

## ABSTRACT

LIANG, WEIZHEN. Mechanisms Controlling Ammonia/um Dynamics in Broiler Litter. (Under the direction of Dr. Sanjay B. Shah and Dr. John J. Classen).

Ammonia emission from broiler house has many negative environmental and public health impacts. In broiler litter, uric acid and urea hydrolyze to ammonium ( $\text{NH}_4^+$ ) and a fraction of  $\text{NH}_4^+$  converts to ammonia ( $\text{NH}_3$ ) depending on pH, temperature, and TAN (total ammoniacal-N =  $\text{NH}_4^+\text{-N}$  +  $\text{NH}_3\text{-N}$ ) concentration. Ammonium undergoes solid-liquid partitioning and the  $\text{NH}_3$  fraction is partitioned among the solid, liquid and gas phases in the litter, which can be calculated using the dissociation constant and Henry's Law constant. However, there are few studies on ammonia/um sorption in broiler litter and values of dissociation constant and Henry's Law constant developed for aqueous solutions may not be appropriate for modeling the fate of  $\text{NH}_4^+$  and  $\text{NH}_3$  in litter system. Ammonium partitioning was measured at different pH values, ammonia sorption was calculated at different moisture contents, and dissociation constant and Henry's Law constant in broiler litter were quantified. In broiler litter, Freundlich, linear and Temkin isotherm provided the best fits at pH of 4, 6, and 7, respectively while in broiler cake, linear isotherm provided the best fit at all pH values; overall, due to its simplicity, the linear isotherm was the most suitable for simulating  $\text{NH}_4^+$  partitioning in broiler litter and cake. Under the test conditions, ammonia sorption increased with moisture content from 0% to 25% and maximum of ammonia sorption was 4,230 mg/kg at 25% moisture content and then decreased with increasing moisture content from 35% to 55%. Litter at 0% moisture content adsorbed >2,800 mg/kg of ammonia, more than sorbed by litter with moisture content at or above 45%. Dissociation constant in litter slurry is  $1.02 \times 10^{-10}$ , 20% of the dissociation constant in aqueous solution, while Henry's Law constant (0.0158 atm/M) in litter slurry was

close to the  $K_h$  (0.0164 atm/M) in aqueous solution. Drying broiler litter at 70°C for 16 h resulted in complete moisture removal with a small loss of C and moderate loss of TAN. Moisture content in broiler litter determined by conventional method needs to be adjusted due to the C and N losses. Better understanding of the mechanisms controlling  $\text{NH}_4^+$  and  $\text{NH}_3$  fate and transformation in broiler litter and cake will allow improved simulation of litter N dynamics.

Mechanisms Controlling Ammonia/um Dynamics in Broiler Litter

by  
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# 1 Introduction

## Ammonia production by livestock

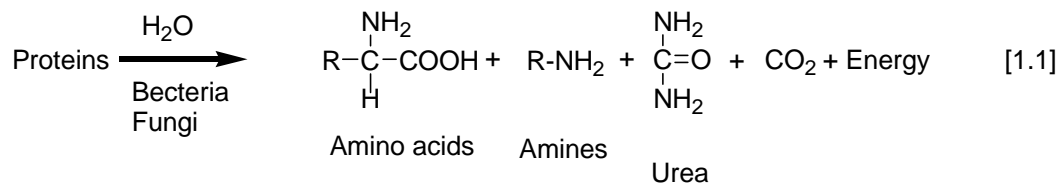
Intensive production of livestock in the USA has raised serious environmental concerns with the public because of its impacts on the environment (Liu et al. 2007). It is estimated that in the US 71% of  $\text{NH}_3$  emissions comes from livestock (EPA, 2004). Ammonia emissions from poultry farms were estimated to 26% of livestock emission in 2010 and 29% in 2015 (EPA, 2005) and ammonia emission is mainly from broiler litter (Reece et al. 1980).

Broilers (meat birds) are raised on bedding material, e.g., wood shavings. Over time, feces, spilled water and feed, and feathers accumulate in the bedding material. Whole-house broiler litter can be divided into fresh cake on the surface and litter below. The cake is largely composed of feces, water, and spilled feed, while the litter underneath also has bedding material. Differences in the ammonia content of poultry feces are due to the differences in feed composition, nutrient digestibility, fiber content in the diet, flock number, time in storage and storage condition (Krogdahl and Dalsgard, 1981) and ventilation rate (Gates et al., 2000).

The nitrogen (N) in broiler litter can be present in various forms- such as uric acid ( $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$ ), urea ( $\text{CO}(\text{NH}_2)_2$ ), ammonia ( $\text{NH}_3$ ), ammonium ( $\text{NH}_4^+$ ), nitrite ( $\text{NO}_2^-$ ), and nitrate ( $\text{NO}_3^-$ ). Uric acid was identified as the major N source (50% of the N content) in poultry manure (Lacy et al., 2004). Twenty percent of total Kjeldahl nitrogen (TKN, the sum of organic N and total ammoniacal N) in broiler litter is ammonium ( $\text{NH}_4^+$ ). Microorganisms and enzymes (ex: uricase and urease) present in litter are responsible for the decomposition

of N species in the litter (Lacy et al., 2004). The main microbial processes that affect ammonia fate in animal waste include aerobic and anaerobic degradation of organic matter, for example, urea and uric acid hydrolysis, nitrification, and denitrification processes (Rotz, 2004).

Ammonia is mainly generated through the breakdown of urea and uric acid by the enzymes urease and uricase, respectively (Lacy et al., 2004). Undigested proteins (organic N) in feces and spilt feed can also break down to release  $\text{NH}_3$ . The proteins in the feed and feces are broken down by heterotrophic bacteria and fungi and become amino acid and amines which further decompose to  $\text{NH}_4^+$  by heterotrophs as shown in equations [1.1], [1.2] and [1.3] (Tisdale et al., 1993). The process of microbial conversion of the organic N to ammonia or ammonium is called ammonification (mineralization) and the microbes are called ammonifying bacteria. The mineralization is from organic substrate (uric acid, urea) to inorganic N ( $\text{NH}_4^+$ ), and the process is affected by several factors, including pH value, moisture content, C/N ratio, available nutrient and particle size (Nodar et al., 1990).



### **On-farm and Off-farm impacts of ammonia**

In broiler house, NH<sub>3</sub> levels commonly reached 50 ppm and were as high as 200 ppm in poorly ventilated houses (Carlile, 1984). High concentration of ammonia in animal houses attacks the eyes and respiratory system of farm animals and workers, thus putting them at risk. Many studies have shown that high levels of NH<sub>3</sub> in poultry houses can reduce feed efficiency, growth rate and egg production (Reece et al., 1980, Caveny et al., 1981, Deaton et al., 1984).

Ammonia volatilization is a major environmental and ecological concern associated with poultry houses (Moore, 1998). Many negative impacts of NH<sub>3</sub> emissions from animal feeding operations on the environment and ecology, e.g. soil acidification, water eutrophication, and particulate matter (PM) have been widely reported (Draaijers et al., 1989). Soil acidification occurs when NH<sub>4</sub><sup>+</sup> is converted to nitrate, which is an acid-forming reaction (Breemen et al., 1982). In the atmosphere, ammonia adsorbs onto acidified droplets (i.g. NO<sub>x</sub> or SO<sub>x</sub> compounds) to form very fine ammonium aerosols (e.g. ammonium nitrate or ammonium sulfate) that will cause haze (Arogo et al., 2001). In addition, N deposition in atmosphere alters the species composition and biodiversity of ecosystems, cause soil acidification and eutrophication as well as leaching of N to surface and ground waters (Kangas and Sanna, 2001). Due to its environmental impacts and its role in PM formation, there has been considerable emphasis on controlling NH<sub>3</sub> emissions from farms.

### **Regulating ammonia emission**

While the EPA has not regulated emissions from animal feeding operations (AFOs), though recently, it has shown interest in regulating AFOs under the Clean Air Act (CAA).

The EPA announced an Air Quality Compliance (AQC) Agreement with AFOs in 2005 (EPA, 2005) to measure air emissions from AFOs and develop an effective regulatory program. As a provision of the AQC, the EPA established a monitoring program NAEMS (National Air Emission Monitoring Study) to monitor emissions and develop standard methodologies for estimating emissions, including ammonia.

Under NAEMS, three broiler farms in California were monitored (NAEMS, Purdue University). There are thousands of broiler farms all over the US that vary widely in management, construction, and climate conditions. Therefore, applying emissions based on measurements from three broiler farms to the broiler industry in the US may not be representative. Therefore, there may be need for physically-based modeling of ammonia emissions, taking into account litter properties, environmental conditions, and management factors.

### **Mechanism of ammonia and ammonium balance**

There are many factors that affect ammonia and ammonium balance: pH, temperature, moisture content, TAN concentration, carbon/nitrogen ratio, oxygen level, substrate concentration, and concentrations of some cations in litter. The most significant factors are pH, temperature, moisture content and TAN concentration.

Depending on pH and temperature, a fraction of  $\text{NH}_4^+$  converts to  $\text{NH}_3$  and their ratio is described by dissociation constant ( $K_d$ ) (eq. [1.4]). In broiler litter, a portion of  $\text{NH}_4^+$  dissolves in the liquid phase while a portion adsorbs to the solid phase. Partitioning between liquid and adsorbed phases for  $\text{NH}_4^+$  can be estimated by using a suitable adsorption isotherm.

$$K_d = \frac{[\text{NH}_3]_{(\text{aq})}[\text{H}^+]}{[\text{NH}_4^+]_{(\text{aq})}} \quad [1.4]$$

A portion of  $\text{NH}_3$  stays in the gas phase but a fraction of  $\text{NH}_3$  adsorbs to litter while the remainder dissolves in liquid phase. Depending on pH, moisture content, and temperature, a fraction of  $\text{NH}_3(\text{aq})$  in litter will convert to  $\text{NH}_3(\text{g})$  that can be explained by Henry's law constant ( $K_h$ ) (eq. [1.5]). Figure 1-1 shows the mechanisms controlling ammonia and ammonium balance in broiler litter. For example, as pH and temperature increases, more  $\text{NH}_4^+(\text{aq})$  becomes  $\text{NH}_3(\text{aq})$  as explained by  $K_d$ , and consequently, more  $\text{NH}_3(\text{aq})$  converts to  $\text{NH}_3(\text{g})$  as explained by  $K_h$ . Therefore, ammonia volatilization increases in alkaline or high temperature condition.

$$K_h = \frac{[\text{NH}_3]_{(\text{g})}}{[\text{NH}_3]_{(\text{aq})}} \quad [1.5]$$

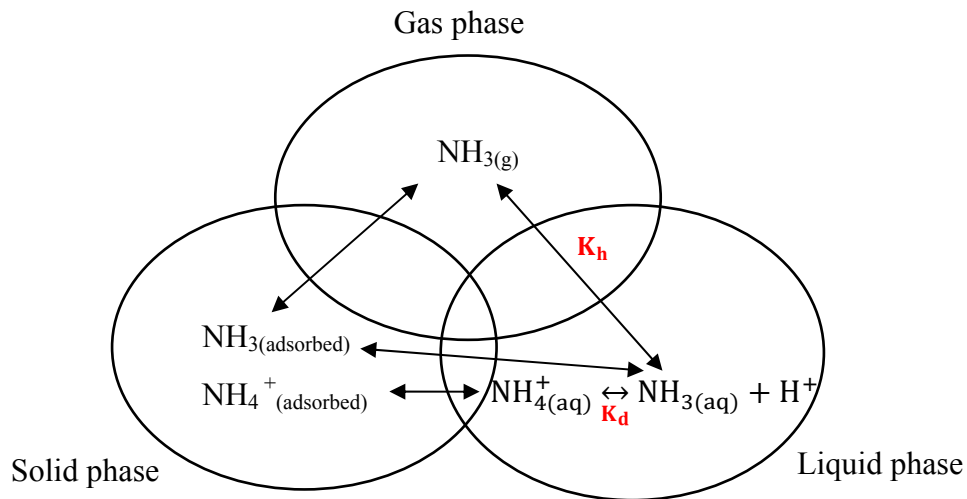


Figure 1-1 Illustration of the mechanisms governing ammonia and ammonium balance in broiler litter

Besides temperature, high TAN concentration in broiler litter could also influence the Henry's law constant, dissociation constant, and the generation and diffusion of ammonia. The values of the  $K_d$  and  $K_h$  of ammonia in text books are applicable in dilute solutions (Snoeyink and Jenkins, 1982); however, the TAN concentration in broiler litter is much higher than what could be considered a dilute solution. Therefore, determining adequate  $K_d$ ,  $K_h$  and ammonia/um sorption for broiler litter is important to accurately model ammonia generation in broiler litter.

To model ammonia/um fate accurately, it is important to have accurate knowledge of the properties of broiler litter, such as total N, total C, etc. During the drying process, mass loss includes not only moisture but also N and C losses; therefore, litter moisture content will be overestimated. Consequently, C and N concentrations, expressed on dry weight basis will be underestimated. The degree of underestimation will depend on the drying temperature. In most studies (Pote et al., 2009, Webb and Hawkes, 1985, Hamilton and Sims, 1995), litter was dried in 100°C or 105°C in convective oven, using the same drying method as soil. Drying at higher temperatures may result in excessive loss of C and N, while low temperature drying may result in incomplete moisture removal. Also, excessive loss of C may reduce the negative charges on organic C, which will affect some mechanisms, such as adsorption. Drying at low temperature (i.e. room temperature) may result in mineralization, nitrification and denitrification, which would affect concentrations of specific N species. Therefore, selecting an appropriate drying temperature and reducing the confounding effects of C and N losses may result in improved understanding of N transformation processes.

Although there have been many studies on monitoring ammonia emission from broiler houses, there are only a few studies on drying temperatures and modeling ammonia/um dynamics in broiler litter. Ammonium adsorption isotherms developed for soils have been used in broiler litter and ammonia adsorption in broiler litter was assumed to be zero. The dissociation constant and Henry's Law constant measured in aqueous solutions are not appropriate for use in broiler litter. Therefore, studies on drying temperature and mechanisms governing ammonia/um dynamics in broiler litter are required for modeling ammonia fate and transport in broiler litter.

### **Research Objectives**

The goal of this research is to understand mechanisms that govern ammonia and ammonium dynamics in broiler litter. Specific objectives are to:

- 1) determine drying temperature-time impact on moisture, N, and C losses in broiler litter;
- 2) model ammonium adsorption in broiler litter and cake as impacted by different pH values (pH 4, 6 and 7);
- 3) model ammonia absorption and adsorption at different moisture contents (0%, 15%, 25%, 35%, 45%, and 55%); and
- 4) quantify dissociation constant of ammonium and Henry's Law constant of ammonia in broiler litter.



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## **2 Drying Temperature and Time Impacts on Moisture, Carbon, and Nitrogen Losses from Broiler Litter**

### **Abstract**

Determination of accurate drying temperature – time combination for broiler litter moisture content is important for research. While drying at higher temperatures may result in excessive loss of carbon (C) and nitrogen (N), low temperature drying may result in incomplete moisture removal. Loss of C and N during drying can also confound moisture losses and reduce accuracy of calculation of the chemical composition of the litter. In this study, 50-g broiler litter samples were dried in flasks placed in water bath with forced air at 25°C for 48 h, 50°C for 24 h or 70°C for 16 h in triplicate. Carbon and ammonia-N losses from the litter samples and in the ambient air were determined. Broiler litter was also dried in petri dishes at room temperature for 48 h and in a convective oven at 70°C to constant weight; however, C and N losses were not determined in those treatments. Total losses of C and N were 0.7 to 3.1% and 6.9 to 13.8%, and losses increased with drying temperature. Drying broiler litter at 70 °C for 16 h resulted in complete moisture removal with a small loss of C and moderate loss of ammonia-N. Drying at lower temperatures resulted in incomplete moisture removal. Adjusted for C and N losses, moisture contents of the litter was reduced by nearly 3% resulting in actual dry basis chemical concentrations being increased by the same amount.

## Introduction

Broiler chickens are raised on a bedded floor (e.g., wood shavings) and the resulting litter that consists of feces, spilled feed and water, feather, and bedding material is usually disposed off through land application because of its fertilizer value. For some research objectives, it is important to quantify broiler litter moisture content accurately because litter chemical properties have to be expressed on dry basis moisture content. Conventionally, broiler litter moisture content may be expressed on dry basis (  $MC_{db}$ , eq. [2.1]) or wet basis ( $MC_{wb}$ , eq. [2.2]).

$$MC_{db} = \left( \frac{\text{initial mass} - \text{final mass}}{\text{final mass}} \right) \times 100(\%) \quad [2.1]$$

$$MC_{wb} = \left( \frac{\text{initial mass} - \text{final mass}}{\text{initial mass}} \right) \times 100(\%) \quad [2.2]$$

In eq. [2.1] and [2.2], the terms initial mass and final mass denote masses of litter sample before and after drying at some temperature-time combination. While moisture content of plant and waste samples (including broiler litter) is frequently expressed on wet basis, expressing on a dry basis allows for comparison with other studies.

Unlike the standard practice of drying mineral soils at 105 °C to constant weight for moisture content determination, there are no widely accepted drying temperature-time combinations for broiler litter moisture content determination. Broiler litter contains much higher concentrations of organic carbon (C) and nitrogen (N) species, including a large percentage of ammonia/um. During drying, some of C and ammonia can be lost and when losses of moisture, C, and N are not separated, moisture loss will be overestimated as is clear from eq. [2.1]. Confounding moisture loss with losses of C and N could be a much bigger

concern in broiler litter than soil since broiler litter contains much higher concentrations of C and N (particularly, the fraction that can be lost during drying) than soil.

Therefore, knowledge about drying temperature-time combination for broiler litter samples may not only save time and resources but also avoid the confounding effects of C and N losses on the chemical composition of the samples. Hence, the overall objective of this study was to determine the effects of different drying temperature-time combinations on moisture, C, and N losses. The specific objectives of this study were to:

- (a) determine moisture, C, and N losses in broiler litter dried at 25°C for 48 h, 50°C for 24 h, and 70°C for 16h;
- (b) compare moisture contents using the above treatments with the control treatment, i.e., drying temperature of 70°C to constant weight; and
- (c) determine the error in calculating moisture content of broiler litter due to losses of C and N confounded with moisture loss.

## Literature review

Due to differences in their chemical compositions, drying temperature-time combinations for mineral soil and broiler litter will likely differ. In this chapter, research on drying temperature-time combinations for soil and animal waste were reviewed.

The standard method for measurement of soil moisture content is to dry the sample at 105°C to constant weight (Carter and Gregorich, 2006). Some physical change may happen when drying at such a high temperature. Dissolved inorganic materials will become more concentrated and may ultimately precipitate (Bohn et al., 1985). Dissolved organic materials may coagulate, as they become more concentrated (Bohn et al., 1985). However, drying the largely organic broiler litter at 105°C may result in change in its properties to a much greater extent than would happen with the largely mineral matrix of soil. Mills and Jones (1996) reported that drying plant samples at high temperatures lead to thermal breakdown and volatile loss of some constituents.

Drying temperature will likely affect the concentrations of C and N in broiler litter. Broiler litter is high in total ammoniacal N (TAN=ammonia-N+ ammonium-N) and increased drying temperature will result in greater conversion of ammonium to ammonia and its subsequent volatilization. Hence, loss of volatile C and N along with moisture may confound moisture content determination of litter samples. Further, if oven-dry litter samples are required for further analyses, high-temperature drying may change the inherent structure and character of the litter sample. For example, Carter and Gregorich (2006) reported that solid organic C deformed and became hydrophobic during high-temperature drying.



In many studies ( e.g. Pote et al. 2009; Webb and Hawkes, 1985, Hamilton and Sims, 1995), livestock waste was dried at 100°C or 105°C similar to soil. Wolf et al. (1997) measured total solid content of liquid manure at three drying temperature-time combinations: 110°C - 6 h, 70°C – 16 h and 50°C – 24 h. In the Wolf et al. (1997) drying experiment, minimum drying time for each temperature was determined by drying the sample to constant weight. Residual moisture content after achieving constant weight at 50°C and 70°C was determined by comparison with the 110°C moisture content. Wolf et al. (1997) reported that drying at 110°C – 6 h or 70°C -16 h and 50°C - 24h removed moisture completely. However, Hoskins et al. (2003) reported that the moisture removal in liquid manure was not complete when drying at 70°C for 16 h. Obviously, the nature of waste or manure and perhaps, the type of oven (forced convection vs. natural convection) are factors that influence the effectiveness of drying temperature – time combination on complete moisture removal.

Carbon and N are important constituents of broiler litter accounting for 23% and 3%, respectively, of total solids (NCSU, 2011). However, there are no studies that evaluated the impact of drying temperature and time combination on C (as CO<sub>2</sub>) and N (as ammonia as well as amines). Quantification of volatile C and N losses could improve estimation of litter moisture content.

## **Materials and Method**

### **Sample preparation**

Broiler litter and cake used in this study were obtained from a broiler farm in Duplin Co., North Carolina. The samples were placed in black plastic bags and transported on ice to the lab. The litter and cake were passed through a 2-mm sieve to remove large clumps and then thoroughly mixed, separately. Thereafter, the cake and litter were preserved at low temperature (-18°C) in a freezer to suspend microbial and enzymatic activities until start of the experiments.

The drying experiments were conducted at the Air Quality R&D Facility. Chemical analyses were performed at Environmental Analysis Lab (EAL) in the Biological and Agricultural Engineering Dept.

### **Determination of initial litter properties**

The sieved broiler litter and cake were analyzed for pH, TAN, nitrate ( $\text{NO}_3^-$ -N), total Kjeldahl N (TKN), total carbon (TC), specific surface area (SSA) using methods described in Table 2-1. Except for SSA which was analyzed at the Biomass research center, all analyses were performed at the EAL. Cation exchange capacity analysis was not performed because broiler litter has very high concentrations of organic compounds with decomposed materials which have large functional groups, which would result in large concentrations of soluble salts in (S. M. Hassan, March 31, 2011, personal communication, Dept. of Soil Science,

University of Georgia). Thus, the CEC measurements would have been higher than upper limit of measurement of the machine (W. P. Miller, March 31, 2011, personal communication, Dept. of Soil Science, University of Georgia).

Table 2-1 Analytical methods used for analysis of broiler litter and cake constituents

Parameter	Method	Method detection limit (MDL)	Reference
TKN (Total Kjeldahl N)	Persulfate digestion and ammonia salicylate method	0.037 mg/L	EPA Manual 351.2 (1979) with slight modifications including dialysis or Standard Methods 4500-N <sub>org</sub> B (1998)
TAN (Total Ammoniacal Nitrogen)	Ammonia-salicylate method	0.016 for 0-2 mg/L 0.124 for 0-100 mg/L	EPA Method 351.2 (1979) or Standard Methods 4500-NH <sub>3</sub> G (1998), with slight modifications including dialysis
NO <sub>3</sub> <sup>-</sup> / NO <sub>2</sub> <sup>-</sup> -N	Cadmium reduction method	0.011mg/L	EPA Method 351.2 (1979), Technicon Industrial Method No. 100-70W (1973), or Standard Methods 4500- NO <sub>3</sub> <sup>-</sup> E (1998), with slight modifications including dialysis
pH	Electrometric Method	Not available	EPA Method 150.1 (1979) or Standard Methods 4500-H <sup>+</sup> B pH value (1998)
Total Carbon	Combustion and oxidation method	Not available	EPA Method 415.1 (1974)

Surface area	Brunauer, Emmett and Teller (BET) surface area analysis	0.01m <sup>2</sup> /g	Micrometrics Gemini VII 2390
Electrical conductivity	YSI Model 33 S-C-T Meter	10 μmhos/cm	EPA Method 9050

### Moisture, C, and N loss determination

The five treatments evaluated in this study are listed below.

1. Treatment 1: Drying at 70°C for 16 h
2. Treatment 2: Drying at 50°C for 24 h
3. Treatment 3: Drying at 25°C for 48 h
4. Treatment 4: Drying at room temperature (~22°C) for 48 h
5. Treatment 5: Drying at 70°C to constant weight

Each treatment was replicated three times and before starting the study, the litter was removed from freezer and allowed to equilibrate to room temperature for 30 min. In Treatment 1 through 3, in addition to moisture loss, CO<sub>2</sub> and ammonia losses were also determined during the drying process and thus required a different experimental set-up vs. Treatment 4 and 5.

In Treatment 1 though 3, 50 g of sieved field-moist broiler litter sample was placed in a 500 mL glass flask in a 0.5-cm layer; this flask was placed in a water bath to control temperature (Figure 2-1). Two CO<sub>2</sub> scrubbers (polycarbonate flasks) each containing 250 mL of 2M sodium hydroxide (NaOH) solution were placed downstream of the flask containing the litter to absorb CO<sub>2</sub> released by the litter during drying (Carter and Gregorich, 2006). The

two CO<sub>2</sub> scrubbers were used sequentially assuming that any CO<sub>2</sub> not trapped in the primary scrubber would be trapped in the secondary scrubber. There was enough NaOH available to absorb 3,000 mg of CO<sub>2</sub>-C which would equal approximately 23% of C in the litter. Two boric acid (2% w/v) scrubbers (polycarbonate flask), each containing 250 mL of acid solution were placed following the CO<sub>2</sub> scrubbers to trap ammonia (and amines) released by the litter during drying (Fig. 2-1). Shah et al. (2006) reported that acid scrubbers were very efficient with the primary scrubber trapping > 97% of the ammonia. While C and N losses during drying were also estimated based on C and N concentration changes during drying, due to the high variability in C and N concentrations in litter, the scrubber provided more reliable information on CO<sub>2</sub> and ammonia losses.

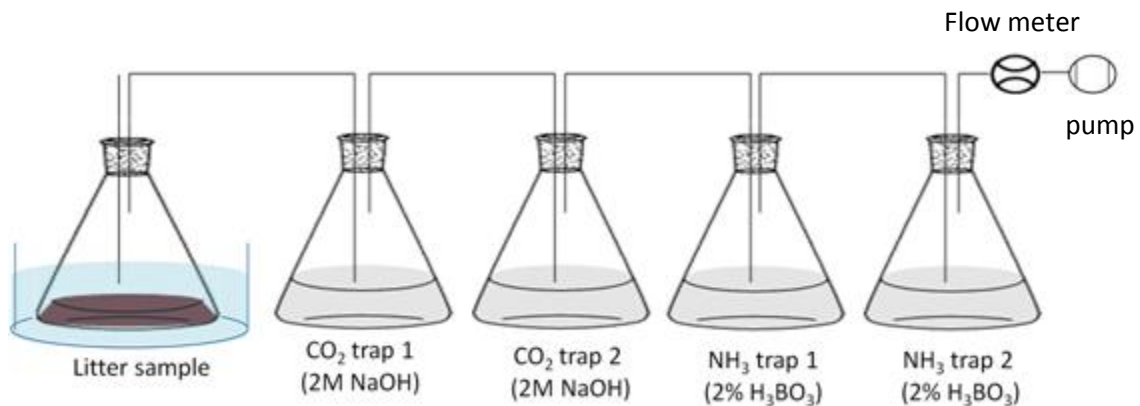


Figure 2-1 Experimental set-up of drying experiment for Treatments 1 through 3

Room air (118 mL/min) was drawn first into the flask containing litter and then into the CO<sub>2</sub> and NH<sub>3</sub> scrubbers with a vacuum pump which was run on a 90% duty cycle (270 s ON and 30 s OFF) using a timer. To minimize drawing air from over the water bath, the air inlet line was made longer and located away from the water bath. A flow meter (Make:

Gilmont Instrument; Model: GF-8321-1401; Accuracy:  $\pm 5\%$ ) equipped with a valve was connected downstream of the CO<sub>2</sub> and NH<sub>3</sub> scrubbers to monitor and control the airflow rate at 118 mL/min (Figure 2-1). To ensure that no condensate dripped back into the flask during drying, a light bulb covered with an aluminum foil was used to heat the outlet line from the flask containing litter.

Ambient air (118 mL/min) was also sampled for CO<sub>2</sub> and NH<sub>3</sub> using a single scrubber for each gas. A blank sample was used as baseline to adjust the NH<sub>3</sub> and CO<sub>2</sub> concentrations in the ambient air to account for contamination during solution preparation.

