Application of nanofiltration for concentration of sodium sulfate waste solution

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ABSTRACT

Nanofiltration was successfully applied to pre-concentrate waste sodium sulfate solution. Reducing salt discharge to the environment is important from both an economical and ecological point of view. Two commercial membranes: NF-270 (DOW FilmTec) and MPS-34 (KOCH) were characterized in flat-sheet and tested in spiral-wound configuration. In the pressure range of 10–40 bar, both permeation flux and salt retention were found to decrease significantly with increasing feed concentration and decreasing driving force. To maintain a high concentration of Na_2SO_4 (up to 110 g/l) and low salt content in permeate (below 0.3 g/l Na_2SO_4), a two-stage process was proposed and verified.

Keywords: Nanofiltration; Sodium sulfate; Wastewater treatment; Recovery

1. Introduction

Disposal of saline effluents is an increasing issue worldwide, both due to environmental awareness and stringent legislation. Large quantities of waste sodium sulfate solutions are generated in many branches of industry, including production of: viscose fibers, synthetic silica, fatty acids, cyclohexanone and catalysts. Although Na_2SO_4 emissions does not pose a direct threat to human health, salt discharge should be avoided to reduce salinity of surface waters. Waste salt load should be reduced to meet national discharge limits (usually below 500 mg/l for sulfates and below 800 mg/l for sodium). Sulfate content can be reduced i.e. by treatment with lime or by ion-exchange, but both processes generate additional wastes [1]. As industrial wastewaters containing Na_2SO_4 originate mostly from the final neutralization of wastewater stream and in many cases are diluted, thus their processing requires significant amounts of energy. On the other hand, recovery of sodium sulfate from such waste is considered uneconomical, due to its low market price. As a result, in industrial practice these solutions are usually combined with other wastewater and transferred to a effluent treatment plant without further processing. To protect surface waters and the environment, new methods to reduce salt discharge should be developed.

Electromembrane techniques, namely membrane electrolysis, electro-electrodialysis or bipolar membrane electrodialysis allows for salt splitting to recover the originating acid and/or base [2–5]. Our previous work [6–8] focused on use of electro-electrodialysis (EED) in which in a three-compartment stack, ions from waste salt are transported through the ion-exchange membrane toward the corresponding electrode compartments, where they

recombine with ions generated by water electrolysis to form products – acid and base. EED enabled the conversion of waste Na_2SO_4 solutions into sulfuric acid and sodium hydroxide, up to 15%. Such products can possibly be re-used in the neutralization process that generates the waste Na_2SO_4 solution or within the plant. However, the efficiency of electromembrane salt splitting increases with the concentration of waste salt [3,6]. Pre-concentration for subsequent waste sodium sulfate processing can be done by a pressure-driven membrane processes that are increasingly being used in industrial separation technologies, especially regarding diluted solutions [9]. These continuous separation techniques can be carried out under mild conditions, have low energy consumption and can be easily scalable and integrated with other unit processes [9]. Such an integrated system not only enables high Na_2SO_4 removal efficiency, but also the reuse of water.

Nanofiltration (NF) seems to be the most suitable pressure-driven membrane process for pre-concentration of sodium sulfate [10,11]. Due to the presence of surface charge, the separation mechanism in NF is the combination of a molecular sieving characteristic of ultrafiltration, and a solution-diffusion mechanism found in reverse osmosis (RO), additionally including the Donnan exclusion of charged particles [9,12,13]. This complex mechanism is also the reason that performance of NF membranes, especially in the separation of mixtures, is hard to predict by a model. Surface charge of NF membrane, originating from fixed ionic groups incorporated in membrane structure, leads to a higher exclusion of multivalent ions, providing additional selectivity.

NF operates at pressures higher than micro- or ultrafiltration, but lower than RO, and is preferred over RO due to additional separation of multivalent from monovalent ions. The retention of ions by NF membrane is strongly dependent on functional groups of membrane, its surface charge density and on pH and concentration of solution [14–16]. Typically, the rejection of divalent ions of the same charge as the membrane is above 95%, thus high retention of SO_4^{2-} is achieved, especially in diluted solutions [17–20]. Retention of sulfates decreases with feed concentration. Rejection of Na_2SO_4 is mostly the result of repulsion between surface functional groups with negative charge and sulfates from the feed solution and thus retention increases with surface charge [21]. However, this can be decreased by a shell of cations in highly concentrated solutions [22].

The aim of this work was to asses the applicability of nanofiltration to concentrate waste sodium sulfate solutions as a pre-concentration step for further processing by electro-electrodialysis. In experiments performed at lab and module scale, we investigated the effect of module configuration, transmembrane pressure, concentration and hydrodynamic conditions on transmembrane flux and retention of Na_2SO_4 during concentration of waste solution originating from catalyst production.

2. Experimental

Two commercial nanofiltration membranes were used: NF-270 and MPS-34, their properties and operating limits, as given by manufacturers, are presented in Table 1.

Table 1
Properties and operating limits of NF membranes used in the study

	Filmtec NF-270	SelRO MPS-34
Producer	DOW FilmTec	KOCH Membrane systems
Membrane type	Polyamide thin-film composite	Proprietary composite
MWCO, Da	1000	200
p max, bar	41	35
pH operation range	2–11	0–14
T max, °C	45	50
Feed requirements	<5 SDI, <0.1 ppm Cl2	<1 NTU
Max. feed flow rate, l/min	23 (for 2540 modules)	19 (for 2540 modules)

The nanofiltration was conducted in batch mode with feed recirculation. Experiments were performed in the installation presented in Fig. 1, both a flat sheet and spiral wound configuration was used for each membrane; experimental conditions are given in Table 2. Linear flow velocity was in the range 0.1–0.4 m/s. Sulfates were determined by the precipitation method and Na_2SO_4 concentration was calculated based on sulfates. During the NF process, salt concentration increased gradually, but did not exceed 10 wt% Na_2SO_4.

