Report on material properties of conductive membrane for optimal disinfection by-product precursor removal

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08.07.2024 page 2	To address the reviewers' comment: "When updating the deliverable, please include in the history of changes where and what have been added comparing to the initial version of the deliverable. This will facilitate to review the deliverable": Previous "History of Changes" renamed to "History of Versions". "History of Changes" added.
08.07.2024, page 3, Abstract	To address the reviewers' comment "The abstract should be reviewed. It rather stands as an introduction than a summary", the abstract has been thoroughly reviewed and revised to ensure it serves as a concise summary rather than an introduction to better align with the expectations of an abstract.
08.07.24 page 23, 5. Conclusion	A conclusion was incorporated to address the reviewer's comment that "a conclusion should be added."
08.07.24 page 11 & 23, Section 2.5 & 4.1	To address the reviewers' comment: "The report should be reviewed to better outline how the analysis provided in D. 2.2 relates to Tasks 1.1. and 1.2, as per the description of Task 2.2 in the DoA." the material and methods section 2.5 was revised, with an emphasis on the methods used to quantify NOM, highlighting the relationships to the methods developed in WP1. Additionally, section 4.1 was introduced to provide an overview of the membrane's selective NOM removal performance using the previously introduced methods.
08.07.2024 page 10, Section 2.4	To address the reviewers comment: "There is currently a wide range of membranes available on the market, with a high level of maturity. As such, it would also be useful to include a short description on how the membranes were selected." a new paragraph was added explaining the choice of the membranes concerning the intended membrane characteristics affecting the process.

Abstract

In this deliverable, we present findings on the optimal material properties for an adsorptive innovative membrane process with chemical-free regeneration methods. The focus is on utilizing membrane adsorbers to remove the main precursor of disinfection by-products: Natural Organic Matter (NOM). Our study explores the development of nanolayer metal-coated membranes enabling electrically driven adsorptive and desorptive processes that allow for sustainable regeneration without the use of neutral salts. Additionally, the use of external electrodes as an alternative to coating is investigated, offering promising enhancements to the membrane process.

This study focusses into the critical aspects of the membrane adsorbers' properties. Results indicate that a positive zeta potential is advantageous during NOM adsorption, whereas a negative zeta potential led to benefits in regeneration due to weaker bonds of NOM and ion exchange groups of the membrane. External electrodes emerged as more superior compared to nanolayer duplex-coated membranes, particularly when paired with a weakly basic membrane adsorber, unlike strongly basic adsorbers which did not support successful desorption.

The optimal setup identified includes the commercial Sartobind® D membrane adsorber, functionalized with dimethylamines (proto- and deprotonable, isoelectric point 9.1), combined with a graphite fleece working electrode and a sintered steel permeate carrier counter electrode. The membranes pore size (3-5 µm) allows for a purely adsorptive process without steric retention, reducing energy requirements due to high permeability (10,800 L h^{-1} m^{-2} bar^{-1}). Contact angle measurements revealed hydrophilicity with a value of 34.1 °.

Overall, our findings underscore the significant potential of innovative membrane processes with chemical-free regeneration methods for efficient NOM removal, offering a sustainable and effective approach to water treatment.

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Table of contents

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Abbreviations

Ag	Silver
Au	Gold
DBP	Disinfection By-product
DI	Deionized
ECM	Electrically Conductive Membrane
EDA	Ethylenediamine
GA	Grant Agreement
GF	Graphite Felt
EC	European Commission
EDL	Electric Double Layer
e-sorptive	Electro-sorptive
IEP	Isoelectric Point
MF	Microfiltration
MWCO	Molecular Weight Cut-Off
Ni	Nickel
NOM	Natural Organic Matter
PAN	Polyacrylonitrile
PEG	Polyethylene glycol
PES	Polyethersulfone
Pt	Platinum
PVDF	Polyvinylidene fluoride
PWP	Pure Water Permeability
SS	Sintered Steel
SSM	Stainless Steel Mesh
UF	Ultrafiltration

1. Introduction

Disinfection by-products (DBPs) in drinking water pose significant health risks (Richardson, 2003), with natural organic matter (NOM) being a primary precursor for their formation (Hua & Reckhow, 2007; Tak & Vellanki, 2018). Conventional approaches for NOM removal, including coagulation-flocculation, adsorption on activated carbon, and membrane filtration, often fall short due to incomplete NOM removal, high operational costs, and the generation of secondary waste (Matilainen, Vepsäläinen, & Sillanpää, 2010; Matilainen, Vieno, & Tuhkanen, 2006; Tak & Vellanki, 2018). Additionally, the selectivity-permeability trade-off in dense and porous membranes presents a challenge, as ultrafiltration (UF) and microfiltration (MF) offer high fluxes and low operational costs but do not significantly remove NOM (Lin et al., 2016; Siddiqui, Arif, & Bashmal, 2016).

Two innovative adsorptive electrically assisted chemical-free approaches have shown promise in addressing these challenges and are reported in this deliverable:

- Membrane Adsorbers with external electrodes
- Electrically Conductive Membranes (ECM)

Membrane Adsorbers with external electrodes

Functionalized membranes, such as those incorporating affinity and ion-exchange, offer rapid, reliable separation with high volumetric throughputs compared to traditional packed beds (Boi, 2007), making them suitable for a variety of applications including NOM removal. A novel approach for a chemical-free regeneration of these adsorbers includes the application of an electrical potential to external electrodes in close proximity to the membranes surface. The negative applied potential induces the desorption of previously adsorbed anionic compounds. The exact mechanisms underlying this desorption process are not fully understood yet, but potential factors may include electrostatic repulsion, disruption of electrostatic interactions, reduction of oxidized species, reversible electrochemical processes and potential local pH changes at the electrode and thus membrane surface.

Electrically Conductive Membranes (ECM)

The second approach involves rendering membranes electrically conductive to enhance NOM removal through electro-sorption. While various types of ECMs, such as carbon nanotubes and mixed matrix membranes, offer significant benefits for water treatment (Barbhuiya, Misra, & Singh, 2021; Sun et al., 2021; Z. Zhang et al., 2022), this report will specifically focus on the innovative use of duplex-coated membranes with gold and platinum, as developed by Mantel, Benne, Parsin, and Ernst (2018) Usman, Glass, Mantel, Filiz, and Ernst (2024): Coating membranes with platinum or gold, thus providing the necessary conductivity for electro-sorption (e-sorption) processes. This technique not only improves NOM removal efficiency through e-sorption but also mitigates membrane fouling, offering a promising solution to the challenges posed by conventional methods. In the process of e-sorption, charged substances within water, are attracted and bound to the interface of the electrode. This mechanism is distinguished from traditional adsorption by its reliance on the electric field, which exploits the variance in electrical charges. E-sorption can take place either within the electric double layer (EDL) or through a direct chemical connection to the electrode. A notable feature of this process is its reversible nature; substances that are electrochemically adsorbed at the surface of the electrode can revert to their initial state and release from the surface when the electrical potential is no longer applied.

Both approaches are designed to enhance NOM adsorption while minimizing chemical use for regeneration via electro-assisted techniques. The processes differ mainly in terms of when a potential is applied. The e-sorptive process applies a positive potential during adsorption and for regeneration. Then reversing the potential creates electro-repulsive forces, aiding in NOM detachment from the membrane. On the contrary, no potential is applied during adsorption when using non-coated membrane adsorbers with external electrodes. The application of a negative potential to the external electrodes during regeneration for non-coated membrane adsorbers induces similar forces and local pH changes at electrode surfaces with potential impact on desorption.

