

Nanofiltration as an effective method of NaOH recovery from regenerative solutions

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Abstract: The objective of this study was to determine the suitability of the nanofiltration (NF) process to recover the regenerating agent (NaOH) from spent solutions contaminated with organic compounds. NaOH recovery from 2 spent regenerant solutions after cleaning ultrafiltration (UF) membranes (polymeric 30 kDa, ceramic 300 kDa) fouled with natural humic water was carried out using 2 types of NF membranes: NP010P (Na₂SO₄ rejection: 35–75%) and NP030P (Na₂SO₄ rejection: 80–95%). It has been shown that the use of the NP030P membrane allows for very high separation efficiency of organic compounds (up to 97% of color intensity reduction) from the tested solutions. It was also observed that the effectiveness of the process, in addition to the type of membrane used, also depends on the time of NF process – along with the elapsed time of the process, the hydraulic and separation properties of the tested membranes deteriorated. The obtained results showed that the use of both tested NF membranes allows for the recovery of NaOH to a degree that allows its re-use.

Introduction

Water determines life on Earth and is widely used in all branches of the economy. In order to be able to use it safely, raw water should be treated to meet the water quality standards. Depending on the purpose of the water (water supply, cooling, heating, etc.) and the degree of pollution of the water source, more or less effective purification processes are applied. Their selection depends on the costs incurred.

Natural organic matter (NOM) is one of the surface water contaminants that must be removed before the water is supplied to consumers (Matilainen et al. 2011). NOM includes, among others, amino acids, lipids, phenols, sugars, hydrocarbons and humic substances and thus vary in properties (Nebbio and Piccolo 2013). The removal of these compounds is a very important operation due to the safety of human health and proper operation of devices used in water treatment technology (Sillanpää 2015). These substances, in addition to the intense color and unpleasant smell, have an adverse effect during the treatment and distribution of water (Grefte et al. 2013). NOM chemical compounds easily react with oxidants used in water treatment (Matilainen and Sillanpää 2010). As a consequence, during disinfection, undesirable oxidation by-products are formed in the water being a nutrient for bacteria found in water distribution systems (Bond et al. 2014).

NOM removal methods include pressurized membrane processes, in particular ultrafiltration (UF). This process is increasingly used in water treatment facilities. It allows for the removal of many impurities and admixtures from the water, does not cause the transformation of pollutants and prevents

secondary water contamination (Bodzek et al. 2019, Lee and Kim 2014, Yunos et al. 2014).

When membrane processes are used, the membrane fouling can often be observed. This phenomenon is based on depositing on the membrane surface and its pores of some components present in treated waters or sewage. This leads to a decrease in hydraulic membrane efficiency, shortens their lifespan and increases process costs. Membrane fouling is one of the most limiting factors taken into account when using membrane techniques in practice (Sutzkover-Gutman et al. 2010).

The membrane fouling may be reduced or deferred by maintaining appropriate process parameters, periodic membrane cleaning, pretreatment of the feed water, using physical and chemical methods. The most common method of reducing the effects of fouling is chemical cleaning (Porcelli and Judd 2010). Depending on the type of compounds deposited on the surface of the membrane, appropriate chemicals are selected. An important aspect is the tolerance of the membrane material to the given chemicals, the effective removal of the accumulated layer and the restoration of the membrane permeability. The concentration of the cleaning agent and the washing time is also important. During cleaning, there is a reaction between the chemicals and the compounds blocking the surface of the membranes and in this way the fouling layer structure is weakened.

The most commonly used cleaning agent for membranes is concentrated NaOH solution (Lin et al. 2009). Unfortunately, as a result of membrane cleaning, the problem of spent regenerant solutions appears. In the case of NOM removal in

the UF process and subsequent regeneration of the membranes, regeneration solutions will be heavily contaminated with organic compounds. Due to the fact that they are dangerous to the environment, work is being undertaken on the possibility of recovering regenerant solutions by separating any impurities.

One of the methods allowing for regeneration solution recovery is the NF process. Thanks to it, the organic compounds are retained by the membrane and the obtained permeate, devoid of NOM, can be reused for the membrane regeneration. There are reports in the literature (Gésan-Guiziou et al. 2007) on the recovery of cleaning agents from the spent regeneration solutions obtained as a result of cleaning membranes used for milk processing in the dairy industry. However, there is no information regarding the treatment of regenerant solutions contaminated with NOM.

Based on the above, it seemed advisable to determine the suitability of the NF process to recover the regenerating agent from spent solutions contaminated with organic compounds.

