USING A MEMBRANE FILTRATION PROCESS TO CONCENTRATE THE EFFLUENT FROM ALKALINE PEROXIDE MECHANICAL PULPING PLANTS

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Using a multi-effect evaporation system to concentrate the effluent from alkaline peroxide mechanical pulping (APMP) plants is known to require a high energy consumption. In order to improve the situation, a polyethersulfone membrane was used to concentrate the effluent of APMP plants beforehand. An orthogonal experimental design was applied and a mathematical model was established to optimize the filtration parameters. An estimation of potential energy and water savings from this new concentration process was developed. The optimal filtration conditions obtained were: molecular weight cut-off at 10,000 Dalton, trans-membrane pressure at 3 bar, feed temperature at 50°C, cross-flow velocity at 420 rpm, and volume reduction factor at 0.93. The average permeate flux under these conditions was 45.31 l/m^2.h. The total solids content was increased from 14.74 g/l in the feed to 95.04 g/l in the concentrate. The permeate had low total solid contents of 8.75 g/l, Chemical Oxygen Demand of 6696 mg/l, and Biochemical Oxygen Demand of 4383 mg/l. Such qualities would allow the permeate to be reused in the alkaline peroxide mechanical pulping process. With this new concentration process, about 4840.6 kwh energy can be saved and 23.3 m^3 effluent discharge can be reduced for each ton of pulp produced.

Keywords: Alkaline peroxide mechanical pulping; Effluent; Polyethersulfone membrane; Concentrating; Orthogonal experiment; Mathematical model; Energy and water saving

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NOMENCLATURE

APMP   Alkaline peroxide mechanical pulping
BOD   Biochemical oxygen demand
CFV   Cross-flow velocity
COD   Chemical oxygen demand
FT   Feed temperature
J   Average permeate flux, see Eq. 2
MWD   Molecular weight distribution
MWCO   Molecular weight cut-off
PES   Polyethersulfone
TMP   Trans-membrane pressure
VRF   Volume reduction factor, see Eq. 1

INTRODUCTION

During the past 50 years, membrane filtration processes have grown into a billion-dollar industry worldwide (Barzin et al. 2004). They have received even more interest in recent years because of the stringent standards for water supply and effluent discharge. Polymeric membranes have been used for many industry applications, such as micro-filtration, ultra-filtration, reverse osmosis, pervaporation, and gas-vapor separation (Hilal et al. 2004; Braeken et al. 2006). Polyethersulfone (PES), which has a high glass transition temperature of $230^{o}C$, is a closely related derivative of polysulfone. Due to its outstanding characteristics of wide temperature limit, wide pH tolerance, easy membrane fabrication, wide range of pore size, and good chemical resistance (Kim and Kim 2005; Ulbricht et al. 2007; David et al. 2003), it has been widely used as the membrane material in membrane filtration processes (Zhao et al. 2001).

Effluent recycling in the pulp and paper industry has long been an important topic because of the massive amount of water used. Particular attention has been paid to regulations affecting treatment and discharge of the effluent. New and more cost-effective technologies are demanded for the treatment of effluent from the pulp and paper industry. Mills have sought to comply with new regulations by reducing the generation of waste water via process improvement (Wallberg et al. 2001).

The alkaline peroxide mechanical pulping (APMP) process has been widely adopted all over the world due to its advantages of high yield, high brightness, high strength, and low pollution. The effluent of APMP plants comprises those coming from the processes of chip washing, hot-water impregnation, squeezing extrusion, chemical impregnation, and mechanical refining. It is a mixed effluent. To achieve a closed wastewater loop, several APMP plants have attempted to concentrate the total effluent by using multi-effect evaporation systems. The concentrated effluent is then blended with black liquor to feed recovery boilers for alkaline pulping systems. But this process is always associated with very high energy consumption.

For a membrane filtration process to be successfully used in the pulp and paper industry as a kidney, it must be tailored according to its special requirements (Wallberg et al. 2003). The low-cost and easily-fabricated PES membrane, which could produce a reasonably large amount of purified process water and does not foul easily compared to other commercial membranes (Cheryan 1998), is believed to be applicable in the treatment of effluent from APMP plants.

