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NANOFILTRATION – ION EXCHANGE SYSTEM FOR EFFECTIVE SURFACTANT REMOVAL FROM WATER SOLUTIONS

I. Kowalska

Wroclaw University of Technology, Institute of Environment Protection Engineering,
Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland.
Phone: + 48 (71) 320-3639, Fax: + 48 (71) 328-2980
E-mail: izabela.kowalska@pwr.edu.pl

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Abstract - A system combining nanofiltration and ion exchange for highly effective separation of anionic surfactant from water solutions was proposed. The subjects of the study were nanofiltration polyethersulfone membranes and ion-exchange resins differing in type and structure. The quality of the treated solution was affected by numerous parameters, such as quality of the feed solution, membrane cut-off, resin type, dose and the solution contact time with the resin. A properly designed purification system made it possible to reduce the concentration of anionic surfactant below 1 mg L^{-1} from feed solutions containing surfactant in concentrations above the CMC value.

Keywords: Membrane; Resin; Anionic surfactant.

INTRODUCTION

Surfactants are low molecular weight amphiphilic compounds that effectively reduce the surface tension and help formation of emulsions between different liquids. Due to their properties, surfactants are used in almost all fields of industry, including textile, mining, petroleum, metallurgy, plastics and synthetic resins, food processing and detergent manufacturing. Anionic surfactants are commercially the most important class, and the market share is about 50-60% of total production (Patel, 2004). The annual growth of production is estimated to be 3% to 4% per year globally and 1.5% to 2.0% in the European Union. The total production of surfactants in the European Union amounted to 2.92 million tonnes in 2012, with the share of anionic surfactants on a level of 41% (CESIO Statistics, 2012).

Therefore, the effective treatment of wastewater containing surfactants is a very important issue for environmental and economic reasons. Surface active agents are very difficult to remove from water solutions due to their diverse chemical structure and physicochemical properties. Their presence in wastewater treatment plants may result in foaming and inhibition of microorganisms, implying a decrease in treatment efficiency (Oliveira *et al*., 2010). Surfactants are generally removed by biodegradation (Camacho-Muñoz *et al*., 2014; Chen *et al*., 2005), coagulation (Beltrán-Heredia *et al*., 2012; Aboulhassan *et al*., 2006), adsorption (Gupta *et al*., 2003; Hua Wu *et al*., 2001), foaming (Chen, 1994; Lee *et al*.,), advanced oxidation processes (Karci *et al*., 2013; Méndez-Díaz *et al*., 2010) and ion exchange (Yang *et al*., 2006; Yang *et al*., 2007). As attractive techniques for removal of surfactants from aqueous solutions membrane techniques can also be mentioned. 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

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*To whom correspondence should be addressed used in the batch production of surfactants and detergents (Goers *et al*., 2000; Kaya *et al*, 2009; Suárez *et al*., 2012). As the main advantages of the pressure-driven membrane processes for surfactant removal from water solutions their high selectivity without involving phase changes or chemical additives can be mentioned, and thus their greater efficiency in concentrated stream recycling, especially in detergent production plants (Forstmeier *et al*., 2002; Goers *et al*., 2000; Kaya *et al*., 2009).

The most crucial parameters determining the effectiveness of surfactant separation by means of pressure-driven processes is the critical micelle concentration (CMC) and the size of the micelle in comparison with the pore diameters of the membranes. Ultrafiltration effectively remove only micelles and pre-micelles, however the quality of ultrafiltration permeate is generally not satisfactory due to the large permeation of surfactant monomers. To reach a satisfactory low concentration of surfactants in the permeate, a nanofiltration should be applied. However, the literature reports suggest that the effectiveness of surfactant removal by means of nanofiltration depends to a large extent on membrane and surfactant type.

The experiments conducted by Archer *et al.* (1999) revealed that the nanofiltration (NF) process can be applied for pretreatment of industrial effluents containing anionic surfactant up to a concentration of 1 g L^{-1}. Part of the surfactant can be recovered for reuse in the production process and, at the same time, the organic load of the effluent is effectively reduced. The retention of sodium lauryl-ether-sulfate (CMC=300 mg L^{-1} at 20 °C, 385 Da) amounted to 79.1% (membrane SP12, 600-800 Da) and 99.0% (membrane MX07, 300-500 Da) from solutions containing 202.8 mg L^{-1} and 216.8 mg L^{-1}, respectively.

