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Ion-exchange–ultrafiltration system for surfactants removal from water solutions

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ABSTRACT

Studies were performed to determine the effectiveness of hybrid system combining ion exchange and ultrafiltration for surfactant separation from water solutions. During the experiments the influence of membrane cut-off, type of ion-exchange resin, resin dose and contact time was evaluated. The results obtained for the hybrid system were also compared with the effectiveness of the single processes, i.e. ultrafiltration and ion exchange. It was found that the combination of ion exchange and ultrafiltration was more effective in surfactant removal than ultrafiltration process alone. In the hybrid system because of the resin presence, the systematic increase in surfactant separation along with the filtration time was noticed. From among the ion-exchange resins tested the most effective was MIEX® one. For the smallest resin dose equal to 5 cm^3/dm^3 the reduction of anionic surfactants from model solution with concentration of 0.25 CMC reached almost 100% for the hybrid process with 30 kDa polyethersulfone membrane. The retention coefficient of anionic surfactant achieved by the ion-exchange–ultrafiltration system with A100 and A200 resins was lower and amounted to 47% and 94% after 60 min of the process, respectively.

Keywords: Surfactant; Detergent; Ultrafiltration; Membrane; Ion exchange; Hybrid process

1. Introduction

Anionic surfactants are the major class of surface active agents used in detergent formulation and as facilitators in a wide range of industrial applications such as textiles, food, paints, polymers, pharmaceuticals, mining, pulp and paper production. The consumption of surfactants for both industrial and domestic purposes has resulted in worldwide production of approximately 17 million tonnes in 2000 (including soap), with expected future growth rates of 3–4% per year globally and of 1.5%–2.0% in the EU [1].

Due to the diversity of surfactants and their physicochemical properties it is difficult to develop a single and effective treatment method of detergent wastewater. From among techniques which were studied in this research area [2–8] the following can be listed: biodegradation, coagulation, foaming, oxidation, adsorption, ion exchange and membrane processes. Numerous reports indicate that membrane technology is emerging as one of the leading contenders in the recovery of water and concentrated products from the rinsing waters used in the batch production of surfactants and detergents. Micro- and ultrafiltration have been suggested as a means of recovery of surfactants with critical micelle concentrations. If the surfactant concentration is low, that is, monomer concentration, (c < CMC) then nanofiltration has been suggested as an effective removal process. The effectiveness of pressure-driven membrane processes (i.e. UF, NF) is not always efficient enough to discharge the treated detergent effluents directly to the environment. In this connection an additional treatment process to improve the membranes selectivity must be applied. Therefore an ion-exchange–ultrafiltration system would seem to be a very effective solution to this problem.

The article presents a possibility of applying a hybrid system combining ion exchange and ultrafiltration for separation of anionic surfactants from water solutions. The effect of membrane cut-off, type of ion-exchange resin, its dose and contact time was evaluated. The results obtained for the hybrid system were also compared with the effectiveness of the single processes, i.e. ultrafiltration and ion exchange. The maximum ion-exchange capacity of selected resins towards SDBS calculated from Langmuir model was presented.

2. Experimental procedures

2.1. Model solutions

Experiments were carried out on surfactant solutions prepared from distilled water and powdered surfactant. Sodium dodecylbenzenesulfonate (SDBS) was purchased from Sigma and used as such without further purification. The active content was about 80% by wt. and the molecular weight amounted to 348.48 Da. The concentration of SDBS in model solutions amounted to 0.25 CMC, 1.0 CMC and 3.0 CMC. Its critical micelle concentration (CMC) was determined via surface tension measurements using Lauda tensiometr and amounted to 2.29 mmol/dm^3 at 22°C.

The anionic surfactant concentration was measured using potentiometric titrator 785 DMP Titrino (Metrohm).

2.2. Ultrafiltration

The permeation tests were carried out with the use of commercial polyethersulfone membranes (Microdyn-Nadir® GmbH). The main properties of the polymers are shown in Table 1.

Flat sheet membranes were tested in a laboratory set-up, whose main part was an Amicon 8400 cell with the total volume of 0.350×10^{-3} m^3 and a working area of the membrane of 4.54×10^{-3} m^2. In order to maintain a stable concentration of the substances in the feed solution, the permeate was recirculated to a filtration cell (Fig. 1). The filtration experiments were carried out at the transmembrane pressures range of 0.5–3 bar.

