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Interaction between surfactants of different classes and nanofiltration membranes

Interação entre surfactantes de diferentes classes com membranas de nanofiltração

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The presence of surfactants in aquatic environments may alter the water quality parameters. Nanofiltration is a promising technique that can separate surfactants from water with high rejections. Nevertheless, negative charges on nanofiltration membranes could facilitate the occurrence of electrostatic interactions between the charged surfactants and the surface of these membranes, increasing the membrane-fouling tendency. In this work, the interaction of surfactants commonly found in residential laundry wastewater with membranes used in nanofiltration was investigated. For this purpose, the surface, and transport properties of four commercial membranes were analyzed. The zeta potential of the NF90 membrane in the presence of individual and mixture of surfactants was performed to evaluate the effect of adsorption of these surfactants on the performance of the membrane. Additionally, a central composite rotatable design (CCDR) and response surface model were applied to investigate the simultaneous effect of the initial concentration of CTAB and SDS ($[CTAB + SDS]_0$) and pH on the NF90 permeate fluxes and rejections. It was shown that surfactant adsorption varies with the type of surfactant and membrane. Moreover, adsorption played an important role in NF90 membrane fouling, mainly for the cationic surfactant in individual solutions and in the mixture of surfactants. Besides adsorption, pore blocking may have affected the performance of nanofiltration for higher concentrations of surfactants. Finally, by the application of the central composite rotatable design (CCDR), it was possible to find the best conditions of pH and initial concentration of surfactants for achieving higher fluxes and rejections by the NF90 membrane.
Keywords: nanofiltration, surfactants, adsorption.

A presença de surfactantes em ambientes aquáticos altera os parâmetros de qualidade da água. A nanofiltração é uma técnica promissora que separa surfactantes da água com altas rejeições. Todavia, cargas negativas em membranas de nanofiltração facilitam as interações eletrostáticas entre os surfactantes e a superfície dessas membranas, e promovem a incrustação da membrana. Neste trabalho, foi investigada a interação de surfactantes encontrados em efluentes de lavanderias residenciais com membranas de nanofiltração. Para isso, foram analisadas as propriedades de superfície e transporte de quatro membranas comerciais. O potencial zeta da membrana NF90 na presença de surfactantes individuais e na mistura de surfactantes foi obtido para avaliar o efeito da adsorção desses surfactantes no desempenho da membrana. Adicionalmente, um planejamento composto central rotacional (DCCR) e o modelo de superfície de resposta foram aplicados para investigar o efeito simultâneo da concentração inicial de CTAB e SDS ($[CTAB + SDS]_0$) e do pH nos fluxos e rejeições pela NF90. Foi demonstrado que a adsorção de surfactante varia com o tipo de surfactante e membrana. Ademais, a adsorção teve um papel importante na incrustação da membrana do NF90, principalmente para o surfactante catiônico em soluções individuais e na mistura de surfactantes. Além da adsorção, o bloqueio de poros pode ter afetado o desempenho da nanofiltração para maiores concentrações de surfactantes. Por fim, com a aplicação do planejamento composto central rotacional (DCCR), foi possível encontrar as melhores condições de pH e de concentração inicial de tensoativos para obtenção de maiores fluxos e rejeições pela membrana NF90.
Palavras-chave: nanofiltração, surfactantes, adsorção.

1. INTRODUCTION

Increased amounts of wastewater are discharged by laundry processes. In fact, 15 L of water are used for each 1 kg of items cleaned at a laundry facility, which also takes part of 10% of the municipal sewer discharge [1]. In accommodation providers such as residences, hospitals and hotels, 12-25 L kg^{-1} of textile wastewater is produced [2]. The water quality parameters of these wastewaters will vary with the degrees of soiled objects cleaned, and with the type and amount of the detergents used in the cleaning process [3].

Surfactants from different classes are used in laundry detergent formulation, often at concentration ranges varying from 58 to 1,000 mg L^{-1} [4-7]. These surfactants are classified into three groups: anionic, cationic and nonionic, from which anionic and nonionic surfactants are the most employed in laundering processes, while cationic surfactants are reported to present bactericide properties [2]. Besides the presence of surfactants found in the formulation of detergents and softeners, laundry wastewaters may contain suspended solids, salts, nutrients, organic content, and pathogens [8]. Literature also reports the presence of other chemicals such as phosphates and other phosphorous compounds, chlorine bleach, hypochlorite, and fragrances [2].

Among the effects of the presence of surfactants in the aquatic ecosystem is the production of foams that form an insulation layer that blocks oxygen exchange between water and atmospheric air and cause the death of organisms by hypoxia, a change in surface tension that can promote the solubilization of other pollutants, mainly at concentrations above the critical micellar concentration [9], and modification of water quality parameters such as turbidity and pH [2]. Skin irritation and respiratory problems are some of the effects of human exposure to surfactants. As for aquatic organisms, exposure to surfactants may also reduce their resistance to environmental stress and affect their reproduction and growth processes [10].

Owing to the complex composition of laundry wastewaters, and the toxicological effects on humans and the ecosystem, advanced treatment alternatives are required for effectively removing surfactants from water and avoiding their reintroduction into the environment. Most of the remediation technologies to remove surfactants from water include processes such as filtration, flocculation-adsorption, electrocoagulation, electro-oxidation [10], and biological processes that involve the metabolic activity of bacteria or fungi [11].

Nanofiltration (NF) is a membrane process used for the treatment of a great variety of wastewater, especially for the removal of macropollutants. It is a promising alternative for the treatment of effluents with a high content of surfactants, such as laundry wastewater [12-19]. NF is also used for the control of emerging pollutants, such as endocrine disruptors, pharmaceuticals, and personal care products [20]. Nanofiltration membranes have intermediate characteristics between reverse osmosis (RO) and ultrafiltration (UF). Nanofiltration operates at lower pressures than RO and smaller pore sizes than UF membranes, resulting in higher surfactant retention from low to concentrated solutions (not in micelle form) [21, 22]. The surface charges of the nanofiltration membranes affect their separation performance, as well as the tendency of fouling. The interaction between inorganic and organic substances with the membrane surface in aqueous media is dependent on its surface properties, and pH is an important parameter that may affect electrostatic interactions between the charged surfactant and the membrane surface [18]. The study of such properties can be therefore considered an initial step toward a better understanding of membrane transport properties [23].

Fouling is a phenomenon inherent to membrane separation processes, which results in the reduction of permeate flux when operating at constant pressures. Membrane fouling can be related to the accumulation of the effluent components in the pores or surface of the membranes, and due to the adsorption of solutes involving specific or non-specific interactions [3, 24]. Understanding the interactions between the effluent components and the membrane surface is important for fouling evaluation, along with membranes performance tests, to fully explain the adsorption phenomenon.

Surfactants at concentrations above their critical micelle concentration (CMC) may be found in three forms in the aqueous phase: as monomers, as aggregates or adsorbed in the air/water interface [25]. The performance of membrane processes for removing surfactants in the form of aggregates or monomers may differ significantly. Literature reports that the initial concentration of the surfactants in the feed solution may affect the membrane flux because of concentration polarization, adsorption, and micelle formation [26].

Besides the form of surfactants in the aqueous phase, the contact angle and electrostatic interactions between the membrane and the surfactants were also reported to influence the performance of NF processes. For instance, Archer et al. (1999) [12] reported different separation efficiencies of surfactants by Nanofiltration, attributing it to the physical-chemical properties of surfactants and electrostatic interactions between the NF membrane and ionic species in the aqueous phase. Moreover, the hydrophilicity of NF membranes was reported to affect the flux behavior of nanofiltration for rejecting nonionic surfactants [13]. Adsorption of surfactants may occur through their hydrophobic tail or hydrophilic heads, producing a more hydrophobic or hydrophilic top layer on the membrane surface, respectively [27].

