The effect of anionic surfactant on the surface structure of nanofiltration membranes

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The effect of cleaning bath – sodium dodecyl sulphate solution on the surface structure of the polymer membrane used during nanofiltration of concentrated salt solutions have been presented in this paper. It was found that the use of the cleaning bath with sodium dodecyl sulphate caused a significant reduction in the separation and permeability possibilities of tested membrane.

Keywords: nanofiltration membrane, concentrated salt solution, anionic surfactant, scaling

Introduction

Nanofiltration is a membrane pressure technique, which has many applications. Till now, it was successfully applied for treatment of both surface and underground waters [1-3] as well as purification of industrial wastewaters [4,5]. The nanofiltration process was mostly applied for separation of organic compounds, water softening and bacteria removal from water used for housing and industrial purposes [1-3] as well as separation and concentration of metal ions [4,5] and dyes [6,7]. According to the literature data [8-10] and our own investigations [11-13], one of the most important and interesting research area of nanofiltration is connected with separation of mono- and multivalent ions present in salt solutions. The nanofiltration membrane in such processes, according to its ion-selectivity, becomes non-permeable for multivalent ions and permeable for monovalent anions and cations [10,14,15].

The wide application of nanofiltration is limited by reduction of the process efficiency caused by membrane fouling and/or scaling [16,17]. This phenomenon depend strongly on nanofiltration membrane properties [13,15-17]. Membrane charge plays here main role. It is dependent on functional groups present in the membrane structure [12,13] as well as on pH and kind of solution (mainly concentration and salt type) [10,14]. The membrane charge changes dependently on process [18,19] and cleaning bath conditions [20-22]. Our previous investigations [13,18] showed that at low pH positively charged groups appear on nanofiltration membrane surface. They are responsible for adsorption of negatively charged ions on the membrane surface. In consequence, it leads to scaling and reduces membrane selectivity [18]. Change of membrane selectivity strongly influences and changes retention of feed components, what can lead to further increasing of membrane concentration polarization and decreasing its permeability. From the point of view of mono- and multivalent ions (present in salt solutions) separation between permeate and retentate fluxes leaving the membrane module it is useful to keep high membrane permeability and initial selectivity. That is why removal of adsorbed on the membrane surface ions layer seems to crucial for the nanofiltration [18]. Baths based on mineral acids (H₂SO₄, HCl), lye (NaOH) and surfactants are commonly used for the cleaning of polymer nanofiltration membranes [17-24]. Besides of type and density of membrane charge, structure of membrane surface is a main factor for determination of membrane tendency for scaling [25-27]. According to Vrijenhoek et al. [16] and Nanda et al. [17] nanofiltration membranes characterized by less roughness surface showed less fouling and scaling tendency. It is concerning with the fact that both organic and inorganic compounds gathers, in a preferential way, in any cavities of roughness membrane surface [25,26]. That is why the selection of membrane assuring effective nanofiltration should take into account a structure of membrane surface.

Recently, atomic force microscopy (AFM) [13,25,27] and scanning electron microscopy (SEM) [17,18,27] became the most used methods for analysis of membrane surface structure.

Atomic force microscopy allows for determination of average roughness of the membrane surface and such parameters as: maximal and minimal values of deflection, average deviation from the sample profile or determination of a roughness class. The average roughness is determined by the topographic image of the sample. It is a kind of map...
where a certain heights is attached to every point. The averaging of all those data gives an average height of the sample. The difference between the average and local (for each point) height is a roughness measure of the investigated surface [25,27]. Results obtained by the use of atomic force microscopy can be displayed on histogram which represents dependence of sum of number of the surface hills on their heights.

Scanning electron spectroscopy enables visual observation of surface and structural changes of analyzed membrane samples. This technique gives the quantitative analysis on the investigated samples and direct determination of details of the investigated objects [18,27].

The aim of this work was to determine the analysis of structural changes of membrane surface used to nanofiltration of concentrated salt solutions at low pH and cleaned by anionic surfactant bath. During the investigations topographic images and histograms of the tested membrane surfaces as well as their average roughness values has been determined by the use of AFM method. Moreover to support the investigations, SEM images of the tested membrane surfaces have been taken.

