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# The application of nanofiltration in NaOH solution regeneration after ultrafiltration membrane cleaning

A. Urbanowska*, M. Kabsch-Korbutowicz

*Chair in Water and Wastewater Treatment Technology, Faculty of Environmental Engineering, Wroclaw University of Science and Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland, Tel. +48 71 3203639;*
*email: agnieszka.urbanowska@pwr.edu.pl (A. Urbanowska)*

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ABSTRACT

The use of both polymeric and ceramic membranes is quite often limited due to the membrane fouling, which can be prevented by chemical cleaning of the membranes. NaOH solution is the most commonly used chemical for this purpose. Unfortunately, the regeneration of the spent cleaning solutions issue arises. This research attempted to determine the possibility of the recovering the cleaning solution from spent regenerant solutions of various origin using the nanofiltration (NF) process. The results showed that the use of NF membranes allowed for the recovery of NaOH to a degree that enabled its reuse. The type of membrane, the composition of the spent regenerant solution, and the duration of the process determined the efficiency of the regenerating agent recovery. It was shown that the use of the NP030P membrane allowed for a very high organic compound separation efficiency (up to 98%). It was also possible to regenerate a cleaning solution after another regeneration to such an extent that it would be just as effective as a fresh solution. It was also observed during the recovery process that the hydraulic efficiency decreased and the separation properties deteriorated as a result of progressive NF membrane fouling.

*Keywords:* Natural organic matter; Pressure-driven membrane process; Chemical cleaning; NaOH solution recovery

## 1. Introduction

To obtain a high quality of treated water, water treatment plants are modernizing the currently used technology by introducing low-pressure membrane processes, for example, the ultrafiltration (UF) that allows for the removal of many organic and mineral admixtures and impurities [1,2]. Organic pollutants can be of natural or anthropogenic origin and occur in a dissolved or undissolved form in all types of waters on Earth [3]. Natural organic matter (NOM) substances are mainly products of biological synthesis or decomposition, which occur with the participation of microorganisms present in water, soil, animals, and plants [4]. NOMs are a mixture of structurally complex compounds with very diverse properties and a wide range of molecular weights [5]. Although the presence of NOM does not pose a direct threat, it does affect water quality by increasing the formation of disinfection by-products, forming complexes with heavy metals and organic micropollutants, and also supporting bacterial regrowth in the distribution system [6].

A progressive decrease in hydraulic efficiency can often be observed during both polymeric and ceramic membrane operation [7]. This is one of the main limitations of the widespread use of pressure-driven membrane processes [8]. This phenomenon is caused by membrane blocking, which results of the deposition of removed impurities on the membrane surface and in its pores [9]. In the case of low-pressure membrane filtration, NOM is often indicated as a major foulant [3]. The fouling leads to a change in the properties of the membrane, and it is often irreversible. In addition to a

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* Corresponding author.

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decrease in the permeate flux, it also shortens the membrane life time and increases the cost of the process [10]. It is therefore important to limit fouling negative effects and prevent it by applying an appropriate control technique. This can be achieved by chemical cleaning of the membranes [11]. This method is very often used in all operated membrane installations. The selection of chemicals is based on the type of compounds that are deposited on the membrane surface. The chemicals used can be strong and weak bases, acids, detergents, enzymes, disinfectants, and complexants [12]. For membranes fouled by organic substances, NaOH solution is the most commonly used chemical for cleaning [13]. According to the authors own research [14], it allows for full recovery of the initial membrane flux. Unfortunately, as a result of membrane cleaning, spent regenerant solutions are generated. In the case of cleaning polymeric or ceramic membranes used to remove NOM, the spent regenerant will be strongly contaminated with organic compounds. Due to the fact, that a cleaning agent might pose a threat to the environment, an effort is undertaken to recover contaminated solutions by removing organic substances. One of the possible recovery methods is pressure-driven membrane filtration, for example, nanofiltration (NF). Although this process is applied with success in the dairy industry for cleaning agent regeneration [15,16], no literature has been found on the recovery of spent caustic regenerant after NOM-fouled membrane cleaning. The subject seems to be interesting as the main components to be separated in the solution obtained from the cleaning of membranes used for milk treatment are fats and proteins, while in the case of membranes used for water treatment, spent cleaning solutions contain primarily NOM particles. The use of NF should isolate NOM molecules, and thus allows the permeate (NaOH solution), which is devoid of these impurities, to be reused.

Considering the earlier, the authors have attempted to assess the possibility of recovering the caustic cleaning agent from various spent regeneration solutions using the NF process.

## 2. Materials and methods

The spent regenerant solution was obtained after chemical cleaning of two types of UF membranes:

- a polymeric polyethersulfone flat sheet membrane (Microdyn Nadir, Germany),
- a tubular INSIDE CéRAM ceramic membrane (TAMI Industries, France).

The properties of the used membranes are shown in Table 1.