Moreover, although many studies have assessed the effect of the adsorption of individual surfactants and a mixture of surfactants on the performance of nanofiltration processes [13-14, 17-18], the literature still does not cover the application of experimental design to evaluate the simultaneous influence of the initial concentration of surfactants and the influence pH on the performance of nanofiltration processes.

Hence, the present study focuses on evaluating the viability of using nanofiltration for removing surfactants commonly found in laundry processes. For this purpose, the influence of membrane surface properties, the interaction between the surfactants found in real effluents with the membrane surface charge, and membrane performance were investigated. Selected membranes were characterized through contact angle and surface tension. Moreover, performance tests for assessing the flux permeates of CTAB and SDS solutions by nanofiltration membranes and their rejections to single salts and individual solutions of surfactants were investigated. Furthermore, the zeta potential of NF90 membrane in the presence of individual and mixture of surfactants was performed to evaluate the effect of adsorption of these surfactants on the performance of NF90. Finally, the central composite rotatable design (CCDR) and response surface model were applied to investigate the simultaneous effect of the initial concentration of CTAB and SDS ($[\text{CTAB} + \text{SDS}]_0$) and pH on the NF90 permeate fluxes and rejections. As far as we know, these aspects in combination have not been discussed in the literature so far.

2. MATERIAL AND METHODS

2.1 Membranes, chemicals and surfactants

Three nanofiltration membranes and one reverse osmosis (RO) membrane were investigated in this study. Their main characteristics are shown in Table 1. The surfactants cetyltrimethylammonium bromide (CTAB) ($C_{19}H_{42}BrN$) (98%) and sodium dodecyl sulfate (SDS) ($NaC1_2H_{25}SO_4$) (99%) were purchased from Vetec Química (Brazil). The nonionic surfactants Triton X-100 ($C_{14}H_{22}O(C_2H_4O)n(n=9\text{-}10)$) (90%) and Tween 80 ($C_{64}H_{124}O_{26}$) (97%) were obtained from Sigma Aldrich (Brazil) and Tedia (USA), respectively (Figure 1). MgCl2.6H2O (98%), Na_2SO_4 (99%), and NaCl (99%) were provided by Vetec (Brazil); KCl (74-78.1%) was supplied by Reagen (Brazil) and $MgSO_4.XH_2O$, by Sigma Aldrich (Brazil). All the chemicals were used as received. Solutions were prepared with distilled, deionized, and microfiltered water. Moreover, the pH of the solutions was adjusted with solutions of HCl (63%) and NaOH (98%) obtained from Vetec (Brazil).

Table 1: Specifications of the membranes used in the present study.

Membrane	**NF90 (NF)**	**NFS (NF)**	**SR90 (NF)**	**BW30 (RO)**
Manufacturer	Dow Filmtec	Synder	Dow Filmtec	Dow Filmtec
Material	Aromatic polyamide thin film	Polyamide thin film	Polyamide	Polyamide thin film
Maximum Pressure (bar)	41 [25]	41 [25]	41 (b)	41 (b)
pH range	2-11 [25]; 4-11 [26]	3-10.5	5-9 (b)	2-11 (b)
Zeta potential (mV) at neutral pH	−17.5 [26]	−75 [27]	−35.3 (a)	−5.2 [29]
Contact angle	43.2° [29]	28.3° [27]	29.7° (a)	60.8 [29]
Hydraulic permeability (L/(m².h.bar))	5.4 [25]	7.2 (a)	10.79 (a)	3.9 (a)

(a) Measured by the authors; (b) According to the membrane suppliers.

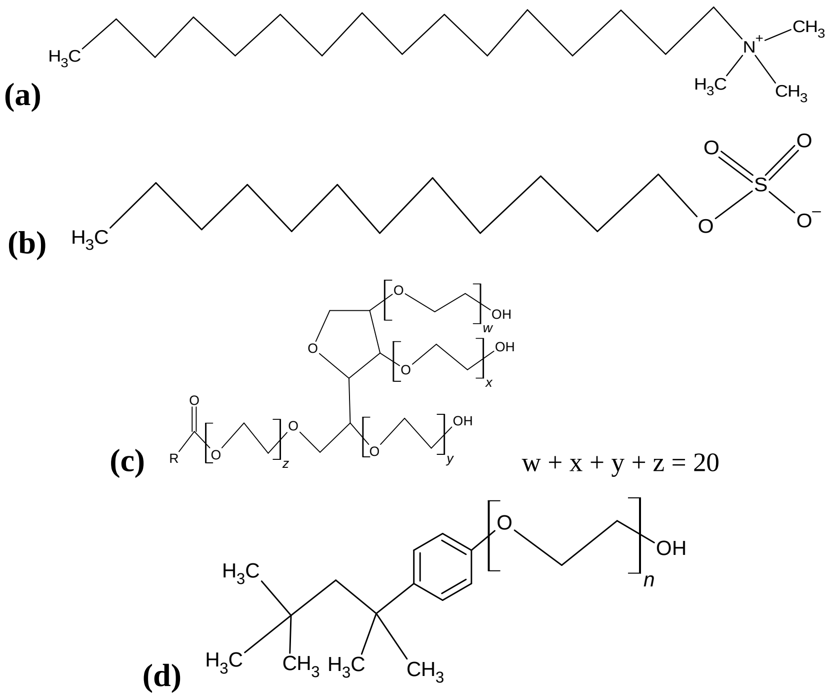

Figure 1: Structures of the surfactants: (a) CTAB; (b) SDS; (c) Tween 80 and (d) Triton X-100.

2.2 Quantification of surfactants

The concentration of the anionic and cationic surfactants was determined from conductivity measurements, using calibration curves obtained in the ranges 0.01-0.06 g L^{-1} and 0.2-1.0 g L^{-1} for CTAB and SDS, respectively.

2.3 Contact angle and surface tension measurements

The static contact angle was obtained by the sessile drop method using a goniometer (Dataphisics OCA 15, Germany) at room temperature. Measurements of the advancing angle after membrane immersion into the surfactant solution and its subsequent drying at room temperature were performed in triplicate. The surface tension was measured using the same device by the pendant drop method, extensively applied in the literature [28-30].

2.4 Zeta potential

The zeta potential of the membranes was determined by the streaming potential method using a SurPASS electrokinetic analyzer (Anton Paar, Austria) equipped with a clamping cell. The streaming potential generated was used to calculate the zeta potential using the Fairbrother-Mastin equation (Equation 1) [30, 31].

$$\left(\frac{\Delta\varphi}{\Delta P}\right) = \zeta\frac{\varepsilon_0\varepsilon_r}{\eta\lambda_0}\left(\frac{\lambda_h R_h}{R}\right) \quad (1)$$

where ζ is the zeta potential (mV), $\Delta\varphi$ is the measured streaming potential in the flow cell (mV), ΔP is the applied pressure (mbar), ε_0 is the vacuum permittivity (As Vm^{-1}), ε_r is the relative dielectric constant of the electrolyte solvent, λ_0 is the bulk conductivity of the circulating electrolyte (mS m^{-1}), λ_h is the conductivity of the electrolytic solution (mS m^{-1}), R_h is the electrical resistance (mV A^{-1}) across the flow channel filled with the highly saline reference solution and R is the electrical resistance (mV A^{-1}) across the flow channel filled with the regular experimental electrolyte. Prior to the sample mounting, the membranes were immersed in the measuring solution for 24 h.

2.5 Permeation tests

Permeation tests were conducted in a nanofiltration unit shown in Figure 2. The solution contained in the feed tank is transferred to the permeation unity containing the flat sheet membrane (effective permeation area = 28 cm^2) by a pump. The pressure is controlled by a valve and the concentrate and permeate streams are recycled to the feed tank. The temperature was kept at 24 ^{o}C by a heat exchanger. For all the experiments, the membranes were initially compacted to achieve a constant permeate flux by permeating pure water at the highest pressure used in the experiments. As for the hydraulic permeability measurements, the pressure was kept at the 5-20 bar range and at room temperature. Otherwise, the pressure was set at 15 bar. The feed rate was 48.8 L h^{-1} in all the experiments.

