



# Selective sodium removal with electrodialysis by modifying concentration gradients using EDTA complexation

Selin Ozkul<sup>a</sup>, Hadar Scharfberg<sup>a</sup>, Roel J.M. Bisselink<sup>b</sup>, Norbert J.M. Kuipers<sup>b</sup>, Harry Bruning<sup>a</sup>, Huub H.M. Rijnaarts<sup>a</sup>, Jouke E. Dykstra<sup>a,\*</sup>

<sup>a</sup> Environmental Technology, Wageningen University & Research, Bornse Weilanden 9, 6708 WG Wageningen, The Netherlands

<sup>b</sup> Food and Biobased Research, Wageningen University & Research, Bornse Weilanden 9, 6708 WG Wageningen, The Netherlands

## ARTICLE INFO

### Keywords:

Electrodialysis  
Sodium removal  
Ion transport  
EDTA complexation  
Selective diffusion  
Desalination

## ABSTRACT

Circular water reuse is often limited by the accumulation of harmful ions and the loss of valuable ions during water desalination. Selective removal of specific ions from water is essential but challenging with conventional desalination technologies, especially for ions with similar properties, such as sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ). In the present study, the use of electrodialysis in combination with EDTA complexation in the concentrate is proposed to selectively remove  $\text{Na}^+$  ions from a multi-ionic solution containing  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{NO}_3^-$  ions. Electrodialysis experiments were conducted at lab-scale at different operational conditions (i.e. solution pH, applied voltage, EDTA/ $\text{Na}^+$  ratio and solution ion composition) to evaluate the selectivity of the proposed process. It was found that a high solution pH ( $>10$ ) and a low applied voltage ( $<0.3$  V per cell pair) is required to maximize the selective transport of  $\text{Na}^+$  ions, while the presence of other metal ions in solution limits the process efficiency. The effect of the proposed process on the transport mechanisms in electrodialysis, which are electromigration, convection and diffusion, was also examined. The provided analysis concluded that the electromigration and convection mechanisms show the largest contribution to the transport of both  $\text{Na}^+$  and  $\text{K}^+$  ions, while the process selectivity is controlled by selective diffusion of ions which is enhanced by EDTA complexation. Finally, the regeneration and recovery of EDTA with acidification was experimentally evaluated at different pH values and different precipitation times; recoveries of  $>95\%$  were achieved with an acidic solution with pH  $< 2$  in 30 min.

## 1. Introduction

Selective removal of ions from a solution is often essential for circular water reuse to prevent the accumulation of harmful ions, such as sodium ( $\text{Na}^+$ ), and the loss of valuable compounds, such as potassium ( $\text{K}^+$ ), which decreases the quality of water [1,2]. Especially in agriculture, reducing the  $\text{Na}^+$  concentration in water to the threshold level is required while keeping the  $\text{K}^+$  concentration as high as possible [3,4]. However, selective separation of ions with similar physicochemical properties (e.g., valency and size) is still a challenge due to the low selectivity of conventional desalination technologies. Electrodialysis (ED) is a water treatment technology that uses ion-exchange membranes (IEMs) to remove charged species from a solution by applying an electric field. The process consists of cation exchange membranes (CEMs) and anion exchange membranes (AEMs) placed in alternating order that allow oppositely charged ions to pass through, creating the diluate and concentrate channels [5–7]. Selective ion removal with ED depends on

various parameters, such as membrane properties and process operational conditions [8], which allows to achieve ion-selective transport by tuning different parameters.

Transport of ions through IEMs in the ED process is determined by three main mechanisms: electromigration due to a potential gradient across the membranes, convection due to water transport through the membranes, and diffusion due to a concentration gradient over the membranes [9–11]. In conventional ED, electromigration and convection enhance the removal of ions that have high affinity and high mobility in the membrane [8,11]. Diffusion, on the other hand, shows opposite trends for the ions with different properties due to the asymmetric concentration profiles building up in the IEMs to maintain electroneutrality. As a result, the ions with a negative concentration gradient (with low affinity, i.e.  $\text{Na}^+$ ) diffuse to the concentrate channel, meanwhile the ones with a positive concentration gradient (with high affinity, i.e.  $\text{K}^+$ ) diffuse to the diluate channel [8,11]. Concentration gradients of the ions over the membranes, which control selective diffusion, are not

\* Corresponding author.

E-mail address: [jouke.dykstra@wur.nl](mailto:jouke.dykstra@wur.nl) (J.E. Dykstra).

<https://doi.org/10.1016/j.seppur.2024.126337>

Received 3 November 2023; Received in revised form 24 December 2023; Accepted 5 January 2024

Available online 7 January 2024

1383-5866/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

only depending on the properties of the ions, but also on their free concentration in the diluate and concentrate. By adjusting the free ion concentration between the two channels in ED, it is, in theory, possible to enhance selective removal of specific ions with low affinity and low mobility which are difficult to be removed by the ED process.

To adjust the free ion concentration in the flow channels, chelating agents may be used. Chelating agents are organic compounds that can bind to metal ions and decrease their free concentration in solution based on their specific formation constants [12]. The agents are being applied in various industries for hardness removal, wastewater treatment and soil remediation [13]. One of the chelating agents that has been widely used in aqueous solutions is **ethylenediaminetetraacetic acid (EDTA)** due to its ability to form a stable metal–ligand complex with many metal species in solution, low biodegradability under natural conditions, and reusability [14–17]. The use of EDTA in combination with ED to improve selective removal of ions from water systems has been previously investigated [18–23]. Cherif et al. has studied the selective separation of  $\text{Ag}^+$  ions from  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  ions based on their different affinities to bind EDTA [18]. Iizuka et al. and Chan et al. have reported the separation of  $\text{Li}^+$  ions from solutions containing  $\text{Co}^{2+}$  [19,20],  $\text{Ni}^{2+}$  and  $\text{Mn}^{3+}$  ions [20]. Separation of ions with the same valency was also investigated by Chaudhary et al. and Tzanetakakis et al. for separation of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions [21,22]. Babilas et al. studied the selective recovery of  $\text{Ni}^{2+}$  from  $\text{Cu}^{2+}$  ions [23]. To our knowledge, selective removal of monovalent ions with ED using EDTA complexation has not been studied before. In the mentioned studies, EDTA is used to change the charge of ions by creating negatively charge metal-EDTA complexes; therefore, the positively charged ions migrate through the CEMs, while the negatively charged complexes are being transported through the AEMs, allowing high metal recoveries of  $> 90\%$  for the ED set-ups with one or two compartments. However, the transport of the metal-EDTA complexes through the AEMs was reported to be slow, which increases the treatment time, limits the total ion removal and reduces the process current efficiency [18]. The EDTA use in the diluate channel can limit the reuse of the diluate solution and its discharge to the environment due to the high pH of the solution that is required for complexation and the possible EDTA presence. The high concentration of EDTA can increase the risk of eutrophication, solubilize contaminant metals and increase their environmental mobility, change soil properties and decrease plant growth [15,24,25]; therefore, the solution with EDTA requires additional treatment prior to discharge to the environment. EDTA can also be recovered from a solution and reused for several cycles without significant loss of its efficiency [26,27]. There are three main methods being used to recover EDTA from a solution: electrochemical reduction, precipitation with zero-valent metals, and acidification [17]. Among them acidification causes less operational problems and is considered to be economically more feasible [17,28].

