Research Article

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The concept of load ratio applied to bioelectrochemical systems for ammonia recovery

Mariana Rodríguez Arredondo,[a,b] Philipp Kuntke,[a] Annemiek ter Heijne[b*] and Cees JN Buisman[a,b]

Abstract

BACKGROUND: The load ratio is a crucial parameter to optimize the current driven recovery of total ammonia nitrogen (TAN) from urine. The load ratio is the ratio between the current density and the TAN loading rate. It is currently not known if the load ratio concept applies to a bioelectrochemical system (BES) because the current density and TAN loading rate cannot be controlled independently.

RESULTS: We found a clear increasing trend in TAN removal efficiency with respect to load ratio in the BES for both human and synthetic urine. The maximum TAN removal efficiency was 60.9% at a load ratio of 0.7, corresponding to a TAN transport rate of 119 gN m^{-2} day^{-1} at an electrical energy input of 1.9 kWh kgN^{-1} (synthetic urine). Low load ratios (<1) were obtained, indicating that the current was not enough to transport all the TAN across the membrane.

CONCLUSIONS: BES and ES show the same general relationship between TAN removal efficiency and load ratio. Therefore, given a stable current density, the concept of load ratio can also predict the TAN removal efficiency in BES. Higher current densities, and insights into the factors limiting current, are needed to increase the load ratio and therefore the TAN removal efficiency.

Supporting information may be found in the online version of this article.

Keywords: ammonia removal; ammonia recovery; urine treatment; bioelectrochemical systems

INTRODUCTION

Around 1–2% of total world energy consumption is used to produce ammonia (NH_3) from atmospheric nitrogen gas (N_2).[1] A large part of this produced reactive nitrogen ends up in the environment, mainly in agricultural waste streams and domestic wastewater.[2,3] At the same time, removing nitrogen compounds from wastewater is one of the most energy-intensive processes for conventional wastewater treatment plants.[4] The widely used nitrogen-removal processes (i.e. nitrification/denitrification and Anammox) in conventional wastewater treatment plants convert usable reactive nitrogen compounds back to inert N_2. In order to reduce the cost and environmental impact of these processes, the focus of technological development has shifted from the removal of nitrogen to the recovery of nitrogen.[5] Direct recovery of nitrogen (i.e. NH_3 stripping, struvite precipitation or ion exchange[6]) from waste streams avoids its conversion first to N_2 and then back to a reactive form.[7]

Two of the newest technologies aiming for the recovery of total ammonia nitrogen [TAN; the sum of NH_3 and ammonium (NH_4^+) nitrogen] from wastewaters are electrochemical systems (ES) and bioelectrochemical systems (BES).[3,7–9] In order to recover a cleaner, purer product, these systems are usually coupled to stripping-absorption units[10–14] or gas-permeable hydrophobic membrane units (TransMembrane ChemiSorption or TMCS).[15–19] The main advantage of these integrated systems is their sustainability: there is no need for the addition of chemicals such as caustics, and useful by-products are obtained (such as electricity or hydrogen).

In general, (bio)electrochemical systems ((B)ESs) consist of an anode connected over an external circuit to a cathode. At the anode, an oxidation reaction occurs, whereas at the cathode a reduction reaction occurs. These reactions are catalysed by different materials, and in the case of bioelectrochemical systems, by electrochemically active microorganisms. The anode pH decreases due to the oxidation reaction leading to proton production,

* *Correspondence to: A ter Heijne, Department of Environmental Technology, Wageningen University, Bornse Weilanden 9, P.O. Box 17, 6700 AA Wageningen, The Netherlands. E-mail: annemiek.terheijne@wur.nl*

a *Wetsus, European Centre of Excellence for Sustainable Water Technology, Leeuwarden, The Netherlands*

b *Department of Environmental Technology, Wageningen University, Wageningen, The Netherlands*

whereas the cathode pH increases due to the hydrogen evolution reaction that leads to hydroxide production.[7] An ion exchange membrane is usually placed between anode and cathode chambers. An insufficient transport of protons and/or hydroxyl ions over these membranes results in pH differences between anode and cathode.[20] In (B)ESs for the recovery of TAN, a cation-exchange membrane (CEM) is used to allow for the transport of NH_4^+ from the feed to the cathode chamber, where it is converted to NH_3 due to the high catholyte pH. The catholyte is then hydraulically connected to a stripping-absorption or TMCS unit for the recovery of NH_3 in an acid. TAN in (B)ESs can be transported over the CEM via diffusion (concentration-gradient induced) and electromigration (current-induced).[21]

