



Selectrodialysis: Fractionation of divalent ions from monovalent ions in a novel electro dialysis stack

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ABSTRACT

In view of wastewater recycling and industrial requirements to valorize nutrients and other valuable ions from waste streams, as well as to refine the product streams, a novel electro dialysis stack, denoted as selectrodialysis, was designed and used for ion fractionation.

In this work, separation of sulphate from a NaCl/Na₂SO₄ mixture is investigated. Prior to the investigation, the selectrodialysis stack was qualitatively tested on a synthetic wastewater to study the potential of ion fractionation by using this novel configuration. Different approaches including changing of pH and current density were used to evaluate the effects on the stack selectivity, the current efficiency and the product (sulphate) purity. Furthermore, the optimized parameters were applied to produce a sulphate-enriched stream from sulphate-free solutions (NaCl solution) in the product stream.

The results show that the sulphate purity can reach over 85% with the current efficiency of over 50%. It is proved that selectrodialysis is feasible and effective for chloride/sulphate fractionation.

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1. Introduction

Organic and inorganic ions are present in most industrial, municipal and natural freshwaters and wastewaters. In view of different applications of these streams, some ions are desired and need to be kept or concentrated but others have to be removed. For example, in the fermentation industry, inorganic salts have to be eliminated from the broth but some useful organic ions should be concentrated as the product [1]. Another example is in drinking water production, where divalent ions (Ca²⁺ and Mg²⁺) should be partially removed but the water salinity should be in a narrow range, and higher than 500 mg L⁻¹ total dissolved solid (TDS) [2], in view of protection of human health.

Several processes have been proposed and used for ion separation and fractionation, including ion exchange, nanofiltration and electro dialysis [3–6]. Ion exchangers are traditionally widely used in industrial applications for specific applications such as deionization (ion sorption), which mainly involve purification rather than fractionation [7–11]. Separation and recovery processes by ion exchange resins need eluents to regenerate these resins; these processes are highly environmentally unfriendly.

Alternatively, charged membranes such as nanofiltration (NF) and ion exchange membranes can be used to selectively remove ions with different charges. NF is a pressure driven membrane process with molecule weight cut off (MWCO) around 200–1000 Da. In NF, the water and around 20–80% of monovalent ions permeate through the membrane due to the pressure gradient whereas the rejection to divalent ions of the same charge to the membrane can reach 95% [12]. In contrast with nanofiltration, ion exchange membranes (electrically charged membranes) generally need an electrical potential as the driving force, which means that the ions are transported through the membrane by an electrical field. Ion exchange membranes are generally very dense with the pore size around 1 nm [13].

Nanofiltration has been reported for ion fractionation in various publications [14–18]. Van der Bruggen et al. [19] reviewed the applications of nanofiltration in pharmaceutical, food and sweetener industries for fractionation of small organic ions and compounds. Umpuch et al. [20] investigated separation of lactate and glucose by nanofiltration with the addition of NaCl/Na₂SO₄. Results show that the maximum separation factor is 1.9 when 0.25 M Na₂SO₄ was added into the 0.1 M glucose and 0.1 M sodium lactate solution. Recently, layer-by-layer nanofiltration membranes were fabricated and studied to achieve a higher selectivity between ions and organic compounds by size exclusion and charge repulsion from different

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layers. Ahmadiannamini et al. [21] investigated multilayered poly-electrolyte complex (PECs) nanofiltration membranes to separate an ion mixture containing Cl^- , SO_4^{2-} and HPO_4^{2-} . The results show that the retention was higher than 86% for SO_4^{2-} and HPO_4^{2-} , and below 25% for Cl^- (separation factor around 5.3). However, a higher product purity may be desired in view of potential industrial applications.

Electrodialysis membranes have ion exchange capabilities and can be of the anion exchange type or the cation exchange type. This process is widely used in water desalting and production of organic acids [22–24]. In general, these membranes do not differentiate between different ions, although some differences in transport rate through the membranes can be observed. These differences, however, do not lead to fractionation of practical use. Some membranes are selective for monovalent (an)ions compared to multivalent (an)ions and the fractionation effect that can be obtained in this way. However, the separation factor is limited and similar to the effect that can be obtained with nanofiltration, as was proven previously by Van der Bruggen et al. [2].

Ion fractionation has a great application potential in various industries but is difficult to achieve, especially to the ions with the same (size and) charge sign. In this study, a novel electrodialysis configuration with a selective removal of ions with the same charge sign was innovated and examined. Fractionation of divalent ions (SO_4^{2-}) from monovalent ions (Cl^-) was investigated by using this specifically designed electrodialysis stack, named “selectrodialysis”.

2. Materials and methods

2.1. The novel electrodialysis stack: selectrodialysis

2.1.1. Configuration

The configuration of selectrodialysis is based on conventional electrodialysis by adding one or more selective membrane(s) between the standard anion- and cation exchange membranes. In Fig. 1, the three-compartment (denoted as the feed, product and brine compartment, respectively) configuration formed by a membrane trio (the standard cation exchange membrane, CM; the standard anion exchange membrane, AM; the monovalent selective anion exchange membrane, MVA) is exhibited. CM and AM are regarded as having no selectivity to their counter-ions; and MVA has a limited selectivity to monovalent anions, i.e., monovalent anions have a higher transport number than multivalent anions in MVA membrane.

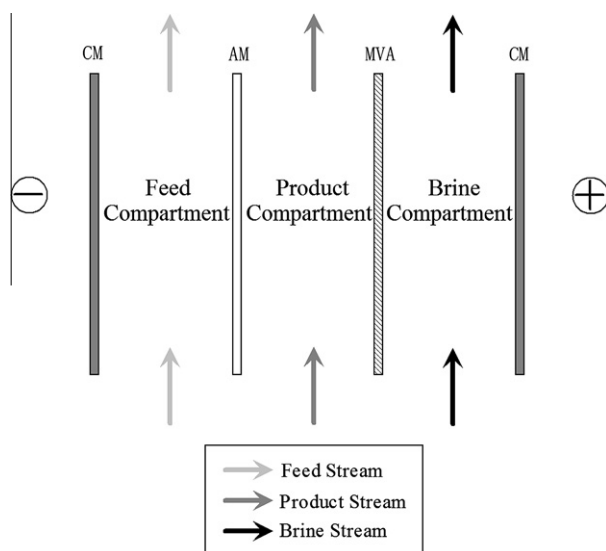


Fig. 1. Basic configuration of selectrodialysis stack to fractionate anions.

2.1.2. Scenario

A basic scenario on the divalent/monovalent anion fractionation by selectrodialysis is shown in Fig. 2: the feed and the product streams comprise the salt mixture with cation A^+ and the same molar concentration (to simplify the calculation) of monovalent anion B^- and divalent anion C^{2-} . The purpose is to enrich divalent anion C^{2-} while to remove monovalent anion B^- in the product compartment. The CM and AM are assumed to be an ideal non-selective cation exchange membrane and an ideal non-selective anion exchange membrane, respectively. The MVA is a monovalent selective anion exchange membrane with a selective factor of ξ . Selective factor (ξ) is a simplified parameter to reflect membrane selectivity, which is calculated by the ion molar amount ratio which two types of ions are transported through the membrane. This CM–AM–MVA unit is a repeating membrane trio in a selectrodialysis stack.

