Direct Electrochemical Oxidation of Ammonia on Graphite as a Treatment Option for Stored Source-Separated Urine

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ABSTRACT

Electrolysis can be a viable technology for ammonia removal from source-separated urine. Compared to biological nitrogen removal, electrolysis is more robust and is highly amenable to automation, which makes it especially attractive for on-site reactors. In electrolytic wastewater treatment, ammonia is usually removed by indirect oxidation through active chlorine which is produced in-situ at elevated anode potentials. However, the evolution of chlorine can lead to the formation of chlorate, perchlorate, chlorinated organic by-products and chloramines that are toxic. This study focuses on using direct ammonia oxidation on graphite at low anode potentials in order to overcome the formation of toxic by-products. With the aid of cyclic voltammetry, we demonstrated that graphite is active for direct ammonia oxidation without concomitant chlorine formation if the anode potential is between 1.1 and 1.6 V vs. SHE (standard hydrogen electrode). A comparison of potentiostatic bulk electrolysis experiments in synthetic stored urine with and without chloride confirmed that ammonia was removed exclusively by continuous direct

oxidation. Direct oxidation required high pH values ($\text{pH} > 9$) because free ammonia was the actual reactant. In real stored urine ($\text{pH} = 9.0$), an ammonia removal rate of $2.9 \pm 0.3 \text{ gN} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ was achieved and the specific energy demand was $42 \text{ Wh} \cdot \text{gN}^{-1}$ at an anode potential of 1.31 V vs. SHE. The measurements of chlorate and perchlorate as well as selected chlorinated organic by-products confirmed that no chlorinated by-products were formed in real urine. Electrode corrosion through graphite exfoliation was prevented and the surface was not poisoned by intermediate oxidation products. We conclude that direct ammonia oxidation on graphite electrodes is a treatment option for source-separated urine with three major advantages: The formation of chlorinated by-products is prevented, less energy is consumed than in indirect ammonia oxidation and readily available and cheap graphite can be used as the electrode material.

KEYWORDS

NoMix technology, nitrogen removal, decentralized, on-site, potential controlled electrolysis, chlorinated by-products

1. INTRODUCTION

The separate collection and treatment of urine and feces (NoMix technology) has emerged as a new field in urban water management (Larsen et al., 2013). NoMix technology allows pollutants to be eliminated more efficiently (Pronk et al., 2007) or nutrients to be recovered from urine with processes such as struvite precipitation (Etter et al., 2011) and nitrification/distillation (Udert and Wächter, 2012). However, in some areas, especially in the cities of industrialized countries, nutrient removal rather than nutrient recovery might be a more economically viable solution. A

promising technology for ammonia removal from urine is electrolysis (Udert et al., 2013) thanks to its high robustness, versatility and amenability to automation (Anglada et al., 2009).

During electrolysis, ammonia is removed by oxidation via two pathways: it is either oxidized indirectly through an oxidation mediator produced on the anode (e.g. active chlorine species: Cl_2 , HOCl or OCl^-) or through direct electron transfer on the anode surface (Anglada et al., 2009).

Both processes can occur during electrolysis of stored urine, because chloride is present in high concentrations (up to $3.8 \text{ gCl}\cdot\text{L}^{-1}$; Udert et al., 2006). Although indirect oxidation is the most common electrochemical process for ammonia removal in wastewaters (Chen, 2004), it has three major disadvantages: (1) toxic chlorinated by-products can be formed, (2) the specific energy demand for ammonia removal is high, and (3) active chlorine can increase electrode corrosion.

Stored urine contains high amounts of organic substances (the chemical oxygen demand (COD) can be as high as $10 \text{ g}\cdot\text{L}^{-1}$, Udert et al., 2006). Thus, the risk of forming chlorinated organic by-products is high (Sirés and Brillas, 2012). Due to the high ammonia concentration, the formation of chloramines is also very likely. Chlorate and perchlorate are other inorganic chlorinated by-products that are formed chemically or electrochemically when chloride is oxidized at elevated anode potentials (Perez et al., 2012).

The specific energy demand is large due to the high cell voltages needed to reach the anode potentials at which active chlorine is formed. The side reactions occurring at elevated anode potentials (e.g. oxygen evolution, Kim et al., 2006) also contribute to the high specific energy demand. The negative effect that active chlorine can have on electrode stability is well known from the chlor-alkali industry (Hamann and Vielstich, 2007), especially in the case of graphite exfoliation (particle detachment caused by intercalated chloride).

In contrast to indirect oxidation, the use of direct oxidation should allow ammonia to be eliminated without producing chlorinated by-products. The specific energy demand can be expected to be lower and electrode corrosion should be reduced. The key to successful direct oxidation is to choose an electrode which is cheap and stable, and which is active and selective with respect to ammonia oxidation (Panizza, 2010). Despite its advantages, direct ammonia oxidation has not received much attention so far for the treatment of wastewaters or urine. One exception is the treatment of ammonia in highly alkaline media with Pt-Ir electrodes (Diaz and Botte, 2012; Boggs and Botte, 2010). The Pt-Ir electrode has the lowest overpotential for direct ammonia oxidation, resulting in high selectivity and a low energy demand. Other studies on direct ammonia oxidation mainly focused on the activity and mechanism of direct electron transfer with boron-doped diamond (BDD) or different types of dimensionally stable anodes (DSAs, Bunce and Bejan, 2011). However, one drawback of all these electrode materials is their high cost.

