



The effects of scale inhibitor ATMP in water on nanofiltration

Xue Han^a, Xian-Qiu Zhang^{a,b,c,*}, Shun-Qing Yang^a, Ming-Xia Du^a

^a*School of Environment, Nanjing Normal University, Nanjing 210023, China, Tel. 13912910492, email: 1074703532@qq.com (X. Han), zhangxianqiu@njnu.edu.cn (X.-Q. Zhang), 724312131@qq.com (S.-Q. Yang), dumingxia_1011@sina.com (M.-X. Du)*

^b*Jiangsu Center for Collaborative Innovation in Geographical Information Resource Development and Application, Nanjing 210023, China*

^c*Jiangsu Key Laboratory of Material Circulation and Pollution Control, Nanjing 210023, China*

Received 30 May 2018; Accepted 5 May 2019

ABSTRACT

As a kind of advanced water purification technology, nanofiltration (NF) has been widely used in the treatment of water. In the NF process, scale inhibitor such as aminotris (methylenephosphonic acid) (ATMP, H₆atmp, H₆L) is commonly added to control scale deposition. However, the impact of ATMP on the separation performance of NF has up to now been unknown. In this study, the impact of ATMP on calcium ion (Ca²⁺) rejection rate and permeate flux of NF 270 membrane were investigated by permeate experiments with different ATMP concentrations. The results showed that ATMP had a significant impact on Ca²⁺ rejection rate, as well as the feed pH. Both a local minimum in rejection rate and a slight maximum in permeate flux appeared at 10 mg·L⁻¹ ATMP, corresponding to the feed pH about 5.5, which may be close to the isoelectric point (IEP) of membrane. When ATMP concentration was below 8 mg·L⁻¹ and above 10 mg·L⁻¹, increasing ATMP concentration would both dramatically enhance Ca²⁺ rejection rate. The main mechanism affecting the performance of NF was electrostatic effect caused by ATMP rather than its chelation effect. Our work demonstrated that in addition to the scale inhibition effect, ATMP in water also had a certain impact on the performance of NF membrane, especially for treating low alkalinity water (contain hardness and SO₄²⁻), and aminotris (methylene phosphonic acid) (ATMP, H₆atmp, H₆L) is preferred to avoid precipitation and improve NF softening and desalination performance.

Keywords: Nanofiltration; Calcium ion; Rejection rate; Permeate flux; pH; Aminotris (methylene-phosphonic acid)

1. Introduction

NF membranes have properties in between those of ultrafiltration (UF) membranes and reverse osmosis (RO) membranes [1]: ① It has a molecular weight cut-off ranging from 200–1000 Da [2]; ② The operation pressure is low and usually less than 1.0 MPa, which is more energy-efficient than RO [3,4]; ③ It offers better rejection performance than UF for treating water containing small molecule substances or ions [5]. In short, NF has significant advantages, making it very promising in the treatment of water including

brackish groundwater softening, removal of heavy metal ions and pretreatment of seawater desalination, etc [6–8].

Separation by NF membranes occurs primarily due to size exclusion and electrostatic interactions. For uncharged molecules, sieving or size exclusion is the main reason for separation; for ionic substances, sieving and electrostatic interaction are the causes of separation. For all applications, membrane surface and pore charge characteristics play an important role in the transport of water and solute molecules through the membrane [9]. For polyamide membranes such as NF 70, 90, 200 and 270 membranes, which possess dissociable carboxylic and amine groups [4,5]. The feed pH can change the properties of these membranes surface charge and pore size, as well as that of solution chemistry

*Corresponding author.

and therefore can affect the membrane separation efficiency [10–13].

In the process of NF, scaling is a very common problem. A widely used technique for controlling scale deposition is an application of chemical inhibitors [14,15]. As an effective scale inhibitor, ATMP is widely used in the NF process [16]. However, the impact of ATMP on the separation performance of NF membranes was still not well investigated.

