Nitrogen Extraction from Water By an Innovative Electrochemical System

Deliverable for action B2

Report on operational experience and performance of NEWBIES on urine

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Introduction

This report covers the progress made and scientific results obtained in the second operational phase of the N.E.W.B.I.E.S. pilot: treatment of source-separated urine at Ecological Housing Community Arneco in Arnhem, the Netherlands.

The primary aim of this second pilot phase was to optimize the operation of the plant, treating source-separated urine, with respect to the project proposal defined key performance indicators. There were most notably (1) load rate (kg N/day), (2) removal/recovery efficiency (percentage of nitrogen removed from the urine and recovered in the product), and (3) energy efficiency (kWh spent per kg N removed/recovered).

In addition, the prior testing period on digestate identified some crucial causes for performance loss in the system, and in this second phase, the system has been adjusted in an attempt to lower these losses. The most notable to this aspect is the development of an adjusted side-plate for the ED stack which aimed for reducing energy efficiency losses due to a phenomenon called "ionic shortcut". This adjusted stack design, from here on referred to as "spider stack" due to its esthetics, has been commissioned during this second phase of the pilot (see also Appendix I). In this report, the performance of the adjusted system is compared to the original design.

To allow for a complete and structured analysis and exploration of the abovementioned issues, the research goals in this second pilot phase were as follows:

1. Wastewater characterization over time
2. Short-term process optimizations (within a CIP cycle)
3. Long-term process characterization and analysis (effectiveness/economics of the used CIP method)
4. Post-mortem analysis of the ED stack to identify "aging" mechanisms

A short explanation as to why the abovementioned four sub-goals were defined as follows:

Wastewater characterization over time

To understand the output dynamics of the system, it is of absolute necessity to know what has been put in. With the site being smaller than anticipated - due to Covid, the pilot was forced to move towards a substantially smaller source of urine than previously set out for - temporal fluctuations in urine composition may be more pronounced.

Short-term process optimizations

An experimental design, adopted from the first operational phase in Girona, but adjusted for the new wastewater characteristics, investigated the within 1 CIP-cycle effects of load rate/load ratio, current density, and donnan/continuous operation on the systems KPIs.

Long-term process characterization and analysis

Although the short-term effect might be positive in terms of instantaneous KPI improvement, it may result in higher CIP demands which overall lead to less beneficial economics and may affect the lifetime of used components (e.g. membranes). After selection of optimal short-term conditions, and achieving reproducible within-CIP cycle results, the impact of CIP was assessed on process economics and long-term system stability was assessed.

Post-mortem analysis of the ED stack

In order to assess with more preciseness the (long-term) effect of the used wastewater on the membrane performance and structure, a similar test was done as performed at the end of the first phase. This cannot be done easily as it requires a lot of work to disassemble the stack and therefore these tests were only performed after the second pilot phase had ended. Results can be compared.

Materials and Methods

ED-stack design: Spider stack versus Original/Old stack

After post-mortem analysis on the stack filled with glass beads showed that the beads blocked off substantial parts of the membrane stack, this stack was returned to the manufacturer for reassembly with adjusted side plates during the first weeks of the pilot testing on urine. Meanwhile, the second stack, which had originally been used before on digestate in the first phase, but which was not equipped with glass beads, was commissioned to start the first tests on urine. After the series of tests used for short-term process optimization had been finished with this original stack, it was replaced by the then-finished “spider stack”, and an identical series of tests was performed on this new stack as well as to compare the performance.

Short-term process optimizations (within-CIP-cycle)

Starting directly after commissioning the pilot plant using the original stack, the effects of current density, load ratio and Donnan/intermittent mode were studied. For these within-CIP-cycle tests, the system was cleaned each time before a run was started. This was done by removing all liquids from the feed and concentrate/TMCS sections, followed by a 15-30mins base wash of the feed section, and a 15-30min acid wash of the concentrate section. After the acid/base wash, the compartments/piping were thoroughly emptied by air sparging and fresh concentrate consisting of demineralized water was used to refill the concentrate/tmcs section. The system was then started with the operational parameters set as per table 1. Any parameters not mentioned were kept unchanged as compared to the operation on digestate (see previous report). Between the experiments, recirculated liquids for the acid stripper (stripper from here on) and electrode rinse solutions (anocatholyte from here on) were kept. The reason for not replacing these two process flows was that (1) for the anocatholyte, the impact of its composition on the system performance is deemed negligible, while (2) for the stripper liquid, its concentration builds up slowly over multiple CIP liquids (as it becomes a very concentrated stream, eventually limited by osmotic water transport) and replacing it each time would result in unrealistically low water fluxes directed towards the product.