Previously, we reported that the selective transport of  $\text{Na}^+$  over  $\text{K}^+$  ions in ED can be achieved by controlling the concentration gradients between the diluate and concentrate channels due to the opposite contribution of the diffusion mechanism to the transport of ions [11]. In the present study on how to achieve selective removal of  $\text{Na}^+$  over  $\text{K}^+$  ions in ED, we investigated the use of selective complexation with EDTA to change the concentration gradients over the IEMs by altering the free ion concentration in the concentrate channel. In the proposed process, ions are being selectively transported as free ions with the help of their opposing concentration gradients in the membranes instead of being carried by EDTA, which aims to avoid the observed problems in previous studies. We conducted ED experiments to evaluate the effect of different operational conditions, such as pH of the solution, the applied voltage and the EDTA concentration on selective ion removal. Moreover, we studied the effect of other ions present in solution, such as lithium ( $\text{Li}^+$ ) and calcium ( $\text{Ca}^{2+}$ ), on the process performance. We provided

theoretical analysis to further study the influence of EDTA use in ED on the individual ion transport mechanisms: electromigration, convection and diffusion, and reported their contributions to selective ion removal. Additionally, we conducted batch experiments to investigate the regeneration and recovery of EDTA by acidification at different values of the solution pH and at different precipitation times to evaluate its reusability in the proposed process.

## 2. Principle: use of EDTA complexation in combination with electro dialysis

In order to achieve selective removal of  $\text{Na}^+$  over  $\text{K}^+$  ions from a solution, we propose ED in combination with complexation in the present study. The proposed process involves creating concentration gradients over the membranes by selectively decreasing the free concentration ratio of  $\text{Na}^+$  over  $\text{K}^+$  ions in the concentrate channel using complexation with EDTA; hence, facilitating the diffusion of  $\text{Na}^+$  ions to the concentrate channel while maintaining the diffusion of  $\text{K}^+$  ions to the diluate channel. In this way, it is possible to selectively remove ions with a negative concentration gradient ( $\text{Na}^+$ ), rather than the ones with a higher affinity and mobility inside the membrane ( $\text{K}^+$ ).

Selective binding of ions depends on the speciation of EDTA in solution, which can be controlled by the solution pH and the formation constants of EDTA with the ions. The EDTA speciation, the complexation of  $\text{Na}^+$  and  $\text{K}^+$  ions, and the free ion ratio in the solution based on the solution pH are presented in Fig. 1. When the pH of the solution is around 2, almost all EDTA in the solution stays in the nonionic  $\text{H}_4\text{EDTA}$  form; the fraction of dissociated forms of EDTA increases with the solution pH. Species such as  $\text{HEDTA}^{3-}$  and  $\text{H}_2\text{EDTA}^{2-}$  predominate at pH values of 3–8; when the pH of the solution is higher than 10, almost all EDTA is dissociated to  $\text{EDTA}^{4-}$ . The complexation reaction of a metal cation ( $M$ ) with EDTA ( $Y$ ) can be described as [29]

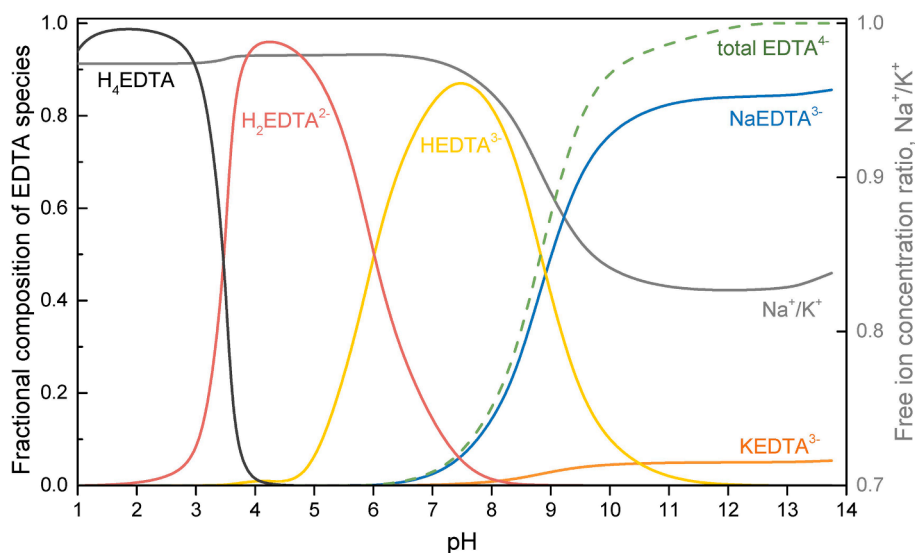


The formation constant ( $K_f$ ), also known as the stability constant, for EDTA complexation reaction, Eq. (1), is defined by [29]

$$K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]}. \quad (2)$$

Higher formation constants,  $K_f$ , indicate stronger tendency to bind that specific ion. Formation constants of EDTA with the metal cations used in the present study are given in Table 1. Since EDTA has a higher formation constant to bind  $\text{Na}^+$  ( $\log(K_f) = 1.86$ ) than  $\text{K}^+$  ions ( $\log(K_f) = 0.8$ ) (Table 1), it forms more complexes with  $\text{Na}^+$  ions in the solution resulting in a lower free  $\text{Na}^+$  concentration. The ratio of  $\text{Na}^+$  ions bound by EDTA increases with increasing pH; and at  $\text{pH} > 10$ , the free concentration ratio of  $\text{Na}^+$  over  $\text{K}^+$  ions in the solution reaches the minimum value (Fig. 1).

