

Effect of interaction between anionic surfactants and poly(piperazine-amide) nanofiltration membranes used for chromium(III) recovery from saline solution

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ABSTRACT

The effect of the anionic surfactant on the permeation properties of the nanofiltration (NF) membranes used for chromium(III) recovery from saline solution at low pH have been presented in this paper. The membrane surface layer performance periodically modified by sodium dodecyl sulphate (SDS) solution has been studied with measurements of zeta potential, atomic force microscopy (AFM) and permeability coefficient of tested membranes. It was found that the membrane surface layer modification by SDS caused a substantial reduction in the possibility of separation of loose NF membrane characterized by a high density of positively charged groups activating under the effect of the low pH of the saline solutions (HL membrane). On the other hand, in the case of dense NF membranes characterized by a strong negatively charged surface (DL membrane) constituting used the SDS improves the separation of chloride and chromium(III) ions. In this case, the surfactant solution also provides a high membrane permeability coefficient behavior over a long period of use. DL membrane modification by SDS allowed both to retain the stable membrane working for a long period and to limit the frequency of the chemical cleaning of this membrane.

Key words | anionic surfactant, chromium(III), nanofiltration membranes

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INTRODUCTION

Nanofiltration (NF) is a pressure driven process, which assures great process selectivity, as well as enables its great efficiency for the separation/concentration of ionic and micromolecular elements of solution (Koltuniewicz & Drioli 2008; Shahmansouri & Bellona 2015). Taking into account these advantages, the NF is successfully applied for the separation of metal ions from industrial wastewaters (Saikaew *et al.* 2010; Al-Rashdi *et al.* 2013; Liu *et al.* 2015). Several other studies (Gomes *et al.* 2010; Kiril Mert & Kes-tioglu 2014) as well as our previous works (Religa *et al.* 2011a; Religa *et al.* 2013) demonstrated very interesting possibilities of NF used for chromium(III) recovery from saline solution characterized by low pH. It was caused by ionoselective properties of NF membranes relying on the fact that univalent ions can to a large extent penetrate through the membrane, while multivalent ions stopped on them (Tanninen *et al.* 2006; Gomes *et al.* 2010). A decrease of permeate flux was observed with time during the nanofiltration of such solutions. It was caused by mineral deposit formation on the membrane surface (i.e. scaling), which

resulted in the change of the kind and the density of the surface charge of the membrane under the low pH (Ju & Hong 2014; Chidambaram *et al.* 2015). One of the ways of maintaining high membrane permeability is using an effective procedure for membranes cleaning. The most appropriate cleaning procedure from one side should enable removal of mineral deposit from the surface and/or porous of membranes letting the initial productivity for their reconstruction. On the other side, it should enable to restoration of primeval charge of membranes enabling selectivity reconstruction. For the effective regeneration of NF membranes the dual-step cleaning procedure is recommended (Al-Amoudi *et al.* 2007; Religa *et al.* 2013). However, repeated cleaning of polymer membranes with aggressive chemicals negatively influences their mechanical stability (Zhao *et al.* 2011; Religa *et al.* 2013). Introduction of the surface active substances into the membrane internal structure could be the other way of creating suitable membrane properties. Surfactants are the group of compounds with high surface activity. The surfactants belong to a broad group of

amphiphilic compounds which, in their asymmetric molecular structure, have both hydrophilic and hydrophobic groups (Kowalska *et al.* 2006). Some researchers have investigated the effect of surfactants as components of the membrane on its structure, morphology and performance (Rahimpour *et al.* 2007; Mansourpanah *et al.* 2011). From these studies, it was found that properties of such membranes are both the consequence of kind of surfactants (cationic, anionic, non-ionic) and concentration of surfactants in the membrane active layer. However, literature review revealed that there is no considerable research about the possibilities of using surfactant solutions for direct NF membrane surface layer modification.

In this study the possibility of modification of surface layer of NF membranes used for chromium(III) recovery from saline solutions at low pH by periodic membrane wetting into anionic surfactant solution was determined.

