Ammonia removal in anaerobic digestion by biogas stripping: an evaluation of process alternatives using a first order rate model based on experimental findings

M. Walker*, K. Iyer, S. Heaven, and C. J. Banks
*Corresponding author - School of Civil Engineering and the Environment, University of Southampton, Southampton, SO17 1BJ, UK

Abstract

The feasibility of biogas stripping to remove ammonia in the anaerobic digestion of source segregated food waste was investigated. It was found in batch experiments that ammonia could be removed from digestate and that the removal followed 1st order kinetics with respect to total ammonia nitrogen concentration. Increasing temperature, biogas flow rate and initial pH all increased removal rates. Using kinetic data gathered in these experiments allowed the integration of ammonia stripping with an anaerobic digestion plant to be modelled for different configurations. Four scenarios were identified: post digestion, *in situ*, side-stream and pre-digestion ammonia removal relating to where in the process the ammonia stripping was performed. The modelling showed that *in situ* ammonia removal may be best able to reduce in-digester ammonia concentrations over a wide range of organic loading rates whereas pre-digestion showed most promise in terms of application due to the flexibility to control each part of the process separately. Further experimental work is required into these scenarios to confirm their viability.

Keywords
Anaerobic Digestion (AD), Ammonia, biogas, stripping, source-segregated food waste (SSFW)

Abbreviations
ABPR   Animal by-products regulations
AD   Anaerobic digestion
Defra   Department for Environment, Food and Rural Affars
FW   Food waste
HRT   Hydraulic retention time
OLR   Organic loading rate
SSFW   Source segregated food waste
TAN   Total ammonia nitrogen
VFA   Volatile fatty acid
VS   Volatile solids

1. Introduction

Food waste (FW) is a major waste stream and its disposal can be problematic due to its high moisture content, bulk density and biodegradability [1]. Furthermore it can contain pathogens, is subject to animal by-products regulations (ABPR) (EC 1069/2009) and in Europe its disposal to landfill is being phased out under the EU Landfill Directive (99/31/EC). When collected as a mixture with municipal and commercial wastes it can complicate or prevent recovery of other potentially valuable materials through contamination by contact with the FW. There is therefore increasing interest in the separate collection and management of source segregated food waste (SSFW) with an emphasis on further recovery of value from this material. The high moisture content and calorific value of FW make suitable for anaerobic digestion (AD) which produces biogas, a biofuel, and the nutrient content makes the digestate suitable to apply to agricultural land as a fertiliser [2].

Despite the advantages of anaerobic digestion (AD) as a treatment technology for SSFW there are potential operational problems due to the high proportion of proteinaceous material in the raw waste [3]. The anaerobic degradation of proteins leads to the release of ammonia which is a necessary nutrient for many organisms in the digester, but in elevated concentrations can be inhibitory, especially in its non-ionised form free ammonia (NH_3) [4]. Most evidence suggests that the acetoclastic methanogens which degrade acetate and produce methane and carbon dioxide are more sensitive to free ammonia than hydrogenotrophic methanogens [5, 6], with inhibitory concentrations of Total Ammonia Nitrogen (TAN) reported in the range of 759-4000 mg N l^{-1} [3, 4, 7-9].

Digesters fed on SSFW have been shown to exhibit symptoms of ammonia toxicity, but these problems may take a long time to cause process failure. The elevated ammonia/ammonium concentration provides buffering capacity that allows digester operation at higher concentrations of volatile fatty acids (VFA) than would be possible in a less buffered system [10-12]; it is only when this buffering capacity is broken by acid accumulation that the pH drops to a point where conditions are unfavourable for methanogenesis. This behaviour has also been seen in the digestion of other nitrogen-rich materials such as cattle slurry [13] and slaughterhouse waste [14]. It would be advantageous to be able to manage the ammonia concentrations in AD such that the problems of its accumulation are avoided, in turn preventing the build-up of VFA. Furthermore, the ability to manage the ammonia content of a digestate will allow higher rates of application in nitrogen sensitive zones under the EU Nitrates directive (91/676/EEC), and balancing of the overall nutrient composition.

Ammonia removal from wastewater and animal slurry has been well studied. Methods used include struvite precipitation [15]; biological ammonia oxidation and denitrification [16]; electrochemical conversion [17]; microwave [18] and ultrasound treatment [19]; and air stripping [20]. The latter is a proven concept for the removal and recovery of ammonia from slurries and wastes: air is blown through the liquid and the free ammonia transfers into the gas phase and can then be captured by absorption downstream. It has been found that the most rapid removal occurs at high temperature, high gas flow rate and high pH [20-22]. The importance of these parameters can be explained using pH equilibrium and phase change theories: pH modifies the ammonia removal behaviour on a chemical basis, by shifting the equilibrium between free ammonia, the volatile form, and ammonium salts which are non-volatile. Temperature alters the same equilibrium slightly, with an increase causing a greater fraction of free ammonia to be present in the digestate; and also has a physical effect in that it increases the saturated vapour pressure of the free ammonia, thus increasing the driving force which allows volatilisation into the gaseous form. Flow rate of gas has no chemical effect on the balance of free/ionic ammonia but instead changes the available surface

interface between the liquid and gaseous phases within the stripping system, such that an increase in flow rate leads to an increase in reaction rate (in this case volatilisation and removal of ammonia).

The aim of this work was to investigate the possibility of in-situ ammonia removal in the anaerobic digestion process itself, as it is during this stage that ammonia is released through hydrolysis and also the point where accumulation occurs leading to process inhibition. The most promising method for direct integration with an anaerobic digestion plant was thought to be gas stripping using biogas as the stripping gas. This has the potential advantage of removing ammonia whilst maintaining an anaerobic environment and keeping the carbon dioxide in equilibrium with the dissolved carbon in the digestate, thus avoiding pH change as demonstrated by de la Rubia et al [23].

