV-spectrophotometer (Shimadzu-UV 360, Japan) at wavelength of 670 nm.

## 3. Results and Discussion

Separation performance is an important parameter in the membrane separation processes and affected by many factors such as trans-membrane pressure, solution temperature and the flow rate and the concentration of the feed solution. Effects of these factors on PVA recovery from the simulated wastewater are investigated. Figure 2 shows the effect of two different trans-membrane pressures on the PVA concentration in the retentate at 75°C and 0.32 m/s feed velocity without addition carboxymethyl cellulose (CMC) as synthetic warp sizing agents in the PVA solution. Figure 2, shows that PVA concentration in the

retentate increases with an increase of the trans-membrane pressure from 1.0 to 2.1 bars. This is due to the distribution of the surface pores size of PES hollow fiber membranes which causes concentration polarization on UF membrane surface. Using carboxymethyl cellulose as synthetic warp sizing agents in the PVA solution, the PVA concentration in the retentate is decreased with two different trans-membrane pressure from 1.0 to 2.1 bars compare with PVA solution without carboxymethyl cellulose (CMC) with the same trend, Figure (3).

The desizing operation is carried out at 70-85°C because of the PVA solution viscosity. The simulated hot desizing wastewater has a temperature of 75°C in this case. Figure 4 and Figure 5 show the effect of the solution temperature on the PVA concentration in the retentate at 1.0 bar pressure and 0.32m/s feed velocity for two different PAV solutions. Figure 4 shows that increasing the solution temperature from 50 to 75°C, the PVA concentration in the retentate increases because of the reduction of the retentate viscosity at high temperatures. The PVA concentration in the retentate was improved using PVA solution without addition of carboxymethyl cellulose (CMC) by the comparison with that used carboxymethyl cellulose (CMC) in Figure 5. It illustrates that UF efficiency increases with a decrease of the solution viscosity and PVA solution without carboxymethyl cellulose (CMC). Figure 6 shows the effect of feed velocity (0.16 and 0.32 m/s) on the PVA concentration in the retentate at operating temperature 75°C and 1.0 bar pressure for PVA solution without carboxymethyl cellulose (CMC). There is an effect of the feed velocity

on the PVA concentration, this fact is that because pumping the solution on the membrane surface sweeps away the accumulated solute (PVA), it results in reducing the hydraulic resistance of the cake and the thickness of the boundary layer. In any case, increasing feed velocity is one of the effective methods to control the effects of concentration polarization. In Figure 7, the effect of feed velocity on the PVA concentration is shown. It can be note that the feed velocity on the PVA recovery decreased with addition of carboxymethyl cellulose (CMC) to the PVA solution.

#### 4. Conclusions

PES hollow fiber ultrafiltration (UF) membrane with 20,000 MWCO was used in this case in order to recover polyvinyl alcohol (PVA) from the simulated desizing wastewater. The investigation was conducted to evaluate effects of process parameters, such as trans-membrane pressure, solution temperature and feed velocity on UF performance using PVA solution with and without addition of carboxymethyl cellulose (CMC) as synthetic warp sizing agents. Experimental results shown that PVA concentration in the retentate, of PES hollow fiber membrane were lower with addition of carboxymethyl cellulose (CMC) in PVA solution. Besides, higher trans-membrane pressure from 1.0 to 2.1 bar, solution temperature 50-75°C, and feed velocity 0.16-0.32 m/s, improved the PVA recovery in two different PVA solutions. PES hollowfiber ultrafiltration process was efficient for PVA recovery from the simulated wastewater using PVA solution with low carboxymethyl cellulose (CMC) concentration as synthetic warp sizing agents.