METHODS

Experimental setup

The experiments were carried out at laboratory scale in cross-flow cell (Figure 1). 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, at transmembrane pressure (TMP) = 14 bar and $Q_R = 800 \text{ dm}^3/\text{h}$. The temperature of

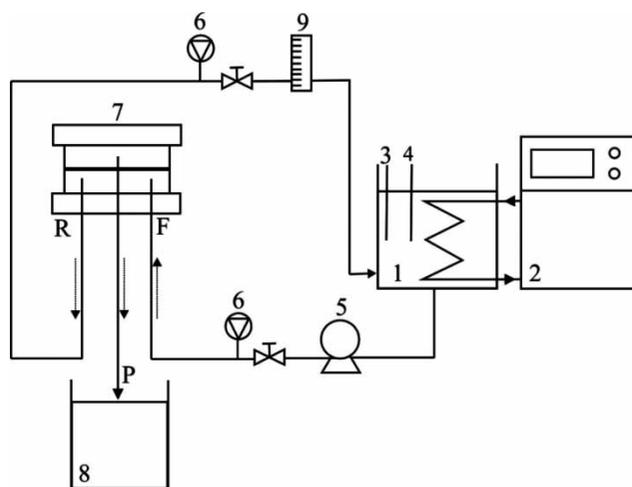


Figure 1 | Schema of the laboratory plant: 1 – feed/retentate tank, 2 – thermostat, 3 – measurement of temperature, 4 – measurement of pH, 5 – high pressure pump, 6 – manometer, 7 – NF membrane cross-flow cell, 8 – permeate tank, 9 – flowmeter, P – permeate, F – feed, and R – retentate.

feed solution during the process was constant and equal to $25 \pm 1 \text{ }^\circ\text{C}$. After the end of the experiments, samples of permeate and retentate have been collected for determination of the chromium(III) and chloride ion concentration.

Two kinds of NF flat sheet membranes (thin film DL and HL) provided by GE Osmonics were used in the experiments. Each of these membranes had an effective area of 0.0155 m^2 . The active layer of the tested NF membranes was made of the poly(piperazine-amide) (Religa *et al.* 2013), whereas the support was made of polysulfone. The HL membrane was characterized by much looser structure of the active layer than the DL membrane (Boussu *et al.* 2008). Membranes used in experiments were also characterized by different isoelectric point (IP) which was 3.0 and 3.3 for DL and HL membrane, respectively (Al-Amoudi *et al.* 2007; Religa *et al.* 2013).

Solutions and chemicals

The feed constituted model saline solution contained $2 \text{ gCr}^{3+}/\text{dm}^3$, $10 \text{ gCl}^-/\text{dm}^3$, $10 \text{ gSO}_4^{2-}/\text{dm}^3$ and characterized by $\text{pH} \approx 4$. The feed solution was prepared using the following chemicals: $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich), pure NaCl (Chempur[®]), pure Na_2SO_4 (Chempur[®]) and demineralized water. For initial pH correction the pure HCl (Lachner) was used. The pH was measured by pH-meter (Mettler Toledo SevenEasy). The composition of the model solution was characteristic for chromium industrial wastewater (Koltuniewicz & Drioli 2008; Gomes *et al.* 2010; Religa *et al.* 2011a).

The anionic surfactants baths – dodecyl sodium sulphate (SDS) solution with concentration $3.5 \cdot 10^{-3} \text{ mol}/\text{dm}^3$, for the period of modification of the tested membranes, was prepared. Membranes were soaked in surfactant bath for 15 minutes and then rinsed by demineralized water. The application of SDS solution with concentration below critical micelle concentration which was $8.1 \pm 0.1 \cdot 10^{-3} \text{ mol}/\text{dm}^3$ (Fuguet *et al.* 2005; Kowalska *et al.* 2006) opposed the formation of micelles and enabled the analysis of the influence of single molecule activity on surface properties of NF membranes (Pontié *et al.* 2008).

Measurement equipment

The chromium(III) ions have been analyzed by spectrophotometer NANOCOLOR UV/VIS using 1,5-difenylokarbazyde method with wave length $\lambda = 540 \text{ nm}$. The chloride ions have been analyzed using the Mohr titration method. Membrane

surface zeta potential was determined by streaming potential using an apparatus and procedure described in the literature (Childress & Elimelech 2000; Religa *et al.* 2013). The membrane surfaces were examined using atomic force microscopy (AFM) SollverBio Instruments NT-MDT. The membrane surfaces were analyzed in a scan size of $10\ \mu\text{m} \times 10\ \mu\text{m}$. The average surfaces roughness of tested membranes was calculated from AFM images using Nova SPM software.