The paper presents data from ammonia stripping experiments using digestate from an anaerobic digester treating source segregated food waste [11]. The kinetic data was then used to model possible methods of integrating this ammonia management technology into an anaerobic digestion plant. The experiments and modelling in this work were carried out at three temperatures commonly associated with anaerobic digestion; 35°C (mesophilic), 55°C (thermophilic) and 70°C (pasteurisation) with pH modified only when this could be feasibly done during the digestion process.

2. Materials and methods

2.1 Batch removal of ammonia using biogas stripping from food waste digestate

Two digestates were used, both taken from an anaerobic digester treating source segregated food waste (Biocycle, Ludlow, UK). The first sample had a TAN concentration of approximately 8000 mg N l^{-1} in which the pH changed from 8.5-9.3 on storage between stripping experiments. The second sample had a TAN concentration of approximately 6000 mg N l^{-1} and a pH of 8.1-8.2.

Ammonia removal was carried out in a water jacketed heated glass column of total volume three litres connected to a closed loop biogas recirculation system with condensate and ammonia traps (Figure 1). The system was primed with a standard biogas mixture of 65% methane, 35% carbon dioxide (BOC, UK) and gas was circulated by a peristaltic pump. A biogas storage bag was included in the loop to provide a reservoir for additional biogas produced by the digestate during the course of an experiment. Two litres of digestate were used in each stripping test, with samples taken during the run to monitor changes in pH and to assess the kinetics of the ammonia removal. At the end of each experiment the TAN concentration in the digestate, water, acid and condensate traps was measured to determine the distribution of ammonia within the system. Where digestate pH was modified this was done using 10M NaOH.

Experiments were carried out at 35°C, 55°C or 70°C, at gas flow rates from 0.125-0.750 litres of biogas per litre of digestate per minute (l l^{-1} min^{-1}), with and without initial pH adjustment. The experimental conditions for each run are given in Table 1. An additional experiment was carried out in which the digestate was spiked with acetic and propionic acid to give concentrations similar to those found in the experiments carried out by de la Rubia et al [23] in which the pH profile during stripping differed from that seen in this study. The VFA addition experiment was performed at 70°C, 0.375 l l^{-1} min^{-1} and without pH modification.

TAN concentration was determined using a Kjeltech steam distillation unit according to the manufacturer's instructions (Foss Ltd, UK). Sample pH was measured using a pH probe connected to a Jenway 3310 pH meter (Jenway, UK). The pH meter was calibrated before use with buffer solutions (pH 4, 7 and 9.2 general purpose grade, Fisher Scientific, UK). Total solids (TS) and volatile solids (VS) content were determined according to Standard Method 2540 G [24]. Volatile fatty acids (VFA) were quantified in a Shimazdu GC-2010 gas chromatograph (Shimadzu, Milton Keynes, UK), using a flame ionization detector and a capillary column type SGE BP-21.

2.2 Modelling the integrated ammonia removal and anaerobic digestion process

A model was developed to simulate the integration of ammonia stripping with anaerobic digestion based on the following assumptions:

1. Ammonia is removed in the stripping reactor such that the TAN decreases exponentially (1st order kinetics). This was shown experimentally in the biogas stripping experiments.
2. The digester and tank volumes are dimensionless and the results from laboratory-based experiments can be scaled up.
3. Ammonia is released into the digester immediately by the incoming food waste; in reality this is not the case, as there is some delay while proteins are hydrolysed; but this time is short relative to the typical retention times in anaerobic digestion.
4. The TAN concentration upon digestion is a characteristic of the feedstock and therefore the TAN of completely hydrolysed food waste digestate is a constant independent of other operating characteristics: in this research 6000 mg N l^{-1} was used. This assumes no hydrolysis inhibition.
5. The digester, mixing tank, ammonia stripping reactor and pasteuriser are completely mixed.
6. The food waste is homogenous and of constant volatile solids (VS) content (217 g VS kg^{-1} fresh matter was used in this work) with a density of 1000 kg m^{-1}, allowing the relation of mass flow and hydraulic characteristics of the systems.

The model was applied to four scenarios that are represented in Figure 2 and described below, with the following common characteristics: biogas is used as the stripping gas; it is bubbled through the digestate before entering an ammonia recovery stage; the biogas production of the plant is unaffected by the stripping process as it is not consumed during ammonia removal.

Scenario 1 – Post digestion ammonia removal
The ammonia stripping reactor is placed after the main anaerobic digester and is operated at 70°C, and additionally acts as a pasteurisation stage. Under the ABPR pasteurisation is obligatory when using mesophilic digestion and to combine it with ammonia removal minimises the energy requirements of the combined process. A proportion of the output digestate from this stage is returned to the start of the process, and mixing of this ammonia-depleted recyclate with incoming food waste reduces the digester ammonia concentration. In this scenario the hydraulic retention time (HRT) of the plant is set by the incoming organic loading rate (OLR) but the digester HRT can be altered by changing the ratio of recycled digestate to incoming food waste. For maximum ammonia reduction in the digester it is preferable to have a high recycle ratio. This presents an operational problem, however, as the recycled digestate has been pasteurised and therefore does not return active anaerobic biomass to the system. The limitation is therefore the minimum digester HRT, which sets the maximum amount of digestate that can be recycled. For process stability a minimum digester HRT of 30 days was assumed. The stripping conditions used in the simulations were 70°C, biogas flow rates of 0.5-0.625 l l^{-1} min^{-1} and pH modification to 14 (as in experimental runs 20.1 and 20.2), giving an ammonia removal time constant of 4 hours, the stripper was operated for 24 hours per batch fill.

Scenario 2 – In situ ammonia removal

The digester is gas mixed and the whole digester becomes a stripping reactor, with ammonia captured in the mixing gas which is subsequently sent to the ammonia removal stage. In this scenario, since there is no digestate recycling, the HRT of the process is set by the OLR. The ammonia stripping system in this case operates at the temperature and pH of the digester, and only the gas flow rate can be changed. The stripping was simulated at 35°C, biogas flow rate of 0.375 l l^{-1} min^{-1} and no pH modification (as per experimental run 0.1), giving an ammonia removal time constant of 595 hours.