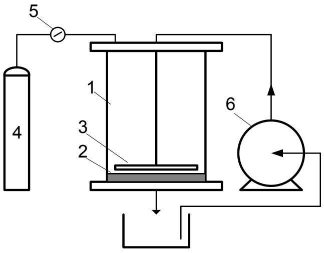

Fig. 1. Laboratory set-up: 1 – filtration cell, 2 – membrane, 3 – stirrer, 4 – gas cylinder, 5 - reducer, 6 – recirculation pump.

During filtration tests the following calculations were done:

- Permeate volume flux (J):

$$J = \frac{V}{t \cdot A} \quad \text{dm}^3/\text{m}^2\text{h} \tag{1}$$

where V is the permeate volume (dm^3), t stands for the time (h), and A denotes the working area of the membrane (m^2).

- Retention coefficient of anionic surfactant (R):

$$R = \frac{c_f - c_p}{c_f} \cdot 100\% \tag{2}$$

where c_f and c_p are the surfactant concentration in the feed and permeate, respectively.

2.3. Ion exchange

The experiments with anion-exchange resins (Table 2) were carried out using a Velp Scientifica JLT4 jar tester. One liter samples of the solution were put into beakers, and the following amounts of resin were added: 2.5, 5, 10 and 20 cm^3/dm^3. The content in the beakers was well mixed at a speed of 150 rpm. After an allotted time of mix-

Table 1
Characteristics of Nadir® ultrafiltration membranes [9]

Membrane type	Membrane material	Cut-off, kDa	Pure water flux$^{1)}$ (dm^3/m^{2}h)	Pure water flux$^{2)}$ (dm^3/m^{2}h)
UP005	Polyethersulfone	5	>30	41
UP010		10	>150	265
UP030		30	>100	345

$^{1)}$ Test conditions: 3 bar, 20°C, stirred cell: 700 RPM
$^{2)}$ Determined by the author. Test conditions: 3 bar, 22°C, stirred cell: 300 RPM

Table 2
Characteristics of anion-exchange resins [10,11]

Parameter	MIEX®	A100	A200
Manufacturer	Orica Watercare	Purolite	Purolite
Type	Strong base anion macroporous	Weak base anion macroporous	Strong base anion gel
Structure	Polyacrylic	Polystyrene crosslinked with divinylbenzene	Polystyrene crosslinked with divinylbenzene
Functional group	Type 1 quaternary ammonia	Tertiary amine	Type 2 quaternary ammonium
Particle size, mm	150–180	725 ± 125	725 ± 125
Total capacity, mmol/cm^3	—	1.3	1.3
Water content, %	—	53-60	45–51
Ion-exchange capacity*, mmol/cm^3	0.398	0.902	1.068

* Determined by the author according to Polish Norm PN-93/C-04860/14

ing (5, 10, 20, 40, 60, 90 and 120 min), the samples of the solution were taken for measurements of the surfactant concentration.

The surfactant uptake (q, mmol/cm^3) on the resin was calculated using the following formula:

$$q = \left(C_i - C\right)\frac{V}{V_J} \tag{3}$$

where C_i (mmol/dm^3) — initial surfactant concentration in the solution, C (mmol/dm^3) - surfactant concentration in the solution at given contact time, V (dm^3) — solution volume, V_J (cm^3) — resin volume.

Ion-exchange isotherms were analyzed using the linear-form of the Langmuir model:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}K_L} + \frac{C_e}{q_{\max}} \tag{4}$$

where q_e (mmol/cm^3) — equilibrium amount of SDBS exchanged on a resin volume of 1 cm^3, C_e (mmol/dm^3) — equilibrium concentration of SDBS in solution, $q_{\max}$ (mmol/cm^3) — maximum uptake of SDBS exchanged on a resin volume of 1 cm^3, K_L — Langmuir constant (dm^3/mmol).

2.4. Ion-exchange–ultrafiltration system

During the hybrid system a mixture of surfactant solution and resin was treated by means of ultrafiltration. Therefore the anion-exchange resin was dosed directly to the filtration cell. The content of the Amicon cell was well mixed. Similarly as in the UF process in order to maintain a stable concentration of the substances in the feed solution, the permeate was recirculated to the filtration cell. After an allotted time of mixing (5, 10, 20, 40 and 60 min), the samples of the solution were taken for measurements of surfactant concentration.

