Application of Ultrafiltration in a Paper Mill: Process Water Reuse and Membrane Fouling Analysis

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High water consumption is a major environmental problem that the pulp and paper industry is facing. Ultrafiltration (UF) can be used to remove the dissolved and colloidal substances (DCS) concentrated during the recycling of white water (the process water) to facilitate the reuse of white water and reduce fresh water consumption. However, membrane fouling limits the application of UF in this industry. In this study, super-clear filtrate obtained from a fine paper mill was purified with a polyethersulfone (PES) ultrafiltration membrane to evaluate the reuse performance of the ultrafiltrate. The membrane foulants were characterized by scanning electron microscopy, energy-dispersive spectrophotometry, attenuated total reflection-fourier transform infrared spectroscopy, and gas chromatography-mass spectrometry. The results indicate that the retention rate of stock and the strength properties of paper increased when the ultrafiltrate was reused in the papermaking process compared to when super-clear filtrate was used. The reversible membrane foulants during ultrafiltration accounted for 85.52% of the total foulants and primarily originated from retention aids, drainage aids, and wet strength resins, while the irreversible adsorptive foulants accounted for 14.48% and mostly came from sizing agents, coating chemicals, and others. Moreover, the presence of dissolved multivalent metal ions, especially Ca^{2+}, accelerated membrane fouling.

Keywords: Paper mill white water; Reuse performance; Dissolved and colloidal substances (DCS); Foulant characterization; Foulant identification; Ultrafiltration

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INTRODUCTION

The exploding world population and industrial establishment has accelerated economic growth in the 21st century, creating global water pollution and water shortage issues. The pulp and paper industry is water use-intensive (Buyukkamaci and Koken 2010), ranking third after the metal and chemical industries in terms of worldwide fresh water consumption (Kaya *et al*. 2010). Water consumption by this industry reaches 15 to 60 m^3 per finished tonne of paper. High fresh water consumption and the accumulation of contaminants during the paper manufacturing process contribute to the large volume of effluent from paper mills. It has been estimated that the effluent of the pulp and paper industry is responsible for 50% of all industrial wastes (Zhang *et al*. 2009), and that the effluent volume and chemical oxygen demand (COD) discharged by this industry can reach 38.5 m^3 and 7.5 kg per tonne of paper, respectively. Recently, the pulp and paper industry has been moving toward more intensive recycling of white water to reduce fresh water uptake and satisfy tightened discharge standards. However, white water cannot be recycled easily because dissolved and colloidal substances (DCS) and electrolytes become enriched with greater white water recycling (Yuan *et al*. 2011; Hubbe *et al*. 2012), adversely affecting paper machine runnability and paper quality (Francis and Ouchi 2001; Whipple and Maltesh 2002; Zhang *et al*. 2007).

The DCS in white water mainly comes from fiber extractives and the chemical additives consumed during manufacturing operations (Hubbe *et al*. 2012). They are also called “anionic trash” because of their negative charge (Miao *et al*. 2012). The DCS are generally stably dispersed in the pulp suspension or white water, easily gathering together and forming non-ionic stickies when operating conditions change; they can also react with electrolytes, especially Ca^{2+} and Mg^{2+} (Ordonez *et al*. 2010; Hubbe *et al*. 2012), which interferes with papermaking because the stickies cannot be effectively controlled by normal chemical methods. Most paper mills employ disc filters to recycle white water fines as much as possible, gaining a certain amount of super-clear filtrate to replace fresh water during paper production. However, DCS and electrolytes cannot be eliminated by disc filters (Ordonez *et al*. 2010). Thus, advanced water treatment technologies are required.

Membrane technologies such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) are becoming more widely applied in process water and effluent purification with the aim of water recycling in the pulp and paper industry (Mänttäri *et al*. 2006; Jönsson *et al*. 2008; Beril Gönder *et al*. 2012; Vergili *et al*. 2012) because such technologies offer a high level of contaminant removal with relatively little energy consumption. Moreover, such technologies require small floor space and are easy to fit into existing mill water circuits (Zhang *et al*. 2009). Currently, UF can be used to remove DCS from white water and render the permeate clean enough to replace fresh water as paper machine shower water (Nuortila-Jokinen *et al*. 2004). The permeate can otherwise be reused if it is RO-treated to remove salts (Zhang *et al*. 2009). However, membrane fouling limits the use of UF at a large scale in pulp and paper mills (Puro *et al*. 2011). According to some studies, DCS (especially fatty and resin acids) (Carlsson *et al*. 1998; Puro *et al*. 2002), Ca^{2+} (Li and Elimelech 2004; Abrahamse *et al*. 2008), and Mg^{2+} (Uyak *et al*. 2014) are enriched in process water and can complex, contributing to pore blocking, cake layer formation, and concentration polarization during ultrafiltration (Wang *et al*. 2013), ultimately reducing filtration efficiency. Currently, UF technology can only be used to filter paper mill effluent that has been pre-treated and meets discharge standards. It would be difficult for pulp and paper mills to afford such great expense in treating such large effluent volumes in the long run.

Research has demonstrated the membrane fouling mechanism (Nuortila-Jokinen and Nyström 1996; Costa *et al*. 2006; Kaya *et al*. 2010; Puro *et al*. 2010; 2011; Peter-Varbanets *et al*. 2011; Zhang *et al*. 2012a) and prevention methods (Costa *et al*. 2006; Pinelo *et al*. 2009; Park *et al*. 2010; Zhang *et al*. 2012a), but the characterization and identification of specific membrane foulants is relatively rare because of the complex composition of white water (Cho *et al*. 1998; Puro *et al*. 2002; Her *et al*. 2007). Furthermore, most existing studies have involved filtering of simulated white water (Elefsiniotis *et al*. 1997) or model foulants (Ramamurthy *et al*. 1995) and evaluated the fouling behavior only by flux and retention measurements. Hence, it is desirable to determine the specific white water fractions responsible for membrane fouling so that measures can be taken to remove them. For example, some anionic components of DCS can be bound to fibers and removed from process water together with the wet sheet when using fixatives with relatively low molecular mass and high cationic charge density

(Miao *et al*. 2012), and dissolved multivalent metal ions such as Ca^{2+} can be removed by a modified natural marcomolecular substance called anionized cationic starch (ACS) (Ye *et al*. 2009; Yuan *et al*. 2012). Such work could make it possible for pulp and paper mills to use UF and RO modules, which up to this point mainly have been used after the wastewater treatment plant. By using the modules earlier in the manufacturing process, it may be possible to benefit the safe and stable operation of a papermaking operation. Reverse osmosis permeate can be reused in the papermaking process because of the relatively low electrical conductivity, and the concentrated retentates of UF may be of value (Puro *et al*. 2011). Numerous environmental and economic benefits may be realized (Pizzichini *et al*. 2005) by reducing fresh water consumption and diminishing organic load for external water treatment (Kaya *et al*. 2010; Beril Gönder *et al*. 2012).