Methodology

The research aimed at determining a potential of the regenerating agent recovery using the NF process was carried out for two spent regenerant solutions obtained after cleaning two NOM-contaminated UF membranes with 0.5 M NaOH solution (20 g/dm³). The properties of these solutions are shown in Table 1.

Feed water used for UF membrane fouling 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 were as follows:

- color: 172.3 gPt·m⁻³,
- UV 254 nm absorbance: 1.218 cm⁻¹,
- DOC: 32.3 gC·m⁻³,
- conductivity: 50 μS·cm⁻¹,
- pH: 5.44,
- temperature: 23°C.

Two types of UF membranes were used to prepare the spent regenerant solutions: a 30 kDa molecular weight cut-off (MWCO) flat sheet PES membrane (Microdyn Nadir) and INSIDE CéRAM 300 kDa MWCO tubular ceramic membrane (TAMI Industries). Their properties are presented in Table 2.

NaOH recovery from 2 spent regenerant solutions was carried out using 2 types of NF membranes: NP010P and NP030P, the properties of which are shown in Table 3.

The UF process was carried out using two lab-scale UF systems. The process with the use of flat sheet PES 30 kDa membrane was realized in dead-end mode in a system equipped with Amicon 8400 stirred cell (Millipore). UF with the use of ceramic Ceram INSIDE 300 kDa membrane was performed in the cross-flow system (J.A.M. INOX PRODUKT). Detailed set-up descriptions can be found in (Urbanowska and Kabsch-Korbutowicz 2016). In cross-flow filtration experiments,

Table 1. Spent regenerant solution characteristics

Solution	Color [gPt·m ⁻³]	UV 254 nm absorbance [cm ⁻¹]	DOC [gC·m ⁻³]	Conductivity [mS·cm ⁻¹]	pH
Solution 1 after cleaning PES 30 kDa membrane	31.92	0.183	10.40	97.5	13.24
Solution 2 after cleaning ceramic 300 kDa membrane	100.34	0.468	24.4	98.4	13.33

Table 2. UF membranes used to prepare spent regenerant solutions (Microdyn Nadir Product Catalogue, Tami Industries Ceram INSIDE Product Catalogue)

Membrane type	Material	Cut-off [kDa]	Max. pressure [MPa]	Max temp. [°C]	pH range	Effective filtration area [cm ²]
Flat sheet organic						
PES 30	polyethersulfone (PES)	30 kDa	–	95	1–14	45.3
Tubular ceramic, 7-channel						
Ceram INSIDE 300 kDa	Al ₂ O ₃ · TiO ₂	300 kDa	< 9	150	0–14	125

Table 3. NF membranes used in the experiments (Microdyn Nadir Product Catalogue, Kovács and Samhaber, 2008)

Membrane type	Material	Na ₂ SO ₄ retention [%]	MWCO [kDa]	Max temp. [°C]	pH range	Effective filtration area [cm ²]
NP010P	polyethersulfone	35–75	1040–1400	95	0–14	45.3
NP030P		80–95	520–700			

tangential flux equal to 1.9 m/s was maintained. TMP 0.2 MPa was used in UF experiments.

The evaluation of the effectiveness of spent regenerant recovery in the NF process was carried out in a lab-scale 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 cm³ 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 color intensity (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.

Results and discussion

Results of preliminary studies aimed at obtaining two types of regeneration solutions for further testing are shown in Fig. 1. It was shown that the membranes made of PES were slightly more susceptible to fouling compared to ceramic membranes.

The relative membrane permeability (J/J_0) for polymer membrane was between 0.16 and 0.6, while for ceramic one from 0.26 to 0.48. The differences of membranes vulnerability to fouling observed for polymeric and ceramic membranes during initial stage of experiments may result from different properties of both membrane materials (polymer vs ceramic) as well as from different hydraulic conditions in installations (dead-end vs cross-flow modes). Despite stirring of feed in the Amicon cell (polymeric membrane) more organic substances may be deposited on the membrane surface and cause the significant decrease of its permeability. The research showed a rapid decrease in the permeate flux in the first minutes of the UF process (about 40 min) for both tested membranes. Further process prolongation resulted in slow stabilization of the flux. A nearly constant permeate flux value was achieved, in the case of polymer membrane, after about 60 min and, in the case of ceramic membrane, after about 150 min.

Analyzing the membrane cleaning dynamics it was noticed that the polymer membranes were cleaned faster. Time required to restore flux to 85% of distilled water flux was about 15–25 min for PES membrane and about 80–120 min for ceramic one. This may have been due to the higher cleaning solution flux for PES membrane. The membrane cleaning itself was not the exact subject of this study: the objective of this process was to collect at least the volume of the solution allowing further testing (400 cm³). For both membranes the time required to obtain such volume was only about 15–20 min.

