Nitrogen Extraction from Water By an Innovative Electrochemical System

Deliverable for action B1

Report on operational experience and performance of NEWBIES on liquid digestate

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The LIFE-NEWBIES project has received funding from the LIFE programme of the European Union

Newbies technology

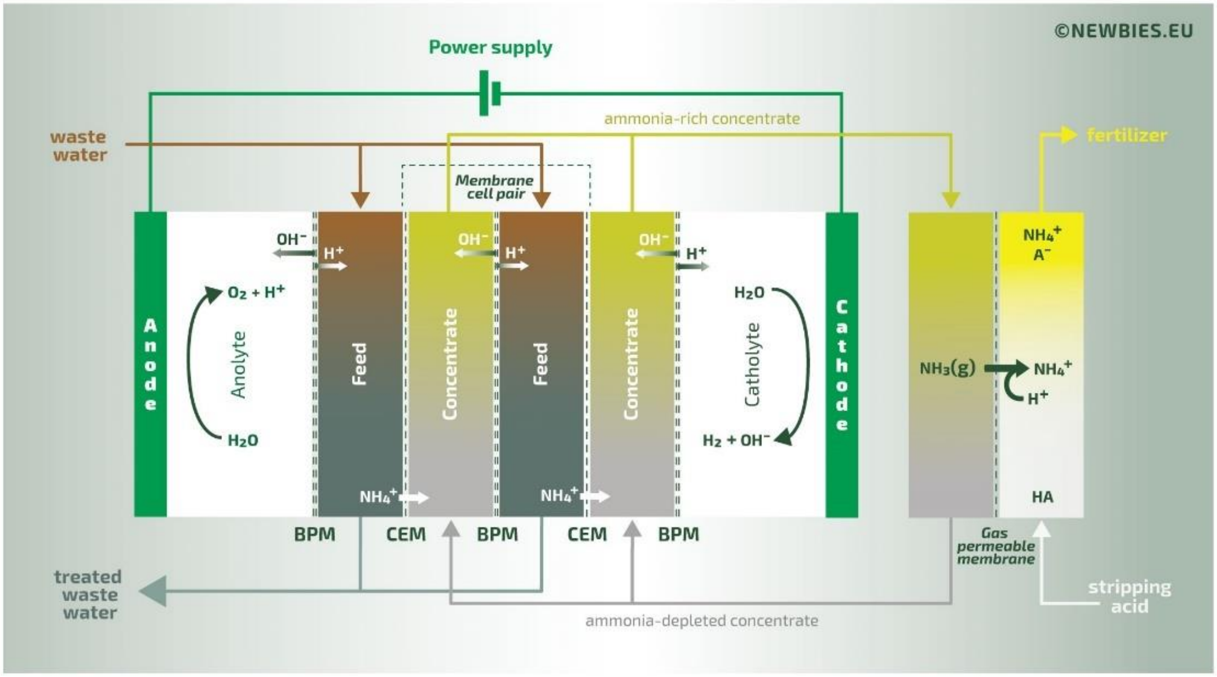

Figure 1. Concept flow diagram of the technology.

Figure 1 provides an overview of the N.E.W.B.I.E.S. process. This process treats digestate from a municipal wastewater treatment plant (WWTP) in Girona, Spain, containing relatively high concentrations of organic nitrogen in the form of ammonia. The digestate initially has a neutral or slightly acidic pH, with the nitrogen present as non-volatile ammonium. The digestate is introduced into an ElectroDialysis (ED) stack in which the ammonium is transported through ion-exchange membranes to a concentrate stream. The concentrate is then introduced into a gas membrane stripper (a process formally known as Trans Membrane ChemiSorption, TMCS), where the gaseous ammonia diffuses across the membrane. Thus, by TMCS, the ammonia is transferred to a product liquid. The driving force of this last extraction is the addition of an external acid, in this example sulfuric acid, yielding a concentrated ammonium sulfate solution as the final product. Clearly visible is the use of bipolar membranes as part of the ED-process. By using bipolar membranes the pH in this concentrate stream is very high. As a result of this high pH, the ammonium is converted into volatile ammonia. This volatilization of organic nitrogen is required for the subsequent TMCS to function properly.

Figure 2. Pilot plant.

Firsts 2 months of operations.

During the first 2 months of operation of the pilot plant, a combination of hardware and software issues had arisen and had to be solved before starting the first experiment. The resulting data of the first characterization experiments showed issues related to an unstable coulombic efficiency and decreasing over time leading to maximum test duration of 6 hours. Also, another issue that prevented the normal functioning of the pilot plant was the deposits of calcareous materials that formed on concentrate pumps and flow meters, eventually leading to pump failure. Since the cleaning procedure was not programmed to clean the cation concentrate recirculation pumps and to get to a first robust system performance characterization, all pre-programmed cleaning procedures were disabled and the system was operated at maximum recirculation flow rates under the continuous supervision of the operator.

Outcomes after the addition of glass beads on the cation concentrate side.

To tackle the issue related to the low and unstable coulombic efficiencies, glass beads were added on the cation concentrate side. This was done to lower the effect of the ion shortcut that the membrane stack was facing. Ion shortcut was due to the fast increase of the cation concentrate conductivity and was the main cause of a fast decrease of the coulombic efficiency (CE) during every test we conducted and of maximum test operation of about 6 hours after which no further ammonia was recovered. The glass beads made it possible to operate the system for a whole day with a more stable CE.