Two solutions of different origin, but with a similar NOM content, were used for UF membrane fouling. Solution A was obtained by adding humic acids (Aldrich, USA) to tap water after dechlorination in the amount of 0.05 g/dm$^3$. Solution B was a natural humic water sampled from a stream flowing from the Great Peat Bog of Batorów (Table Mountains, Poland, sampling point location: 50°27′29.97″ N; 16°23′16.87″ E). The properties of the feed solutions are presented in Table 2.

0.5 M NaOH (20 g/dm$^3$) solution was used to clean the membranes fouled with NOM. As a result of cleaning, the following spent regenerant solutions were collected:

- solution 1: after cleaning membrane PES 50 kDa fouled using solution A,
- solution 2: after cleaning membrane PES 50 kDa fouled using solution B,
- solution 3: after cleaning ceramic 50 kDa membrane fouled using solution A, and
- solution 4: after cleaning ceramic 50 kDa membrane fouled using solution B.

The characteristics of the spent regenerant solutions are given in Table 3.

NaOH recovery from each spent regenerant solution was carried out using two types of NF membranes, NP010P and NP030P, the properties of which are shown in Table 4.

The evaluation of the effectiveness of spent regenerant recovery in the NF process was carried out in a laboratory-scale

Table 1
UF membranes used to prepare spent regenerant solutions [17,18]

| Membrane type | Material | Cutoff (kDa) | Max. pressure (MPa) | Max temp. (°C) | pH range | Effective filtration area (cm$^2$) |
|---|---|---|---|---|---|---|
| Flat sheet organic | | | | | | |
| PES 50 | Polyethersulfone (PES) | 50 kDa | – | 95 | 1–14 | 45.3 |
| Tubular ceramic, 1-channel | | | | | | |
| Ceram INSIDE 50 kDa | $Al_2O_3 \cdot TiO_2$ | 50 kDa | <9 | 150 | 0–14 | 40 |

Table 2
The properties of solutions used to foul membranes

| Solution | Color (g Pt/m$^3$) | UV 254 nm absorbance (cm$^{-1}$) | DOC (g C/m$^3$) | Conductivity (µS/cm) | pH | Temperature (°C) |
|---|---|---|---|---|---|---|
| A | 177.2 | 0.872 | 35.7 | 679 | 5.83 | 23 |
| B | 172.3 | 1.218 | 32.3 | 50 | 5.44 | |

Table 3
Spent regenerant solution characteristics

| Solution | Color (g Pt/m$^3$) | UV 254 nm absorbance (cm$^{-1}$) | DOC (g C/m$^3$) | Conductivity (mS/cm) | pH | Temperature (°C) |
|---|---|---|---|---|---|---|
| 1 | 24.50 | 0.158 | 6.83 | 102.3 | 12.82 | 23 |
| 2 | 36.54 | 0.208 | 13.1 | 111.8 | 13.22 | |
| 3 | 42.94 | 0.233 | 14.9 | 69.9 | 13.17 | |
| 4 | 50.68 | 0.268 | 17.9 | 104.5 | 13.45 | |

Table 4
NF membranes used in the experiments [19]

| Membrane type | Membrane material | $Na_2SO_4$ retention (%) | MWCO (kDa) | Max temp. (°C) | pH range | Effective filtration surface (cm$^2$) |
|---|---|---|---|---|---|---|
| NP010P | Polyethersulfone | 25–40 | 1,040–1,400 | 95 | 0–14 | 45.3 |
| NP030P | | 80–95 | 520–700 | | | |

dead-end NF system equipped with the Amicon 8400 stirred cell. Each new NF membrane was conditioned before the experiments by continuous filtration of the distilled water until a constant permeate flux ($J_0$) was achieved. In the next stage of conditioning, caustic solution containing NOM was filtered in order to ensure the equilibrium of the compound adsorption into and onto the membrane. Finally, the spent regenerant (350 cm$^3$ sample) was subjected to NF (TMP 0.3 MPa) in order to recover the NaOH solution. NF was carried out until 95% of the solution volume passed through the membrane.

The effect of the number of subsequent cleaning solution regenerations on the effectiveness of UF membrane cleaning was determined by comparing the distilled water flux for a fresh membrane with a flux measured for a membrane after a single fouling-cleaning cycle (a new UF membrane was used for each experiment).

The content of organic compounds in the water was determined by measuring the intensity of color (350 nm absorbance), UV 254 nm absorbance, and dissolved organic carbon (DOC) concentration. The color indicates on the presence of a NOM fraction containing chromophore groups (typical for high molecular weight NOM), UV 254 nm absorbance is the measure of the amount of NOM fraction containing aromatic structures, and the DOC concentration determines the total amount of organic compounds. The NaOH concentration in the examined water samples was determined by titrating the diluted sample (1:5) with 1 M HCl, using phenolphthalein as an indicator.