In this work, the super-clear filtrate obtained from a disc filter in fine paper mill was investigated to simulate the actual production situation. An ultrafiltration process was used to separate DCS from the white water, and the reuse performance of the ultrafiltrate was evaluated. Scanning electron microscopy (SEM), attenuated total reflection-fourier transform infrared (ATR-FTIR) spectroscopy, and SEM-energy-dispersive spectrophotometry (EDS) were employed to analyze the membrane fouling characteristics, and gas chromatography-mass spectrometry (GC-MS) was carried out to identify the composition and possible origin of membrane foulants. The aim of the present study was to offer ways to prevent the membrane fouling caused by white water from the fountainhead.

EXPERIMENTAL

Materials

Paper mill super-clear filtrate (obtained from a disc filter fed with white water) used as a feed for the ultrafiltration experiments was supplied by UPM (Changshu) Co. Ltd., China. The main properties of the feed are 412.76 mg/L COD, pH 7.3, 1268 μS/cm electrical conductivity, and 648 NTU turbidity. The feed was stored at 5 °C to preserve its characteristics. The pulp used in the experiment was obtained from the machine chest (UPM, China). The proportion of recycled, coated broke was 17%. A stirred, dead-end UF module (MSC-300 Mosu, China) with a temperature controller was used in this study. The membrane area of this filter was 0.00332 m^2, the volume of the feed vessel was 350 mL, and the pressure range was 0 to 3 bar. The UF membranes (Mosu, China) used were made of polyethersulphone (PES) with a nominal cut-off value of 10 kDa.

Methods

Filtration and adsorption procedures

The membranes were pretreated by rinsing three times in an ultrasonic bath with deionized water for 10 min to remove preservatives (Puro *et al*. 2011). A new piece of membrane was used in each filtration. The deionized water and the super-clear filtrate were heated to 40 °C, a common temperature of paper mill waters.

The feed batch was 300 mL, and 225 mL of permeate was collected during the filtration. Thus, 75 mL remained as concentrated liquor. The experiments were performed at pressures of 1 bar. In the adsorption tests, the UF membranes were soaked in the super-clear filtrate at 40 °C and no pressure was used, and the adsorption time was the same as in the filtrations at 1 bar. Each experiment was replicated three times.

Water analysis and evaluation of ultrafiltrate reuse performance

The fresh water, super-clear filtrate, and ultrafiltrate samples were analyzed. The analysis equipment and methods are shown in Table 1.

Table 1. Equipment and Methods Used in Analysis of Water Samples

Analysis	Equipment/Method (Manufacturer)
pH	MP521 pH meter, 25 °C (Sanxin, China)
Conductivity	MP521 Konduktometer, 25 °C (Sanxin, China)
Turbidity	Hach 2100P Turbidimeter, 25 °C (Hach Company, USA)
Total solid content	dry in oven at 105 °C
Cationic demand	Mütek particle charge detector 03 (Mütek, Germany)
DCS content	Centrifuge at 2000 rpm for 20 min with CR21G III Centrifuge (Hitachi, Japan), then collect the supernatant and dry in oven at 105 °C
COD	Potassium dichromate method

The drainage value and retention rate of the stock can be determined with a dynamic drainage jar (DDJ) (Mütek TM DFR-05 BTG, Germany). The pulp (1% oven-dry consistency, 1000 mL) was diluted with fresh water, super-clear filtrate, or ultrafiltrate samples. Chemicals including 1% cationic starch (CS; National Starch, USA), 0.025% cationic polyacrylamide (CPAM; Ciba, Switzerland) (1000 rpm, 1 min), and 0.05% colloidal silica (Eka Chemicals, Holland) (750 rpm, 20 s) were added, in the order listed, and the drainage value was recorded after stirring for 20 s. The temperature of the pulp was maintained at 20 °C. The retention rate was determined under the same conditions as above.

The moisture content of pulp was diluted to 0.2% with three water samples and handsheets were made according to TAPPI standard T205 sp-02 (2002) using a sheet-making apparatus (RK-2A PTI, Austria) with the same experimental conditions and doses of chemicals as above and 20% added ground calcium carbonate (GCC; Daheng, China) as filler. The tensile index, tearing resistance, folding endurance, Cobb value, and whiteness were tested following TAPPI standards T494 om-01 (2001), T414 om-98 (1998), T511 om-02 (2002), T441 om-98 (1998), and T560 wd-03 (2003), respectively.

SEM and SEM-EDS analysis of UF membranes

The SEM analysis was carried out with a Quanta 200 (FEI, USA) both before and after filtration to provide detailed structural information regarding the membranes. The dried membrane samples were fractured under liquid nitrogen, coated with a thin layer of gold prior to analysis (Gönder *et al*. 2011), and examined at an accelerating voltage of 15 to 20 kV. The EDS was used to determine the inorganic foulants present on the membrane surface.

Isolation and characterization of membrane foulants

The membrane foulants were isolated from the fouled membranes by extraction. The UF membrane sample of 0.00332 m^2 was placed in a Soxhlet extractor and extracted with 50 mL of acetone-water solution (1:9, v/v) for 30 min. After extraction, all of the acetone solution was collected to be concentrated by evaporation and then dried in a nitrogen stream and further vacuum-dried at 40 °C. The samples were then weighed to determine the amount of foulants present in the extracted membrane area.

The samples described above may contain polymeric material from the membranes, potentially harming the gas chromatograph (GC) column. Therefore, the samples were diluted in tert-butylmethylether (MTBE) and extracted a second time with liquid-liquid extraction as described by Örså and Holmbom (1994) to remove any polymeric membrane material (Puro *et al*. 2011). A 1-uL MTBE solution obtained was injected into the GC-MS apparatus (Agilent 6890/5793, USA, equipped with NIST05 mass spectral libraries). The column (HP-5MS Agilent, USA) was a 25 m/0.25 mm I.D. wide-bore capillary with a nonpolar phase film thickness 0.25 μm. The injector temperature was 260 °C. The initial column temperature was 150 °C and was programmed to increase to 230 °C at a rate of 7 °C/min starting 0.5 min after injection. The column then heated to 290 °C at 10 °C/min and maintained at that temperature for 10 min. The detector temperature was 290 °C.