Another problem with direct ammonia oxidation can be the deactivation of the electrode. The thermally decomposed iridium oxide film (TDIROF, a DSA type electrode), was found to be deactivated, presumably due to surface poisoning by adsorbed nitrogen (Kapałka et al., 2011). The same deactivation mechanism had already been reported earlier for platinum and several transition metals (de Vooy et al., 2001). However, not all electrodes were poisoned. Continuously ongoing direct ammonia oxidation has been demonstrated by Bonnin et al. (2008) on Pt-Ir and by Kapałka et al. (2010a) on Ni/Ni(OH)₂ electrodes. Unfortunately, in the latter study it was pointed out that corrosion might be a critical problem with Ni/Ni(OH)₂ electrodes. Amstutz et al. (2012) further showed that ammonia oxidation on TDIROF at high pH values can be inhibited by competing oxidation of carbonate.

Compared to Pt-Ir, BDD or DSA, graphite could be an inexpensive alternative electrode material for direct ammonia oxidation. However, its activity, selectivity and stability for direct ammonia oxidation have not yet been investigated in detail. Candido and Ponciano Gomes (2011) found indications of direct ammonia oxidation during an anodic polarization experiment, but were unable to confirm their findings in cyclic voltammetry (CV) experiments. Zheng et al. (2009) reported the use of graphite for ammonia removal from synthetic urine. However, indirect oxidation via active chlorine was likely to be the main mechanism for ammonia removal since chloride was present and high current densities were applied.

The aim of this study was to evaluate whether direct oxidation of ammonia on isostatically pressed fine-grain graphite is a technically feasible alternative to indirect electrolytic ammonia removal from source-separated urine. The use of direct ammonia oxidation should allow us to work at lower anode potentials, thereby preventing the formation of chlorinated by-products, avoiding graphite exfoliation induced by active chlorine and reducing specific energy demand. We studied the individual and combined reactions of ammonia oxidation and chlorine evolution in cyclic voltammetry experiments to find the anodic potential window for direct ammonia oxidation without concomitant chlorine evolution. In bulk electrolysis experiments, we subsequently evaluated the process stability, selectivity and efficiency of direct ammonia oxidation in synthetic and real stored urine.

2. MATERIAL AND METHODS

2.1. Cyclic voltammetry (CV) experiments

A one-compartment glass cell (50 mL, temperature controlled at 25 ± 0.1 °C with a Colora thermostat, Colora Messtechnik GmbH, Lorch, Germany) was used for CV. The electrolyte

volume was 40 mL. The working electrode was a graphite rod (R 8650, SGL Carbon GmbH, Bonn, Germany). The cross-sectional area with a geometric surface of 0.385 cm^2 was exposed to the electrolyte. The reference electrode was an Ag/AgCl/KCl (Ag/AgCl, 0.21 V vs. SHE, InLab reference pro, Mettler Toledo, Greifensee, Switzerland) placed in a glass-blown Luggin capillary filled with $1\text{ mol}\cdot\text{L}^{-1}\text{ NaClO}_4$. The counter electrode was a graphite bar (Geometric surface area: 8 cm^2 ; R4340, SGL Carbon GmbH, Bonn, Germany). The cell was controlled with a potentiostat using EcmWin software (PGU 10V-1A-IMP-S, EcmWin V2.4, Ingenieurbüro Peter Schrems, Münster, Germany).

NaClO_4 ($1\text{ mol}\cdot\text{L}^{-1}$) was used as the supporting electrolyte (Table 1: “support”). Two solutions were used to study individual reactions of ammonia and chloride: first, $1\text{ mol}\cdot\text{L}^{-1}\text{ NaClO}_4$ with $0.25\text{ mol}\cdot\text{L}^{-1}\text{ NH}_4\text{ClO}_4$ (“support + NH_3 ”) and, second, $1\text{ mol}\cdot\text{L}^{-1}\text{ NaClO}_4$ with $0.085\text{ mol}\cdot\text{L}^{-1}\text{ NaCl}$ (“support + Cl”). The desired pH levels were adjusted with sodium hydroxide. The combined effect of ammonia and chloride was investigated in a solution with $1\text{ mol}\cdot\text{L}^{-1}\text{ NaClO}_4$, $0.25\text{ mol}\cdot\text{L}^{-1}\text{ NH}_4\text{ClO}_4$ and $0.085\text{ mol}\cdot\text{L}^{-1}\text{ NaCl}$ (“support + NH_3 + Cl”). For all conditions, 5 scans were performed in a row at a scan rate of $200\text{ mV}\cdot\text{s}^{-1}$. Unless indicated otherwise, the lower return potential was -1.59 V and the upper return potential (E_{up}) was 2.01 V . The same working electrode was used for all experiments and was cleaned with 5 cycles (between: -1.59 to 2.01 V) in $1\text{ mol}\cdot\text{L}^{-1}\text{ NaClO}_4$ prior to new experiments.