RESULTS AND DISCUSSION

Membrane electrokinetic potential

The influence of SDS solution on the electrokinetic potential of NF membranes tested repeatedly for chromium(III) recovery from saline solutions at low pH was determined. Figure 2 shows the changes of membrane surface charge as confirmed by the obtained results of the zeta potential of new no-modified membranes, and modified membranes

after working at 6 and 20 hours in saline solution. It was found that the conditions in saline solutions, in spite of the modified of membrane by SDS, alters the trend depending on the zeta potential of the pH and the change of the isoelectric point of the tested membrane surfaces. These changes were specific and different for the tested types of membranes. In the case of the DL membrane (Figure 2(a)) it was found that a significant change in its zeta potential, characterized by its own predominant negative active group, occurred after 6 hours in saline solutions. However, the value of zeta potential remained negative for the process conditions at $\text{pH} \approx 4$. Also, the zeta potential observed for the membrane after 20 hours in saline solution was still negative (Figure 2(a)). For the established membrane properties constant operating conditions were observed. The results are shown in Table 1. The DL membrane was characterized by a stable and, at the same time, a high degree of chromium(III) retention. Due to the low chloride retention counteracting the concentration polarization of membrane either the stable permeate flux was observed.

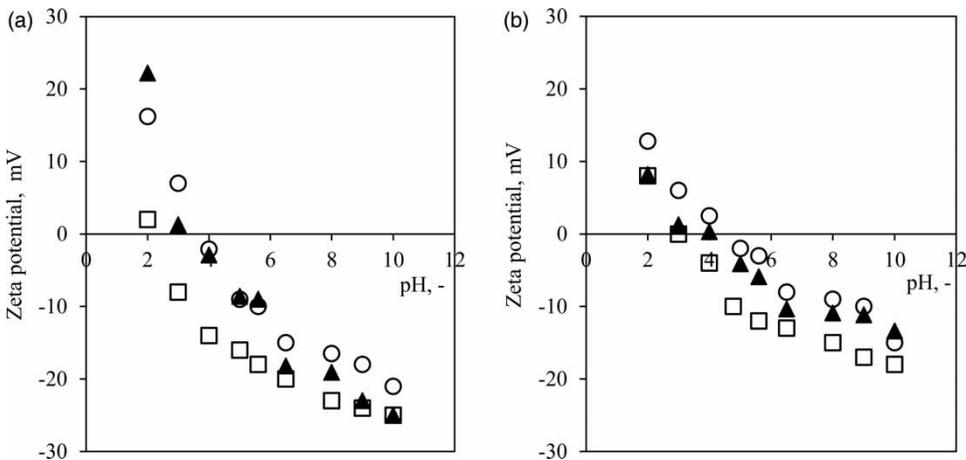


Figure 2 | Zeta potential of new and 'worked' DL (a) and HL (b) membranes at various pH (□ – new-no modified membrane, ▲ – modified membrane after working at 6 hours in saline solution, ○ – modified membrane after working at 20 hours in saline solution).

Table 1 | Performance of the new-no modified membranes and the membranes modified by SDS and frequently used for nanofiltration of saline solution at low pH

	DL membrane			HL membrane		
	J_p $10^6\ \text{m}^3/(\text{m}^2\text{s})$	Retention Cr(III), %	Retention Cl^- , %	J_p $10^6\ \text{m}^3/(\text{m}^2\text{s})$	Retention Cr(III), %	Retention Cl^- , %
New-no modified	28	96	8	21	97	26
Modified after 6 h	28	96	8	21	95	23
Modified after 15 h	28	96	8	20	90	19
Modified after 18 h	26	96	6	20	88	17
Modified after 20 h	26	96	6	20	87	17

In the case of the HL membrane (Figure 2(b)), after 6 hours in saline solution at $\text{pH} \approx 4$, the change of zeta potential from negative to positive for process conditions was observed. It is also characteristic that the membrane zeta potential was changed during the working time, taking more and more positive values (Figure 2(b)).

