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COMMUNICATION

Gas-permeable hydrophobic tubular membranes for ammonia recovery in Bio-Electrochemical Systems.

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The application of a gas-permeable hydrophobic tubular membrane in Bio-Electrochemical Systems enables an efficient recovery of ammonia (NH₃) from the cathode compartment. Due to the Hydrogen Evolution Reaction at the cathode, no chemical addition was required to increase the pH for a continuous NH₃ recovery from wastewater.

1. Introduction

Bio-electrochemical systems (BESs) allow for the recovery of valuable products and energy from wastewater streams¹. BESs use electron active microorganisms to catalyse at least one of the electrode reactions at anode or cathode. There are two basic types of BES; Microbial Fuel Cells (MFCs) are galvanic cells which produce electricity² and Microbial Electrolysis Cells (MECs) are electrolytic cells which produce hydrogen³. BES have been applied for the recovery of ammonia and energy (as electricity or hydrogen gas) from wastewater.^{4,5}

Recently, BESs have been proposed as a suitable technology for the treatment of urine, which allow for nutrient and energy recovery and provide the opportunity for suitable business case to bring BESs to the market.^{5,6}

One of the biggest challenges for the energy efficient recovery of ammonia (NH₃) from wastewater is the energy required for the NH₃ – stripping process.^{7,8} Using BESs the need for chemical addition to raise the pH of the wastewater can be mitigated, but the high energy demand for the supply and recycle of a gas stream to the cathode compartment still remains.⁹⁻¹¹

Transmembrane chemisorption (TMCS) has been described as an alternative method for NH₃ recovery by NH₃-gas transport through a gas-permeable hydrophobic membrane with subsequent NH₃-absorption in a suitable acid solution as ammonium (NH₄⁺).¹² This eliminates the need for high gas flow

Water Impact

Ammonia recovery using Bio-electrochemical systems (BESs) has been investigated by various researchers with promising results. Most of the concepts using Microbial Fuel Cells and Microbial Electrolysis Cells rely on ammonia stripping from the catholyte with subsequent absorption in an acid. However, this requires large volumes of gasses (O₂, N₂, H₂) to be recycled or supplied to the cathode compartment, resulting in potentially high energy demand. Integrating a gas-permeable hydrophobic tubular membrane can lower the energy demand for the ammonia recovery from wastewater and also simplify the design of ammonia recovery systems based on BES. Furthermore, similar approaches for ammonia recovery using Electrochemical System can also benefit from this type of integration.

rates (several L gas/L wastewater) and therefore can lower the energy requirements of the NH₃ recovery.

In this research we report the recovery of NH₃ by means of a TMCS module integrated in the catholyte compartment of an MEC. Ammonium ions are transported from anolyte to catholyte by diffusion and migration. As a result of the pH in the catholyte, ammonium ions are deprotonated to volatile ammonia gas. The ammonia gas in the catholyte diffuses via the nanometer size gas filled pores of the gas-permeable hydrophobic membrane into the acid.

2. Materials and Methods

2.1. Experimental Setup

The experimental setup consisted of a MEC with an integrated TMCS module. Figure 1A illustrates the experimental setup. The MEC was composed of 4 anode and cathode pairs, which were hydraulically and electrically connected in parallel.