The schematic description of the proposed process is shown in Fig. 2. When the chelating agent EDTA is added to the concentrate channel of ED at  $\text{pH} > 8$ , it creates complexes with the ions in solution, decreasing the free ion concentration ratio of  $\text{Na}^+$  over  $\text{K}^+$  ions. As a result, a negative concentration gradient is built for the  $\text{Na}^+$  ions to be selectively transported from the dilute to the concentrate channel, which is the other way around for the  $\text{K}^+$  ions, resulting in selective removal of  $\text{Na}^+$  over  $\text{K}^+$  ions. The negatively charged EDTA species and the metal-EDTA complexes cannot pass through the CEMs and stay in the concentrate channel due to the arrangement of the IEMs in the ED stack, which allows the direct use of the diluate solution without need for further treatment for EDTA. The EDTA in the concentrate solution can be recovered in a post-treatment step.



**Fig. 1.** Fractional composition of EDTA species, Na-EDTA and K-EDTA complexes and the free ion concentration ratio based on the solution pH (prepared using OLI studio software: the total EDTA concentration is 0.1 M, and the total ion concentration, free and in the complex, is 0.5 M for  $\text{Na}^+$  and  $\text{K}^+$ ). At pH 1, the total concentration fraction of  $\text{H}_5\text{EDTA}^+$  and  $\text{H}_6\text{EDTA}^{2+}$  present in solution is  $\sim 0.05$ , and at pH 3.5, the concentration fraction of  $\text{H}_3\text{EDTA}^-$  is  $\sim 0.03$ , since the fractions are low, these species are not included in the figure.

**Table 1**

Formation constants of EDTA with the metal cations used in this study [29].

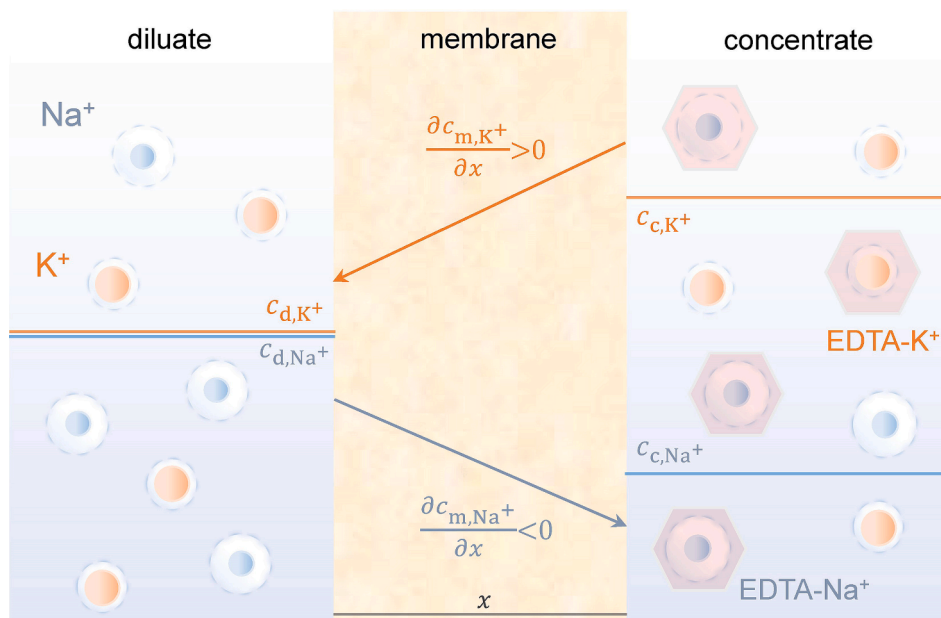
Ion	Formation constants, $\log(K_f)$
$\text{Li}^+$	2.95
$\text{Na}^+$	1.86
$\text{K}^+$	0.80
$\text{Ca}^{2+}$	10.65

### 3. Materials and methods

We conducted batch-mode ED experiments to investigate the effect of EDTA use in the concentrate channel on selective ion removal with different operational conditions and solution ion compositions. Additionally, we evaluated the regeneration and recovery of EDTA by acidification at various pH values and precipitation times.

#### 3.1. Electrodialysis experiments with EDTA

The ED experiments were performed using a laboratory-scale ED unit (PCCell BED 1–3 Compact, PCA GmbH, Germany) including ten



**Fig. 2.** Schematic description of the proposed electrodialysis process in combination with EDTA complexation. EDTA is added to the concentrate channel to increase the free ion concentration of  $\text{K}^+$  over  $\text{Na}^+$  ions, in this way concentration gradients in opposite direction build up inside the membrane ( $\frac{\partial c_{m,i}}{\partial x}$ ) for the ions due to electroneutrality as shown by the arrows. Asymmetric concentration profiles enhance selective transport of  $\text{Na}^+$  ions to the concentrate and of  $\text{K}^+$  ions to the diluate channel.  $x$  is the position inside the membrane;  $c_m$ ,  $c_d$  and  $c_c$  is for the ion concentrations in the membrane, and the diluate and the concentrate channel, respectively.

repeating cell pairs each consisting of one AEM (AMX-fg) and one CEM (CMX-fg) with 8 cm × 8 cm of active membrane area. During each experiment, 1 L of feed solutions were recirculated through the ED stack continuously at a flow rate of 70 L·h<sup>-1</sup> to ensure mixing. A power supply (Votcraft PPS-16005) was used to apply constant voltage during the experiments, and the current is monitored continuously by a digital multimeter (MetraHit 29S). Conductivity, pH, and temperature of the solutions were measured and recorded continuously throughout the experiments with a Hach SensION + MM374. Samples were collected periodically from the diluate solution and analysed using inductively-coupled plasma spectrometry (ICP, PerkinElmer Avio 500) to determine the concentration of cations in the solution. The presence of EDTA in the diluate solution was checked using Raman spectroscopy analysis to detect a possible EDTA-complex transport from the concentrate to the diluate channel, the results are presented in the [supplementary information \(SI\)](#). The temperature of the solutions was controlled at ~ 20 °C with a cooling system throughout the experiments.