## 3. Results

Fig. 1 presents the influence of the NF process duration (permeate recovery rate) on the relative permeate flux changes during spent regenerant recovery from various postregeneration solutions. In regard to obtained results one can say that NPO10P membrane was more prone to fouling as compared with NPO30P membrane. Analyzing hydraulic efficiency of both tested membranes it was shown that the NPO10P membrane transport properties were significantly better than those determined for the NPO30P membrane. The obtained values of the permeate flux ranged from 0.83 to 1.15 m$^3$/m$^2$ d for NPO10P during the initial 20 min of the regeneration, while the NPO30P membrane was characterized by a lower hydraulic efficiency (0.166–0.191 m$^3$/m$^2$ d), which was consistent with other literature reports [20,21]. The explanation of this phenomenon may be the molecular weight cutoff (MWCO) and pore diameters of the tested membranes. Kovács and Samhaber [22] showed that the pore size of NPO10P membranes was higher (MWCO 1,010–1,400 Da, pore diameter 0.80–1.29 nm) than that measured for NPO30P membranes (MWCO 500–700 Da, pore diameter 0.57–0.93 nm), and this may have resulted in a greater flow resistance and thus, in a lower permeability of the NPO30P membrane. In addition, the analysis of the obtained results showed that due to the progressive membrane fouling, the hydraulic efficiency gradually decreased. This effect was clearly visible for all tested configurations, especially after filtering about 50% of the tested solution. It could also be observed that the composition of the recovered regeneration solutions also had a noticeable effect on NF membrane permeability. The permeate flux of the spent regenerant solutions obtained from the membranes fouled with solution A was higher than that obtained for the membranes fouled with the use of solution B. This indicated that the low-molecular-weight fractions present in natural water could intensify the phenomenon of NF membrane blocking [23]. It can be easily seen that the $J/J_0$ values for the postregeneration solutions obtained after cleaning the UF membranes fouled during treatment of water from the Bog were lower (0.6–0.9) than for the solutions contaminated with the Aldrich humic acids (0.65–0.95; values measured after NF of the half of the spent regenerant solution volume).

Apart from changes in the transport properties of the NF membranes used for cleaning solution recovery, fluctuations of membranes separation efficiency during the process were also very important. The comparison of the NOM removal efficiency from the spent regenerant solution using NF membranes is shown in Fig. 2 (for solutions from the cleaning of membranes fouled with solution A) and Fig. 3 (for solutions from the cleaning of UF membranes fouled with solution B).

