Hydrogen production and ammonium recovery from urine by a Microbial Electrolysis Cell


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Abstract

We investigated the use of a Microbial Electrolysis Cell (MEC) for the ammonium removal, COD removal and hydrogen production from five times diluted urine. During operation with a batch cathode, a current density of 23.07 ± 1.15 A m⁻² was achieved corresponding to a hydrogen production rate of 48.6 ± 7.47 m³ H₂ m⁻³ MEC d⁻¹, an ammonium removal rate of 173.4 ± 18.1 g N m⁻² d⁻¹ and a COD removal rate of 171.0 ± 16.9 g COD m⁻² d⁻¹. Ammonia stripping was not possible in the applied MEC and ammonia diffusion from cathode to anode compartment led to a relatively short stable operation period. The stable operation period was prolonged by addition of new cathode media (HRT 6 h), but this resulted in a lower current density (14.64 ± 1.65 A m⁻²), hydrogen production rate (32.0 ± 0.89 m³ H₂ m⁻³ MEC d⁻¹), ammonium removal rate (162.18 ± 10.37 g N m⁻² d⁻¹) and COD removal rate (130.56 ± 4.45 g COD m⁻² d⁻¹).

1. Introduction

On average one person excretes 1.5 L of urine per day, which corresponds with about 1 volume% of the total produced domestic wastewater. At the same time approximately 80% of the total amount of nitrogen (N) present in this wastewater originates from urine [1,2]. Most nitrogen in urine is found in the form of urea. In the presence of the enzyme urease, urea is hydrolysed to ammonia and carbamate, whereas carbamate further decomposes to bicarbonate and ammonia [3]. As a result of this hydrolysis and subsequent decompositions, ammonia and ammonium account for 90% of the nitrogen in urine [4]. Conventionally, nitrogen compounds are removed from wastewater as they increase the risk of eutrophication of receiving water bodies. At the same time large amounts of nitrogen fertilizers are produced and applied in agriculture. In 2012 approximately 10.5 Mt N based fertilizers were used in the EU [5].

Removal or recovery of nitrogen from wastewater and urine is energy intensive; conventional nitrification and denitrification requires 45 kJ g⁻¹ N removed, nitrogen removal by the Sharon and Anammox process requires 16–19 kJ g⁻¹ N removed, while ammonia recovery by NH₃ stripping requires an even higher 32.5 kJ g⁻¹ N recovered [2].

Recent work has demonstrated that ammonia can be recovered in a bioelectrochemical system (BES), in this case a Microbial Fuel Cell (MFC), in which no power was consumed but a net energy production of 3.46 kJ g⁻¹ N recovered was achieved [6]. BES are an emerging field focussing on various applications, which are ranging from energy [7,8] and...

A BES consists of two electrodes; an anode and a cathode which are often separated by an ion selective membrane. At the anode, bacteria catalyse the oxidation of organic matter to electrons, carbon dioxide and protons. In the absence of an electron acceptor (oxygen) at the anode, the electrons are transferred by the bacteria to the electrode and are transported via the electrical circuit to the cathode. At the cathode a reduction reaction takes place. In case of an MFC, oxygen is reduced to water and hydroxyl ions are produced [12]. The electron transport over the electrical circuit induces an ion transport over the ion exchange membrane to compensate for the negative charge transport (electrons) and maintain electro neutrality of the system [13–15]. Due to the hydroxyl ion production the pH in the cathode chamber increases and ammonium (NH₄⁺) transforms into volatile ammonia (NH₃), which can be recovered from the cathode compartment by NH₃ stripping [6, 16]. In case of a Microbial Electrolysis Cell (MEC), water is reduced to hydrogen and hydroxyl ions at the cathode [9]. The use of an MEC instead of an MFC for recovery of ammonia from urine can have distinct advantages. The hydrogen gas production eliminates the need of aeration of the cathode, which is necessary in an MFC based ammonium recovery concept, and the produced hydrogen gas has a higher economic value than electricity [17]. Furthermore, the produced hydrogen gas in the cathode can aid in the removal of ammonia from the liquid phase of the cathode and thereby increase the driving force for removal of ammonium from the anode compartment [18]. Finally, the applied voltage allows for higher current densities to be gained, which increases the ammonium transport and removal rate [17].

In this work we demonstrate the use of an MEC for the treatment of urine. This manuscript shows that hydrogen can be produced and ammonium can be recovered from urine at the same time. The performance of the MEC was assessed by the current density, the coulombic efficiency, the hydrogen production rate, the cathode efficiency, the ammonium removal rate, ammonium removal efficiency, COD removal rate, COD removal efficiency and the energy requirement of the MEC.