To characterize the functional groups of the foulants, an ATR-FTIR apparatus (FTIR-650, China) was used to analyze the surface of both pristine and fouled membrane samples.

RESULTS AND DISCUSSION

Reuse Performance of Process Water Treated by Ultrafiltration

The ultrafiltrate of white water is clean enough to meet the demands of most positions of usage in the papermaking process because of the effective separation of macromolecular solutes and colloids. This study analyzed the quality of fresh water, super-clear filtrate, and its ultrafiltrate and determined the impacts of each water sample on stock and paper properties to evaluate the reuse performance of ultrafiltrate of super-clear filtrate. The results of the water analysis are shown in Table 2.

Table 2. Parameters of Fresh Water and Super-clear Filtrate Before and After Ultrafiltration

Parameter	Super-clear Filtrate	Ultrafiltrate	Fresh Water
COD (mg/L)	412.76	117.76	2.00
pH	7.3	7.3	7.2
Turbidity (NTU)	648	0.80	0.42
Total solids content (mg/L)	1420	680.0	193.3
DCS content (mg/L)	1200	680.0	- *
Cationic demand (μeq/L)	178	13.0	-2.3
Conductivity (μS/cm)	1268	1047	140.7

* This parameter was not analyzed, because there is no DCS (which were concentrated during the recycling of white water) in fresh water.

The quality of ultrafiltrate improved dramatically relative to the initial super-clear filtrate, as shown in Table 2. The COD of the ultrafiltrate decreased by 71.5% as compared to that of the super-clear filtrate, indicating that most organic contaminants in the feed were removed by UF treatment, although the value is still higher than that of fresh water. The turbidity and total solid content of super-clear filtrate were dramatically decreased by UF, which demonstrated the effective removal of macromolecular colloids (Yuan *et al*. 2011). Zhang *et al*. (2012b) found that the paper machine, the application of paper additives, and paper properties performed well when reusing white water with DCS below 900 mg/L. According to the results of this experiment (Table 2), the cationic demand of the ultrafiltrate decreased by 92.7% and the DCS content of the ultrafiltrate can be controlled to within this effective scope. However, the UF process cannot remove electrolytes; the slight drop in the conductivity of the ultrafiltrate may be due to the polyelectrolyte complexes of DCS with a few electrolytes, which can be removed by UF membranes. High conductivity limits the reuse of ultrafiltrate to some extent (Yuan *et al*. 2011), but it is possible for the ultrafiltrate to be reused at a position with higher demand if further treated by NF and RO.

Table 3. Impact of Fresh Water and Super-clear Filtrate Before and After UF on Stock and Paper Properties

Parameters		Super-clear Filtrate	Ultrafiltrate	Fresh Water
Stock Properties	Total retention rate (%)	69.1	82.7	86.5
	Ash retention rate (%)	43.6	58.3	61.3
	20s drainage value (mL)	408	418	434
Paper Properties	Tensile index ($N\cdot m\cdot g^{-1}$)	29.07	31.23	31.64
	Tearing resistance ($mN\cdot m^{2}\cdot g^{-1}$)	5.00	6.00	6.10
	Folding endurance (number of times)	6.00	8.00	9.00
	CIE whiteness (%)	84.73	83.87	84.12

The impact of each of the water samples on stock and paper properties are shown in Table 3. The retention rate of stock was increased greatly when the ultrafiltrate was reused to dilute pulp compared with the direct reuse of super-clear filtrate, and the value was close to that when fresh water was used. A recent study demonstrated that DCS adsorb onto the surface of cationic additives before fibers and can form deposits with electrolytes (especially Ca^{2+} or other multivalent ions), hindering connections between fibers and adsorption between fibers and additives (Yuan *et al*. 2011) and contributing to the loss of fines from the wire. The UF treatment can remove a large amount of the DCS present in super-clear filtrate, ultimately increasing the stock retention rate, the total retention rate, and the ash retention rate by 19.7 and 33.7%, respectively. The DCS have adverse effects on stock drainage, to some degree (Dai *et al*. 2008), but the reuse of ultrafiltrate resulted in only a minor increase in drainage value.

As shown in Table 3, the strength properties of the paper increased dramatically when the ultrafiltrate was used compared with the direct reuse of super-clear filtrate, mainly because the residual fillers and DCS in super-clear filtrate obstruct connections between fibers. Removing these contaminants with UF can increase the binding force between fibers and improve paper strength. The reuse of ultrafiltrate had a slight negative impact on the whiteness of the paper, and the whiteness of the paper made with super-clear filtrate was higher than that made with ultrafiltrate or fresh water. This is likely because the dyes absorbed on the surface of fillers and DCS remained in the super-clear filtrate.

SEM and EDS Analysis of Pristine and Fouled Membranes

To visualize the fouling on the UF membrane surface and pores caused by process waters, SEM images were generated before and after filtration. Figure 1 shows the SEM images of both pristine and fouled membranes.

