

Toward circular greenhouse wastewater reuse: advancements in cation exchange membranes for selective Na⁺/K⁺ separation using electrodialysis systems

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ABSTRACT

Driven by the growing need for alternative water sources and forthcoming stringent nutrient discharge regulations, there is growing interest in developing selective membrane solutions to facilitate circular greenhouse wastewater reuse (as emphasized in the European Union's Horizon 2020 ULTIMATE project). For electrodialysis systems, sodium (Na⁺) over potassium (K⁺) selective membranes are essential to achieve minimal liquid discharge. This study addresses the challenge of developing selective, efficient, and scalable Na⁺/K⁺ cation exchange membranes. State-of-the-art cation exchange membrane developments were reviewed and the functionalization of commercial membranes with crown ethers was identified as a promising approach. Two crown ether-modified membranes (15-crown-5 (15C5) and 18-crown-6 (18C6)) were developed, characterized, and tested with equimolar and greenhouse wastewater binary feed ratios. While the results demonstrated low overall selectivity, the 15C5-modified membrane showed a marginal enhancement in K⁺ selectivity, suggesting the need for further optimization. The study concludes with recommendations for the future development of Na⁺/K⁺ selective membranes, highlighting the potential of machine learning approaches to expedite progress. This research provides a foundational step toward practical and scalable Na⁺/K⁺ ion separation solutions, for achieving minimal liquid discharge in greenhouse horticulture.

Key words: circular economy, electrodialysis, greenhouse horticulture, ion exchange membrane modification, Na⁺/K⁺ selective crown ethers

HIGHLIGHTS

- There is growing interest in developing Na⁺/K⁺ selective cation exchange membranes (CEMs) for minimal liquid discharge from greenhouse wastewater.
- The advances in Na⁺/K⁺-selective CEMs are reviewed in this study, focusing on the selectivity–resistance–scalability trade-off.
- Crown ether–modified CEMs were developed, characterized and evaluated.
- Low selectivity was observed, with 15-crown-5-modified membrane showing marginal enhancement in K⁺ selectivity.
- Recommendations for improving Na⁺/K⁺ selective CEMs and machine learning-driven optimization strategies were discussed.

INTRODUCTION

Fresh water consumption has been steadily increasing globally due to population growth and rapid economic development. While global water withdrawal is dominated by agriculture at 69%, in Europe, industrial consumption can go up to 57% (Chaudhuri 2014). In both cases, the wastewater is mostly discharged after being used. The generated wastewater has promising potential to serve as a source of reusable water, valuable components, and energy for the agricultural and industrial sectors, but this remains largely underexplored. Sectorial collaboration to minimize waste and maximize resource efficiency, leading to economic benefits and reduced environmental impact is a strategy known as industrial symbiosis (IS) (Chertow

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2000). A specific variation of IS is water smart industrial symbiosis (WSIS), where wastewater not only plays a key role as a reusable resource but also as a vector for energy and materials to be extracted, treated, stored, and reused within the same sector or across other industries. This approach is exemplified by the European Union-funded Horizon 2020 research project ULTIMATE, which demonstrates WSIS applications across diverse (industrial) sectors (Ultimate 2020). Among the practical case studies developed within ULTIMATE, the research presented in this paper forms a part of a greenhouse sector-focused case study aimed at optimizing the water and nutrient cycles to achieve WSIS.

In the Netherlands, greenhouse horticulture is an advanced and important economic sector characterized by high production rates and, consequently, high input of resources (Van der Salm *et al.* 2020). In recent years, this sector has faced challenges related to water scarcity and stringent regulation on nutrient discharge, prompting the need for smart alternatives to minimize discharge and maximize resource recovery from greenhouse wastewater. To close the water and nutrient cycle, the generated wastewater is (i) treated to prevent the accumulation of undesired constituents such as Na^+ (Voogt & Sonneveld 1997) and (ii) disinfected to prevent plant pathogen proliferation. Na^+ presents the main challenge, as its accumulation is known to hinder plant growth. It is not actively absorbed by crops and eventually limits the reusability of reclaimed water and resources, as most crops have a low tolerance for Na^+ ions (as low as <0.1 mmol/L) (Guleria *et al.* 2024). Furthermore, a range of nutrients is added to the source water to sustain crop growth, nutrients that can be reused. Therefore, there is a need to investigate processes that can selectively separate Na^+ , while retaining/separating other ions such as nutrients from greenhouse wastewater.

These challenges have propelled the exploration of electrically driven membrane separation technologies for selective Na^+ separation, such as electrodialysis (ED). ED operates by applying an electric potential across ion exchange membranes (IEMs) arranged between anode and cathode electrodes. In a conventional ED system, alternating cation and anion exchange membranes selectively allow cations to move toward the cathode and anions toward the anode. This migration results in the concentration of ions in specific compartments, effectively separating them from the feed solution. ED's potential for ion-selective separation, lower brine production, low fouling, and high energy efficiency can make it more beneficial compared to other treatment processes, for certain applications (Strathmann 2010). Recent studies at pilot scale employing conventional IEMs demonstrated higher water reuse feasibility and lower specific energy consumption (0.24 kWh/m³) from greenhouse wastewater compared to other technologies such as reverse osmosis (Guleria *et al.* 2024). Conventional IEMs are limited by ion selectivity. Given this, important plant nutrients, including potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), nitrate (NO_3^-), sulfate (SO_4^{2-}), and phosphate (PO_4^{3-}) remain in the concentrate together with the undesired Na^+ ions. Moreover, studies with monovalent-divalent selective ion exchange (IEX) membranes at the laboratory scale have demonstrated the selective separation of monovalent cations including Na^+ and K^+ , and retention of divalent Ca^{2+} and Mg^{2+} cations in the diluate for reuse as irrigation water from greenhouse wastewater. The best-performing membrane demonstrated 1.6–3.2 Na^+ for Ca^{2+} ions and 2.4–7.6 Na^+ for Mg^{2+} ion selectivity (Ahdab *et al.* 2021). To further optimize resource recovery (separating Na^+ from all the other valuable cations) and move toward minimal liquid discharge in the greenhouse horticulture sector, selectively differentiating between Na^+ and K^+ ions is required. However, the effectiveness of currently available conventional and monovalent-divalent selective commercial IEMs to selectively separate monovalent-monovalent cations is limited by their physical and chemical properties.