The complexity of reactions occurring in (B)ESs and the interdependence of the parameters involved make the complete, large-scale recovery of TAN a challenge.[17,19] The load ratio was recently identified as a crucial parameter to optimize the recovery of TAN in an ES treating urine.[19] The load ratio is the ratio between the current density and the TAN loading rate of the system. In theory, one mole of electrons is needed to remove one mole of TAN, given that under acidic conditions (commonly found in the anode) all TAN is present as NH_4^+. Accordingly, three conditions can be defined: a load ratio <1 describes a situation in which the current density is not enough to transport all of the TAN in the system; a load ratio of 1 describes a situation in which the current density and the TAN loading rate are equal; and a load ratio >1 describes a situation in which the current density is higher than the TAN loading rate, so that ideally all TAN could be transported. The higher the load ratio, the higher the removal efficiency of the system, but also the higher the energy input. Therefore, working at an optimum load ratio allows maximum TAN removal efficiency at minimal energy input.[19]

The load ratio can be manipulated either by changing the current density (such as in an electrochemical system) or the TAN loading rate. In an ES, the load ratio can be easily manipulated, because both the applied current density and the TAN loading rate can be controlled independently. In a BES, however, the current density and the TAN loading rate cannot be controlled independently. We recently investigated the influence of the load ratio in a ES,[19] but the application of the load ratio concept in a BES has not been studied. In a BES, the current density depends on the oxidation of organic matter (COD) by microorganisms. The oxidation of organic matter by microorganisms, in turn, depends on the amount and nature of organic compounds, anode potential and other factors also affecting the microorganisms, such as pH.[22–24] At the same time, the COD:TAN ratio of a certain wastewater is fixed, so manipulating the TAN loading rate also would affect the COD loading and therefore the current density. The load ratio, thus, might be a difficult parameter to control in a BES.

The goal of this study was to investigate the validity and applicability of the concept of load ratio in a BES treating urine. BESs with integrated TMCS units were run on human urine and synthetic urine at different dilutions, flow rates and modifications (such as reduced TAN concentration, lower pH and feeding the effluent of the cell) in order to obtain a variety of load ratios.

MATERIALS AND METHODS

Experimental set-up

The experiments were performed in microbial electrolysis cells (MECs) coupled to hydrophobic, gas-permeable membrane modules, also called TMCS units. The cathode chamber of each cell was hydraulically connected to an individual TMCS unit as described previously.[19] The catholyte (cathode electrolyte) was recirculated over the TMCS unit for the recovery of NH_3 in sulfuric acid.[16,19] The set-up scheme and reactions occurring at the anode and the cathode can be found in the Supporting Information (Fig. S1).

Three MECs were used in total, one for each experimental run. Each cell consisted of two titanium plates (16 cm x 16 cm) with a machined flow field (10 cm x 10 cm x 0.2 cm) coated with a thin Pt layer (50 g m^{-2}) (Magneto Special Anodes BV, Schiedam, The Netherlands). The platinized flow field served as an anodic current collector or as a cathode (acting as a catalyst for a hydrogen evolution reaction). Graphite felt (FMI Composites Ltd., Galashiels, Scotland) was used as the anode, whereas the cathode was either the platinized flow field itself or a 100-µm titanium mesh (10 x 10 cm) with a ruthenium mixed metal oxide (RuMMO) coating (Magneto Special Anodes BV). Both cathode materials are known as excellent catalysts for hydrogen evolution.[25] The hydraulic volume of the anode chamber, including the recirculation vessel, was 200 mL. The hydraulic volume of the cathode chamber, including the recirculation vessel and the volume encased in the TMCS unit, was 300 mL. Anode and cathode chambers were separated by a cation exchange membrane (Nafion®117, Ion Power GmbH, Germany) with a projected surface area of 0.01 m^2 (same as anode and cathode). Spacer material (PETEX 07-4000/64, Sefar BV, Goor, The Netherlands) was placed on both anode and cathode sides of the membrane.