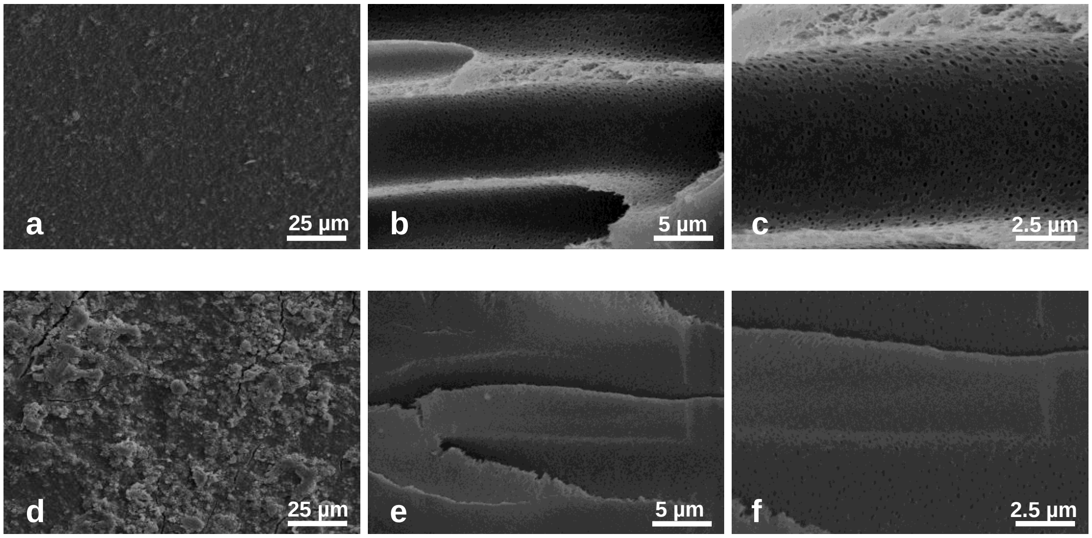

Fig. 1. SEM images of (a) pristine UF membrane surface; (b) cross-section of pristine membrane; (c) cross-section of pristine membrane; (d) fouled membrane surface fed with super-clear filtrate; (e) cross-section of fouled membrane fed with super-clear filtrate; and (f) cross-section of fouled membrane fed with super-clear filtrate

As can be seen from the SEM images in Fig. 1, the pristine UF membrane, with its asymmetric and compact cortical structure, had a clean, smooth surface (Fig. 1a). The sublayer inside the membrane had many finger-like holes (Fig. 1b) with homogeneous and compact pores on their walls (Fig. 1c); most macromolecular colloids can be retained by these pores. However, morphological variations occurred on the fouled membranes (Figs. 1d, 1e, and 1f). A thick fouling layer was formed on the surface of the membrane after ultrafiltration of the super-clear filtrate. Deposition can also be seen in the form of nodules and aggregates (Fig. 1d). The inside diameter of the finger-like holes visually decreased (Fig. 1e) and the size of pores clearly visible before ultrafiltration seemed to decrease, with some even disappearing as a result of pore blocking (Fig. 1f). Low-molecular weight materials entered into the holes during the earlier stage of ultrafiltration and adsorbed onto the hole walls or blocked the pores, inhibiting flux. Simultaneously, the macromolecular contaminants were retained on the surface of the membrane and gradually formed a cake layer as ultrafiltration continued. The results above agree with those of Kaya (2010) in the SEM measurements of a NF membrane fed with white water. According to recent studies, pore blocking can occur during the filtration of pulp and paper mill wastewater by UF even at optimal operating conditions (Gönder *et al*. 2012).

Springer *et al*. (1985) reported that Na^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, and some other ions accumulate during white water recirculation, and that these ions affect the ultrafiltration process. An EDS analysis was performed to detect the elements present on the surfaces and cross-sections of pristine and fouled PES membranes, in conjunction with the SEM observation, to explore the influence of metal ions on membrane fouling. The results and EDS spectra are presented in Table 4 and Fig. 2, respectively.

Table 4. Elemental Composition of Pristine and Fouled Membranes

Element	Pristine Membrane				Fouled Membrane			
	Membrane Surface		Cross-section		Membrane Surface		Cross-section	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
C	40.18	53.07	56.81	67.69	36.18	46.69	52.34	64.87
O	35.15	34.85	29.09	26.02	47.84	46.36	27.98	26.03
S	20.52	10.15	13.15	5.87	3.73	1.80	17.86	8.29
Cl	0.53	0.24	0.41	0.17	0.35	0.15	0.58	0.24
Na	0.70	0.49	0.24	0.15	1.06	0.71	0.31	0.20
Ca	2.64	1.04	0.31	0.11	10.35	4.00	0.76	0.28
Mg					0.19	0.12	0.09	0.06
Al	0.28	0.16			0.25	0.14		
Fe							0.08	0.02

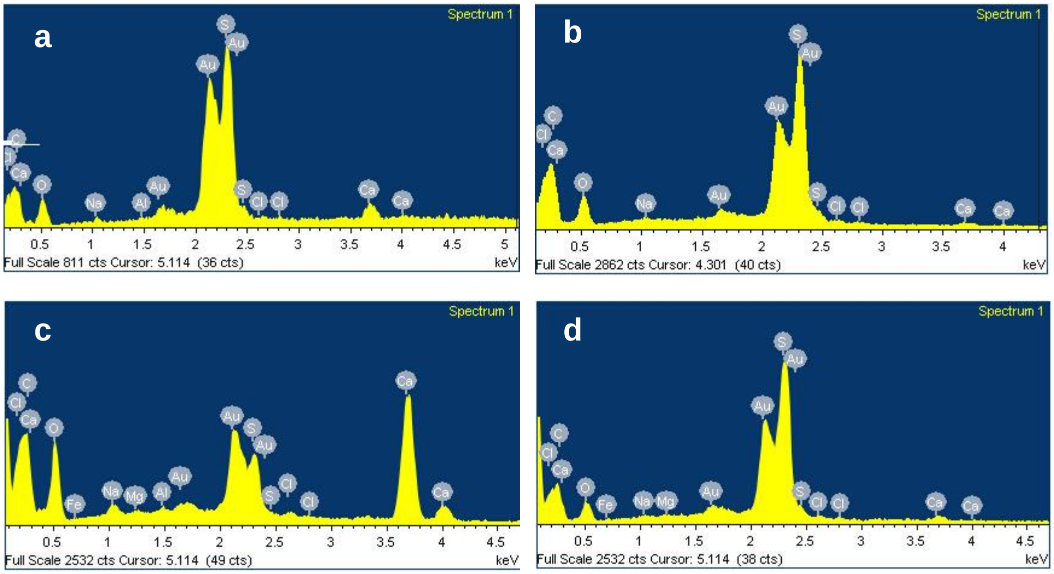

Fig. 2. EDS spectra of (a) pristine membrane surface; (b) cross-section of pristine membrane; (c) fouled membrane surface; and (d) cross-section of fouled membrane

As can be seen in Table 4, carbon, oxygen, and sulfur were the main elements detected in the pristine PES membrane, which agrees with the elemental composition of the PES. However, the elemental proportion on the surface was different from that on the cross-section of the membrane, and trace amounts of sodium, calcium, and aluminum were detected in the pristine membrane, and these can be mainly attributed to the phase-inversion membrane preparation method. The carbon, oxygen, and sulfur contents in the fouled membrane fed with super-clear filtrate were different from those in the pristine PES membrane, and the sodium, calcium, magnesium, and iron contents increased, due to the coexistence of PES material and foulants including organic and inorganic materials.