The tested NF membranes had an active layer made of the poly (piperazine-amide) (Religa *et al.* 2013). A characteristic feature of such type of polymer is the presence of two functional groups – the carboxyl and amino – that are activated under the influence of solution pH (Pontié *et al.* 2008; Jahanshahi *et al.* 2010). During the wetting of tested HL membrane in a SDS solution at $\text{pH} = 8$ some surfactant molecules were adsorbed on the membrane surface. Adsorption of anionic surfactant molecules on weakly negatively charged membrane surface was reported by other research groups (Childress & Elimelech 2000). Under the process conditions, both the low pH and presence of salt in the solution contributed to the reduction in the critical micelle concentration of surfactant (Umlong & Ismail 2007; Sammalkorpi *et al.* 2009). Consequently, the partial SDS particles desorption occurred from the membrane surface. Simultaneously, at low pH, membrane amino groups become more active which caused the membrane surfaces to become more positively charged. According to results of our previous works (Religa *et al.* 2013b; Religa *et al.* 2013), positively charged surface contributes to the formation of the ionic adsorption layer on the membrane surface, which is accompanied by an increase of membrane concentration polarization. At the same time, the interaction between hydrophilic, negative charged part of SDS and positively charged membrane surface get very active (Childress & Elimelech 2000). Probably hemimicelles structure are locally formed on the membrane surface. Hemimicelles result from the surfactant ions associated with each other

to remove their hydrocarbon chains from the bulk water and, hence, to reduce the free energy of the system. Appearance of hemimicells changed the electrokinetic balance especially as a result of the interaction between the positive ions and the negative micellar structures. Excess of negative charge in the feed caused the increase in the potential difference on both sides of the membrane and thus forced the negative chloride ions permeation. The obtained results as summarized in Table 1 confirmed the significant decrease of chloride ion retention in the case of HL membrane modified by the solution prepared on the basis of the anionic surfactant. The negative phenomenon that accompanied the changes described above was a decrease of chromium(III) retention. The possible cause of this phenomenon is an increase of ions flux of the particular charge. In the present case, the negative chloride ions, facilitates the penetration of opposite charge ions to the internal structure of the membrane (Mansourpanah *et al.* 2011). Thus, a loss of membranes selectivity was observed in the case of positive chromium(III) ions. Additionally, the interaction polymer-surfactant caused looseness of the membrane structure and favored the penetration of multivalent ions (Mansourpanah *et al.* 2011) in the tested case, i.e. the chromium(III) ions.

Membrane permeability

The topographical images of the membranes were made by using AFM (Figures 3 and 4) and an average roughness of membrane surface was measured. The comparison between the new HL membrane and membrane modified by the SDS solution after 20 hours working in saline solutions, showed changes in an average roughness value (Figure 3). The obtained results showed increase of the average membrane surface roughness from 24.0 nm (indicated for the new membrane) to 39.0 nm for the membrane after 20 hours of

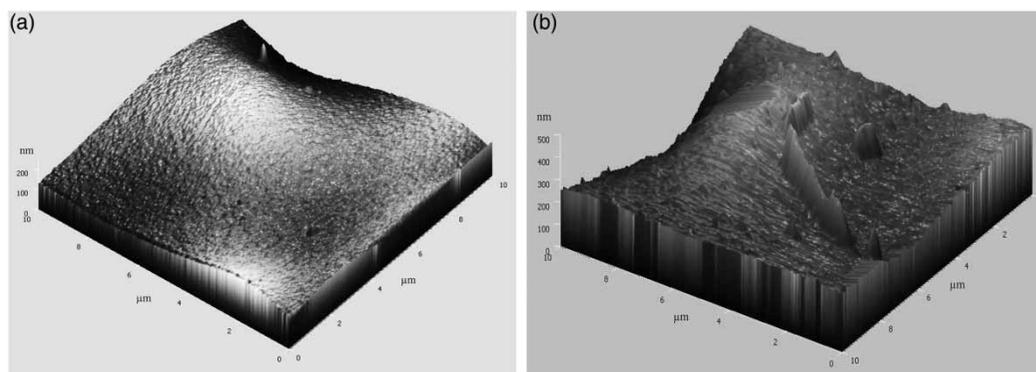


Figure 3 | AFM images of HL membrane surfaces: new-no modified (a) and modified after working at 20 hours in saline solution (b).