Each TMCS unit consisted of a tubular polyproplylene membrane (pore size 200 nm, type Accurel PP V8/HF, CUT Membrane Technology GmbH, Germany) encased in a custom-made membrane module. The TMCS membrane has an outer surface area of 0.04 m^2. It was operated in crossflow mode, with the catholyte on the inner and the acid on the outer side of the TMCS membrane. The acid recirculation vessel was placed on top of a magnetic stirring plate in order to provide better mixing.

Anode and cathode potentials were measured *versus* reference electrodes (Ag/AgCl 3 mol L^{-1} KCl, +0.2 V *versus* NHE, QM711X, ProSense BV, Oosterhout, The Netherlands), which were placed in the respective electrolytes near the inlet of anode and cathode chambers. The anode potential was controlled by a potentiostat (KP 07, Bank 116 Elektronik - Intelligent Controls GmbH, Pohlheim, Germany). Temperature and pH of both anolyte (anode electrolyte) and catholyte were measured by pH meters (Orbisint CPS11D sensor with Liquisys M COM 253 transmitter, Endress + Hauser BV, Naarden, The Netherlands) placed in each recirculation vessel. A data logger (Memograph M RSG40, Endress + Hauser BV) recorded each minute the anode and cathode potentials, anode and cathode pH and temperature, cell voltage and current density.

Two peristaltic pumps (Masterflex L/S, Metrohm Applikon BV, Schiedam, The Netherlands) were used in each system: one to provide fresh anolyte continuously and the other to recirculate anolyte, catholyte and acid through the TMCS unit.

Both anode and cathode recirculation vessels had a gas vent connected to a water lock to let CO_2, CH_4 and H_2 escape and to prevent O_2 from coming into the system.

Media composition and inoculation

Media composition

Pre-treated human urine and synthetic urine were used as stock solutions to prepare varied anolyte inflows. Human urine was collected from the water-free urinals (Urimat®, Biocompact,

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Table 1. Overview of experiments performed in each run

Run	Influent	Dilution or conditions tested	Duration (days)	TAN loading rate (g m^{-2} day^{-1})	J (A m^{-2})	L_N (–)
1	Urine	5x	16	61–78	3.3–4.5	0.6–0.8
		2.5x	21	76–82	2.6–3.5	0.4–0.6
		2.5x, lower flowrate	14	59–63	2.3–2.7	0.5
		–	13	73–81	0.5–0.8	0.1
		Lower pH (7.6)	42	74–83	0.5–0.6	0.1
		+60 mmol L^{-1} acetate	15	75–80	0.4–0.5	0.1
2	Urine 70% less TAN	5x	7	49–80	5.9–9.2	1.5
	Urine	34% TAN removed (5x), 6x, 7.5x, effluents, different flowrates	51	109–565	0.9–5.0	0.0–0.6
	Synthetic urine	33% TAN removed (9x), 9x, 4x, 2x	21	139–226	5.1–10.6	0.4–0.7
3	Urine 70% less TAN	5x	7	49–80	5.9–9.5	1.5
	Urine[a]	34% TAN removed (5x), 6x, 7.5x, effluents, different flowrates	62	109–449	1.1–6.3	0.0–0.7
	Synthetic urine	33% TAN removed (9x), 9x, 4x, 2x	30	137–226	1.4–3.1	0.1–0.3

The experiments were separated in three categories: urine, urine 70% less TAN and synthetic urine. In each category, different dilutions, flow rates and modifications (such as different pH or using collected effluent) were tested. The urine from which 34% of the TAN was removed is included in the category 'urine'. The range of TAN loading rate tested, as well as the range of current density (J) and load ratio (L_N) obtained are shown.
[a] Anode potential was −0.4 V during 34 days, instead of −0.3 V as for the rest of the experiments.

Rotterdam, The Netherlands) installed in the male bathrooms of the Wetsus building (Leeuwarden, The Netherlands). The collected urine was stored in a tank for approximately 7 days, and later pre-treated by struvite precipitation and filtration to remove phosphate as described previously.[19] The composition of the pre-treated human urine can be found in Table S1. The synthetic urine stock was adapted from Ledezma *et al.*[26] by reducing the amounts of acetate and TAN. This was done to match the chemical oxygen demand (COD) and TAN concentration of the pre-treated human urine used in this study. The carbon source was ammonium acetate, whereas the TAN came from three sources: the ammonium acetate, ammonium hydroxide and ammonium bicarbonate. The complete recipe can be found in Table S2.

