

Electrochemically-assisted ammonia recovery from wastewater using a floating electrode

Tim H. Muster and Johannes Jermakka

ABSTRACT

This work presents and explores a novel methodology for the removal and recovery of ammonia from wastewater based upon two mechanisms: electrochemical oxidation and a previously unreported electrochemically-assisted surface transfer mechanism. Recovery of ammonia is enabled by placing a porous cathodic electrode at the wastewater-air interface. In this configuration, the cathode creates local alkalinity and an electric field that draws ammonium ions towards the wastewater-air interface, resulting in near-linear reductions of dissolved ammonium irrespective of concentration. This approach leads to significant ammonia recovery without the need for ion-exchange membranes. In addition, anodic reactions that simultaneously occur at depth in the wastewater induce ammonia oxidation in accordance with proven mechanisms. The floating electrode approach offers improved ammonia removal efficiency in comparison to electrooxidation. Trials conducted on synthetic wastewater ($900 \text{ mg NH}_4^+\text{-N l}^{-1}$) and filtered anaerobic centrate ($560 \text{ mg NH}_4^+\text{-N l}^{-1}$) demonstrated ammonia concentration decreases up to $216 \text{ mg l}^{-1} \text{ hr}^{-1}$ and $110 \text{ mg l}^{-1} \text{ hr}^{-1}$, respectively, under the application of 5 mA cm^{-2} current density. The technology would be best used to treat municipal and industrial wastewaters possessing high ammonia concentration, including anaerobic digester centrate and urine, and offers potential to assist in removing ammonia from environmental waters.

Key words | air-stripping, ammonia recovery, electrochemical nutrient removal, electrochemical oxidation, resource recovery, wastewater treatment

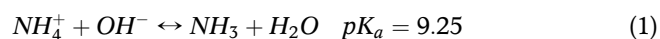
Tim H. Muster (corresponding author)
CSIRO Land and Water,
Gate 3, Waite Road,
Urrbrae 5064,
South Australia,
Australia
E-mail: tim.muster@csiro.au

Johannes Jermakka
VTT Technical Research Centre of Finland,
P.O. Box 1000,
FI-02044 VTT,
Espoo,
Finland

INTRODUCTION

The removal of nitrogen from wastewater is a significant task that is required to avoid the environmental costs associated with toxicity and eutrophication of receiving waterways. Raw municipal wastewater contains significant amounts of nitrogen (up to 70 mg l^{-1}), the majority of which presents itself in the form of ammonia (Tchobanoglous *et al.* 2004). While ammonia is a bulk commodity that is produced using energy-intensive Haber-Bosch synthesis, its recovery from wastewater is not widely practiced. The large majority of treatments for municipal wastewater rely on biological processes that convert ammonia to nitrogen gas, which is released back to the atmosphere. There are very few approaches that are able to recover ammonia; the most common approaches on an industrial scale are ammonia stripping by either vacuum (Fassbender 2001) and sparging (Sagberg *et al.* 2006). Other

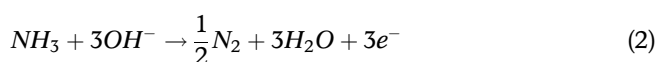
approaches have explored the adsorption of ammonia to surfaces such as zeolites (Mercer *et al.* 1970). Developing technologies have sought the use of gas (Membrana 2009) and cationic permeable membranes (Desloover *et al.* 2012, 2015; Ippersiel *et al.* 2012). With the exception of adsorption, all other methods require the addition or generation of alkaline conditions to assist with volatilisation due to ammonium/ammonia equilibria (Lide 2011):



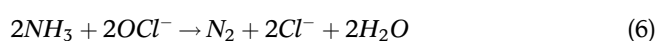
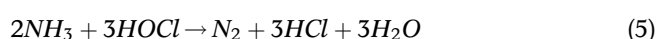
Each method for recovering ammonia faces the challenge of overcoming the high water solubility of ammonia (i.e. Henry's Law constant for ammonia is 59 M atm^{-1} , which is considerably higher than for CO_2 and O_2 (0.036 and $0.0013 \text{ M atm}^{-1}$, respectively) (Lide 2011). This work

explores a new methodology to extract and capture ammonia as a potential resource while simultaneously removing it from wastewater based upon two mechanisms: electrooxidation and a previously unreported electrochemically-assisted ammonia recovery (EAAR) air-stripping mechanism.

