



Load ratio determines the ammonia recovery and energy input of an electrochemical system



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ABSTRACT

Complete removal and recovery of total ammonia nitrogen (TAN) from wastewaters in (bio)electrochemical systems has proven to be a challenge. The system performance depends on several factors, such as current density, TAN loading rate and pH. The interdependence among these factors is not well understood yet: insight is needed to achieve maximum ammonium recovery at minimal energy input. The aim of this study was to investigate the influence of current density and TAN loading rate on the recovery efficiency and energy input of an electrochemical cell (EC). We therefore defined the load ratio, which is the ratio between the applied current and the TAN loading rate. The system consisted of an EC coupled to a membrane unit for the recovery of ammonia. Synthetic wastewater, with TAN concentration similar to urine, was used to develop a simple model to predict the system performance based on the load ratio, and urine was later used to evaluate TAN transport in a more complex wastewater. High fluxes (up to $433 \text{ gN m}^{-2} \text{ d}^{-1}$) and recovery efficiencies (up to 100%) were obtained. The simple model presented here is also suited to predict the performance of similar systems for TAN recovery, and can be used to optimize their operation.

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1. Introduction

Nitrogen removal from wastewaters is necessary to prevent the pollution of receiving water bodies. Nitrogen, on the other hand, is an essential nutrient for plants, so it is used in the production of fertilizers to increase food production. Both the removal of nitrogen compounds from wastewater and their production are energy intensive (Matassa et al., 2015; Maurer et al., 2003). Energy use for the removal and production of nitrogen compounds can be reduced by recovering these from wastewater. In domestic wastewater, most of the nitrogen can be found in the form of ammonium (NH_4^+) or ammonia (NH_3), depending on the temperature and pH (von Sperling, 2007). The combination of both NH_4^+ and NH_3 is referred to as total ammonia nitrogen (TAN). Direct recovery of TAN from wastewater can save resources by creating a shortcut in the nitrogen cycle: it accomplishes removal and eliminates the need of an artificial nitrogen fixation process (Rodríguez Arredondo et al.,

2015).

(Bio)electrochemical systems ((B)ESs) have been proposed as an energy-efficient alternative to recover TAN from wastewater (Desloover et al., 2012; Kuntke et al., 2012; Ledezma et al., 2015; Rodríguez Arredondo et al., 2015). These systems consist of two electrodes: an anode, where an oxidation reaction takes place, and a cathode, where reduction occurs. Energy from the wastewater can be recovered in the form of electricity or chemicals (such as H_2) depending on the cathodic reaction (Logan et al., 2008). In bioelectrochemical systems (BESs), at least one of the reactions taking place at the electrodes is catalysed by microorganisms; while in electrochemical systems (ES) all reactions are purely electrochemical and no microorganisms are involved. In the case of TAN recovery in ES, water electrolysis usually takes place, where oxygen is produced at the anode and H_2 is produced at the cathode.

The anode and cathode chambers of (B)ESs are often separated by an ion exchange membrane (Logan et al. 2006, 2008). When the electrons produced in the oxidation reaction flow through an external circuit from anode to cathode, ions in solution migrate

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through this ion exchange membrane to maintain electroneutrality (Rozendal et al., 2007). In (B)ESs for the recovery of TAN, a cation exchange membrane (CEM) is used to allow the transport of NH_4^+ in the wastewater from anode to cathode. In the cathode chamber, the NH_4^+ removed from the wastewater is converted to volatile NH_3 due to the high pH of the catholyte (cathode electrolyte) (Kim et al., 2008). To strip the NH_3 out of the catholyte effectively, an additional gas flow or stripping process is needed (Dykstra et al., 2014; Kuntke et al., 2014). The NH_3 is then recovered as gas or absorbed into an acid.

TAN has successfully been recovered from nitrogen-rich wastewaters (like anaerobic digestate or urine) by the combination of (bio)electrochemical systems with either stripping-absorption (Desloover et al., 2012; Luther et al., 2015) or gas-permeable hydrophobic membranes (TransMembrane ChemiSorption, or TMCS) (Kuntke et al., 2016). Complete TAN removal (how much TAN is removed from the wastewater) and recovery (how much TAN is recovered in the acid or as gas) in these integrated systems, however, has proven to be a challenge. As examples, an ES coupled to a stripping-absorption unit treating urine obtained an average TAN removal efficiency of 75% and an average recovery efficiency of 57% (Luther et al., 2015); while a BES coupled to a gas-permeable membrane unit obtained an average of 42% removal efficiency and a maximum recovery of 49% (Kuntke et al., 2016).

In order to be effectively recovered, TAN needs to be transported from anode to cathode. It has been shown that TAN transport across the CEM is determined by several factors, such as current density, TAN loading rate, pH and continuous removal of NH_3 from the cathode by the stripping or membrane unit (Desloover et al., 2012; Kuntke et al., 2011, 2012). The interdependence among these factors, however, is currently not well understood: insight is needed to achieve maximum TAN recovery at minimal energy input. In steady-state, NH_4^+ is the main charge carrier, since it is the only ion effectively removed from the catholyte (by stripping or any other means); however, at a certain point (limiting current density), the NH_4^+ gets depleted at the membrane surface (anode side), causing other ions to transport the charge. This phenomenon can cause the membrane potential, and therefore, the total energy input, to increase steeply. The limiting current density itself depends on, among others, the bulk concentration and the electrolyte flow rate (Długoński et al., 2010). Thus, both current density and loading rate can affect the system performance. We therefore defined the load ratio (L_N) as the ratio between the current density and TAN loading rate, in order to study its relation to TAN transport.