3. Results and discussion

3.1. Ultrafiltration

Separation properties of the ultrafiltration membranes during the permeation tests are presented in Fig. 2. Comparing the separation properties of the membranes with different cut-off values, it can be inferred that the greater the molecular weight cut-off of the membranes (the more spongy the structure and the larger the pore size), the less effective the SDBS separation from the water solutions. This phenomenon was especially pronounced for the concentration below the CMC value. This can be exemplified by the SDBS retention coefficient reaching approximately 80%, 52% and 23% for 5, 10 and 30 kDa membrane, respectively. For solutions with surfactant concentrations of 1.0 CMC and 3.0 CMC, the drop in the surfactant retention with the increase in cut-off value was less pronounced and the SDBS retention coefficient amounted to 87–94%, 68–81% and 65–85% for 5, 10 and 30 kDa membrane, respectively. At the same time the retention coefficient of SDBS from model solutions was stable during the filtration process for all membranes tested.

The separation properties of the membranes during permeation of surfactant solutions can be attributed to several phenomena, such as sieving mechanism, concentration polarization, membrane fouling and interactions between surfactant and membrane. For the lowest surfactant concentration (i.e. 0.25 CMC), the high surfactant retention was mainly connected with the pre-micelles formation in the concentration polarization layer on the membrane surface which can convert to micelles [12]. For the concentration close to the CMC value, as a result of the micelle creation, the separation increased (especially for 30 kDa membranes). Taking into account the radius of the SDBS micelle (22 Å) [13] and its average molecular weight (which is about 50 times greater than the molecu-

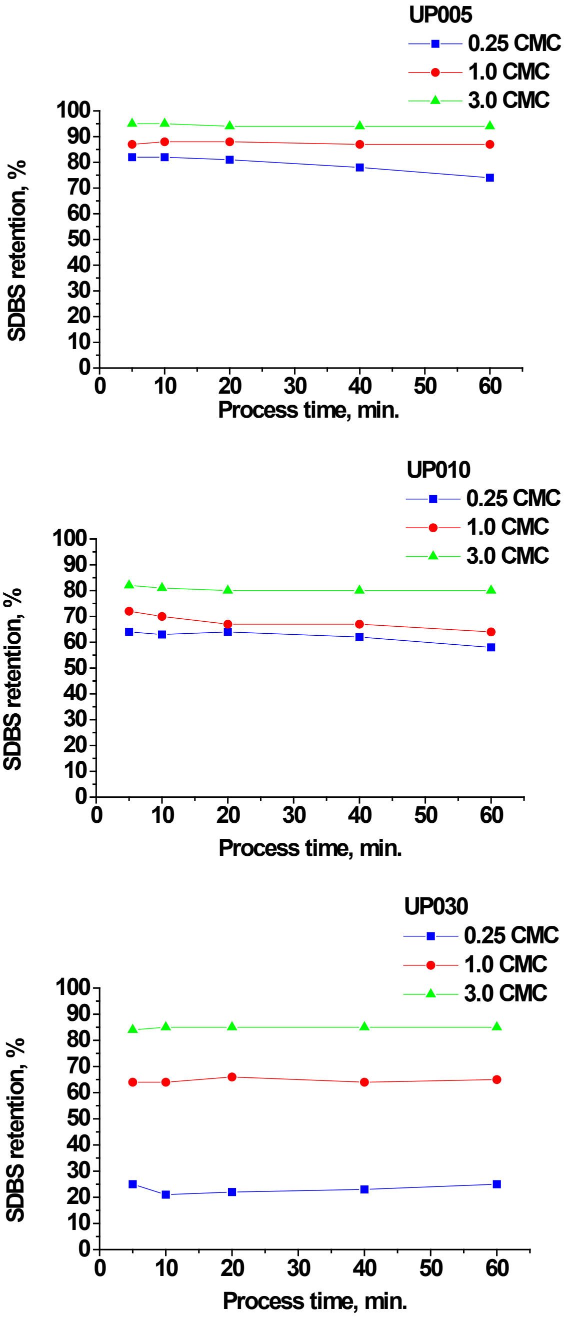

Fig. 2. SDBS retention during the ultrafiltration process.

lar weight of SDBS molecule [14]), a conclusion can be drawn that the sieving mechanism is predominant during the surfactant separation by polymer membranes, especially in the concentration range above the critical micelle concentration.