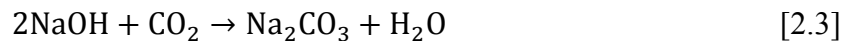
At the end of the drying run, final broiler litter mass were measured to determine the combined mass losses of moisture, CO<sub>2</sub>, and ammonia. Masses of liquid in the scrubbers were also determined gravimetrically. The mass of CO<sub>2</sub>-C absorbed in the scrubbers (or blank) determined as described in the following section to obtain a direct measure of CO<sub>2</sub> loss. Ammonia (plus amines), as ammonium-N concentration in the scrubber or blank solution was determined using ion chromatography (MDL=0.01 mg-N/L). Based on the mass (or volume, assuming specific gravity was unity) of the solution, the mass of ammonium-N in the scrubber or blank was determined. The dried litter samples were also analyzed for TC, TKN, and TAN as described in Table 2-1; comparison of these constituents before and after drying gave another measure of C and N losses due to drying.

In Treatment 4 (room temperature- 48 h), a 0.5cm layer of litter was dried in ambient air for 48 h in a 15-cm diameter petri dish to compare difference in mass loss vs. Treatment 1 through 3. In Treatment 5, 20 g of litter spread to a depth of 0.5 cm was dried at 70 °C for 16 h in a convection oven. After weighing, the litter samples were returned to the oven and dried

for another 1 h; this process of repeated until the mass changed by <0.1 mg in mass. However, the additional drying resulted in virtually no change in mass. The reduced mass after drying to constant weight in Treatment 5 represented the total moisture (plus some CO<sub>2</sub>-C and ammonia-N) in the litter sample.

### **Determination of carbon dioxide (CO<sub>2</sub>) released during drying**

The method described by Carter and Gregorich, (2006) was used to determine the mass of CO<sub>2</sub> released during drying of the litter. When CO<sub>2</sub> reacts with NaOH, the following chemical reaction results.



In equation [2.3], because of the high molarity of the NaOH solution, it was assumed that all CO<sub>2</sub> was consumed. After each drying experiment, the volumes of the two CO<sub>2</sub> scrubbers were measured. Twenty milliliters of the solution from each scrubber or blank was drawn separately and diluted to 100 mL in a volumetric flask. Forty milliliters of this diluted sample was drawn, and mixed with 8 mL 0.05M barium chloride (BaCl<sub>2</sub>). Barium chloride reacts with Na<sub>2</sub>CO<sub>3</sub> to form insoluble barium carbonate (BaCO<sub>3</sub>), which was filtered out. Three drop of phenolphthalein indicator was added to the filtrate and titrated with 0.1M HCl solution until the solution returned clear when the phenolphthalein end point (pH 8.3 to 10) (Carter and Gregorich, 2006) was reached as the OH<sup>-</sup> in the solution was completely neurealized by HCl. Mass of CO<sub>2</sub> was determined as shown in eq. [2.4] and [2.5]

$$M_{\text{ambient air}} = \frac{44^{\text{g}}/\text{mol} \times (V_b - V_a) \text{ml} \times 0.001^{\text{l}}/\text{ml} \times 0.1^{\text{mol}}/\text{l} \times 2.5 \times 5 \times 12.5}{2} \quad [2.4]$$

$$M_{\text{sample}} = \frac{44^{\text{g/mol}} \times (V_a - V_s) \text{ml} \times 0.001^{\text{l/ml}} \times 0.1^{\text{mol/l}} \times 2.5 \times 5 \times 12.5}{2} \quad [2.5]$$

where

$M_{\text{ambient air}}$  = mass of  $\text{CO}_2$  in the ambient air scrubber, g;

$M_{\text{sample}}$  = mass of  $\text{CO}_2$  in scrubber, g;

$V_b$  = volume of 0.1M HCl consumed in blank sample, mL;

$V_a$  = volume of 0.1M HCl consumed in ambient air sample, mL; and

$V_s$  = volume of 0.1M HCl consumed in primary or secondary scrubber, mL. The numerical terms in the equation [2.4] and [2.5] are molecular weight of  $\text{CO}_2$  (44 g/mole), extraction ratio of 2.5 to represent the 40 mL aliquot extracted from 100 mL; dilution ratio of 5 to present dilution of 20 mL → to 100 mL; and an extraction ratio of 12.5 to denote the full volume 250 mL of the scrubber solution from which a → 20 mL aliquot was taken. Equation [2.3] shows that for each mole of  $\text{CO}_2$  trapped in the NaOH, 2M of NaOH will be converted to  $\text{Na}_2\text{CO}_3$ . Therefore, the total  $\text{CO}_2$  produced is twice the depletion of NaOH in the trap and thus, the denominator has 2. Carbon lost as  $\text{CO}_2$ -C was assumed to have come from the solid litter, while  $\text{O}_2$  came from the air. Carbon dioxide released from the litter could have also been dissolved in the litter liquid film that was liberated during the drying process. Carbon lost from solid matrix and dissolved  $\text{CO}_2$  were both included in total C measurement.

### **Determination of water loss and moisture content**

Moisture lost was calculated as shown in eq. [2.6].

$$M_{\text{H}_2\text{O}} = \Delta M - N_{\text{NH}_3} - M_{\text{CO}_2\text{-C}} \quad [2.6]$$



In eq. [2.6],

$\Delta M$  = difference between initial and final masses of litter, g;

$M_{H_2O}$  = moisture lost, g;

$M_{NH_3}$  = mass of  $NH_3$  lost, g; and

$M_{CO_2-C}$  = mass of  $CO_2-C$  lost, g.

### **Statistical analyses**

The mass losses of  $CO_2-C$ ,  $NH_3-N$ , and moisture were calculated separately in each treatment (Treatment 1 through 3). Treatment means (Treatment 1 through 3) were compared using analysis of variance (ANOVA) using SAS (SAS, 2009); if the null hypothesis was rejected (i.e., at least one treatment was different), Tukey's minimum significant difference (MSD) test was used for means comparison using SAS program (SAS, 2009). Moisture losses from Treatments 3 and 4 were compared using t-test. Similarly, moisture losses from Treatment 1 and 5 were also compared using t-test. Treatment 1 and 5 were also compared using t-test. An alpha value of 0.05 was used throughout this study.

## Results and Discussion

In results and discussion, the five treatments are defined below.

Treatment 1: Drying at 70°C for 16 h (70°C-16 h)

Treatment 2: Drying at 50°C for 24 h (50°C-24 h)

Treatment 3: Drying at 25°C for 48 h (25°C-48 h)

Treatment 4: Drying at room temperature (~22°C) for 48 h (room temperature-48 h)

Treatment 5: Drying at 70°C to constant weight (70°C to constant weight)

The properties of broiler litter are shown in Table 2-2. The analytical methods were described in Table 2-1.

Table 2-2. Mean ( $\pm$ SD) (n=3) litter properties (wet basis)

	TKN <sup>1</sup>	TAN <sup>2</sup>	NO <sub>3</sub> /NO <sub>2</sub> N <sup>3</sup>	TC <sup>4</sup>
	mg/kg	mg/kg	mg/kg	mg/kg
Litter	24,797	3,579 $\pm$ 49	13.99	260,900

<sup>1</sup>TKN: Total Kjeldahl N

<sup>2</sup>TAN: Total ammoniacal N

<sup>3</sup>NO<sub>3</sub>/NO<sub>2</sub>N: nitrate N

<sup>4</sup>TC: Total C

Figure 2-2 compares the moisture losses (based solely on mass change during drying, without accounting for C and N losses) in Treatment 1 through Treatment 5. There were significant treatments effects (ANOVA) (SAS, 2009) on moisture content loss (Figure 2-2).

Since Treatment 1 and 5 were not significantly different (Figure 2-2), Treatment 1 (70 °C -16 h), with a 50-g moist sample resulted in complete moisture removal even though Treatment 1 (70°C -16 h) used a different drying system than a conventional convective oven [Treatment 5 (70°C to constant weight), 20-g moist sample]. Mass losses in the remaining treatments were: Treatment 2 (50°C-24 h)>Treatment 4 (room temperature-48 h)>Treatment 3 (25°C-48 h); however, none of these treatments provided complete moisture removal and should not be used to determine moisture content of broiler litter.

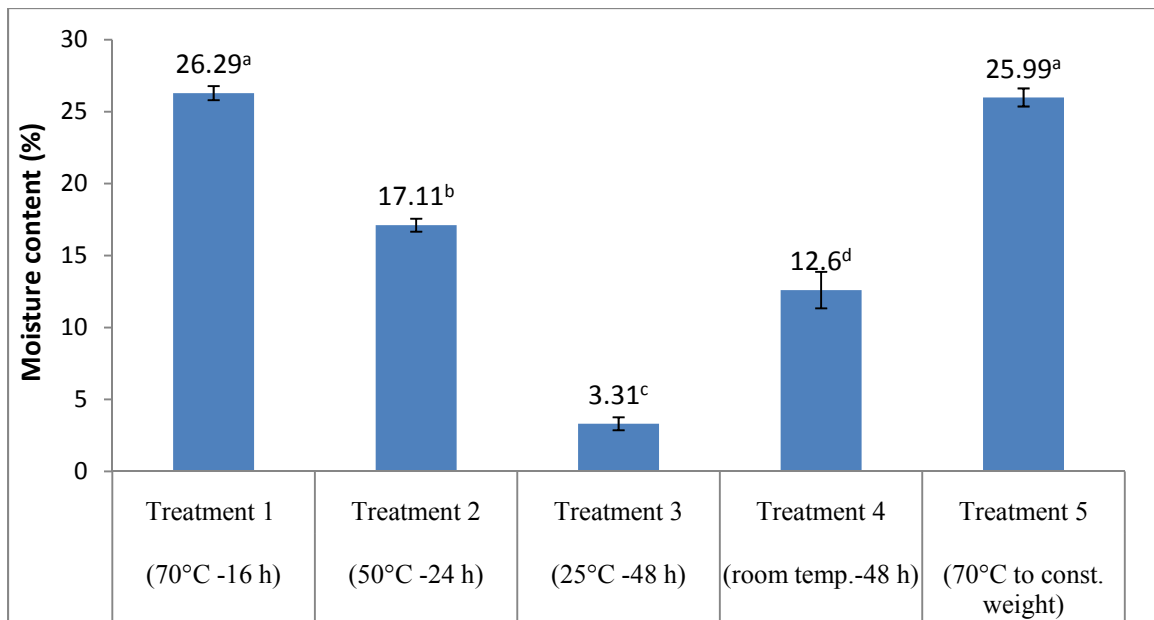


Figure 2-2 Comparison of mass losses (as percent of final mass) from Treatment 1 through Treatment 5. Each value is a mean of three replicates and the error bars show SD. Treatment means followed by the sample alphabet are not significantly different at  $\alpha=0.05$  (Tukey's MSD = 2.0%)

Figure 2-2 showed that drying broiler litter at 70°C for 16 h removed moisture completely because Treatment 1 (70°C-16 h) and Treatment 5 (70°C to constant weight) resulted in mass losses that are not significantly different. Hoskins et al. (2003) reported that the moisture removal in liquid manure was not complete when drying at 70°C for 16 h but this temperature – time treatment resulted in complete moisture removal in this study. This may be due to the different characteristics of liquid manure (high moisture content) and broiler litter (low moisture content).

Total C losses (as percent of initial TC) in Treatments 1 through 3 (70°C-16 h, 50°C - 24 h, and 25°C -48 h) were significantly different from one another ( $p=0.003$ ), with C losses increasing with drying temperature (Fig. 2-3). Total C losses were only 0.7 to 3.1% of initial total C concentration, lower than N (Fig. 2-3). There was a significant treatment effect on ammonia-N during drying ( $p=0.05$ ) (Fig. 2-3). Ammonia-N losses were significantly higher with Treatment 3 (25°C- 48 h) vs. Treatment 1 (70°C- 16 h) though Treatment 1 (70°C- 16 h), Treatment 2 (50°C- 24 h), and Treatment 3 (25°C- 48 h) were not significantly different from one-another (Fig. 2-3).

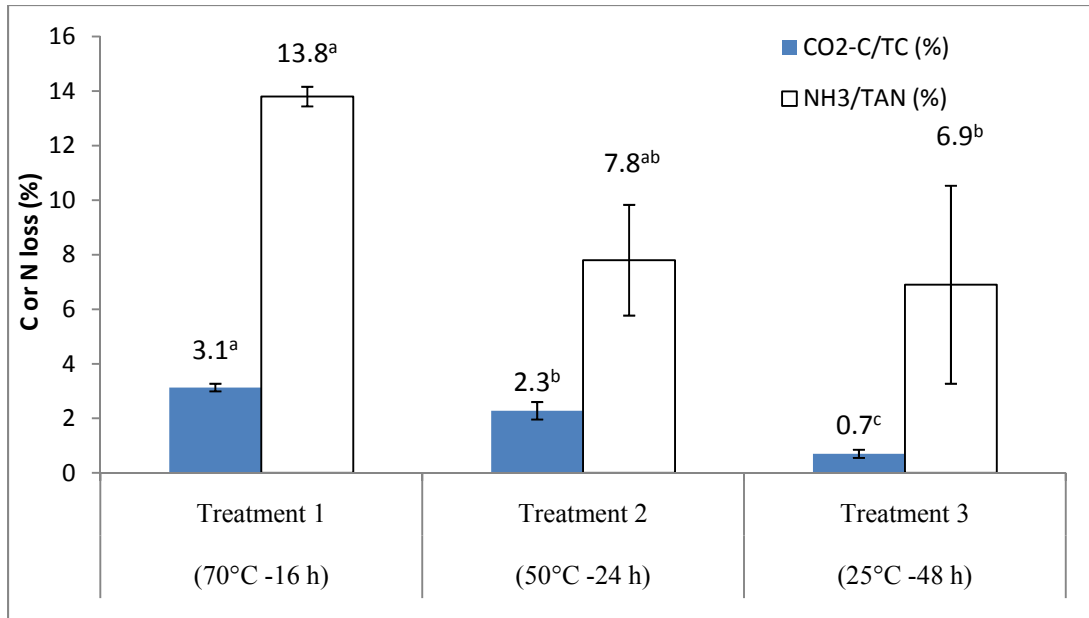


Figure 2-3 Comparison of mass C and ammonia-N losses as percent of initial TC and TAN concentrations, respectively, from Treatment 1 through Treatment 3 (70°C-16 h, 50°C-24 h, 25°C-48 h) . Each value is a mean of three replicates and the error bars show SD. Treatment means for the same constituent (C or N) followed by the sample alphabet are not significantly different at  $\alpha=0.05$  (Tukey's MSD = 0.6% for C and 6.0% for ammonia-N)

Carbon losses increased 228% when drying at 50°C vs. 25°C because the organic C in broiler litter biodegraded more rapidly as enzyme and microbial activities increase with temperature. Also, more carbon dioxide dissolved in the liquid film was liberated at 50°C vs. 25°C because more moisture was evaporated. In Treatment 1 (70°C-16 h), as the temperature was increased to 70°C, C losses increased 35% over Treatment 2 (50°C-24 h) because complete moisture removal was incomplete. However, difference in C loss between

Treatment 1 (70°C-16 h) vs. Treatment 2 (50°C-24 h) was much lower than between Treatment 2 (50°C-24 h) vs. Treatment 3 (25°C-48 h) because greater microbial inactivation at 70°C vs. 50°C probably resulted in reduced CO<sub>2</sub> release due to respiration.

In Treatment 1 (70°C-16 h), the percentage of adjusted moisture content is 22.5% (Figure 2-4). Therefore, from a 50-g moist sample, 11.25 mL of water was evaporated and 1.53 g of CO<sub>2</sub>-C was liberated, based on the experimental data.

The solubility of carbon dioxide in water at 25°C is 1.8 g/L (Carroll et al., 1991). Even assuming that CO<sub>2</sub> solubility would be the same in the broiler litter liquid fraction with its high ionic concentration, there was probably ~0.02 g of dissolved CO<sub>2</sub> in the litter prior to drying. Therefore, no more than 1.5% CO<sub>2</sub> released from the litter was likely CO<sub>2</sub> gas released from the liquid fraction when the moisture evaporated, and most of the C came from the solid litter fraction.

Nitrogen losses with 25 °C vs. 50 °C were not significantly different (Fig. 2-3). However, as the temperature was increased to 70°C, and all of the litter moisture was evaporated, a large portion of dissolved ammonium converted to ammonia and was liberated as was all the dissolved ammonia in the litter moisture. Therefore, at 70°C, N losses doubled compared to 25°C and 50°C. Lower variability in the C and N losses in Treatment 1 (70°C - 16 h) vs. Treatment 2 (50°C - 24 h) and 3 (25°C - 48 h) (Fig. 2-3) provide more confidence that subtracting the C and N losses from total mass loss would provide reliable moisture content values.

From Figure 2-4, it is clear that Treatment 1 (70°C-16 h, not adjusted for C and N losses) and Treatment 5 (70°C to constant weight) are not significantly different in terms of

moisture content, but Treatment 1 (70°C-16 h, not adjusted for C and N losses) and Treatment 1 (70°C-16 h, adjusted for C and N losses) were significantly different ( $p < 0.01$ ). When moisture content was adjusted for C and N losses (using eq. [2.6] as numerator in eq. [2.1]), the adjusted moisture content of Treatment 1 was reduced significantly by nearly 3.5% to 3.8% (Fig. 2-4). Hence, it seems clear that accounting for losses of C and N could improve moisture content estimation in broiler litter.

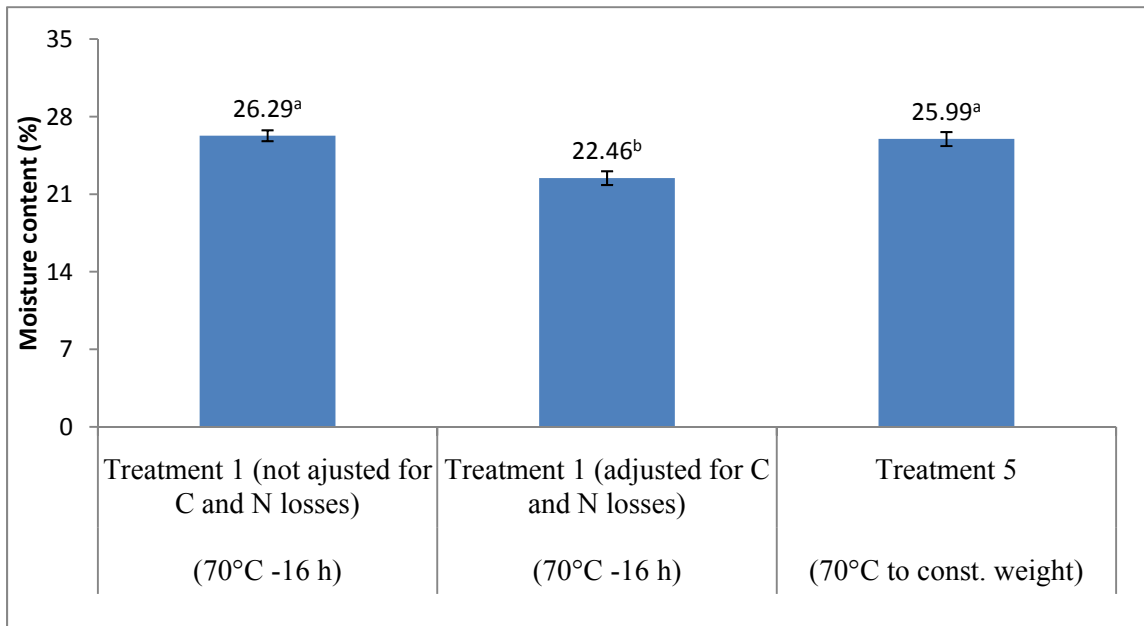


Figure 2-4 Comparison of moisture contents (as percent of final mass) in Treatment 1 and Treatment 5. Each value is a mean of three replicates and the error bars show SD.

Treatment means followed by the sample alphabet are not significantly different at  $\alpha = 0.05$  (Tukey's MSD = 1.5%)

Table 2-3 shows the N species and C concentrations calculated on dry basis, based on both gross moisture content (26.3%) and net moisture content (22.5%). It is clear from Table 2-3 that using gross MC resulted in overestimation of the N species and C concentrations by

3% (vs. using the net MC). While an overestimation of 3% may seem small, using the net MC approach could be meaningful when an accurate mass balance of N and C species is required while comparing two treatments with different moisture contents. Such an approach could also be useful when comparing treatments that could affect moisture content and/or pH (hence, ammonia to ammonium ratio) of the waste.

Table 2-3. Mean ( $\pm$ SD) litter properties (wet basis, gross moisture content, net moisture content)

	TKN <sup>1</sup>	TAN <sup>2</sup>	NO <sub>3</sub> /NO <sub>2</sub> N <sup>3</sup>	TC <sup>4</sup>
	mg/kg	mg/kg	mg/kg	mg/kg
Wet basis	24,797	3,579 $\pm$ 49	13.99	260,900
Gross moisture content (26.3%)	31,319	4,520 $\pm$ 62	17.67	329,516
Net moisture content (22.5%)	30,376	4,384 $\pm$ 60	17.14	319,603

<sup>1</sup>TKN: Total Kjeldahl N

<sup>2</sup>TAN: Total ammoniacal N

<sup>3</sup>NO<sub>3</sub>/NO<sub>2</sub>N: nitrate N

<sup>4</sup>TC: Total C

The litter samples after drying using Treatment 1 (70°C-16 h) had TAN concentration (dry basis, adjusted for C and N losses) of 3,779 $\pm$ 60 mg/kg; subtracting the final concentration (Table 2-3, 4,384 $\pm$ 60 mg/kg) from the initial concentration yielded the TAN concentration (505 $\pm$ 60 mg/kg) lost during drying. Based on the TAN trapped by the



scrubbers, the Treatment 1 (70°C-16 h) samples lost  $520 \pm 7$  mg/kg of TAN during drying. Since the TAN lost calculated using the two methods were within 3% of one-another, it seemed that the scrubber, with lower SD, gave reliable estimate of TAN loss during drying.

Drying broiler litter spread at a depth of 0.5 cm at 70°C for 16 h in a forced convection oven resulted in complete moisture removal with a small loss of C and moderate loss of N. When accurate concentrations of C and N are required to compare treatments with different moisture contents and volatile N fractions, adjusting for C and N losses could increase the accuracy of measurements.

Most C lost in broiler litter was from solid fraction. Most N lost was in the form of ammonia. Ammonia adsorbed on the broiler litter solid matrix the form of ammonia that was first followed by ammonia in the liquid phase that became volatilized, as temperature increased. According to the chemical balance, some ammonium would form ammonia in liquid phase and then become ammonia, which was also lost.

## **Conclusions**

1. Drying broiler litter at 70 °C for 16 h in a forced convection oven when spread at a depth of 0.5 cm resulted in complete moisture removal and is thus recommended for drying broiler litter. Drying at lower temperature (25 or 50 C) for longer times resulted in incomplete moisture removal.
2. Drying at 70 °C for 16 h resulted in total losses of C and N of 3.1 and 13.8%, respectively. Most C lost was from solid fraction and most N lost was ammonia in broiler litter.
3. Compared with dry basis MC of 26.3% based solely on mass differences during drying at 70 °C for 16 h, adjusting for C and N losses resulted in a dry basis MC of 22.5%. Hence, when treatments with different moisture contents and volatile N fractions require comparison, accounting for C and N losses during drying may improve the accuracy of measurement.

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### **3 Dissociation Constant of Ammonium and Henry's Law Constant of Ammonia in Broiler Litter**

#### **Abstract**

Ammonia ( $\text{NH}_3$ ) emission from poultry houses is a major air quality concern. In poultry litter, uric acid and urea hydrolyze to ammonium ( $\text{NH}_4^+$ ) and a fraction of  $\text{NH}_4^+$  converts to  $\text{NH}_3$ ; the  $\text{NH}_4^+$  -  $\text{NH}_3$  equilibrium in the litter depends on pH, temperature, moisture content, ionic concentration, carbon/nitrogen (C/N) ratio, oxygen level, substrate concentration, and some cations. The dissociation constant ( $K_d$ ) that controls  $\text{NH}_4^+$  -  $\text{NH}_3$  equilibrium developed for aqueous solutions may not apply to broiler litter which has much higher ionic concentration. Similarly, Henry's law constant ( $K_h$ ) which describes the equilibrium of  $\text{NH}_3$  between the liquid and gas phases in aqueous solution with free liquid surface may not apply to broiler litter. Therefore,  $K_d$  and  $K_h$  developed for aqueous solutions may not be appropriate for modeling the fate of  $\text{NH}_4^+$  and  $\text{NH}_3$  in litter system. In this study,  $K_d$  and  $K_h$  in broiler litter were measured in replicated lab experiments. Dissociation constant in litter slurry was  $1.02 \times 10^{-10}$ , 20% of the dissociation constant in aqueous solution, which may be due to the ammonia/um adsorption on the solid matrix and reduced activity coefficient. Henry's Law constant (0.0158 atm/M) in litter slurry was similar to  $K_h$  (0.0164 atm/M) in aqueous solution. Determination of dissociation constant and Henry's constant for broiler litter will allow more accurate simulation of litter nitrogen dynamics.

## Introduction

Ammonia (NH<sub>3</sub>) emission from poultry houses is a major air quality concern. In poultry litter, uric acid and urea in the feces or spilled feed hydrolyze to ammonium (NH<sub>4</sub><sup>+</sup>) and a fraction of NH<sub>4</sub><sup>+</sup> converts to NH<sub>3</sub> (eq. [3.1]); the NH<sub>4</sub><sup>+</sup>- NH<sub>3</sub> equilibrium in aqueous solutions is governed by the dissociation constant (K<sub>d</sub>) (eq. [3.2]) (Snoeyink and Jenkins, 1982) which depends on pH, temperature, and ionic concentrations. At 25°C, the dissociation constant (K<sub>d</sub>) of ammonium in dilute solution is 5.01×10<sup>-10</sup> (Snoeyink and Jenkins, 1982). However, it is unclear if K<sub>d</sub>, developed for aqueous solutions would apply to broiler litter that has high solids content and ionic concentrations. In eq. [3.2], units of all the species are molar concentrations.



$$K_d = \frac{[\text{NH}_3(\text{aq})][\text{H}^+]}{[\text{NH}_4^+(\text{aq})]} \quad [3.2]$$

Ammonia in solution is not only in equilibrium with NH<sub>4</sub><sup>+</sup> but also in equilibrium with NH<sub>3</sub> at the liquid-air interface (eq. [3.3]). The concentration of ammonia in the gas and liquid phases is related by the Henry's law constant (K<sub>h</sub>, atm/M) (eq. [3.4]). In dilute solutions, the concentration of ammonia in solution is linearly related to its concentration in the air above the liquid surface (eq. [3.4]) (Snoeyink and Jenkins, 1982).



$$K_h = \frac{[\text{NH}_3(\text{g})]}{[\text{NH}_3(\text{aq})]} \quad [3.4]$$

Henry's law constant can also be presented with  $[\text{NH}_3]_{(\text{aq})}$  in the numerator and  $[\text{NH}_3]_{(\text{g})}$  in denominator (atm/M). Hence, Henry's law constant can be expressed in various dimensions (Ni, 1999), for example, M/atm,  $\frac{\text{mol}/\text{m}^3}{\text{mol}/\text{m}^3}$  (dimensionless), and  $\frac{\text{atm}\cdot\text{m}^3}{\text{mol}}$ . The  $K_h$  of ammonia in dilute solution is 0.016 atm/M at a temperature of 25 °C (Betterton, 1992).

It is unclear if  $K_d$  (eq. [3.2]) developed for dilute aqueous solutions or  $K_h$  (eq. [3.4]) which requires a free liquid surface will apply to broiler litter. This objective of this research is to quantify  $K_d$  and  $K_h$  in broiler litter in replicated lab experiments.

## Literature review

Factors that affect ammonium-ammonia equilibrium are discussed here. Selected studies on determination of  $K_d$  and  $K_h$  with emphasis on livestock waste are also presented.