Comparison of the NaOH recovery efficiency with the use of NF membranes is presented in Fig. 2.

The obtained results show that at a constant transmembrane pressure, the type of NF membrane used was a decisive factor for the NaOH recovery efficiency. For both tested solutions it was found that the use of the NP010P membrane resulted in inferior permeate quality. For example, for the solution 1 and the NP010P membrane, the values of absorbance, color and DOC coefficients obtained were up to 79.2%, 89.5% and 67.7%, while for the NP030P membrane: 96.4%, 96.2% and 90.0% respectively. The better separation properties of the NP030P

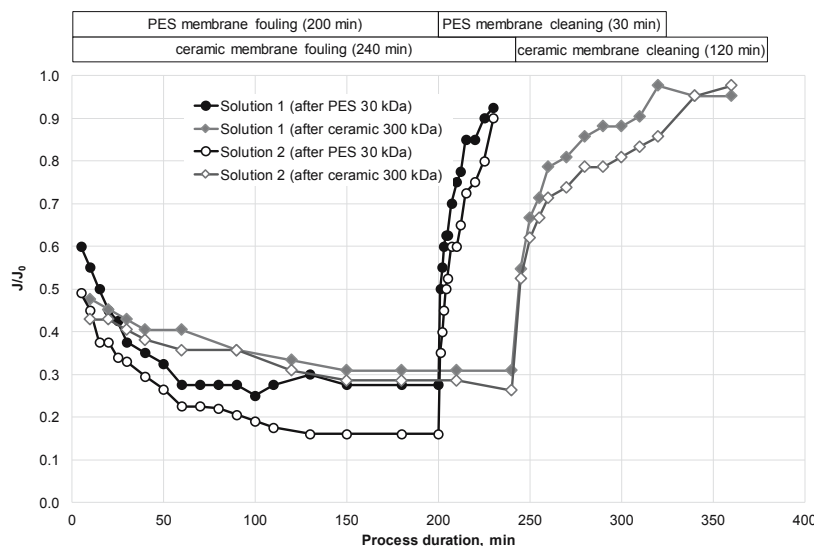


Fig. 1. Membrane fouling and cleaning: relative permeate flux for various membranes and solutions

