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Treatment of Aqueous Ionic Surfactant Solutions by Dynamic Ultrafiltration

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Abstract: This paper investigates the reduction of concentration of an ionic surfactant (sodium dodecyl benzene sulfonate) present in an aqueous solution by ultrafiltration. A dynamic filtration system consisting of a metal disk rotating near a flat circular organic membrane was used in this study. Membranes cut off tested were 10, 20, and 50 kDa. The maximum rejection rate was 92% at 10 kDa. Permeate fluxes kept increasing with transmembrane pressure until at least 1400 kPa, reaching 400 $Lh^{-1}m^{-2}$ at 10 kDa and 950 at 50 kDa for a rotation speed of 1000 rpm. However, raising the rotation speed above 500 rpm at 900 kPa had only a moderate effect on performance, indicating probably strong interactions between surfactant molecules and the membrane and that the permeate flux was mostly limited by pressure.

Keywords: Ionic surfactants, SDBS, ultrafiltration, micelles

INTRODUCTION

Surfactants can be found in wastewater from several industries such as textile, paper, detergents, and food processing. They are used as emulsifiers, cleaning, and wetting agents and for grease removal. The use of surfactants has reached 17 million tons in the year 2000 worldwide and increases by 3 to 4% per

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year (1). Due to their wide use and resistance to biodegradation, untreated surfactants are commonly found in large quantities in industrial or urban wastewaters. It is thus important to treat wastes containing surfactants for both economical and environmental reasons. Present waste rejection regulations call for a reduction of surfactant residual concentrations in view of their noxiousness. There seems to be a lack of reliable and accurate data on their real concentrations in industrial effluents, as these residual concentrations depend on local conditions and the type of treatment performed (2).

Membrane separation has been considered as one of best methods for treating liquid or gas effluents. In addition, ultrafiltration (UF) is well-suited for recovery of organic compounds. The recent development of new membranes with specific properties has opened the way to surfactant reduction in liquid wastes (3–6). However, the efficiency of conventional crossflow-filtration is limited by severe concentration polarization due to physicochemical interactions with the membrane.

UF of sodium dodecylsulfate (SDS) has been carried out by Azoug et al. (3) using a zirconium ceramic membrane. After measuring hydraulic permeabilities of their membrane for different solutions, they showed that the membrane resistance depended upon the ion concentration, more specifically that of free ions DS^- and Na^+ and to a lesser extent on the spherical micelles of the surfactant. Mizoguchi et al. (4) investigated the UF of a solution containing a non-ionic surfactant (LDAO) at a concentration near the critical micellar concentration (CMC) using an organic hydrophilic membrane (Amicon, USA). A drop in the permeate flux was observed when the surfactant concentration was close to the CMC. They concluded that this drop was due to the formation of pre-micelles at the membrane surface. Majewska-Nowak et al. (5) have also ultrafiltered SDS solutions using polyethersulfone, polysulfone, cellulose acetate, and aromatic polyamide membranes. They showed that the rejection rate of SDS molecules was a function of the membrane material and its hydrophilic or hydrophobic properties. They found that polyethersulfone and polysulfone membranes gave the highest recovery of SDS. However, they observed that a large increase in SDS concentration reduced the membrane permeability and its SDS rejection. In a recent paper, Fernandez et al. (6) investigated the influence of surfactant nature, feed flow rate, temperature, and pressure on permeate flux with a ZrO_2 tubular mineral membrane. They used both an ionic surfactant (SDS) and a non ionic one (Tergitol NP-9). They found strong interactions between these surfactants and the membrane surface. Highest retention rates were observed with the SDS. They attributed this result to electrostatic repulsive forces between negatively charged SDS micelles in the polarization layer on the membrane.

Due to their chemical structure, surfactants get strongly adsorbed at interfaces and form aggregates, even at small concentrations. When their concentration reaches the CMC, they form micelles, while above the CMC, monomers and micelles are in equilibrium. Thus the transformation of the surfactant plays a major role in solute-membrane interactions which govern

UF performance (7, 8). Moreover, according to Bylin and Jonsson (9), the enhancement of concentration polarization created by surfactant adsorption at the membrane will strongly affect the permeate flux and rejection.