It is clear that the presence of most metal elements on the membrane surface, especially calcium, increased drastically following ultrafiltration and that most were higher than those of the cross-section. Multivalent metal ions, especially Ca^{2+}, can easily disturb the stability of DCS *via* a Ca-DCS complex and aggregate formation, thus being retained on the membrane surface (Bobacka *et al*. 1998). Meanwhile, electrostatic repulsion between anionic hydrophobic colloids and negatively-charged, hydrophilic PES membrane prevented the colloids from entering into membrane pores, thus contributing to the fouling layer on the membrane surface formed by the complexing of rejected colloids with metal ions in the feed (Kim and Jang 2006). Sodium ions (Na^+), present at relatively high concentration in the super-clear filtrate, existed in a free form so they cannot be removed by ultrafiltration and only an insignificant amount of sodium was detected in the fouled membrane. The results suggest that membrane fouling because of the instability and aggregation of DCS can theoretically be prevented by controlling the content of multivalent metal ions, especially Ca^{2+}, in the white water.

ATR-FTIR Analysis of Pristine and Fouled Membranes

The major or representative functional groups of the pristine and fouled membrane samples were analyzed with ATR-FTIR spectroscopy and are compared in Fig. 3.

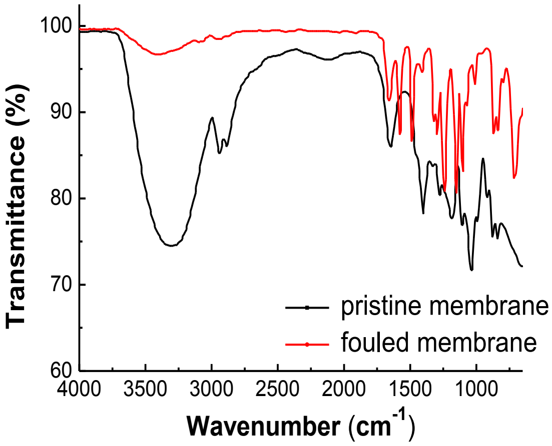

Fig. 3. ATR FTIR-spectra of pristine and fouled membranes fed with super-clear filtrate

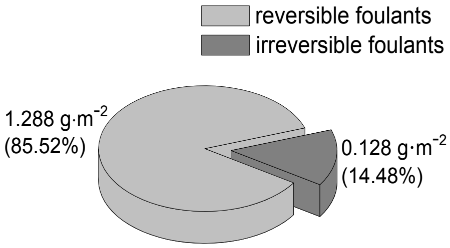

Fig. 4. Content of UF membrane PES foulants

As is shown in Fig. 3, the pristine membrane exhibited IR peaks representing aromatic double bonded carbons (3320 cm^{-1}), aromatic bands (1643 cm^{-1}), and the =C–H bonds of p-disubstituted benzene (841 cm^{-1}), suggesting the presence of an aromatic ring structure within the membrane material. The above-mentioned peaks, as well as the distinct absorption peaks ascribed to the stretching vibration of =C–O–C from aromatic ether (1040 cm^{-1}) and to the symmetric vibration of SO_2 groups (1272 cm^{-1}), all agree with the functional groups of PES material of the membrane (Cho *et al*. 1998). However, the peaks at 3320 and 1040 cm^{-1} and the C–H bond peaks from methyl groups (around 2940, 2880, and 1400 cm^{-1}) disappeared in the spectra of the fouled membrane, resulting from the covering of the membrane surface with foulants. In addition, new peaks representing aromatic bands (around 1580 and 1490 cm^{-1}), the C–O bonds of hydroxy acids or the C–N bonds of amide group (1230 cm^{-1}), and the C-O vibrations of esters or acid anhydride (1160 cm^{-1}) appeared in the spectra of the fouled membrane, indicating trace residues of organic foulants from the super-clear filtrate, potentially originating from the polyacrylamide retention and drainage aids, internal sizing agents, coating latex, or elsewhere. The specific origin cannot be identified by ATR-FTIR analysis because of the complexity of the components in white water.

Quantitative Analysis and Identification of Membrane Foulants

Membrane fouling, consisting of both reversible and irreversible fouling, occurred during the ultrafiltration of white water. Reversible fouling was caused by pore blocking, concentration polarization, or a gel layer forming on the membrane surface and can be easily cleaned. Irreversible fouling resulted from adsorption of foulants onto membrane pores and can only be remedied by chemical cleaning, a key limitation of the UF membrane application.

Figure 4 illustrates that the total amount of membrane foulants present after filtration of super-clear filtrate was 1.506 g/m^2, of which 1.288 g/m^2 (85.52%) were reversible foulants and 0.128 g/m^2 were (14.48%) irreversible foulants.

The GC-MS can be used to determine the specific chemical components within the membrane foulants. Because the chemical additives consumed in UPM are already known, the possible origins of the component corresponding to each peak can be inferred from the GC-MS results and the amount of each component present can be calculated according to the relative peak area. According to the analysis of the main peaks in the total ion chromatograms (Figs. 5 and 6), the main components and possible origins of total foulants and adsorptive foulants are presented in Tables 5 and 6, respectively.