Kertész *et al.* (2008) studied the recovery of anionic surfactant (CL80, CMC=2100 mg L^{-1} at 20 °C) with the use of a DL composite membrane with a theoretical $MgSO_4$ retention of 96%. The removal efficiency of surfactant (CL80) from solutions containing 500-5,000 mg L^{-1} exceeded 94%.

Kaya *et al.* (2006) investigated the effectiveness of three NF membranes (N 30F, 400 Da; NF PES 10, 1000 Da; XN 45, 200 Da) for removal of anionic (linear alkyl benzene sulfonate, sodium dodecylether sulfate) and nonionic (nonylphenol ethoxylate) surfactants from model solutions. The highest retentions of linear alkyl benzene sulfonate (CMC=640 mg L^{-1}, 322 Da, C_i=500 mg L^{-1}) and sodium dodecylether sulfate (CMC=300 mg L^{-1}, 384 Da, C_i=200 mg L^{-1}) of around 97-98% were achieved for NF PES10 and N 30F. The removal efficiency of nonylphenol ethoxylate (CMC=60 mg L^{-1}, 645 Da, C_i=50 mg L^{-1}) ranged from 46% to 93% for NF PES10 and XN 45, respectively.

Korzenowski *et al.* (2012) studied the effectiveness of FilmTec membranes (NF-90, NF-200 and NF-270) for removal of anionic surfactants (linear alkyl benzene sulfonate and sodium dodecylether sulfate) with a content of 430 mg L^{-1} from model solutions and detergent wastewater. Removal of anionic surfactants, expressed as total organic carbon, exceeded 95% for model solutions and 92% for detergent wastewater.

In recent years, more attention has been given to removing anionic surfactants from aqueous solutions by means of ion exchange (IE). The main reasons for the attractiveness of ion-exchange resins are their properties (high exchange capacity, high porosity and surface area) (Yang *et al*., 2006) and the satisfactory level of surfactant elution from the polymer structure during the regeneration stage (Kowalska, 2012; Yang *et al*., 2007).

In the experiments carried out by Schouten *et al.* (2007), the maximum exchange capacity of linear alkyl benzene sulfonate on synthetic resins varied from 420 mg g^{-1} to 1210 mg g^{-1} for Amberlyst A21 and Amberlite IRA-900, respectively. The studies of Yang *et al.* (2006, 2007) showed that the adsorbed amount of anionic surfactant on the resins increased with increasing surface area of the polymer and the highest exchange capacities of 864 mg sodium 6-dodecyl benzenesulfonate g^{-1} (Yang *et al*., 2006) and of 4986 mg sodium 1-dodecyl benzenesulfonate g^{-1} (Yang *et al*., 2007) were achieved on XAD-4 (styrene-divinyl-benzene polymer) resin with a surface area of 880 m^2 g^{-1}.

In view of the above, a system combining nanofiltration and ion exchange for highly effective separation of anionic surfactant was proposed.

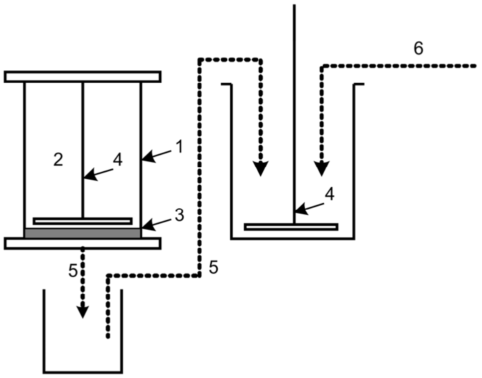
Surfactants rejected during the NF stage can be reused in the production process, while the second purification stage with the use of ion-exchange resins is regarded as a post-treatment process with the purpose of obtaining a high quality water.

EXPERIMENTAL

Experiments were carried out on surfactant solutions prepared from distilled water with a conductivity of 1.7 μS cm^{-1} and powdered surfactant. Sodium dodecylbenzenesulfonate (SDBS) was purchased from Sigma and used as such without further purification. The active content was about 80% by weight and the molecular weight amounts to 348.48 Da. The critical micelle concentration (CMC) of the surfactant was determined from measurements of the surface tension and amounted to 800 mg L^{-1}. The SDBS concentration in the solutions was determined by potentiometric titration using a 785 DMP Titrino titrator (Metrohm). The concentration of SDBS in model solutions ranged from 0.025 CMC (20 mg L^{-1}) to 3.0 CMC (2400 mg L^{-1}).

