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SEPARATION OF ANIONIC SURFACE-ACTIVE AGENTS IN AN INTEGRATED ION EXCHANGE– SEDIMENTATION–ULTRAFILTRATION PURIFICATION SYSTEM

The efficiencies of separation of anionic surface-active agents (ASAAs) from aqueous solutions below the critical micelle concentration were determined in an integrated purification system combining ion exchange, sedimentation and ultrafiltration. The tests were carried out using five types of anion-exchange resins (strongly and weakly basic) and flat polyethersulfone membranes with cut-off values of 5, 10 and 30 kDa. Combination of ion exchange and low-pressure membrane separation processes was found to facilitate effective separation of ASAAs from aqueous solutions below the critical micelle concentration. Integration of both unit processes was observed to be most beneficial in the case of membrane with the highest cut-off (30 kDa), which was characterized by low ASAA retention factors when ultrafiltration was carried out as a standalone process. The presence of the ion-exchange resin was also found to allow a significant reduction in membrane fouling and retention of high hydraulic efficiency.

1. INTRODUCTION

In order to enhance the efficiency of removal of microcontaminants from aqueous solutions, membrane techniques are increasingly used in combination with other individual purification processes. Appropriately designed systems allow us to maximize the benefits of individual purification processes, both classic and membrane ones while significantly reducing their disadvantages [1]–[3]. Due to numerous benefits of integrated systems involving membranes, many studies are conducted to develop such methods, including methods for purifying solutions containing surface active agents [4]–[8].

Combination of ultrafiltration and ion exchange is one of possible solutions of the problem of separation of anionic surface-active agents (ASAAs) from solutions below the critical micelle concentration (CMC). As shown by the studies [9]–[13], the standalone

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process of ultrafiltration is a satisfactory method for separating surface-active agent micelles from solutions at concentrations equal to or greater than that of the CMC. In cases where the concentration of surface-active agents is lower, high-pressure separation techniques (nanofiltration, reverse osmosis) are suggested for effective separation processes.

The literature reports [14]–[16] also suggest that using synthetic ion-exchange resins for separation of ionic SAAs leads to better results than using typical adsorbents due to a significantly larger sorption capacity as a result of high porosity and specific surface area, stable chemical structure and the possibility of appropriately modifying the polymer with respect to the number and type of functional groups.

The goal of the studies was to determine the efficacy of elimination of ASAAs from aqueous solutions at concentrations below the critical micelle concentration in an integrated purification system combining ion exchange and ultrafiltration. The effect of the type of anion-exchange resin and the membrane cut-off value on the efficacy of the proposed purification system was studied.

2. MATERIALS AND METHODS

2.1. TEST SOLUTIONS

Subject to the tests were model solutions of anionic surface-active agent (sodium dodecylbenzenesulfonate (SDBS), 348.48 Da) at concentration of 0.25 CMC. The critical micelle concentration (equal to ca. 800 g/m^3) was determined from the measurements of the surface tension of the solution. The concentration of the anionic surface-active agent in the solutions was determined by potentiometric titration using a 785 DMP Titrino titrator (Metrohm). Product purity determined from the alkylbenzenesulfonate content was 80%, with higher and lower homologs of the compound detected [17].

2.2. ION-EXCHANGE RESINS

The tests were carried out using five types of anion-exchange resins with characteristics presented in table 1. 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 [18], [19].

The ion-exchange process was carried out in 2 dm^3 reactors containing 1 dm^3 of the solution and charged with resin doses of 2.5, 5, 10 and 20 cm^3 . The reactors were

placed on Velp Scientifica JLT 4 stirrer and stirred at the rotational speed of 150 rpm, which ensured the suspension and uniform distribution of the resin within the entire volume of the solution. Samples were collected for determination of ASAA concentrations after pre-defined mixing periods (5–60 min.).

Table 1

Characteristics of anion exchange resins*

Resin	Type	Structure	Functional group	Particle size (μm)	SDBS exchange capacity* (mmol/cm^3)
MIEX [®] Orica Watercare	strong base	macroporous polyacrylic	type 1 quaternary ammonium	150–180	0.365
Purolite [®] A100	weak base	macroporous polystyrene crosslinked with divinylbenzene	tertiary amine	725 ± 125	0.109
Purolite [®] A200	strong base	gel polystyrene crosslinked with divinylbenzene	type 2 quaternary ammonium	725 ± 125	0.121
Purolite [®] A400	strong base	gel polystyrene crosslinked with divinylbenzene	type 1 quaternary ammonium	725 ± 125	0.139
Wofatit [®] SBW	strong base	gel polystyrene crosslinked with divinylbenzene	type 1 quaternary ammonium	300–1200	0.155

* Exchange capacity of the resins with regard to SDBS determined from the Langmuir isotherm method.