Over recent years, in the fields of using membrane filtration processes to treat the effluents coming from pulp and paper mills, researchers in Lappeenranta University of Technology (Finland) and Lund University (Sweden) have done many studies. Their studies mainly have focused on the treatments of kraft black liquor (Wallberg and Jönsson 2003; Holmqvist et al. 2005; Wallberg et al. 2005), bleaching effluent (Fälth et al. 2001) and white water of paper machines (Huuhilo et al. 2001; Mänttäri et al. 1997). The material of membrane they adopted are both polymeric and ceramic (Wallberg and Jönsson 2003; Holmqvist et al. 2005; Wallberg et al. 2005). The filtration performance of using polyvinilidene fluoride (PVDF) membrane cooperating with polyethyleneimine (PEI) and polyvinylalcohol (PVA), which were used as water-soluble polymeric macroligands, to remove trace metals and *COD* from pulp and paper industrial

wastewater were discussed by the researchers in the University of Maringa (Brazil) (Vieira et al. 2001). As a new synthetic polymer, PES has been widely used as membrane material for various applications such as biomedicine, food, hemodialysis, plasma separator, and water purification. But its contact with pulp and paper industry applications is rarely reported. The relatively studies of PES membranes applied in the pulp and paper industry have mainly emphasized the fouling and cleaning of the membrane but not the treatment of the effluent coming from APMP plant (Väisänen et al. 2002; Maartens et al. 2002). In this study an orthogonal experimental design is used as a new attempt for optimizing the filtration conditions of membranes.

The objective of this work is to use an economical membrane filtration process to pre-concentrate the effluent from APMP plants. The pre-concentrated effluent then enters a multi-effect evaporation system for further concentration. The permeate is evaluated relative to its reuse in the APMP pulping process. The ultimate goal is to reduce the energy and water consumption and effluent discharge in APMP plants. Specifically, six types of flat-sheet membranes with different model numbers were applied to concentrate APMP plant's effluent. An orthogonal experimental design was applied, and a mathematical model was established to optimize the filtration parameters. Estimation of energy and water saving from this new concentration process was also developed.

EXPERIMENTAL

Materials

Apparatus

A cross-rotational flat-sheet filter (MSC 300), manufactured by Mosu Membrane, China, was used in this work. MSC 300 is a laboratory-scale filter with a 350 cm^3 stirred dead-end and a membrane area of 0.0031 m^2. It is made of polymethyl methacrylate with magnetic stirring, as shown in Fig. 1.
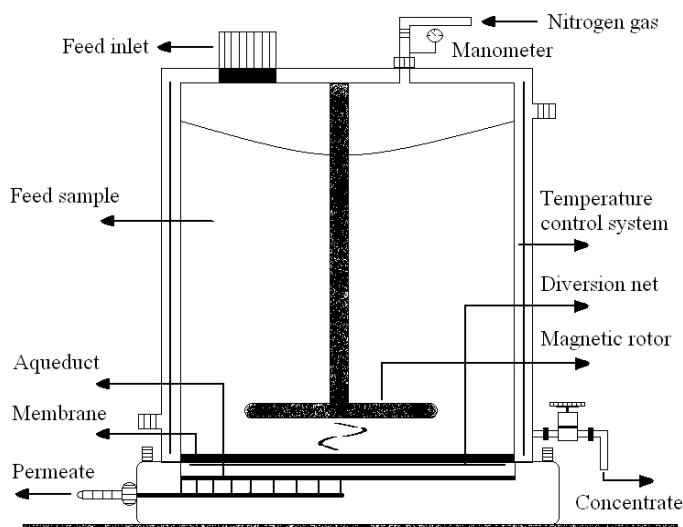

Fig. 1. MSC300 cross-rotational flat-sheet filter

The trans-membrane pressure can be adjusted within 0 to 3 bar. The maximum speed of the rotor is 430 rpm, which corresponds to a cross-flow velocity of 1.12 m/s on the rotor tip. Its trans-membrane pressure is controlled by nitrogen gas and the feed temperature is maintained by an automatic temperature-control system with cooling water and a heater.

Membrane

Six types of flat-sheet membranes with different model numbers, produced by Sepro Membrane and Microdyn-Nadir, USA, were used in this study. Table 1 shows their characteristics.

Table 1. Characteristics of the Flat-Sheet Membranes Used

Manufacturer	Sepro			Microdyn-Nadir		
	PES 2	PES 5	PES 10	UH030	UH050	US100
Material (active/support)	PES/PO	PES/PO	PES/PO	PESH/PO	PESH/PO	PSH/PO
$MWCO$ (Dalton)	2,000	5,000	10,000	30,000	50,000	100,000
Thickness (µm)	165	165	165	270	270	270
pH [a]	2-10	2-10	2-10	1-14	1-14	1-14
Temp. max (℃)	50	50	50	90	90	90
PWF [b] ($l/m^2/h$)	60	140	210	250	500	800
Retention (%)	75 (2K PEG)	93 (5K PEG)	95 (10K PEG)	85 (PVP K30)	79 (PVP K30)	75 (PVP K30)
a *pH* was measured at 20 ℃						
b *PWF* was measured under the conditions: *TMP* at 2 bar, *FT* at 25 ℃, *CFV* at 0 rpm						
PO: Polyolefin, PWF: Pure water flux, PEG: Polyethylene glycol, PVP: Polyvinylpyrrolidone						

Effluent

The APMP plant's effluent came from Sun Paper Co., China. Generally speaking, the main components in the effluent were typically carbohydrates, extractives, lignin, low-molecular weight organic acids, proteins, and inorganic ions. The effluent, pre-treated with a 150µm bend screen, was used as the feed for the membrane filtration concentration experiments. The main parameters of the feed were measured before the concentrating experiments. Table 2 presents the average values of different parameters of the feed.

