

Ammonia recovery from anaerobically digested cattle manure by steam stripping

L. Zeng, C. Mangan and X. Li

Alberta Research Council Inc., Vegreville, AB T9C 1T4, Canada (E-mail: lzeng@arc.ab.ca)

Abstract Ammonia recovery from anaerobically digested cattle manure effluents through steam stripping was studied at a stripping tower temperature of 98–99 °C and a steam–water ratio approximately 56–72 g/L. The digested manure effluents were first treated by microfiltration and then the permeate was used as feed in steam stripping. The stripping performance was evaluated under different feed pH values, ammonia concentrations and temperatures. The increase of the initial feed pH does not significantly improve ammonia stripping efficiency due to the fact that the stripped effluent pH is increased during steam stripping. This suggests that steam stripping of anaerobically digested manure effluents for ammonia recovery may not need pre-raised pH. In contrast, the pH value of the synthetic ammonia wastewater containing NH_4Cl dramatically decreases after steam stripping. Increasing the feed temperature slightly improves ammonia stripping efficiency, but reduces the concentration of the recovered ammonia in the condensate due to an increased condensate volume at a higher feed temperature. Therefore, the feed temperature should be controlled at an optimum point that can compromise the condensate ammonia concentration and the ammonia stripping efficiency. Experimental results indicate that recovery of ammonia from anaerobically digested cattle manure effluents as NH_4OH is technically feasible.

Keywords Ammonia removal and recovery; anaerobic digestion; cattle manure; steam stripping

Introduction

Anaerobic digestion of agricultural and municipal wastes has been widely used for biogas production and considered as a viable technology for waste disposal. However, anaerobic digestion alone does not completely address the challenges associated with those wastes. Significant amounts of nitrogen, phosphorus and other plant nutrients always remain in the digestate, which are valuable resources for plant growth but also pose-potential risk of contamination to water bodies if improperly managed. Therefore, effective recovery of nutrients from the digested effluents becomes necessary for pollution control and environmental sustainability.

Nitrogen in the ammonia form can be removed from wastewater or effluents through three basic groups of processes: physical/chemical processes, biological processes, or hybrids of the two. The practical methods mainly include biological nitrification-denitrification, air stripping, steam stripping, ion exchange, reverse osmosis, struvite precipitation, volatilization, and breakpoint chlorination (Reeves, 1972; USEPA, 1974, 1994; Marr and Koncar, 1993; Water Environment Federation, 1998). Several of those mentioned methods, such as stripping, ion exchange, reverse osmosis and struvite precipitation, can also recover ammonium. Ammonia stripping by air or steam is a relatively simple process that can be controlled for efficient ammonia removal and recovery.

Although both air stripping and steam stripping are similar gas–liquid mass transfer processes, steam stripping is essentially a distillation process that takes place at higher temperatures than air stripping, usually close to the boiling point of water. An important benefit of steam stripping is that no off-gas treatment is required, since the off-gas vapors can be condensed into a small amount of concentrated liquid stream. As a separation

technology, steam stripping has long been used in the chemical process industry. In recent years, it has been increasingly applied to pollution control, particularly for the removal of volatile organic compounds (VOCs) from contaminated water (Hassan and Timberlake, 1992; Hwang *et al.*, 1992a,b; Bravo, 1994; Dvorak *et al.*, 1996). Steam stripping was studied for ammonia removal from different wastewaters: sour water in petroleum industry (Darton *et al.*, 1978), wastewater from a metal extraction process (Wickramanayake *et al.*, 1992), sludge treatment reject water (Teichgräber and Stein, 1994; Janus and van der Roest, 1997), reverse osmosis retentate of domestic wastewater (Bilstad, 1995), coke plant wastewater (Minhalma and de Pinho, 2002, 2004). Ammonia nitrogen could be recovered in the off-gas condensate as enriched NH_4OH solution after stripping (Teichgräber and Stein, 1994). However, little data are available for steam stripping of anaerobically digested manure effluents.