As a pre-treatment before NF processing, filtration of waste solution through 5 and 1 µm candle filters was used to remove any solid particles. For lab-scale experiments this pretreatment was sufficient and no flux decline due to fouling/scaling was observed. After experiments, membranes were rinsed with demineralised water.

In experiments to determine the effect of linear flow velocity on permeation flux, model Na_2SO_4 solutions were used, prepared from analytical grade salt (POCH, Poland). For experiments with NF-270 membrane, both at lab and module scale, the feed was waste Na_2SO_4 solution originating from Fe–Cr catalyst production. Prior to discharge, this waste solution was alkalized and filtered, thus metallic contaminants are mostly removed, to trace levels. The processed waste solution contained 2.6 wt% of Na_2SO_4 and had a pH of about 9. For experiments with MPS-34, the feed was permeate collected from NF-270, as preliminary research
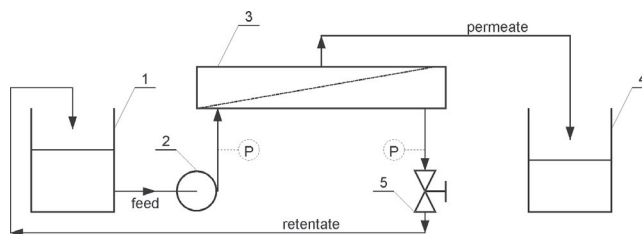

Fig. 1. Scheme of the experimental NF installation. 1- feed recirculation tank, 2-pump, 3-membrane module, 4-permeate tank, 5-pressure control valve.

Table 2
Experimental conditions

Scale	Laboratory	Module
Configuration	Flat-sheet	Spiral-wound
Membrane type	NF–270, MPS–34	NF–270, MPS–34
Module	Sepa CF II (Sterlitech Corp., USA)	Type 2540: length 40", Diameter 2.5"
Membrane active surface area, m²	0.014	2.6 (NF–270) 1.6 (MPS–34)
Applied trans-membrane pressure, bar	10–40	10–40
Operation mode	Batch	Batch
Initial feed composition	2.6 wt% of Na₂SO₄, pH c.a. 9	2.6 wt% of Na₂SO₄, pH c.a. 9
Initial feed volume, liters	4	100
Feed temperature, °C	30	35

Fig. 2. Permeation flux through investigated NF membranes as a function of transmembrane pressure.

demonstrated unacceptably low permeate flux for solutions containing above 2.6% Na₂SO₄. In both experiments, feed was thermostated.

3. Results and discussion

To apply nanofiltration to concentrate solutions of sodium sulfate, we investigated the effect of membrane module configuration, transmembrane pressure, concentration and hydrodynamic conditions on transmembrane flux and retention of Na₂SO₄. The initial study was conducted at a lab scale to characterize the performance of membranes (Section 3.1) and the results were verified at spiral-wound modules (Section 3.2).

3.1. Membrane performance

Performance of the NF separation process is characterized by two main parameters: permeation flux and retention coefficient, both membrane-dependent. The first, defined as the volume of permeate flowing through the membrane per unit area per unit time, describes the process productivity. Retention factor (R) describes membrane and process selectivity:

$$R = \frac{C_n - C_p}{C_n} = 1 - \frac{C_p}{C_n} \tag{1}$$

where C_n – concentration of Na₂SO₄ in the feed stream; C_p – concentration of a Na₂SO₄ in the permeate.

3.1.1. Productivity: permeation flux

Permeability of membranes was determined in a Sepa flat sheet module with deionized water as a feed solution. Fig. 2 shows the flux as a function of transmembrane
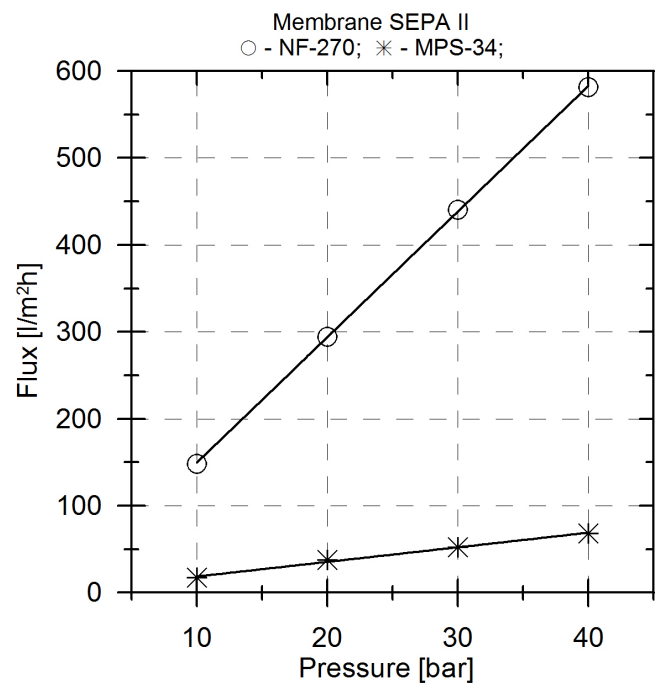
pressure. Permeation flux in both cases is proportional to the driving force (transmembrane pressure). The investigated membranes differ in structure, expressed by molecular weight cut-off (MWCO). This parameter–the lowest molecular weight of solute in which 90% of the solute is retained by the membrane – is often used to approximate the "density" of membrane's structure. As can be expected, more dense MPS-34 membrane (characterized by lower MWCO, 200 Da) is less permeable and the flux is smaller than through NF-270 (with MWCO of 1000 Da).

