Ammonium recovery and energy production from urine by a microbial fuel cell

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**A B S T R A C T**

Nitrogen recovery through NH₃ stripping is energy intensive and requires large amounts of chemicals. Therefore, a microbial fuel cell was developed to simultaneously produce energy and recover ammonium. The applied microbial fuel cell used a gas diffusion cathode. The ammonium transport to the cathode occurred due to migration of ammonium and diffusion of ammonia. In the cathode chamber ionic ammonium was converted to volatile ammonia due to the high pH. Ammonia was recovered from the liquid–gas boundary via volatilization and subsequent absorption into an acid solution. An ammonium recovery rate of 3.29 gN m⁻² (vs. membrane surface area) was achieved at a current density of 0.50 A m⁻² (vs. membrane surface area). The energy balance showed a surplus of energy 3.46 kJ g⁻¹, which means more energy was produced than needed for the ammonium recovery. Hence, ammonium recovery and simultaneous energy production from urine was proven possible by this novel approach.

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**1. Introduction**

1.1. Nitrogen

Ammonium is an essential nutrient and an important nitrogen source for plants. Here “ammonium” refers to the sum of volatile NH₃ and ionic NH₄⁺; the specific chemical formula are used to distinguish between NH₃ and NH₄⁺. Ammonium based fertilizers are applied on large scale to increase crop yields and to ensure a high food production. The production of ammonium fertilizer is dependent on the Haber–Bosch process, wherein N₂ is fixated as NH₃. After consumption of the produced food, nitrogen compounds (i.e., ammonia, nitrite, nitrate, etc.) end up in wastewater. These nitrogen compounds are removed as N₂ in wastewater treatment plants (WWTPs) by nitrification/denitrification or the Anammox process. The Haber–Bosch process and nitrogen removal are energy intensive and therefore costly. Energy can be saved by a direct NH₃ recovering from wastewater. The main obstacles for ammonium recovery from wastewater are low nitrogen concentration and large volumes of wastewater to be processed, which result in a high energy demand (Maurer et al., 2003).

Focussing on the composition of wastewater, 75% of the nitrogen load to a conventional WWTP originate from urine (Larsen and Gujer, 1996). However, urine only contributes 1% to the volume of the wastewater. On an average urine contains 1 g L⁻¹ phosphorus, 9 g L⁻¹ nitrogen and 10 g L⁻¹ COD.

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Due to these high concentrations, urine can be considered as a valuable resource for nitrogen, phosphorus and energy recovery. Urine can be easily separated and kept concentrated by the use of separation toilets and water free urinals.

In fresh urine most of the nitrogen is found in the form of urea ((NH₂)₂CO). Urea is hydrolysed by the bacterial enzyme urease to NH₃ and carbamate, whereas carbamate hydrolysis further to NH₃ and bicarbonate (Mobley and Hausinger, 1989). Urease is produced by bacteria found in the sanitary installation and storage tank. As a result of the decomposition of urea, the pH of the urine increases and triggers the precipitation of salts (i.e., MgNH₄PO₄·6H₂O, Ca₁₀(PO₄)₆(OH)₂, CaCO₃, etc.) (Udert et al., 2003). Ammonium concentrations up to 8.1 g L⁻¹ can be found in urine (Maurer et al., 2006).

### 1.2. Microbial fuel cell

Microbial fuel cells (MFCs) are an emerging technology with a wide range of applications (Hamelers et al., 2010). In MFCs, bacteria catalyze the oxidation of organic substrate (i.e., acetate) and produce electrons at the anode according to:

\[
\text{CH}_3\text{COO}^- + 4\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + 8\text{e}^- + 9\text{H}^+
\]  

(1)

The electrons are used to reduce an electron acceptor (i.e., O₂) at the cathode. Given the neutral to alkaline environment (pH ≥ 7) of the cathode, the reduction of oxygen results in the production of hydroxyl according to:

\[
\text{O}_2 + 4\text{e}^- + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^-
\]  

(2)

Anode and cathode are often separated by an ion exchange membrane (Logan et al., 2006). Ion exchange membrane and the cathode-electrode can be combined to form so-called membrane electrode assembly (MEA) (Larminie and Dicks, 2003; Pham et al., 2005; Prakash et al., 2010). In an MEA the membrane separates the anode from the cathode and serves as an ion conductor, while the electrode can be directly exposed to the gas phase (air-cathode).

### 1.3. Ammonium recovery by an MFC

The principle of ammonium recovery by an MFC was reported in literature (Kuntke et al., 2011) using a sacrificial K₃Fe(CN)₆-cathode and synthetic wastewater. Recently, ammonium has been reported as a proton shuttle (between anode and cathode) and ammonium recovery was demonstrated by stripping from a synthetic wastewater (Cord-Ruwisch et al., 2011). The feasibility of using highly diluted (0.035 vol/vol) urine solutions as fuel in MFCs has been reported in literature (Ieropoulos et al., 2012). The aim of this study is to investigate ammonium recovery from real undiluted urine using a more sustainable air-cathode under high NH₃ concentration and high pH. Therefore, ammonium recovery and energy production were studied not only from synthetic urine but also from real urine. The obtained results were compared to previous work (Kuntke et al., 2011). Furthermore, the energy demand for this ammonium recovery (kJ g⁻¹) was calculated and compared to the energy demand of conventional NH₃ stripping process. The new MFC facilitated ammonium recovery concept is shown in Fig. 1a.