Experiments were carried out at various conditions: applying constant voltage of 1.5, 2.3 and 3 V, using concentrate solutions with pH of 8.5, 10 and 13.1, and EDTA/Na<sup>+</sup> ratio of 0.3, 0.5 and 1, and having Ca<sup>2+</sup> and Li<sup>+</sup> ions in the solution. The solutions were prepared using demineralized water with reagent-grade nitrate (NO<sub>3</sub><sup>-</sup>) salts, K<sub>2</sub>EDTA and H<sub>4</sub>EDTA. The pH of the concentrate solution was set using KOH and NaOH as the base. The details of the experimental conditions can be found in [Table S1](#) in the SI. The experiments were evaluated considering the ion concentration ratio in the diluate solution, process selectivity and the total ion removal of the ED process. The process selectivity ( $\beta$ ) is calculated for Na<sup>+</sup> over K<sup>+</sup> ions as a function of time using [8]

$$\beta_{\text{Na}^+/\text{K}^+} = \frac{J_{\text{Na}^+} c_{\text{d},\text{K}^+}}{J_{\text{K}^+} c_{\text{d},\text{Na}^+}} \quad (3)$$

where  $c_{\text{d},i}$  is the concentration of ion  $i$  in the diluate channel and  $J_i$  is the flux of ion  $i$  from the diluate to the concentrate channel calculated by dividing the ion mass decrease in the diluate channel by membrane area and time interval between the measurements. The total ion removal ( $IR_t$ , %) is determined by

$$IR_t = \frac{c_{\text{d},0} - c_{\text{d},t}}{c_{\text{d},0}} \cdot 100 \quad (4)$$

where  $c_{\text{d},0}$  and  $c_{\text{d},t}$  are the total Na<sup>+</sup> and K<sup>+</sup> ion concentration in the diluate solution at the start of the experiment and time  $t$ .

### 3.2. Regeneration of EDTA with acidification

The regeneration of EDTA was studied by conducting batch acidification experiments where the EDTA in the solution was precipitated in the non-ionic form, H<sub>4</sub>EDTA, at low pH. The effect of the final solution pH (0.5 – 3) and the time for precipitation (10 – 210 mins) on EDTA recovery was investigated. Each solution was prepared using 0.1 M NaNO<sub>3</sub>, KNO<sub>3</sub> and H<sub>4</sub>EDTA, and the pH of the solutions was set to be > 10 using 0.2 M NaOH and KOH to start the complexation of EDTA with the ions. After complexation, nitric acid (HNO<sub>3</sub>, 65 % w/w) was used to start the acidification of EDTA and was slowly added to the solutions while stirring until the pH of the solution becomes stable; the acidic solutions were left for precipitation for varying times. The precipitated EDTA was then separated from the solution by vacuum filtration using a 0.45 μm membrane filter (Whatman ME 25/21 ST) and flushed with demineralized water repeatedly to collect the precipitated EDTA as much as possible. Thereafter, the filtered EDTA was dried in an oven at 105 °C for at least 18 h. After drying and cooling, the net precipitated EDTA was weighed and compared to the initial amount of EDTA added to the solution. The EDTA recovery ( $R_{\text{EDTA}}$ , %) was calculated using

$$R_{\text{EDTA}} = \frac{m_{\text{dry}}}{m_{\text{add}}} \cdot 100 \quad (5)$$

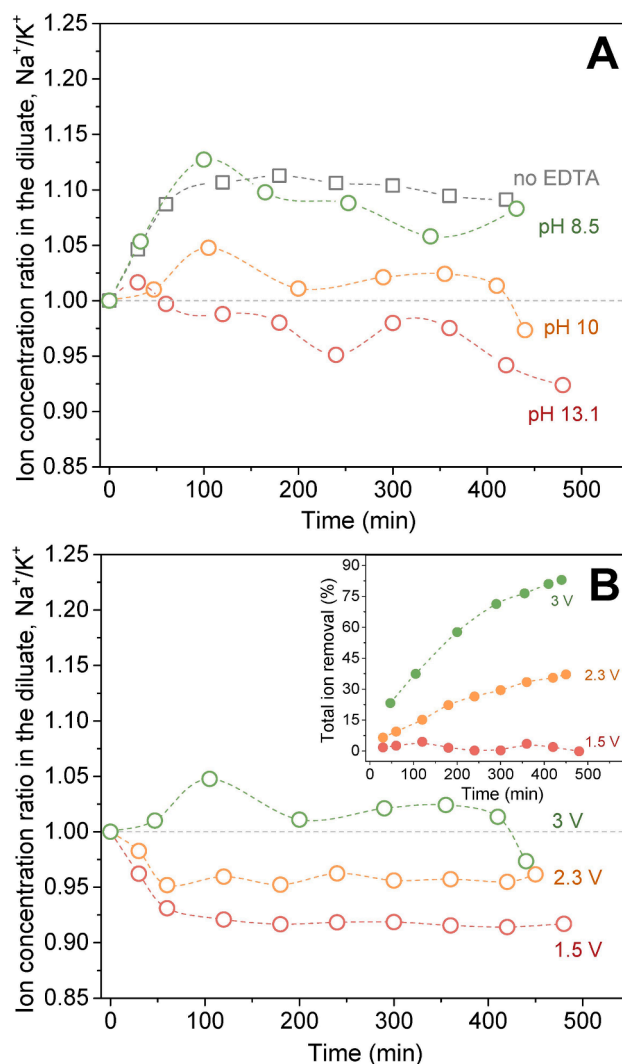
where  $m_{\text{add}}$  is the weight of EDTA added to the solution in the beginning of the experiments, and  $m_{\text{dry}}$  is the weight of the net precipitated EDTA.

## 4. Results and discussion

### 4.1. Effect of process operational conditions on selective ion transport: pH, applied voltage and EDTA amount

The ED experiments were conducted to investigate the effect of the concentrate solution pH and the applied voltage on selective transport of Na<sup>+</sup> and K<sup>+</sup> ions in presence of EDTA at three different pH values in the alkaline range (8.5, 10 and 13.1), and three different applied voltages (1.5, 2.3 and 3 V). Selective ion removal is evaluated based on the concentration ratio of Na<sup>+</sup> over K<sup>+</sup> ions in the diluate channel during process operation and the obtained results are presented in [Fig. 3](#). Created concentration profiles inside the membranes at the start of the experiments based on the solution pH is given in [Figure S2](#); current density data during the experiments based on the applied voltage is given in [Figure S3](#) in the SI.