Permeation flux measured for water is the highest possible flux under applied transmembrane pressure. The presence of solute greatly reduces the flux, building up osmotic pressure, which decreases effective pressure, that is transmembrane pressure minus the osmotic pressure and permeate pressure. Osmotic pressure of Na₂SO₄ solutions can be calculated in a wide range of concentrations by the following equation [23]:

$$\pi = 0.246 \frac{RT}{V_w} \omega^{0.95} \tag{2}$$

where R – gas constant (8.314 J/(mol·K)), T – absolute temperature (K), V_w – molar volume of water (1.8·10⁻⁵ mol/m³), ω – mass fraction of Na₂SO₄ in solution (kg/kg).

To achieve acceptable flux through MPS-34 membrane, permeate from NF-270 was used as a feed, not the original waste solution (as in case of NF-270). Figs. 3 and 4 show the effect of transmembrane pressure and concentration on flux for Na₂SO₄ solution for NF-270 and MPS-34 membranes, respectively.

The flux decreases in a non-linear way with increasing concentration of Na₂SO₄ in a feed due to the increasing role of concentration polarization: mass accumulation
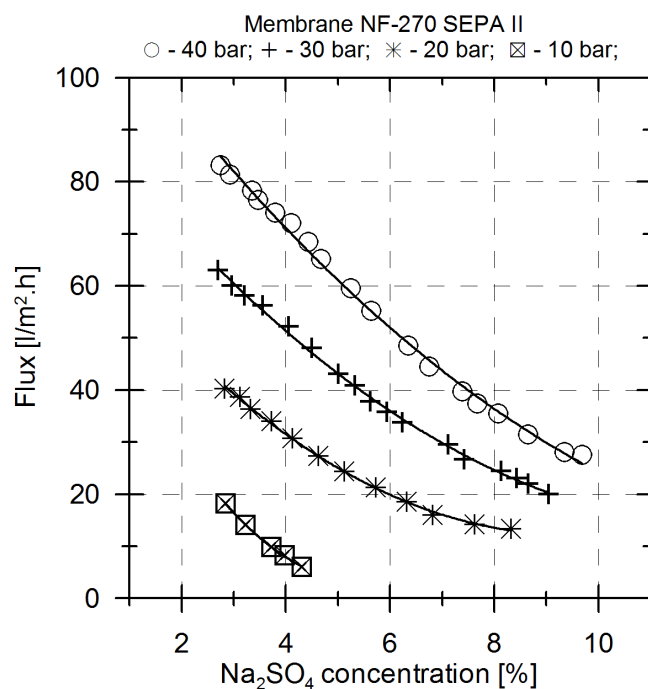
Fig. 3. The effect of transmembrane pressure and feed concentration on permeation flux for NF-270 membrane. Linear flow velocity 0.2 m/s.
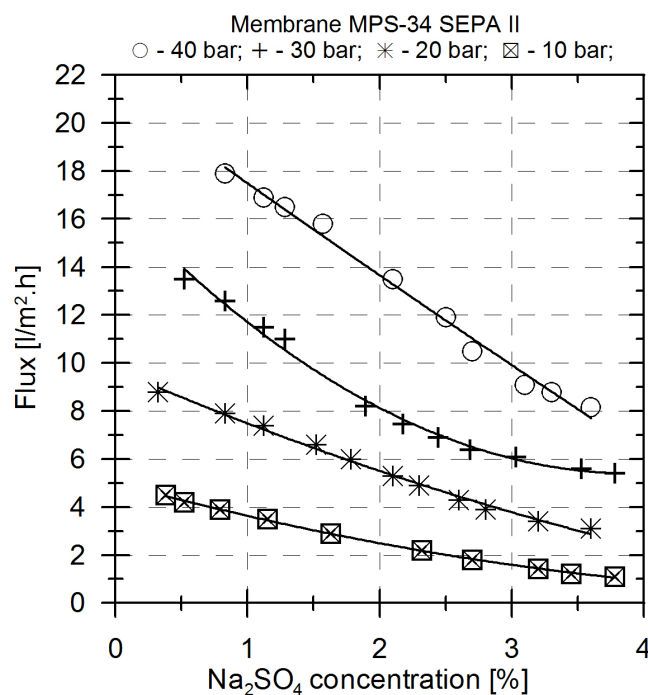

Fig. 4. The effect of transmembrane pressure and feed concentration on permeation flux for MPS-34 membrane. Linear flow velocity 0.2 m/s.

on membrane surface hinders permeate flux by increasing osmotic pressure difference across the membrane and thus decreasing driving pressure [24,25]. Minimizing concentra-

tion polarization is one of the most important objectives in designing and engineering membrane separation systems. A few approaches can be applied to improve hydrodynamic conditions to increase mixing at the membrane surface, among them are: increasing linear flow velocity, increasing the temperature, using pulsating flow, modifying the surface of a spacer or membrane, introducing gas bubbles or ultrasounds [24]. We investigated the effect of linear flow velocity on permeation flux for four various feed concentrations (Fig. 5 and 6).

Flow velocity affects the thickness of the boundary layer: the higher the cross flow velocity, the thinner the boundary layer and resulting concentration polarisation. As can be seen in Figs. 3 and 4, for low pressures and diluted solutions, permeate flux is proportional to the driving force – the applied transmembrane pressure. When transmembrane pressure is high and feed is concentrated, the retentate flux does not increase linearly with pressure. The transport across NF membrane is limited by the resistance of the boundary polarization layer. Increasing the linear flow velocity decreases thickness of the boundary polarization layer, thus the resistance of mass-transport approaches value resulting from the properties of the membrane itself. As in Figs. 5 and 6 for both membranes in study increasing the retentate linear flow velocity above 0.2 m/s does not further affect the flux. To minimize the concentration polarization, feed linear flow velocity should be maintained at 0.2 m/s.