At the anode, electrons are produced (Eq. (1)) and transported via an external load (resistor) to the cathode, where oxygen is reduced (Eq. (2)). The electron transport induces a charge transport (i.e., anion or cation transport) across the membrane to maintain the charge neutrality of the system. In case of the applied Cation Exchange Membrane (CEM), cation transport (i.e., H3O⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, NH₄⁺) occurs from the anode chamber through the CEM to the cathode chamber (migrational flux) and leads with time to a concentration gradient between cathode and anode chamber of the MFC. The pH in the cathode chamber increases during operation, due to the production of hydroxyls (OH⁻) according to Eq. (2).

Fig. 1 — (a) Schematic representation of the processes involved in the ammonium recovery using an MFC; (b) Schematic representation of the experimental setup for ammonium recovery using an MFC.
and a migrational transport of cations other than $\text{H}_2\text{O}^+$ and NH$_3^+$. During continuous MFC operation an equilibrium will be reached, where forward (anode to cathode) migrational flux and backward (cathode to anode) diffusion flux of cations will be equal and a maximum concentration of cations and OH$^-$ in the cathode chamber is reached. At this point the cathode pH remains stable, because the constant production of OH$^-$ leads to a diffusion flux of OH$^-$ from cathode to anode (Rozendal et al., 2006; Sleutels et al., 2009a).

The high pH in the cathode chamber results in to a formation of volatile NH$_3$. NH$_3$ is stripped (Cord-Ruwisch et al., 2011) from the liquid–gas boundary at the MEA by the air stream supplied to air-cathode. Subsequently, NH$_3$ can be recovered from the gas stream leaving the cathode by adsorption in an acid as NH$_4^+$. Therefore, this innovative concept couples energy production from urine by an MFC with NH$_3$ stripping.

2. Materials and methods

2.1. MFC design and experimental setup

The applied MFC was of a two chamber design similar to recently published work (Jeremiasse et al., 2010). The MFC was made from two identical Plexiglas plates (21 cm × 21 cm), each plate contained one flow through chamber (10 cm × 10 cm × 0.2 cm) with a 9 channel inlet and 9 channel outlet for flow distribution. In the anode chamber (volume 20 mL), graphite felt (100 cm$^2$ thickness 3 mm, National Electrical Carbon BV, Hoorn, The Netherlands) was used as the anode. The anode chamber and the cathode chamber (volume 20 mL) were separated using a MEA. The MEA (100 cm$^2$) was produced by hot pressing (5 min, 140 °C, 534 bar) a platinum coated (20 g m$^{-2}$) titanium fine mesh (Dexmet, Magneto Special Anodes B.V., Schiedam, The Netherlands) into a Nafion N117 (Dupont, Geneva, Switzerland) CEM using a Labopress P 400 S (Vogt Maschinenbau GmbH, Berlin, Germany). Anode (graphite felt) and cathode (Pt coated Ti felt) were each contacted via 4 Pt/Ir (80/20) wires (0.025 cm diameter, Advent Research Materials, Oxford, UK) to the outside of the MFC. Anode media was recirculated at 80 mL min$^{-1}$ through the MFC using a peristaltic pump (Masterflex, Vernon Hills, USA). New influent was supplied at a flow rate of 1 mL min$^{-1}$ by another peristaltic pump. The total volume of the anode was 250 mL, including tubes (PTFE $(10 \text{ cm}^2)$ with a 9 channel inlet and 9 channel outlet). Air was supplied to the MEA in the cathode chamber at a flow rate of 10 mL min$^{-1}$ using a compressor (Kaeser Sigma SM 9, USA), a multistage pressure regulator (VWR, The Netherlands) and a PTFE needle valve (VWR, The Netherlands) for flow control. The gas stream from the cathode was channeled through two 500 mL gas washing bottles with filter disks (Schott Duran®), VWR, The Netherlands) placed in series. The first bottle was filled with boric acid (20 $\text{g L}^{-1}$) to collect the volatile NH$_3$ as NH$_4^+$ (adsorption bottle). The boric acid was renewed periodically. The gas stream from the adsorption bottle was channeled to a second bottle filled with a 0.4M $\text{H}_2\text{SO}_4$ to prevent contamination of boric acid with ammonia from the laboratory environment. Fig. 1b presents the scheme of the experimental setup.