2.2. Bulk electrolysis experiments

In these experiments, a 400 mL glass cell was filled with 300 mL solution and covered with a Plexiglas lid to prevent ammonia volatilization. Two graphite plates (R 4340, SGL Carbon GmbH, Bonn, Germany) with an exposed surface of 20 cm^2 served as the anode and cathode,

respectively. The graphite was connected to a copper wire with silver epoxy glue (EPO-TEK E4110, Epoxy Technology, Billerica, USA) and sealed onto PVC plates with silicon glue (CAF 1, Bluestar silicones, Saint-Fons cedex, France). The distance between the electrodes was 1 cm. The reference electrode was a Hg/Hg₂SO₄/K₂SO₄ (MSE, 0.64 V vs. standard hydrogen electrode (SHE), Ref 601, Radiometer analytical, France) placed in a glass-blown Luggin capillary filled with saturated K₂SO₄. All electrode potentials were recalculated to values against SHE. The solution was stirred with a magnetic stirrer and the temperature was controlled with a thermostat (25 ± 0.1 °C, Colora thermostat, Colora Messtechnik GmbH, Lorch, Germany). Aliquots of the solution (10 to 15 mL) were taken with a syringe through a needle permanently placed in the electrolysis cell. The samples were filtered (0.45 µm, Chromafil GF/PET, Macherey-Nagel, Düren, Germany) before chemical analysis (see below).

The anode potential (E_a) was controlled and measured continuously with a potentiostat (PGU 10V-1A-IMP-S, Ingenieurbüro Peter Schrems, Münster, Germany) and the current was recorded with the same device. The cell voltage was recorded with a data logger on a high impedance analogue input (Mikromec multisens, Technetics, Freiburg, Germany). The temperature and pH were measured continuously (SenTix 41 connected to pH 196, WTW, Weilheim, Germany) and recorded with the data logger. Conductivity was measured with a handheld meter (TetraCon 325 connected to Cond 340i, WTW, Weilheim, Germany).

Synthetic urine was prepared on the basis of the composition of stored urine given by Udert et al. (2006). Acetate was chosen as the only organic substance. Since low removal rates had to be expected, the ammonia and acetate concentrations were reduced to shorten the duration of the experiments. Chloride was completely eliminated from one solution to suppress indirect

oxidation (Table 1). The recipes for the synthetic urine are given in the supplementary information (Table A.1).

Electrolysis of real urine was performed with urine from the women's collection tank in the main building at Eawag (Table 1). In this experiment, the weight change of the anode and the cathode was monitored and six organic by-products (dichloromethane, trichloromethane, tetrachloromethane, 1,2-dichloroethane, 1,2-dichloropropane, chlorobenzene) previously observed during electrolysis at elevated anode potentials were analyzed after extraction from the solution with dodecane (see below). The electrodes were weighed before and after electrolysis on a precision balance (Ag204 DeltaRange, Mettler-Toloedo GmbH, Greifensee, Switzerland). Before weighing, the electrodes were dried for 30 minutes at 105 °C.

2.3. Chemical analyses

Chloride, phosphate, sulfate and nitrate were analyzed by ion chromatography (881 compact IC pro, Metrohm, Herisau, Switzerland) while ammonia and nitrite were analyzed photometrically with a flow injection analyzer (standard operating procedures: 45-1 and 45-3, FOSS, Hillerød, Denmark). Free and total chlorine, COD and nitrite at very low concentrations were measured with photometric cuvette tests (LCK 310, LCK 514 and LCK 341, Hach Lange, Berlin, Germany). Free and total chlorine as well as total COD were analyzed in unfiltered samples. The standard deviations of the chemical analyses were less than 5%.

Organic chlorinated by-products were extracted by adding 0.9 mL of the unfiltered sample to 0.9 mL dodecane in a gas chromatography / mass spectrometry (GC/MS) glass screw-cap vial. The sample was taken with a gastight glass syringe. The GC/MS vials were shaken for 10 seconds and the solvents were allowed to separate for 30 minutes. Thereafter, 0.8 mL of the segregated

dodecane phases on top of the sample were pipetted into another GC/MS glass screw-cap vial (1.5 mL). The dodecane samples were stored in a freezer (-20 °C) until analysis with GC/MS. 1 µL of the dodecane sample was analyzed with a Thermo Scientific DSQII single quadrupole GC/MS (Restek, Bellefonte, USA). The samples were injected into the column with a CTC CombiPAL auto-sampler. The temperature increased from 40 °C (constant for 1 min) to 140 °C at 10 °C·min⁻¹ and from 140 °C to 200 °C (constant for 20 min) at 40 °C·min⁻¹. The column was a RTX-VMS, 60 m x 0.32 mm I.D. with 1.8 µm film thickness (Restek). Helium (100 kPa) was used as the carrier gas. The transfer line had a temperature of 220 °C and the MS source temperature was set at 250 °C. The relative standard deviation of the GC/MS analysis was less than 3.6% for all compounds.

2.4. Calculations

2.4.1. Cyclic voltammetry

The polarization of the graphite electrodes during cyclic voltammetry led to high background currents ($i_{support}$ [mA cm⁻²]). To obtain the current caused by ammonia oxidation during the CV in ammonia-containing electrolyte, the current measured in the electrolytes without ammonia or chloride was subtracted from the original current ($i_{support+NH_3}$, [mA cm⁻²]). The peak current density of ammonia oxidation (i_{peak} [mA cm⁻²], Figure 2) was then obtained by evaluating the maximum of the corrected current (Equation 1).

$$i_{peak} = \max(i_{support+NH_3} - i_{support}) \quad (1)$$

The mole fraction of NH₃, f_{NH_3} [%], was calculated as a function of the pH from the measured total ammonia concentrations $S_{NH,tot}$ with the chemical speciation software PHREEQC (Parkhurst

and Appelo, 1999). Activity coefficients were calculated using the Pitzer approach with a database extended by Pitzer parameters for ammonium and perchlorate (Kapałka et al., 2010a).