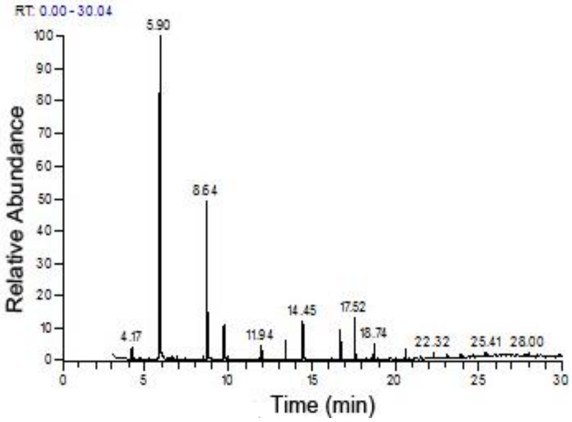

Fig. 5. The total ion chromatogram of total foulants

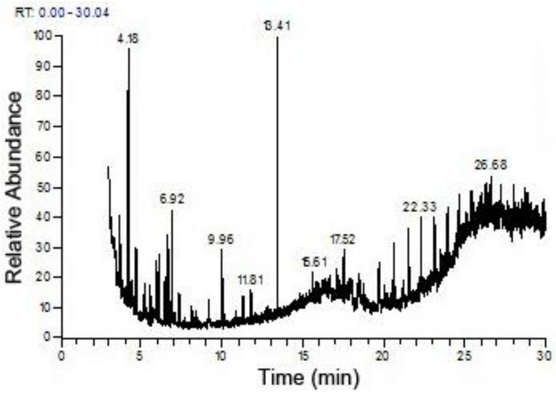

Fig. 6. The total ion chromatogram of adsorptive foulants

Table 5. Main Components and Possible Origins of Total Foulants of UF Membrane

RT (min)	Relative Content (%)	Compound Name	Formula	Possible Origin
5.90	61.21	N-isopropyl-acrylamide	$C_6H_{11}NO$	polyacrylamide
8.64	16.06	1,1,4,7,7-pentamethyl diethylenetriamine	$C_9H_{23}N_3$	polyamide polyamine epichlorhydrin (PAE) resin
13.41	1.52	Butylated Hydroxytoluene	$C_{15}H_{24}O$	oxidant for polyester or resin
17.52	3.14	Phthalic acid diisobuty esterl	$C_{16}H_{22}O_4$	plasticizer

As shown in Fig. 5 and Table 5, the main causes of filtration membrane fouling were N-isopropyl-acrylamide and 1,1,4,7,7-pentamethyl diethylenetriamine. These had contents of 0.922 and 0.242 g/m^2, respectively, calculated according to their peak areas.

Table 6. Main Components and Possible Origins of Adsorptive Foulants of UF Membrane

RT (min)	Relative Content (%)	Compound Name	Formula	Possible Origin
3.65	6.54	4-hydroxy-4methyl-2-pentanone	$C_6H_{12}O_2$	antiseptics
6.46	2.68	2,4,4-trimethyl-2-pentene	C_8H_{16}	plasticizer
6.61	5.32	Dicyclopentadiene	$C_{10}H_{12}$	polyester resin surface sizing agent
6.92	7.87	2-isopropyl-cyclohexanol	$C_9H_{18}O$	plasticizer; surfactant
7.36	1.89	2,6-dimethylhepta-1,3,5-triene	C_9H_{14}	surfactant
9.19	2.77	3,7-dimethyl-1,7-octanedio	$C_{10}H_{22}O_2$	plasticizer; dispersant; defoaming agent
9.96	3.93	Dicyclopentadiene	$C_{10}H_{12}$	polyester resin surface sizing agent
13.41	12.43	Butylated Hydroxytoluene	$C_{15}H_{24}O$	oxidant for polyester or resin
15.61	2.06	2,6-di-tert-butyl-4-(dimethylaminomethyl)p	$C_{17}H_{29}NO$	oxidant for polyester or resin
17.08	1.93	Phenanthrene	$C_{14}H_{10}$	polyester resin surface sizing agent; dye
17.53	2.39	Dibutyl phthalate	$C_{16}H_{22}O_4$	plasticizers or biocide
18.43	2.59	Hexadecanoic acid	$C_{16}H_{32}O_2$	emulsifying agent; internal sizing agent

It can be inferred from knowledge of the paper additives used that the N-isopropyl-acrylamide may come from the polyacrylamide, widely used as retention and drainage aid or a reinforcing agent by the paper industry. Diethylenetriamine is a main component in the organic synthesis of the PAE resin used as wet strength agent (Obokata and Isogai 2004), so the 1,1,4,7,7-pentamethyl diethylenetriamine likely originates from the inefficient production of PAE resins.

It can be clearly seen from Fig. 6 and Table 6 that the adsorptive foulants were complex, though their absolute contents were relatively low. Butylated hydroxytoluene may come from an oxidant for a polyester or resin; the dicyclopentadiene may be derived from unsaturated polyester resins released mainly by surface sizing agents. In addition, the plasticizer shown in Table 6 may come from coating latexes released by the coated broke recovery process or from sizing agents. The hexadecanoic acid may originate from dispersants, emulsifying agents, or internal sizing agents and the phenanthrene may come from polyester resin surface sizing agents or dyes.

The specific components of ultrafiltration membrane foulants from fine paper mill white water mostly orginate from the chemical additives used in the paper manufacturing process and their ineffective manufacture and use, rather than from wood extractives. This finding disagrees with the preceding results of a study of ultrafiltration of ground wood mill (GWM) circulation water (Puro *et al*. 2002).

CONCLUSIONS

1. The quality of ultrafiltrates improved significantly following UF of paper mill super-clear filtrate by PES membranes with a cut-off value of 10 kDa.

2. The DCS content in ultrafiltrate can be controlled to within a stable range, with slight decreases in conductivity, using ultrafiltration.
3. When ultrafiltrate was reused in the papermaking process, the retention rate of stock increased greatly over the value achieved with the direct reuse of super-clear filtrate and was close to the value achieved when fresh water was used.
4. The increase in the drainage value of stock following ultrafiltration was slight, whereas the paper strength properties increased dramatically and the whiteness was slightly reduced.
5. Reversible fouling was the major form of fouling during ultrafiltration of super-clear filtrate and included deposits of foulants on the membrane surface and pore blocking. Reversible membrane foulants accounted for 85.52% (1.288 g/m^2) of the total membrane foulants, while irreversible adsorptive foulants accounted for 14.48% (0.218 g/m^2).
6. The membrane foulants during the filtration of super-clear filtrate mainly originated from the chemical additives used in paper manufacturing process and their ineffective use. The reversible membrane foulants came mostly from retention and drainage aids, reinforcing agents, and wet strengthening resins whereas the irreversible adsorptive foulants (which play a pivotal role in limiting UF technology application) came mainly from sizing agents, coating chemicals, dispersants, and other sources.
7. Dissolved multivalent metal ions, especially Ca^{2+}, accelerated membrane fouling *via* the formation of a Ca-DCS complex and the formation of aggregates that were retained on the membrane surface.
8. The key to preventing membrane fouling in the ultrafiltration of paper mill process water is reducing the dissolved multivalent metal ion content (especially Ca^{2+}) and the amount of paper additives lost in the white water during pretreatment. Another helpful technique would be to choose membrane cleaning protocols according to the characteristics of the membrane foulants.
9. The insights gained from this study can make it possible for the pulp and paper industry to reduce its fresh water consumption and use UF, currently used following the waste water treatment plant, earlier in the manufacturing process.