The integrated purification process was carried out on a laboratory scale according to the design presented in Figure 1. In the first stage of experiments, model surfactant solutions were purified using flat-sheet NF membranes (Table 1) placed in an Amicon 8400 cell.

The permeation tests were conducted at the trans-membrane pressure ΔP = 3 bar, achieved by force using compressed technical-grade nitrogen. Next, the obtained permeates were further purified in the ion exchange process on MIEX®, A100, A200, A400, and SBW resins (Table 2). The resin dose in the vessel tests was 2.5, 5, 10, and 20 mL per 1 L of the purified solution. After pre-defined mixing times (5-60 min), water samples were collected for analysis. All experiments were performed in duplicate.



1. Amicon 8400 cell;
2. feed solution;
3. nanofiltration membrane;
4. stirrer;
5. permeate stream;
6. dose of ion-exchange resin.

Figure 1: Schematic diagram of the laboratory set-up

Table 1: Nadir® nanofiltration membranes.

Membrane type	Membrane material	Na_2SO_4 retention (%)	Pore radius [a] (nm)	MWCO [a] (Da)	Surface charge	Pure water flux [b] (L m^{-2} h^{-1})
NP010	polyethersulfone	25–40	0.80-1.23	1010-1400	negative	22
NP030	polyethersulfone	80–95	0.59-0.93	500-700	negative	4.5

[a] From Ref. [Kovács and Samhaber, 2008]
[b] Determined by the author. Test conditions: 3 bar, 22 °C, stirred cell: 300 RPM.

Table 2: Characteristics of anion exchange resins.

Resin	Type	Structure	Resin grain size, μm	SDBS exchange capacity[a], mg mL^{-1}
MIEX® Orica Watercare	strong base	macroporous polyacrylic	150-180	127
Purolite® A100	weak base	macroporous polystyrene crosslinked with divinylbenzene	600-850	38
Purolite® A200	strong base	gel polystyrene crosslinked with divinylbenzene	600-850	42
Purolite® A400	strong base	gel polystyrene crosslinked with divinylbenzene	600-850	48
Wofatit® SBW	strong base	gel polystyrene crosslinked with divinylbenzene	300-1200	54

[a] Determined by the author from the Langmuir isotherm method (Kowalska, 2009)

SDBS exchange capacity (Table 2) was determined according to the procedure which was precisely described in a previous studies (Kowalska, 2009). Isotherms of the ion exchange process were carried out in triplicate for a resin dose of 10 mL L^{-1} and surfactant concentrations in the range of 0.1-3.0 CMC (80-2400 mg L^{-1}). Ion-exchange isotherms were analyzed using the linear-form of the Langmuir model:

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

where:
q_e (mg mL^{-1}) – equilibrium amount of SDBS exchanged on a resin volume of 1 cm^3 calculated using the following formula:

$$q_e = (C_i - C_e)\frac{V}{V_J} \tag{2}$$

where:
C_i (mg L^{-1}) - initial surfactant concentration in the solution,
C_e (mg L^{-1}) - equilibrium concentration of SDBS in solution,
V (L^{-1}) - solution volume,
V_J (mL) - resin volume,
q_{max} (mg mL^{-1}) - maximum uptake of SDBS exchanged on a resin volume of 1 cm^3,
K_L (L mg^{-1}) - Langmuir constant.

Besides classic anion-exchange resins (A100, A200, A400, and SBW), the MIEX® resin, containing a magnetic component incorporated within the polymer structure, was used. Owing to such a modification of the polymeric material, individual resin grains act like magnets, are able to form heavy aggregates, and are effectively separated from water.

The efficiency of the purification system was determined based on the following expressions:

- Surfactant removal efficiency (R, %):

$$R = \frac{c_i - c}{c_i} \cdot 100 \tag{3}$$

where c_i and c are the surfactant concentration in the feed solution and treated solution, respectively.

- Relative permeability of membranes (%):

$$RF = \frac{J}{J_{H2O}} \cdot 100 \tag{4}$$

where J denotes the permeate volume flux after time t=60 min. to the initial distilled water flux (J_{H2O}) which was determined for the brand-new membrane under specified process conditions (Table 1).