2.2. MFC operation

The MFC was inoculated using effluent of another active MFC operated at 30 °C on synthetic media with acetate (Kuntke et al., 2011). The anode potential of the MFC was measured via a Haber–Luggin capillary relative to an Ag/AgCl reference electrode (−0.200 V vs. NHE, ProSense QiS, Oosterhout, The Netherlands). The anode pH was measured using an Orbisint CPS11D pH electrode connected to a Liquisys M CPM 253 transmitter (Endress + Hauser B.V., Naarden, The Netherlands). The cell voltage, anode potential and the pH in the anode chamber were recorded in a 5 s interval using an Ecograph T data logger (RSG 30, Endress + Hauser B.V., Naarden, The Netherlands). The anode and the cathode were connected through an external resistor.

The experiment consisted of two parts. In part one, synthetic urine was used to study the effects of anode ammonium concentration and electron transport rate (current density) on ammonium transport. In part two, the feasibility of this ammonium recovery and energy production by an MFC was studied under realistic conditions using real urine.

The effects of an increasing anode ammonium concentration on the ammonium recovery was studied at a high external resistance 1 kΩ. The effects of the electron transport rate on the ammonium recovery was studied at constant anode ammonium concentration and a decreasing external resistance. Further details about part one of this experiment are given in Table 1.

The synthetic urine contained 1.36 g $\text{L}^{-1}$ $\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$, 0.74 g $\text{L}^{-1}$ $\text{KCl}$, 0.58 g $\text{L}^{-1}$ $\text{NaCl}$, 0.68 g $\text{L}^{-1}$ $\text{KH}_2\text{PO}_4$, 0.87 g $\text{L}^{-1}$ $\text{K}_2\text{HPO}_4$, 0.28 g $\text{L}^{-1}$ $\text{NH}_4\text{Cl}$, 0.1 g $\text{L}^{-1}$ $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.1 g $\text{L}^{-1}$ $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.1 mL $\text{L}^{-1}$ of a trace element mixture (Sleutels et al., 2009b). The ammonium concentration was increased by addition of NH$_4$Cl. All chemicals were purchased at VWR (Amsterdam, The Netherlands) in analytical grade. The synthetic urine had a measured COD of 600 mg $\text{L}^{-1}$.

On day 77 the influent was changed to real urine and one day later the effluent of the MFC was connected to the influent tank to recycle the same batch urine over a longer period of time. The ammonium concentrations in the urine batch were expected to decline at a moderate rate based on the expected produced currents and previous experiments (Kuntke et al., 2011). Therefore, the same batch of urine can be recycled for longer periods without the risk of depleting the urine batch of COD or ammonium. Two batches of urine (each 9 L) were used during part two of the experiment. This urine (from 60 persons 6 female and 54 male) was collected at Landustrie B.V. (Sneeck, The Netherlands) by DeSaH B.V. (Sneeck, The Netherlands) using separation toilets (Villeroy & Boch Gustavsberg AB, Gustavsberg, Sweden) and Urimat® eco, water free urinals (Biocompact Environmental Technology B.V., Rotterdam, The Netherlands). The urine was pretreated by centrifugation at 8000 rpm for 5 min (Avanti J-26XP, Beckman Coulter, USA) to remove particulate matter, suspended particles and crystals (i.e., struvite).
Table 1 - Ammonium concentration, applied external resistances during the experiment, conductivity influent and pH of the influent.

<table>
<thead>
<tr>
<th>Time (d)</th>
<th>Anode ammonium concentration (gNH₄ L⁻¹)</th>
<th>External resistance (Ω)</th>
<th>Conductivity influent (mS cm⁻¹)</th>
<th>pH influent (⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–6</td>
<td>0.07c</td>
<td>1000</td>
<td>5.4</td>
<td>7.0</td>
</tr>
<tr>
<td>7–14</td>
<td>0.07</td>
<td>1000</td>
<td>5.4</td>
<td>7.0</td>
</tr>
<tr>
<td>15–20</td>
<td>0.5</td>
<td>1000</td>
<td>9.1</td>
<td>7.0</td>
</tr>
<tr>
<td>21–27</td>
<td>1.0</td>
<td>1000</td>
<td>13.3</td>
<td>7.0</td>
</tr>
<tr>
<td>28–34</td>
<td>2.0</td>
<td>1000</td>
<td>21.5</td>
<td>6.9</td>
</tr>
<tr>
<td>35–41</td>
<td>3.0</td>
<td>1000</td>
<td>29.2</td>
<td>6.9</td>
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<td>42–48</td>
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<td>37.2</td>
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<td>4.0</td>
<td>500</td>
<td>37.2</td>
<td>6.8</td>
</tr>
<tr>
<td>56–62</td>
<td>4.0</td>
<td>250</td>
<td>37.2</td>
<td>6.8</td>
</tr>
<tr>
<td>63–76</td>
<td>4.0</td>
<td>100</td>
<td>37.2</td>
<td>6.8</td>
</tr>
<tr>
<td>77–119</td>
<td>4.05b</td>
<td>500</td>
<td>35.0</td>
<td>8.85</td>
</tr>
<tr>
<td>120–135</td>
<td>3.96b</td>
<td>250</td>
<td>35.0</td>
<td>8.85</td>
</tr>
<tr>
<td>136–149</td>
<td>4.05b</td>
<td>250</td>
<td>35.0</td>
<td>8.85</td>
</tr>
<tr>
<td>150–160</td>
<td>4.01a</td>
<td>100</td>
<td>35.0</td>
<td>8.85</td>
</tr>
</tbody>
</table>

a Inoculation.

b 1st batch real urine.

c 2nd batch real urine.