Ammonia nitrogen in wastewater is present as ammonium ions (NH_4^+) and aqueous ammonia (NH_3) that is volatile. The equilibrium between NH_4^+ and NH_3 in the aqueous solution is strongly dependent on pH and temperature (Emerson *et al.*, 1975). At pH below 7, ammonia nitrogen exists essentially in the NH_4^+ form regardless of temperature. With pH increase, the amount of NH_4^+ decreases. The same occurs with an increase in temperature. Both increases in pH and temperature, in turn, favor the ammonia stripping process.

In the effluents from anaerobic digestion of cattle manure, high concentrations of ammonia nitrogen, often over 2000 mg/L, exist in a complex matrix and are due to the release of large amounts of ammonia through break down of organic nitrogen compounds in anaerobic digestion. The purpose of this research was to study the feasibility of steam stripping of ammonia from anaerobically digested cattle manure effluents. Batch steam stripping experiments with digested cattle manure effluents were conducted in a pilot packed stripping tower to determine the effects of the feed pH, ammonia concentration, and temperature on ammonia recovery. The obtained results could provide a further understanding of ammonia removal and recovery from anaerobically digested animal manure.

Materials and methods

Digested manure effluents

Anaerobically digested cattle manure effluents were obtained from an Integrated Manure Utilization System (IMUS) demonstration plant, located at Vegreville, Alberta, Canada. The manure effluents were centrifuged on-site with a commercial solid bowl centrifuge before being transported to the laboratory. This centrifuged digested manure (CDM) effluent was further treated by microfiltration (MF). The permeate collected from MF membrane treatment was used as feed for steam stripping. Major chemical and physical properties of this permeate are given in Table 1.

The actual ammonia concentration in the feeding solution for steam stripping was approximately 910 mg/L as $\text{NH}_3\text{-N}$ after storing for a few weeks in a cold room at 4 °C. For experiments with higher initial ammonia concentrations, ammonium chloride (NH_4Cl) was directly added into the MF permeate to make up the required ammonia concentrations. For comparison, stripping experiments were also conducted using synthetic wastewater containing 1000–2500 mg $\text{NH}_3\text{-N/L}$, which was prepared by dissolving NH_4Cl (BDH, Analytical reagent, 99.5% min) in tap water.

Stripping apparatus and procedures

The experimental setup for steam stripping consisted mainly of a stripping tower, a feed tank with a heating element, a liquid feeding pump, a steam input line, and a water-jacketed

Table 1 Chemical and physical properties of permeate from microfiltration of centrifuged digested cattle manure effluent

Item	Unit	Value ^a	SD
NH ₃ -N	mg/L	956	44
PO ₄ ³⁻	mg/L	27	12
SO ₄ ²⁻	mg/L	21	8
Ca	mg/L	63	26
Mg	mg/L	41	8
K	mg/L	1904	121
Na	mg/L	618	47
Cl	mg/L	1089	51
pH		8.14	0.30
TS	mg/L	6905	456
TSS ^b	mg/L	102	
TDS	mg/L	6803	371
Alkalinity	CaCO ₃ mg/L	5493	469
Turbidity	ntu	69	15
Conductivity	μS/cm	13610	740

^aAverage value from 5 samples

^bBy difference of TS and TDS. NO₃⁻ and NO₂⁻ were not detected in all samples

condenser. The stripping tower made of brass pipes had an internal diameter (ID) of 4.5 cm, a height of 1.8 m in the packing zone and 0.31 m in the extended zone above packing. A piece of liquid distribution tubing was centrally installed at a location 0.1 m above the packing in the stripping tower. The stripping tower was packed with 3/8" ceramic Berl saddles in a total packed volume of 2.8 L. It was wrapped with heating tapes and fiberglass insulating sheets and its internal temperature was controlled by a temperature controller. The liquid feed tank was mechanically stirred and heated by a controlled heating plate. Several thermocouples were installed to measure temperatures at the inlet, outlet and middle of the stripping tower and inside the feed tank. Gauges were used for measuring the pressure at the bottom and top of the stripping tower.