### Factors affecting ammonia and ammonium equilibrium

There are many factors that affect  $\text{NH}_3$  and  $\text{NH}_4^+$  balance: pH, temperature, moisture content, ionic concentration, carbon/nitrogen (C/N) ratio, oxygen level, substrate concentration, and presence and concentrations of some cations. The most significant factors are pH, temperature, moisture content, and ionic concentration (e.g., TAN concentration).

(1) pH: As is clear from eq. [3.2], increase in pH results in conversion of  $\text{NH}_4^+$  to  $\text{NH}_3$  in the solution ( $\text{NH}_{3(\text{aq})}$ ). Since  $\text{NH}_{3(\text{aq})}$  is in equilibrium with  $\text{NH}_{3(\text{g})}$ , following Henry's law (eq. [3.4]), increase in pH will increase  $\text{NH}_3$  volatilization. Therefore, ammonia volatilization is higher in alkaline soils than in acidic soils (Singandhupe and Rajput, 1989). However, pH affects N transformation and dynamics in other ways that can indirectly impact ammonia-ammonium equilibrium and ammonia volatilization. Decreasing pH to acidic levels may reduce ammonia generation due to the inhibition of bacteria and enzyme activities. Biologically, when litter pH <6, ammonification stopped due to the inhibition of bacteria and enzyme activities (Weaver and Meijerhof, 1991). The optimum pH for nitrification was 7-8 and it was observed that nitrification rate was inhibited under acidic conditions because nitrifying bacteria were inhibited (Tarre and Green, 2004). Nitrification is comprised of two oxidation steps: conversion of ammonium to nitrite and then, nitrite to nitrate. Nitrate formation will reduce the amount of ammonium in the system and more ammonia will be



converted to ammonium. Under acidic condition ( $\text{pH} < 6.5$ ), nitrification process ceases and over 99% of the TAN is in the ammonium form, which may result in more ammonium adsorption on solid matrix (Tarre and Green, 2004). Therefore, as is the case in dilute solutions, ammonia volatilization in litter systems is reduced in an acid environment.

(2) Ionic concentration: Ionic strength of the solution will also affect the  $\text{NH}_4^+ - \text{NH}_3$  equilibrium (Snoeyink and Jenkins, 1982). Equation [3.2] is only applicable for dilute solution, in which ions behave independently and it is assumed that the activity coefficients are unity (Snoeyink and Jenkins, 1982). However, as the concentrations of ions increase, electrostatic interactions between the ions also increase and the activity of ions becomes less than their measured concentration. Therefore, in eq. [3.5], the activity coefficient ( $\gamma$ ) is less than 1 and the new dissociation constant ( $K'_d$ ) is corrected as eq. [3.6] (Snoeyink and Jenkins, 1982) and new Henry's law constant is corrected as eq. [3.7] (Snoeyink and Jenkins, 1982). While  $K_d$  and  $K_h$  apply to dilute solution,  $K'_d$  and  $K'_h$  apply to solutions with high ionic concentration.

$$\{i\} = \gamma_i [i] \quad [3.5]$$

$$K'_d = \frac{\gamma_{\text{NH}_3} [\text{NH}_3] \gamma_{\text{H}^+} [\text{H}^+]}{\gamma_{\text{NH}_4^+} [\text{NH}_4^+]} \quad [3.6]$$

$$K'_h = \frac{[\text{NH}_3]_{(g)}}{\gamma_{\text{NH}_3} [\text{NH}_3]_{(aq)}} \quad [3.7]$$

The activity coefficient (eq. [3.5]) can be calculated by the extended Debye-Huckel approximation equation, which requires the ionic strength ( $\mu$ ) of the solution. The ionic strength of the solution can be calculated using total dissolved solids (TDS) concentration or electrical conductivity (Snoeyink and Jenkins, 1982). The activity coefficient decreases as

the ionic strength of a solution increases. Therefore,  $K_d$  of ammonium and  $K_h$  of ammonia may change with TDS concentration.

(3) Temperature: Temperature increases dissociation constant, Henry's Law constant, and microbial production of ammonia/um (up to a certain optimum temperature). As is clear from the well-known Arrhenius equation (eq. [3.8]), as temperature increases, more molecules are on the higher energy level and obtain activation energy; therefore, chemical reaction rate also increases (Snoeyink and Jenkins, 1982) and chemical reaction moves toward higher entropy. When temperature increases, eq. [3.1] is driven more rapidly from left to right, because the right side has more independently moving molecules, which has higher entropy level. As more  $\text{NH}_{3(\text{aq})}$  forms, more  $\text{NH}_{3(\text{g})}$  (eq. [3.3]) is released due to the high entropy of gas phase. Hence, when temperature increases,  $K_d$  and  $K_h$  increase, resulting in greater  $\text{NH}_3$  emission from broiler litter.

$$k = Ae^{-E_a/RT} \quad [3.8]$$

where

$k$ =rate of chemical reaction;

$T$ =temperature, K;

$A$ =pre-exponential factor;

$E_a$ =activation energy; and

$R$ =ideal gas law constant.

Biologically, the optimum temperatures for nitrifying bacteria and mineralizing bacteria are 35°C and 45°C, respectively, in soil (Myers, 1975). In concentrated chicken manure (not litter, which has a large fraction of bedding material, e.g., wood shavings),

Hashimoto and Ludington (1971) reported that

$K'_d = \frac{1}{6} \times 10^{-(0.0897 + \frac{2729}{T})}$ , where T is temperature (K). In diluted swine manure (1% solid

content), Zhang (1992) reported that  $K'_h = 1.1561e^{\frac{-4151}{T}}$ ,  $\frac{\text{atm}}{\text{mg/L}}$ , where T is temperature (K).

In both equations, activity coefficients were considered implicitly.

(4) Moisture content: Moisture is essential for microbial activity. Reduced moisture content may decrease biological activity, though higher moisture content can decrease porosity, and hence, oxygen supply slowing down enzymatic and microbial activities. Weaver and Meijerhof (1991) reported that 45% to 75% was the optimal moisture content range for microbial and enzyme activities, which increased ammonia levels in the gas phase. Carr et al. (1990) reported that at very high moisture level, ammonia emissions decreased. Carr et al. (1990) also reported that maintaining litter moisture content below 30% (dry basis) helped control ammonia emission.

(5) TAN concentration: Ammonium concentration in broiler litter is much higher than what could be considered a dilute solution and Ni (1999) reported that  $K_d$  and  $K_h$  in manure slurries are different from those in dilute solution. Ni (1999) also reported that if TAN is less than 1000 mg/L in liquid manure, no serious error will result if Henry's law is used to predict gas phase concentration.

(6) C/N ratio: Carbon is important for microbes to produce energy and nitrogen is essential for building cell proteins. As broiler litter contains organic carbon materials, microorganisms consume the available organic carbon and take up ammonium needed for proteins. Increased

N immobilization will result in reduced ammonia release from litter. Kirchmann (1985) found that if the C/N ratio was more than 50, ammonia loss was negligible.

(7) Substrate inhibition: High concentration of uric acid and urea may inhibit the growth of the ammonifying bacteria through substrate inhibition. Singh and Nye (1984) obtained a maximum rate at a urea concentration of about 0.2 M of N in the soil solution was adequate for ammonifying bacteria (Michaelis Menten equation); higher N concentrations reduced the activity of the ammonifying bacteria.

(8) Cations: Cations (such as zinc and copper) have a dual effect on microbial growth. If the concentrations are optimal, these cations become trace elements for microbial growth (Juliastuti et al., 2003). However, if these ions are present in higher concentrations, they may inhibit nitrification process. Juliastuti et al. (2003) reported that when  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  concentrations exceeded 0.05 mg/L and 0.35 mg/L, respectively, nitrification was inhibited in soil.

### **Dissociation constant of ammonium**

A few studies have evaluated  $K_d$  values of ammonium in livestock manure or waste. Hashimoto and Ludington (1971) measured  $K_d$  of  $\text{NH}_4^+$  on chicken manure slurry at room temperature. The slurry was first aerated to convert organic N to TAN and then transferred to a reaction vessel. Sodium hydroxide was added to raise the pH of the slurry. Hashimoto and Ludington (1971) reported that the decrease in TAN concentration with time in chicken manure followed the first order differential equation. The  $K'_d$  ( $9.529 \times 10^{-11}$ ) of  $\text{NH}_4^+$  in

chicken manure slurry at room temperature was one-sixth the value of  $K_d$  in dilute anhydrous ammonia solution (Hashimoto and Ludington, 1971).

Arogo et al. (2003) measured  $K_d$  of  $\text{NH}_4^+$  in swine anaerobic lagoon liquid and deionized water at different temperatures. The experiment was conducted in a convective emission chamber for 3 h with samples of lagoon liquid. At the end of experiment, TAN and pH were measured and then  $K'_d$  was calculated. As pH was greater than 10.5, ammonium concentration was neglected. Arogo et al. (2003) reported that  $K_d$  values for lagoon liquid were about 50% of the value in deionized water at 25°C ( $3.39 \times 10^{-10}$ ) and 35°C but 94% of the value in deionized water at 15°C.

Zhang (1992) reported that  $K'_d$  in diluted finishing pig manure (1% solid content) was one-fifth ( $1.143 \times 10^{-10}$ ) the magnitude compared with that of  $\text{NH}_3$  in water at room temperature. The experiments were also conducted at high pH values (pH=9.45-12.55) (Zhang, 1992).

There are no studies on measurement of  $K'_d$  and  $K'_h$  values in poultry litter that are higher in C/N than chicken manure; C/N will likely affect dissociation constant. Therefore, there is need to measure dissociation constant in broiler litter.

### **Henry's law constant of ammonia**

Some studies on calculating Henry's law constant in animal waste systems are discussed. Beutler and Renon (1978) provided a method to calculate  $\text{NH}_3\text{-H}_2\text{S-H}_2\text{O}$ ,  $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ , and  $\text{NH}_3\text{-SO}_2\text{-H}_2\text{O}$  vapor liquid equilibrium between 0 and 100 °C in high

concentration of acid solution. Beutler and Renon (1978) reported that the value of Henry's constant equation was a function of temperature. Olesen and Sommer (1993) used the Beutler and Renon (1978) equation ( $K_h=0.0164$  atm/M at 25°C) to model ammonia volatilization in stored pig slurry. The value of Henry's constant obtained from the Beutler and Renon (1978) equation was close to that measured in dilute solution (Olesen and Sommer, 1993). The Henry's law constant ( $K'_h$ , atm/M) modeled by Olesen and Sommer (1993) in swine slurry at different temperatures (T, K) as expressed in eq. [3.9].

$$\ln(K_h) = 160.559 - \frac{8621.06}{T} - 25.6767\ln T + 0.035388T \quad [3.9]$$

Anderson et al. (1987) determined Henry's constants for four gases: carbon dioxide, methane, ammonia and hydrogen sulfide at pH 6.5 in swine manure. Henry's constant of ammonia was a function of temperature and was affected by the fraction of CO<sub>2</sub> and H<sub>2</sub>S. However, this equation only applied when pH was less than 6.5; for pH values higher than 7.5, it required revision because the fraction of CO<sub>2</sub> and H<sub>2</sub>S would be reduced (Anderson et al., 1987).

Pagans et al. (2006) measured ammonia sorption isotherm at different moisture content on biofilter media and found that the experimental data could be modeled with Henry's Law. Different media had different Henry's Law constant values and were higher than or similar to ammonia in pure water. Pagans et al. (2006) hypothesized that water in organic matrix was present in the form of a biofilm, the absorption capacity of which could be altered according to the chemical composition of the biofilm. The study by Pagans et al. (2006) showed that Henry's law constant could change in three-phase systems and with moisture content in such systems. Therefore, there is need to measure  $K'_h$  in broiler litter.

## Materials and Method

Broiler litter and cake used in this study were obtained from a broiler farm in Duplin Co., North Carolina. The samples were placed in black plastic bags and transported on ice to the lab, and preserved at low temperature (-18°C) in a freezer to suspend microbial and enzymatic activities. The litter (or cake) was passed through a 2-mm sieve to remove large clumps and then thoroughly mixed. Thereafter, the cake and litter were again stored in the freezer until start of the experiments. Before conducting  $K_d$  and  $K_h$  experiment, litter were allowed to equilibrate to room temperature.

The dissociation constant and Henry's constant experiments were conducted at the Air Quality R&D Facility. Samples for TAN concentration were analyzed at the Biological and Agricultural Engineering Department's Environmental Analysis Lab (EAL).

### Dissociation constant ( $K_d$ )

The dissociation constant of ammonium in litter was measured at room temperature (26°C). Field-moist broiler litter was used instead of oven-dried litter in this study to replicate the conditions in broiler houses. In a study that was replicated three times, 150 g of sieved (2-mm) litter were mixed with 450 mL of deionized, distilled water (DDW) in a glass jar (8.5 cm diameter, 16 cm height) on a stirrer 5 min. The resulting slurry completely filled the glass jar, leaving no headspace for ammonia to accumulate; the jar was sealed using Parafilm®. Because Parafilm® is permeable to water vapor (1 g/m<sup>2</sup>-d) (<http://www.2spi.com/catalog/supp/parafilm-m-permeability-properties.php>) and water vapor and ammonia have similar properties (e.g., size of molecules and polarity), it may also some

ammonia to escape. Because there was no headspace, and ammonia diffusivity in liquid several orders of magnitude lower than air, very little ammonia may have escaped through the Parafilm®. Unionized ammonia and pH in the slurry were measured with ammonia combination ion selective electrode (Make: Fisher Scientific, Model: 13-620-508; Range:  $5 \times 10^{-7}$  M to 1M) and pH electrode, respectively, that were introduced through the Parafilm® (Fig. 3-1). The gaps around the electrodes were sealed with Parafilm® to keep the system air-tight.



Figure 3-1 Experiment design of dissociation constant. At left is the pH electrode, and at right is ammonia electrode)

A higher ratio of litter to DDW to achieve moisture contents comparable to broiler houses would have been used if there had been an alternative to the ion selective electrode for measuring ammonia gas dissolved in the liquid phase of unsaturated broiler litter. Before



conducting the experiment, the calibration curve (eq. [3.10]) for the ion selective electrode was developed for a range of  $\text{NH}_{3(\text{aq})}$  concentrations ( $10^{-7}\text{M}$ ,  $10^{-3}\text{M}$ ,  $10^{-2}\text{M}$ ,  $10^{-1}\text{M}$ ). The ion selective electrode gave a very good fit ( $R^2 \approx 1$ ) between the analog output (y, mV) and  $\text{NH}_{3(\text{aq})}$  standard concentration (C, M).

$$y_{(\text{mv})} = -22.05 \ln(C) - 222.5 \quad (r^2 = 1.00) \quad [3.10]$$

The experiment was conducted until the value of  $\text{NH}_3$  combination ion selective electrode approached equilibrium indicating that ammonia and ammonium in the slurry were in equilibrium. Thereafter, TAN was analyzed in EAL. Dissociation constant was calculated (eq. [3.12]) in molar concentration (M) by substituting eq. [3.11] in eq. [3.2].

$$[\text{TAN}] = [\text{NH}_3\text{-N}]_{(\text{aq})} + [\text{NH}_4^+\text{-N}]_{(\text{aq})} \quad [3.11]$$

$$K'_d = \frac{[\text{NH}_3\text{-N}]_{(\text{aq})}[\text{H}^+]}{\text{TAN} - [\text{NH}_3\text{-N}]_{(\text{aq})}} \quad [3.12]$$

In eq. [3.12],  $K'_d$  implicitly accounts for ionic effects on ammonia-ammonium equilibrium. Thereafter,  $K'_d$  of  $\text{NH}_4^+$  on broiler litter slurry was adjusted for temperature ( $26^\circ\text{C}$ ,  $299.15\text{K}$ ) using eq. [3.13] that correlates  $K_d$  with temperature (T, K) proposed by Jayaweera and Mikkelsen (1990). Finally,  $K'_d$  of ammonium in broiler litter slurry was compared to  $K_d$  of ammonium in DDW.

$$K_d = 10^{-(0.0897 + \frac{2729}{T})} \quad [3.13]$$

### Henry's Law constant ( $K_h$ )

The Henry's Law constant for ammonia in field-moist broiler litter was measured in triplicate at room temperature (23°C). Sieved (2-mm) litter (150 g) was mixed with 450 mL of DDW in a glass jar (8.5 cm diameter, 16 cm height) on a stirrer for 5 min. This jar was placed in an air-tight plastic container (Make: Lock & Lock; dimensions: 45 cm L×29 cm W× 23.5 cm H; volume of 20.8 L) (Fig. 3-2). The container had three holes, one for inserting the ion selective electrode (Make: Fisher Scientific, Model: 13-620-508; Range:  $5 \times 10^{-7}$ M to 1 M) for measuring ammonia gas in the slurry, the second for drawing out the air to sample for ammonia concentration, and the third was for recirculating the sampled air back into the container for maintaining neutral pressure (Fig. 3-2). Ammonia gas concentration in the container was measured every minute by a photoacoustic spectrophotometer (Make: LumaSense Technologies Inc., Ballerup, Denmark, Model: INNOVA, Model: 1421, Detection limit for ammonia: 0.2 ppm at 20°C and 1 atmosphere of pressure, Dynamic range: 4 orders of magnitude) and also recorded by the INNOVA 1412. The experiment was conducted until the headspace ammonia concentration reached equilibrium and remained constant for 30 min. During the experiment,  $\text{NH}_{3(\text{aq})}$  concentrations in the slurry were also recorded regularly. At the end of experiment, TAN in the litter slurry was measured in the EAL.

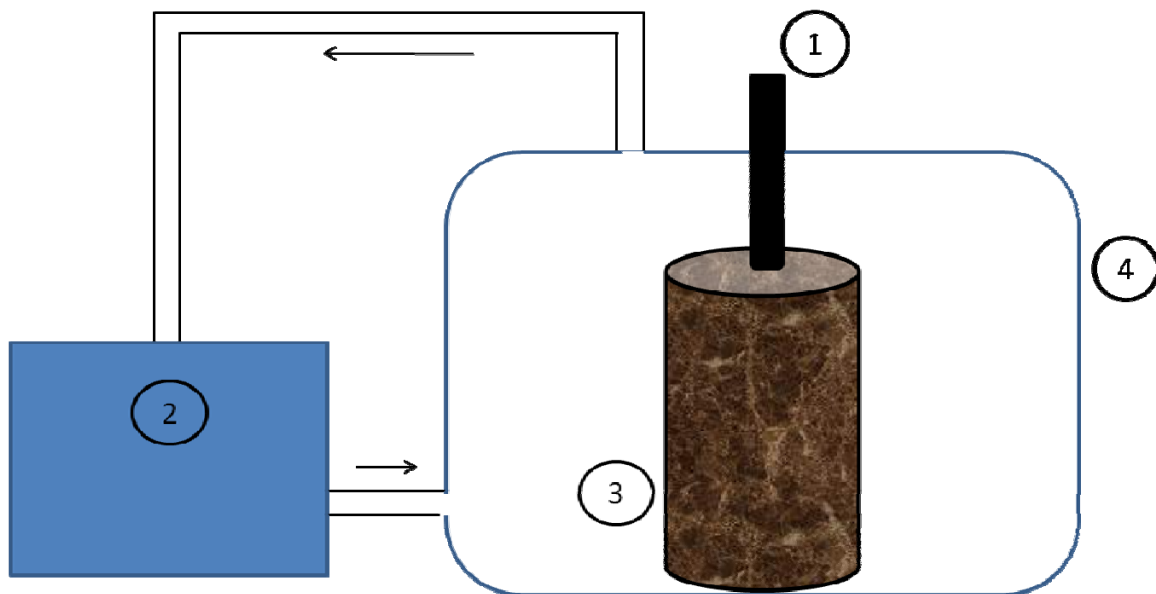


Figure 3-2 Experiment design of Henry's law constant (1) NH<sub>3</sub> combination ion selective electrode (2) photoacoustic sensor (3) litter sample (4) plastic container

In eq. [3.14],  $K'_h$  is calculated in atm/M because it implicitly accounts for ionic effects on NH<sub>3(g)</sub>-NH<sub>3(aq)</sub> equilibrium. Thereafter,  $K'_h$  was compared to  $K_h$  of NH<sub>3</sub> in DDW.

$$K'_h = \frac{[\text{NH}_3]_{(g)}}{[\text{NH}_3]_{(aq)}} \quad [3.14]$$

Since  $K_h$  is temperature-dependent, the empirical equation by Dasgupta and Dong (1985) was used to compare the experimental value ( $K'_h$ ) and theoretical value ( $K_h$ , atm/M) as a function of temperature (T, K).

$$\ln(K_h) = \frac{4092}{T} - 9.7 \quad [3.15]$$

## Results and Discussion

The results of dissociation constant and Henry's constant experiments are discussed in this chapter. The dissociation constant,  $K'_d$  of ammonium in broiler litter slurry was compared to  $K_d$  of ammonium in deionized water. Henry's constant,  $K'_h$  of ammonia in broiler litter slurry was also compared to  $K_h$  of ammonia in deionized water.

### Dissociation constant

The theoretical dissociation constant ( $K_d$ ) (eq. [3.13],  $5.01 \times 10^{-10}$ ) of ammonium in water and experimental dissociation constant ( $K'_d$ ) of ammonium in broiler litter slurry are presented in Table 3-1. Dissociation constant for broiler litter slurry was only 20% of  $K_d$  in aqueous solution (Table 3-1). The equilibrium ammonia and pH data are shown in Appendix A.

Table 3-1 Comparison of theoretical aqueous dissociation constant ( $K_d$ ) and experimental dissociation constant ( $K'_d$ ) at 25 °C for ammonium in broiler litter slurry.

pH <sup>1</sup>	[NH <sub>3</sub> -N] (M)	[NH <sub>4</sub> -N] (M)	$K'_d$	$K_d$
7.33±0.02 <sup>2</sup>	(2.02±0.10)×10 <sup>-4</sup>	(9.40±0.3)×10 <sup>-2</sup>	(1.02±0.05)×10 <sup>-10</sup>	5.01×10 <sup>-10</sup>

<sup>1</sup>pH was determined in 1: 3 (litter : water ) suspension

<sup>2</sup> Mean±SD (n=3)

Hashimoto and Ludinton (1971) reported that  $K'_d$  in chicken manure was 17% of that in aqueous solution ( $K_d$ ). Zhang (1992) reported  $K'_d$  that in liquid swine manure was 20% of the value in aqueous solution. Arogo et al. (2003) reported that  $K'_d$  in swine lagoon liquid

was 50% of the value of  $K_d$ . Differences in  $K'_d$  values among the different studies were probably due to different TDS concentrations. The  $K'_d$  calculated in this study is close to the results of Hashimoto and Ludington (1971) and Zhang (1992). In field conditions (e.g. broiler house), the moisture content in broiler litter may be in the range of 20% to 40% (dry basis), which is lower than this study. The  $K'_d$  in broiler litter under field conditions may be lower than what was measured in this study because TDS in broiler litter (under field condition) would be higher in due to much lower moisture content resulting in lower activity coefficient (eq. [3.6]).

Arogo et al. (2003) reported  $K'_d$  in swine lagoon was reduced to 50% of that in aqueous solution due to TAN adsorption on suspended solids. The adsorbed ammonium may not dissociate and convert to ammonia to be available to volatilize. Broiler litter, which has a much lower moisture content than liquid swine waste, will contain much higher concentrations of ammonium and other ions in the liquid fraction. As the concentration of these ions increase, electrostatic interactions between the ammonium ions becomes much lower than its analytical concentration. The electrical conductivity of broiler litter slurry (litter: water=1:3) was 8,933  $\mu\text{mhos/cm}$  ( $n=3$ ), which was indicative of high ionic concentration in litter slurry. These reasons may explain the much lower value of  $K'_d$  in broiler litter slurry vs.  $K_d$  in aqueous solution. Therefore, when N modeling is applied to broiler litter,  $K'_d$  should be reduced in light of these findings.

### Henry's Law constant

The theoretical Henry's Law constant ( $K_h$ ) of ammonia in water (0.0178 atm/M, adjusted for temperature using eq. [3.15]) and experimental Henry's Law constant of ammonia in broiler litter slurry ( $K'_h$ ) are presented in Table 3-2. The equilibrium liquid and gas concentration of ammonia recorded by the ammonia electrode and photoacoustic sensor are shown in Appendix B.

Table 3-2 Comparison of theoretical Henry's Law constant in aqueous solution ( $K_h$ ) and experimental Henry's Law constant for ammonia in broiler litter ( $K'_h$ ) at 25 °C

pH <sup>1</sup>	TAN (M)	[NH <sub>3</sub> ] <sub>(aq)</sub> (M)	P <sub>NH<sub>3</sub></sub> (atm)	K' <sub>h</sub> (atm/M)	K <sub>h</sub> (atm/M)
7.38±0.04 <sup>2</sup>	1604±55	(2.72±0.14)×10 <sup>-4</sup>	(4.29±0.02)×10 <sup>-6</sup>	0.0158±0.0008	0.0164

<sup>1</sup>pH was determined in 1: 3 (litter : water ) suspension.

<sup>2</sup>Mean±SD (n=3)

Henry's Law constant for broiler litter slurry was 96% of  $K_h$  (using eq. [3.15]) and 99% of  $K_h$  for Betterton's (1992) result. Oleson and Somer (1993) reported that  $K'_h$  in swine slurry is 0.0166 atm/M at 25°C. Hence,  $K'_h$  in this study was very close in value of reported values of  $K_h$  in dilute aqueous solution. In contradiction to Ni (1999) who reported that  $K_h$  applied to dilute solution of up to 1,000 mg/L, in this study,  $K_h$  applied to TAN concentration >1600 mg/L. Under field conditions, broiler litter has lower moisture content (20%-40%) than was used in this study, which may increase TDS concentration in broiler litter (field condition). High TDS concentration will reduce activity coefficient; therefore,  $K'_h$  in broiler litter may be higher than observed in this study (eq. [3.14]).

The differences in  $K_d$  and  $K_h$  between aqueous solution and broiler litter slurry could be due to two factors. Firstly, adsorption of ammonium and ammonia by the organic matter complex reduced their availabilities for conversion and release (Arogo et al., 2003). Second, the presence of other ions in solution probably greatly reduced the activity coefficient of ammonium (Snoeyink and Jenkins, 1982), thereby reducing formation of ammonia in the liquid phase. Reduced ammonia formation in the liquid phase probably reduced ammonia transfer to the air. The findings of this study indicate that in broiler litter, it may be acceptable to use  $K_h$  developed for aqueous solutions though there is need for additional validation.

## Conclusions

1. Dissociation constant ( $K'_d$ ) in litter slurry was  $1.02 \times 10^{-10}$ , 20% of the dissociation constant ( $K_d$ ) in aqueous solution which may be due to ammonium adsorption onto solid matrix and reduced activity coefficient.
2. Henry's Law constant ( $K'_h$ ) (0.0158 atm/M) in litter slurry is close to the Henry's law constant ( $K_h$ ) (0.0164 atm/M) in aqueous solution and so, it may be acceptable to use  $K_h$  developed for aqueous solutions though there is need for additional validation.