This paper describes an investigation on the impact of different ATMP concentrations on Ca^{2+} rejection rate and permeate flux by permeate experiments, and the chelation effect and electrostatic effect by ATMP were also discussed. Hopefully the experiment results would be useful for practical engineering application of NF.

2. Materials and methods

2.1. Chemicals and materials

2.1.1. Chemicals

All chemicals used were of analytical grade except for ATMP. ATMP (molecular weight 299 Da) is an industrial product with a content of 50% (Aladdin Industrial, China). Calcium chloride (CaCl_2) and ATMP were used for the preparation of the feed water. The pH was adjusted by 10% sodium hydroxide (NaOH) or 10% hydrochloric acid (HCl). The chemicals used to measure Ca^{2+} concentration were: Calcium carbonate (CaCO_3); 1% methyl red reagent; 10% ammonia solution; ethylene diaminetetra (acetic acid) disodium salt, $\text{Na}_2\text{H}_2\text{edta}\cdot 2\text{H}_2\text{O}$ ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8\cdot\text{Na}_2\cdot 2\text{H}_2\text{O}$); Ammonia-ammonium chloride buffer solution (pH = 10.0) and Chrome black T. The deionized water used in this study was prepared by RO.

2.1.2. NF membrane

The NF membrane used in this study was labeled NF 270 membrane, manufactured by Dow Company (USA). It

is a semi-aromatic polyamide membrane with pore radius about 0.4 nm [17,18], and it is a “loose” NF membrane characterized with low sodium chloride (NaCl) rejection rate and high pure water permeability [19].

2.2. Membrane set-up and filtration test

2.2.1. Membrane set-up

The experimental set-up is schematically described in Fig. 1. Basically, it has seven parts: feed tank, permeate tank, retentate tank, pump, membrane test cell, pressure gauge and pressure regulating valve. Membrane test cell was made by Nitto Denko (Japan), with a size of 21 cm × 8.5 cm × 6.5 cm and the effective area of 81.6 cm².

2.2.2. Filtration test

ATMP was added to the 3 mmol·L⁻¹ CaCl_2 solution to achieve the ATMP concentration of 0, 4, 8, 10, 12, 16 and 20 mg·L⁻¹, respectively. After that, the solution was stirred for 30 min, and then was let to equilibrate for 24 h before experiment starts. Before each filtration test, 2 L CaCl_2 and ATMP solution was added into the feed tank. Also, a new membrane coupon (81.6 cm²) was loaded into the cell. Initially, both permeate and retentate circulated back to the feed tank for 10 min to maintain the feed concentration constant, and then, permeate and retentate were collected separately for 10 min. For all filtration tests, the operating pressure and the feed temperature were controlled at 0.55 MPa and about 20°C, respectively.

Ca^{2+} concentration was determined by EDTA titration and permeate volume was measured by a cylinder. The pH was monitored by a pH meter (PHS-3C, INESA Scientific Instrument CO., Ltd, China) and temperature was observed by a thermometer. The rejection rate of Ca^{2+} was calculated according to Eq. (1):