2. Material and methods

2.1. Setup and experimental procedures

The experimental setup consisted of a 2 chamber MEC (Fig. 1A) made from titanium (Magneto Special Anodes, Schiedam, The Netherlands) with platinum (Pt) coated flow fields using 2.5 μm Pt coating (50 g Pt/m²). The flow field of the anode was 100 × 100 × 4 mm (40 mL), with 8 channels at the inlet and outlets over which the flow was distributed. The cathode flow field was 100 × 100 × 1 mm (10 mL) with one channel at the inlet and outlet on opposite sides of the flow field. The anode consisted of a graphite felt 100 × 100 × 2.8 mm (Morgan AM&T Swansea, UK). The graphite felt was compressed with spacer material (thickness 1 mm, 64% open; PETEX 07-4000/64, Sefar

![Fig. 1](image-url) A) schematic representation of the MEC, B) the experimental used during the experiment. The dashed line in indicates the configuration during experiment D, where the cathode media was replenished.
Anode and cathode potentials were measured individually with Ag/AgCl 3 M KCl reference electrodes (+200 mV Vs NHE, Prosense QiS, Oosterhout, The Netherlands) through a capillary filled with 3 M KCl connected to the MEC. The MEC was connected to a potentiostat (KP 07, Bank Elektronik Intelligent Controls GmbH, Pohlheim, Germany) in a two electrode mode (Endress + Hauser, Naarden, The Netherlands). The temperate of the MEC was controlled at 30 °C. Anode and cathode potentials were measured individually using an Ecograph T, RSG30 data logger (Endress + Hauser, Naarden, The Netherlands). The headspace was 600 mL. The gas outlet of the flask was connected via a second flask (0.5 L) filled with 100 mL 20 g L−1 H3BO3 to a gas flow meter (Milligascounter, Ritter, Bochum, Germany). Liquid samples of the catholyte (cathode media) were taken via a sample port in the catholyte recycle and gas samples from the headspace were taken through a septum from the head space of the recycle flask.

Anode and cathode potentials were measured individually with Ag/AgCl 3 M KCl reference electrodes (+200 mV Vs NHE, Prosense QiS, Oosterhout, The Netherlands) through a capillary filled with 3 M KCl connected to the MEC. The MEC was connected to a potentiostat (KP 07, Bank Elektronik Intelligent Controls GmbH, Pohlheim, Germany) in a two electrode mode at a constant applied voltage of 1.0 V. The current was measured using the current output connection of the potentiostat. The current, applied voltage, anode potential, cathode potential, anode pH and cathode pH were recorded in a 10 min interval using an Ecograph T, RSG30 data logger (Endress + Hauser, Naarden, The Netherlands). The temperature of the MEC was controlled at 30 °C (±1 °C) using electrical heated pads connected to both anode and cathode sides of the MEC. The MEC was inoculated with effluent of an operational MEC [19]. Over a period of 6 weeks the applied cell voltage (Ecell) was step wise (100 mV) increased from 0.6 V to 1.0 V. Then four different experiments at Ecell of 1.0 V were performed to assess the possibility of the MEC to produce hydrogen and recover ammonium from urine. Table 1 shows these experiments and the experimental parameters.

Table 1 – Experimental design.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Feed stream</th>
<th>HRT anolyte</th>
<th>HRT catholyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Synthetic wastewater</td>
<td>1 h</td>
<td>–a</td>
</tr>
<tr>
<td>B</td>
<td>5x diluted urine</td>
<td>2 h</td>
<td>–a</td>
</tr>
<tr>
<td>C</td>
<td>5x diluted urine</td>
<td>1 h</td>
<td>–a</td>
</tr>
<tr>
<td>D</td>
<td>5x diluted urine</td>
<td>1 h</td>
<td>6 h</td>
</tr>
</tbody>
</table>

*a Batch cathode operation.*
coulombic efficiency ($\eta_{\text{CE}}$), which was determined from the measured current and the removed COD as described by Logan et al. [9]. The volumetric hydrogen production rate ($\text{m}^3 \text{H}_2 \text{m}^{-3} \text{MEC d}^{-1}$) was determined from the measured volume of hydrogen produced during stable operation over a period of one hour, multiplied by 24 h d$^{-1}$ and normalized for the specific volume of the MEC (50 mL). The ammonium removal efficiency ($\eta_{\text{NH}_4^+ - \text{N}}$) was determined from the difference in measured ammonium–nitrogen concentration of the influent and effluent of the anode compartment. The ammonium removal rate ($\text{g N m}^{-2} \text{d}^{-1}$) was determined from the difference in the measured ammonium–nitrogen concentration ($\text{g N L}^{-1}$) of the influent and effluent of the anode compartment, which was normalized to the projected membrane surface area (0.01 m$^2$) and the hydraulic loading rate of the MEC (L d$^{-1}$).