Electrooxidation has been heavily researched for the decomposition of chloride and nitrogen compounds, and the removal of wide-ranging contaminants and colour from wastewater (Cho *et al.* 2010). The overall oxidation of ammonia to nitrogen gas can be described according to Equation (2) (Kim *et al.* 2006):



The specific mechanisms for ammonia oxidation are, however, dependent upon the choice of electrode, the presence of oxidative species and the pH of the wastewater. Bunce & Bejan (2011) recently reviewed the mechanisms of ammonia reduction. Ammonia may be directly oxidized under alkaline conditions to form near-pure N_2 at applied potentials that avoid water oxidation. Where water oxidation occurs, typically at potentials $>1.3 V_{\text{SHE}}$, the likelihood of alternative product formation (i.e. NO_2^- , NO_3^- , NO , N_2O) is increased. The ability to form these products is significantly decreased, however, in acidic electrolytes. It is also noted that conversion efficiency is dependent upon the concentration of gaseous ammonia and not ammonium, where the proposed direct oxidation occurs initially via adsorption of NH_3 onto the electrode surface (Kapalka *et al.* 2010; Bunce & Bejan 2011). In addition to direct oxidation at the electrode surface, the presence of chloride in solution has a significant effect on conversion rates. Chloride ion concentrations in the range of 0.01–0.17 M have a beneficial influence on conversion to N_2 due to the oxidation of chloride to hypochlorite (Equations (3) and (4)), and subsequent oxidation of ammonia according to Equations (5) and (6) (Kim *et al.* 2006; Cho *et al.* 2010):



The equilibria of $\text{Cl}_2/\text{HClO}/\text{ClO}^-$ is influenced by pH; where $\text{pH} < 3.3$ favours Cl_2 , $3.3 < \text{pH} < 7.5$ HClO , and $\text{pH} > 7.5$ ClO^- (Anglada *et al.* 2009). Thermodynamically, the oxidation of ammonia is more favourable than both chloride and water, occurring practically at overpotentials of approximately $0.06 V_{\text{SHE}}$, $1.36 V_{\text{SHE}}$ and, $1.5 V_{\text{SHE}}$, respectively (Anglada *et al.* 2009; Bunce & Bejan 2011). The kinetics of each oxidative process are somewhat dependent upon the choice of electrode, applied potential and solution composition.

The electrolytic decomposition of ammonia has been undertaken in solutions of varying chloride concentration using Ti/RuO₂-Pt electrodes as anode and Ti as cathode (Ding *et al.* 2010). Current densities in the range of 5–15 mA.cm⁻² were applied and ammonia removal increased with increasing current density and chloride ion addition. An optimum ammonia removal was achieved using 0.3 g l⁻¹ NaCl and a current density of 10 mA cm⁻². Under these conditions, ammonia was found to oxidise to nitrite and then further to nitrate. Some denitrification (NO_3^- conversion to N_2) was thought to occur (at the cathode). Li *et al.* used modelling to predict that optimal ammonia removal could be achieved using 0.31 g l⁻¹ NaCl, 42.75 mA cm⁻² for 101 minutes, at which point the ammonia and nitrate concentrations would be reduced to 0 and 1.1 mg l⁻¹, respectively (Li *et al.* 2011).

Almost all electrochemical processes applied to wastewater have attempted to remove ammonia from solution, including the considerable configurations of bioelectrochemical systems and electrodialysis that use ion exchange membranes to accumulate ammonium ions into the alkaline catholyte of the electrochemical half-cell (Cord-Ruwisch *et al.* 2011; Desloover *et al.* 2012; Ippersiel *et al.* 2012). The alkaline conditions then promote transfer of ammonia to the vapour phase for potential recovery via traditional stripping approaches. Li *et al.* reported that ammonia could be removed, but not recovered, via electrochemical application to an undivided electrolyte (Li *et al.* 2011). However, here we demonstrate that by placing a porous cathodic electrode at the wastewater-air interface according to the schematic in Figure 1, it is possible to utilise the highly localised alkaline surface layer to strip ammonia directly from the surface of wastewater without the use of ion-exchange membranes and without air-sparging through the wastewater. The combination of ammonia release at the floating cathodic electrode and ammonia oxidation at the anodic electrode offers a new approach for utilisation in wastewater treatment, the recovery of ammonia, and the remediation of environmental waters.