The results showed that at pH 8.5 the concentration of Na<sup>+</sup> ions in the diluate channel remains higher than the concentration of K<sup>+</sup> ions



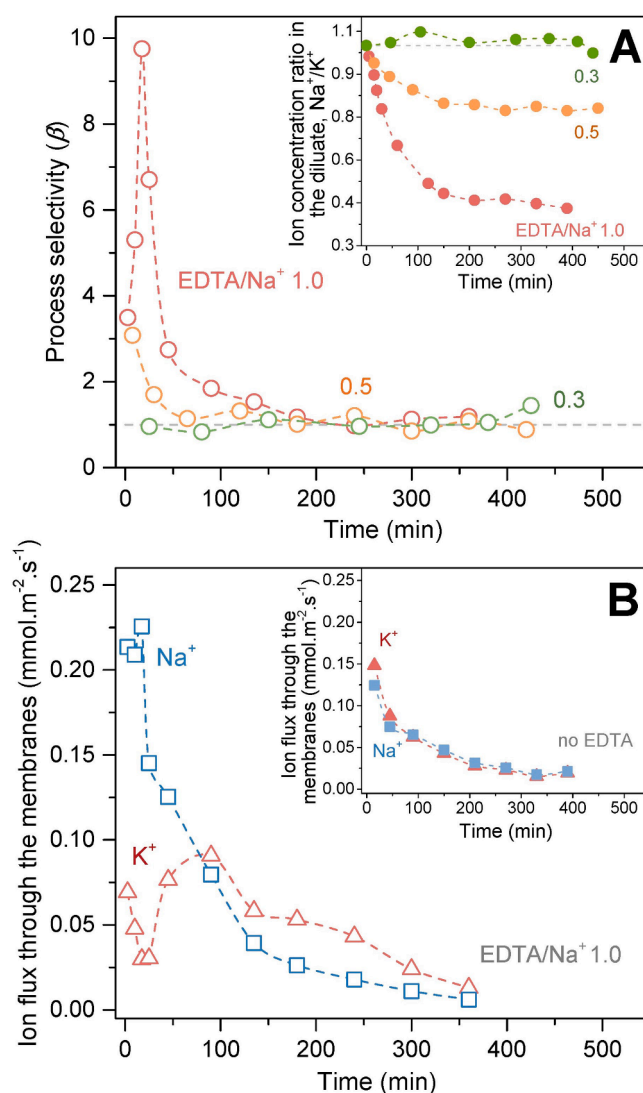
**Fig. 3.** Effect of operational conditions on selective ion removal with EDTA in electro dialysis: pH (A) and applied voltage (B) at pH 10. All diluate solutions include 0.1 M Na<sup>+</sup> and 0.1 M K<sup>+</sup> ions. The pH of the concentrate solution deviates, during operation, max. 10 % from the starting pH. Markers: experimental data, dashed lines serve to guide the eye.

during operation, which suggests that more  $K^+$  ions are being removed and selectively transported to the concentrate channel (Fig. 3A). At pH 8.5, H-EDTA<sup>3-</sup> is the most dominant specie in solution (Fig. 1), resulting in limited complexation of the monovalent ions by EDTA<sup>4-</sup>. Therefore, the effect of the concentration gradient on selective transport is limited, and the experiments conducted at pH 8.5 show similar selective ion transport as the experiments where no EDTA was added to the concentrate channel (Fig. 3A). When the solution pH is increased to 10, selective transport of  $Na^+$  ions is enhanced and the ratio of  $Na^+$  over  $K^+$  ions in the diluate channel decreases to values below 1 during operation. The effect of EDTA on selective ion transport in ED is more evident when the pH of the solution was increased to 13.1, decreasing the ratio of  $Na^+$  over  $K^+$  ions in the diluate solution for 15 % compared to the experiments with no EDTA addition. The results showed that selective transport of  $Na^+$  over  $K^+$  ions can be achieved with the enhanced concentration gradient of  $Na^+$  ions created by EDTA addition to the concentrate channel at  $pH > 10$ .

The applied voltage is another important operational parameter which can influence the mechanisms that govern ion transport and the related selective ion removal using EDTA in ED. The results presented in Fig. 3B showed that with the decreasing applied voltage from 3 V to 1.5 V, the concentration ratio of  $Na^+$  over  $K^+$  ions in the diluate solution decreases. When the applied current density is low (Figure S3), the contribution of diffusion to ion transport can overcome electromigration, which favours the selective transport of  $K^+$  over  $Na^+$  ions [11], and can control the selective ion removal in ED. As a result, the selective transport of  $Na^+$  ions to the concentrate channel increases, causing a decreasing concentration in the diluate solution.

Even though the results showed higher selective transport of  $Na^+$  ions while applying 1.5 V, the total ion removal from the diluate solution according to Eq. (4) was close to zero during operation, whereas at 2.3 V only 37 % of the ions were removed at the end of the process operation (Fig. 3B). Low total ion removal indicates that the applied current is too low to create enough force to drag all ions from the diluate to the concentrate channel to overcome the diffusion of the ions from the concentrate to the diluate channel. As a result, during process operation, the total ion removal alternated with local minima and maxima that represent the turning points where electromigration and back diffusion were overruled by each other (inset Fig. 3B). Especially at 1.5 V, the ion concentration ratio in the diluate channel decreases without significant total ion removal (~5%), which indicates that the  $Na^+$  ions are transported from the diluate to the concentrate channel, while the  $K^+$  ions move from the concentrate to the diluate channel resulting in the exchange of ions without a change in the total ion concentration.

The influence of the amount of EDTA in the concentrate channel on selective ion removal was also investigated; the experiments were conducted using EDTA/ $Na^+$  ratio of 0.3, 0.5 and 1. The results of the process selectivity, the ion concentration ratio in the diluate channel and the ion fluxes are presented in Fig. 4; the created concentration profiles at the start of the experiments are given in Figure S4 in the SI. Selective removal of  $Na^+$  ions increases with the EDTA/ $Na^+$  ratio in the concentrate channel (Fig. 4A) due to the bigger concentration differences over the membranes. The process shows the highest  $Na^+$  selectivity in the beginning of the experiments, when the created concentration gradient is at the peak, increasing up to 10 for the experiment with the ratio of 1. Towards halfway operation the total ion removal reaches values up to ~75 %, after that the process selectivity stays around 1, showing no significant selective removal. As a result of the preferential removal of  $Na^+$  ions, the ion concentration ratio of 0.4 is reached in the diluate channel at the end of the experiments (Fig. 4A). According to the study of Qian et al., the irrigation water should contain less than 4 mM of  $Na^+$  ions and > 6 mM of  $K^+$  ions to be able to meet the  $Na^+$  concentration limit (~20 mM) after accumulation and to sustain the optimal  $K^+$  concentration [3]. Our results show that with a single stage of the proposed process it is possible to keep the  $Na^+$  concentration at ~2.5 mM while maintaining the required  $K^+$  concentration in water, which would allow



**Fig. 4.** Effect of EDTA amount on selective ion removal with EDTA in electro-dialysis at 3 V and pH 10. All diluate solutions include 0.1 M  $Na^+$  and 0.1 M  $K^+$  ions. The pH of the concentrate solution deviates, during operation, max. 10 % from the starting pH. Markers: experimental data, dashed lines serve to guide the eye.

to reuse the treated water for several cycles.