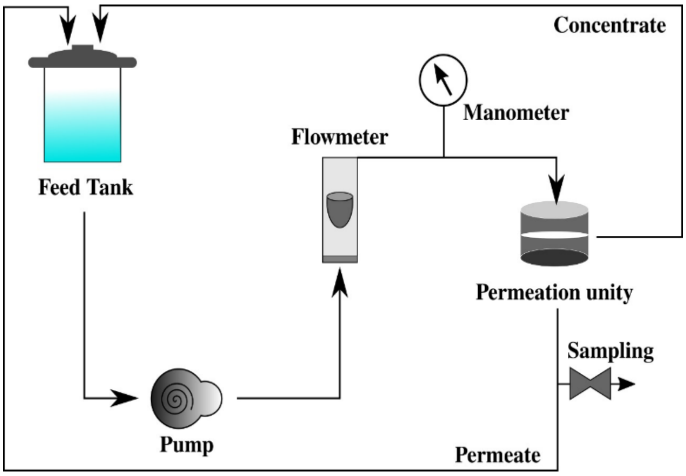

Figure 2: Scheme of the nanofiltration unit used in the experiments.

The permeate flux was determined as follows (Equation 2) [24]:

$$J_p = \frac{V_p}{t \; x \; A_M} \qquad (2)$$

Where:
J_p = permeate flux (L m^{-2} h^{-1});
V_p= volume of the permeate collected as a function of time (t) (L);
A_M= area of the membrane (0.0028 m²).

Moreover, the permeability was obtained from flux and trans-membrane pressure data, according to Equation 3 [32]:

$$J = P.\Delta P \qquad (3)$$

Where:
J = permeate flux (L m^{-2} h^{-1});
P = permeability (L m^{-2} h^{-1} bar^{-1});
ΔP = transmembrane pressure (bar).

Also, ions rejection (R%) was calculated from conductivity measurements, as shown in Equation 4 [33]:

$$R_{\%} = \left(\frac{Condutivity_{feed} - Condutivity_{permeate}}{Condutivity_{feed}}\right) x \; 100 \qquad (4)$$

2.6 Central composite rotatable design and response surface model

The central composite rotatable design (CCDR) (Table 2) and response surface model were applied to find the best conditions of initial CTAB and SDS concentrations and pH for achieving higher permeate fluxes and rejections by the NF90 membrane. The characteristics and advantages of this experimental design are fully covered in our previous work [34].

Table 2: Experimental design (CCDR) applied for removing the mixture of CTAB and SDS from water by the application of nanofiltration using NF90 membrane.

	X_1: [CTAB + SDS]$_0$ (mg L^{-1})		X_2: pH			
Exp.	**Codified values of X_1**	**Real values of X_1**	**Codified values of X_2**	**Real values of X_2**	***Rejections of CTAB and SDS (%)***	***Permeate flux for CTAB and SDS (L m^{-2} h^{-1})***
1	-1	390	-1	4.9	89.4	8.6
2	1	1,726	-1	4.9	94.0	4.3
3	-1	390	1	9.1	93.0	7.5
4	1	1,726	1	9.1	89.0	6.4
5	-1.41	116	0	7.0	81.0	8.6
6	1.41	2,000	0	7.0	86.0	6.4
7	0	1,058	-1.41	4.0	89.0	8
8	0	1,058	1.41	10.0	87.0	8.6
9	0	1,058	0	7.0	94.0	8.6
10	0	1,058	0	7.0	94.0	8.6
11	0	1,058	0	7.0	95.0	8.6

Two independent variables were selected such as the total concentration of surfactants CTAB and SDS (X_1) and pH (X_2) of the solution, and the other variables were maintained constant throughout the experiments (pressure at 15 bar and temperature 24 ºC). A total of 11 experiments were performed, including a triplicate to assess the experimental error. The minimum and maximum values of the total concentration used (including equal amounts of SDS and CTAB added to the solutions) were selected according to the respective concentrations of anionic and cationic surfactants in laundry effluents [4-7]. Moreover, equal amounts of CTAB and SDS were added to the solution, to evaluate the simultaneous influence of CTAB and SDS on the performance of NF90, at the same initial concentration. As for the pH, the range 4-10 was selected according to the specifications of the membrane. Moreover, response variables such as rejection (%) and permeate fluxes (L m^{-2} h^{-1}) were evaluated to investigate the performance of NF90 for removing surfactants from synthetic solutions produced by the mixture of surfactants. Finally, the results were treated by the software Statgraphics®, generating polynomial regression models that were adjusted to the experimental results by applying the least squares method.

3. RESULTS AND DISCUSSION

3.1 Surface tension and contact angle

To shed light on the hydrophilicity of the membranes, and possible electrostatic interactions between the membranes and the surfactants, the contact angle of pure water and surfactant solutions with the membrane surfaces were measured (Table 3). For NF90 and NFS membranes, contact angles were found in the literature. In this study, information regarding the surface tensions and concentrations of surfactants evaluated in this study are shown in Table 3. Higher concentrations of anionic surfactants are usually applied in laundering processes due to the higher dosage of powder/liquid detergents compared to those of the softeners [35]. Also, according to Table 3, only the nonionic surfactant Tween 80 is present at concentrations higher than the critical micelle concentration (CMC), and therefore, may also be in the form of micelles in the bulk solution.

Table 3: Water contact angles and contact angles of individual solutions of surfactants on the surface of NF90, NFS, BW30 and SR90 membranes, at pH 6-7.

Membrane	**Water**	**CTAB** (58 mg L^{-1})	**SDS** (1000 mg L^{-1})	**Triton X-100** (58 mg L^{-1})	**Tween 80** (58 mg L^{-1})
NF90	43.2° [29]	60.5°	58.2°	14.1°	55.5°
NFS	28.3° [27]	39.0°	8.3°	14.7°	57.0°
BW30	53.7°	60.1°	41.3°	24.0°	53.2°
SR90	29.7°	10.3°	18.2°	20.1°	48.3°

In addition, as shown in Table 3, pure water contact angles are lower than 90°, confirming their hydrophilicity. After immersion in CTAB solutions ($[CTAB]_0$ = 58 mg L^{-1}), an increase in contact angles and more hydrophobic surfaces of NF90, NFS, and BW30 membranes were observed. In the study of Boussu et al. (2007) [27], the water contact angle of the NF270 membrane was 27°, increasing to 33° after contact with the cationic cetrimide solution. According to the authors, the negative top layer of the NF270 membrane attracted the positively charged head of the cetrimide molecule, resulting in the adsorption of the surfactant. Moreover, Childress and Elimelech (2000) [36] observed adsorption of the cationic surfactant DTAB onto the NF-55 membrane surface due to electrostatic attraction, and further formation of hemimicelle. Oppositely, the hydrophilicity of the SR90 membrane increased after contact with the cationic surfactant. This behavior is explained by the association of surfactant ions to remove their hydrocarbon chains from the bulk and reduce the free energy of the system. This effect was also reported by Boussu et al. (2007) [27] for the Desal51HL and NFPES10 membranes after contact with cetrimide solution at a concentration lower than the CMC.

In terms of the changes observed for the anionic surfactant SDS, contact angles of the membranes NFS, BW30, and SR90 were lowered significantly after contact with SDS solutions. The increase in hydrophilicity of these membranes is explained by the adsorption of surfactant molecules by hydrophobic interactions through the hydrophobic tail, exposing their polar negative heads to the bulk, as also observed by Childress and Elimelech (2000) [36] for the NF55 membrane after contact with SDS solution at pH around 8. Interestingly, after contact with the anionic surfactant solution, the NF90 membrane showed to be more hydrophobic, which may be attributed to the lower negative surface charge of the NF90 membrane at the pH of the measurements (between 6-7) [27], as well as the direction of the surfactant along the surface of the membrane [37] that could lead to lower interactions between the hydrophobic tail and the surface of the membrane.

