Introduction

Numerous microcontaminants that leak into the environment due to extensive anthropogenic activities are responsible for the constantly deteriorating condition of water reserves. Among the particularly troublesome microcontaminants are surfactants (surface active agents), which cause extensive foaming in natural reservoirs and wastewaters mainly in areas of turbulent flow [1]. Moreover, surfactants increase the solubility of many hazardous microcontaminants (PCBs, pesticides, mineral oils), thus enhancing their ability to penetrate into living organisms and increasing their toxicity [1, 2]. Surfactants may have a toxic impact on organisms comprising the aquatic biocenosis, but most of them are not acutely toxic to organisms at environmental concentrations. Lewis [3, 4] has summarized the chronic and sublethal toxicities of surfactants to aquatic animals and stated that chronic toxicity of anionic and non-ionic surfactants occurs at concentrations usually greater than 0.1 mg/dm³.

Due to their many useful properties, surfactants are used in nearly all branches of industry, including the textile, mining, and oil industries, metallurgy, foodstuffs, plant protection agents, agriculture, and zootechnics. The largest amounts of surfactants are used as synthetic washing agents in laundries and households [5].

Detergent production plants, textile manufactures, and laundries generate large amounts of wastewaters with concentrations of microcontaminants (including surfactants) largely exceeding the acceptance limits defined by standards in force. Significant reduction of the levels of these microcontaminants is required before the wastewaters are discharged into the sewage systems or into the surface waters. Due to diverse chemical structures of surface active agents, as well as to their varying physical properties and concentrations in aqueous solutions, identification of an
optimum method for surfactant removal is a complex issue. Surfactant microcontamination is removed by processes that are also recommended for elimination of other organic microcontaminants, but each of these methods has its merits and limitations. Among the currently employed processes in the treatment of wastewaters containing surfactants, the most common are biological methods based on active sludge. Removal of nonionic and anionic surfactants from raw domestic wastewater in wastewater treatment plants amounts to 67-90% and 93-99%, respectively [6]. Application of biological methods for the treatment of industrial wastewater with high concentrations of surfactants is problematic due to their toxicity to activated sludge and foam production.

From among other techniques studied in this field, we can mention oxidation [7, 8], coagulation using coagulants or combinations of coagulants and polyelectrolytes [9], adsorption [10, 11], ion exchange [12, 13], and membrane processes [14, 15].

Without a doubt, high pressure membrane processes are attractive separation techniques; however, it should be underlined that among factors that affect the high capital and exploitation costs of nanofiltration and reverse osmosis systems are relatively low permeate flux values, leading to the increase in the membrane area required for the process. On the other hand, use of low-pressure membrane separation processes (MF and UF) for detergent-containing wastewater treatment is not always sufficiently effective for achieving acceptable levels of organic contaminants, such as surfactants, when discharging wastewaters into sewage or surface waters. In wastewater treatment, low-pressure membrane processes are used as pre-treatment before the nanofiltration and reverse osmosis stage.

This article presents the possibility of applying pressure membrane processes (ultrafiltration) for separation of anionic surfactants from aqueous solutions in a system integrated with ion exchange that constitutes a highly effective final purification stage.

### Materials and Methods

#### Model Solutions

Experiments were carried out on surfactant solutions prepared from distilled water (conductivity of 1.7 μS/cm) 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. Product purity determined from the alkybenzenesulfonate content was 80%, with higher and lower homologs of the compound detected. The concentration of SDBS in model solutions amounted to 0.25 CMC, 1.0 CMC, and 3.0 CMC. The pH of the feed solutions subjected to a sequential ultrafiltration – ion exchange purification system amounted to 9.2, 10.2, and 10.9, respectively.

The critical micelle concentration (CMC), defined as the concentration of surfactants above which micelles form, equal to ca. 2.29 mmol/dm³. The CMC value was determined from the measurements of the surface tension of the solution. The tests were performed by du Noüy ring method using a semiautomatic Lauda tensometer at 22°C. The maximum force required to raise the ring from the liquid’s surface was measured. A standard platinum–iridium ring with radius of 9.6 mm and wire diameter of 0.2 mm was used in this method. Surface tension data were recorded as the average values of three measurements on solutions of SDBS. In order to perform the correction for the measured interfacial tension data, the Lunkenheimer factors were used [16].

The anionic surfactant concentration in the solutions was determined by potentiometric titration using a 785 DMP Titrino titrator (Metrohm).

### Membranes

The permeation tests were carried out using flat-sheet polyethersulfone and cellulose Microdyn-Nadir® membranes with cut-off values of 5, 10, and 30 kDa. The membranes are formed on a highly porous polypropylene substrate, which significantly enhances their mechanical durability. The main properties of the polymers are shown in Table 1.