**Material and method**

The experiments were carried out at laboratory scale in cross flow system equipped with SEPA CF (GE Osmonics) which scheme and detailed description can be found in our previous paper [13]. All experiments were performed at TMP = 14 bar and QR = 800 dm³/h. The temperature of feed solution during the process was constant and equal to 25±1°C. The feed constituted model saline solution containing 2 g Cr³⁺/dm³, 10 g Cl⁻/dm³ and 10 g SO₄²⁻/dm³ and characterized by pH ≈ 4. The composition of model solution was characteristic of chromium industrial wastewater [1,11]. All experiments were performed in batch concentration mode, i.e. the permeate stream was collected in the permeate tank, whilst retentate stream was recycled to the feed/retentate tank. The nanofiltration flat sheet membrane was studied. For this purpose, using an atomic force microscope (AFM) and scanning electron microscopy (SEM).

The tested membrane surfaces were examined using atomic force microscopy (AFM) and scanning electron microscopy (SEM).

The AFM images were performed with SollverBio Instruments NT-MDT. The cantilever was made out of Si with a spring of a 4.4 N/m and a nominal tip apex radius of 10 nm. The membrane surfaces were analyzed in a scan size of 10 μm x 10 μm. The average surfaces roughness of tested membranes were calculated from AFM images using Nova SPM software.

The SEM images were determined by scanning electron microscope PHENOM G2 (FEI). For SEM analysis, the deposition of a gold layer of about 2 nm in thickness was done using K550x Sputter Coater (Technologies Quorum).

**Results and discussion**

The effect of concentrated salt solutions and cleaning bath – sodium dodecyl sulphate solution on the surface structure of the polymer nanofiltration membrane was studied. For this purpose, using an atomic force microscope (AFM) were made topographical images and histograms the surface of tested membrane: new, after 6 and 20 hours in concentrated salt solutions at low pH and cleaning by the sodium dodecyl sulphate solution (Fig. 1). Then, using the software Nova SPM determined average roughness values which summarized in Table 2. The obtained results showed a significant effect of sodium dodecyl sulphate on structure of nanofiltration membranes repeatedly used for chromium(III) and chloride concentration. The samples of permeate, feed and retentate have been analyzed using the following methods:

- chromium(III) – spectrophotometer NANOCOLOR UV/VIS using 1,5-difenylkarbazide method with wave length λ = 540 nm,
- chlorides – the Mohr titration method.

The feed solution has been prepared using the following chemicals: CrCl₃·6H₂O (Sigma-Aldrich), pure NaCl (Chem pur®), pure Na₂SO₄ (Chem pur®) and the deionized water (after RO system = 46.1 μS/cm, pH = 7.9). The feed solution was characterized by pH = 4. For initial pH correction the pure HCl (Lachner) was used. The pH was measured by pH-meter (Mettler Toledo SevenEasy).

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**Table 1. Characteristic of nanofiltration membrane used in the experiments**

<table>
<thead>
<tr>
<th>Surface material</th>
<th>Poly(piperazine-amide)</th>
</tr>
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<tbody>
<tr>
<td>Support material</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>Type of membrane</td>
<td>Thin film</td>
</tr>
<tr>
<td>Cut-off (g/mol)</td>
<td>150-300</td>
</tr>
<tr>
<td>Permeability coefficient 10⁻⁸ (m³/m²·s·bar)</td>
<td>3.5</td>
</tr>
<tr>
<td>pH range</td>
<td>3-9</td>
</tr>
<tr>
<td>Max. temperature (°C)</td>
<td>50</td>
</tr>
<tr>
<td>Max. pressure (bar)</td>
<td>40</td>
</tr>
<tr>
<td>Isoelectric point (pH)</td>
<td>3.3 [12]</td>
</tr>
<tr>
<td>Zeta potential (mV) (pH=4, t=25°C)</td>
<td>-4.0 [12]</td>
</tr>
</tbody>
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The effect of anionic surfactant on the surface structure of nanofiltration membranes

separation of chromium(III) and chloride ions from the concentrated salt solutions at low pH. The analysis of the AFM images membranes: new and after 6 and 20 hours in concentrated salt solutions and cleaned sodium dodecyl sulfate allowed to conclude the increase corrugations of the surface (Fig. 1), and thus there was a significant increase in the average roughness of the membrane after repeated used and cleaned by SDS solution (Table 2). The average roughness determined from AFM images were 24.0, 25.6 and 39.0 nm for the membrane: new, after 6 and 20 hours of working in concentrated salt solution and cleaning solution of sodium dodecyl sulfate, respectively. According to Arnold et al. [24] and Petkova et al. [25] concluded that the observed structural changes of the tested membrane,

