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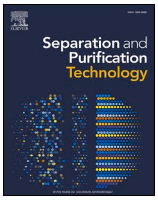

Effluent pH correlates with electrochemical nitrogen recovery efficiency at pilot scale operation

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ABSTRACT

A bipolar electrodialysis (BP-ED) pilot plant including 3.15 m^2 of cation exchange membrane and bipolar membrane each was operated for ammonia recovery. The pilot treated source-separated diluted urine (1 gNH_4^+/L). Previously found set operation parameters for lab-scale such as current density and nitrogen load did not directly influence the stack performance. However, the effluent pH was directly related to the removal efficiency of the system. 80% nitrogen removal was achieved at a set effluent pH of 4. Operating under an effluent pH control strategy was more effective to control NH_4^+ removal than controlling current density or nitrogen loading, as it accounts for fluctuation in wastewater availability and composition. The pilot plant removed up to 88% of the NH_4^+ from urine and recovered around 700 g/day (from 1 m^3 of urine). This was a significant improvement compared to the pilot plant previous performance on digestate. The energy consumption was around 13 Wh/g_N. The overall current efficiency was ~40% with most losses caused by parasitic ionic shortcut currents occurring at the hydraulic manifolds of the BP-ED stack. Therefore, the energy demand can be further decreased by preventing these ionic shortcuts in the new cell designs.

1. Introduction

Most of the nitrogen is produced in the Haber-Bosch (HB) process [1]. The HB process was first demonstrated in 1909, and by 1913, ammonia was already produced at an industrial scale [1–4]. As the natural nitrogen reserves (such as nitre deposits) were depleted there was an urgent need for the fast rollout of a process that could serve as a viable alternative for fertilizer production. The HB process is widely applied and remains almost unaltered after 100+ years. Nowadays, our attention has been slowly shifting from purely producing to also recovering nitrogen as the HB process is energy-intensive, and the natural gas required for the process is unevenly distributed worldwide [2,5,6]. Further, the intensive use of N fertilizers is disrupting ecosystems through eutrophication [7–9].

Ammonia recovery using electrochemical systems was previously demonstrated at lab-scale [10–13]. Yet, only a limited number of pilot studies were conducted. Ward et al used a 30 cell pair electrodialysis (ED) unit (total membrane area of 7.2 m^2) for nutrient recovery (i.e., concentrated nitrogen and potassium product) [14]. Ferrari et al combined an electrodialysis with bipolar membranes cell including 65 cell pairs (3.15 m^2 membrane area) with two liquid/liquid membrane contactors [15]. The pilot produced a concentrated ammonium sulphate product. Nevertheless, both pilot installations demonstrated relatively short operation and performance decrease throughout the experiment.

Implementing a new technology like electrochemical systems for nitrogen recovery needs continuous further development. Certain features need to be optimized, such as operational flexibility, sustainability, safety, and economic competitiveness [16,17]. So far, electrochemical systems in full-scale as treatment applications are rarely implemented successfully [18–20]. However, the success of electrochemical nitrogen recovery depends on the performance at larger scale (removal/recovery, rate, and energy).

Abbreviations: BP-ED, Bipolar electrodialysis pilot plant; BPM, Bipolar membranes; CEM, Cation exchange membranes; CIP, Cleaning in place; ED, Electrodialysis; HB, Haber-Bosch process; j, current density; LLMC, Liquid/Liquid membrane contactors; L_N, Load ratio; PID controller, proportional–integral–derivative controller; PLC, programmable logic controller.