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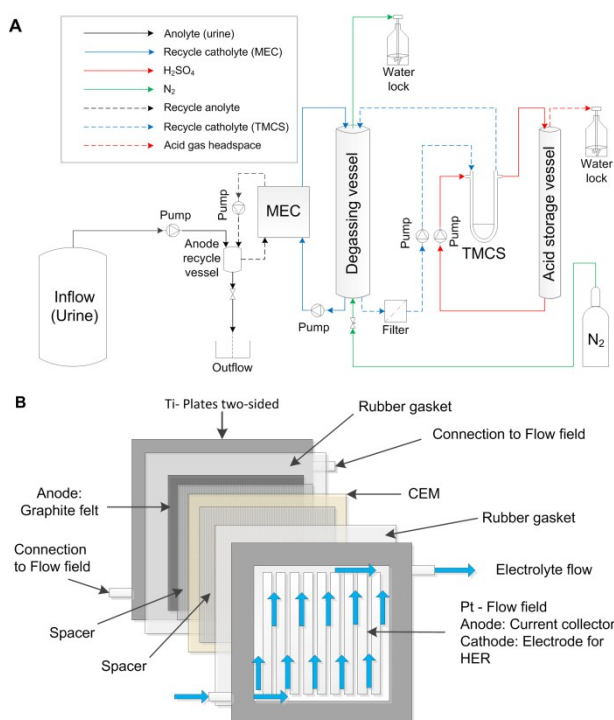


Figure 1A Schematic representation of the experimental setup. The experimental setup was operated at atmospheric conditions with 1 to 5 mbar pressure increase due to the water locks. Figure 1B schematic representation of one cell pair of the MEC and the flow of the electrolyte in the machined and platinized flow field.

The MEC was operated in parallel configuration in which each individual titanium plate either served as anode or cathode housing. Each titanium plate (dimensions 28 cm x 28 cm x 0.8 cm) had a machined and platinized flow field (10 g m⁻²) with the following dimensions 20 cm x 20 cm x 0.3 cm on both sides. The platinized flow fields define a flow path for the electrolyte. At the anode side, the flow field also served as the anodic current collector, where the graphite electrode is placed upon. At the cathode side, the flow field also served as catalyst for the Hydrogen Evolution Reaction (HER). Figure 1B illustrates one cell pair of the MEC and shows the flow of the electrolyte through one of the half cells (anode or cathode).

The Titanium plates were supplied by Magneto Special Anodes B.V. (Schiedam, The Netherlands). The anode electrodes were composed of a graphite felt (GFD 2.5, SGL Group, Bonn, Germany) with the dimensions of 20 cm x 20 cm. The total anode surface area was 0.16 m². Anode and cathode pairs were separated by a cation exchange membrane (CEM, Ralex CMH-PP, Mega a.s., Czech Republic). Silicone rubber gaskets (0.5 mm, MVQ Silicone, ERIKS, The Netherlands) were used to ensure water tightness. All 4 anode compartments were fed in parallel with inflow from a common anolyte recycle vessel (0.9 L). Each anode and cathode compartment (8) was equipped with Ag/AgCl reference electrodes (QM710X, Q-i-s, Oosterhout, The Netherlands). Similarly, the 4 cathodes compartments were fed in parallel with an inflow from a common recycle vessel. The recycle vessel (degassing vessel) had a volume of 1.5 L and a 1 L headspace, including a heating jacket for temperature control (LGS, Ubbena, The Netherlands). The cathode compartment was operated in a

batch mode while the catholyte was recycled over a gas-permeable hydrophobic tubular membrane module on the shell side. Inside the gas-permeable hydrophobic tubular membrane (lumen side of the TMCS module) a 1 M sulphuric acid solution was recycled from an acid storage vessel (similar to degassing vessel). The sulphuric acid was used for absorption of ammonia resulting in an ammonium sulphate solution over time. All chemicals used were of analytical grade.

Four Masterflex pumps (L/S Digital Drive 600, Metrohm Applikon BV, Schiedam, The Netherlands) were used to supply the inflow from the storage tank to the system and different recycle flows over the anodes, cathodes and the gas-permeable hydrophobic tubular membrane module (shell and lumen side). Polyethylene (PE) tubing was used for the gas and liquid transport (DN04/06, Em-Technik, Germany) in the experimental setup. The anode compartment had a hydraulic volume of 1.35 L, whereas the total volume of the anodes (inside the MEC) was 0.32 L.

N₂ from a Nitrogen generator was supplied to the cathode compartment at 2 to 5 mL min⁻¹ to remove any oxygen from the headspace and provide oxygen free conditions for the HER.