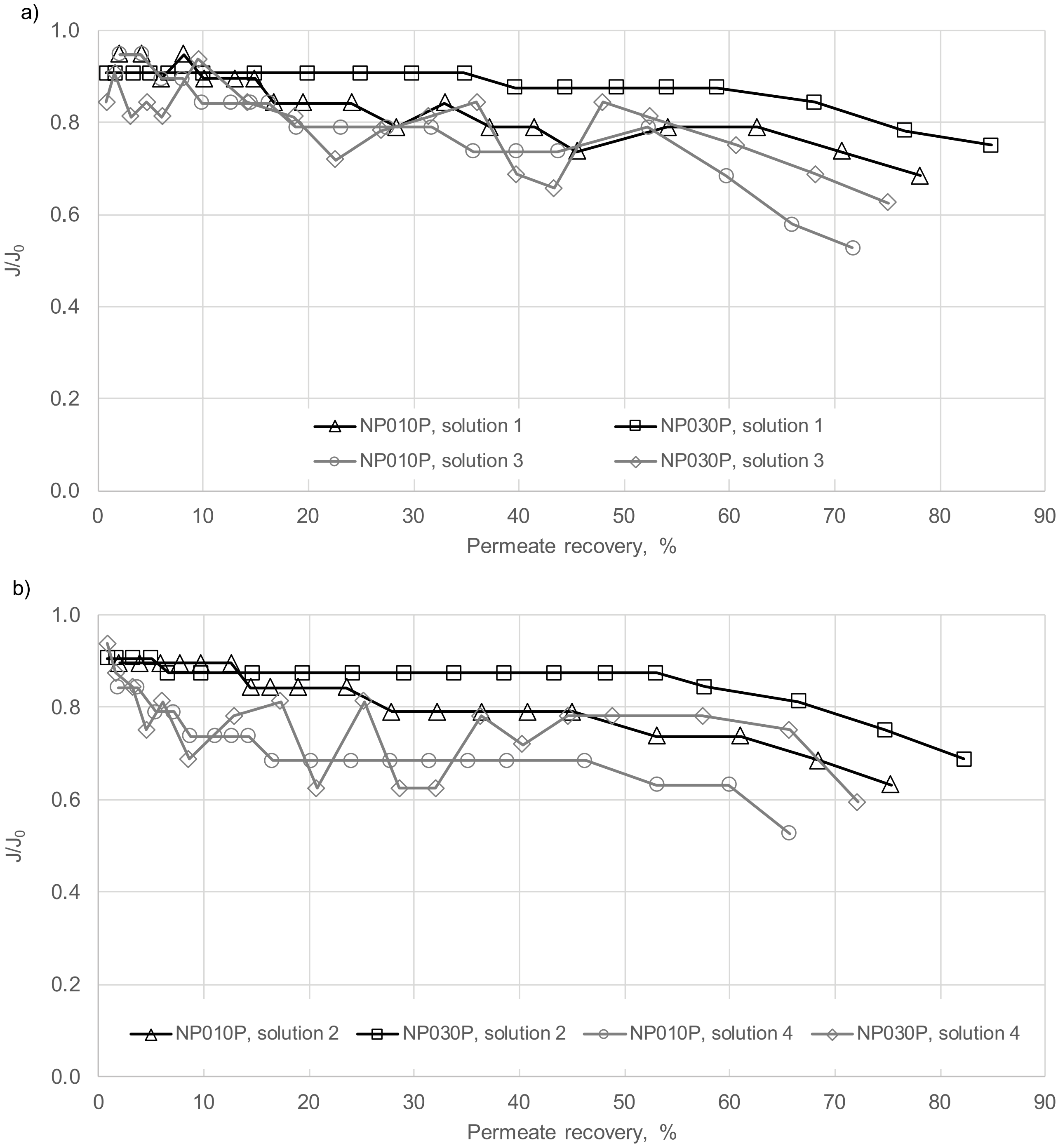

Fig. 1. Relative permeate fluxes during NF of spent regenerant filtration generate during cleaning of UF membranes fouled with the use of solution A (a) and solution B (b).

The values of the color and UV absorbance retention coefficients obtained for both the NF membranes and for the various spent regenerant solutions show that at a constant TMP pressure, the NF membrane type and the composition of the purified solution determined the efficiency of NaOH recovery. For all tested postregeneration solutions, it was observed that the use of the NPO10P membrane resulted in a deterioration of the permeate quality when compared with the NPO30P membrane. For example, the NPO30P membrane allowed for a color and absorbance retention of up to 95.4% and 93.3% to be achieved for solution 2, while for the NPO10P membrane the values were 90.8% and 84.1%, respectively. The better separation properties of the NPO30P membrane could have resulted of the denser structure of the membrane [22]. For both tested membranes the increase in the permeate recovery rate resulted in the decrease of NOM

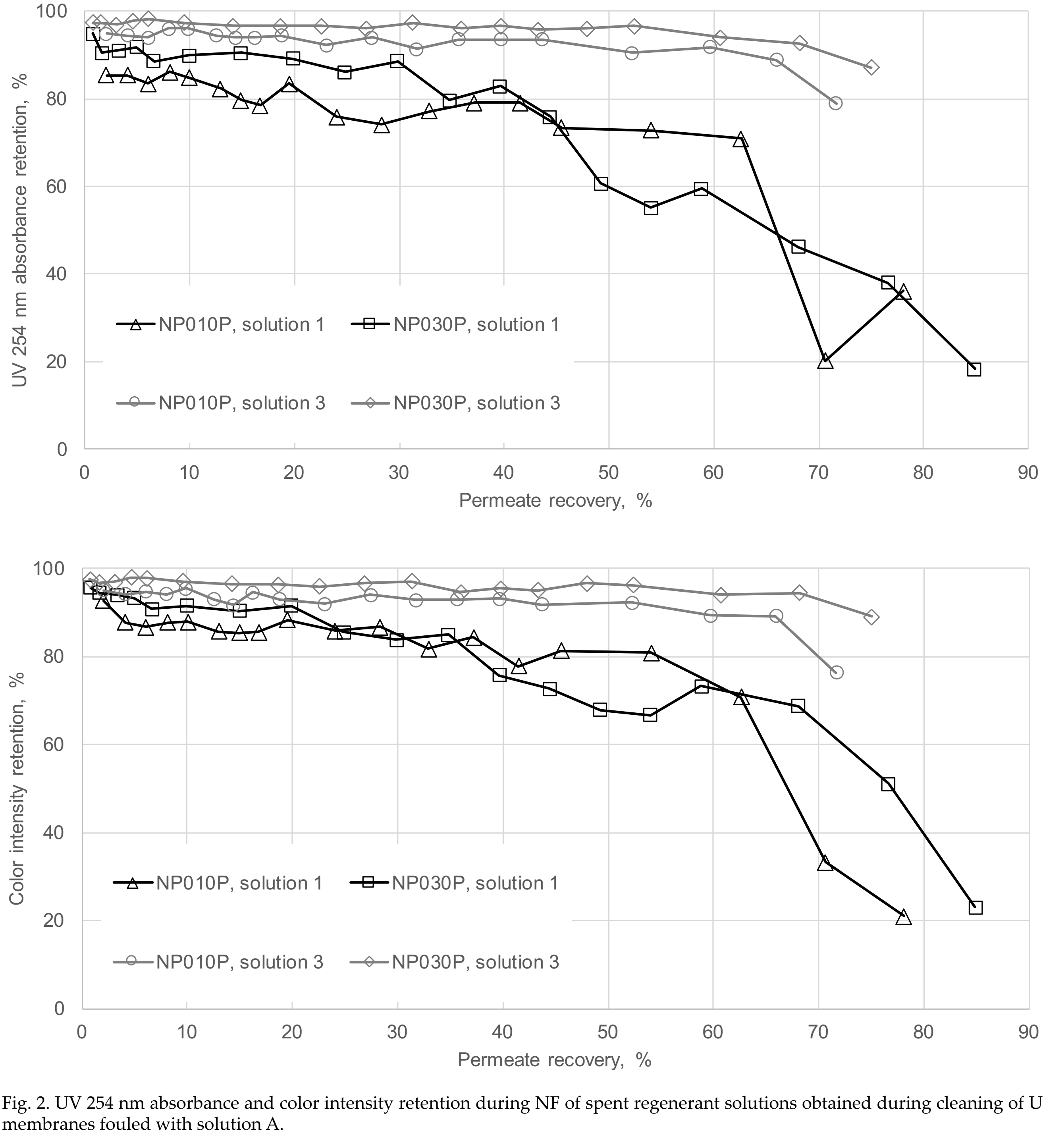

Fig. 2. UV 254 nm absorbance and color intensity retention during NF of spent regenerant solutions obtained during cleaning of UF membranes fouled with solution A.