Table 2 presents key parameters measured in the real urine after centrifugation.

2.3. Chemical analysis

The urine was analyzed for the concentration of relevant cations, anions and COD after centrifugation. An ICP-OES, type Perkin Elmer Optima 5300 DV (Waltham, Massachusetts, USA) was used to determine cation concentrations. An ion chromatograph, type Metrohm IC Compact 761 (Schiedam, The Netherlands) was used to determine anion concentrations. The COD was analyzed using test kit LCK 303 (Dr. Lange, HACH, Loveland, Colorado, USA) and a spectrophotometer HACH XION 500 (HACH, Loveland, Colorado, USA). Ammonium concentrations from the absorption bottle were measured throughout the experimental time to determine ammonium transport numbers. Samples of the influent and anode media were filtered (0.45 μm, PTFE syringe filters, VWR, Amsterdam, The Netherlands) prior to analysis. All samples were analyzed in duplicate. The conductivity was determined using a conductivity electrode QC281x and a controller P 862 (ProSense BV – QiS, Oosterhout, The Netherlands).

2.4. Calculation

The current density was calculated according to:

\[ I = E_{cell} R^{-1} A^{-1} \]

where \( I \) (A m⁻²) is the current density, \( E_{cell} \) (V) is the cell voltage, \( R \) (Ω) is the external resistance and \( A \) (m²) is the surface area of the membrane (equal to the projected anode surface area). The power density (W m⁻²) is calculated according to:

\[ P = I \cdot E_{cell} \]

From the recorded (pH and anode potential) and calculated (current density and power density) parameters average values and standard deviation were calculated based on the results obtained during a specific set of operation conditions (applied concentration or resistance) over a certain period of time (as indicated in Table 1). The amount of produced charge (\( Q_e \)), expressed in coulombs (C), was calculated according to:

\[ Q_e = \int_0^t i dt \]  

(3)

Where \( i \) is the current (A) produced by the MFC over a certain sampling period. The transport of ammonium from anode to cathode was determined indirectly by measuring the ammonium concentration in the gas washing bottle filled with boric acid. The ammonium transport (\( Q_{NH_4} \)) is presented as charge transport, which is expressed in coulombs (C) and was calculated according to:

\[ Q_{NH_4} = (c_{NH_4} - c_{NH_4_1}) \cdot V \cdot z_{NH_4} \cdot F \]

(4)

Where, \( c_{NH_4} \) (mol L⁻¹) is the concentration of ammonium at the end of a certain sampling period, \( c_{NH_4_1} \) (mol L⁻¹) is the concentration of ammonium at the start of a certain sampling period, \( V \) (L) is the volume of the boric acid used in the adsorption bottle, \( z_{NH_4} \) (⁻) is the charge of the NH₄⁺ and \( F \) is the Fricke constant.
Faraday constant (96,485 C mol⁻¹). The Coulombic efficiency (η_CE) was calculated according to:

\[
\eta_{CE} = \frac{Q_e}{F b (\frac{1}{M_{O_2}}) \Delta COD \cdot V}
\]

(5)

Where \(Q_e\) is the amount of produced coulombs during a specific time period (Eq. (3)), \(b\) is the amount of electrons (4) exchanged per mole of \(O_2\), \(F\) is the Faraday constant, \(M_{O_2}\) is the molar mass of oxygen, \(\Delta COD\) is the change in the measured COD during a specific time period and \(V\) is the volume of the urine (9 L).

The NH₃ content (%) present in solution at a specific pH was calculated according Eq. (6) based on a \(pK_A\) of 9.24 (at 25 °C) (Tchobanoglous et al., 2003).

\[
\text{NH}_3 \text{ content} = 100 \left[ 1 + \frac{10^{-\text{pH}}}{10^{-pK_A}} \right]
\]

(6)

The ammonium recovery rate (gN d⁻¹ m⁻²), which is based on the daily measured ammonium transport and the membrane surface area was calculated according to:

\[
\text{Recovery rate} = \frac{\Delta (m_i)}{A_M}
\]

(7)

Where \(\Delta (m_i)\) is the transported amount of NH₄⁰ or NH₃ amount (gN d⁻¹) and \(A_M\) is the membrane area (m²).