The purpose of this deliverable is to lay the foundational groundwork for the development of a chemical-free technique for the removal of NOM utilizing (electro-)sorptive membranes within Case Study #1. A critical initial step in this development process involves the selection of an appropriate porous membrane. This deliverable will detail the influence of material properties on the processes and properties of the chosen membrane, marking a significant phase in Task 2.2. By understanding the interplay between membrane characteristics and NOM removal & regeneration efficiency, safeCREWs case study site can better tailor these innovative approaches to meet the demands and address the limitations of conventional NOM removal methods.

The membrane's properties have been thoroughly analysed to assess their suitability for (electro)sorption processes and its potential efficacy in electrically induced NOM regeneration. This includes evaluating the base material used in the membrane support and filtration layer, examining surface morphology through SEM imaging, determination of the Molecular Weight Cut-Off (MWCO), measuring hydrophilicity via contact angle measurements, and determining intrinsic charge using zeta-potential analysis. Additionally, FTIR spectroscopy will be employed to assess membrane functionalization, providing insights into chemical composition and surface modification.

2. Material and Methods

The experimental set-ups and the application of electrical potentials of the two approaches in order to enhance the adsorption capacity and achieve chemical-free regeneration are to be further explained. The applied potentials during both adsorption and regeneration processes are depicted in Figure 1.

Firstly, duplex coated membranes were developed with the aim of augmenting the intrinsic adsorption capacity. This was achieved by applying an electrical potential to induce e-sorptive forces. In the case of duplex coated membranes, a cell potential of up to +2.5 V was applied during adsorption, while a cell potential of up to -2.5 V was employed during regeneration (Figure 1A).

Additionally, to achieve chemical-free regeneration, the alternative method utilizing external electrodes was implemented. Here, during adsorption, no potential is applied, and the removal is solely a plain adsorptive process due to the intrinsic adsorptive properties of the membrane adsorber. However, for regeneration, a consistent -2.5 V cell potential was applied to induce desorption of NOM through electro-repulsive forces (Figure 1B).

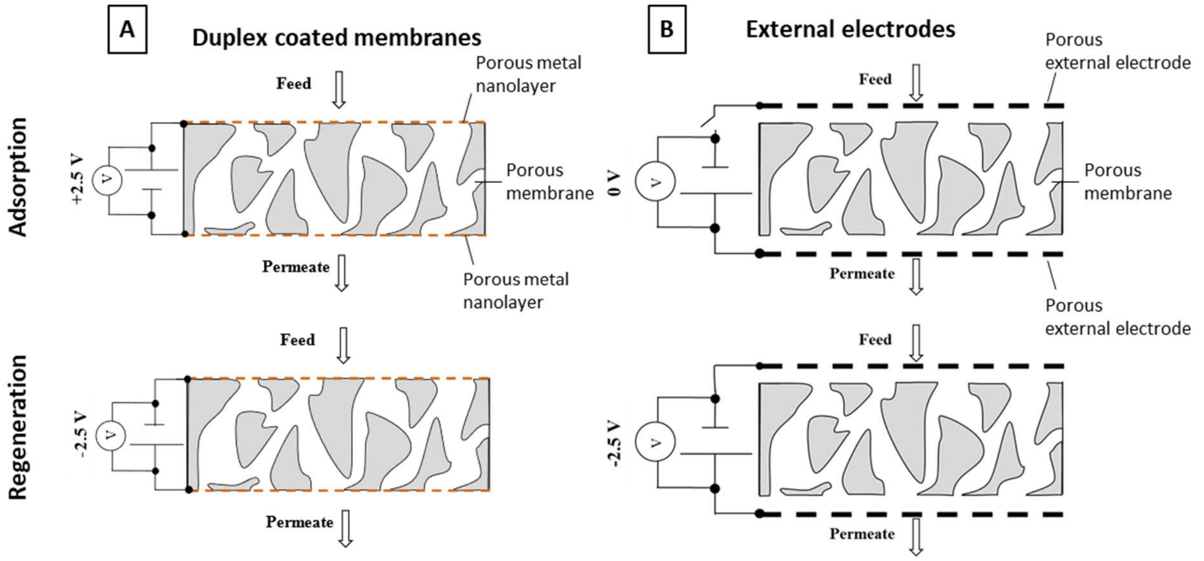

Figure 1: Depiction of applied potential during adsorption and regeneration processes for (A) Duplex coated membranes, employing a +2.5 V potential during adsorption and -2.5 V during regeneration, and (B) No external electrode potential applied during adsorption and utilizing -2.5 V for regeneration (adapted from Mantel (2022b) with modifications)

2.1. Fabrication of duplex coated EMCs

The fabrication of ECMs involved multiple processes utilizing four different metal coatings: Silver, gold, and platinum via sputter deposition, as extensively described in Mantel et al. (2018) and Usman et al. (2024) and a nickel coating technique adapted from Bell, Sengpiel, and Wessling (2020). While the coating process was successful for most membrane base materials, cellulose-based membranes exhibited a tendency to swell upon contact with water. Consequently, after the coating process and wetting of the membrane, detachment of the coating layer was observed due to swelling. To address this issue, the different technique, adapted from Bell et al. (2020), was employed for coating with nickel. This approach aimed to assess the performance of cellulose-based membranes as ECMs while mitigating the challenges associated with swelling-induced coating detachment.

2.1.1. Sputter Deposition Technique

A Sputter Coater SCD 005 (Baltec Inc., Balzers, Liechtenstein), a bench-scale sputtering device, facilitated the deposition of thin films through DC magnetron sputtering. This technique ensured uniform and controlled application of the coatings onto the membrane surfaces. Silver, gold and platinum were tested. An extensive description of the procedure can be found in Mantel et al. (2018) and Usman et al. (2024).

2.1.2. Nickel coating

Prior to coating with nickel, the membranes underwent a cleaning process to ensure optimal adhesion of the nickel. A degreasing solution consisting of sodium carbonate, sodium metasilicate pentahydrate, and sodium lauryl sulfate (all Carl Roth GmbH, Karlsruhe, Germany) in deionized water (DI) was used. Ultrasonic agitation was applied to thoroughly clean the membranes. The nickel was applied onto the membrane surfaces using an impregnating solution followed by a reduction solution as described in Bell et al. (2020). This ensured even distribution and adherence of the coatings. After coating application, the membranes were rinsed with pure water to remove any residual solutions.

2.2. External electrodes

In the investigation of external electrodes (see Figure 1.B), various methodologies were explored. Within the experimental setup, a sintered steel permeate carrier (Sterlich, Kent, WA, USA) was employed as the counter electrode. To serve as working electrodes in the feed channel, different materials were tested. These included Sigracell® graphite felts (SGL Carbon, Germany) and stainless steel meshes with various mesh sizes.

2.3. Membrane Properties

2.3.1. Permeability

Pure water permeability (PWP) measurements were conducted to gain insights into membrane pore size and density, as well as benchmarking and performance evaluation. A higher PWP indicates either a lower number of larger pores or a higher number of smaller pores. PWP assessment was performed on both uncoated and conductive membranes, as well as in setups with external electrodes, all evaluated in dead-end mode. The obtained PWP values were utilized to assess the influence of the coating with respect to following properties: coating layer thickness, type of metal used for coating, as well as the impact of external electrodes on membrane PWPs.