To futher increase the CE and lower the energy consumption, another operational strategy was investigated. When a current is applied, a concentration gradient of cations builds up between catholyte and feed solution. When no current is applied, cations diffuse back to the feed solution from the catholyte as a result of the concentration difference. These cations will be exchanged for other cations (including NH_4^+) to maintain the electroneutrality: a phenomenon known as Donnan Dialysis. For this reason Donnan Dialysis was explored as a strategy to enhance the NH_4^+ removal efficiency.

The optimum operating parameters we found are shown in Table 1.

Table 1. Optimum operating parameters for the NEWBIEs pilot-plant treating digestate at WWTP Girona

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Name	PSU	Feed pump	Load ratio
Donnan 75A/m2	75A/m2 (20 sec ON, 60 sec OFF)	50 L/h	1.37

With these parameters, it was possible to reach 40% CE, which slowly decreased to 30% in 24 hours. When the system was operated without the glass beads, the maximum CE was 20%, suggesting that there was a significant ion short circuit in the initial design of the pilot plant.

After adding the glass beads, the main issue was caused by the scaling in the cation concentrate membranes and recirculation pumps which prevented the operation of the system after 24 hours due to the steep increase in cell voltage and the blockage of the TMCS and cation concentrate recirculation pumps. The scaling was caused by the high concentration of calcium (up to 80 mg/L) in the digestate. For this reason, an acid rinse of the complete cation concentrate line (membranes, pumps, and valves) was necessary to allow the normal operation of the recirculation pumps, valves, and membranes and prevent their damage.

To assess the system stability and reproducibility of tests, several tests were run. System was operated every day at the same condition and rinsing the system (cation concentrate side-acid rinse, feed ED side-base rinse) before starting every run. As shown in Figure 3, after each run there was an increase in total cell potential (and consequently decrease in CE), making the process more energy demanding.

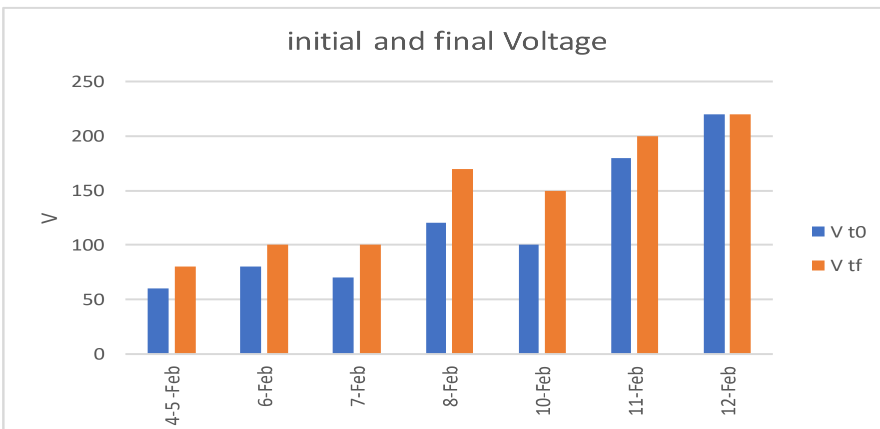


Figure 3. initial and final voltage during the firsts test with glass beads.

After the last run, every compartment (including anode and cathode) was checked and rinsed (including an acid rinse for the feed ED compartment and a base rinse or the cation concentrate).

The reason for the increase of the voltage was found in a scaling formation on the Feed side that was increasing the resistance of the membranes.

Since this moment, the cleaning procedure was changed and was operated as follows:

1. Base rinse of the feed ED (only stack);
2. Acid rinse of the cation concentrate (complete cation concentrate line);

❖ Acid rinse of the feed compartment and line by filling the feed ED vessel and recirculating the acid till its conductivity reached a plateau. The reason behind the scaling issue on the feed compartment was not observed before and could be caused by the glass beads that made possible to increase the operational duration to levels not tested before.

Feed Characterization.

The centrifuges of Girona's WWTP treating the digestate were working twice per day. A 10 m^3 tank was used to collect the liquid digestate. Another purpose of the tank was to settle the solid fraction of the liquid digestate before entering the pilot plant and thus reduce the clogging of the ED stack. Figure 4 shows the sedmentation of solids in the liquid digestate. The settleability of the solids present in the liquid digestate was high. This sedimentation step resulted to be essential to prevent the clogging of the 5 μm filters at the entrance of the pilot plant and the continuous functioning of this technology.

0 min 1 min 3 min 6 min 10 min 30 min

Figure 4. Settleability of liquid digestate

Table 2 – Ion concentrations in digestate from WWTP Girona with standard deviation during tests 1 to 8.

Na mg/L	$N\text{-}NH_4$ mg/L	K mg/L	Mg mg/L	Ca mg/L	Cl mg/L	$S\text{-}SO_4$ mg/L	$P\text{-}PO_4$ mg/L
84.6 ± 10	484.9 ± 39.6	117.7 ± 5.9	21.6 ± 4.9	65.4 ± 11.4	170.3 ± 32.5	2.2 ± 0.8	18.4 ± 5.1

Table 2 shows average ions concentrations with standard deviation in liquid digestate. Concentration of ions during tests described in Table 1 was constant. The ammonium concentration in the liquid digestate of Girona's WWTP was lower than expected (the expected concentration was over 1 g N-NH4/L) while concentration of other cations was higher than expected. Relatively constant composition of the digestate in terms of $N\text{-}NH_4^+$ concentration and concentrations of other cations made it possible to compare results from tests with the different operational conditions described in Table 1.