Nonionic surfactants were reported to interact with hydrophobic groups of membrane surfaces through London and van der Waals interactions [13], therefore, the surfactant hydrophobic tails have a higher tendency to adsorb onto the hydrophobic groups of the membrane surface. Nevertheless, the nonionic surfactants Triton X-100 and Tween have shown opposite effects on the contact angle of the membranes evaluated in this study. For instance, contact angles of the membranes with Triton X-100 were lowered in comparison to those of pure water, while higher contact angles were observed after immersion of the membranes in surfactant solutions of Tween 80, compared to those of pure water (Table 3). Tween 80 is at a concentration higher than its CMC, and therefore, the formation of micelles of Tween 80 molecules may have occurred, generating a layer with the tail groups of Tween 80 oriented to the bulk of the solution [38], which explains the higher contact angles observed. On the other hand, adsorption of hydrophobic tails of Triton X-100 molecules by hydrophobic interactions [27], and with the hydrophobic groups exposed to the bulk of the solution may have increased the hydrophilicity of the membranes.

3.2 Performance tests of nanofiltration membranes

The effect of charged surfactants CTAB ($[CTAB]_0$ = 58 mg L^{-1}) and SDS ($[SDS]_0$ = 1,000 mg L^{-1}) on the performance of nanofiltration membranes was explored (Figure 3). For all the membranes tested, permeate fluxes of SDS were greater than those achieved for CTAB. Also, from Table 3, contact angles of NFS, BW30, SR90 decreased significantly after contact with SDS solution at the same initial concentration, indicating a higher hydrophilicity of these membranes. Therefore, it appears that adsorption of SDS on these membranes makes them more hydrophilic, increasing permeate fluxes. This effect was also observed by Nguyen et al. (2015) [38] during ultrafiltration of nonionic surfactants. The authors observed stable or higher fluxes than the pure water flux during ultrafiltration of nonionic surfactants.

Oppositely, membranes NF90, NFS, and BW30 after contact with solutions of CTAB at initial concentration of 58 mg L^{-1} had their hydrophobicity increased, due to the adsorption of these surfactants on the membrane surface. Even at concentrations lower than CMC, surfactants may decrease permeation fluxes during nanofiltration processes, due to the strong electrostatic interaction between the negative membranes and the positive charged cationic surfactant. For instance, previous studies observed a significant decline in permeate fluxes of surfactants at concentrations lower than their CMC, due to the formation of hemimicelles at the solid/solution interface [13].

Also worth of mentioning is that the highest fluxes for SDS and CTAB were achieved by SR90 and NFS membranes, respectively. However, for the purpose of real effluents containing higher surfactants of both CTAB and SDS, SR90 membrane is recommended, due to its higher hydrophilicity after contact with both surfactants (Table 3).

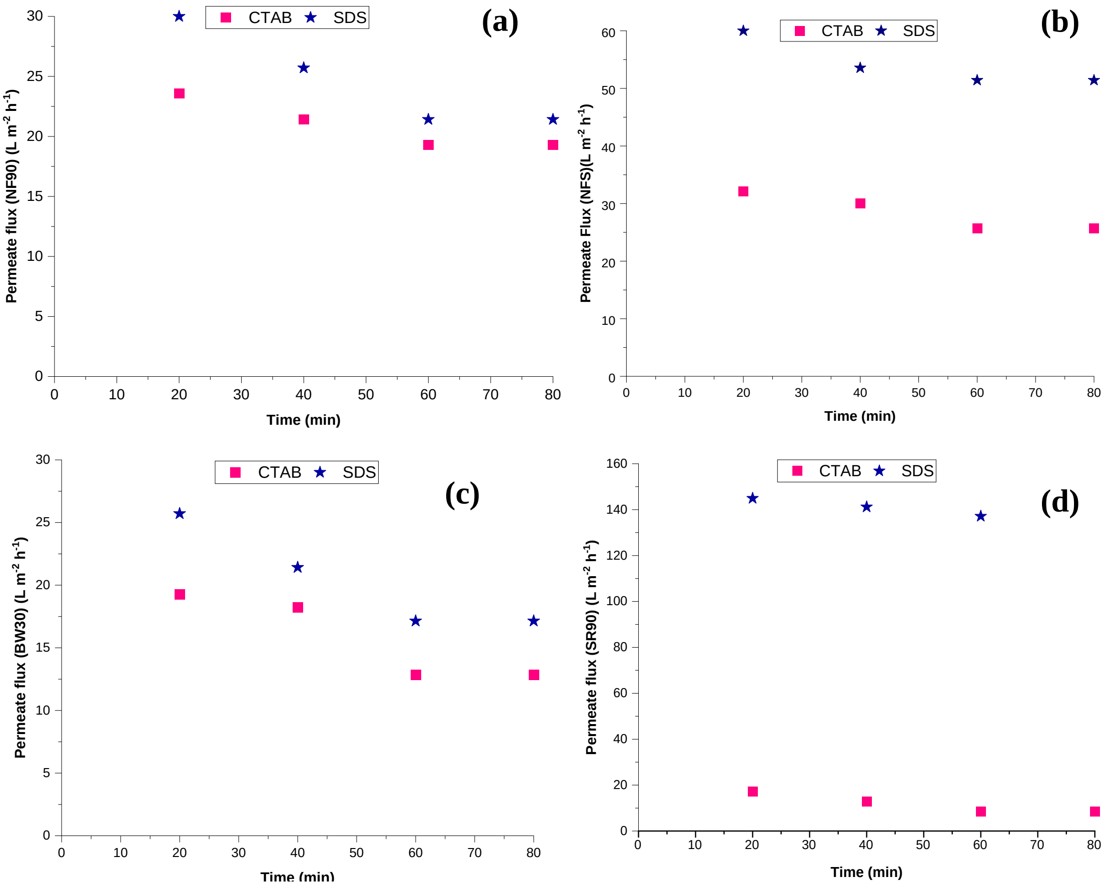

Figure 3: Permeate fluxes of anionic and cationic surfactants by NF90 (a), NFS (b), BW30 (c) and SR90 (d) membranes.

3.3 Rejection of single salts and individual solutions of surfactants

Besides the high hydrophilicity observed for the SR90 membrane (Table 3), other factors such as the composition and morphology of the selective layer [39], as well as the structure of NF membranes [40] may result in different membrane permeabilities. In this study, the performance of the NF90, BW30, NFS and SR90 membranes for rejecting salts and surfactants was investigated. Membranes were initially characterized in terms of the hydraulic permeability, rejections to the individual solutions of surfactants, and permeate fluxes calculated by Equation 2, Equation 3 and Equation 4, respectively. Permeabilities of NF90, BW30, NFS and SR90 were 2.5, 3.9, 7.2 and 10.8 L m^{-2} h^{-1} bar^{-1}, respectively, so the highest permeability was observed for the SR90 membrane (Figure 4).

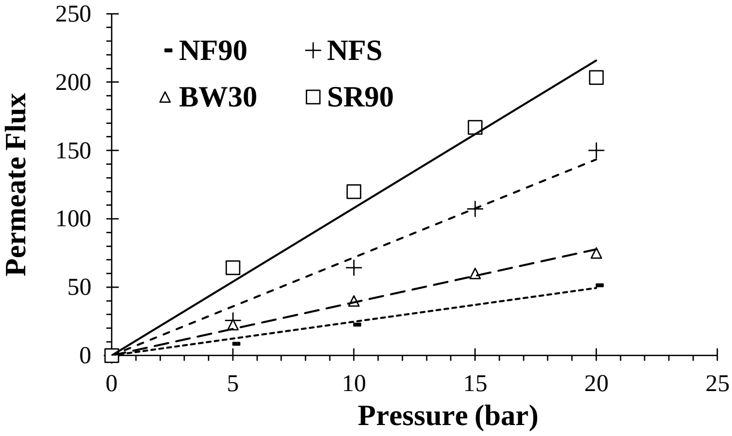

Figure 4: Water permeate flux as a function of the transmembrane pressure and permeability data. Feed flow rate: 48.8 L h^{-1}.

