

## Sizing Agents Recovery By Ultrafiltration: Effects of Operating Conditions

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### ABSTRACT

The recycling of polyvinyl alcohol, polyacrylate and carboxymethylstarch based sizing agents by ultrafiltration, and the parameters influencing the process were investigated in this study. The performance of the ultrafiltration process has been comparatively investigated at four different temperatures, 20°C, 30°C, 60°C and 90°C, and six different time periods, 0 to 240 minutes with 40 minutes intervals. The effect of a lubricant has also been investigated. Results indicate a considerable increase in concentrate concentration with prolonged operating times and elevated temperatures. The use of lubricant did not have a considerable effect on UF recovery efficiency, however, it passed to the permeate at elevated temperatures resulting in decrease in the COD charge reduction.

**Key Words:** Recycling, membranes, wax, sizing agents, ultrafiltration.

**Abbreviations:** COD:chemical oxygen demand, CMS: carboxymethylstarch, PVA: polyvinyl alcohol, PAA: polyacrylate, UF: ultrafiltration.

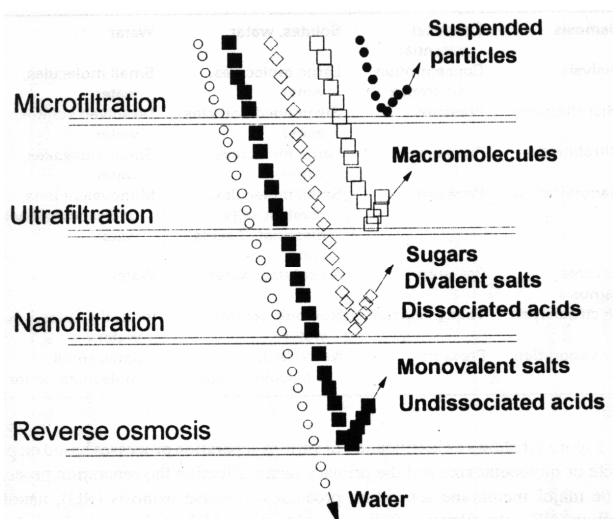
### INTRODUCTION

#### Membrane Filtration

Membranes are made of several materials in several configurations and they can be thought as a kind of filter under certain pressure. The most important duty of a membrane is to act as a selective barrier (Cheryan 1998).

Membrane filters are usually used to separate the compounds of dimensions smaller than 10 micrometer from the liquor. The flow on the membrane surface is in two directions; parallel to the membrane axis and in a radial direction (cross-flow). Particles having greater dimensions than the membrane pores are held-back on the surface of the membrane and carried out by the parallel flow and collected as concentrate. Particles having smaller molecular sizes than the membrane pores pass through the membrane with the cross-flow and collected as permeate. Consequently, the molecules in the liquor are separated physically according to their molecular dimensions (Dickenson 1997; Scott 1998).

The most popular membrane processes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) which separate the compounds in the liquor according to molecular dimensions under hydrostatic pressure. Figure 1 illustrates the separating action according to the pore size.



**Figure 1.** The separation of the membranes according to their pore dimensions (Cheryan 1998)

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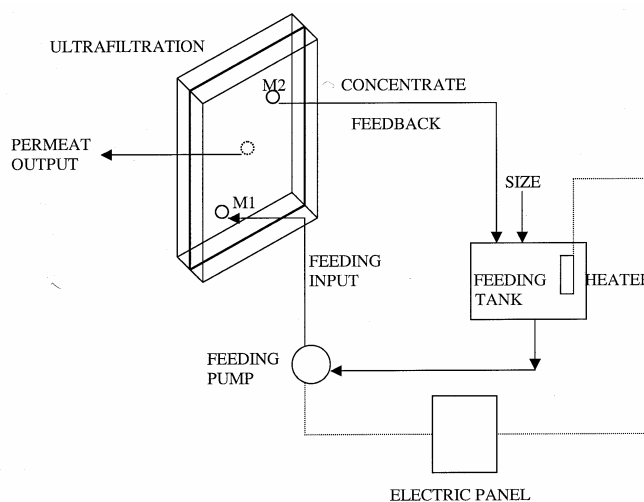


Figure 2. UF apparatus

### Ultrafiltration Process

The pore dimensions of the ultrafiltration membrane is 0,001-0,02 micrometers and separates the molecules having 300-300 000 g mol<sup>-1</sup> molecular weights. It removes colloidal materials, proteins, viruses and macromolecules. Operating pressures ranges from 1 to 7 bar (Chermisnoff 1995).

