

Membrane technology for the purification of solutions containing cationic surfactant

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Abstract

The objective of the study was to evaluate the effectiveness of cationic surfactant (Tequat LC90i, TEAQ) removal from aqueous solutions with the use of tubular ceramic ultrafiltration and microfiltration modules. Research included an assessment of the feed solution parameters (surfactant concentration, presence of electrolyte) and process conditions (transmembrane pressure and linear velocity) on the transport and separation properties of the membranes. It was found that pressure-driven membrane processes enable cationic surfactants solutions purification — TEAQ retention coefficients exceeded 80%.

Keywords: esterquat, quaternary ammonium compound, ceramic membranes, fabric softener

1. Introduction

Due to the positive charge of the molecule, cationic surfactants have found applications in many industries. A particular group of the cationic surfactants are esterquats. Triethanolamine-based esterquat (TEAQ) has been the primary ingredient in European fabric softeners (Friedli et al., 2002). The softening action of esterquats is based on lubricating properties of facilitate the fiber sliding within the fabric structure. Cationic surfactant-contaminated wastewater may be generated in facilities producing detergents, laundries, textile facilities or households; however the surfactant content in particular wastewater differs and may be in the range from a few to thousands g m⁻³. Water consumption reduction and wastewater reuse are general trends in most of countries both for environment secure and economics. Application of membrane-based techniques allows to achieve the goal of valuable ingredients recovering from wastewater and production of highquality water that may be use in further factory operations. Several data report high efficiency of ceramic membranes application in anionic and nonionic surfactants removal from water - Fernández et al. (2006) tested ceramic ultrafiltration membrane Membralox for anionic surfactants removal. High retention (up to 70%) was achieved for solutions characterized by the low contaminant concentration (below the CMC value).

2. Experimental procedures

Cationic surfactant Tequat LC90i, TEAQ (Dihydrogenated Tallowethyl Hydroxyethylmonium Methosulfate & Ditallowethyl Hydroxyethylmonium Methosulfate) solutions in concentration of 50, 100, 250, 500 and 1000 mg L⁻¹ were used in the tests. Dynamic light scattering (Malvern Zetasizer Nano ZS, wavelength 532 nm) method was conducted for surfactants physical properties determination. Surfactant critical micelle concentration (CMC) amounted to 0.026 \pm 0.0067 g m⁻³ and the micelle size distribution was 115.9 \pm 6.9 nm. TEAQ concentration in the samples was monitored by TOC measurements (HACH IL550 TOC-TN).

Three tubular ceramic modules (CéRAM INSIDE®, Table 1) were used in the experiments. The tests were performed in a continuous batch concentration mode, with the retentate recirculation from the membrane back to the feed tank under transmembrane pressure (TMP) of 0.3 MPa. The volume of the feed amounted to 8 L.

Table 1. Characteristics of tubular ceramic membranes CéRAM INSIDE® (Tami Industries)

Parameter	Value		
Pore diameter (µm)/ cut-off (kDa)	0.45 μm	0.14 μm	150 kDa
Number of channels	7	7	1
Inner channel diameter (mm)	6	2	2
Filtration area (m ²)	0.0130	0.0130	0.005

3. Results

Figure 1 presents averaged retention coefficients of TEAQ obtained in 120-minutes experiments. As can be seen, very satisfactory results were achieved for all tested modules and the initial surfactant concentration did not significantly affect the separation. General tendency that the lower size of the membrane pores, the higher retention coefficients was noted – 95% of TEAQ

was removed from the solution of 1000 mg L⁻¹ both for 150 kDa and 0.14 μm membranes. Taking into account the TEAQ micelle size (115.9 nm) and microfiltration membrane pore size (Table 1), the retention coefficients obtained are surprisingly high. Analysis of modules permeability during the processes shows that the presence of TEAQ in the treated solution strongly deteriorated hydraulic properties of the membranes (analysis of relative flux which is process flux to distilled water flux ratio expressed in percent) - for membrane 150 kDa and TEAQ initial concentrations of 100-1000 mg L⁻¹ relative flux did not exceed 23%. The hydraulic efficiency showed membrane characterized by the greatest pore size, i.e. 0.45 µm (relative flux above 50% for solutions of 50-500 mg L 1), however when the concentration increased to 1000 mg L-1 a sharp drop in relative flux was observed for this membrane. It is very probable that due to fouling the membrane pores reduced their sizes (comparing to virgin membranes), thus separation of lower-size particles was performed with high efficiency.