In terms of salt rejections (Figure 5), initial concentration of the salts $MgCl_2$, $MgSO_4$, and Na_2SO_4 was approximately 2 g L^{-1}, while initial SDS and CTAB concentrations were 1 g L^{-1}. The pH of the solutions was about 7.5, though the isoelectric point of nanofiltration and reverse osmosis membranes is around 4.7 [41]. Higher rejections of $MgCl_2$, $MgSO_4$, and Na_2SO_4 were observed for BW30 membrane, which corresponds to the unique characteristics of reverse osmosis membranes [23], while NF90 presented the highest rejections towards CTAB and SDS.

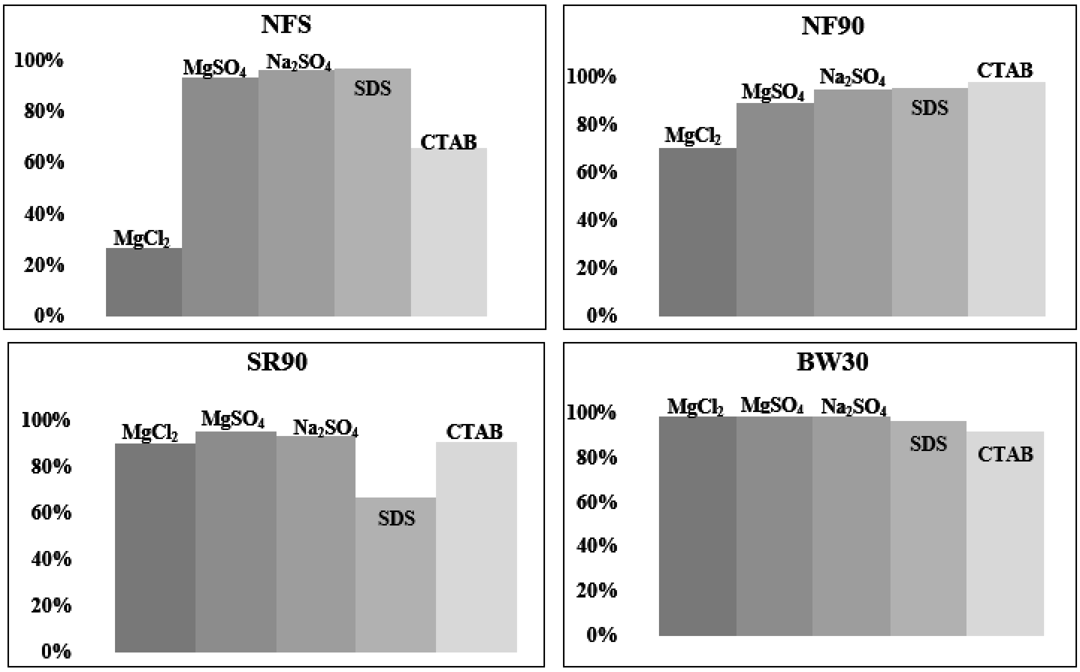

Figure 5: Membranes rejections to salts (at initial concentrations of 2 g L^{-1}) and surfactants (1 g L^{-1}). Experimental conditions: pressure of 15 bar and feed flow rate of 48.8 L h^{-1}.

In general, results have shown that Na^+ was satisfactorily rejected by the NFS, NF90, SR90 and BW30 membranes. However, in terms of Mg^{2+} rejections, higher rejections were achieved by SR90 and BW30 membranes, when compared to those obtained by NF90 and NFS membranes. This behavior could be explained the smallest pore size of SR90 and BW30 membranes, or to the higher electrostatic interaction between the NF90 and NFS membranes and the Mg^{2+}, resulting in a reduction of the salt rejection for these membranes. Thabo et al. (2021) [42] also observed higher rejections of Na^+ in NF270 and NF90 membranes and lower rejections of Mg^{2+}, attributing this result to the charge effects of these membranes governed by Donnan exclusion.

As for CTAB and SDS rejections, CTAB is at a concentration higher than its CMC (Table 4), therefore, the formation of micelles may have occurred. In fact, higher rejections of CTAB were observed for SR90 membrane, in comparison to the rejection of SDS solution. This effect could be attributed to the formation of a closed packed layer on the membrane surface [43], leading to higher rejections [12]. Oppositely, NFS membrane has shown higher SDS rejection when compared to CTAB rejection by the same membrane. According to Al-Amoudi and Lovitt (2007) [23], even at concentrations lower than the CMC, SDS can adsorb onto the negative surface of nanofiltration membranes by an ion exchange mechanism and lead to a higher concentration and further micellization of SDS near the membrane surface, which could have led to higher rejections [12].

Table 4: Surface tension of the aqueous surfactant solutions.

	CMC (mg/L)	**Concentration (mg/L)**	**Concentration (mmol/L)**	**Surface Tension (mN/m)**
Cationic surfactant (CTAB)	335-365	58	0.16	68.2
Anionic surfactant (SDS)	2,019-2,884	1,000	3.47	52.0
Nonionic surfactant (Tween 80)	13-15	58	0.04	47.2
Nonionic surfactant (Triton X-100)	125	58	0.09	30.5

*The CMC values were taken from the product specification sheets.

Finally, the similar rejections of SDS and CTAB by NF90 and BW30 membranes, with a slightly higher rejection of salts by the BW30 were observed in this study. Interestingly, Zhang et al. (2020) [44] also observed similar rejections of the herbicide 2-methyl-4-chlorophenoxyacetic acid by NF90 membrane and RO membranes. Therefore, it can be concluded that nanofiltration and RO membranes may achieve similar rejections for some organic compounds, depending on the operational conditions applied, and characteristics of the organic compound to be removed.

3.4 Zeta potential and adsorption of surfactants and their mixtures on NF90 membrane

NF90 membrane was chosen for further evaluation of the adsorption of the surfactants CTAB, SDS, Tween80 and their mixture by measurements of zeta potential (Figure 6). The concentration of these surfactants was selected according to their occurrence in real effluent, as previously stated.

