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Flux decline control in nanofiltration of detergent wastewater by a shear-enhanced filtration system

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ABSTRACT

Treatment of wastewater containing a cleaning-in-place detergent was investigated by using a rotating disk module equipped with a nanofiltration (NF) membrane. At a rotational speed of 2000 rpm, a pH 7.2 and 25 °C, the permeate flux reached a plateau at 350 Lm^{-2} h^{-1} above 35 bar while rejection of conductivity and COD were respectively 93 and 97%. When a pretreatment by ultrafiltration (UF) was carried out before the NF, the NF flux increased linearly with TMP to reach 450 Lm^{-2} h^{-1} at 40 bar while COD of NF permeate was a little lower than without pretreatment. Both permeate flux and conductivity rejection increased with increasing pH. High membrane shear rates prevented flux decline with time, as surfactant molecules were dragged away from membrane surface, preventing surfactant aggregates formation. The disk rotational speed necessary for flux stability increased with TMP from 1000 rpm at 10 bar to 2000 rpm at 30 bar. Increasing feed pH had a similar effect by enhancing electrostatic repulsion between surfactant molecules and membrane. Raising the temperature to 45 °C increased the permeate flux to over 500 Lm^{-2} h^{-1} at 30 bar and 2000 rpm. This work confirms the high performance of high shear dynamic filtration in detergent wastewater treatment by NF system both in terms of permeate flux and ion and COD rejections due to reduction in concentration polarization, so that a UF pretreatment was not necessary.

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1. Introduction

The detergent industry, manufacturing liquid dishwasher detergents, shower gel and shampoo, generates a large amount of wastewater containing a large amount of surfactant, which mostly results from cleaning-in-place (CIP) and disinfecting procedures after every change of product. This effluent can cause significant environmental problems because surfactants are hazardous and toxic to aquatic life and soils [1]. Therefore, a number of technologies were used to purify detergent wastewater, such as chemical flocculation, foam fractionation, Fenton oxidation [2], aerobic biodegradation [3] and membrane filtration [4]. Economic considerations require that both recyclable water and organic compounds recovery are achieved in the treatment of CIP wastewater. Thus, membrane technology is the only one satisfying these two requirements simultaneously, as surfactants can be concentrated by ultrafiltration (UF) and/or nanofiltration (NF) for reutilization while permeate can be reused as CIP water [5–8].

Although UF separates and concentrates surfactant micelles efficiently when surfactant concentration at membrane surface is above the critical micelle concentration [9], its permeate is still not reusable [4]. However, NF, as a technology using both electric charge (Donnan effect) and pore size (sieving effect), can better reject small molecules of molecular mass up to 200 g mol^{-1} and ions than UF and is preferable to treat detergent wastewater with a low surfactant concentration. Archer et al. [10] first tested the performance of several NF membranes for filtrating an anionic surfactant solution, and showed that surfactant rejection could reach 99% for a certain NF membrane. Cornelis et al. [6] found that NF membranes with lower contact angle and molecular weight cutoff (MWCO) were more desirable, and NF270 was thought to be the most suitable membrane due to its high water permeability and antifouling property among NF membranes. Kaya et al. [11] reported that negative charged membranes were adapted to separation of anionic surfactants but non-ionic surfactants should be treated by uncharged membranes. Due to the outstanding surfactant rejection by NF, Goers and Wozny [4] proposed a two-step UF/NF-system for product recovery from detergent wastewater, where UF was used to concentrate a solution containing surfactant and a NF step was necessary for water purification. Furthermore, a two-step NF process was also presented for improving

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Nomenclature

A	effective membrane area (m^2)
CIP	cleaning-in-place
COD	chemical oxygen demand (mgO$_2$ L^{-1})
J	permeate flux (Lm^{-2} h^{-1})
k	velocity factor (0.89 for this system)
L_p	pure water permeability (Lm^{-2} h^{-1} bar^{-1})
p_c	peripheral pressure (bar)
R	module housing inner diameter (m)
R_{app}	apparent rejection (%)
RDM	rotating disk membrane
t	filtration time (h)
TMP	transmembrane pressure (bar)
V_O	initial feed volume (L)
V_p	permeate volume (L)
V_C	concentrate volume (L)
VRR	volume reduction rate
X_f	COD or conductivity in feed
X_p	COD or conductivity in permeate

Greek letters

γ_m	mean shear rate at membrane (s^{-1})
ρ	fluid density (g L^{-1})
ν	fluid kinematic viscosity (m^2 s^{-1})
ω	angular velocity (rad s^{-1})

permeate water quality, and both model and real detergent wastewaters were treated using this new strategy [8,12].

However, a major limitation in applying NF technology to treat wastewater is the flux decline due to concentration polarization and membrane fouling, especially for detergent wastewater because surfactant molecules tend to assemble at interfaces [9]. Wendler et al. [13] found that, when permeate flux increased to more than 60 Lm^{-2} h^{-1}, a "dilution effect" due to permeate flux increase as the permeate was diluted by increasing water flux at a higher pressure, was defeated by the higher concentration polarization as more solutes passed through the membrane, and, thus, surfactant concentration in permeate rose. According to data reported by Kaya et al. [11], the permeate flux decreased to 20–80% of initial values (30–170 Lm^{-2} h^{-1}) after 200 min of NF of anionic or non-ionic surfactant at 12 bar. While operating at a much higher permeate flux, Kertész et al. [14] found that the flux declined by as much as 50% in 15 min when initial flux was about 500 Lm^{-2} h^{-1}. The flux decline was mainly caused by surfactant adsorption on membrane surface or pores wall at a high permeate flux [9,15]. Moreover, these results were obtained in treatment of model surfactant solutions, and because of the complex composition of real wastewater, flux decline was thought to be more serious when a real detergent wastewater was concentrated by NF. Therefore, Gönder et al. [8] recently optimized the filtration conditions to control flux decline in concentration of shampoo CIP wastewater by NF, and found that, operating at neutral pH, low temperature and small pressure were more desirable. However, a very effective method to control flux decline is to increase the shear rate at membrane surface, which can prevent the deposition of surfactant molecules at membrane surface, thus decreasing concentration polarization and fouling. Because of the strong adsorption and agglomeration properties of surfactants [9], once an adsorption layer of surfactant forms on the membrane when the membrane shear rate is not high enough, other surfactant molecules in bulk solution easily aggregate on the adsorption layer, and the concentration polarization layer thickens, or transforms into a gel layer. This was the reason why the flux declined so severely in preceding studies [8,11,14].