3. Results and discussion

3.1. Ammonium recovery from synthetic urine

In part one of the experiment, first the effect of an increasing anode ammonium concentration and then the effect of an increasing current density on the ammonium transport were investigated. Fig. 2a shows the average anode potential and the average current density reached at constant external resistance (1 kΩ) at increasing anode ammonium concentrations.

The current density stabilises above an ammonium concentration of 1 gN L⁻¹ and shows a peak at an ammonium concentration of 2 gN L⁻¹. At 2 gN L⁻¹ an average current density of 59 mA m⁻² and an average power density of 34.22 mW m⁻² were obtained. The measured average anode potential shows only a marginal increase with an increasing anode ammonium concentration. The results show that no adverse effects were found in the tested ammonium concentration range. This observation is in agreement with earlier published work (Kuntke et al., 2011). However, these results are in contrast to the reported ammonium toxicity in a single chamber MFC (Nam et al., 2010).

For all applied anode ammonium concentrations, the relation between ammonium transport and produced charge is shown in Fig. 2b. A direct linear relation (\(R^2 = 0.995\)) was found between ammonium transport and produced charge in these experiments. Independent of the ammonium concentration, 30% (slope = 0.30) of the produced charge was used for ammonium transport to the cathode.

Fig. 3a shows measured average anode potential, current density and average power density obtained at higher current densities and a constant anode ammonium concentration (4 gN L⁻¹).

At an increasing current density (from 0.1 to 0.47 A m⁻²), a slight increase of the anode potential was observed (from -0.42 to -0.39 A m⁻²). A power density of 222 mW m⁻² was measured at a current density of 0.47 A m⁻² under the given operational conditions. The obtained current densities in this work were found to be lower than the current density obtained in previous work (Kuntke et al., 2011). This difference can be explained by the respective cathode systems used in the experiments. The air-cathode is affected by the conditions (e.g., pH, low buffer concentration, oxygen supply) found in the MFC (Zhao et al., 2006), whereas the K₃Fe(CN)₆-cathode is not limited by these conditions.

![Fig. 2 – (a) Average anode potential and average current density with standard deviation obtained at 1 kΩ and at increasing ammonium concentrations (day 7–48 synthetic urine); (b) Ammonium transport against produced charge from day 7 until day 48.](image-url)
The relation between ammonium transport and produced charge at these current densities is shown in Fig. 3b. A direct linear relation ($R^2 = 0.998$) was found between ammonium transport and produced charge in these experiments at the different current densities. The ammonium transport increased together with produced charge. Independent of the current density, 31% (slope 0.31) of the produced charge from synthetic urine was used to transport ammonium. The ammonium transport using a K$_3$Fe(CN)$_6$-cathode was reported to be 50% of the produced charge (Kuntke et al., 2011). This difference could be caused by the difference in MFC designs. The advantage of the air-cathode is the removal of NH$_3$ from the cathode by the supplied air (Kim et al., 2008). In a K$_3$Fe(CN)$_6$-cathode, ammonium is concentrated in the cathode and needs to be separated from K$_3$Fe(CN)$_6$ in an additional step (i.e., NH$_3$ stripping). Since the pH of the K$_3$Fe(CN)$_6$-cathode does not increase during operation, chemicals need to be added prior to NH$_3$ stripping.

The ammonium transport was found to be independent from the anode ammonium concentration and increases with current density. This successfully demonstrates the principal of ammonium recovery and energy production from synthetic urine by an MFC using an air-cathode system.

### 3.2. Ammonium recovery from real urine

In part two of the experiment, ammonium recovery from real urine was investigated. Fig. 4a shows the measured average anode potential, current density and power density obtained during experiments with real urine.

A stable anode potential was observed, at increasing current density. A power density of 250 mW m$^{-2}$ was
measured at a current density of 0.50 A m\(^{-2}\) under the given operational conditions. Although a more complex substrate was used comparable current densities and power densities were obtained during the operation on real urine and synthetic urine. This shows that the biomass was able to use real urine as a substrate. The anode potentials were lower during the operation on real urine compared to operation on synthetic urine. This decrease in anode potential can be explained by the change in the anode pH. Fig. 4b shows the average recorded anode pH during the experiments. The anode pH during operation on synthetic urine was 6.8 ± 0.1 and the anode pH during operation on real urine was 8.85 ± 0.1. The anode pH remained stable at 8.85 during the operation on urine, because of the high concentration of buffer present. The two buffers present were ammonium—ammonia (pK\(_A\) = 9.24) with a concentration of 0.29 mol L\(^{-1}\) and bicarbonate—carbonate (pK\(_A\) = 10.33) with a concentration of 0.25 mol L\(^{-1}\).