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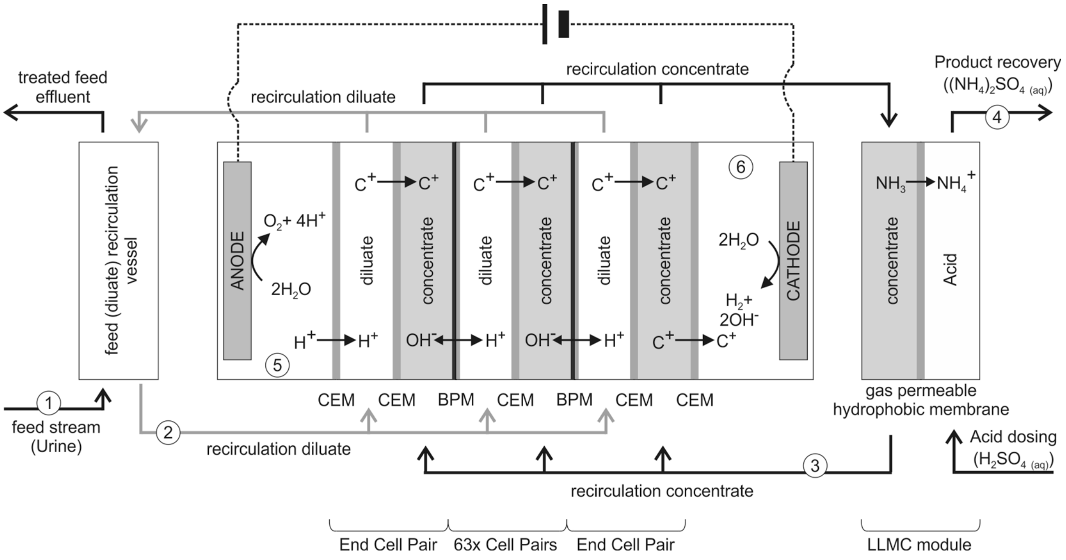

Fig. 1. Adapted from Ferrari et al., 2022 (CC-BY 4.0) [15]. The urine was supplied to the diluate compartments of the electrochemical cell. The current was applied to drive the ammonium in the urine through the cation exchange membranes into the concentrate solution. The concentrated solution is rich in ammonia gas due to the high pH. As a concentration gradient forms, the ammonia gas is extracted from the concentrate solution to concentrated sulphuric acid by using liquid/liquid membrane contactors [15,21].

Table 1
Average urine composition collected at Arneco.

Analyte	Average Concentration (mg/L)
Chloride	344.3 ± 60.0
Nitrate	10.5
Phosphate	74.0 ± 16.2
Sulphate	216.0 ± 62.4
Inorganic Carbon	471.2 ± 61.9
Total Carbon	750.7 ± 100.3
Sodium	241.4 ± 38.5
Ammonium	921.9 ± 155.7
Potassium	258.3 ± 42.5
Magnesium	often below 10 mg/L
Calcium	often below 10 mg/L *

* Rarely 30 mg/L of Calcium were measured on the influent stream.

Table 2
Summary of the operational conditions conducted at the NEWBIES pilot plant when supplied with urine. The performance was characterized regarding current density (j), Load Ratio (L_N), intermittent and continuous current mode (CC), pH control with fixed j and intermittent current mode.

Variable of interest	Studied Range	Fixed parameter
j (A/m^2)	50, 100, and 200	L_N
L_N (-)	0.5, 1, 1.5, and 2.5	j
Current mode	CC, 50% intermittent and 75% intermittent	j & L_N
pH Control	pH effluent adjusted to 4	50% intermittent & j = 100 A/m^2

This study used the same bipolar electrodialysis pilot plant (Pilot BP-ED) used by Ferrari et al for ammonia recovery from source-separated urine. In contrast to the previous study, we explored how a pH-controlled operation mode improves the ammonium recovery and energy demand. We characterized the pilot plant performance regarding current efficiency, energy consumption, and nitrogen removal and identified new challenges of up-scaling for the (BP-) ED technology.