Advanced membrane engineering comes forth as a pivotal approach to address these limitations, integrating membrane design and process development to enhance the selectivity and efficiency for such applications. Recently, several studies have attempted to develop Na^+/K^+ selective membranes (Casadella *et al.* 2016; An *et al.* 2019; Yang *et al.* 2019; Qian *et al.* 2020; Krishna *et al.* 2022). These studies give invaluable insights into the complex separation mechanisms that can selectively separate Na^+ and K^+ ions. However, these membranes are mostly developed at a small scale, can be complex and expensive to fabricate, and are not tested under real conditions. Thus, the question remains: how can a selective, efficient, and upscalable Na^+/K^+ membrane be developed, and how would they perform in practical conditions (e.g., particularly, resource recovery from greenhouse wastewater)? In addition, could machine learning (ML) approaches leapfrog their development? This paper investigates the developments in modifying and fabricating cation exchange membranes (CEMs) for selective Na^+/K^+ separation for ED systems, focusing on circular greenhouse wastewater reuse. Specifically, this paper aims to first provide a state-of-the-art overview of CEMs development for selective Na^+/K^+ separation. Then, a promising modification method, namely, functionalization and characterization of commercial membranes comparing two crown ethers (K^+ selective and Na^+ selective) is proposed, upscaled, and investigated for equimolar and greenhouse wastewater feed ratios. Lastly, current limitations and future perspectives in achieving more efficient, scalable, and selective Na^+/K^+ separation for greenhouse horticulture applications, including potential modeling approaches are elaborated.

BACKGROUND ON Na^+/K^+ SELECTIVE MEMBRANE DEVELOPMENT

Ion-selective membranes (ISMs) play a critical role within ED systems by leveraging selective permeability and an external electric field to drive ion transport. The selectivity is achieved through embedded fixed charged groups within the membrane material, which interact with counterions while excluding co-ions. Key principles, such as Donnan equilibrium and membrane potential, contribute to the selective ion transport, while minimizing the transport of water and co-ions. Charge-based selectivity allows membranes with fixed charges to attract oppositely charged ions while repelling others, favoring monovalent over multivalent ions. Ion size and hydration also play a role, with smaller hydration shells facilitating faster ion transport, for ion–ion separation. Furthermore, membrane structure, including pore size and surface charge, influences ion separation by controlling interactions with hydrated ions. Commercially, monovalent–divalent ion separating membranes have been developed, but ion–ion separating membranes remain a challenge due to similarity in properties, complex ion transport mechanisms, and scaling challenges.

Developing ion–ion selective membranes can be achieved by surface modification and/or by synthesizing new membranes with an engineered physical–chemical separation mechanism. Specific ion selectivity is achieved through pore-size sieving, electrostatic repulsion, or specific interaction effects (Strathmann 2010). The pore-size sieving effect, the improvement of crosslinking degree (Jackson & Nelson 2019), and the formation of separated hydrophilic/hydrophobic structures (Yang *et al.* 2019) are the main approaches to altering the structures of the membrane matrix to achieve ion perm-selectivity. For ions with the same charge, specifically Na^+ and K^+ , separation is challenging, and selectivity based on size and ionic charge is ineffective as both ions possess similar charge (+1), crystal radii, hydrated radii, and IEX equilibrium coefficients (Zhang *et al.* 2021). The literature has established that precise, selective pathways based on ion-hydrated radii are key to such separations.

Table 1 provides an overview of the properties of common ions found in greenhouse wastewater. Ions with larger hydrated radii are hindered in passing through smaller pores compared to ions with smaller radii. Furthermore, with a larger hydrated radius, ions need to partially shed their hydration shell to penetrate a smaller pore. This implies that the ion dehydration energy is a significant factor in determining the rate and selectivity of ion transport of similar monovalent ions (Tang & Bruening 2020). For the case of Na^+ and K^+ , the difference in their hydration energy (-295 and -430 kJ mol^{-1} for K^+ and Na^+ , respectively) can potentially be exploited to achieve their separation. Recent studies have shown that materials such as crown ethers, supported liquid membranes, and graphene-oxides are promising approaches. Table 2 provides an extensive overview of recent literature on the development of ion–ion selective membranes focused on Na^+ and K^+ separation.

From Table 2 it can be inferred that there are very few studies on the development of Na^+/K^+ selective membranes. Furthermore, no specific membrane development method performs satisfactorily overall (++ for all categories), i.e., high selectivity, low resistance or good permeability, and ease of scalability. It should be noted that there are inconsistencies in the methodology adopted for assessing the membrane selectivity as observed across the literature, specifically for calculating and determining ion–ion perm-selectivity (e.g., a range of setups, experimental conditions, and calculation methods are used). There is a need for a consistent protocol for determining and comparing the performance of ion–ion selective membranes being developed. Nonetheless, the zeolite membrane (ZM), supported liquid membrane (SLM), polymer inclusion membrane (PIM), and polypyrrole (PPy) membrane electrode show high selectivity. However, they have high resistance (sometimes not measured), or complex synthesis or fabrication methods, i.e. described in academic research and not yet scaled for large-scale production. The crown ethers co-modification (CECM), saloplastic (SL), and crown ether impregnation (CEI) membranes have relatively simple synthesis or fabrication methods (replicable for industrial standard) and lower resistance; however, they exhibit only acceptable selectivity (less than the average of 3.4). Considering the selectivity–resistance–scalability

Table 1 | Properties of common ions (Tang & Bruening 2020) found in greenhouse wastewater

Cation	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	NO_3^-	Cl^-	SO_4^{2-}
Ionic crystal radii, r (Å)	0.95	1.33	1.48	0.99	0.65	2.64	1.81	2.90
Effective hydrated radius, r' (Å)	3.58	3.31	3.31	4.12	4.28	3.35	3.32	3.79
Molar Gibbs hydration energy, ΔG_{hyd} (kJ/mol)	-430	-295	-285	-1,505	-1,830	-300	-340	-1,080
Diffusion coefficient, D at 25 °C (10^{-9} $\text{m}^2 \text{s}^{-1}$)	1.334	1.957	1.957	0.792	0.706	1.902	2.032	1.065

Table 2 | Overview of recent literature on the development of ion–ion selective membranes focused on Na⁺ and K⁺ separation