Steam was delivered at about 10 psig to the bottom of the stripping tower by a steam input line from a central boiler. The liquid stream was pumped with a Masterflex pump from the feed tank to the top of the stripping tower and flowed out from the bottom of the tower to a separate storage tank. The exhaust steam out of the stripping tower was condensed in the condenser and collected in a condensate container.

Experimental methods

Steam stripping experiments were conducted under different conditions including the feed pH, feed concentration, and feed temperature. In each experiment, about 8.5 L of liquid was loaded in the feed tank. Its pH was pre-adjusted to a designated value between 8.2 and 11 with 10 mol l⁻¹ NaOH solution. For all experiments, the liquid feeding flowrate was approximately 140 mL/min and the steam input flowrate was approximately 10,000–12,000 mL/min, providing a steam-water ratio approximately at 70–86 (vol/vol) or expressed as 56–70 kg/m³. The stripping tower temperature was controlled at 98–99 °C, whereas the feed temperature was controlled at 79–81 °C, unless stated elsewhere. Each stripping experiment ran for about 40 min after the stripping tower reached steady-state operation, and the stripped effluent and condensate were sampled 4 times in an interval of 8 min for ammonia and pH measurements. An average and standard deviation were calculated from these four samples to represent the results under the tested conditions.

For experiments evaluating the pH effect, the feed solutions in a concentration of 910 NH₃-N mg/L were pre-adjusted to different pH values between 8.2 and 11. For experiments

evaluating the effect of the feed ammonium concentration, a series of feed solutions having different initial ammonia concentrations between 910 and 45,000 $\text{NH}_3\text{-N}$ mg/L and pH 8.2–8.5 were used. Those feed solutions were made by dissolving different amounts of NH_4Cl into the MF permeate. For experiments evaluating the effect of the feed temperature, different feed temperatures from 40 to 80 °C were used, whereas the feed solution had a concentration of 910 $\text{NH}_3\text{-N}$ mg/L and pH 8.2.

Stripping experiments were also conducted in a circulation mode, i.e. circulating stripped liquid, in which the stripped liquid was delivered back to the feed tank during the experiments, maintaining pH in the feed tank by adding 10 mol l^{-1} NaOH solution. Each circulation experiment ran for about 90 min after the stripping tower reached steady-state operation.

Analytical methods

The ammonia concentrations of liquid samples during experiments were measured by an ammonia-selective electrode and expressed as ammonia nitrogen ($\text{NH}_3\text{-N}$, mg/L). Some stripped effluent samples with the ammonia concentrations below 50 mg/L were analyzed by an ion chromatograph (Dionex ICS-1000) for NH_4^+ . Other ions such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , PO_4^{3-} , SO_4^{2-} , NO_3^- and NO_2^- in manure effluents were measured by the same ion chromatograph. Several properties such as pH, total solids, total dissolved solids, alkalinity, turbidity and conductivity were determined by standard methods (*Standard Methods for the Examination of Water and Wastewater*, 1995).

Results and discussion

Effect of the feed pH

The experimental results obtained with the feeding solution containing 910 mg/L $\text{NH}_3\text{-N}$ at different pH are shown in Figure 1. Three curves in the figure represented the changes of the condensate ammonia concentration, stripped effluent ammonia concentration, and effluent pH vs. feed pH. The ammonia concentration in the condensate increased with pH. This increase was more significant at pH between 10 and 11 than between 8.2 and 10. With the present stripping tower settings, the ammonia concentration in the condensate