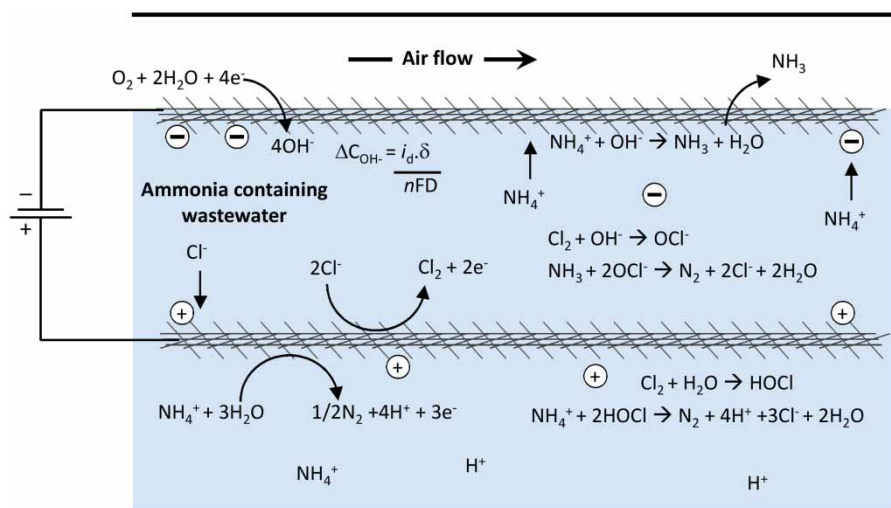


Figure 1 | Mechanistic example of electrochemically-assisted ammonia removal/recovery processes.

MATERIALS AND METHODS

An electrochemical cell was constructed from 110 mm diameter PVC tubing, which was cut to a length of 135 mm and sealed with a circular base and air-tight screw cap (further detail is available in the Supplementary Information, Figure S1, available with the online version of this paper). Electrodes were circular sections of 0.1 cm thick ruthenium/iridium oxide coated titanium mesh (CC87, Electro Coating Technologies, Australia) with a radius of 5.5 cm. The active electrode surface area for each electrode was estimated, using grey-scale thresholding of an optical image, to be 111.0 cm² (Schneider *et al.* 2012). During experiments, the working electrode (WE) was polarised cathodically while the counter electrode (CE) acted as the anode. A silver/silver chloride reference electrode was mounted midway between the WE and CE electrodes.

The cell was filled with 570 ml of wastewater solution, the air outlet was connected to a one litre glass bubbling cylinder filled with 570 ml of dilute H₂SO₄ solution, and the air inlet was connected to a mass flow controller (Omega, USA) supplying ambient air at 1 or 20 L min⁻¹. A constant current of 0, 1, 2 or 5 mA cm⁻² was applied between the electrodes using a Princeton Applied Research PAR273 potentiostat. 0.2 ml liquid samples were taken from the cell via a syringe port and from the H₂SO₄ solution at regular intervals.

An artificial inorganic wastewater solution based on OECD suggested guidelines was prepared containing 50 mM NH₄Cl, 1 mM CaCl₂·2H₂O, 1 mM MgSO₃·7H₂O, 15 mM KH₂PO₄, 5 mM Na₃PO₄·12H₂O and 2 mM NaCl (OECD 2001). It had a total nitrogen content of 0.05 M, conductivity of 7,000 mS m⁻¹ and pH of 7.0. Filtered anaerobic

centrate from Suomenoja WWTP, Espoo, Finland was sampled and used within 24 h of sampling. The centrate had a typical concentration of 22 mg PO₄³⁻P l⁻¹, 49 mg Cl l⁻¹, 560 mg NH₄⁺-N l⁻¹, 0.2 mg NO₃⁻-N l⁻¹ and 0.2 mg NO₂⁻-N l⁻¹, conductivity of 630 mS m⁻¹ and pH of 7.4.

Ammonium, nitrate, nitrite, phosphate and chloride were measured using a Hach-Lange spectrophotometer with Hach-Lange test kits LCK303, LCK341, LCK339, LCK349 and LCK311, respectively.

RESULTS

Studies using synthetic wastewater

Figure 2 demonstrates that the application of electrochemical current leads to a decrease in the ammonium ion concentration in the test cell. Where no current is applied, no ammonia is removed from the cell. The rate of ammonia removal is increased with increased current density. The application of 5 mA cm⁻² resulted in a decrease in ammonia concentration from 50 mM to approximately 20 mM over an 8-hr period (equivalent to 75 mg l⁻¹ hr⁻¹).

Cathodic potentials were at maximum -4 V/Ag/AgCl, which suggests that oxidation of both chloride and water should occur. A faint smell of chlorine emanated from the receiving solution, accompanied by a slow reduction in chloride concentration that occurred with time (i.e. 53 mM to 46 mM over 8 hrs). The presence of nitrate and nitrite in the solution was determined to be 6 × 10⁻² mM and 4 × 10⁻¹ mM after 8 hrs, suggesting that low amounts of