S. No.	Membrane	Application	Methodology	Separation mechanism	Selectivity	Remarks	Reference
1	ZM	Extracting K ⁺ from seawater	Synthesized with a double hydrothermal method on an α -Al ₂ O ₃ plate	Hydrated ion size exclusion: Membrane channel diameters of 0.59–0.70 nm, allowing selective K ⁺ entry due to its smaller hydrated diameter	7.62 (K ⁺ /Na ⁺), 68.43 (K ⁺ /Mg ²⁺), and 162.92 (K ⁺ /Ca ²⁺)	Selectivity ++ Resistance -- Scalability -- Add: high feed conc., complex synthesis, no resistance analysis	An <i>et al.</i> (2019)
2	CECM	Binary and ternary synthetic streams (K ⁺ , Li ⁺ , Na ⁺ , Mg ²⁺)	Co-deposition-modified CEMs with crown ethers and PDA	Pore size sieving effect: 15C5 selectively forms 1:1 or 2:1 ‘sandwich’ host–guest complex with K ⁺	Li ⁺ /K ⁺ : pristine (1.18), modified (2.87) Na ⁺ /K ⁺ : pristine (0.63), modified (1.45)	Selectivity + Resistance + Scalability ++ Add: easy modification, scalable, stability uncertain	Yang <i>et al.</i> (2019)
3	SLM	K/Na separation with greenhouse drain water	Membrane support (ACCUREL) was submerged in the organic solvent (combinations of NPOE, NaBARF, and crown ether) held by capillary forces	Interaction between host/guest molecule and mobility of the (partly dehydrated) ionic species. The crown ether only slightly improves K ⁺ selectivity	K ⁺ /Na ⁺ : 6	Selectivity ++ Resistance -- Scalability -- Add: highest selectivity, resistance and scalability issues, crown ether had no significant effect	Qian <i>et al.</i> (2020)
4	SL	Na/K separation from greenhouse drain water	Polyelectrolyte complex of polystyrene sulfonate and polyvinylamine in the monomer ratio 1:2.5 hot-pressed to form a dense SL	K ⁺ (softer water shell) vs Na ⁺ (harder shell) leads to kinetic selectivity. PSS-PVA leads to improved K ⁺ selectivity by amine groups’ polarity and their interaction with OH ⁻ ions	Na ⁺ /K ⁺ : commercial membranes 1.32 ± 0.1, SL 1.80 ± 0.33 (resistance-based selectivity)	Selectivity + Resistance + Scalability + Add: synthesis method, scalable, nontoxic	Krishna <i>et al.</i> (2022)

5	PIM	K ⁺ from metal ions present in urine (K ⁺ , Na ⁺ , and NH ₄ ⁺)	2-NPOE used as plasticizer to cellulose triacetate (CTA) used as polymer and dicyclohexan-18C6 used as carrier	Co-transport and complexation with the crown ether main transport mechanism with ultrapure water in receiving phase	K ⁺ /Na ⁺ : 27.9 NH ₄ ⁺ /Na ⁺ : 295	Selectivity ++ Resistance -- Scalability - Add: unstable, no resistance measured, scalability can be an issue	Casadella <i>et al.</i> (2016)
6	PPy membrane electrode	K ⁺ /Na ⁺ separation from demi water and seawater	PPy on a stainless steel wire mesh using a novel redox transistor electro dialyzer and PPy/modified active carbon (M-AC) membrane electrode	Due to its smaller hydrated ionic radius and lower hydration energy, K ⁺ diffuses more easily onto the PPy membrane electrode. Further improved by stronger electrostatic attraction between K ⁺ and the counterion	K ⁺ /Na ⁺ : 2.18	Selectivity ++ Resistance - Scalability - Add: small-scale assessment, difficult to upscale	Zhou <i>et al.</i> (2020)
7	CEI	K ⁺ /Na ⁺ salt separation	Crown ethers 15C5 and 18C6 were impregnated in the commercial membrane and added to the mixed salt solution for ED	Complex formation between crown ethers and alkali-metal cations is related to the inner diameter of the ether and the crystal radii of the cations. K ⁺ form more stable complexes with 18C6 than sodium ions, thus they were difficult to exchange with the membrane	K ⁺ /Na ⁺ ratio was 2.66 without 18C6 and 1.62 with 18C6 (100 g/L).	Selectivity + Resistance + Scalability ++ Add: small scale, scalable, crown ether 18C6 was Na ⁺ selective and 15C5 showed no selectivity	Sata <i>et al.</i> (2000)

Note: The weightage in the remarks section is quantified as follows: **Selectivity** (average of all data = 3.4): - - (< nonmodified membrane), - (= nonmodified membrane), + (between nonmodified and average selectivity (3.4)), and ++ (> average selectivity (3.4)); **Resistance** (based on measured values): - - (not measured), - (< twofold of the nonmodified membrane), + (up to twofold of the nonmodified membrane), and ++ (> twofold of the nonmodified membrane); **Scalability** (based on methodology): - - (only described in academic research), - (described in academic research but not used for large-scale production), + (described in academic research with similarities to industry standard application), and ++ (close to industry standard e.g., by only additional modification step(s)).

PSS-PVA, polystyrenesulfonate-polyvinylamine.

trade-off for developing Na⁺/K⁺ selective membrane, the methodology for CE (co-deposition-modified CEMs with crown ethers and polydopamine (PDA)) showed promise and was further developed and studied in this work by employing surface modification (Luo *et al.* 2018). Two crown ether compounds; Na⁺ selective (15-crown-5 (15C5)) and K⁺ selective (18-crown-6 (18C6)) known for their selective binding with Na⁺ and K⁺ ions, respectively, due to their cavity size, were chosen for fabricating the modified membranes. For optimizing nutrient recovery from greenhouse wastewater, separating Na⁺ (i.e., harmful for crop growth) from K⁺ (nutrient for fertilizer) or vice versa is crucial. Thus, these crown ethers were selected and compared. Developing and characterizing modified membranes with these two distinct crown ethers allows for the evaluation of their efficacy in enhancing selectivity and ion transport properties. This is elaborated on in the next section.

MATERIALS AND METHODS

Based on the assessment in the previous section, commercial CEMs were modified with two types of crown ether compounds. The aim is to assess the influence of upscaling membrane functionalization for Na⁺/K⁺ separation using crown ethers. The methodology, characterization, and results are discussed in further detail in the following sections.

Reagents and membranes

For the modification, materials used were dopamine hydrochloride (98%), 4'-aminobenzo-15-crown-5 (98%), 4'-aminobenzo-18-crown-6 (98%), polyethyleneimine (PEI) (98%), glutaraldehyde (GA), tris(hydroxymethyl)aminomethane (99.5%), hydrogen peroxide (99.5%), concentrated hydrochloric acid (HCl, 99.5%), tris-HCl buffer solution (99.5%), potassium chloride (99.5%), sodium chloride (99.5%), sodium sulfate (99%), and copper(II) sulfate pentahydrate (99.5%), which were received from Merck Netherland. Deionized (DI) water was used throughout the experiments. Commercial membranes (FUJIFILM, the Netherlands) were used for the modification, and their specifications and properties are provided in Supplementary material S1. The membrane modifications were performed using an in-house apparatus (Supplementary material S2).