Therefore, for controlling flux decline in filtration of detergent wastewater by NF, besides optimizing operating conditions such as pH, temperature and pressure, it is important to employ high shear rates at membrane surface.

All previous studies about treatment of detergent wastewater by NF used crossflow membrane modules, which could only produce moderate shear rate, due to pressure drop limitation. A shear-enhanced filtration system, which consists in creating the membrane shear rate by a rotating disk, or by rotating or vibrating the membranes, can be operated at a very high shear rate (1–3×10^5 s^{-1}), thus reducing concentration polarization effectively [16]. This filtration system was proved to be successful for treatment of wastewater [17,18] and represents a good choice in order to purify detergent wastewater with high efficiency. In this study, a rotating disk membrane (RDM) module was used to treat a real detergent wastewater, and a NF270 membrane was chosen, based on previous research [6]. The effect of UF pretreatment and operating conditions on NF permeate flux and rejection was investigated in short tests. In order to control flux decline during filtration of detergent wastewater by NF, a series of longer experiments under different rotational speeds, transmembrane pressure (TMP), pH and temperature was performed. The present work aims at understanding the mechanism of flux decline in membrane filtration of surfactant-containing effluents and to develop treatment of detergent wastewater by NF.

2. Materials and methods

2.1. Experimental set-up and membranes

The RDM module, shown in Fig. 1, has been designed and built in our laboratory [19]. A flat membrane, with an effective area of 176 cm^2 (outer radius R_1 = 7.72 cm, inner radius R_2 = 1.88 cm), was fixed on the cover of the cylindrical housing in front of the disk. The disk equipped with 6 mm-high vanes can rotate at adjustable speeds, ranging from 500 to 2500 rpm, inducing very high shear rates on the membrane. As described previously in [18], the module was fed from a thermostatic and stirred tank containing 12 L of fluid by a volumetric diaphragm pump (Hydra-cell, Wanner, USA). The peripheral pressure (p_c) was adjusted by a valve on outlet tubing and monitored at the top of the cylindrical housing by a pressure sensor (DP 15–40, Validyne, USA), and the data was collected automatically by a computer. The permeate was collected in a beaker placed on an electronic scale (B3100 P, Sartorius, Germany) connected to a computer in order to measure the permeate flux.

A UP005P (Nadir) membrane, made of hydrophilic polyethersulfone (PES) with 5 kDa MWCO was used as a pretreatment step. A NF270 (Dow-Filmtec) was chosen for the 2nd step because of its outstanding advantages in flux and antifouling performance for surfactant solutions according to a previous study [6]. Based on the manufactures' data sheet and literature [20], the properties of UF and NF membranes are shown in Table 1.

2.2. Detergent wastewater

Dishwasher detergent CIP wastewater was collected from a detergent factory located in Compiégne (France) in two different batches. This liquid dishwasher detergent was made of anionic surfactants. The effluent was pre-filtered by two sieves with pore size of 0.25 mm and 0.10 mm (Prolabo, Paris, France). According to the factory's information, this effluent mainly contains: sodium dodecyl sulfate (molecular weight $\approx$288 g mol^{-1}), linear alkylbenzene sulfonate (323 g mol^{-1}), 2-bromo-2-nitro-1,3-propanediol (200 g mol^{-1}), limonene (136 g mol^{-1}), sodium
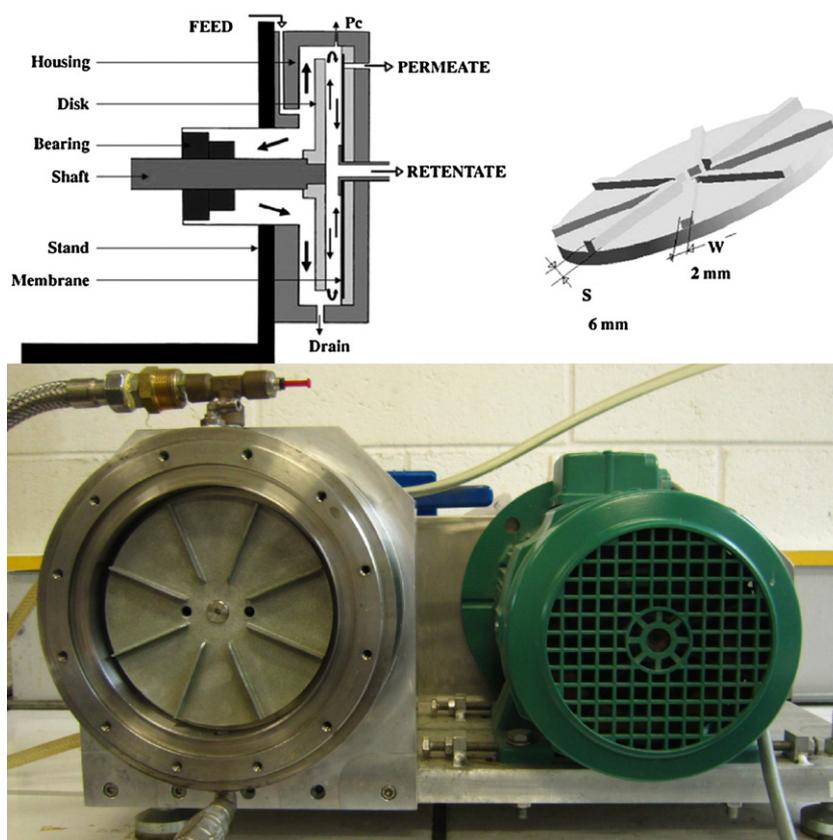
Fig. 1. Schematic and photo of the rotating disk module (RDM) and the disk with vanes.

Table 1
Properties of UF and NF membranes [20].

Index	UP005P	NF270
Membrane material	Polyethersulphone	Polyamide
Molecular weight cutoff (Da)	5000	150–200
L_p[a] ($Lm^{-2}\,h^{-1}\,bar^{-1}$) 25 °C	18–20	11.3 ± 0.3
Max. temperature (°C)	95	45
Max. pressure (bar)	NA	41
Contact angle (sessile drop) (°)	NA	30
Zeta potential (mV)	NA	+7.2 (pH 4), −10.9 (pH 6.7)
Isoelectric point (pH)	NA	5.3

[a] Pure water permeability, NA: not available.

Table 2
Main characteristics of detergent wastewater.