In order to limit concentration polarization and membrane fouling, it is necessary to create at the membrane a high shear rate without resorting to a large feed flow rate which would result in a large transmembrane pressure at the inlet part of the module. Dynamic filtration, which creates high membrane shear rates by moving parts independently of feed flow therefore looks promising for this application (10, 11). Dal-Cin et al. (10) have ultrafiltered oil-water emulsions using a Spintek dynamic filtration module with rotating circular 20 cm in diameter membranes mounted on spinning disks and generating shear rates of the order of 105 s^{-1}. They used polyethersulfone membranes of 35 and 50 kDa cut-off. They observed that, above a speed of 800 rpm, concentration polarization or gel formation was minimal and that the flux remained pressure limited up to 3200 kPa. They obtained permeate fluxes ranging from 70 Lh^{-1} m^{-2} at 800 rpm to 108 at 1800 rpm and a pressure of 2500 kPa. Viadero et al. (11) also used a Spintek high shear rotary UF module equipped with 0.11 μm ceramic disk membranes. They concluded that it was possible to concentrate oil suspended in water beyond typical operating limits of conventional UF modules.

In this paper, we present the results of UF of an ionic surfactant solution using a dynamic filtration module consisting in a metal disk rotating near a flat circular organic membrane. The shear rate in the module can be further augmented at the same speed by fitting the disk with eight radial vanes which increase the fluid angular velocity in the gap between the disk and membrane (12). Our goal was to investigate the influence of internal hydrodynamics and physicochemistry on the performance of the system for UF of surfactant solutions. The surfactant selected for this study is sodium dodecyl benzene sulfonate (SDBS)for which few results are available. This surfactant is commonly employed in the detergent industry.

MATERIAL AND METHODS

Test Fluid

The SDBS characteristics are given in Table 1. Aqueous solutions were prepared by mixing the SDBS in deionized pure water. Concentrations were

Table 1. Characteristics of SDBS surfactant

Surfactant	Chemical formula	MW (Da)	CMC (mML^{-1})	Supplier
SDBS	$CH_3(CH_2)_{11}C_6CH_4\ SO_3\ Na$	348.48	2.1	Sigma

equal or higher than the CMC, since for concentrations below CMC, nanofiltration is preferred for surfactant recovery from aqueous solutions.

Analyses

The SBDS concentration was measured using a CG 855 conductimeter, (Konductometer GmbH, Germany). Since it is ionic, its concentration is proportional to its conductivity and the device was calibrated from samples with known concentrations. The value of CMC was deducted from surface tension measurements with a Krus K100 tensiometer (Germany). Viscosimetric measurements were performed on rotational viscometer Visco Star Plus (Fungilab, Barcelona, Spain). Rejection rates R were calculated from permeate (C_p) and retentate (C_r) concentrations using:

$$R\% = (C_r - C_p)/C_r \tag{1}$$

Filtration System

This system consists of a rotating disk module in stainless steel shown in Fig. 1, designed and built in our laboratory, which has been already described by Frappart et al. (13) and can sustain pressures of up to 3000 kPa. The module was equipped with a single polyethersulfone (PES) organic membrane with an area of 188 cm^2 (outer radius = 7.75 cm; inner

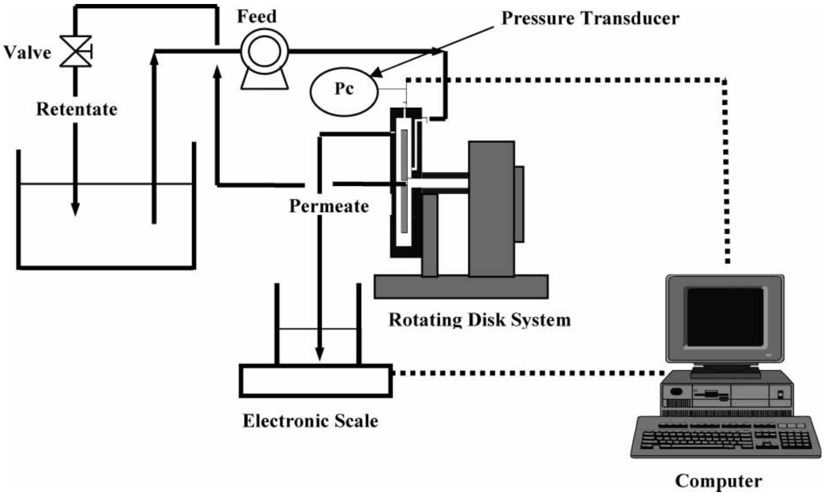

Figure 1. Schematic of rotating disk filtration system.