3.2. Ion exchange

The exchange isotherms of surfactant removal on anion-exchange resins are presented in Figs. 3 and 4. The results indicate that the surfactant amount exchanged from water solution rose with increasing of initial surfactant concentration and with decreasing of resin dose as a result of increasing in driving force. It was also stated that the surfactant amount exchanged on the resins increased with time for any initial concentration. For applied resins most of exchange took place within the first 30–40 min. (75–80% of uptake) and then the removal rate became slow and a plateau of surfactant separation was attained. For the lower initial surfactant concentrations and for the higher resin doses the equilibrium time was faster achieved as a result of the competition weakness for the active sites. From among resins tested the lowest equilibrium time (on a level of 10 min) was achieved by

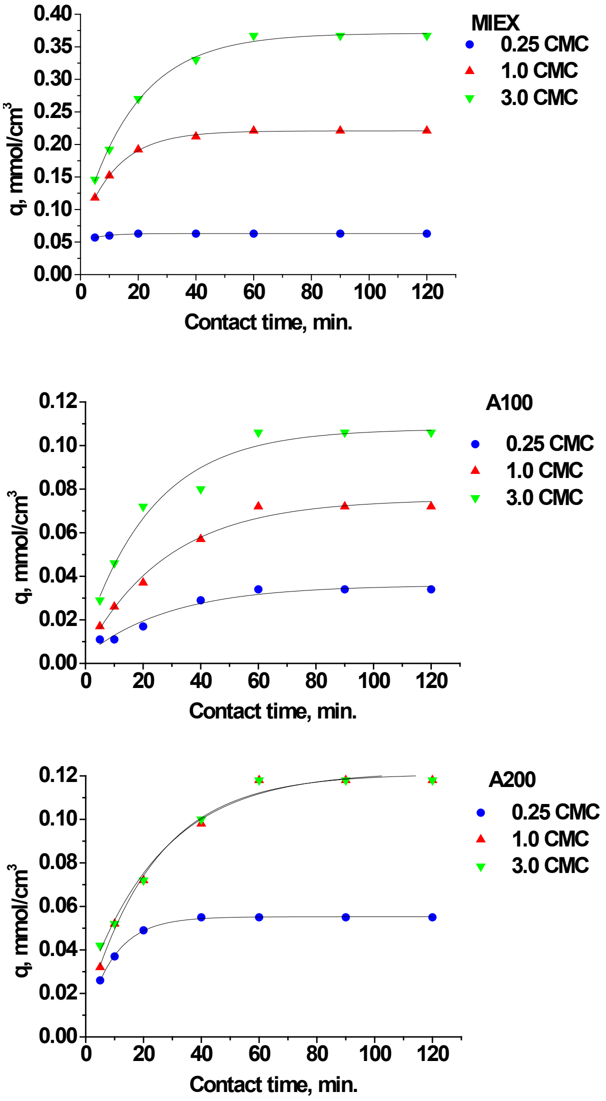

Fig. 3. Effect of contact time and initial surfactant concentration on the SDBS exchange on anion-exchange resins (resin dose: 10 cm^3/dm^3).

