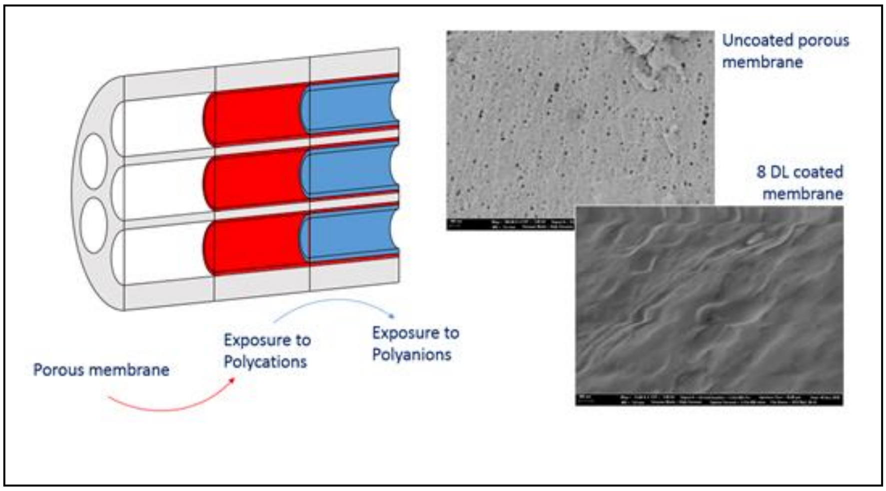
2.2 SULEMAN: Treatment of Groundwater with increased Sulfate Concentration – Innovative options and limits of a resource and energy efficient drinking water management



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Introduction

Increased sulfate (SO_4^{2-}) concentrations in raw waters for drinking water applications can be an upcoming challenge for water suppliers. Current commercially available processes for the reduction of the sulfate content are low pressure reverse osmosis (LPRO)/nanofiltration (NF) and ion exchange (IE). These technologies though, can cause high specific energy consumption and can be challenging to estimate regarding process stability and cost development.

Research Goals

Aim of the project is to provide reliable statements on sulfate removal of the currently available technologies, based on experimental data from pilot plants. Furthermore, an innovative membrane process is developed by modification of ultrafiltration (UF) hollow fiber membranes, which combines advantages of NF with those of a UF process. All processes are evaluated through life cycle assessment.

Approach

For the development of the innovative membrane, UF hollow fiber membranes (Multibore® membranes, DuPont, inge GmbH) are modified using the Layer-by-Layer (LbL) technique. During the modification process, the virgin membrane with a negative surface charge is first exposed to a polycationic solution (1 g/L poly-diallyl-dimethylammonium chloride (PDADMAC, molecular weight 400-500 kDa, Sigma-Aldrich Inc.) in 0.1 M NaCl) for 10 min. Due to electrostatic effects and the release of counterions into solution, polycations adsorb onto the membrane surface, leading to a positive surface charge. The membrane is then exposed to an anionic solution (1 g/L poly-sodium 4-styrenesulfonate (PSS, molecular weight 1000 kDa, Sigma-Aldrich Inc.) in 0.1 M NaCl), also for 10 min. These polyelectrolytes (PE) also adsorb onto the membrane surface, again leading to a charge reversal, resulting in a negative surface charge. Repeating this procedure allows to build up a dense polyelectrolyte multilayer (PEM) film on top of the active membrane surface, taking over the membrane separation properties. At the DVGW research centre TUHH, experiments are conducted in lab scale to identify influencing factors during modification and filtration. Furthermore, membrane modules (15 fibers with 7 capillaries and 1.5 m length) are operated in pilot scale in waterworks to allow reliable statements about the long-term behaviour and stability.

Recent Results

In lab scale, the modified membranes showed good SO_4^{2-} rejection (~ 90 %) and permeability (~ 15 L/(m² h bar)) in the range of commercially available NF-membranes. To evaluate the long-term behaviour, the pilot plant was connected to partially treated water after aeration and sand filtration in a Hamburg waterworks. Selected water parameters for the inlet of the plant and operational parameters for three trial periods are listed in table 1 and table 2 respectively.

Table 1: Selected water constituents for the inflow to the pilot plant in mg/L; average values for n=14 throughout trial periods P 1 - 3

Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	SiO_2	K^+	HCO_3^-	Sr^{2+}	$Ks_{4,3}$	TDS
54.5 +/- 4.7	280 +/- 16	167 +/- 6	10.0 +/- 0.2	30.3 +/- 2.2	21.0 +/- 0.1	2.6 +/- 0.0	156 +/- 24	0.7 +/- 0.0	2.9 +/- 0.0	589 +/- 85

Table 2: Operation parameters for the three different trial periods (P1-3); CF-velocity: mean crossflow velocity between membrane inlet and outlet; WCF: Water conversion factor; hydr. BW: interval of hydraulic backwash

Period		1	2	3
Flux	L/(m² h)	30	30	30
CF velocity	m/s	1	1	0.6
WCF	%	75	75	75
hydr. BW	1/d	0	2	2

Figure 1 shows rejections for selected substances in regard of the feed concentration at the inlet of the membrane capillaries (left), and the applied TMP and permeability (normalised to 25 °C) (right).