radius = 0.5 cm). This membrane is fixed on the cover of the cylindrical housing in front of the disk. The axial gap between membrane and disk was about 8 mm. The disk is fixed on a rotating shaft which is linked by a belt to an electrical motor. The shaft can rotate at adjustable speeds, ranging from 500 to 2500 rpm. The module was fed from a thermostated and stirred tank containing 12 L of fluid by a volumetric diaphragm pump. The peripheral pressure (p_c) was measured at the top of the cylindrical housing by a Validyne DP15 (Validyne Corp. Northridge, CA) pressure transducer. The permeate flow rate was measured by collecting the permeate in a beaker continuously weighted on an electronic scale (Sartorius, Germany) connected to a microcomputer calculating the derivative of the collected volume with respect to time and providing a value of flux every ten seconds if needed. The permeate flux was then measured after a stabilized period of ten minutes. PES membranes of 50, 20, and 10 kDa, supplied by Alting (Strasbourg), were used in the tests in order to find the optimal cut-off. Tests were carried out at a temperature of 24–25°C and at initial concentration or a volume reduction ratio (VRR, determined from the ratio of initial to final volume) of 1 with permeate and retentate recycling or by increasing the VRR without permeate recycling. Although membranes could be regenerated, a new one was used for each test.

Internal Hydrodynamics

The fluid flow between the disk and the membrane has been described by Bouzerar et al. (12). The inviscid core rotates at the angular speed $k\omega$ where ω is the disk angular speed and k the velocity coefficient which depends on the disk shape, 0.45 for a flat smooth disk and from 0.6 to 0.84 for a disk equipped with eight 6 mm high vanes (13). The pressure distribution in this inviscid core is obtained from Bernoulli's equation as

$$p(r) = 1/2\rho k^2\omega^2 r^2 + p_0 \tag{2}$$

where p_0 is the pressure at the center of the membrane, equal to the pressure in the housing when the disk is at rest. Since the pressure p_c at the disk rim $r = R$ can be measured, it is possible to determine k from p_0 and p_c using Eq. (2). Since the permeate is collected at atmospheric pressure, the mean transmembrane pressure can be obtained from integrating Eq. (2) over the membrane to give

$$p_{tm} = p_c - 1/4\rho k^2\omega^2 R^2 \tag{3}$$

The maximum shear rate occurs at disk rim and is given by (12)

$$\gamma_m = 0.0296\nu^{-0,8}(k\omega)^{1,8}R^{1,6} \tag{4}$$

RESULTS AND DISCUSSION

Variation of Permeate Flux and Rejection Rate with Transmembrane Pressure and Membrane Cut-off

This variation during tests at constant SDBS concentration equal to CMC with permeate recycling is presented in Fig. 2 for 10, 20, and 50 kDa membranes using a disk equipped with vanes rotating at a speed of 1000 rpm. The transmembrane pressure (TMP)was progressively augmented from a minimum of 300 kPa in 100 kPa steps of 15 min duration to obtain a stabilized flux. The flux increased nearly linearly with pressure for the 10 and 20 kDa membranes (pressure limited regime), since in this case the surfactant molecules are not adsorbed at the membrane, while at 50 kDa the rate of flux increase decayed at above 800 kPa as a transition towards the mass transfer regime occurred, as was also observed in (14, 15).

As expected, permeate fluxes increased significantly with the membrane cut-off, reaching 950 Lh^{-1} m^{-2} at 50 kDa versus 700 at 20 kDa and 410 at 10 kDa, at the maximum pressure of 1400 kPa.

The variation of rejection rate is represented in Fig. 3 for the same tests as in Fig. 2. This rejection rate, measured when the flux was stabilized at each TMP increment, reached 92% for the 10 kDa membrane above 300 kPa, versus 70 to 78% for the 20 kDa one. The rejection rate was lowest at 50 kDa (around 52–55%) and nearly independent of pressure. These results can be explained by the molecular weights of monomers and micelles. Micelles, which are spherical with a molecular weight of 15.7 kDa (16, 17)

