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Recovery of sulfuric acid and ammonia from scrubber effluents using bipolar membrane electrodialysis: Effect of pH and temperature

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ABSTRACT

Simulated ammonium sulfate scrubber effluent was treated using bipolar membrane electrodialysis (BPMED) to recover sulfuric acid for reuse in the scrubber, and ammonium hydroxide as a product, without using any chemicals. The effect of pH and temperature of the feed solution on the energy consumption of the BPMED and the purity of the recovered acid and base were investigated in batch experiments. Experiments were conducted during a 3-hour period using a scrubber effluent with the following characteristics: 50 g/L ammonium sulfate, pH ranging from 1 to 5 and temperature ranging from 20 °C to 30 °C. The energy consumption at pH 5 was lower than that at pH 1, i.e., 6.9 MJ/kg SO_4^{2-} and 7.7 MJ/kg SO_4^{2-}, respectively. The purity of the acid recovered from the feed solution with a pH of 5 was 36 %, whereas the feed with a pH of 1 resulted in an acid purity of 72 %. These values corresponded to a mass of ammonia diffusion of 6.9 g and 2.3 g, respectively. The purity of the base recovered from the feed with a pH of 5 was 84 %, whereas this was 69 % for the feed with a pH of 1. Higher temperature of the feed solution, i.e., 30 °C compared to 20 °C, resulted in a lower energy consumption: 7.1 MJ/kg SO_4^{2-} compared to 9.5 MJ/kg SO_4^{2-}, respectively. The temperature had a very limited effect on the acid and base purities, with values ranging from 80 % to 82 % for the acid, and from 33 % to 36 % for the base. Our study demonstrated the effective application of BPMED for the treatment of simulated acidic scrubber effluent, with simultaneous recovery of ammonia and sulfuric acid.

1. Introduction

To limit ammonium (NH_4^+) release to the aqueous environment, residual water with high nitrogen concentrations is treated before discharge. Recovery of NH_4^+ from ammonium rich streams is commonly achieved by using a combination of air stripping and acid scrubbing technologies [1–4]. During the stripping process, the NH_4^+ in the residual water is stripped in the form of ammonia gas (NH_3) [5,6]. The latter reacts with acid present in the scrubber to produce ammonium salt [7,8].

However, the operation of a scrubber requires a substantial amount of acid (3.7 kg H_2SO_4 (96 %)/kg NH_4^+-$N_{recovered}$) [9]. Sulfuric acid (H_2SO_4) is mostly used in the industry for the scrubbing process because it is a strong acid, easier to handle than for instance hydrochloric acid (HCl), and less expensive than alternative acids [10]. Ammonium sulfate ($(NH_4)_2SO_4$) is produced through the reaction of H_2SO_4 with NH_3-rich stripping gas during the scrubbing process. This chemical compound is widely used as a mineral fertilizer, and its market value varies depending on the region (70 – 110 €/ton for $(NH_4)_2SO_4$ (40 %)) [9]. In most cases, the income generated from the sales of $(NH_4)_2SO_4$ offsets the costs associated with the purchase and use of sulfuric acid [9]. However, a reduction in operational expenditures (OPEX) can be achieved by utilizing bipolar membrane electrodialysis (BPMED) to recover both H_2SO_4 and NH_4OH from the scrubber effluent. The recovered acid can be recycled, enabling its reuse in the scrubber, while the by-product NH_4OH can be utilized in the manufacturing of mineral fertilizer, thus resulting in a reduction of OPEX for operating the scrubber.

BPMED is a membrane technology that produces acid and base from the corresponding salt under a direct electric field [11]. A BPMED stack consists of cation-exchange membranes (CEMs), anion-exchange membranes (AEMs), and bipolar membranes (BPMs). A BPM dissociates water in the presence of an electric field to produce hydroxide ions (OH^-) and protons (H^+) [12]. BPMED can simultaneously recover NH_4^+ in the form of ammonium hydroxide (NH_4OH) and H_2SO_4 from an

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$(NH_4)_2SO_4$ solution. NH_4^+ ions migrate through the CEMs to the base compartment and combine with the OH^- produced by the BPMs to form NH_4OH, whereas the sulfate ions (SO_4^{2-}) migrate through the AEMs to the acid compartment and combine with the H^+ produced by the BPMs to form H_2SO_4 [13].

Recently, BPMED technology has gained increasing attention for treating industrial effluents [14–19]. Several studies have evaluated the application of BPMED to recover ammonium hydroxide and acids such as HCl, HNO_3, and H_2SO_4 from industrial streams containing ammonium chloride, ammonium nitrate, and ammonium sulfate, respectively [13,20–22].

Recovering H_2SO_4 in-situ using BPMED is expected to be more cost effective and energy friendly than purchasing H_2SO_4 for the scrubber. The energy consumption and purity of the recovered acid depend on the pH, temperature and composition of the salt stream to be treated [23–25]. The energy consumption of BPMED while treating the ammonium salt solution is affected by the competition between H^+ and NH_4^+ during their migration through the membrane from the feed solution to the base compartment [23,25]. The study of Guan et al. [23] focused on a rather narrow initial pH range of the feed solution (pH 2.5 to 4.0). In contrast to Guan et al. [23], Szczygielda & Prochaska [25], using alpha-ketoglutaric acid, reported that a higher initial pH of the feed solution, up to pH 5, results in lower purity of the acid recovered by BPMED. In addition, higher temperature results in a lower proton leakage from the acid to the diluate compartment, through the anion exchange membrane, resulting in higher acid concentration [26]. Besides, higher temperature results in a reduction in the membrane's stack resistance, and thus a lower energy consumption [24]. However, the energy consumption does not infinitely decrease with an increase in temperature due to the loosening of the porous matrix structure of the membranes when operating above a certain temperature [23]. To the best of our knowledge, there is a lack of studies that assessed the energy consumption associated with the treatment using BPMED of ammonium salt scrubber effluents at different pH and temperatures. Furthermore, there is a lack of studies assessing the effect of pH and temperature of such effluents on the purity of the recovered H_2SO_4 and NH_4OH. In addition, no studies have investigated ammonia (NH_3) diffusion from the base compartment to the acid compartment at different pH and temperature.