3.1.2. Selectivity: salt retention

Molecular weight cut off can be used to characterize the structure of NF membrane and predict the flux. However, rejection of ionic components is mainly the result of electrostatic repulsion between the fixed ions on NF membrane surface and the ions from solution [9,12]. Nevertheless, for tight NF membranes, size exclusion can provide an additional effect [12,13]. The effect of concentration and pressure on the Na_2SO_4 retention is shown in Figs. 7 and 8. For both membranes in the study, retention of salt increases with transmembrane pressure (by 10–20% in tested range 10–40 bar), but also a steep and non-linear decrease in retention with concentration is observed. With an increase in concentration and decrease in transmembrane pressure, the permeate contains more salt, and instead of water recovery, additional waste is being generated, not meeting salt discharge limits.

3.1.3. The effect of concentration

Typically, the rejection of a sulfate ion approaches 95%, although at lower concentrations than reported herein [12,17]. For NF-270, membrane, salt retention when feed concentration reaches 8 wt% dropped to c.a 55–70%, for pressure in the range of 10–40 bar, respectively.

In the case of membranes with surface charge, this effect is attributed to decrease in charge density of the membrane (repulsive forces, Donnan exclusion) by either (i) screening of the membrane's fixed ions by counter-ions from the solution, (ii) distortion of the surface charge of the membrane, (iii) distortion of dielectric exclusion, (iv)
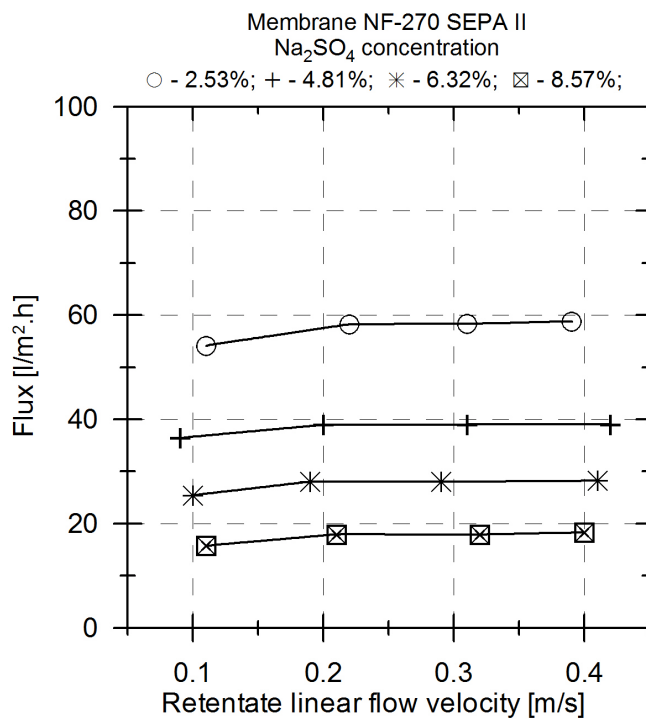
Fig. 5. The effect of feed concentration and retentate linear flow velocity on permeation flux for NF-270 membrane, pressure 30 bar.
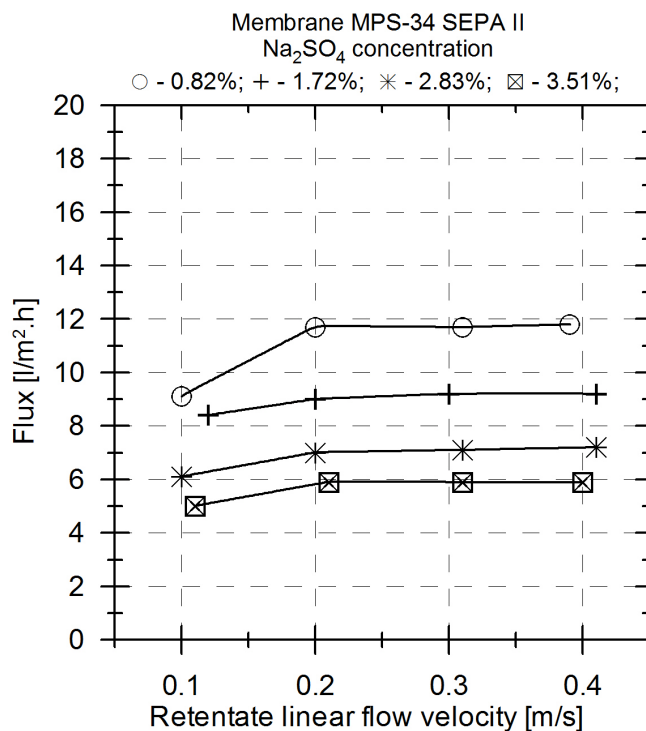

Fig. 7. The effect of concentration and pressure on the Na_2SO_4 retention for NF-270 membrane.