By applying an electrical potential, anions are attracted to the anode whereas cations are attracted to the cathode. m , n denote to the molar amount of anions transported during a certain period of time. In the feed compartment, cations are transported through the CM membrane to the brine compartment, while anions are transported through the AM to the product compartment. Since the AM is an ideal non-selective membrane, the same amount (m) of anion B^- and C^{2-} is transported through the AM to the “product”. Meanwhile, due to the electroneutrality in the feed solution, $3m$ of A^+ pass through the CM to the “brine”.

x and y refer to the molar amount of the cation A^+ and anion B^- , respectively, in the initial product stream. In order for the charge balance to be closed in this compartment, the number of moles of C^{2-} should be $(x - y)/2$. During the time period, the product compartment receives the same amount (m) of B^- and C^{2-} and meanwhile has to transfer $3m$ equivalent of anions through the MVA membrane to the brine compartment. The concentration of cation A^+ (x) in the product stream remains the same, since both sides of the product compartment are (ideal) anion exchange membranes. Due to the electroneutralization effect in the product stream, the overall anion equivalent molar amount should be x .

On the other hand, because MVA is a monovalent selective membrane, more B^- passes through the MVA than C^{2-} . Thus, it is expected to obtain an increased concentration of multivalent anion C^{2-} in this compartment. When n moles of C^{2-} penetrate the MVA membrane and reach the brine compartment ($m > n$), the retained amount of C^{2-} in the product compartment is $m - n$. Thus, the

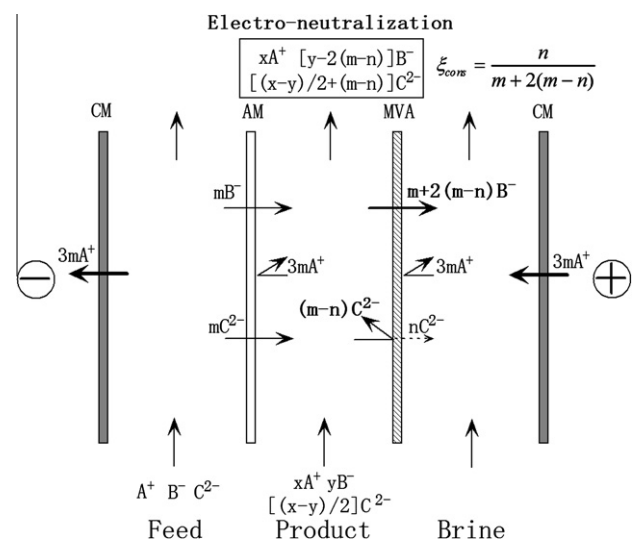


Fig. 2. Schematic diagram of a cell trio in selectrodialysis stack and the working principle.

number of moles of B^- transported to the brine compartment is $m + 2(m - n)$.

The membrane selective factor for C^{2-} towards B^- can be expressed as:

$$\xi_{\text{cons}} = \frac{n}{m + 2(m - n)}$$

Note that the membrane selective factor, as defined above, is a parameter to reflect the membrane selectivity, and this parameter is different with “separation efficiency” which defined in Section 2.

Thus, in the product stream (volume V), the initial molar amount of A^+ , B^- and C^{2-} is x , y , and $(x - y)/2$, respectively. Assume that the MVA membrane selective factor ξ is constant during the experiment. The concentration of the anion C^{2-} increases after a period t , from $c_C(0) = \frac{(x-y)/2}{V}$ to $c_C(t) = \frac{(x-y) + (m-n)t}{V}$; meanwhile, the concentration of anion B^- from $c_B(0) = \frac{y}{V}$ decreases to $c_B(t) = \frac{y-2(m-n)t}{V}$. After a period t' , the concentration of B^- decreases to $c_B(t') = \frac{y-2(m-n)t'}{V}$ and the concentration of C^{2-} increases to $c_C(t') = \frac{(x-y) + (m-n)t'}{V}$. Therefore, the concentration of anion B^- decreases and the concentration of anion C^{2-} increases in the product compartment as a function of time, until the concentration of anion B^- in the selector is depleted.

In conclusion, the amount of the anions B^- and C^{2-} which transport through the product compartment to the brine compartment is determined by:

- 1) Electro-neutralization: as no cation can migrate through the anion exchange membranes, the amount of the total charge equivalence (T_{eq}) of the outgoing anions from the product through the MVA membrane should be the same as the T_{eq} of the incoming anions, i.e., $T_{\text{eq}} = 3m$.
- 2) The membrane selective factor: as the MVA membrane is a monovalent selective membrane, more B^- will penetrate through the MVA membrane than C^{2-} . The MVA membrane selective factor to the divalent anion C^{2-} towards monovalent anion B^- is denoted as ξ ($\xi < 1$), which is dependent on the experimental conditions (ξ_{cons}).

2.2. Experimental setup

2.2.1. Preliminary experiments

Prior to the experiments in this investigation, the electrodialysis stack performance was initially examined by an experiment on a custom build stack with synthetic wastewater. The stack configuration is shown in Fig. 1. The active surface area of each membrane was 0.0180 m^2 and the spacer width between two membranes was 10 mm. In this stack, two standard cation exchange membranes (CM), one standard anion exchange membrane (AM) and one monovalent selective anion exchange membrane (MVA) were installed. The water contained four different anions: chloride, nitrate, sulphate and phosphate. The initial concentrations of the four ions were 7.61, 0.32, 4.48 and 0.43 mmol L^{-1} , respectively. The volumes of the feed, product and brine were 9, 3 and 3 L, respectively. The initial compositions of these three streams were the same. $0.1 \text{ M Na}_2\text{SO}_4$ was used as the electrolyte rinsing solution. Current density of 28 A m^{-2} was chosen as the constant current during the experiment. The experiment was run in batch mode and all the streams were recirculated during the experiment. The initial pH of all streams was around 7 and was not adjusted during the experiment.

2.2.2. Study of chloride/sulphate separation

A lab-scale electrodialysis apparatus was used in this work. For each membrane, the active surface area was 0.0064 m^2 and the

Table 1

Information on PCA standard cation and anion exchange membranes and monovalent selective anion exchange membranes.

Membrane	Thickness (μm)	Ion exchange capacity (meq g^{-1})	Chemical stability (pH)	Perm-selectivity	Functional groups	Area resistance ($\Omega \text{ cm}^2$)
PC-SK (CM)	130	ca. 1	0–11	>0.96	$-\text{SO}_3\text{Na}$	0.75–3
PC-SA (AM)	90–130	ca. 1.5	0–9	>0.93	$-\text{NR}_4\text{Cl}$	1–1.5
PC-MVA	100	ca. 1	0–7	>0.97	N/A	N/A

spacer channel width between two membranes was 0.5 mm. There were three cell trios in the stack, each cell trio containing a feed, a product and a brine compartment. In total three pieces of standard anion exchange membrane (AM), three pieces of monovalent selective anion exchange membrane (MVA) and four pieces of standard cation exchange membrane (CM) were used. Thus, the total active membrane surface area was 0.0192 m^2 . Information about the membranes is given in Table 1, which was provided by the manufacturer. The membranes and the stack (ED-64 004) were supplied by PCA–Polymerchemie Altmeier GmbH and PCell GmbH, Heusweiler, Germany.