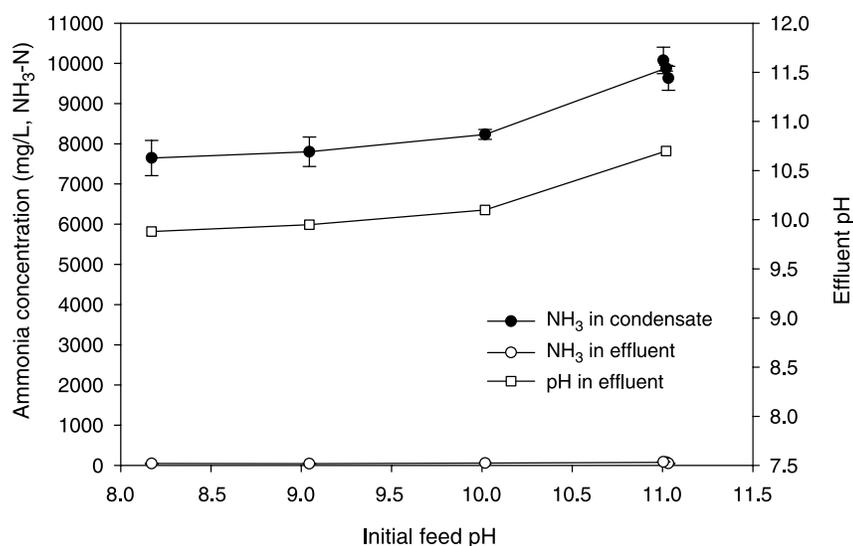


Figure 1 Effect of pH in the feeding solution on steam stripping of ammonia at an initial ammonia concentration of 910 mg/L and temperature of 80 °C

was about 9 to 11 times that in the feeding solution. Correspondingly, the residual ammonia concentration in the stripped effluents significantly decreased to approximately 31–78 mg/L at different feed pH values. The ammonia removal efficiency was between 91% and 96% for those stripping runs. In addition, the pH measurement showed that the stripped effluent pH was higher than the feed pH when the feed pH was below 10. Particularly, the stripped effluent pH reached 9.88 when the original MF permeate without any pH adjustment was taken as feed that had an initial pH of 8.2. In contrast, several similar experiments of steam stripping with NH_4Cl solution showed a dramatic decrease of pH in the stripped effluent after stripping.

The pH rise in the stripped effluent is an important feature associated with steam stripping of digested manure solution compared with that of NH_4Cl solution. This difference should be attributed to the fact that the anaerobically digested manure solution contains a considerable amount of dissolved CO_2 . During steam stripping, the dissolved CO_2 in the digested manure solution is also released and subsequently the pH is increased, although the release of NH_3 causes a pH decrease in the stripped liquid phase. However, the net change of pH in the stripped effluent was an increase under the present experimental conditions when the feed pH was below 10. The pH increase after stripping was further confirmed by experiments with bubbling air through the same feeding solution at room temperature. In those experiments, pH increased gradually from 8.25 to 9.25 along with air bubbling. The critical implication from those results is that steam stripping of anaerobically digested manure effluents for ammonia recovery may not need to pre-raise pH. For reducing operation cost, the steam stripping of digested manure solution is preferably operated without any prior pH adjustment.

In addition, the released CO_2 , if its concentration is too high, may form NH_4HCO_3 precipitants with NH_3 in the condensate to block flow pipes. Blockage of several pipes by NH_4HCO_3 precipitants was observed during operation of steam stripping of sludge treatment reject water (Teichgräber and Stein, 1994).