Methods

Before each filtration, a fresh membrane was first stabilized with distilled water under the conditions of 2 bar, 25℃, and 0 rpm until its pure water flux remained stable. Meanwhile, the pure water flux was also measured. During the membrane filtration concentration process, the concentrate was retained in the dead-end cell and the permeate was collected from the outside. The endpoint of every concentration experiment was determined by the volume reduction factor, which is the volume ratio between the permeate and the initial feed.

Table 2. Characteristics of the Feed Used in the Concentration Experiments

Parameters	Average values
Total solid, g/l	14.74±0.23
Total organic matter, g/l	8.04±0.02
Ash content, g/l	6.11±0.05
Heating value, kJ/g	12235±651
COD, mg/l	12147±846
BOD, mg/l	5035±382
pH	7.68±0.10
Conductivity, mS/cm	7.42±0.04
Colour, PtCo	856.25±28.20

Molecular weight distribution

In order to determine the molecular weight distribution of the effluent from APMP plants, an indirect ultra-filtration method was used to fractionate the feed (which is the effluent pre-treated with a 150μm bend screen) after it was diluted by 5,000 times with distilled water in order to possibly reduce the errors caused by the fouling problems. 20 ml pre-treated effluent was used in every experiment. The ultra-filtration procedure started with a MWCO 100,000 Dalton membrane. The permeate was then concentrated again with a MWCO 50,000 Dalton membrane, and then in sequence with a MWCO 30,000, 10,000, 5,000, and finally, a MWCO 2,000 Dalton membrane. The contents of total solids in the samples were measured and calculated according to the method described by Henning et al. (1997). The experiments of the molecular weight distribution were repeated three times in all and we used the average value of the two closer results for the final result.

Preliminary selection of membranes

Six types of flat-sheet membranes with different model numbers were experimented separately in the concentration process under the same filtration conditions, which are: *TMP* at 2 bar, *FT* at 25°C, *CFV* at 420 rpm, and *VRF* at 0.9. Based on the experimental results, three of them were selected for further orthogonal experiments. Samples taken from the feed, concentrate, and permeate were analysed to obtain the following values: average permeate flux, total solids, *COD*, and *BOD*.

Orthogonal experiment

An orthogonal experiment was carried out to obtain the optimal filtration conditions for the concentration process of the effluent. Four parameters including *MWCO*, *TMP*, *FT*, and *CFV*, were used in the orthogonal experimental design. The average permeate fluxes and the retentions of total solid, *COD* and *BOD* of all samples were measured. Experiments were conducted with the three pre-selected membranes chosen above. The trans-membrane pressures used varied from 1 bar, 2 bar and 3 bar, which were the typical pressures used in ultra-filtration process. The feed temperatures

were set at 25 °C, 40 °C, and 55 °C, respectively, which are within the possible temperature range for the effluent from APMP plants. All of the concentration processes were carried out at the cross-flow velocities of 200, 310, and 420 rpm, mainly because the previous experiments have shown that the average permeate fluxes obtained under these cross-flow velocities differed considerably.

Optimal VRF

The degree of concentration is usually expressed as the volume reduction factor in ultra-filtration processes. The volume reduction factor is an important factor in this concentration process, as it relates to concentration effect and production cost. An experiment for optimal volume reduction factor was performed based on the optimal filtration conditions obtained from the orthogonal experiment. A mathematical model was developed using MATLAB 7.8 software to calculate the optimal volume reduction factor.

Analysis

Samples of the feed, concentrate, and permeate were all measured to obtain the values of total solid, total organic matter, ash content, heating value, *COD*, *BOD*, *pH*, conductivity, and colour. Total solid and ash content were analysed according to the SFS 3008 standard method. Total organic matter was calculated as the difference between total solids and ash content. Heating value analysis was carried out using a GR-3500 oxygen bomb calorimeter according to the ISO 1928 - 1995 standard method. *COD* was measured according to the SFS 5504 standard method. *BOD* was analysed according to the ISO 5815 - 1, 2: 2003 standard method. The *pH* was determined according to the UDC 663. 6: 543. 06 standard method. Conductivity was analysed using the ISO 7888-1985 standard method. Colour was analysed according to the ISO 7887 - 1985 standard method.