### Ion-Exchange Resins

The tests were carried out using five types of anion-exchange resins with characteristics presented in Table 2. 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.

SDBS exchange capacity was determined according to the procedure described in previous studies [17]. Ion-exchange isotherms were analyzed using the linear-form of Langmuir model.

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### Table 1. Nadir® ultrafiltration membranes.

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Membrane material</th>
<th>Cut-off (kDa)</th>
<th>Pure water flux (dm³/m²·h)*</th>
<th>Pure water flux (dm³/m²·h)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>UP005</td>
<td>polyether-sulfone</td>
<td>5</td>
<td>&gt;30</td>
<td>41</td>
</tr>
<tr>
<td>UP010</td>
<td></td>
<td>10</td>
<td>&gt;150</td>
<td>265</td>
</tr>
<tr>
<td>UP030</td>
<td></td>
<td>30</td>
<td>&gt;100</td>
<td>345</td>
</tr>
<tr>
<td>UC005</td>
<td>cellulose</td>
<td>5</td>
<td>&gt;25</td>
<td>45</td>
</tr>
<tr>
<td>UC010</td>
<td></td>
<td>10</td>
<td>&gt;40</td>
<td>82</td>
</tr>
<tr>
<td>UC030</td>
<td></td>
<td>30</td>
<td>&gt;300</td>
<td>1244</td>
</tr>
</tbody>
</table>

*The catalogue of Nadir® membranes. Test conditions: 3 bar, 20°C, stirred cell: 700 RPM.
**Determined by the author. Test conditions: 3 bar, 22°C, stirred cell: 300 RPM.
where:

\[ q_e = \frac{1}{q_{\text{max}} K_L} + \frac{C_e}{q_{\text{max}}} \]  

(1)

\[ q_e = \left( C_i - C_e \right) \frac{V}{V_j} \]  

(2)

...where:

\( q_e \) (mmol/cm\(^3\)) – equilibrium amount of SDBS exchanged on a resin volume of 1 cm\(^3\) calculated using the following formula:

\( C_e \) – initial surfactant concentration in the solution, (mmol/dm\(^3\))

\( C_e \) – equilibrium concentration of SDBS in solution, (mmol/dm\(^3\))

\( V \) – solution volume, (dm\(^3\))

\( V_j \) – resin volume, (cm\(^3\))

\( q_{\text{max}} \) – maximum uptake of SDBS exchanged on a resin volume of 1 cm\(^3\), (mmol/cm\(^3\))

\( K_L \) – Langmuir constant (dm\(^3\)/mmol)

The Integrated Purification System

The integrated purification process was carried out in laboratory scale according to the design presented in Fig. 1. Model surfactant solutions at concentrations of 0.25, 1.0, and 3.0 CMC were preliminarily purified using flat-sheet ultrafiltration membranes. The transport and separation properties of the membranes were tested in Amicon 8400 filtration cells. The process of filtration of surfactant solutions was conducted at the transmembrane pressure \( \Delta P = 3 \) bar, achieved by force using compressed technical-grade nitrogen. After the filtration process, membranes were regenerated using 0.1 n NaOH, as recommended by the manufacturer.

Next, the obtained permeates were further purified in the ion exchange process on MIEX\(^*\), A100, A200, A400, and SBW resins. The resin dose in the vessel tests was 2.5, 5, 10, and 20 cm\(^3\) per 1 dm\(^3\) of the purified solution. After pre-defined mixing times (5-60 min.), water samples were collected for analysis.

The efficiency of the ultrafiltration and the integrated purification system was determined based on the following expressions [18]:

- Surfactant removal efficiency (R, %):

\[ R = \frac{c_i - c}{c_i} \cdot 100 \]  

(3)

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

- Permeate volume flux (\( J \), dm\(^3\)-m\(^{-2}\)-h\(^{-1}\)):

\[ J = \frac{1}{A} \frac{dV}{dt} \]  

(4)