3. Results and discussion

In this work we demonstrate the use of an MEC for the treatment of urine. This manuscript shows that hydrogen can be produced and ammonium can be recovered from urine simultaneously. The performance of the MEC was assessed by the current density, the coulombic efficiency, the hydrogen production rate, the cathode efficiency, the ammonium removal rate, ammonium removal efficiency, COD removal rate, COD removal efficiency and the energy requirement of the MEC.

3.1. Urine treatment in MECs produces high current densities

Fig. 2 shows the average measured current density ($\text{A m}^{-2}$) and average anode pH ($\text{pH}$) during the 4 different experiments. During 6 days of operation on synthetic wastewater (Fig. 2A), a current density of 8 $\text{A m}^{-2}$ was produced at a stable pH of 5.6 ± 0.1 in the anode. When the feed was switched to diluted urine and the HRT was increased to two hours, the current density increased to 16 $\text{A m}^{-2}$. After 96 h of stable operation the current density decreased to 11 $\text{A m}^{-2}$. While the current decreased, the pH increased from 5.6 to 9 which corresponds to the pH of the diluted urine used as the feed stream.

After both the anolyte and catholyte were refreshed and the HRT was lowered to one hour, the current density increased to 23 $\text{A m}^{-2}$ and remained stable for 72 h and then decreased to 7.6 $\text{A m}^{-2}$. During the increase in current density the pH of the anode first decreased from 9 to 7 and then again showed a drastic increase to pH 9 at the same time as the current dropped. The first decrease in anode pH was caused by acidification of the urine as a result of the proton production. The pH increase could be caused by the diffusion of ammonia.
from cathode to anode, counteracting the acidification of the anolyte [16,22].

In order to test this hypothesis, a new batch of diluted urine was supplied (HRT of 1 h) and the cathode media was constantly replenished by adding new cathode media at a flow rate of 1.3 mL min⁻¹ (HRT of 6 h) (Fig. 2D). With this new batch of diluted urine and the constantly replenished cathode the current density increased to 15 A m⁻² in the course of 7 days (168 h), afterwards the current density started decreasing to 8 A m⁻². Again, when a new batch of diluted urine was supplied the current density increased to 16 A m⁻² and remained stable for 6 days (144 h) in this case.

The obtained current densities with the diluted urine (experiments B, C and D) were up to three times higher than the current density obtained with synthetic wastewater (experiment A) at higher (experiment B) or equal (experiment C and D) HRTs. Also the measured pH in the anode during stable operation with synthetic wastewater was significantly lower than the measured pH in the anode during stable operation on diluted urine. The diluted urine provided more buffering capacity during the operation resulting in a neutral to slightly alkaline pH in the anode [16,22,23]. This finding is consistent with recent work energy production from urine by MFCs [8].

### 3.2. Urine treatment in MEGs allows high ammonia recovery

The average ammonium removal (\(\eta_{\text{NH}_4^-\text{N}}\)) during the different experiments was about 30%. The ammonium removals during experiments A, B and C show a larger fluctuation compared to experiment D, which can be seen by the relative high standard deviations (Table 3).

The ammonium removal efficiencies during experiment A, B and C were 27.8 ± 10.8%, 32.6 ± 17.0% and 34.3 ± 2.3%, respectively. The relative large standard deviations correspond to a large variation in the ammonium removal rate. The ammonium removal rate decreases during each experiment, whereas the highest removal rates were measured during the start of an experiment. In experiment D during which the cathode media was constantly replenished, the high ammonium removal efficiencies from the anode could be maintained throughout the entire experimental period. Table 2 shows the determined removal rates during the different experiments at the start, in the middle and at the end of the experiments.

