Scaling of nanofiltration membranes used for chromium(III) ions recovery from salt solutions
A. Kowalik-Klimczak and P. Gierycz

ABSTRACT
The effect of membranes’ structure on the efficiency of chromium(III) ions recovery from salt solution at low pH and the efficiency of chemical cleaning of these membranes were analyzed in this work. The nanofiltration membranes (DL and HL) used in this study were provided by GE Osmonics. The DL membrane had an irregular, dense support layer structure, while the HL membrane had a loose one. In the case of the DL membrane, it was found that, under tested solutions, the layer of mineral scale formed on the surface gradually decreases the membrane permeability coefficient. In the case of the DL membrane, the scaling was observed only on the surface. On the other hand, a small roughness (118 Å) and low density charge (zeta potential at level –4) of the HL membrane causes an uneven growth in deposits and, consequently, irregular nature of the surface structure which hinders the removal of accumulated sediment from the tested membranes’ surface. Additionally, the loose structure of the support layer of HL membrane contributes to its internal scaling. Consequently, the permanently loose structure of the HL membrane permeability coefficient was observed.

Key words | AFM, chromium(III), NF membranes, salt solution, scaling, SEM

INTRODUCTION
Chromium wastewater is treated by methods such as adsorption, chemical precipitation, biological degradation, ions exchanges and electrocoagulation (Kotuniewicz & Drioli 2008; Aoudj et al. 2015; Cheballah et al. 2015). Recently, nanofiltration especially has been widely used for recovery of metal ions, including chromium, from wastewater (Wang et al. 2007; Gomes et al. 2010; Religa et al. 2013; Kirin Mert & Kestioglu 2014). Recovery of metal ions depends on the ability of the membrane to maintain a high permeability in the nanofiltration process (Religa et al. 2011a; Al-Rashdi et al. 2013; Liu et al. 2015a, 2015b). The permeability of the membrane lowers and the filter cake is formed on the membrane surface during the filtration (Vrijenhoek et al. 2001; Lau & Ismail 2009; Ju & Hong 2014; Chidambaram et al. 2015). The composition of the wastewater containing metal ions contributes to the formation of a mineral filter cake on the membrane surface, i.e. scaling (Van de Lisdonk et al. 2001; Religa et al. 2011b, 2013). According to previous studies (Religa et al. 2011a, 2013), we knew that the membrane surface charge causes the formation of scaling on the nanofiltration membranes used for chromium(III) recovery from salt solution at low pH. The presence of charged groups contributes to the adsorption of ions (presented in the solutions) on the nanofiltration membranes (Petrinic et al. 2007; Bruni & Bandini 2008; Szymczyk et al. 2010; Religa et al. 2011b). Moreover, the results of previous studies (Religa et al. 2013) confirm the different decreases in permeability coefficient in the case of membranes with the same surface charge. In turn, an analysis of membrane surface properties found a significant effect of roughness nanofiltration membrane on its scaling sensitivity (Vrijenhoek et al. 2001; Nanda et al. 2008, 2010). These researchers found that the higher the roughness of the membrane, the greater the tendency to scaling, because the high roughness of the membrane promotes the development of the surface (Vrijenhoek et al. 2001; Nanda et al. 2008, 2010). In turn, it facilitates the adsorption of the solution components in contact with the membrane and consequently leads to the formation of a scale layer on the membrane surface.

The aim of the study was to determine the effect of the nanofiltration membranes’ structure on the efficiency of chromium(III) ions recovery from salt solution at low pH and the efficiency of chemical cleaning of the membranes used.
METHODS

The commercial nanofiltration flat sheet membranes (DL and HL) with an area of 0.0155 m² provided by GE Osmonics were analyzed in this work. The characteristics of tested membranes are presented in Table 1. Both tested nanofiltration membranes had an active layer made of poly(piperazine-amide) and an isoelectric point (IP) equal to about 3.0. The main differences between the tested membranes are the surface roughness and the support layer internal structure. The DL membrane had a very irregular, dense support layer structure, while the HL membrane had a loose one (Kowalik-Klimczak et al. 2016).

In this work, the surface roughness, structure and permeability coefficients of tested membranes were analyzed. Surface roughness was determined by atomic force microscopy (AFM) (SoliverBio Instruments NT-MDT). The cantilever was made out of Si with a spring of 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 × 10 μm. HITACHI S3500N scanning electron microscope (SEM) with a Scotty type thermal field emitter (SU-70 model) was used to record the SEM images of the microstructure of the cross-section membranes. The analysis was carried out in a vacuum condition (1 × 10⁻⁶ Pa) at an accelerating voltage of 15 kV and a secondary electron reception angle of 30°. The membrane samples were coated with an approximately 2 nm-thick layer of gold using BAL-TEC SCD 050 Sputter Coater from Quorum Technologies. The per-membrane surfaces were characterized by a pH of 4. The main differences between the tested membranes were the surface roughness and the support layer internal structure. The DL membrane had a very irregular, dense support layer structure, while the HL membrane had a loose one (Kowalik-Klimczak et al. 2016).