Ca^{2+}, Mg^{2+} and K^+ carbonates are formed at pH above pH 7. However, to ensure ammonia stripping (pKa=9.26), the pH of the cation concentrate needs to be higher than pH 8. Thus, the cations transported from the feed solution to the cation concentrate will always precipitate under conditions required for ammonia stripping. Also, divalent cations will have higher transport numbers compared to ammonium. Thus, the N: Ca, Mg, K, Na ratio determines the number and amount of cleaning agent needed per kg of N recovered.

Experimental Plan.

Table 3. – Tests description.

#	Description	PSU	Feed pump	Load ratio
Test 1	Donnan 50A/m2 (20 sec ON, 60 sec OFF)	50A/m2 (25% time)	132 L/h (25% time)	1.37
Test 2	Donnan 50A/m2 (20 sec On, 60 sec OFF)	50A/m2 (25% time)	100 L/h (25% time)	1.82
Test 3	Donnan 75A/m2 (20 sec ON, 60 OFF)	75A/m2 (25% time)	200 L/h (25% time)	1.37
Test 4	Donnan 100 A/m2 (20 sec ON, 60 OFF)	100 A/m2 (25% time)	200 L/h (25% time)	1.82
Test 5	Donnan 75A/m2 (20 sec ON, 60 OFF) Cations concentrate pH (t0) = 7.5	75A/m2 (25% time)	200L/h (25% time)	1.37
Test 6	Continuous 50A/m2	50A/m2	132 L/h	1.37
Test 7	Continuous 50A/m2	50A/m2	100 L/h	1.82
Test 8	Continuous 75 A/m2	75A/m2	150 L/h	1.82

The experimental plan describes a multifactorial design in which 3 different variables were studied (load ratio, current density, and operational mode) (Table 3).

The load ratio (LR) is a crucial parameter to optimize the current-driven recovery of total ammonia from the feed and is equal to the ratio between the current density and the NH_4^+ loading rate (Rodríguez Arredondo et al. 2019). In this experimental plan, it was decided to investigate the effect of LR 1.4 and 1.8. This LR is higher to the usually selected LR in previous studies ((Rodrigues et al. 2020) and was selected due to the lower N: Ca, Mg, K ratio that characterized the treated liquid digestate.

The current densities that were selected were 50, 75, and 100 A/m2.

The operational modes investigated were continuous mode and Donnan mode. In continuous mode, recirculation pumps are working in continuous and current is always in ON mode. In Donnan mode, while the recirculation pumps are always working, the current and the feed pump alternates 20 seconds of ON mode and 60 seconds of OFF mode. When no current is applied, cations that are highly concentrated in the cations concentrate tend to diffuse back to the feed ED solution because of the concentration difference. These cations are then exchanged with other cations to maintain electroneutrality, a phenomenon called Donnan dialysis. In these tests, Donnan mode was applied to study its effects on NH_4^+ recovery and energy expenditure and compare it with the tests in continuous mode.

Test 5 has the same operational conditions as test 3 with the exception of the initial pH. In this test the initial pH was highr (pH 7.5) compared to the other tests (<6.0) to verify wether a low initial cation concentrate pH is a limiting factor for the process.

Results

Figures 5, 6, and 7 show the main results of the tests carried out. Results are divided into two main groups, results from the experiments conducted in Donnan mode (test 1 to 5), and experiments run in continuous mode (test 6 to 8). This division was made to better represent the results due to different test duration (test at Donnan mode lasted 24 hours, with current working 25% of the time, while test in continuous lasted 6 hours). For the experiments in Donnan mode, the results are shown as average values per hour, considering both ON and OFF periods.

All tests were operated as planned (24 hours for Donnan tests and 6 hours for the continuous test), except for tests 4 and 5 that were interrupted before the experiments could be finished due to the higher initial cation concentrate pH and thus more pronounced scaling.

Figure 5 shows results of NH_4^+ removal efficiencies from Donnan mode experiments at different test durations. Removal efficiencies depended on the LR. Results with LR 1.4 had an initial removal efficiency of around 40% for samples at 2 hours for Donnan tests and 1 hour for continuous tests during the first two samples and decreased to around 20% for samples at 20 hours for Donnan tests and 5 hours for continuous tests. In the test 3 the removal efficiency at the end of the experiment was somewhat higher, 31%. For tests with LR equal to 1.8, the removal efficiencies were higher, 55-60%, during the first 2 hours for tests in Donnan mode and 0.5 hours for tests in continuous mode, and were then lowered to 50-55% and 30-35% for samples at 4 and 20 hours for Donnan tests and 1 and 5 hours for continuous tests. Test 8 yielded somewhat higher ammonia removal efficiency (45%) after 5 hours of operation. The NH_4^+ removal decreased over the operational time in all runs, with the highest NH_4^+ removal achieved at the beginning of each run. This was a consequence of intense membrane fouling and scaling, that gradually worsened the reactor performance and had a detrimental impact on the removal and recovery of ammonia.

The product showed an average concentration of 26 g N-NH_4^+/ L (≈122 g ammonium sulfate / L).