2.3.2. Contact Angle

CA measurement served as a means to evaluate the hydrophilicity of the membranes, both with and without coating, utilizing both the sessile drop and captive bubble methods (Baek, Kang, Theato, & Yoon, 2012; W. Zhang, Wahlgren, & Sivik, 1989). In the sessile drop method, membrane cutouts were placed on a holder. Droplets of DI water were then carefully deposited onto the membrane active layer using a syringe. Subsequently, these droplets were captured through imaging and further processed using software for contact angle determination.

Conversely, the captive bubble method involved submerging membrane cutouts in DI water. Small air bubbles were then gently placed onto the membrane surface using a J-shaped needle. The CAs of these bubbles on the membrane surface were then measured to assess the hydrophilicity of the membrane.

2.3.3. Zeta Potential

The zeta potential analysis provides fundamental insights into the surface charge properties of the membranes, thereby investigating their inherent sorption characteristics. Additionally, it is an important parameter for assessing both the electro-sorptive and desorptive process.

Incorporating the methodologies described in Mantel et al. (2018) and Usman et al. (2024), the analysis of zeta potential for uncoated and coated membranes was conducted using a Surpass (Anton Paar GmbH, Graz, Austria) in a 1 mol L^{-1} KCl solution. Before analysis, membranes were prepared by cutting them into gap cell dimensions (20 mm x 10 mm) and allowing them to equilibrate in pure water. The measurement procedure was initiated at alkaline pH and involved incremental titration with HCl until reaching acidic pH.

2.3.4. Molecular Weight Cut-Off

Molecular weight cut off (MWCO) is essential for UF and MF membranes because it determines the size of molecules that can pass through. This helps in assessing whether the retention during operation is due to the e-sorptive process or steric retention. Polyethylene glycol (PEG) standards with varying molecular weights: 12.3, 26.1, 42.7, 98, and 200 kDa, along with a dextran standard weighing 130 kDa (PSS Polymer Standards Service GmbH, Mainz, Germany) as described in Mantel et al. (2018).

2.3.5. ATR-FTIR spectra

ATR-FTIR spectroscopy served as a tool for understanding the chemical composition and functional groups within the membranes. By comparing the spectra of untreated membranes with those that underwent functionalization, the efficacy of the modification process was rigorously assessed (Glass et al., 2021). Alterations in peak intensities and positions associated with distinct functional groups were analyzed to gauge the extent of modification induced by the functionalization process.

2.4. Tested Membranes

This report extensively evaluates various membranes to ascertain optimal performance, drawing insights from ongoing investigations and previous studies. A diverse range of membranes, including those fabricated from polyamide, nylon, polyethersulfone (PES), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), and regenerated cellulose, were subjected to rigorous assessment. Each membrane's characteristics and performance were assessed to establish correlations between membrane properties and functionality. A comprehensive overview of the membranes tested is provided in Table 1:

Table 1: Overview of tested and reviewed membranes

Membrane	Manufacturer	Base material
Microlon 50	Membrana	Polyamide
Microlon 05[2]	Membrana	Polyamide
Nylon plus	Roche	Polyamide/Nylon
ROTI®Nylon (neutral)	Carl Roth	Polyamide/Nylon
ROTI®Nylon plus	Carl Roth	Polyamide/Nylon
UP150[1]	Microdyn Na.	Polyethersulfone
UP150 + Cysteamine	Microdyn Na.	Polyethersulfone
UV150	Microdyn Na.	PVDF
DuraPES200	Membrana	Polyethersulfone
DuraPES200 + Cysteamine	Membrana	Polyethersulfone
PAN-NH_2[3]	HZG[5]	Polyacrylonitrile
PAN virgin[3]	HZG[5]	Polyacrylonitrile
PAN-EDA[3]	HZG[5]	Polyacrylonitrile
PAN-NaOH[3]	HZG[5]	Polyacrylonitrile
Sartobind® Q[4]	Sartorius	Regenerated cellulose
Sartobind® STIC	Sartorius	Regenerated cellulose
Sartobind® D[4]	Sartorius	Regenerated cellulose

[1](Mantel et al., 2018); [2](Mantel, Jacki, & Ernst, 2021); [3](Usman et al., 2024); [4](Wullenweber, Bennert, Mantel, & Ernst, 2024), [5](Glass et al., 2021)

Choice of membranes:

The selection of the membranes studied was based on the availability of diverse options in both the commercial market and custom-tailored ion exchange membrane synthesis/fabrication. A key factor in this selection was the charge of the membrane, as functionalization with positive or negative groups is essential for the sorptive process. Based on these properties, the membranes were pre-selected. Two positively charged membranes with different pore sizes, Microlon 50 and Microlon 05, were investigated. Additionally, Nylon Plus from Roche, a commercially available positively charged membrane, and ROTI®Nylon Plus, along with ROTI®Nylon (neutral) as a reference, were examined.

Furthermore, the impact of a negative charge on the process was identified by a study using the UP150 (polyethersulfone) membrane from Microdyn-Nadir GmbH. Further studies aimed to investigate the effects of various functionalization, with either strongly or weakly basic groups, on the process. For this purpose, PAN was chosen as the base material. The selection of PAN-based membranes was based

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on the findings by Glass et al. (2021), who highlighted that PAN is easier to chemically modify due to the presence of a nitrile group. Various modification reactions for substances containing nitrile groups, such as PAN, are well-documented (El Newehy & Alamri, 2014; Scharnagl & Buschatz, 2001). Finally, based on the studies of PAN experiments, commercially available products with both strong and weak basic functional groups, but with significantly higher adsorption capacities than custom-made ones, were sought. For this, ion-exchange membrane adsorbers, intended for use in membrane chromatography, were pre-selected. Chen et al. (2023) provides an overview of the available models and manufacturers on the market. Broadly, there are three products available: (i) Sartobind from Sartorius Stedim, (ii) Mustang from Pall Corporation and (iii) Natrix Separations Inc.. However, the production of basic Mustang and Natrix in flat sheet format has been discontinued, leading to the selection of the Sartobind® D and Q membranes from Sartorius GmbH (Göttingen, Germany).

2.5. Adsorption Experiments

Experiments were conducted to assess the adsorption efficiency, capacity and regeneration of the membranes. As a model substance for NOM, the International Humic Substances Society (IHSS, USA) NOM isolate 2R101N Suwannee River Natural Organic Matter (SRNOM) was used, which has been extensively characterized in the literature (Green, McInnis, Hertkorn, Maurice, & Perdue, 2015). To evaluate NOM content, Dissolved Organic Carbon (DOC) was quantified using a Shimadzu TOC analyzer. For dynamic experiments related to breakthrough curves, Ultraviolet-254 (UV254) absorbance was measured with a spectrophotometer (Hach Lange GmbH, Düsseldorf, Germany). The UV254 was assessed as a reliable indicator of organic compounds (Weishaar et al., 2003). Not only were the bulk parameters DOC and UV254 used to evaluate the performance of NOM removal, but also the methods developed in Tasks 1.1 and 1.2 for more precise specification and fingerprinting of NOM and its link to DBP precursor fractions. As described in the method by Wullenweber et al. (2024), fluorescence spectroscopy using an Aqualog fluorescence spectrophotometer (HORIBA, Osaka, Japan) and liquid chromatography-organic carbon detection (LC-OCD) (DOC Labor Huber, Karlsruhe, Germany) were applied to investigate the selectivity of DBP precursor removal. Adsorption tests were performed using flat sheet membranes set up in a dead-end configurations as described in Mantel et al. (2022), Usman et al. (2024) and Wullenweber et al. (2024).