Fig. 6. The effect of feed concentration and retentate linear flow velocity on permeation flux for MPS-34 membrane, pressure 30 bar.
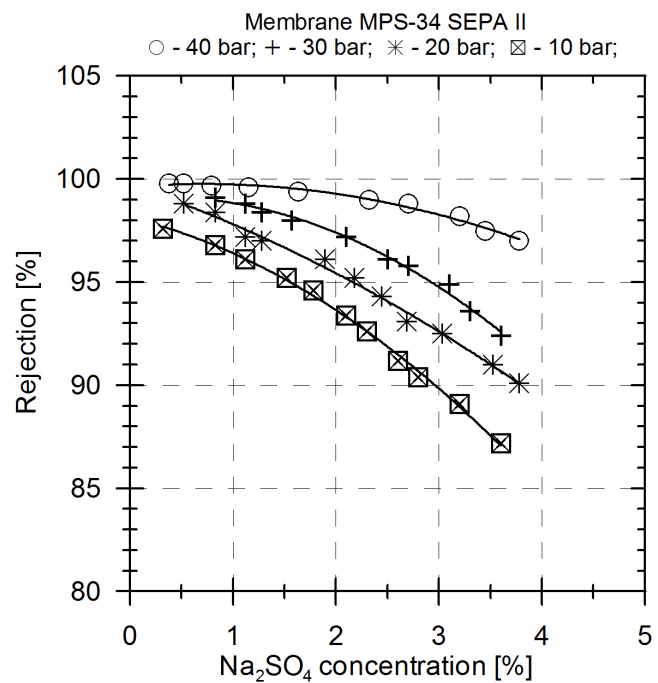
Fig. 8. The effect of concentration and pressure on the Na_2SO_4 retention for MPS-34 membrane.

adsorption of ions from the solution [14,26]. As salt transport is less hindered by the membrane charge, the retention decreases.

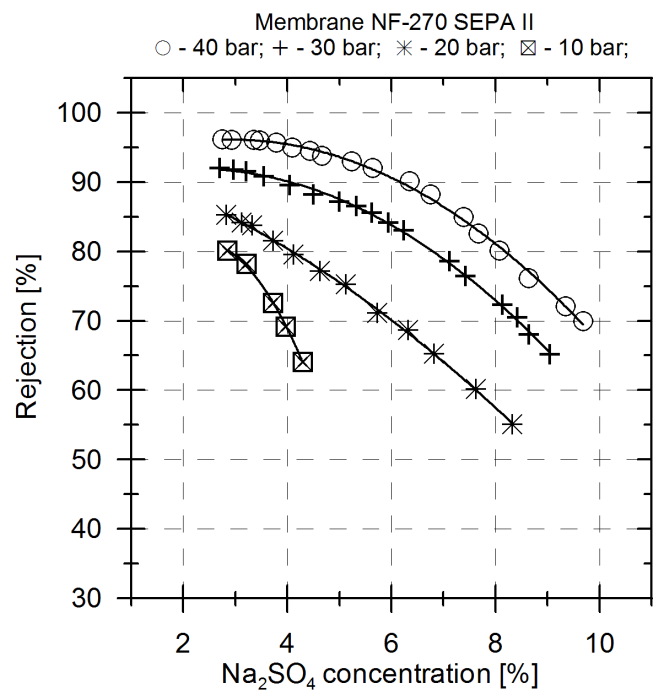### 3.1.4. The effect of effective pressure on permeation flux

The driving force of membrane filtration is a pressure difference across the membrane. The effective pressure is the difference between applied pressure and osmotic pressure difference between the feed and permeate:

$$P_{effective} = \Delta P - \Delta \pi \qquad (3)$$

Due to concentration polarization mass is accumulated at the membrane surface and concentration locally increases. Differences of osmotic pressure across membrane increase, reducing effective (driving) pressure and therefore, the permeate flux.

The effect of effective pressure difference on the permeation flux for NF-270 and MPS-34 in a flat-sheet membrane module configuration is presented in Figs. 9 and 10, respectively. The osmotic pressure was calculated according to Eq. (2). Within applied pressure range (10 to 40 bar), at low retentate concentrations (up to 3.0% and 1.5% respectively) dependence has linear character. Under these conditions, the permeation flux depends on the membrane permeability. Along with increasing concentration, permeation flux decreases and dependence diverge .

3.2. Two stage NF concept and module-scale results

Salt concentration and membrane structure are the crucial factors limiting the effectiveness of concentration of waste Na_2SO_4 solution by affecting both the productivity (Figs. 3 and 4) and the selectivity (Figs. 7 and 8) of the process. The tested NF membranes differ in properties and structure. NF-270 is highly permeable with rather low salt retention, especially in the case of a more concentrated feed. The fluxes obtained with MPS-34, under comparable transmembrane pressure and feed concentration (2.6–4%), were clearly lower but salt retention was higher. Also, from data presented in section 3.1, simultaneously maintaining high salt concentration in the retentate and low in the permeate is impossible. This can be overcome by two-stage NF. In the first stage, membranes with higher MWCO should be used to efficiently concentrate the effluent and maintain high permeate flux. The concentration of salt in the retentate after the first stage is suitable for further Na_2SO_4 processing, e.g. by electro-electrodialysis [3,6]. Permeate from the first stage contains significant amounts of salt and is directed to the second stage, where NF membranes with lower MWCO are used. It is preferred to use NF instead of RO in the second stage, due to additional rejection of sulfates (as multivalent ions) and higher permeability, resulting in higher permeate flux under the same applied pressure. Permeate from the second stage meets the discharge limits and retentate is returned to the first stage of NF separation. This concept was verified at bench scale with industrial, spiral wound membranes.