Modifications were made to the stocks of human urine and synthetic urine before feeding them to the BES (Table 1). Depending on the experiment, these modifications included dilution, pH adjustment and reduction of the TAN concentration. The reduction of the TAN concentration was achieved, in the case of human urine, by pre-treatment with the TMCS. In the case of synthetic urine, the TAN concentration in one experiment was reduced by 33% by adding half of the ammonium bicarbonate. For some human urine experiments, the effluent from the BES was collected and later fed back to the cell.

The catholyte consisted of a 0.01 mol L^{-1} NaCl solution. One litre of 1 mol L^{-1} H_2SO_4 was used as the acid for absorption in the TMCS unit.

Inoculation and start-up

The cell from the first run was inoculated with effluent from an active, acetate oxidizing bioanode. The two other cells (second and third run) were inoculated with a mixture of two effluents: 20 mL effluent from an active, acetate oxidizing bioanode and 10 mL effluent from a bioanode previously running on urine (cell from first run). For the start-up period, synthetic wastewater (composition in Table S3) with 10 mmol L^{-1} sodium acetate as the carbon source was used. All cells were started up with cell potential control at −0.5 V. After stable current densities were established, the configuration was changed to anode potential control. The bioanode from the first run was constantly poised at a potential of −0.35 V *versus* Ag/AgCl and later changed to −0.3 V *versus* Ag/AgCl. For the second and third runs, the bioanodes were initially poised at a potential of −0.4 V *versus* Ag/AgCl and gradually increased to −0.3 V *versus* Ag/AgCl. After a start-up period of *c.* 1 month in all cases, pre-treated urine was introduced.

System operation

Each experimental run lasted 5 months. The second and third runs were performed at the same time. After the start-up phase of each run, the anode potential was constantly controlled at −0.3 V *versus* Ag/AgCl. There was an exception in which, due to deterioration in performance, the bioanode of cell 3 was controlled at −0.4 V *versus* Ag/AgCl for 34 days.

The temperature of the cells was controlled (30.3 ± 0.3°C). The anode chambers had a continuous inflow of anolyte (inflow rate), whereas both the cathode chamber and TMCS unit were operated in batch mode. All three liquids (anolyte, catholyte and acid) were recirculated over their respective chambers at either 70 mL min^{-1} (first run, and first 67 days of the second and third runs) or 140 mL min^{-1} (after 67 days of the second and third runs). The anolyte inflow rates were varied throughout the experiments (ranging from 0.2 to 6.3 mL min^{-1}), which resulted in varied current densities and load ratios as shown in Table 1. In most of the experiments, water transport over the TMCS membrane was observed. Catholyte was added once the volume was <100 mL, and the acid volume was lowered if it was >1.1 L or renewed if it contained more than 14 gTAN L^{-1}. Both the catholyte and acid solutions were continuously sparged with a very low amount of N_2 gas (≤2 mL min^{-1}) to maintain anaerobic conditions.

After the start-up phase of the first run, the synthetic wastewater was switched to 5x diluted urine and gradually changed to undiluted urine, while trying to maintain TAN loading rates constant, as shown in Table 1.

After the start-up phase of the second and third runs, the synthetic wastewater was first switched to 5x diluted urine containing 70% less TAN, followed by other experiments with 5x diluted urine containing 34% less TAN, and later urine in different dilutions and other amendments; see 'Media composition' section above. Part of the TAN in urine was removed to manipulate the TAN loading rate

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in order to test different load ratios. Afterwards, experiments with synthetic urine at different dilutions were performed (Table 1). All experiments performed with pre-treated human urine, with the exception of the one with 70% less TAN, are referred to as 'urine' experiments. The experiments performed without TMCS or in which the TMCS was not working are not taken into account in Table 1 or the results.

The three BESs were operated on a large variety of operational condition (i.e. synthetic urine, pre-treated urine, different dilutions, adjustments in pH, TAN and COD concentration). Those conditions were categorized as seen in Table 1.

Sampling and chemical analysis

Samples were taken after a minimum of four hydraulic retention times (HRTs) after a parameter was changed. For each condition, two to seven samples were taken from the inflow and each recirculation vessel (anolyte, catholyte and acid), with a sampling interval of at least 24 h.