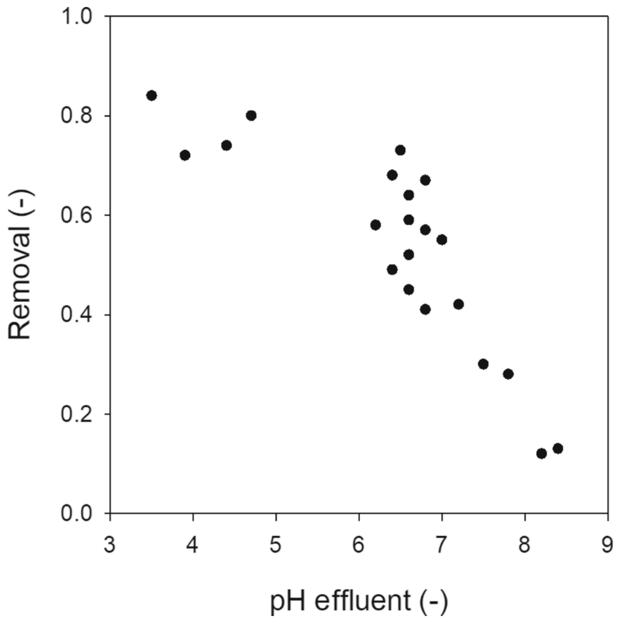

Fig. 2. Nitrogen removal efficiency in function of the effluent pH. Higher ammonium removal efficiency was measured at lower effluent pH of the effluent.

Table 3
Pilot performance under pH controlled operation in terms of Ammonia removal efficiency, energy demand, mass nitrogen recovered, and volume of urine treated.

Run	j (A/m^2)	Removal Efficiency (-)	Energy (Wh/g_N)	Mass recovered (g_N/d)	Volume treated (L/d)	Mass loaded (g_N/L)
1	100	0.80	13.6	348.8	630	434
2	100	0.88	13.4	269.6	423	307
3	100	0.83	12.7	702.5	1000	848

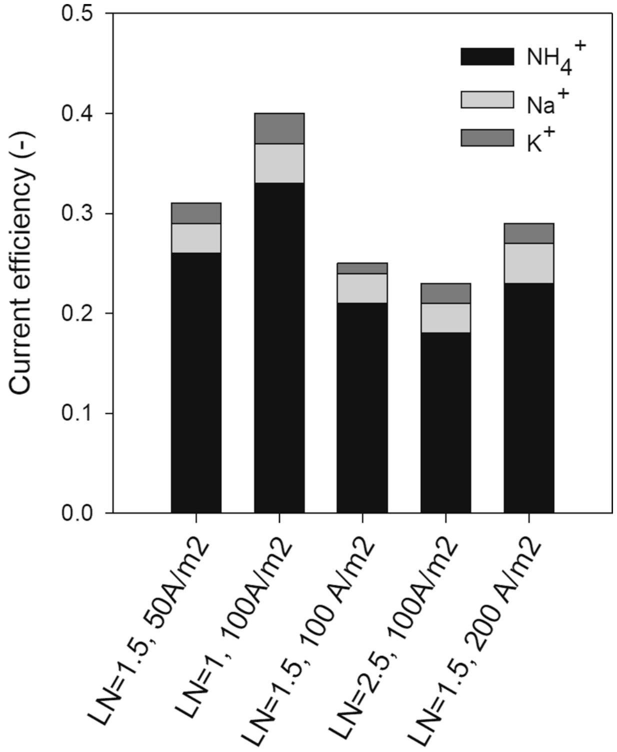

Fig. 3. Ion current efficiency for the ions transported over the CEM (NH_4^+, Na^+, and K^+), at different j (50, 100, and 200 A/m^2) and L_N (1, 1.5 and 2.5). Calcium and magnesium current efficiencies were not included as these ion concentration were below detection range. Overall, the total current efficiency were often below 0.4 (40%).

2. Materials and methods

2.1. Setup configuration

A pilot-scale BP-ED cell unit consisting of a cross-flow stack (22 cm × 22 cm) provided by REDstack BV (Sneek, The Netherlands) and two liquid/liquid membrane contactors (LLMC modules, 2.5 × 8 in., type EXF, 3 M Liqui- Cel™, NC, USA) were used in the pilot plant for ammonium recovery. The pilot installation is illustrated in Fig. 1.