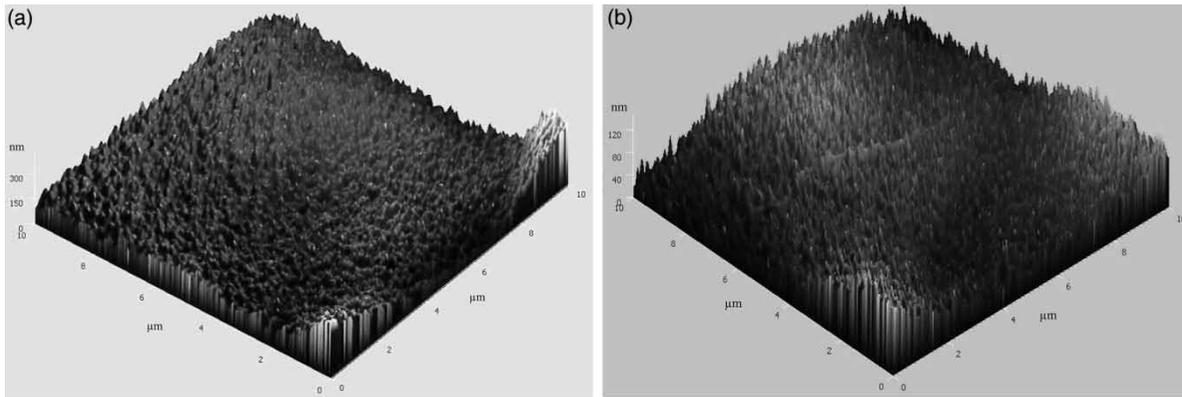


Figure 4 | AFM images of DL membrane surfaces: new-no modified (a) and modified after working at 20 hours in saline solution (b).

use. Similar results concerning the changes in the average roughness values obtained after addition of anionic surfactant to the polymer membrane were noted in other investigations (Rahimpour *et al.* 2007; Mansourpanah *et al.* 2011). The AFM images indicated significant differences in the observed changes of the heights and in the heights adjacent surfaces (Figure 3). Thus, in this situation, the average roughness determined for HL membranes is regarded as the theoretical values, particularly during long periods of membrane use.

In the case of the DL membrane surface (Figure 4), the analysis of AFM images showed that the characteristic change for the HL membrane, in this case, are intermittent. DL membrane was characterized by an uneven but

uniform structure over the entire surface. In the case of a DL membrane, changes of the average roughness from 27.2 nm (indicated for the new membrane) to 37.8 nm for the membrane after 20 hours immersion in saline solution and modified by the SDS solution were observed. Such a structure was also observed in the case of a DL membrane cleaning by the caustic and mineral acid baths (Religa *et al.* 2013). Therefore, in the case of DL membrane modified by the SDS solution, the average roughness changes were probably associated with incomplete stripping of the mineral deposits formed on the membrane surface.

The observed changes in the surface of new and repeatedly used DL and HL membranes during nanofiltration of

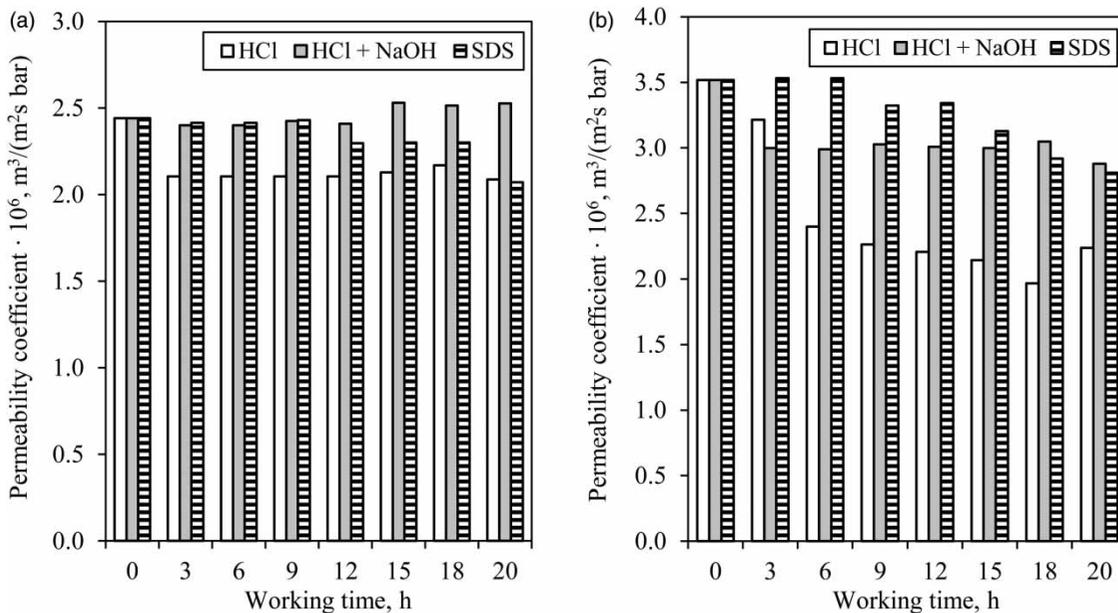


Figure 5 | Correlation between the permeability coefficient of DL (a) and HL (b) membranes after cleaning with HCl, HCl and NaOH or modified by SDS vs. working time in saline solution at low pH.