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Appendix A Partial pressure of ammonia in the headspace and broiler litter slurry

pH in dissociation constant study

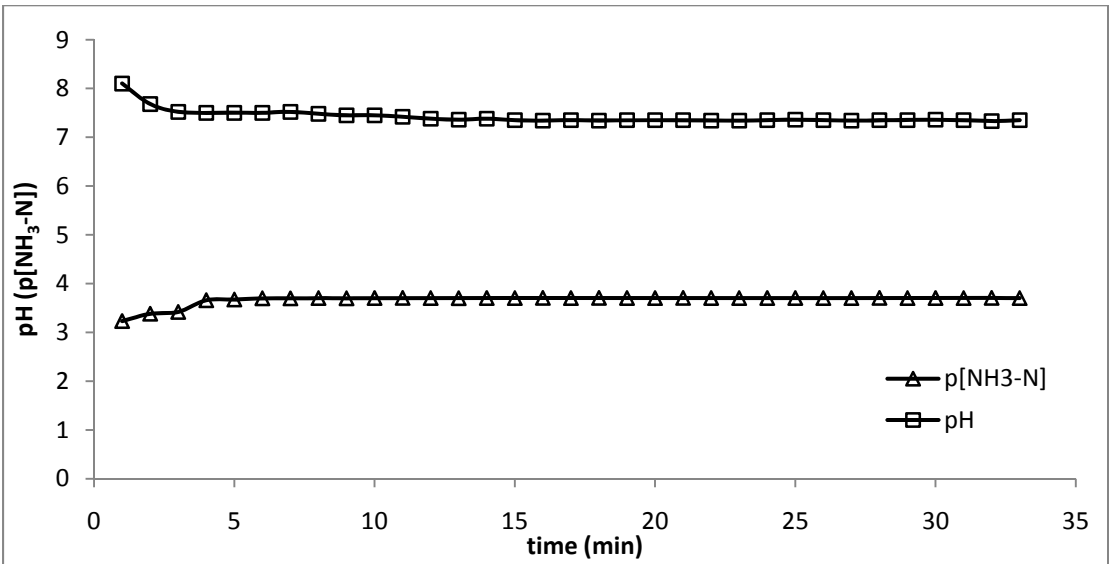


Figure A-0-1 Ammonia concentration and pH vs. time (sample 1)

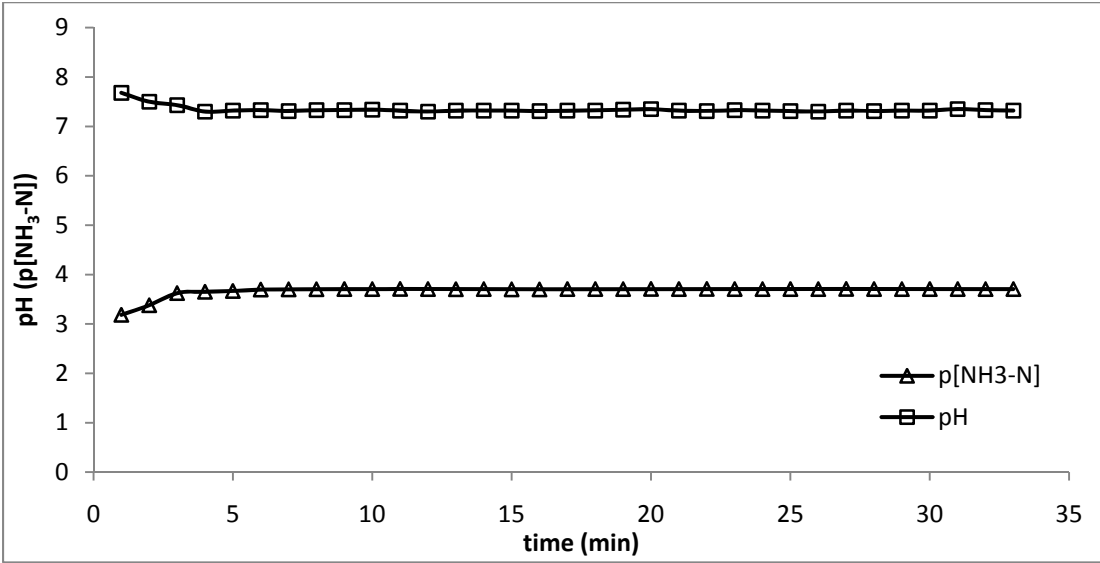


Figure A-0-2 Ammonia concentration and pH vs. time (sample 2)

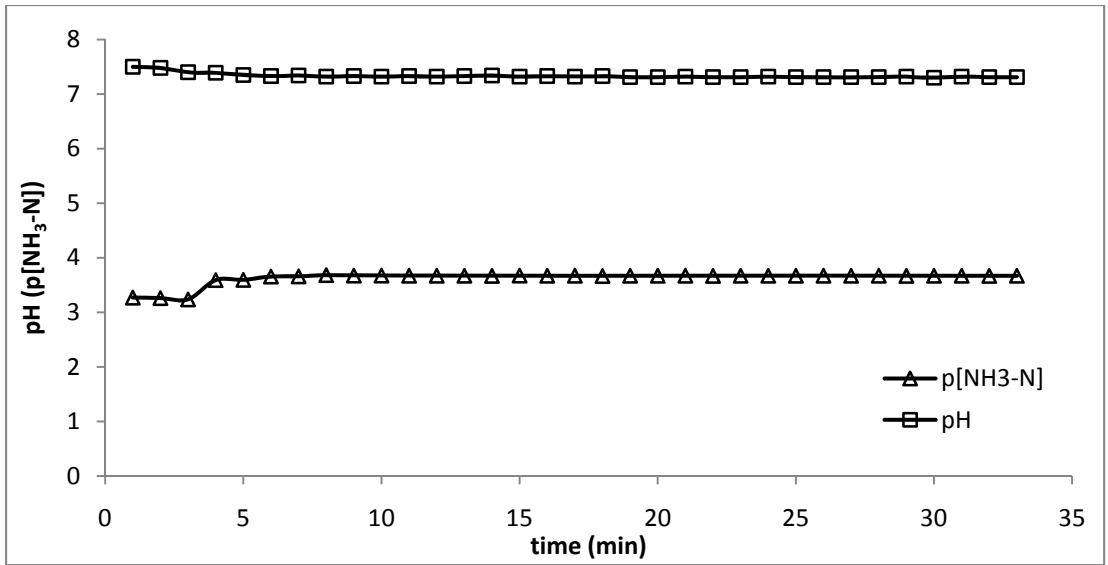


Figure A-0-3 Ammonia concentration and pH vs. time (sample 3)

**Appendix B Determination of Henry's Law constant in broiler litter slurry**

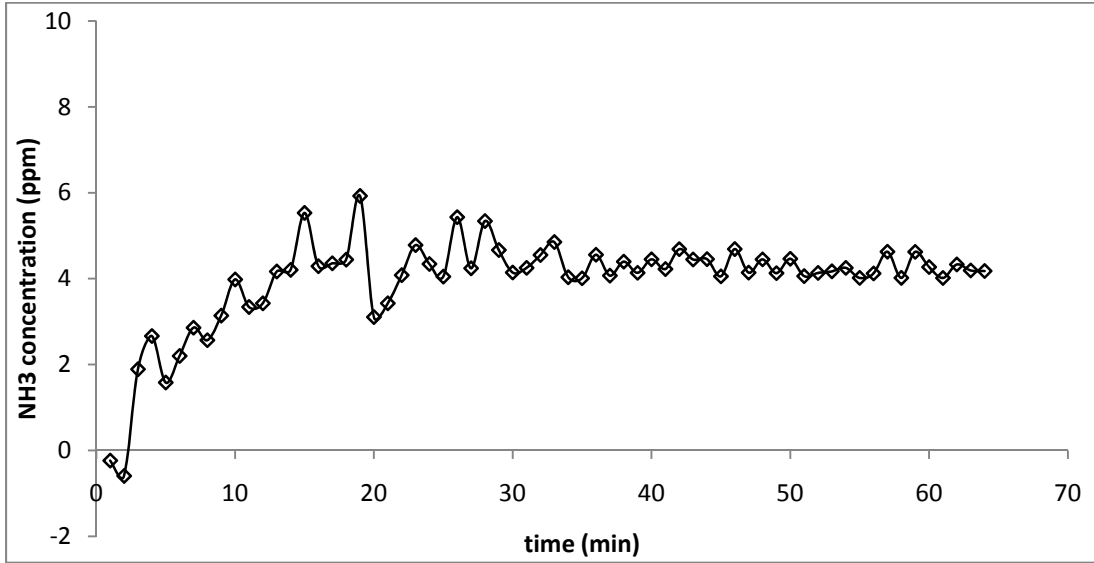


Figure B-0-1 Ammonia gas concentration (ppm) vs. time (sample 1)

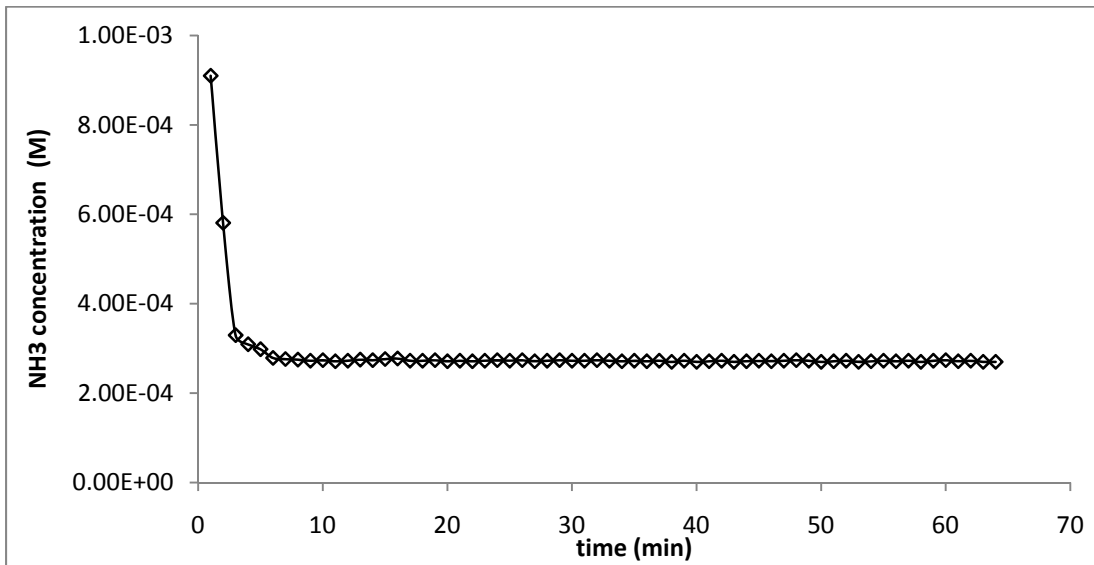


Figure B-0-2 Dissolved ammonia concentration (M) vs. time (sample 1)

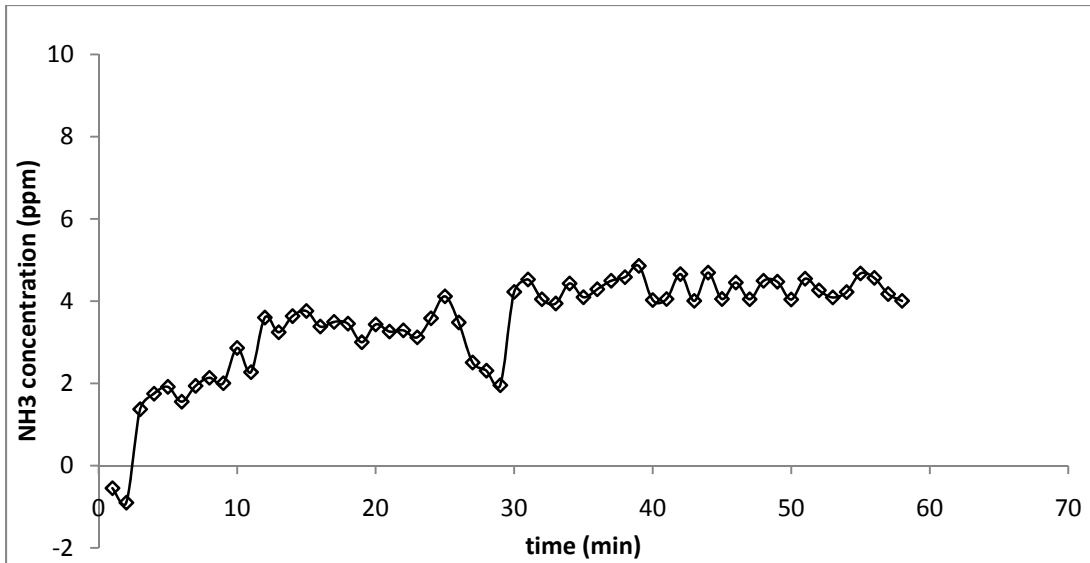


Figure B-0-3 Ammonia gas concentration (ppm) vs. time (sample 2)

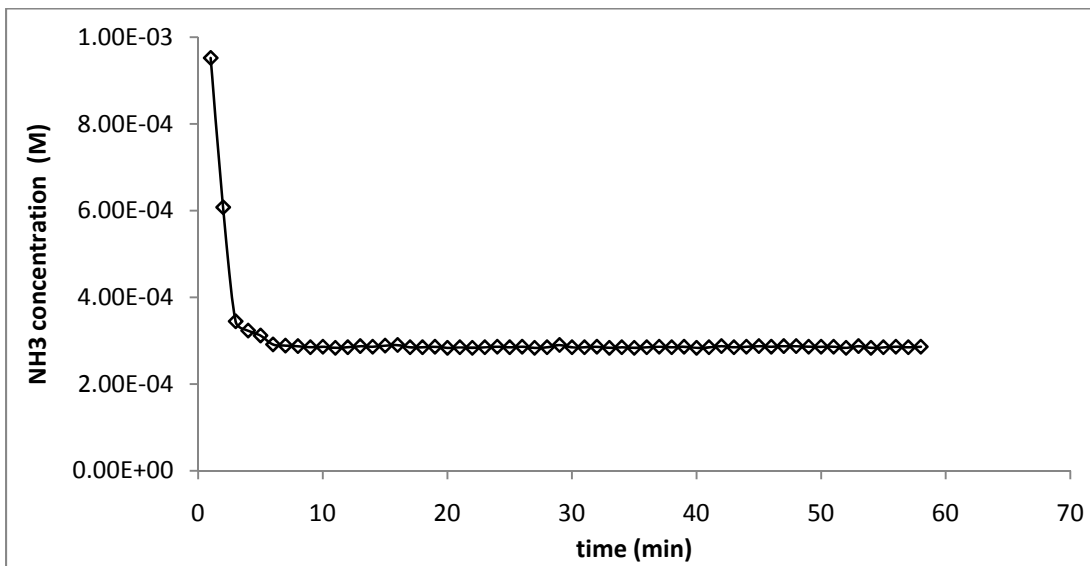


Figure B-0-4 Ammonia liquid concentration (M) vs. time (sample 2)

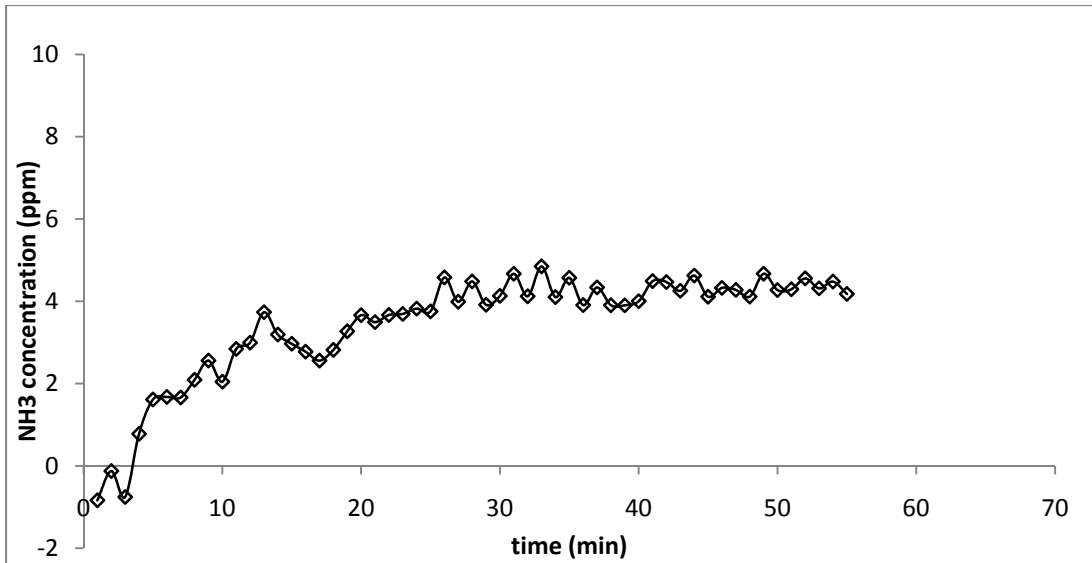


Figure B-0-5 Ammonia gas concentration (ppm) vs. time (sample 3)

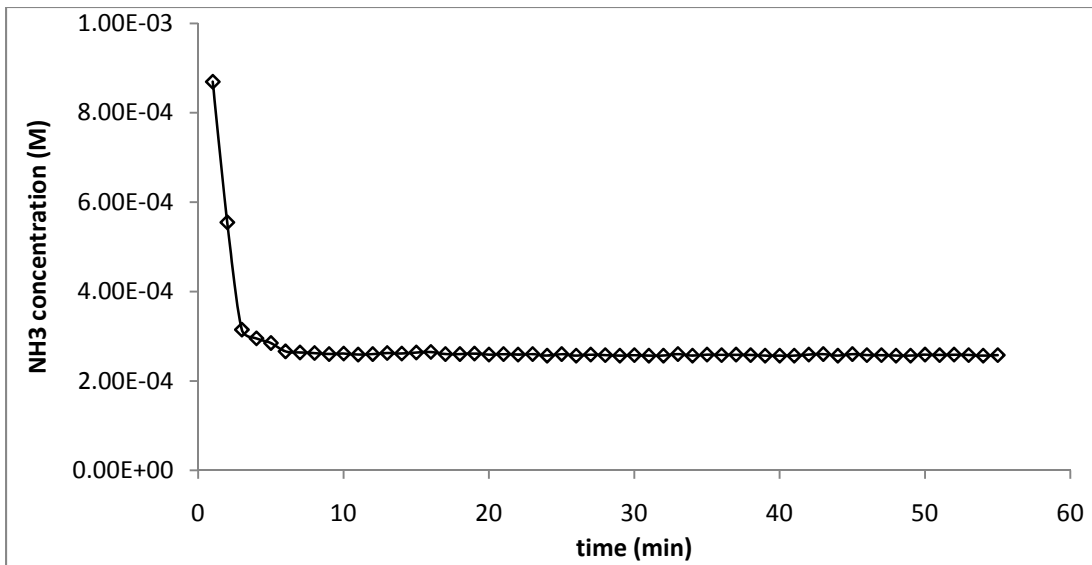


Figure B-0-6 Ammonia liquid concentration (M) vs. time (sample 3)



## 4 Ammonium and Ammonia Sorption on Broiler Litter and Cake

### Abstract

Ammonia emission from broiler houses is a major concern because of its impacts on the environment. To reduce ammonia emissions, it is necessary to understand the fate of ammonia/um in the broiler litter. In broiler litter, uric acid and urea hydrolyze to ammonium ( $\text{NH}_4^+$ ) and a fraction of  $\text{NH}_4^+$  converts to ammonia depending on pH and temperature. Further,  $\text{NH}_4^+$  undergoes solid-liquid partitioning and the ammonia fraction is partitioned among the solid, liquid and gas phases in the litter. Ammonium partitioning between solid and liquid phases in boiler cake (primary feces and spilled feed on the surface) and litter (dissolved fecal constituents and bedding beneath the cake) were measured at different pH values and dissolved ammonium concentrations. In broiler litter, Freundlich, linear and Temkin isotherm provided the best fit at pH of 4, 6, and 7, respectively. In broiler cake, linear isotherm provided the best fir at pH 4, 6, and 7. Overall, for both broiler cake and litter, the linear isotherm is appropriate for modeling ammonium partitioning between the dissolved and adsorbed phases because of its accuracy and simplicity. Ammonia partitioning among solid, liquid, gas phases was also measured using litter with different moisture contents. Ammonia sorption increased with moisture content from 0% to 25% and maximum of ammonia sorption was 4,230 mg/kg at 25% moisture content and then decreased with increasing moisture content from 35% to 55%. Litter at 0% moisture content adsorbed >2,800 mg/kg of ammonia, more than sorbed by litter with moisture content at or above 45%. The results of ammonium and ammonia sorption studies on litter will provide information to simulate litter nitrogen dynamics more accurately.

## Introduction

Broiler litter contains many different nitrogen (N) species and two of those important species are uric acid and urea. In litter, uric acid and urea hydrolyze to ammonium ( $\text{NH}_4^+$ ) and a fraction of  $\text{NH}_4^+$  converts to ammonia ( $\text{NH}_3$ ) depending mainly, on pH and temperature. Further,  $\text{NH}_4^+$  undergoes solid-liquid partitioning while the  $\text{NH}_3$  fraction is partitioned among the solid, liquid and gas phases in the litter; a large fraction of the ammonia may be released inside the broiler house and then exhausted into the environment. Ammonia release into the broiler house and its subsequent emission are concerns because of its impacts on bird health as well as the environment. To reduce ammonia production and emissions, it is necessary to understand the fate of ammonia/um in the litter. However, many different mechanisms that govern ammonia/um in the litter are not clearly understood or have not been quantified or modeled. For example, current model of ammonium adsorption isotherm in litter use the Freundlich isotherm developed for soil (reference) and ammonia adsorption onto the solid litter matrix is assumed to be zero (Liu et al., 2009).

Ammonium partitioning between solid and liquid phases in broiler cake (primarily, feces, and spilled feed on the surface) and litter (dissolved fecal constituents, some feces, and bedding beneath the cake) will be affected by both pH and dissolved ammonium concentration. Suitable adsorption isotherms for ammonium in broiler cake and litter can be modeled using linear regression and non-linear regression as has been done for other adsorbents (Kumar et al., 2006, 2008).

Ammonia partitioning among solid, liquid, and gas phases will also occur in litter and this will be affected by the litter moisture contents. If there is no moisture, only adsorption will occur though this unlikely to happen in practice except on the litter surface in empty houses. However, if there is moisture, ammonia gas will be partitioned among all three phases. Therefore, in addition to adsorption, absorption will also be a significant mechanism for ammonia transfer from the gas phase to the material (Pagans et al., 2006).

Hence, better understanding of ammonium partitioning between the solid and liquid phases and ammonia adsorption on the solid litter fraction will improve the ability to simulate litter nitrogen (N) dynamics more accurately. The specific objectives of this study are to:

- (1) model ammonium adsorption in broiler litter and cake as impacted by different pH values (pH 4, 6 and 7) and
- (2) model ammonia absorption and adsorption at different litter moisture contents (0%, 15%, 25%, 35%, 45%, and 55%).

## **Literature review**

Most studies on ammonium and ammonia adsorption are focused on soil or other materials, and there is little information about those mechanisms in broiler litter or cake. There has been some research on ammonia adsorption on solid organic matrices; though it is unclear if they are applicable to broiler litter because broiler litter has very high levels of background ammoniacal-N. Selected studies are presented below. But first, the theory of adsorption as well as the difference between adsorption and absorption are discussed briefly to provide some background.

### **Adsorption vs. Absorption**

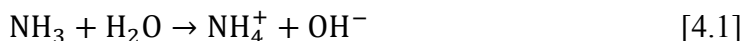
Adsorption is the process by which ions or molecules present in one phase (liquid or gas) tend to attach on the surface of another phase (solid). The material being attached is the adsorbate and the adsorbing solid is called the adsorbent. Absorption occurs when a molecule diffuses through the stagnant film into the bulk liquid (Cooper and Alley, 2002). Therefore, adsorption is a surface phenomenon that involves either a solid or liquid surface (very thin film). In general, as the concentration of the species in solution or gas increases, the adsorbed and absorbed concentrations also increase.

There are three types of adsorption: physical, chemical, and exchange (Sawyer and McCarty, 1978). Physical adsorption is nonspecific and reversible and is due to weak forces, such as Van der Waals' forces between molecules (Sawyer and McCarty, 1978). Van der Waals' forces result when two neighboring atoms (polar or non-polar) attract each other by fluctuating charges. The adsorbed molecule is not affixed to a particular site on the solid

surface, but is free to move over the surface. In addition, the adsorbed material may condense and form multiple layers on the surface of the adsorbent (Sawyer and McCarty, 1978).

Chemical adsorption is less reversible and involves stronger forces than physical adsorption due to the formation of chemical bonds on the surface (Bohn et al., 1985). The distinction between chemical adsorption and physical adsorption is the same as that between chemical and physical interactions (IUPAC, 2001). The adsorbed material normally forms a layer over the surface which is only one molecule thick, and the molecules are not free to move from one surface site to another (Sawyer and McCarty, 1978; Bohn et al., 1985). Physical and chemical adsorptions are not easily distinguished, especially those involving strong hydrogen (H) bonds (IUPAC, 2001). Hydrogen bonding is considered either chemical reaction (Brancato et al., 2002) or a subset of Wan der Waals forces (Sparks, 2004). In this study, it is assumed that H bonding results in chemical adsorption. An example of chemical adsorption in broiler litter could be adsorption of ammonium ions by some carboxyl groups ( $\text{COO}^-$ ) through covalent bonding.

Exchange adsorption is also characterized by electrical attraction between the adsorbate and the adsorbent, but this attraction is due to ion exchange. Ions of a substance attach on the surface as a result of electrostatic attraction to sites of opposite charge on the surface, i.e., acid-base reaction (Bohn et al., 1985). An example of ion exchange adsorption is shown in eq. [4.1] as might happen on the broiler litter surface in a moist environment, where a single layer of water molecules adsorb ammonia, which is readily reversible.



Unlike adsorption, absorption is not a surface phenomenon and involves bulk liquid as absorbent. Absorption can be physical or chemical, depending on whether there is chemical reaction forming bonds and producing new products (Shiflett and Yokozeki, 2010). An example of physical absorption of a gas into a liquid is the absorption of ammonia into water ( $\text{NH}_{3(\text{g})} \leftrightarrow \text{NH}_{3(\text{aq})}$ ) where no new product is formed. Equation [4.1] can also be an example of chemical absorption when the absorbent is bulk liquid and not the liquid surface. Compared to the ion exchange adsorption, chemical absorption occurs in bulk liquid and is less reversible. In this study on ammonia partitioning, sorption is used to include both adsorption and absorption when it is not possible to separate the surface phenomenon from the bulk phenomenon.

### **Factors affecting ammonia and ammonium sorption**

The main factors that affect ammonia and ammonium sorption are pH, temperature, and moisture content. As pH increases, the fraction of ammonia in the solution containing ammonia and ammonium increases, which reduces ammonium adsorption on solid matrix as the dissolved ammonium converts to ammonia.

Adsorption is also affected by temperature. For example, a decrease in adsorption efficiency and effectiveness is generally observed with increasing temperature (Rosen, 2004). Diffusive mass transfer increases with temperature because gas solubility. For ammonia/ammonium sorption, as temperature increases, molecules become more active and more  $\text{NH}_{3(\text{aq})}$  forms  $\text{NH}_{3(\text{g})}$  in the atmosphere, which results in reduced adsorption. Therefore, physical absorption,

and to a lesser extent, chemical absorption, as applied to ammonia dissolved in litter moisture would also decrease with increased temperature.

Gibbs free energy (G) is affected by change in temperature (eq. [4.2]) (Snoeyink and Jenkins, 1982). Gibbs free energy can determine whether the reaction proceeds spontaneously or not.

$$\Delta G = \Delta H - T\Delta S \quad [4.2]$$

In eq. [4.2],  $\Delta G$  = change in Gibbs free energy (kcal/mol);  $\Delta H$  = change in enthalpy (kcal/mol);  $T$  = temperature, K; and  $\Delta S$  = change in entropy (kcal/mol-T). A negative value of  $\Delta G$  indicates spontaneous adsorption (Kumar et al., 2007) which is also an exothermic reaction, meaning that the chemical compounds move toward a lower energy state.

When moisture is present, both absorption and adsorption may be significant mechanisms for ammonia transfer from gas phase to solid-liquid matrix (Pagans et al., 2006). Absorption includes dissolution (i.e.  $\text{NH}_{3(\text{g})} \rightarrow \text{NH}_{3(\text{aq})}$ ), conversion (i.e. ammonia forms ammonium), and biodegradation (i.e. nitrification process,  $\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$ ). While dissolution is physical absorption, conversion, and degradation are examples of chemical absorption. Pagans et al. (2006) observed that ammonia biological absorption was considered as the predominant mechanism at 65.8% moisture content in biofilter.

## Theories of adsorption isotherm

Partitioning between the dissolved and adsorbed phases can be modeled using adsorption isotherms. Adsorption isotherms are divided into two categories: two-parameter isotherms and three-parameter isotherms.

### *Two parameter adsorption isotherm*

Based on the review of literature, six widely-used equilibrium isotherms are discussed below.