separation efficiency (expressed as UV 254 nm absorbance or color intensity).

It was found that the effectiveness of organic compounds separation from a spent regenerant was significantly determined by their origin. The color and absorbance retention coefficients during purification of the solutions obtained from cleaning the UF membranes fouled with solution A, and also of those containing Aldrich humic substances, were noticeably higher than for those fouled with solution B (NOM particles from the peat-bog). For example, the efficiency of the NPO30P membrane ranged, for a 30% permeate recovery rate, from 83.8% to 95.6% for color removal and from 86.1% to 94.9% for UV absorbance decrease for solution 1, and respectively from 81.6% to 95.4% and from 80.8% to 93.3% for solution 2. A similar tendency could also be observed for the NPO10P membrane: 86.7%–92.7% and 77.2%–85.4%, and 81.6%–90.8% and 75.5%–84.1%, respectively. This could be explained, as it was the case when examining the transport

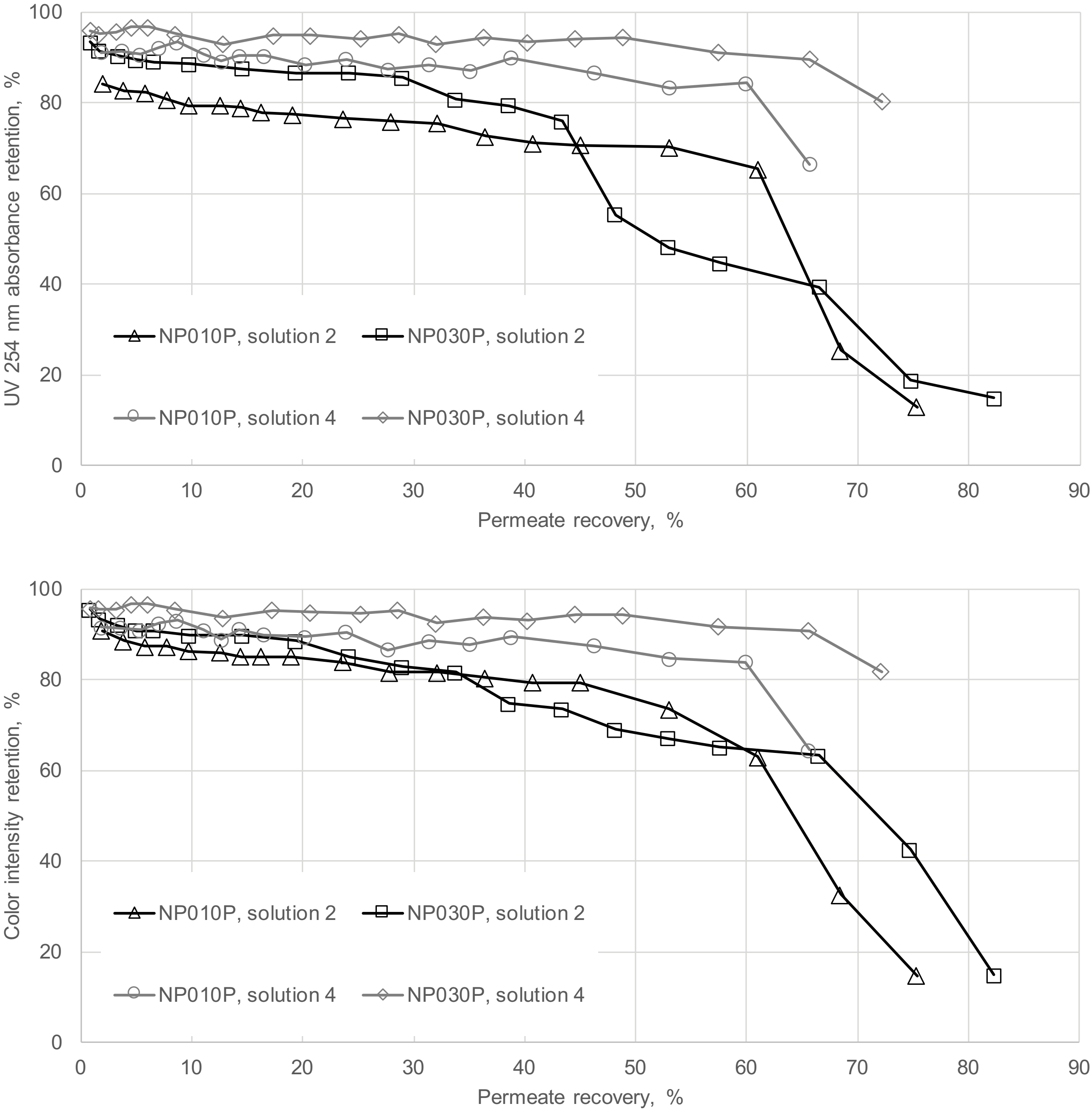

Fig. 3. UV 254 nm absorbance and color intensity retention during NF of spent regenerant solutions obtained during cleaning UF membranes fouled with solution B.