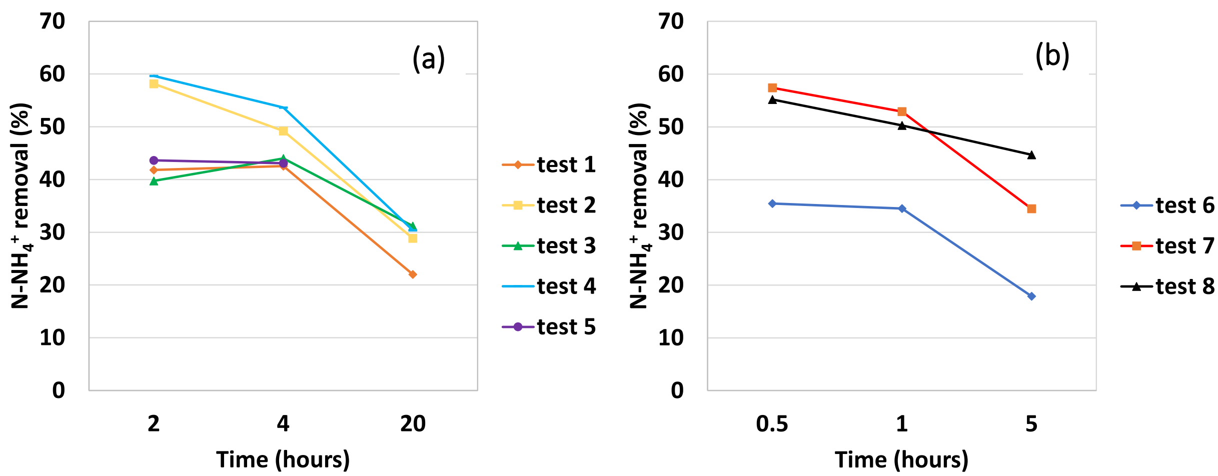
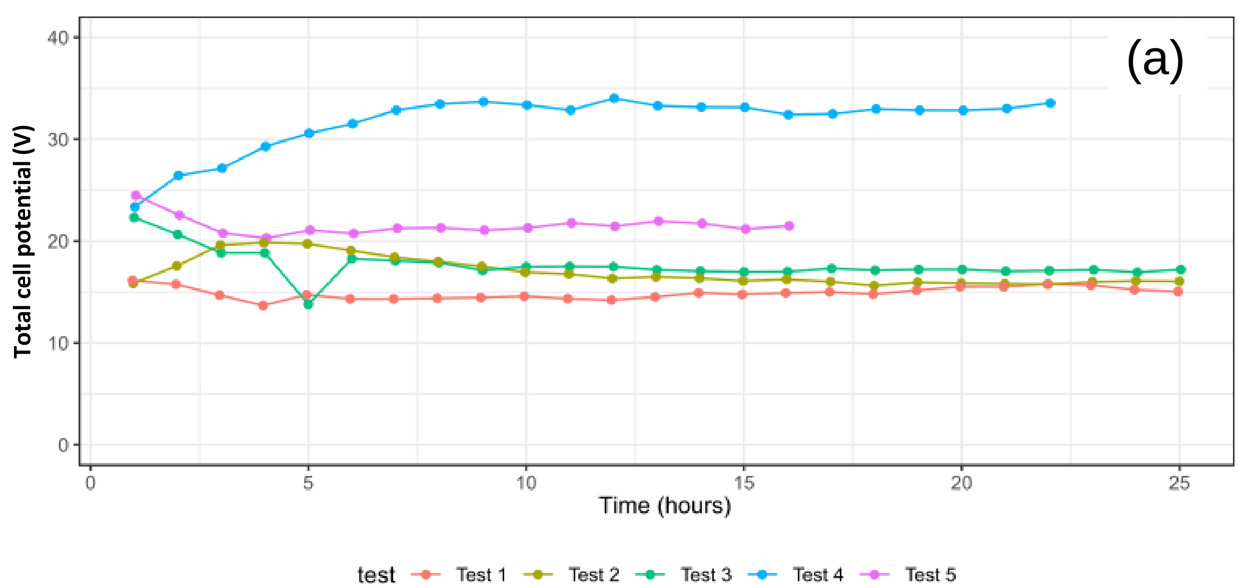


Figure 5. NH_4^+ removal efficiency from the liquid digestate for Donnan tests (a) for continuous tests (b).

When comparing the voltage of tests in continuous (Figure 6a) and Donnan mode (Figure 6b) it is visible how Donnan mode enabled to maintain the total cell potential relatively constant and at lower values (15-35 V) compared with the continuous mode of operation (50-280 V?)). For tests in continuous mode, lower applied current and lower LR led to lower voltage needed to keep the current density constant. For tests in Donnan mode lower current led to lower voltage and, at same current, lower load ratio led to lower voltage.