(1) Langmuir isotherm: This Langmuir isotherm was initially derived for the adsorption of gases by solids by Langmuir based on the assumption of monolayer adsorption (Bohn et al., 1985). It is expressed as (Bohn et al., 1985):

$$r = \frac{Q_0 b C}{1 + b C} \quad [4.3]$$

where  $r$  = adsorbed concentration on medium, mg/kg;  $Q_0$  = adsorption maximum at fixed temperature (assumed to be monolayer coverage of adsorbent surface), mg/kg;  $b$  = parameter related to net enthalpy of adsorption, L/mg; and  $C$  = dissolved concentration at equilibrium, mg/L.

The Langmuir adsorption isotherm was based on three assumptions (Bohn et al., 1985): (i) a constant energy of adsorption that is independent of the extent of surface coverage; (ii) no interaction between adsorbate molecules; and (iii) maximum adsorption occurs when there is a complete monomolecular layer on adsorbent surfaces. Langmuir isotherm can describe adsorption over a portion of adsorption range and can also predict the



maximum adsorption. Equation [4.3] is rearranged in the linear form as eq. [4.4], where  $C/r$  versus  $C$  yields a straight line with a slope  $1/Q_0$  and an intercept  $1/Q_0b$ :

$$\frac{C}{r} = \frac{1}{Q_0b} + \frac{C}{Q_0} \quad [4.4]$$

(2) Freundlich isotherm: The Freundlich isotherm (Montgomery, 1985) is widely used for modeling partitioning between liquid and solid phases, and is expressed as follows:

$$r = K_f C^{(1/n)} \quad [4.5]$$

where  $K_f$  = Freundlich partition coefficient, L/kg;  $1/n$  = Freundlich exponent, while the other terms were defined earlier. The Freundlich isotherm is often expressed in its logarithmic form (eq. [4.6]) to obtain a straight line with slope  $1/n$  and an intercept of  $\log K_f$ .

$$\log r = \log K_f + \frac{1}{n} \log C \quad [4.6]$$

If the data does not fit the Langmuir adsorption isotherm, the less demanding Freundlich adsorption isotherm can often be used successfully (Bohn et al., 1985) but it lacks theoretical foundation. The only assumption is that the decrease in energy of Freundlich adsorption with increasing surface coverage is due to surface heterogeneity (Bohn et al., 1985). The drawback of Freundlich isotherm is that it cannot be extrapolated beyond the experimental range because it does not predict a maximum adsorption capacity.

(3) Linear isotherm: This isotherm (eq. [4.7]) is obtained when  $n$  is set equal to 1 in the Freundlich isotherm (eq. [4.5]), and would thus, apply to low concentrations.

$$r = K_L C \quad [4.7]$$

In eq. [4.7],  $K_L$  = linear partition coefficient, L/kg and the other terms were defined earlier.

(4) Temkin isotherm: Temkin and Pyzhev (Allen et al., 2004) considered the effects of adsorbate interaction on adsorption and proposed that these interactions produced heat, and adsorption of all molecules in the layer would decrease due to adsorbent-adsorbate interaction. Adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (Kundu and Gupta, 2006). The Temkin isotherm is used for modeling partitioning between liquid and solid phase in soil and is expressed as (Allen et al., 2004):

$$r = \frac{RT}{b} (\ln AC) \quad [4.8]$$

where A= equilibrium binding constant, L/kg; b = variation of adsorption energy, J/mol; R= idea gas law constant 8.31 J/mol-K; T = temperature, K; and other terms were defined earlier.

The Temkin isotherm is often expressed in its logarithmic form (eq. [4.9]) to linearize it with slope  $RT/b$  and intercept of  $RT \ln A/b$ . The adsorption data can be analyzed according to eq. [4.9] in expanded form to determine constants b and A.

$$r = \frac{RT}{b} (\ln A) + \frac{RT}{b} (\ln C) \quad [4.9]$$

### ***Three parameter adsorption isotherm***

(1) Redlich-Peterson isotherm: Redlich and Peterson (1959) proposed an empirical equation with three parameters, which can be used to represent adsorption equilibrium over a wide concentration range like the Langmuir adsorption isotherm. The equation is expressed as (Kumar et al., 2006):

$$r = \frac{K_R C}{1+bC^\beta} \quad 0 \leq \beta \leq 1 \quad [4.10]$$

where  $K_R$ = Redlich-Peterson partition coefficient;  $b$  = a constant parameter, L/mg;  $\beta$ =a constant parameter between 0 and 1; and other terms were defined earlier.

Equation [4.10] can be reduced to a linear isotherm at low adsorbate concentration when  $\beta=0$  and to the Freundlich isotherm at high adsorbate concentration ( $0<\beta<1$ ); it becomes the Langmuir isotherm when  $\beta=1$  (Alihosseini et al., 2010). The linearization of eq. [4.10] gives the following relationship:

$$\frac{C}{r} = \frac{1}{K_R} + \frac{b}{K_R} C^\beta, \quad 0 \leq \beta \leq 1 \quad [4.11]$$

Plotting  $C/r$  against  $C^\beta$  yields a straight line with slope  $b/K$  and an intercept  $1/K$ .

(2) Toth isotherm: The Toth isotherm (eq. [4.12]) was developed to improve the fitting of the Langmuir isotherm to experimental data based on the existence of heterogeneity on the adsorbent surface (Toth, 2000).

$$r = \frac{K_T C}{(a+C^t)^{1/t}}, \quad 0 < t \leq 1 \quad [4.12]$$

In eq. [4.12],  $K_T$ = maximum adsorption capacity, mg/kg;  $a$ = adsorptive potential constant, (mg/L);  $t$ = the heterogeneity coefficient of the adsorbent, which is between 0 and 1; while the other terms were defined earlier. Toth (2000) proposed that most sites had sorption energies lower than the maximum adsorption energy. If the surface is homogeneous,  $t=1$ , and the Toth equation reduces to the Langmuir equation (eq. [4.3]). Equation [4.12] can be reduced to a linear isotherm as shown below.

$$\left(\frac{C}{r}\right)^t = \frac{a}{K_T^t} + \left(\frac{1}{K_T}\right)^t C^t \quad [4.13]$$

Plotting  $\left(\frac{C}{r}\right)^t$  against  $C^t$  yields a straight line with slope  $\left(\frac{1}{K_T}\right)^t$  and intercept  $\frac{a}{K^t}$ . However, eq. [4.13] also has three unknown parameters equation and therefore, a optimization procedure is required to maximize  $R^2$  to obtain the best fit.

Linear regression was the most frequently used method to determine the best fit isotherm (Kumar and Porkodi, 2006). Linear regression can be used for two-parameter isotherms but sometimes is not applicable to three-parameter isotherms (Kundu and Gupta, 2006). Kumar and Sivanesan (2005) showed that depending on the way the isotherm equations are linearized, error distribution may occur (discussed in Results and Discussion). Thus, the non-linear regression method was proposed to obtain equilibrium isotherm parameters for two-parameter and three-parameter adsorption isotherms (Kundu and Gupta, 2006). Kundu and Gupta (2006) also reported that evaluating experimental data with both linear and non-linear regression analyses ensured better results. The six isotherms were used to analyze the data using both linear regression and non-linear regressions (discussed in Material and Method).

### **Ammonium and ammonia adsorption on different materials**

There are no studies modeling ammonia/um adsorption on broiler litter or cake, though there are studies of ammonia/um adsorption on soil and some organic materials. In the following paragraphs, selected adsorption studies on different materials that could be relevant to this research are reviewed.

Kinniburgh (1986) measured potassium ( $K^+$ ) and copper ( $Cu^{2+}$ ) adsorption on soil at five pH values (pH 2, 4, 6, 8, 10) and reported that Langmuir and Freundlich isotherms were the two most commonly used adsorption isotherms. The maximum adsorption capacity of  $K^+$  was 193 mg/kg. The two isotherms fit a wide variety of adsorption data and since both isotherms could be transformed to linear forms, their two parameters could be easily estimated by linear regression (Kinniburgh, 1986).

Witter and Kirchman (1989) measured ammonia and ammonium adsorption on peat, zeolite, and basalt at different pH values and different ammonia concentrations in desiccators. Adsorbed ammonium (or ammonia) concentrations were calculated from the reduction of ammonium (or ammonia) in solution. The Langmuir isotherm provided the best fit for ammonium adsorption and 1<sup>st</sup> order model provided the best fit for ammonia adsorption (Witter and Kirchman, 1989).

Kithome et al. (1999a) modeled ammonium adsorption in zeolite as affected by pH (4 to 7) and ammonium concentration. Adsorbed ammonium concentration was calculated from the reduction of ammonium in the solution. Adsorption increased with pH and  $NH_4^+$  adsorption capacity was 14,000 mg N/kg at pH of 7. Ammonium adsorption fitted both Langmuir and Freundlich isotherms very well (Kithome et al. 1999a).

Kithome et al. (1999b) studied ammonium adsorption and pH buffering capacity of coir. Ammonium adsorption capacity of coir was 7,778 mg N/kg at pH of 5. As pH increased, there was a consistent increase in the adsorption. The Langmuir and Temkin isotherm provided better fits compared with the Freundlich and Redlich isotherms (Kithome et al., 1999b).

Helminen et al. (2000) measured ammonia adsorption on zeolite, alumina, silica gel, and activated carbon at partial pressure from 1 to 100 kPa. At room temperature, ammonia adsorbed most strongly on zeolites. However, at 100°C, the adsorption was greatest on activated carbon, followed by zeolites, silica and alumina. Adsorption was poor at low pressure. Linear isotherms described ammonia adsorption on all the materials (Helminen et al., 2000).

Liu and Lo (2001) studied ammonium adsorption in zeolite as affected by time and particle size. Ammonium adsorption increased with decreasing zeolite particles size with powdered zeolite <500µm having the highest ammonium adsorption capacity. Rate of adsorption of ammonium was rapid for the first 4 h and decreased gradually thereafter. Langmuir isotherm provided excellent fit for the first 4 h and adsorption capacity was between 14,350 and 17,810 mg/kg (Liu and Lo, 2001).

Mervosh (2003) measured sorption of two herbicides (isoxaben and oryzalin) on four different soils (at field moisture contents) at pH 5-6. Four different concentrations of the two herbicides were added to the soil samples and the sorbed herbicide content was determined by difference of initial concentration and equilibrium concentration in aqueous phase. The Freundlich and linear isotherms best explained the results. The linear isotherm showed an intercept because the soil samples contained residual herbicides concentrations (Mervosh, 2003).

Pagans et al. (2006) determined ammonia adsorption on biofilter media (coconut, bark, prunings, and peat) at four moisture contents: 0%, 37.5%, 65.8% and 88.1% at 25°C. The media were dried at 105°C for 24 h prior to the study. The experimental setup was a

closed system; ammonia was pumped through the flask until its concentration in the headspace reached equilibrium. When ammonia concentration in the headspace reached 400-500 mg/m<sup>3</sup>, equilibrium and maximum adsorption were achieved. At 0% moisture content, both the Langmuir and Freundlich isotherms fitted the ammonia adsorption data and maximum adsorption capacity, calculated with Langmuir isotherm varied from 1.06 to 1.81mg NH<sub>3</sub>/g dry medium. In moist samples, Henry's law equation explained adsorption and absorption (Pagans et al., 2006).

Guo et al. (2007) measured adsorption of K<sup>+</sup> and ammonium ions in waste water onto zeolite at pH values of 6 and 9 for 18 h. Ammonium and K<sup>+</sup> adsorption reached equilibrium within 1 h. The results showed that Langmuir, Freundlich, Langmuir-Freundlich and Toth isotherms all fitted (all R<sup>2</sup> > 0.96) the data, but the three-parameter Langmuir-Freundlich and Toth isotherms had higher R<sup>2</sup> (>0.996) than the two-parameter isotherms (Guo et al., 2007).

Although many studies have been done on adsorption isotherm in different materials, no studies that evaluated ammonium and ammonia adsorption on broiler litter could be located in the literature. The adsorbents discussed in the above studies had low concentrations of ammonium and ammonia. However, because background total ammoniacal N (TAN=ammonia-N + ammonium-N) concentrations are very high in broiler litter, there is need to research ammonium adsorption on broiler litter.

## **Materials and Method**

Broiler litter and cake used in this study were obtained from a broiler farm in Duplin Co., North Carolina. The samples were placed in black plastic bags and transported on ice to the lab, and preserved at low temperature (-18°C) in a freezer to suspend microbial and enzymatic activities. The litter (or cake) was passed through a 2-mm sieve to remove large clumps and then thoroughly mixed. Nine-hundred grams of litter and 700 g cake were spread out to a depth of ~1 cm in separate stainless steel trays and oven-dried to constant weight at 70 °C for 16 h; prior work had shown that this time-temperature combination resulted in complete drying. Thereafter, the cake and litter were again stored in the freezer until start of the experiments.

The ammonium and ammonia adsorption experiments were conducted at the Air Quality R&D Facility. Samples for ammonium and ammonia adsorption were analyzed at the Environmental and Agricultural Testing Service (EATS) at the Department of Soil Science and in the Biological and Agricultural Engineering Environmental Analysis Lab (EAL). The properties of litter and cake after oven drying at 70°C are shown in Table 4-1. The analytical methods used are shown in Chapter 2 Table 2-1. Both experiments were conducted with oven-dried samples to reduce TAN levels as much as possible without changing the sorption-relevant properties of the litter and cake.



Table 4-1. Mean ( $\pm$ SD) (n=3) litter and cake properties on dry weight basis except pH and EC. The litter and cake were oven-dried at 70 °C for 16 h prior to analysis.

	TKN <sup>1</sup>	TAN <sup>2</sup>	NO <sub>3</sub> /NO <sub>2</sub> N	pH <sup>3</sup>	TC <sup>4</sup>	Surface area	EC <sup>5</sup>
	mg/kg	mg/kg	mg/kg		mg/kg	m <sup>2</sup> /g	μmhos/cm
Litter	27391±5380	3602±90	BDL <sup>7</sup>	7.3±0.2	275,400	1.99±0.07	8933±115
Cake	37112±2359 <sup>6</sup>	3136±86	BDL <sup>7</sup>	7.3±0.2	276,200	2.71±0.01	-

<sup>1</sup>TKN: Total Kjeldahl N

<sup>2</sup>TAN: Total Ammoniacal N

<sup>3</sup>pH was determined in 1: 5 (litter : water) suspension.

<sup>4</sup>TC: Total C

<sup>5</sup>EC: Electrical conductivity

<sup>6</sup>Mean±SD

<sup>7</sup>BDL: Below detection limit

### **Ammonium adsorption**

The ammonium adsorption experiment was conducted at room temperature (25±2 °C). Ammonium adsorption was evaluated for TAN concentrations approximately 100% to 200% (in increments of 20%) above background TAN concentrations, on oven-dry broiler litter (Table 4-2) or cake (Table 4-3). The rationale for selecting the range of added ammonium concentrations is discussed below. The desired TAN concentrations were

obtained by preparing six different concentrations of aqueous TAN solution and adding to the broiler litter samples. The aqueous TAN solutions were obtained by dissolving ammonium chloride (NH<sub>4</sub>Cl) powder (USP/FCC/EP certified) in deionized, distilled water (DDW). There were 36 treatments conducted in triplicate for both litter and cake at three pH values (4, 6, and 7) for a total of 108 experiment units (EUs). A higher pH value was not considered because formation and release of ammonia would be greater as pH increased, thus increasing uncertainty in modeling adsorption. Reported average pH values for broiler litter (n=18) and cake (n=4) were 7.4 and 7.6, respectively (S. B. Shah, June 10, 2010, personal communication, North Carolina State University), which are reasonably close to the highest pH value used in this study. Low pH values in litter and cake can occur when acidifiers are used to reduce ammonia formation in litter houses.

Table 4-2. Added TAN concentrations at six different levels to broiler litter (TAN background concentration (TAN<sub>back</sub>) = ~36 mg/10 g litter, Table 4-1)

TAN added (mg/10 g dry litter)	Increased TAN percentage in sample above TAN <sub>back</sub>
33.0	91.6%
42.0	116.6%
46.2	128.3%
52.5	145.8%

Table 4-2 continued

58.8	163.2%
65.5	181.8%

Table 4-3. Added TAN concentrations at six different levels to broiler cake (TAN background concentration ( $TAN_{back}$ ) = ~31.4 mg/10 g litter, Table 4-1)

TAN added mg/10 g dry cake (mg)	Increased TAN percentage in samples above $TAN_{back}$
33.0	105.4%
42.0	133.9%
46.2	147.3%
52.5	167.4%
58.8	187.5%
65.5	209.1%

At different levels of TAN addition, with the background TAN concentrations included, the broiler litter and cake samples had TAN concentrations in range of ~6,900 to

10,500 and 6,440 to 9,690 mg/kg, respectively. In commercial houses with heavy broilers (63-d flock, 4 kg ea.), TAN concentration in broiler cake was 8,500 mg/kg (oven-dry basis) (average of five flocks) (S. B. Shah, June 10, 2010, personal communication, NCSU). Also, TAN in broiler litter is slightly higher than cake (NCSU, 2011). While background TAN concentrations in the litter and cake were very low compared with the values reported by Shah, added TAN levels provided a wide range of realistic TAN concentrations in the cake and litter (Table 4-2 & 4-3) to model the partition of ammonium between the solid and liquid phases of broiler litter and cake.

In each EU, 10-g of oven-dry litter or cake was mixed with 35 mL of TAN solution (of the desired concentration, Table 4-2 and Table 4-3) and 15 mL of certified buffer solution (Fisher Scientific) to maintain the desired pH (4, 6, or 7) in a glass culture tube (75mL), stoppered, and stirred for 3 min on a stirrer. The suspension was allowed to settle for 6 h (Liu and Lo, 2001) to allow the dissolved and adsorbed phases to equilibrate and then filtered through membrane filter (particle retention: 20-25  $\mu\text{m}$ ). An aliquot (1-2 mL) of the filtrate was drawn and its final TAN (dissolved phase) and nitrate ( $\text{NO}_3^-$ ) concentrations were measured at EATS using Cd reduction method (EPA Method 351.2, 1979). Even though no nitrification was expected because the samples had been dried at 70 C for 16 h), nitrate concentration was measured to confirm that the nitrification did not occur during the experiment.

Based on literature review (e.g., Witter and Kirchman, 1989), mass of ammonium adsorbed by the sample was calculated from the reduction of ammonium concentration

between the initial and equilibrium solutions. Mass balance, taking into account the concentrations and volume of liquid (50 mL, including buffer solution) and mass of litter or cake was used to calculate the adsorbed ammonium concentration.

Reece et al. (1980) reported that at pH below 7, 99.9% of the TAN in solution was in the  $\text{NH}_4^+$  form. Therefore, ammonia concentration was ignored in the mass balance (eq. [4.14]).

$$\text{TAN}_{\text{adsorbed}} = \text{TAN}_{\text{background}} + \text{TAN}_{\text{added}} - \text{TAN}_{\text{dissolved}} \quad [4.14]$$

In equation [4.14],  $\text{TAN}_{\text{adsorbed}}$  = the mass of ammonium adsorbed on litter or cake, mg;  $\text{TAN}_{\text{background}}$  = the TAN mass in dried litter or cake, mg;  $\text{TAN}_{\text{added}}$  = the mass of  $\text{NH}_4\text{Cl-N}$  added to sample, mg; and  $\text{TAN}_{\text{dissolved}}$  = the mass of TAN in filtrate, mg. Finally,  $\text{TAN}_{\text{adsorbed}}$  was expressed on concentration basis.

### **Statistical analyses**

Six widely-used adsorption isotherms, that included four two-parameter isotherms (-Langmuir, Freundlich, linear, and Temkin ) and two three-parameter isotherms (Redlich and Toth ) were examined for their abilities to model ammonium adsorption onto litter or cake as a function of initial or equilibrium dissolved concentration at pH values of 4, 6, and 7 at room temperature ( $25 \pm 2^\circ\text{C}$ ). Both, linear and non-linear regressions were used to analyze the data, as discussed below. Then ammonium adsorption isotherm that provided the best fit for the broiler litter or cake data was selected.

### *Linear regression*

The isotherm parameters were transformed to their linear forms for the determination of parameters by linear regression. The solid phase adsorbed concentration was plotted against liquid phase equilibrium concentration. The quality of the isotherm fit to the experimental data and hence the isotherm parameters obtained using linear regression were assessed based on the magnitude of the correlation coefficient ( $R^2$ ) with the most appropriate isotherm giving an  $R^2$  value closest to unity.

### *Non-Linear Regression*

Error functions were defined to enable the optimization process to determine and evaluate the fit of the isotherm equation to the experimental data. Five different error functions (discussed below) were examined for each isotherm and the isotherm parameters were determined by minimizing each error function across the liquid-phase concentration range (Kundu and Gupta, 2006; Kumar et al., 2006, 2008; Allen et al., 2004; Alihosseini et al., 2010) using the solver add-in in Microsoft Excel 2007.

(a) Error of the sum of squares (ERRSQ):

This widely used error function is expressed as (Kumar et al., 2006):

$$\text{ERRSQ} = \sum_{i=1}^n (r_{\text{calc}} - r_{\text{meas}})_i^2 \quad [4.15]$$

where n: number of samples;  $r_{\text{calc}}$ : equilibrium concentration of ammonium calculated from the applied model, mg/kg; and  $r_{\text{meas}}$ : equilibrium concentration of ammonium adsorbed from experiment, mg/kg. This error function has one major drawback: the calculated isotherm parameters provide a better fit at the higher end of the liquid-phase concentration range (Kumar et al., 2006). This is because as the concentration increases, the magnitude of the errors also increases, which may result in increased square of the errors.

(b) Sum of square of the average squares of the errors (ERAV):

This error function (eq. [4.16]) minimizes the fractional error distribution across the entire concentration range. If model outputs are close to the experimental data, ERAV will be a small number (Kundu and Gupta, 2006).

$$\text{ERAV} = \left[ \frac{1}{n} \sum_{i=1}^n (r_{\text{calc}} - r_{\text{meas}})^2 \right]^{1/2} \quad [4.16]$$

(c) Hybrid fraction error function (HYBRID):

This error function (eq. [4.17]) was developed in order to improve the fit of the ERRSQ method at low concentration values. In this method, each ERRSQ value is divided by the measured adsorbed concentration (Kundu and Gupta, 2006). The term n-p in the denominator of eq. [4.17] is degrees of freedom for the system, where n is the number of data points and p the number of unknown parameters in the isotherm.

$$\text{HYBRYID} = \frac{100}{n-p} \sum_{i=1}^n \left[ \frac{(r_{\text{meas}} - r_{\text{calc}})^2}{r_{\text{meas}}} \right] \quad [4.17]$$

(d) Marquardt's percent standard deviation (MPSD):

This error function is similar to a geometric mean error distribution which has been modified to allow for the number of degrees of freedom of the system (Alihosseini et al., 2010).

$$\text{MPSD} = 100 \left( \sqrt{\frac{1}{n-p} \sum_{i=1}^n \left[ \frac{(r_{\text{meas}} - r_{\text{calc}})^2}{r_{\text{meas}}} \right]} \right) \quad [4.18]$$

(e) Sum of the absolute errors (EABS):

In this error function (eq. [4.19]) the approach is similar to the ERRSQ method. Isotherm parameters determined using this method provide a better fit as the magnitude of the errors increase biasing the fit toward at high concentration data (Kumar et al., 2006).

$$\text{EABS} = \sum_{i=1}^n |r_{\text{calc}} - r_{\text{meas}}| \quad [4.19]$$

Since the application of these five different error functions will produce five sets of isotherm parameters, it is difficult to identify an overall optimum parameter set. Therefore, to perform a meaningful comparison between the parameter sets, for each parameter set for each isotherm a procedure of normalizing and summing the error results was adopted resulting in ‘sum of the normalized errors (SNE)’ (Kundu and Gupta, 2006). The formula used to calculate SNE is shown in Results and Discussion. This method allows a direct comparison of the errors and hence identifies the isotherm parameters that will provide the closest fit to the measured data (Kundu and Gupta, 2006). After calculating the error function for each isotherm, if the values of parameters obtained by linear regression and non-linear regression are similar, it can be inferred that the isotherm gives a reasonable approximation to the optimum parameters (Kundu and Gupta, 2006, Kumar et al., 2006, Alihosseini et al., 2010).



### **Ammonia adsorption**

Oven-dried litter (see properties in Table 4-1) was used in the ammonia adsorption experiment. Before conducting the experiment, the broiler litter was removed from the freezer and brought to room temperature by placing on the table for 30 min. Ammonia adsorption on broiler litter was evaluated at five different moisture contents (dry basis), namely, 0%, 15%, 25%, 35%, 45%, and 55% at room temperature.

An air-tight plastic container (Make: Lock & Lock; dimensionless: 45 cm L×29 cm W× 23.5 cm; Volume of 20.8 L) was used. The container had three ports, one for adding the ammonia source, the second for drawing out the air to sample for ammonia concentration, and the third for returning the sampled air into the container for maintaining neutral pressure (Fig. 4-1).

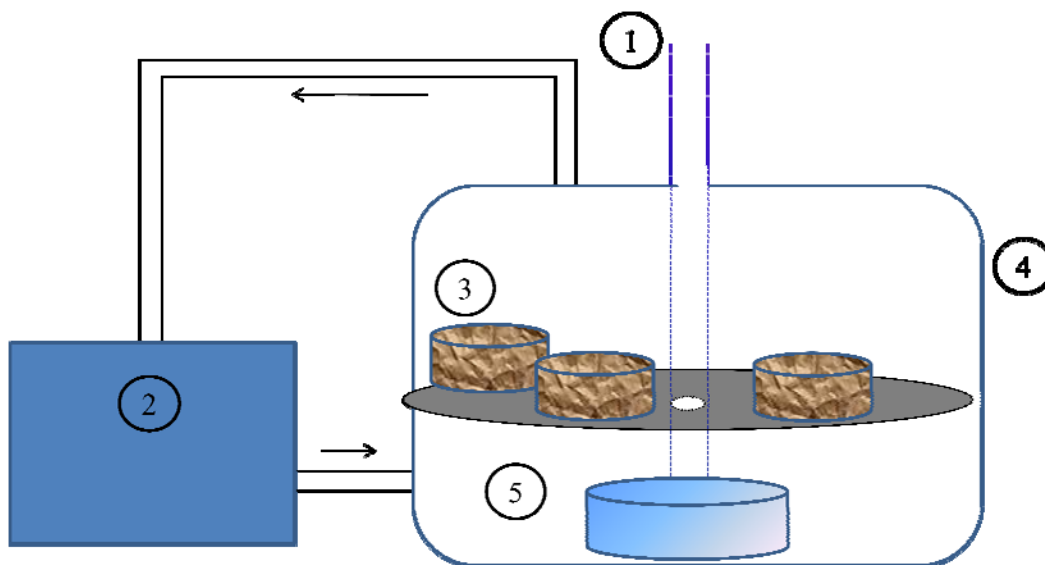


Figure 4-1 Setup for ammonia adsorption measurement where (1)  $\text{NH}_4\text{Cl}_{(\text{aq})}$  added, (2) photoacoustic sensor, (3) litter in petri dishes, (4) air-tight plastic container, and (5) NaOH solution.

Dry (0 % moisture content) or moistened litter (10 g oven-dry litter plus DDW) samples were placed in petri dishes (15 cm diameter) in triplicate (Figure 4-1). For example, whereas for the 0% moisture content, only 10 g of dry litter was used, for 25 % moisture content, 10 g of dried litter was mixed with 2.5 g DDW. The litter was spread to a height of ~ 2 mm in the petri dish to maximize litter exposure to ammonia and minimize pores within the litter layer. Three litter samples were elevated above the glass jar (6.3 cm diameter and 8.5 cm height) (shown as part # 5 in Figure 4-1) containing 200 mL of 8M NaOH. The internal surface of the container and petri dishes were passivated by wiping with 2M NaOH solution to prevent ammonia adsorption.

At the start of each run (for a particular moisture content), following Pagans et al. (2006), to achieve equilibrium and maximum adsorption, adequate volume of 8% (w/v)  $\text{NH}_4\text{Cl}$  was added to the  $\text{NaOH}$  solution in the glass jar (Figure 4-1) to produce  $\sim 480 \text{ mg/m}^3$  of ammonia in the headspace. A photoacoustic spectrophotometer (Make: LumaSense Technologies Inc., Ballerup, Denmark, Model: INNOVA, Model: 1421, Detection limit for ammonia: 0.2 ppm at  $20^\circ\text{C}$  and 1 atmosphere of pressure, Dynamic range: 4 orders of magnitude) was used to monitor ammonia concentration.