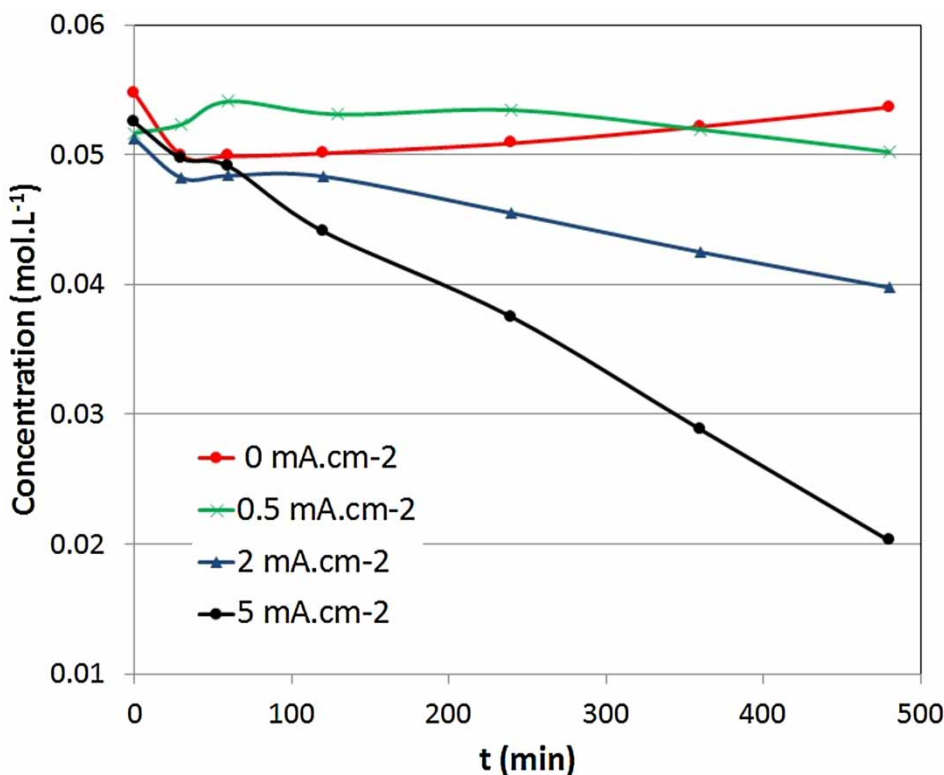
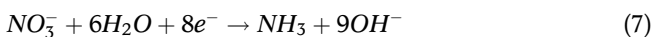


Figure 2 | Ammonium ion concentration in synthetic wastewater as a function of time (t). Air flow = 20 l min⁻¹, pH_{initial} = 6.77.

other water soluble oxidised forms of nitrogen are produced from (electro)chemical reactions (further data available in Supplementary Information, Figures S2 and S5, available with the online version of this paper).

The ability of ammonia to be removed at the cathode-wastewater-air interface, and subsequently recovered in a dilute sulfuric acid solution, was investigated. According to Figure 3, approximately 55% of the ammonia decrease is recovered in the receiving sulfuric acid solution, and the remainder is primarily removed as N₂ by anodic oxidation processes. This shows that the electrochemical reactions occurring at cathodic electrode can enhance both ammonia removal and lead to its recovery.

Vanlangendonck *et al.* suggest two main reactions can occur at the cathode under typical electrolysis conditions (Vanlangendonck *et al.* 2005):



Due to the configuration of the cathode at the wastewater-air interface, the most abundant reaction is that of

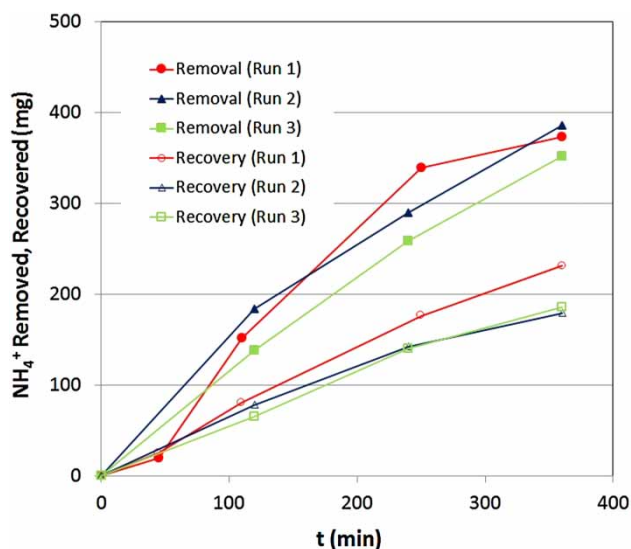


Figure 3 | Ammonia removal from synthetic wastewater solution and recovery into a dilute sulphuric acid solution. 5 mA cm⁻² electrochemical current. Air flow = 20 l min⁻¹, pH_{initial} = 6.77.