In this study, we performed lab scale experiments to investigate the effects of the initial pH of the feed solution and the temperature on two key performance variables: the purity of the recovered H_2SO_4 and NH_4OH and the energy consumption during BPMED of the $(NH_4)_2SO_4$ scrubber effluent. Furthermore, we assessed the NH_3 diffusion from the base to the acid compartment at different pH and temperature. Initial pH of the feed solution and temperature have an impact on the transport of ions, and as a result have an impact on i) the energy consumption during BPMED of the $(NH_4)_2SO_4$ scrubber effluent, ii) the purity of the recovered products, and iii) NH_3 diffusion from the base to the acid compartment. $(NH_4)_2SO_4$ scrubber effluent is typically acidic and has usually a temperature of about 70 °C. Membrane scaling is not likely to occur when this scrubbing effluent that is virtually free of multivalent cations, is used as the feed solution for BPMED. For the experiments, an $(NH_4)_2SO_4$ feed solution with a pH in the range 1 to 5 was investigated. The maximum investigated temperature was set to 30 °C because the reported membrane stability was limited to 30 – 35 °C.

2. Materials and methods

2.1. Materials

A lab-scale 64004 electrodialysis cell was used, purchased from PCCell (Heusweiler, Germany), consisting of a Pt/Ir- (platinum/iridium) coated titanium anode and a V4A steel cathode. A three-compartment cell arrangement was used, consisting of an acid compartment, a base compartment and a diluate compartment, also called salt compartment. A BPMED membrane stack consisting of ten cell triplets was used. Each cell triplet consisted of an anion exchange membrane (AEM), a cation exchange membrane (CEM) and a bipolar membrane (BPM). PC 100D AEMs, PC-SK CEMs, and PC Bip BPMs were used, purchased from PCCell (Heusweiler, Germany). The main characteristics of the ion exchange membranes provided by PCCell (Heusweiler, Germany) are shown in Table 1. Fig. 1 depicts the BPMED membrane stack used for the experiments. Anion exchange end membranes (AEEMs) were chosen over cation exchange end membranes (CEEMs) to limit the accumulation of NH_4^+ in the electrode rinse solution (ERS) and also to keep the sodium ions (Na^+) in the ERS. PC 100D AEEMs were used, purchased from PCCell (Heusweiler, Germany). The active membrane surface area of each membrane was 8x8 cm^2. The membranes and electrodes were separated by 0.5 mm thick silicon/polyethylene sulfone spacers with a void fraction of 59 %.

The feed/diluate solution was stored in a 1-liter borosilicate bottle. The acid solution, base solution, and ERS were stored in 0.5-liter borosilicate bottles. The solutions were continuously mixed by magnetic stirrers on a mixing plate with the same settings for all experiments. The solutions were recirculated through the BPMED membrane stack by a calibrated peristaltic Watson-Marlow 520S pump with separate Watson-Marlow 313 pump heads for each solution. For all experiments, the cross-flow velocity of each stream was set to 2 cm s^{-1}, corresponding to a pump flow rate of 16.9 L h^{-1}. A TENMA 72–1330 power supply was used with an electric current and electric potential range of 0.0 – 15.0 A and 0.0 – 60.0 V, respectively. Fig. 2 shows a schematic representation of the complete experimental BPMED set-up, similar to the set-up used by van Linden et al. [27].

The following reagents were used in the experiments: $(NH_4)_2SO_4$ salt (≥99 %), sodium sulfate (Na_2SO_4) salt (≥99 %), H_2SO_4 (2.5 M), and NH_4OH (25 %). These reagents were used to prepare the initial solutions used in the acid, base, and diluate compartments and ERS. All the reagents were supplied by Sigma Aldrich (Zwijndrecht, The Netherlands).

2.2. Analytical methods

The diluate, acid, base and ERS pH and electrical conductivities (EC) were measured in the respective bottles, using WTW Multi 3620 IDS multimeters, connected to calibrated IDS SenTix 940 pH meters and TetraCon 925 EC meters, respectively. The temperature of the solutions was monitored by using the temperature sensors present in the IDS SenTix 940 pH meters or TetraCon 925 EC meters. Calibrated volumetric cylinders were used to determine the solution volumes at the beginning and end of the experiments. Finally, NH_4^+ concentrations were measured using a Metrohm 883 cation system Ion Chromatography (IC) with a cation column (C6 150/4.0) and SO_4^{2-} concentrations were measured using a Metrohm 818 anion system IC with an anion column (A Supp 5 150/4.0).

2.3. Experimental methods

Batch experiments to investigate the effects of the initial pH of the feed solution and temperature were performed by using the experimental set-up shown in Fig. 2. The following pH values of the feed were investigated: 1, 2, 3, 4, and 5; and the following temperatures were investigated: 20 °C, 25 °C and 30 °C. All experiments to investigate the effect of the initial pH of the feed were conducted at a temperature of 25 ± 2 °C, while the experiments to investigate the effect of temperature were conducted with a feed solution of pH = 5 and in a temperature-controlled room. The initial feed solution contained 50 g of $(NH_4)_2SO_4$ in 1 L of demi water. The pH of the initial feed was manually adjusted using H_2SO_4 (2.5 M). The initial acid and base solution contained 0.66 g of $(NH_4)_2SO_4$ in 0.5 L of demi water (0.01 M $(NH_4)_2SO_4$). The initial ERS consisted of 1 M Na_2SO_4 (addition of 71 g of Na_2SO_4 to 0.5 L of demi water). The ERS was acidified to a pH of 2 using H_2SO_4 (2.5 M) to minimize the net H^+ leakage from the acid to the ERS compartment

Table 1
Main characteristics of ion exchange membranes provided by PCCell (Heusweiler, Germany) and utilized in the experiments.

Membrane	Thickness (μm)	Area resistance (Ω cm^2)	Water content (wt%)	Ion exchange capacity (meq.g^{-1})		Transport number (–)
				Strong basic	Weak basic	
AEM (PC 100D)	100–160	~ 5	~ 50	~ 1.2	~ 0.7	>0.94
CEM (PC-SK)	100–120	~ 2.5	~ 9	–		>0.95
BPM (PC Bip)	~ 120	–	~ 30	–		–