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REFERENCES CITED

Abrahamse, A. J., Lipreau, C., Li, S., and Heijman, S. (2008). "Removal of divalent cations reduces fouling of ultrafiltration membranes," *J. Membr. Sci.* 323(1), 153-158. DOI: 10.1016/j.memsci.2008.06.018

Bobacka, V., Nasman, J., and Eklund, D. (1998). "Interactions between cationic starch and anionic trash of a peroxide-bleached TMP at different salt concentrations," *J. Pulp Pap. Sci.* 24(3), 78-81.

Buyukkamaci, N., and Koken, E. (2010). "Economic evaluation of alternative wastewater treatment plant options for pulp and paper industry," *Sci. Total Environ.* 408(24), 6070-6078. DOI: 10.1016/j.scitotenv.2010.08.045

Carlsson, D. J., Dal-Cin, M. M., Black, P., and Lick, C. N. (1998). "A surface spectroscopic study of membranes fouled by pulp mill effluent," *J. Membr. Sci.* 142(1), 1-11. DOI: 10.1016/S0376-7388(97)00305-0

Cho, J., Amy, G., Pellegrino, J., and Yoon, Y. (1998). "Characterization of clean and natural organic matter (NOM) fouled NF and UF membranes, and foulants characterization," *Desalination* 118(1), 101-108. DOI: 10.1016/S0011-9164(98)00100-3

Costa, A., Depinho, M., and Elimelech, M. (2006). "Mechanisms of colloidal natural organic matter fouling in ultrafiltration," *J. Membr. Sci.* 281(1-2), 716-725. DOI: 10.1016/j.memsci.2006.04.044

Dai, H., Qian, M., and Ye, C. (2008). "The effects of dissolved and colloidal substances on water retention value and drainage performance of fiber fines," *Transactions of China Pulp and Paper* 23(3), 77-79. DOI: 10.3321/j.issn:1000-6842.2008.03.018

Elefsiniotis, P., Hall, E. R., and Johnson, R. M. (1997). "Removal of contaminants from recirculated white water by ultrafiltration and/or biological treatment," *Can. J. Chem. Eng.* 75(1), 88-94. DOI: 10.1002/cjce.5450750115

Francis, D. W., and Ouchi, M. D. (2001). "Effect of dissolved and colloidal solids on newsprint properties," *J. Pulp Pap. Sci.* 27(9), 289-295.

Gönder, B. Z., Arayici, S., and Barlas, H. (2011). "Advanced treatment of pulp and paper mill wastewater by nanofiltration process: Effects of operating conditions on membrane fouling," *Sep. Purif. Technol.* 76(3), 292-302. DOI: 10.1016/j.seppur.2010.10.018

Gönder, B. Z., Arayici, S., and Barlas, H. (2012). "Treatment of pulp and paper mill wastewater using utrafiltration process: Optimization of the fouling and rejections," *Ind. Eng. Chem. Res.* 51(17), 6184-6195. DOI: 10.1021/ie2024504

Her, N., Amy, G., Plottu-Pecheux, A., and Yoon, Y. (2007). "Identification of nanofiltration membrane foulants," *Water Res.* 41(17), 3936-3947. DOI: 10.1016/j.watres.2007.05.015

Hubbe, M. A., Sundberg, A., Mocchiutti, P., Ni, Y., and Pelton, R. (2012). "Dissolved and colloidal substances (DCS) and the charge demand of papermaking process waters and suspensions: A review," *BioResources* 7(4), 6109-6193. DOI: 10.15376/biores.7.4.6109-6193

Jönsson, A. S., Nordin, A. K., and Wallberg, O. (2008). "Concentration and purification of lignin in hardwood kraft pulping liquor by ultrafiltration and nanofiltration," *Chem. Eng. Res. Des.* 86(11), 1271-1280. DOI: 10.1016/j.cherd.2008.06.003

Kaya, Y., Gönder, B. Z., Vergili, I., and Barlas, H. (2010). "The effect of transmembrane pressure and pH on treatment of paper machine process waters by using a two-step nanofiltration process: Flux decline analysis," *Desalination* 250(1), 150-157. DOI: 10.1016/j.desal.2009.06.034

Kim, I. S., and Jang, N. (2006). "The effect of calcium on the membrane biofouling in the membrane bioreactor (MBR)," *Water Res.* 40(14), 2756-2764. DOI: 10.1016/j.watres.2006.03.036

Li, Q., and Elimelech, M. (2004). "Organic fouling and chemical cleaning of nanofiltration membranes: Measurements and mechanisms," *Environ. Sci. Technol.* 38(17), 4683-4693. DOI: 10.1021/es0354162

Mänttäri, M., Viitikko, K., and Nyström, M. (2006). "Nanofiltration of biologically treated effluents from the pulp and paper industry," *J. Membr. Sci.* 272(1), 152-160. DOI: 10.1016/j.memsci.2005.07.031

Miao, Q., Huang, L., and Chen, L. (2012). "Advances in the control of dissolved and colloidal substances present in papermaking processes: A brief review," *BioResources* 8(1), 1431-1455. DOI: 10.15376/biores.8.1.1431-1455

Nuortila-Jokinen, J., Mänttäri, M., Huuhilo, T., Kallioinen, M., and Nyström, M. (2004). "Water circuit closure with membrane technology in the pulp and paper industry," *Water Sci. Technol.* 50(3), 217-227.

Nuortila-Jokinen, J., and Nyström, M. (1996). "Comparison of membrane separation processes in the internal purification of paper mill water," *J. Membr. Sci.* 119(1), 99-115. DOI: 10.1016/0376-7388(96)00118-4

Obokata, T., and Isogai, A. (2004). "1H-and 13C-NMR analyses of aqueous polyamideamine-epichlorohydrin resin solutions," *J. Appl. Polym. Sci.* 92(3), 1847-1854. DOI: 10.1002/app.20166

Ordóñez, R., Hermosilla, D., and Blanco, A. (2010). "Replacement of fresh water use by final effluent recovery in a highly optimized 100% recovered paper mill," *Water Sci. Technol.* 62(7), 1694-1703. DOI: 10.2166/wst.2010.933

Örsa, F., and Holmbom, B. (1994). "A convenient method for the determination of wood extractives in papermaking process waters and effluents," *J. Pulp Pap. Sci.* 20(12), J361-J366.