Effect of the feed ammonia concentration

The experimental results obtained at three feed ammonia concentrations with feed pH of 8.2–8.5 and temperature of 80 °C are shown in Figure 2. The ammonia concentration in

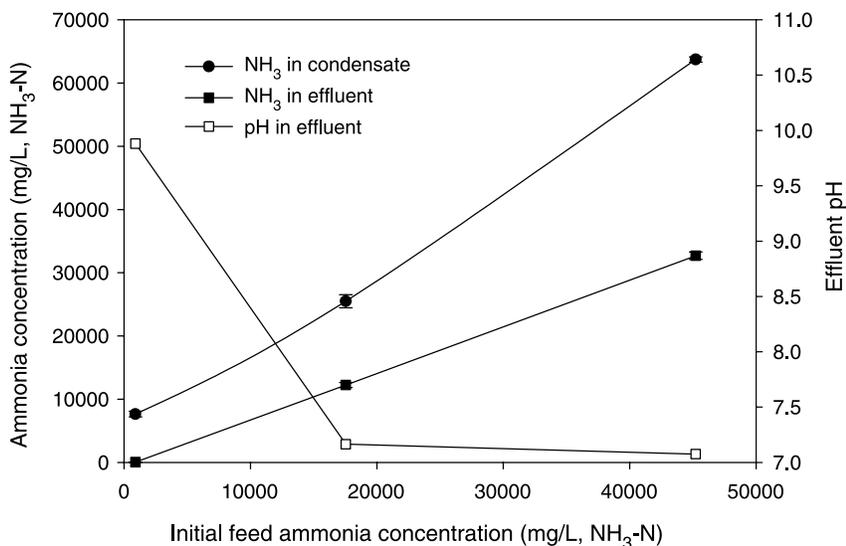


Figure 2 Effect of the feed ammonia concentration on steam stripping of ammonia

the condensate increased with the increase of the feed ammonia concentration, but not as significantly as shown in Figure 1, except for the experiment with the lowest ammonia feed concentration. This was caused by not maintaining a higher pH inside the stripping tower as indicated by a lower pH in the stripped effluent in Figure 2, evidently due to a large addition of NH_4Cl in the feed for increasing the initial ammonia concentration. As previously shown, the stripped effluent pH was increased after steam stripping of digested manure solution, while the stripped effluent pH no longer increased when a large amount of NH_4Cl was added into the same digested manure solution. These results suggest that maintaining a certain pH (for instance, 9.0 or above) during steam stripping be important for efficient ammonia removal. As shown in Figure 2, the residual ammonia in the stripped effluent increased with the increase of the feed ammonia concentration. Similarly, an early simulation of steam stripping with sour water showed that the effluent ammonia concentration was increased with the feed ammonia concentration (Melin *et al.*, 1975).

Effect of the feed temperature

The experimental results obtained with different feed temperatures at pH 9.0 are shown in Figure 3. The ammonia concentration in the condensate was considerably decreased with an increase of the feed temperature. It was 20,800 mg/L at the feed temperature of 40 °C and decreased to 7800 mg/L at the feed temperature of 80 °C. This was due to a considerably increased condensate rate or water evaporation rate (volume per unit time) at a higher feed temperature as indicated in Figure 4. However, the measured ammonia stripping rate as shown in Figure 4 was slightly higher at the higher feed temperature. Meanwhile, the ammonia concentration in the stripped effluent decreased from 120 mg/L to 30 mg/L when the feed temperature increased from 40 °C to 80 °C. The stripped effluent pH remained between 9.6 and 10.0 when the feed temperature changed (Figure 3).

For steam stripping of aqueous solution, increasing the feed temperature can increase water evaporation and thus the condensate volume. From the point view of obtaining a high ammonia concentration in the recovered condensate, a lower feed temperature may be beneficial. However, a dramatic deterioration in stripping performance may occur