Fig. 3 shows the schematic diagram of the apparatus and one cell trio configuration of the electrodialysis stack. The electrical field was supplied by a DC adjustable power supply (CNRood 0–20 V, 10 A, Zellik, Belgium). For all of the experiments an electrode rinsing solution (“Rinsing” in Fig. 3) of $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ and a volume of 3 L was used. The concentrations of feed, product and brine were $8 \text{ mmol L}^{-1} \text{ Na}_2\text{SO}_4$ and $8 \text{ mmol L}^{-1} \text{ NaCl}$, except specified. The initial pH of product was adjusted by 0.1 M NaOH or HCl (analytical grade). The volume of the feed and the brine was 60 L and the product volume was 3 L to eliminate ion depletion of the feed and a possible back diffusion from the brine compartment due to the concentration build-up.

Different currents (0.1–0.4 A, i.e., current densities 15.6 – 62.5 A m^{-2} accordingly) were used in the experiments to determine the current density effect on the electrodialysis performance; during each experiment, the applied current was kept constant. On the other hand, different pH values were kept in the product stream to find out the pH effect on the performance; during each experiment, the applied pH was kept constant. The flow rate and pressure were monitored by flow meters (Georg Fischer, Schaffhausen, Switzerland) and mechanical pressure gauges (ERIKS 0–1.5 Bar, Alkmaar, the Netherlands). As illustrated in Fig. 3, the sulphate ions are expected to be retained and to be concentrated in the product compartment, while the chloride ions will be “excluded” to the brine compartment. As the sodium ions being retained in the product stream, the total molar equivalent is constant (cation leakage is negligible, according to the fact that the AM and MVA membrane permselectivity to cations >0.93).

As instructed in the product manual of ED-64 004, the suggested flow rate is 4 – 8 L h^{-1} per cell, i.e., 12 – 24 L h^{-1} for a stack with three cell trios. Therefore, the flow rates were set to 22 L h^{-1} for the feed, product and brine compartments (the fluid velocity in the spacer was 0.051 m s^{-1} and the Reynolds number $Re \approx 4080$, the spacer mesh was not taken into account) and 150 L h^{-1} for the electrode rinsing compartment. In some experiments, the pH of the product stream needed to be adjusted, this was done by a 40 mM NaOH solution (analytical grade) and a Black Stone BL 7917 pH Measuring & Dosing System as the automatic regulator.

Different experiments were performed to investigate transport properties of chloride and sulphate in the electrodialysis stack. The concentration of chloride and sulphate in the product was plotted as a function of time, current density and pH. During the

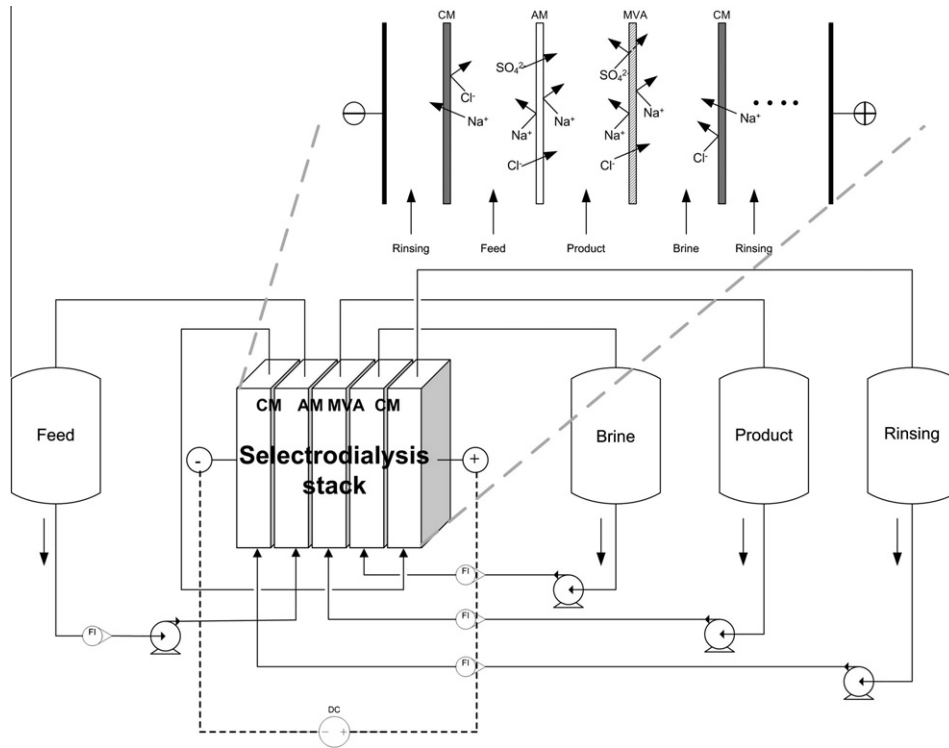


Fig. 3. Schematic diagram of the electrodialysis stack and system.

experiments, samples were taken on an hourly basis with a volume of 20 ml. The total sampling volume was within 5% of each stream volume.

2.3. Analytical methods

The anion concentrations were measured with ion chromatography (DX-120 Ion chromatography with IONPAC AS11-HC Analytical Column, DIONEX, USA). The sample preparation for IC consisted of diluting the experiment sample with Millipore Milli-Q deionized water according to the expected concentration. A 20 mM NaOH eluent was used for the measurements. The eluent was degassed by immersing into an ultrasonic bath for minimum one hour prior to use for the IC. Analytical reagent grade chemicals were used for the preparation of all the solutions, eluent and standards.

2.4. Data analysis

The current density ($A m^{-2}$) was calculated as the quotient of the applied current (I) and the membrane surface area (S).

The current efficiency of ion A (negative charge in this study) was calculated as the ratio of the electrical charge used for the transport of ion A to the total electrical current charge. Assuming the applied current being constant, the current efficiency of ion A (η_A) can be calculated as:

$$\eta_A = \frac{-z_A \frac{\Delta m_A(t)}{M_A} F}{nIt} \times 100(\%) \quad (1)$$

where $\Delta m_A(t)$ is the weight of transferred ion, z_A is the charge number of ion A (negative charge), M_A is molar mass of ion A , F is the Faraday constant, I is the applied current, t is the time period, n is the number of cell trios in the ED stack. $\Delta m_A(t)$ can be calculated from the equation below, where m_A^0 is the initial amount of ion A :

$$\Delta m_A(t) = m_A^0 - c_A(t)V_0 \quad (2)$$

The current efficiency of Cl^- and SO_4^{2-} was calculated from the concentration increase of these ions in the brine vessel. Since only chloride and sulphate ions were present in the system, the overall current efficiency of the stack is the sum of the current efficiencies of Cl^- and SO_4^{2-} .