Scenario 3 – Side-stream ammonia removal

This configuration is similar to scenario 1 except that the stripping reactor and pasteuriser are separate. Stripping takes place as a side-stream process to the main digestion, in batch or continuous mode, with the transfers of digestate between the stripping reactor and main digester being of equal volume but other conditions being flexible: the residence time in the ammonia stripping reactor can be altered by changing the flow of digestate between the two reactors or by changing their relative sizes. The conditions of the stripping process may have implications for the active biomass in the digester, similar to the case where a high temperature and high flow rate process is used as in scenario 1. In the simulations the relative size of the stripping reactor was varied between 1/10 and 1/100 of the main digester. It was assumed that the stripping reactor was filled with digestate daily and operated constantly for a 24-hour period, with stripping conditions of 70°C, biogas flow rate of 0.375 l l^{-1} min^{-1} and no pH modification (as per experimental run 6.1), giving an ammonia removal time constant of 17.7 hours.

Scenario 4 – Pre-digestion ammonia removal

This scenario relies on the release of ammonia during a short anaerobic hydrolysis stage, with subsequent removal in a stripping reactor. As in scenario 3 the design is flexible and would need optimisation to the degradation characteristics of the food waste. Parameters that can be varied are: the residence time in the hydrolysis stage; the residence time in the stripping reactor; and the conditions of ammonia stripping. In initial simulations the effectiveness of the hydrolysis was varied by changing the TAN concentration leaving this step between 0-6000 mg N l^{-1} i.e. between no hydrolysis and complete hydrolysis of the proteinaceous fraction of the food waste. Stripping was modelled at 70°C, biogas flow rates of 0.5-0.625 l l^{-1} min^{-1} and pH modification to 14 (as per experimental runs 20.1 and 20.2), giving an ammonia removal time constant of 4 hours. In the later simulations, and for comparison with the other scenarios, a hypothetical plant was designed to give a hydrolysis tank HRT of 2 days and a batch time in the ammonia stripper of 8 hours at an OLR of 5 kg VS m^{-3} d^{-1}. In these simulations hydrolysis and therefore TAN production was assumed to follow 1st order kinetics with a time constant of 0.35 d^{-1}.

The characteristics of each scenario were investigated separately before being compared under given conditions for OLR of 1-6 kg VS m^{-3} d^{-1}.

3. Results and discussion

3.1 Batch removal of ammonia using biogas stripping from food waste digestate

The results of the ammonia stripping experiments are shown in table 1. For each experimental run an ammonia removal time constant was calculated for using the measurements of TAN and fitting an

exponential decay curve (i.e. 1st order kinetics): these are tabulated along with the respective correlation coefficients (r^2). An example of this process is shown in Figure 3 for experimental run 3.1, where the time coefficient of the equation is 0.031 and the reciprocal of this gives the ammonia removal time constant of 32.3 hours. The correlation coefficients (r^2) for these curve fits ranged from 0.73 to 1.00 but in most cases were above 0.95 indicating that an exponential decay function gave a satisfactory representation of the physical behaviour. This allows quantitative comparison between experimental runs with different initial and final conditions.

The ammonia removal time constants for experimental runs without pH modification were plotted against biogas flow rate in Figure 4. The data follows the trends previously observed by de la Rubia et al [23]: an increase in biogas flow rate (or in temperature, when compared with runs 0.1 and 1.1 in Table 1) led to an increase in the ammonia removal rate. The range of flow rates in these experiments, up to 0.75 l l^{-1}min^{-1}, was greater than previously used, however. It can be seen that increasing the gas flow rate above 0.375 l l^{-1}min^{-1} has little impact on the rate of removal as saturation is reached. The time required for cessation of ammonia removal at 70 °C was between 30 and 80 hours.

Addition of alkali to modify the initial pH was shown to have a strong effect on the TAN removal kinetics, as seen in experimental runs 11-14 and 18-20. The time for removal decreased from 30-80 hours to around 4-20 hours. This is in agreement with the theory that increasing the pH leads to a greater proportion of free ammonia and therefore to more rapid removal. At high alkali dosages experimental problems were encountered due to excessive foaming, and antifoam (J-QUELL 19, J1 Technologies, UK) was used to prevent this.

Table 2 shows an example of the partitioning of the TAN on a concentration basis for runs 12.1 and 12.2, demonstrating that the ammonia captured in the condensation and water traps can reach very high concentrations; TAN concentrations of 35 and 21 g N l^{-1} respectively. Additionally the results show that most of the ammonia had been removed from the gas flow before the acid trap, suggesting that it could be omitted from the system without having a major impact of the process. This would reduce risks and cost associated with acid use on an industrial scale.

3.2 Effect of VFA on ammonia stripping

The results in Table 1 show a difference in behaviour of the two digestates under similar ammonia stripping conditions. This was thought to be due to the higher VFA concentration in digestate 2, although the digestates 1 and 2 had different TS contents of 5.50 and 3.14% respectively.

In the experiment where digestate 2 was spiked with VFA, the effect of this on the ammonia stripping can be clearly seen in Figure 5. The VFA reduced the pH of the digestate, causing a pH swing as the ammonia was removed. This prevented the removal of ammonia below a TAN of 4300 mg N l^{-1}, compared with a final TAN concentration of 1090 mg N l^{-1} when no VFA was added. This explains some apparent discrepancies between the previous work and current findings [23], and is an important result since it has implications for the use of ammonia stripping to recover food waste digesters that have already accumulated high concentrations of VFA: in these conditions gas stripping is less effective and is unlikely to reduce TAN concentrations to less than 4000 mg N l^{-1}.

The main reason for differences in ammonia removal from both digestates under similar conditions was thought to be the different VFA concentrations in these digestates, although it is also possible that

digestate TS could influence this. The interaction between the gas bubbles and the digestate may be affected by the digestate physical characteristics, including its solids content and viscosity, but further investigation of this was outside the scope of the current work.