The BP-ED unit included, an anode compartment, 65 cell pairs of diluate and concentrate compartments, and a cathode compartment. The cell pairs were separated on one side by bipolar membranes (BPM) (FBM-PK, Fumatech GmbH, Germany) and on the other side CEM (FKB-PK130, Fumatech GmbH, Germany). The BPMs generate protons and hydroxide to diluate and concentrate, respectively (Fig. 1). NH_4^+ is transported through the CEM from the diluate to the concentrate (towards the cathode). The diluate and concentrate compartments were created using polypropylene spacers (22 cm × 22 cm, thickness 0.05 cm, 53% open area) with a silicon gasket layer at two opposing sides for sealing (DEUKUM GmbH, Frickenhausen, Germany). The anode and cathode were two platinized titanium electrodes (22 cm × 22 cm MAGNETO Special Anodes B.V., Schiedam, The Netherlands). The anode and cathode compartments were shielded from the cell pairs to minimize the transfer of chloride ions by two Nafion N117 membranes (22 cm × 22 cm, Fuelcellsetc, TX, USA). The streams supply and recirculation and current supply are described in detail in Appendix A. After each run, a Clean In Place (CIP) strategy previously described by Federico et al was performed to guarantee the performance was not compromised [15].

2.2. Operational conditions

The pilot plant was supplied with urine collected in urine diverting toilets (Ecoflush, Wostman Ecology AB, Saltsjö-Boo, Sweden) installed in 15 households at Arneco (Arnhem, The Netherlands). The toilets have a separate collection for urine and apply a minimal flushing volume of 200 mL, therefore collecting diluted urine. The complex produces on average 100 L of diluted urine per day. To prevent filter clogging and increase the amount of NH_4^+ available, the urine was first collected in a 1 m^3 storage tank that allowed for urea hydrolysis and settling suspended solids (Fig. 1). The urine composition is provided in Table 1.

The performance of electrochemical systems is affected by the mode of operation (continuous or intermittent), current efficiency, and nitrogen loading (Load Ratio - L_N) [21–23]. Firstly, we characterized the influence of current density (j), loading, and mode of operation on the pilot BP-ED system (Table 2). After characterization the pilot was also operated under pH control, as we observed that the removal efficiency is related to the effluent pH. This was only possible after implementing a PID feedback loop in the pilot plant operation system. The PID controller regulated the influent feed rate to assure a pre-set pH value of the effluent at the end of an intermittent current cycle. The current was

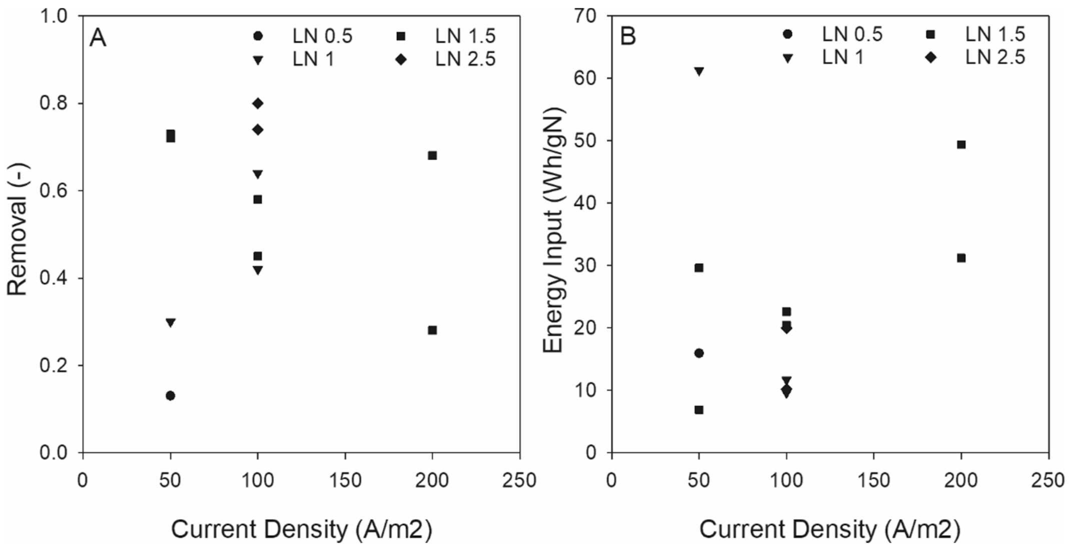

Fig. B1. Nitrogen removal efficiency (A) and energy input (B) at different current densities (50, 100, and 200 A/m^2). The current density effect was demonstrated at some different Load ratios (L_N – 0.5, 1, 1.5, and 2.5) and in duplicate.