3. Results

3.1. Evaluation of ECM fabrication methods and external electrodes

Conductivity is one of the primary factors for assessing the results of the coating. Therefore, selected findings will be presented. As reported in Mantel et al. (2018), Mantel, Benne, and Ernst (2021), Mantel (2022a) for gold coating and in Usman et al. (2024) for platinum coating the layer thickness of the coated nanolayer has significant influence on the conductivity. The conductivities for UP150 membrane with 5, 10, 15, 40 nm Au-layer and 40 nm layer for the M5 membrane, as well as 10 and 20 nm Pt layers for the PAN-EDA are shown in Figure 2. It becomes apparent that, for the reported results, both gold and platinum coatings exhibit a plateau in conductivity improvement beyond a certain thickness, nearly reaching the conductivity of elemental gold and platinum. It is presumed that this occurs at a thickness of approximately 20 nm. Furthermore, as depicted in Mantel et al. (2018) and Usman et al. (2024), a thickness greater than 10 nm is necessary to achieve a uniform coating that is uninterrupted.

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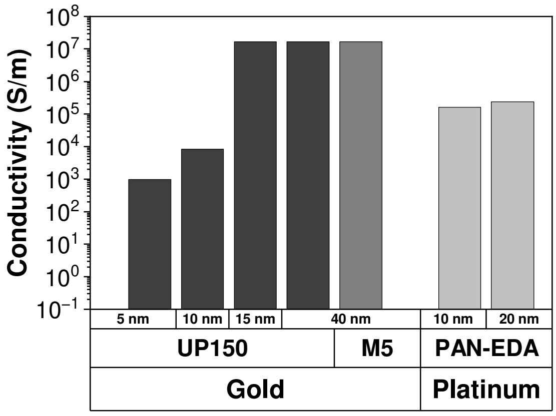
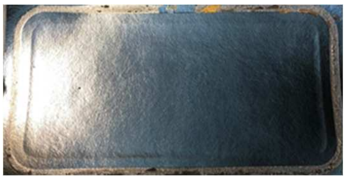


Figure 2: Conductivity of different membranes coated with: UP150 5,10,15 nm Gold (Mantel et al., 2018), UP150 40nm Gold (Mantel, 2022a); M5 40 nm Gold (Mantel, Jacki, & Ernst, 2021) and Pan-EDA with 10, 20 nm Platinum (Usman et al., 2024)

Besides conductivity, the stability of the coated layer is crucial. While both gold and platinum allowed for both sorption and desorption, the use of silver led to corrosion and the formation of silver chloride in solution, as reported in Usman et al. (2024). Additionally, Table 2 demonstrates that at a potential of 2 V, slight detachment of the gold coating was observed after regeneration, with a further increase to 2.5 V resulting in more extensive detachment. In contrast, platinum exhibited notable stability, even under cyclic usage, at this potential.

Table 2 Stability of 20 nm coated layers under different potentials

Au-sputtered		**Pt-sputtered**
After use at 2 V	After use at 2.5 V	After use at 2.5 V
		

For the regenerated cellulose membranes, an immediate detachment of gold as well as platinum was observed after wetting with water due to the swelling of the cellulose. While the coating with nickel enables an e-sorptive and -desorptive process, it was shown that conductivity modification of cellulose-based membranes also works. However, application of nickel in the drinking water sector is not feasible due to health aspects and regulations regarding approved substances.

A summary of the decision-making process for selecting the coating metal is presented in the following Table 3:

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Table 3: Summary of coating material evaluation

Coating material	Stability of coating	Electrical conductivity	Remarks
Nickel (Ni)	-	+	Health risks and regulatory limitations due to toxicity
Silver (Ag)[1]	-	+	Corrosion leading to detachment of silver chloride
Gold (Au)[2]	o	+	Limited stability at potentials >2.0 V and reduced long-term stability.
Platinum (Pt)[1]	+	+	

[1](Usman et al., 2024), [2](Mantel et al. 2018; Mantel et al. 2021; Mantel 2022)

The utilization of external electrodes for potential-driven regeneration was explored using various electrode types as depicted in the Table 4. Across all tested setups, employing the sintered steel permeate carrier as a counter electrode yielded promising results in terms of stability, electrical conductivity, and surface area. Although stainless steel meshes demonstrated satisfactory performance, the significantly higher surface area of graphite felt rendered it superior to the mesh. While the mesh could serve as a counter electrode, the felt proved unsuitable as a counter electrode due to anodic instability and signs of dissolution.

Table 4: Comparison of external electrode performance

External electrode	Stability	Electrical conductivity	Surface area	Remarks
Stainless steel mesh	+	+	+	
Graphite felt	o	+	++	Anodically unstable at higher potentials
Sintered steel permeate carrier	+	+	+	

The steric retention of natural organic matter (NOM) by UF and MF membranes is negligible (Lin et al., 2016; Siddiqui et al., 2016), , given the variation in molecular sizes of NOM, which typically range between 1 and 100 kDa (Ericsson & Trägårdh, 1997)(Song, Shao, He, Hou, & Chao, 2011)(Song et al., 2011)(Song, Shao, He, Hou, & Chao, 2011)(Song et al., 2011). However, it is necessary to investigate the extent to which the coating influences the MWCO. The findings presented in Mantel et al. (2018) suggest that the MWCO is not significantly altered by the gold coating. It can be inferred that the sputter deposition of gold forms a porous layer on the membrane's separating surface. While this layer slightly increases filtration resistance, it has minimal impact on the membrane's inherent steric retention and properties. The determination of the MWCO for commercial Sartobind membranes with pore sizes of 3-5 µm posed challenges due to the relatively large pore sizes. Traditional methods for MWCO determination rely on the passage of molecules with known sizes through the membrane, however, membranes with these pore sizes exceed the molecular sizes of interest. Therefore, it can be assumed that for these membranes, steric retention of NOM is not present.

3.2. Permeability

To assess the influence of the electroconductive layer on the membranes, as well as the external electrodes on the membrane filtration process, permeability was evaluated. Selected values are depicted in Figure 3.A for coated membranes and Figure 3.B for the use of external electrodes (working electrode: graphite felt, counter electrode: sintered steel permeate carrier). Considering the permeabilities, it becomes evident that the process with external electrodes is superior. The coating led to a decrease in permeability of 15-30 %. However, no significant changes were observed for the external electrodes. Furthermore, it is noteworthy that the functionalization of the membranes also influences permeability, as seen in the comparison of PAN-NaOH and PAN-EDA to virgin PAN.