Equation (7), where oxygen reduction occurs and leads to the generation of a localised alkaline region. The mechanism of ammonia recovery at the cathode has four important processes:

1. Non-limited supply of oxygen to the cathode such that the production of hydroxyl ions is efficient.
2. Hydroxyl ions convert ammonium ions to gaseous ammonia within the localised alkaline zone.
3. Gaseous desorption of ammonia at the wastewater-air interface.
4. The application of an electric field that attracts positively-charged ammonium ions to the negative (cathode), which also reduces the need for mixing of the solution.

These four processes are optimised where the cathode is floated on the surface of the wastewater. Ammonia removal was measured to be $215 \text{ mg l}^{-1} \text{ hr}^{-1}$ with a floating cathode (whereby the meniscus of the water met with the top of the electrode) and was shown to decrease to $68 \text{ mg l}^{-1} \text{ hr}^{-1}$ when immersed 0.6 mm in the solution (further detail is provided in Supplementary Information, Figure S3, available online). At the same time, the relative amount of ammonia recovered significantly decreased.

The influence of air flow rate on removal/recovery efficiency was also explored. Using identical conditions to those used to derive the data for Figure 2 but with an air flow rate of 5 L min^{-1} , no difference in total ammonia removal was observed (within error) as can be seen in Supplementary Information, Figure S4 (available online); however, the total amount of ammonia recovered at the reduced air flow rate was <5% of ammonia removed. In comparison, the ammonia recovery percentage at an air flow rate of 20 l min^{-1} was $54 \pm 8\%$. Further work is warranted to better understand the importance and control of air flow.

Anaerobic digester centrate from Suomenoja municipal WWTP

In order to assess the viability and transferability of the novel electrochemical approach to real wastewater, experiments were performed using filtered anaerobic centrate obtained from the Suomenojan wastewater treatment plant. An initial experiment was undertaken using a 5 mA cm^{-2} electrochemical current and an airflow rate of 20 l min^{-1} . Under these conditions, there was considerable foam generation at the wastewater-air interface. The ammonia concentration decreased by approximately $110 \text{ mg l}^{-1} \text{ hr}^{-1}$ (6.5 mM hr^{-1}) from a starting concentration of 560 mg l^{-1} . This compares to removal efficiencies of 72 to $216 \text{ mg l}^{-1} \text{ hr}^{-1}$ (4 to 12 mM) under identical conditions from the synthetic wastewater composition, originally containing 900 mg l^{-1} . The varied removal rate from the latter

represents the extremes of the electrode being slightly submerged at 0.6 mm and floating, respectively.

During treatment of the wastewater centrate, the levels of other ions were found to vary. As expected, the chloride ion concentration decreased upon the application of the electrochemical current. The chloride concentration in the centrate was considerably lower than that of the synthetic formulation (i.e. 1.4 mM versus 0.051 M). Nitrite levels were low both before and after treatment, maintaining levels below 0.002 mM. Nitrate levels were initially 0.1 mM and increased to 0.2 mM during the 3.5 hour experiment (see Supplementary Information, Figure S5, available online).

DISCUSSION

Anodic electrochemical oxidation

Ammonia oxidation can arise from either direct oxidation or through chemical oxidation. A faint smell of chlorine was noticed when using synthetic wastewater, suggesting the formation of Cl_2 . Monitoring of chloride ion concentrations showed a slow loss from solution, confirming Cl_2 emission from the electrochemical cell. While the formation of Cl_2 is favoured at low pH (i.e. $\text{pH} < 3.3$) and would certainly exist in high concentrations around the anodic electrode, the major oxidant in the wastewater bulk is likely to be HClO (Equation (4)).

The influence of chloride on the electrochemical oxidation was not explored, however; slightly higher ammonia removal rates were achieved during experiments on the synthetic wastewater, which had high chloride concentrations (0.051 M) in comparison to the anaerobic centrate with its low chloride (0.0014 M). This is likely to be associated with the mechanisms described by Equations (3)–(6), leading to higher removal efficiencies at the anode.

Analysis of nitrite and nitrate during several experiments demonstrated that very low levels were obtained. Low rates of water oxidation, and also high alkalinity, act to minimise the generation of oxidised nitrogen compounds, whose formation would be detrimental for practical application. These observations match literature reports that suggest N_2 to be the main product from electrooxidation (Pressley *et al.* 1972).

Cathodic removal and recovery of ammonia

The novel approach to ammonia removal and recovery at a floating cathodic electrode is demonstrated in Figure 3 to

operate at higher efficiency than electrooxidation processes, showing recoveries of over 55%. The efficiency of electrochemical oxidation is typically evaluated against the three electron conversion of ammonia to N_2 in Equation (1) (Kim *et al.* 2006). The relationship between electrical energy and ammonia removal at the cathode is, however, complicated by the indirect mechanism of: (i) creation of hydroxyl ions, (ii) conversion of ammonium to ammonia, (iii) air-stripping of ammonia. The fundamental exchange of electrons to create alkalinity is for each electron to create one hydroxyl, which in turn may lead to one ammonia molecule being released into the air stream. This theoretically suggests that ammonia removal at the cathode may be three times more efficient than electrooxidation, and the combined process should require just two electrons to remove one ammonia molecule.