$$\text{Rejection rate}(\%) = (1 - C_p / C_f) \times 100 \quad (1)$$

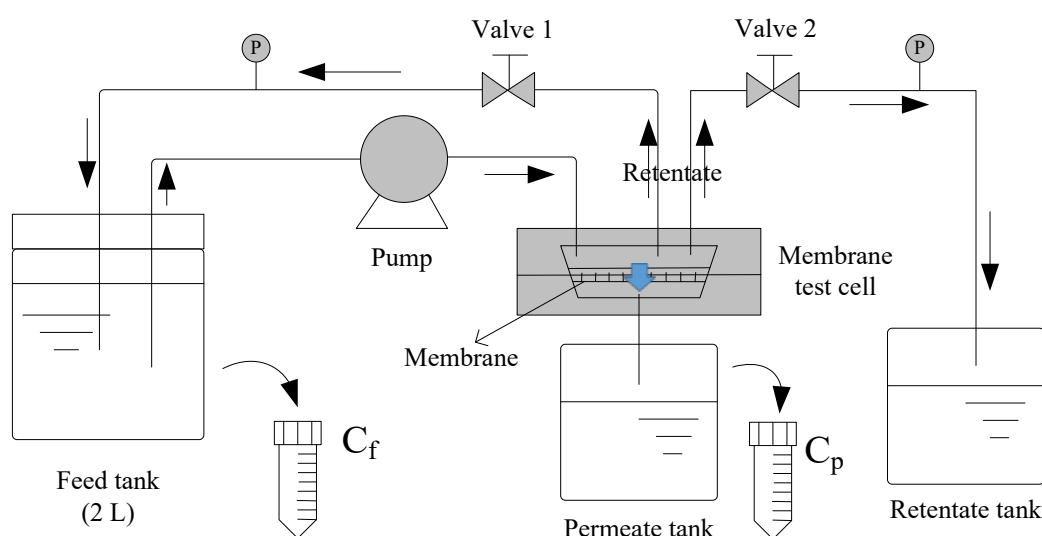


Fig. 1. Membrane testing set-up.

where C_p is the concentration of Ca^{2+} in permeate ($\text{mg}\cdot\text{L}^{-1}$); C_f is the concentration of Ca^{2+} in feed ($\text{mg}\cdot\text{L}^{-1}$).

Permeate flux was calculated according to Eq. (2):

$$J = \frac{V_t}{A \times t} \quad (2)$$

where J is the permeate flux ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$); V_t is a permeate volume change within 10 min (L); A is membrane area (m^2); t is filtration time (h).

3. Results and discussion

3.1. Impact of ATMP concentration on membrane performance

Fig. 2a demonstrates that ATMP concentration had a significant impact on Ca^{2+} rejection rate. On the whole, the rejection rate increased obviously with ATMP concentration increasing. However, a very interesting phenomenon is that, a local minimum in rejection rate (Fig. 2a) and a slight maximum in permeate flux (Fig. 2b) appeared at $10 \text{ mg}\cdot\text{L}^{-1}$ ATMP. When ATMP concentration was below $8 \text{ mg}\cdot\text{L}^{-1}$ and above $10 \text{ mg}\cdot\text{L}^{-1}$, increasing ATMP concentration would both dramatically enhance Ca^{2+} rejection rate (Fig. 2a).

It is known that ATMP molecule contains three active phosphate groups ($-\text{PO}_3\text{H}^-$) offering three potential reacting sites with Ca^{2+} [20], which could have an impact on the membrane performance. Moreover, ATMP is a hexavalent acid, which could cause the feed pH to drop. From Fig. 2, we can see that the feed pH dropped from 6.83 to 4.12 with the ATMP concentration increasing from 0 to $20 \text{ mg}\cdot\text{L}^{-1}$. The feed pH was about 5.5 at $10 \text{ mg}\cdot\text{L}^{-1}$ ATMP, which may be close to the isoelectric point (IEP) of membrane. This is in a good agreement with Mänttari et al., who reported that this membrane has an IEP between pH 5.0 and pH 6.0 by measuring the zeta-potential of NF 270 membrane [21]. However, Lin et al. [22] showed that the IEP of NF 270 membrane is near pH 4.0. The difference may be caused by different solution systems [23] and measurement errors [21]. It is clear that changes in feed pH can cause changes in electrostatic effects. Accordingly, two mechanisms caused by ATMP are plausible: chelation effect (Section 3.2) and electrostatic effect (Section 3.3).