Table C1

Summary of all experiments performed and the respective performance regarding ammonium removal, current efficiency (for ammonium and total), energy consumption, mass recovered and loaded per day, and volume treated per day. The values presented are the average over the period considered.

Mode	j A/m^2	L_N	pH effluent	Removal	t_{NH4+}	t_i total	Energy Wh/g_N	Total mass recovered g_N/day	Volume treated L/day	Mass loaded g_N/day
CC	50	1.5	6.5	0.73	0.26	0.31	29.6	678.0	730	935
CC	50	1.5	3.9	0.72	0.20	0.25	6.9	510.8	730	713
CC	100	1	6.6	0.64	0.33	0.40	9.6	1684.8	2193	2632
CC	100	1	7.2	0.42	0.19	0.20	11.7	991.7	2192	2345
CC	100	1.5	6.2	0.58	0.21	0.25	20.4	1082.0	1461	1870
CC	100	1.5	6.6	0.59	0.25	0.29	19	1322.1	1461	2250
CC	100	1.5	6.6	0.45	0.18	0.21	22.6	934.4	2023	2064
CC	100	2.5	4.7	0.80	0.18	0.22	20.0	938.2	877	1175
CC	100	2.5	4.4	0.74	0.13	0.16	10.2	686.7	877	929
CC	200	1.5	6.4	0.68	0.23	0.29	49.4	2321.3	2922	3419
Intermittent 50%	100	1.5	6.6	0.52	0.19	0.20	9.7	499.4	731	958
Intermittent 50%	100	1.5	6.4	0.49	0.17	0.15	9.5	480.2	726	987
Intermittent 50%	100	1.5	6.8	0.57	0.27	0.30	5.4	693.0	1027	1222
Intermittent 50%	100	2.5	3.5	0.84	0.20	0.25	6.1	500.4	579	596
Intermittent 75%	100	1.5	6.8	0.67	0.28	0.32	3.7	362.3	364	538
Intermittent 75%	100	1.5	6.8	0.41	0.16	0.18	2.1	216.9	358	529
Intermittent 75%	100	1.5	7.0	0.55	0.22	0.15	1.3	276.5	504	504
pH control	100	n/a	–	0.80	0.14	0.16	13.6	348.8	630	434
pH control	100	n/a	–	0.88	0.11	0.11	13.4	269.6	423	307
pH control	100	n/a	–	0.83	0.28	0.31	12.7	702.5	1000	848

applied in intermittent mode (50%, current on: 45 s and current off: 45 s) and at 100 A/m^2 during the pH-controlled runs. The length of the experiment was chosen as to allow uninterrupted operation given the available urine buffer at the site (~1 m^3).

2.3. Analysis and measurements

Samples from the influent, effluent, concentrate, anolyte/catholyte, and acid were taken and analysed. All samples were filtered through a 0.45 μm filter prior to analysis and analysed in duplicate. Cations (NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}) and anions (SO_4^{2-}, PO_4^{3-}, NO_2^-, NO_3^- and Cl^-) were analysed using a Metrohm Compact IC Flex 930 instrument with a cation column (Metrosep C 4-150/4.0) and a Metrohm Compact IC 761 instrument with an anion column (Metrosep A Supp 5-150/4.0), respectively. Total and Inorganic carbon were measured using TOC-L CPH, Shimadzu BENELUX, 's-Hertogenbosch (The Netherlands).

Conductivity and pH of all process streams were measured and recorded per second by the PLCs data acquisition software (Labview) using in-line sensors (Easysense pH 32 and Inpro7100i, Mettler-Toledo,).

2.4. Calculations

All performance indicators (current efficiency, energy input, and removal efficiency) were calculated as described in [21].

3. Results & discussion

3.1. Electrochemical systems performance can be improved by setting the effluent pH (diluate).

Unlike lab-scale studies, current and nitrogen loading (L_N) did not directly influence ammonia removal (Appendix B) [23]. Nevertheless, during the characterization, a relation between nitrogen removal efficiency and the effluent pH of the stack was observed.