Index	Batch 1	Batch 2
Surfactant type	Anionic	Anionic
Dry matter (g L^{-1})	26.12	21.32
Conductivity (ms cm^{-1})	5.01	6.22
COD (mgO$_2$ L^{-1})	54,000	43,500
pH	7.2	7.5

chloride and sodium sulfate. The main characteristics of the detergent wastewater are described in Table 2 and show a high initial COD.

2.3. Experimental procedure

A new membrane was used for each group of experiments to ensure the same initial membrane conditions for the entire study.

The membranes were soaked in deionized water for at least 48 h prior to use, and pre-pressurized with deionized water for 30 min under a pressure of 40 bar (10 bar for UF membrane) at 25 °C. After stabilization, the pure water flux of membranes was measured at five pressures of 20, 16, 12, 8, 4 bar for NF (10, 8, 6, 4, 2 bar for UF) to calculate water permeability (L_p). Before the experiments started, the feed was heated to selected temperature and pH was adjusted with 1 M NaOH and 1 M HCl to specific values as required, during which the feed was fully recycled in the system at zero TMP, and this process lasted about 10 min for each test to ensure that surfactant pre-adsorption on membrane was similar. Then experiments were performed at a feed flow rate of 180 L h^{-1} in three series: short-term full recycle tests, long-term full recycle tests and concentration tests.

2.3.1. Series 1: short tests with full recycling (using batch 1)

This series was performed with permeate and concentrate recycling in order to investigate the effect of TMP, rotational speed, pH and temperature at a constant feed concentration. For each group of experiments, with the same membrane and test fluid, TMP was increased in steps, but rotational speed was decreased in steps except if stated otherwise. This procedure minimized the possible effect of concentration polarization or/and fouling formed at the previous test point on the next one, and the experimental protocol will be defined in more details later in each section. Samples were all collected in permeate 10 min after the beginning of each TMP increment or rotational speed decrease in order to have stabilized flux and transmission conditions. However, for some cases, the permeate flux could not stabilize after 10 min filtration, or even in a longer time, and therefore, not all data for short-term tests were measured at steady-state.

2.3.2. Series 2: long tests with full recycling (using batch 1)

This series was carried out in total recirculation mode like Series 1, with a rotational speed first set to its maximum value and then decreased in steps. Tests were conducted at each rotational speed for 1 h and after 4 h continuous operation, the rotational speed was returned to its initial value (maximum one) and kept for 30 min to see whether the initial permeate flux could be recovered. Permeate samples were collected for analysis every 15 min. This procedure was performed under different TMP, pH and temperatures in order to examine the effect of operating conditions on flux decline.

2.3.3. Series 3: concentration mode (using batch 1 and 2)

In this series, permeate was not returned to feed tank and a 12 L feed was concentrated to 2 L at constant conditions (2500 rpm, 30 bar, pH 7.5, 35 °C). Samples were collected in permeate every half unit of volume reduction rate (VRR). Finally, the concentrate was conserved in a refrigerator for 48 h and the supernatant was taken out for analysis.

After each series of tests, at rotational speed of 500 rpm, the filtration system was flushed with deionized water for more than 6 times until the rinsing water came out clear (a small amount of foam was difficult to avoid), and L_p was measured to know the degree of irreversible fouling. Then, the membrane was soaked in deionized water at a pH of 4.5 for a night and L_p was measured again in the next day morning. In some cases this pH was adjusted to 8–9 to prevent membrane permeability from decaying during preservation.

2.4. Analytical methods

Turbidities of the concentrate and the permeate were measured with a Ratio Turbidimeter (Hach, USA). COD was measured using Nanocolor Kits (Machery-Nagel, Hoerdl, France) in order to quantify organic matter concentration. The total relative error on COD was estimated to be 8%. Conductivity was measured with multi-range conductivity meter (HI 9033, Hanna, Italy) and pH was measured with pH Meter (MP 125, Mettler Toledo, Switzerland). Dry mass was determined by measuring the weight loss with a digital precision scale (AR2140, Ohaus, USA) after drying samples at 105 ± 2 °C for 5 h in an oven.

2.5. Calculated parameters

The permeate flux (J) was calculated by:

$$J = \frac{1}{A}\frac{dV_p}{dt} \tag{1}$$

where A is the effective membrane area, V_p is the total volume of permeate, and t is the filtration time.

The pure water permeability (L_p) was calculated as follows:

$$L_p = \frac{J}{TMP} \tag{2}$$

The mean TMP is obtained by integrating the local pressure over the membrane area as follows [19]:

$$TMP = p_c - \frac{1}{4}\rho k^2 \omega^2 R^2 \tag{3}$$

where ρ is the density of the fluid, k is the velocity factor (0.89 for this system), ω is the disk angular velocity and R is the housing inner diameter.

The membrane mean shear rate (γ_m) can be calculated by the following equation [16].

$$\gamma_m = 0.0164 R^{8/5}(k\omega)^{9/5}\nu^{-4/5} \tag{4}$$

where ν is the fluid kinematic viscosity. Table 3 shows the mean shear rate on the membrane at various speeds for RDM module.

Table 3
Mean shear rate on the membrane for RDM module assuming ν is 0.89×10^{-6} m^2 s^{-1} at 25 °C.

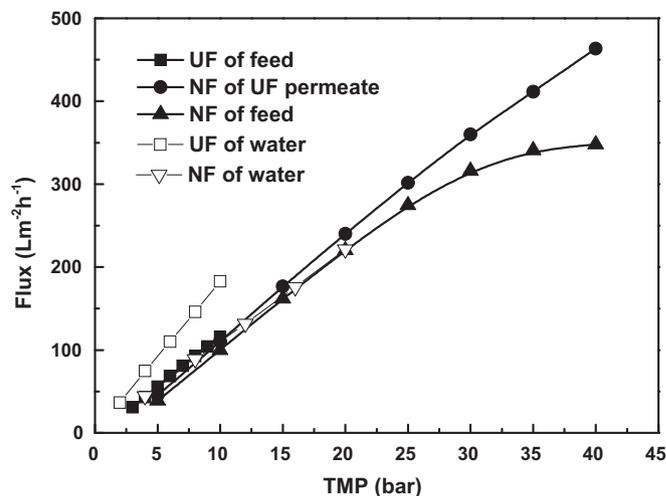| Rotational speed (rpm)	500	1000	1500	2000	2500
γ_m ($\times 10^5$ s^{-1})	0.17	0.60	1.24	2.08	3.11

Fig. 2. Permeate flux as a function of TMP for different feeds and membranes. Rotational speed = 2000 rpm; pH 7.2; temperature = 25 °C.