3.2. Chelation effect by ATMP

In order to further investigate the chelation effect on Ca^{2+} rejection rate, a series of experiments were carried out with the feed pH 5.5 (close to the IEP of membrane), as shown in Fig. 3. The results showed that Ca^{2+} rejection rate increased slowly and permeate flux was almost unchanged with ATMP concentration increasing. ATMP is known to form compounds with Ca^{2+} such as CaH_3L^- , $\text{CaH}_2\text{L}^{2-}$ and CaHL^{3-} (L represents ATMP) [24,25]. At higher pH (about pH 9) and in the presence of a large excess of calcium, ATMP could form two insoluble salts: $\text{Ca}_3(\text{atmp})_3\text{H}_2\text{O}$ and $\text{Ca}_5(\text{atmp})_2\text{H}_2\text{O}$ [26,27]. However, insoluble salts should not be formed in this experimental system (pH = 5.5, $[\text{Ca}^{2+}] = 3 \text{ mmol}\cdot\text{L}^{-1}$ and $[\text{ATMP}] = 0\text{--}20 \text{ mg}\cdot\text{L}^{-1}$) according to [27]. It is obvious that the molecular size of chelates (Ca-ATMP complexes) is much larger than that of free calcium ions, which could lead to an increase in the space steric hindrance [28–30] and finally result in an increase in the rejection rate [31,32]. However, our experimental results demonstrated that the chelation effect by ATMP was small. According to chemical equilibrium, ATMP and calcium ions mainly form

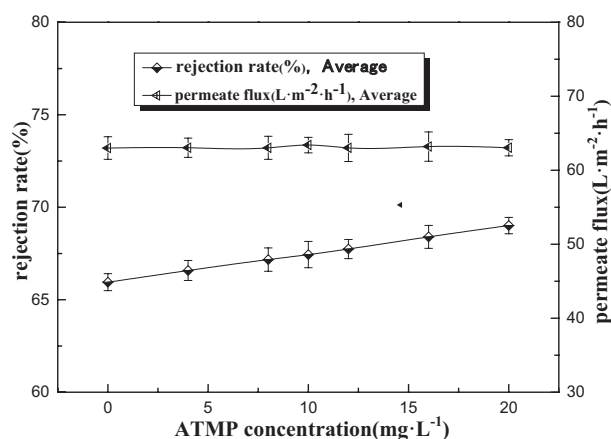


Fig. 3. Chelation effect on Ca^{2+} rejection rate and permeate flux at the feed pH 5.5.

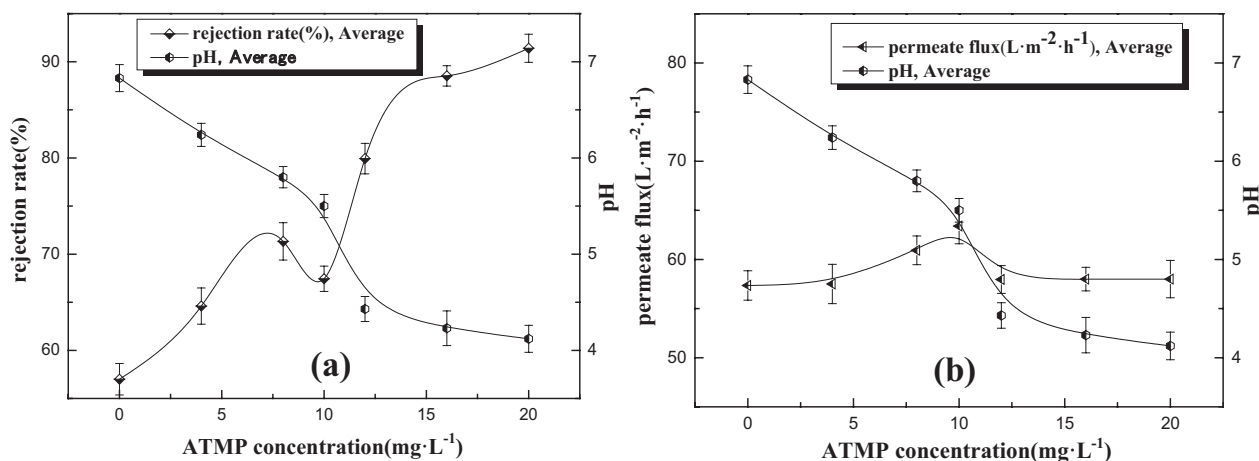


Fig. 2. Impact of ATMP concentration on membrane performance and feed pH.

complexes of a mole ratio of 1:1, so $20 \text{ mg}\cdot\text{L}^{-1}$ ATMP ($0.07 \text{ mmol}\cdot\text{L}^{-1}$) could only combine $0.07 \text{ mmol}\cdot\text{L}^{-1}$ Ca^{2+} from totally $3 \text{ mmol}\cdot\text{L}^{-1}$ present in the solution (c.a. 2.33%) [27], which is in a good agreement with our experimental results.