2.4.2. Bulk electrolysis experiments

The removal or production rate of a substance x per electrode surface $r_{A,x}$ [$\text{gN} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$] was calculated from the slope s_x [$\text{gN} \cdot \text{d}^{-1}$] of the linear regression of the remaining mass of substance x (including mass in removed samples) vs. time as:

$$r_{A,x} = s_x \cdot \frac{1}{A} \quad (2)$$

where A [m^2] is the anode surface area.

The yields Y_x [%] of nitrite and nitrate were estimated from the concentration of substance x , S_x [$\text{mgN} \cdot \text{L}^{-1}$] in the cell at a time t [s] and the total ammonia concentration $S_{NH,tot}$ [$\text{mgN} \cdot \text{L}^{-1}$] in the cell by:

$$Y_x = \frac{S_x(t) - S_x(0)}{S_{NH,tot}(0) - S_{NH,tot}(t)} \quad (3)$$

The yield of the gaseous nitrogen species $Y_{N,gas}$ was estimated from the following mass balance:

$$Y_{N,gas} = 100 - Y_{NO_2^-} - Y_{NO_3^-} \quad (4)$$

Under the assumption that all ammonia not converted to nitrate or nitrite was oxidized to N_2 , the total current efficiency (CE , in %) was estimated as:

$$CE_{tot}(t) = CE_{NO_3^-}(t) + CE_{NO_2^-}(t) + CE_{N_2}(t) \quad (5)$$

216 where

$$217 \quad CE_x(t) = \frac{\Delta m_x(t) \cdot v_{e^-,x} \cdot F}{M_N \cdot Q(t)} \quad (6)$$

218 and

$$219 \quad CE_{N_2}(t) = \frac{(\Delta m_{NH_{tot}}(t) - \Delta m_{NO_3^-}(t) - \Delta m_{NO_2^-}(t)) \cdot v_{e^-,N_2} \cdot F}{M_N \cdot Q(t)} \quad (7)$$

220 Here $\Delta m_x(t)$ [gN] is the mass of substance x produced in the cell until a time t , and $v_{e^-,x}$ [mole⁻
221 ·molN⁻¹] is the number of electrons used per mole of ammonia oxidized to nitrate, nitrite or
222 molecular nitrogen, respectively. F is the Faraday constant (96,485 C·mole⁻¹), M_N the molecular
223 weight of nitrogen (14 gN·molN⁻¹) and $Q(t)$ the transported charge.

224 The current efficiency for organic substance removal was estimated on the basis of COD
225 measurements:

$$226 \quad CE_{COD}(t) = \frac{\Delta m_{COD}(t) \cdot F}{TOD_{e^-} \cdot Q(t)} \quad (8)$$

227 As with the nitrogen species, $\Delta m_{COD}(t)$ [gO₂] is the mass of COD removed until a time t . TOD_{e^-}
228 is the theoretical oxygen demand of one mole of electrons (8 gO₂ mol⁻¹).

229 The transported charge Q [C] was calculated from the current I [A] as:

$$230 \quad Q(t) = \int_0^t I(t) dt \quad (9)$$

The specific energy demand for ammonia removal E_{sp} [Wh·gN⁻¹] was calculated from the average electrical power $\overline{U \cdot I}$, which was calculated as the average of the product of the cell voltage U [V] times the current I [A] up to a time t as:

$$E_{sp} = \frac{\overline{U \cdot I} \cdot t}{\Delta m_{NH,tot} \cdot 3600 \frac{s}{h}} \quad (10)$$

3. RESULTS

3.1. Direct ammonia oxidation on graphite anodes

The voltammogram in the presence of ammonia at pH 9 showed a clear anodic peak (a1), which was not observed in the supporting electrolyte without ammonia (Figure 1). This peak can be attributed to direct ammonia oxidation starting at an onset potential of 1 V. When a potential of 1.8 V was reached, the voltammograms with and without ammonia overlapped again, indicating the end of ammonia oxidation. The backward scans in the experiments with an upper return potential (E_{up}) of 2.01 V showed the same cathodic peak (c1) between 1.7 and 1.4 V with and without ammonia. However, when E_{up} was decreased to 1.81 V, no cathodic peak was visible in the backward scan, although the anodic ammonia oxidation peak was present in the forward scan. The cathodic peak c1 was most likely caused by surface functional groups on the graphite (hydroxyl, carbonyl and carboxyl groups), which are formed in the forward scan (Rueffer et al., 2011) above a potential of 1.8 V. Figure 2 shows the peak current density of ammonia oxidation as a function of the bulk pH value in nine CV scans: the peak currents follow the mole fraction of NH₃, which indicates that NH₃ was the reacting compound.

3.2. Ammonia oxidation on graphite in the presence of chloride

The CV results with respect to chloride oxidation in the absence of ammonia are presented in Figure 3A. Figure 3B shows how chloride and ammonia oxidation interact if both substances are present. The presence of chloride alone resulted in a strong increase of anodic currents above an E_a of 1.6 V in the forward scans, which indicates that chloride oxidation started at this potential. In the backward scans, the cathodic peak c1 vanished. Instead, a cathodic peak (c2) occurred between 1.2 and 0.75 V. The height of this peak depended on E_{up} and disappeared when E_{up} was smaller than 1.6 V. These observations indicate that the presence of chloride resulted in oxidation products (most likely Cl_2 , HOCl or OCl^-), which were reduced during the backward scan.