3.3 Modelling the integrated ammonia removal and anaerobic digestion process

Scenario 1 – Post digestion ammonia removal
Figure 6 shows accumulation in a digester with initial TAN concentration of 500 mg N l^{-1}, representing a digester inoculated with municipal sewage sludge digestate. Organic loading rates of 1-6 kg VS $m^{-3}d^{-1}$ were modelled with an ammonia removal time constant of 4 hours corresponding to a temperature of 70°C and a biogas flow rate of 0.375 l l^{-1} min^{-1}. The retention time of the digester was set to 30 days by altering the ratio of recycled digestate to incoming feedstock, making the volume of digestate recycled between 6.23-0.21 times the volume of the fresh feed. The steady state TAN concentration was reached after 100-120 days and increased from 831 to 4977 mg N l^{-1} with increasing loading rate from 1 to 6 kg VS m^{-3} d^{-1}. This corresponds to reductions in digester TAN concentrations of 86-17% respectively relative to a digester without ammonia stripping.

The variation in performance can be attributed to the different volumes of recycled digestate. The ratio of recycled digestate to fresh FW feed is chosen such that the HRT in the digester is at a safe minimum, which in this case was set at 30 days. At 1 kg VS m^{-3} d^{-1} the whole system HRT was 217 days and the recycle ratio (volume recycled: volume fresh feed) was 6.23, meaning that fresh food waste with an TAN production potential of 6000 mg N l^{-1} is diluted with 6.23 volumes of digestate with a TAN concentration only 0.2% of that in the digester. At the highest OLR, however, the dilution is only 0.21 volumes which led to the higher steady state TAN concentration. The final loading limit on the system is 7.24 kg VS m^{-3} d^{-1}, at which point the HRT of the whole system is 30 days and no digestate could be recycled without reducing the digester HRT below this value.

The post digestion removal scenario requires in the pasteurisation of excess digestate, since some of the output from the stripper/pasteuriser is recycled, and will therefore increase the heat load of the anaerobic digestion plant. In the worst case, at 1 kg VS m^{-3} d^{-1} the heat load of the stripper/pasteuriser is increased by a factor of 7.23 relative to scenario 2. This may be acceptable in some circumstances where sufficient waste heat is available.

Scenario 2 – In situ ammonia removal
Figure 7 shows the results for OLR of 1-6 kg VS m^{-3} d^{-1} with an initial TAN concentration of 500 mg N l^{-1}. The ammonia removal time constant in this case was 595 hours corresponding to a digester temperature of 35°C and a biogas flow rate of 0.375 l l^{-1} min^{-1}. Despite the constant being two orders of magnitude higher than in the post digestion stripping scenario, the final TAN concentrations at all loading rates are lower. The TAN concentration in the digester was 629-2510 mg N l^{-1} equating to removals of 90-58% respectively relative to no intervention at the same OLR. In this scenario the ammonia removal is simply related to the HRT of the system: at shorter retention times (higher OLR) the digestate spends less time in the stripping system (the digester) and therefore the final TAN concentration is higher. The retention time of the digester for scenario 2 was set by the incoming volume of food waste (i.e. by the OLR) and varied between 217 and 36 days.

In contrast to scenario 1 there is no additional heat load on the plant but pumping requirements are much greater, by a factor of 15 (as the stripping reactor in scenario 1 is 1/30 the size of the digester and operates at twice the specific biogas flow rate).

Scenario 3 – Side-stream ammonia removal

This configuration is similar to the post-digestion removal except that it offers a greater degree of flexibility by operating the stripping system independently of the pasteuriser. Figure 8 shows the results of the modelling where the stripping reactor was modelled as a semi-continuous process filled and discharged once every 24 hours. The volume of the stripping system relative to the digester volume was adjusted in a range between 1/10 and 1/100. In each case the batch time of the stripping reactor was constant at 24 hours, equivalent results could be obtained by adjusting the batch time and keeping the volume of the stripping system constant. The system was modelled using an ammonia removal time constant of 17.7 hours equivalent to a temperature of 70°C and a biogas flow rate of 0.375 l l^{-1} min^{-1}. As was expected the results showed that the larger the stripping system, relative to the size of the digester, the lower the resulting concentration of TAN. At an OLR of 3 kg VS m^{-3} d^{-1} the effect of changing the stripping system volume from 1/100 to 1/10 was to reduce the TAN concentration from 3984 to 991 mg N l^{-1}, corresponding to a change in TAN removal from 34-83% relative to no stripping.

For comparison scenario 3 was modelled for a single case and compared on a performance basis (digester TAN concentration) with all the other scenarios (Figure 9). The stripping system, with a volume of 1/30 the digester, was filled daily and operated continuously between filling operations which were assumed to be instant. Again stripping was modelled with an ammonia removal time constant of 17.7 hours as per experimental run 6.1. The results of this simulation are that for OLR of 1-6 kg VS m^{-3} d^{-1} the TAN concentration was 942-3166 mg N l^{-1} corresponding to TAN removals of 84-47% respectively relative to no intervention.

It should be noted that the mode of operation of the side-stream ammonia stripping system may have implications for the biological stability of the system since the digester effective HRT can go below 30 days (including both the effluent and stripping system flows). Further testing would be required to ascertain whether stable digestion could be maintained with the stripping system in operation and with associated disruptions to the biomass e.g. temperature, pH shifts etc. The energy requirements of this scenario depend on the temperature, biogas flow rate, relative size and digestate flow rate in the stripping system.

Scenario 4 – Pre-digestion ammonia removal

The operation of scenario 4 requires selection of a design residence time and therefore of the relative volumes of the hydrolysis reactor (or mixing tank) and the ammonia stripping reactor. In a particular installation, once these volumes have been set the residence times then depend only on the OLR of the system. This scenario assumes that hydrolysis of proteins and ammonia release occurs in a relatively small hydrolysis reactor. Whilst there is evidence that this could occur in the low pH environment found in this type of reactor [25], initial experiments with food waste showed that only 15% of the potential TAN concentration is released in a low pH short retention time reactor, probably due to pH inhibition [26]. It is likely that some form of pH control, through chemical additions or digestate recycle, would be needed for effective ammonia release in the hydrolysis step. Recycling large volumes of digestate to the hydrolysis reactor would make this scenario similar to scenario 3.