Fig. 1. AFM images of tested membrane surfaces: new (a), after 6 (b) and 20 (c) hours working in concentrated salt mixture solution and cleaning with sodium dodecyl sulphate (SDS)
Anna Kowalik-Klimczak, Paweł Religa, Paweł Gierycz, Marta Bojarska

and hence increase in the average roughness of the surface caused by the adsorption of sodium dodecyl sulphate molecules on the surface. A characteristic feature of the changes in the surface structure of a loose NF membrane was uneven spatial distribution changes. The analysis of histograms obtained by AFM (Fig. 1) leads to the conclusion that the observed increase in the hills formed on the surface with working time and subsequent cleanings using sodium dodecyl sulphate. Probably it was caused by the subsequent adsorption of sodium dodecyl sulphate particles on the surface of the tested membrane. At the same time reduced the number which indicates the connection of single bulge in the tight structure – folds. The interactions surfactant-polymer can significantly contribute to changes in the surface properties of polymer membranes, which have a direct effect on the permeability and selectivity of the membranes [28,29].

Additionally of AFM analysis were surface images of tested membranes made by using scanning electron microscope (Fig. 2). SEM images analysis confirmed the formation on the tested membrane surface the numerous changes unevenly distributed in the shape of folds. Similar observations were noticed after the addition of surfactant to the membrane polymer by other research group [30-32].

The observed changes in the surfaces of tested membrane repeatedly used during the nanofiltration of concentrated salt solutions and cleaned with sodium dodecyl sulphate (SDS) was accompanied by adverse changes in its selectivity (Table 3). The particles of the surfactant adsorbed on the membrane surface during the cleaning formed unstable layer, which established the process conditions (pH ≈ 4) contributes to the relaxation of the structure [30-32]. Negative phenomenon that accompanied the changes described was a decrease in retention of ions present in concentrated salt solutions (Table 3). Therefore, a decrease distribution of chloride and chromium(III) ions between permeate and retentate streams leaving the tested nanofiltration module was observed.
The effect of anionic surfactant on the surface structure of nanofiltration membranes

Application of the cleaning bath constituting an anionic surfactant (sodium dodecyl sulphate) has caused the decrease in tested membrane permeability for demineralized water (Fig. 3). Probably, the surfactant molecules adsorbed on the surface as a result of interaction with the membrane material caused relaxation of its structure which provided a constant of permeate flux despite appearing the appearance of sediment on the mineral layer deposition. Unfortunately, the continue using a further use of the membrane and cleaned it in a bath prepared on the basis of with SDS caused a decrease in the permeability coefficient. Probably, relaxation of the membrane structure facilitated the penetration of the ions present in solution into the membrane structure. As a result of interaction of ions with the charge of the membrane, occurred their adsorption ions into occurred in the membrane structure, and thus its scaling into the internal structure (Fig. 4). This irreversible process of internal membrane pores blocking caused probably a significant and rapid loss of tested membrane permeability coefficient.

Conclusions

The changes of nanofiltration membrane structure, characterized by a loose external layers used to during nanofiltration of concentrated salt and cleaned by sodium dodecyl sulphate solution have been analyzed. The tested membrane surface interacted with the surfactant used what resulted in further destruction (more loose) of the external layers structure. It caused the strong decrease of both chloride and chromium(III) ions retention. Easy permeation of ions present in the investigated systems into the membrane structure caused their inside adsorption in the membrane and led to the membrane scaling. Consequently, a decrease of permeability coefficient for demineralized water was observed. The obtained results led to conclusion that the use of cleaning bath formed from anionic surfactant caused a significant reduction in the separation possibility of tested nanofiltration membranes. That is why a further investigations concerning other cleaning baths enabling for proper cleaning of the membranes used for nanofiltration processes of concentrated salt solutions at low pH is absolutely needed.
Acknowledgements
This work was financially supported by the Project No 504/M/1070/0112/000.

References