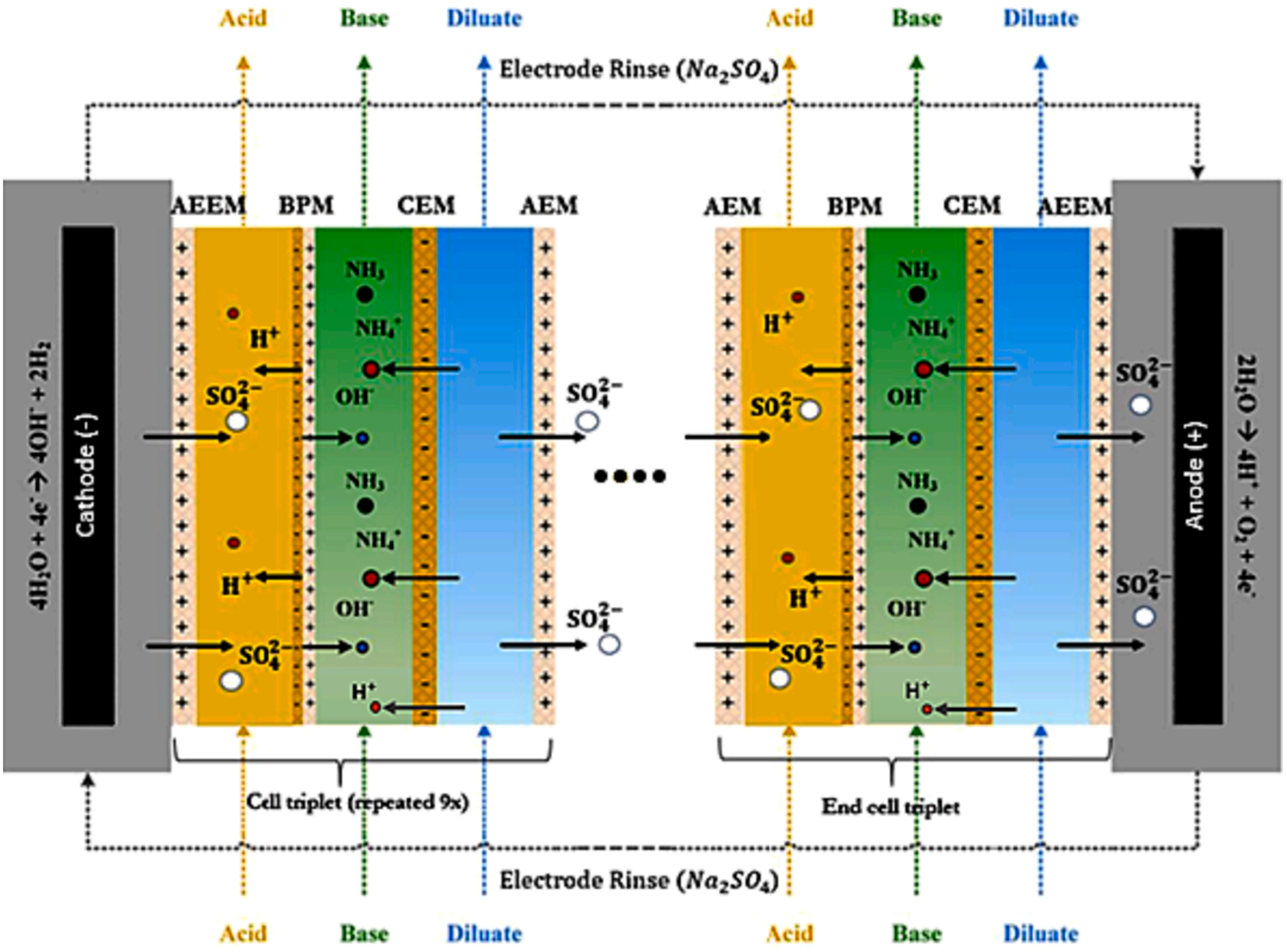

Fig. 1. Schematic overview of the three compartment BPMED cell configuration and the ions transport under the application of an electric current. In the acid compartment, H^+ combines with SO_4^{2-} to form H_2SO_4, while in the base OH^- combines with NH_4^+ to form NH_4OH. The base is rich in $NH_{3\ (aq)}$ due to the high pH. Figure is adapted from van Linden et al. [27].

through the AEEM. This adjustment allowed to mitigate the impact of the Grotthus mechanism or co-ion leakage [26], resulting in a decrease in the H^+ concentration gradient between the acid and ERS during the experiment and thus minimizing the net H^+ leakage from the acid to the ERS. The applied current density was 187.5 A/m^2, which corresponded to the limiting current density (LCD) for 90 % NH_4^+ removal. The batch experiments were carried out for a duration of 180 min. Solution samples (2 mL) were taken every 20 min during the experimental run. Solution volumes were measured at the beginning and end of each batch experiment to determine the water balance. NH_4^+ and SO_4^{2-} concentrations were measured at the beginning, every hour, and at the end of each batch experiment to assess the NH_4^+ and SO_4^{2-} mass balance. Moreover, the current and electric potential were automatically logged every 5 s on a laptop. Finally, the pH and EC of the diluate, acid, base, and ERS were also logged every 5 s.

2.4. Performance indicators

The performance of BPMED for the recovery of H_2SO_4 and NH_4^+ from $(NH_4)_2SO_4$ scrubber effluents was evaluated based on acid current efficiency and electrochemical energy consumption. The acid current efficiency was determined using equation (1) [28].

$$\eta_{acid} = \frac{Z\cdot F\cdot n_{SO_4^{2-},a}}{N\cdot\sum_{t=0}^{t}(I_{\Delta t}\cdot \Delta t)}.100\%, \tag{1}$$

where η_{acid} = acid current efficiency (unitless), z = ion valence (unitless, $z = 2$ for SO_4^{2-}), F = Faraday constant (unit: C.mol^{-1}, F = 96,485 C. mol^{-1}), $n_{SO_4^{2-},a}$ = amount of SO_4^{2-} transported from the diluate to the acid (unit: mol), N = number of cell triplets in the BPMED membrane stack (unitless, $N = 10$), $I_{\Delta t}$ = average electric current during each time