Ultrafiltration membranes are designed for parallel flow mode. Such systems have the advantage of long life, since they can be cleaned and renewed (Scott 1998).

Membranes are made of several materials like polysulphone, polyethersulphone, polyamide, cellulose acetate, ceramics and aluminum oxides. Ultrafiltration membranes are generally polymeric membranes but there are also inorganic and ceramic membranes (Wang and Cheryan 1995)

### Size Recovery by Ultrafiltration

The ultrafiltration process for the recycling of sizing agents, which enables to make significant reductions in wastewater pollution, has been in use in German textile mills since 1987. This method has met a general acceptance among other size recycling methods because of its high efficiency (Trauter 1990). The washing liquor is pumped under pressure through diaphragms in the UF method. The far smaller molecules of the washing water pass through the diaphragms, while the macromolecules of the size are held back in the process. Thus, the separation of the size substance and water occurs. After the ultrafiltration, the recovered sizing agent can be reused for sizing. The washing water is returned to the washing process, thus forming a closed recycling cycle that enables the textile mill to eliminate most of the sizing agent out of the wastewater. The basic prerequisite for every recycling operation is based on the type of sizing agent: the sizing agent should not exhibit any uncoverable change in its structure during the desizing process. All starch sizes which are degraded enzymatically or after an acid/alkaline hydrolysis are basically unsuitable for recycling and they can not be reused even if they are recovered (Tarakcioglu 1986; Duran and Ekmekçi 1995). In addition, surfactant and alkali addition is a general practice in desizing process to increase the efficiency of the process. Nevertheless, such substances should not be presented in the sizing agent. Therefore, the desizing process has to be carried out without the use of these substances if the size will be recovered. Size recovery and reuse can only be possible with the sizing agents that can be desized without any viscosity loss from the woven fabric (Duran and Ekmekçi 1995). The sizing agents should be largely resistant to the mechanical and thermal stresses of the recovery process. Heat stability deserves particular attention for recycling of sizing agents because the molecules of the sizing agents are exposed to temperatures of 80°C or more for a relatively long time in the vat and in the dryer of the storage tanks before and after the UF. When mixed sizes are recovered, it should be ensured that the components are readily compatible and have approximately the same solubility (Trauter 1990; 1993).

The effect of temperature, operating time and size auxiliaries (lubricant and detergent) on the UF for the PVA, CMS and PAC sizing agents and the environmental charge of the size liquors were investigated in this study. Especially the effect of auxiliaries was investigated through using a neutral wax.

## MATERIALS AND METHODS

### *Materials*

Three different types of sizing agents; polyvinyl alcohol, polyacrylate and carboxymethylstarch, were subjected to recycling by ultrafiltration in this study. Polyvinyl based sizing agent (partially (88%) hydrolyzed) was supplied by Lamberti, carboxymethylstarch was based on potato starch ether and supplied by Emsland-Starke GMBH, acrylic polymer sodium salt sizing agent was supplied by Cesalpinia Chemicals s.p.a.. Overwax G (neutral wax, Lamberti) was used as the lubricating agent.

### *UF Apparatus*

UF apparatus designed for laboratory studies was manufactured by Saygın Environment and Energy Systems Corporation and it is shown in Figure 2. Manometers on the apparatus were Pakkens manometers and had the maximum degree 16 kg cm<sup>-2</sup> pressure. The pump was a Deng Yuan TYP 2600 model pump.

Desizing liquor in the feeding tank is fed to the membrane by the pump under the feeding tank. The far smaller water molecules which can pass through the membrane pores leaves the system from the permeate output and the sizing agent solution which can not pass through the membrane pores leaves the system from the concentrate output. Concentrate output is send back to the storage tank. The polymeric structure of the UF membrane was polysulphone and the temperature limits were 90-100°C while the pH range was 0,5-13.

The membrane was cleaned with distilled water after every run, regardless from fouling of the membrane. The cleaning of the membrane was performed by running the device with distilled water at room temperature for 15 minutes.

### *Methods*

Three initial solutions containing 1,5%(w/v) PVA, 2,5%(w/v) CMS and 2,5%(w/v) PAC were prepared for the experiments. In addition, 0,5 g L<sup>-1</sup> Overwax was also added to the solutions which were prepared to investigate the effect of lubricant. The PAC sizing agent solution also included 2 g L<sup>-1</sup> detergent (anionic) since it is recommended to use detergents in desizing processes of PAC. The spectrophotometric absorbance and concentration and also the COD values of the recycled liquors were measured after the treatments carried out at four different temperatures and six different operating times.