The ion flux results presented in Fig. 4B shows that in the first hours of the process operation without EDTA, the flux of  $K^+$  is higher than the flux of  $Na^+$  ions due to the higher selectivity of the conventional CEMs towards  $K^+$  ions [30]. After 120 min, the total  $Na^+$  flux becomes higher than the  $K^+$  flux as a result of the naturally built-up concentration gradient in the membranes by ion removal during process operation. Note that without EDTA, there is no concentration gradient in the beginning of the experiments, thus diffusion does not have a significant contribution to selective ion removal. With the EDTA addition to the concentrate channel, the flux trends of the  $Na^+$  and  $K^+$  ions switch. This can be explained by the change of the mechanisms that govern selective ion transport. In the beginning of the experiments, lower  $K^+$  flux is observed due to the positive concentration gradient created by the EDTA, causing diffusion of  $K^+$  ions in the opposite direction of the ion removal, from the concentrate to the diluate channel, decreasing its total flux. Meanwhile, the  $Na^+$  flux remains higher since its diffusion occurs in the same direction as the ion removal, facilitating selective removal of  $Na^+$  ions. Later on in the experiment, the created concentration gradient decreases, consequently, the flux of  $Na^+$  ions becomes lower than the

flux of  $K^+$  ions. The detailed analysis on the contributions of the transport mechanisms on selective ion removal for the cases with and without EDTA is provided in Section 4.3.

#### 4.2. Effect of solution ion composition on selective ion transport: $Li^+$ and $Ca^{2+}$ presence

The effect of the presence of additional ions in solution on the selective  $Na^+$  ion removal with EDTA in ED is investigated. The experiments were conducted with different solutions including either  $Li^+$  (0.05 M) or  $Ca^{2+}$  (0.01 M) ions; the ion concentration ratio results are presented in Fig. 5. The presence of both ions in solution limits the use of the proposed process to enhance selective  $Na^+$  removal, since EDTA in the solution tends to bind more strongly to  $Li^+$  and  $Ca^{2+}$  ions (Table 1). As a result, the negative concentration gradient that enhances the selective ion removal shifts to either  $Li^+$  or  $Ca^{2+}$  ions, instead of  $Na^+$  ions. In addition, the  $Na^+$  complex of EDTA is considered weak and less stable compared to the ones with  $Li^+$  and  $Ca^{2+}$  ions [31]. Hence, EDTA complexation with  $Na^+$  is not enough to create the required concentration gradient over the membranes to enhance the selective  $Na^+$  ion transport. The inhibition of the selective  $Na^+$  removal is more clear for the experiment with  $Li^+$  ions, where the ion ratio in the diluate solution stays even higher than the experiment when no EDTA is added to the concentrate channel (Fig. 5). A similar trend is observed for the experiment with the  $Ca^{2+}$  ion present in the beginning of the experiment even though the  $Ca^{2+}$  ion concentration in the solution is relatively low (0.01 M), due to the much higher affinity of EDTA towards divalent ions than monovalent ions [29]. The selective transport of  $Na^+$  ions increases at  $\sim 40$  min, when 90 % of the  $Ca^{2+}$  ions is removed from solution, showing that the treatment of divalent ions is required to be able to effectively remove  $Na^+$  ions from solution with the proposed process.

#### 4.3. Theoretical analysis: Influence of EDTA on ion transport mechanisms in ED

Theoretical analyses were performed to evaluate the effect of EDTA complexation on the selective ion transport mechanisms in ED using the process model developed in our previous study based on extended Nernst-Planck equation and Donnan equilibrium [11]. The data analysis was done using the reported membrane properties (except the membrane-water friction) and following the same approach as described

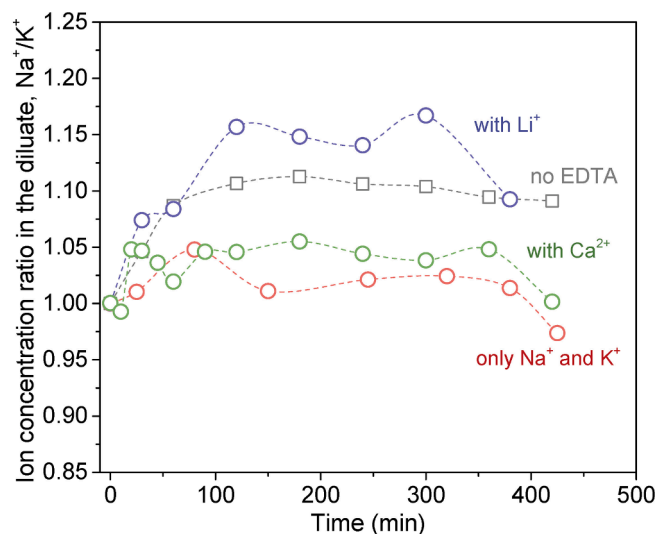


Fig. 5. Effect of  $Li^+$  (0.05 M) or  $Ca^{2+}$  (0.01 M) ions in solution on the selective removal of  $Na^+$  with EDTA in electrodialysis at 3 V and pH 10. The pH of the concentrate solution deviates, during operation, max. 10 % from the starting pH. Markers: experimental data, dashed lines serve to guide the eye.

in Section 4.3 in Ref. [11]. The input for the free ion concentrations in the concentrate channel is calculated using OLI studio software when EDTA is present in the solution. The validation of the model predictions by the experimental data is given in Figure S5 in the SI with the used membrane-water fractions. The total ion flux and the contributions of the three ion transport mechanisms, i.e., electromigration, convection and diffusion on selective ion transport was evaluated. The results of the  $Na^+$  and  $K^+$  ion fluxes during ED operation with and without EDTA are presented in Fig. 6. Without EDTA use in the concentrate channel, the electromigration and convection show the biggest contributions to ion transport, favouring the removal of the  $K^+$  ions due to its ion properties, such as high affinity to the membrane surface groups and high mobility inside the membranes. Meanwhile, diffusion results in opposite contributions to the transport of  $Na^+$  and  $K^+$  ions, favouring the removal of  $Na^+$  ions, however, it is not dominant enough to determine the overall process selectivity with the lowest contribution (Fig. 6A).

When EDTA is added to the concentrate channel, the total  $Na^+$  ion flux in the beginning of the experiment increases  $\sim 2.5$  times, meanwhile the total  $K^+$  ion flux decreases  $\sim 2.5$  times. With the resulting concentration gradient, diffusion becomes the leading transport mechanism for both ions, facilitating selective  $Na^+$  ion removal. The results show that the ion transport in the proposed process is mainly controlled by the mechanisms of electromigration and convection; however, the process selectivity is determined by the diffusion mechanism.