2.3. ULTRAFILTRATION MEMBRANES

The tests were carried out using Microdyn-Nadir[®] polyethersulfone membranes with cut-off values of 5, 10 and 30 kDa (table 2). The membranes are formed on a highly porous polypropylene substrate, which significantly enhances their mechanical durability (figure 1). Separation properties of the polymers were tested in a laboratory setup, Amicon 8400 ultrafiltration cell being the main component.

Table 2

Characteristics of Nadir[®] polyethersulfone ultrafiltration membranes [20]

Membrane type	Cut-off (kDa)	Pure water flux ($\text{dm}^3/\text{m}^2\text{h}$)*	Polymer properties
UP005	5	41	hydrophilic, high chemical resistance pH range: 0–14 max. temperature: 95 °C
UP010	10	265	
UP030	30	345	

* Determined by the author. Test conditions: 3 bar, 22 °C, stirred cell: 300 rpm.

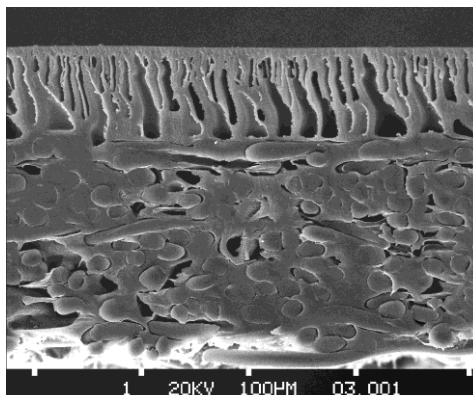


Fig. 1. SEM of UP membrane cross-section ($\times 280$)

2.4. THE INTEGRATED PURIFICATION SYSTEM

The separation efficiency of ASAA was assessed in an integrated system whose operation consists in ion exchange, sedimentation and ultrafiltration. Solutions purified in the ion-exchange processes were submitted to ultrafiltration. In this embodiment, the ion-exchange process was carried out in finite volume conditions for 20 min at resin doses of $5 \text{ cm}^3/\text{dm}^3$. After a pre-defined mixing period, the mixture was subjected to sedimentation lasting for 30 min. Next, the clarified liquid was submitted to further purification by ultrafiltration.

3. RESULTS

3.1. ION EXCHANGE

The kinetic curves obtained are presented in figure 2. The efficacy of separation of the ASAA from aqueous solutions increased with the increase in the time of contact between the resin and the macroanions and in the dose of the resin used. The ion exchange was most intense at the initial stage of the process. Then, the dynamics of ASAA ion exchange slowed down and the process reached equilibrium. Of all the ionites used, MIEX[®] resin had the shortest equilibrium times – for the resin dose of $10 \text{ cm}^3/\text{dm}^3$, the equilibrium concentration was reached after ca. 10 minutes. In the case of strongly alkaline gel resins (A200, A400 and SBW), the time to equilibrium was about 40 minutes, while in the case of the weakly alkaline A100 it was ca. 60 minutes.