The closed system was operated in a fume hood and air from inside was transported to the INNOVA 1421 for sampling and recirculated back into the container. Ammonia concentrations were sampled every minute and the data were stored in the INNOVA 1421. The experiment continued until ammonia concentration in the chamber reached  $480 \pm 24 \text{ mg/m}^3$  ( $691.5 \pm 34.5 \text{ ppm}$ ) and remained stable for 30 min indicating that equilibrium had been reached between the adsorbed and/or dissolved phases on the one hand and the gas phase on the other hand.

At the end of the run, 10 mL of deionized, distilled water and 20 mL of 3M  $\text{KCl}$  solution (Kithome et al. 1999a, b) was added to the litter in the petri dish to prevent desorption of ammonia. Thereafter, the pH of the resulting slurry was measured with a pH electrode (Make: Fisher Scientific, Model: pH/ATC electrode, Range: 0 to 14). The slurry was transferred to a polycarbonate flask, ensuring that no litter was left in the petri dish. The three flasks for a particular moisture content were placed on a shaker for 1 h and then filtered

through separate membrane filters (Particle retention: 20-25  $\mu\text{m}$ ). A 5 mL aliquot of the filtrate was drawn, diluted five volumes, and analyzed for TAN in the EAL.

Masses of adsorbed and dissolved ammonia were calculated by N mass balance, dissociation constant ( $K_d = 1.02 \times 10^{-10}$ ) and the ammonium adsorption isotherm. The method of calculation was different for the oven dry litter (0% moisture content) vs. moist litter as discussed below.

(1) Oven-dry litter (0% moisture content):

When there is no moisture, ammonia is held on the solid litter surface only through adsorption. The N mass balance (eq. [4.20]) was used to calculate the adsorbed mass of ammonia on oven-dry broiler litter. It was assumed that all of the  $\text{NH}_4\text{Cl}$  dissociated into ammonia and volatilized due to the high pH of NaOH. The pH of the NaOH- $\text{NH}_4\text{Cl}$  solution (used to produce ammonia) was 14.85 at equilibrium (calculated using the charge balance equation). Since at a pH of 14.85,  $\frac{\text{NH}_3(\text{aq})}{\text{NH}_4^+(\text{aq})}$  is 358084, it was assumed that the residual  $\text{NH}_4\text{Cl}$  in the NaOH jar could be neglected; this assumption was also applied to the N mass balance performed using moist litter (below).

$$\text{NH}_3 - \text{N}_{\text{ads}} = (\text{NH}_3 - \text{N}_{\text{add}}) + \text{TAN}_{\text{back}} - \text{TAN}_{\text{meas}} - (\text{NH}_3 - \text{N}_{\text{head}}) \quad [4.20]$$

In eq. [4.20],  $\text{NH}_3 - \text{N}_{\text{ads}}$ =ammonia-N adsorbed on litter, mg;  $\text{NH}_3 - \text{N}_{\text{add}}$ = ammonia-N generated using  $\text{NH}_4\text{Cl}_{(\text{aq})}$ , mg;  $\text{TAN}_{\text{back}}$ = TAN in dried litter, mg;  $\text{TAN}_{\text{meas}}$ = TAN concentration measured in filtrate, mg; and  $\text{NH}_3 - \text{N}_{\text{head}}$ =ammonia-N concentration in headspace at equilibrium, mg. The headspace (or net) volume occupied by the air-ammonia

mixture was obtained by subtracting the volumes of the petri dishes, the NaOH jars, and three capped jars (for supporting the petri dishes) from the total internal volume of the container (16.4 L).

(2) Moist litter (15%-55% moisture content):

If moisture is present in the litter, some ammonia gas will dissolve in the liquid phase and form ammonium while a fraction of the remaining ammonia will adsorb to the solid phase; some ammonia may also adsorb on the surface of water molecules. A fraction of dissolved ammonium will adsorb onto broiler litter. Therefore, when litter is moist, in addition to ammonia adsorption, ammonia absorption, ammonia-ammonium equilibrium, and ammonium solid-liquid partitioning should be considered. Equation [4.21] shows the mass balance of N species in the whole system.

$$\text{NH}_3 - \text{N}_{\text{ads}} = (\text{NH}_3 - \text{N}_{\text{add}}) + \text{TAN}_{\text{back}} - (\text{NH}_3 - \text{N}_{\text{head}}) - (\text{NH}_4^+ - \text{N}_{\text{aq}}) - (\text{NH}_4^+ - \text{N}_{\text{ads}}) - (\text{NH}_3 - \text{N}_{\text{aq}}) \quad [4.21]$$

In eq. [4.21],  $\text{NH}_3 - \text{N}_{\text{ads}}$ =ammonia-N adsorbed on litter, mg;  $\text{NH}_3 - \text{N}_{\text{add}}$ = ammonia generated using  $\text{NH}_4\text{Cl}$ , mg;  $\text{TAN}_{\text{back}}$ = background TAN in dried litter, mg;  $\text{NH}_3 - \text{N}_{\text{head}}$ =ammonia-N concentration in headspace at equilibrium, mg;  $\text{NH}_4^+ - \text{N}_{\text{aq}}$ = ammonium-N concentration in dissolved phase, mg;  $\text{NH}_4^+ - \text{N}_{\text{ad}}$ = ammonium-N adsorbed onto litter, mg; and  $\text{NH}_3 - \text{N}_{\text{aq}}$ =ammonia-N concentration in dissolved phase, mg. There were two forms of inorganic N ions ( $\text{TAN}_{\text{meas}}$ ) in the liquid phase,  $\text{NH}_4^+ - \text{N}_{\text{aq}}$  and  $\text{NH}_3 - \text{N}_{\text{aq}}$  shown in eq. [4.22] in concentration form; their concentrations were not separately measured but estimated as shown in eq. [4.23] & [4.24] (Snoeyink and Jenkins, 1982).

$$[\text{TAN}_{\text{meas}}] = [\text{NH}_3\text{-N}]_{(\text{aq})} + [\text{NH}_4^+\text{-N}]_{(\text{aq})} \quad [4.22]$$

$$[\text{NH}_3\text{-N}] = \frac{K_d}{[\text{H}^+] + K_d} \times [\text{TAN}_{\text{meas}}] \quad [4.23]$$

$$[\text{NH}_4^+\text{-N}] = \frac{[\text{H}^+]}{[\text{H}^+] + K_d} \times [\text{TAN}_{\text{meas}}] \quad [4.24]$$

In equations [4.22], [4.23], and [4.24],  $[\text{TAN}_{\text{meas}}]$  = TAN concentration measured in liquid phase, M;  $[\text{NH}_3\text{-N}]$  = ammonia-N concentration in liquid phase, M;  $[\text{NH}_4^+\text{-N}]$  = ammonium-N concentration in liquid phase, M;  $[\text{H}^+]$  = hydrogen ion concentration, M; and  $K_d$  = dissociation constant,  $1.02 \times 10^{-10}$  at a temperature of 25°C. While  $K_d$  for ammonium is  $10^{-9.3}$  at 25°C in aqueous solution, in litter it was measured to be  $1.02 \times 10^{-10}$ , 20% of  $K_d$  in aqueous solution in Chapter 3.

The Langmuir adsorption isotherm was applied to eq. [4.21] to estimate  $\text{NH}_4^+ - \text{N}_{\text{ads}}$  from  $\text{NH}_4^+ - \text{N}_{\text{aq}}$  using equations [4.3], [4.23], and [4.24] as shown in eq. [4.25]. As discussed later, while the Temkin isotherm provided the best fit of ammonium adsorption on broiler litter at pH 7 for equilibrium concentrations ranging from 750 mg/L to 1200 mg/L, the equilibrium concentrations of ammonium in this experiment ranged between 1000 mg/L to 2500 mg/L, which required application of the Langmuir isotherm.

$$\text{NH}_3\text{-N}_{\text{ads}} = \text{NH}_3\text{-N}_{\text{add}} + \text{TAN}_{\text{back}} - \text{NH}_3\text{-N}_{\text{head}} - \left( \frac{[\text{H}^+]}{[\text{H}^+] + K_d} \times [\text{TAN}_{\text{meas}}] \times V \times m_w \right) -$$

$$\left[ \frac{Q_0 b \left( \frac{[\text{H}^+]}{[\text{H}^+] + K_d} \times [\text{TAN}_{\text{meas}}] \times m_w \right)}{1 + b \left( \frac{[\text{H}^+]}{[\text{H}^+] + K_d} \times [\text{TAN}_{\text{meas}}] \times m_w \right)} \right] \times m - \left( \frac{K_d}{[\text{H}^+] + K_d} \times [\text{TAN}_{\text{meas}}] \times V \times m_w \right) [4.25]$$

In equation [4.25],  $V$  = total volume of solution, L;  $m$  = mass of litter sample, kg; and  $m_w$  = molecular weight of N, 14,000 mg/mol.

Ammonia/um absorption and adsorption concentrations were plotted against moisture content. Ammonia adsorbed phase concentration was also plotted against moisture content.

## **Results and Discussion**

The results of the ammonium and ammonia sorption studies are presented and discussed in this chapter. In the ammonium adsorption study on litter and cake, six isotherms were evaluated using both linear and non-linear regressions to calculate parameters at different pH values. The parameters of the different adsorption isotherms were also compared. In the ammonia adsorption study, adsorbed and absorbed concentrations of ammonia in litter at different moisture contents were calculated and discussed.

### **Ammonium adsorption on broiler litter**

The experimental data were modeled using six adsorption isotherms as shown below. Based on very low nitrate-N plus nitrite-N concentrations ( $0.63 \pm 0.83$  mg/L,  $n=3$ ), it was assumed that nitrification was negligible.

### *Linear regression method*

The linear plot of  $r$  (mg/kg) vs.  $C$  (mg/L) is shown in Figure 4-2 and the linear isotherm parameters  $K_L$  and  $b$  for pH 4, 6 and 7 on litter are presented in Table 4-4. Higher  $R^2$  (0.96 and 0.92) at pH values of 6 and 7 indicated that the linear isotherm provided a good model of the adsorption at those pH values but not as much at pH of 4. Figure 4-2 shows that even when equilibrium TAN concentration increased to 850 mg/L (total TAN concentration of 8,500 mg/kg which was high, though realistic), ammonium desorption occurred at all pH values. The values of  $r$  (mg/kg) below the dashed line in Figure 4-2 indicate desorption; e.g., when  $r$  is 3,500 mg/kg, about ~102 mg/kg of ammonium-N was desorbed given that the background TAN in broiler litter was 3,602 mg/kg (Table 4-1). Background TAN concentration was included in the  $r$  (Fig. 4-2 y-axis) in this study as was also done by Kithome et al. (1999a, b); however, their background concentrations were very low unlike this study. The linear isotherm parameters and  $R^2$  values are presented in Table 4-4.



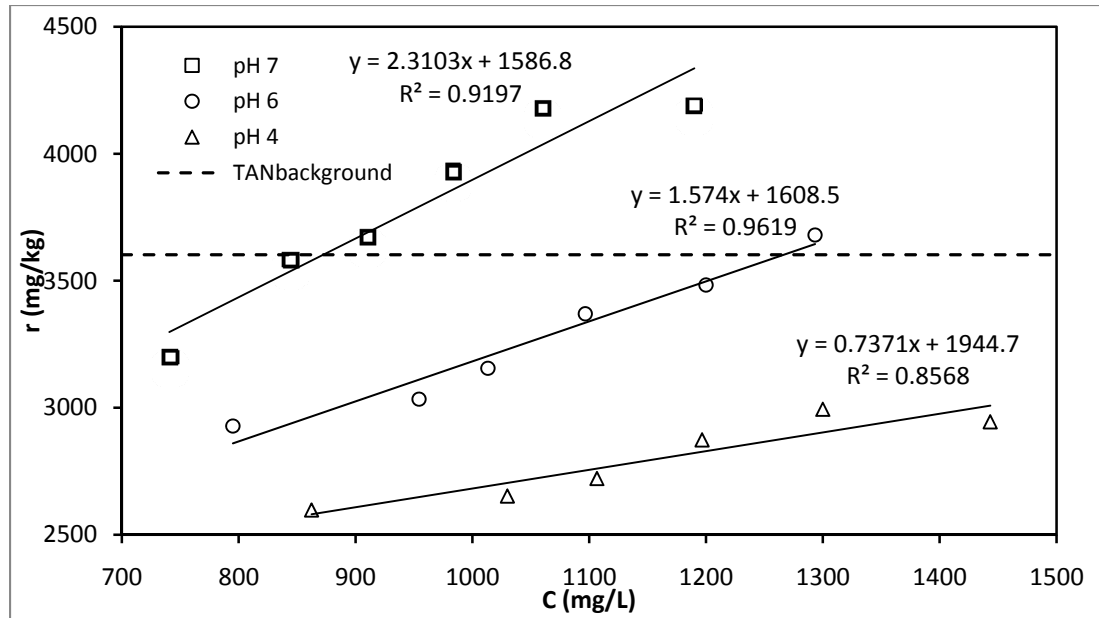


Figure 4-2 Linear isotherms of  $\text{NH}_4^+$  adsorption on broiler litter. The terms are C: equilibrium concentration (mg/L) and r: adsorbed ammonium concentration (mg/kg). If the value of r is below the dashed line, it indicates that desorption has occurred.

Table 4-4. Estimated parameters for linear isotherm (eq. [4.7]) of ammonium adsorption on broiler litter

pH	$K_L$ (L/kg)	b (mg/kg)	$R^2$
4	0.74	1994.7	0.86
6	1.57	1608.5	0.96
7	2.31	1586.8	0.92

Increasing pH resulted in greater  $\text{NH}_4^+$  adsorption on broiler litter (Fig. 4-2). There are two possible explanations for this observation. The first is that the number of hydrogen ion

(H<sup>+</sup>) is greater at lower pH and the size of H<sup>+</sup> ions are smaller than NH<sub>4</sub><sup>+</sup> and can thus, more easily occupy adsorption sites on litter, resulting in NH<sub>4</sub><sup>+</sup> desorption in broiler litter at pH of 4. Second, some carboxyl functional group (R-COO<sup>-</sup>) would be protonated at lower pH, forming R-COOH, which indicates that more hydrogen ions are adsorbed resulting in greater ammonium ions desorption.

Most studies in soil used linear isotherm to fit experimental data only when concentrations were low because linear isotherms are generally applied under low concentration conditions. However, in broiler litter, the linear isotherm modeled NH<sub>4</sub><sup>+</sup> adsorption and desorption on litter well. Mervosh (2003) reported that the linear isotherm adequately described adsorption of two herbicides on soil.

Based on higher R<sup>2</sup>, the Langmuir isotherm fitted the experimental results slightly better than the linear isotherm (Figure 4-3). The Langmuir isotherm parameters Q<sub>0</sub> and b calculated from its linear transformation (eq. [4.4]) are presented in Table 4-5. The NH<sub>4</sub><sup>+</sup> adsorption capacity (Q<sub>0</sub>) of broiler litter, calculated using the Langmuir isotherm, increased with pH (Fig. 4-3).

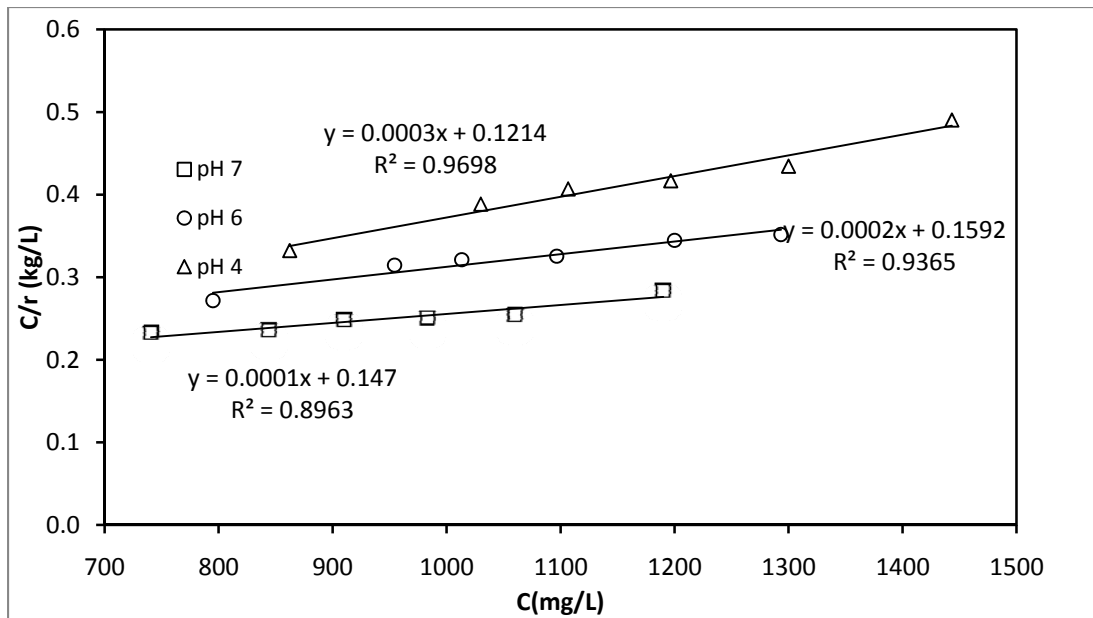


Figure 4-3 Langmuir isotherms of  $\text{NH}_4^+$  adsorption on broiler litter. The terms are C: equilibrium concentration (mg/L) and r: adsorbed or desorbed ammonium concentration (mg/kg).

Table 4-5 Estimated parameters for Langmuir isotherm Eq. [4.3] of ammonium adsorption on broiler litter

pH	$Q_0$ (mg/kg)	b (L/kg)	$R^2$
4	3333	$2.47 \times 10^{-3}$	0.97
6	5000	$1.26 \times 10^{-3}$	0.94
7	10000	$6.80 \times 10^{-4}$	0.90

Kithome et al. (1999a) reported that the  $\text{NH}_4^+$  adsorption capacity of coir was 7,778 mg N/kg at pH of 5 and for zeolite it was 9,600, 12,700, and 14,000 mg N/kg, respectively, at pH of 4, 6, and 7. Kirchmann and Witter (1989) reported that  $\text{NH}_4^+$  adsorption capacity of peat was 23,400 mg/kg at neutral pH. Hence, broiler litter had adsorption capacity of 10000 mg/kg which was lower than that of coir, zeolite, or peat.

The Freundlich isotherm also fitted the experimental data ( $R^2 = 0.87$  to  $0.94$ ) (Fig. 4-4). Although the  $R^2$  values of Freundlich and Langmuir isotherms are close (Fig. 4-3 and 4-4), the logarithmically transformed Freundlich expression is less sensitive to changes in variables; therefore, Langmuir isotherm may provide better results (Kithome et al., 1999a).

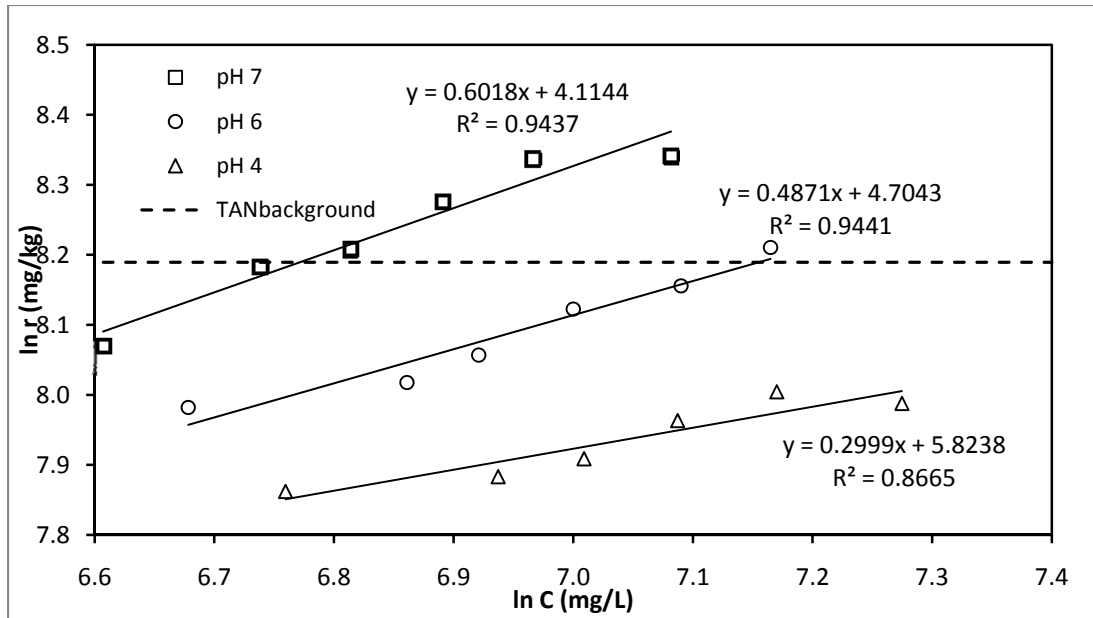


Figure 4-4 Freundlich isotherm of  $\text{NH}_4^+$  adsorption on broiler litter. The terms are C: equilibrium concentration (mg/L) and r: adsorbed or desorbed ammonium concentration (mg/kg).

The Freundlich isotherm constant  $K_f$  and  $n$  calculated from linear transformation (eq. [4.6]) are presented in Table 4-4. The Freundlich parameters  $K_f$  and  $n$  are reasonable compared to other studies (Kithome et al., 1999b; Kirchmann and Witter, 1989). For example,  $K_f$  and  $n$  of  $\text{NH}_4^+$  adsorption are 55 L/kg and 1.5, respectively, for zeolite (Kithome et al., 1999b) and 500.6 L/kg and 2.1, respectively, for coir (Kirchmann and Witter, 1989).

Table 4-6 Estimated parameters for Freundlich isotherm (eq. [4.5]) of ammonium adsorption on broiler litter

pH	$K_f$ (L/kg)	n	$R^2$
4	338.25	3.33	0.87
6	110.42	2.05	0.94
7	61.22	1.66	0.94

The Temkin isotherm also successfully described the experimental data with  $R^2$  values ranging from 0.86 to 0.95 (Fig. 4-5; Table 4-7). Plotting  $r$  (mg/kg) versus  $\ln(C)$  (mg/L) by linear transformation [eq. 4.9] also yielded a straight line (Figure 4-5).

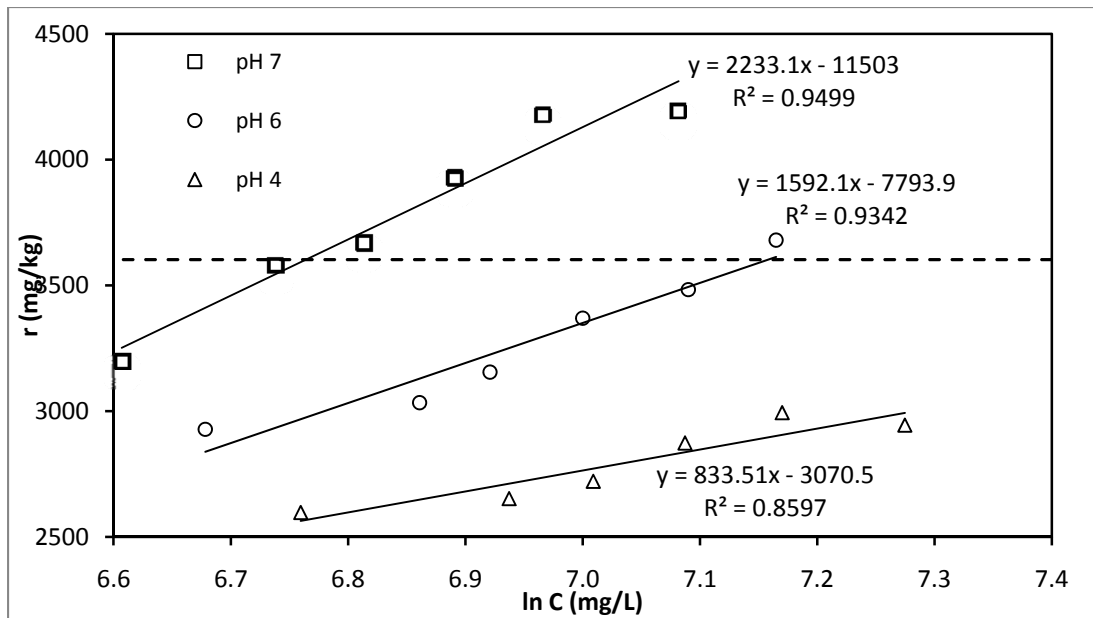


Figure 4-5 Temkin isotherm of  $\text{NH}_4^+$  adsorption on broiler litter. The axis labels include C: equilibrium concentration (mg/L) and r: adsorbed or desorbed ammonium concentration (mg/kg).

Table 4-7 Estimated parameters for Temkin isotherm (eq. [4.8]) of ammonium adsorption on broiler litter.

pH	A (L/kg)	b (J/mol)	R <sup>2</sup>
4	0.025	2.971	0.86
6	0.007	1.555	0.93
7	0.006	1.109	0.95

The Temkin isotherm adsorption energy (b) values in Table 4-7 for all pH values were positive indicating that the reaction was exothermic (Hamdaoui and Naffrechoux, 2007).

The adsorption energy produced at pH 4 was greater than at 6 or 7, meaning that the adsorbed ammonium was more stable at pH 4.

The linear plot of  $C/r$  (kg/L) against  $C^\beta$  (mg/L) <sup>$\beta$</sup>  for the three parameter Redlich-Peterson isotherm is shown in Figure 4-6 and its linear transform (eq. [4.11]) parameters are presented in Table 4-8. Because  $\beta$  was equal to zero at pH of 6,  $C^\beta$  was 1, which resulted in an  $R^2$  of infinity; therefore, the Redlich-Peterson isotherm was not evaluated at pH of 6. The  $\beta$  values in Table 4-8 indicate that the Redlich-Peterson isotherm resembles the Langmuir isotherm at pH of 7 and the Freundlich isotherm at pH 4. The values of  $\beta$  are 0 and 1 at pH 6 and pH 7, respectively; therefore, it would seem that the linear and Langmuir isotherms are appropriate for pH of 6 and 7, respectively.



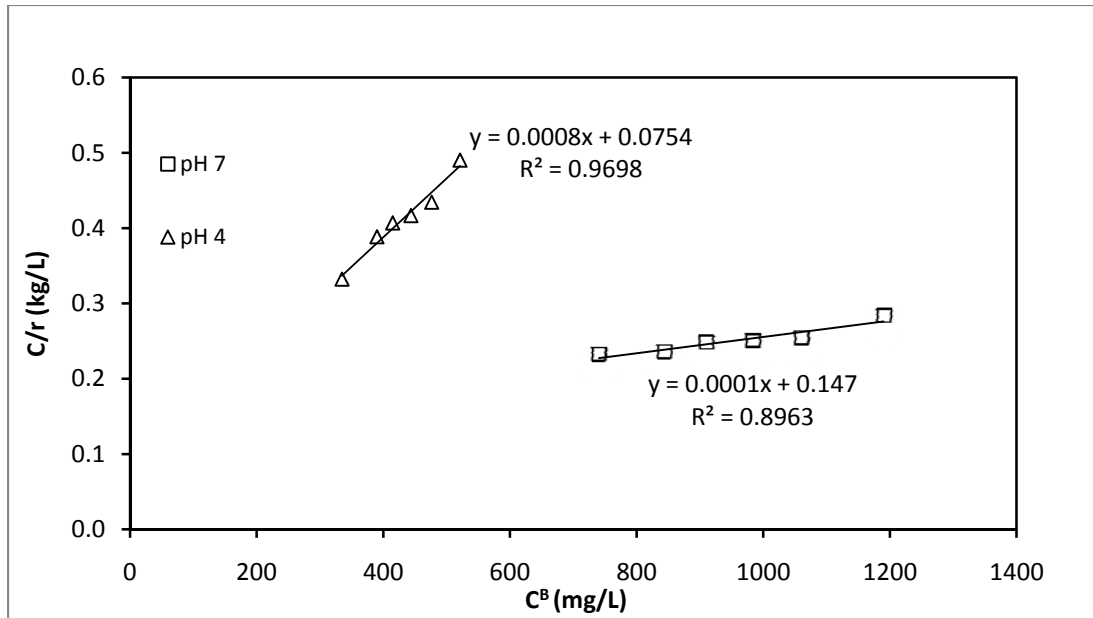


Figure 4-6 Redlich-Peterson isotherm of  $\text{NH}_4^+$  adsorption on broiler litter. The axis labels include C: equilibrium concentration (mg/L), r: adsorbed or desorbed ammonium concentration (mg/kg), and  $\beta$ : a parameter between 0 and 1.