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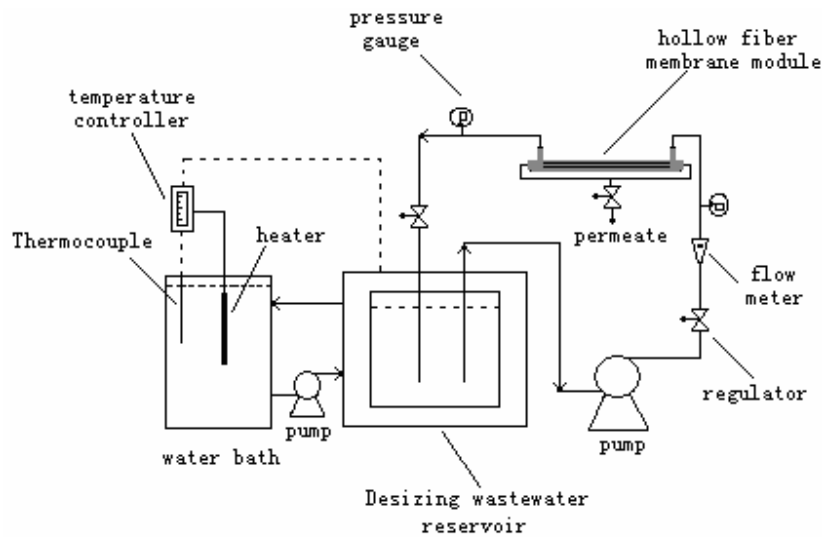
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**Figure (1) Schematic diagram of the experimental system used for hollow fiber ultrafiltration experiments**

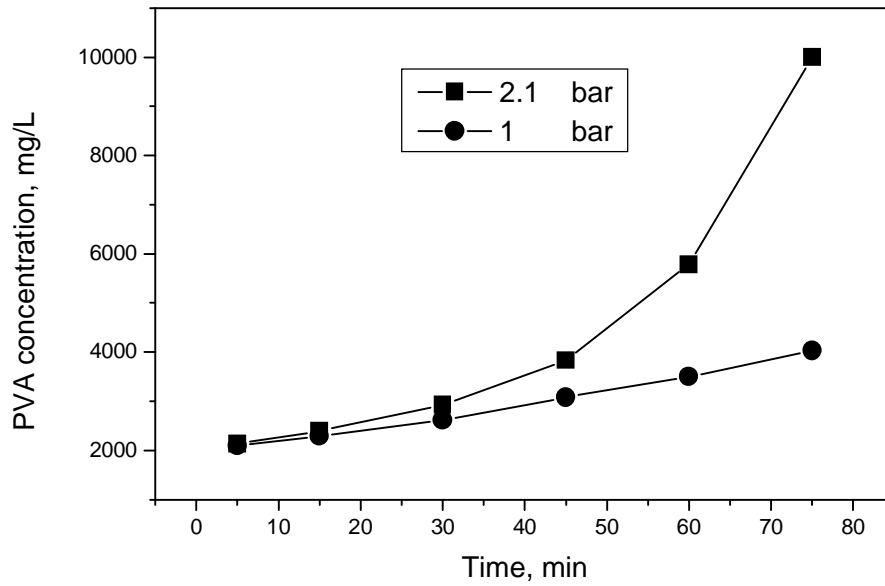


Figure (2) Effect of trans-membrane pressure on the PVA concentration using (PVA: Water) as desizing solution