The normalized current efficiency (N-CE) is introduced to illustrate in particular the efficiency of the current to transfer SO_4^{2-} from the feed compartment and to retain it in the product compartment, or to exclude Cl^- from the product compartment towards the brine. The N-CE of ion A during a time period i (τ_A^i) was calculated as:

$$\tau_A^i = \frac{-Z_A V_p (|\Delta c_A^i|) F}{nIt} \times 100(\%) \quad (3)$$

where V_p denotes to the volume of the product, $|\Delta c_A^i|$ is the absolute value of the concentration difference at a period i of ion A in the product vessel. In this study, i refers to a time interval between two samples. Due to electro-neutralization in the product compartment, the concentration differences of Cl^- and SO_4^{2-} follow the correlation:

$$|c_{Cl^-}^i - c_{Cl^-}^0| = 2 |c_{SO_4^{2-}}^i - c_{SO_4^{2-}}^0| \quad (4)$$

$$\text{i.e., } \tau_{Cl^-} = \tau_{SO_4^{2-}} \quad (5)$$

The membrane selectivity, represented as membrane separation efficiency, was calculated by the method introduced by Van der Bruggen et al. [2]. In this method, the separation efficiency S between component A and B is evaluated as:

$$S_B^A(t) = \frac{(c_A(t)/c_A(0)) - (c_B(t)/c_B(0))}{(1 - c_A(t)/c_A(0)) + (1 - (c_B(t)/c_B(0)))} \quad (6)$$

The range of S_B^A is from -1 to 1 . If ion A is transported slower than ion B , the S_B^A value is between 0 to 1 ; if ion B is transported slower, then the S_B^A is between -1 to 0 .

Sulphate is expected to concentrate in the product compartment, thus, the sulphate concentration and the purity in the product vessel is one of the most important concerns in this research. Sulphate purity ($\sigma_{SO_4^{2-}}$, %) was calculated as:

$$\sigma_{SO_4^{2-}} (\%) = \frac{c_{SO_4^{2-}}}{c_{Cl^-} + c_{SO_4^{2-}}} \cdot 100 \quad (7)$$

The mass balance of chloride and sulphate in the feed, product and brine was made in all experiments to verify whether any leakage occurred in the experiment and to ensure the data quality. The results show that no leakage was observed and the mass balance is satisfactory (deviation less than 5%).

3. Results and discussion

3.1. Conventional ED for ion separation and preliminary electrodialysis experiments

3.1.1. Conventional ED for ion separation

Conventional ED was studied by several researchers to fractionate ions from aqueous solutions. Sata et al. [25] investigated separation of chloride and sulphate by modifying the membrane surface with different methods. The results show that a relative transport number of sulphate to chloride was achieved between 0.2 and 0.8. Zhang et al. [26] reported the separation efficiency of the PC-SA (standard anion exchange membrane) and PC-MVA (monovalent selective anion exchange membrane) membrane to chloride and sulphate is strongly affected by pH and current density. The separation efficiency of the PC-SA membrane varied from 0.02 to 0.84 and of the PC-MVA membrane varied from 0.33 to 0.89. Although the research shows that it is possible to separate divalent ions (e.g., sulphate) from monovalent ions (e.g., chloride), the membrane selectivity is still very limited. This means that, in

view of the target ion purity, only a rough mixture is obtained by the conventional ED process, from either the diluate or the concentrate side.

On the other hand, in view of the ion concentration, the target ions can not be concentrated in the diluate since all the ions in the feed (diluate) solution are migrated to the concentrate stream by the electrical field applied in a conventional ED. Thus, it is not possible to really “fractionate” the ions from the solution by conventional electro dialysis.

3.1.2. Preliminary electrodialysis experiment

A three-compartment ED was hypothesized to fulfill the requirements for feed desalination and ion fractionation. Mass balance was checked in the entire experiment.

It can be seen that the multivalent ions were concentrated after the experiment of around 800 minutes: the concentrations of phosphate and sulphate were increased to 245% and 161% of their initial concentrations, respectively; while the concentrations of monovalent ions, i.e., chloride and nitrate, both decreased to 44% of their initial concentrations. The results qualitatively and quantitatively show that the multivalent ions can be selectively concentrated in the product stream by electrodialysis. However, the mechanisms of selective ion migration should be known in detail. This was studied in further experiments. (See Fig. 4).

3.2. Electrodialysis performance at various pH's and current densities

Previous studies [26–28] show that the MVA membrane selectivity is affected by both pH and current density. According to the stack configuration of electrodialysis, sulphate is retained due to the selectivity of the MVA membrane in the product compartment. Thus, the performance of electrodialysis using a range of applied parameters (i.e., pH and current density) was

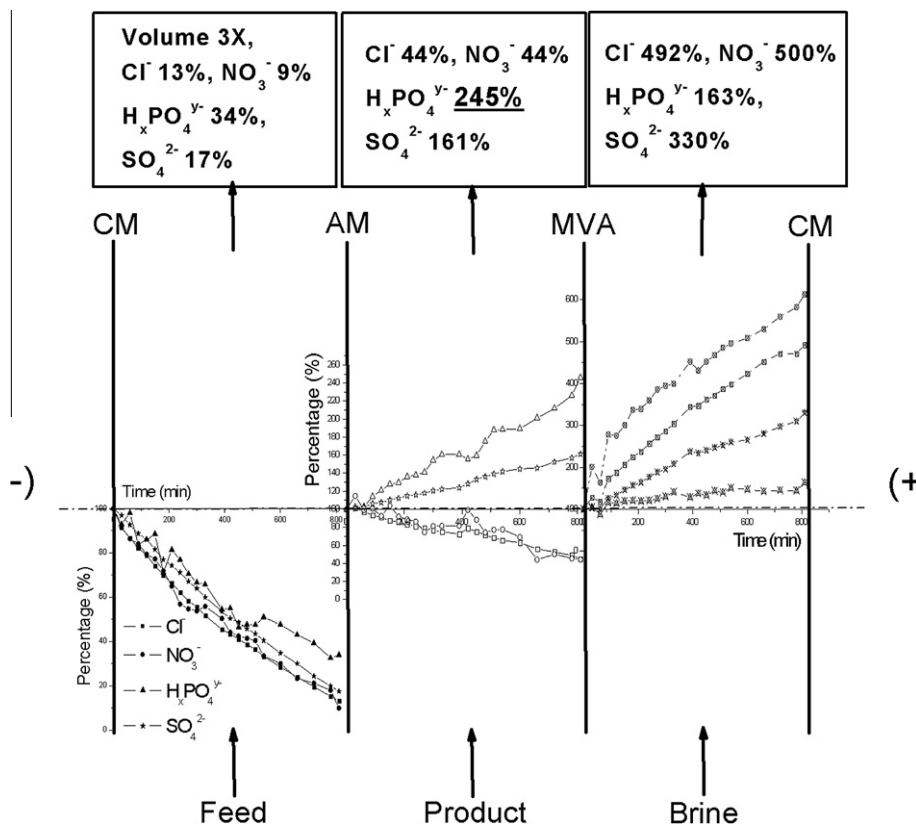


Fig. 4. The initial experiment of electrodialysis – fractionation of multivalent ions from monovalent ions on a synthetic wastewater.