- Permeate volume flux (J, L m^{-2} h^{-1}):

$$J = \frac{1}{A}\frac{dV}{dt} \tag{5}$$

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

RESULTS AND DISCUSSION

Separation properties of NF membranes are presented in Figure 2. In a wide range of concentration, SDBS retention coefficients were very similar and amounted to 88.2-93.9% and 90.0-95.6% for NP010 and NP030, respectively. The dense structure of the membranes' active layer ensured effective separation of both surfactant monomers and micelles; however the highest retention coefficients were noted for concentrations above the CMC as a result of micelle formation. Comparing the physical radius of the SDBS micelle (2.2 nm (Jönsson and Jönsson (1999)) and its average molecular weight (which is 50 times greater than the molecular weight of the SDBS molecule) with the pore diameters of the membranes (and their average MWCO) (Tab. 1), it can be supposed that the sieving mechanism is predominant during surfactant separation above CMC. For surfactant concentrations far below the CMC value, the high surfactant retention is associated with both hydrophobic and electrostatic interactions between anionic surfactant monomers and the membrane, endowed with a large negative charge.

With increasing concentration of SDBS in the feed, a decrease in membrane permeability compared with distilled water was observed (Figure 3). When the concentration of SDBS reached the CMC, a slight increase in hydraulic efficiency of the membrane occurred. The phenomenon can be associated with the electrostatic repulsion between negatively charged micelles which probably results in creation of a less compact polarization layer. The looseness of the layer on the membrane surface effectively facilitates the solvent transport.

Despite these high retention coefficients, with increasing SDBS concentration in the feed, significant leakage of monomers to the permeate side was observed. The concentration determined in the treated solutions was in the range 1.3-145 mg L^{-1} and 1.2-106 mg L^{-1} for NP010 and NP030, respectively.

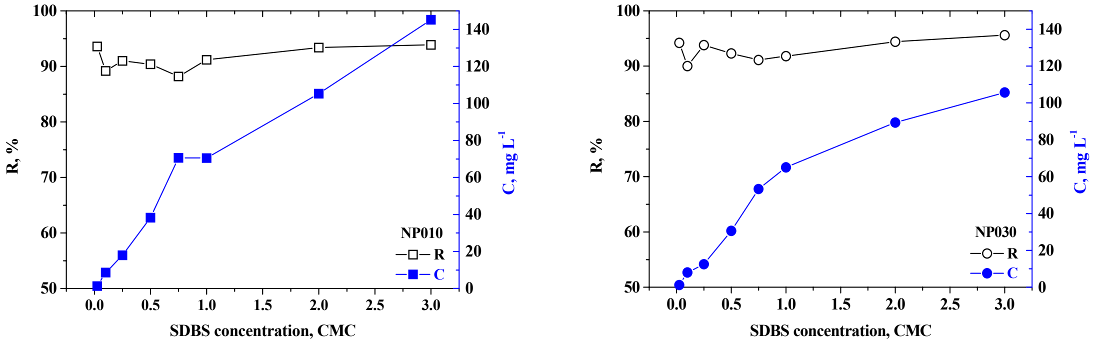


Figure 2: Removal efficiency of SDBS in the nanofiltration process.

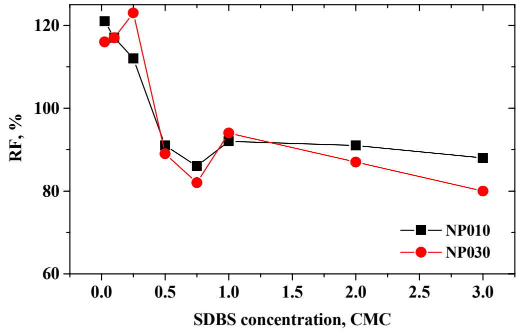


Figure 3: Relative permeability of nanofiltration membranes.

To achieve the acceptable concentration of surfactants in wastewater discharged into sewage or surface waters, ion exchange was implemented as an effective post-treatment process. The efficiency of ion exchange was dependent on the following parameters: quality of the solution to be purified, the type of ion-exchange resin and its dose, and the solution contact with the resin. SDBS removal efficiency greatly depended on the type of the anion-exchange resin and, according to the exchange capacity (Table 2), the resins are arranged in the following order: MIEX®>SBW>A400>A200>A100.