The immersion depth of the electrode was shown to control the efficiency of the process, which reinforces the benefit of placing the cathode at the wastewater-air interface. The pH at the cathodic electrode can be estimated using the following equation:

$$i_c = \frac{n.F.D.\Delta C_{OH^-}}{\delta} \quad (9)$$

where i_c is the current density (A), n is the number of electrons exchanged per unit of OH^- produced (1), F is Faraday's constant ($94,685 \text{ A.s.mol}^{-1}$), D is the diffusion constant of hydroxyl species (moving away from the electrode and into the bulk $\sim 6.65 \times 10^{-5} \text{ cm}^2.\text{s}^{-1}$), ΔC_{OH^-} is the change in hydroxyl ion concentration across the diffusion layer (mol.cm^{-3}) and δ is the diffusion layer thickness in cm. δ for stagnant water has been estimated to be between 10 and 100 μm (Buchheit *et al.* 1999).

Figure 4 shows the modeled relative efficiency of ammonia removal at the wastewater-air interface as a function of electrode immersion depth. For the model, it is assumed that the diffusion of H^+ and OH^- ions acts to decrease the pH linearly away from the electrode according to Ficks Law, $d = (2Dt)^{0.5}$, where d is the immersion depth and D is the rate of diffusion. The pH of the localised solution at the interface is decreased as the electrode is immersed to a greater depth, resulting in a decreased concentration of ammonia relative to the ammonium ion concentration. The model suggests that efficient performance of a floating cathode can be achieved where immersion is $< 0.4 \text{ mm}$.

For the majority of experiments, the reduction in ammonia occurred linearly with time, suggesting concentration-independent removal. Several authors (Vanlangendonck

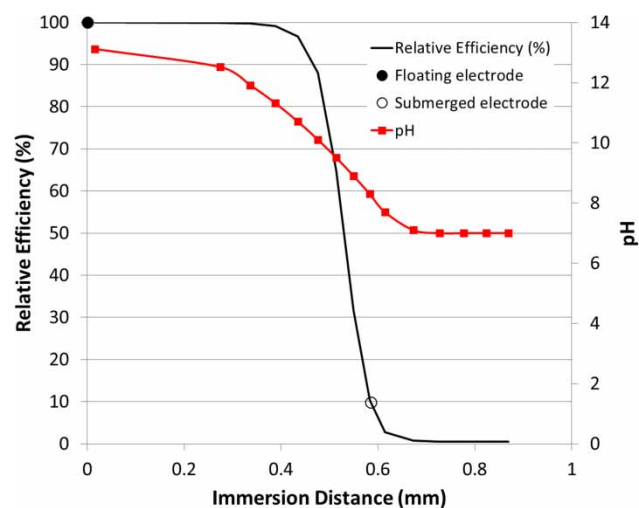


Figure 4 | Modelled relative efficiency (against floating electrode) for ammonia recovery at the cathode. Circular data points represent 0.6 mm immersion and floating electrode data from Figure S3 (available with the online version of this paper).

et al. 2005; Li & Liu 2009) have demonstrated that the electrooxidation of ammonia from solution occurs linearly with time. Vanlangendonck *et al.* (2005) suggest this is due to the constant formation of HOCl and its subsequent ability to oxidise ammonia through Equations (3)–(6), which then regenerates chloride ions to maintain the constant reaction rate. It is also proposed that the applied electric field acts to transport positively-charged ammonium ions toward the negatively-charged cathode. This enables a consistently high concentration of ammonia to accumulate at the wastewater-air interface, allowing removal to occur.

Overall efficiency of ammonia removal and recovery

The overall efficiency of electrical energy can be estimated by taking into account the theoretical requirement of two electrons to remove one ammonia molecule from solution. In the present work, 3.2 electrons were required to remove one ammonia molecule, which equates to a theoretical electrical efficiency of 63% and an energy cost of 29.3 kWh. $\text{kg}^{-1} \text{ N}$ to remove nitrogen. This efficiency compares well against other reported electrochemical treatments for wastewater (Kim *et al.* 2006; Desloover *et al.* 2015). The total energy cost exceeds that reported by Ippersiel *et al.* (2012) for combined electrodialysis and air-stripping (18 kWh. $\text{kg}^{-1} \text{ N}$ removed), however, additional chemical costs to overcome low recovery efficiencies were not reported and accounted for by Ippersiel *et al.* (2012). Desloover *et al.* reported the ammonia concentration to be achieved using 13–18 kWh. $\text{kg}^{-1} \text{ N}$, with air stripping requiring a further

9 kWh.kg⁻¹ N to enable nitrogen recovery (Desloover *et al.* 2012, 2015).