The aim of this study was to investigate the influence of current density and TAN loading rate on the TAN recovery efficiency and energy input of an electrochemical system. The system consisted of an electrochemical cell (EC) coupled to a TMCS unit for the recovery of ammonia. An EC was chosen instead of an MEC (Kuntke et al., 2016) to be able to work at high and constant currents, which is needed to study the effects of current in combination with TAN loading on TAN transport. Whereas the main difference between the EC and the MEC is the anodic oxidation reaction (water oxidation vs. organic carbon source), other aspects are similar: hydrogen evolution reaction at the cathode (Kelly and He, 2014; Rodríguez Arredondo et al., 2015) and high pH at the cathode (Gildemyn et al., 2015). Synthetic wastewater, with TAN concentration similar to urine, was used to develop a simple model to predict the performance of the system based on the load ratio, and urine was later used to evaluate TAN transport in a more complex wastewater.

2. Materials and methods

2.1. Experimental setup

The experiments were performed in an EC coupled to a membrane module (TMCS unit) (Fig. 1). The catholyte was recirculated via the TMCS unit for recovery of NH_3 . The TMCS unit contains a tubular hydrophobic membrane through which ammonia (gas) can pass and then be absorbed by an acid. This configuration was chosen since it has been proven to effectively remove ammonia from the catholyte, facilitating the overall TAN removal and recovery (Kuntke et al., 2016).

The electrochemical cell consisted of two poly (methyl methacrylate) (PMMA) panels (21 cm × 21 cm) which encased the anode and the cathode. Titanium mesh electrodes with a 50 g m^{-2} platinum coating (Magneto Special Anodes, The Netherlands) were used as anode and cathode. The dimensions of the anode and cathode chambers are 10 cm × 10 cm × 0.2 cm. 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). 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 240 mL.

The TMCS unit used in this study consisted of a tubular polypropylene membrane (pore size 200 nm, type Accurel PP V8/HF, CUT Membrane Technology GmbH, Germany) encased in a custom-made membrane module (Kuntke et al., 2016). 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.

Anode and cathode potential were measured versus reference electrodes (Ag/AgCl 3 M KCl, +0.2 V vs. NHE, QM711X, ProSense BV-QiS, Oosterhout, The Netherlands), which were placed in the respective electrolytes near the inlet of anode and cathode chambers. The reference electrodes were connected to a high impedance preamplifier (Ext-Ins technologies, Leeuwarden, The Netherlands). Electrical current was controlled by an external power supply (ES 030-5, Delta Elektronika BV, Zierikzee, The Netherlands).

Temperature and pH of both anolyte (anode electrolyte) and catholyte were measured by pH meters (Orbisint CPS11D sensor with Lquisys M COM 253 transmitter, Endress+Hauser BV, Naarden, The Netherlands) placed in each recirculation vessel. A data logger (Memograph M RSG40, Endress + Hauser BV, Naarden, The Netherlands) recorded each minute the anode and cathode potentials, cell voltage and anode and cathode pH.

Two peristaltic pumps (Masterflex L/S, Metrohm Applikon BV, Schiedam, The Netherlands) were used in the system: one to provide fresh anode medium continuously and the other to recirculate both anolyte and catholyte. A diaphragm pump (SIMDOS 10, KNF Flodos AG, Sursee, Switzerland) was used to recycle the acid through the TMCS unit.

2.2. System operation

The system was operated at room temperature ($23.4 \pm 1.1 \text{ }^\circ\text{C}$). The anode chamber of the electrochemical cell had a continuous inflow of fresh medium (anolyte inflow rate), while 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 70 mL min^{-1} . Two anolyte inflow rates were used: 1.1 mL min^{-1} and 0.2 mL min^{-1} , resulting in an HRT of 3.0 and 16.7 h.

The effluent from the anode chamber was collected in a closed container sealed with a water lock. Both anode and cathode