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

<table>
<thead>
<tr>
<th>Resin</th>
<th>Type</th>
<th>Structure</th>
<th>Functional group</th>
<th>Particle size, mm</th>
<th>Ion-exchange capacity*, mmol/cm(^3)</th>
<th>SDBS exchange capacity**, mmol/cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIEX(^*) Orica Watercare</td>
<td>strong base</td>
<td>macroporous polyacrylic</td>
<td>type 1 quaternary ammonium</td>
<td>150-180</td>
<td>0.398</td>
<td>0.365</td>
</tr>
<tr>
<td>Purolite(^*) A100</td>
<td>weak base</td>
<td>macroporous polystyrene crosslinked with divinylbenzene</td>
<td>tertiary amine</td>
<td>725±125</td>
<td>0.902</td>
<td>0.109</td>
</tr>
<tr>
<td>Purolite(^*) A200</td>
<td>strong base</td>
<td>gel polystyrene crosslinked with divinylbenzene</td>
<td>type 2 quaternary ammonium</td>
<td>725±125</td>
<td>1.068</td>
<td>0.121</td>
</tr>
<tr>
<td>Purolite(^*) A400</td>
<td>strong base</td>
<td>gel polystyrene crosslinked with divinylbenzene</td>
<td>type 1 quaternary ammonium</td>
<td>725±125</td>
<td>1.090</td>
<td>0.139</td>
</tr>
<tr>
<td>Wofatit(^*) SBW</td>
<td>strong base</td>
<td>gel polystyrene crosslinked with divinylbenzene</td>
<td>type 1 quaternary ammonium</td>
<td>300-1,200</td>
<td>1.130</td>
<td>0.155</td>
</tr>
</tbody>
</table>

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

\**Determined by the author from the Langmuir isotherm method [17]

![Fig. 1. Schematic diagram of the laboratory set-up.](image-url)
• Relative permeability of membranes (%):

\[ RF = \frac{J}{J_{H2O}} \times 100 \]  

...where: \( J \) denotes the permeate volume flux after time \( t \) to the initial distilled water flux. The relative permeability of membranes is the measure of the permeate volume flux decline during the ultrafiltration process.

**Results and Discussion**

The use of an integrated purification system allowed us to enhance the efficiency of surfactant separation by combining two separation mechanisms of molecular sieving and ion exchange. Overall efficiency of such a purification system was determined by numerous parameters, such as quality of the solution to be purified, type of the membrane material, membrane cut-off value, the type of ion-exchange resin, its dose, and solution contact time of the ion-exchange resin.

Separation properties of the ultrafiltration membranes during filtration tests are presented in Figs. 2 and 3. The quality of the permeate after the ultrafiltration process was significantly dependent on the cut-off value and the polymer material of the membrane. Highest quality of the permeate was achieved upon the use of a polyethersulfone membrane with low cut-off values (UP005). Retention coefficients achieved for surfactant solutions with concentrations of 0.25 CMC, 1.0 CMC, and 3.0 CMC were approximately 80%, 87%, and 94%, respectively. The increase in membrane cut-off values and the use of regenerated cellulose as the membrane polymer led to significant reduction in quality of the obtained permeate and, therefore, a more concentrated solution was subjected to the ion exchange process. For example, the efficiency of SDBS elimination on a UC005 membrane for solutions with concentrations of 0.25 CMC, 1.0 CMC, and 3.0 CMC was 37%, 49%, and 74%.

Comparisons of the efficiency of the surfactant removal from aqueous solutions using membranes with different cut-off values showed that the increase in the membrane cut-off value resulted in a significant reduction in separation, especially for concentrations below CMC. For concentrations above CMC, the reduction in the surfactant retention coefficient (due to the size of micelle being formed) was less pronounced when the membrane cut-off value was increased from 5 kDa to 30 kDa. The analysis of relative permeability of the membranes showed that the reduction in hydraulic efficiency was more evident in the case of membranes with higher cut-off values, which were more prone to fouling due to easier access of surfactant monomers to large membrane pores (Table 3).

<table>
<thead>
<tr>
<th>Membrane</th>
<th>0.25 CMC</th>
<th>1.0 CMC</th>
<th>3.0 CMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>UP005</td>
<td>98</td>
<td>79</td>
<td>80</td>
</tr>
<tr>
<td>UP010</td>
<td>75</td>
<td>76</td>
<td>79</td>
</tr>
<tr>
<td>UP030</td>
<td>78</td>
<td>60</td>
<td>43</td>
</tr>
<tr>
<td>UC005</td>
<td>99</td>
<td>102</td>
<td>94</td>
</tr>
<tr>
<td>UC010</td>
<td>99</td>
<td>96</td>
<td>92</td>
</tr>
<tr>
<td>UC030</td>
<td>89</td>
<td>70</td>
<td>48</td>
</tr>
</tbody>
</table>
As shown by previous studies [19], the efficiency of surfactant separation in the ultrafiltration process is not only due to the pore size reduction in the process of monomer adsorption, but also due to pre-micelle and micelle formation in the membrane polarization layer. The obtained results led to the conclusion that the molecular sieving mechanism is of great significance in separation of surfactants by ultrafiltration. However, the overall separation effect is determined by the resultant hydrophobic and electrostatic interactions (between individual surfactant monomers and between surfactant monomers and the membrane).