Three types of membranes samples were analyzed as follows:

- new membrane – unused membranes;
- membranes after wetting for 20 h in salt solution – membranes after wetting in model solution containing 2 gCr³⁺/dm³, 10 gCl⁻/dm³, 10 gSO₄²⁻/dm³ and characterized by pH ≈ 4;
- membranes after working for 20 h in salt solution and cleaning according to dual step procedure – membranes after nanofiltration of model solution containing 2 gCr³⁺/dm³, 10 gCl⁻/dm³, 10 gSO₄²⁻/dm³ characterized by pH ≈ 4 in a laboratory installation described in the work by Religa & Kowalik-Klimczak (2015) and cleaned by NaOH followed by HCl as described in Religa et al. (2015).

The model solution was prepared using the following chemicals: CrCl₃·6H₂O (Sigma-Aldrich), pure NaCl (Chempur®), pure Na₂SO₄ (Chempur®) and deionized water. For initial pH correction, pure HCl (Lachner) was used. The pH was measured by pH-meter (Mettler Toledo SevenEasy).

RESULTS AND DISCUSSION

Membrane surface roughness

In the first stage, the surface roughness of new membranes and the membranes after wetting in saline solution characterized by a pH ≈ 4 were examined. The changes in the surface roughness of the tested membranes were determined on the basis of topographic images determined by AFM. The results obtained are summarized in Figures 1 and 2.

In the case of new membranes, it was found that the surface of the HL membrane had a lower roughness than the surface of the DL membrane. Similar results were obtained

Table 1 | Characteristics of nanofiltration membranes used in the experiments

<table>
<thead>
<tr>
<th>Active layer</th>
<th>Support layer</th>
<th>MWCO (Da)</th>
<th>Surface roughness (Å)</th>
<th>Isoelectric point</th>
<th>Zeta potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>DL</td>
<td>Thin film PPZ</td>
<td>Dense PSU</td>
<td>147</td>
<td>3.0</td>
<td>-13</td>
</tr>
<tr>
<td>HL</td>
<td>Thin film PPZ</td>
<td>Loose PSU</td>
<td>118</td>
<td>3.3</td>
<td>-4</td>
</tr>
</tbody>
</table>

PPZ, poly(piperazine-amide); PSU, polysulfone.

aRoughness measurements with tapping mode AFM for scan area of 10 μm × 10 μm.

bZeta potential measured in 0.001 M KCl solution for pH = 4.
in other studies (Boussu et al. 2005, 2007, 2008). Furthermore, based on the analysis of AFM images (Figures 1 and 2), it was found that in the case of the DL membrane, the surface roughness was characterized by higher uniformity than the HL membrane. For both tested membranes, after wetting for 20 h in a saline solution at low pH, a change of the surface structure was observed (Figures 1(b) and 2(b)). The changes in the surfaces of tested membranes were caused by the mineral scale layer which was formed on their surfaces under process conditions in the saline solution. The active layers of the tested membranes were made of poly(piperazine-amide) (Boussu et al. 2005; Al-Amoudi et al. 2007; Tang et al. 2009a, 2009b; Religa et al. 2013). This polymer contains hydrophilic functional groups, which become carriers of negative charges (Al-Amoudi et al. 2007; Bruni & Bandini 2008; Religa et al. 2013) in the solution conditions (pH ≈ 4). The presence of negatively charged groups was caused by the absorption of chromium (III) ions present in the saline solution. The multivalent ions strongly interact with the charged surfaces of nanofiltration membranes (Bruni & Bandini 2008; Szymczyk et al. 2010; Religa et al. 2013). The formation of the adsorption layer and the high concentration of salt present in the tested solution favor the formation of mineral scale layer which alters the surface roughness of the tested membranes (Vrijenhoek et al. 2007; Boussu et al. 2007).

The differences in the surface roughness of the tested membranes were a result of the solutions’ composition contacting with the membrane, electrokinetic properties of the membranes, as well as the initial roughness of their surfaces. The high surface area and charge density of the DL membrane (Table 1) was accompanied with a uniform adsorption of ions which favored the profile smoothing the surface structure (Figures 1 and 2). The irregularities designated for the DL membrane after wetting in saline solution were significantly lower than in the new membrane.

On the other hand, in the case of HL membrane characterized by a lower surface roughness and a slightly negative

![Figure 1](image1.png)  
**Figure 1** | AFM images of DL membranes: (a) new and (b) after wetting in salt solution.