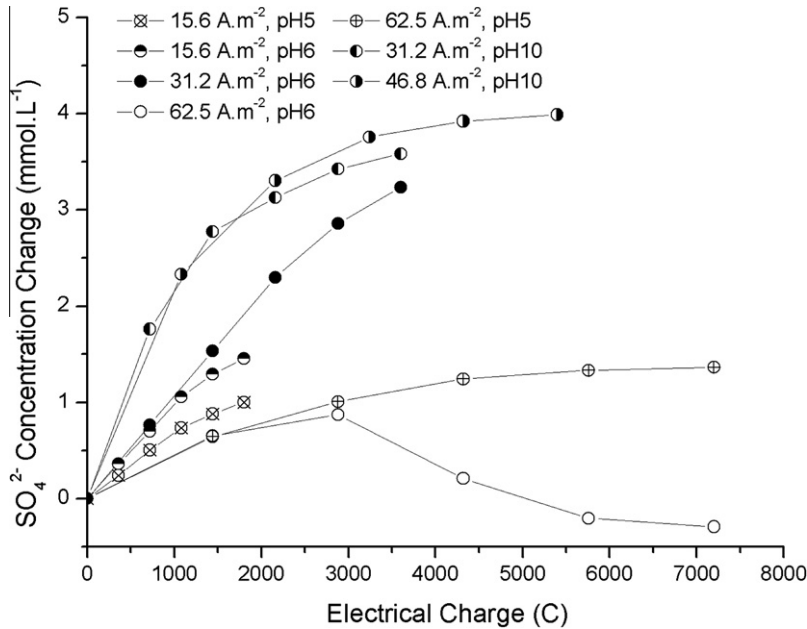


Fig. 5. Sulphate concentration changes in the product as a function of electric charge (C) under different pH and current density.

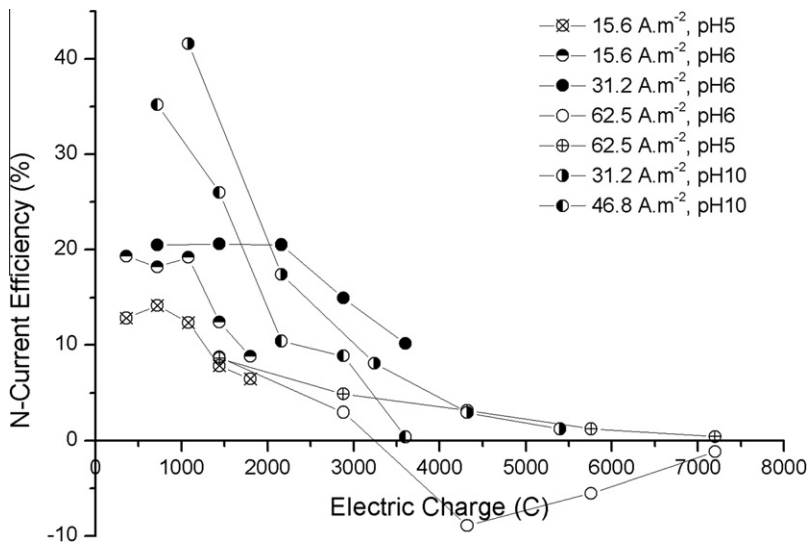


Fig. 6. N-current efficiency of SO_4^{2-} in the product compartment as a function of electric charge (C) under different pH and current density.

investigated in a systematic experimental design using well-defined synthetic chloride/sulphate solutions.

Fig. 5 illustrate the profiles of sulphate concentration change as a function of electric charge (C, Coulomb) in the product (the stream enriched with sulphate) at pH 5, 6, 10 and current 0.1–0.4 A (i.e., current density $15.6\text{--}62.5\text{ A m}^{-2}$). The initial concentration of Cl^- and SO_4^{2-} in these experiments was 8 mmol L^{-1} . As shown, SO_4^{2-} has the highest concentration increase (4 and 3.5 mmol L^{-1}) at 0.2 A (31.2 A m^{-2} , pH 10) and 0.3 A (46.8 A m^{-2} , pH 10) after 3000 C electric charges were transferred, respectively. The SO_4^{2-} concentration at 31.2 A m^{-2} and pH 6 finally increases around 3.1 mmol L^{-1} . The concentration increases by 1.3, 1.3 and 0.9 mmol L^{-1} at 0.4 A (62.5 A m^{-2}) and pH 5, at 15.6 A m^{-2} and pH 6 and at 15.6 A m^{-2} and pH 5, respectively. In the experiment at 62.5 A m^{-2} and pH 6, the SO_4^{2-} concentration increases by 0.8 mmol L^{-1} after 3000 C, but finally decreases to below the initial concentration after over 7000 C electric charges transferred. This

may due to the experiment failure or the measurement errors happened.

In view of these facts, the higher the pH of the product stream, the higher the SO_4^{2-} concentration can be reached, i.e., the final concentration of sulphate in the product has a strongly positive correlation with the pH. This is due to the observation that the MVA membrane has a higher selectivity at a higher pH, as pointed out by previous research [26–28].

On the other hand, the profile implies that a plateau is reached for the experiments at 31.2 A m^{-2} and pH 10 and at 46.8 A m^{-2} and pH 10. At the contrary, the experiments at 15.6 A m^{-2} and pH 6 and at 31.2 A m^{-2} and pH 6 have not reached a plateau yet. It can also be concluded that the experiment with a lower current can obtain a higher plateau at the same pH (e.g., the experiment at 31.2 A m^{-2} has a higher plateau than the one at 46.8 A m^{-2} and pH 10).

The results show a fact that the sulphate was concentrated in the product stream, as hypothesized.

For a deeper understanding of the separation mechanisms in the product compartment, the N-CE was used. As mentioned above, this factor aims to illustrate the efficiency of current in particular to transfer SO_4^{2-} from the feed compartment and retain it in the product compartment, or to exclude Cl^- from the product compartment to the brine. Therefore, N-CE is a reflection of the selectrodialysis stack efficiency. Fig. 6 show the N-CE curves of sulphate and chloride, respectively, as a function of transferred electric charge, at different current and pH.

It can be seen from Fig. 6 that the two experiments at pH 10 have the highest initial N-CE and both of their N-CE drops to around zero after 3600 and 5400 C, respectively. On the other hand, the two experiments with current density 62.5 A m^{-2} have the lowest N-CE value. The other three experiments operated at a lower current density (15.6 and 31.2 A m^{-2}) still kept higher current efficiency at the end of the experiments. This reveals that the selectrodialysis stack has a higher normalized current efficiency at higher pH and/or lower current density.

Furthermore, the AM and MVA membrane selectivity was also investigated. Generally, the results show that the AM membrane has almost no selectivity (the value is in the range of -0.2 to 0.2) between chloride and sulphate ions. The MVA membrane selectivity increases if a higher pH and/or lower current is applied. The MVA shows a selectivity of around 0.7 at pH 10 at 31.2 and 46.8 A m^{-2} .