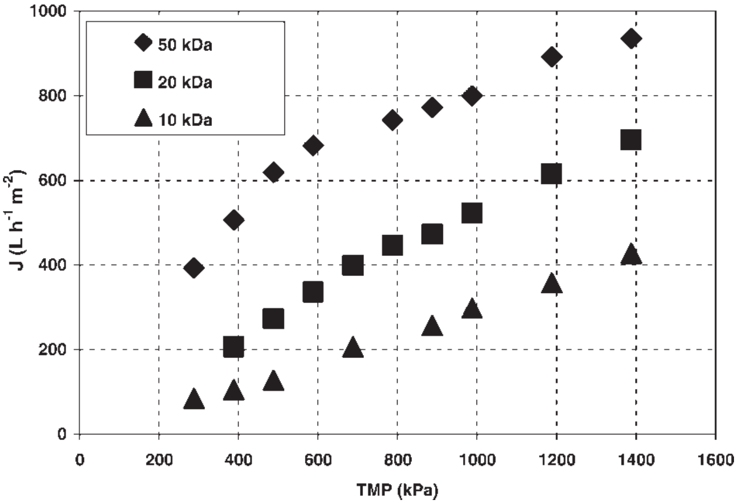

Figure 2. Variation of permeate flux versus TMP for various cut-offs. N = 1000 rpm, VRR = 1, SDBS = 1 CMC, disk with 6 mm vanes.

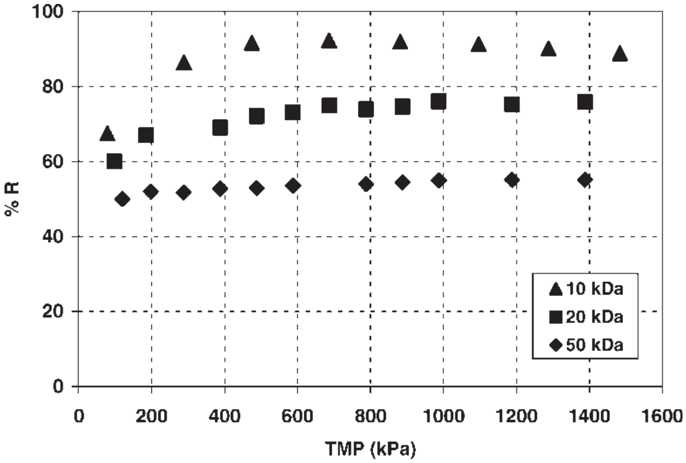

Figure 3. Effect of membrane cut-off on SDBS rejection. SDBS = 1CMC, N = 1000 rpm T = 25°C, VRR = 1, disk with 6 mm vanes.

were completely rejected by the 10 kDa membrane and only monomers with a MW of 348 Da were transmitted, while, with the 20 and 50 kDa membranes, micelles were partially transmitted.

Effect of SDBS Concentration on Variation of Permeate Flux and Rejection with Transmembrane Pressure

This effect on the permeate flux is represented in Fig. 4 for the 10 kDa membrane using concentrations equal to the CMC and twice the CMC. The permeate fluxes are identical with both concentrations until a pressure of 700 kPa, then the flux at the higher concentration becomes a little smaller, due to the presence of monomers and a higher micelle concentration.

Corresponding surfactant rejections are shown in Fig. 5. They are very close for both concentrations and lie between 80 and 90%, but the rejection rate seems a little less at 2 CMC below 300 kPa and above 1000 kPa, due probably to the presence of monomers which have a higher transmission than micelles.

Variation of Permeate Flux with Rotation Speed

Figure 6 displays the variation of permeate flux and TMP with rotation speed at a peripheral pressure of 900 kPa for the three membranes at a temperature of 24°C. The transmembrane pressure decays slightly with increasing pressure from 930 kPa at 250 rpm to 850 at 2500 rpm due to the Bernoulli effect according to Eq.(3). It is seen that, even with the 50 kDa membrane,