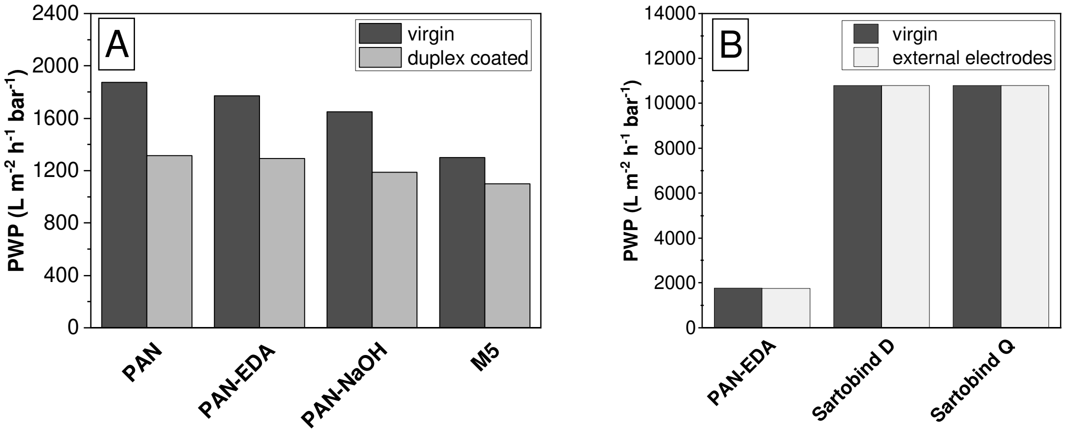

Figure 3: Pure Water Permeabilities of (A) virgin and duplex coated membranes: PAN[1], PAN-EDA[1], PAN-NaOH[1] (each 20 nm Pt), M5[2] (40 nm Ag) and (B) of virgin and in external electrode set-up membranes: PAN-EDA, Sartobind® D[3] and Sartobind® Q[3]. External electrodes on the feed side graphite felt and permeate site sintered steel permeate carrier. ([1]adapted from Usman et al. (2024); [2]adapted from Mantel, Jacki, and Ernst (2021); [3]adapted from Wullenweber et al. (2024))

3.3. ATR-FTIR spectroscopy

The analysis of membrane functionalization plays a pivotal role in assessing their performance. ATR-FTIR is an analytical technique for assessing molecular alterations in the membrane. By exploiting the characteristic vibrational modes of functional groups, ATR-FTIR enables precise identification and quantification of chemical changes occurring during membrane modification. The application and assessment via ATR-FTIR will be illustrated by the example of the virgin PAN and PAN-NaOH functionalization as reported in Kishore Chand et al. (2022) and PAN-EDA membrane reported in Glass et al. (2021). In both publications, it was demonstrated that successful membrane functionalization compared to the virgin membranes could be assessed by the scans. The NaOH-functionalized membranes, as depicted in Kishore Chand et al. (2022), showed stretching vibrations of the OH groups indicated by peaks at 3332 cm^{-1}. Similarly, Glass et al. (2021) evidenced successful functionalization with EDA through the peaks at wavelengths observed at 3364 cm^{-1} and 1650 cm^{-1}. This underscores the utility of ATR-FTIR scans as a valuable tool for selecting the optimal membrane for the process.

3.4. Zeta potential:

It has been demonstrated that for intrinsic sorption, potential-driven regeneration with external electrodes, as well as e-sorption & -desorption with duplex coated membranes, the functionalization and thus the charge of the membranes significantly influence the processes. Therefore, the following selected data, as reported in Usman et al. (2024) and Wullenweber et al. (2024), will present the zeta potentials of selected membranes. In Figure 4, the zeta potentials of PAN, PAN-NaOH, PAN-EDA, Sartobind® D (weakly basic, functionalized with diethylamines) and Q (strongly basic, functionalized with quaternary amines) are displayed. PAN represents a base membrane without modification, while PAN-NaOH and PAN-EDA are functionalized with NaOH and ethylenediamine (EDA), respectively, as shown in Glass et al. (2021). It is evident that both NaOH and EDA functionalization alter the zeta potential to higher values. Particularly, the EDA functionalization levels the potential to positive values below a pH of 7.5.

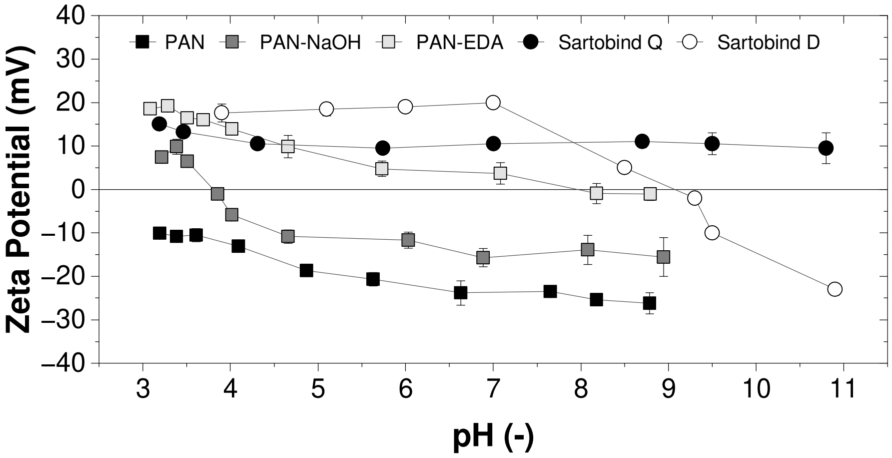

Figure 4: Zeta potentials of PAN base membranes: Virgin PAN, PAN-NaOH and PAN-EDA (Usman et al., 2024). As well as Zeta potentials of the Sartobind® D and Sartobind® Q Membrane (adapted from *Wullenweber et al. (2024))*

Additionally, the isoelectric points (IEP), the points of zero charge, are displayed in Table 5 for these membranes. The Sartobind® D membrane is proto- and deprotonable depending on pH. The assessed IEP through zeta potential is 9.1, thus it is positively charged below the pH of the IEP and negatively charged above it. The Sartobind® Q membrane does not have an IEP; it exhibits positive potentials across the entire measurement range.

Table 5: Isoelectric-Point: : Virgin PAN, PAN-NaOH and PAN-EDA (Usman et al., 2024). As well as Zeta potentials of the Sartobind® D and Sartobind® Q Membrane (*Wullenweber et al. 2024)*

Membrane	IEP
PAN	-
PAN-NaOH	3.7
PAN-EDA	7.8
Sartobind® D	9.1
Sartobind® Q	-

3.5. Intrinsic & E-sorption

The adsorption capacities for DOC SRNOM per square meter of the introduced membranes are depicted in Figure 5. In Usman et al. (2024), the intrinsic sorption characteristics of membrane materials, including virgin PAN and modified PAN are discussed. Loading capacity experiments without external applied potentials were conducted. Virgin PAN membranes showed no NOM removal during dead-end filtration and PAN-NaOH membrane exhibiting minimal intrinsic adsorption. In contrast, PAN-EDA membranes initially demonstrated significantly higher intrinsic NOM adsorption attributed to primary amine functional groups. This suggests that a positive zeta potential at the feed's pH, as observed at pH 7 due to the presence of amines, is a necessary requirement for effective intrinsic sorption. However, the limited intrinsic NOM adsorption performance of PAN-EDA suggests weak electrostatic attraction due to only a slight difference between the membrane's IEP and the feed solution's pH, potentially resulting in insufficient positively charged sites for effective sorption of negatively charged NOM.