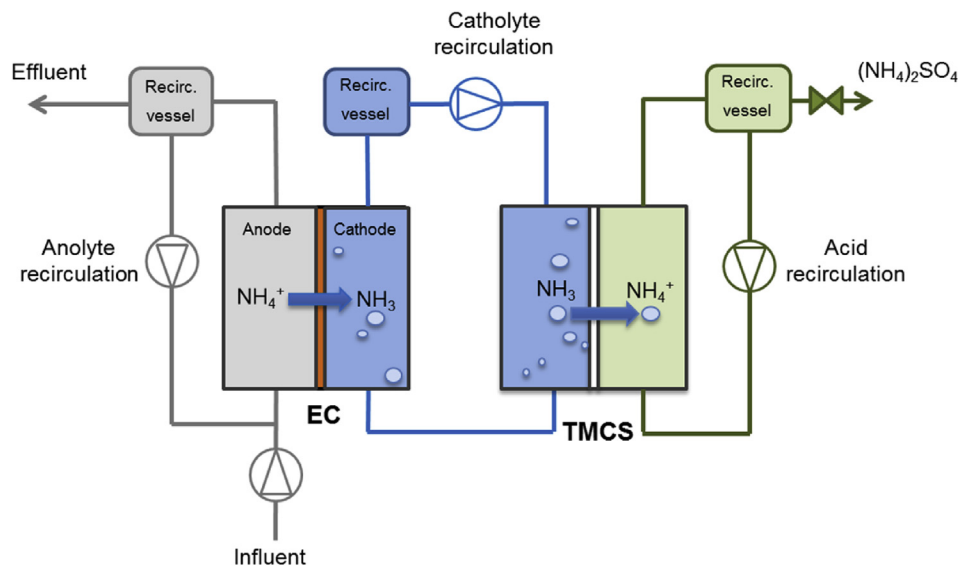


Fig. 1. Schematic representation of experimental setup. EC = Electrochemical Cell; TMCS = TransMembrane Chemisorption. There were two membranes in the system: a cation exchange membrane in the EC and a gas-permeable hydrophobic membrane in the TMCS unit.

recirculation vessels had a vent to let the produced gasses escape.

Steady-state was defined as the situation in which anode and cathode pH, as well as anode and cathode potentials were stable. After taking two samples in steady-state, the experiment was finished.

2.3. Media composition

Two types of wastewater were used as anolyte during the experiments: a simplified synthetic wastewater and pre-treated human urine. The synthetic wastewater consisted of 13.7 g L^{-1} $(\text{NH}_4)_2\text{CO}_3$ and 4.6 g L^{-1} Na_2CO_3 (0.14 and 0.04 M, respectively). This composition was chosen to have similar concentrations of TAN and Na^+ compared to urine (Kuntke et al., 2012), but with only one competing cation (Na^+) to simplify the study of ammonium transport. Sodium was chosen as the competing cation due to its high predominance in urine. The pH of the synthetic wastewater was 9.3 ± 0.1 . Urine was collected from the water-free urinals (Urimat[®], Biocompact, Rotterdam, The Netherlands) installed in the male bathrooms of Wetsus (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 (Kuntke et al., 2014). Struvite precipitation was performed at a molar ratio of 1.3:1 (Mg:P) using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ as the magnesium source. After precipitation, the urine was filtered through a $10 \mu\text{m}$ cartridge filter (Van Borselen Filters, Zoetermeer, The Netherlands) to remove the struvite crystals. The urine was used in the experiments immediately after filtration ($\text{pH } 9.2 \pm 0.1$). The composition of the pre-treated urine can be found in Table A.1 (Appendix A).

The catholyte was a 0.09 M NaOH solution, in order to have the same sodium concentration in both anolyte and catholyte. One litre of 1 M H_2SO_4 was used as the acid for absorption in the TMCS unit. The anode chamber, cathode chamber, and the TMCS unit were emptied completely and filled with fresh media before starting a new experiment.

2.4. Experimental plan

Eight experiments were performed with synthetic wastewater,

as shown in Table 1. Two of these experiments were performed with no applied current (open circuit) to investigate TAN transport by diffusion. The other six experiments were performed to study TAN transport in dependence of applied current density. These six experiments resulted in three sets of conditions with respect to the applied current density: balanced TAN loading (“sufficient”), excess TAN loading (“excess”) and insufficient TAN loading (“deficit”). These conditions are defined by the parameter load ratio (L_N), which is a relation between the applied current and the TAN loading rate (both expressed in A m^{-2}) (Equation (1)):

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

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

Therefore, a L_N lower than 1 means that there is more TAN than the current can transport (“excess”), whereas a L_N higher than 1 means that the TAN is limiting (“deficit”). A load ratio equal to zero describes open circuit experiments ($j_{\text{applied}} 0 \text{ A m}^{-2}$). A L_N of 1 describes a situation in which the TAN loading and the applied current are equal (“sufficient”). Due to variations in the TAN concentration, however, it is challenging to achieve a load ratio of exactly 1.0. Thus, the load ratios close to 1 are also considered as “sufficient”.

The synthetic wastewater experiments were used to study and model the TAN transport processes in the system. Afterwards, three experiments were performed with urine (Table 1) to evaluate TAN transport in a more complex mixture of ions and to observe how these results fit to the model obtained with synthetic wastewater. These three experiments were chosen based on the fact that the application of (B)ESs for the treatment of urine has the objective of achieving high TAN removal efficiencies and transport rates, which implies “sufficient” or “deficit” load ratios.

2.5. Sampling and chemical analysis

Before starting each experiment, samples were taken from the influent container and recirculation vessel of both anode and cathode. At the completion of one hydraulic retention time (HRT), a sample was taken from the anolyte recirculation vessel and from the acid. Two samples were taken from the recirculation vessel of both anode and cathode at steady state (determined by a constant anode and cathode pH, as well as anode and cathode potentials) within a period of 15–20 min. Steady state was reached within 20–40 h, depending on the experiment. A final sample was taken from the acid and the anolyte effluent container, and the experiment was finished immediately afterwards.

The samples were filtered through 0.45 μm filters (PTFE syringe filters, VWR International B.V., Amsterdam, The Netherlands) prior to analysis. TAN and sodium concentrations for the synthetic wastewater experiments, as well as chloride, nitrite, nitrate, sulphate, potassium, magnesium and calcium concentrations from the urine experiments were measured by ion chromatography in duplicate. The ion chromatographs used were the Metrohm Compact IC Flex 930 with a cation column (Metrosep C 4- 150/4.0) and the Metrohm Compact IC 761 with an anion column (Metrosep A Supp 5- 150/4.0), both equipped with conductivity detectors. The acid samples from the TMCS were analysed by a cuvette test kit for ammonium (LCK 303, spectrophotometer XION 500, Dr. Lange Nederland B.V., The Netherlands).