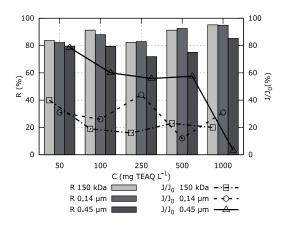


Figure 1. TEAQ retention coefficient (R) and relative flux (J/J_0) versus initial surfactant concentration.

Surfactants-based products often contains inorganic salts therefor it is important to examine the effect of these substances on membrane process efficiency. The 60-minutes experiments with the use of 0.14 μm module and NaCl addition in doses of 0.5, 1 and 3 g L⁻¹ were performed. The data obtained is presented in Table 2. As can be seen, a slight worsening of the TEAQ separation due to presence of NaCl occurred; however, the most significant impact was seen in terms of relative flux. For all tested TEAQ concentrations relative flux deterioration comparing to the single-ingredient solutions was noted. The most significant drop was seen for the highest salt content $-\ J/J_0$ value decreased from 31 to 24, from 44 to 10 and from 31 to 12% for solutions of initial TEAQ concentration equal to 50, 250 and 1000 mg L⁻¹, respectively. The presence of electrolyte caused diminishing the electrostatic repulsion between ionic particles of surfactant, as a result micellar forms were less compact and stable. Moreover, electrolyte effect on surfactants CMC decrease is well known (Basara et.al, 2004). Concluding, more number of smaller micellar forms or

even surfactants monomers/di-mers/tri-mers existed in treated solution having easier access to membrane pores, inducting more intensive pore clogging.

Table 2. Effect of NaCl on TEAQ removal efficiency, module $0.14~\mu m$, TMP= 0.3~MPa

Salt conc. (g L ⁻¹)	TEAQ conc. (mg L ⁻¹)	R (%)	J/J ₀ (%)
0.5	50	83	14
	250	77	15
	1000	86	17
1	50	79	18
	250	76	20
	1000	91	17
3	50	78	24
	250	73	10
	1000	90	12

In order to limit the fouling phenomena, changes in process performance (ex. linear velocity or TMP) may be introduced. The tests were performed for 0.14 µm module and the initial TEAQ concentration of 50 mg L⁻¹. The first part was performed under the constant TMP of 0.2 MPa and for five values of linear velocity (1.25, 1.80, 2.8, 4.4 and 5.7 m s⁻¹). It was noted that implementation of the highest value of linear velocity (5.7 m s⁻¹) allow to limit the decrease in relative flux – after 60- min filtration, J/J₀ amounted to 62% while for the remaining values of linear velocity J/J_0 was below 32%. At turbulent flow, fouling was limited due to surfactant washing out. The second part of the test included evaluation the TMP effect on relative flux. Linear velocity was at the level of 4.1-4.5 m s⁻¹ and the TMP values were equal to 0.13, 0.17, 0.23, 0.30 and 0.43 MPa. It was found that increasing TMP resulted in relative flux deterioration - for the TMP of 0.43 MPa, averaged J/J₀ amounted to 17%.

References

Basara C.A, Karagunduzb A., Cakicic A., Keskinler B. (2004), Removal of surfactants by powdered activated carbon and Microfiltration, *Water Research*, **38**, 2117–2124

Friedli F.E., Koehle H.J., Fender M., Watts M., Keys R., Frank P., Toney C.J., Doerr M. (2002), Upgrading Triethanolamine Esterquat Performance to New Levels, *Journal of Surfactants and Detergents*, **5** (3), 211-216.

Fernández E., Benito J.M., Pazos C., Coca J. (2005) Ceramic membranes ultrafiltration of anionic and nonionic surfactant solutions, *Journal of Membrane Science* **246** (1), 1–6.

Acknowledgments

The financial support of the Faculty of Environmental Engineering (Wroclaw University of Science and Technology, grant no. 0402/0098/18) is greatly appreciated