The apparent rejections (R_{app}) of COD and conductivity are defined as:

$$R_{app}(\%) = \left(1 - \frac{X_p}{X_f}\right) \times 100 \tag{5}$$

where X_p and X_f are the COD or conductivity in permeate and feed, respectively.

The volume reduction rate (VRR) is defined as:

$$VRR = \frac{V_o}{V_c} \tag{6}$$

where V_O is initial feed volume and V_C concentrate volume.

3. Results and discussion

3.1. Effect of UF pretreatment on permeate flux and rejection

We compare here two processes, the first consisting in a single NF step and the second in a pretreatment by UF before the NF step. These tests were carried out in full recycle mode at a constant rotational speed of 2000 rpm, and TMP was increased in steps from 5 to 40 bar. As seen in Fig. 2, without pretreatment the permeate flux reaches a plateau of 350 Lm^{-2} h^{-1} at 35 bar while, after UF pretreatment, the NF permeate increased linearly with TMP until 40 bar reaching 470 Lm^{-2} h^{-1}, because of organic matter removal in the NF feed by UF. The NF permeate flux of 2nd process was even a little larger than the water flux. This was caused by improved wettability of the NF membrane surface through adsorption of surfactant monomers on hydrophobic group, thus leading flux to increase above pure water flux [6] and also by the high shear rate produced by RDM module, which prevented concentration polarization from increasing with TMP. As shown in Fig. 3, for UF, the rejection of conductivity was very low but COD rejection was near 90%. Conductivity rejections in NF were similar for the two processes, reaching 93% above 30 bar while it was below 38% for UF. COD rejection by NF shown in Fig. 3b was higher in 1st process at 97% against 70–80% in 2nd one. However, due to the COD rejection by UF of near 90%, NF
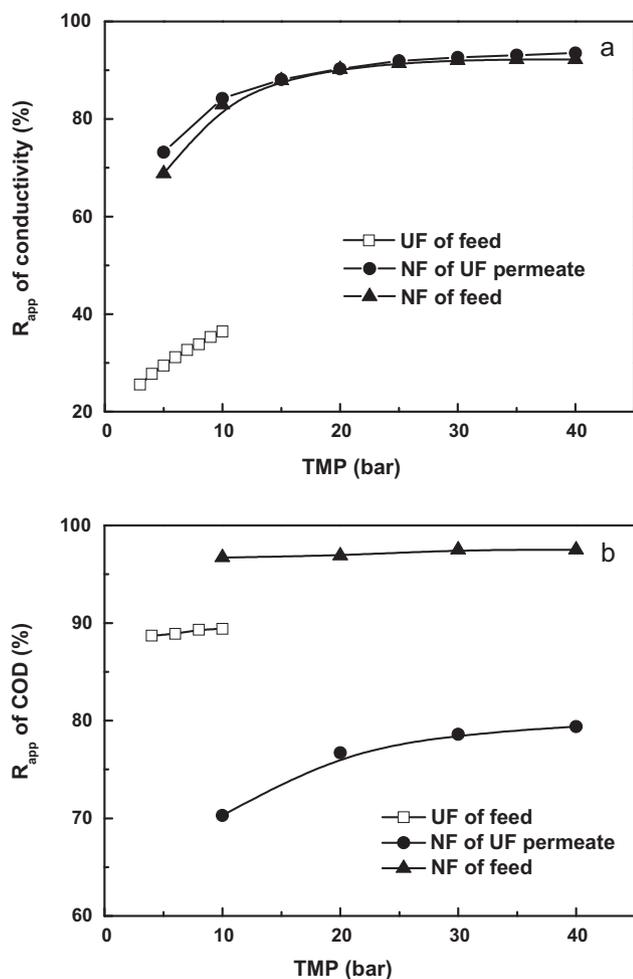
Fig. 3. Observed rejection of conductivity (a) and COD (b) for UF and NF at different TMP. Rotational speed = 2000 rpm; pH 7.2; temperature = 25 °C.

Fig. 4. Effect of rotational speed on permeate flux (a) and conductivity rejection (b) of NF270. pH 7.2; temperature = 25 °C.

permeate COD was still lower in 2nd process at 1264 mg/L versus 1361 mg/L without UF.

3.2. Effect of operating conditions on permeate flux and rejection (Series 1)

3.2.1. Effect of rotating speed

Higher rotational speeds produce higher shear rates across membrane, reducing solutes accumulation at membrane surface and thus decrease osmotic pressure differences across the membrane, leading to higher permeate flux at same TMP [18]. Fig. 4a shows the effect of rotational speed on permeate flux for NF of detergent wastewater in short tests (Series 1). The rotational speed was first set to 2500 rpm and permeate flux and conductivity retention were measured at TMP of 10, 15, 20, 25, 30 bar and these tests were repeated at 2000, 1500, 1000 and 500 rpm. At 2500 rpm, the flux increased nearly linearly with TMP to reach 340 Lm^{-2} h^{-1}, while it reached a plateau at 25 bar and speeds of 1000 and 500 rpm. The effect of rotational speed and TMP on conductivity rejection is shown in Fig. 4b. This rejection increased with speed and TMP and reached 92% at 2000 rpm, meaning that higher rotational speed not only improved flux but also permeates quality. At speeds of 1000 and 500 rpm, the rejection decreased above 20 bar. According to previous studies [18,21], a rotational speed of around 2000 rpm seemed to be a good compromise between low energy consumption, high permeate flux and high rejection and was selected for use in further study.
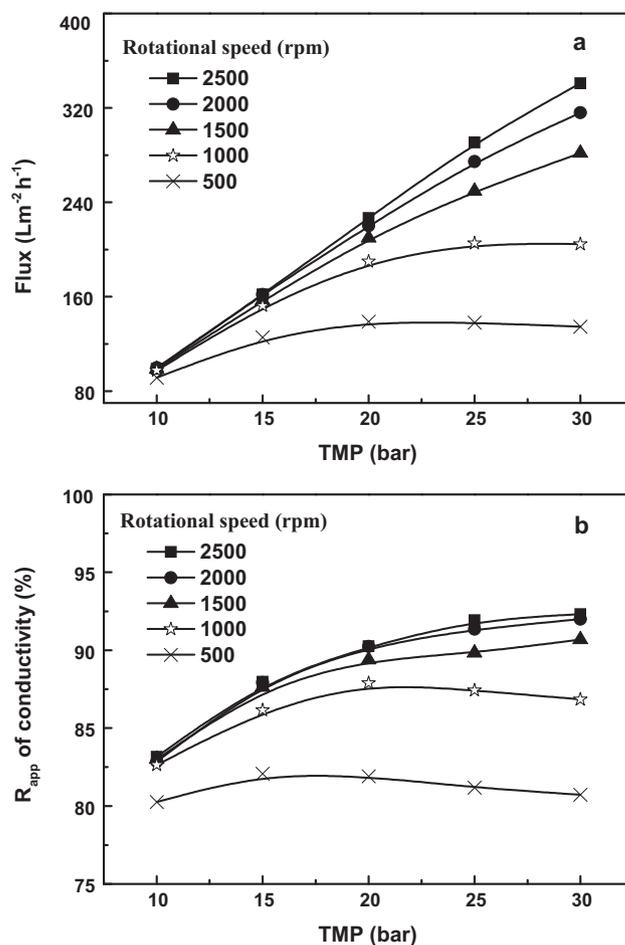
3.2.2. Effect of pH