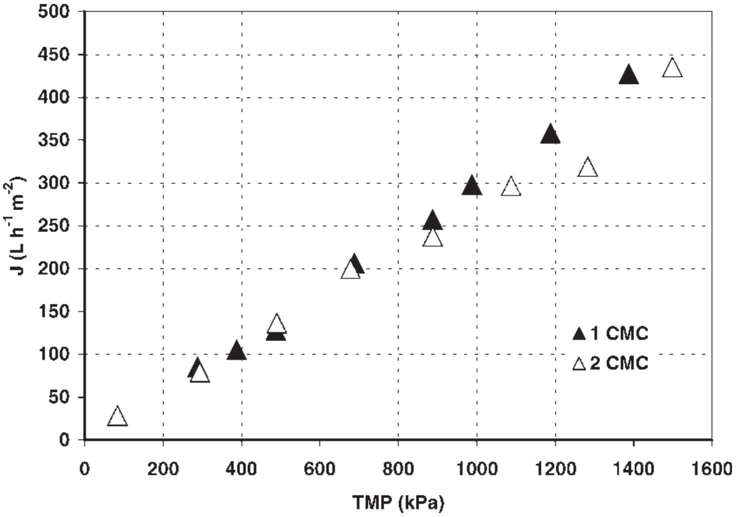

Figure 4. Variation of permeate flux versus TMP for SDBS concentration = 1 CMC and 2 CMC N = 1000 rpm, VRR = 1, 10 kDa membrane, disk with 6 mm vanes.

the flux is almost independent of rotation speed above 500 rpm, since at 900 kPa the flux is mainly governed by TMP. It is also possible that the effect of shear rate on permeate flux was small and offset by the decrease of TMP at large speed, but this result shows that the SDBS concentration polarization layer is

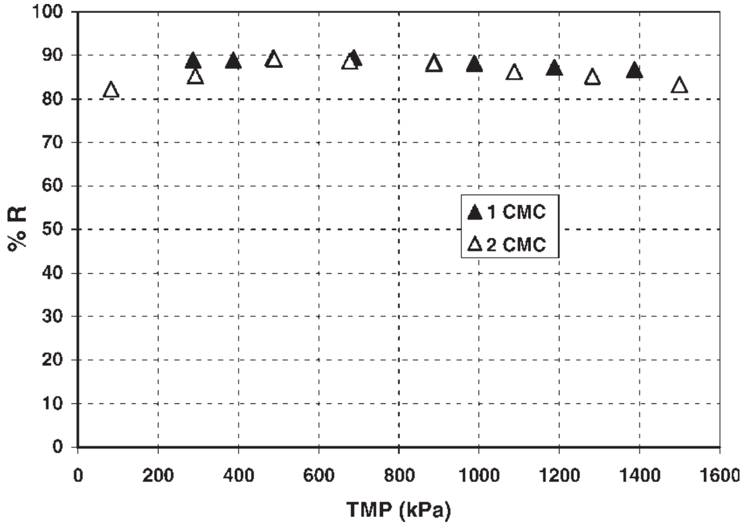

Figure 5. Variation of SDBS rejection with TMP at 1 CMC and 2 CMC, N = 1000 rpm and T = 25°C, VRR = 1, 10 kDa membrane disk with 6 mm vanes.

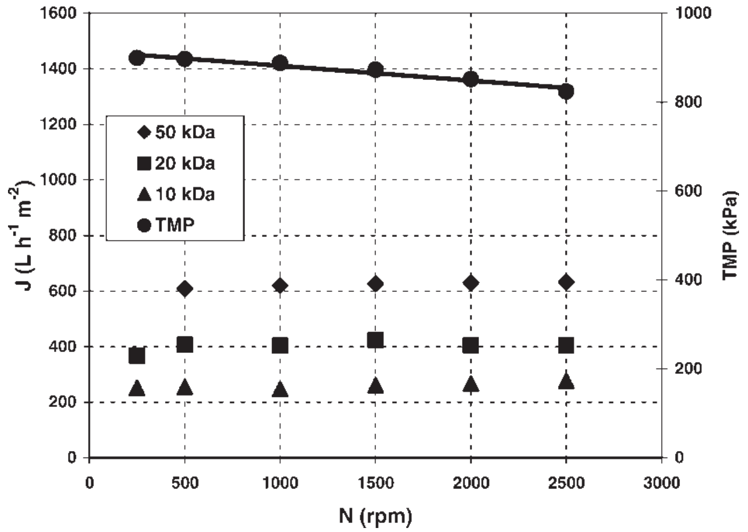

Figure 6. Variation of permeate flux versus disk rotation speed at various membrane cut-offs. SDBS=1 CMC, Pc = 900 kPa, T = 24°C, VRR = 1, disk with 6 mm vanes.

not easily reduced by the high shear rates due possibly by strong interactions between the membrane and surfactant molecules. Table 2 lists values of the permeate flux, and membrane shear rates for the various rotation speeds, and for two values of p_c equal to 900 and 1200 kPa for the three membranes, confirming the small effect of shear rate on the flux. This effect was, however, larger at 1200 kPa and for the 50 kDa membrane as the transition to mass transfer limited regime has begun in this case, as seen in Fig. 2.