Kinetic tests (Figure 4) showed that the highest exchange rate was obtained for the MIEX® resin. For a resin dose of 10 mL L^{-1} the surfactant exchange equilibrium was achieved after 5 min; while the gel resins (A200, A400 and SWB) and the weak base resin (A100) needed 40 min and 60 min. to reach equilibrium, respectively. Compared to other resins, the MIEX® one is characterized by the lowest size of resin grain and the highest specific surface area. These two parameters facilitate access of ions to the resin active sites and shorten their diffusive transport. After reaching a state of equilibrium, strong base resins (MIEX®, A200, A400 and SBW) reduced the SDBS concentration in the purified solutions to a very similar level (below 3.0 mg L^{-1}); this was caused by the incomplete saturation of the active sites of ion exchangers. However, the use of A100 resin reduced the SDBS concentration to a level below 10 mg L^{-1}.

It was also shown that SDBS removal may be controlled by the amount of ion exchange resin (Figure 5). A significant increase in the quality of the solution was achieved by an increase in the dose of the ion-exchange resin.

A decrease in the ratio of resin dose to surfactant concentration resulted in a higher saturation of resin grain surface by SDBS ions and thus intensified the driving force for the ion-exchange process, which is the electrical potential difference between two phases – the ion-exchanger and the external liquid. Due to the higher resin saturation, an increase in the exchange capacity per unit volume (Figure 6) and the elongation of the equilibrium time (Figure 7) occurred.

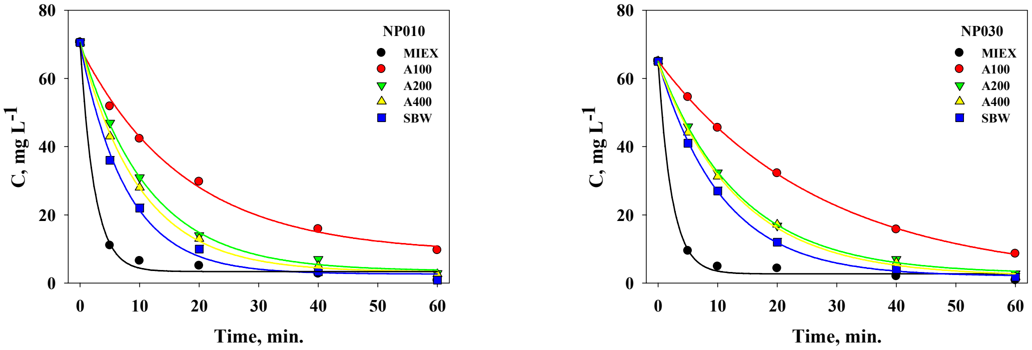


Figure 4: Removal efficiency of SDBS in the NF-IE process (feed conc.: 1 CMC, resin dose: 10 mL L^{-1}).

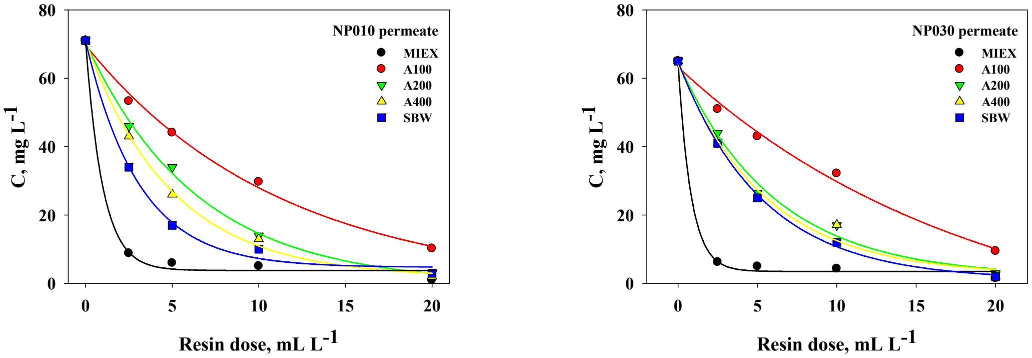


Figure 5: Removal efficiency of SDBS in the NF-IE process (feed conc.: 1 CMC, contact time: 20 min).