The color reaction with iodoboric acid was used for the quantitative determination of polyvinyl alcohol sizes. In the presence of iodine and boric acid, polyvinyl alcohol forms a stable green-blue color complex. After calibration series have been prepared, the intensity of the iodoborax acid complex formed was determined colorimetrically by a UV spectrophotometer (UV-1601 Shimadzu) at 690 nm wavelength. The concentrate and permeate concentrations were determined from the standard series calibration graph.

A similar method to the quantitative determination of PVA sizes was used for the quantitative determination of carboxymethylstarch. CMS sizes form a stable blue color complex with iodine solution and the intensity of the color complex formed was determined colorimetrically by a UV spectrophotometer (UV-1601 Shimadzu). The concentrate and permeate CMS concentrations were determined using the standard series calibration graph at 690nm.

The quantitative determination of polyacrylic sizes was made gravimetrically. The PAC concentrations were determined from the standard series calibration graph.

COD tests were performed according to the Standard Methods for the Examination of Water and Wastewater/5220 B Open Reflux Method.

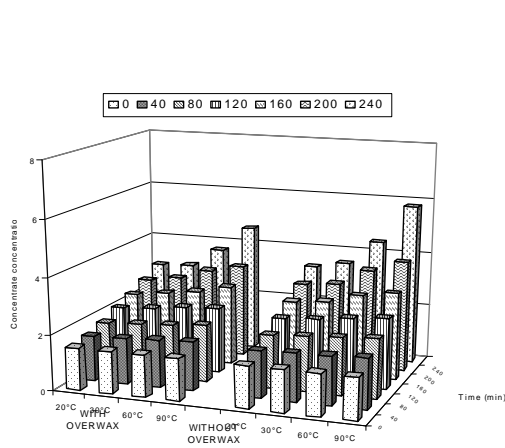
## RESULTS AND DISCUSSION

### **Effects of Operating Parameters on the Recovery of PVA, CMS and PVA Sizes by UF**

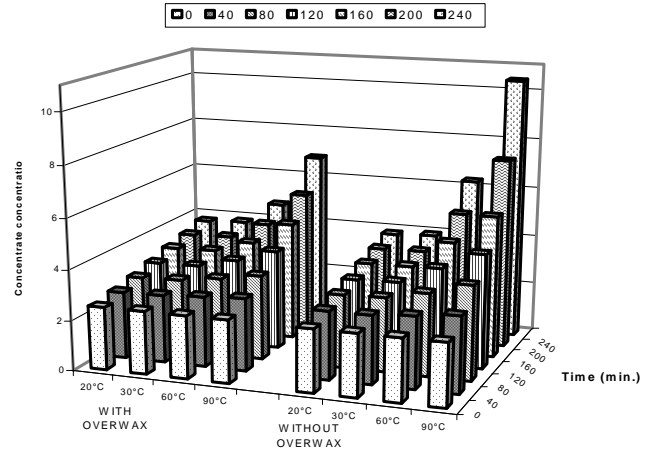
The recovery of PVA sizes by UF was investigated at four different temperatures and six different operating times. The recovery of PVA sizes with and without Overwax at 20°C, 30°C, 60°C and 90°C are shown on Figure 3. An increase in the temperature and operating time results in an increase in the concentration of the concentrate. Nevertheless, the use of Overwax decreases the efficiency of the UF process. This negative effect increases especially at prolonged operating times. The concentrate concentrations of the PVA regenerates with and without Overwax were statistically different at %5 level approving the negative effect of Overwax.

The recovery of CMS sizes by UF was investigated at four different temperatures and six different operating times. The recovery of CMS sizes with and without Overwax at 20°C, 30°C, 60°C and 90°C are

shown on Figure 4. The increase in the temperature and operating time contributes to the concentration of the concentrate. On the other hand, the use of Overwax does not considerably affect the UF efficiency at lower temperatures although it has a negative effect at high temperatures, 60°C and 90°C. This negative effect increases as the operating time is prolonged.