Concentration Tests

These tests were carried out on 10 kDa membrane without permeate recycling to the feed tank, so that the volume reduction ratio (VRR) increased during the

Table 2. Variations of permeate flux with shear rate for various membranes

Rotation speed (rpm)	Shear rate $\gamma\,(s^{-1})$	Pc = 900 kPa [J (Lh^{-1}m^{-2})]			Pc = 1200 kPa [J (Lh^{-1}m^{-2})]		
		10 kDa	20 kDa	50 kDa	10 kDa	20 kDa	50 kDa
500	27637	255	403	609	347	566	816
1000	96237	248	406	619	349	612	1005
1500	199668	262	417	626	350	616	1065
2000	199668	268	419	629	366	619	1098
2500	500753	277	423	623	363	619	1122

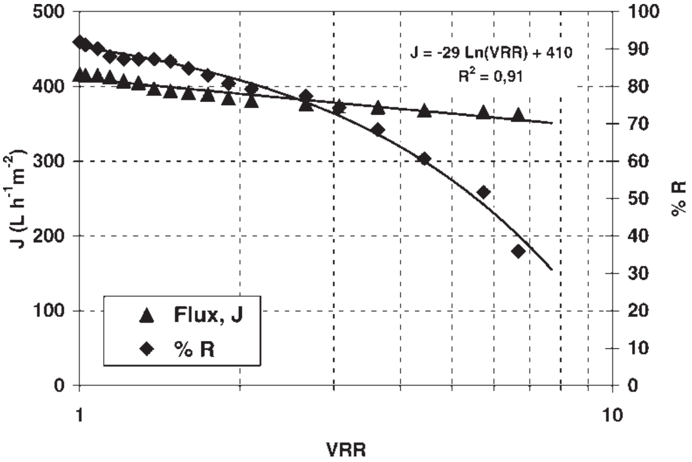

Figure 7. Variation of permeate flux and SDBS rejection with volume reduction ratio For N = 1000 rpm, a 10 kDa membrane, T = 24°C, Disk with 6 mm vanes. TMP = 1400 kPa.

test to reach about 9. As seen in Fig. 7, the permeate flux decreases relatively little with increasing VRR, as it is often the case in dynamic filtration (13). In addition, Table 3 shows that the solution viscosity does not rise very much with increasing concentration, as also observed by Guo et al. (18). This decay is a linear function of log (VRR) above VRR = 2 with a mass transfer coefficient equal to 29 $Lh^{-1} m^{-2}$, indicative that the flux was governed by mass transfer. The SDBS rejection decreases with increasing VRR and more rapidly at high VRR. This is in contrast to the UF of usual fluids such as protein solutions, for which rejection increases with VRR due to increased membrane fouling. So this unexpected observation may be due to changes in the physicochemistry of the surfactants such as transformation of micelles into monomers with higher transmission under shearing action or the formation of a coalescent layer at the membrane (19). A membrane cut-off below 10 kDa would have probably increased the rejection at large VRR, but at the expense of a lower permeate flux.

Table 3. Viscosities of SDBS solutions

Concentration (mML^{-1})	1.05	2.1	4.2	10.5	21	44	105	210
Viscosity (mPa · s)	0.87	0.90	0.93	0.98	1.04	1.07	1.22	2.10

CONCLUSION

This study has confirmed the potential of dynamic filtration with a rotating disk module for ultrafiltration of surfactant solutions, as it can yield very large permeate fluxes when the transmembrane pressure is increased to 1400 kPa, even at moderate rotation speeds such as 500 rpm, corresponding to an azimuthal velocity of 4 ms^{-1} for the disk rim. The specific energy consumed by disk friction per m^3 of permeate was not measured in this study, but it can be estimated from a previous investigation (20), after adjusting the viscosity to the present case, to be around 3 kWh m^{-3} for a module in which a disk with vanes was rotating at 1000 rpm. A good rejection, of around 92%, was obtained with a 10 kDa membrane at an optimal pressure of 700 kPa. But the behavior of our SDBS solution during high shear UF was different of that of particle suspensions or protein solutions, concerning the effect of rotation speed on the flux or the rejection decay at high concentration. Thus further studies of the physicochemical properties of SDBS solutions seem necessary.

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