2.6. Calculations

The equations for the calculations of removal efficiency of TAN (RE_{TAN} , how much was removed from the TAN that entered the system), recovery efficiency of TAN (how much of the TAN supplied via the anolyte inflow was recovered in the acid), flux of TAN over the CEM (J_{TAN}), flux of NH_3 over the TMCS membrane ($J_{\text{NH}_3, \text{TMCS}}$), transport efficiency of NH_4^+ ($tE_{\text{NH}_4^+}$) and transport energy input can be found in [Appendix A](#).

2.7. Model development

A simple removal efficiency model was derived (Equation (2); derivation shown in [Appendix A](#)) based on the anode and cathode mass balance equations, the transport equations for the NH_3 and NH_4^+ fluxes, and initial assumptions of: i) steady state and ii) completely mixed anode and cathode chambers. Assumption i) implies 100% transport efficiency for NH_4^+ , since it is the only ion effectively removed from the catholyte, by the TMCS unit, at steady state.

Table 1

Experiments performed in the study and their load ratio (L_N). Sufficient, deficit and excess refer to the TAN loading with respect to the applied current. Synthetic wastewater and urine were used as anolyte.

$j_{\text{applied}} \text{ A m}^{-2}$	$Q_{\text{anode}} = 0.2 \text{ mL min}^{-1}$		$Q_{\text{anode}} = 1.1 \text{ mL min}^{-1}$	
	L_N	Condition	L_N	Condition
0	0.00	Diffusion	0.00	Diffusion
10	1.20	Sufficient	0.22	Excess
20	2.54	Deficit	0.45	Excess
50	6.16	Deficit	1.33	Sufficient
20	2.72	Deficit (urine)	–	–
50	6.48	Deficit (urine)	1.18	Sufficient (urine)

$$RE_{\text{TAN, model}} = ((1 - \beta) * L_N + \beta * \gamma) * 100 \quad (2)$$

where $RE_{\text{TAN, model}}$ (%) is the predicted removal efficiency of TAN, L_N (–) is the load ratio (Equation (1)), and β (–) and γ (–) are parameters described by Equations (3) and (4), respectively.

$$\beta = \frac{k_m}{k_m + K_g} \quad (3)$$

where k_m (m s^{-1}) is the mass transfer coefficient of ammonia through the CEM and K_g (m s^{-1}) is a term which includes the gas transfer coefficient of ammonia through the TMCS (Equation (A.15)).

$$\gamma = \frac{K_g * A_m * f_{\text{NH}_3, \text{anode}}}{Q_{\text{anode}}} \quad (4)$$

where A_m (0.01 m^2) is the surface area of the CEM, Q_{anode} ($\text{m}^3 \text{ s}^{-1}$) the anolyte inflow rate and $f_{\text{NH}_3, \text{anode}}$ (–) the fraction of NH_3 in the anolyte.

The experimental data of synthetic wastewater were used to estimate the model parameters β and γ (Equations (3) and (4), respectively). K_g was determined by plotting the TMCS flux ($J_{\text{NH}_3, \text{TMCS}}$, in $\text{mol N m}^{-2} \text{ s}^{-1}$) against the NH_3 concentration in the catholyte (mol m^{-3}). K_g is the slope of the linear regression curve.

After obtaining K_g , γ was calculated for each experimental point. Only the current-induced experiments were included in the model. Then, an optimum β was obtained by minimizing the sum of the squares of the differences between the experimental removal efficiencies and Equation (2). Once the optimal β was obtained, we calculated k_m . Equation (2) was then used to predict the removal efficiency of the system depending on the load ratio.

3. Results and discussion

3.1. TAN flux over the CEM equals TAN flux over the TMCS

There are two fluxes of nitrogen in the system: TAN over the cation exchange membrane (J_{TAN}) and NH_3 over the TMCS membrane ($J_{\text{NH}_3, \text{TMCS}}$). When both fluxes are the same, steady state is reached. [Fig. 2](#) shows that there is a direct linear relationship with a slope of 1.06 and a R^2 of 0.98 for the synthetic wastewater data points. The slope shows that the flux over the cation exchange membrane was around 6% higher than the one over the TMCS, which indicates near steady state. The system thus effectively transported ammonia from the influent to the acid. This was also the case for urine as influent, as both fluxes across CEM and TMCS membrane were similar, too.

3.2. Load ratio is an essential parameter to assess TAN removal efficiency and transport energy input

To study TAN removal efficiency and energy input under different experimental conditions, we defined the load ratio, which is the ratio between the applied current (in A m^{-2}) and the TAN loading rate (in A m^{-2}) (Equation (1)). The main trends and figures are shown in this section, while all results are summarized in [Table A.2](#).