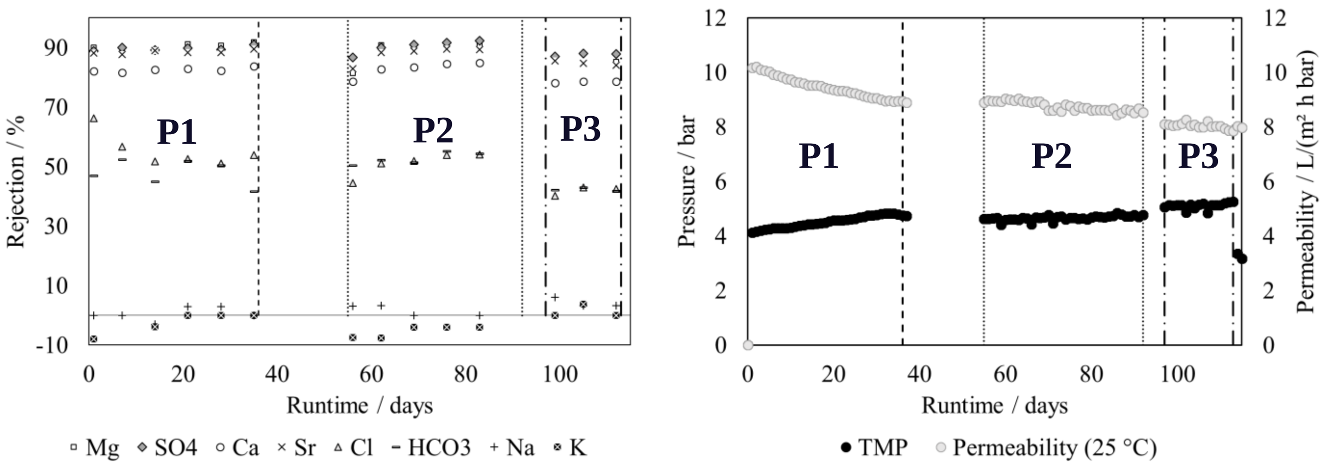

Figure 1: Removal efficiency for different ions (left), and transmembrane pressure (TMP) and permeability (normalised to 25 °C) (right) during operation in the waterworks; operation parameters for the different periods (P1-3) are listed in table 2.

SO_4^{2-} rejection in the pilot tests with a real water matrix reached similarly high rejection as lab scale tests with ~ 90 % in the first trial period. Additionally, other divalent ions were also rejected to a high extend (85 – 90 %), while monovalent anions showed rejection rates of approx. 50 %. Monovalent cations were either not rejected or even showed negative rejection due to the Donnan-Effect. The TMP increased during the first phase, while permeability decreased. This could be attributed to accumulations of mostly inorganic foulants (i.e. $BaSO_4$) on the membrane surface.

During the second period, the membranes were hydraulically backwashed (hydr. BW) in a regular interval of 12 hr. This hydr. BW did not influence the membrane rejection behaviour, indicating that the LbL layer remained stable. Additionally, as TMP increase and permeability decrease could be mitigated, hydr. BW did show a positive influence on process stability.

In the third period, the crossflow (CF) velocity was reduced from 1 m/s to 0.6 m/s, which caused a rejection decrease of divalent ions and monovalent anions. The rejection decrease is attributed to the effect of concentration polarization (CP). Due to the laminar flow, a concentration gradient builds up for rejected ions from the bulk feed solution to the membrane surface (CP). It is directly dependent on the CF velocity, with an increasing CP and increased ion concentration at the membrane surface at decreasing CF velocity. Increased concentrations also lead to a higher osmotic pressure, counteracting against the applied TMP. Therefore, the TMP increased, when decreasing the CF velocity in P 3.

Conclusion and Outlook

LbL modified membranes could be operated with real water matrix over several months. Hereby, high sulfate, as well as other divalent ion rejection was achieved. Hydraulic Backwash was beneficial to achieve a stable process and mitigate permeability decrease. However, the rejection behaviour did show an influence related to the CF velocity. Therefore, the influence of CF velocity on the membrane operation and rejection behaviour for different substances is part of ongoing investigations.

Project Partners

Project Coordination

DVGW
DVGW-Forschungsstelle TUHH
Technische Universität Hamburg

Project Partners

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