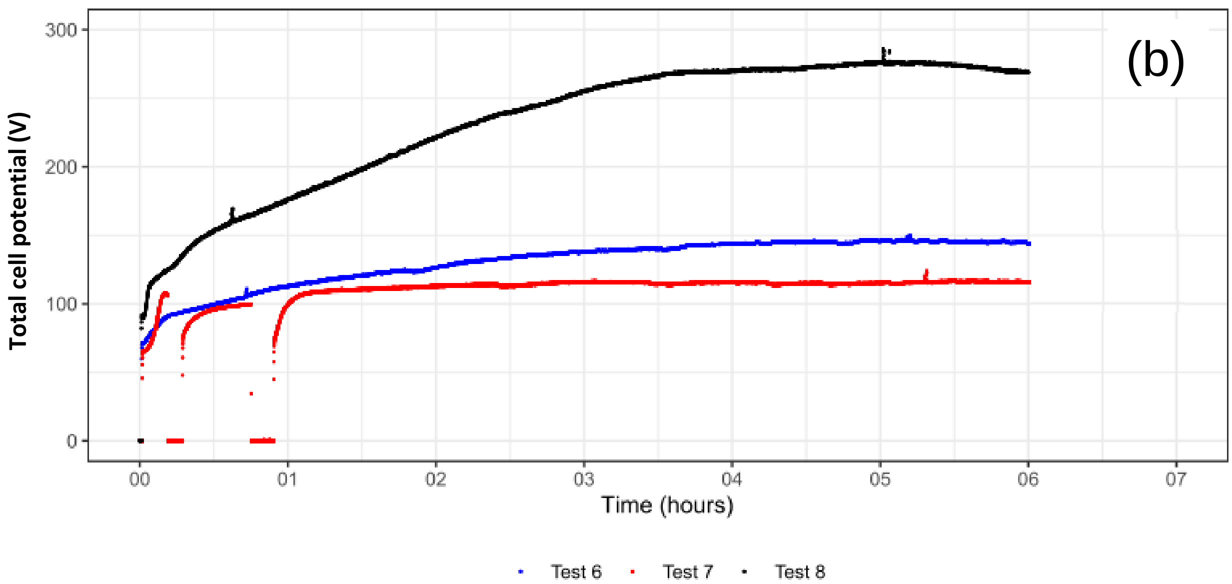


Figure 6. Average total cell potential per hour for the experiments run in Donnan mode (a) Total cell potential for the experiments run in continuous mode (b).

Figure 7 shows the energy (in MJ) needed to recover 1 kg of nitrogen, calculated based on the total cell potential at each of the current densities applied. Due to the intermittent application of current, the energy consumption was significantly lower for the experiments run in Donnan mode.

The benefits of operating the system in Donnan mode were already pointed out in the study by Rodrigues et al. (2020) in which a similar system configuration was used. In this study, Donnan mode operation increased the transport of ammonium from feed to cathode and consequently the total ammonia nitrogen removal. Additionally, it resulted in lower energy consumption for TAN removal.

For tests in continuous mode, test 7 resulted in less energy expenditure compared test 6. Both tests were run at a current density of 50 A/m2, but with the LR higher for test 7 (1.82) compared with test 6 (LR=1.37) because of the lower feed flow rate. Higher concentration of divalent cations might explain why a higher load ratio is needed when operating the system at a lower current density.

Donnan mode resulted in lower energy expenditure with the best result given by test run at LR of 1.4 (test 1, 3, and 5). The dependence of the energy expenditure on the load ratio are highlighted by test 1 and 2. Indeed, operating the system at 50 A/m2 and a load ratio of 1.4 (test 1) resulted in higher energy efficiency compared to operating the system at the same current density but at 1.8 of load ratio. Under these conditions , systems showed similar nitrogen recovery but a higher voltage during test 2.. Test 5 was run to check whether a higher initial cation concentrate pH (pH 7.5 instead of pH 5) could further shift the NH_4^+-NH_3 equilibrium toward NH_3 to increase the ammonia recovery during the process. This test resulted in higher energy expenditure and also to a lower experiment duration.

