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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 L m^{-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 L m^{-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 L m^{-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.

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 cut-off (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 ($1–3 \times 10^5\,s^{-1}$), 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-filtrated 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 ≈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