Membrane surface modification methodology

The modification was applied to commercial membranes and two crown ether complexes: 4'-aminobenzo-15C5 and 4'-aminobenzo-18C6, based on the literature (Torun 1994; Sata *et al.* 2000; Yang *et al.* 2019; Warnock *et al.* 2021). Tris-HCl buffer solution was prepared by dissolving 1.22 g of tris(hydroxymethyl)aminomethane in 1 L of distilled water and adjusting the pH to 8.5 (10 mM) with concentrated HCl. The resulting solution was stored at room temperature. Co-deposition solutions with PDA were prepared by dissolving in 200 ml tris-HCl buffer solution (pH ~8.5, 10 mM): 0.298 g of 15C5/DA or 0.345 g of 18C6/DA, 0.4 g of dopamine hydrochloride, and 0.250 g of CuSO₄·5H₂O. The solution was completed with 0.4 mL of H₂O₂. The PEI/DA solution was prepared by dissolving in 200 mL tris-HCl: 0.2 g of PEI, 0.4 g of dopamine hydrochloride, and 0.250 g of CuSO₄·5H₂O. Then, 0.4 mL of H₂O₂ was added. Following this, 2.5 wt% GA aqueous solution was prepared by adding 10 mL of GA (50 wt%) to 190 mL of distilled water.

CEMs (11 × 11 cm²) were horizontally immersed into the freshly prepared 15C5/DA or 18C6/DA co-deposition solution for 6 h at 25 °C. The membranes were then washed and immersed into the freshly prepared PEI/DA solution for 6 h at 25 °C. The modified membrane was washed with DI water three times before being immersed into the freshly prepared GA aqueous solution for 30 min at 50 °C. Finally, the treated membrane was rinsed three times and stored in DI water for further characterization and performance evaluation (Figure 1).

Morphology and structure characterization

The morphology and structure of the membranes were characterized using infrared spectroscopy and scanning electron microscopy. To examine the chemical structure of the membrane surface, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) in the spectral range 4,000–400 cm⁻¹ was used (Nicolet iS50, Thermo-Fisher Scientific). The distribution of elements in the cross-section of both nonmodified and modified CEMs was observed using a scanning electron microscope (SEM, SU8010 Hitachi, Japan). An energy-dispersive X-ray (EDX) detector (AMETEK Inc., USA) was utilized to analyze the elemental composition of the membranes. In addition, the hydrophilicity of the membranes was assessed using static water contact angle measurements with an optical contact angle goniometer (Krüss, DSA25). All samples were characterized after drying in a vacuum dryer for over 24 h.



Figure 1 | Images of the nonmodified (left) and crown ether–modified membranes (15C5 (middle) and 18C6 (right)). All membranes were of size $11 \times 11 \text{ cm}^2$.

Water uptake characterization

Water uptake (WU) refers to the water absorbed by the membrane (relative to the dry membrane) after it is immersed in water for 24 h. First, the membranes were dried for 24 h at 42°C and weighed. In the next step, the samples were immersed in water for 24 h at 25°C . The wet membrane samples were dried with filter paper to remove additional moisture and weighed. WU is determined using Equation (1), where W_{wet} (g) and W_{dry} (g) are the weight of the wet and dry membranes, respectively.

$$\text{WU} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)$$

IEC capacity characterization

IEC capacity (IEC) refers to the number of fixed charges per unit weight of dry polymer (W_{dry} , g) and is determined by experimental titration (Strathmann 2010). To measure IEC, nonmodified and modified membranes were equilibrated for approximately 24 h in 1 M HCl to exchange all cations in the membrane matrix with H^+ . After this, the membranes are washed with DI water to remove the residual H^+ from the membrane surface. The membrane is further immersed in a 1 M NaCl solution for 24 h to release H^+ into the solution. The IEC of each sample is determined by back titration with a known volume (V_{NaOH} , L) of 10 mM NaOH (C_{NaOH} , mmol/L). Equation (2) gives the equation to determine the IEC (mmol/g) values.

$$\text{IEC} = \frac{C_{\text{NaOH}} \times V_{\text{NaOH}}}{W_{\text{dry}}} \quad (2)$$

Electrical resistance characterization

The surface resistance of the modified and nonmodified membranes was measured using the current interrupt method (Mosquera-Romero *et al.* 2022). The electrochemical cell consisted of two chambers (0.2 L) with end plates on each side and two frames (internal dimensions $5 \times 20 \times 2 \text{ cm}^3$) placed in parallel in the middle (Supplementary material S3). The materials for the anode and cathode were $5 \times 20 \text{ cm}^2$ Ti/RuO₂ (MMO Magneto) and a $5 \times 20 \text{ cm}^2$ stainless steel mesh (AISI 316L mesh size 495 μm , wire thickness 200 μm ; Solana) respectively. Two reference electrodes (RE-1B and ALS) comprising of Ag/AgCl (3 M KCl, +0.21 V vs. SHE) as working electrode (Rref2) and counter electrode (Rref1) were installed at an approximately 0.3 cm distance from the anode and cathode. For stability verification, the electrodes were checked against the standard calomel electrode. The membranes with a membrane area (A_m) of 64 cm^2 were placed in the middle of the cell, dividing the cathode and anode compartments. Voltage for the cells was supplied by a potentiostat (Biologic, the Netherlands). A solution of 0.5 M NaCl or KCl was pumped through the compartments with a continuous flow rate of 100 mL/min with a peristaltic pump (Masterflex L/S) for both compartments. Resistance (R_i) of the membrane ($\Omega \text{ cm}^2$) was determined using the following equation:

$$R_i = (R_{\text{ref2}} - R_{\text{ref1}}) \times A_m \quad (3)$$

Monovalent selectivity characterization

To assess the separation performance and transport of ions, pristine and modified membranes were tested in a six-compartment cell setup with two solutions: an equimolar binary composition of Na^+ and K^+ (1:1) and greenhouse wastewater with a Na^+/K^+ ratio of 1:0.3 (Guleria *et al.* 2024) (Supplementary material S4). The perm-selectivity of Na^+ and K^+ for the nonmodified, DA, 15C5, and 18C6 membranes was measured at a constant current of 5 mA/cm^2 at room temperature (current-voltage curves for the nonmodified and modified membrane are given in Supplementary material S5). The ion flux across the membranes, indicated by a change in concentration (mmol/L) in the concentrate cell, is given by the following equation:

$$J_i = \frac{V dC_i}{A dt} \quad (4)$$

J_i ($\text{mmol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) is the flux of the cation i (Na^+ or K^+), V (L) is the volume of the concentrate compartment, A is the membrane working area (0.0064 m^2), and dC_i/dt (mmol/L) is the concentration change of ion i over time. The perm-selectivity P_j^i between two ions i and j was calculated using the following equation, where $\Delta C_{i,j}$ is the concentration difference of each of the ions determined by ion chromatography. All data points were collected in duplicates.