In order to model this scenario it was first necessary to calculate digester TAN concentrations for various degrees of hydrolysis in the first step, to establish the TAN concentration entering the stripping reactor;

and to determine the amount of time the digestate spends in the stripping reactor. Stripping in this case was modelled under the same conditions as scenario 1 (as per run 20.1/20.2) assuming an ammonia removal time constant of 4 hours based on a temperature of $70^{\circ}C$ and a biogas flow rate of $0.375l \ l^{-1} \ min^{-1}$. The results are shown in Figure 10, and it can be seen that the effectiveness of the hydrolysis process is the most critical factor: if the nitrogen remains as proteins or amino acids throughout the hydrolysis step it cannot be removed by the stripping stage, and therefore ends up as ammonia in the digester.

For further modelling of scenario 4 a particular design case was chosen based on residence times in the hydrolysis and stripping reactor of 2 days and 8 hours respectively at an OLR up to 6 kg VS $m^{-3} \ d^{-1}$. The calculation steps, which assume both hydrolysis and TAN release are 1st order with a time constant of 0.35 d^{-1}, are shown in table 3. The results show digester TAN concentrations between 750-3379 mg N l^{-1} corresponding to removals of 88-44% relative to a digester without stripping. Figure 9 shows the results compared with the other removal scenarios. The results for an OLR of 5 kg VS $m^{-3} \ d^{-1}$ require a hydrolysis tank 9.2% and stripping reactor 0.77% of the size of the main digester. If the size of the hydrolysis and stripping reactors is doubled (giving residence times of 4 days and 16 hours respectively at 5 kg VS $m^{-3} \ d^{-1}$) the performance of the system improves, giving TAN removals of 93-68% relative to no intervention.

Of the scenarios modelled the applicability of pre-digestion ammonia stripping is associated with the most uncertainty. There is insufficient experimental data to predict whether ammonia can be fully released in a hydrolysis reactor, without excessive use of chemicals to control pH. Furthermore large concentrations of VFA would be expected in the effluent from the hydrolysis reactor which could impact the stripping process as was observed in the experimental work. Further experimental work is required to verify this application. However pre-digestion shows most promise in terms its degree of operational flexibility, allowing the hydrolysis and stripping systems to be designed independently: this would permit operational control of the TAN and therefore free ammonia concentration in the digester to that required for a particular OLR. None of the other scenarios provide this since they are all subject to operational limits: scenarios 1 and 3 from the deactivation of biomass due to the high temperature stripping process and scenario 2 by the temperature of stripping *in situ* and the relatively short HRT at high OLR.

4. Conclusion

In all experimental runs it was possible to reduce the TAN concentration in the digestate by biogas stripping, which suggests that this technology may be viable as a tool for ammonia management in AD to relieve toxicity and manage digestate ammonia concentration. The kinetic of the TAN removal process was shown to approximate 1st order decay over a wide range of conditions of temperature and gas flow rate. At 35 and 55 °C the removal time constants were in the order of 600 hours, whereas at 70 °C this could be reduced to around 15-17 hours at a suitable flow rate. With pH adjustment by the addition of 10M NaOH the time constant could be further reduced, to 3.9 hours at 70°C. The main interfering factor in ammonia removal appeared to be high concentrations of VFA which led to a characteristic small initial pH increase followed by a sharp swing to a lower pH, resulting in cessation of the ammonia removal process and leaving TAN concentration of around 4000 mg N l^{-1} in the digestate.

The results of the modelling showed that ammonia removal in an integrated process was achievable in all of scenarios considered. I*n situ* ammonia removal showed the greatest ammonia removal over a wide range of OLR, whereas pre-digestion ammonia removal allowed the most operational flexibility and design since the unit processes of ammonia release, removal and anaerobic digestion could be operated

independently. Further experimental work is required to design an optimised pre-digestion ammonia removal system. In terms of energy inputs in-situ ammonia removal would involve a large pumping load on the digestion plant which may make the treatment unfeasible. Similarly the other scenarios required varying amounts of additional heat, as stripping would be performed at 70°C. An energetic analysis of the scenarios would be required before recommendations on larger-scale testing could be made.

5. Acknowledgements

6. References

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Tables and Figures

Table 1 Experimental results of batch ammonia stripping experiments with digestates 1 and 2