Moreover, the purity of SO_4^{2-} in the product was compared. As illustrated in Fig. 7, the experiments at pH 10 exhibit the highest sulphate purity: 85% and 87% for the experiment at 31.2 and 46.8 A m^{-2} , respectively. Both experiments reach a plateau after 3000 C electric charges transferred. The experiments at 15.6 and 31.2 A m^{-2} at pH 6 show a similar plot: 68% and 70% of sulphate purity is reached after 1800 and 3600 C , respectively, and does not form a plateau yet. The experiments with a lower pH and a higher current exhibit a poor SO_4^{2-} purity. It can be concluded that a higher SO_4^{2-} purity in the product can be obtained under a higher pH and/or a lower current density.

3.3. Influence of total salinity in product compartment

Based on the investigation, optimized values for pH and current to produce a sulphate enriched stream from a sulphate-free

solution (pure NaCl solution) in the product compartment were as follows: pH = 10, current = 0.2 A (current density 31 A m^2). In this investigation, two experiments under the same current density and the same pH were carried out and were compared. The feed and brine both consisted of $8 \text{ mmol L}^{-1} \text{ Na}_2\text{SO}_4$ and $8 \text{ mmol L}^{-1} \text{ NaCl}$, and both volumes were 60 L . The only difference of these two experiments was the concentration of Cl^- in the 3 L pure NaCl solution (12 and 24 mmol L^{-1} , respectively) as the initial product stream. These two concentrations were chosen was based on the fact that the equivalent concentration for all the other experiments ($8 \text{ mmol L}^{-1} \text{ SO}_4^{2-}$ and $8 \text{ mmol L}^{-1} \text{ Cl}^-$) was 24 mmol L^{-1} as monovalent anion. Thus, a full equivalent concentration ($24 \text{ mmol L}^{-1} \text{ NaCl}$, denoted as Exp-Full) and a half equivalent concentration ($12 \text{ mmol L}^{-1} \text{ NaCl}$, denoted as Exp-Half) were chosen for these initial product stream.

Furthermore, the overall current efficiency of the selectrodialysis stack in these two experiments were calculated and the results show that the efficiencies were over 90% and water splitting rate was very low (pH was constant) during the MVA membrane showed a high selectivity (over 0.8).

3.3.1. The experiment with $24 \text{ mmol L}^{-1} \text{ NaCl}$ solution as the initial product stream (denoted as Exp-Full)

The concentration profiles of chloride and sulphate ion, and the sulphate purity in the product vessel as a function of time, are shown in Fig. 8(a). The Cl^- concentration drops from 24 to 2 mmol L^{-1} after 5 hours. Meanwhile, the SO_4^{2-} concentration increases from 0 to 11 mmol L^{-1} . This implies that the experiment did not reach the final stage (the plateau of the curve). Theoretically, if the concentration of Cl^- drops to zero, the concentration of SO_4^{2-} should reach 12 mmol L^{-1} , due to the principle of electro-neutrality in the product compartment. The purity of SO_4^{2-} in the product reaches 85% after 5 hours. It is expected that a higher purity can be reached if the experiment lasted longer. It can also be seen from Fig. 8 (a) that the concentration profiles of chloride and sulphate are linear during the first 240 min (4 hours).

Fig. 8(b) illustrates the correlations between the current efficiency of Cl^- , N-CE of Cl^- and MVA membrane selectivity as a function of time. The current efficiency of Cl^- was more than 80% during the experiment. This means that the current efficiency of

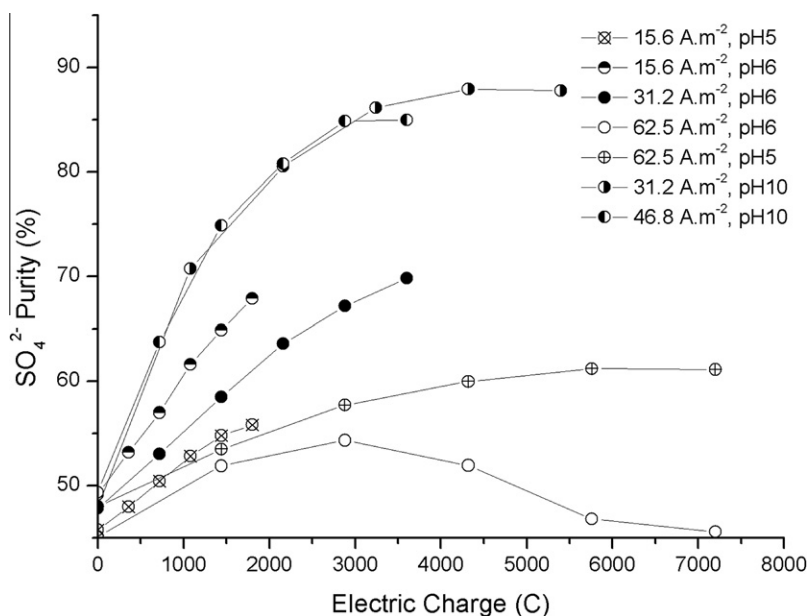


Fig. 7. SO_4^{2-} purity as a function of electric charge in the product.