Because NF270 is a charged membrane and anionic surfactant was contained in our detergent wastewater, pH is an important factor that influences the electrostatic interaction between surfactant and membrane. A filtration test with full recycling was carried out at a rotational speed of 2000 rpm, and TMP was increased in steps from 10 to 30 bar using three feeds with different pH of 4.5, 7.2 and 9.9. As seen in Fig. 5a, permeate fluxes were close at pH 4.2 and 7.2, while at a pH of 9.9 and above 20 bar, the flux increased almost linearly and faster than for lower pH, indicating that a higher pH can alleviate concentration polarization of surfactant molecules. The effect of pH on conductivity rejection was more important as seen in Fig. 5b. With increase of TMP, the rejection of conductivity rose from 80% to 88% at pH 7.2 and even more at pH 9.9, while it rose from 40% to 60% only at pH 4.5 which could be explained by their different electrostatic effects. Since the isoelectric point of NF270 is pH 5.3 (Table 1), the membrane will be positively charged at a pH of 4.5. But the anionic surfactant was negatively charged, and therefore, electrostatic attraction between solutes and membrane resulted in the lowest rejection of conductivity. For pH 7.2 and 9.9, both surfactants and membrane were negatively charged, and these surfactants were rejected by an electrostatic repulsion force.

3.2.3. Effect of temperature

These experiments were performed in full recycling mode at constant rotational speed and pH, and permeate flux and conductivity retention at different temperatures were measured as TMP rose from 10 to 30 bar. Increasing temperature decreased fluid
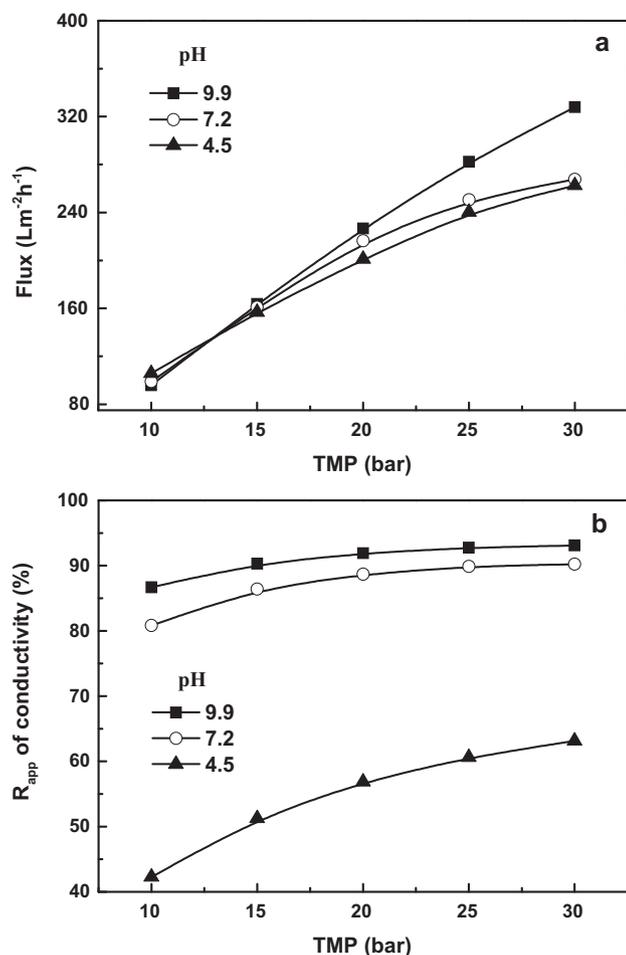
Fig. 5. Effect of pH on permeate flux (a) and conductivity rejection (b) of NF270. Rotational speed = 2000 rpm; temperature = 25 °C.

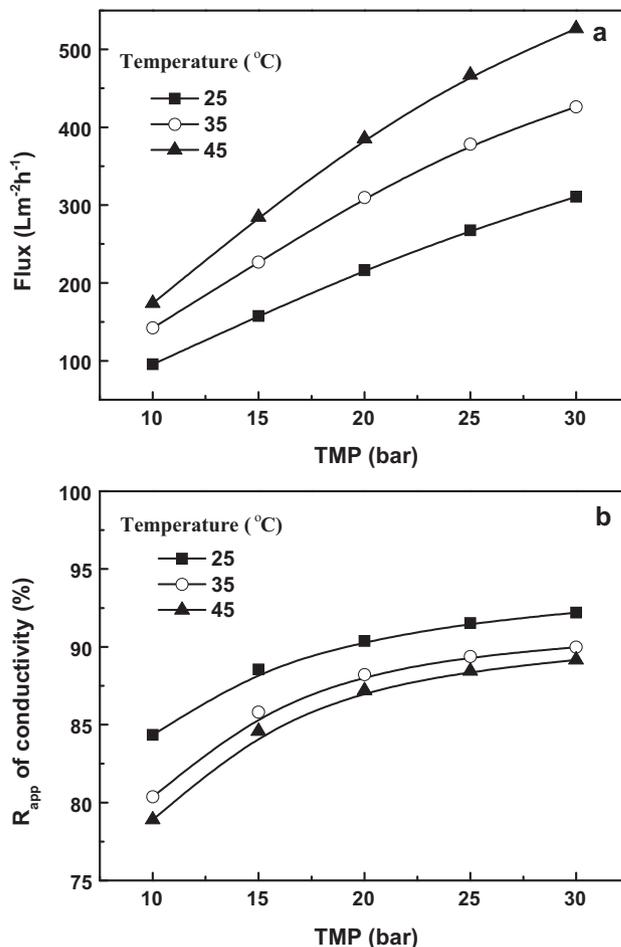**Fig. 6.** Effect of temperature on permeate flux (a) and conductivity rejection (b) of NF270. Rotational speed = 2000 rpm; pH 7.2.

viscosity, and increased the flux as shown in Fig. 6a. Since diffusion coefficients increase with temperature, concentration polarization is reduced by enhanced back transport, and solutes pass through the membrane more easily, decreasing conductivity rejection as seen in Fig. 6b. Therefore, these two factors caused the flux to increase with temperature.