$$P_j^i = \frac{J_i \Delta C_j}{J_j \Delta C_i} \quad (5)$$

RESULTS AND DISCUSSION

Membrane surface characterization

ATR-FTIR was conducted to analyze the pristine and modified CEMs. Figure 2 shows the FTIR spectra of the pristine, DA-modified, and crown ether-modified membranes (15C5 and 18C6). A strong peak at $1,057 \text{ cm}^{-1}$ indicates the sulfonated group vibration of the pristine CEM membrane (Sharma *et al.* 2018). Peaks at 950 and $1,130 \text{ cm}^{-1}$ are attributed to $-\text{CH}_2-$ and ether functional group ($\text{C}-\text{O}-\text{C}$) stretching from the crown ether ring vibrations for the modified membranes (Kim *et al.* 2015; Yang *et al.* 2019). The peak at $2,850 \text{ cm}^{-1}$ is characteristic for the $\text{C}-\text{H}$ bond stretch (Kim *et al.* 2015). The stretched peak at $3,500 \text{ cm}^{-1}$ corresponds to the $\text{O}-\text{H}$ bond in the sulfonate group, where the pristine membrane shows a narrower peak due to a weaker moist adsorption from the base commercial membrane (Yang *et al.* 2021). Peaks at $1,550 \text{ cm}^{-1}$ depict the $\text{N}-\text{H}$ shearing vibrations from DA, PEI, and CE modifications (Zhang *et al.* 2014).

Furthermore, the chemical composition of the membranes was qualitatively analyzed using SEM-EDX at $100\times$ magnification (Table 3 and Figure 3). Carbon atoms are more abundant along the reinforcing fibers of the membrane. The other atoms (O, N, S) are uniformly distributed. After the first coating, the number of N atoms increased, and the number of S

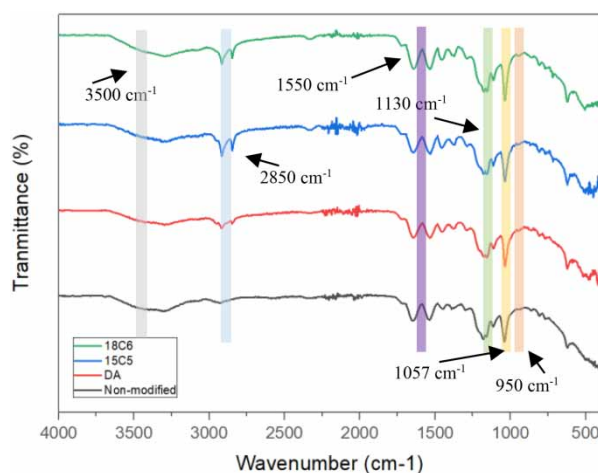
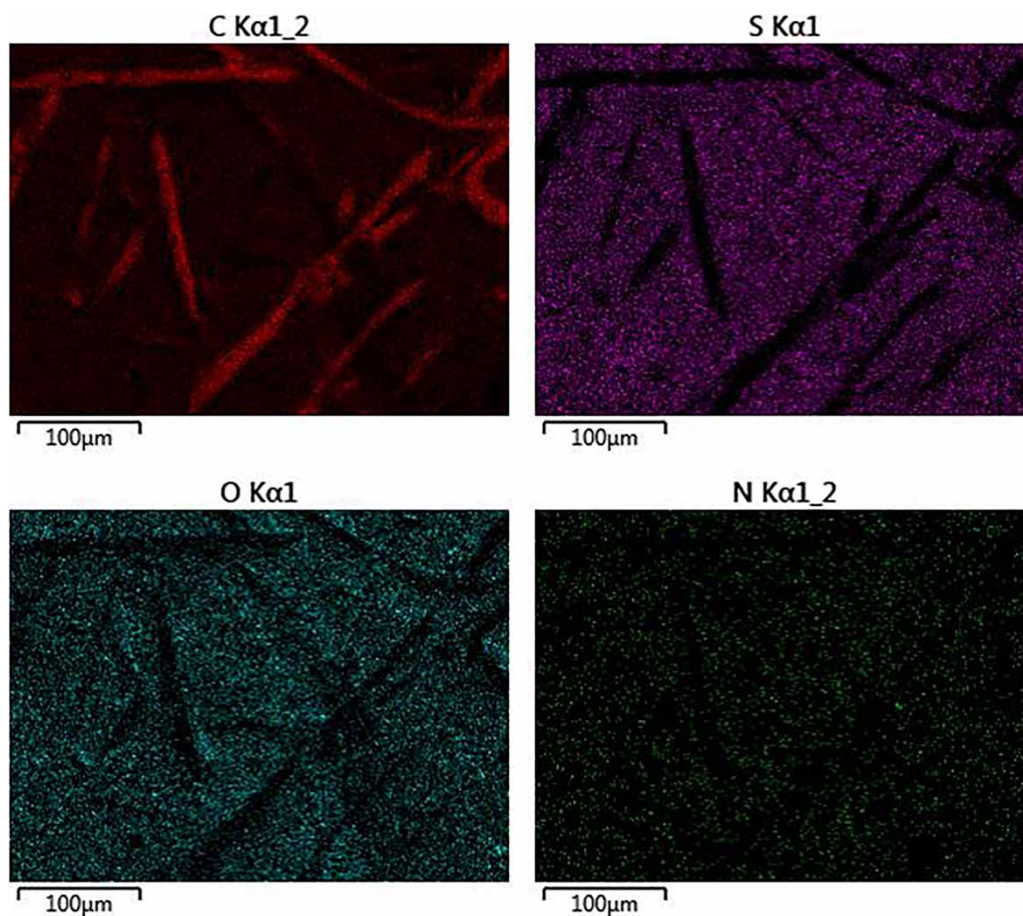


Figure 2 | FTIR spectra of the nonmodified CEM, DA-modified membrane, 15C5-modified membrane, and 18C6-modified membrane.

Table 3 | SEM-EDX analysis for nonmodified, DA-modified, and crown ether-modified membranes (15C5 and 18C6)

Membrane	C (%)	O (%)	N (%)	S (%)	C/O	C/N	O/N
Nonmodified CEM	63.0	25.2	6.8	4.9	2.5	9.3	3.7
DA	63.8	22.6	8.2	4.3	2.8	7.8	2.8
15C5	64.2	22.2	7.9	4.0	2.9	8.1	2.8
18C6	65	22.4	7.1	3.8	2.9	9.2	3.2

**Figure 3** | Surface elemental mapping images of the 15C5-modified membranes (analysis for all the membranes is given in Supplementary material S6).

and O atoms decreased. This indicates the presence of DA, which contains more N and less S and O than the membrane matrix. For the crown ether-modified membranes, the C/O ratio increased slightly from 2.5 to 2.9, and the O/N ratio increased from 2.8 to 3.2 compared to the DA membrane. This can be attributed to the higher O element and N element in the 15C5/18C6 molecule. Thus, the shifts in absorption bands and changes in chemical composition indicate modifications in functional groups and potential structural rearrangements. These structural changes were further supported by variations in membrane resistance, IEC and perm-selectivity, elaborated in the following sections.