properties of NF membranes, by the presence of small molecular weight fractions and other inorganic ions in the post-cleaning solutions of membranes fouled with the peat-bog water. This in turn may have affected both, the spatial configuration of organic particles and surface charge, which may have facilitated transport of organic substances throughout the membrane. It must not be forgotten that there are three major interactions affecting solute-membrane rejection: steric hindrance, electrostatic repulsion, and hydrophobic interactions.

It was also noticed that the color intensity retention coefficient values were slightly higher than those for UV absorbance, which indicated that substances containing chromophore groups were preferentially rejected by membranes.

As the process of NaOH recovery was realized in the dead-end mode, it was also very important to analyze whether the filtration process duration affected the effectiveness of the elimination of organic substances from the spent regenerant solutions. The obtained results of the changes in the color intensity and UV absorbance retention coefficients showed

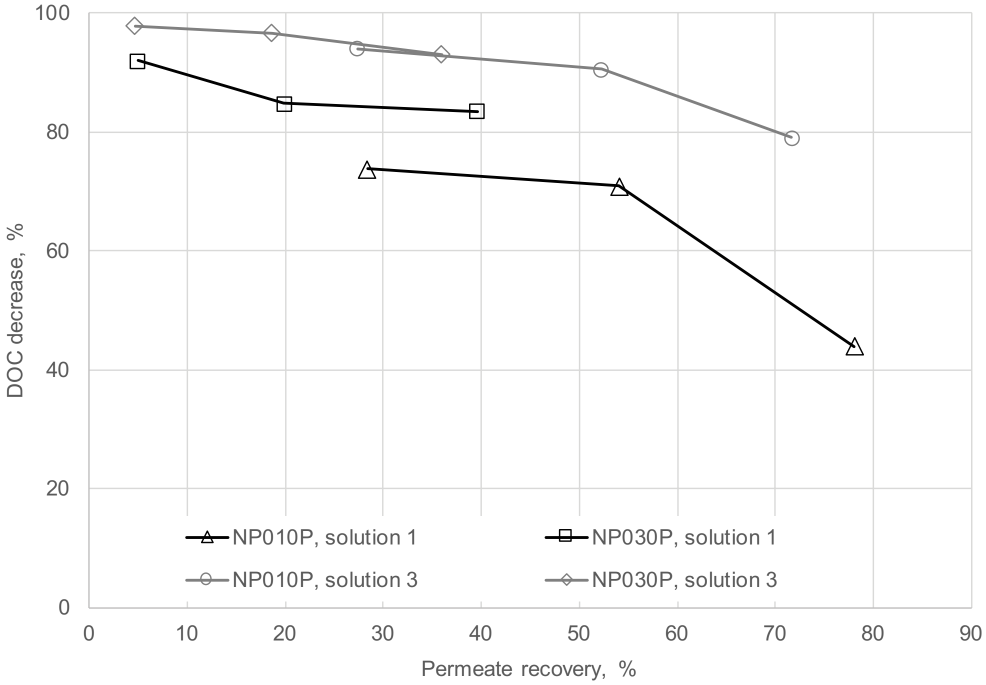

Fig. 4. DOC removal during NF of spent regenerant solutions obtained during cleaning of UF membranes fouled with the use of solution A.

that along with the elongation of the process, and thus with the feed solution concentration, the separation properties of both NF membranes deteriorated. It was also observed that approximately 45%–70% of the solution intended for regeneration was well cleaned – the effectiveness of the separation of impurities on the membrane was almost unchanged over time. However, during the regeneration of the remaining volume of the solution, a decrease in the retention coefficients of both measured parameters was observed.

The analogous conclusions, as in the case of changes in the color intensity and UV absorbance, could be drawn when analyzing changes in the DOC content of the permeate (Fig. 4). It was also influenced by the NF membrane type and the composition of organic compounds in the feed. For example, the DOC removal coefficient, depending on the type of spent regenerant solution, varied from 43.9% to 94.0% for the NPO10P membrane and from 81.8% to 97.9% for the NPO30P membrane.

Hence, when NF membranes are considered to be used for NOM contaminated caustic solution regeneration, apart from membrane type and NOM properties, concentration factor/permeate recovery rate has to be taken into account.