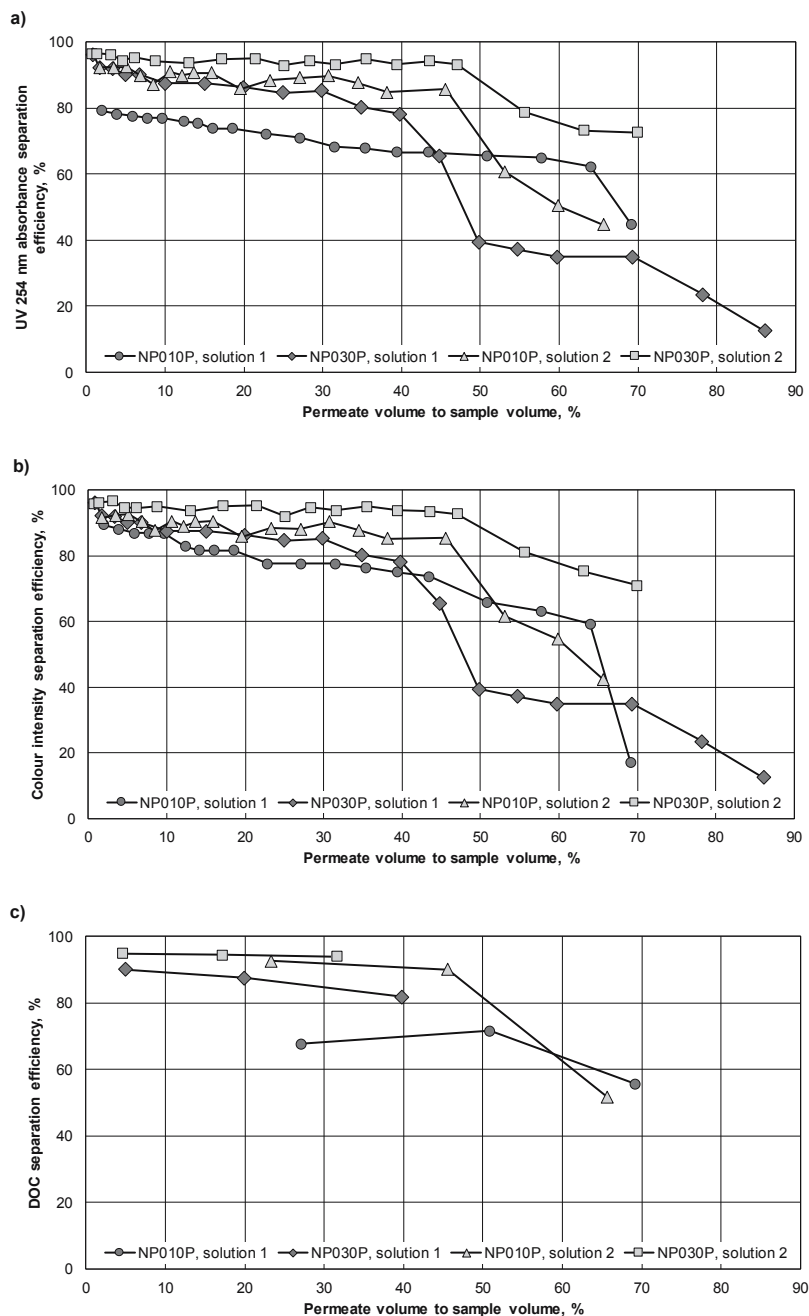


Fig. 2. UV 254 nm absorbance (a), color intensity (b) and DOC concentration (c) removal during NF of spent regenerant solutions obtained by cleaning UF membranes

membrane may have resulted from the more dense structure of this membrane (Kovács and Samhaber 2008). It was also observed that the values of the color retention coefficients were slightly higher than the others, which indicates that substances containing chromophore groups are removed preferentially on the membranes.

The impact of filtration time on the effectiveness of organic substances separation from spent regenerant solution is also significant. It was found that along with the process duration, and thus with the increasing concentration of feed solutions, the separation properties of both NF membranes deteriorated. In addition, it was noted that about 45–70% of the initial solution volume to be regenerated was cleaned well enough: the effectiveness of NOM separation was high and almost

constant over time, but further regeneration of the remaining volume resulted in a decreased separation efficiency.

Table 4 presents changes in the solution pH and the NaOH concentration during the spent regenerant solutions treatment using NF membranes: the obtained test results show that these factors are constant during the recovery. It can only be observed that the solution pH after cleaning was slightly lower than that for fresh solution. NaOH retention was different depending on the type of NF membrane and was in the range of 9–11% for the NP010P membrane and 3–7% for the NP030P membrane. Similar effects were observed for both recovery solutions. It may have resulted from the difference in MWCO of these membranes and is consistent with others findings (Arkell et al. 2013).

In order to analyze the NF membranes transport properties and assess their susceptibility to fouling, the influence of the process duration on the permeate flux during regenerant recovery was examined. The obtained test results are shown in Fig. 3.

It was observed that the NP010P membrane transport properties were significantly better than determined for the NP030P membrane. The values of the permeate flux were around 0.83–1.15 m³/m²·d in the initial 20 min of regeneration process for the NP010P membrane. However, the use of the NP030P membrane resulted in a hydraulic performance around 0.140–0.191 m³/m²·d. The observed trend is consistent with literature reports (Córdova et al. 2016). It can be explained by membrane MWCO and pore diameters. According to (Kovács and Samhaber 2008), the pore size of the NP010P membranes

fits in the range of 1010–1400 Da with diameter 0.80–1.29 nm and is higher than that measured for the NP030P membrane (MWCO 500–700 Da with a pore diameter in the range of 0.59–0.93 nm). It can result in a greater flow resistance and thus lower permeability of NP030P membrane. In addition, it has been shown that with the progressing membrane fouling, hydraulic efficiency is gradually decreasing. This effect was found for both tested membranes and solutions after passing approximately 50% of the solution volume.

In order to restore the original properties of the cleaning solutions, studies on the effectiveness of their repeated cleaning were carried out. For this purpose, the NF membranes were tested against the relative permeability value and whether cleaning properties of recovered solution deteriorated with subsequent regeneration (Fig. 4).