Physiochemical properties

WU and IEC analysis were conducted to determine the membrane performances in terms of exchangeable ionic sites and the percentage of the hydrophilic domain within the membrane matrix. Figure 4 presents the IEC and WU results for the

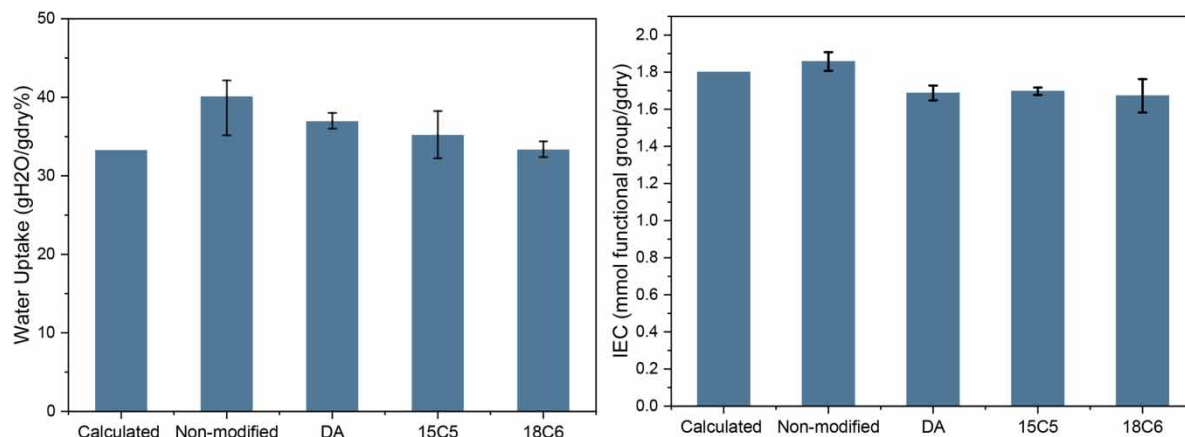


Figure 4 | WU and IEC results for the theoretically calculated, nonmodified, DA-modified, and crown ether-modified membranes (15C5 and 18C6).

nonmodified, DA-modified, and crown ether-modified membranes. Both WU and IEC decreased with the DA and crown ether modifications. For a membrane to be considered an IEM, IEC is typically expected to be between 1 and 3 mmol functional groups/g dry membrane (Strathmann 2010). The modified membranes fell within the range for ED applications. A 10% reduction in IEC was observed with the co-deposition-modified membranes (nonmodified: 1.86 mmol/g, DA: 1.68 mmol/g, 15C5: 1.68 mmol/g, and 18C6: 1.67 mmol/g). This reduction may be due to the interaction of positive PEI-derived amine groups on the surface of the membrane and the permeation of small DA molecules into the membrane, which interact with the sulfonated groups. The positive amine groups on PEI would attract and bind with the negatively charged sulfonated groups within the membrane. This binding can cause a partial charge neutralization and reduction in the free volume/pore size within the membrane, potentially altering the IEC (Yao *et al.* 2013).

WU reflects the hydrophilic character and the presence of water in the membrane cavities. After a single modification with DA, WU decreased by 7.5% in comparison to the nonmodified membrane and after the 15C5/DA and 18C6/DA modification, WU decreased by 12.5 and 17.5%, respectively. Overall, with the modification steps, there is more accumulation and interaction of modified media in the membrane (Luo *et al.* 2020; Yang *et al.* 2021), impacting the physiochemical performance of the membranes.

Electrical resistance properties

The electrical resistance indicates the required energy for the ED process. The electrical resistance of the nonmodified, DA-modified, and crown ether-modified membranes is provided in Figure 5. The nonmodified membrane had a resistance of 5.6 Ω cm² (specifications of the commercial CEM given in Supplementary material S1). With the modifications, the resistance of the membranes increased up to 20 and 23% for the 15C5- and 18C6-modified membranes. This can be attributed to the increase in membrane thickness due to modification layers on the modified membranes and some deposition of modification compounds within the membrane structure. Furthermore, co-deposition media on the membrane surface will penetrate into the inner matrix of the membrane, partially inhibiting cation migration and leading to higher resistance (Yao *et al.* 2013). From these results, it can also be seen that the increase in resistance is in line with the decrease in IEC and WU.

Monovalent cation selectivity

ED experiments were conducted to investigate the separation of Na⁺/K⁺ ions for the pristine and modified membranes. Figure 6 shows the perm-selectivity and ion fluxes obtained with equimolar Na⁺:K⁺ (1:1) and greenhouse wastewater with Na⁺:K⁺ (1:0.3) feed ratios for the nonmodified and modified membranes. The nonmodified membranes show low selectivity with both the equimolar initial feed $P_{Na^+}^{K^+} = 0.93 \pm 0.03$ and greenhouse initial feed $P_{Na^+}^{K^+} = 1.08 \pm 0.02$. For the crown ether-modified membranes, the selectivity for 15C5 was $P_{Na^+}^{K^+} = 0.95 \pm 0.15$ with the equimolar feed composition and $P_{Na^+}^{K^+} = 1.02 \pm 0.016$ for the greenhouse feed composition. The highest selectivity was observed to be slightly increased for K⁺ ions for the equimolar initial feed ($P_{Na^+}^{K^+} = 1.1$). It was expected that the K⁺ ion would form complexes with the functionalized

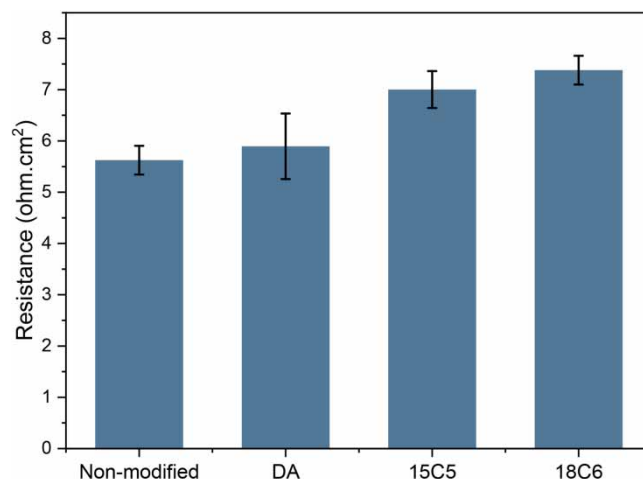


Figure 5 | Electrical resistance results for the nonmodified, DA-modified, and crown ether-modified membranes (15C5 and 18C6).