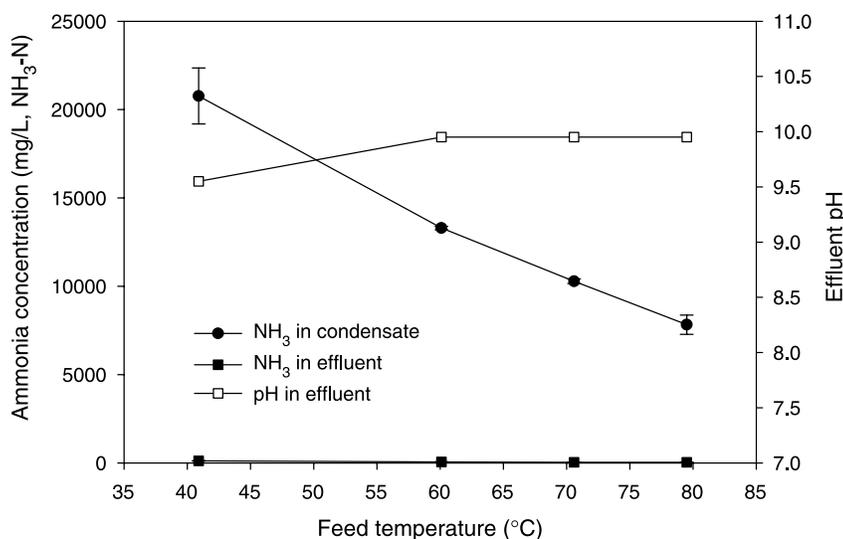


Figure 3 Effect of the feed temperature on steam stripping of ammonia

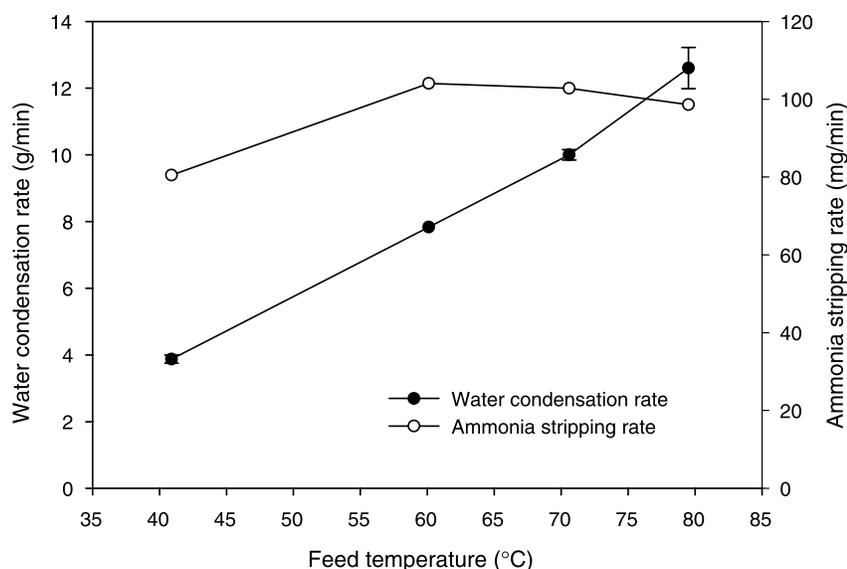


Figure 4 Effect of the feed temperature on condensation rate and ammonia stripping rate

once the feed temperature is reduced such that more than approximately 70% of the total steam is condensed in the stripping tower (Melin *et al.*, 1975). Therefore, the feed temperature should be controlled at an optimum point that can compromise the condensate ammonia concentration and the ammonia stripping efficiency. Under the present experimental settings, this optimum temperature is approximately between 50 and 55 °C which is correspondent to the crossing point of the condensate ammonia concentration curve and the ammonia stripping rate curve. Furthermore, a rectification tower or section can be used in a steam stripping process for further concentrating ammonia in the condensate (Teichgräber and Stein, 1994).