The experimental design as adopted and adjusted can be found in table 1 below.

Table 1. Pilot plant operational parameters during the second pilot phase – urine treatment

run#	Variable of interest	Operational Current density (A/m^2)	Load ratio	Power Supply duty cycle (%)
1	Current density	50	1.5	1
2		100	1.5	1
3		200	1.5	1
4	Load ratio	100	1	1
5		100	1.5	1
6		100	2.5	1
7	Donnan mode	100	1.5	0.25
8		100	1.5	0.5
9	Validation	100	1.5	0.25
*****	**Extra (DD)**	**100**	**2.5**	**0.5**

During each of the runs as indicated in table 1, liquid samples were taken from all process flows as soon as in-line measured variables (ECs, pHs and most notably, sulfuric acid pumping rate) had stabilized/flattened out. Depending a bit on the condition tested this took place between 2-6 hours after the system was started. These samples were filtered (0.22um) and stored in refrigerator for later compositional analysis. These samples were then analysed for:

- Total Inorganic / Organic Carbon (TIC/TOC)
- Ion Chromatography for cations: Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_3^+
- Ion Chromatography for anions: Cl^-, NO_2^-, NO_3^-, PO_4^{2-}, SO_4^{2-}
- Ion Chromatography for VFAs: Acetic acid, Propionic acid, Butyric acid
- ICP-MS for elemental analysis of: Ca, Fe, K, Mg, Na, P, S, Si

The in-line process data, consisting of real-time measurements for all process flows of (a) pH, (b) electrical conductivity, (c) net resulting water flux (using recirculated volume level control), (d) measured voltage and current as applied by the power supply, and (e) – specifically for the stripper section – acid dosing was monitored using the Labview-based integrated software package from Pro Control, The Netherlands. The measurement interval for data logging was set to 1 second. In addition to these key variables, other relevant operational data like recirculation water fluxes (L/h) was monitored to check for mechanical blocking or pump malfunctioning (which didn't occur during the tests performed).

The inline measured data was – partially due to its high temporal resolution – processed with open-source mathematical software package R (www.r-project.org). The script used for the calculation/determination of the relevant fluxes and KPIs can be found in Appendix II. In short, the script plotted all in-line measured data for the operational period, and asks the user to select a time window within which averages are obtained for all recorded process variables, plus calculated averages for (a) effective feed pump rate, (b) applied voltage, (c) applied current, (d) **apparent** recovery efficiency by means of acid dosing, (e) **apparent** product concentration, (f) **apparent** recovery energy efficiency, (g) water fluxes for cation concentrate, catholyte, stripper and acid sections.

The averages obtained using the R-script for the different water fluxes as they occurred, were used in conjunction with the chemical composition data to calculate the **direct** removal/recovery/energy efficiencies. The direct product concentration was directly obtained from the IC analysis of the product. These “direct” measures ideally should correspond well to the “apparent” calculated values, provided the assumption of the sampled liquid composition being in a more or less steady-state at the time of sampling, was correct.

Long-term process characterizations (between CIP cycle analysis)

After the short-term experiments had been finished and results analysed, the operational conditions were determined for during the long-term process characterization. Although initially it was foreseen for these experiments the system would be operated with a constant load rate, the short-term optimizations in combination with the wastewater compositional analysis as it was performed over time, showed that for more consistent removal efficiency / effluent quality, the pH of the effluent could be used as an adequate feedback variable. For this reason, before the long-term process characterizations, a PLC-software modification was made to make use of this. As operation by Donnan exchange (intermittent mode) turned out to result overall in longer duty cycles, with higher energy efficiency and potentially high removal efficiency, it was made in a way that adequate pH control could be obtained with the system operating in Donnan mode. To this means, an automated cycle was developed in which feed pump, power supply and effluent valve operated as per figure 1 below.