[Fig. 3](#) shows the experimental data for TAN removal efficiency (RE_{TAN}) as a function of the load ratio. At L_N much higher than 1, there is limited TAN compared to the applied current, and for synthetic wastewater this resulted in TAN removal efficiencies between 99% and 100%. For L_N lower than 1, there is excess TAN compared to the applied current, and therefore, TAN removal

efficiencies were much lower. In a situation where current is applied, TAN is transported through the membrane by a combination of migration (current-induced) and diffusion (concentration gradient-induced). At L_N 0, no current is applied, so RE_{TAN} is determined by diffusion alone. The model, as seen in Fig. 3, is well suited to describe the relation between load ratio and TAN removal efficiency.

A RE_{TAN} of 100% would be expected at a L_N of 1 in steady state, since at this load ratio the applied current equals the TAN supplied. Our experiments show, however, that the system needs to be operated at a load ratio higher than 1 to achieve complete TAN removal, because ammonia diffusion from cathode to anode also contributes to TAN transport. When NH_3 diffuses through the CEM from cathode to anode, it is protonated to NH_4^+ when close to the anode (Liu et al., 2016), so energy is spent in transporting NH_4^+ back to the cathode.

In addition to TAN removal, the load ratio is also a useful parameter to assess energy efficiency. The transport energy input is defined here as the electrical energy input to the EC that was used for transport processes, independent of the reactions occurring at the electrodes. Therefore, it only takes into account the potential loss due to the transport of ions through the membrane ($E_{transport}$, measured as the potential difference between the reference electrodes) and the potential loss due to the pH gradient over the membrane ($E_{\Delta pH}$) (Sleutels et al., 2009). Values for $E_{transport}$, E_{pH} (along with final anolyte and catholyte pH) and the total electrical energy input can be found on Table A.3. Fig. 4 shows the relation between the load ratio (L_N) and transport energy input for the recovery of TAN.

In our experiments with synthetic wastewater, at $L_N < 1.2$, the energy input for transport of TAN was minimal (see insert in Fig. 4), but the TAN removal efficiency was low (Fig. 3). At $L_N > 1.2$, the applied current was higher than the current that can be carried by NH_4^+ . This resulted in depletion of NH_4^+ at the membrane surface (anode side), and therefore higher energy input for TAN transport.

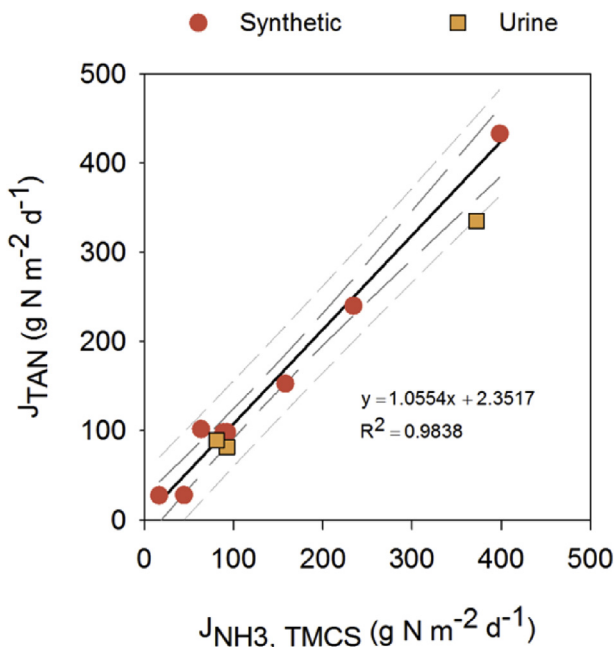


Fig. 2. TAN flux over the cation exchange membrane (J_{TAN}) against NH_3 flux over the TMCS membrane ($J_{NH_3, TMCS}$). The regression line was fitted only for the synthetic wastewater points for modelling purposes. Long-dashed and short-dashed curves represent the 95% confidence interval and 95% prediction interval for the linear regression, respectively. This figure shows that the system was near steady state.

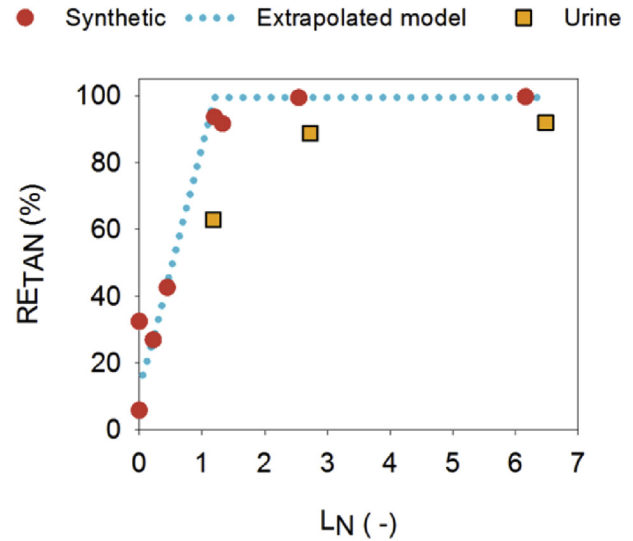


Fig. 3. TAN removal efficiency (RE_{TAN}) with respect to load ratio (L_N). L_N is the ratio between the applied current and the TAN loading rate, both in units of $A m^{-2}$. The synthetic wastewater data set was used for modelling purposes. The dotted line depicts the model results. Data points at 0 load ratio belong to the open circuit experiments and are not fitted in the model. The model based on the load ratio can accurately describe the system performance in terms of removal efficiency.