Calculation

The volume reduction factor was calculated using Eq. (1), where V_p is the permeate volume (l) and V_f the initial volume of feed (l).

$$VRF = \frac{V_p}{V_f} \qquad (1)$$

The average permeate flux at a specific *VRF* (l/m^2.h) was calculated by Eq. (2), where *V* was the permeate volume (l), *S* the filtration area (m^2), and *t* the filtration time (h).

$$J = \frac{V}{S \times t} \qquad (2)$$

The retention of total solids, *COD*, and *BOD* (R_{TS}, R_{COD}, R_{BOD}, %) at a specific *VRF* were calculated according to Eqs. (3)-(5), where $C_{p.TS}$ is the content of total solids in permeates (mg/l) and $C_{c.TS}$ the content of total solid in concentrates (mg/l); $C_{p.COD}$ is the

value of *COD* in permeates (mg/l), and $C_{c.COD}$ the value of *COD* in concentrates (mg/l); $C_{p.BOD}$ is the value of *BOD* in permeates (mg/l), and $C_{c.BOD}$ is the value of *BOD* in concentrates (mg/l).

$$R_{TS} = \left(1 - \frac{C_{p.TS}}{C_{c.TS}}\right) \times 100\% \tag{3}$$

$$R_{COD} = \left(1 - \frac{C_{p.COD}}{C_{c.COD}}\right) \times 100\% \tag{4}$$

$$R_{BOD} = \left(1 - \frac{C_{p.BOD}}{C_{c.BOD}}\right) \times 100\% \tag{5}$$

The production cost of organic fuel can be calculated by Eq. (6) (Zhang 2009):

$$Pc = \frac{Cc + Oc}{m_{organics} \times H_{fuel}} \tag{6}$$

where *Pc* is the production cost, *Cc* the capital cost, *Oc* the operating cost; $m_{organics}$ is the amount of organics in the concentrate and H_{fuel} the net heating value of the fuel, i.e., the heating value of organics in the concentrate minus the heating value needed for the evaporation of water in the concentrate during combustion. H_{fuel} is given by,

$$H_{fuel} = H_{organics} \times X_{organics} - 20.5 \times [1 - TS] \tag{7}$$

where $H_{organics}$ is the heating value of organics in the concentrate, $X_{organics}$ is the weight percentage of organics, and *TS* the content of total solid in the concentrate. In Eq. (7), the contribution of other substances besides organics (mainly extractives and inorganic ions) to the heating value of the concentrate was assumed to be negligible. This was an acceptable assumption, as organics make up 90-95% of the total solid content at volume reduction factor 0.9. The heating values of lignin and carbohydrates are 25.5 MJ/kg and 12.5 MJ/kg, respectively (Grace et al. 1989). The value of 20.5 MJ/kg was used in the calculations based on the proportion of lignin and carbohydrates in hardwood.

The influence of the *VRF* on *TS* can be expressed with Eq. (8) as:

$$TS = TS_0 \times \left(\frac{1}{1-VRF}\right)^R \tag{8}$$

where TS_0 is the initial total solid content in the feed, and *R* the observed retention of total solid. The constant *R* can be determined by fitting Eq. (8) to the experimental data shown in Table 11, using nonlinear regression.

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RESULTS AND DISCUSSION

Molecular Weight Distribution

Figure 2 shows the molecular weight distribution of all components in the diluted effluent. The proportion of the components with molecular weight larger than 10,000 Dalton was 85.1%, in which 28.8% were larger than 100,000 Dalton, 21.6% were between 100,000 Dalton and 50,000 Dalton, 11.4% were between 50,000 Dalton and 30,000 Dalton, and 23.3% were between 30,000 Dalton and 10,000 Dalton. Only 14.9% of the components in the diluted effluent were smaller than 10,000 Dalton. This result indicated that the molecular weight of all the components in the diluted effluent fell mainly in the range of larger than 10,000 Dalton. There were relatively less components in the effluent whose molecular weight was smaller than 10,000 Dalton. Attempts to determine the molecular weight distribution of all components in the effluent of APMP plants directly were not successful, because the contents of the components were too high. The form of all components in the un-diluted effluent should be more complex than that in the diluted one (Liu et al. 2004; Ahn et al. 1998). Due to the influences of other experimental factors, for instance, the fouling problems, the practical cut-off values of membranes, the measurement conditions, and the used model substance, the results obtained by this measurement are approximate and only used for guiding the preliminary selection of membranes in this study.
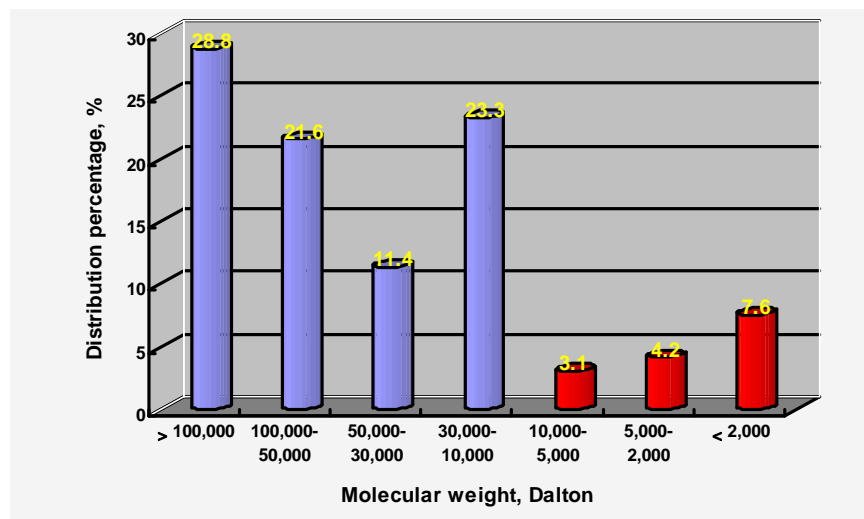