	Temp (°C)	Flow Rate ($l\,l^{-1}\,min^{-1}$)	Alkali addition	Length of run (hrs)	Initial		Final		Time constant (hours)	r^2	% N-NH$_3$ Removed
					pH	TAN ($mg\,N\,l^{-1}$)	pH	TAN ($mg\,N\,l^{-1}$)			
Digestate 1											
0.1	35	0.375	N	306.3	8.43	7189	8.87	4318	595.0	0.98	40
1.1	55	0.125	N	120.1	8.46	7479	8.89	6155	699.6	0.91	18
2.1	70	0.125	N	97.5	8.70	7743	8.49	446	30.7	0.96	94
3.1	70	0.125	N	118.5	8.49	7798	9.36	285	32.3	0.96	96
4.1	70	0.375	N	30.0	8.50	7764	8.86	1090	15.1	0.99	86
5.1	70	0.250	N	63.5	8.65	7810	8.89	497	22.1	0.99	94
6.1	70	0.375	N	28.8	8.50	7847	8.99	1585	17.7	1.00	80
7.2	70	0.500	N	24.4	8.59	8076	9.04	1963	17.5	1.00	76
8.2	70	0.625	N	44.7	8.62	8245	7.98	773	17.7	0.97	91
9.2	70	0.375	Y	6.3	12.18	6783	10.99	1539	4.2	1.00	77
10.1	70	0.750	N	22.7	8.45	8821	9.03	6925	17.8	0.97	21
10.2	70	0.750	N	52.0	8.45	8821	8.01	470	17.1	0.97	95
11.1	70	0.125	Y	64.9	10.19	7815	10.36	1706	45.2	0.93	78
11.2	70	0.125	Y	89.8	10.19	7815	10.12	551	36.0	0.91	93
12.1	70	0.250	Y	55.1	10.25	8134	10.30	235	15.3	0.96	97
12.2	70	0.250	Y	55.3	10.25	8134	10.18	202	15.0	1.00	98
13.1	70	0.250	Y	71.8	11.43	5816	11.18	357	27.8	0.73	94
13.2	70	0.375	Y	71.9	10.32	6232	10.41	191	8.2	0.74	97
14.1	70	0.375	Y	22.8	13.86	5404	11.28	281	7.8	0.96	95
14.2	70	0.375	Y	22.9	13.86	5404	11.36	391	8.9	0.95	93
Digestate 2											
15.1	70	0.125	N	98.5	8.20	5978	8.57	1389	64.2	0.99	77
15.2	70	0.250	N	98.5	8.20	5978	7.63	1302	66.9	0.98	78
16.1	70	0.375	N	52.9	8.13	5834	8.82	1701	41.8	1.00	71
16.2	70	0.500	N	52.9	8.13	5834	8.13	1664	36.0	0.95	71
17.1	70	0.625	N	48.5	8.24	5849	7.86	1395	33.4	0.98	76
17.2	70	0.750	N	45.3	8.24	5948	7.85	1937	37.8	0.80	67
18.1	70	0.375	Y	18.8	12.24	4328	11.18	537	9.2	0.99	88
18.2	70	0.500	Y	18.8	12.24	4328	11.28	458	8.6	0.98	89
19.1	70	0.375	Y	11.2	9.15	5258	9.96	2587	15.7	0.99	51
19.2	70	0.500	Y	11.2	9.06	5045	9.93	2214	13.0	0.98	56
20.1	70	0.500	Y	6.3	14.56	4764	12.08	1044	4.1	1.00	78
20.2	70	0.625	Y	6.3	14.61	4976	11.84	940	3.7	0.99	81

Table 2 Ammonia concentrations for run 12.1 and 12.2

TAN concentration (mg N l^{-1})	R1	R2
Initial Digestate	8877	8877
Final Digestate	256	221
Acid trap	7681	7430
Water trap	19301	20996
Condensate trap	29227	34978
Crystals (with water)	330	240

Table 3 Modelling of pre-digestion hydrolysis and ammonia removal over a range of loading rate from 1-6 kg VS m^{-3} d^{-3}

Organic loading rate (kg VS m^{-3} d^{-1})	1	2	3	4	5	6
Hydrolysis tank size (% main digester)	9.2	9.2	9.2	9.2	9.2	9.2
Hydraulic retention time of hydrolysis tank (days)	20	10	6.7	5	4	3.3
TAN concentration in hydrolysis tank (input to ammonia stripper, mg N l^{-1})	5250	4667	4200	3818	3500	3231
Ammonia stripper size (% of main digester)	0.77	0.77	0.77	0.77	0.77	0.77
Batch time of ammonia stripper (hours)	40	20	13.3	10	8	6.7
TAN concentration after stripping (mg N l^{-1})	0.24	31	150	313	474	610
TAN concentration in digester (mg N l^{-1})	750	1365	1948	2495	2974	3379
Ammonia removal (% removal c.f. no intervention)	87.5	77.3	67.5	58.4	50.4	43.7
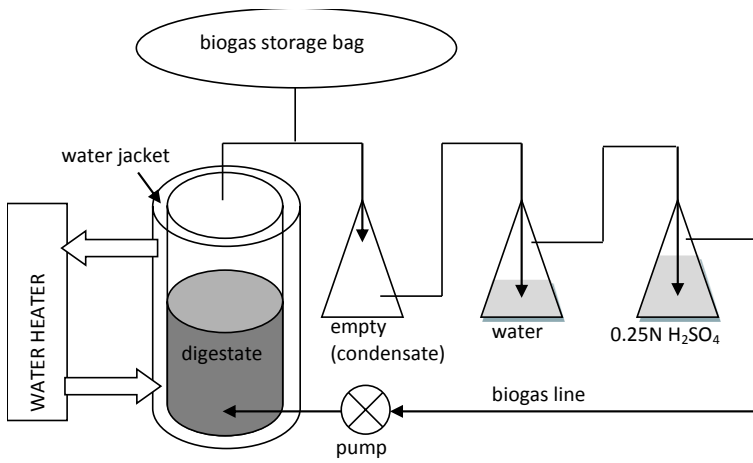
Figure 1 Ammonia stripping equipment