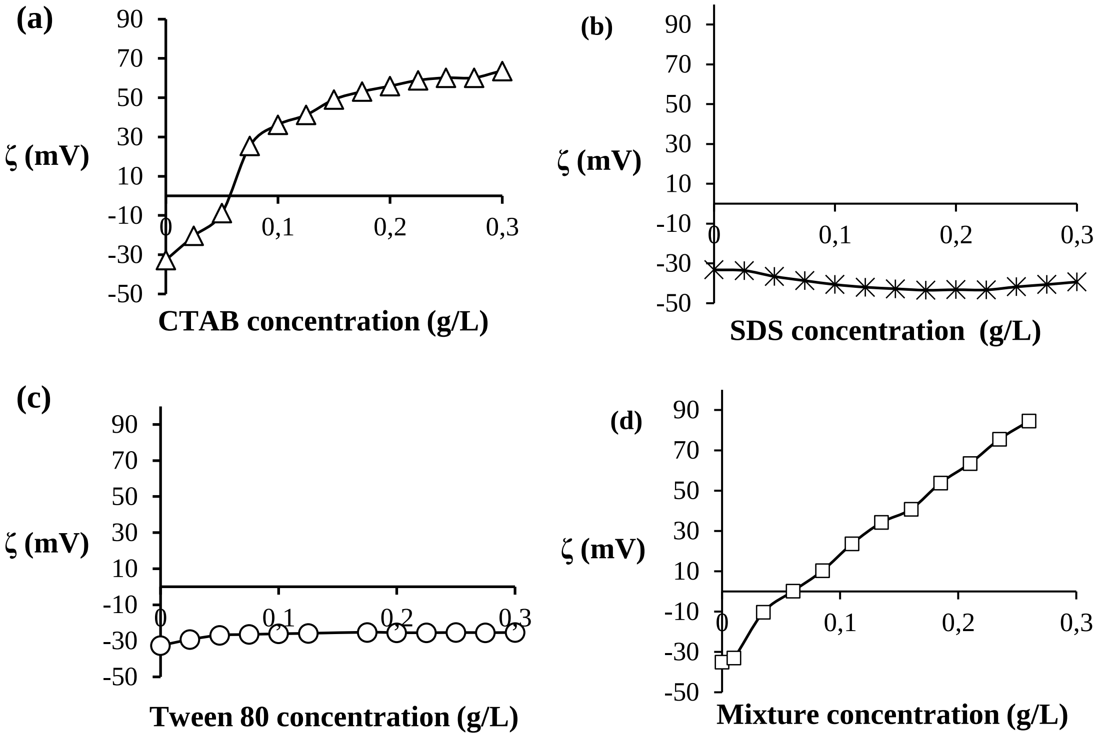

Figure 6: Zeta Potential of the NF90 membrane as a function of surfactants concentrations, (a) CTAB, (b) SDS, (c)Tween 80 and (d) mixture of surfactants (equal mass proportion of each surfactant in the solution) (pH 6-7).

At the initial pH of the aqueous solutions prepared (6-7) the NF90 membrane is expected to present negative charge (Table 1). However, the presence of surfactants may alter the zeta potential of nanofiltration membranes due to the formation of a new layer at the interface [31]. Figure 6a shows that at initial CTAB concentrations around zero, the zeta potential of NF90 was predominantly negative. Nevertheless, with increasing CTAB concentrations to values higher than 0.05 g L^{-1}, positive values of the zeta potential were achieved, reaching a maximum of approximately 70 mV. This behavior suggests the formation of a positive layer on the surface of the NF90 membrane, which is in accordance with the change observed in the contact angle of this membrane after contact with CTAB solution.

As for SDS and Tween80 surfactants, the observed zeta potential of the membrane was predominantly negative (Figure 6b and Figure 6c, respectively), though a slight increase in positive charges on the surface of the membrane occurred as the concentration of these surfactants increased to values up to 0.05 g L^{-1} and 0.2 g L^{-1}, respectively. This behavior was also identified by the slight change in contact angle of the NF90 membrane after contact with the solutions of SDS and Tween 80, increasing from 43.3° to 58.2° and 55.2°, respectively. Therefore, possible interactions between the hydrophobic tail of SDS molecules, and hydrophobic interactions of Tween 80 with the negative surface of the NF90 membrane may have occurred, leading to the decrease in the zeta potential magnitude.

Finally, the zeta potential of the NF90 membrane increased linearly with the increase in initial concentration of the surfactants in the mixture (Figure 6d). A similar behavior was observed for the individual solution of CTAB, suggesting that the adsorption of CTAB is dominant in the mixture, when compared to the adsorption of SDS. This behavior is expected given the strong electrostatic attraction between the oppositely charged head of the cationic surfactants.

3.5 Effect of pH and initial concentration of surfactants on the performance of NF90 membrane

NF90 was chosen to further clarify the impact of initial concentration of surfactants and the pH on the rejections and permeate fluxes of CTAB and SDS (Table 1). Moreover, among nanofiltration membranes, NF90 has shown the highest rejections towards CTAB and SDS (Figure 5). For this aim, experiments were carried out by following a DCCR for the for the mixture of CTAB and SDS $[\text{CTAB+ SDS}]_0$.

3.5.1 Permeate flux of the mixture CTAB and SDS by the NF90 membrane

Regarding the permeate fluxes of the mixture of surfactants after 80 minutes of permeation, the ANOVA has indicated that the negative effect of $[\text{CTAB + SDS}]_0$ was statistically significant (F test, and p-value < 0.05), as also shown by the Pareto chart (Figure 7 and Table 5). Moreover, a determination coefficient of $R^2 = 0.816$ was obtained by the response surface model (Eq. 5). Figure 8 shows the response surface and contour plot.

$$\text{Permeation flux (L m}^{-2}\text{ h}^{-1}) = 8.538 - 1.065X_1 + 0.249X_2 - 0.829X_1^2 - 0.401X_2^2 + 0.8X_1X_2 \quad (5)$$

Where X_1 is the total concentration of CTAB and SDS, and X_2 is the pH of the solution.

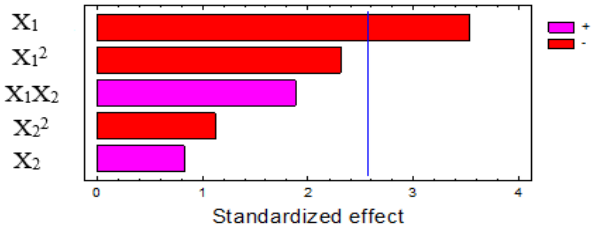

Figure 7: Pareto chart of standardized effects for permeate fluxes of mixed surfactants by NF90 membrane.

Table 5: ANOVA for permeate fluxes of mixed surfactants by NF90 membrane.

Source	**Sum of squares**	**Df**	**Mean square**	**$F_{\text{-ratio}}$**	**p-value**
X_1	9.06246	1	9.06246	12.52	0.0166
X_2	0.494994	1	0.494994	0.68	0.4460
X_1^2	3.85303	1	3.85303	5.32	0.0692
X_1X_2	2.56	1	2.56	3.54	0.1188
X_2^2	0.904399	1	0.904399	1.25	0.3145
Total error	3.61977	5	0.723954		
Total (corr.)	19.7473	10			