The samples were filtered through 0.45-µm filters (PTFE syringe filters, VWR International BV, Amsterdam, The Netherlands) before analysis. COD concentration (inflow, anolyte and catholyte), as well as TAN concentration from the acid samples were measured using photometric test kits (LCK 514 and LCK 303, spectrophotometer XION 500, Dr. Lange Nederland BV, The Netherlands). TAN concentrations from the inflow, anolyte and catholyte samples in the first run also were measured as described previously. In the second and third runs, TAN, cations and anions were measured by ion chromatography as described earlier.[19]

Calculations

The load ratio was calculated as described previously by Rodriguez Arredondo *et al.*[19] The load ratio is the relation between the current density and the TAN loading rate, both expressed in A m^{-2} [Eqn (1)]:

$$L_N = \frac{j_{applied}}{C_{anolyte\ inflow,TAN} * Q_{anode} * \frac{F}{A_m}} \quad (1)$$

where $j_{applied}$ is the applied current (A m^{-2}), $C_{anolyte\ inflow,\ TAN}$ is the molar concentration of TAN in the anolyte inflow (mol m^{-3}), Q_{anode} the anolyte inflow rate (m^3 s^{-1}), F the Faraday constant (96 485 C mol^{-1}) and A_m the surface area of the cation exchange membrane (0.01 m^2).

The equations for TAN removal efficiency (RE_{TAN}), TAN transport rate over the CEM (J_{TAN}), TAN transport efficiency (tE_{TAN}) and total energy input can be found in the Supporting Information.

RESULTS AND DISCUSSION

Clear increasing trend in TAN removal efficiency with load ratio

The current density from the BESs ranged, on average, from 0.4 to 10.6 A m^{-2}, and resulted in varying load ratios (Table 1). The load ratio is the ratio between the current and the TAN loading rate, both expressed in A m^{-2}. As seen in Fig. 1, there was a clear increasing trend in TAN removal efficiency with respect to load ratio for both human and synthetic urine. The maximum removal efficiency was 60.9% for a load ratio of 0.68. In some cases, TAN removal efficiency was lower than expected. This occurred in two specific situations: (i) when NH_3 was not effectively removed from the catholyte by the TMCS, and (ii) for urine with the lowest TAN concentration (urine 70% less TAN).

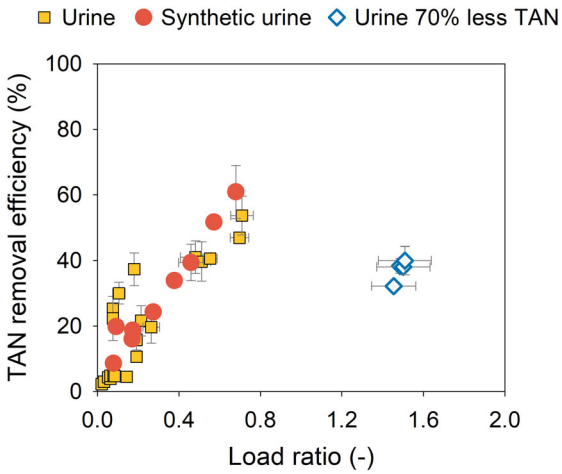

Figure 1. TAN removal efficiency with respect to load ratio from a bioelectrochemical system treating real and synthetic urine at different dilutions, and urine with 70% less TAN (pre-treated with a TMCS).

Negative TAN removals were observed for the situation without a TMCS, or when the TMCS was not operational (data not shown). This was caused by diffusion of TAN from the cathode chamber back into the anode chamber when TAN was not effectively removed from the catholyte.[21,27,28]

The experiments with urine with 70% less TAN in Fig. 1 show the highest load ratio. The general expected trend is for the TAN removal efficiency to increase with the load ratio, reaching a maximum and then stabilizing. For that reason, these experiments were expected to result in the highest TAN removal efficiencies, yet this was not the case. In these experiments, the initial TAN concentration was the lowest: 199.6 ± 7.3 mg L^{-1}. This low TAN concentration was the result of a pre-treatment step, in which *c.* 70% of the TAN in urine was removed with a TMCS, the pH was adjusted with NaOH and then the urine was diluted five times. For this reason, the proportion of NH_4^+ compared to other ions was much lower than in other experiments, which lead to the relatively high transport of other ions. Therefore, even though the current density was sufficient to transport all the TAN (load ratio higher than 1), the lower TAN transport efficiency resulted in an overall lower TAN removal efficiency.