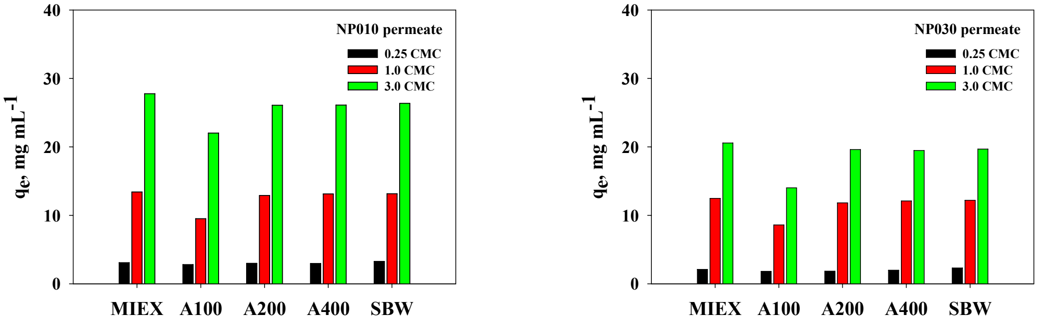


Figure 6: The effect of SDBS feed concentration on removal efficiency (resin dose: 5 mL L^{-1}, contact time: 60 min).

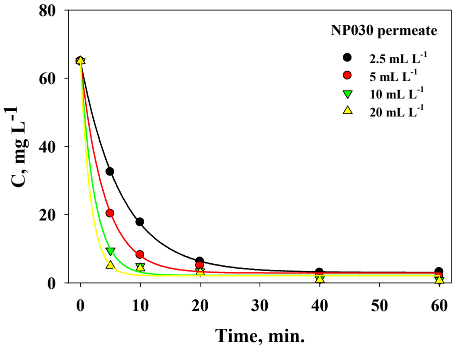


Figure 7: The effect of MIEX resin dose on SDBS removal efficiency (feed conc.: 1 CMC).

CONCLUSIONS

The NF-IE system allows effective anionic surfactant removal from water solutions by combining the two separation mechanisms of molecular sieving and ion exchange. With appropriately selected process parameters, the concentration of SDBS can be reduced below 1 mg L^{-1}. Overall efficiency of the integrated purification systems was determined by numerous parameters, such as surfactant concentration in the feed solution, membrane cut-off, resin type and dose and the solution contact with the resin. The efficiency of the NF-IE system can be arranged for each tested membrane, depending on the resin type used in the experiments in the following order: MIEX®>SBW>A400>A200>A100. Taking into account the membrane type, the best separation coefficients were achieved by a purification system with the more dense NP030 membrane.

REFERENCES

Aboulhassan, M. A., Souabi, S., Yaacoubi, A., Baudu, M., Removal of surfactant from industrial wastewaters by coagulation flocculation process. International Journal of Environmental Science and Technology, v. 3, p. 327-332 (2006).

Archer, A. C., Mendes, A. M., Boaventura, A. R., Separation of an anionic by nanofiltration. Environmental Science and Technology, v. 33, p. 2758-2764 (1999).

Beltrán-Heredia, J., Sánchez-Martín, J., Barrado-Moreno, M., Long-chain anionic surfactants in aqueous solution. Removal by *Moringa oleifera* coagulant. Chemical Engineering Journal, v. 180, p. 128-136 (2012).

Camacho-Muñoz, D., Julia, M., Juan, L. S., Aparicio, I., Esteban, A., Occurrence of surfactants in wastewater: hourly and seasonal variations in urban and industrial wastewaters from Seville (Southern Spain). Science of the Total Environment, v. 468-469, p. 977-984 (2014).

Chen, H. J., Tseng, D. H., Huang, S. L., Biodegradation of octyl-phenol polyethoxylate surfactant Triton X-100 by selected microorganisms. Bioresource Technology, v. 96, p. 1483-1491 (2005).

Chen, S., Modeling surfactant removal in foam fractionation: I - Theoretical development. Aquacultural Engineering, v. 13, p. 163-181 (1994).

Forstmeier, M., Goers, B., Wozny, G., UF/NF treatment of rinsing waters in a liquid detergent production plant. Desalination, v. 149, p. 175-177 (2002).

Goers, B., Mey, J., Wozny, G., Optimised product and water recovery from batch-production rinsing waters. Waste Management, v. 20, p. 651-658 (2000).