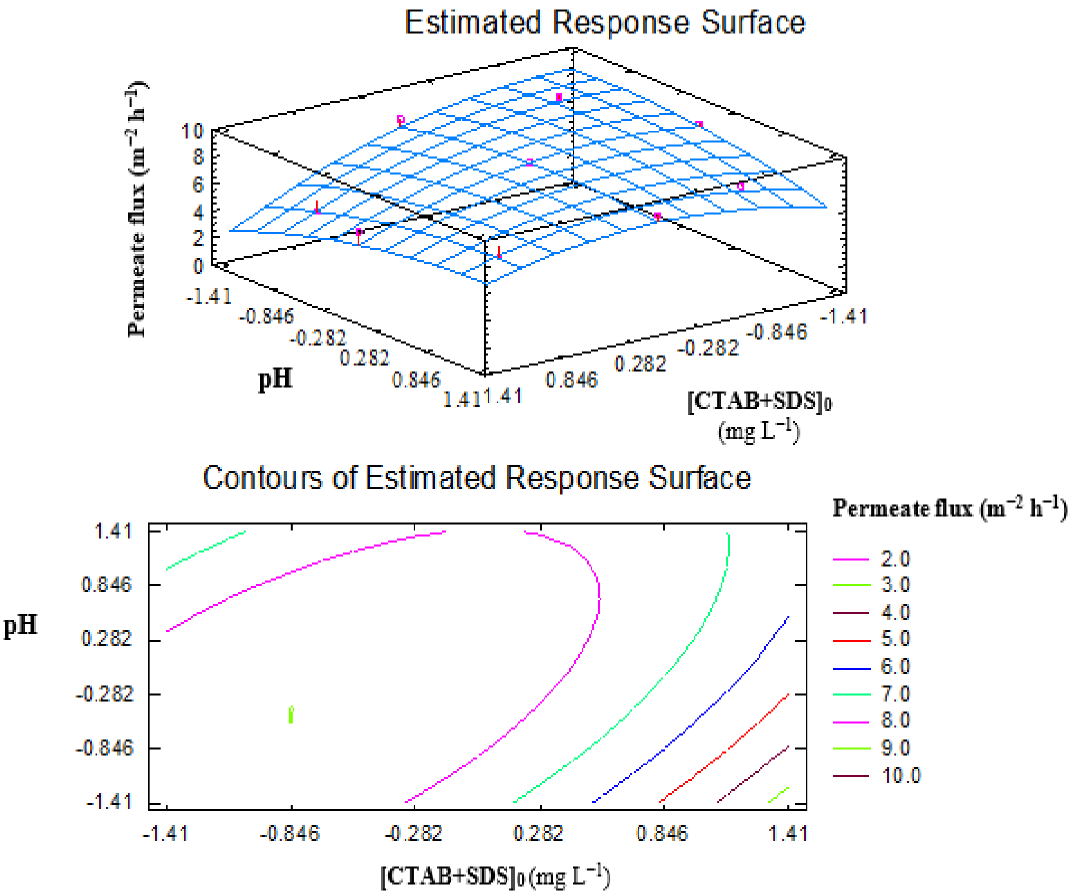

Figure 8: Response surface and contour plot for permeate flux of mixed surfactants by NF90 membrane, varying X_1 from -1.41 to 1.41 and X_2 from -1.41 to 1.41.

As observed in Table 2, the lowest permeate flux was 4.3 L m^{-2} h^{-1} obtained at experimental conditions of experiment 2: [CTAB + SDS]$_0$ and pH values of 1,726 mg L^{-1} and 4.9, respectively. Nevertheless, with decreasing [CTAB + SDS]$_0$ to 390 mg L^{-1} in experiment 1, at the same pH (4.9), permeate flux has doubled to 8.6 L m^{-2} h^{-1}. The same negative effect of [CTAB + SDS]$_0$ was observed in experiments 3 and 4, when increasing pH to 9.1. In fact, increasing the initial concentration of the surfactants from 390 to 1,726 mg L^{-1}, declined permeate flux from 7.5 to 6.4 L m^{-2} h^{-1}. At neutral pH (7), permeate flux also decreased from 8.6 to 6.4 L m^{-2} h^{-1} as [CTAB + SDS]$_0$ increased from 116 to 2,000 mg L^{-1}. This effect is explained by the adsorption of these surfactants at their micellar concentration, as observed in contact angle (Table 3) and zeta potential of NF90 membrane shown in Figure 6a and Figure 6b. Besides the interaction of these charged surfactants with the nanofiltration membrane, interactions between the surfactants may also occur, resulting in pore obstruction and flux decline [27].

Boussu et al. (2007) [27] observed a decrease in relative fluxes of the hydrophilic membrane Desal51HL as initial concentration of the anionic and cationic surfactants sodium dodecylbenzenesulfonate (SDBS) and cetrimide increased from 20 to 70 mg L^{-1}, at pH 6. In addition, Kowalska (2014) [45] evaluated the application of the nanofiltration-ion exchange system for removing surfactants from water, and as initial SDBS concentration increased in the feed solution from 1.3 to145 mg L^{-1} for NP010 membrane and from 1.2 to 106 mg L^{-1} for NP030 membrane, the permeabilities of these membranes were decreased [45].

However, permeate flux was 8.6 L m^{-2} h^{-1} as initial [CTAB + SDS]$_0$ was 1,058 mg L^{-1} and pH values were 7 (experiment 8) or 10 (experiments 9-10). This result shows that the negative effect of increasing initial concentration to 1,058 mg L^{-1} of these surfactants does not occur at pH values of 7 and 10. Luo et al. (2012) [18] evaluated the permeate fluxes of NF270 membrane at different pH values for removing anionic surfactants from water. The authors observed similar permeate fluxes at pH 4.2 and 7.1, and a significant increase in permeate fluxes as pH changed to 9.9, suggesting a lower concentration polarization of surfactant molecules at higher pH values. Boussu et al. (2007) [27] observed higher hydrophilicity of different nanofiltration membranes after contact with the anionic surfactant SDBS and the cationic surfactant cetrimide solutions at high pH, attributing this behavior to the hindered formation of hemimicelles when increasing pH from 6 to 7.

In summary, it can be concluded that permeate fluxes of NF90 were severely declined in the presence of the mixture of surfactants when compared the fluxes achieved for single solutions of surfactants (Figure 3), which could be attributed to the stronger adsorption of surfactant mixtures, as observed by Liu and Kim (2009) [46]. In fact, pore blocking of surfactant on the membrane surface and within membrane pores may also lead to permeate flux reductions [47]. Finally, the best conditions of $[CTAB + SDS]_0$ and pH, for achieving the highest permeate flux (9 $L\ m^{-2}\ h^{-1}$) for the mixture of surfactants by the NF90 membrane were found by the model, corresponding to values of $[CTAB + SDS]_0 = 426.2$ mg L^{-1} (X_1: −0.94841) and pH = 5.2 (X_2: −0.63422), respectively. Therefore, these experimental conditions must be suitable for the application of nanofiltration of laundry wastewaters containing both classes of surfactants.

3.5.2 Rejections of the mixture CTAB and SDS by the NF90 membrane

Regarding the rejections of the mixture of surfactants, the ANOVA has indicated that the positive effect of $[CTAB + SDS]_0$ was statistically significant (F test, and p-value < 0.05), as also shown by the Pareto chart (Figure 9 and Table 6). Moreover, a determination coefficient of $R^2 = 0.896$ was obtained by the response surface model (Eq. 6). Figure 10 shows the response surface and contour plot.

$$\text{Rejections (\%)} = 86.58 + 5.27X_1 - 0.94X_2 - 0.42X_1^2 + 1.66X_2^2 - 0.20X_1X_2 \quad (6)$$

Where X_1 is the total concentration of CTAB and SDS, and X_2 is the pH of the solution.

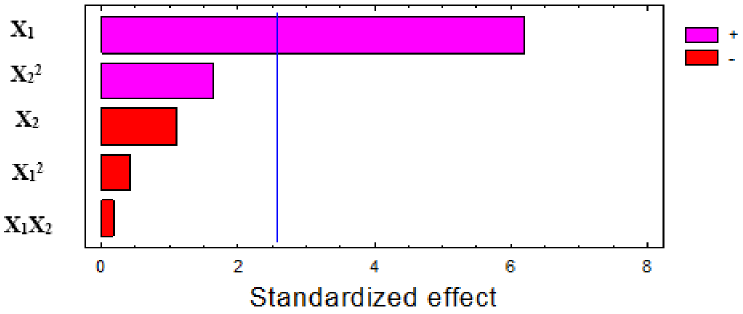

Figure 9: Pareto chart of standardized effects for rejections of mixture of surfactants by NF90 membrane.

Table 6: ANOVA for rejections of mixture of surfactants by NF90 membrane.