A power supply (ES 030-5, Delta Elektronika, The Netherlands) was used to apply a constant voltage to the MEC. The electrical connection of the 4 cell pairs (8 electrodes) was carried out by means of 2 identical aluminium blocks (8 cm x 8 cm x 4 cm) with each 5 drilled connections in geometric alignment, connected by 7 identical isolated cables (50cm x 0.1mm² - 4 mm connector, Hirschmann, Germany).

The pH and temperature were measured in the anode recycle vessel and degassing vessels using pH electrodes (CPS11D) and a two channel transmitter (Liquiline CM442, Endress+Hauser, Germany). Applied voltage, anode and cathode potentials, current, pH and temperature of the anode and the cathode were recorded with a datalogger (Memograph M RSG40, Endress+Hauser, Germany).

The TMCS module was constructed from a polypropylene (pore size 200 nm, type Accurel PP V8/ HF) membrane fibre (CUT Membrane Technology GmbH, Düsseldorf, Germany), housed in a custom-made membrane module and operated in cross flow mode. The TMCS module had a total shell side (outer) membrane surface area of 374 cm².

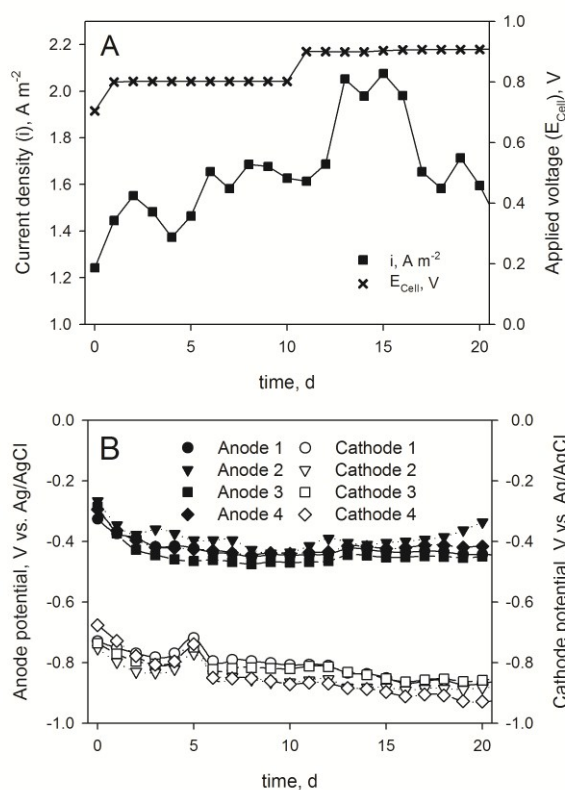


Figure 2A Applied cell voltage and measured current density. Figure 2B measured anode and cathode potentials during the experimental period.

2.2. BES operation

The BES was previously operated on wastewater (diluted urine) and was originally inoculated with effluent from an active cell also operating on urine.⁹ Anode, cathode and acidic solution were recycled over their respective vessels at a flow rate of 50 mL min^{-1} . The anodes were fed from the storage tank (50L) at an inflow rate of 4 mL min^{-1} . During the experiment the ammonium concentration in the acid was measured on weekdays. The sulphuric acid renewed when the NH_4^+ concentration exceeded 15 gN L^{-1} , before the acid reached saturation to ensure sufficient absorption capacity.

The cathode recycle and acid recycle vessel were temperature-controlled to $25 \pm 1^\circ\text{C}$ using a water bath DC10-K10 (Thermo Scientific HAAKE, Germany) to ensure equal temperature and prevent a water vapour gradient across the gas-permeable hydrophobic tubular membrane, and thus minimising the risk of water vapour transport from either side of the membrane. Samples were taken on weekdays from the anode influent, anode effluent, cathode compartment and the acidic compartment to determine the BES performance.