Fig. 2 shows the nitrogen removal efficiency in function of the effluent pH. Overall, we observed higher removal at lower effluent pHs. Ammonium removals of up to 80% were obtained when the pH of the effluent was around 4. Decreasing the alkalinity of the solution improves first the conversion of NH_3 to NH_4^+. Second, it was previously demonstrated how in order to remove all ammonium ions from the diluate solution, all other cations needed to be depleted as well [24].

Unlike previously observed at lab-scale, the removal efficiency was not directly correlated with load ratio or current density. This shows that the simplistic load ratio model previously described by Rodriguez-Arredondo et al 2017 has a limitation for the application on this more complex and variable wastewater (source separated urine). Rodriguez-Arredondo et al model was developed/validated for a more simple and defined solution with little fluctuations, often obtained by pretreatments and or synthetic formulations [22,23]. Therefore, a pilot operation under less controlled conditions requires a different and more simplistic approach, such as the pH control strategy.

3.2. High removal was achieved using effluent pH for process control.

Considering optimization between nitrogen recovery and energy consumption (Appendix C), the pilot operation was set for a j = 100 A/m^2 and 50% intermittent mode. Additionally, the PLC was set to achieve an effluent pH of 4. The urine supply was controlled to guarantee the desired pH. Table 3 summarizes the pilot plant performance under these setting.

The pilot showed stable operation throughout these runs while removing up to 88% of the ammonium nitrogen from the influent and consuming on average 13 Wh/gN. The treated solution contained between 100 and 150 mg/L NH_4^+. This is a significant improvement compared to the 60% removal efficiency decreasing throughout the experiment to 30% achieved in the same pilot plant. According to the influent volume supplied and removal efficiency, the pilot was removing up to 700 g_N/day; a promising result compared with the operation using digestate (~560 g_N/day in continuous mode and ~130 g_N/day in intermittent mode) [15].

The energy consumption was comparable to Anammox combined with the Haber-Bosch process [25,26]. In direct comparison with lab-scale electrochemical systems, the energy consumption was higher (~2x) [12,27,28].

During operation, an ammonium sulphate solution was produced (~145 g/L, pH = 3.5). This means the ammonium in urine was concentrated from around 1 g/L up to 40.6 g/L. The concentrated stream recirculating over the BP-ED cell had a residual ammonium concentration, around ~1.2 g NH_4^+/L. Previous work by Rodrigues et al demonstrated that although acidic, the fertilizers produced by such BP-ED can be used for crop growth [29]. This combined electrochemical cell with LLMC can generate a product is free of unwanted sodium, as previously reported by [14].

3.3. Upscaling electrochemical systems for ammonia recovery leads to lower current efficiency due to ionic shortcut currents.

Fig. 3 shows the current efficiency for ammonium, sodium, and potassium at different j (50, 100 and 200 A/m^2) and L_N (1, 1.5 and 2.5).

The ion transport was determined by measuring the change of ionic composition between influent and effluent. The sum of the current efficiency of all ions (ratio between charged removed over charged supplied) was often below 0.4 (40%) (Fig. 3). Even considering the effect of L_N and j on the charge transported over the CEMs, this current efficiency is significantly lower than reported in previous studies [21,28]. Around 0.6 (60%) of the total charge transport could not be quantified based on the composition difference between influent and effluent and the corresponding applied current. Ammonium was the main ion responsible for the charge transport in the BP-ED stack. Calcium and magnesium were often below the detection range, and the other cations (sodium and potassium) accounted for less than 0.1 (10%) of the charge transport. The transport of anions was not detected. Previous studies reported up to 0.3 (30%) charge loss due to proton transport, ammonia diffusion, and/or anions leakage at similar operation conditions [21,30,31]. As the pH of the concentrated stream was alkaline (pH ~10), a similar undesired transport of protons or ammonia diffusion could be considered. Nevertheless, the current efficiency is much lower than expected.

In this study, parasitic ionic shortcut currents through manifolds were the main phenomena causing the charge losses as proton transport, ammonia diffusion and anion leakage influences were not dominant. First, the pH of the diluate solution is not low enough for protons to play a substantial role in charge transfer (Appendix C). Secondly, ammonia diffusion was low as most nitrogen removed was measured in the acidic recovered solution. Finally, a low and constant amount of anions was detected in the concentrate solution. A small anion leakage is expected as the CEM and BPM are known to have high permselectivity, but they cannot explain the low current efficiency [32].