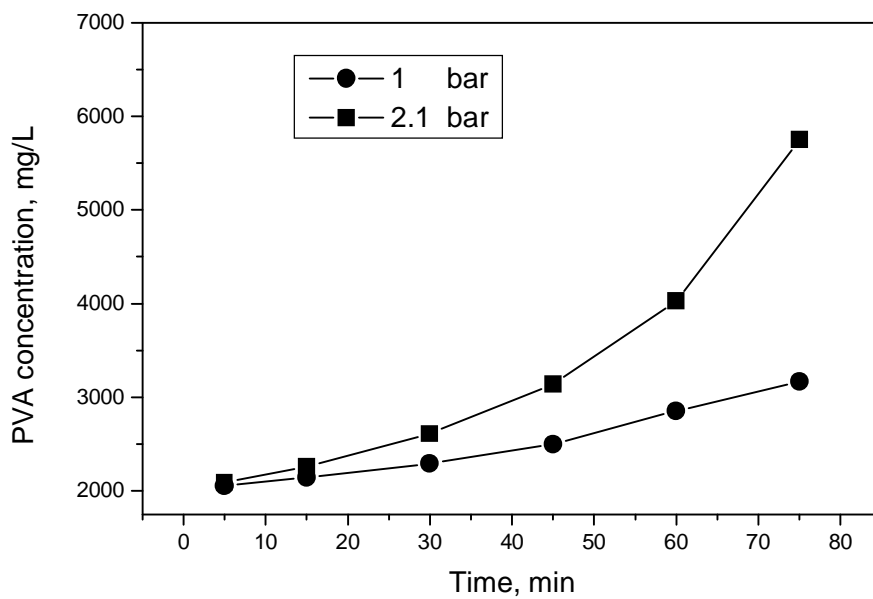


Figure (3) Effect of trans-membrane pressure on the PVA concentration using (PVA: CMC: Water) as desizing solution

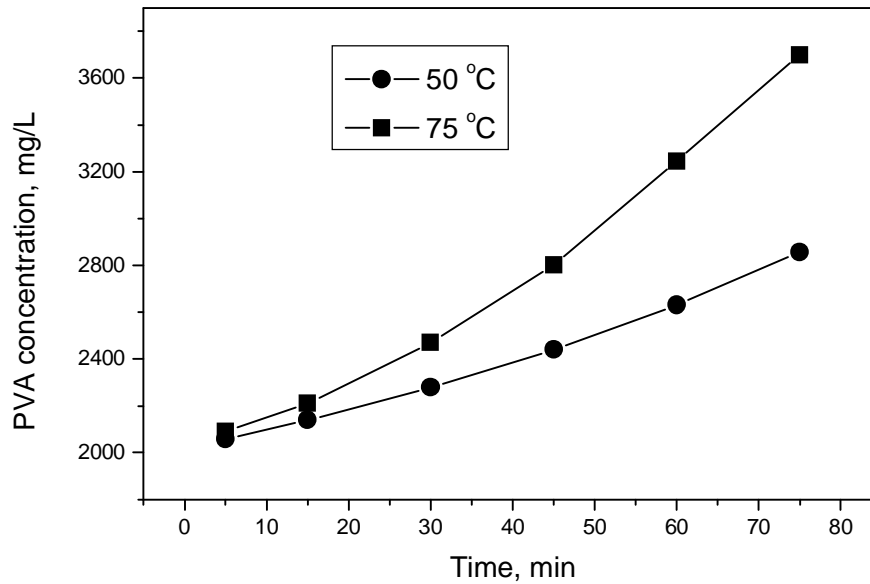


Figure (4) Effect of operating temperature on the PVA concentration using (PVA: Water) as desizing solution

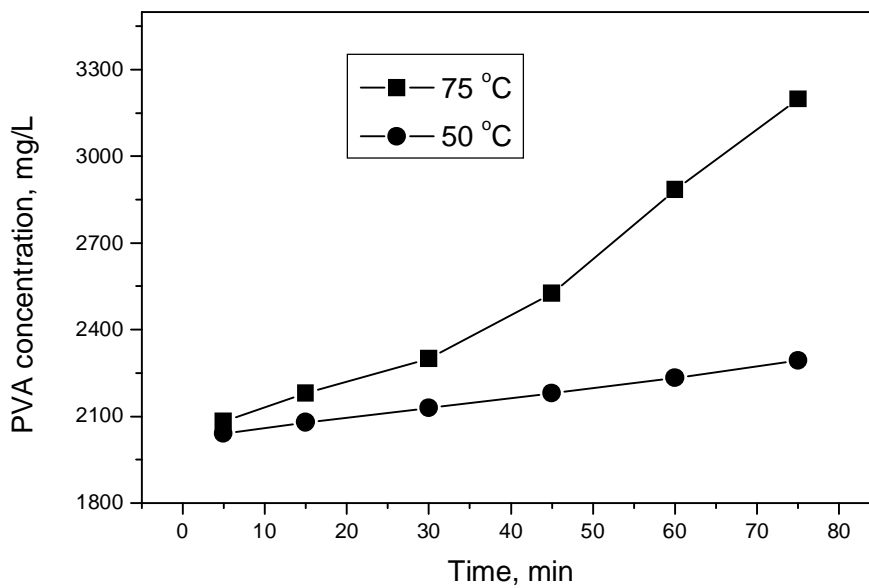


Figure (5) Effect of operating temperature on the PVA concentration using (PVA: CMC: Water) as desizing solution