3.3. Effect of operating conditions on flux variation with time (Series 2)

3.3.1. Effect of rotating speed at various TMP

If the shear rate produced by disk rotation is not large enough to remove solutes away from membrane, surfactant molecules are first adsorbed at membrane surface, then aggregate together due to the hydrophobic interaction, inducing a continuous flux decline [9,10]. As shown in Fig. 7a, at a TMP of 10 bar, a disk rotating at 1000 rpm or more can prevent solutes aggregation and keep the permeate flux constant at about 108 Lm^{-2} h^{-1}, while it decays rapidly to 80 Lm^{-2} h^{-1} at 500 rpm. At a TMP of 20 bar (Fig. 7b), a rotational speed of at least 1500 rpm is required for maintaining flux stability. At 1000 rpm the flux decayed by 30% and raising the speed to 2500 rpm restored the flux to its 1500 rpm value, but not the initial one. At TMP = 30 bar, (Fig. 7c) the necessary speed for flux stability was 2000 rpm. If the shear rate was not high enough to disperse the surfactant molecules at membrane, the permeate flux decreases at higher TMP. For example, the permeate flux at 1000 rpm and 30 bar (Fig. 7c) dropped to 130 Lm^{-2} h^{-1} after 1 h, and was lower than the flux at 1000 rpm and 20 bar of 140 Lm^{-2} h^{-1}

(Fig. 7b). Therefore, increasing shear rate was the most effective method to control flux decline in NF of detergent wastewater. Conductivity rejection decayed a little at low rotational speed and was less affected than the flux.

3.3.2. Effect of rotation speed at different pH and temperatures

These effects on permeate flux are represented in Figs. 7c and 8 at a TMP of 30 bar. Fig. 8a shows the variation of flux with rotational speed at 25 °C and pH 9.8, which can be compared with Fig. 7c showing the same variation at a pH of 7.2. The comparison of these two profiles shows that permeate flux is higher at pH 9.8, and decays less with time at speeds of 1500 and 1000 rpm. The flux decay at the end of 1000 rpm period relatively to final flux at 2500 rpm was 45% at pH 9.8 versus 57% at pH 7.2. On the one hand, at an alkaline pH, the NF270 membrane would swell and its permeability would increase [20,23]. On the other hand, electrostatic repulsion among surfactant molecules, and between membrane and surfactant molecules, became stronger with increase of pH. Therefore, at pH 9.8, the filtration resistances of concentration polarization and membrane decreased, resulting in a higher and more stable permeate flux.

The effect of a temperature change from 25 °C to 35 °C is illustrated in Figs. 7c and 8b. As expected, the permeate flux at 2500 rpm during the first hour was higher, 390 Lm^{-2} h^{-1} at 35 °C instead of 330 Lm^{-2} h^{-1} at 25 °C. The second difference was that the flux stabilized with time at 2000 rpm at 25 °C while it kept decreasing at 35 °C. This result was compatible with that of Kaya et al. [12] and Gonder et al. [8], but the reasons were different, as they employed
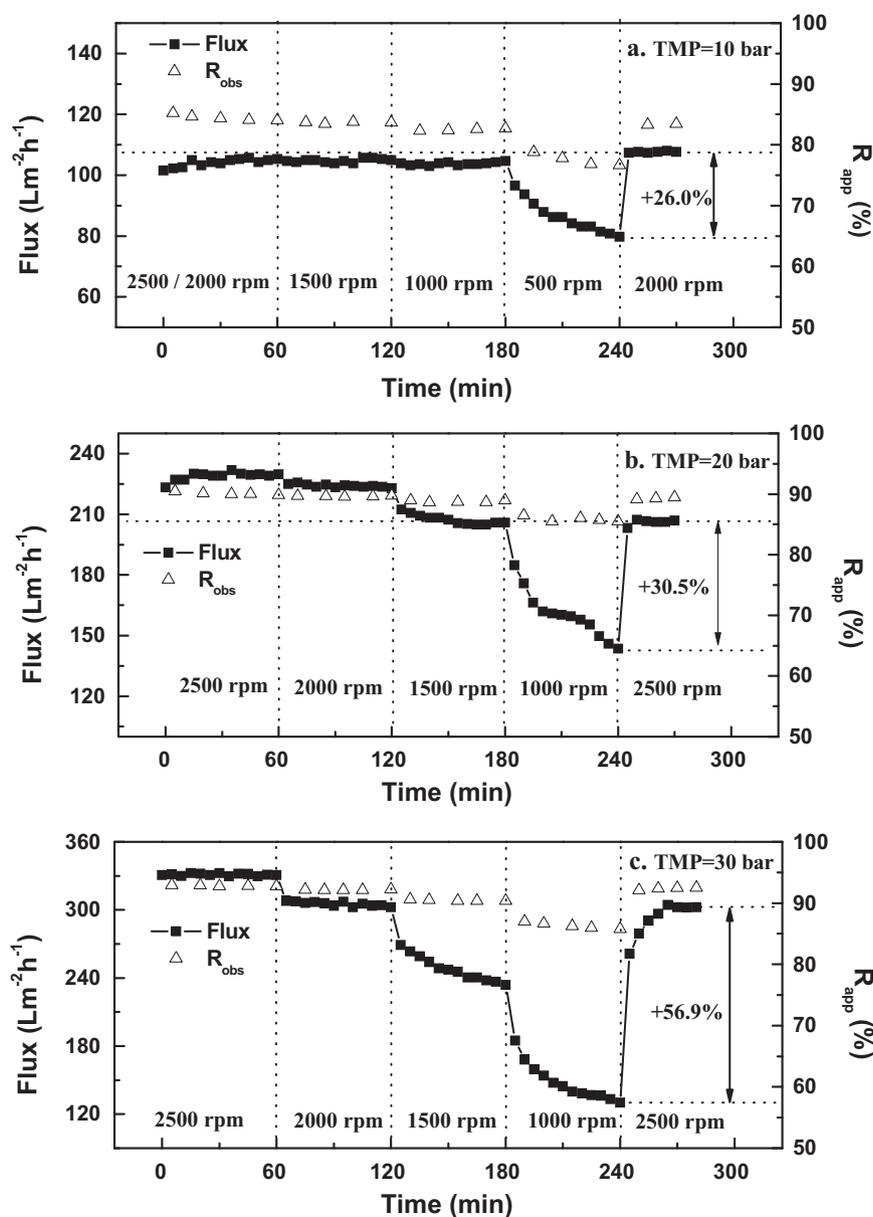
Fig. 7. Effect of TMP and rotational speed on flux decline at pH 7.2 and temperature = 25 °C. (a) 10 bar; (b) 20 bar; (c) 30 bar.