3.3. Electrostatic effect caused by ATMP

In order to investigate the electrostatic effect on Ca^{2+} rejection rate, comparative experiments were carried out with $4 \text{ mg}\cdot\text{L}^{-1}$ ATMP (a) and without ATMP (b) (blank) at the same conditions, bearing different pH ranging from 3 to 10 and the results are illustrated in Fig. 4a and Fig. 4b, respectively.

It can be seen from Fig. 4a that Ca^{2+} rejection was the lowest and permeate flux was the highest at around pH 5.5 (close to the IEP). The similar appearance has been reported by Childress and Elimelech [9] and Qin et al. [33]. When the pH dropped from the IEP to lower values, the amine functional groups on membrane surface could protonate ($\text{H}^+ + \text{solid} - \text{C}(\text{O}) - \text{NH}^- \leftrightarrow \text{solid} - (\text{C}(\text{O}) - \text{NH}_2^+)$) and resulted in more positive charge, which has been demonstrated by measuring zeta-potential [21]. In this case, electrostatic repulsion was generated between Ca^{2+} and membrane surface charge, which led to high rejection rate. When the pH shifted from the IEP to higher values, the carboxyl groups on membrane surface could deprotonate ($\text{solid} - \text{COOH} \rightarrow \text{solid} - \text{COO}^-$) and resulted in more negative charge, which caused the electrostatic attraction generate between Ca^{2+} and membrane surface charge. In the latter case, Ca^{2+} rejection rate declined slowly with the rise of feed pH, as shown in Fig. 4b, which was agree with Chen [34]. It should be noted that the solubility ($Q_c = 3 \times 10^{-11}$) of Ca^{2+} and OH^- in this experiment was smaller than the solubility product constant ($K_{sp} = 4.7 \times 10^{-6}$). Therefore, no insoluble solid $\text{Ca}(\text{OH})_2$ formed in this experiment.

However, when ATMP was added, Ca^{2+} rejection rate increased slightly and the permeate flux declined slightly with the rise of feed pH, as shown in Fig. 4a. This results may be attributed to two mechanisms: 1) ATMP and Ca^{2+} could form insoluble solids ($\text{Ca}_3\text{L}_{\text{solid}}$) in the presence of a large excess of calcium. At pH above 9.0, almost all ATMP molecules exist in the system as insoluble solid form [27]. Therefore, the insoluble solids were capable to accumulate

on the membrane surface; 2) Bridging effect of free Ca^{2+} [35], which associates the CaH_3L^- , $\text{CaH}_2\text{L}^{2-}$ and CaHL^{3-} (L represents ATMP) with a small number of $\equiv\text{COO}^-$ groups on the clean membrane surface, and this could lead to the pore size of the membrane reduced. Both of the above situations caused an increase in rejection and a decrease in permeate flux. But ATMP could still achieve the goal of scale inhibition by getting adsorbed onto the nuclei and thus blocking the active growth sites, or by effectively reducing the number of the nuclei [36].

It can be seen that when using ATMP as a NF scale inhibitor, attention should be paid to pH control, especially for water with low alkalinity (contain hardness and SO_4^{2-}), and acid type ATMP (H_6L) is preferred to avoid precipitation and improve NF softening and desalination performance.