Ammonia stripping with circulation of liquid stream

Steam stripping experiments with liquid circulation were performed with different initial feed pH between 8.2 and 10.3 under a feed temperature of 80 °C. The average residence time of the liquid stream in the stripping tower was about 7–9 min. The results of the condensate NH_3 concentration, feed NH_3 concentration, feed pH and effluent pH for the experiment with an initial feed pH of 8.2 are shown in Figure 5. The ammonia concentration in the condensate gradually decreased as the ammonia concentration in the circulated feed decreased with the increase of the stripping time. Correspondingly, the effluent ammonia concentration decreased and thus the total ammonia removal efficiency was increased with stripping time. Both the effluent pH and feed pH were increased with stripping time, and the effluent pH was higher than the feed pH. The ammonia concentration in the stripped effluent decreased to 13 mg/L after 90 min of stripping. Experimental results obtained at higher initial feed pH values are similar to those shown in Figure 5, except that the effluent ammonia concentration after 90 min of stripping reached 4 mg/L in the experiment with an initial feed pH of 10.3.

Although it is generally accepted that the higher feed pH is beneficial to ammonia stripping, the present stripping experiments using digested manure solution did not show significant difference when the initial feed pH changed from 8.2 to 10.3. These results confirmed that steam stripping of ammonia from anaerobically digested manure solution may not need pre-raised pH.

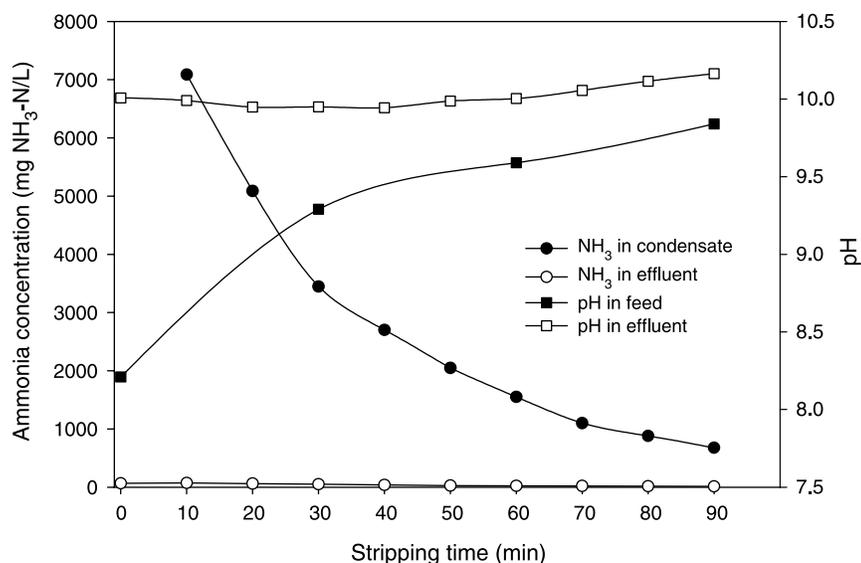


Figure 5 Steam stripping of ammonia with circulation of the liquid stream at an initial feed pH of 8.2

Conclusions

The following conclusions for steam stripping of ammonia from anaerobically digested cattle manure effluents can be drawn:

- The increase of the feed pH does not significantly improve ammonia stripping efficiency due to the fact that the pH of the digested manure solution increases during stripping. This significant pH increase in the stripped effluents makes it possible that steam stripping of anaerobically digested manure effluents for ammonia recovery does not need pre-raised pH.
- The attempt to evaluate the effect of the initial ammonia concentration were not completely successful owing to difficulty in maintaining a high pH inside the stripping tower, caused by a large addition of NH_4Cl in the feed.
- Increasing the feed temperature increases ammonia stripping efficiency, but decreases the recovered ammonia concentration in the condensate, due to the increases of the condensate volume. For obtaining a high ammonia concentration in the collected condensate, the feed temperature should be controlled at an optimum point that can compromise the condensate ammonia concentration and ammonia stripping efficiency.
- Ammonia nitrogen can be recovered as NH_4OH in the condensate after steam stripping.

Acknowledgements

The authors gratefully acknowledge the financial support for this project from Alberta Research Council Inc. and Highland Feeders Ltd. Thanks are also extended to Brett Kotelko and Luhong Zhang for assistance with experiments in this study.