Gupta, S., Pal, A., Ghosha, P. K., Bandyopadhyaya, M., Performance of waste activated carbon as a low-cost adsorbent for the removal of anionic surfactant from aquatic environment. Journal of Environmental Science and Health Part A, v. 38, p. 381-397 (2003).

Hua, Wu S., Pendleton, P., Adsorption of anionic surfactant by activated carbon: Effect of surface chemistry, ionic strength, and hydrophobicity. Journal of Colloid and Interface Science, v. 243, p. 306-315 (2001).

Jönsson, A. S., Jönsson, B., The influence of nonionic and ionic surfactants on hydrophobic and hydrophilic ultrafiltration membranes. Journal of Membrane Science, v. 56, p. 49-76 (1991).

Karci, A., Arslan-Alaton, I., Bekbolet, M., Advanced oxidation of a commercially important nonionic surfactant: Investigation of degradation products and toxicity. Journal of Hazardous Materials, v. 263, p. 275-282 (2013).

Kaya, Y., Barlas, H., Arayici, S., Nanofiltration of Cleaning-In-Place (CIP) wastewater in a detergent plant: Effects of pH, temperature and transmembrane pressure on flux behaviour. Separation and Purification Technology, v. 65, p. 117-129 (2009).

Kaya, Y., Aydiner, C., Barlas, H., Keskinler, B., Nanofiltration of single and mixture solutions containing anionics and nonionic surfactants below their critical micelle concentrations (CMCs). Journal of Membrane Science, v. 282, p. 401-412 (2006).

Kertész, S., László, Z., Horváth, Z. H., Hodúr, C., Analysis of nanofiltration parameters of removal of an anionic detergent. Desalination, v. 221, p. 303-311 (2008).

Korzenowski, C., Martins, M. B. O., Moura Bernardes, A., Zoppas Ferreira, J., Duarte, E. C. N. F., Norberta De Pinho, M., Removal of anionic surfactants by nanofiltration. Desalination and Water Treatment, v. 44, p. 269-275 (2012).

Kovács, Z., Samhaber, W., Characterization of nanofiltration membranes with uncharged solutes. Membrántechnika, v. 12, p. 22-36 (2008).

Kowalska, I., Anionic surfactant removal by ion exchange. Ochrona Srodowiska, v. 31, p. 25-29 (2009).

Kowalska, I., Regeneration of ion-exchange resins used for the separation of anionic surfactants from aqueous solutions. Ochrona Srodowiska, v. 34, p. 39-42 (2012).

Lee, J., Maa, J. R., Separation of a surface active solute by foam fractionation. International Communications in Heat and Mass Transfer, v. 3, p. 465-473 (1986).

Méndez-Díaz, J., Sánchez-Polo, M., Rivera-Utrilla, J., Canonica, S., von Gunten, U., Advanced oxidation of the surfactant SDBS by means of hydroxyl and sulphate radicals. Chemical Engineering Journal, v. 163, p. 300-306 (2010).

Oliveira, L. L., Costa, R. B., Duarte, I. C. S., Luiz Silva, E., Varesche, M. B. A., Anaerobic degradation of linear alkylbenzene sulfonate in fluidized bed reactor. Brazilian Journal of Chemical Engineering, v. 27, p. 539-543 (2010).

Patel, M., Surfactant based on renewable raw materials. Carbon dioxide reduction potential and policies and measures for the European Union. Journal of Industrial Ecology, v. 7, p. 46-62 (2004).

Schouten, N., van der Ham, L. G. J., Euverink, G-J. W., de Haan, A. B., Selection and evaluation of adsorbents for the removal of anionic surfactants from laundry rinsing water. Water Research, v. 41, p. 4233-4241 (2007).

Suárez, L., Díez, M. A., Garcia, R., Riera, F. A., Membrane technology for the recovery of detergent compounds: A review. Journal of Industrial and Engineering Chemistry, v. 18, 1859-1873 (2012).

Yang, W. B., Li, A., Fan, J., Yang, L., Zhang, Q., Adsorption of branched alkylbenzene sulfonate onto styrene and acrylic ester resins. Chemosphere, v. 64, p. 984-990 (2006).

Yang, W. B., Xia, M., Li, A., Yang, L., Zhang, Q., Mechanism and behavior of surfactant adsorption onto resins with different matrices. Reactive and Functional Polymers, v. 67, p. 609-616 (2007).