4. Conclusion

In this study, permeate experiments were conducted with different ATMP concentrations in the $3 \text{ mmol}\cdot\text{L}^{-1}$ CaCl_2 solution to study the impact of ATMP on the separation performance of NF. The results showed that ATMP had a significant impact on Ca^{2+} rejection rate, as well as the feed pH. A local minimum in rejection rate and a slight maximum in permeate flux appeared at $10 \text{ mg}\cdot\text{L}^{-1}$ ATMP, corresponding to the feed pH about 5.5, which may be close to the isoelectric point (IEP) of membrane. When ATMP concentration was below $8 \text{ mg}\cdot\text{L}^{-1}$ and above $10 \text{ mg}\cdot\text{L}^{-1}$, increasing ATMP concentration would both dramatically enhance the Ca^{2+} rejection rate. The main mechanism affecting the performance of NF was electrostatic effect caused by ATMP rather than its chelation effect. These results indicate that ATMP in water could have a certain influence on NF separation performance, especially for treating low alkalinity water, and acid type ATMP (H_6L) is preferred to avoid precipitation and improve NF softening and desalination performance.

Acknowledgments

This work was financially supported by Jiangsu province "six top talent program" (184080H102207), Research

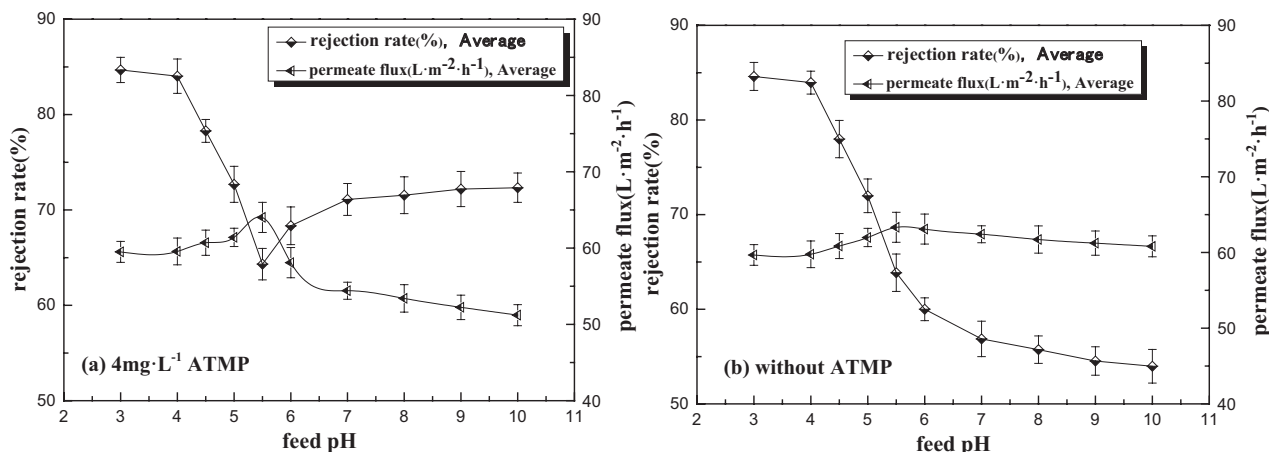


Fig. 4. Electrostatic effect on Ca^{2+} rejection rate and permeate flux with $4 \text{ mg}\cdot\text{L}^{-1}$ ATMP (a) and without ATMP (b).

Fund of Nanjing Normal University (2011105XGQ0084) and the National Water Pollution Control and Treatment Science and Technology Major Project (2017ZX07203-003).