The anode potential (Logan et al., 2006) decreases with a decreasing proton concentration (due to the high pH) at the anode according to:

\[
E_{\text{Anode}} = E_0 - \frac{R T}{n F} \ln \left( \frac{[\text{CH}_3\text{COO}^-]}{[\text{HCO}_3^-] [\text{H}^+]^n} \right)
\]

Where \(E_{\text{Anode}}\) (V) is the standard potential of the anode reaction, \(R\) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \(T\) the temperature (K), \(n\) the number of electrons transferred per reaction (mol), \(F\) the Faraday constant (96,485 C mol\(^{-1}\)), \([x]\) the concentration (mol L\(^{-1}\)) of the reactants (x).

High ammonium concentrations have been reported to inhibit microbial processes and to influence the performance of anaerobic digestion (Braun et al., 1981; van Velsen, 1981). Generally, the NH\(_3\) form has been reported to be more toxic than the NH\(_4\) form (Koster and Koomen, 1988). The anolyte ammonium concentration was measured after 2 days of operation and from the result the NH\(_3\) concentration in the anode was 1.15 g N L\(^{-1}\) as a result of the anode pH. However, no toxic effects on the biological processes in the MFC were found, since the anode potential remained stable at increasing current densities and power densities. These results are in contrast to report ammonium toxicity in a single chamber MFC (Nam et al., 2010), which showed that already a low NH\(_3\) concentration can be toxic. However, the operational condition (start up, cell type) and the inoculums (possible adaptation to a high ammonium concentration) were different in the respective works. No published information was found on MFC operation at high ammonium concentrations at alkaline pH condition (pH ≥ 8.5) for comparison.

Although similar current densities were obtained with synthetic urine and real urine, the daily ammonium transport was significantly higher in experiments with real urine (Table 3).

Also the relation between ammonium transport and produced charge was different during the operation on real urine (Fig. 5).

A slope of 1.32, 0.81 and 0.53 was found at a current density of 0.11, 0.22 and 0.50 A m\(^{-2}\), respectively. A slope higher than 1.00 shows that more coulombs of ammonium were transported than coulombs of electrons were transported. Therefore, the ammonium transport cannot solely originate from migrational transport. Since convection transport of ammonium is impossible through a CEM, the ammonium transport is limited to migration and diffusion. The explanation for this difference in ammonium transport is diffision of NH\(_3\). NH\(_3\) diffusion through perfluorosulfonic ion exchange membrane (“Nafion”) has been reported in literature (He and Cussler, 1992; Tricoli and Cussler, 1995; Vorobiev and Beckman, 2002). At a pH ≤ 7 (operation on synthetic urine) less than 0.7% of the ammonium is present as NH\(_3\). Whereas at a pH of 8.85 (operation on urine) 28.5% of the ammonium is present as NH\(_3\) (see Eq. (6)).

The NH\(_3\) diffusion (\(n_{\text{NH}_3, \text{diff}}\)) can be determined by calculation, because the total ammonium transport (\(n_{\text{NH}_3, \text{total}}\)) is equal to the sum of NH\(_3\) diffusion and NH\(_4\) migration (\(n_{\text{NH}_4, \text{mig}}\)).

\[
\tag{9}
\begin{align*}
\bar{n}_{\text{NH}_3, \text{total}} &= \bar{n}_{\text{NH}_3, \text{diff}} + \bar{n}_{\text{NH}_4, \text{mig}} \\
\bar{n}_{\text{NH}_4, \text{mig}} &= \alpha \bar{n}_{\text{e}}
\end{align*}
\]

Where \(\bar{n}_{\text{NH}_3, \text{total}}\) (mmol d\(^{-1}\)) is the measured total ammonium transport, \(\bar{n}_{\text{NH}_3, \text{diff}}\) (mmol d\(^{-1}\)) is the NH\(_3\) diffusion and \(\alpha\) is

Table 3 – Average ammonium transport (C d\(^{-1}\)) and the average produced charge (C d\(^{-1}\)) during operation on synthetic urine (4 gN L\(^{-1}\)) and real urine at the respective current densities.

<table>
<thead>
<tr>
<th></th>
<th>Synthetic urine</th>
<th>Real urine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Q_{\text{NH}_3}) (C d(^{-1}))</td>
<td>(Q_e) (C d(^{-1}))</td>
</tr>
<tr>
<td>0.10</td>
<td>27 ± 5</td>
<td>85 ± 5</td>
</tr>
<tr>
<td>0.22</td>
<td>61 ± 2</td>
<td>185 ± 3</td>
</tr>
<tr>
<td>0.47</td>
<td>117 ± 13</td>
<td>406 ± 8</td>
</tr>
</tbody>
</table>

Fig. 5 – Ammonium transport against produced charge at different current densities during operation on real urine.
a factor and \( n_A \) (mmol d\(^{-1}\)) is amount of transported electrons (measured current). \( n_{NH_4} \) and \( \alpha \) were determined using the amount of transported electrons and total ammonium transport obtained during the experiments at different current densities. \( n_{NH_4} \) was 0.995 ± 0.06 mmol d\(^{-1}\) (equal to 96 ± 6 C d\(^{-1}\)) and \( \alpha \) was 0.31 ± 0.01. Hence, the diffusion of \( NH_3 \) from the anode to cathode chamber affects the total ammonium transport. As shown in Section 3.1, similar \( \alpha \) values (i.e., 0.30 and 0.31) were obtained during experiments using synthetic urine.