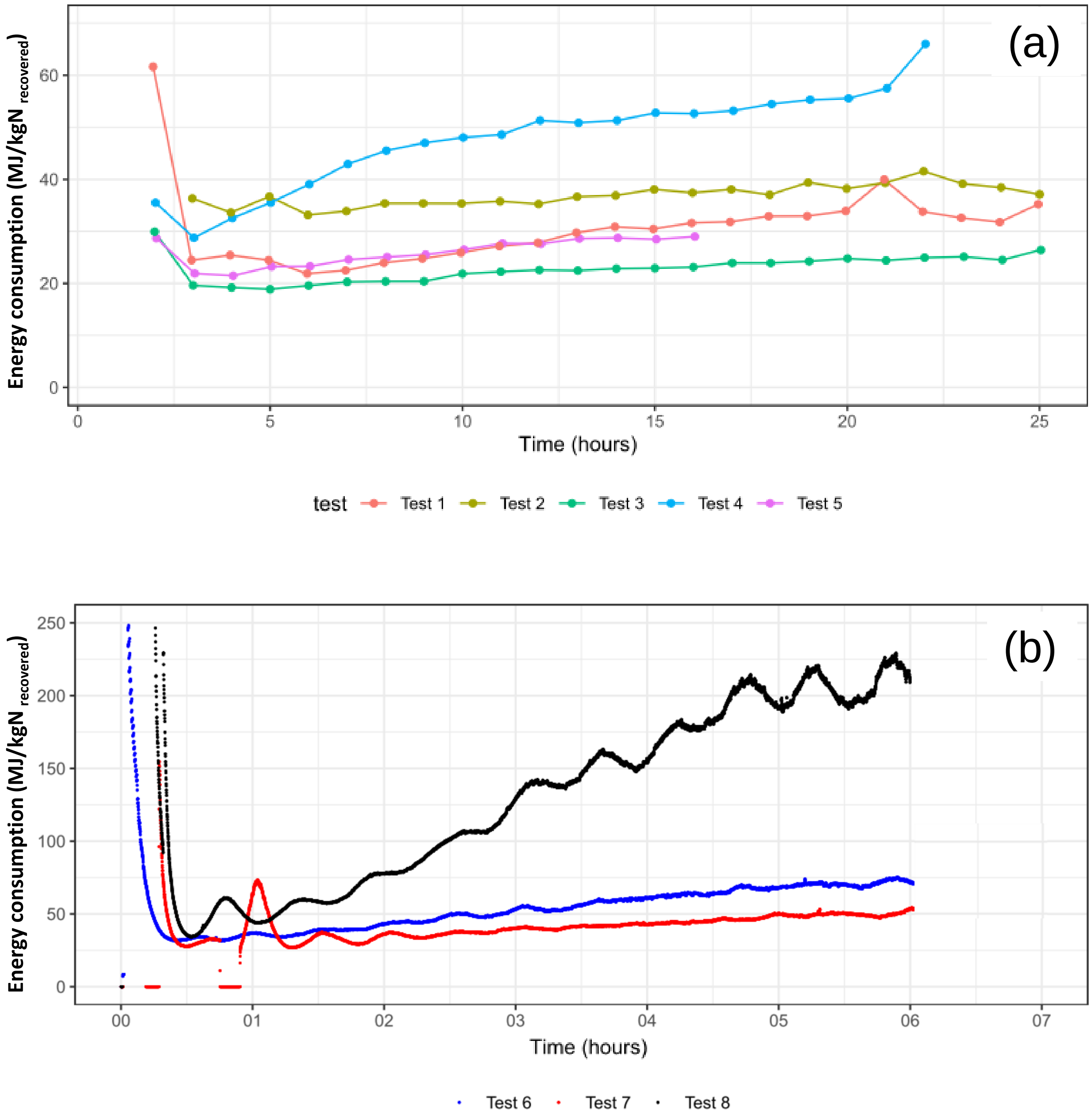


Figure 7. Average energy demand per hour per kg of nitrogen recovered for the experiments run in Donnan mode (a) energy demand per kg of nitrogen recovered for the experiments run in continuous mode (b).

*The energy demands were calculated considering only the total cell potential, current, and the nitrogen recovered.

Table 8 shows the results of minimum and maximum pH and conductivity for feed, feed ED and cation concentrate compartments for each test. The initial pH and conductivity were continuously increased to reach maximum values at the end of each experiment (Table 8). Minimum and maximum values of cation concentrate conductivity represent the initial and final values of the experiment, respectively. Higher pH leads to a decrease in conductivity due to the precipitatation of cations at higher pH. Indeed test 5 ended before the selected duration (17 hours instead of 24 hours). This was caused by the scale formation which blocked the cation concentrate recirculation pumps which occurred at 17.2 mS/cm. Test 4 was also not completed because the recirculation pumps stopped working at 21.5 h, when cation concentrate conductivity was 25.8 mS/cm. Higher conductivity at the end of the test 4 compared to tests 1, 2, 3 and 5 was likely due due to the difference of initial pH which was tested in test 5. Tests in continuous mode showed higher maxim cation concentrate pH compared to tests in Donnan mode due to the continuous OH- formation at the cathode.

Table 8. Minimum and maximum pH and conductivities of feed, feed ED, and cation concentrate solution for each test.

		pH		Conductivity (mS/cm)	
		min	max	min	max
test 1	Feed	7.8	8.0	3.5	3.7
	Feed ED	6.3	7.0	2.4	4.6
	Cat Conc	5.1	8.7	3.6	21.9
test 2	Feed	7.8	7.9	3.5	3.7
	Feed ED	5.9	7.0	1.8	5.2
	Cat Conc	2.7	8.7	3.2	21.7
test 3	Feed	7.9	8.0	3.9	4.2
	Feed ED	6.4	7.7	2.1	4.8
	Cat Conc	4.5	9.5	1.1	23.7
test 4	Feed	7.4	7.6	3.9	4.1
	Feed ED	5.9	7.6	1.5	4.6
	Cat Conc	5.0	9.4	5.4	25.8
test 5	Feed	7.7	7.9	3.9	4.1
	Feed ED	6.3	7.5	2.2	4.5
	Cat Conc	7.5	9.7	1.5	17.2
test 6	Feed	7.8	7.9	3.6	3.8
	Feed ED	6.4	7.8	2.7	4.1
	Cat Conc	5.8	9.8	5.9	14.5
test 7	Feed	7.7	7.8	3.6	3.8
	Feed ED	5.8	7.3	1.8	4.5
	Cat Conc	5.8	9.7	3.7	16.6
test 8	Feed	7.8	7.9	3.5	3.7
	Feed ED	5.9	7.9	1.8	4.3
	Cat Conc	5.8	10.1	3.7	12.6