References

- [1] A.W. Mohammad, M.S. Takriff, Predicting flux and rejection of multicomponent salts mixture in nanofiltration membranes, *Desalination*, 157 (2003) 105–111.
- [2] N.S. Kotrappanavar, A.A. Hussain, M.E.E. Abashar, I.S. Al-Mutaz, T.M. Aminabhavi, M.N. Nadagouda, Prediction of physical properties of nanofiltration membranes for neutral and charged solutes, *Desalination*, 280 (2011) 174–182.
- [3] T. Uruse, J. Oh, K. Yamamoto, Effect of pH on rejection of different species of arsenic by nanofiltration, *Desalination*, 117 (1998) 11–18.
- [4] K.P.M. Licona, L.R. de O. Geaquinto, J.V. Nicolini, N.G. Figueiredo, S.C. Chiapetta, A.C. Habert, L. Yokoyama, Assessing potential of nanofiltration and reverse osmosis for removal of toxic pharmaceuticals from water, *J. Water Process Eng.*, 25 (2018) 195–204.
- [5] C. Zeng, S. Tanaka, Y. Suzuki, S. Fujii, Impact of feed water pH and membrane material on nanofiltration of perfluorohexanoic acid in aqueous solution, *Chemosphere*, 183 (2017) 599–604.
- [6] Y. Song, T. Li, J. Zhou, Z. Li, C. Gao, Analysis of nanofiltration membrane performance during softening process of simulated brackish groundwater, *Desalination*, 399 (2016) 159–164.
- [7] B.A.M. Al-Rashdi, D.J. Johnson, N. Hilal, Removal of heavy metal ions by nanofiltration, *Desalination*, 315 (2013) 2–17.
- [8] D. Zhou, L. Zhu, Y. Fu, M. Zhu, L. Xue, Development of lower cost seawater desalination processes using nanofiltration technologies - A review, *Desalination*, 376 (2015) 109–116.
- [9] A.E. Childress, M. Elimelech, Relating nanofiltration membrane performance to membrane charge (electrokinetic) characteristics, *Environ. Sci. Technol.*, 34 (2000) 3710–3716.
- [10] Z. Wang, K. Xiao, X. Wang, Role of coexistence of negative and positive membrane surface charges in electrostatic effect for salt rejection by nanofiltration, *Desalination*, 444 (2018) 75–83.
- [11] Z. Wang, G. Liu, Z. Fan, X. Yang, J. Wang, S. Wang, Experimental study on treatment of electroplating wastewater by nanofiltration, *J. Membr. Sci.*, 305 (2007) 185–195.
- [12] L.B. Chaudhari, Z.V.P. Murthy, Treatment of landfill leachates by nanofiltration, *J. Environ. Manage.*, 91 (2010) 1209–1217.
- [13] G.T. Ballet, L. Gzara, A. Hafiane, M. Dhahbi, Transport coefficients and cadmium salt rejection in nanofiltration membrane, *Desalination*, 167 (2004) 369–376.
- [14] K.I. Popov, N.E. Kovaleva, G. Ya. Rudakova, S.P. Kombarova, V.E. Larchenko, Recent state-of-the-art of biodegradable scale inhibitors for cooling-water treatment applications, *Therm. Eng.*, 63 (2016) 122–129.
- [15] X. Li, H. Shemer, D. Hasson, R. Semiat, Characterization of the effectiveness of anti-scalants in suppressing scale deposition on a heated surface, *Desalination*, 397 (2016) 38–42.
- [16] Y. Tang, W. Yang, X. Yin, Y. Liu, P. Yin, J. Wang, Investigation of CaCO₃ scale inhibition by PAA, ATMP and PAPEMP, *Desalination*, 228 (2008) 55–60.
- [17] L. Yang, J. Zhou, Q. She, M.P. Wan, R. Wang, V.W.-C. Chang, C.Y. Tang, Role of calcium ions on the removal of haloacetic acids from swimming pool water by nanofiltration: mechanisms and implications, *Water Res.*, 110 (2017) 332–341.
- [18] L. Yang, Q. She, M.P. Wan, R. Wang, V.W.-C. Chang, C.Y. Tang, Removal of haloacetic acids from swimming pool water by reverse osmosis and nanofiltration, *Water Res.*, 116 (2017) 116–125.
- [19] T. Arumugham, N.J. Kaleekkal, D. Rana, Fabrication of novel aromatic amine functionalized nanofiltration (NF) membranes and testing its dye removal and desalting ability, *Polym. Test*, 72 (2018) 1–10.