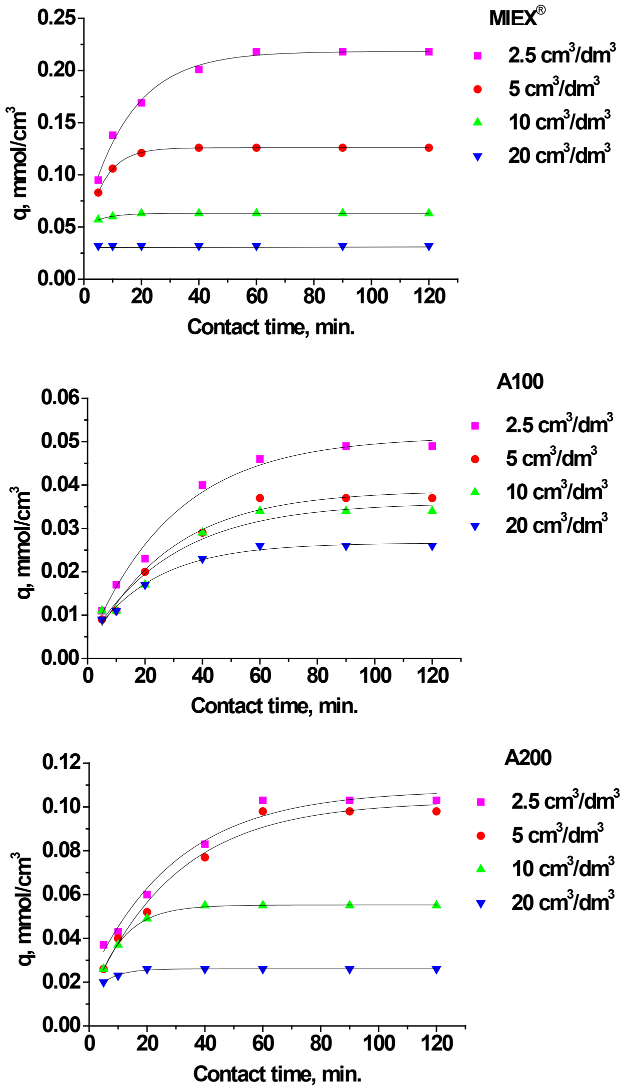

Fig. 4. Effect of contact time and resin dose on the SDBS exchange on anion-exchange resins (surfactant concentration: 0.25 CMC).

MIEX® resin. The equilibrium time attained by A200 and A100 resins amounted to 40 min and 60 min, respectively.

The results of the experiments confirmed that the effectiveness of ion exchange was strongly influenced by resin type, i.e. kind of functional group and its basicity, mean size of resin beads and polymer structure. It can be easily noticed that the most effective was MIEX® resin which is strong base macropurous resin with the smallest mean size of beads. This is explained by the fact that organic anions, such as anionic surfactant, can diffuse easier within macropourus structure for the active sites. The second strong base gel resin, i.e. A200, was not as effective in surfactant separation as MIEX® one what was connected with the more dense polymer structure and the larger size of beads. On the basis of the Langmuir model, the anion-exchange resins were ranked according to SDBS exchanging capacity as follows: MIEX® (0.365 mmol/cm^3) > A200 (0.121 mmol/cm^3) > A100 (0.109 mmol/cm^3).

The large differences in the observed capacities of ion-exchange resins (A200 and A100) towards SDBS ions and the ion-exchange capacities (determined towards chlorides and sulfates) may be explained by the restricted access of surfactant monomers with the significant linear dimension to the active sites of gel resins (A200) characterized by a high degree of cross-linking and thus by low porosity of the polymer. In the case of A100 macroporous resin, its pores are large enough to allow fast diffusion of surfactant monomers to the active sites without the swelling process; however, the weak base anion-exchange resins are characterized by the lower selectivity of the weak acid anions.

The obtained similar capacity values for the third resin tested (MIEX®), i.e. 0.365 mmol/cm^3 and 0.398 mmol/cm^3, confirming the above mentioned discussion. Namely, the high efficiency of the MIEX® resin should be mainly associated with the polymer structure and its basicity. The very small resin bead size, and the macroporous structure, provides effective exchange of surfactant monomers. As well as, the strong base resin is highly selective for the weak acid anions.

3.3. Ion-exchange–ultrafiltration system

The application of the ion-exchange–ultrafiltration system was more effective in surfactant removal than the ultrafiltration process alone (Fig. 5). In the hybrid system because of the ion-exchange resin presence, the systematic increase in surfactant separation along with the filtration time was noticed. It was stated that the hybrid process was strongly influenced by the resin type. From among ion-exchange resins tested in the hybrid system, the most effective was magnetic ion-exchange one (MIEX®). For the smallest resin dose equal to 5 cm^3/dm^3, the reduction of anionic surfactants from the model solution with the concentration of 0.25 CMC reached almost 100% for the hybrid system with 30 kDa polyethersulfone membrane. However the separation effectiveness of the hybrid system was mainly contributed to the presence of ion-exchange resin, and the membrane separated only the saturated resin from the solution. The ion-exchange process with MIEX® resin enabled just a few percent lower separations. For the ion-exchange–ultrafiltration system with A200 resin, the surfactant retention coefficient amounted to 94% after 60 min of the process. In the case of processes working independently, surfactant removal reached 25% and 90% for UF and IE, respectively. The worst surfactant separation from the model solutions was achieved by means of the hybrid system with A100 resin on a level of 47%.