The analysis of changes in the pH and concentration of NaOH during the cleaning of the spent regeneration solution in the NF process was also performed (Table 5). None of those parameters significantly changed during the recovery process. It was observed that the pH of regenerated cleaning solution was slightly lower than that for the fresh cleaning solution. NF of the spent regenerant resulted in a slight decrease of the NaOH content in the recovered solution. It was observed that NaOH retention depended on the type of NF membrane, and was in a range of 9%–11% for the NPO30P membrane and 3%–7% for the NPO10P membrane. This may have resulted of the difference in the MWCO of these membranes and it was consistent with other findings [20]. This effect was independent of the type of recovered solution.

It was crucial to verify whether multiple regenerations of the NaOH solution used for cleaning membranes did not change its properties. The experiments carried out on the

Table 5
pH and NaOH concentration values measured during the spent regenerant recovery using NF membranes

| Spent regenerant solution | pH | | NaOH concentration (g/dm$^3$) | |
|---|---|---|---|---|
| | NPO10P | NPO30P | NPO10P | NPO30P |
| 1 | 13.27–13.46 | 13.23–13.40 | 18.56–18.56 | 17.96–17.98 |
| 2 | 13.28–13.44 | 13.28–13.32 | 18.74–19.24 | 17.82–18.04 |
| 3 | 13.29–13.29 | 13.17–13.29 | 18.69–18.96 | 17.82–17.90 |
| 4 | 13.21–13.21 | 13.27–13.42 | 18.70–19.28 | 17.84–17.96 |

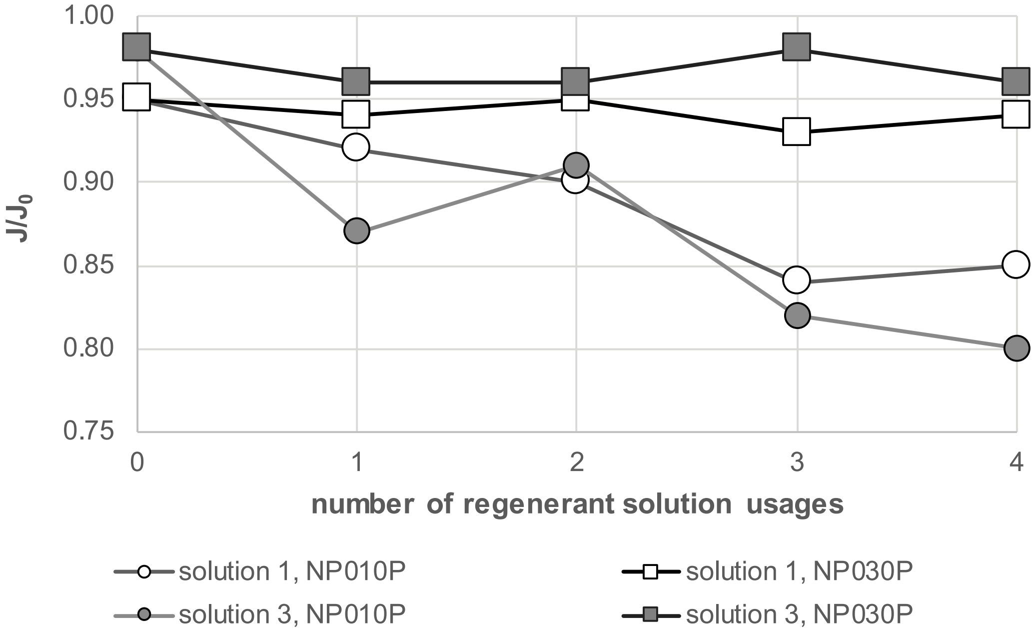

Fig. 5. The influence of multiple regeneration of NaOH cleaning solution on the recovery of transport properties of PES 50 membrane.

effectiveness of repeated recovery of spent cleaning solutions using NF membranes and the possibility to restore their original capabilities showed, that along with subsequent regeneration, cleaning properties of the regenerant solution may have also been changed. The results presented in Fig. 5, obtained for solutions after regeneration of 50 kDa PES membrane, clearly show that the use of the NPO30P membrane for cleaning solution recovery allowed to obtain NaOH solution, after its subsequent use, almost as effective as the fresh one. It was noticed that the $J/J_0$ values for the PES 50 membrane cleaned with a recovered solution ranged from 0.93 to 0.95, while for the ceramic 50 kDa membrane the values were 0.96–0.98. It was also found that the use of the NPO10P membrane caused a slightly worse effect in recovering the solution's initial cleaning properties. Low MW NOM particles, which remained in the cleaning solution after its treatment with the use of NPO10P membrane, may have been responsible for UF membranes fouling and thereby decreased permeate flux. It is easy to notice a decrease in UF membrane permeability with subsequent recovery cycles. In this case, the $J/J_0$ for the fresh cleaning solution fluctuated in a range of 0.95–0.98, while after the fourth regeneration it dropped to 0.80–0.85. This may have been due to the weaker separation properties of the NPO10P membrane when compared with the NPO30P membrane.