In these experiments, where energy input for transport increases steeply, the RE_{TAN} reached values close to 100%. At L_N around 1, however, 92–94% TAN removal efficiencies were already achieved, even though the energy input for transport was considerably lower than that for $L_N > 1.2$. Thus, working at higher load ratios than the ‘limiting’ one does not provide an advantage anymore: it costs more energy, and no considerable increase in removal efficiency can be achieved.

3.3. System performance using urine

For the experiments with urine, a similar trend in transport energy input was observed (Fig. 4), although at $L_N > 1.2$ it was considerably lower than for synthetic wastewater. In the two urine cases with $L_N > 1.2$, the potential loss due to transport was 10–30 times lower than the corresponding synthetic wastewater cases (Table A.3). The reason for a lower $E_{transport}$ in the urine experiments may be related to the difference in composition between synthetic wastewater and urine. Urine contains a more complex mixture of ions than the synthetic wastewater (K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , etc.), so its conductivity is higher, which affects transport losses. In the urine case at L_N 1.18, the transport energy input was higher than its synthetic counterpart because the TAN removal efficiency was relatively low (63% vs. 92% for synthetic), resulting in higher transport energy input per kg TAN removed.

The experiments with urine and synthetic wastewater also showed a similar trend regarding TAN removal efficiency (Fig. 3). Higher load ratios resulted in higher RE_{TAN} , even though removal efficiencies with urine were lower than those with synthetic wastewater. The reason for this lower removal efficiency could be explained by the presence of chloride (Cl^-). Urine contains Cl^- , which can potentially be oxidized electrochemically to produce chlorine (Cl_2). Chloride oxidation can result in hypochlorite production, which can react with the ammonium in the anolyte to form chloramines (Dbira et al., 2014; Kapařka et al., 2010; Putnam, 1971; Radjenovic and Sedlak, 2015; Zöllig et al., 2015). The chloramine formation decreases the amount of NH_4^+ available for transport, which would result in lower TAN removal efficiency.

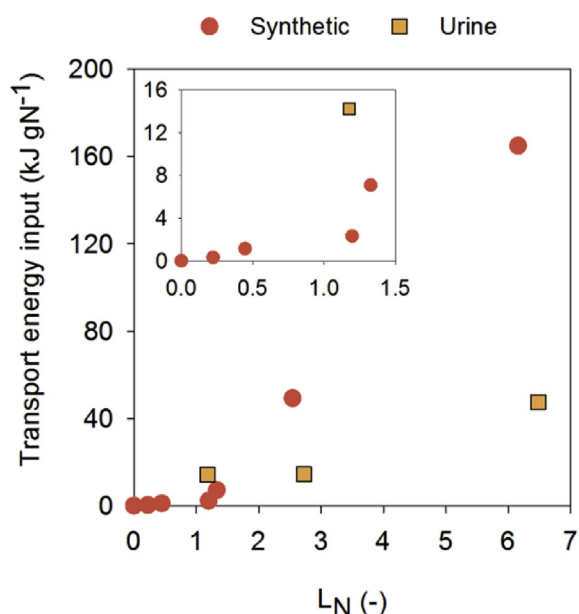


Fig. 4. Energy input used to transport TAN (in kJ per g N removed) with respect to load ratio (L_N). L_N is the ratio between the applied current and the TAN loading rate, both in units of A m^{-2} . The transport energy input takes into account only the potential losses due to transport and pH gradient over the membrane. This figure shows that working at load ratios much higher than the 'limiting' one (1.2) costs considerably more energy, even though no considerable increase in removal efficiency can be achieved.

Hypochlorite can also oxidise the ammonium to nitrogen (Candido and Gomes, 2011; Kapaika et al., 2010; Kim et al., 2005), in which case the TAN would be removed as N_2 gas, but not recovered in the acid. Chloride concentration was measured in the three urine experiments, and only in the case of the highest L_N (6.48) a decrease in chloride concentration was found (see Table A.4). The experiment at L_N 6.48 is also the one in which the difference between TAN removal and recovery efficiencies was the highest from the data set (Table A.2), and where the highest anode potential (1.874 V vs. Ag/AgCl) was measured. The above suggests that chloride oxidation might have occurred and, since the TAN was removed but not found back in the acid, it was probably removed as N_2 gas. The presence of Cl^- in urine might therefore have affected the performance of the system, resulting in lower removal efficiencies and also deviations from the model based on chloride-free synthetic wastewater.

3.4. TAN flux and transport efficiency performance

The TAN flux (J_{TAN}) is the total flux of ammonium and ammonia that was transported from the anode to the cathode chamber through the CEM. Fig. 5A shows J_{TAN} for all experiments, plotted as function of the load ratio. When no current is applied (L_N 0), only diffusion determines the overall membrane transport process. For this reason, J_{TAN} for both diffusion experiments was the same ($27 \text{ gN m}^{-2} \text{ d}^{-1}$). The effect of applied current on J_{TAN} was clearly seen at the high inflow rate experiments (1.1 mL min^{-1}) with synthetic wastewater. At this inflow rate there was sufficient (or excess) TAN in the system, so the flux increased with increasing applied current, as expected. On the other hand, for the low inflow rate experiments (0.2 mL min^{-1}), the effect of applied current density was not apparent due to the TAN limitation in the system, meaning that already at the lowest current, TAN flux was highest. The highest flux obtained was $433 \text{ gN m}^{-2} \text{ d}^{-1}$, corresponding with the experiment at the highest inflow rate and applied current ($L_N = 1.33$).