When ammonia and chloride were present, the anodic ammonia oxidation peak a1 appeared exactly as in the case when no chloride was present. Once the onset potential for chloride oxidation (1.6 V) was exceeded, higher anodic currents were measured than in electrolytes that contained no chloride. The identical occurrence of the peak a1 indicates that direct ammonia oxidation took place without any interfering oxidation of chloride between 1 V and 1.6 V. Chloride oxidation most likely started above 1.6 V, resulting in increased anodic currents. In the backward scan, both cathodic peaks c1 and c2 appeared if the upper return potential was 2.01 V. However, they were smaller than the peaks in the experiments, when only ammonia or chloride was present in the electrolytes. The peak c1 most likely resulted from the reduction of the same functional groups on graphite as hypothesized for Figure 1. The peak c2 likely originated from products of chloride oxidation, as shown in Figure 3A. In contrast to the case when only chloride was present, c2 disappeared completely with an upper potential limit of 1.81 V. This indicates that no chloride oxidation products (Cl_2 , HOCl or OCl^-) were produced at anode potentials below 1.81 V if ammonia was present.

3.3. Bulk electrolysis of synthetic stored urine

To determine the influence of chloride on ammonia removal at anode potentials below the chloride oxidation potential, bulk electrolysis experiments were conducted at $E_a = 1.31$ V in synthetic urine solutions with and without chloride. Figure 4 shows that ammonia was removed steadily in both experiments. At the end of the experiment, 38 ± 2 % of the initial ammonia was removed, of which 77 ± 4 % was oxidized to gaseous nitrogen species (not measured), 21 ± 2 % to nitrate and 2 ± 2 % to nitrite (not shown). In a control experiment without applied voltage, the ammonia concentration remained constant for 45 hours, indicating that ammonia loss by volatilization was negligible.

Ammonia removal proceeded at rates of 7.1 ± 0.5 $\text{gN} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (without chloride) and 6.2 ± 0.4 $\text{gN} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (with chloride). A student t-test revealed that these two rates are not significantly different ($\alpha = 0.05$). Nitrate production rates reached values of 1.1 ± 0.05 $\text{gN} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (without chloride) and 1.2 ± 0.06 $\text{gN} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (with chloride). Free chlorine did not exceed 0.2 $\text{mgCl}_2 \cdot \text{L}^{-1}$ and total chlorine was not higher than 0.4 $\text{mgCl}_2 \cdot \text{L}^{-1}$ in both experiments, while the chloride concentration was constant in the experiment with chloride (3340 ± 40 $\text{mgCl} \cdot \text{L}^{-1}$).

The specific energy demand for ammonia removal was 37 $\text{Wh} \cdot \text{gN}^{-1}$ without chloride while 35 $\text{Wh} \cdot \text{gN}^{-1}$ were needed with chloride. The current efficiencies for nitrate production were 21% (without chloride) and 27% (with chloride), and total current efficiencies for ammonia removal were 48% (without chloride) and 56% (with chloride).

No exfoliated graphite was observed in either experiment. Visual inspection of the solution revealed negligible turbidity and no graphite particles. In the experiment with chloride, where

stronger graphite exfoliation would be expected, the COD values did not increase (860 ± 16 $\text{mgO}_2 \text{ L}^{-1}$).

3.4. Bulk electrolysis of real stored urine

Real stored urine was treated at the same anode potential of $E_a = 1.31 \text{ V}$ to validate the results obtained with synthetic urine solutions. Indeed, the ammonia concentration profile in Figure 5 shows that ammonia was removed steadily from real urine. The removal rate was $2.9 \pm 0.3 \text{ gN} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$. The nitrate concentration was below the detection limit and the nitrite concentration did not exceed $0.3 \text{ mgN} \cdot \text{L}^{-1}$ in any sample. The products of ammonia oxidation in real urine must have been mainly gaseous nitrogen species (not measured). Organic substances (Figure 5) were removed at a rate of $20.6 \pm 3.5 \text{ gCOD m}^{-2} \cdot \text{d}^{-1}$ during the first four days of electrolysis. It was also during this period of time that the pH and the current density decreased, whereas both variables were constant after day four until the end of the experiment (Figure 5).

The chloride concentration increased from 1200 to $1880 \text{ mgCl} \cdot \text{L}^{-1}$, probably due to electrolyte leakage from the pH probe. Free and total chlorine measurements could not be interpreted unambiguously due to a strong matrix effect in real urine. (Figure B.2, supplementary information). The selected chlorinated organic compounds (dichloromethane, trichloromethane, tetrachloromethane, 1,2-dichloroethane, 1,2-dichloropropane, chlorobenzene) as well as chlorate and perchlorate were below the detection limits in all samples. This strongly suggests that neither active chlorine nor chlorinated by-products were formed.

The specific energy demand in real urine was higher than in synthetic urine solutions, with $42 \text{ Wh} \cdot \text{gN}^{-1}$ needed to remove the first 12% of ammonia nitrogen. The higher energy demand resulted from a lower total current efficiency of 33% and a higher cell voltage due to the lower

conductivity of real urine. The gravimetric corrosion assessment showed a weight loss of the anode of $2.8 \text{ mg} \cdot \text{g}^{-1}$ and a weight gain of the cathode of $1.5 \text{ mg} \cdot \text{g}^{-1}$ (Figure 6). No graphite particles were noticed in the solution, which indicates that graphite exfoliation did not take place.