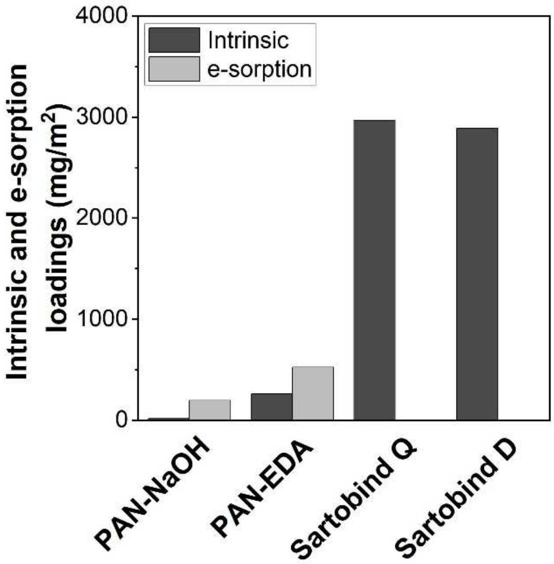

Figure 5: Intrinsic and e-sorptive loading capacties of NOM: PAN-NaOH and PAN-EDA (adapted from Usman et al. (2024)). As well as of the Sartobind® D and Sartobind® Q Membrane (adapted from Wullenweber et al. (2024))

Additionally in Usman et al. (2024) the influence of the functionalization on electro-sorption is reported, after application of an external applied potential of +2.5 V. Results showed minimal NOM e-sorption in the virgin ECM PAN membrane, whereas significantly enhanced NOM adsorption was observed in e-sorptive duplex coated PAN-NaOH and PAN-EDA membranes compared to their virgin counterparts (see Figure 5). This highlights the crucial role of surface charge in e-sorptive NOM removal. The improved NOM e-sorption in the modified PAN membranes is attributed to induced electrostatic interactions between negatively charged organic molecules and externally anodically charged ECMs. Specifically, the presence of amines and its derivatives, along with the carboxyl groups in the membrane matrix, enhances NOM e-sorption properties due to their high polarizability, facilitating charge separation and promoting NOM e-sorption through electrostatic interactions. Conversely, the nitrile group in the PAN membrane itself, with low polarizability, is not benefical to ECM development. Notably, the ECM PAN-EDA membrane exhibited the most significant increase in NOM sorption, owing to combined contributions from intrinsic adsorption and e-sorption properties. These findings reported in Usman et al. (2024) indicate that functionalities like derivates of ammonia are imperative to induce e sorp characteristics, thereby a slightly positive surface charge at feeds pH is not a must but may contribute to increased e-sorption capacity. This is comparable with the reported findings from Mantel, Jacki, and Ernst (2021) that the M5 membrane with an intrinsic positive surface charge showed a significant increase in loading trough the e-sorptive process.

On the other hand, the commercially available cellulose-based membrane adsorbers Sartobind® D and Q exhibited significantly higher intrinsic capacities compared to the conductive e-sorptive membranes (see Figure 5). This is attributed to the substantially higher degree of functionalization in the manufacturing process, highlighting the potential to use these membranes for purely intrinsic adsorption applications without the need for capacity enhancement by e-sorption.

3.6. E-Desorption

The influence of surface charge on e-desorption can be illustrated using PAN-EDA and PAN-NaOH membranes as depicted in Usman et al. (2024). In the regeneration UV254 curves shown in Figure 6.A, it is evident that PAN-EDA allowed for a higher concentration during regeneration, mainly due to the fact that the maximum loading during adsorption was also greater. Comparing the e-desorption efficiencies presented in Figure 6.B, it becomes clear that PAN-NaOH achieved a higher e-desorption (>90 %) compared to PAN-EDA (63 %). While a positive surface charge was advantageous during both intrinsic and e-sorption, a negative charge proved beneficial here. The reason is likely that interactions between the membrane and negatively charged species are weaker with negative surface potentials, allowing for easier desorption of substances.

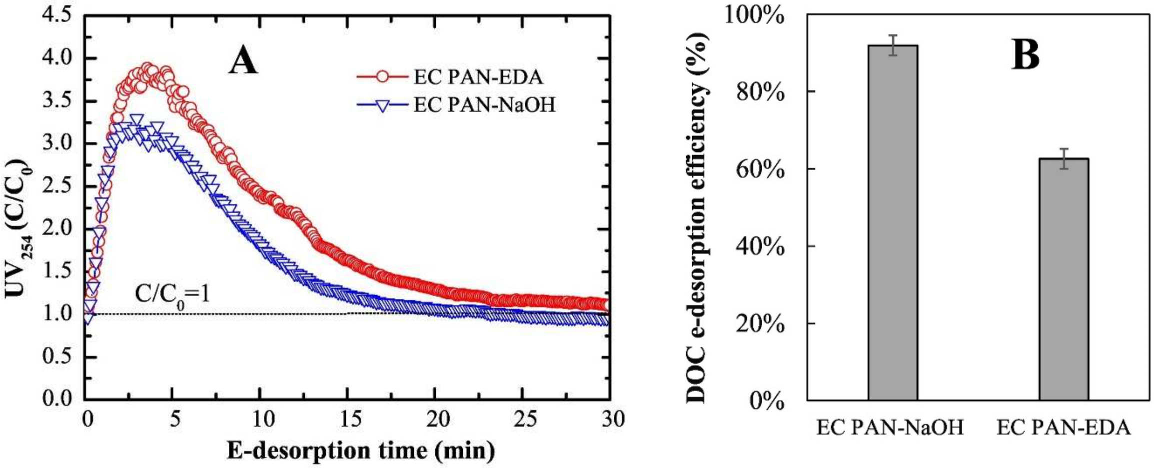

Figure 6: (A) UV254 e-desorption regeneration curves for 20 nm Pt duplex coated PAN-EDA and PAN-NaOH; (B) E-Desorption efficiency of 20 nm Pt duplex coated PAN-EDA and PAN-NaOH at -2.5 V applied potential. (Adapted from Usman et al. (2024))

3.7. Influence of Zeta Potential and functionalization on potential driven regeneration with external electrodes

The dynamic breakthrough curves without applied potential at the external electrodes during adsorption phase for uncoated Sartobind® D and Q are depicted in Figure 7.A. It is evident that both membranes exhibited similar performance, likely due to their positive zeta potential and comparable grade of functionalization. However, in Figure 7.B, the regeneration curves following the application of a -2.5 V potential to the external electrodes are shown. It is noticeable that only the weakly basic membrane begins desorbing. Hence, it can be presumed that for potential-driven regeneration with external electrodes, a weakly basic membrane is necessary, while a strongly basic one shows no significant effect. A potential explanation is that the electrostatic repulsive forces in the emerging electric field are too weak compared to the binding energy on the strongly basic membrane. Additionally, local pH changes at the electrodes and consequently on the membrane surface may occur, ultimately influencing the zeta potential and thereby the charge of the weakly basic membrane, leading to desorption induction. Nevertheless, the proof of principle is demonstrated that potential-driven desorption with external electrodes is feasible for the Sartobind® D.

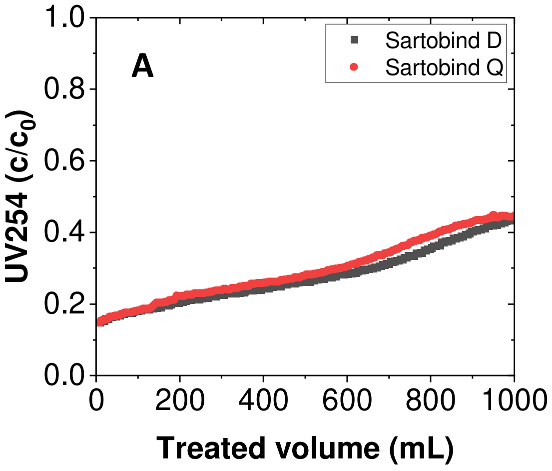

Figure 7: (A) Dynamic breakthrough curves for the intrinsic adsorption of UV_{254} active NOM compounds for Sartobind® D and Q membranes. (B) Regeneration UV254 curves after application of -2.5 V at the external electrodes.

This project has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No 101081980.