Table 4-8 Estimated parameters for Redlich-Peterson isotherm (eq. [4.10]) of ammonium adsorption on broiler litter

pH	$K_R$	b	$\beta$	$R^2$
4	13.26	$1.06 \times 10^{-2}$	0.86	0.97
6	N/A	N/A	0	N/A
7	6.8	$6.8 \times 10^{-4}$	1.00	0.90

The three-parameter Toth isotherm was also used to model the experimental data and the linear plot of  $\left(\frac{C}{r}\right)^t$  against  $C^t$  is shown in Figure 4-6 and the linear transform parameters

(eq. [4.13]) are presented in Table 4-9. The results show that the isotherm is similar to Langmuir isotherm at pH 4 and 7 ( $t=1$ ). Because  $t = 0$  at pH of 6, the linear isotherm seemed the most appropriate at that pH.

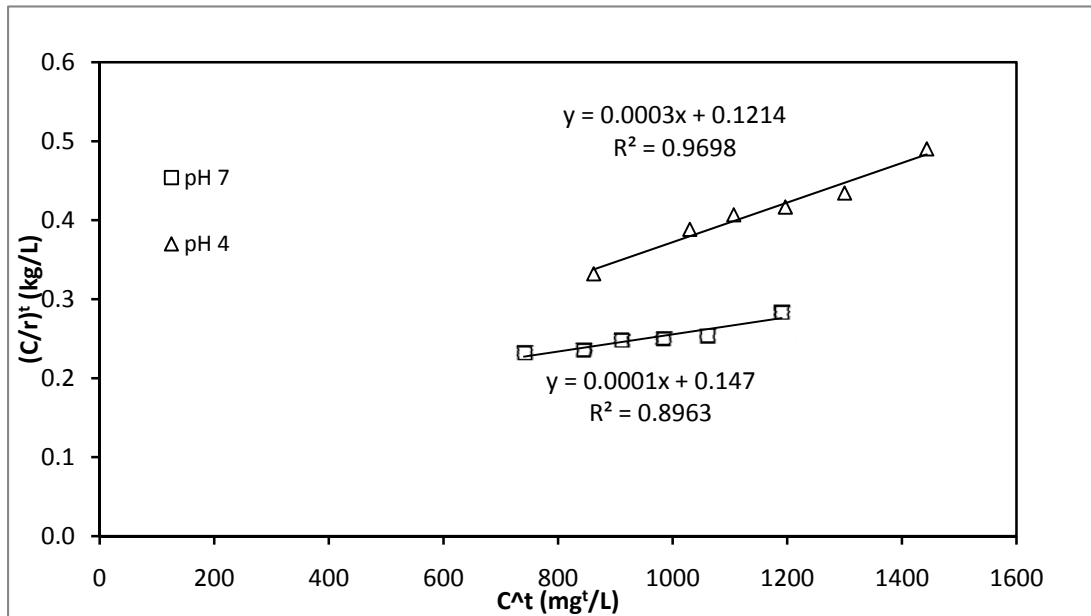


Figure 4-7 Toth isotherm of  $\text{NH}_4^+$  adsorption on broiler litter. The axis labels include C: equilibrium concentration (mg/L), r: adsorbed or desorbed ammonium concentration (mg/kg), and t = the heterogeneity coefficient of the adsorbent, which is between 0 and 1.

Table 4-9 Estimated parameters for Toth isotherm (eq. [4.12]) of ammonium adsorption on broiler litter

pH	$K_t$ (mg/kg)	a (mg/L)	T	$R^2$
4	3333.33	404.67	1.00	0.97
6	N/A	N/A	0	N/A
7	10000	1470	1.00	0.90

In linear regression, the isotherm giving an  $R^2$  value closest to unity is considered to provide the best fit. Thus, Langmuir, Redlich-Peterson and Toth isotherms could be said to have provided the best fit at pH 4 because they all gave the highest and identical  $R^2$  value (0.97). The linear and Temkin isotherms provided the best fits at pH of 6 and 7, respectively.

However, from Figure 4-8, it is clear that the Langmuir isotherm did not fit the experimental data at pH 4 despite the highest  $R^2$ . The linear regression method introduced an offset or drift between the modeled and measured values as shown in Figure 4-8.

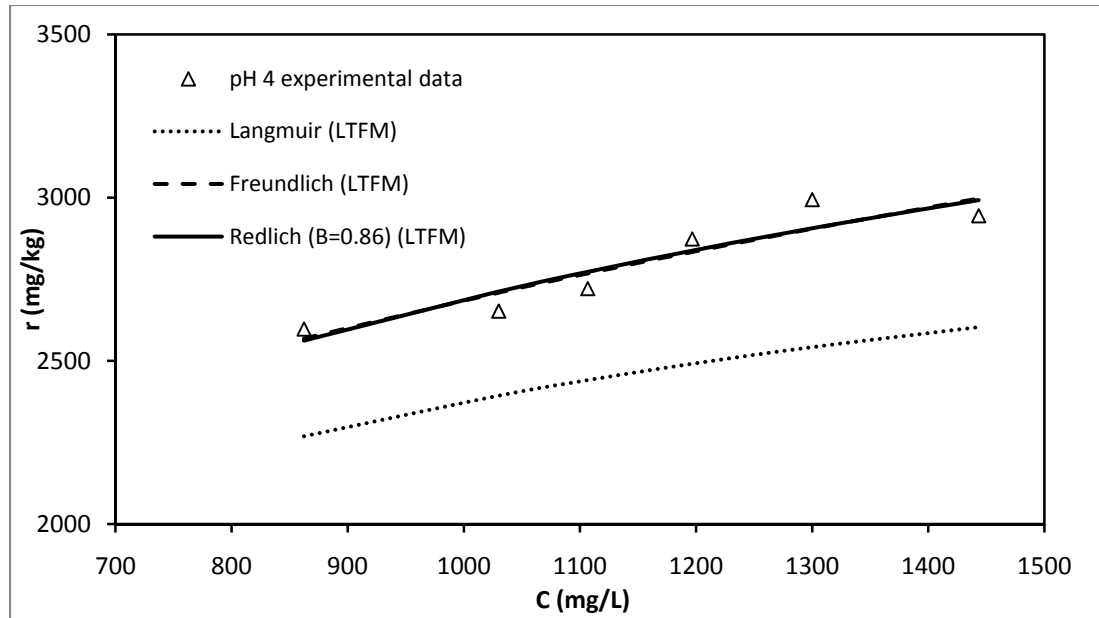


Figure 4-8 Isotherms of  $\text{NH}_4^+$  adsorption on broiler litter using linear regression at pH of 4. The axes are C: equilibrium concentration (mg/L) and r: adsorbed or desorbed ammonium concentration (mg/kg). The Redlich-Peterson and Freundlich isotherm lines are coincident.

In the Redlich-Peterson isotherm, because the value of parameter  $\beta$  was 0.86, it reduced to Freundlich isotherm. . The experimental data were better explained by the Freundlich isotherm than Langmuir isotherm at pH of 4, even though the  $R^2$  for Langmuir isotherm was higher. Due to concerns of such bias inherent in linear regression, the parameter sets for each isotherm were also determined using non-linear regression. Most studies (Kundu and Gupta, 2006, Allen et al., 2004) used non-linear regression to calculate Redlich-Peterson and Toth isotherms to avoid the drift (offset) errors.

### *Non-linear regression method*

In order to analyze the impact of different error functions on the isotherms, and minimize the error between the experimental data and the isotherms, non-linear regression was used. When the parameters obtained by linear and non-linear regressions were similar, it could be inferred that the isotherm simulated partitioning between the solid and liquid phases accurately (Kundu and Gupta, 2006).

The six isotherms parameters for broiler litter at pH of 4 determined by non-linear regression using five error functions (ERRSQ, ERAV, HYBRID, MPSD, EABS) are presented in Table 4-10. The non-linear regression was obtained using the Solver add-in in Microsoft 2007. In Table 4-10, the column headings LTFM, ERRSQ, ERAV, HYBRID, MPSD, and EABS were used to calculate the parameters and the row headings ERRSQ, ERAV, HYBRID, MPSD and EABS were used to evaluate the error based on the obtained parameters (Allen et al., 2004). Take linear isotherm in Table 4-10 as an example. The parameters (shaded)  $K_L$  (0.74) and  $b$  (1994.68) were calculated while minimizing the error function ERRSQ ( $ERRSQ = \sum_{i=1}^n (r_{calc} - r_{meas})_i^2$ ). Those parameters ( $K_L$  and  $b$ ) were then used to calculate the various error functions, e.g., using those parameters in the linear isotherm and comparing the measured and modeled values using the error function HYBRID

(HYBRYID =  $\frac{100}{n-p} \sum_{i=1}^n \left[ \frac{(r_{meas} - r_{calc})^2}{r_{meas}} \right]$ ) yielded 164.71 (Table 4-10).

Table 4-10 Linear and non-linear adsorption isotherm parameters and errors calculated using different error functions for broiler litter at pH of 4.

Linear isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
K <sub>L</sub>	0.74	0.74	0.74	0.74	0.74	0.83
b	1944.70	1944.68	1944.68	1943.70	1943.70	1801.33
R <sup>2</sup>	0.86					
ERRSQ	19025.13	19025.12	19025.12	19032.36	19032.36	27996.13
ERAV	56.31	56.31	56.31	56.32	56.32	68.31
HYBRID	164.72	164.71	164.71	164.65	164.65	244.35
MPSD	128.34	128.34	128.34	128.32	128.32	156.32
EABS	309.38	309.38	309.38	309.36	309.36	330.19
(SNE) <sup>7</sup>	<b>3.936</b>	<b>3.936</b>	<b>3.936</b>	<b>3.936</b>	<b>3.936</b>	5
Langmuir isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
Q <sub>0</sub>	3333.33	3981.89	3980.78	3970.23	3970.22	3970.00
b	2.47E-03	2.08E-03	2.08E-03	2.10E-03	2.10E-03	2.19E-03
R <sup>2</sup>	0.97					
ERRSQ	720520.30	18982.71	18982.66	18993.67	18993.54	25760.03
ERAV	346.54	56.25	56.25	56.26	56.26	65.52
HYBRID	6359.90	167.97	167.96	167.87	167.87	232.80
MPSD	797.49	129.60	129.60	129.56	129.56	152.58
EABS	2043.57	320.04	319.93	318.99	318.99	316.23
(SNE) <sup>7</sup>	5	0.534	0.534	<b>0.533</b>	<b>0.533</b>	0.608

Table 4-10 continued

Freundlich isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
K <sub>f</sub>	338.25	337.05	337.27	338.21	345.51	345.51
n	3.33	3.33	3.33	3.33	3.33	3.40
R <sup>2</sup>	0.87					
ERRSQ	18520.44	18519.62	18519.61	18527.04	18526.95	31520.61
ERAV	55.56	55.56	55.56	55.57	55.57	72.48
HYBRID	161.93	161.97	161.97	161.90	161.90	271.85
MPSD	127.25	127.27	127.27	127.24	127.24	164.88
EABS	313.94	314.24	314.19	313.88	313.93	308.30
(SNE) <sup>7</sup>	3.721	3.722	3.721	<b>3.720</b>	3.721	4.981
Temkin isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
b	2.97	2.97	2.97	2.98	2.98	3.24
A	2.51E-02	2.51E-02	2.51E-02	2.55E-02	2.55E-02	3.28E-02
R <sup>2</sup>	0.86					
ERRSQ	18637.37	18637.35	18637.36	18646.71	18646.71	25606.43
ERAV	55.73	55.73	55.73	55.75	55.75	65.33
HYBRID	163.80	163.80	163.80	163.71	163.71	219.99
MPSD	127.98	127.98	127.98	127.95	127.95	148.32
EABS	316.58	316.60	316.64	315.85	315.85	302.29
(SNE) <sup>7</sup>	4.188	4.188	4.188	<b>4.186</b>	<b>4.186</b>	4.955

Table 4-10 continued

Redlich-Peterson isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
K <sub>R</sub>	13.26	13.38	14.54	13.95	13.07	17.45
b	1.06E-02	1.05E-02	1.30E-02	1.17E-02	9.85E-03	5.37E-02
β	0.86	0.86	0.84	0.85	0.67	0.67
R <sup>2</sup>	0.97					
ERRSQ	37358.68	18680.93	18656.98	18676.40	18696.50	38619.85
ERAV	78.91	55.80	55.76	55.79	55.82	80.23
HYBRID	324.16	164.39	164.09	164.16	164.42	350.15
MPSD	180.05	128.21	128.10	128.12	128.23	187.12
EABS	347.15	317.58	317.37	316.93	317.19	378.81
(SNE) <sup>7</sup>	4.756	3.172	<b>3.169</b>	<b>3.169</b>	3.172	5.000
Toth isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
t	1.00	1.00	0.90	0.79	0.80	0.81
K <sub>T</sub>	3333.33	3333.33	4150.11	4365.75	4323.68	4323.00
a	404.67	404.67	230.32	110.15	120.39	120.00
R <sup>2</sup>	0.97					
ERRSQ	720520.301	720530.59	18888.89	18807.276	18829.5332	25972.17
ERAV	346.54	346.54	56.11	55.99	56.02	65.79
HYBRID	6359.90	6359.99	166.92	165.96	166.02	234.39
MPSD	797.49	797.50	129.20	128.83	128.85	153.10
EABS	2043.57	2043.58	319.28	318.07	317.51	316.29
(SNE) <sup>7</sup>	4.999	5.000	0.533	0.531	<b>0.530</b>	0.609



<sup>1</sup>LTFM: Linear transform

<sup>2</sup>ERRSQ: Error of the sum of squares, (eq. [4.15])

<sup>3</sup>ERAV: Sum of square of the average squares of the errors, (eq. [4.16])

<sup>4</sup>HYBRID: Hybrid fraction error function, (eq. [4.17])

<sup>5</sup>MPSD: Marquardt's percent standard deviation, (eq. [4.18])

<sup>6</sup>EABS: Sum of the absolute errors, (eq. [4.19])

<sup>7</sup>Sum of normalized error

After calculating all error values, the normalized error for each error function was obtained by dividing that value by the maximum absolute error value in that row (from ERRSQ to EABS); thereafter, sum of normalized error (SNE) was obtained by adding up all the normalized error values in that column (Kumar et al., 2006). For example, the error (19025.12, shaded in Table 4-10) obtained using the error function ERRSQ obtained when ERRSQ was used to calculate the linear isotherm parameters was normalized by dividing it by the maximum absolute error that row (i.e., 27996.13 obtained using EABS, Table 4-10). Thereafter, the SNE value of 3.936 in ERRSQ (shown in shaded) was calculated as:  $\left(\frac{19025.12}{27996.13} + \frac{56.31}{68.31} + \frac{164.71}{244.35} + \frac{128.34}{156.32} + \frac{309.38}{330.19} = 3.936\right)$ . The smallest SNE value (shown in bold) among all error functions indicated that the parameters calculated by this error function provide the best results (Kumar et al., 2006).

From Table 4-10, it is clear that the parameters for the Langmuir, Redlich-Peterson, and Toth isotherms obtained by non-linear regression are not similar to one-another and have no similarity with the linear transform (LTFM) values. Therefore, these three isotherms do not adequately describe ammonium adsorption. This is why several research reports (e.g.,

Kumar et al., 2006) suggested that non-linear regression was better for obtaining isotherm parameters because linearization of non-linear experimental data resulted in the drift (offset) error.

For the linear and Temkin isotherms, the parameters obtained by all error functions, except EABS were close to the LTFM values and both isotherms provided very good fit of ammonium adsorption on broiler litter. For linear isotherm in Table 4-10, all the error function except EABS provided the lowest SNE and identical value. For the Temkin model, the HYBRID and the MPSD methods yielded the lowest SNE.

The parameters of the Freundlich isotherm obtained by non-linear regression (particularly, with HYBRID) are quite similar to the linear transform values (Table 4-10). Thus, it can be inferred that the Freundlich isotherm modeled ammonium adsorption at pH of 4 very well. Based on the error values, the quality of the isotherm fit can be arranged in order of increasing error values, and the three best isotherms were Freundlich<Temkin<linear. Hence, the Freundlich isotherm provided the best fit of ammonium adsorption and desorption on broiler litter at pH of 4.

The parameters for the six isotherms of ammonium adsorption from broiler litter at pH of 6 were determined using non-linear regression with the five error functions (Table 4-11) identical to pH of 4 presented in Table 4-10. Since the parameter  $\beta$  for Redlich-Peterson and parameter  $t$  for Toth isotherm approach 0, both isotherms approximate the linear isotherm at pH of 6. Since the parameters for the Redlich-Peterson and Toth isotherms obtained by error functions are not similar to one-another, these isotherms do not adequately describe ammonium adsorption on litter at pH of 6.

Table 4-11 Linear and non-linear isotherm parameters and errors calculating using different error functions for broiler litter at pH of 6

Linear isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
K <sub>L</sub>	1.57	1.57	1.57	1.56	1.56	1.58
b	1608.50	1608.53	1608.50	1622.95	1622.95	1587.20
R <sup>2</sup>	0.96					
ERRSQ	15627.78	15580.04	15580.04	15617.28	15617.27	16930.15
ERAV	51.04	50.96	50.96	51.02	51.02	53.12
HYBRID	126.04	125.94	125.94	125.67	125.67	135.72
MPSD	112.27	112.22	112.22	112.10	112.10	116.50
EABS	278.25	278.20	278.20	278.45	278.45	278.10
(SNE) <sup>7</sup>	4.775	<b>4.769</b>	4.770	4.771	4.771	4.999
Langmuir isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
Q <sub>0</sub>	5000.00	6520.70	6546.58	6420.11	6432.61	5001.99
b	1.26E-03	9.65E-04	9.57E-04	9.95E-04	9.91E-04	1.78E-03
R <sup>2</sup>	0.94					
ERRSQ	1198654.61	26803.64	26810.87	26899.36	26874.31	64721.42
ERAV	446.96	66.84	66.85	66.96	66.93	103.86
HYBRID	8971.38	216.42	216.82	215.68	215.69	466.86
MPSD	947.17	147.11	147.25	146.86	146.86	216.07
EABS	2627.20	350.95	350.83	351.39	351.34	510.87
(SNE) <sup>7</sup>	5.000	<b>0.484</b>	0.485	0.485	0.485	0.761

Table 4-11 continued

Freundlich isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
K <sub>f</sub>	110.42	99.61	99.63	103.83	110.00	110.00
n	2.05	1.99	1.99	2.02	2.02	2.05
R <sup>2</sup>	0.94					
ERRSQ	20915.07	20597.07	20597.04	20649.33	20651.85	21317.42
ERAV	59.04	58.59	58.59	58.66	58.67	59.61
HYBRID	166.86	166.55	166.55	166.04	166.04	168.95
MPSD	129.17	129.05	129.05	128.86	128.85	129.98
EABS	315.42	314.62	314.62	314.95	314.95	315.38
(SNE) <sup>7</sup>	4.953	<b>4.925</b>	<b>4.925</b>	<b>4.925</b>	4.926	4.999
Temkin isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
b	1.56	1.55	1.55	1.58	1.58	1.52
A	7.48E-03	7.47E-03	7.47E-03	7.71E-03	7.71E-03	7.02E-03
R <sup>2</sup>	0.93					
ERRSQ	26908.77	26908.54	26908.55	27006.54	27008.14	28810.62
ERAV	66.97	66.97	66.97	67.09	67.09	69.29
HYBRID	215.71	215.75	215.75	214.95	214.95	231.71
MPSD	146.87	146.88	146.88	146.61	146.61	152.22
EABS	351.24	351.27	351.27	350.57	350.56	352.45
(SNE) <sup>7</sup>	4.793	4.793	4.793	<b>4.791</b>	<b>4.791</b>	5

Table 4-11 continued

Redlich-Peterson isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
K <sub>R</sub>		10.52	81.12	57.44	51.08	16.08
b		0.02	0.68	0.43	0.37	0.04
β		0.71	0.52	0.53	0.66	0.66
ERRSQ		23128.25	20827.19	20996.17	21038.65	23787.28
ERAV		62.09	58.92	59.16	59.22	62.96
HYBRID		186.75	168.33	168.76	169.13	186.79
MPSD		136.66	129.74	129.91	130.05	136.67
EABS		330.34	316.13	317.14	317.44	326.45
(SNE) <sup>7</sup>	N/A	4.958	<b>4.618</b>	4.636	4.643	4.988
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
t		0.58	0.53	0.53	0.44	0.48
K <sub>T</sub>		11117.24	11999.55	12000.00	14999.75	13999.94
a		57.10	39.16	38.64	20.92	38.64
ERRSQ		24135.36	23745.42	23744.15	23329.47	25135.55
ERAV		63.42	62.91	62.91	62.36	64.72
HYBRID		196.17	191.50	191.39	187.00	202.19
MPSD		140.06	138.38	138.34	136.75	142.19
EABS		335.23	334.04	334.04	331.29	331.73
(SNE) <sup>7</sup>	N/A	4.895	4.833	4.832	<b>4.766</b>	4.989

<sup>1</sup>LTFM: Linear transform

<sup>2</sup>ERRSQ: Error of the sum of squares, (eq. [4.15])

<sup>3</sup>ERAV: Sum of square of the average squares of the errors, (eq. [4.16])

<sup>4</sup>HYBRID: Hybrid fraction error function, (eq. [4.17])

<sup>5</sup>MPSD: Marquardt's percent standard deviation, (eq. [4.18])

<sup>6</sup>EABS: Sum of the absolute errors, (eq. [4.19])

<sup>7</sup>Sum of normalized error

The parameters of the Langmuir isotherm obtained by LTFM and those from error functions are very different at pH of 6 (Table 4-11) as with pH of 4 (Table 4-10), and thus, Langmuir isotherm also does not fit the adsorption data. The parameters of linear, Freundlich, and Temkin isotherms calculated using the error functions, ERRSQ, ERAV and HYBRID produced good fits for the adsorption data. Based on the error values, the quality of the isotherm fit can be arranged in order of increasing error values as: linear < Freundlich < Temkin. Therefore, the linear isotherm provided the best fit for ammonium adsorption and desorption on broiler litter at pH of 6.

Following the same procedures used for pH of 4 and 6 described earlier, the parameters for the six isotherms for ammonium adsorption on broiler litter at pH of 7 was determined using non-linear regression with the five error functions (Table 4-12). The parameter sets for the Redlich-Peterson isotherm calculated using the different error functions are different from one-another as well as from LTFM (Table 4-12). However, the parameter sets for Toth isotherm calculated using the different error functions are quite similar to one-another as well as to LTFM; further, the  $t$  values of the Toth isotherm calculated using the error functions are close to unity (Table 4-12), which indicates that the Toth isotherm may be similar to Langmuir or Freundlich isotherms for this pH. The parameter sets of Freundlich isotherm obtained by error functions for pH of 7 are not similar

to one-another or to LTFM except ERRSQ and ERAV that are very similar to one-another (Table 4-12).

Table 4-12 Linear and non-linear isotherm parameters and errors calculated using different error functions for broiler litter at pH 7

Linear isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
K <sub>L</sub>	2.32	2.32	2.32	2.36	2.36	2.11
b	1577.50	1577.47	1577.45	1536.87	1536.86	1800.18
R <sup>2</sup>	0.92					
ERRSQ	57660.90	57660.89	57660.89	57899.67	57899.85	66386.22
ERAV	98.03	98.03	98.03	98.23	98.23	105.19
HYBRID	366.28	366.27	366.26	364.55	364.55	450.26
MPSD	191.38	191.38	191.38	190.93	190.93	212.19
EABS	517.43	517.43	517.43	515.57	515.57	527.20
(SNE) <sup>7</sup>	4.497	4.497	4.497	<b>4.493</b>	<b>4.493</b>	5.000
Langmuir isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
Q <sub>0</sub>	10000.00	9160.29	9160.37	9233.86	9237.12	9237.12
b	6.80E-04	7.48E-04	7.48E-04	7.37E-04	7.36E-04	7.51E-04
R <sup>2</sup>	0.90					
ERRSQ	133025.64	40052.82	40050.85	40159.97	40152.29	49997.61
ERAV	148.90	81.70	81.70	81.81	81.80	91.28
HYBRID	861.49	250.71	250.80	250.47	250.46	322.37
MPSD	293.51	158.34	158.37	158.26	158.26	179.55

Table 4-12 continued

EABS	732.34	437.10	437.08	436.74	436.71	435.19
(SNE)	5.000	<b>2.277</b>	<b>2.277</b>	2.278	<b>2.277</b>	2.569
Freundlich isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
K <sub>f</sub>	61.22	70.30	70.33	66.13	341.27	341.27
n	1.66	1.72	1.72	1.69	1.69	2.82
R <sup>2</sup>	0.94					
ERRSQ	49013.53	48163.07	48163.11	48353.61	48352.30	183352.70
ERAV	90.38	89.59	89.59	89.77	89.77	174.81
HYBRID	304.95	304.17	304.25	303.02	303.02	1354.86
MPSD	174.63	174.40	174.43	174.07	174.07	368.08
EABS	474.44	477.52	477.51	476.22	476.22	786.09
(SNE)	2.087	2.081	2.081	2.080	<b>2.079</b>	5.000
Temkin isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
b	1.11	1.11	1.11	1.10	1.10	1.08
A	5.79E-03	5.78E-03	5.79E-03	5.68E-03	5.68E-03	5.62E-03
R <sup>2</sup>	0.95					
ERRSQ	37317.46	37315.70	37315.62	37406.46	37407.90	48543.84
ERAV	78.86	78.86	78.86	78.96	78.96	89.95
HYBRID	231.76	231.74	231.73	231.14	231.15	306.87
MPSD	152.24	152.23	152.23	152.03	152.03	175.18
EABS	419.37	419.17	419.21	417.10	417.04	413.35
(SNE)	4.270	4.269	4.270	<b>4.264</b>	<b>4.264</b>	4.986



Table 4-12 continued

Redlich-Peterson isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
K <sub>R</sub>	6.80	6.88	8.10	7.92	7.71	6.55
b	6.80E-04	7.56E-04	3.53E-03	3.32E-03	2.60E-03	1.34E-03
β	1.00	1.00	0.83	0.83	0.90	0.90
R <sup>2</sup>	0.90					
ERRSQ	133025.64	40024.32	42312.13	42402.76	41985.48	66640.09
ERAV	148.90	81.67	83.98	84.07	83.65	105.39
HYBRID	861.49	251.16	265.98	264.77	262.57	405.29
MPSD	293.51	158.48	163.09	162.72	162.04	201.32
EABS	732.34	437.45	449.32	448.08	446.39	433.10
(SNE)	5.000	<b>2.278</b>	2.360	2.360	2.344	2.956
Toth isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
t	1.00	1.00	1.00	0.97	0.94	0.95
K <sub>T</sub>	10000.00	9677.38	9659.32	9332.08	9817.27	10000.03
a	1470.00	1467.32	1462.78	1107.43	916.33	1000.34
R <sup>2</sup>	0.90					
ERRSQ	133025.64	41405.85	41328.45	40223.74	40664.12	54661.85
ERAV	148.90	83.07	82.99	81.88	82.32	95.45
HYBRID	861.49	255.44	255.07	252.32	253.36	348.99
MPSD	293.51	159.83	159.71	158.85	159.17	186.81
EABS	732.34	434.37	434.45	438.39	438.74	435.22
(SNE)	5	2.303	2.301	<b>2.285</b>	2.294	2.689

<sup>1</sup>LTFM: Linear transform

<sup>2</sup>ERRSQ: Error of the sum of squares, (eq. [4.15])

<sup>3</sup>ERAV: Sum of square of the average squares of the errors, (eq. [4.16])

<sup>4</sup>HYBRID: Hybrid fraction error function, (eq. [4.17])

<sup>5</sup>MPSD: Marquardt's percent standard deviation, (eq. [4.18])

<sup>6</sup>EABS: Sum of the absolute errors, (eq. [4.19])

<sup>7</sup>Sum of normalized error

From Table 4-12, it is clear that the parameter sets for Langmuir, linear, and Temkin isotherms calculated using the different error functions are more similar to one-another. The lowest value of SNE was obtained using ERRSQ, ERAV and MPSD for the Langmuir isotherm and HYBRID and MPSD for the linear and Temkin isotherms. Based on the error values, the Temkin isotherm provides the best fit for ammonium adsorption on broiler litter at pH of 7, followed by Langmuir, and linear isotherms, respectively.