Fig. 2. Molecular weight distribution of the components in the diluted effluent

Preliminary Selection of Membranes

Table 3 presents the concentrating effects of the six types of flat-sheet membranes that have different model numbers. With the decrease of molecular weight cut-off, the values of total solid, *COD*, and *BOD* in the concentrate increased correspondingly, while the same numbers in the permeate decreased gradually. The average permeate flux, which relates to energy consumption and equipment investment, was an important factor in this concentration process. The average permeate flux was always higher than 41.78 l/m^2.h when the molecular weight cut-offs of membranes were larger than 10,000 Dalton. But it

decreased rapidly to only 3.20 l/m^2.h when the molecular weight cut-off was at 5,000 Dalton (PES 5) and to 2.88 l/m^2.h when the molecular weight cut-off was at 2,000 Dalton (PES 2). So PES 5 and PES 2 were obviously not suitable for the concentration process of APMP effluent, because their average permeate fluxes were too low. Considering the molecular weight distribution of the components in the APMP effluent and the fact that the concentration effects of Model UH030 and Model PES 10 were fairly similar, Model UH030 can be excluded from further study as well. Therefore, only three flat-sheet membranes, those are Models US100, UH050 and PES 10, were chosen for the further optimization with orthogonal experiment design.

Table 3. Concentrating Effects * of the Six Types of
Flat-Sheet Membranes with Different Model Numbers

Model numbers	MWCO (Dalton)	J (l/m^2.h)		Total solid (g/l)	COD (mg/l)	BOD (mg/l)
US100	100,000	41.78	Concentrate	60.34	56037	13358
			Permeate	1.20	9951	5842
UH050	50,000	48.02	Concentrate	66.28	69422	15680
			Permeate	1.22	8938	5394
UH030	30,000	45.40	Concentrate	71.65	71210	16350
			Permeate	1.19	8020	5360
PES 10	10,000	43.98	Concentrate	71.67	72839	17525
			Permeate	1.15	6885	4383
PES 5	5,000	3.20	Concentrate	72.38	72568	17629
			Permeate	0.97	5912	4067
PES 2	2,000	2.88	Concentrate	73.45	74987	18000
			Permeate	0.85	4865	3898
* Filtration conditions: *TMP* at 2 bar, *FT* at 25 ℃, *CFV* at 420 rpm, *VRF* at 0.9						

Orthogonal Experiment

For the design and discussion of the orthogonal experiment, readers are referred to Sun (1998). According to relevant research on pulping or papermaking effluent filtrations, 0.9 might be a suitable value of volume reduction factor with a comprehensive consideration of energy consumption and equipment investment (Holmqvist et al. 2005; Sun 1998; Nuortila-Jokinen et al. 1998). So, in the orthogonal experiments, it was preliminary assumed that the optimal volume reduction factor was 0.9. There were four factors, including the four filtration parameters: *MWCO, TMP, FT*, and *CFV*, and three levels which were designed in the orthogonal experiment, as can be seen in Table 4. Table 5 is the orthogonal experimental schedule designed for a series of tests of optimizing filtration parameters. The final results of the orthogonal experiment are presented in Table 6. Table 7 presents the influences of four parameters on the average permeate flux during the concentration process. Different *R* values showed that feed temperature and cross-flow velocity were the more active factors affecting the increase of average permeate flux. With the increase of feed temperature (from 20°C to 50°C) and