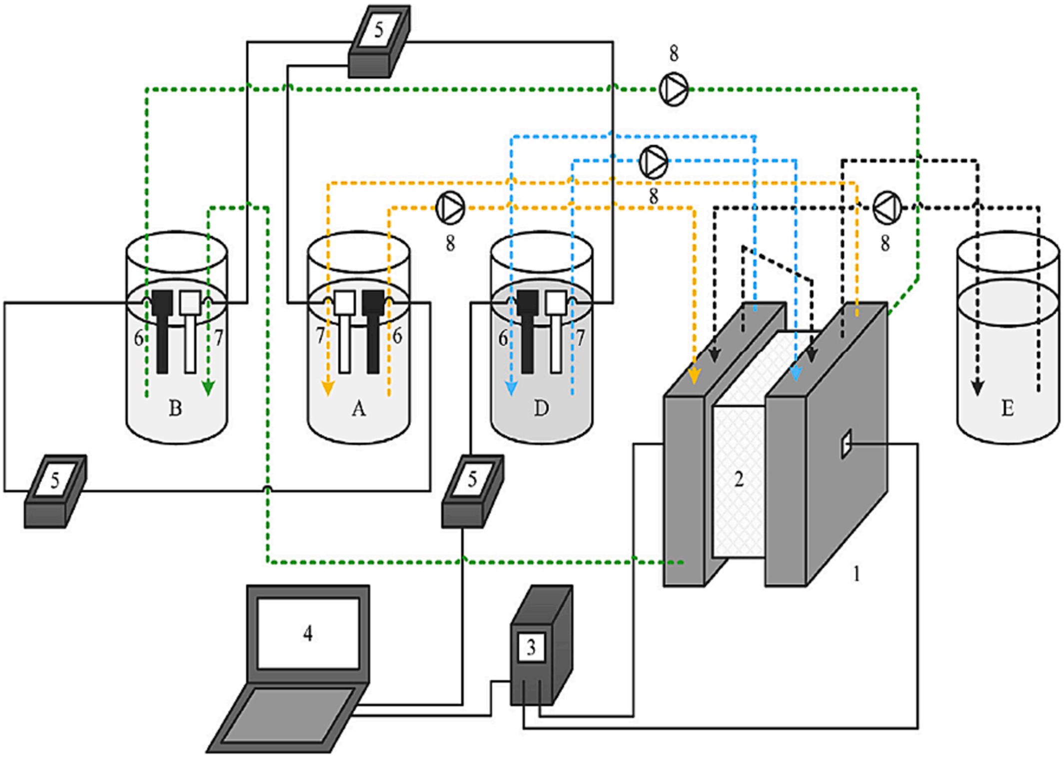

Fig. 2. Schematic representation of BPMED experimental set-up: 1) cell, 2) BPMED membrane stack, 3) power supply, 4) laptop, 5) multi-meters, 6) EC-sensors, 7) pH-sensors, 8) peristaltic pumps, and diluate (D), acid (A), base (B) and electrode rinse solution (E) [27].

interval (unit: A), and Δt = time interval (unit: s).

The electrochemical energy consumption for the treatment of $(NH_4)_2SO_4$ scrubber effluents by BPMED was calculated as in equation (2).

$$E = \frac{\sum_{t=0}^{t}(U_{\Delta t}\cdot I_{\Delta t}\cdot \Delta t)}{m_{SO_4^{2-},a}} \tag{2}$$

where$E$ = electrochemical energy consumption (unit: J/g-$SO_4{}^{2-}$), $U_{\Delta t}$ = average electric potential during each time interval (unit: V), $m_{SO_4^{2-},a}$ = mass of recovered $SO_4{}^{2-}$ in the acid compartment (unit: g-$SO_4{}^{2-}$).

Moreover, the purities of the recovered acid and base were assessed. The purity is defined as the concentration of acid or base over the total concentration of ions present in the solution, as shown in the following equations:

$$P_{acid} = \frac{C_{H_2SO_4}}{C_T}.\ 100\% \tag{3}$$

$$P_{base} = \frac{C_{NH_4OH}}{C_T}.\ 100\% \tag{4}$$

where P_{acid} = the purity of the acid (unit: %), $C_{H_2SO_4}$ = concentration of sulfuric acid in the acid (unit: mol/L), C_T = total concentration of identified ions in the respective compartment (unit: mol/L)), P_{base} = the purity of the base (unit: %), and C_{NH_4OH} = concentration of ammonia solution in the base (unit: mol/L).

Furthermore, the distributions of NH_4^+ and SO_4^{2-} across the diluate, acid, and base compartments were determined to analyse (i) the NH_4^+ and SO_4^{2-} transport from the diluate to the base and acid compartment, respectively, (ii) the NH_3 diffusion and NH_4^+ leakage from the base to the acid compartment through the BPM [11], (iii) NH_3 diffusion from the base to the diluate compartment through the CEM, (iv) SO_4^{2-} leakage from the acid to the base compartment through the BPM [11], and (v) the possible leakage of ionic species (NH_4^+ and SO_4^{2-}) from the base and acid to the diluate [27] and vice versa that took place after a specific duration of the experiment. The final fraction of NH_4^+ and SO_4^{2-} in the 3 compartments was calculated by using the following equations:

$$\text{Final fraction of } NH_4^+ = \frac{m_{sNH_4^+\ at\ t=180\ min}}{m_{DNH_4^+\ at\ t=0\ min}}.\ 100\%, \tag{5}$$

$$\text{Final fraction of } SO_4^{2-} = \frac{m_{sSO_4^{2-}\ at\ t=180\ min}}{m_{DSO_4^{2-}\ at\ t=0\ min}}.\ 100\%, \tag{6}$$

where Final fraction of NH_4^+ = fraction of NH_4^+ at 180 minutes (unit: %), $m_{sNH_4^+\ at\ t=180\ min}$ = mass of NH_4^+ in respective compartment at 180 minutes (unit: g), $m_{DNH_4^+\ at\ t=0\ min}$ = total initial mass of NH_4^+ in feed (unit: g), Final fraction of SO_4^{2-} = fraction of SO_4^{2-} at 180 minutes (unit: %), $m_{sSO_4^{2-}\ at\ t=180\ min}$ = mass of SO_4^{2-} in respective compartment at 180 minutes (unit: g), $m_{DSO_4^{2-}\ at\ t=0\ min}$ = total initial mass of SO_4^{2-} in feed (unit: g).

3. Results and discussion

3.1. Final NH_4^+ and SO_4^{2-} distribution

All reported values represent the mean of duplicate experiments. The final NH_4^+ and SO_4^{2-} distribution over the diluate, acid, and base reflected the net NH_4^+ and SO_4^{2-} transport, including NH_3 diffusion and SO_4^{2-} leakage that was observed after an experimental period of 180 min. Fig. 3A shows the NH_4^+ distribution over the diluate, acid, and base compartment at different pH feed solutions. The temperature was set to 25 ± 2 °C. Higher pH of the feed solution, i.e., pH 5 compared to pH 1, resulted in a lower fraction of NH_4^+ in the diluate at the end of the experiments: 2 % compared to 58 %, respectively. This means that 98 % and 42 % of the NH_4^+ was transported from the feed at pH 5 and pH 1, respectively. The observed lower fraction of NH_4^+ removed from the diluate with pH 1 feed solution can be attributed to the high ion-competition between H^+ and NH_4^+ for their transport over the