The transport efficiency refers to the contribution of an ion to the total charge transport across the CEM. In one experiment with TAN in excess (synthetic wastewater, 1.1 mL min^{-1} and 10 A m^{-2} , L_N 0.22) the transport efficiency of NH_4^+ was higher than 100%; likely due to the effect of diffusion. This study shows that the highest TAN removal efficiencies were obtained at the lowest NH_4^+ transport efficiencies ($t_{\text{E}_{\text{NH}_4^+}}$) (Fig. 5B), which is in agreement with other studies (Desloover et al., 2012; Luther et al., 2015). High TAN removal efficiencies, however, were also obtained at high NH_4^+ transport efficiencies (Fig. 5B). This fact indicates that transport efficiency alone is not well suited to predict how much TAN the system can remove.

The three experiments at L_N around 1 showed very different TAN fluxes (Fig. 5A). On one hand, the experiment with synthetic wastewater at 0.2 mL min^{-1} (L_N 1.20) had a lower TAN flux compared to the two experiments at 1.1 mL min^{-1} (L_N 1.33 and 1.18 for synthetic wastewater and urine, respectively), which is explained by the fact that there was less TAN entering the system (low inflow rate). On the other hand, J_{TAN} for the urine experiment at 1.1 mL min^{-1} (L_N 1.18) was lower than the corresponding synthetic (L_N 1.33). The TAN flux for the urine experiment at L_N 1.18 might be lower than its synthetic one because its NH_4^+ transport efficiency was lower (Fig. 5B). In the case of the lowest inflow rate the transport efficiency of NH_4^+ for urine and synthetic are similar, which relates to their similar TAN fluxes.

Transport efficiency is dependent on both current density and TAN loading rate. In TAN limited systems, the current carries more charge than can be supplied via TAN, and the result is that other ions are transported across the CEM. This can be seen in Fig. 5B, where the lowest transport efficiencies coincide with the cases in which TAN was limiting: all TAN was removed, so other ions contributed to the charge transport. Transport efficiency calculations show that 53–100% of the total charge (in the cases of load ratios lower than 1.3) was carried by NH_4^+ . The transport efficiency of other ions (i.e. K^+ , Na^+ and H^+/OH^-) is shown in Fig. A.1. Thus, the combination between TAN loading rate and current, as reflected in the load ratio, is essential to draw conclusions on the system's performance.

3.5. High removal and recovery efficiencies are achieved in the EC-TMCS system

Overall, high removal and recovery efficiencies were achieved except for the situations with TAN in excess. Even though from Fig. 5B it is clear that in these situations most of the current was used to transport ammonium (highest $t_{\text{E}_{\text{NH}_4^+}}$), the applied current was not enough to remove all TAN.

As seen in the open circuit experiments, the system was able to remove part of the TAN without applying any current (Fig. 3). Diffusion showed to account for a substantial part of the TAN removal in the system, especially in the case of the low inflow rate. A RE_{TAN} of 32% was obtained in the 0.2 mL min^{-1} open circuit experiment, while for the 1.1 mL min^{-1} it resulted in 6%. This difference might be due to the longer hydraulic retention time of the lower inflow rate (16.7 vs. 3 h). Previous studies using MECs or ECs using recovery methods other than the TMCS obtained similar removal efficiencies even under influence of combined diffusion and migration (Desloover et al., 2012; Kuntke et al., 2014).

Most of the TAN removed from the system (84% or more) was recovered in the acid in all cases, with the urine experiment at 0.2 mL min^{-1} and 50 A m^{-2} showing the lowest recovery. This was probably due to chloride oxidation, as mentioned in Section 3.4. In two cases, recoveries were slightly higher than removals (Table A.2). Whereas the removal efficiency is calculated based on steady state measurements, the recovery efficiency is determined

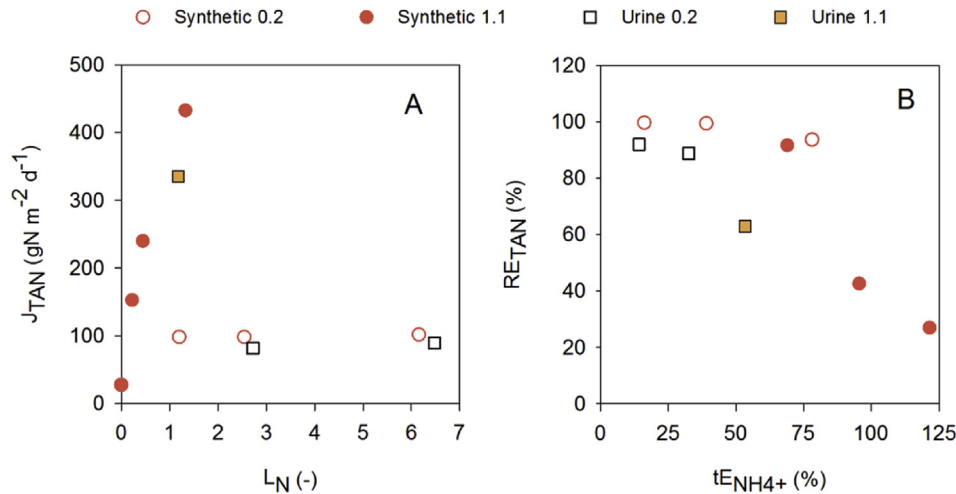


Fig. 5. (A) TAN flux over the cation exchange membrane (J_{TAN}) against load ratio (L_N). (B) TAN removal efficiency (RE_{TAN}) in relation to NH_4^+ transport efficiency (tE_{NH4+}). L_N is the ratio between the applied current and the TAN loading rate, both in $A\ m^{-2}$. In the legend, 0.2 and 1.1 represent the anolyte inflow rate ($mL\ min^{-1}$). The effect of applied current density is not apparent in A) for the low inflow rate due to TAN limitation in the system. In B), it can be seen that high removal efficiencies can be obtained at both high and low transport efficiencies.