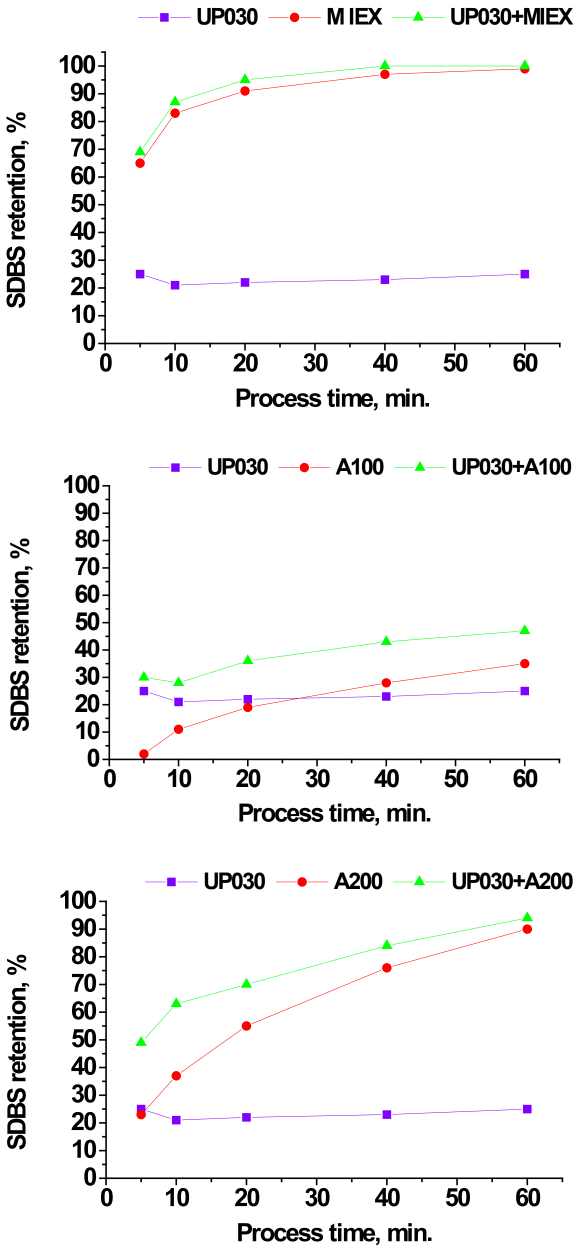

Fig. 5. SDBS retention during the ion-exchange–ultrafiltration system with UP030 membrane (resin dose: 5 cm^3/dm^3; surfactant concentration: 0.25 CMC).

3.4. *Regeneration of waste resin*

The current stage of experiments is involved in evaluation of the effective method of surfactant elution from the saturated resin matrix. The preliminary tests for MIEX® and A100 resin proved that application of 12% NaCl solution (according to Orica Watercare recommendation) was highly effective in resin regeneration (96% and 95% of elution rate for MIEX and A100, respectively). However, the elution rate for A200 resin was lower (62%) and therefore the modification of the regeneration procedure should be applied.

Based on the results presented it can be stated that surfactant elution was mainly influenced by the resin type. In the case of macropurous resins, i.e. MIEX® and A100, the pores are large enough to allow fast diffusion of surfactant monomer exchanged by the regenerating agent. However, the diffusion of surfactant monomers from the exchange site of gel resin (A200) to the resin grain surface was restricted as a result of low porosity of the polymer. One may also suspect that that lower elution rate achieved for A200 could be connected with stronger hydrophobic interaction between the SDBS chains and polymer chains.

The regeneration process allowed for successful reuse of macroporous resins in the hybrid process (Fig. 6). The results indicate that the multiple resin regeneration has no effect on the effectiveness of the SDBS retention.

4. Conclusions

Surfactant separation during the ultrafiltration process was significantly influenced by the membrane cut-off. It was stated that the greater the molecular weight cut-off of the membranes, the less effective the SDBS separation from the water solutions. This phenomenon was especially pronounced for the concentration below the CMC value. For surfactant solutions around and above CMC value as a result of micelle formation, the drop in surfactant retention with the increase in cut-off value was less pronounced.