When compared against reports of the relative efficiency of biological processes to remove N, it is apparent that electrochemical approaches are uncompetitive against biological deammonification processes, which are reported to remove ammonia with as little energy as 1.2 kWh.kg⁻¹ N (Wett *et al.* 2010). With regards to the value of ammonia through recovery, the Haber-Bosch process is reported as being an energy-intensive means to produce ammonia, requiring some 8 kWh.kg⁻¹ (De Beer 2000). The relatively low energy cost of producing bulk ammonia compared to the costs to remove ammonia using electrochemical approaches suggest that a step change in technology is required to warrant its recovery.

Practical considerations and future work

The practical utilisation of the EAAR process reported here will be dependent upon maximising its advantages while minimising disadvantages. The key advantages and disadvantages of electrooxidation processes have been documented by Anglada *et al.* (2009). Advantages include: robustness, versatility, low temperature and pressure requirements, and amenability to automation. Disadvantages are predominantly associated with the high cost of electrical energy consumption. The EAAR approach maintains the advantages listed above, and furthermore it demonstrates significant improvement in the efficiency of ammonia removal from wastewater over conventional electrooxidation processes, requiring 2:1 electron:ammonia rather than 3:1). The present approach also achieves ammonia recovery without the use of expensive ion-exchange membranes and/or chemical addition to achieve a high solution pH.

Additional disadvantages of EAAR are largely due to the placement of the cathodic electrode at the wastewater-air interface. The removal of ammonia from the bulk only occurs at the surface in a two-dimensional arrangement, which limits the volume of wastewater that can be treated by a set electrode area. This effect may however be less of a disadvantage due to the movement of ammonium ions toward the surface under the applied electric field. Further work is required to develop workable configurations for the process. An additional complication is the ability to float the cathodic electrode on the surface of the wastewater, which may require the development of novel low-density electrodes and/or engineered means to maintain optimal positioning of the electrode. Further advancement of the fundamental concepts of EAAR would benefit from greater knowledge of the influence of the cathodic electrode area

and porosity, conductivity, chloride ion concentration and wastewater alkalinity. Finally, the influence of the air-flow rate required for optimal ammonia recovery requires further investigation, as does the cost associated with air flow.

Electrochemical methods for wastewater treatment are likely to be confined to decentralised treatment operations, where small scale treatment can be automated in a robust manner. One such example may be the localised treatment of urine or blackwater. In this case, the greater energy costs for electrochemical treatment may be justified by a saving in capital, maintenance and labour costs.

CONCLUSIONS

A novel method for the removal and recovery of ammonia from wastewater has been demonstrated through the floating of a cathodically-polarised porous electrode on the surface of wastewater.

The approach offers improved removal efficiency in comparison to electrooxidation, and furthermore, the combination of floating electrode and anodic electrooxidation mechanisms offer possible synergies in enhancing the overall efficiencies of electrochemical treatment of wastewater.

In comparison to existing electrochemical treatments, it also does not require the use of ion-exchange membranes in order to recover ammonia. The method utilises local pH increases, as opposed to the generation of bulk alkalinity.

Linear reductions of NH₄⁺ in wastewater were observed irrespective of concentration, suggesting the electric field creates a continuous flux of NH₄⁺ to the cathode-wastewater-air interface, where NH₃ can pass into the vapour phase.

Further development is required to better understand air flow requirements, electrode design and wastewater composition effects on efficiency.

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REFERENCES

- Anglada, A., Urriaga, A. & Ortiz, I. 2009 Contributions of electrochemical oxidation to wastewater treatment: fundamentals and review of applications. *Journal of Chemical Technology and Biotechnology* **84** (12), 1747–1755.