Effect of TAN transport efficiency on TAN removal efficiency

The transport efficiency shows the contribution of an ion to the total charge transport across the membrane. According to our previous study,[19] the load ratio is better suited as a single parameter to predict TAN removal efficiency than the TAN transport efficiency. Our current results on BESs (Fig. 2) support this finding. In Fig. 2, no defined relationship can be observed between the transport efficiency and TAN removal efficiency. Even though most of the charge was transported by ammonium in the majority of the experiments (TAN transport efficiencies between 50% and 100%), the TAN removal efficiencies varied widely.

Transport efficiencies >100%: diffusion and charge exchange

The data points in Fig. 2 with TAN transport efficiencies >200% correspond to the data points in Fig. 1 with load ratios <0.2 and higher TAN removal efficiencies than others. One of the reasons for transport efficiencies >100% is diffusion. The contribution of diffusion compared to migration increases at low current

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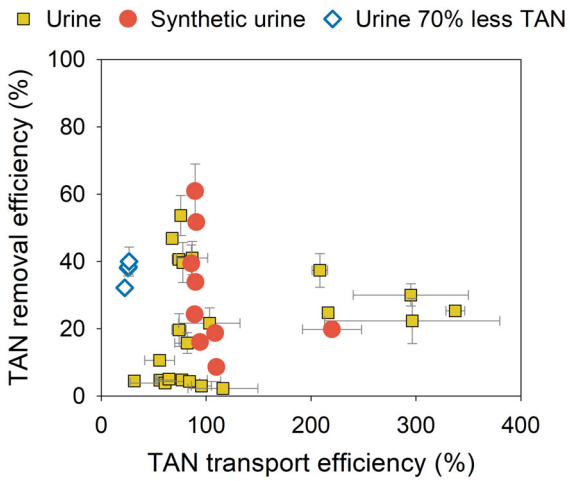

Figure 2. TAN removal efficiency with respect to transport efficiency from a bioelectrochemical system treating real and synthetic urine at different dilutions and urine with 70% less TAN (pre-treated with a TMCS).

densities.[14,21,29] Some of the data points in Fig. 2 with transport efficiencies >200% were the ones with the lowest current densities overall: 0.5–0.7 A m^{-2}. Therefore, even though the load ratio was very low because of the low current, the TAN removal efficiency was high because of the contribution of diffusion.

Another reason for transport efficiencies >100% is the charge exchange process.[30,31] When cations other than NH_4^+ (such as Na^+ and K^+) diffuse from cathode to anode, an equivalent amount of NH_4^+ is transferred from anode to cathode to maintain electroneutrality. That was the case in another experiment: the concentration of competing cations (Na^+ and K^+) in the catholyte was much higher than in the anolyte, promoting their diffusion from cathode to anode (Fig. S2B; experiment 4). To maintain electroneutrality, an equivalent amount of NH_4^+ can diffuse from anode to cathode, which resulted in transport efficiencies higher than 100%.

Transport efficiencies <30%: ionic composition

The transport efficiency is influenced, among other factors, by the ionic composition (in this case, the proportion of NH_4^+ compared to other competing ions, such as Na^+ and K^+). The experiments in which the urine was pre-treated to remove 70% of the TAN resulted in the lowest transport efficiencies. As mentioned previously, even though the current density was sufficient to transport all the TAN (load ratio >1), mostly other cations were transported across the CEM, resulting in an overall lower TAN removal efficiency.

This can be explained by the ionic composition of the feed. The mole fraction of TAN to the total cations ($n_{TAN}/n_{total\ cations}$) in the experiments with 70% less TAN was around three times lower than for the rest of the experiments (mole fractions were 0.23 and 0.69, respectively). Other studies have shown that high TAN removal efficiencies (>60%) can be achieved at low transport efficiencies (15–30%), but in those cases the mole fraction of TAN was higher (from 0.38 to 0.70).[10,12,19] Therefore, a much higher load ratio (higher current density) is required to reach high TAN removal efficiencies in this situation (low TAN mole fractions), which will increase the energy demand. These results show that even though the load ratio is a crucial parameter to optimize the operation of the nitrogen-recovery system, there are limitations to this simple model. As shown in this and earlier studies,[19] the wastewater composition (i.e. TAN concentration relative to other cations) does affect the current density required to reach high recoveries. Therefore, the model needs to be adapted to the specifics of the wastewater.