The overall membrane/compartment resistance was high (around 41 Ω), as 65 cell pairs are stacked. Additionally, the use of CEM/BPMs cell pairs have large resistance compared to normal ED (AEM/CEM) scenarios [33]. As, the diluate solution has a low conductivity (between 2 and 6 mS/cm) and the concentrate liquid has a high conductivity (higher than 20 mS/cm) salt bridges can form across the inlet manifolds or across the outlet manifolds. Instead of crossing the cation exchange membranes, the ions moved through the liquid from one compartment to another. This was not observed in earlier test with a similar stack design and only 6 cell pairs at the lab-scale [21]. This illustrates, it is essential to test technologies at larger pilot scale. Until further improvements are made in the cell design, cells with larger dimensions and less stacked cell pairs should be considered as a mitigation strategy. Although the current efficiency aforementioned was particularly low for an BP-ED, we achieved up to 88% removal and energy below 13.4 Wh/g_N comparable with previous studies [10–12,27].

Nevertheless, the simplicity of having an on/off system (no biology involved) that reaches equilibrium after a short period of time and can be controlled by an in-situ variable (effluent pH), makes BP-ED an attractive option for ammonia recovery of concentrated wastewater streams.

4. Conclusion

Nitrogen removal from buffered organic waste streams using bipolar electrodialysis systems has a high correlation with the effluent pH. Therefore, pilot-plants can be operated under pH control at a set current density. At pH 4, more than 80% of the nitrogen was removed and recovered. The energy consumption of electrochemical systems can be further improved by reducing ion shortcut currents through the manifolds and thereby improving current efficiencies.

CRediT authorship contribution statement

Mariana Rodrigues: Methodology, Investigation, Writing – original draft, Visualization, Conceptualization. **Sam Molenaar:** Methodology, Investigation, Conceptualization. **Joana Barbosa:** Investigation. **Tom Sleutels:** Writing – review & editing, Supervision. **Hubertus V.M. Hamelers:** Writing – review & editing, Resources, Supervision, Project administration, Funding acquisition. **Cees J.N. Buisman:** Writing – review & editing, Supervision. **Philipp Kuntke:** Writing – review & editing, Resources, Supervision, Funding acquisition, Conceptualization.

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

The research data underlying this work is available at https://doi.org/10.4121/20310099

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Appendixes

Appendix A

The urine was supplied to the diluate compartment using a membrane pump (DDA 200–4, Grundfos Nederland B.V., Almere, The Netherlands). The 0.1 M Na_2SO_4 electrolyte solution (used as an electrolyte for both anode and cathode) was recirculated using a membrane pump (DDA 200–4, Grundfos). Membrane pumps (DDA 200–4) were also used to recirculate the diluate solution the concentrate solution and supply two LLMCs. The LLMCs were connected in parallel. Here, ammonia diffused through the LLMCs and reacted with sulphuric acid forming ammonium sulphate (Fig. 1). Concentrated sulphuric acid (37%, v/v) was continuously added by a membrane pump (DDA7.5–16, Grundfos) to form a concentrated ammonium sulphate solution and maintain the product pH at 2.5. The ammonium and other cations are transported through the CEM due to the current supplied to the ED module using a current supply (SM15K Delta Elektronika, Zierikzee, The Netherlands), with an upper limit of 330 V. A custom made PLC (Pro Control BV, De Rijp, the Netherlands) controlled all pilot functions (pumps, power supply, cleaning) and recorded operational data (volume, conductivity, pH, applied current and voltage). After each run, a cleaning was applied in situ by flushing the diluate compartments with 1 M NaOH to remove organic fouling and flushing the concentrate compartments and TMCS units and lines with 1 M HCl to remove inorganic scaling deposits. The CIP was previously described [15]. For example, a pressure increase in the concentrate compartment indicated the formation of inorganic scaling, which was a previously observed phenomena obstructing the membranes [15]. The membranes were restored with the acid rinse solution during CIP.

Appendix B

Fig. B1 shows the energy consumption and nitrogen removal efficiency when the ED stack is operated continuously at different current.

Appendix C

(See Table C1)

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