![Figure 2](image2.png)  
**Figure 2** | AFM images of HL membranes: (a) new and (b) after wetting in salt solution.
zeta potential under the experiment conditions (Table 1) than the DL membrane, uneven growth surface corrugations without specific quantities of growth were observed (Figure 2(a) and 2(b)). Based on the analysis of surface changes of the tested new (Figures 1(a) and 2(a)) and wetting in salt solution (Figures 1(b) and 2(b)) membranes, it was found that the higher the initial surface roughness and higher charge density of the DL membrane promoted the formation of uniform, spatially aligned layers of mineral deposits on the surface. Whereas the low density of surface charge and, at the same time, a very small roughness of HL membrane caused an uneven growth in deposits and, consequently, the formation of irregular structure on its surface. The changes of tested nanofiltration membranes’ structure due to interaction with components of salt solutions are shown in Figure 3(a) and 3(b).

**Membrane permeabilities**

Based on the results compiled in Figure 4, it was found that a new HL membrane had a higher permeability coefficient of the deionizer water than the DL membrane. Similar results were obtained by other researchers (Al-Amoudi et al. 2007, 2008). This was probably due to the fact that the support layer of the HL membrane was characterized by looser structure than the DL membrane (Figure 3). In this situation, the facilitation of penetration of the ions present in salt solution into the structure of the HL membrane was found (Figure 3(b)). Similar results were observed in other studies (Afonso 2006; Li & Elimelech 2006). Moreover, an active layer of the HL membrane was characterized by higher density of amine (-NH₂) groups than carboxyl (-COO⁻) groups (Religa & Kowalik-Klimczak 2015). As a result of interaction of ions with the positive charge of the membrane, the adsorption of ions occurred in the membrane structure, and thus its scaling into the internal structure. This irreversible process of internal membrane pores blocking probably caused a significant and rapid loss of tested membrane permeability coefficient (Figure 4). Therefore, scaling had a negative impact on the productivity and efficiency of the chromium(III) ions recovery from salt solution in the nanofiltration process (Religa et al. 2011a, 2013).

The retrieval of the high permeability coefficient of nanofiltration membranes used for chromium(III) ions recovery from salt solutions was possible by the use of a dual-step cleaning by NaOH followed by HCl (described in the work of Religa et al. 2013). The confirmation of such an approach was also a recovery of the initial DL membrane permeability coefficient (Figure 4). It was due to the fact that, in the case of DL membrane, we are likely dealing with scaling only on the surface, which can be easily removed by the adopted cleaning procedure (Religa et al. 2013). The chemical cleaning contributes to the
diversification of the profile of the membrane surface. The character of the membrane roughness is equivalent to that of a new membrane surface roughness, indicating efficient removal of the adsorbed layer of mineral scale (Figure 5).

Analysis of the surface roughness character of the HL membrane used for chromium(III) ions recovery from salt solution and cleaning according to the adopted procedure, found that its surface was visibly smoothed and was accompanied by limited but significant corrugations (Figure 5). Despite a good level of scale washout from the membrane surface, a significant decrease in permeability coefficient was observed (Figure 4). Probably, it was irreversible scaling of membrane that prevented the recovery of the initial permeability coefficient. This means that for chromium(III) ions recovery from salt solutions at low pH, nanofiltration membranes having a dense support layer structure should be preferably used, because they prevent the deposition of mineral scale in the membrane interior.

**CONCLUSIONS**

Based on the obtained results, it was found that high initial surface roughness and a high charge density of nanofiltration membrane used for chromium(III) ions recovery from salt solutions at low pH caused the formation of a uniform, spatially aligned layer of mineral deposits on the surface. The membrane, cleaned with a dual-step method, was characterized by the ability to recover its original roughness, indicating efficient removal of the adsorbed layer of mineral deposits from the membrane surface. The confirmation of such an approach was also the recovery of the initial membrane permeability coefficient. In the case of this type of membrane, we are likely dealing with only scaling on the surface. On the other hand, the low roughness and, at the same time, a very low surface charge density of nanofiltration membranes caused uneven growth of the scale and, consequently, the formation of irregular structures on the surface; and, therefore, the removal of accumulated sediment from the surface of the tested membrane. Additionally, the loose structure of the support layer of this type of membrane contributed to scaling in its internal structure. Consequently, the membrane permanently decreased the permeability coefficient.
coefficient. This means that for chromium(III) ions recovery from wastewater characterized by high salinity and low pH, nanofiltration membranes with a high surface area and compact internal structure should be used. This membrane structure prevented blocking inside of the membrane. Consequently, it allows for a long-term and stable performance of the process and promotes effective chemical cleaning of the membrane.

REFERENCES

Religa, P., Kowalik, A. & Gierycz, P. 2011b A new approach to chromium concentration from salt mixture solution using nanofiltration. Separation and Purification Technology 82, 114–120.


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