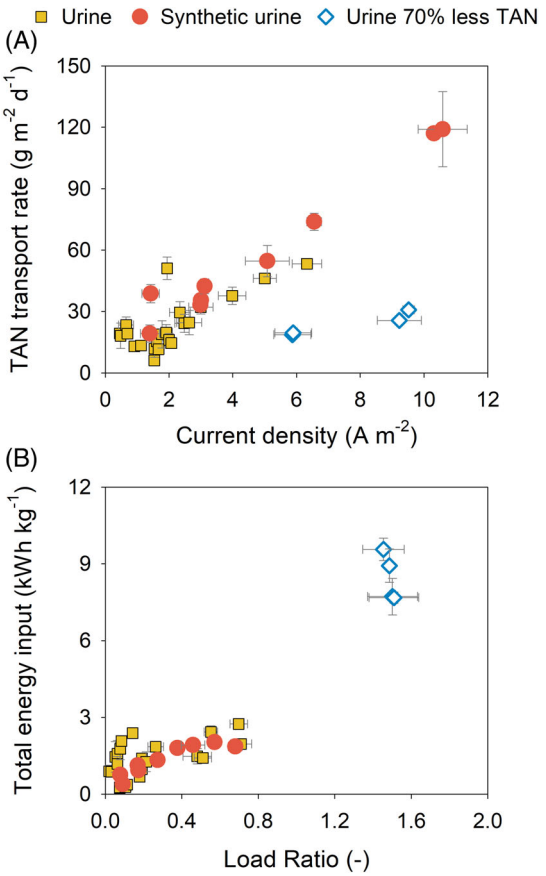

Figure 3. (A) TAN transport rate with respect to current density and (B) total energy input with respect to load ratio from a bioelectrochemical system treating real and synthetic urine at different dilutions and urine with 70% less TAN (urine was pre-treated with a TMCS).

The relationship between the load ratio and the total energy input

There is a linear increase in TAN transport rate (or flux) with current density, as expected [Fig. 3(A)]. Again, the urine experiments with the lowest TAN concentration (urine 70% less TAN) were the exception to this trend. These experiments showed lower TAN fluxes than other urine experiments, even at higher current densities. Therefore, a higher current density is needed to remove the same amount of TAN from a stream with a low TAN concentration compared to a stream with a high TAN concentration. As a result, the energy input for TAN recovery is higher [Fig. 3(B)]. For some experiments the urine was pre-treated with the TMCS to remove *c.* 34% of the initial TAN, resulting in a TAN mole fraction of 0.46 (1.5 times lower than the other urine experiments). However, this did not seem to have an effect as radical on the overall performance as the experiments with 70% less TAN (mole fraction of 0.23).

In our previous study with an ES,[19] a 'limiting' load ratio (1.2) was found. This meant that working at a load ratio higher than the limiting one costed more energy without providing a considerable increase in removal efficiency. In the present study, except for the urine with 70% less TAN, there was no steep increase of energy input with load ratio at any point [Fig. 3(B)]. Because we did not