## 4. Conclusions

The research presented in this paper allowed for the following conclusions to be drawn:

- both examined NF membranes could be effectively used for NaOH recovery from various spent cleaning solutions contaminated with NOM substances, however, better purification results were obtained for the denser NPO30P membrane,
- the effectiveness of the process was depended on such parameters as: the type (i.e., the properties of NOM fraction) of membrane used, the composition of the spent regenerant solution purified and the permeate recovery rate,
- better transport and separation properties of NF membranes were obtained when the spent regenerant solution obtained from cleaning membranes contaminated with bigger NOM particles (solution A) was treated, than when the solution obtained from during smaller natural NOMs removal (despite similar contents of NOM),
- prolonged NF in the dead-end mode led to a deterioration of the hydraulic and separation properties of used membranes, and
- it was proven that it was possible to regenerate a cleaning solution to such an extent that it would be almost as effective as a fresh one.

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## References

[1] K.J. Howe, D.W. Hand, J.C. Crittenden, R.R. Trussell, G. Tchobanoglous, Principles of Water Treatment, John Wiley & Sons, Hoboken, NJ, 2012.

[2] A.W. Zularisam, A.F. Ismail, R. Salim, Behaviours of natural organic matter in membrane filtration for surface water treatment – a review, Desalination, 194 (2006) 211–231.

[3] N.H. Lee, G. Amy, J.-P. Croué, H. Buisson, Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM), Water Res., 38 (2004) 4511–4523.

[4] N.S. Bolan, D.C. Adriano, A. Kunhikrishnan, T. James, R. McDowell, N. Senesi, Dissolved organic matter: biogeochemistry, dynamics, and environmental significance in soils, Adv. Agron., 110 (2011) 1–75.

[5] A. Matilainen, M. Vepsäläinen, M. Sillanpää, Natural organic matter removal by coagulation during drinking water treatment: a review, Adv. Colloid Interface Sci., 159 (2010) 189–197.

[6] A. Matilainen, E.T. Gjessing, T. Lahtinen, L. Hed, A. Bhatnagar, M. Sillanpää, An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment, Chemosphere, 83 (2011) 1431–1442.

[7] B. Hofs, J. Ogier, D. Vries, E.F. Beerendonk, E.R. Cornelissen, Comparison of ceramic and polymeric membrane permeability and fouling using surface water, Sep. Purif. Technol., 79 (2011) 365–374.

[8] S. Shirazi, C.-J. Lin, D. Chen, Inorganic fouling of pressure-driven membrane processes – a critical review, Desalination, 250 (2010) 236–248.

[9] W. Guo, H.-H. Ngo, J. Li, A mini-review on membrane fouling, Bioresour. Technol., 122 (2012) 27–34.

[10] W. Gao, H. Liang, J. Ma, M. Han, Z. Chen, Z. Han, G. Li, Membrane fouling control in ultrafiltration technology for drinking water production: a review, Desalination, 272 (2011) 1–8.

[11] X. Shi, G. Tal, N.P. Hankins, V. Gitis, Fouling and cleaning of ultrafiltration membranes: a review, J. Water Process Eng., 1 (2014) 121–138.

[12] N. Porcelli, S. Judd, Chemical cleaning of potable water membranes: a review, Sep. Purif. Technol., 71 (2010) 137–143.

[13] H. Yamamura, K. Kimura, Y. Watanabe, Seasonal variation of effective chemical solution for cleaning of ultrafiltration membrane treating a surface water, Sep. Purif. Technol., 132 (2014) 110–114.

[14] A. Urbanowska, M. Kabsch-Korbutowicz, Cleaning agents efficiency in cleaning of polymeric and ceramic membranes fouled by natural organic matter, Membr. Water Treat., 7 (2016) 1–10.

[15] G. Gésan-Guiziou, N. Alvarez, D. Jacob, G. Daufin, Cleaning-in-place coupled with membrane regeneration for re-using caustic soda solutions, Sep. Purif. Technol., 54 (2007) 329–339.

[16] Intermasz – Application of Membranes in Cleaning Agent Regeneration (in Polish), Available at: http://intermasz.com/index.php?site=4&id=27&id2=46&z=50.

[17] Microdyn Nadir Product Catalogue, Available at: http://www.microdyn-nadir.com/fileadmin/user_upload/downloads/catalogue.pdf.

[18] Tami Industries Ceram INSIDE Product Catalogue, Available at: https://www.sepra.it/en/ceramic-tubular-membranes-p-47-s-18.html.

[19] Microdyn Nadir Membrane Data Sheets, Available at: https://www.lenntech.com/products/microdyn.htm.

[20] A. Arkell, H. Krawczyk, J. Thuvander, A.-S. Jönsson, Evaluation of membrane performance and cost estimates during recovery of sodium hydroxide in a hemicellulose extraction process by nanofiltration, Sep. Purif. Technol., 118 (2013) 387–393.

[21] T. Coskun, E. Debik, N.M. Demir, Treatment of olive mill wastewaters by nanofiltration and reverse osmosis membranes, Desalination, 259 (2010) 65–70.

[22] Z. Kovács, W. Samhaber, Characterization of nanofiltration membranes with uncharged solutes, Membrántechnika, 12 (2008) 22–36.

[23] A. Urbanowska, M. Kabsch-Korbutowicz, Isolation and fractionation of humic substances present in water with the use of anion-exchange resins and ultrafiltration, Braz. J. Chem. Eng., in press