Scenario 1

Scenario 1 Post digestion ammonia removal

Scenario 2 *In situ* ammonia removal

Scenario 3 Side-stream ammonia removal

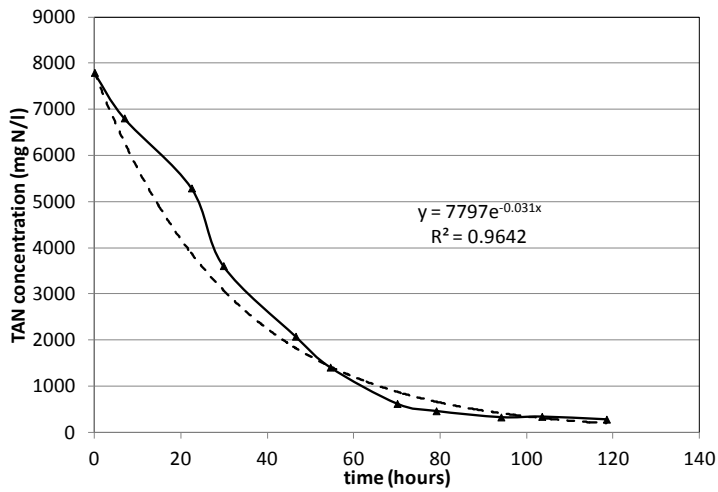**Scenario 4** Pre-digestion ammonia removal
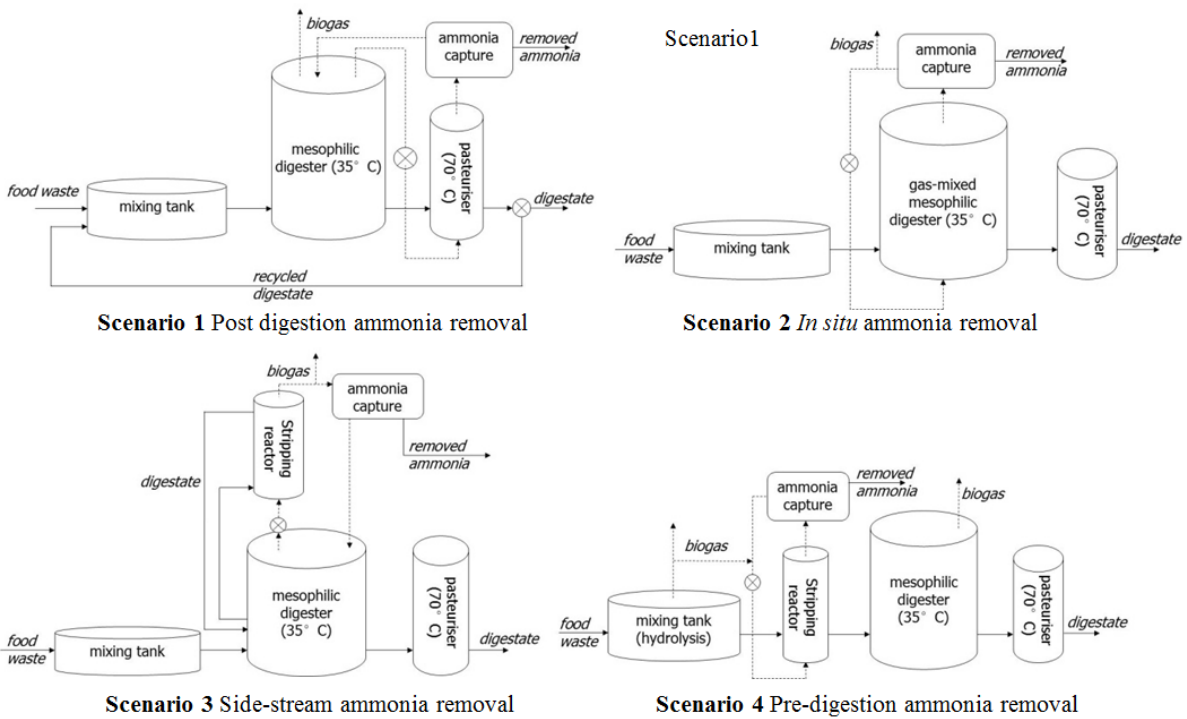
Figure 2 Ammonia removal scenarios modelled

Figure 3 Exponential fit of experimental data (70ºC, gas flow rate 0.125 1 l^{-1} min^{-1}, no pH modification) to an exponential decay coefficient
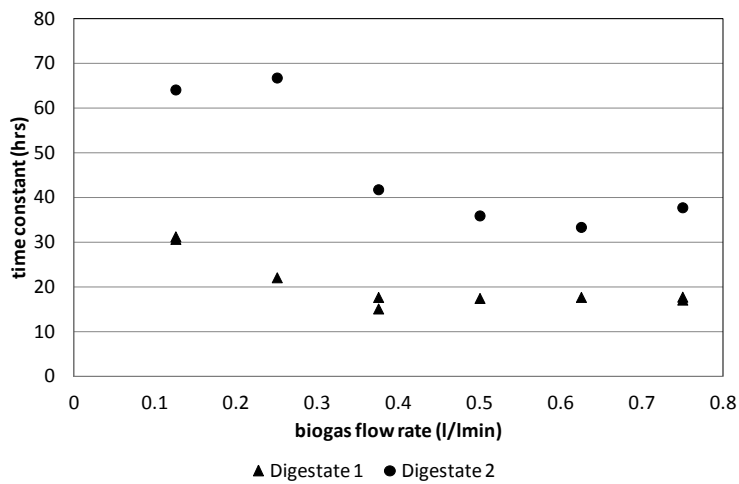