4. Membrane selection for the application in Case Study#1

We have discussed the selection of the coating, the external electrodes and the influence of the zeta potential as critical factors for a successful chemical-free regeneration. To facilitate the selection of the optimal membrane for continued research, the following section provides a consolidated overview of all membranes previously examined. Table 6 summarizes membranes utilized as duplex-coated ECMs, highlighting their application potential and performance metrics. Conversely, Table 7 focuses on membranes evaluated for potential-driven regeneration using external electrodes. Both tables encompass a comprehensive evaluation of each membrane's suitability for the intended applications, presenting essential details such as the membrane identification, manufacturers, base materials, metal coatings investigated (for Table 6), external electrodes used (for Table 7), permeabilities, zeta potentials at pH 7, and pore sizes. This structured comparison aims to guide the selection for future research efforts in safeCREWs case study #1 for a chemical free removal of NOM.

The zeta potential has emerged as a crucial membrane property influencing the success of both introduced methods. Additionally, the choice of base material was pivotal for the application of sputter deposition in the fabrication of ECMs. While the Sartobind® membranes, with their high degree of functionalization, delivered the highest loading capacities in terms of intrinsic adsorption, the swelling of cellulose post-sputter deposition coating rendered them unsuitable for this application. An alternative coating method using nickel was deemed impracticable due to the toxicological properties of nickel, rendering it unsuitable for drinking water applications.

Conversely, PAN-EDA membranes demonstrated superior loading capacities for both intrinsic adsorption and electro-sorption, primarily due to the functionalization with amine groups and their resulting zeta potential. Despite PAN-NaOH achieving higher e-desorption rates (likely due to its lower zeta potential), PAN-EDA was rated more favorably in the evaluation. This preference was based on the comparatively low adsorption loadings of PAN-NaOH, underscoring the significance of optimizing both the zeta potential and the base material.

For the chemical-free regeneration using external electrodes, the Sartobind® Q membrane exhibited no desorption capabilities, while the PAN-EDA membrane achieved only limited desorption. However, as demonstrated in this report, the Sartobind® D membrane was capable of desorbing a significant majority of the previously adsorbed dissolved organic carbon by applying a potential to the external electrodes. This significant difference in desorption efficiency highlights the importance of membrane selection and the potential of the Sartobind® D.

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Table 6: Overview of duplex coated membranes and their properties (tested or from literature): Base material, coating, permeability, zeta potential, pore size, and e-sorption & -desorption performance

Membrane	Manufacturer	Base material	Coating	Permeability (LMH/bar)	ζ potential at pH 7 (mV)	Pore Size (nm)	E-Sorption & -desorption
Microlon 50	Membrana	Polyamide	Au	3000	+13.5	~100	**+**
Microlon 05[2]	Membrana	Polyamide	Au	1400	+13.5	~40	**+**
Nylon plus	Roche	Polyamide/Nylon	Au	3900	-2	450	**+**
ROTI®Nylon (neutral)	Carl Roth	Polyamide/Nylon	Au	~4000	-30	450	**o**
ROTI®Nylon plus	Carl Roth	Polyamide/Nylon	Au	~4000	+2	450	**+**
UP150[1]	Microdyn Na.	Polyethersulfone	Au	280	-28	23	**-**
UP150 + Cysteamine	Microdyn Na.	Polyethersulfone	Au	280	-11	23	**o**
UV150	Microdyn Na.	PVDF	Au	280	-33	23	**-**
DuraPES200	Membrana	Polyethersulfone	Au	25000	-42	200	**-**
DuraPES200+ Cysteamine	Membrana	Polyethersulfone	Au	25000	-30	200	**o**
PAN-NH$_2$[3]	HZG[4]	Polyacrylonitrile	Au/Pt	1700	+9	25	**o**
PAN virgin[3]	HZG[4]	Polyacrylonitrile	Au/Pt	1870	-33	25	**-**
PAN-EDA[3]	HZG[4]	Polyacrylonitrile	Au/Pt/Ag	1770	+10.5	25	**++**
PAN-NaOH[3]	HZG[4]	Polyacrylonitrile	Au/Pt	1650	-17.5	25	**o**
Sartobind® Q	Sartorius	Reg. cellulose	Ni	10800	+13	>3000	**-**
Sartobind® STIC	Sartorius	Reg. cellulose	Ni	10800	+7	>3000	**+**
Sartobind® D	Sartorius	Reg. cellulose	Ni	10800	+20	>3000	**+**

[1](Mantel et al., 2018); [2](Mantel, Jacki, & Ernst, 2021); [3](Usman et al., 2024); [4](Glass et al., 2021)

Table 7 Overview of all tested membranes with external electrodes and their properties: Base material, coating, permeability, zeta potential, pore size, and sorption & -desorption performance

Membrane	Manufacturer	Base material	External Electrodes[5]	Permeability (LMH/bar)	ζ potential at pH 7	Pore Size (nm)	Sorption & E-desorption
Sartobind® Q	Sartorius	Reg. cellulose	SSM, SS, GF	10800	+13	3000	**o**
Sartobind® D	Sartorius	Reg. cellulose	SSM, SS, GF	10800	+20	3000	**++**
PAN-EDA	HZG[4]	Polyacrylonitrile	SSM, SS, GF	1100	+10.5	25	**o**

[4](Glass et al., 2021); [5] SSM: Stainless steel mesh, SS: Sintered steel; GF: Graphite felt

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To aid the decision-making process for the membrane and method to be further pursued in Case Study #1, permeability considerations are also important. This report has comprehensively demonstrated that the coating process for producing ECMs leads to a loss in permeability, resulting in higher energy costs and reduced operational efficiency. Furthermore, the coating process itself is significantly more labor- and cost-intensive compared to the use of external electrodes. Additionally, it has been observed that the coating stability for silver and gold is fragile, suggesting that in real-world applications, the platinum layer might also compromise its mechanical stability in the presence of particles, among other factors. These considerations further underscore the advantages of opting for the method involving external electrodes.

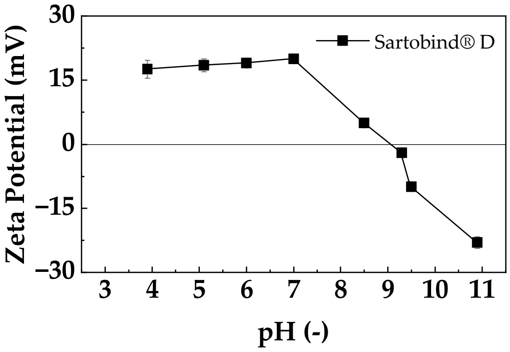
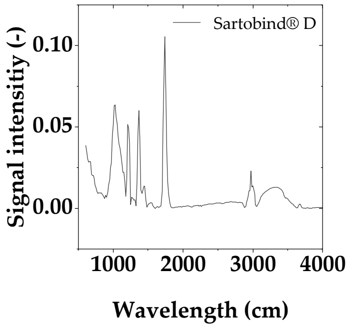
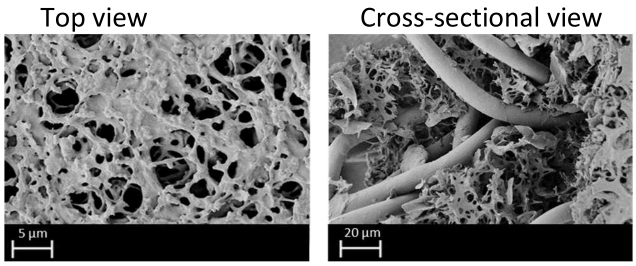
In summary, the configuration with external electrodes outweighs its advantages, as it simplifies the process and does not result in any loss of permeability, thus avoiding increased energy consumption. Therefore, the decision for further investigations, considering all factors, is made in favor of the Sartobind® D, a weakly basic membrane functionalized with diethylamines.