cross-flow velocity (from 200 rpm to 420 rpm), the average permeate flux increased quickly. To the contrary, the influences of molecular weight cut-off and trans-membrane pressure on average permeate flux were relatively small. So the optimal combination in terms of the average permeate flux was $A_1B_1C_3D_3$. Table 8 shows the influences of four parameters on R_{TS}. The changes of R indicated that feed temperature was the most important factor affecting the decrease of R_{TS}. With the increase of feed temperature (from 20 ^{o}C to 50 ^{o}C), the R_{TS} decreased quickly. The trans-membrane pressure was also a significant factor during the concentration. The cross-flow velocity and the molecular weight cut-off were relatively inactive. Therefore, the optimal combination in terms of R_{TS} was $A_1B_3C_1D_3$. Likewise, Table 9 and Table 10 display the influences on R_{COD} and R_{BOD}, respectively. The decrease of R_{COD} and R_{BOD} had a similar trend as the R_{TS}'s. Table 9 indicates that feed temperature was the most active factor. The contributions of trans-membrane pressure, cross-flow velocity, and molecular weight cut-off were relatively small. The optimal combination in terms of R_{COD} was $A_1B_3C_1D_1$. On the other hand, the molecular weight cut-off and the trans-membrane pressure were the more important factors affecting R_{BOD}. Feed temperature and cross-flow velocity were relatively inactive, as can be seen in Table 10. So the optimal combination in terms of R_{BOD} was also $A_1B_3C_1D_1$.

Two major competing factors that determine whether membrane filtration process can be applied in the pulp and paper industry are average permeate flux and environmental benefit. Keeping high average permeate flux and high retention are two aspects which must be considered comprehensively when determining the optimal filtration conditions. Based on the orthogonal experimental results, the molecular weight cut-off had a significant effect on R_{BOD} and was inactive to J, R_{TS} and R_{COD}. Therefore 10,000 Dalton was chosen for the optimal membrane molecular weight cut-off. *TMP* was an important factor affecting R_{TS}, R_{COD}, and R_{BOD}. So 3 bar was chosen for the optimal *TMP*. With the increase of feed temperature, J increased, but R_{TS}, R_{COD}, and R_{BOD} decreased. Considering the actual temperature of APMP effluent and the fact that the average permeate flux is the decisive factor, 50 ^{o}C was determined to be the optimal feed temperature. The cross-flow velocity had the most important effect on the average permeate flux, so 420 rpm was chosen for the optimal cross-flow velocity. Therefore, the optimal filtration conditions obtained were: *MWCO* at 10,000 Dalton, *TMP* at 3 bar, *FT* at 50 ^{o}C and *CFV* at 420 rpm (1.1 m/s on the rotor tip), which is combination $A_1B_3C_3D_3$.

Table 4. Factors and Levels of the Orthogonal Experimental Design

levels\Factors	A *MWCO* (Dalton)	B *TMP* (bar)	C *FT* (℃)	D *CFV* (rpm)
1	10,000	1	20	200
2	50,000	2	35	310
3	100,000	3	50	420

Table 5. Orthogonal Experimental Schedule for Optimizing Filtration Parameters

Tests\Factors	A MWCO (Dalton)	B TMP (bar)	C FT (℃)	D CFV (rpm)
Test 1	1 (10,000)	1 (1)	1 (20)	1 (200)
Test 2	1 (10,000)	2 (2)	2 (35)	2 (310)
Test 3	1 (10,000)	3 (3)	3 (50)	3 (420)
Test 4	2 (50,000)	1 (1)	2 (35)	3 (420)
Test 5	2 (50,000)	2 (2)	3 (50)	1 (200)
Test 6	2 (50,000)	3 (3)	1 (20)	2 (310)
Test 7	3 (100,000)	1 (1)	3 (50)	2 (310)
Test 8	3 (100,000)	2 (2)	1 (20)	3 (420)
Test 9	3 (100,000)	3 (3)	2 (35)	1 (200)
* Other filtration condition: VRF at 0.9				

Table 6. Results of the Orthogonal Experiment for Optimizing Filtration Parameters

Results\Tests	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9
J (l/m^2.h)	17.08	38.20	50.16	45.46	30.56	27.90	41.52	32.04	22.68
R_{TS} (%)	85.55	77.55	85.40	78.57	80.66	85.82	77.81	84.00	80.19
R_{COD} (%)	90.00	81.33	87.96	83.47	84.10	88.97	82.08	86.75	85.34
R_{BOD} (%)	63.71	51.59	63.69	47.89	51.57	63.89	40.74	41.04	51.64

Table 7. Factor Analysis of J

Analysis items\Factors	A MWCO (Dalton)	B TMP (bar)	C FT (℃)	D CFV (rpm)
Average K1	35.146	34.686	25.674	23.440
Average K2	34.640	33.600	35.446	35.874
Average K3	32.080	33.580	40.746	42.554
Range R	3.066	1.106	15.072	19.114
Optimal combination	D>C>A>B		$A_1B_1C_3D_3$	