from the increase in TAN concentration in the sulphuric acid solution over the whole experimental period, which may result in small imbalances.

3.6. Load ratio as a parameter of comparison to other studies

Usually, it is difficult to find a good measure of comparison between different (bio)electrochemical systems for TAN removal and recovery, since different hydraulic retention times, current densities and inflow TAN concentrations are used. We propose here the use of the load ratio as a fair parameter of comparison. It is important to take into account, however, that steady-state situations are essential for these comparisons to be valid.

Fig. 6 compares the model developed here to the results obtained in four recent studies for the recovery of ammonia: one of an EC attached to a stripping-absorption unit in which synthetic urine and real urine were used (Luther et al., 2015), another one in which an MEC was coupled to a TMCS unit (such as the one used in this study) (Kuntke et al., 2016), one in which an MEC and an EC attached to a stripping-absorption unit treated synthetic wastewater (Gildemyn et al., 2015) and one in which an EC coupled to the same stripping-absorption units used in the other two studies treated digestate (Desloover et al., 2012). These studies were chosen because they are similar to this work in terms of the use of an integrated system in the cathode for the recovery of NH_3 . The data points are calculated based on the inflow TAN concentrations, inflow rates, current densities and removal efficiencies provided by the different studies. As in the case of urine shown in Fig. 3, the data points do not match completely, because the model is fitted to our synthetic wastewater data. It is expected then, that with varying systems and wastewater composition, the optimum load ratio will change. The RE_{TAN} determined in the first two studies (Kuntke et al., 2016; Luther et al., 2015), however, is similar to what would be expected by using the model. The other two studies differ significantly from the model, due to, among other reasons, some complications during the experiments (such as a low stripping-absorption efficiency) and varying wastewater composition (Desloover et al., 2012; Gildemyn et al., 2015). The simple model presented here is therefore also suited to predict the performance of other optimally functional and similar systems for TAN recovery.

This model based on the load ratio provides a reasonable

description of the expected outcomes in terms of removal efficiency and the threshold in which the system can be optimally operated. Since the focus of this study was to design a simple steady-state model to describe a complex system, the model may be further optimized by taking into account other processes occurring in the system, such as ionic speciation.

4. Conclusions

- The load ratio (ratio between applied current and TAN loading rate) is an essential parameter to assess TAN removal efficiency and energy input of current-driven processes.

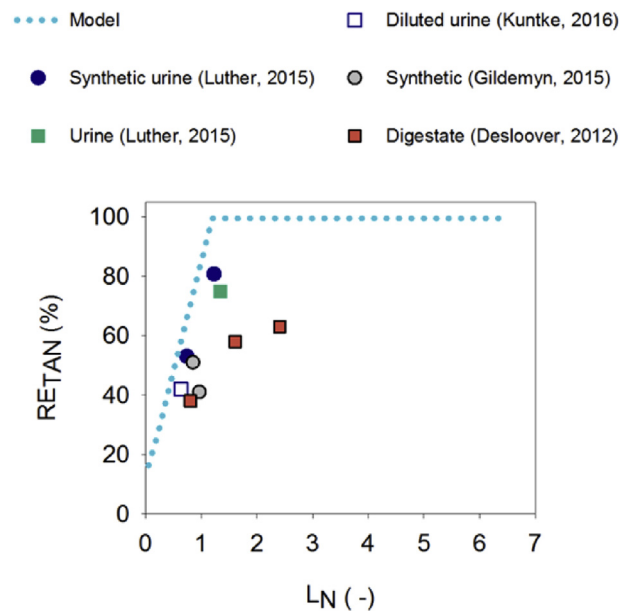


Fig. 6. TAN removal efficiency (RE_{TAN}) with respect to load ratio (L_N). L_N is the ratio between the applied current and the TAN loading rate, both in units of $A\ m^{-2}$. The dotted line is the model developed in this study, while the other data points are based on four other studies.

- Working at higher load ratios than the 'limiting' one does not provide an advantage anymore: it costs more energy, and no considerable increase in removal efficiency can be achieved.
- A RE_{TAN} of 100% would be expected at a L_N of 1 in steady state, since at this load ratio the applied current equals the TAN supplied. Our experiments show, however, that the system needs to be operated at a load ratio higher than 1 to achieve complete TAN removal, because ammonia diffusion from cathode to anode also contributes to TAN transport.
- A similar trend in system performance was observed for both synthetic wastewater (with TAN and sodium concentrations similar to urine) and urine.
- The model based on the load ratio described well the experimental data, is also suited to predict the performance of similar systems for TAN recovery, and can be used to optimize their operation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.12.051>.

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