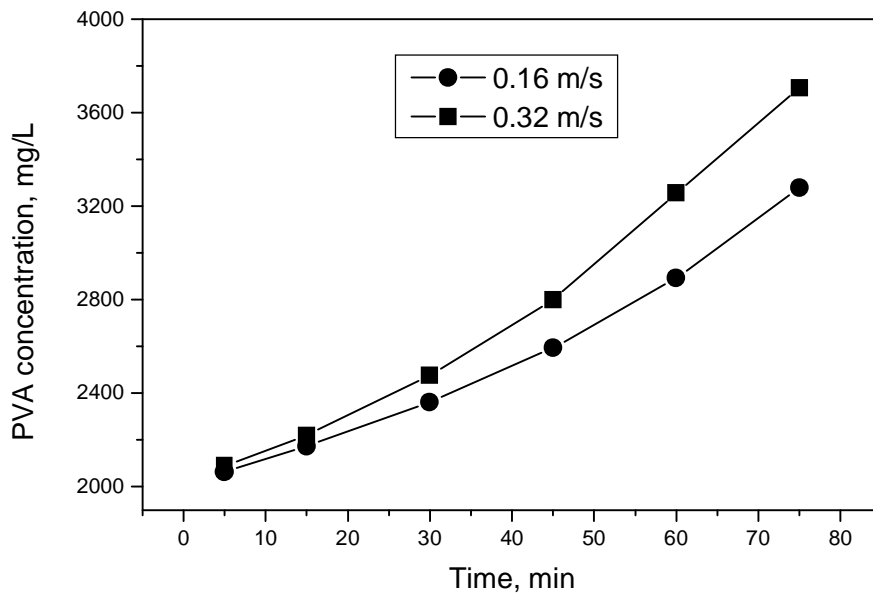


Figure (6) Effect of feed flow rate on the PVA concentration using (PVA: Water) as desizing solution

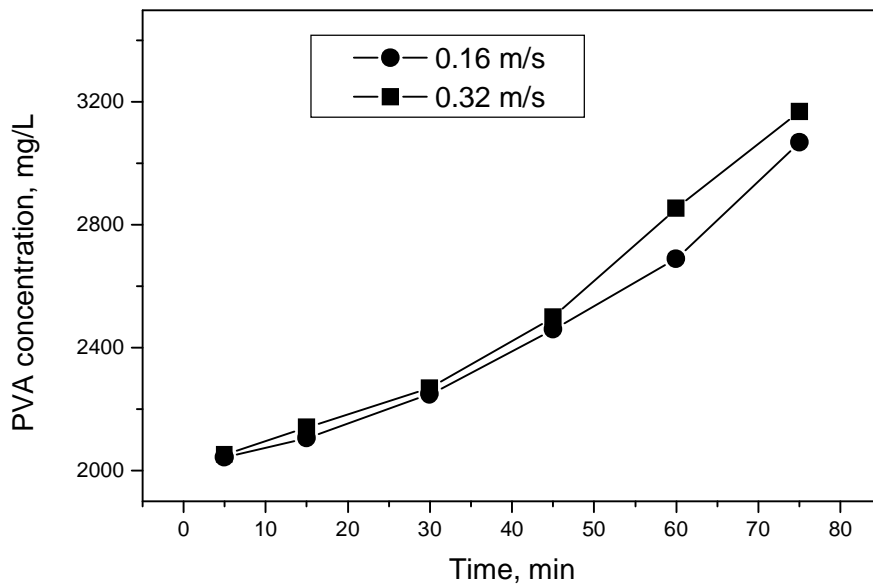


Figure (7) Effect of feed flow rate on the PVA concentration using (PVA: CMC: Water) as desizing solution