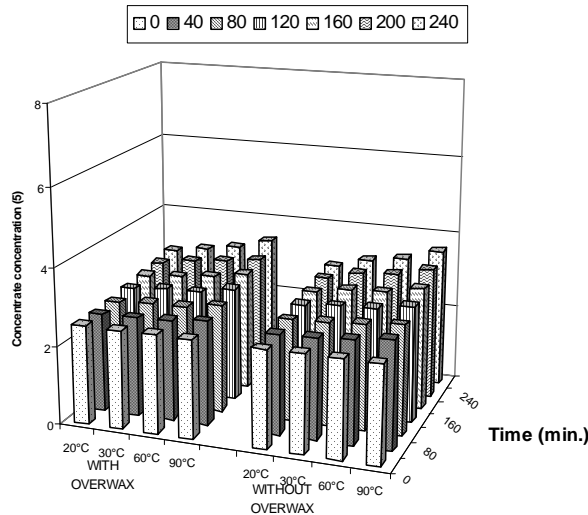


**Figure 3.** The concentration-time-temperature interaction of the PVA size regenerate with and without Overwax



**Figure 4.** The concentration-time-temperature interaction of the CMS size regenerate with and without Overwax.

The recovery of PAC sizes by UF was also investigated at four different temperatures and six different operating times. The recovery of PAC sizes with and without Overwax at 20°C, 30°C, 60°C and 90°C are shown on Figure 5. The increase in the temperature and operating time contributes to the concentration of the concentrate. It is somewhat deceiving although the use of Overwax seems to have no effect on the UF efficiency. The reason of such closer values is due to the effect of the addition of detergent to the PAC size liquor in the desizing bath. Thus, it can be concluded that the chemicals used in desizing baths also decrease the UF efficiency in addition to the use of lubricating agents.



**Figure 5.** The concentration-time-temperature interaction of the PAC size regenerate with and without Overwax

***Effect of Operating Time***

When the size concentrate concentration-operating time interaction is concerned, an increase in the size concentrate concentration is observed with the prolonged operating times. The longer the operating time, the higher the increase in size concentrate concentration. However, longer operating times means higher operating costs, therefore, the operating time should be prolonged until the size concentrate concentration reaches the levels to be reused in the sizing baths.

### ***Effect of Temperature***

Trials were performed at four different temperatures. Results indicated a rapid increase at the concentrate concentration according to the rise in temperature showing that the temperature is a basic factor in the UF process of the recovery of sizing agents in case of concentrate efficiency. When referred to individual sizing agents, the concentrate concentration showed a similar increase for the different temperatures for PVA size. For CMS size, there is not a considerable difference between the concentrate concentrations at room temperatures, 20°C and 30°C, although a great difference occurs at high temperatures, 60°C and 90°C. This is due to the dramatic decrease of viscosity at elevated temperatures. There were not significant changes in the concentrations of the PAC size concentrate due to the increase in temperature.

Statistical evaluation indicated a difference at 5% level on the UF size recovery process between the studied temperatures. The best UF recovery results were obtained at 90°C. A linear increase in the concentrate concentration was observed at low temperatures although the increase was not linear at elevated temperatures (60°C-90°C). These results are in agreement with those of Lin and Lan (1995).

### ***Effect of Sizing Agents***

The statistical evaluation for 240 minutes operating time showed that different sizing agents gave different UF recovery efficiency results at 5% level. The highest recover rates were obtained with CMS size.

### ***Effect of Size Auxiliaries***

The presence of size auxiliaries, lubricant and detergent, did have a negative effect on UF size recovery efficiency. The concentrate efficiency increases at elevated temperatures, on the other hand, the lubricating agents pass to the permeate at the increased temperatures because of the reduced viscosity. Therefore, the COD charge reduction decreases to an extent of 10%. Therefore, the use of lubricants in sizing baths and the use of detergents and wetting agents in desizing baths should be avoided if the size regenerates will be sent to the UF system.

### **COD Values of the Permeate and Concentrate of PVA, CMS and PAC Regenerates**

The COD values of the permeate of the PVA, CMS and PAC sizes after 240 minutes operating time are given in Table 1.