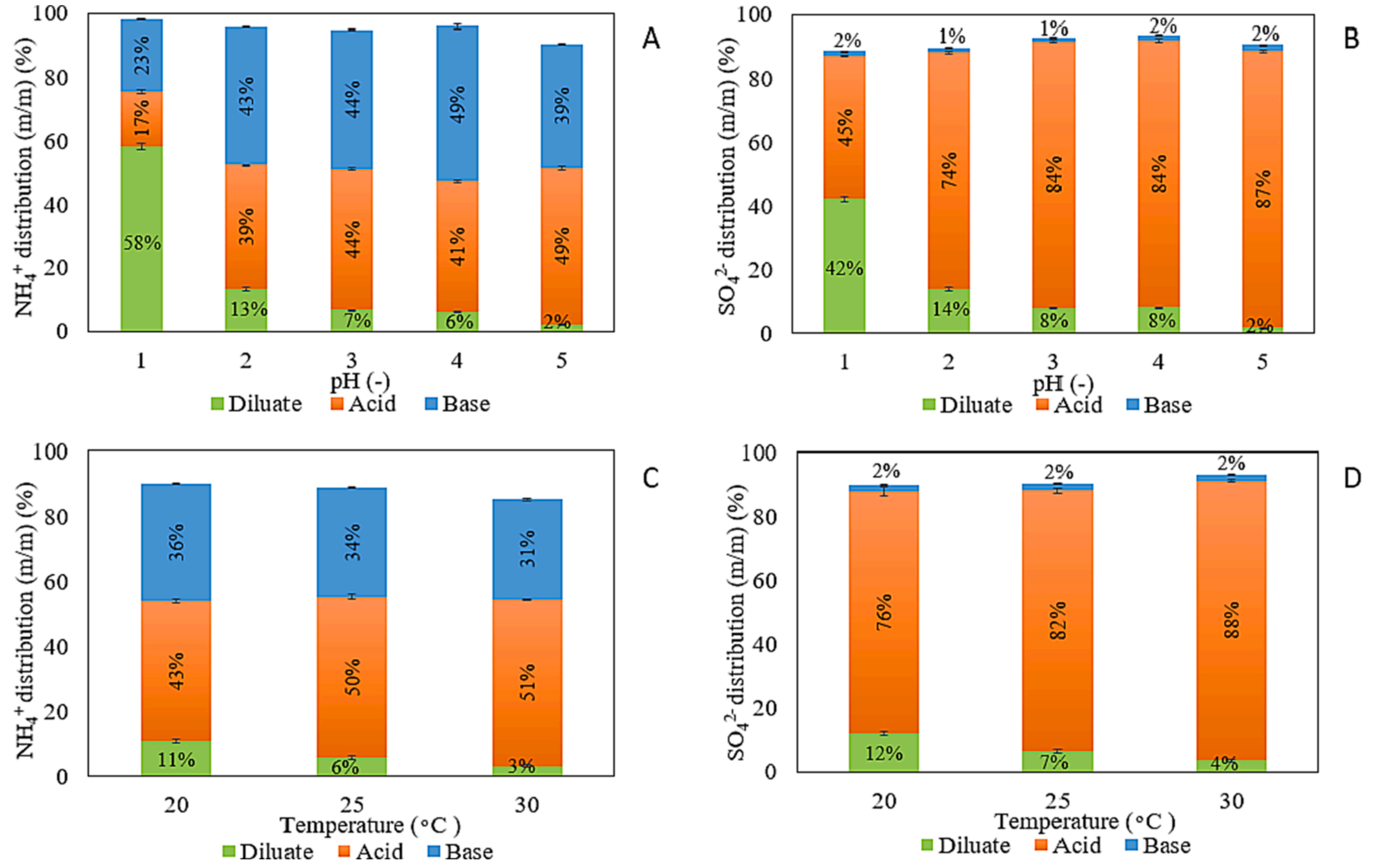

Fig. 3. Distribution of NH_4^+ and SO_4^{2-} originating from feed solution of 50 g/L $(NH_4)_2SO_4$ after 180 min at different initial pH of the feed solution (A and B) and temperature (C and D). The pH experiments (A and B) were conducted at a temperature of 25 ± 2 °C and the temperature experiments (C and D) were conducted at a pH of 5. Average values of the duplicate experiments are presented, along with the minimum and maximum values (outer values of error bars).

membrane [23]. Moreover, it can be observed that 40 – 50 % of the transported NH_4^+ from the feed ended up in the acid compartment via diffusion from the base to the acid compartment. During BPMED treatment of ammonium salts, gaseous NH_3 is formed in the base compartment, which can freely diffuse through the BPMs to the acid compartment. In the study of van Linden et al. [27], the NH_3 concentration in the diluate was always lower than that in the acid, which suggests that ammonia diffuses from the base compartment, through the BPMs to the acid compartment. The higher the NH_3 concentration in the base, the higher the NH_3 diffusion from the base to the acid [20]. In our current study, higher pH of the feed solution, i.e., pH 5 compared to pH 1, resulted in a higher mass of NH_3 that diffused from the base to the acid: 6.9 g compared to 2.3 g, respectively, as shown in Table S1 in Supporting Information. Note that there was no accumulation of NH_4^+ in the electrode rinse solution at the end of the experiments because of the AEEMs used in the BPMED membrane stack, which is in line with the study of van Linden et al. [27].

Fig. 3B shows the SO_4^{2-} ions distribution over the diluate, acid, and base compartment at different pH feed solutions after an experimental period of 180 min. The temperature was set to 25 ± 2 °C. The fraction of SO_4^{2-} recovered in the acid compartment with a pH of 5 was 87 %, whereas this was 45 % for the feed with a pH of 1. H_2SO_4 has a pKa of 2.0 [29], which means that below pH = 2 the fraction bisulfate (HSO_4^-) relative to sulfate (SO_4^{2-}) becomes larger than equimolar. Lorrain et al. [30] state that the HSO_4^- ion does not cross the AEM, instead it dissociates at the solution-membrane interface into a proton and a SO_4^{2-} ion that crosses the AEM. This implies that with increasing pH, the concentration of HSO_4^- in solution becomes lower and, correspondingly, the concentration of already available SO_4^{2-} in solution becomes higher, resulting in a higher mass of SO_4^{2-} recovered in the acid. However, the observed low SO_4^{2-} removal when working with pH 1 feed cannot be entirely attributed to the higher ratio of HSO_4^- to SO_4^{2-}. Note that the feed solution was acidified using H_2SO_4 and thus pH 1 feed had a higher net mass of SO_4^{2-} compared to the other investigated feed solutions.

Fig. 3C shows the NH_4^+ distribution over the diluate, acid and base at different temperatures after a period of 180 min, whereas Fig. 3D presents the SO_4^{2-} distribution at different temperatures after 180 min. The initial pH was set to 5. Higher temperature of the feed solution, i.e., 30 °C compared to 20 °C, resulted in a higher fraction of transported NH_4^+: 97 % compared to 89 %, respectively. Furthermore, the fraction of NH_4^+ present in the acid compartment due to NH_3 diffusion from the base compartment, when treating a feed solution at 30 °C, was higher than with a feed solution at 20 °C: 51 % and 43 %, respectively, corresponding to a mass of 7.1 g and 6.0 g, respectively (Table S2 in Supporting Information). Notably, there is almost 10 % more NH_3 than NH_4^+ in a basic solution at pH 10 when temperature increases from 20 °C to 30 °C, thus increasing the fraction of NH_3 that can diffuse into the acid compartment. In addition, from Fig. 3D it can be observed that the fraction of recovered SO_4^{2-} in the acid compartment at 30 °C was higher than that at 20 °C: 88 % and 76 %, respectively. The mobility of ions increases with temperature [24], which might explain the higher removal of NH_4^+ and SO_4^{2-} from the feed in the present study.