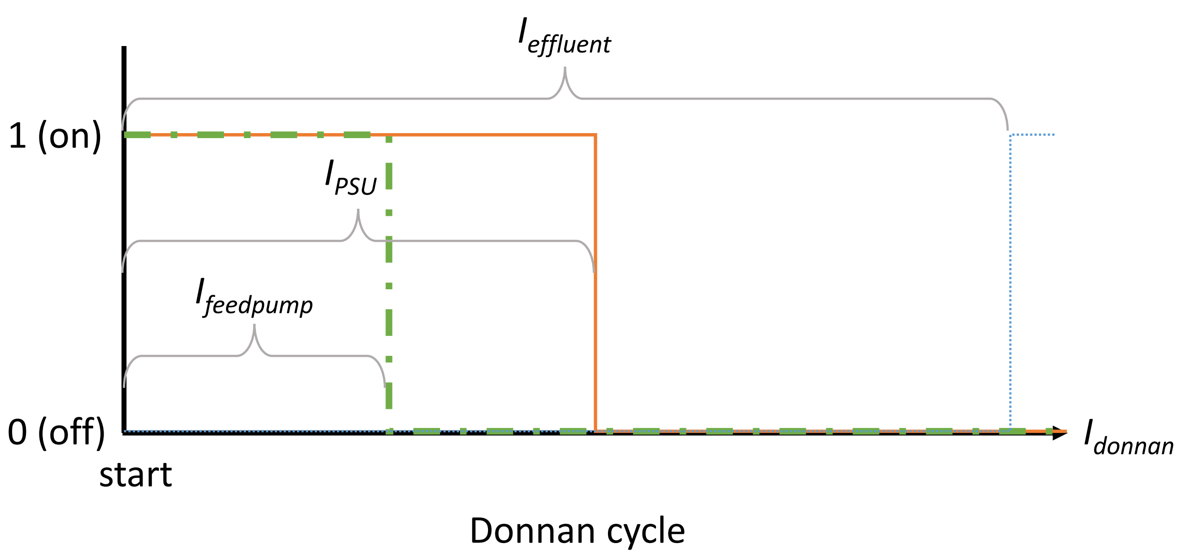


Figure 1 *Starting a Donnan cycle, the feed pump (green, dashed) and PSU (orange) were active (on, 1), with the feed effluent valve (blue, dashed) closed (off, 0). After the interval Ifeedpump, the feed pump was deactivated while the power supply continued until interval IPSU had expired. Just before the end of the cycle (I_{donnan}) the effluent valve would open after Ieffluent had expired and drained the recirculated feel volume back to its lower point before a new Donnan cycle would commence. For the PID feedback loop, the pH as measured at the end of the Donnan cycle was used as input for the PID control, and the resulting output was translated into an adusted $I_{feedpump}$. This made sure effluent as it was drained at the end of a Donnan cycle always had the desired pH value.*

With the pH control added as a new feature, the prolonged runs were conducted at an operational current density of 100A/m2, a Donnan PSU duty cycle of 50% (I_{donnan}=90s, I_{psu}=45s), pH effluent regulated by the control loop at pH=4, feed pump operational flowrate fixed at 150L/h (when ON) and all other operational parameters (recirculation flow rates, pH of stripping liquid etc.) were left unchanged. However, in addition to the conditions set for the within-CIP experiments, the automated CIP handler was now activated. The relevant parameters were set to perform the CIP routine as soon as the applied voltage would exceed 150V. During CIP, the concentrate sides of both the stack and TMCS were cleaned with an HCl rinsing solution, which was recovered for later reuse after each CIP-cycle. During one out of four CIP cycles, the Feed side of the ED stack was rinsed with a 0.5M NaOH solution and also this liquid was recovered at the end of the CIP cycle for reuse later. In contrast to the short-term experiments, the automated procedure reused the cation concentrate liquid after CIP had been finished. This led to the gradual conductivity increase of the cation concentrate. As the automated CIP cycle hadn't foreseen in the cleaning of all tubing and pumps, these were exposed to progressive scaling throughout the operation of the pilot and eventually – after several automated CIPs – the cation concentrate had to be drained and the whole section rinsed with the acidic CIP solution to clean it. After this manual procedure, the cation concentrate sections were refilled using demi-water. Throughout the long-term characterization, liquid samples were taken after (SR1) two and (SR2) three automated CIP cycles, and just before a new automated CIP cycle after the system had been cleaned manually (SR3). By sampling the system during different "states of dirtiness" it is hoped a good insight is obtained into the impact scaling and higher conductivity of the cation concentrate has on overall system performance.