Table 4. pH and NaOH concentration values measured during spent regenerant recovery using NF membranes

NF membrane	NP010P		NP030P	
solution	pH	NaOH concentration [g/dm ³]	pH	NaOH concentration [g/dm ³]
Solution 1	13.28–13.44	18.74–19.24	13.28–13.32	18.74– 9.24
Solution 2	13.34–13.39	19.24–19.28	13.24–13.28	17.82–17.90

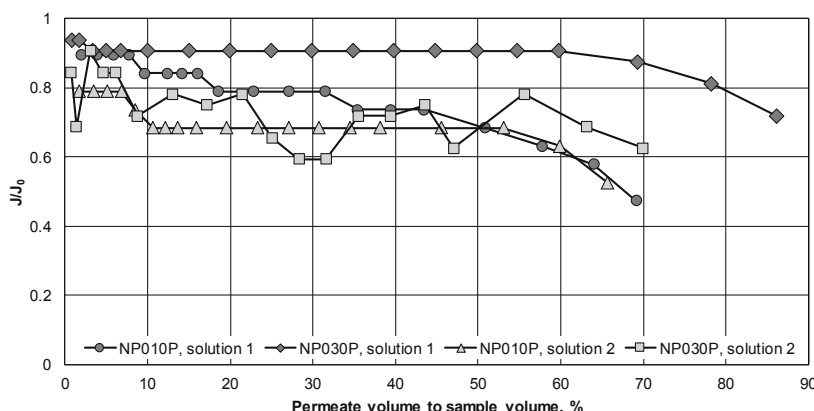


Fig. 3. Relative permeate fluxes during NF of spent regenerant filtration generated during cleaning of fouled UF membranes

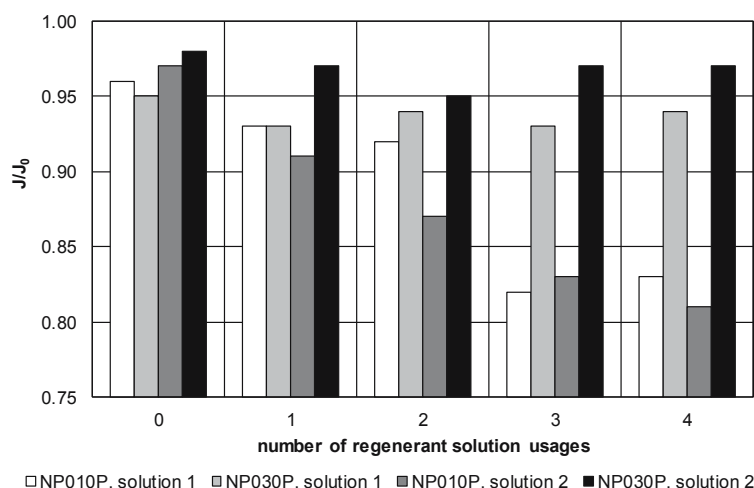


Fig. 4. The influence of multiple regeneration of NaOH cleaning solution on the recovery of transport properties of PES 30 kDa membrane

The results show that the use of NP030P NF membrane allows for obtaining cleaning solution as efficient as the fresh solution after subsequent cleaning-regeneration cycles. It was also noticed that the use of NP010P NF membrane did not allow for restoring original cleaning properties. In this case, a decrease in permeability of membranes was visible along with subsequent recovery cycles. The J/J_0 values obtained after the usage of NP030P membrane ranged from 0.93 to 0.98, while for the NP010P membrane it dropped to the value from the range 0.82–0.96. The reason for this phenomenon may be better separation properties of NP030P membranes when compared to NP010P membranes.

Conclusions

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

- both tested NF membranes can be successfully used for NaOH recovery, but the denser NP030P membrane proved to be more effective,
- the efficiency of the process is influenced by such parameters as the membrane type and the process duration: NF process prolongation resulted in deterioration of both hydraulic and separation properties of the tested membranes,
- it was shown that it was possible to regenerate a cleaning solution with the use of NP030P membrane so it would be almost as effective as a fresh one.

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Proces nanofiltracji jako efektywna metoda odzysku NaOH z roztworów poregeneracyjnych

Streszczenie: W przeprowadzonych badaniach określono przydatność procesu nanofiltracji (NF) do odzysku czynnika regenerującego (NaOH) z roztworów poregeneracyjnych zanieczyszczonych związkami organicznymi. Uzyskane wyniki pokazały, że użycie obu testowanych membran nanofiltracyjnych (NP010P oraz NP030P) pozwala na odzysk NaOH w stopniu pozwalającym na jego ponowne użycie. Wykazano, że zastosowanie membrany NP030P pozwala na uzyskanie bardzo wysokiej skuteczności separacji związków organicznych (do 97% usunięcia barwy) z testowanych roztworów. Zaobserwowano również, że skuteczność procesu, oprócz rodzaju użytej membrany, zależała także od czasu prowadzenia nanofiltracji – wraz z upływającym czasem procesu pogarszały się właściwości hydrauliczne i separacyjne testowanych membran.