Table 8. Factor Analysis of R_{TS}

Analysis items\Factors	A MWCO (Dalton)	B TMP (bar)	C FT (℃)	D CFV (rpm)
Average K1	82.833	80.643	85.123	82.657
Average K2	81.683	80.737	81.290	82.133
Average K3	80.667	83.803	78.770	80.393
Range R	2.166	3.160	6.353	2.264
Optimal combination	C>B>D>A		$A_1B_3C_1D_3$	

Table 9. Factor Analysis of R_{COD}

Analysis items\Factors	A MWCO (Dalton)	B TMP (bar)	C FT (℃)	D CFV (rpm)
Average K1	86.430	87.423	88.573	86.480
Average K2	85.513	85.183	84.713	86.060
Average K3	84.723	84.060	83.380	84.127
Range R	1.707	3.363	5.193	2.353
Optimal combination	C>B>D>A		$A_1B_3C_1D_1$	

Table 10. Factor Analysis of R_{BOD}

Analysis items\Factors	A MWCO (Dalton)	B TMP (bar)	C FT (℃)	D CFV (rpm)
Average K1	59.753	59.830	56.213	55.640
Average K2	54.450	50.780	52.090	52.073
Average K3	44.473	48.067	50.373	50.963
Range R	15.280	11.763	5.840	4.677
Optimal combination	A>B>C>D		$A_1B_3C_1D_1$	

Optimal *VRF*

Capital cost is, in most cases, the dominating cost for an ultra-filtration plant. It comprises the cost of membranes and equipment. The operating cost consists of mainly power consumption, replacement of membrane, maintenance, cleaning, and labor costs, where power consumption is affected by volume reduction factor. In a specific process, the capital cost and all operating cost other than power consumption are all constant. So a trend line expressing the relationship between volume reduction factor and production cost can be fitted with MATLAB 7.8. This is presented in Fig. 3.

Table 11. The Influence of *VRF* on Concentration Effect

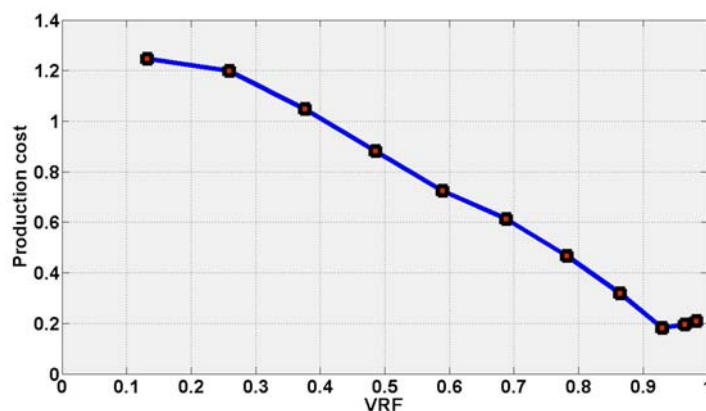| VRF	Time (h)	J (l/m².h)	Total solid in the concentrate (g/l)	Power consumption (kwh)
0.13	0.5	56.84	17.24	10.75×10^{-3}
0.26	1	56.78	17.26	10.35×10^{-3}
0.38	1.5	53.24	19.30	10.10×10^{-3}
0.49	2	49.68	21.33	9.40×10^{-3}
0.59	2.5	47.10	25.45	9.20×10^{-3}
0.69	3	44.52	29.56	9.05×10^{-3}
0.78	3.5	41.30	38.23	8.90×10^{-3}
0.87	4	36.12	55.21	8.75×10^{-3}
0.93	4.5	32.38	95.04	8.65×10^{-3}
0.97	5	15.48	175.79	17.10×10^{-3}
0.98	5.5	7.74	333.88	34.9×10^{-3}

Fig. 3. Relationship between *VRF* and production cost of organic fuel

Before reaching 0.93, the production cost decreases gradually with increasing *VRF*. But after that point, the production cost started to increase slowly. Meanwhile, the average permeate flux decrease more quickly. So 0.93 was determined to be the optimal *VRF* for this concentration process. The obtainment of optimal volume reduction factor was partly based on the calculation methods in the reference (Holmqvist et al. 2005).

Verification Experiment

A verification experiment was repeated immediately after obtaining the optimal filtration conditions and volume reduction factor. Table 12 shows the final concentration effect of APMP effluent. The average permeate flux under these conditions was 45.31 l/m^2.h. The content of total solid was raised from 14.74 g/l in the feed to 95.04 g/l in the concentrate. The heating value of effluent was increased from 12.23 kJ/g to 15.39 kJ/g, indicating that the utilization value of APMP plant's effluent was enhanced. The permeate had a low total solid content of 8.75 g/l, *COD* of at 6696 mg/l, and *BOD* of 4383 mg/l, and was likely to be directly reused in APMP pulping process for wet feed preparation, coarse pulp washing or lime mud washing according to the results of the later permeate reuse experiments (Zhang 2009).