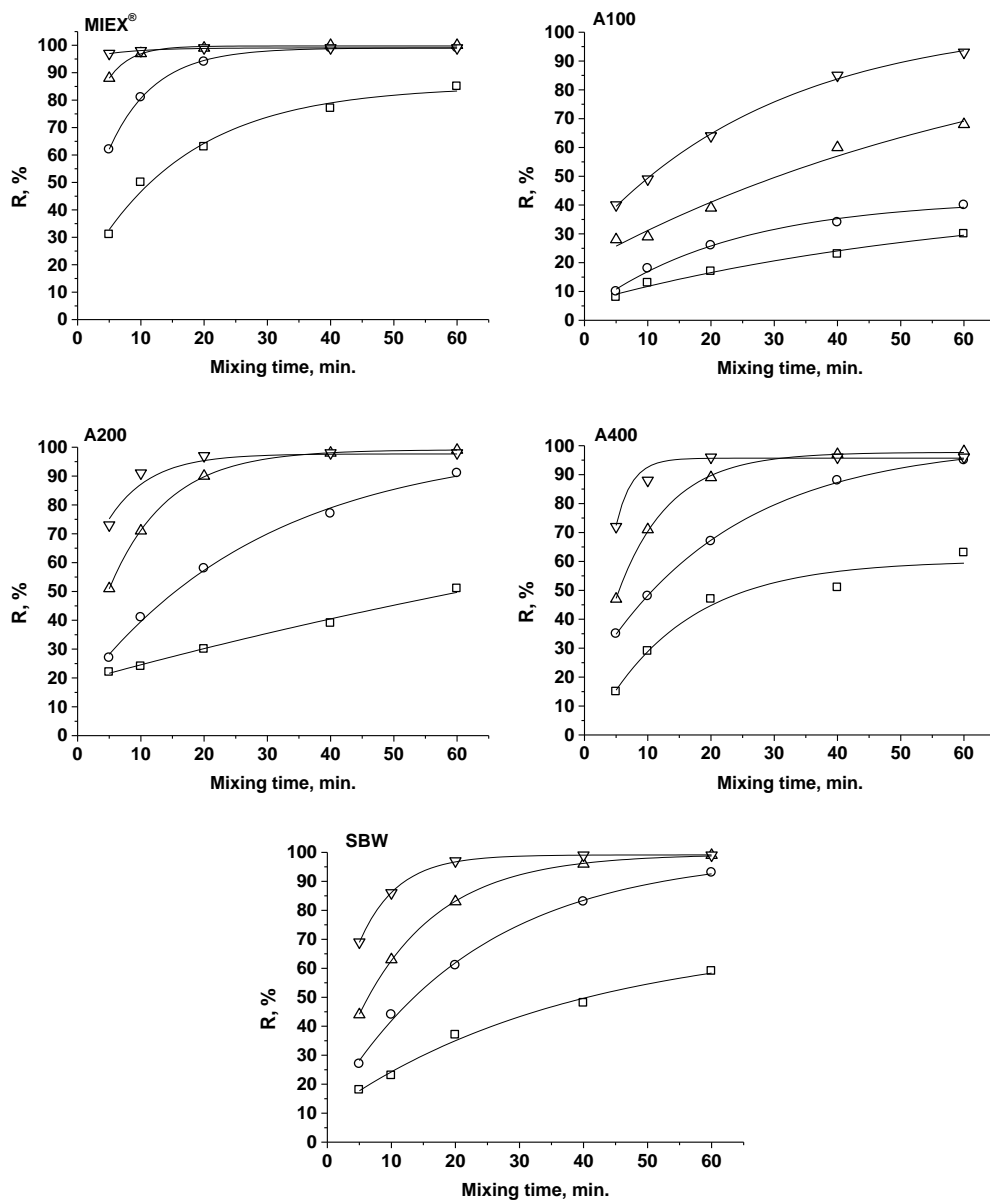


Fig. 2. The effect of contact time and ion-exchange resin dose on the efficiency of SDBS separation ($\square 2.5 \text{ cm}^3/\text{dm}^3$; $\circ 5 \text{ cm}^3/\text{dm}^3$; $\Delta 10 \text{ cm}^3/\text{dm}^3$; $\nabla 20 \text{ cm}^3/\text{dm}^3$)

The test showed that the strongly alkaline MIEX[®] was most efficient in exchanging the ASAA ions. Using 5 cm^3 of the resin per 1 dm^3 of the purified solution allowed an increase in ASAA separation efficiency from 62% to 99% after mixing

times of 5 and 40 minutes, respectively. The remaining strongly alkaline ion-exchange resins (A200, A400 and SBW) and the weakly alkaline resin were characterized by lower dynamics of ASAA ion exchange and lower separation efficiency. At the resin dose of $5 \text{ cm}^3/\text{dm}^3$, the efficiency of ASAA separation changed in the following ranges: 27–91% (A200), 35–95% (A400), 27–93% (SBW) and 10–40% (A100) after mixing times of 5 and 60 minutes, respectively.