4. DISCUSSION

4.1. Activity and selectivity of graphite for direct ammonia oxidation in stored urine

The activity of graphite for direct ammonia oxidation is clearly demonstrated by our CV results in Figure 1. The onset potential of 1 V is in good agreement with the onset potential found by Candido and Ponciano Gomes (2011) in a linear potential sweep experiment at pH 9.4. In contrast to our measurements, Candido and Ponciano Gomes (2011) did not observe clear ammonia peaks in their CV. We assume this is due to the use of a low upper return potential (only 1.34 V) in their experiment. The data presented in Figure 2 further shows that the reactive compound for direct ammonia oxidation is NH_3 , as has been demonstrated for other electrode materials such as TDIROF, $\text{Ni}/\text{Ni}(\text{OH})_2$ and BDD (Kapařka et al., 2011; Kapařka et al., 2010a; Kapařka et al., 2010b).

The results from the potentiostatic bulk electrolysis experiments in synthetic and real stored urine show that ammonia can be oxidized continuously on the graphite surface via the direct oxidation pathway. A considerable amount of ammonia was oxidized to nitrate in synthetic urine but not in real urine. Unfortunately, very little is known about nitrate formation during direct oxidation of ammonia and our data as well do not allow an in-depth discussion of the formation of nitrate which would make any interpretation of the data speculative. This phenomenon could be subject of a follow-up study.

In contrast to other electrode materials, the graphite anodes were not poisoned nor did competing carbonate oxidation suppress ammonia oxidation completely as observed with TDIROF (Amstutz et al., 2012). Synthetic urine in particular contained large amounts of inorganic carbon and the initial pH was high. Thus, carbonate was present but its oxidation was too slow, if it occurred at all, to interfere with the direct ammonia oxidation. Poisoning was frequently observed with other electrode materials such as noble or transition metals (de Vooy et al., 2001). On these electrodes, strongly adsorbed elementary nitrogen blocked the active sites if ammonia was completely dehydrogenated during anodic oxidation. This kind of surface poisoning does not seem to occur with graphite. Otherwise, the ammonia removal rate and the nitrate production rate in the bulk electrolysis experiments would have changed with time. Our CVs in the presence and absence of ammonia (Figure 1) support this conclusion because the current densities were the same as soon as the ammonia oxidation peak was passed during the forward scan. If nitrogen were to poison the graphite surface, the oxidation of adsorbed nitrogen in the forward scan and the reduction of the oxidized nitrogen in the backward scan would produce a modified current profile as observed with platinum (de Vooy et al., 2001).

The graphite anodes were not very selective for ammonia oxidation: with synthetic urine, the current efficiencies did not exceed 56% and in the experiment with real stored urine the current efficiency was as low as 33%, indicating important side reactions. The most probable of these are the oxidation of organic substances, the oxidation of the graphite itself and the evolution of oxygen through water splitting. In the bulk electrolysis of real urine, the strong removal of organic substances during the first four hours would have required a current efficiency of 104% if anodic oxidation alone were responsible. Thus, organics were not removed by anodic oxidation alone in that period. COD may also have been removed cathodically by adsorption,

which would explain the weight gain of the cathode. Another possible process is biological COD removal, but in that case we would not expect the process to stop after four days.

The current efficiency for ammonia oxidation was 32% in the period from day four to fourteen. Accordingly, the oxidation of organic substances cannot be the sole process responsible for the low current efficiency. According to Rueffer et al. (2011), the oxidation of graphite itself (mineralization to CO₂) occurs together with the evolution of oxygen from water splitting above potentials of 0.94 V. This anode potential is exceeded in our experiments. The weight loss of the anode measured in the experiment with real stored urine would require a charge of 0.5 Ah if the oxidation of graphite to CO₂ was the responsible process. Since the total charge was 1.65 Ah, the mineralization of graphite could account for about one third of the anodic current. The competition of direct ammonia oxidation, CO₂ formation and oxygen evolution on carbon fibers was pointed out by Webster et al. (2012). The low current efficiency for ammonia oxidation therefore most probably resulted from a combination of organics oxidation, graphite mineralization and oxygen evolution.

4.2. Influence of chloride on direct ammonia oxidation in stored urine

Janssen and Hoogland (1970) established the following mechanism for chlorine evolution:

However, chloride ions are well known for their adsorption property in the inner Helmholtz plane by contact adsorption before faradaic currents occur (Bockris and Reddy, 1974). It has to be assumed that chloride ions are also present in direct contact with the graphite surface at

potentials below 1.6 V. Therefore, the presence of chloride could have affected the direct ammonia oxidation in two ways: (1) it could have led to indirect oxidation increasing the ammonia removal and nitrate production with a risk of chlorinated by-product formation, or (2) the adsorption of chloride ions could have blocked active sites for direct ammonia oxidation, leading to decreased ammonia removal and nitrate production. Our results show that neither of these two scenarios was the case at anode potentials below 1.6 V. Three observations lead to this conclusion and are explained in the following subsection.

4.2.1. Influence of chloride below 1.6 V

(i) The CV in Figure 3A does not show additional faradaic currents due to chlorine evolution in the forward scans compared to the CV in the supporting electrolyte up to potentials of 1.6 V. The reactions according to equations (11) and (12) thus did not take place until 1.6 V was reached. This conclusion is also supported by the fact that no reduction peak c2 appeared when the upper return potential was 1.6 V. In contrast, higher upper return potentials showed additional faradaic currents in the forward scans once 1.6 V was passed due to reactions (11) and (12). As a consequence, the reduction peak c2 was observed due to the reduction of Cl_{ad} and Cl_2 (or HOCl , OCl^-) in the backward scan.