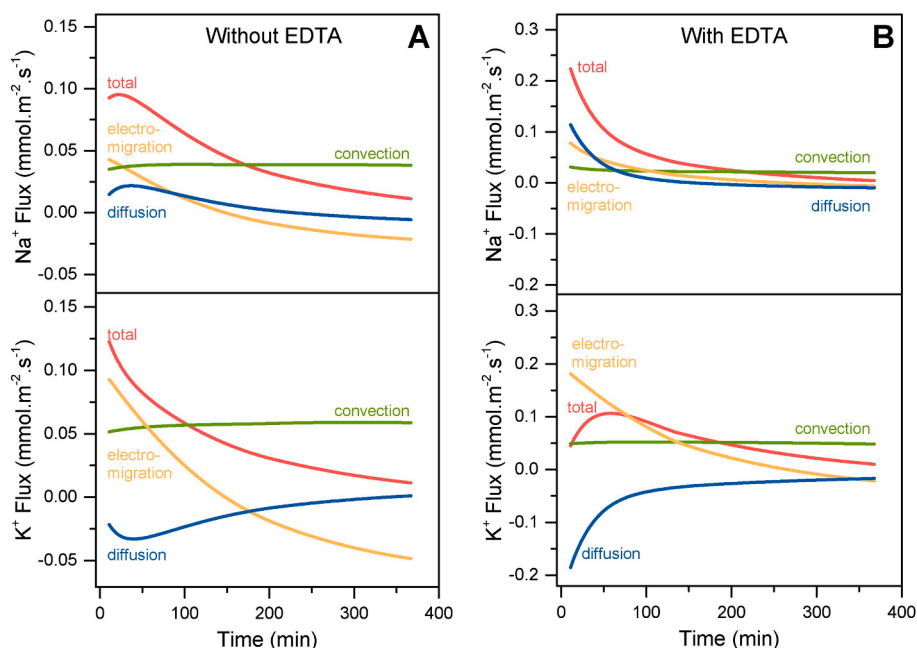
#### 4.4. Recovery of EDTA

The regeneration and recovery of EDTA was evaluated by acidification experiments performed at different pH values and with varying precipitation times. The recovery percentage of EDTA was calculated for each condition using Eq. (5), and the results are presented in Table S2 in the SI. In general, higher recovery rates were obtained when the final pH of the solution is lower than 2 with the average values of 97.5 % for  $pH < 2$  and 80.9 % for  $pH \geq 2$ . Moreover, the results on the effect of the precipitation time on EDTA recovery show that the recovery of  $> 95$  % can be achieved in 30 mins at  $pH < 2$ , meanwhile the highest recovery reached when  $pH > 2$  is 92 %, which took 3 h of precipitation time (Table S2).

Although Goel et al. reported that 5–6 h is required for 95 % recovery of 0.1 M EDTA by de-chelating nickel ions ( $Ni^{2+}$ ) at pH 2 [28], the de-complexation of  $Na^+$  and  $K^+$  ions is achieved  $\sim 10$  times faster in the present study. The  $Na^+$  and  $K^+$  ions have weaker bonds with EDTA [31] as compared to  $Ni^{2+}$  ions ( $\log(K_f) = 18.4$ ) [29] due to its higher valency, which can explain a faster de-complexation process for  $Na^+$  and  $K^+$ . For the ions that are weakly bound with EDTA, such as monovalent ions, relatively shorter times can be estimated to reach maximum EDTA recovery. The recovered EDTA is expected to maintain its performance for multiple cycles of reuse with high complexation efficiency [17,28].

## 5. Conclusions

In the present study, we used the electrodialysis process in combination with EDTA complexation in the concentrate channel to enhance the removal of  $Na^+$  ions from a solution including  $K^+$  ions by selective diffusion. The effect of different operational conditions on selective  $Na^+$  removal is evaluated by electrodialysis experiments. The experimental results show that, with EDTA complexation, the selectivity of the conventional electrodialysis process can be switched, and  $Na^+$  over  $K^+$  removal can be achieved. Also, a high solution pH ( $> 10$ ) and a low applied voltage ( $< 3$  V) are required to respectively increase EDTA complexation and enhance selective diffusion to maximize the  $Na^+$  selectivity of the process. On the other hand, it was observed that the presence of metal ions in solution, other than of  $K^+$  ions, limits the selective diffusion of  $Na^+$  ions. The theoretical analysis on the contributions of transport mechanisms on removal of  $Na^+$  and  $K^+$  ions shows that electromigration and convection have the largest contribution to the



**Fig. 6.** Theoretical calculations for the contributions of the various ion transport mechanisms in electrodesalination: electromigration, convection and diffusion without EDTA (A) and with EDTA (B) for Na<sup>+</sup> and K<sup>+</sup> mixtures at 3 V and pH 10.

transport of both Na<sup>+</sup> and K<sup>+</sup> ions with EDTA complexation. Meanwhile, the process selectivity is controlled by selective diffusion of Na<sup>+</sup> ions enhanced by EDTA complexation. Finally, EDTA recovery of 95 % was achieved in 30 min at solution pH < 2 by regeneration experiments.

#### CRediT authorship contribution statement

**Selin Ozkul:** Conceptualization, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **Hadar Scharfberg:** Conceptualization, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **Roel J.M. Bisselink:** Conceptualization, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **Norbert J.M. Kuipers:** Conceptualization, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **Harry Bruning:** Conceptualization, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **Huub H.M. Rijnaarts:** Conceptualization, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **Jouke E. Dykstra:** Conceptualization, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

#### Acknowledgements

We would like to thank Julian Zamudio Pineres for his help with the Raman spectroscopy analysis. This project was funded by the Dutch Topsector AgriFood “Natte Stroom” (DFI-AF-18003).

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2024.126337>.