High efficacy of MIEX[®] resin was due to the smaller particle size, compared to those of other resins (table 1). Smaller ionite grain diameters lead to reduction in the time of the diffusive transport of ions from the ionite grain surface to the exchange site, and subsequently in the time of the diffusive transport of the displaced ions back to the grain surface. The magnetic MIEX[®] resin is also characterized by higher specific surface area compared to other ionites, resulting in an increased access of the exchanged ions to the active sites. The remaining strongly alkaline ion-exchange resins were characterized by much lower efficiency of macroanion separation and slower process dynamics. This was due to restricted access of monomers to active sites of ion-exchange resins characterized by high degree of polymer cross-linking. The lowest efficacy of macroporous, weakly alkaline A100 resin was in turn associated with its lower selectivity towards weak acid anions.

3.2. ULTRAFILTRATION

The efficacy of the separation of ASAA from model solutions below the critical micelle concentration is presented in figure 3. Comparison of the efficacies of the separation of ASAA from aqueous solutions obtained using polyethersulphone membranes of different cut-off values shows that the increase in the cut-off value leads to an evident impairment of separation. The use of the tight UP005 membrane ensured high SDBS retention factor of 82%, while the efficacies of ASAA separation on membranes of higher porosity were much lower and equaled 46% and 22% for UP010 and UP030 membranes, respectively.

The analysis of transport properties of the membranes showed a reduction in the volumetric flux of the permeate in the SDBS ultrafiltration process compared to the flux of distilled water ($J/J_{\text{H}_2\text{O}}$). 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 ASAA monomers to large membrane pores.

The efficacy of separation using the polyethersulfone membranes tested is the result of hydrophobic and electrostatic interactions between the separated component and the polymeric material, as well as of the sieving mechanism. In the case of ASAA solutions below the CMC, micellar structures may form as a result of local increase in ASAA concentration in the paramembrane layer. However, the sieving mechanisms of the formed premicelles and micelles would be of less significance from the standpoint

of overall separation in the case of the membranes of higher cut-off values, i.e. the membranes of looser polymeric structure.

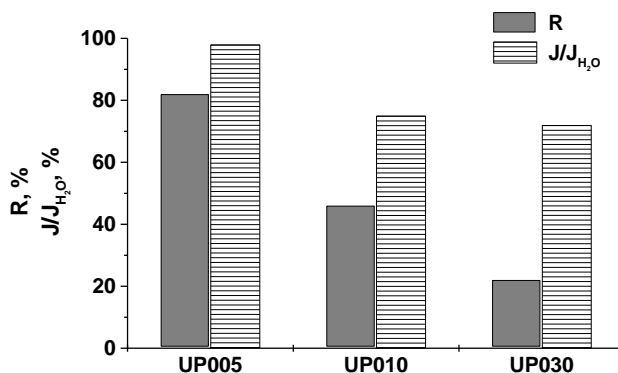


Fig. 3. SDBS retention factor (R , %) and relative membrane permeability (J/J_{H_2O}) as functions of polymer cut-off values ($\Delta P = 0.3$ MPa)

3.3. INTEGRATED PURIFICATION SYSTEM

The results obtained for the standalone ultrafiltration system suggest that satisfactory separation of ASAA from aqueous solutions below critical micelle concentration is possible when tight membranes of relatively low hydraulic efficiency are used. On the other hand, the ion-exchange process is effective when the fine grain magnetic MIEX[®] resin is used, which requires additional filtration stage (to eliminate ionite loss) or large doses of conventional ionites. Therefore, the efficiencies of the separation of ASAA from aqueous solutions were verified for the integrated purification systems.

The test results (figures 4 and 5) showed that the use of the integrated purification system allowed us to enhance the efficiency of ASAA separation compared to individual purification processes. A particularly beneficial effect was obtained for an integrated system with a membrane of the highest cut-off value (30 kDa), which was characterized by low ASAA retention factors when ultrafiltration was carried out as a standalone process. The use of ion exchange and sedimentation as preliminary purification processes allowed us to enhance the efficacy of separation compared to standalone ultrafiltration stage by 75%, 37%, 56%, 64% and 59%, respectively, for MIEX[®], A100, A200, A400 and SBW resins (at resin dose of 5 cm³/dm³ and the resin-solution contact time of 20 minutes). Of note is the fact that in the case of conventional resins, the overall separation was the result of ion exchange and ultrafiltration. The contribution of UF to the overall process efficacy increased with the reduction in membrane, i.e. in the average pore size.