**Table 1.** The COD values of the permeate of the PVA, CMS and PAC sizes after 240 minutes operating time

Initial COD charge (mg L <sup>-1</sup> )	Permeate (mg L <sup>-1</sup> )	Temperature			
		20°C	30°C	60°C	90°C
<b>PVA size</b>					
Regenerate without overwax (4047,4)	Permeate COD	145,1	176,5	194,4	587,3
	% COD reduction	96,4	95,6	95,2	85,5
Regenerate with overwax (4126,7)	Permeate COD	142,8	148,3	309,5	968,2
	% COD reduction	96,5	96,4	92,5	76,5
<b>CMS size</b>					
Regenerate without overwax (2841,0)	Permeate COD	182,0	210,3	352,0	437,0
	% COD reduction	93,6	92,6	87,6	84,6
Regenerate with overwax (4183,0)	Permeate COD	98,5	286,1	409,0	924,2
	% COD reduction	97,6	93,2	90,2	77,9
<b>PAC size</b>					
Regenerate without overwax (3742,3)	Permeate COD	189,9	277,2	462,0	575,0
	% COD reduction	94,9	92,6	87,7	84,6
Regenerate with overwax (3925,1)	Permeate COD	191,3	315,0	497,2	714,2
	% COD reduction	95,1	92,0	87,3	81,8

The COD values of the PVA regenerate could be reduced at a large extend, 85,5-96,4% of the COD charge of the regenerate including lubricant and 76,5-96,5% of the COD charge of the regenerate without lubricant. Although the size concentration in the permeate increases at elevated temperatures and prolonged operating times, the operating time has to be prolonged in order to obtain a certain concentration of the concentrate. This situation slightly increases the COD values, however, 85,5% COD charge reduction can still be achieved in consideration with the initial COD value. This reduction level is 76,5% at the liquors including lubricant.

The COD values of the CMS regenerate could be reduced at a level of 84,6-93,6% for the COD charge of the regenerate including lubricant and 77,9-97,6% for the COD charge of the regenerate without lubricant. The use of lubricant resulted in a loss about 10% on the COD charge reduction for both types of sizes.

The COD values of the PVA regenerate could also be reduced at a large extend, 81,8-95,1% of the COD charge of the regenerate including lubricant and 84,6-94,9% of the COD charge of the regenerate without lubricant.

A COD charge reduction to a very large extend occurred when the initial feeding liquor and permeate output liquor from the UF system was compared. The increase of the temprature resulted in increases in the COD charges. The size concentration in the permeate showed an increase as the temperature increased due to the decomposition of larger sizing agent molecules to smaller ones, hence decreasing the viscosity. The decreased viscosity resulted in an increase in the COD charges. Statistical evaluation indicated that the most appropriate temperature for concentrate efficiency was 90°C, but a decreases by 10% in COD charge reduction also occurred at this temperature when compared to lower temperatures. Nevertheless, the total COD charge removal was still very high in the environmental view. The use of size auxiliaries increased the COD charges. The COD charge reduction decreased to 76,5% for PVA, 77,9%for CMS and 81,8% for PAC in presence of auxiliaries.

## CONCLUSION

It can be stated that the process temperature is a basic parameter for UF size recovery processes and when considered the usual temperatures for desizing processes at practice is 60-80°C, it should be useful to send the desizing liquor continuously to the UF system to increase the UF efficiency. The use of auxiliaries, like lubricants at sizing baths and detergents at desizing baths, should be avoided to reduce the permeate charge.

## REFERENCES

- Chermisnoff P.N. (1995). *Solids/Liquids Separation*. Technomic Publishing Company, Lancaster.
- Cheryan M. (1998). *Ultrafiltration and Microfiltration Handbook*. Technomic Publishing Company, Lancaster.
- Dickenson T.C. (1997). *Filters and Filtration Handbook*. Elsevier Science Ltd., U.K.
- Duran K., and Ekmekçi A. (1995). Sizing Agents at the Ecological Point of View, SAGEM/Education Pub. No:155, Bursa.
- Lin S.H., and Lan W.J. (1995). Polyvinyl Alcohol Recovery by Ultrafiltration: Effects of Membrane Type and Operating Conditions, *Separation Technology* 5(2): 97-103.
- Scott K. (1998). *Handbook of Industrial Membranes*. Elsevier Science Ltd., U.K.
- Tarackcioglu I. (1986). *Textile Treatment and Machines-Part 3*, Aracilar Publishing Co., Izmir.
- Trauter J. (1993). Use of Ultrafiltration for Recycling Sizing Agents and Indigo, *Melliand Textilberichte* 74(6): 559-562.
- Trauter J. (1990). Technological and Economic aspects of Recycling Sizing Agents. *Melliand Textilberichte* 71(1): 17-23.
- Wang L.K., and Cheryan M. (1995). Application of Membrane Technology in Food Industry for Cleaner Production. In: *Proceedings of the Second International Conference on Minimisation and Clean Production*, Book of Papers, Barcelona, pp333-346.