saline solutions and modified by the SDS solution was accompanied by a reduction of demineralized water permeability coefficients determined by the ratio $J_P = f(\Delta P)$ of the tested membranes (Figure 5).

The HL membrane operating during 20 hours in saline solution and modified by SDS solution was characterized by a permeability coefficient remaining at a level comparable to the dual-step bathing procedure and was significantly higher than the permeability coefficient of the tested membrane repeatedly used and cleaned only with HCl (Figure 5(b)). However, the nature of these changes was significantly different. In the initial period of use (about 10 hours) the permeability coefficient remained unchanged. This indicated that the surfactant adsorbed layer on membrane surface successfully prevent its scaling. But, conversely, the surfactant molecules adsorbed on the membrane surface as a result of interaction with the membrane material caused relaxation of its structure (Childress & Elimelech 2000; Mansourpanah *et al.* 2011). Unfortunately, a further use of the membrane and modified in a bath prepared with SDS caused a decrease in the permeability coefficient. Probably, relaxation of the loose HL membrane structure facilitated the penetration of the ions present in the solution into the membrane structure. As a result of interaction of ions with the charge of the membrane, their adsorption occurred in the membrane structure, and thus led to scaling into the internal structure. As a consequence, this irreversible process of internal membrane pore blocking caused a significant and rapid loss of HL membrane permeability coefficient (Figure 5(b)).

Whereas in the case of the DL membrane, the changes of its permeability coefficient and nature were the same as in the case of these type of membranes repeatedly used and cleaned with HCl (Figure 5(a)). It suggests that the interaction between surfactant and membrane surface prevent quite well the scaling of DL membrane. On the other hand, despite these interactions, the dense DL membrane structure successfully prevents the multivalent ion penetration into this and irreversible membrane blocking.

CONCLUSIONS

The effect of the anionic surfactant solution periodically used for NF membrane rinsing on its permeation properties during recovery of chromium(III) from saline solution at low pH was determined. Specific interactions between the tested membranes and the anionic surfactant were found.

The comparison of the effect selected cleaning baths and membrane modification by SDS solution on the separation ability of DL and HL membrane separation was done. Results obtained for the new membrane and membrane used for nanofiltration of saline solutions at low pH and cleaning with HCl, HCl and NaOH or modified by SDS solution enabled the assumption that membrane modification with a solution of SDS is preferred in the case of a DL membrane. DL membrane modification by SDS allowed both retention of the stable membrane working for a long period, and to limit frequency of the chemical cleaning of this membrane. However, in the case of the HL membrane using SDS solution for its modification leads to destabilization of operating membrane working. This phenomenon is a consequence of the additional membrane loose structure under the influence of membrane-surfactants interaction. Such interactions facilitate multivalent anions penetration into the internal HL membrane structure and its irreversible scaling. As a consequence the decrease of process efficiency was observed.

REFERENCES

- Al-Amoudi, A., Williams, P., Mandale, S. & Lovitt, R. W. 2007 Cleaning results of new and fouled nanofiltration membrane characterized by zeta potential and permeability. *Separation and Purification Technology* **54**, 234–240.
- Al-Rashdi, B. A. M., Johnson, D. J. & Hilal, N. 2013 Removal of heavy metal ions by nanofiltration. *Desalination* **315**, 2–17.
- Boussu, K., Vandecasteele, C. & Van Der Bruggen, B. 2008 Relation between membrane characteristics and performance in nanofiltration. *Journal of Membrane Science* **310**, 51–65.
- Chidambaram, T., Oren, Y. & Noel, M. 2015 Fouling of nanofiltration membranes by dyes during brine recovery from textile dye bath wastewater. *Chemical Engineering Journal* **262**, 156–168.
- Childress, A. E. & Elimelech, M. 2000 Relating nanofiltration membrane performance to membrane charge (electrokinetic) characteristic. *Environmental Science & Technology* **34**, 3710–3716.
- Fuguet, E., Ràfols, C., Rosés, M. & Bosch, E. 2005 Critical micelle concentration of surfactants in aqueous buffered and unbuffered systems. *Analytica Chimica Acta* **548**, 95–100.
- Gomes, S., Cavaco, S. A., Quina, M. J. & Gando-Ferreira, L. M. 2010 Nanofiltration process for separating Cr(III) from acid solutions: Experimental and modelling analysis. *Desalination* **254**, 80–89.
- Jahanshahi, M., Rahimpour, A. & Peyravi, M. 2010 Developing thin film composite poly(piperazine-amide) and poly(vinyl-alcohol) nanofiltration membranes. *Desalination* **257**, 129–136.
- Ju, Y. & Hong, S. 2014 Nano-colloidal fouling mechanisms in seawater reverse osmosis process evaluated by cake