The urine was collected from the male employees of Wetsus by means of water-free urinals (Urimat®, Biocompact, The Netherlands) and stored in a polyvinyl chloride (PVC) vessel. The urine was pre-treated by struvite precipitation and subsequent filtration as previously described.⁹ The anolyte inflow was prepared by dilution of the pre-treated urine 5x with deionized water to mimic a wastewater.

2.3. Chemical analysis

Samples from the anode influent, anode effluent, cathode compartment and the acid compartment were analysed according to standard methods¹³ for relevant parameter such as COD, ammonium-nitrogen, cations and anions concentration as previously described.⁹ All samples were analysed in duplicate after filtration by 0.45 μm membrane filters. The pH of the collected samples was analysed with a weekly calibrated sensor (ProfiLine pH/Cond 3320 WTW, Germany).

Samples from the headspace were analysed with a gas chromatograph (μGC Varian CP 4900, Agilent Technologies, US) for the gas composition).

2.4. Calculations

The performance of the BES was analysed by determining the current density (i), coulombic efficiency (CE), COD removal (R_{COD}) from the influent, ammonia recovery (R_{N}) from the influent, and ammonia transport efficiency over the CEM (η_{N}) in accordance with described methods.⁹ The energy requirement for the ammonium recovery was calculated based on the removed ammonium nitrogen and the electrical energy input of the MEC.

3. Results and discussion

3.1. MEC performance

The MEC performance was assessed by the measured current density and the anode and cathode potentials. Figure 2A shows the current density determined over the 20-day experiment. Although the measured current density (average $1.7 \pm 0.21 \text{ A m}^{-2}$) was considerably lower than earlier reported current densities in BES treating urine⁹, the system showed a stable operation during the whole experimental period. Figure 2B shows the corresponding anode and cathode potentials during the experimental period also indicating a stable operation.

3.2. COD and Ammonium removal and efficiencies

Figure 3A and Figure 3B show the COD and ammonium removal as well as the coulombic and ammonium transport efficiency over the CEM. Coulombic efficiency (η_{CE}) and COD removal (η_{COD}) indicate stable operation. On average a coulombic efficiency of $78 \pm 10\%$ and a COD removal of $40 \pm 5\%$ were obtained, which are comparable to earlier reported results for BES operating on urine.⁹

The average ammonium nitrogen removal throughout the experimental period of 20 days was $42 \pm 6\%$, while the highest removal reached was 51% on day 4 and 15 in this continuous feed BES system.

The ammonium transport efficiency over the CEM was on average $70 \pm 17\%$, whereas the highest transport efficiency was 104%, showing that ammonium was the main contributor to the charge transport over the CEM.

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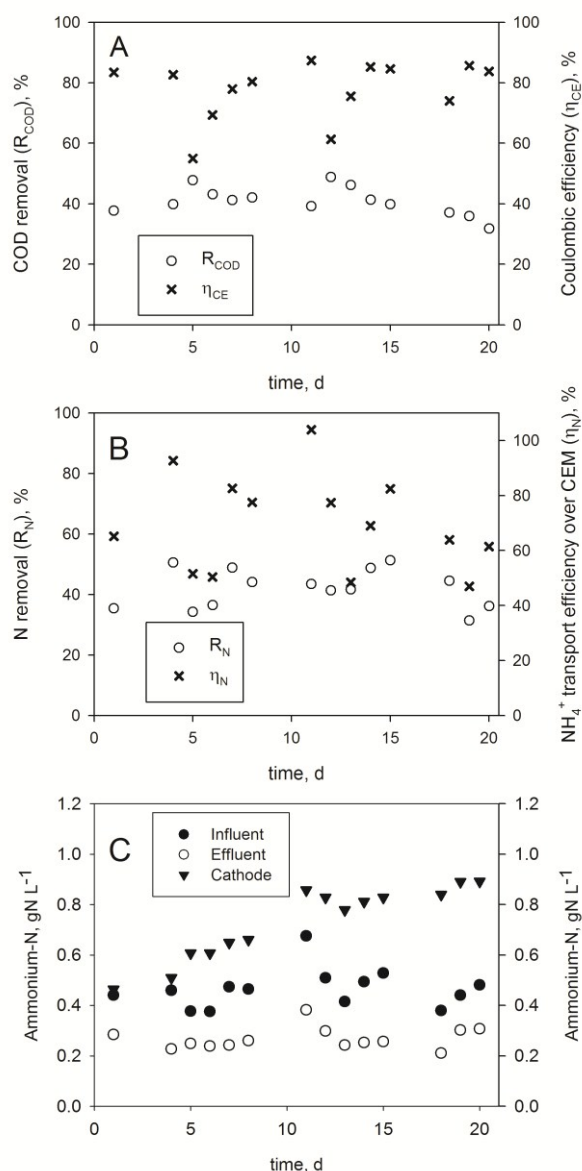