3.2.1. Performance of spiral wound membranes

The effect of concentration and transmembrane pressure on permeation flux for NF-270 2540 and MPS-34 2540 membranes is presented in Figs. 11 and 12, and on retention in Figs. 13 and 14, respectively. Permeation flux increases significantly with transmembrane pressure and decreases with feed concentration. Salt retention increases with pressure and decreases with feed concentration. The mechanism is the same as described in paragraph 3.1: concentration polarization and decreased repulsion. More interesting is that for both membranes tested, their performance in a flat-sheet and spiral wound configuration were similar, in terms of both per-
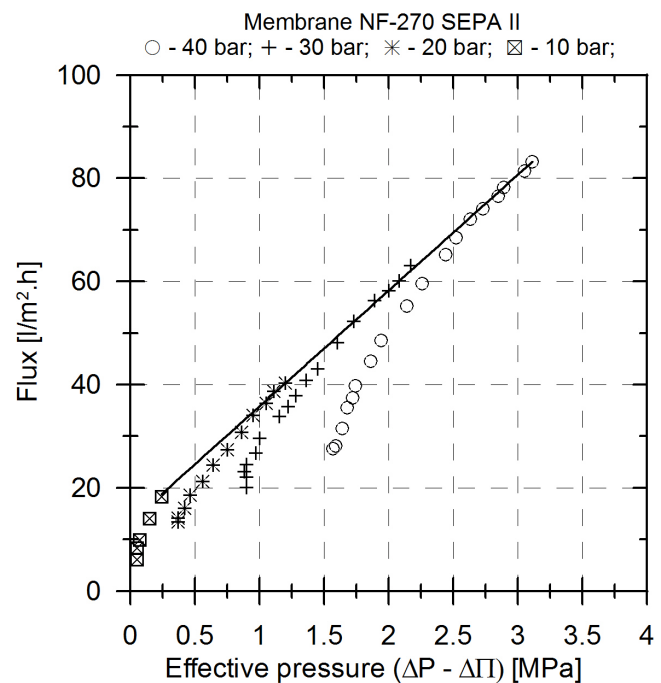

Fig. 9. The effect of effective pressure on the permeation flux for NF-270 membrane. Linear flow velocity 0.2 m/s.
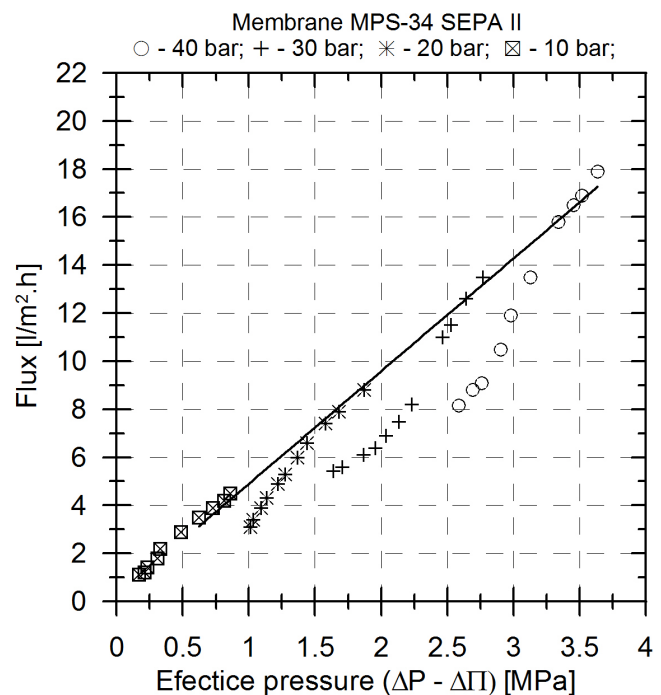

Fig. 10. The effect of effective pressure on the permeation flux for MPS-34 membrane. Linear flow velocity 0.2 m/s.