Post mortem analysis of membranes/membrane characterization

After finishing a series of short-term optimization runs using the original (old) stack, this stack came free as the spider stack was commissioned. The original stack was then brought back to the manufacturer for disassembly and a visual inspection of the present scaling/fouling was performed first. Based on this, some CEM and BPM membranes were taken out and cleaned by extensive acid/base washing (in 0.5M solutions of HCl and NaOH respectively), each wash consisting of a 2-day soak in plenty of solution. After this, these selected membranes were stored in 10g/L Na_2SO_4 solution until characterization tests were done.

For characterization, a 15x15cm piece was cut out from the membrane under investigation and it was mounted in a conventional ED(BM) plate and frame stack, as per diagram below:

Results

NEWBIES Pilot – urine stage: main results

he results obtained during the pilot operation while supplied with urine were the combination of two data sources. The pilot system recorded every second different variables, including current, voltage, inflow, pH of all streams, etc. From here it was possible to extract performance parameters such as Coulombic efficiency, Product concentration and Energy consumption (Figure 2a, b and c).

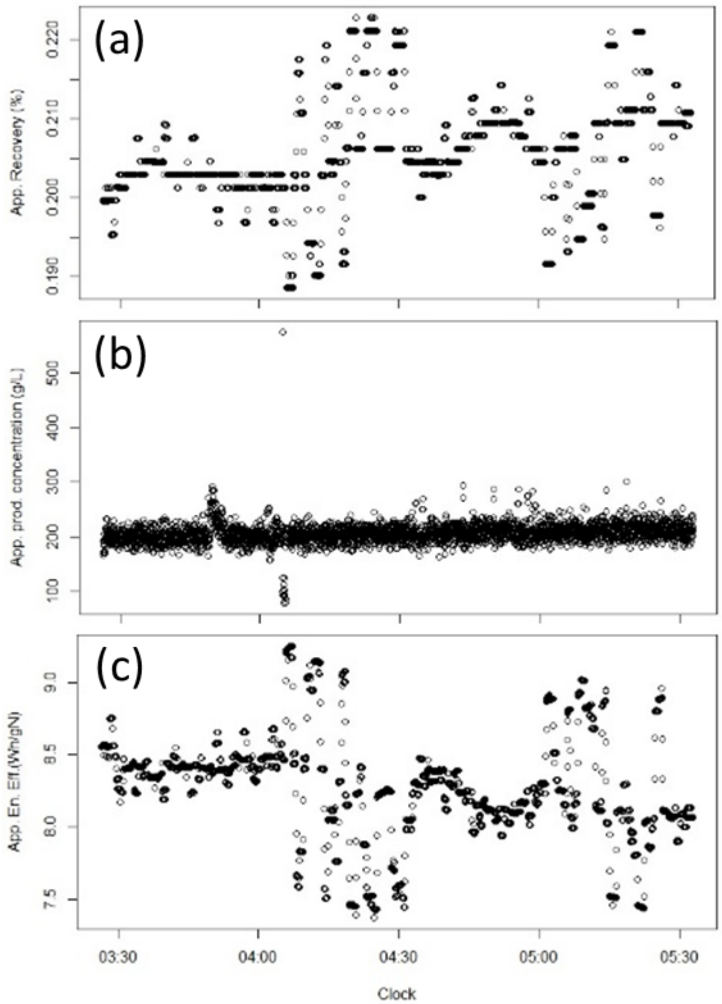


Figure 2 Performance parameters such as recovery , product concentration, and energy consumption (Figure 2a, b and c).

As these values are extrapolated, we verified the results by analyzing samples extracted at different operation conditions for different analytes (cations, anions, elements, carbon, COD, etc.). From the analyzed samples we also calculated Coulombic efficiency, Product concentration and Energy consumption as well as, Removal efficiency. The main results and conclusions are presented below.

Several conditions were tested regarding current and nitrogen load to assess the cell performance.

Table 1 shows the runs performed for both cell designs used. Some extra runs were tested for insight into the new design (lower load ratio, continuous operation, etc.). It was previously described the current applied to an electrochemical cell or the loaded amount of nitrogen (Load Ratio) influences performance parameters such as removal/recovery efficiency, the Coulombic efficiency, the product concentration, and the energy input. Moreover, operating at different conditions implies a different treatment capacity (L/day) and consequently product formed (gN/day).

The S Runs also described in this report are not included in the table as they were uniquely performed with the new cell design.