3.2. Acid current efficiency and electrochemical energy consumption

Fig. 4A shows the acid current efficiency and Fig. 4B shows the electrochemical energy consumption for the treatment of $(NH_4)_2SO_4$ scrubber effluents by BPMED using different initial pH of the feed and a fixed temperature of 25 ± 2 °C. Higher pH of the feed solution, i.e., pH 5 compared to pH 1, resulted in a higher acid current efficiency and lower

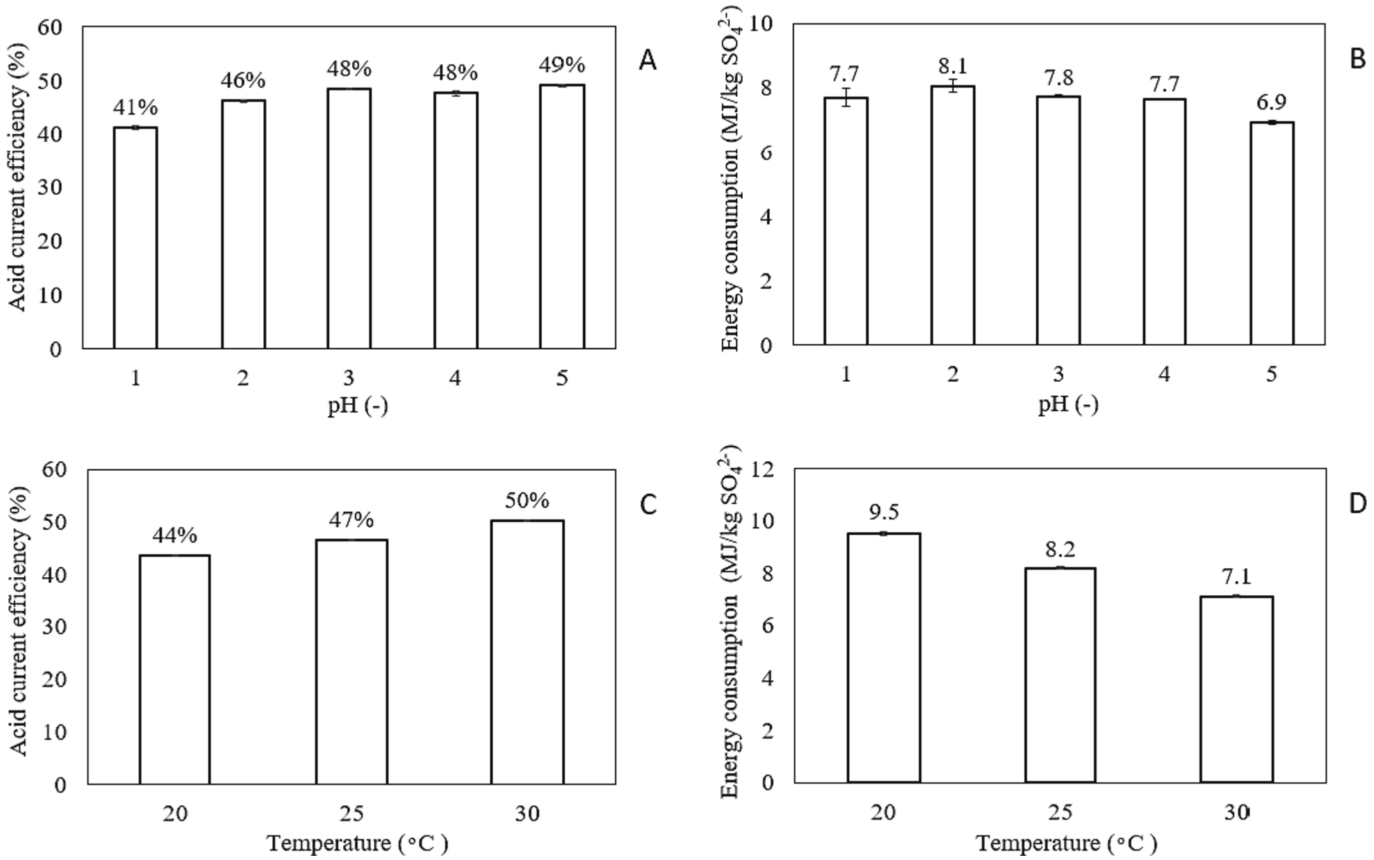

Fig. 4. Acid current efficiency and electrochemical energy consumption at different initial feed solution pH (A and B), and temperature (C and D) using 50 g/L $(NH_4)_2SO_4$ feed solution. The pH experiments (A and B) were conducted at a temperature of 25 ± 2 °C and the temperature experiments (C and D) were conducted at a pH of 5. Average values of the duplicate experiments are shown, along with the minimum and maximum values (outer values of error bars).

energy consumption: 49 % compared to 41 % and 6.9 MJ/kg SO_4^{2-} compared to 7.7 MJ/kg SO_4^{2-}, respectively. The higher current efficiency and lower energy consumption for pH 5 feed solution compared to pH 1 feed are likely related to the higher mass of SO_4^{2-} recovered in the acid compartment with pH 5 feed solution compared to pH 1, i.e., 31.7 ± 0.2 g SO_4^{2-} compared to 26.6 ± 0.2 g SO_4^{2-}, respectively. However, it remains unclear why a higher acid current efficiency and lower energy consumption was observed for the pH 5 feed solution, because the electrical resistance of the BPMED membrane stack when operating with a pH 5 feed should have been higher than with a pH 1 feed. Notably, the EC of the diluate, acid and base for the pH 5 feed solution experiments was lower than that of the pH 1 feed (Fig.S1 in Supporting Information), and the average electric potential across the BPMED membrane stack during the experiment with a pH 5 feed was higher than that of a pH 1 feed, 16.9 ± 1.3 V compared to 16.3 ± 1.7 V (Fig. 5A). The energy consumption with a feed solution of pH 2 was higher than that at pH 1: 8.1 MJ/kg SO_4^{2-} and 7.7 MJ/kg SO_4^{2-}, respectively. The lower energy consumption for the feed solution at pH 1, compared to pH 2, is probably due to the lower electrical resistance of the BPMED membrane stack when operating with pH 1 feed. The higher EC of the diluate, acid and base for pH 1 feed solution experiments (Fig.S1 in Supporting Information) may have led to the reduction in electrical resistance of the