References

- Bilstad, T. (1995). Nitrogen separation from domestic wastewater by reverse osmosis. *J. Membrane Sci.*, **102**, 93–102.
- Bravo, J.L. (1994). Design steam strippers for water treatment. *Chem. Eng. Progress*, **12**, 56–63.
- Darton, R.C., van Grinsven, P.F. and Simon, M.M. (1978). Development in steam stripping of sour water. *Chem. Eng (London)*, **339**, 923–927.

- Dvorak, B.I., Lawler, D.F. and Speitel, G.E. Jr. (1996). Niche for steam stripping in treating dilute SOC-contaminated waters. *J. Environ. Eng.*, 871–874.
- Emerson, K.R., Russo, R.C., Lund, R.E. and Thurston, R.V. (1975). Aqueous ammonia equilibrium calculations: effect of pH and temperature. *Can. J. Fish. Res. Board Can.*, **32**(12), 2379–2383.
- Hassan, S.Q. and Timberlake, D.L. (1992). Steam stripping and batch distillation for the removal and/or recovery of volatile organic compounds from industrial wastes. *J. Air Waste Manage. Assoc.*, **42**, 936–943.
- Hwang, Y.-L., Keller, G.E. II and Olson, J.D. (1992a). Steam stripping for removal of organic pollutants from water. 1. Stripping effectiveness and stripper design. *Ind. Eng. Chem. Res.*, **31**(7), 1753–1759.
- Hwang, Y.-L., Olson, J.D. and Keller, G.E. II (1992b). Steam stripping for removal of organic pollutants from water. 2. Vapor-liquid equilibrium data. *Ind. Eng. Chem. Res.*, **31**(7), 1759–1768.
- Janus, H.M. and van der Roest, H.F. (1997). Don't reject the idea of treating reject water. *Water Sci. Technol.*, **35**(10), 27–34.
- Marr, R. and Koncar, M. (1993). Recovery of ammonia from industrial wastewater. *Int. Chem. Eng.*, **33**(3), 416–425.
- Melin, G.A., Niedzwiecki, J.L. and Goldstein, A.M. (1975). Optimum design of sour water strippers. *Chem. Eng. Process*, **71**(6), 78–82.
- Minhalma, M. and de Pinho, M.N. (2002). Development of nanofiltration/steam stripping sequence for coke plant wastewater treatment. *Desalination*, **149**, 95–100.
- Minhalma, M. and de Pinho, M.N. (2004). Integration of nanofiltration/steam stripping for the treatment of coke plant ammoniacal wastewaters. *J. Membrane Sci.*, **242**, 87–95.
- Reeves, T.G. (1972). Nitrogen removal: a literature review. *J. Wat. Pollut. Control Fed.*, **44**, 1895–1908.
- Standard Methods for the Examination of Water and Wastewater* (1995). 19th edn, America Public Health Association/America Water Works Association/Water Environment Federation, Washington DC, USA.
- Teichgräber, B. and Stein, A. (1994). Nitrogen elimination from sludge treatment reject water—comparison of the steam-stripping and denitrification processes. *Water Sci. Technol.*, **30**(6), 41–51.
- USEPA (1974). *Physical-chemical nitrogen removal: wastewater treatment*. U.S. Environmental Protection Agency, prepared by Gordon Culp, EPA 625/4-74-008.
- USEPA (1994). *Nitrogen Control*, Technomic Publishing Co., Inc., Lancaster, USA. U.S. Environmental Protection Agency.
- Water Environment Federation (1998). *Biological and Chemical Systems for Nutrient Removal*, Water Environment Federation, VA, USA. A special publication.
- Wickramanayake, G.B., Evers, D.P., Kittel, J.A. and Gavaskar, A. (1992). *Bench-scale evaluation of ammonia removal from wastewater by steam stripping*. U.S. Environmental Protection Agency, EPA 600/S2-91/046