#### References

- [1] Y.D. Ahdab, G. Schucking, R. Danyal, J.H. Lienhard, Treatment of greenhouse wastewater for reuse or disposal using monovalent selective electrodesalination, *Desalination* 507 (2021) 115037.
- [2] W. Voogt, E.A. Van Os, Strategies to manage chemical water quality related problems in closed hydroponic systems, *Acta Hort.* 927 (2012) 949–956.
- [3] Z. Qian, H. Miedema, L.C.P.M. de Smet, E.J.R. Sudholter, Modelling the selective removal of sodium ions from greenhouse irrigation water using membrane technology, *Chem. Eng. Res. Des.* 134 (2018) 154–161.
- [4] A. Krishna, H.J. Zwijnenberg, S. Lindhoud, W.M. de Vos, Sustainable K<sup>+</sup>/Na<sup>+</sup> monovalent-selective membranes with hot-pressed PSS-PVA saloplastics, *J. Membr. Sci.* 652 (2022) 120463.
- [5] J.M.A. Juve, F.M.S. Christensen, Y. Wang, Z.S. Wei, Electrodesalination for metal removal and recovery: A review, *Chem. Eng. J.* 435 (2022) 134857.
- [6] S. Al-Amshawe, M.Y.B. Yunus, A.A.M. Azoddein, D.G. Hassell, I.H. Dakhil, H. Abu Hasan, Electrodesalination desalination for water and wastewater: A review, *Chem. Eng. J.* 380 (2020) 122231.
- [7] K. Tado, F. Sakai, Y. Sano, A. Nakayama, An analysis on ion transport process in electrodesalination desalination, *Desalination* 378 (2016) 60–66.
- [8] T.M. Mubita, S. Porada, P.M. Biesheuvel, A. van der Wal, J.E. Dykstra, Strategies to increase ion selectivity in electrodesalination, *Sep. Purif. Technol.* 292 (2022) 120944.
- [9] S. Castano Osorio, P.M. Biesheuvel, E. Spruijt, J.E. Dykstra, A. van der Wal, Modeling micropollutant removal by nanofiltration and reverse osmosis membranes: considerations and challenges, *Water Res.* 225 (2022) 119130.
- [10] Y.S. Oren, P.M. Biesheuvel, Theory of Ion and Water Transport in Reverse-Osmosis Membranes, *Phys. Rev. Appl.* 9 (2018) 024034.
- [11] S. Ozkul, J.J. van Daal, N.J.M. Kuipers, R.J.M. Bisselink, H. Bruning, J.E. Dykstra, H.H.M. Rijnaarts, Transport mechanisms in electrodesalination: The effect on selective ion transport in multi-ionic solutions, *J. Membr. Sci.* 665 (2023) 121114.
- [12] V.L. Snoeyink, D.W. Jenkins, *Water Chemistry*, John Wiley & Sons, New York, 1980.
- [13] I.S.S. Pinto, I.F.F. Neto, H.M.V.M. Soares, Biodegradable chelating agents for industrial, domestic, and agricultural applications—a review, *Environ. Sci. Pollut. Res.* 21 (2014) 11893–11906.

- [14] K. Rekab, C. Lepeyre, F. Goettmann, M. Dunand, C. Guillard, J.M. Herrmann, Degradation of a cobalt(II)-EDTA complex by photocatalysis and H<sub>2</sub>O<sub>2</sub>/UV-C. Application to nuclear wastes containing <sup>60</sup>Co, *J. Radioanal. Nucl. Chem.* 303 (2015) 131–137.
- [15] C. Oviedo, J. Rodriguez, EDTA: The chelating agent under environmental scrutiny, *Quim Nova* 26 (2003) 901–905.
- [16] K. Zhang, Z.W. Dai, W.L. Zhang, Q. Gao, Y. Dai, F. Xia, X.J. Zhang, EDTA-based adsorbents for the removal of metal ions in wastewater, *Coord. Chem. Rev.* 434 (2021) 213809.
- [17] T.T. Lim, P.C. Chui, K.H. Goh, Process evaluation for optimization of EDTA use and recovery for heavy metal removal from a contaminated soil, *Chemosphere* 58 (2005) 1031–1040.
- [18] A.T. Cherif, A. Elmidaoui, C. Gavach, Separation of Ag<sup>+</sup>, Zn<sup>2+</sup> and Cu<sup>2+</sup> ions by electro dialysis with monovalent cation specific membrane and EDTA, *J. Membr. Sci.* 76 (1993) 39–49.
- [19] A. Iizuka, Y. Yamashita, H. Nagasawa, A. Yamasaki, Y. Yanagisawa, Separation of lithium and cobalt from waste lithium-ion batteries via bipolar membrane electro dialysis coupled with chelation, *Sep. Purif. Technol.* 113 (2013) 33–41.
- [20] K.H. Chan, M. Malik, G. Azimi, Separation of lithium, nickel, manganese, and cobalt from waste lithium-ion batteries using electro dialysis, *Resour. Conserv. Recycl.* 178 (2022) 106076.
- [21] A.J. Chaudhary, J.D. Donaldson, S.M. Grimes, N.G. Yasri, Separation of nickel from cobalt using electro dialysis in the presence of EDTA, *J. Appl. Electrochem.* 30 (2000) 439–445.
- [22] N. Tzanetakakis, W.M. Taama, K. Scott, R.J.J. Jachuck, R.S. Slade, J. Varcoe, Comparative performance of ion exchange membranes for electro dialysis of nickel and cobalt, *Sep. Purif. Technol.* 30 (2003) 113–127.
- [23] D. Babilas, J. Muszynski, A. Milewski, K. Lesniak-Ziolkowska, P. Dydo, Electro dialysis enhanced with disodium EDTA as an innovative method for separating Cu(II) ions from zinc salts in wastewater, *Chem. Eng. J.* 408 (2021) 127908.
- [24] M. Sillanpaa, Environmental fate of EDTA and DTPA, *Rev Environ Contam Toxicol* 152 (1997) 85–111.
- [25] M.F. Jaramillo, I. Restrepo, Wastewater Reuse in Agriculture: A Review about Its Limitations and Benefits, *Sustainability* 9 (2017) 1734.
- [26] Q.W. Wang, J.J. Chen, Recovery of EDTA from soil-washing wastewater with calcium-hydroxide-enhanced sulfide precipitation, *Chemosphere* 237 (2019) 124286.
- [27] S.M. Wu, Y. An, J.L. Lu, Q.M. Yu, Z. He, EDTA-Na<sub>2</sub> as a recoverable draw solute for water extraction in forward osmosis, *Environ. Res.* 205 (2022) 112521.
- [28] S. Goel, K.K. Pant, K. Nigam, Extraction of nickel from spent catalyst using fresh and recovered EDTA, *J. Hazard. Mater.* 171 (2009) 253–261.
- [29] D.C. Harris, *Quantitative Chemical Analysis*, 7th ed., W.H. Freeman and Co., New York, 2007.
- [30] T. Luo, S. Abdu, M. Wessling, Selectivity of ion exchange membranes: A review, *J. Membr. Sci.* 555 (2018) 429–454.
- [31] M. Chen, R.S. Reid, Solution Speciation in the Aqueous Na(I)-Edta and K(I)-Edta Systems, *Canadian J. Chem.-Revue Canadienne De Chimie* 71 (1993) 763–768.