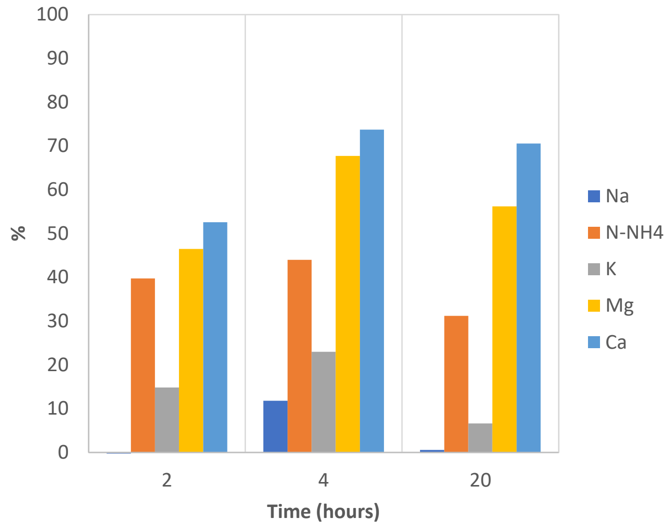
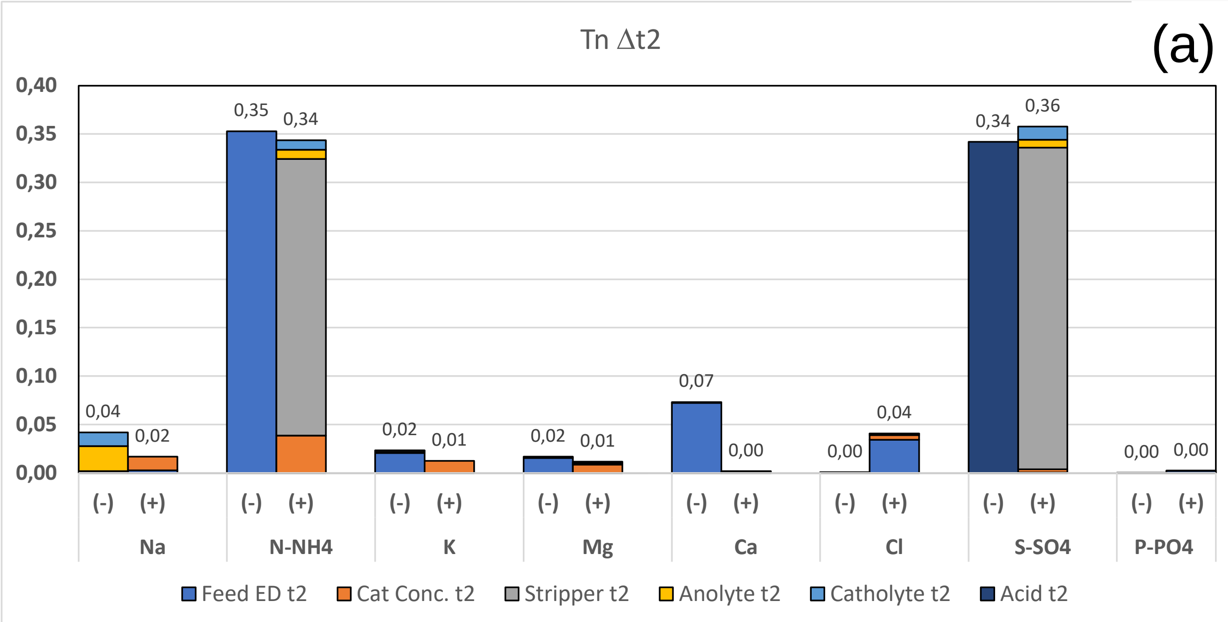


Figure 8. Cations removal efficiency during test 3

Higher overall cation removal efficiency was obtained at the end of the test 3 (Fig. 8). The relatively high concentration of other cations in the feed solution is probably the main cause for the lower ammonium removal. The maximum ammonium removal is 45%.

Figure 10 shows the results of the ion transport number which represents the fraction of the total electrical current carried in an electrolyte by a given ionic species. For every ion species, there is a bar showing the negative results (ion specie leaving the corresponding compartment) and a positive bar (ion specie entering/accumulating in the corresponding compartment). These graphs show results in the time interval between 2 and 4 hours since the test started (Δt2) that is the interval when the coulombic efficiency was at the highest values and between 4 and 20 hours since the test started (Δt3).



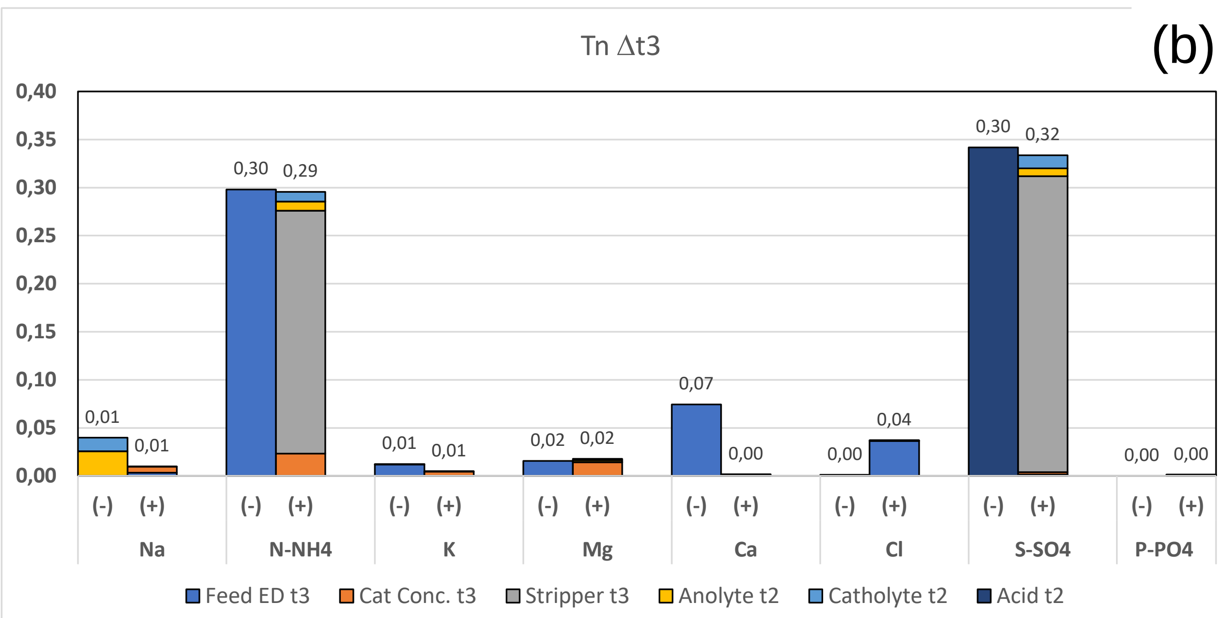


Figure 9. Transport number during Δt2 (a) and Δt3 (b).