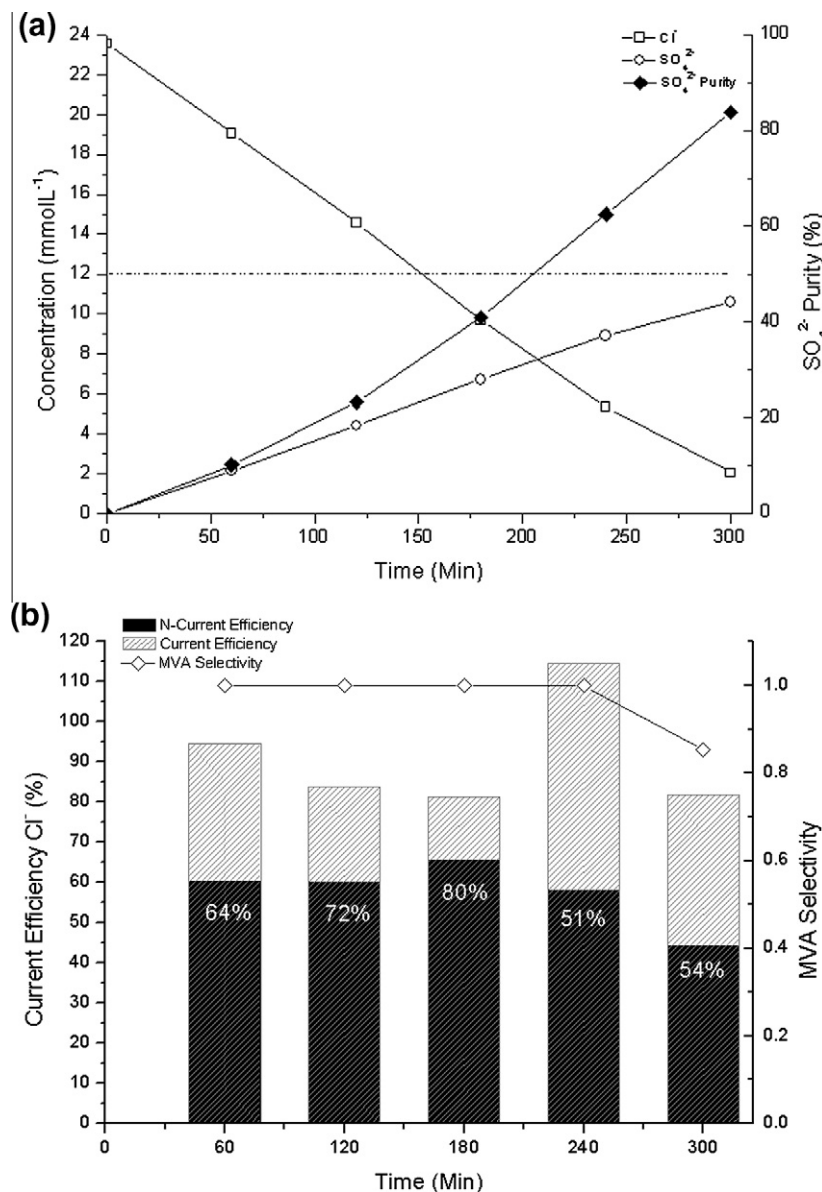


Fig. 8. Exp-Full: (a) the concentration profiles of chloride and sulphate ion, and the sulphate purity in the product vessel as a function of time; (b) the correlations between the current efficiency of Cl⁻, N-current efficiency of Cl⁻ and MVA membrane selectivity as a function of time.

sulphate was less than 20%, which indicates that most of the sulphate ions were retained in the product compartment and that only a very small amount of sulphate went to the brine compartment. On the other hand, the N-CE of chloride was more than 50% (i.e., the stack efficiency was more than 50%) during the experiment. This means that most of the applied current was used to enrich sulphate in the product compartment. Moreover, the MVA membrane selectivity was close to 1 from the beginning until 4 hours and declined to 0.85 in the fifth hour.

3.3.2. The experiment with 12 mmol L⁻¹ NaCl solution as the initial product stream (denoted as Exp-Half)

Similarly, as shown in Fig. 9 (a), the Cl⁻ concentration drops from 12 to 0.8 mmol L⁻¹ after 5 hours. Meanwhile, the SO₄²⁻ concentration increases from 0 to 5.6 mmol L⁻¹. It is obvious that the experiment has reached the final stage and a plateau is formed. 6 mmol L⁻¹ is the theoretical maximum concentration of SO₄²⁻, but the plateau value is 5.6 mmol L⁻¹. This is attributed to a continuous flux (electro-migration under the current of 0.2 A) of chloride ions from the feed compartment.

The purity of SO₄²⁻ in the product reaches 85% after 5 hours and also forms a plateau. Similar as Fig. 8(a), the concentration profiles of chloride and sulphate in Fig. 9(a) are linear during the first 120 min.

In Fig. 9(b), the current efficiency of Cl⁻ declines from 90% to 55% during the experiment. This means that, the current efficiency of sulphate increases from around 10% to around 50%, which indicates that the retention of sulphate ion in the product compartment declines during the experiment. Furthermore, the N-CE of chloride decreases from 69% to almost zero after 5 hours. This means that the stack efficiency was getting worse and worse and almost no sulphate can be further retained in the product compartment at the end of the experiment. Correspondingly, the MVA membrane selectivity declines from 0.85 to zero after 4 hours. This implies that the MVA membrane selectivity is not only affecting the experiment progress but also is affected by the progress.

3.3.3. Comparison of the two experiments

Since the only difference of these two experiments was the initial concentration of NaCl in the product stream, the voltage as a

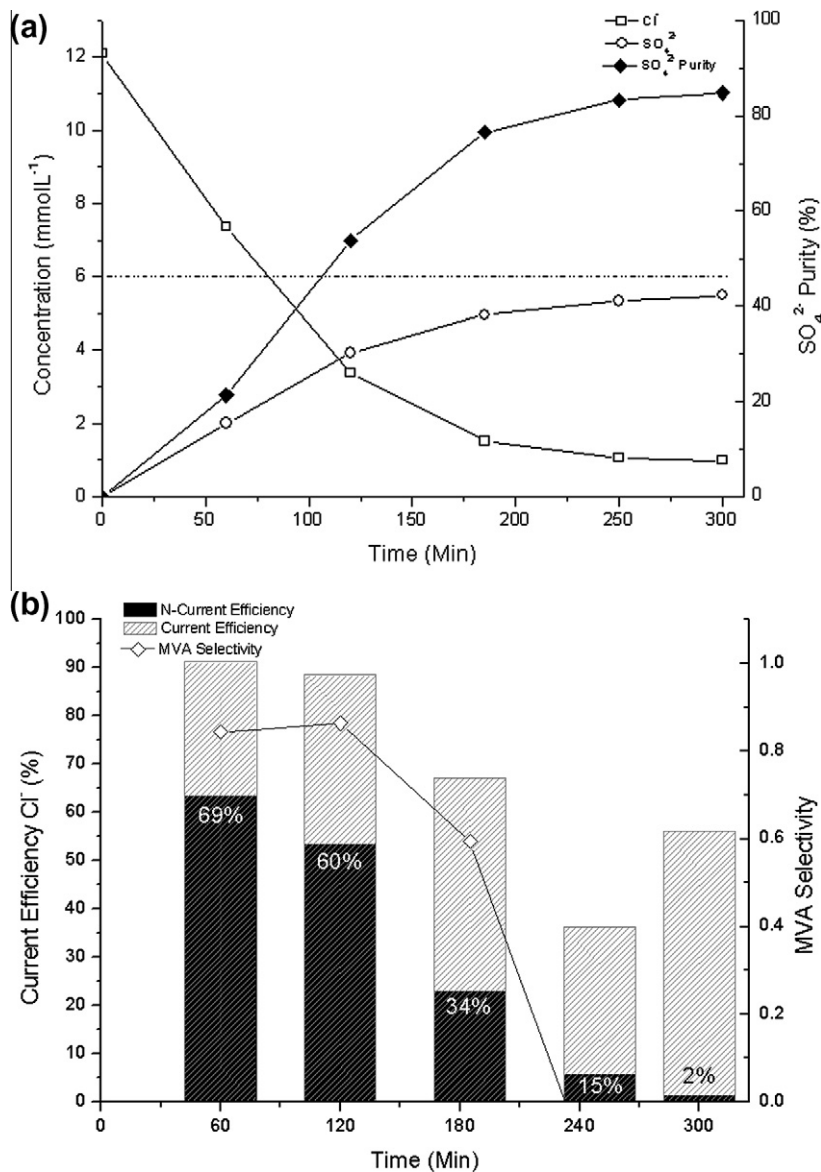


Fig. 9. Exp-Half: (a) the concentration profiles of chloride and sulphate ion, and the sulphate purity in the product vessel as a function of time; (b) the correlations between the current efficiency of Cl⁻, N-current efficiency of Cl⁻ and MVA membrane selectivity as a function of time.

function of time, the ion concentration profiles and the SO₄²⁻ purity are further compared to evaluate the possibility to simulate the electrodesialysis process.

Fig. 10 exhibits the voltage plots of these experiments: the voltage of Exp-Full was stable during the first 3 hours and gradually increased from then on; the voltage of Exp-Half increased from the beginning of the experiment. The increase of the voltage was not due to the depletion of the feed, since the concentration of the feed stream was sufficient (60 L) and almost constant during these two experiments. This phenomenon can be explained by the fact that sulphate ions are more difficult to migrate through the MVA membrane. Therefore, Fig. 10 indicates that as the portion of SO₄²⁻ increased in the product stream (the SO₄²⁻ enriched stream), the resistance of the stack was also increased.