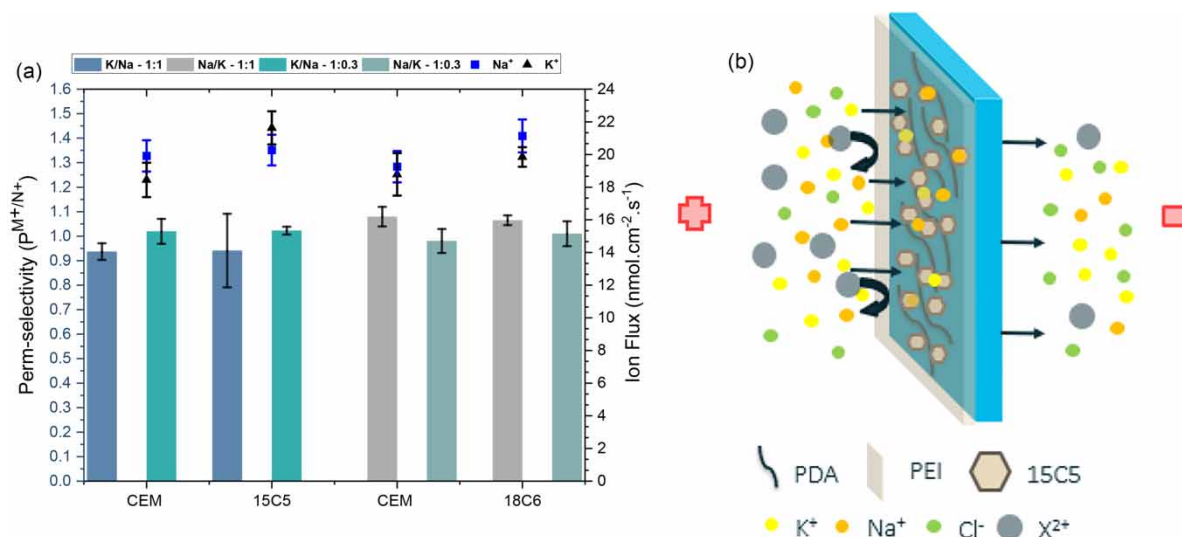


Figure 6 | (a) Perm-selectivity (P^{M^+/N^+}) and ion flux of the nonmodified and modified membrane (15C5 and 18C6) conducted with an equimolar NaCl and KCl solution (Na:K; 1:1) and a greenhouse wastewater solution (Na:K; 1:0.3). M^+ and N^+ depict Na⁺ and K⁺, to show target ion selectivity over the other based on the crown ether used for membrane modification. (b) Graphical depiction of the possible Na⁺/K⁺ ionic separation of the 15C5 crown ether-modified membranes. PDA, polydopamine; PEI, polyethyleneimine; 15C5, functionalized benzo 15-crown-5; X²⁺, divalent cations; and other symbols, hydrated monovalent ions. Possible enhanced K⁺ selectivity can be attributed to the lower interaction energy of K⁺ ions in a 2:1 host-guest interaction between crown ether molecules, compared to the ion-cavity interaction with a single crown ether. K⁺ also has lower dehydration energy, allowing easier transport through membrane channels. Alternatively, 15C5 crown ether may form more stable complexes with Na⁺, reducing Na⁺ mobility relative to K⁺.

crown ether cavity (Supplementary material S8); however, minimal or no improvement in selectivity was observed after the modifications. Selective separation of Na⁺/K⁺ is challenging due to the similarity in molecular properties between the two ions in aqueous systems. Yang *et al.* (2019) observed a K⁺ selectivity of 0.63 for pristine CEM increasing to 1.45 for the 15C5 crown ether-modified membrane. For 18C6 runs, the perm-selectivity values observed were $P_{Na^+}^{K^+} = 1.06 \pm 0.02$ and $P_{Na^+}^{K^+} = 1.01 \pm 0.05$ for equimolar and greenhouse wastewater binary feed compositions, respectively. Tas *et al.* (2017) reported selectivity of K⁺ over Li⁺ with synthesized 18C6 crown ether-modified membranes; however, this was only for the initial stages of the experiments. This was attributed to the reduced availability of crown ether binding sites over time and the increase in hydrophobicity affecting the relative mobility of the ions (Supplementary material S7). Interestingly, Sata *et al.* (2000)

have previously reported an approximately 40% decrease in $P_{Na^+}^{K^+}$ with 18C6 (100 g/L) compared to modified commercial membranes, possibly caused by the reduced mobility of K^+ within the membrane phase due to the formation of a more stable complex with the crown ether as compared to Na^+ , as indicated by the increased electrical resistance of the membrane during ED.

In this study, a slightly enhanced selectivity for K^+ with the 15C5-modified membrane was observed, but this was lower than reported in the literature for equimolar feed solutions and insignificant for the greenhouse binary feed. This result contrasts with the expected selectivity and permeation of Na^+ based on the 15C5 crown ether's cavity size (Torun 1994), and similar findings have been reported in recent studies (Yang *et al.* 2019; Qian *et al.* 2020). These studies suggest that the crown ether promotes host-guest molecules interactions and facilitates the mobility of partially dehydrated target ionic species across the membrane. The energy needed for partial dehydration when entering the membrane should be compensated for by crown ether oxygen and cation interaction, thus favoring the specific ion partitioning over the membrane. Contrary to expectation, the observed trends may be explained by the lower interaction energy of K^+ ion sandwiched (2:1 host-guest interaction) between crown ether molecules in comparison to the ion-cavity ring interaction with a single crown ether molecule, as reported in literature (Kim *et al.* 1999; Yang *et al.* 2019). K^+ has a lower dehydration energy, as smaller hydrated radii ions with lower hydration-free energy can more readily transport through the membrane channels (Epszstein *et al.* 2019). Alternatively, 15C5 crown ether molecule might be interacting with Na^+ , forming more stable complexes than K^+ ions, decreasing their mobility through the membrane. However, it should be noted this was reported in the literature for membranes comprising of 100 g/L crown ether concentration as compared to <10 g/L for this study (Sata *et al.* 2000). The effectiveness of cation separation by crown ether-modified membranes relies on their arrangement on the membrane surface to create precise pathways for selective transport. The specific binding affinity of crown ethers depends on the match between the size of the cation and the cavity size of the crown ether (the cavity diameter and donor atom type of the crown ether, as well as the size and charge of the metal ion), with additional complexity from interactions with solvents and ions (Gromov *et al.* 2021). Thus, strategic incorporation of the crown ether ligands in the polymer network along with optimized copolymerization (controlled integration of various functional groups within the membrane) can potentially enable efficient ion separation by selectively binding Na^+/K^+ .