The membrane Sartobind® D has undergone thorough characterization for NOM removal, with detailed findings published in Wullenweber et al. (2024) and main findings summarized in Table 8. Constructed from reinforced stabilized cellulose, this membrane offers a sturdy base material for filtration application. The functionalization with diethylamines is supported by the ATR-FTIR spectral data shown in Table 8, which display characteristic absorption bands at 3364 cm^{-1} and 1650 cm^{-1}. These bands are likely indicative of the stretching motions associated with amines and amidines (N=C-N), suggesting the modification of the membrane (Ko, Choi, Park, & Woo, 2004). The SEM images reveal a pore size distribution ranging from 3-5 µm, indicating little to no steric removal of NOM. However, the significantly large pore size favors the high permeability and highlights the low energy consumption. The NOM removal must be attributed to an adsorptive process. Moreover, SEM analysis also highlights the incorporation of polyester fleece reinforcement within the membrane structure, enhancing its mechanical stability and longevity. This reinforcement is crucial for ensuring the membrane's resilience to physical stresses encountered during filtration processes.

The membrane's hydrophilic nature, exemplified by a measured contact angle of 34.1 °, further contributes to its permeability. However, it's noteworthy that the main driver behind the membrane's exceptional permeability remains its high pore size. This is evidenced by a high PWP value of 10800 L/(h m^2 bar).

Furthermore, the membrane exhibits a favorable zeta potential behavior. It demonstrates a positive zeta potential above the IEP of pH = 9.1 and a negative surface charge at higher pH values. This property makes it well-suited for drinking water treatment within the typical pH range of 6.5-8.5. Moreover, its weakly basic nature enables the potential-driven regeneration method. This unique combination of properties ensures its compatibility with the pH conditions prevalent in drinking water treatment processes while also allowing for efficient regeneration through potential-driven methods.

Table 8: Properties of the Sartobind® D membrane as specified by the manufacturer and adapted from Wullenweber et al. (2024)

Characteristic	Value
Membrane material[1]	Reinforced stabilized cellulose
Adsorption area/ equivalent volume ratio[1]	36.4 cm^2/mL
Norminal pore size[1]	3-5 µm
Membrane thickness[1]	~ 250 µm
pH stability[1]	Short term: 2-14 Long term: 2-12
Porosity[2]	~ 78
Contact angle[3]	34.1 °
Pure Water Permeability[3]	10800 L/(h m^2 bar)
IEP[3]	9.1
Zeta Potential[3]	
ATR-FTIR-Spectra	
SEM-Images[3]	

[1]Manufacturer; [2]Tatárová, Dreveňák, Kosior, and Polakovič (2013); [3]Wullenweber et al. (2024)

This project has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No 101081980.

4.1 Evaluation of selective NOM fraction removal using advanced characterization methods

The results from Tasks 1.1 and 1.2 demonstrate that LC-OCD is a powerful tool for examining the removal of specific fractions of natural organic matter (NOM), which can be correlated with various classes of disinfection by-products (DBPs). As reported in Wullenweber et al. (2024) Figure 8 presents the composition of the studied SRNOM feed into its fractions according to Huber, Balz, Abert, and Pronk (2011), including biopolymers (BP), humic substances (HS), building blocks (BB), and low molecular weight (LMW) neutrals and acids. The data reveals that in the model water, HS constitutes the largest fraction at approximately 65 %, followed by BB and LMW neutrals. It was shown that for both selected membranes, D and Q, nearly the entire HS fraction could be removed. BB were more effectively removed by membrane D compared to membrane Q, with removal efficiencies of 61 % and 46 %, respectively.

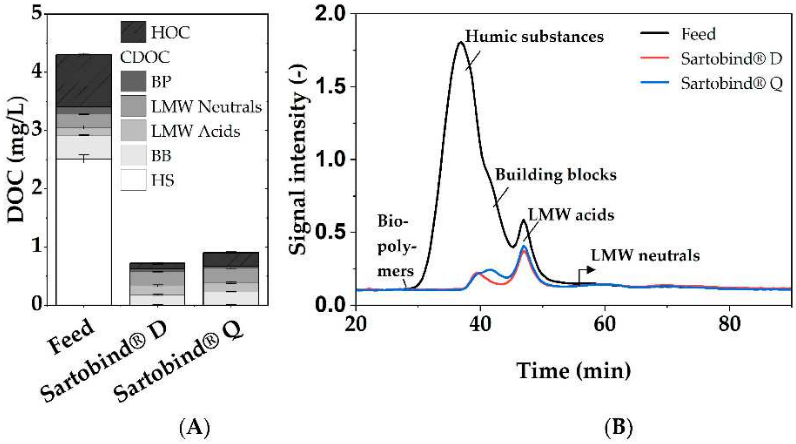


Figure 8: (A) Fractionation of the SRNOM Feed DOC and (B) LC-OCD chromatograms of the SRNOM Feed and Sartobind D and Q permeates (Wullenweber et al. 2024)

Fluorescence spectroscopy revealed further details of NOM removal. As reported by Wullenweber et al. (2024), the overall fluorescence signal reduction was stronger for Sartobind® D compared to Sartobind® Q. Notably, peak M, representing humic substance NOM, was better removed by D than by Q. The fluorescence excitation−emission matrix (EEM) analysis aligns with the LC-OCD and UV254/DOC findings. Sartobind® D achieved an 84 % reduction in peak M compared to 74 % for Sartobind® Q. This could be attributed to the difference in BB removal, which has similar characteristics to humics.

HS possess a negative charge, making them highly adsorbable to positively functionalized amines. This property explains the high removal efficiency of HS observed in the study. This underscores the choice of our membranes. The ability to remove HS is significant because as shown in Task 1.2 the HS is the main precursors to trihalomethanes (THMs). Therefore, the effectiveness of membranes D and Q in removing HS indicates their potential in reducing the formation of THMs in treated water.

5. Conclusion

This report investigated two methods to evaluate the impact of membrane properties on their performance. Using porous membrane adsorbers with either a conductive metal nanolayer or external electrodes demonstrated the potential for chemical-free regeneration using only an electrical potential. The zeta potential emerged as a crucial membrane characteristic influencing the success of both methods. Additionally, the choice of base material was pivotal for applying sputter deposition to fabricate electroconductive membranes. Materials that swell in aqueous media, such as cellulose, were found unsuitable for sputtering to enhance conductivity. However, the commercial membrane adsorber Sartobind® D could be effectively regenerated using external electrodes, making the process simpler and favourable. The high permeability (10,800 L h^{-1} m^{-2} bar^{-1}), functionalization with weakly basic ethylenediamine leading to a positive zeta potential below pH 9.1 and its high adsorption capacity, and availability in a flat sheet design, which were key factors that led to the selection of this membrane. The flat sheet design is essential in this context, offering the advantage of a uniform membrane thickness of approximately 250 µm. This uniformity allows for the application of a directed electric field across the entire membrane and enables the electrodes to be placed in close proximity to the membrane. Additionally, the Sartobind® D membrane could selectively and almost completely remove humic substances, identified as the main precursors of THMs, due to the predominantly negative charge of humic substances and the positive charge of the membrane, thus effectively reducing the potential for DBP formation.

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