The ammonium removal rates for the experiments A, B and C were decreasing over the course of the respective experiment leading to the effective back transport (\(\text{NH}_3\) diffusion) of ammonium from cathode to anode. This can be seen by the negative ammonium removal rates determined at the end of these experiments. The obtained removal rates from experiment D show no such decrease. The measured ammonium concentrations in the anode and cathode compartment confirm the build-up of an ammonium gradient between anode compartment and cathode compartment. At the end of experiment A, B and C, the ammonium concentration in the cathode compartment was up to 10 times higher than the ammonium concentration in the anode compartment. Although the pH of the cathode media during the different experiments was higher than \(pK_a\) of ammonia (\(pK_a = 9.24\)) (see Table 4), an effective ammonium removal via \(\text{NH}_3\)-stripping from the cathode was not possible. This shows that the applied MEC design was not suitable for \(\text{NH}_3\)-stripping. An enhanced design for the ammonium stripping, similar to the work of Desloover et al. [18], which includes a recycle of the hydrogen for stripping would possibly allow for a more effective \(\text{NH}_3\)-stripping. An average ammonium removal rate of 171.4 g N m⁻² d⁻¹ was determined during experiment D. This ammonium removal rate was higher than the ammonium transport number reported by Desloover et al. [18], who reported an ammonium nitrogen flux (over the membrane) of about 120 g N m⁻² d⁻¹ and at an applied current density of 10 A m⁻², which can be explained by the different composition of the wastewater and the higher current density during our experiments.

### 3.3. High hydrogen production rates are possible from the treatment of urine

Fig. 3 shows the obtained average volumetric hydrogen production rates (Q₂₃) and the average required energy input for the hydrogen production.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Start (g N m⁻² d⁻¹)</th>
<th>Middle (g N m⁻² d⁻¹)</th>
<th>End (g N m⁻² d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>16.8</td>
<td>9.0</td>
<td>−0.4</td>
</tr>
<tr>
<td>B</td>
<td>129.4</td>
<td>53.6</td>
<td>−16.02</td>
</tr>
<tr>
<td>C</td>
<td>186.1</td>
<td>160.6</td>
<td>−59.8</td>
</tr>
<tr>
<td>D</td>
<td>197.4</td>
<td>175.0</td>
<td>167.8</td>
</tr>
</tbody>
</table>

* Cathode media HRT 6 h.

![Fig. 3](image_url) – Average volumetric hydrogen production rates (\(Q_{H_2}\)) at average current densities and average energy requirement for hydrogen production obtained during stable operation in the different experiments. *Cathode media HRT 6 h.
The highest volumetric hydrogen production rate was obtained during operation on five times diluted urine in experiment C. The average volumetric hydrogen production rate in experiment C was 48.6 ± 7.47 m³ H₂ m⁻³ MEC d⁻¹ and required an average energy input of 2.38 ± 0.20 kWh m⁻³ H₂. This volumetric hydrogen production rate was three times higher than the hydrogen production during operation on synthetic wastewater.

The highest volumetric hydrogen production rate (50.8 m³ H₂ m⁻³ MEC d⁻¹ at 24 A m⁻²) and the corresponding energy requirements (2.3 kWh m⁻³ H₂) obtained during the experiments with diluted urine were similar to the production rates (50 m³ H₂ m⁻³ MEC d⁻¹ at 22.8 A m⁻²) and energy requirements (2.6 kWh m⁻³ H₂) reported in literature for a comparable MEC type [24,25]. This shows that urine can be considered as a suitable feed stream for hydrogen production in an MEC. Additional enhancements to the hydrogen production rate might be obtained by using a catalyst with a higher specific surface area and catalytic activity such as nickel foam [24] or mixed metal alloys [25,26].

### 3.4. MEC performance parameters

Table 3 shows the related performance parameters of the MEC such as current density (j), hydrogen recovery (ηCat), coulombic efficiency (ηCE), COD removal (ηCOD) and ammonium removal (ηNH₄⁻N) obtained during stable operation in different experiments.

The results show that throughout the stable operation of the MEC in the different experiments high cathode efficiencies (ηCat) and Coulombic Efficiencies (ηCE) were achieved. An average cathode efficiency of 89.3% was determined over the different experiments. This seems reasonable considering the measured hydrogen gas concentration (>95% H₂ in headspace) and the measured gas volumes.

![](https://example.com/table-3.png)

* Cathode media HRT 6 h.

The obtained coulombic efficiencies during the experiments were higher than 80%, which shows that the bacteria growing on the anode were able to utilize most of the available oxidizable organic material for current generation.

An important parameter to describe the efficiency of wastewater treatment systems is the removal rate of COD and the COD removal efficiency. The highest COD removal efficiency (ηCOD = 46.1 ± 1.2%) was measured during experiment B at a current density of 15.81 ± 0.1 A m⁻² (HRT of 2 h), which corresponds to a COD removal rate of 116.3 g COD m⁻² d⁻¹ (23.3 kg COD m⁻³ MEC d⁻¹). An even higher COD removal rate of 171.0 g COD m⁻² d⁻¹ (34.2 kg COD m⁻³ MEC d⁻¹) was obtained during experiment C at a current density of 23.1 ± 0.1 A m⁻² (HRT of 1 h), but at a lower COD removal efficiency (36.7 ± 4.7%). The obtained COD removal rates were found to be significantly higher than the reported COD removal rate by Gil-Carrera et al. [27], who reported a COD removal rate of 0.5 g L⁻¹ (0.5 kg COD m⁻³ MEC d⁻¹) during treatment of raw municipal wastewater at an HRT of 10 h in a pilot scale system (reactor volume 10 L).