Figure 3A COD removal efficiency and Coulombic efficiency. Figure 3B nitrogen removal efficiency and ammonium transport efficiency over the CEM. Figure 3C ammonium-nitrogen (NH_3 -N and NH_4^+ -N) concentration in anode influent, anode effluent and catholyte.

While higher ammonium removal efficiencies have been achieved previously at higher current densities in (Bio-) Electrochemical Systems, the charge transport reported in this work was found to be higher than in these respective works.^{9, 14, 15}

3.3. Ammonium recovery

The pH measurements showed that the anolyte inflow was stable around 9.16 ± 0.16 , the anolyte effluent was stable around 7.19 ± 0.3 and the catholyte pH was stable around 9.46 ± 0.19 . Therefore, ammonium-nitrogen (i.e. NH_3 & NH_4^+) present in the inflow was transported as NH_4^+ from anode to cathode over the CEM, from where it was removed as NH_3 over the gas-permeable hydrophobic tubular membrane and concentrated as NH_4^+ in the sulphuric acid.

Figure 3C shows the ammonium nitrogen (NH_3 -N and NH_4^+ -N) concentration during the experiment. The ammonium nitrogen concentration in the anolyte effluent and the catholyte were on average $42 \pm 6\%$ lower and $59 \pm 33\%$ higher than in the anolyte influent.

The highest NH_4^+ -N concentration reached in the acid was 22.5 gN L^{-1} , which corresponds to a concentration factor of 45 times NH_4^+ -N concentration in the corresponding inflow of the BES. About 95% of ammonium nitrogen removed from the anolyte during this period (day 11 to 15) was recovered in the sulphuric acid. Overall a maximum ammonium recovery of 49% from the influent was reached on day 15, which is slightly lower than the 57% recovery reported in Electrochemical System (ES)¹⁵. These results show that it is possible to concentrate ammonium nitrogen from the anolyte in the acid. Additionally, our experimental setup is less complex than other experimental setups using gas recirculation^{14, 15} or multiple absorption vessel¹¹. While sulphuric acid is a practical solution for ammonium recovery, alternatives (i.e. phosphoric acid or nitric acid) should be considered in order to produce a high value fertilizer.

The limitation of this BES was the relative low current density reached in the experiments, whereas high NH_4^+ transport efficiency over the CEM ($\sim 70 \pm 17\%$) and good recoveries from the catholyte were achieved ($\sim 95\%$).

3.4. Energy demand

The energy demand for the ammonium removal was on average $2.49 \pm 0.67 \text{ kWh g}_N^{-1}$, which is considerably lower than the energy demand of ES (i.e., 5 to 12 kWh g_N^{-1})^{14, 15} and only slightly higher than other BES ($1.35 \pm 0.39 \text{ kWh g}_N^{-1}$)¹⁰ operating at higher current densities. However, the lower energy demand of the BES was a result from the constantly replenished catholyte, leading to lower potential losses.⁹ Potential benefits on the energy demand of the ammonium recovery from the produced hydrogen were not considered in our experiments. Furthermore, a detailed energy analysis should also include the energy for pumps (inflow and recycling).