Figure 4 Variation in the ammonia removal time constant with biogas flow rate for D1 and D2
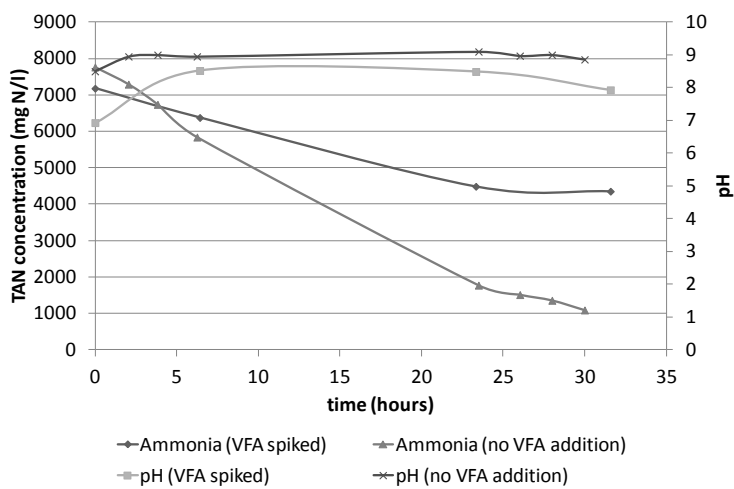
Figure 5 Effect of VFA on ammonia stripping (70ºC, gas flow rate 0.375 1 l^{-1} min^{-1}, no pH modification)
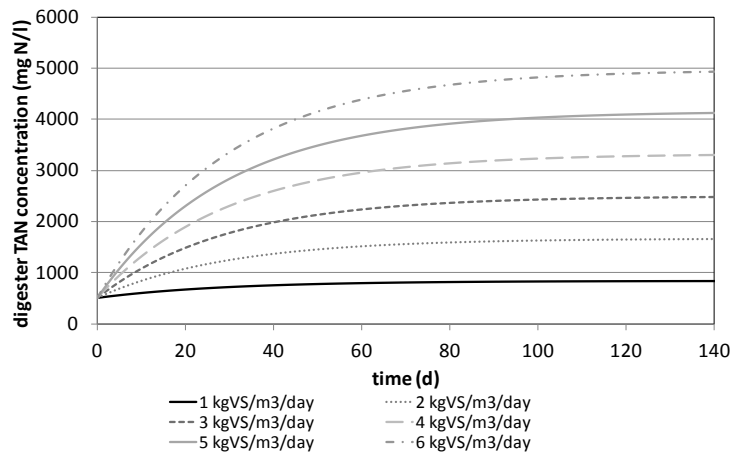
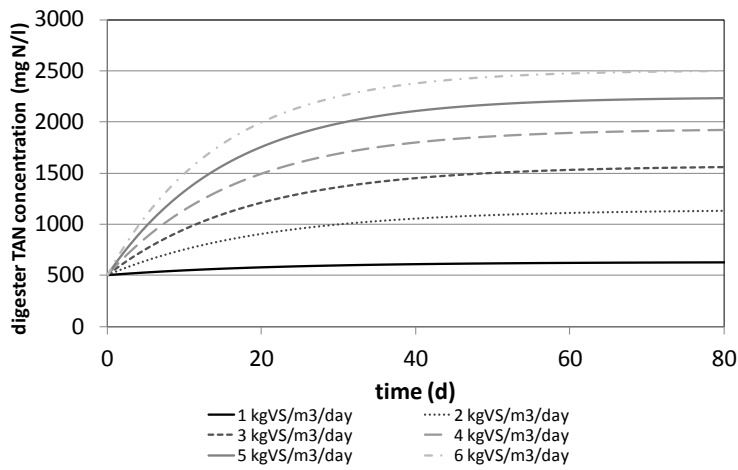Figure 6 Results from the modelling of scenario 1 at loading rates of 1-6 kg VS $m^{-3}d^{-1}$

Figure 7 Results from the modelling of scenario 2 at loading rates of 1-6 kg VS $m^{-3}d^{-1}$
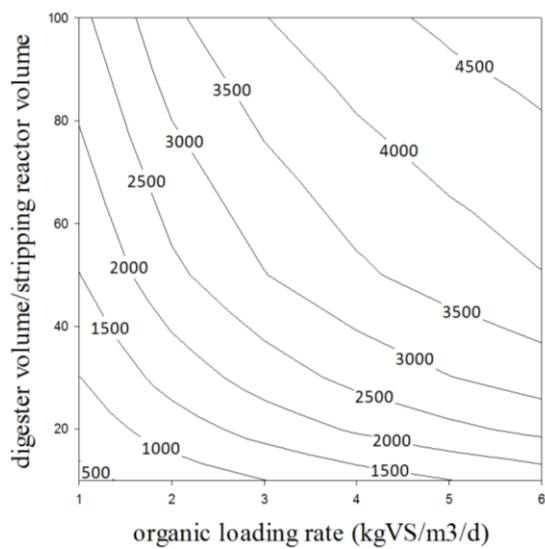

Figure 8 Digester TAN concentration (mg N l^{-1}) at different organic loading rates using a side stream stripping process between 1/10 to 1/100 of the volume of the digester.
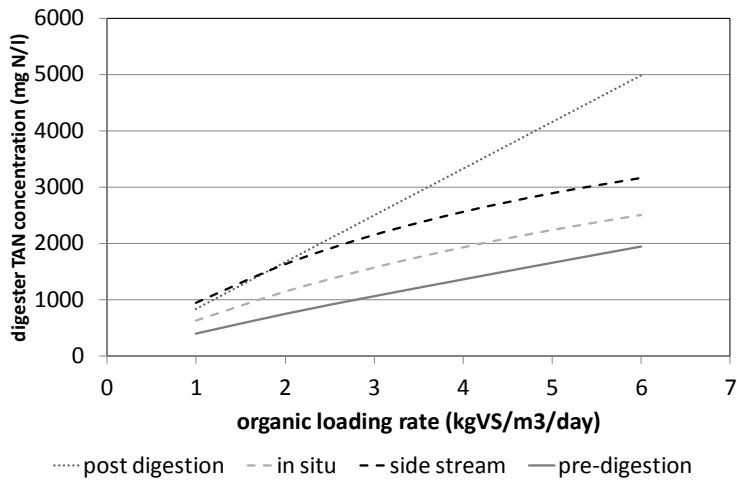
Figure 9 Comparison of digester ammonia concentrations with the four ammonia removal scenarios at organic loading rates of 1-6 kg VS m^{-3} d^{-1}
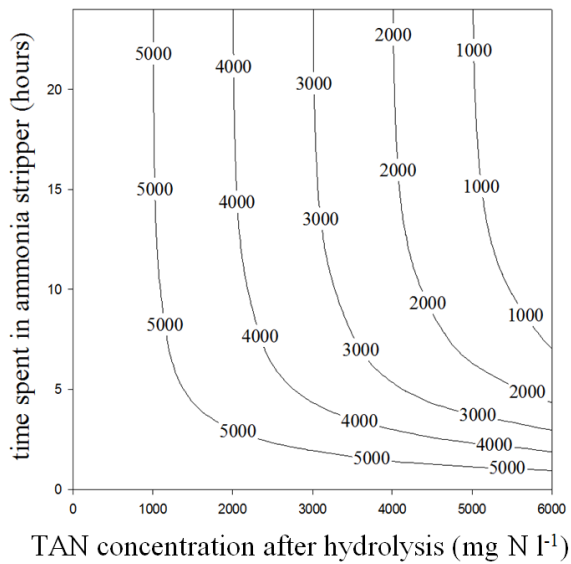

Figure 3 Contour plot of digester TAN concentration (mg N l^{-1}) for differing degrees of ammonia release during hydrolysis and time spent in a pre-digestion ammonia stripper.