Table 12. Characteristics of the Feed, Concentrate and Permeate after the Concentration Experiment under the Optimal Filtration Conditions and *VRF*

Parameters	Average values		
	Feed	Concentrate	Permeate
Total solid (g/l)	14.74±0.23	95.04±0.56	8.75±0.12
Total organic matter (g/l)	8.04±0.02	65.75±0.03	4.02±0.02
Ash content (g/l)	6.11±0.05	29.27±0.02	4.73±0.01
Heating value (kJ/g)	12.23±0.30	15.39±0.45	9.36±0.19
COD (mg/l)	12147±846	90961±1006	6696±578
BOD (mg/l)	5035±382	19479±459	4383±152
pH	7.68±0.10	7.73±0.05	7.91±0.04
Conductivity (mS/cm)	7.42±0.04	11.46±0.02	7.14±0.01
Color (PtCo)	856.3±28.2	9156.3±34.5	171.9±12.4

Economic Benefits Calculation

The benefits in energy-saving and discharge reduction for every ton of APMP pulp produced using this new concentration process under its optimal conditions and volume reduction factor can be calculated based on the data in Table 12. Assume that there is 25 m^3 effluent generated for each ton of pulp produced. When the content of total solid is increased from 14.74 g/l in the feed to 95.04 g/l in the concentrate: 1) the heat energy used to vaporize 1 kg effluent in five-effect evaporation station is about 2256/3.5=645 kJ/kg effluent, converting into power 645/3600=0.179 kwh/kg effluent; thus the reduced usage of steam is 0.179×23.3×1000=4171 kwh/t pulp; where 2256 kJ/kg is the latent heat of vaporization of steam, 3.5 kg effluent/kg steam the evaporation efficiency of five-effect multi-effect evaporation station, 1 kwh=3600 kJ, 23.3 m^3 the permeate coming from the 25 m^3 total effluent. 2) Assume that the specific heat of the effluent with the content of total solid between 14 g/l and 95 g/l is 3.85 kJ/kg. ^{o}C; the heat energy used to preheat the permeate from 50 ^{o}C to 75 ^{o}C, converting into power, is about [3.85×23.3×1000×(75-50)]/3600=623 kwh/t pulp; so the reduced energy used in preheating effluent is 623 kwh/t pulp; 3) the energy consumption used to transport effluent from APMP plant to five-effect evaporation station is 2 kwh/t effluent; thus the reduced power used to transport the effluent is 23.3×2=46.6 kwh/t pulp. 4). Because of the reuse of all permeate, the reduced discharge of effluent is about 23.3 m^3. These results are summarized as below (converting into power):

1) Reducing the usage of steam by 4171 kwh/t pulp;
2) Reducing the energy used in warming-up effluent by 623 kwh/t pulp;
3) Reducing the power used to transport the effluent by 46.6 kwh/t pulp;
4) Reducing the discharge of effluent by 23.3 m^3 .

With this new concentration process, 92.9% of the water in the effluent can be removed. In an APMP plant that has an annual pulp production capacity of one million tons, for instance, 4.84 billion kwh power could be saved. The capital investment for multi-effect evaporation system could also be decreased by 90% correspondingly. The discharge of effluent could be reduced by 23.3 million m^3 per year. More details about the economic calculation can be found in the following reference (Zhang 2009).

These data suggest that the technology to concentrate APMP plant's effluent using ultra-filtration using PES flat-sheet membrane has a great potential for industrial-scale application. Of course, pilot plant trials are needed for further validation.

CONCLUSIONS

1. The potential to use ultra-filtration with PES flat-sheet membranes to concentrate an APMP plant's effluent was investigated. The optimal filtration conditions obtained were: *MWCO* at 10,000 Dalton, *TMP* at 3 bar, *FT* at 50 ^{o}C, and *CFV* at 420 rpm. The optimal volume reduction factor calculated was 0.93 when the concentration effect and production cost were also considered. The average permeate flux under the optimal conditions and optimal volume reduction factor was 45.31 l/m^2.h, and the content of total solid was raised from 14.74 g/l in the feed to 95.02 g/l in the concentrate. The permeate had a low contents total solid at 8.75 g/l, *COD* at 6696

mg/l and *BOD* at 4383 mg/l, and could be directly reused in APMP pulping process for wet feed preparation, coarse pulp washing or lime mud washing.

2. Using this concentration process under its optimal conditions and optimal volume reduction factor, APMP mills could save 4840.6 kwh power and reduce 23.3 m^3 effluent discharge for every ton of pulp produced, and the capital investment in multi-effect evaporation system could also be decreased by 90%.

ACKNOWLEDGMENTS

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