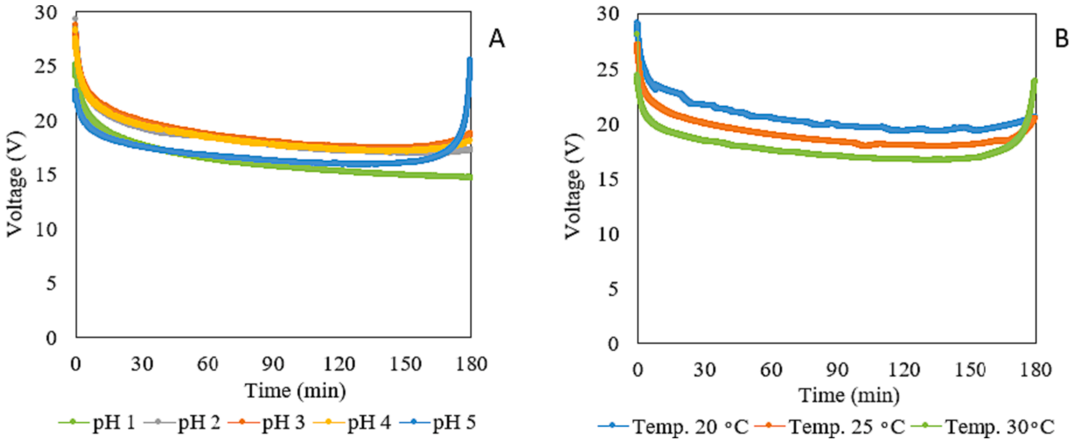

Fig. 5. Electric potential across the BPMED membrane stack during the experiments at different initial feed solution pH (A), and temperature (B). The pH experiments (A) were conducted at a temperature of 25 ± 2 °C and the temperature experiments (B) were conducted at a pH of 5.

BPMED membrane stack. The average electric potential across the BPMED membrane stack during the experiment with pH 1 feed was 16.3 ± 1.7 V, whereas this was 18.3 ± 1.6 V for the feed with a pH of 2 (Fig. 5A).

Fig. 4C and 4D show the acid current efficiency and energy consumption at different temperatures (20 °C, 25 °C, and 30 °C) and initial pH set to 5. Higher temperature of the feed solution, i.e., 30 °C compared to 20 °C, resulted in a higher acid current efficiency and lower energy consumption: 50 % compared to 44 % and 7.1 MJ/kg SO_4^{2-} compared to 9.5 MJ/kg SO_4^{2-}, respectively. The lower energy consumption at higher temperature was due to the increase in acid current efficiency and decrease in the electrical resistance of the BPMED membrane stack. The average electric potential across the membrane stack with the feed at 30 °C was 17.7 ± 1.3 V, whereas this was 20.5 ± 1.4 V with the feed at 20 °C (Fig. 5B).

3.3. Purity of H_2SO_4 and NH_4OH recovered by BPMED

Fig. 6A shows the purity of the acid and base at different initial feed solution pH. The temperature was set to 25 ± 2 °C. The purity of the acid recovered from the feed solution with a pH of 5 was 36 %, whereas the feed with a pH of 1 yielded an acid purity of 72 %. The purity of the base recovered from the feed with a pH of 5 was 84 %, whereas this was 69 % for the feed with a pH of 1. The diffusion of dissolved NH_3 from the base solution to the acid solution, via the BPMs, as already mentioned in section 3.1, is the cause of the lower purity of the acid at higher pH. On the other hand, the purity of the base solution was higher at higher pH feed solution because the fraction mass of NH_4^+ transported from feed to base relative to mass of SO_4^{2-} leaked from feed to base was larger than equimolar. The mass of NH_4^+ transported to the base compartment from the feed solution with a pH of 5 was 5.4 ± 0.0 g, whereas this was 3.1 ± 0.0 g for the feed with a pH of 1. The mass of SO_4^{2-} that leaked from the acid to the base solution for the feed with a pH of 5 was 0.7 ± 0.1 g, whereas this was 0.9 ± 0.0 g for the feed with a pH of 1. The difference in mass of SO_4^{2-} that leaked from the acid to the base solution at different pH feed solutions was insignificant. Note that these leakages are not severe when considering that 31.7 g of SO_4^{2-} were recovered in the acid compartment for the feed with a pH of 5, and 26.6 g of SO_4^{2-} were recovered in the acid compartment for the feed with a pH of 1, as mentioned in section 3.2. The mass of SO_4^{2-} that leaked from the acid to the base solution for the feed with a pH of 5 represented 2.2 % of the SO_4^{2-} recovered in the acid compartment, whereas this was 3.4 % for the feed with a pH of 1. The incomplete permselectivity of the ion-exchange layers of the BPM makes SO_4^{2-} susceptible to leak through the BPM from the acid to base compartment [11].

The purity of the acid and base with pH 5 feed solution at different temperatures was also investigated (Fig. 6B). Notably, according to Fig. 6B, the temperature had a very limited effect on the purities of the acid and base, which ranged 80 – 82 % and 33 – 36 % for the acid and base, respectively.

3.4. Overall discussion and future outlook

This study showed that BPMED can effectively be used to simultaneously remove NH_4^+ from acidic scrubber effluent, recover H_2SO_4 in-situ for scrubbing, and recover NH_4OH. By increasing the pH of the feed solution, the energy consumption of BPMED of $(NH_4)_2SO_4$ scrubber effluent can be decreased. In the study by Zhang et al. [31] various ion-exchange membranes were utilized, revealing significant differences in membrane resistance even when working at the same pH. This observation highlights the dependency of membrane resistance on membrane type, indicating that the use of alternative membranes to the ones employed in our study may lead to further reduction in energy consumption of BPMED of $(NH_4)_2SO_4$ scrubber effluents.

Moreover, we showed that the pH of the feed solution significantly influenced the purities of the H_2SO_4 and NH_4OH recovered by BPMED. However, since the recovered H_2SO_4 will be used as scrubber liquid, its scavenging capacity to absorb volatile NH_3 is likely more important than its purity.

Experiments performed at different temperatures showed that the energy consumption decreased with increasing temperature. However, BPMED membranes loose stability at temperatures exceeding 35 °C. Note that the targeted scrubber effluent is warm (70 °C) and cooling to 30 °C is energetically not very efficient. Therefore, development of thermostable membranes for high temperature treatment, will facilitate the application of BPMED technology in scrubber liquid loops, which are commonly characterized by temperatures exceeding 35 °C. Such development will provide further insights into the effect of temperature on the energy consumption during BPMED of $(NH_4)_2SO_4$ scrubber effluents.