The ion-exchange experiments indicated that the surfactant amount exchanged by the unitary volume of resin (1 cm^3) rose with increasing of the initial surfactant concentration and with decreasing of the resin dose. It was also stated that the surfactant amount exchanged by the resins increased with time for any initial concentra-

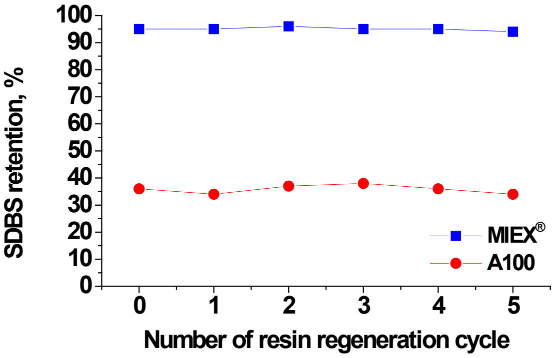

Fig. 6. Effect of the number of resin regeneration cycles on SDBS retention during the ion-exchange–ultrafiltration system with UP030 membrane (resin dose: 5 cm^3/dm^3; surfactant concentration: 0.25 CMC; process time: 20 min).

tion. The results of the experiments confirmed that the effectiveness of ion exchange was strongly influenced by the resin type. The most effective was MIEX® resin which is a strong base macropurous resin with the smallest mean size of beads.

The ion-exchange–ultrafiltration system was more effective in surfactant removal than the ultrafiltration process alone. In the hybrid process because of the ion-exchange resin presence, the systematic increase in surfactant separation along with the filtration time was noticed. From among the hybrid systems tested, the most effective was one with MIEX® resin.

Acknowledgements

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References

[1] M. Patel, Surfactants based on renewable raw materials. Carbon dioxide reduction potential and policies and measures for the European Union, J. Ind. Ecol., 7 (2004) 46–62.

[2] M.J. Scott and M.N. Jones, The biodegradation of surfactants in the environment, Biochim. Biophys. Acta, 1508 (2000) 235–251.

[3] A. Adak, M. Bandyopadhyay and A. Pal, Removal of anionic surfactant from wastewater by alumina: a case study. Colloids Surfaces A: Physicochem. Eng. Aspects, 254 (2005)165–171.

[4] S. Boonyasuwat, S. Chavadej, P. Malakul and J.F. Scamehorn, Anionic and cationic surfactant recovery from water using a multistage foam fractionator, Chem. Eng. J., 93 (2003) 241–252.

[5] W. Xiao-Jun, S. Yang and M. Jun-Sheng, Combined Fenton oxidation and aerobic biological processes for treating a surfactant wastewater containing abundant sulfate, J. Hazard. Mater., 160 (2008) 344–348.

[6] S.H. Wu and P. Pendleton, Adsorption of anionic surfactant by activated carbon: Effect of surface chemistry, ionic strength, and hydrophobicity, J. Colloid Interface Sci., 243 (2001) 306–315.

[7] W.B. Yang, A. Li, J. Fan, L. Yang and Q. Zhang, Mechanism and behavior of surfactant adsorption onto resins with different matrices, React. Funct. Polym., 67 (2007) 609–616.

[8] I. Kowalska, Surfactant separation in pressure-driven membrane processes. Environ. Prot. Eng., 34 (2008) 105–113.

[9] Microdyn-Nadir® GmbH catalogue

[10] www.miexresin.com

[11] Purolie® catalogue

[12] K. Mizoguchi, K. Fukui, H. Yanagishita, T. Nakaneb and T. Nakata, Ultrafiltration behavior of a new type of non-ionic surfactant around the CMC, J. Membr. Sci., 208 (2002) 285–288.

[13] A.S. Jönsson and B. Jönsson, The influence of nonionic and ionic surfactants on hydrophobic and hydrophilic ultrafiltration membranes, J. Membr. Sci., 56 (1991) 49–76.

[14] S. Kumar, D. Sharma and D. Kabirud, Small-angle neutron scattering studies on sodium dodecylbenzenesulfonate-tetra-n-butylammonium bromide systems, J. Surf. Det., 9 (2006) 77–82.