(ii) The forward scans in the electrolyte that contained ammonia and chloride (Figure 3B) were identical to those in the electrolyte that contained only ammonia (Figure 1) up to a potential of 1.6 V. Thus, ammonia was either oxidized at different active sites than those adsorbing chloride or the oxidation happened at adsorbed chloride ions or both, resulting in the same ammonia oxidation currents as on the bare graphite surface.

(iii) In the potentiostatic bulk electrolysis experiments with synthetic urine presented in Figure 4, ammonia removal and nitrate production were not influenced significantly by the presence of chloride. The very low amounts of free and total chlorine found in these experiments support this interpretation.

4.2.2. Influence of chloride above 1.6 V

Above 1.6 V, our CVs clearly show interactions of chlorine evolution and ammonia oxidation. The missing reduction peak c2 with $E_{up} = 1.81$ V in Figure 3B may have resulted from two possible processes. If ammonia was oxidized at adsorbed chloride, the presence of ammonia could prevent the oxidation of the chloride by replenishing the chloride electrons while being oxidized at the same time. Another possible process could be that chloride was oxidized in the reactions (11) and (12) to active chlorine, which immediately reacted with ammonia. Both processes can explain why no reduction peak c2 was observed, namely because no Cl_{ad} and Cl_2 (or HOCl or OCl^-) were present during the backward scan.

The occurrence of the reduction peaks c1 and c2 in the backward scan of Figure 3B with $E_{up} = 2.01$ V most likely resulted from the fact that ammonia was completely used up at a certain point of the forward scan. This resulted in the formation of surface functional groups (hydroxyl, carbonyl and carboxyl groups) as in the supporting electrolyte, and of Cl_{ad} and Cl_2 in the forward scans. These products were reduced in the corresponding reduction peaks c1 and c2 in the subsequent backward scan. The fact that c1 was observed in Figure 3B but not in Figure 3A shows that the formation of surface functional groups was prevented if only chloride was present but not when ammonia was also available. This could be an indication of competitive adsorption of chloride and ammonia leading to surface functional groups at active sites initially occupied by

ammonia, whereas the surface is not functionalized at chloride adsorption sites. Such a mechanism requires strong adsorption of NH_3 , which was reported by Pittman Jr et al. (1999) at lateral planes of carbon fibers.

4.3. Direct ammonia oxidation as a treatment process for stored urine

The direct ammonia oxidation process on graphite has the advantage that no chlorinated by-products can be formed. The CV in chloride containing electrolyte showed that direct ammonia oxidation is feasible in the potential window from 1 to 1.6 V with no concomitant chlorine evolution. This was confirmed in the bulk electrolysis experiments with synthetic and real stored urine. As a consequence, no chlorinated organics were measured and chlorate and perchlorate were not produced either.

We estimated an electricity demand of $42 \text{ Wh} \cdot \text{gN}^{-1}$ with direct ammonia oxidation, which is about eleven times more than in conventional nitrification/pre-denitrification of domestic wastewater ($3.9 \text{ Wh} \cdot \text{gN}^{-1}$; Maurer et al., 2003). This high energy demand was due to the anodic and cathodic overpotentials as well as the ohmic resistance in the solution. A considerable part of the energy losses had to be attributed to the low CE. As discussed in Section 4.1, organic oxidation and graphite mineralization to CO_2 were probably the responsible side reactions. Energy requirements can be minimized if a cathode material is chosen with a lower overpotential for hydrogen formation (e.g. stainless steel). The ohmic resistance can be diminished with a smaller electrode gap in an improved cell design.

The corrosion, and especially the exfoliation, of the graphite anode was significantly reduced because the anode potential was low and because the formation of active chlorine was hindered. Other important aspects used to determine the applicability of direct ammonia oxidation are the

fate of the oxidized nitrogen and the nitrogen removal rate. A considerable amount of ammonia was oxidized to volatile nitrogen compounds. It cannot be excluded that NO_2 and N_2O were formed, as was found at BDD (Michels et al., 2010). However, it was demonstrated that the main gaseous nitrogen product from direct ammonia oxidation is molecular nitrogen (Webster et al., 2012; Michels et al., 2010). Thus, it is very likely that N_2 was the main gaseous nitrogen compound in our experiments.

Direct ammonia oxidation was slow ($2.9 \pm 0.3 \text{ gN} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, real stored urine) compared to indirect oxidation at an elevated anode potential ($126 \pm 6.7 \text{ gN} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, supplementary information), but was still slightly faster than in conventional surface-based biological systems ($2.5 \text{ gN} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$; Tchobanoglous et al., 2003). Assuming a urine volume of $1.5 \text{ L} \cdot \text{p}^{-1} \cdot \text{d}^{-1}$ with an ammonia concentration of $8.1 \text{ gN} \cdot \text{L}^{-1}$ (Udert et al., 2006), the necessary graphite surface area is $4.2 \text{ m}^2 \cdot \text{p}^{-1}$ for complete direct ammonia oxidation at the observed rate in real urine. In conventional bipolar cells, surface-to-volume ratios of $100 \text{ m}^2 \cdot \text{m}^{-3}$ can be achieved (Hamann and Vielstich, 2007), resulting in a liquid reactor volume of $42 \text{ L} \cdot \text{p}^{-1}$. Space requirements for the actual treatment facility would be higher. This footprint can be reduced by increasing the ammonia removal rate. We currently prepare a manuscript (Zöllig et al., in preparation) in which we discuss in detail whether this could be achieved by optimizing the hydraulic conditions in the electrolysis cell.