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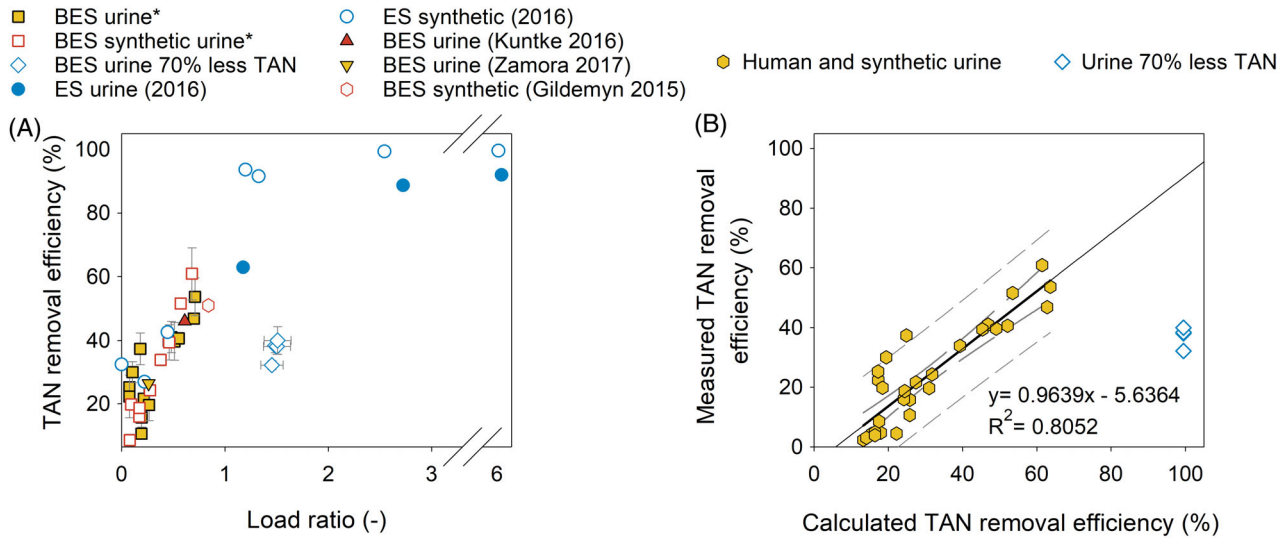

Figure 4. (A) TAN removal efficiency with respect to load ratio in bioelectrochemical systems (BES) and electrochemical systems (ES) based on this study and four other different studies. This study (*) used a BES to treat real and synthetic urine at different dilutions, and urine with 70% less TAN (pre-treated). (B) Correlation between the predicted and the measured TAN removal efficiency in this BES study. The predicted TAN removal efficiency was calculated using the load ratio model based on ES experiments.[19] Long-dashed and short-dashed curves represent the 95% confidence interval and 95% prediction interval for the linear regression, respectively.

obtain load ratios >0.8, an optimal or limiting load ratio was never reached.

TAN removal efficiency was limited in a BES: high load ratios cannot be achieved

Figure 4 compares the results from this study with similar BES studies for TAN recovery and with the results in our previous ES study. The selected studies also use an integrated system in the cathode for the effective recovery of NH_3 (such as stripping-absorption or a TMCS unit). The load ratio was calculated with the data provided by these studies. The results from these studies were similar to ours (except for the 70% less TAN cases), and follow the general trend of increasing TAN recovery with increasing load ratio. This trend is the same for both BES and ES. Higher TAN removal efficiencies were achieved with an ES compared to the BESs, due to the higher load ratios obtained.

As observed in Fig. 4(A), a load ratio <1.5 was obtained in all of our bioelectrochemical experiments. Except for the experiments at the lowest TAN concentration, the load ratio in all experiments was <0.8. This also was the case in other studies of BESs for TAN recovery.[11,16,17] At these load ratios, the current was not high enough to transport all ofthe TAN across the membrane.

Figure 4(B) shows the correlation between the predicted TAN removal efficiencies (using the load ratio model based on ES experiments[19]) and the measured TAN removal efficiencies in this study. Overall, a good correlation ($R^2 = 0.81$) was found. The slope of the linear regression was lower than one (0.96), which means that, in general, the prediction slightly overestimates the actual TAN removal efficiency. Therefore, the concept of load ratio is a useful tool to predict the TAN removal efficiency in BESs, too; however, it was not possible in this study to achieve high TAN recovery efficiencies (maximum of 47% for human diluted urine and 60% for synthetic urine). The reason for this is the lack of control of the current density due to microbial processes involved in a BES, compared to an ES.

For the load ratio (and therefore the TAN removal efficiency) to increase, higher current densities are needed. In ESs, higher load ratios can be achieved by applying higher current densities without the dependence on COD removal. As mentioned earlier, the current density in a BES depends on the oxidation of organic matter by microorganisms, which in turn depends on the amount and nature of organic compounds, anode potential and other factors also affecting the microorganisms, such as pH (Table S4). Compared to an ES, a BES offers a lower energy input[16] and an effluent with a lower COD load. In these BES experiments, the COD removal efficiencies were usually <40% (data not shown). High coulombic efficiencies (>60%, data not shown) were obtained in most cases, meaning that most of the COD consumed was converted to electric current. For this reason, more insights are needed into what is limiting the removal of COD and its relation with TAN removal.

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Supporting Information

Supporting information may be found in the online version of this article.

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