High-quality solutions were obtained by employing the ion exchange process for final purification of the membrane permeates (Figs. 4 and 5). For instance, the use of an integrated purification system with a UP005 membrane allowed for surfactant removal efficiency of over 97%, 96%, 98%, 95%, and 98% for MIEX®, A100, A200, A400 and SBW resins, respectively, at the contact time of 20 min. The use of an integrated purification system with a membrane having the worst separation properties (UC030) allowed for surfactant removal efficiency of over 96%, 55%, 82%, 88%, and 91% for MIEX®, A100, A200, A400...
and SBW resins, respectively, at contact time of 20 min. The retention coefficients of surfactant were found to largely depend on the type of the anion-exchange resin and its ion-exchange capacity toward surfactant (SDBS). Similarly as for an individual ion-exchange process (Table 2), the efficiency of the sequential purification system was arranged in the following order (according to the resin type being used): MIEX® > SBW > A400 > A200 > A100.

The significantly higher surfactant exchange rate and efficiency of the magnetic MIEX® resin should be associated with the lower size of grains, compared to other resins (Table 2). Lower ionite grain diameters result in shortening both the duration of the diffusive transport of the ion from the ionite grain surface to the exchange site, and then the duration of the diffusive transport of the displaced ion to the grain surface. Compared to other ionites, the magnetic MIEX® resin is also characterized by higher specific surface area, increasing the access of the ions to the active sites.

The remaining strong-alkaline ion-exchange resins were characterized by lower ion-exchange capacity toward SDBS, as well as by lower process dynamics. A surprisingly high value of maximum exchange capacity toward SDBS of 0.109 mmol/cm³ was obtained for weak-alkaline resin A100. Considering the significant linear dimension of an SDBS molecule (22 Å), one should assume that in case of gel resins characterized by a high degree of cross-linking and thus by lower porosity, access to the active sites was restricted. On the other hand, the macroporous resin pore diameters (usually larger than 20 nm, i.e. ten times larger than the diameter of the apparent pores of gel ionites) are large enough that fast in-grain diffusion to the ion-active sides may occur without the swelling process. The restricted access of monomers to the active sites of gel resins (A200, A400, and SBW), and the lower selectivity of the weak alkaline resin toward weak acid anions may explain the large differences in the observed ion-exchange capacities of the ionites and the useful ion-exchange capacity (Table 2). One may also suspect that the maximum ion-exchange capacity of the ionites toward SDBS is determined not only by the “pure” ion exchange process, but also by sorption between the hydrophobic surfactant chains and polymer chains.

The efficiency of the sequential purification system was also determined by the dose of the ion-exchange resin (Table 4) and the duration of contact between the resin and the organic macromolecules (Fig. 6). A significant increase in the quality of the solution was achieved with the increase in the dose of the ion-exchange resin and the duration of contact with the surfactant anions (so that equilibrium can be achieved).

<table>
<thead>
<tr>
<th>Sequential system</th>
<th>Resin dose, cm³/dm³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>UP010+MIEX®</td>
<td>87</td>
</tr>
<tr>
<td>UP010+A100</td>
<td>71</td>
</tr>
<tr>
<td>UP010+A400</td>
<td>78</td>
</tr>
<tr>
<td>UC010+MIEX®</td>
<td>53</td>
</tr>
<tr>
<td>UC010+A100</td>
<td>36</td>
</tr>
<tr>
<td>UC010+A400</td>
<td>44</td>
</tr>
</tbody>
</table>

Table 4. Surfactant removal efficiency (%) in a sequential ultrafiltration ion exchange purification system as a function of resin dose (contact time: 20 min., surfactant concentration: 1.0 CMC).

Fig. 5. Surfactant removal efficiency (%) in a sequential ultrafiltration ion exchange purification system (membrane material: cellulose, contact time: 20 min., resin dose: 20 cm³/dm³, 1 – MIEX®, 2 – A100, 3 – A200, 4 – A400, 5 – SBW).
Conclusions

The use of an integrated purification system allowed us to enhance the efficiency of surfactant separation compared to individual purification processes by combining two surfactant separation mechanisms of molecular sieving and ion exchange. Membrane processes allowed for removal of significant loads of anionic surfactants present in the solution in the forms of micelle, pre-micelle, and monomers, so that the starting concentrations of contaminants in solutions submitted to the ion exchange process could be significantly lower.

Overall efficiency of the integrated purification systems was determined by numerous parameters such as quality of the solution to be purified, type of the polymer membrane material, membrane cut-off value, and type, dose, and solution contact time of the ion-exchange resin. The obtained results allowed for listing the integrated systems in the following descending efficiency order depending on the resin being used: MIEX® > SBW > A400 > A200 > A100.

Acknowledgements

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References