5. CONCLUSIONS

We investigated whether direct ammonia oxidation on graphite electrodes is a technically feasible alternative to indirect oxidation with active chlorine to remove ammonia from source separated urine. We found that this process is promising for the following reasons:

- Direct ammonia oxidation on graphite works at comparatively low anode potentials (1 – 1.6 V vs. SHE). No chlorine evolution occurs in this potential range. As a consequence, no chlorinated by-products are formed as is the case with indirect oxidation. Furthermore, the specific energy demand for ammonia removal is reduced compared to indirect oxidation because lower cell voltages are required.
- The low potentials reduce graphite corrosion, since the exfoliation of graphite particles is prevented. This makes it possible to use readily available and cheap graphite as an electrode material for the process, although it has to be regarded as a consumable due to the mineralization to CO₂. The graphite electrode is not deactivated by nitrogen poisoning as frequently observed with other electrodes. Instead we found that the graphite electrode is continuously active for direct ammonia oxidation, leading to surface-specific removal rates that are slightly higher than in conventional biological surface-based nitrogen removal systems.

The challenge in applying direct ammonia oxidation efficiently for the treatment of stored urine lies in the low removal rates and the still high specific energy demand. Further research should focus on the causes of these low removal rates and on reducing the energy demand. This should include the question of whether direct ammonia oxidation is limited by electron transfer kinetics or by diffusion.

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Table 1: Composition of the electrolytes used for CV and solutions used in the bulk electrolysis experiments (calculated from amounts of substances added or *measured values*). The electric conductivity was temperature-compensated for 25 °C. Standard deviations due to measurement uncertainties were less than 5%. The pH values in synthetic urine are high because little acetate and ammonia was added. ¹⁾below detection limit; ²⁾ NaOH for pH adjustment not considered

		Electrolytes for cyclic voltammetry				Synthetic urine solutions		Real urine
		Support	Support + NH ₃	Support + Cl	Support + NH ₃ + Cl	Without chloride	With chloride	
Organics	[mgCOD·L ⁻¹]	0	0	0	0	800	832	1460
Total ammonia	[mgN·L ⁻¹]	0	3500	0	3500	420	406	1550
Sodium	[mg·L ⁻¹]	23000 ²⁾	23000 ²⁾	25000 ²⁾	25000 ²⁾	7590	9410	670
Potassium	[mg·L ⁻¹]	0	0	0	0	2190	3710	560
Nitrate	[mgN·L ⁻¹]	0	0	0	0	0	0	< 10 ¹⁾
Nitrite	[mgN·L ⁻¹]	0	0	0	0	0	0	< 0.02 ¹⁾
Chloride	[mg·L ⁻¹]	0	0	3020	3020	0	3910	1200
Phosphate	[mgP·L ⁻¹]	0	0	0	0	527	527	
Carbonate	[mg·L ⁻¹]	0	0	0	0	16500	16500	
Sulfate	[mg·L ⁻¹]	0	0	0	0	1540	1540	230
Perchlorate	[mg·L ⁻¹]	99500	124000	99500	124000	0	0	
Conductivity	[mS·cm ⁻¹]					27.5	37.0	17.1
Initial pH	[-]	9.0	9.0	8.8	9.0	9.4	9.6	9.0

Figure 1

Figure 1: 5th scan of cyclic voltammograms in the supporting electrolyte (support, Table 1), and the supporting electrolyte with ammonia (support + NH₃, Table 1) recorded on graphite. Scan rate: 200 mV·s⁻¹; pH = 9; T = 25 °C.

Figure 2

Figure 2: Peak current density of ammonia oxidation on graphite (Δ) and the mole fraction of ammonia (solid line) as a function of pH in supporting electrolyte with ammonia (support + NH_3 , Table 1). Scan rate: $200 \text{ mV}\cdot\text{s}^{-1}$; $T = 25 \text{ }^\circ\text{C}$.

Figure 3

Figure 3: 5th scan of cyclic voltammograms in the supporting electrolyte (support, Table 1), A: Chloride containing electrolyte (support + Cl, Table 1) and B: Chloride and ammonia containing electrolyte (support + Cl + NH₃, Table 1) recorded on graphite. Scan rate 200 mV·s⁻¹, pH = 9, T = 25 °C.

Figure 4

Figure 4: Concentration profiles during potentiostatic electrolysis of synthetic stored urine at $E_a = 1.31\text{ V}$ with graphite anodes. Without chloride: (♦) ammonia and (▲) nitrate. With chloride: (◇) ammonia and (Δ) nitrate. $T = 25\text{ }^{\circ}\text{C}$.

Figure 5

Figure 5: Potentiostatic electrolysis of real stored urine at $E_a = 1.31$ V. A: Concentration profiles of total ammonia nitrogen (♦), total COD (■) and dissolved COD (●); B: pH and C: Current density. $T = 25$ °C.

Figure 6

Figure 6: The mass of anode and cathode before (black) and after (grey) electrolysis of real stored urine at $E_a = 1.31$ V. Error bars denote the standard deviation of three independent measurements.