- Buchheit, R. G., Montes, L. P., Martinez, M. A., Michael, J. & Hlava, P. F. 1999 **The electrochemical characteristics of bulk-synthesized Al_2CuMg** . *Journal of the Electrochemical Society* **146**, 4424–4428.
- Bunce, N. J. & Bejan, D. 2011 **Mechanism of electrochemical oxidation of ammonia**. *Electrochimica Acta* **56**, 8085–8093.
- Cho, J. H., Lee, J. E. & Ra, C. S. 2010 **Effects of electric voltage and sodium chloride level on electrolysis of swine wastewater**. *Journal of Hazardous Materials* **180** (1–3), 535–541.
- Cord-Ruwisch, R., Law, Y. & Cheng, K.-Y. 2011 **Ammonium as a sustainable proton shuttle in bioelectrochemical systems**. *Bioresource Technology* **102**, 9691–9696.
- De Beer, J. 2000 **Potential for Industrial Energy-Efficiency Improvement in the Long Term**. *Eco-Efficiency in Industry and Science*. Kluwer Academic Publishers, Dordrecht, The Netherlands. pp. 170–210.
- Desloover, J., Woldeyohannis, A. A., Verstraete, W., Boon, N. & Rabaey, K. 2012 **Electrochemical resource recovery from digestate to prevent ammonia toxicity during anaerobic digestion**. *Environmental Science and Technology* **46**, 12209–12216.
- Desloover, J., De Vrieze, J., Van de Vijver, M., Mortelmans, J., Rozendal, R. & Rabaey, K. 2015 **Electrochemical nutrient recovery enables ammonia toxicity control and biogas desulfurization in anaerobic digestion**. *Environmental Science and Technology* **49**, 948–955.
- Ding, D., Feng, C., Guo, X. & Li, M. 2010 **Study on ammonia-nitrogen removal in wastewater using electrochemical method**. *Bioinformatics and Biomedical Engineering*. In: *4th International Conference, Chengdu*, 18–20 June 2010.
- Fassbender, A. 2001 **Thermoenergy ammonia recovery process for municipal and agricultural wastes**. *The Scientific World* **1** (S2), 908–913.
- Ippersiel, D., Mondor, M., Lamarche, F., Tremblay, F., Dubreuil, J. & Masse, L. 2012 **Nitrogen potential recovery and concentration of ammonia from swine manure using electro dialysis coupled with air stripping**. *Journal of Environmental Management* **95**, S165–S169.
- Kapalka, A., Cally, A., Neodo, S., Comminellis, C., Wächter, M. & Udert, K. M. 2010 **Electrochemical behavior of ammonia at $\text{Ni}/\text{Ni}(\text{OH})_2$ electrode**. *Electrochemistry Communications* **12**, 18–21.
- Kim, K. W., Kim, Y. J., Kim, I. T., Park, G. & Lee, E. H. 2006 **Electrochemical conversion characteristics of ammonia to nitrogen**. *Water Research* **40**, 1431–1441.
- Li, L. & Liu, Y. 2009 **Ammonia removal in electrochemical oxidation: mechanism and pseudo-kinetics**. *Journal of Hazardous Materials* **161**, 1010–1016.
- Li, M., Feng, C., Zhang, Z., Liu, X., Ma, W., Xue, Q. & Sugiura, N. 2011 **Optimization of electrochemical ammonia removal using Box-Behnken design**. *Journal of Electroanalytical Chemistry* **657** (1–2), 66–73.
- Lide, D. R. 2011 *CRC Handbook of Chemistry and Physics*. 91st edn, online version. CRC Press, Boca Raton, FL, USA.
- Membrana 2009 **Using ‘TransMembraneChemiSorption’ (TMCS) for ammonia removal from industrial waste waters**. www.liqui-cell.com (accessed 23 April 2014)
- Mercer, B. W., Ames, L. L., Touhill, C. J., Van Slyke, W. J. & Dean, R. B. 1970 **Ammonia removal from secondary effluents by selective ion exchange**. *Water Pollution Control Federation Journal* **42** (2), R95–R107.
- OECD 2001 *OECD Guideline for the Testing of Chemical: Simulation Test – Aerobic Sewage Treatment*. OECD Standard 303.
- Pressley, T. A., Bishop, D. F. & Roan, S. G. 1972 **Ammonia-nitrogen removal by breakpoint chlorination**. *Environmental Science and Technology* **6** (7), 622–628.
- Sagberg, P., Ryrfors, P. & Berg, K. G. 2006 **Ten years of operation of an integrated nutrient removal treatment plant: ups and downs, part 2: sludge and side stream treatment**. *Water Science & Technology* **53**, 83–90.
- Schneider, C. A., Rasband, W. S. & Eliceiri, K. W. 2012 **NIH Image to ImageJ: 25 years of image analysis**. *Nature Methods* **9**, 671–675.
- Tchobanoglous, G., Burton, F. L. & Stensel, H. D. 2004 *Wastewater Engineering: Treatment and Reuse*. 4th edn, Metcalf & Eddy, Inc., McGraw Hill, Boston.
- Vanlangendonck, Y., Corbisier, D. & Van Lierde, A. 2005 **Influence of operating conditions on the ammonia electro-oxidation rate in wastewaters from power plants (ELONITATM technique)**. *Water Research* **39**, 3028–3034.
- Wett, B., Nyhuis, G., Takacs, I. & Murthy, S. 2010 **Development of enhanced deammonification selector**. In: *WEFTEC Proceedings, 2010*. Water Environment Federation, Alexandria, VA, USA.

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