4. Conclusions

Our results show that gas-permeable hydrophobic membranes can be successfully employed in BES for ammonium recovery from wastewater. The energy demand of this system is considerably lower than the energy demand of an ES for ammonium recovery. Furthermore, gas-permeable hydrophobic membranes could be either directly integrated in the cathode compartment or be part of the recycle stream of the catholyte, resulting in less complex treatment systems. These configurations can also be beneficial for other (bio-) electrochemical systems in order to simplify the design of the ammonium recovery step. Although the results are promising, further research will be necessary to increase ammonium removal rates.

Notes and references

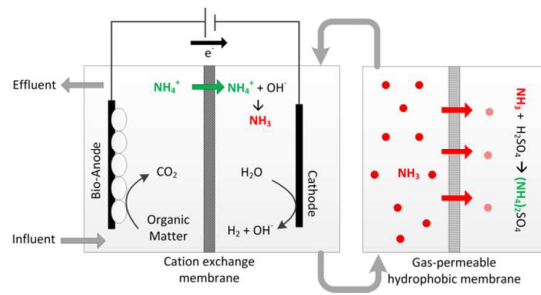
‡ Calculated from the reported values in Kuntke *et al.*, 2014.¹⁰

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1. H. V. M. Hamelers, A. Ter Heijne, T. Sleutels, A. W. Jeremiasse, D. Strik and C. J. N. Buisman, *Applied Microbiology and Biotechnology*, 2010, **85**, 1673-1685.
2. B. E. Logan, B. Hamelers, R. A. Rozendal, U. Schröder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete and K. Rabaey, *Environ. Sci. Technol.*, 2006, **40**, 5181-5192.
3. B. E. Logan, D. Call, S. Cheng, H. V. M. Hamelers, T. H. J. A. Sleutels, A. W. Jeremiasse and R. A. Rozendal, *Environmental Science & Technology*, 2008, **42**, 8630-8640.
4. P. T. Kelly and Z. He, *Bioresource Technology*, 2014, **153**, 351-360.
5. M. Rodriguez Arredondo, P. Kuntke, A. W. Jeremiasse, T. H. J. A. Sleutels, C. J. N. Buisman and A. ter Heijne, *Environmental Science: Water Research & Technology*, 2015, **1**, 22-33.
6. P. Ledezma, P. Kuntke, C. J. N. Buisman, J. Keller and S. Freguia, *Trends in biotechnology*.
7. M. Maurer, W. Pronk and T. A. Larsen, *Water Research*, 2006, **40**, 3151-3166.
8. M. Maurer, P. Schwegler and T. A. Larsen, *Water Science and Technology*, 2003, **48**, 37-46.
9. P. Kuntke, T. H. J. A. Sleutels, M. Saakes and C. J. N. Buisman, *International Journal of Hydrogen Energy*, 2014, **39**, 4771-4778.
10. P. Kuntke, K. Śmiech, H. Bruning, G. Zeeman, M. Saakes, T. Sleutels, H. Hamelers and C. Buisman, *Water Research*, 2012, **46**, 2627-2636.
11. X. Wu and O. Modin, *Bioresource Technology*, 2013, **146**, 530-536.
12. M. Ulbricht, J. Schneider, M. Stasiak and A. Sengupta, *Chemie Ingenieur Technik*, 2013, **85**, 1259-1262.
13. L. S. Clesceri, A. D. Eaton, A. E. Greenberg, A. P. H. Association, A. W. W. Association and W. E. Federation, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, 1998.

14. J. Desloover, A. Abate Woldeyohannis, W. Verstraete, N. Boon and K. Rabaey, *Environmental Science & Technology*, 2012, **46**, 12209-12216.
15. A. K. Luther, J. Desloover, D. E. Fennell and K. Rabaey, *Water Research*, 2015, **87**, 367-377.



Integration of a gas-permeable hydrophobic membrane in the cathode compartment of a Bio-Electrochemical System enables efficient ammonia recovery from wastewater.