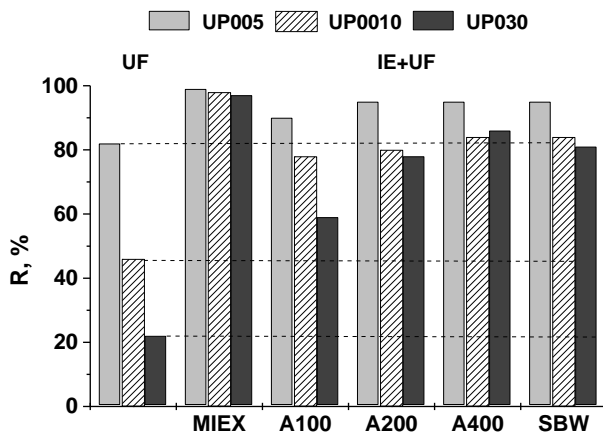


Fig. 4. The efficacy of SDBS separation (R , %) in standalone ultrafiltration process and in integrated purification systems

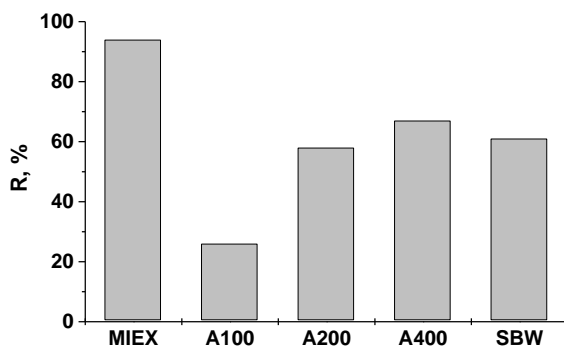


Fig. 5. The efficacy of SDBS separation (R , %) in standalone ion-exchange process (contact time: 20 min.; resin dose: $5 \text{ cm}^3/\text{dm}^3$)

On the other hand, in the case of systems integrated with the magnetic MIEX[®] resin, ion exchange was the separation mechanism that was predominant in the overall process efficacy. The use of an additional barrier in the form of a membrane leads only to a 3% increase in the ASAA separation efficacy. However, the membrane allowed elimination of the loss of the ionite that remained in the solution after sedimentation, which was a particular problem in the case of ion exchange carried out in finite volume conditions using the fine grain MIEX[®] resin.

For ASAA concentrations below the CMC, the presence of the ion-exchange resins allows significant separation of macroions. Thus, reduction in membrane fouling was achieved due to low impurity load at the further stage of the process of purifying the solutions using the ultrafiltration membranes (figure 6). The membrane fouling reduction was more evident in the case of membranes with high cut-off values.

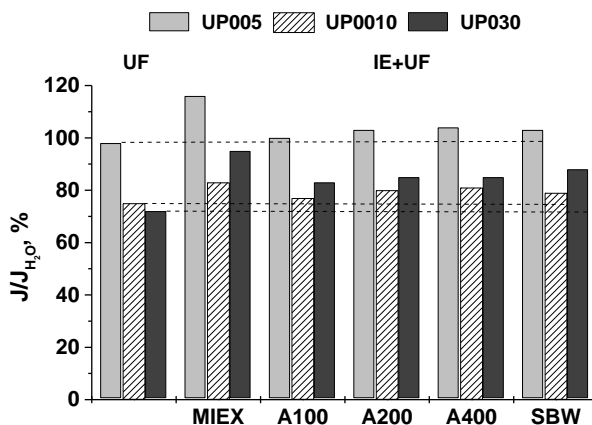


Fig. 6. Relative permeability of membranes (J/J_{H_2O}) in standalone ultrafiltration process and in integrated purification systems

On the other hand, in the case of tight membranes (5 kDa), the volumetric flux of the permeate was slightly larger than the flux of the distilled water for a new membrane. This phenomenon may be associated with hydrophilization of the polymeric material due to hydrophobic interactions between ASAs and the membrane and due to nearly complete reduction in membrane pore blocking.