Fujifilm IEMs used in this study are less hydrophobic as they are typically produced using a technique where an ion-exchangeable polymer is applied as a coating over three-dimensional structured nanofibers, which serve as an internal framework. Consequently, the entire surface of the membranes is covered by the ion-exchangeable polymer, creating a more hydrophilic surface. Thus, the extent of ion partition by exploiting partial dehydration is not fully realized. Alternatively, to improve this, infusing the porous substrate with a UV-cross-linkable electrolyte and crosslinking agent monomers, followed by UV curing and surface polishing, could expose more hydrophobic polyolefin support, creating a predominantly hydrophobic membrane (Akter & Park 2023). No significant change in the flux was observed for both modified membranes compared to the unmodified membrane (Figure 6). A slight increase in the flux of K^+ was recorded for the 15C5-modified membrane, corroborating the selectivity observations. The low IEC and high resistances play a role in the complexation of target ions and limit their transfer rate in the membrane phase. However, no significant differences were observed in the flux of the ions for both membranes. Yang *et al.* (2019) observed similar results with sulfonated polysulfone (SPSF)-based crown ether-modified CEMs.

Future perspective for Na^+/K^+ ion separation for practical application

Instead of developing novel membranes, selective separation of Na^+/K^+ might be achieved by ion-selective process technologies such as Donnan dialysis (DD) and IEX. DD leverages the differential migration of ions across a membrane driven by concentration gradients that can be tailored for Na^+/K^+ separation by choosing inputs and operating parameters with specific IEX properties (Chen *et al.* 2023). However, IEX systems can be designed with resins that interact with Na^+ and less with K^+ , though the challenge lies in achieving and maintaining high selectivity under operational conditions (Dupont 2019). Future studies will focus on technologies for high Na^+/K^+ ion separation, specifically for application in the greenhouse horticulture sector. While the literature and experimental approaches are invaluable in developing novel selective membranes, as evidenced by the body of literature ('Background on Na^+/K^+ selective membrane development' section) and experimentation ('Materials and methods' section), designing IEMs design for Na^+/K^+ selective membranes present significant hurdles. Synthesizing and validating possible combinations of membrane polymers and ionophores can be laborious, time-consuming, and expensive. Therefore, theoretical and ML models promise to improve the development of selective

IEM materials and membranes. Successful research with these approaches has been reported in membrane design (Yin *et al.* 2024), gas-separating membranes (Yuan *et al.* 2021), and fuel cell development (Li *et al.* 2021). However, very few studies have used these methods for ISM development. No investigations related to selectivity for Na⁺/K⁺ separation have been reported to the best of the authors' knowledge.

For the accurate discovery of selective membranes using computational methods, high-quality and standardized data are crucial. Essential steps include preprocessing data from different sources and implementation of feature engineering to identify key descriptors of selective membrane designs, given that data are often limited particularly for ISMs (Cai *et al.* 2020; Yin *et al.* 2024). This emphasizes the need to conduct pertinent experiments and manage the data in a comprehensible and reusable database. Conversely, feature engineering refers to a technique, commonly used in the field of MLL, to find specific membrane material descriptors. The latter is relevant to the desired ISM pathways, which include (i) pore size and hydrophobicity: to control pore size and uniformity for high ion selectivity; (ii) surface charge: the impact of functional group charges on ion affinity; (iii) polymer blend: morphological aspects of the polymer; (iv) driving force: the effect of applied potential difference on ion mobility; and (v) computation simulations: an underexplored feature, data from molecular dynamics (MD), density functional theory, and computational chemistry (e.g., atomic radius, valency, electronegativity) to estimate the molecular structural characteristics and interactions. In addition, existing open-source computational chemistry databases such as Pymatgen, AFLOWLIB, and NanoHUB can be leveraged (Cai *et al.* 2020). Furthermore, quantitative structural property relationship, a promising method to study ligands with high selectivity toward specific ions, can aid in discovering new material. This approach has been demonstrated for Li⁺/Na⁺ (Solov'ev *et al.*) and Mg²⁺/Ca²⁺ separation (Martyanko *et al.* 2020). This enables the addition of more potential features. With the availability of such datasets, ML models can potentially be applied to improve the accuracy of predicting the selectivity of a proposed membrane composition. Previously reported promising ML methods include metal-organic framework (MOF) material discovery for a gas separation membrane using Random Forest, membrane fabrication for macromolecules with a Bayesian optimization algorithm and coarse-grained MD (Wang *et al.* 2020), high-performance polymer prediction with Gaussian process regression and chemical structure fingerprinting (Barnett *et al.* 2020), ion retention prediction with artificial neural networks, and inverse design with genetic algorithms (Ritt *et al.* 2022). In combination, publicly available standardized datasets on platforms like GitHub can accelerate selective membrane development (Yin *et al.* 2024). Finally, in small-set data applications (e.g., <200 samples), limitations in data availability can hinder the applicability of ML models. To overcome this, data augmentation and iterative model training and assessment with synthetic samples can potentially provide an optimal number of the least number of required samples to reach a performance threshold (Tian *et al.* 2023). Thus, to develop highly selective Na⁺/K⁺ membranes by engineering the surface and molecular structure, specifically to optimize the selectivity–resistance–scalability trade-off, ML-powered ISM methods (Supplementary material S9) can significantly aid future research.

CONCLUSIONS

There is growing interest in developing selective membrane solutions to facilitate water reuse and material recovery, e.g., in the context of industrial symbiosis (IS). In the H2020 EU funded ULTIMATE project, the efficient separation of Na⁺/K⁺ ions using ED, specifically for circular greenhouse wastewater reuse, was investigated. One approach to achieve selective separation is the application of selective membranes. Reviewing of previous experimental work, this research identified surface modification with crown ethers (15C5 and 18C6) as the most promising development approach for Na⁺/K⁺ separation membranes with potential for application at a relevant scale under process conditions. This was concluded on the basis of a selectivity–resistance–scalability assessment of the available synthesis methods for selective membranes. Commercial membranes were successfully functionalized with crown ethers (15C5 and 18C6) and characterized. Both membranes showed low selectivity for equimolar and greenhouse wastewater ratio feeds. Marginally enhanced selectivity of K⁺ was observed with the 15C5-modified membrane, potentially attributed to partially dehydrated ion size exclusion or mobility retardation due to stable complexation with the target ion. The selectivity achieved is insufficient to meet the requirements of the greenhouse application. To better understand the potential of crown ether–functionalized membranes for selective Na⁺/K⁺ separation, future research should focus on the strategic incorporation of crown ether ligands into the polymer matrix. Optimizing copolymerization and precisely integrating functional groups within the membrane could improve ion separation efficiency by selectively binding Na⁺ and K⁺ ions, for this challenging separation. A deeper understanding of ion interactions with selective binding sites, as well as optimizing nanochannel spacing for enhanced ion-binding affinity, will be crucial for advancing this

technology. Furthermore, understanding the fundamental separation mechanism and the membrane development process can significantly benefit from ML-assisted membrane approach, specifically in combination with computational methods and data augmentation techniques. Finally, process technologies such as DD and IEX could be explored for efficient Na^+ / K^+ separation for practical application from greenhouse wastewater.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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