To determine \( NH_3 \) diffusion experimentally, synthetic urine (ammonium concentration (4 g N L\(^{-1}\)) without NaCH\(_3\)COO·3H\(_2\)O) was prepared according to details given in section 2.2 and adjusted to the desired pH using 1M NaOH. The setup was identical to the MFC setup, while anode and cathode were not connected by an external circuit. No ammonium transport was measured during 7 days of operation at an anode pH of 7. A diffusional ammonium transport of 1.03 ± 0.05 mmol d\(^{-1}\) (equal to 100 ± 5 C d\(^{-1}\)) was measured during 7 days of operation at an anode pH of 8.8.

The \( NH_3 \) diffusion accounts for 42.2% of the ammonium transport measured at the highest current density, whereas at lower current densities \( NH_3 \) diffusion is the dominant ammonium transport mechanism.

### 3.3. Ammonium recovery rates

The ammonium recovery rates were determined according to Eq. (7). The highest ammonium recovery rate was 3.29 g\(_{NH_4}\) d\(^{-1}\) m\(^{-2}\) at a current density of 0.50 A m\(^{-2}\). This recovery rate can be divided into \( NH_3 \) diffusion (concentration gradient and pH dependent) and \( NH_4^+ \) migration (current density and concentration dependent). Fig. 6 shows the ammonium recovery rates with the respective \( NH_3 \) transport and \( NH_4^+ \) transport obtained during the experiments on real urine.

Higher ammonium recovery rates can be reached by increasing the current density or increasing the \( NH_4^+ \) diffusion.

### 3.4. Energy analysis for ammonium recovery by MFC

The energy analysis for ammonium recovery by MFC was performed at the highest current density (highest ammonium recovery) for an MFC, operated on real urine, with a membrane surface area of 1 m\(^2\) and compared to conventional \( NH_3 \) stripping. The energy demand of the ammonium recovery by MFC was calculated based on aeration, the energy demand for ammonium recovery (adsorption in H\(_2\)SO\(_4\)) and the energy production of the MFC. The energy demand for aeration (\( E_{aeration} \) (kJ g\(^{-1}\)) of the scaled-up MFC was calculated according to:

\[
E_{aeration} = \frac{\Delta P \cdot Q \cdot 86400}{\eta \cdot A_M \cdot recovery \ rate}
\]

Where \( \Delta P \) is the measured pressure drop in the gas diffusion cathode 2.0 \( 10^{-7} \)N m\(^{-2}\) in a single cell, \( Q \) is the air flow \( (1.67 \ 10^{-7} \text{ m}^3 \text{ s}^{-1}) \), \( \eta \) is the pump efficiency (conservatively chosen 0.8), \( A_M \) is the membrane area (0.01 m\(^2\)), 86,400 (s d\(^{-1}\)) is the amount second per day and recovery rate \((g_{NH_4} \text{ d}^{-1} \text{ m}^{-2})\) is the ammonium recovery rate (Eq. (7)). The \( \Delta P \) measured in a single cell is representative for a scaled-up MFC, which is a stack of identical cells with similar geometry to the here applied prototype. An energy demand for aeration of 10.93 kJ g\(_{NH_4}\) was calculated. Details about the energy demand of conventional \( NH_3 \) stripping, including chemical usage (CaO and H\(_2\)SO\(_4\)) and aeration were obtained from literature (Maurer et al., 2003). The comparison between ammonium recovery by MFC and conventional \( NH_3 \) stripping is shown in Table 4.

These results highlight the advantages of the MFC facilitated ammonium recovery over the conventional \( NH_3 \) stripping. The ammonium recovery by MFC requires less energy for aeration. The MFC produces energy and no CaO (or NaOH) addition is necessary for the \( NH_4^+ \) stripping. Therefore, a net energy yield of −3.46 kJ g\(_{NH_4}\) was calculated for ammonium recovery by MFC, whereas the conventional \( NH_3 \) stripping needs 32.5 kJ g\(_{NH_3}\) (Maurer et al., 2003).