meation flux and salt retention. This is despite differences in hydrodynamic conditions in both configurations [27]. Similar conclusions were drawn in [28,29], where flat-sheet and spiral wound configuration performance was compared, (albeit in a much lower concentration range), and indicates that lab-scale experiments remains useful to designing a full-scale plant.
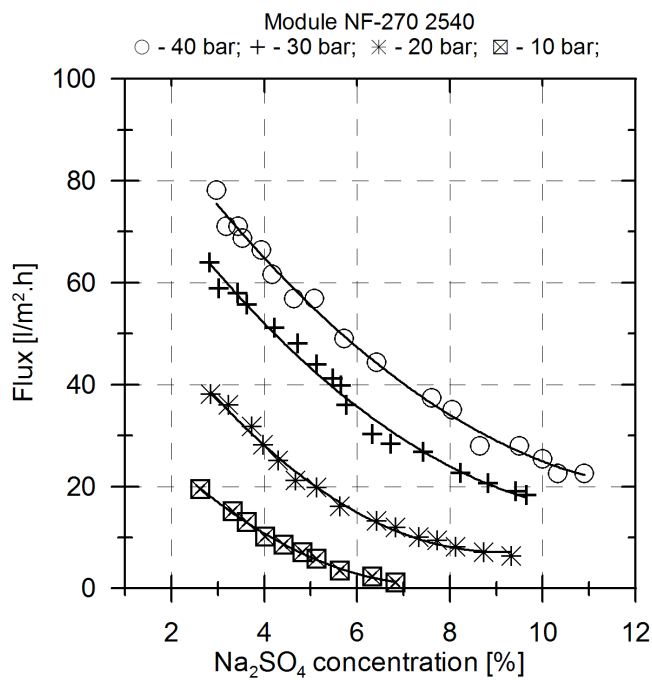
Fig. 11. The effect of transmembrane pressure and feed concentration on permeation flux for NF-270 2540 membrane module.
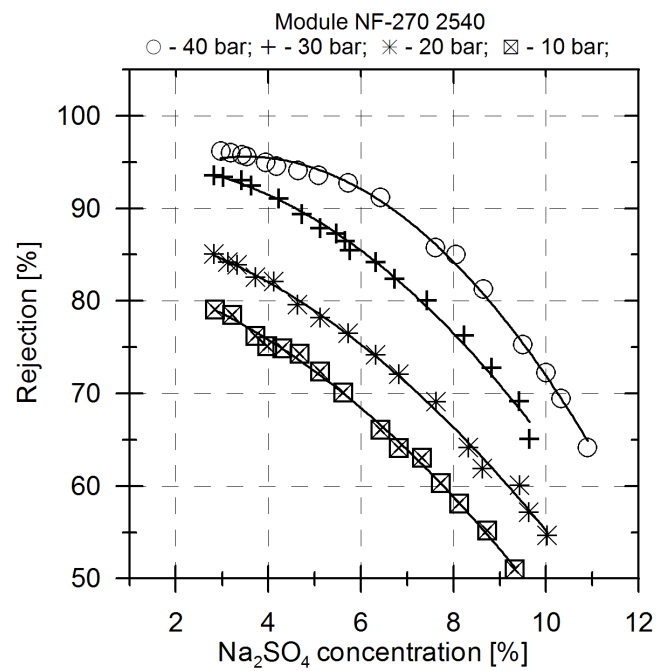
Fig. 13. The effect of concentration and pressure on the Na_2SO_4 retention for NF-270 2540 membrane module.
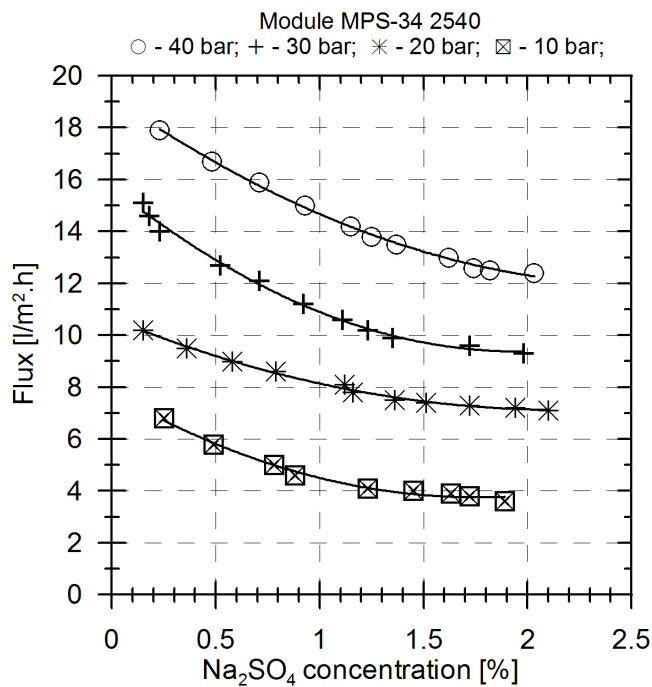
Fig. 12. The effect of transmembrane pressure and feed concentration on permeation flux for MPS-34 2540 membrane module.
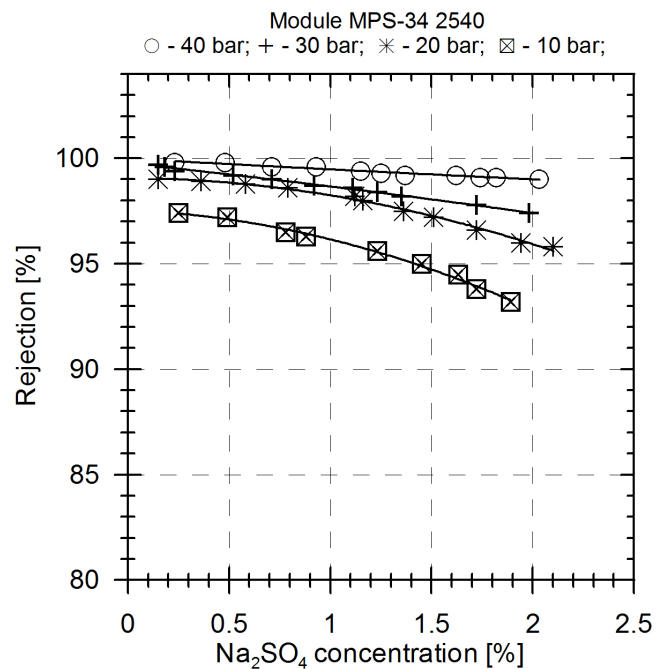
Fig. 14. The effect of concentration and pressure on the Na_2SO_4 retention for MPS-34 2540 membrane module.

3.2.2. Integrated system for treatment of waste Na_2SO_4 solution

EED allows for the splitting of waste salt and recovery of the acid and base from which this salt originate; the performance of this process and concentration of acid and base possible to obtain increases with concentration of waste salt [3,6].

A two-stage NF concentration can be incorporated into an integrated system with EED to concentrate both waste solution and effluent from EED. Such a NF system is comprised of three basic operations, as shown schematically in Fig. 15:

- Feed preparation: waste solution originating from catalyst production (2.6 wt% of Na_2SO_4) is mixed with

diluate from the EED process and retentate from the 2nd stage of NF and used as a feed for the 1st NF stage. A microfilter is used to prevent solid particles from entering the NF module.

- 1st stage of NF (concentration): an averaged solution from the feed preparation step is used as a feed in this stage. NF-270 (MWCO 1000 Da, DOW FilmTec) spiral wound membrane is used. Permeate (1 wt% of Na_2SO_4) is sent to the 2nd stage of NF. Retentate is mostly recirculated, the part with a concentration of 8 wt% of Na_2SO_4 is sent to EED.
- 2nd stage of NF (purification): the aim of this stage is to demineralize water to levels meeting national discharge standard requirements. Retentate form the 1st stage is used as a feed and MPS-34 (MWCO 200 Da, KOCH) spiral wound membrane is used. Retentate (2.6 wt% of Na_2SO_4) is partially recirculated to the 1st NF stage, permeate (<0.3 g/l Na_2SO_4) can be used as process water.