Source	Sum of squares	Df	Mean square	F_{-ratio}	p-value
X_1	222.054	1	222.054	38.51	0.0016
X_2	7.07124	1	7.07124	1.23	0.3186
X_1^2	1.02095	1	1.02095	0.18	0.6914
X_1X_2	0.164025	1	0.164025	0.03	0.8727
X_2^2	15.4925	1	15.4925	2.69	0.1621
Total error	28.8344	5	5.76688		
Total (corr.)	278.702	10			

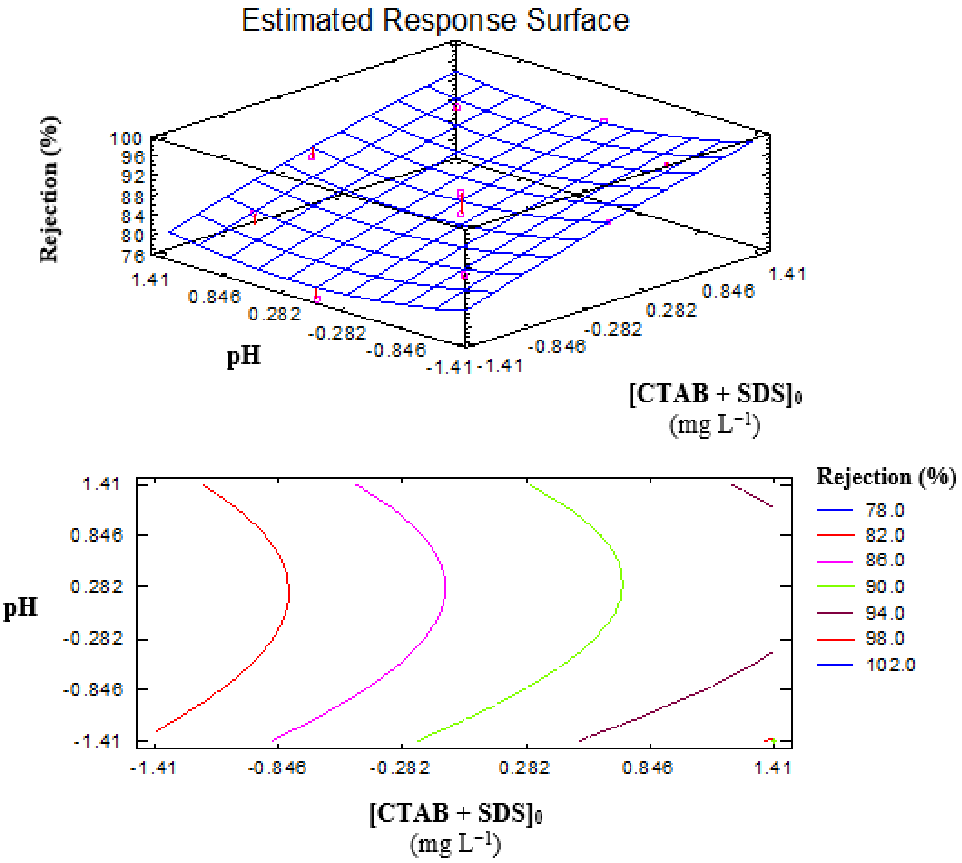

Figure 10: Response surface and contour plot for rejections of mixed surfactants by NF90 membrane, varying X_1 from -1.41 to 1.41 and X_2 from -1.41 to 1.41.

In general, NF90 membrane rejections towards the mixture of surfactants varied between 81 to 95% and showed to be similar to the rejections obtained for individual solutions of CTAB and SDS (Figure 5). The highest rejection was achieved at experimental conditions of pH 7 and $[CTAB + SDS]_0$ of 1,058 mg L^{-1}, corresponding to a rejection of 95%. Similar rejections were achieved (93-98%) by permeation with Desal 5 DL nanofiltration membrane of a real effluent containing a mixture of nonionic surfactants [13]. This result is important and proves the efficiency of NF90 for removing a mixture of surfactants.

Also worth of mentioning is that the positive effect of increasing $[CTAB + SDS]_0$ on the rejections of NF90 was more pronounced at pH 4.9 (experiments 1 and 2), pH 7 (between experiments 5 and 6, and between experiments 5 and 9,10,11). Among experiments 1 and 2, as $[CTAB + SDS]_0$ increased from 390 to 1,726 mg L^{-1} at pH 4,9, NF90 membrane rejection was improved, increasing from 89.4 to 94 %, respectively. A slight increase in rejection was also achieved within experiments 5 and 6, with increasing $[CTAB + SDS]_0$ from 116 to 2,000 mg L^{-1} at pH 7, while the highest increase was observed between experiment 5 and the triplicate of the central point (experiments 9, 10 and 11). In fact, rejection was increased from 81 to 86% within experiments 5 and 6, and from 81% to (94 ± 0.6)% for experiments 5 and under the conditions of the central point (experiments 9, 10 and 11). As for the pH, the opposite effect was observed, and increasing pH has led to lower rejections, except for conditions of higher concentrations of $[CTAB + SDS]_0$, such as 1,058 and 1,726 mg L^{-1}.

The higher rejections observed with increasing initial concentration of SDS and CTAB in the mixture are explained by the important role of adsorption of these surfactants and the occurrence of pore blocking on the membrane surface. Also, it can be assumed that the cationic surfactant exerted greater influence on adsorption, due to the higher rejections (Figure 5) and significant decline in permeate fluxes of single CTAB solutions (Figure 3a) by NF90 membrane.

Finally, the best conditions of $[CTAB + SDS]_0$ and pH, for rejecting 98.2 % of the surfactants by the NF90 membrane were found by the model, corresponding to values of $[CTAB + SDS]_0$ = 1,000 mg L^{-1} (X_1: 1.41) and pH = 4.0 (X_2: −1.41), respectively. Therefore, these experimental conditions must be suitable for the application of nanofiltration of laundry wastewaters containing both classes of surfactants.

4. CONCLUSIONS

The class of the surfactants and their initial concentration in the solution, as well as the membrane type, play an important role in the interaction between the membrane and the surfactant. In this study, results have shown that anionic and cationic surfactants at concentrations lower than their CMC adsorbed onto the surface of most of the membranes through electrostatic interaction, while hydrophobic interactions were responsible for the adsorption of nonionic surfactants. Nevertheless, at concentrations higher than the CMC, surfactants in the form of micelles may form a layer on the surface of the membrane, which may also lead to changes in contact angle and hydrophilicity of the membranes.

In addition, permeate fluxes of SDS were higher than those observed for CTAB solutions for all the membranes tested. However, in terms of rejections, NF90 and BW30 membranes have shown the highest rejections to Na_2SO_4 and to individual solutions of CTAB and SDS, suggesting a similarity between the RO membrane BW30 and the nanofiltration membrane NF90 in selectivity towards Na^+ and ionic surfactants.

Moreover, the change in the zeta potential for individual CTAB solutions followed a similar behavior for the mixture of surfactants, suggesting that the adsorption of the cationic surfactant was predominant in the mixture of surfactants. This effect is expected and occurs due to the strong electrostatic attraction between the oppositely charged head of the cationic surfactants and the negative membrane.

In terms of the experimental design, results have shown that the independent variable $[CTAB + SDS]_0$ negatively affected the permeate fluxes of the NF90 membrane, at low pH values, due to the adsorption of these surfactants on the surface of the membrane and pore blocking at concentrations higher than the CMC. Oppositely, while increasing $[CTAB + SDS]_0$ and pH values up to 7 or 10, permeate flux was stabilized, due to the lower concentration polarization of surfactant molecules at higher pH values, and lower formation of hemimicelles at high pH values.

On the other hand, higher $[CTAB + SDS]_0$ was found to improve the retentions of NF90 leading to higher rejections by the membrane at a range of pH correspondent to 4-10. Furthermore, for the mixture of surfactants, the best conditions of $[CTAB + SDS]_0$ and pH for achieving a permeate flux of 9 L m^{-2} h^{-1} and a rejection of 98.2 % are $[CTAB + SDS]_0$ = 426.2 mg L^{-1} (X_1: −0.94841) and pH = 5.2 (X_2: −0.63422), and $[CTAB + SDS]_0$ = 1,000 mg L^{-1} (X_1: 1.41) and pH = 4.0 (X_2: −1.41), respectively.

Finally, since the interaction of surfactants and membranes may result in the fouling of nanofiltration membranes, this study is a first step toward providing a better understanding of these phenomena and allowing the application of these systems for the treatment of real wastewaters containing high concentrations of surfactants.

5. ACKNOWLEDGMENTS

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