Based on the transport number results (Figure 9):

- NH_4^+: transport number is 0.35 for Δt2 and is lowered to 0.3 for Δt3 because of the increase of the scale formation during the last part of the test. For Δt2 from the 40% of NH_4^+ removed from the feed, 6% accumulates in the cation concentrate without passing through the TMCS membrane, 5.5 % accumulates in the catholyte/anolyte and the rest 88.5% pass the TMCS and leaves the system with the product.
- Na^+, K^+, Mg^{2+}, Ca^{2+}: The amount of these cations that is removed from the feed solution does not seem to accumulate in any other compartment. Indeed the sum of the negative contribution is not equal to the sum of the positive contribution with the first being higher. While these ions pass from the Feed ED through the membrane and accumulate in the cation concentrate when their concentration increases and helped by the high pH, they form carbonate scale which precipitates lowering their concentration present in the soluble form.
- Cl^-, PO_4^{3-}: completely washed out by the system confirming the good cation membranes functioning.
- SO_4^{2-}: leaves the acid vessel to accumulate in the stripper to keep the stripper pH at the set operational stripper pH (2.5). A small fraction is present diffuses through the TMCS membranes and accumulates in the cation concentrate and the catholyte/anolyte.

The amount of nitrogen recovery was assessed for the continuous tests (Test 6, 7 and 8). In Table 9 is presented the amount of N recovered during the tests conducted in continuous operation. These tests lasted for 6 h and then a cleaning was needed due to the scaling produced on the membranes. In the table is also added the N recovery value per day although this value is an extrapolation of the results obtained for 5 h. For this calculation, the time used for cleaning has not been taken into account and therefore this number would only be valid if a pre-treatment of the digestate to remove scalants would be in place and the plant could run in continuous mode without requiring the cleaning of the membranes. The results obtained are lower than the objective of the project of recovering of 1Kg N/day from the different waste streams treated, and this is due to the fact that the % of N removed decreases along the experiment due to the scaling problems explained before.

Table 9. Nitrogen recovery obtained from the digestate under continuous operation.

Tests	**Digestate (L/h)**	**N-NH_4^+ feed (mg N/L)**	**N-load (g/h)**	**N-removed* (%)**	**Recovery in 5h (real data, Kg N)**	**Recovery in 24 h (calculated) (Kg/d)**
Test 6	132	485	64	42	0.134	0.645
Test 7	100	485	48.5	48	0.116	0.559
Test 8	150	485	72.75	50	0.181	0.873

*Average value from the whole test.

Conclusions

Newbies pilot plant was able to recover the nitrogen present in the form of ammonium in the liquid digestate produced by the centrifuges of Girona's WWTP. The main results obtained were:

- Donnan operational mode showed better results in terms of energy demand per kg of nitrogen recovered being in the range 20-70 MJ/kg$N_{recovered}$, whereas continuous mode of operation resulted in the energy consumption of 25-225 MJ/kg$N_{recovered}$. This result was due to the back diffusion of the cations from the cation concentrate solution to the feed ED solution that were partially exchanged with NH_4^+ during the off current interval.
- Reducing the ion shortcut by the addition of glass beads was of major importance to increase process performance and stability.
- Increasing the initial cation concentrate pH resulted in higher energy consumption per kg of nitrogen recovered and faster scale formation.
- The product showed a concentration of 26 g N-NH_4^+/ L(≈122 g ammonium sulfate / L) for every condition tested.
- Running the system in Donnan mode (25% ON) at 75 A/m^2 and with a LR of 1.4 (Test 3) resulted in the lower energy demand per kg of nitrogen recovered.
- Running the system in Continuous mode at 75 A/m2 and with an LR of 1.8 (Test 8) resulted in the highest nitrogen recovery (~ 0.9 kg N-NH_4^+/day).
- Maximum ammonium coulombic efficiency obtained was 40% under optimum conditions (Donnan 75 A/m^2, 1.37 LR)
- High concentration of divalent cations in the liquid digestate was a major problem for pilot plant operation leading to scaling issues, pump failure and lower ammonium transport over the cation exchange membranes. was significant fouling and scaling in the pilot plant. This was due to the relatively high concentration of Ca^{2+} and Mg^{2+} present in the anaerobic digestate. This required an establishment of frequent cleaning procedures with acid and base solutions and prevented a continuous operation of the pilot plant. To run the process without frequent interruptions due to cleaning, complex waste streams such as digestate would need to be first pretreated to remove the calcium, magnesium and other scalants. Nevertheless, the conducted tests allowed evaluating the impact of current density, loading and current supply regime (i.e. Donnan vs continuous) on ammonia recovery
- Higher N: Ca, Mg, K, Na ratio in the feed should lead to higher recoveries and increase system performances.

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