4. SUMMARY

The tests performed showed that combination of the ion-exchange process and the low-pressure membrane separation process allowed effective separation of ASAs from aqueous solutions below the critical micelle concentration. Integration of both unit processes was observed to be most beneficial in the case of membranes with the highest cut-off (30 kDa), which was characterized by low ASAA retention factors when ultrafiltration was carried out as a standalone process. The presence of the ion-exchange resin was also found to allow a significant reduction in membrane fouling and retention of high hydraulic efficiency. In the case of the fine grain MIEX[®] resin, characterized by the highest dynamics and efficacy of ASAA macroion exchange in aqueous solutions, the presence of an additional barrier in the form of a membrane allowed us to eliminate the loss of the ionite remaining in solution following sedimentation.

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REFERENCES

- [1] VAN DER BRUGGEN B., CURCIO E., DRIOLI E., *Process intensification in the textile industry: the role of membrane technology*, Journal of Environmental Management, 2004, 73, 267–274.
- [2] RAJCA M., BODZEK M., KONIECZNY K., *Modeling of efficiency of ultrafiltration and microfiltration in natural water treatment*, Ochrona Środowiska, 2008, 30 (1), 13–20 (in Polish).
- [3] KONIECZNY K., RAJCA M., BODZEK M., KWIECIŃSKA A., *Water treatment using hybrid method of coagulation and low-pressure membrane filtration of efficiency of ultrafiltration and microfiltration in natural water treatment*, Environment Protection Engineering, 2009, 35 (1), 5–22.
- [4] AKBIL BASAR C., KARAGUNDUZ A., ÇAKICI A., KESKINLER B., *Removal of surfactants by powdered activated carbon and microfiltration*, Water Research, 2004, 38, 2117–2124.
- [5] GONZALEZ S., PETROVIC M., BARCELO D., *Evaluation of two pilot scale membrane bioreactors for the elimination of selected surfactants from municipal wastewaters*, Journal of Hydrology, 2008, 356, 46–55.
- [6] SEO G.T., LEE T.S., MOON B.H., LIM J.H., *Ultrafiltration combined with ozone for domestic laundry wastewater reclamation and reuse*, Water Supply, 2001, 5–6, 387–392.
- [7] SOSTAR-TURKA S., PETRINICA I., SIMONIC M., *Laundry wastewater treatment using coagulation and membrane filtration*, Resources, Conservation and Recycling, 2005, 44, 185–196.
- [8] ZHANG H., QUAN X., CHEN S., ZHAO H., ZHAO Y., *The removal of sodium dodecylbenzene sulfonate surfactant from water using silica/titania nanorods/nanotubes composite membrane with photocatalytic capability*, Applied Surface Science, 2006, 252, 8598–8604.
- [9] GOERS B., MEY J., WOZNY G., *Optimised product and water recovery from batch-production rinsing waters*, Waste Management, 2000, 20, 651–658.
- [10] KOWALSKA I., *Surfactant separation in pressure-driven membrane processes*, Environment Protection Engineering, 2008, 34 (2), 105–113.
- [11] TU Z., DING L., FRAPPART M., JAFFRIN M.Y., *Studies on treatment of sodium dodecyl benzene sulfonate solution by high shear ultrafiltration system*, Desalination, 2009, 240, 251–256.
- [12] KERTÉSZ SZ., LÁSZLÓ ZS., HORVÁTH ZS.H., HODŰR C., *Analysis of nanofiltration parameters of removal of an anionic detergent*, Desalination, 2008, 221, 303–311.
- [13] 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, 2006, 282, 401–412.
- [14] YANG W.B., LI A., FAN J., YANG L., ZHANG Q., *Mechanism and behavior of surfactant adsorption onto resins with different matrices*, Reactive and Functional Polymers, 2007, 67, 609–616.
- [15] YANG W.B., XIA M., LI A., YANG L., ZHANG Q., *Adsorption of branched alkyl-benzene sulfonate onto styrene and acrylic ester resins*, Chemosphere, 2006, 64, 984–990.
- [16] SCHOUTENA N., VAN DER HAMB L.G.J., EUVERINKA G.-J.W., DE HAANC A.B., *Selection and evaluation of adsorbents for the removal of anionic surfactants from laundry rinsing water*, Water Research, 2007, 41, 4233–4241.
- [17] The catalogue of Sigma products.
- [18] <http://www.miexresin.com/>
- [19] KABSCH-KORBUTOWICZ M., KOZAK A., KRUPIŃSKA B., *Ion exchange–ultrafiltration integrated process as a useful method in removing natural organic matter from water*, Environment Protection Engineering, 2008, 33 (2), 79–93.
- [20] The catalogue of Nadir® membranes.