1. The current density affects the removal efficiency and increases energy consumption.

j (A/m^2)		Actual Load Ratio	Removal (-)	Coulombic efficiency (-)	[(NH4)2SO4] (g/L)	Energy (Wh/gN)	Total mass recovered (g/day)
50	**Old**	2.7	0.71	0.16	69.5	10.0	665.4
	SS	3.6	0.71	0.23	205.5	8.0	508.4
100#	**Old**	2.7	0.56	0.22	182.2	13.4	1053.3
	SS	2.5	0.44	0.22	188.6	13.1	917.5
200	**Old**	3.0	0.67	0.27	140.2	19.5	2302.8
	SS	2.2	0.27	0.22	246.2	21.8	1241.2

Note: The runs marked with # are the same one and they are repeated for comparison.

From the table, we can see a summary of several stable runs performed at the intended constant Load Ratio of 1.5 at different current densities for the stack design used in Girona (Old) and the new stack design (SS). These runs were performed without interruption for cleaning for a variable amount of hours while there was urine available. The actual Load Ratio was calculated as the urine composition suffered fluctuations during the time the pilot was in Arnhem. In this case, the intended Load Ratio was 1.5, but the pilot was mostly operated at 2.5-3 as the urine was a bit more diluted than expected. Nevertheless, the effect of current density was possible to observe. From the table, we can observe that the removal efficiency seems to decrease with current density, while the energy consumption increases. A phenomenon somehow expected from the literature. The Coulombic efficiency was often similar and between 0.2-0.3. This means that 30% of the total charge applied is used to transport ammonium. Finally, the product concentration increased with current density. Although not necessarily expected but beneficial, this can happen as the cation exchange membranes have a different transport rate than the TMCS one (gas permeable membrane). Additionally, as the pilot capacity increases with current density, more mass was recovered per day even though the removals might be lower.

Hence, it was concluded that the pilot should not be operated at very extreme current densities.

2. A higher nitrogen load (Load Ratio) increased the removal and decreased the Coulombic efficiency, at the same current density.

LN		**Actual Load Ratio**	**Removal (-)**	**Coulombic efficiency (-)**	**[(NH4)2SO4] (g/L)**	**Energy (Wh/gN)**	**Total mass recovered (g/day)**
0.5		0.7	0.13	0.18	117.2	15.9	437.8
1	**Old**	1.9	0.63	0.33	309.0	9.1	1655.7
	SS	2.2	0.42	0.19	269.7	10.3	999.1
1.5 #	**Old**	2.7	0.56	0.21	182.2	13.4	1053.3
	SS	2.5	0.44	0.18	188.6	13.1	917.5
2.5	**Old**	4.3	0.79	0.18	109.3	11.4	924.8
	SS	5.5	0.73	0.13	265.3	10.5	686.1

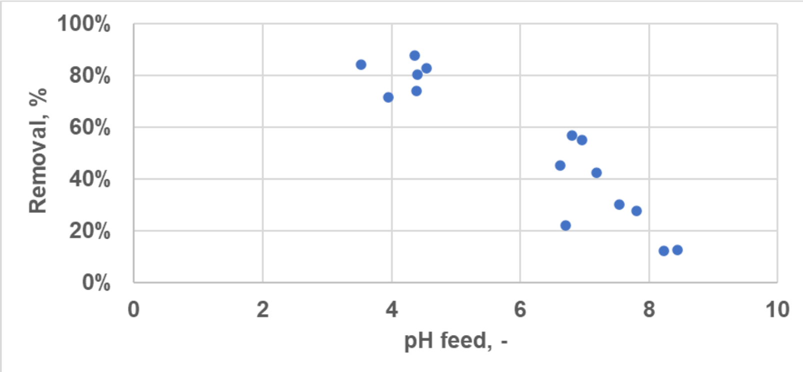
In the same way, constant current density was tested. From the previous runs, it was established the pilot should be operated not higher than 100 A/m2 and therefore the effect of Load Ratio was tested at this current density. Here, the intended Load Ratio was again not the actual one, but it is possible to see that increasing from 0.7 to Load Ratio 5.5, the cell performance changed. The removal efficiency increased with a Load Ratio up to 79%, while the energy consumption was rather stable. The Coulombic efficiency decreases as expected since with a high Load Ratio less nitrogen is loaded into the system. The influence on the product concentration was not so clear but again, most products had more than 200 g of ammonium sulphate per liter. The mass recovered per day was low at a low Load Ratio, since the removal is very low and also decreased for a higher load ratio since not so much nitrogen is supplied to the system.