- [20] R. Pairat, C. Sumeath, F.H. Browning, H.S. Fogler, Precipitation and dissolution of calcium - ATMP precipitates for the inhibition of scale formation in porous media, *Langmuir*, 13 (1997) 1791–1798.
- [21] M. Mänttari, A. Pihlajamäki, M. Nyström, Effect of pH on hydrophilicity and charge and their effect on the filtration efficiency of NF membranes at different pH, *J. Membr. Sci.*, 280 (2006) 311–320.
- [22] Y.-L. Lin, P.-C. Chiang, E.-E. Chang, Removal of small trihalomethane precursors from aqueous solution by nanofiltration, *J. Hazard. Mater.*, 146 (2007) 20–29.
- [23] A.E. Childress, M. Elimelech, Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes, *J. Membr. Sci.*, 119 (1996) 253–268.
- [24] B. Zhang, L. Zhang, F. Li, W. Hu, P.M. Hannam, Testing the formation of Ca-phosphonate precipitates and evaluating the anionic polymers as Ca-phosphonate precipitates and CaCO₃ scale inhibitor in simulated cooling water, *Corros. Sci.*, 52 (2010) 3883–3890.
- [25] K.I. Popov, H. Rönkkömäki, L.H.J. Lajunen, Critical evaluation of stability constants of phosphonic acids, *Pure Appl. Chem.*, 73 (2001) 1641–1677.
- [26] R. Zhang, Z. Zhu, S. Deng, et al. Study on the coordination chemistry of ATMP with calcium ion and magnesium ions in aqueous solution, *J. Ind. Water Treat.*, 23 (2003) 27–29 (in Chinese).
- [27] K.I. Popov, M.S. Oshchepkov, N.A. Shabanova, Yu.M. Dikareva, V.E. Larchenko, E. Ya. Koltinova, DLS study of a phosphonate induced gypsum scale inhibition mechanism using indifferent nanodispersions as the standards for light scattering intensity comparison, *Int. J. Corros. Scale Inhib.*, 7 (2018) 9–24.
- [28] B. Cuartas-Urbe, M.C. Vincent-Vela, S. Álvarez-Blanco, M.I. Alcaina-Miranda, E. Soriano-Costa, Prediction of solute rejection in nanofiltration processes using different mathematical models, *Desalination*, 200 (2006) 144–145.
- [29] N. Ali, A.W. Mohammad, A.L. Ahmad, Use of nanofiltration predictive model for membrane selection and system cost assessment, *Separ. Purif. Tech.*, 41 (2005) 29–37.
- [30] A.W. Mohammad, A modified Donnan-steric-pore model for predicting flux and rejection of dye/NaCl mixture in nanofiltration membranes, *Separ. Sci. Technol.*, 37 (2002) 1009–1029.
- [31] A. Hafiarle, D. Lemordant, M. Dhahbi, Removal of hexavalent chromium by nanofiltration, *Desalination*, 130 (2000) 305–312.
- [32] I.C. Escobar, S. Hong, A.A. Randall, Removal of assimilable organic carbon and biodegradable dissolved organic carbon by reverse osmosis and nanofiltration membranes, *J. Membr. Sci.*, 175 (2000) 1–17.
- [33] J.-J. Qin, M.H. Oo, H. Lee, B. Coniglio, Effect of feed pH on permeate pH and ion rejection under acidic conditions in NF process, *J. Membr. Sci.*, 232 (2004) 153–159.
- [34] X.F. Chen, G. Yang, W.H. Xing, N.P. Xu, Effect of pH and salt on the performance of DK nanofiltration membrane, *J. Nanjing Univ. Technol. (Natural Science Ed.)*, 35 (2013) 43–47 (in Chinese).
- [35] Q. Li, M. Elimelech, Organic fouling and chemical cleaning of nanofiltration membranes: measurements and mechanisms, *Environ. Sci. Technol.*, 38 (2004) 4683–4693.
- [36] K.I. Popov, M.S. Oshchepkov, E.Ya. Afanas'eva, E.Ya. Koltinova, Yu.M. Dikareva, H. Rönkkömäki, A new insight into the mechanism of the scale inhibition: DLS study of gypsum nucleation in presence of phosphonates using nanosilver dispersion as an internal light scattering intensity reference, *Colloids Surfaces*, 560 (2019) 122–129.