Furthermore, the energy consumption can be decreased by increasing the flow rate and the initial salt concentration in the feed [21,23,32], which results in lower electrical resistance of the BPMED membrane stack and lower electrical resistance of the solutions in different compartments [21,32,33]. In addition, the concentrations of the acid and base in their respective compartments will increase as the flow rate and the initial ammonium salt concentration in the feed increases [21,22,34]. The latter will probably result in higher NH_3 diffusion [20] and NH_4^+ leakage from the base compartment to the acid compartment and SO_4^{2-} leakage from the acid compartment to the base compartment, leading to lower purity of the acid and base produced.

Finally, the recovery of H_2SO_4 from acidic scrubber effluent (pH = 5

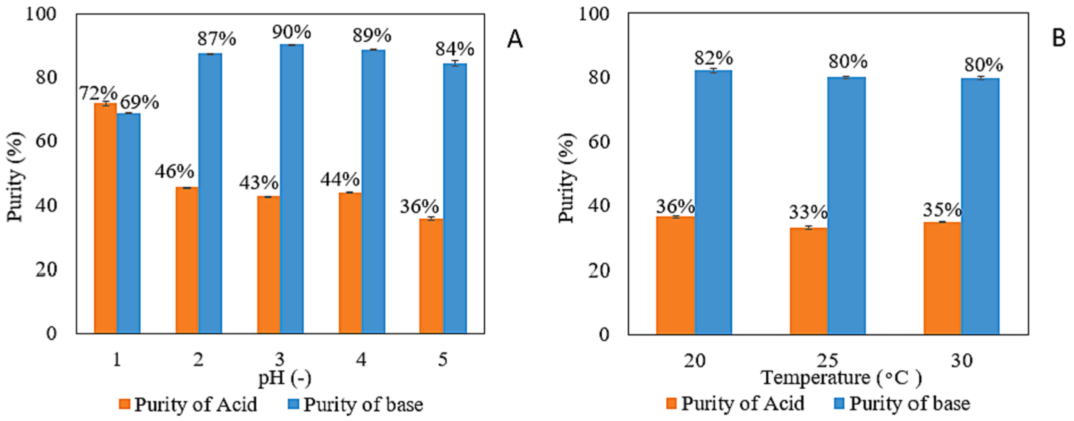

Fig. 6. Purity of acid and base at different initial feed solution pH (A), and temperature (B). The pH experiments (A) were conducted at a temperature of 25 ± 2 °C and the temperature experiments (B) were conducted at a pH of 5. Average values of the duplicate experiments are presented, along with the minimum and maximum values (outer values of error bars).

and temperature = 30 °C) using BPMED resulted in costs for energy consumption comparable to costs for purchasing H_2SO_4 for the scrubber, 0.2 €/kg SO_4^{2-} (considering an electricity cost of $0.1/kWh [35], which currently is at the low level in Europe) compared to 0.2 €/kg H_2SO_4 (96 %) [9]. Notably, the pH of the recovered H_2SO_4 was between 0.9 and 1.0. In addition to the recovery and reuse of H_2SO_4, BPMED also allows the recovery of ammonia from the $(NH_4)_2SO_4$ scrubber effluent. Notably, ammonia recovery using BPMED is more energy intensive than ammonia production from the Haber Bosch process that currently uses methane cracking for hydrogen production with an energy requirement of 27.4 – 31.8 MJ/kg NH_3 [36–38]. However, in the future, the hydrogen used for the Haber Bosch process will likely be produced from water electrolysis [39], with an energy requirement of 38.2 MJ/kg NH_3 [36]. This development positions BPMED as an energetically competitive candidate for ammonia recovery.

4. Conclusions

This study investigated the effects of the initial pH of the feed solution (pH 1 – 5) and the temperature (20 – 30 °C) on the purity of the recovered H_2SO_4 and NH_4OH, as well as the energy consumption during BPMED of the $(NH_4)_2SO_4$ scrubber effluent. The results demonstrate the feasibility of H_2SO_4 recovery with simultaneous NH_4OH production from spent scrubber effluents. Feed solution pH and temperature had a distinct effect on process performance and the following conclusions were drawn:

- The energy consumption for H_2SO_4 recovery was 6.9 MJ/kg SO_4^{2-} for a pH 5 feed solution and 7.7 MJ/kg SO_4^{2-} for a pH 1 feed solution. These values corresponded to an acid current efficiency of 49 % and 41 %, respectively. Notably, the ratio SO_4^{2-}/HSO_4^- increased with increasing pH, impacting the current efficiency.
- The acid purity of the recovered H_2SO_4 was 72 % while treating a pH 1 feed solution and reached 36 % for a pH 5 feed. The reduced purity was attributed to diffusive NH_3 transport from the base to the acid compartment.
- Competing ion transport reduced the fraction of NH_4^+ removal from the feed at low pH; while a 98 % removal was reached for pH 5 feed, it dropped to 42 % for pH 1. Also the base purity was distinctly higher for pH 5 feed solution compared to pH 1.
- Temperature had a positive effect on process performance. The energy consumption for H_2SO_4 recovery was 7.1 MJ/kg SO_4^{2-} for a feed solution at 30 °C, whereas this was 9.5 MJ/kg SO_4^{2-} for a feed solution at 20 °C. The lower energy consumption at higher temperature was attributed to the increase in acid current efficiency, which was 50 % at 30 °C compared to 44 % at 20 °C, and a decrease in the electrical resistance of the BPMED membrane stack.
- An increase in temperature from 20 °C to 30 °C resulted in a higher fraction of NH_4^+ and SO_4^{2-} removal from the diluate, with values increasing from 89 % to 97 % and from 88 % to 96 %, respectively. The higher removal of NH_4^+ and SO_4^{2-} from the diluate at higher temperature may be attributed to the increased mobility of ions. These observations were consistent with fractions of NH_4^+ in the acid due to NH_3 diffusion of 43 % and 51 %, respectively.
- Overall, a feed solution with a pH 5 and a temperature of 30 °C will yield the most energy efficient H_2SO_4 recovery using BPMED. These conditions will result in the highest base purity but lowest acid purity.

CRediT authorship contribution statement

Dhavissen Narayen: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft. **Eline van Berlo:** Formal analysis, Investigation, Methodology. **Jules B. van Lier:** Supervision, Writing – review & editing. **Henri Spanjers:** Supervision, 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.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2024.126605.

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