In the proposed process, the only products are: concentrated sodium sulfate solution directed to the EED stage, and a permeate with low salt content, which can be re-used, e.g. for the preparation of solutions or in the production of deionized water. The overall recovery rate of Na_2SO_4 exceeds 95%. The mass balance of the process is shown in Table 3. As the balance unit, 1000 kg of a waste sodium sulfate solution originating from catalyst production (2.6 wt% of Na_2SO_4) was used.
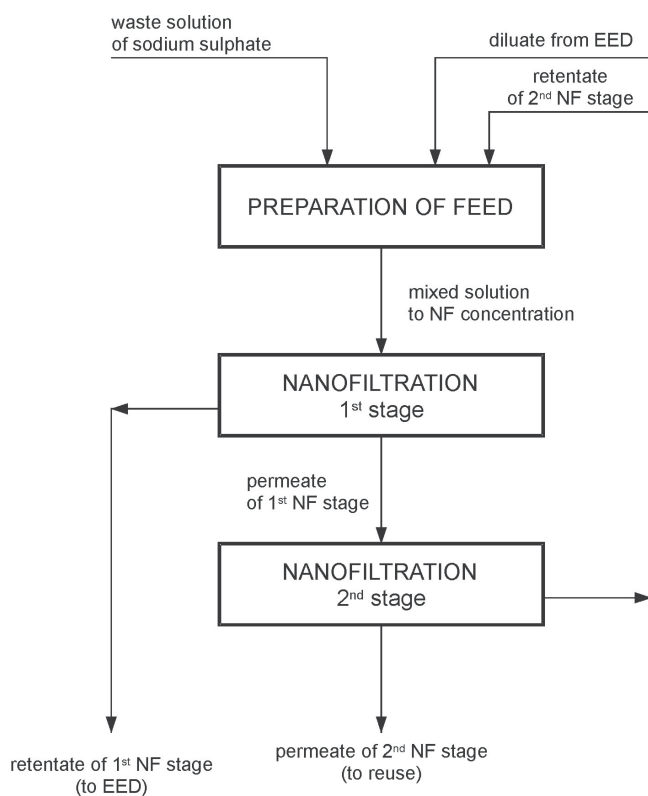

Fig. 15. Schematic diagram of the two stage NF process for concentration of waste Na_2SO_4 solution.

Table 3
Mass balance of waste sodium sulfate concentration by two stage NF

Operation, stream	Total, kg	Compound, kg	
		Na_2SO_4	H_2O
Feed preparation, inlet	1 762	46	1 716
– waste soln. of Na_2SO_4	1 000	26	974
– retentate of 2nd NF st. (to 1st NF st.)	422	11	411
– diluate from EED	340	9	331
Outlet	1 762	46	1 716
– mixed soln. to NF concentration	1 762	46	1 716
Nanofiltration 1st stage, inlet	1 762	46	1 716
– mixed soln. to NF concentration	1 762	46	1 716
Outlet	1 762	46	1 716
– retentate of 1st NF st. (to EED)	433	35	398
– permeate of 1st NF st.	1 329	11	1 318
Nanofiltration 2nd stage, inlet	1 329	11	1 318
– permeate of 1st NF st.	1 329	11	1 318
Outlet	1 329	11	1 318
– retentate of 2nd NF st. (to 1st NF st.)	422	11	411
– permeate of 2nd NF st. (to reuse)	907	0	907

4. Conclusions

Reducing salt discharge to the environment is important from both an economical (fees for discharge of salts paid by industrial emitters) and ecological (reducing mineralization of surface waters) point of view. This can be done more easily by coupling various separation processes. In this study, nanofiltration was successfully applied to concentrate the waste sodium sulfate solution originating from catalyst production. A lab-scale frame-plate module was used to characterize the performance of selected NF membranes. Both permeation flux and salt retention was found to decrease significantly with feed concentration. To maintain the high permeation flux at higher feed concentration, higher transmembrane pressure has to be applied. To achieve a high concentration of concentrate (up to 10 wt%) and low salt content in permeate (below 0.3 g/l Na_2SO_4), a two-stage NF process was proposed. Such a process can be used in a wide range of feed concentrations as a pre-concentration step for subsequent waste solution processing. In the proposed solution, further processing includes electro-electrodialysis (EED) to recover the originating acid and base. The feed is 2.6 wt% solution of Na_2SO_4. Retentate from the 1st NF stage (c.a. 8 wt% Na_2SO_4), the main product of NF concentration unit, is directed to EED processing. Permeate is directed to the 2nd NF stage,

where it is further demineralized to generate water meeting national discharge standard criteria and concentrate, which is recirculated into the 1st NF stage. In an integrated NF-EED system for waste treatment, the overall recovery and conversion rate of Na_2SO_4 exceeds 95%. The obtained results can be the basis for the design and construction of a pilot scale installation for the concentration and treatment of waste sodium sulfate solutions.

Symbols

C_n	–	Concentration of Na_2SO_4 in the feed stream;
C_p^n	–	Concentration of a Na_2SO_4 in the permeate
R^p	–	Gas constant (8.314 J/(mol·K))
T	–	Absolute temperature (K)
V_w	–	Molar volume of water ($1.8 \cdot 10^{-5}$ mol/m³)
ω	–	Mass fraction of Na_2SO_4 in solution (kg/kg)
ΔP	–	Transmembrane pressure (MPa)
$\Delta\pi$	–	Transmembrane osmotic pressure (MPa)

Acknowledgements

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