- resistance simulator-modified fouling index nanofiltration. *Desalination* **343**, 88–96.
- Kiril Mert, B. & Kestioglu, K. 2014 Application of nanofiltration and reverse osmosis for tanning wastewater. *International Journal of Environmental Research* **8**, 789–798.
- Koltuniewicz, A. B. & Drioli, E. 2008 *Membrane in clean technology. Theory and practice*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.
- Kowalska, I., Majewska-Nowak, K. & Kabsch-Korbutowicz, M. 2006 Influence of temperature on anionic surface active agent removal from a water solution by ultrafiltration. *Desalination* **198**, 124–131.
- Liu, T. Y., Bian, L. X., Yuan, H. G., Pang, B., Lin, Y. K., Tong, Y., Van Der Bruggen, B. & Wang, X. L. 2015 Fabrication of a high-flux thin film composite hollow fiber nanofiltration membrane for wastewater treatment. *Journal of Membrane Science* **478**, 25–36.
- Mansourpanah, Y., Alizadeh, K., Madaeni, S. S., Rahimpour, A. & Soltani Afarani, H. 2011 Using different surfactants for changing the properties of poly(piperazineamide) TFC nanofiltration membranes. *Desalination* **271**, 169–177.
- Pontié, M., Dach, H., Leparç, J., Hafsi, M. & Lhassani, A. 2008 Novel approach combining physico-chemical characterizations and mass transfer modelling of nanofiltration and low pressure reverse osmosis membranes for brackish water desalination intensification. *Desalination* **221**, 174–191.
- Rahimpour, A., Madaeni, S. S. & Mansourpanah, Y. 2007 The effect of anionic, non-ionic and cationic surfactants on morphology and performance of polyethersulfone ultrafiltration membranes for milk concentration. *Journal of Membrane Science* **296**, 110–121.
- Religa, P., Kowalik, A. & Gierycz, P. 2011a Application of nanofiltration for chromium concentration in the tannery wastewater. *Journal of Hazardous Materials* **186**, 288–292.
- 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.
- Religa, P., Kowalik-Klimczak, A. & Gierycz, P. 2013 Study on the behavior of nanofiltration membranes using for chromium (III) recovery from salt mixture solution. *Desalination* **315**, 115–123.
- Saikaew, W., Mattaraj, S. & Jiraratananon, R. 2010 Nanofiltration performance of lead solutions: effects of solution pH and ionic strength. *Water Science and Technology: Water Supply* **10**, 193–200.
- Sammalkorpi, M., Karttunen, M. & Haataja, M. 2009 Ionic surfactant aggregates in saline solutions: sodium dodecyl sulfate (SDS) in the present of excess sodium chloride or calcium chloride. *The Journal of Physical Chemistry B* **113**, 5863–5870.
- Shahmansouri, A. & Bellona, C. 2015 Nanofiltration technology in water treatment and reuse: applications and costs. *Water Science and Technology* **71**, 309–319.
- Tanninen, J., Mänttari, M. & Nyström, M. 2006 Effect of salt mixture concentration on fractionation with NF membranes. *Journal of Membrane Science* **283**, 57–64.
- Umlong, I. M. & Ismail, K. 2007 Micellization behaviour of sodium dodecyl sulfate in different electrolyte media. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **299**, 8–14.
- Zhao, C., Nie, S., Tang, M. & Sun, S. 2011 Polymeric pH-sensitive membranes – A review. *Progress in Polymer Science* **36**, 1499–1520.

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