Table 4 shows the average anode pH, anode potential, cathode pH, and cathode potential during stable operation of the different experiments. An anode potential of −0.365 ± 0.008 V vs Ag/AgCl was measured during stable operation on synthetic wastewater, while an anode potential between −0.42 and −0.484 V vs Ag/AgCl was measured during stable operation on diluted urine. Although this work was performed with diluted urine and using a CEM instead of an AEM, the obtained current densities are comparable to the current densities obtained by Jeremiasse et al. [24,25]. This shows that urine is a good feed stream for hydrogen production, but long term stability of the system is still an important issue. The stable operation periods, during which high current densities were obtained, are still relatively short (96 h in experiment B and 72 h in experiment C) and decreased with

<table>
<thead>
<tr>
<th>Exp.</th>
<th>HRT (h)</th>
<th>j (A m⁻²)</th>
<th>pH anode</th>
<th>EAnode (V)</th>
<th>pH cathode</th>
<th>ECathode (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>144</td>
<td>8.25 ± 0.35</td>
<td>5.6 ± 0.1</td>
<td>−0.365 ± 0.008</td>
<td>12.0 ± 0.1</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>96</td>
<td>15.81 ± 0.10</td>
<td>7.9 ± 0.7</td>
<td>−0.484 ± 0.045</td>
<td>13.5 ± 0.2</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>72</td>
<td>23.07 ± 1.15</td>
<td>7.4 ± 0.4</td>
<td>−0.469 ± 0.044</td>
<td>11.6 ± 0.2</td>
</tr>
<tr>
<td>D²</td>
<td>1</td>
<td>288</td>
<td>14.64 ± 1.65</td>
<td>7.5 ± 0.3</td>
<td>−0.420 ± 0.027</td>
<td>9.7 ± 0.1</td>
</tr>
</tbody>
</table>

* Cathode media HRT 6 h.

* vs Ag/AgCl.
the increasing current density. As shown during experiment D, the period of stable operation can be extended when the cathode media is a constantly replenished by adding new cathode media, but this also results in lower current density (14.64 ± 1.65 A m⁻²).

4. Perspectives

During stable operation on five times diluted urine (experiment D) a current density of 14.64 ± 1.65 A m⁻² was achieved corresponding to a hydrogen production rate of 32.0 ± 0.89 m³ H₂ m⁻³ MEC d⁻¹ at an energy input of 2.32 ± 0.1 kWh m⁻³ H₂. An ammonium removal rate of 162.18 ± 10.37 g N m⁻² d⁻¹ and a COD removal rate of 130.56 ± 4.45 g COD m⁻² d⁻¹. The achieved current density and ammonium removal rates exceed by far the ammonium recovery rates presented in our earlier work [6]. Therefore, these results highlight the advantages of the MEC ammonium recovery concept over the MFC ammonium recovery concept. Before this technology can be applied on a larger scale an efficient ammonium stripping concept has to be incorporated with the MEC. An example for an ammonia stripping concept was proposed by Desloover et al. [18], which will enhance the ammonium recovery and result in ammonium rich concentrate. With this enhancement in place, it might be possible to prolong the performance as obtained during experiment C. During experiment C, a current density of 23.07 ± 1.15 A m⁻² was achieved corresponding to a hydrogen production rate of 48.6 ± 7.47 m³ H₂ m⁻³ MEC d⁻¹ at an energy input of 2.38 ± 0.20 kWh m⁻³ H₂, an ammonium removal rate of 173.4 ± 18.1 g N m⁻² d⁻¹ and a COD removal rate of 171.0 ± 16.9 g COD m⁻² d⁻¹. Furthermore, the operation of the MEC needs to be further optimized to allow for maximum ammonium removal from anode to cathode compartment. Currently, only 34.2% of the ammonium is removed (removal efficiency during experiment D) from the anode which limits the possible recovery of ammonium from the cathode. The ammonium recovery can be enhanced in two ways. First, the COD removal should be optimized, with a special focus on conversion of the chemical energy to electrical energy, to allow for more migrational transport of ammonium ions. Second, an effective NH₃-stripping process should be applied to remove ammonium from the cathode and thereby promoting ammonium diffusion over the membrane. An MEC based ammonium recovery technology can be a promising concept, but further research is necessary to allow it become a competitive ammonium recovery technology.

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REFERENCES