Park, C., Hong, S., Chung, T. H., and Choi, Y. (2010). "Performance evaluation of pretreatment processes in integrated membrane system for wastewater reuse," *Desalination* 250(2), 673-676. DOI: 10.1016/j.desal.2009.03.023

Peter-Varbanets, M., Margot, J., Traber, J., and Pronk, W. (2011). "Mechanisms of membrane fouling during ultra-low pressure ultrafiltration," *J. Membr. Sci.* 377(1-2), 42-53. DOI: 10.1016/j.memsci.2011.03.029

Pinelo, M., Jonsson, G., and Meyer, A. S. (2009). "Membrane technology for purification of enzymatically produced oligosaccharides: Molecular and operational features affecting performance," *Sep. Purif. Technol.* 70(1), 1-11. DOI: 10.1016/j.seppur.2009.08.010

Pizzichini, M., Russo, C., and Meo, C. D. (2005). "Purification of pulp and paper wastewater, with membrane technology, for water reuse in a closed loop," *Desalination* 178(1-3), 351-359. DOI: 10.1016/j.desal.2004.11.045

Puro, L., Tanninen, J., and Nyström, M. (2002). "Analyses of organic foulants in membranes fouled by pulp and paper mill effluent using solid-liquid extraction," *Desalination* 143(1), 1-9. DOI: 10.1016/S0011-9164(02)00215-1

Puro, L., Kallioinen, M., Mänttäri, M., Natarajan, G., Cameron, D. C., and Nyström, M. (2010). "Performance of RC and PES ultrafiltration membranes in filtration of pulp mill process waters," *Desalination* 264(3), 249-255. DOI: 10.1016/j.desal.2010.06.034

Puro, L., Kallioinen, M., Mänttäri, M., and Nyström, M. (2011). "Evaluation of behavior and fouling potential of wood extractives in ultrafiltration of pulp and paper mill process water," *J. Membr. Sci.* 368(1-2), 150-158. DOI: 10.1016/j.memsci.2010.11.032

Ramamurthy, P., Poole, R., and Dorica, J. G. (1995). "Fouling of ultrafiltration membranes during treatment of CTMP screw press filtrates," *J. Pulp Pap. Sci. 21*(2), J50-J54.

Springer, A. M., Dullforce, J. P., and Wegner, T. H. (1985). "The effects of closed white water system contaminants on strength properties of paper produced from secondary fiber," *TAPPI J.* 68(4), 78-82.

TAPPI T205 sp-02. (2002). "Forming handsheets for physical tests of pulp," *TAPPI Press*, Atlanta, GA.

TAPPI T414 om-88. (1988). "Internal tearing resistance of paper (Elmendorf-type method)," *TAPPI Press*, Atlanta, GA.

TAPPI T441 om-98. (1998). "Water absorptiveness of sized (non-bibulous) paper and paperboard (Cobb test)," *TAPPI Press,* Atlanta, GA.

TAPPI T494 om-01. (2001). "Tensile breaking properties of paper and paperboard (using constant rate of elongation apparatus)," *TAPPI Press*, Atlanta, GA.

TAPPI T511 om-02. (2002). "Folding endurance of paper (MIT Tester)," *TAPPI Press*, Atlanta, GA.

TAPPI T560 wd-03. (2003). "CIE whiteness and tint of paper and paperboard (using d/0º, diffuse illumination and normal viewing)," *TAPPI Press*, Atlanta, GA.

Uyak, V., Akdagli, M., Cakmakci, M., and Koyuncu, I. (2014). "Natural organic matter removal and fouling in a low pressure hybrid membrane systems," *The Scientific World J.* 2014, 1-11. DOI: 10.1155/2014/893203

Vergili, I., Kaya, Y., Sen, U., Gönder, Z. B., and Aydiner, C. (2012). "Techno-economic analysis of textile dye bath wastewater treatment by integrated membrane processes under the zero liquid discharge approach," *Resour. Conserv. Recycl.* 58, 25-35. DOI: 10.1016/j.resconrec.2011.10.005

Wang, X., Sun, H., Fang, C., Wang, Z., and Gao, X. (2013). "Preparation and characterization of antibacterial polyethersulfone (PES) UF membrane," *Technol. Water Treat.* 39(4), 45-48. DOI: 10.3969/j.issn.1000-3770.2013.04.011

Whipple, W. L., and Maltesh, C. (2002). "Adsorption of cationic flocculants to paper slurries," *J. Colloid Interf. Sci.* 256(1), 33-40. DOI: 10.1006/jcis.2001.7867

Ye, C., Dai, H., and Wang, C. (2009). "Study on the ACS as adsorbent of calcium ions," *Trans. China Pulp Paper* 24(1), 85-90. DOI: 10.3321/j.issn:1000-6842.2009.01.019

Yuan, G., Dai, H., Ye, C., Zhang, Y., and Wang, Z. (2011). "Adsorption of Ca (II) from aqueous solution onto cellulosic fibers and its impact on the papermaking process," *BioRes.* 6(3), 2790-2804. DOI: 10.15376/biores.6.3.2790-2804

Yuan, G., Dai, H., and Zhang, Y. (2012). "Mathematical analysis of calcium ions controlling by ACS," *Trans. China Pulp Paper* 27(1), 1-7. DOI: 10.3969/j.issn.1000-6842.2012.01.001

Zhang, H., He, Z., Ni, Y., Hu, H., and Zhou, Y. (2007). "Characteristics of dissolved and colloidal substances in high yield pulp and their impact on filler retention," *Appita J.* 60(5), 390-395.

Zhang, Y., Ma, C., Ye, F., Kong, Y., and Li, H. (2009). "The treatment of wastewater of paper mill with integrated membrane process," *Desalination* 236(1-3), 349-356. DOI: 10.1016/j.desal.2007.10.086

Zhang, Y., Cao, C., Feng, W., and Xu, M. (2012a). "Chemical cleaning of a polyethersulfone membrane used for concentrating the effluent from alkaline peroxide mechanical pulping plants," *Environ. Eng. Sci.* 29(11), 1020-1025. DOI: 10.1089/ees.2011.0431

Zhang, M., Wang, R., Qin, Y., Ma, X., and Ma, M. (2012b). "Application of DCS control in closed white water circulation in a high-speed twin wire paper machine," *China Pulp & Paper Ind.* 33(18), 50-52. DOI: 10.3969/j.issn.1007-9211.2012.18.013

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