<table>
<thead>
<tr>
<th>Table 4 – Detailed energy analysis for conventional ( NH_3 ) stripping and ammonium recovery by MFC.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH(_4) recovery by MFC</td>
</tr>
<tr>
<td>Aeration (kJ g(_{NH_4}))</td>
</tr>
<tr>
<td>Energy production (kJ g(_{NH_4}))</td>
</tr>
<tr>
<td>CaO (kJ g(_{NH_4}))</td>
</tr>
<tr>
<td>H(_2)SO(<em>4) (kJ g(</em>{NH_4}))</td>
</tr>
<tr>
<td>Net energy yield (kJ g(_{NH_4}))</td>
</tr>
</tbody>
</table>

a (Maurer et al., 2003).
b Not required.
3.5. Perspectives for the ammonium recovery by MFC

One drawback of the ammonium recovery by MFC is that only 31% of the produced electrons ($\eta_e \leq 0.31$) were used for transport of ammonium. This limits the total amount of ammonium which can be transported by migration. The measured COD of the urine (3.9 g L$^{-1}$) shows that a maximum of 0.49 mol of electrons (per litre urine) can be produced and therefore only 0.15 mol of NH$_4^+$ (50%) can be recovered. The COD in the urine batches was monitored during the experiments, after COD decreased to 1.5 g L$^{-1}$ the urine batch was changed. A Coulombic efficiency of 10% was calculated during the operation on real urine at the highest current density, which shows that further improvements are needed. An electricity production coupled to ammonium, as shown recently (He et al., 2009), was not possible in this tested prototype MFC, because the anode was anaerobe and no nitrite was measured during experiments. The total ion transport through the membrane can be influenced by the ion concentration at the anode and cathode (Rozendal et al., 2006). A lower NH$_4^+$ concentration at the cathode compared to the anode leads to NH$_3$ diffusion. At the same time the ammonium transport is influenced by the NH$_3$ diffusion through the membrane. Therefore, ammonium needs to be removed from the cathode at a high rate to increase the total ammonium transport.

To become a competitive ammonium recovery technology, the ammonium recovery rate ($g_\text{NH}_4$ m$^{-2}$ h$^{-1}$) must be increased. Since a higher current density leads to a higher rate of NH$_4^+$ transport, this can be achieved by increasing the current densities of the MFC. Recent literature reports current densities up to 5.5 A m$^{-2}$ for a scaled-up MFC (Ter Heijne et al., 2011) and 22.8 A m$^{-2}$ for a Microbial Electrolysis Cell (Jeremiasse et al., 2010) on a similar cell design. Although these current densities were reached using synthetic media, it shows that high current densities can be reached in bioelectrochemical systems.

The potential ammonium recovery efficiency ($\eta_{\text{NH}_4}$) was calculated on basis of the measured Coulombic efficiency ($\eta_{\text{CE}}$), the measured ratio of charge transport ($Q_{\text{NH}_4}$) to produced charge ($Q_e$) during experiments on real urine and the realistic concentration of ammonium ($C_{\text{NH}_4-N} = 8.1$ g L$^{-1}$) and COD (10 g L$^{-1}$) found in urine (Maurer et al., 2006) for a scaled-up MFC according to:

$$\eta_{\text{NH}_4} = \frac{b}{Q_e} \cdot \eta_{\text{CE}} \cdot \frac{Q_{\text{NH}_4}}{M_{\text{NH}_4}} \frac{C_{\text{NH}_4-N}}{M_N} \quad (12)$$

Where $b$ is the amount of electrons (4) exchanged per mole of $O_2$, $M_{\text{O}_2}$ is the molar mass of $O_2$, $M_{\text{N}}$ is the standard atomic weight of nitrogen, $\eta_{\text{CE}}$ is the Coulombic efficiency (0.1) and $Q_{\text{NH}_4}/Q_e$ is ratio of total ammonium transport to produced charge (0.53). A potential ammonium recovery efficiency of 11.4% was found. The low Coulombic efficiency and the relative low total ammonium transport to produced charge ratio are the limiting factors for the recovery of ammonium by MFC. The Coulombic efficiency can be increased by limiting unwanted biomass growth (i.e. methanogens), due to an optimized operational control (i.e. lower retention time of anolyte) of the MFC (Hamelers et al., 2010). Further investigation on ammonium recovery and Coulombic efficiency will be performed on a scaled-up version of this promising new technology.

The precipitation of crystals (e.g. struvite) inside MFCs is an important issue to consider when using highly concentrated streams (like urine) as a fuel. As a pretreatment step, partial removal of phosphorus, can be necessary to avoid precipitation inside the MFC. In this work, the precipitated crystals were removed from the hydrolyzed urine to avoid scaling inside the MFC. No further precipitation inside the MFC was observed during the experiments.

4. Conclusions

This work demonstrates successfully the principal of simultaneous ammonium recovery and energy production from real urine using an MFC. The electrons needed for the transport of NH$_4^+$ from anode to cathode are produced by microorganisms on the anode. Additional NH$_3$ diffusion enhances the total ammonium transport to the cathode. NH$_3$ stripping from the liquid–gas boundary at the cathode occurs due to the localized high pH and the aeration of the gas diffusion cathode. The energy analysis shows that this technology can be a sustainable ammonium recovery technology. Further improvements to the ammonium transport rates are necessary, in order to become a competitive ammonium recovery technology.

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References

He, Z., Kan, J., Wang, Y., Huang, Y., Mansfeld, F., Nealsion, K.H., 2009. Electricity production coupled to ammonium in...