a concentration mode and, in the same time period, higher temperature to treat a higher volume, and higher feed concentration in retentate. This was the reason why flux decline was larger at higher temperature in their study. While in our study, a full recycling mode was used and all the conditions were the same, except for temperature, and the flux decline at 2000 rpm in Fig. 8b just resulted from the higher temperature. However, when rotational speeds decreased to 1500 rpm and 1000 rpm, flux decline at 25 °C was found (Fig. 7c), even larger than that at 35 °C. These could be explained by a competition between flux increase and diffusion enhancement, both induced by higher temperature, that a higher flux produced more severe concentration polarization, but a higher back diffusion decreased concentration polarization, and at high rotational speed, the former effect was dominant, but at lower rotational speed, the latter one became important. Moreover, higher temperature could decrease the adsorption and aggregation of surfactants on membrane due to higher diffusion, thus alleviating gel formation (flux decreased by 8.0% at 35 °C, but 9.5% at 25 °C when rotational speed was returned to 2500 rpm).

Although the initial permeate flux was not fully recovered at the end all tests when speed was raised to 2500 rpm, the gel layer could be broken up by water rinse, and as shown in Fig. 9, membrane water permeability before and after use were almost the same, even a little higher after use for membranes a and e. The explanation may be that, first, surfactant molecules were negatively charged, and the electrostatic repulsion among molecules in aggregates made the gel layer easier to scatter; secondly, the gel layer was formed by some aggregates with the hydrophilic head-group towards the solution and with the hydrophobic part hidden in the interior [9], and thus these dense clusters were easy to dissolve in deionized water. Therefore, a high shear rate could well control flux decline during NF of detergent wastewater and membrane fouling could be fully removed by several simple water rinses.

3.4. Effect of membrane storing modes on flux decline

Because membrane permeability was fully recovered by water rinse, it was possible to reuse membranes without any chemical
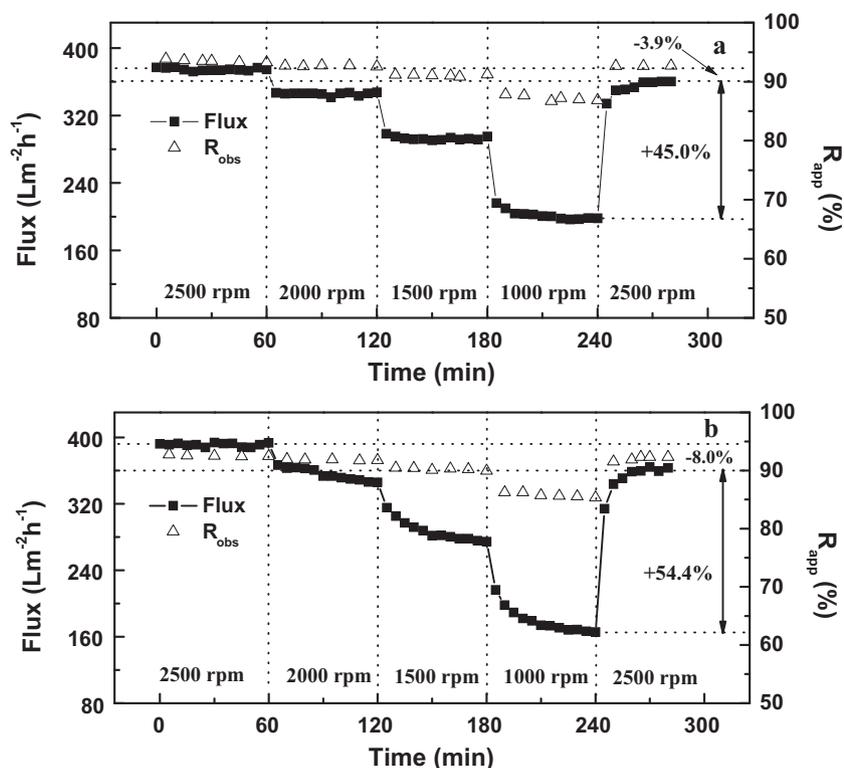
Fig. 8. Effect of pH and temperature on flux decline at TMP = 30 bar. (a) pH 9.8, temperature = 25 °C; (b) pH 7.2, temperature = 35 °C.
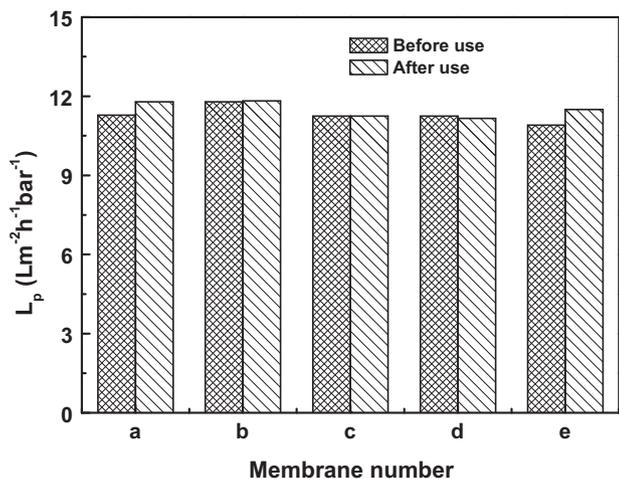

Fig. 9. Comparison of membrane water permeability before and after use (these membranes were used in tests of Figs. 7 and 8).

cleaning. However, after a night of storing in deionized water (pH 4.5), both water permeability and permeate flux decreased, as seen in Fig. 10a, while conductivity rejection increased, indicating that the membrane was fouled during storing. When the pH of storage water was adjusted to 8–9, feed flux reduction was smaller and no water flux reduction occurred (see Fig. 10b). This result was

confirmed in several subsequent experiments. The acid pH of storage water and few surfactants remaining in system might be the reason for flux decline after storing. The membrane was positively charged at a pH 4.5 lower than isoelectric point of NF270 (see Table 1), and anionic surfactants were drawn to the membrane by electrostatic attraction; furthermore, NF270 membrane pores may shrink at an acid pH condition [22], and thus the surfactant molecules adsorbed on pore wall would cross-link and then plug the membrane pores, thus decreasing membrane permeate flux and increasing conductivity rejection. Therefore, membranes for treatment of detergent wastewater should be soaked in water with alkaline pH when not in use.