Furthermore, Fig. 11(a) compares the concentration profiles of Cl⁻ and SO₄²⁻ of these two experiments. As shown, a linear correlation can be seen from 0–120 min in Exp-Half, and from 0–240 min in Exp-Full. After the linear period, the plots start to form a plateau. The result indicates that the initial product concentration has a proportional correlation with the progress of the experiment. Thus,

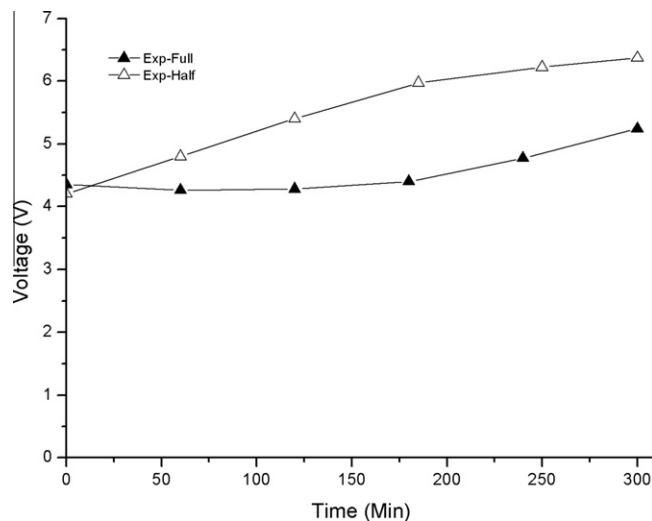


Fig. 10. Comparison of the voltage as a function of time during the experiment Exp-Full and Exp-Half.

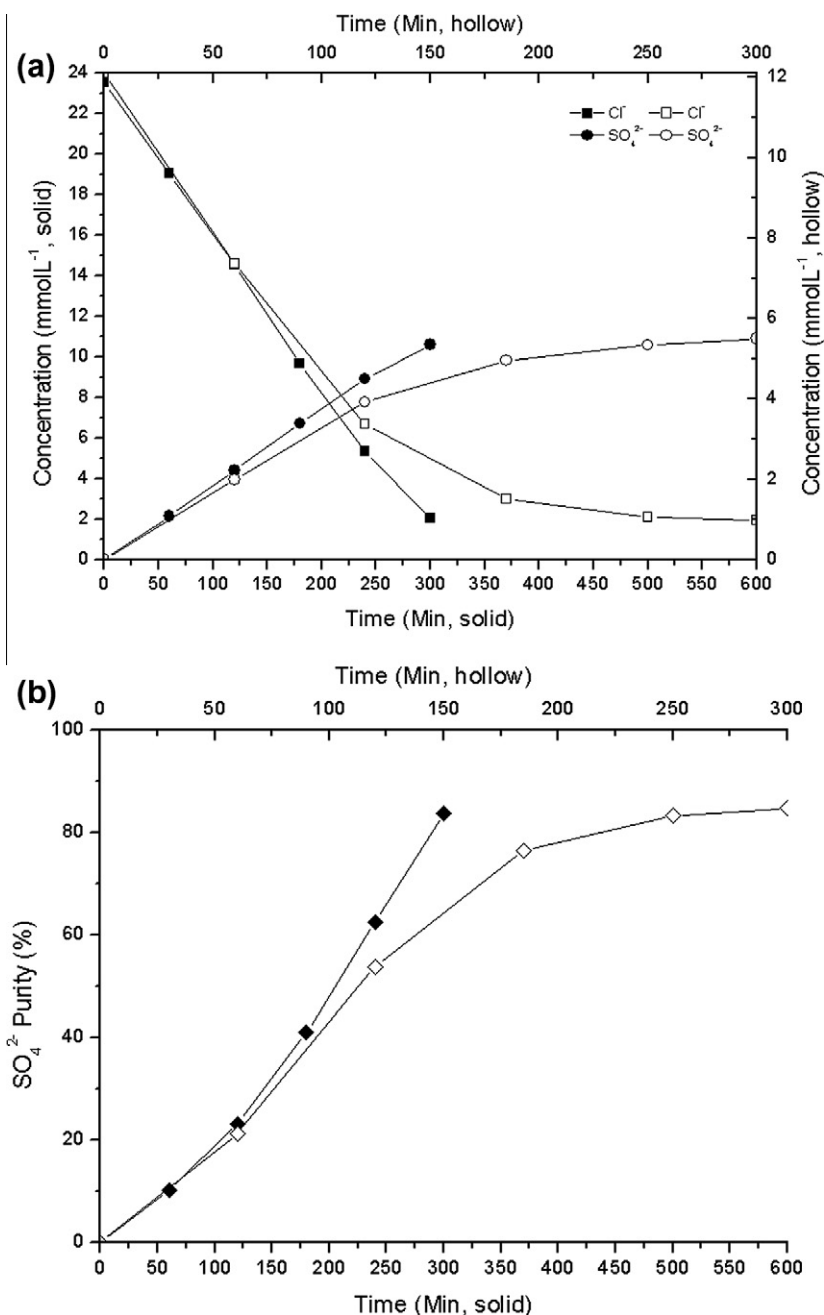


Fig. 11. Comparison of Exp-Half and Exp-Full: (a) the ion concentration profiles; (b) SO_4^{2-} purity; as a function of time.

it can be predicted that Exp-Full will reach the final point at around 600 min. Fig. 11 (b) compares SO_4^{2-} purity of the two experiments. A similar conclusion can be drawn that after 600 min Exp-Full can obtain the highest sulphate purity. Furthermore, the purity will be higher than 85%.

This work is considered to fractionate the ions with different charge numbers. The membrane selectivity to different ions can be attributed to charge difference, size exclusion, hydrophilicity difference, or other characteristics of the membranes and the ions. Recently, some investigations have been reported on separation of charged organic compounds by electro dialysis-based processes [29–31]. Therefore, more study is necessary to be carried out to fractionate different inorganic and/or organic ions or small charged proteins on the basis of their different sizes, hydrophilicity or other characteristics.

4. Conclusion

This work qualitatively and quantitatively demonstrated the potential of electro dialysis: fractionation of multivalent ions from monovalent ions on the synthetic wastewater. It was found that the higher the pH of the product stream, the higher the SO_4^{2-} concentration can be reached. The results also imply that the electro dialysis stack has a higher current efficiency at higher pH. Moreover, two experiments with different total salinity in the product compartment under the optimized conditions were carried out and were compared. The results show that the sulphate purity can reach over 85% and the electro dialysis process can be predicted under the optimized conditions. This investigation thus proves that electro dialysis is feasible and effective to fractionate divalent ion (SO_4^{2-}) from monovalent ion (Cl^-) in the mixture.

Based on the results of this work, further investigations will be carried out to fractionate different inorganic and/or organic ions or small charged proteins on the basis of their different sizes, hydrophilicity or other characteristics.

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