3. Donnan decreased the energy consumption of the system.

Mode		**Actual Load Ratio**	**Removal (-)**	**Coulombic efficiency (-)**	**[(NH4)2SO4] (g/L)**	**Energy (Wh/gN)**	**Total mass recovered (g/day)**
50% DD – LN=2.5	**SS**	4.2	0.84	0.20	213.2	6.1	498.7
25% DD	**Old**	1.9	0.66	0.28	147.9	2.6	355.7
	SS	2.2	0.54	0.22	281.4	3.0	273.9
50% DD	**Old**	2.7	0.50	0.19	133.6	6.8	478.3
	SS	2.5	0.56	0.27	214.3	5.7	684.9
Continuous #	**Old**	4.3	0.56	0.21	182.2	13.4	1053.3
	SS	5.5	0.44	0.18	188.6	13.1	917.5

Apart from the effect of current and loading, it was also tested the effect of operating continuously or in Donnan dialysis. Donnan dialysis is when no current is applied to the system, but due to a concentration gradient previously formed between a concentrated and a diluted compartment, ions can be exchanged between the two compartments. Again at 100 A/m2 and constant Load Ratio around 2 it was possible to observe that the parameter Donnan Dialysis affects the most is energy consumption. By operating in Donnan, we benefit from this gradient and consume less energy while removing the same amount of nitrogen. Additionally, as no new feed is supplied while the power is off, the mass recovered during operation with Donnan dialysis was lower.

4. We established a relation between pH of the effluent (feed) and removal.



While analyzing other variables the pilot recorded (such as pH), it was possible to observe that only when the pH of the effluent (feed) is equal or lower than 4, higher removals were obtained. This allows us to also conclude that our pilot is being efficient if we control this parameter.

5. While selecting the best operation conditions, the pilot was operated continuously for 3 different runs (Run S) and treated a high volume of urine.

			%	g/L	Wh/g_N	g/day
	Intended LN	**Actual Load Ratio**	**Removal**	**[(NH4)2SO4]**	**Energy input**	**mass recovered NH_4^+**
Run 2 #	1.5	2.5	45	188.61	13.1	936.4
Run 9	2.5	4.2	84	213.19	8.3	501.5
Run S1	2.5	5.8	80	146.78	10.2	399.2
Run S2	2.5	0.9	88	149.71	12.9	325.2
Run S3	2.5	0.8	83	134.85	8.8	703.5

From the previous data, we conclude the best would be to combine 100A/m2, Load Ratio 2.5 and pH feed=4 by controlling the supply and power of the electrochemical cell (to a certain extent use Donnan while operating continuously). The result was 3 continuous runs where up to 88% of the nitrogen was removed from the influent while consuming 12.9 Wh/gN. A significant improvement when compared with the runs previously described. Here, the product concentration was relatively lower as well as the mass recovered per day. Nevertheless, in Run S3 83% of nitrogen was removed at 8.8 Wh/gN while recovering 703.5 gN per day. A very close result to what the project's KPI proposed.

Conclusions

For the tested conditions, the pilot system removed up to 88% of the ammonium in the influent while consuming on average 9 kWh/gN, within the expected proposed KPIs. The system performed best at higher load ratio (2.5), low current densities and in Donnan mode. The product concentration is around 200g/L of ammonium sulphate (aq.). The Coulombic efficiency of both stacks was not higher than 30%. It was independent of load ratio and current density. The design changes on the redesigned stack (spider) did not significantly change the system performance. Ionic short circuit might not be the only phenomena influencing the low Coulombic efficiency or the changes implemented in the new design were not sufficient to address this issue.

The tested parameters give useful insight about electrochemical systems as well as the challenges of a pilot scale for this technology. On one hand, an operation at high current density and low Load Ratio is desired as the pilot treated more volume of urine per day and consequently more nitrogen was recovered. On the other hand, at the same high current density and low Load Ratio, the removal efficiency is not so high. If this is not the last treatment urine will go through, a 50% removal will not be an issue. Using Donnan 50% of the time might be a bit extreme, but to have the system working in “pulse” for current can help lowering the energy consumption of the high current densities and improving the removal.