3.5. Concentration of detergent wastewater by NF (Series 3)

Using a high rotational speed (2500 rpm) and moderate temperature (35 °C), concentration of detergent wastewater was carried out with a NF270 membrane. Two batches were tested without adjusting the pH but only data for batch 2 are shown in Fig. 11 and Table 4. The flux decreased linearly with VRR in semi-log coordinates when VRR increased from 1.1 to 4.8, which corresponded to the mass transfer limited regime [18]. When VRR exceeded 4.8, membrane shear rate decreased due to increase of solution viscosity, and thus the flux dropped rapidly. Conductivity rejection also decreased because salt concentration in retentate went up and the charge screening effect by salt ions rose with VRR [23].

Table 4

Main characteristics of feed, permeate and retentate for concentration of detergent wastewater by NF270 at VRR = 6.

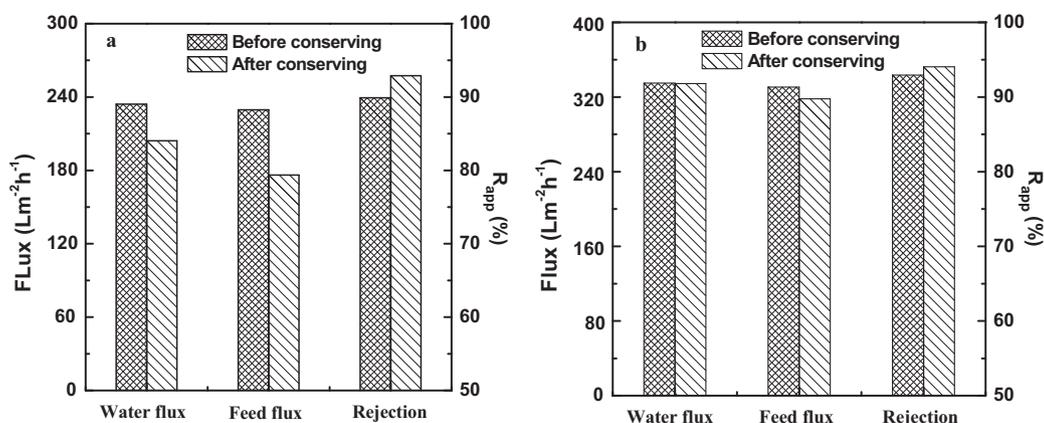| Index	Feed	Permeate	Retentate	Retentate after sedimentation
Dry matter (g L^{-1})	21.32	1.88	108.9	101.7
Conductivity (ms cm^{-1})	6.22	2.38	18.44	18.25
COD (mgO$_2$ L^{-1})	43,500	2600	2,37,000	2,17,500
pH	7.5	7.1	8.0	8.0

Fig. 10. Effect of storing water pH on membrane performance. (a) Storing water at pH 4.5, testing TMP = 20 bar; (b) storing water at pH 8.8, testing TMP = 30 bar. Feed: unadjusted batch 1.
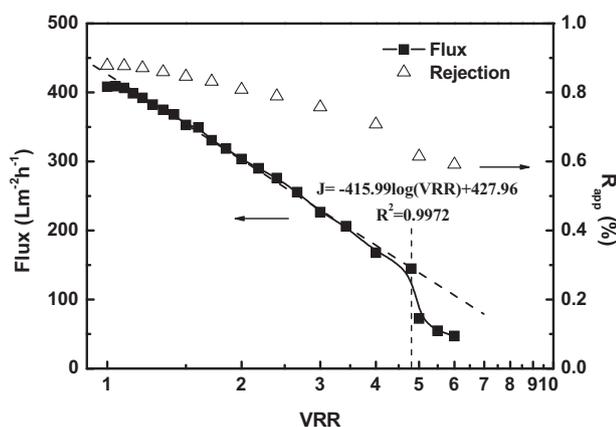

Fig. 11. Permeate flux and conductivity rejection as a function of volume reduction ratio in semi-log coordinates. Feed: unadjusted batch 2; rotational speed = 2500 rpm; TMP = 30 bar, temperature = 35 °C.

Table 4 shows the main characteristics of feed, permeate, concentrate at VRR = 6, before and after sedimentation. Permeate conductivity was 38% of feed one, while permeate COD was about 6% of feed one, and the permeate water was very clear. This permeate might be reused as CIP cleaning water or further purified by reverse osmosis membrane to improve its quality. It was also found that, after sedimentation for 48 h in a refrigerator, some surfactant solutes in the concentrate precipitated due to the supersaturation of surfactants. These precipitated surfactants could be extracted for reuse and the concentration process could be continued to increase recovery of surfactants.

4. Conclusions

These results confirm the high performance of high shear dynamic filtration in detergent wastewater treatment by NF system both in terms of permeate flux and ion and COD rejection. Increasing rotational speed increased permeate flux and solutes rejection by decreasing concentration polarization, especially at a high TMP. Using suitable TMP and rotational speeds permitted to keep permeate flux constant for a long time. An acid pH (4.5) decreased solutes rejection by NF and clearly induced membrane fouling, while an alkaline pH had a cleaning effect on membrane. Acid water could not be used for storing NF270 membrane after filtrating detergent wastewater because it would cause a flux decline after storage. A higher temperature increased the permeate flux and prevented gel layer formation, but lowered solutes rejection.

The fouling layer formed in this process was not very compact and could be broken up by water rinse, and thus membrane permeability could be fully recovered without any chemical cleaning. When detergent wastewater was concentrated to VRR = 6 (COD = 237 g L^{-1}), the flux still remained at 47 Lm^{-2} h^{-1} due to the high shear rate. Although pretreatment by UF of detergent wastewater increased the NF flux at high TMP, the gain in final conductivity and COD rejection in NF permeate was probably not sufficient to justify the cost of this UF step. But the slight flux decline, easy membrane regeneration and the high rejection make this shear-enhanced NF filtration system viable to treat detergent wastewater.

Acknowledgments

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