Based on the values of the linear isotherm parameters, it is clear that the adsorption/desorption process of  $\text{NH}_4^+$  onto litter is a pH and  $\text{NH}_4^+$  concentration-dependent phenomenon. Ammonium adsorption increased with pH from 4 to 7. The Freundlich, linear, and Temkin isotherms were the best fit of ammonium adsorption at pH of 4, 6 and 7, respectively.

## Ammonium adsorption on Broiler Cake

### *Linear regression method*

The linear plot of  $r$  (mg/kg) vs.  $C$  (mg/L) shown in Figure 4-10 indicated that ammonium adsorption occurred in broiler cake at all three pH values. The highest  $r^2$  at pH of 7 (vs. other pH values) indicated that the linear isotherm provided a good model of the ammonium adsorption broiler cake. Figure 4-10 shows that adsorbed  $\text{NH}_4^+$  concentration increased with equilibrium  $\text{NH}_4^+$  concentration. Increasing solution pH value resulted in greater  $\text{NH}_4^+$  adsorption on broiler cake due to reduction in  $\text{H}^+$  which would have competed with  $\text{NH}_4^+$  for adsorption sites. The linear isotherm parameters  $K_L$  and  $b$  for pH through 7 on broiler cake are presented in Table 4-13.

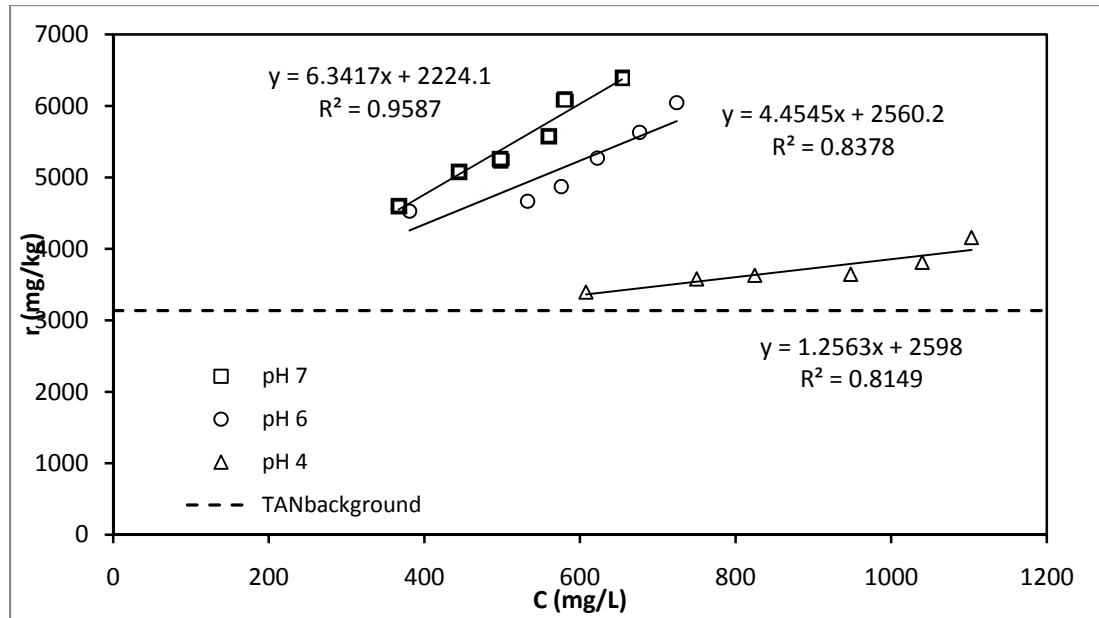


Figure 4-10 Linear isotherm of  $\text{NH}_4^+$  adsorbed on broiler cake. The axes are C: equilibrium concentration (mg/L) and r: adsorbed ammonium concentration (mg/kg).

Table 4-13 Estimated parameters for linear isotherm (eq. [4.7]) of ammonium adsorption on broiler cake.

pH	$K_L$ (L/kg)	b (mg/kg)	$r^2$
4	1.2563	2598	0.81
6	4.4545	2560.2	0.84
7	6.3417	2224.1	0.96

Based on higher R, at pH of 4, the Langmuir adsorption isotherm modeled  $\text{NH}_4^+$  adsorption on broiler cake better than at the higher pH values (Figure 4-11). As expected, the  $\text{NH}_4^+$  adsorption capacity ( $Q_0$ ) of broiler cake, calculated using the Langmuir isotherm,

increased with pH (Table 4-14). Comparison with published literature (Kithome, 1999 b) indicated that  $\text{NH}_4^+$  adsorption capacity of broiler cake (12,500 mg/kg at pH of 7) was lower than coir, zeolite or peat but higher than broiler litter (10,000 mg/kg at pH of 7, Table 4-5). The reason for higher adsorption capacity of cake than litter will be discussed later.

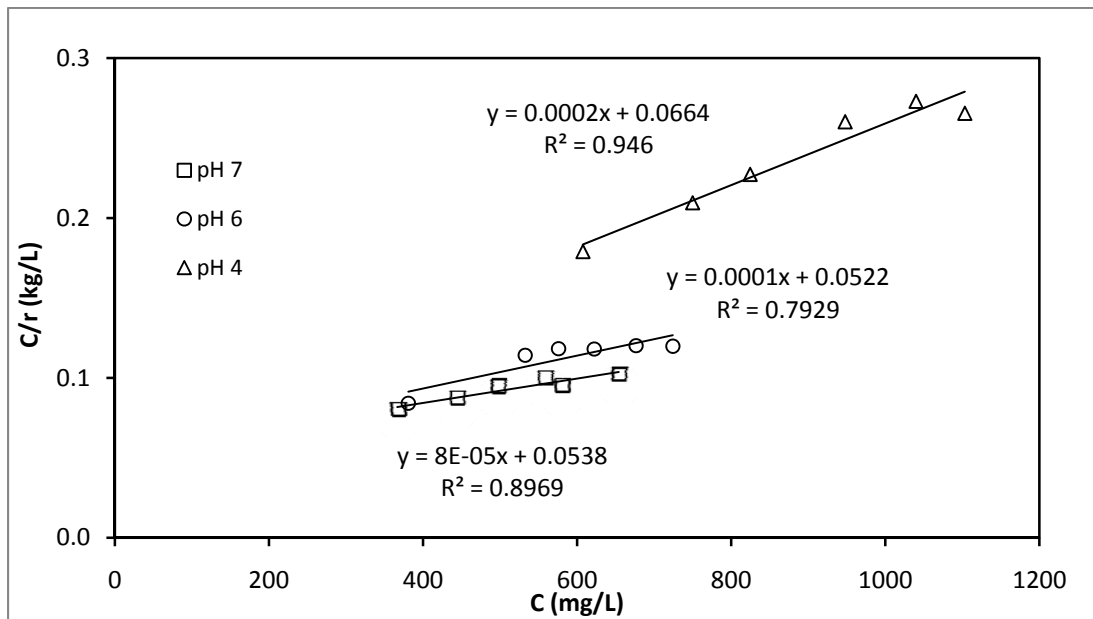


Figure 4-11 Langmuir isotherms of  $\text{NH}_4^+$  adsorption on broiler cake. The axes are C: equilibrium concentration (mg/L) and r: adsorbed or desorbed ammonium concentration (mg/kg).

Table 4-14 Estimated parameters for Langmuir isotherm (eq. [4.3]) of ammonium adsorption on broiler cake.

pH	$Q_0$ (mg/kg)	$b$ (L/kg)	$r^2$
4	5,000	$3.01 \times 10^{-3}$	0.95
6	10,000	$1.92 \times 10^{-3}$	0.79
7	12,500	$1.49 \times 10^{-3}$	0.90

The Freundlich adsorption isotherm fitted the experimental data of ammonium adsorption on broiler cake at pH of 7 very well ( $R^2=0.96$ ), but the fits at pH of 4 and 6 were not as good (Figure 4-12). The Freundlich isotherm parameters  $K_f$  and  $n$  (Table 4-14) seemed reasonable compared with other studies (Kithome et al., 1999a, b; Kirchmann and Witter, 1989).

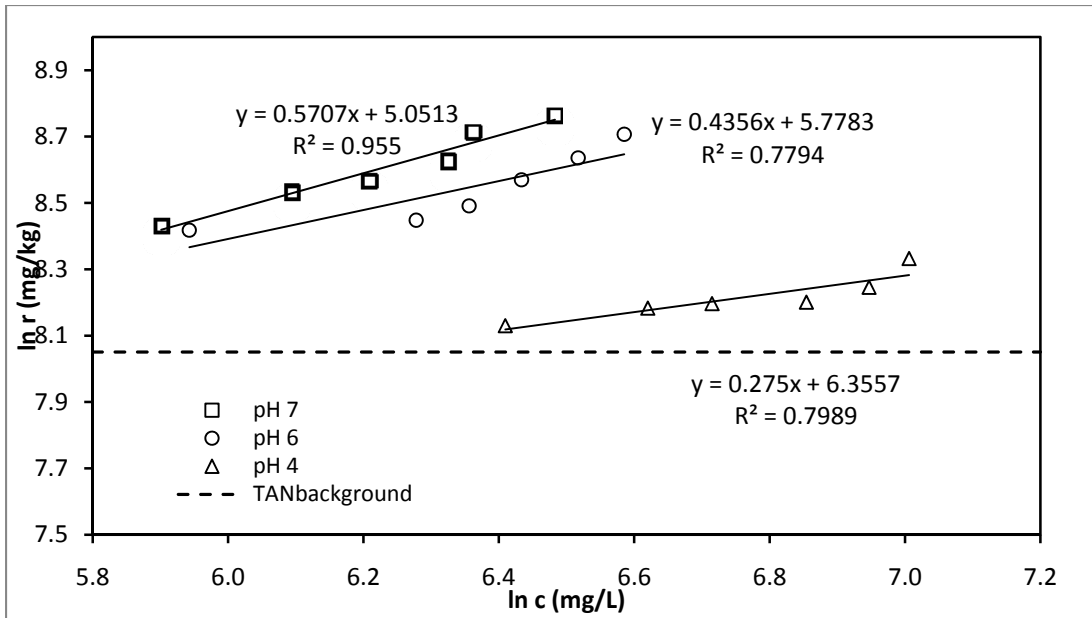


Figure 4-12 Freundlich isotherms of  $\text{NH}_4^+$  adsorption on broiler cake. The axes are C: equilibrium concentration (mg/L) and r: adsorbed or desorbed ammonium concentration (mg/kg).

Table 4-15 Estimated parameters for Freundlich isotherm (eq. [4.5]) of ammonium adsorption on broiler cake.

pH	$K_f$ (L/kg)	n	$r^2$
4	575.77	3.64	0.80
6	323.21	2.30	0.78
7	156.23	1.75	0.96

The Temkin isotherm modeled ammonium adsorption on broiler cake at pH of 7, much better ( $R^2 = 0.94$ ) than for pH of 4 and 6, that seemed to be non-linear (Figure 4-13).

The Temkin adsorption energies (b) (Table 4-16) were positive for all three pH values in broiler cake, indicating that the adsorption was exothermic (Hamdaoui and Naffrechoux, 2007). The highest adsorption energy at pH of 4 meant that the final state of adsorption was the most stable at pH of 4 vs. 6 or 7.

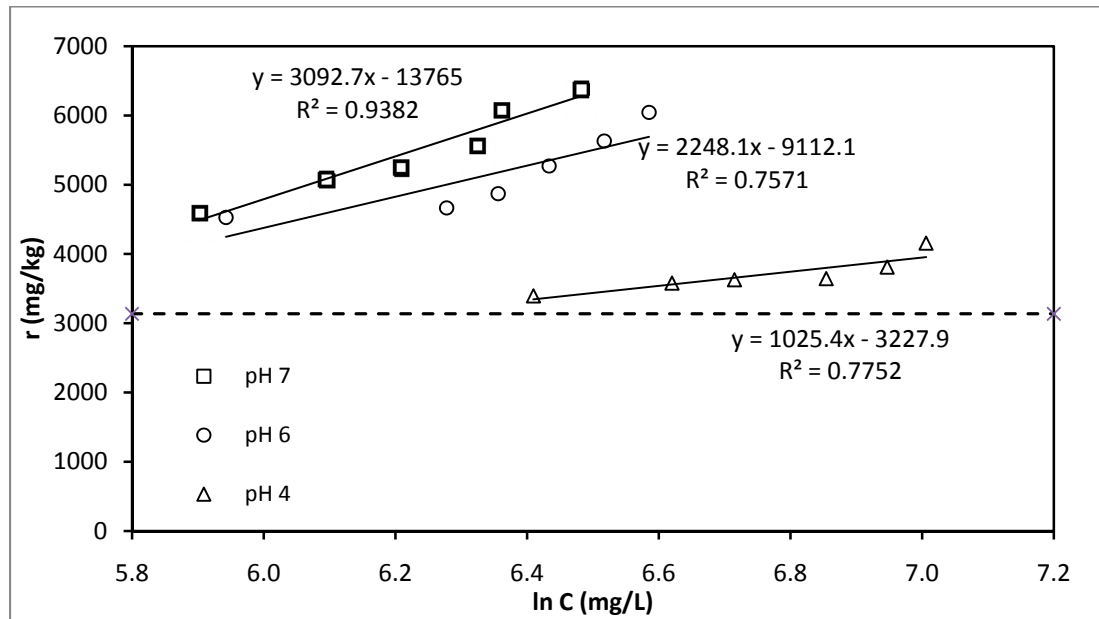


Figure 4-13 Temkin isotherm of  $\text{NH}_4^+$  adsorption on broiler cake. The axes are C: equilibrium concentration (mg/L) and r: adsorbed or desorbed ammonium concentration (mg/kg).



Table 4-16 Estimated parameters for Temkin isotherm (eq. [4.8]) of ammonium adsorption on broiler cake.

pH	A (L/kg)	b (J/mol)	R <sup>2</sup>
4	0.043	2.42	0.78
6	0.017	1.10	0.76
7	0.012	0.80	0.94

The value of  $\beta$  in the Redlich-Peterson isotherm and value of  $t$  in the Toth isotherm are both 0 at all three pH values; thus,  $C^\beta$  (Redlich-Peterson) and  $C^t$  (Toth) are 1 resulting in  $R^2$  of infinity. Based on the linear regression  $R^2$  values, it would seem that the linear isotherm was reasonable for modeling ammonium adsorption on broiler cake at pH of 6 and 7. However, linearization sometimes affects the normality assumptions of the least squares and the error distribution is changed. Due to the inherent bias resulting from linearization, linear regression may not be appropriate technique to predict optimum isotherm, especially calculating three-parameter isotherm. At pH of 4, the Langmuir isotherm had the highest  $R^2$  value.

### *Non-linear regression method*

The parameters for the six isotherms for modeling ammonium adsorption on broiler cake at pH of 4 using non-linear regression (five error functions) are presented in Table 4-17. The parameters for the linear, Langmuir and Freundlich isotherms obtained using several

error functions are close to those obtained through linear transformation (Table 4-17), and therefore, these isotherm provide good fit of ammonium adsorption broiler cake. Based on the error values, the linear isotherm provided the best fit of ammonium adsorption on broiler litter at pH of 4, followed by the Freundlich and Langmuir isotherms, respectively. The parameter  $\beta$  in the Redlich-Peterson isotherm calculated using all five of the error functions ranged between 0.73 and 0.74 (Table 4-17), not 1. Hence, the Freundlich isotherm, rather than the Langmuir isotherm simulated the experimental data better.

Table 4-17 Linear and non-linear isotherm parameters and errors calculated using different error functions for broiler cake at pH of 4

Linear isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
$K_L$	1.26	1.26	1.26	1.23	1.23	1.25
b	2598.00	2597.95	2597.93	2620.87	2620.87	2600.66
R <sup>2</sup>	0.81					
ERRSQ	62434.91	62434.88	62434.88	62625.17	62625.17	62675.84
ERAV	102.01	102.01	102.01	102.16	102.16	102.21
HYBRID	401.17	401.15	401.15	399.92	399.92	400.88
MPSD	200.29	200.29	200.29	199.98	199.98	200.22
EABS	489.38	489.37	489.38	479.13	479.13	485.84
(SNE) <sup>7</sup>	4.994	4.994	4.994	<b>4.973</b>	<b>4.973</b>	4.992
Langmuir isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
Q <sub>0</sub>	5000.00	5100.95	5100.42	5037.91	5037.74	4939.71

Table 4-17 continued

b	3.01E-03	3.10E-03	3.10E-03	3.24E-03	3.24E-03	3.36E-03
R <sup>2</sup>	0.95					
ERRSQ	144965.45	82752.02	82751.97	83055.67	83055.43	94022.54
ERAV	155.44	117.44	117.44	117.65	117.65	125.18
HYBRID	926.03	530.40	530.37	528.35	528.35	587.60
MPSD	304.31	230.30	230.30	229.86	229.86	242.40
EABS	731.23	567.58	567.46	552.45	552.39	535.25
(SNE)	5.000	3.432	3.432	<b>3.411</b>	<b>3.411</b>	3.617
<b>Freundlich isotherm</b>						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
K <sub>f</sub>	575.77	538.17	537.66	565.32	575.00	575.00
n	3.64	3.51	3.51	3.60	3.60	3.65
R <sup>2</sup>	0.7989					
ERRSQ	72156.04	71777.97	71778.12	72011.44	72011.47	75790.64
ERAV	109.66	109.38	109.38	109.55	109.55	112.39
HYBRID	459.01	460.50	460.54	458.88	458.88	477.37
MPSD	214.24	214.59	214.60	214.21	214.21	218.49
EABS	514.37	531.00	531.22	518.70	518.69	510.60
(SNE)	<b>4.838</b>	4.867	4.867	4.843	4.843	4.961
<b>Temkin isotherm</b>						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
b	2.42	2.42	2.42	2.48	2.48	2.97
A	4.29E-02	4.29E-02	4.29E-02	4.73E-02	4.73E-02	9.39E-02
R <sup>2</sup>	0.7752					

Table 4-17 continued

ERRSQ	75843.07	75842.50	75842.50	76098.08	76098.24	93283.78
ERAV	112.43	112.43	112.43	112.62	112.62	124.69
HYBRID	485.38	485.30	485.30	483.61	483.61	571.17
MPSD	220.31	220.30	220.29	219.91	219.91	238.99
EABS	540.30	540.30	540.29	526.88	526.88	448.39
(SNE)	4.486	4.486	4.486	<b>4.461</b>	<b>4.461</b>	4.830

Redlich-Peterson isotherm

	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
$K_R$		183.39	183.35	178.92	183.25	183.39
b		0.28	0.30	0.27	0.28	0.28
$\beta$		0.74	0.73	0.74	0.74	0.74
$R^2$						
ERRSQ		72742.83	72394.70	72657.17	72629.71	76478.83
ERAV		110.11	109.84	110.04	110.02	112.90
HYBRID		463.00	464.61	463.03	462.93	482.34
MPSD		215.17	215.55	215.18	215.16	219.62
EABS		520.04	534.31	521.51	521.75	516.13
(SNE)		<b>4.839</b>	4.864	4.841	4.840	4.966

Toth isotherm

	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
t		0.86	0.78	0.78	0.96	0.84
$K_T$		5406.62	5530.17	5530.17	5073.07	4999.28
a		132.99	70.41	70.41	233.67	83.55
$R^2$						

ERRSQ	81262.29	80402.07	80402.07	82910.29	90420.52
ERAV	116.38	115.76	115.76	117.55	122.76
HYBRID	522.76	512.49	512.49	525.88	559.95
MPSD	228.64	226.38	226.38	229.32	236.63
EABS	569.16	546.17	546.17	543.89	471.77
(SNE)	4.747	4.664	<b>4.663</b>	4.738	4.829

<sup>1</sup>LTFM: Linear transform

<sup>2</sup>ERRSQ: Error of the sum of squares, (eq. [4.15])

<sup>3</sup>ERAV: Sum of square of the average squares of the errors, (eq. [4.16])

<sup>4</sup>HYBRID: Hybrid fraction error function, (eq. [4.17])

<sup>5</sup>MPSD: Marquardt's percent standard deviation, (eq. [4.18])

<sup>6</sup>EABS: Sum of the absolute errors, (eq. [4.19])

<sup>7</sup>Sum of normalized error

In Figure 4-14, instead of linear regression, non-linear regression was applied to the ammonium adsorption data to avoid the drift. Use of the HYBRID error function (non-linear regression) to calculate the parameters of the linear isotherm provided a better fit at pH of 4 than Langmuir isotherm using linear regression (Figure 4-14).

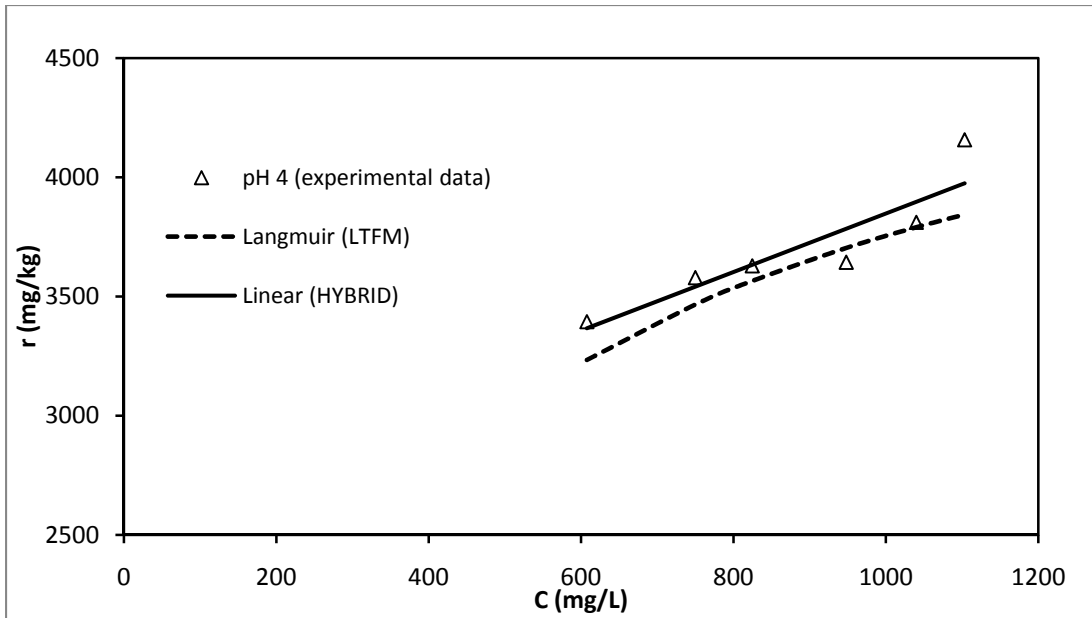


Figure 4-14 Linear isotherm and experimental data derived by linearization of Langmuir isotherm. The axes are C: ammonium equilibrium concentration (mg/L) and r: concentration of ammonium adsorbed on broiler cake (mg/kg).

The parameters for six isotherms for modeling ammonium adsorption on broiler cake at pH of 6 using non-linear regression (five error functions) are presented in Table 4-18. The parameters calculated using the five non-linear error functions for the Redlich-Peterson isotherm showed the greatest variability (Table 4-18). The parameter  $t$  in the Toth isotherm determined by the five error functions were  $<1$  (Table 4-18); hence, the isotherm is similar to Freundlich isotherm than Langmuir isotherm.

Table 4-18 Linear and non-linear isotherm parameters and errors calculated using different error functions for broiler cake at pH of 6

Linear isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
K <sub>L</sub>	4.45	4.45	4.45	4.29	4.29	4.33
b	2560.20	2560.16	2560.16	2645.25	2645.25	2699.14
R <sup>2</sup>	0.84					
ERRSQ	283014.23	283013.77	283013.77	285467.43	285467.45	311283.11
ERAV	217.18	217.18	217.18	218.12	218.12	227.77
HYBRID	1426.58	1426.76	1426.76	1415.46	1415.46	1586.85
MPSD	377.70	377.73	377.73	376.23	376.23	398.35
EABS	1169.10	1169.08	1169.08	1177.31	1177.31	1175.32
(SNE)	<b>4.702</b>	4.703	4.703	4.711	4.711	4.998
Langmuir isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
Q <sub>0</sub>	10000.00	9574.90	9574.92	9135.48	9134.97	10000.90
b	1.92E-03	2.04E-03	2.04E-03	2.26E-03	2.26E-03	1.79E-03
R <sup>2</sup>	0.79					
ERRSQ	466494.43	434615.62	434615.62	438847.68	438856.62	494622.96
ERAV	278.84	269.14	269.14	270.45	270.45	287.12
HYBRID	2399.09	2182.72	2182.72	2162.74	2162.74	2461.00
MPSD	489.80	467.20	467.20	465.05	465.05	496.08
EABS	1484.26	1461.28	1461.28	1470.92	1470.93	1445.19
(SNE)	4.877	<b>4.629</b>	<b>4.629</b>	4.636	4.636	4.974

Table 4-18 continued

Freundlich isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
K <sub>f</sub>	323.21	243.16	243.22	277.33	277.04	277.04
n	2.30	2.08	2.08	2.18	2.18	2.16
R <sup>2</sup>	0.78					
ERRSQ	365957.71	354761.59	354761.46	358019.96	357953.82	387746.71
ERAV	246.97	243.16	243.16	244.27	244.25	254.21
HYBRID	1786.87	1785.16	1785.12	1769.78	1769.79	1975.61
MPSD	422.71	422.51	422.51	420.69	420.69	444.48
EABS	1333.88	1315.15	1315.17	1324.31	1324.20	1321.99
(SNE)	4.771	4.712	<b>4.711</b>	4.719	4.719	4.991
Temkin isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
b	1.10	1.10	1.10	1.15	1.15	1.11
A	1.74E-02	1.74E-02	1.74E-02	1.93E-02	1.92E-02	1.70E-02
R <sup>2</sup>	0.76					
ERRSQ	423651.45	423651.28	423651.28	427528.18	427535.31	462388.08
ERAV	265.72	265.72	265.72	266.94	266.94	277.61
HYBRID	2097.64	2097.94	2097.94	2079.77	2079.77	2225.95
MPSD	458.00	458.03	458.03	456.04	456.04	471.80
EABS	1446.28	1446.29	1446.29	1444.00	1444.00	1445.95
(SNE)	4.787	4.787	4.787	<b>4.785</b>	4.786	5.000
Redlich-Peterson isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>



Table 4-18 continued

$K_R$	33.24	108.52	88.13	79.52	13.70	
b	0.03	0.30	0.19	0.16	0.02	
$\beta$	0.73	0.57	0.60	0.57	0.57	
$R^2$						
ERRSQ	388948.88	362521.35	368407.37	369692.20	951719.53	
ERAV	254.61	245.81	247.79	248.22	398.27	
HYBRID	1947.79	1825.11	1822.34	1828.82	5234.67	
MPSD	441.34	427.21	426.89	427.65	723.51	
EABS	1382.03	1329.44	1344.01	1346.40	1176.33	
(SNE)	3.030	<b>2.899</b>	2.920	2.926	4.851	
Toth isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
t	0.91	0.90	0.90	0.91	0.91	0.90
$K_T$	10211.98	10439.94	10007.49	9764.79	10000.28	
a	267.67	258.71	240.41	265.16	265.12	
$R^2$						
ERRSQ	426769.90	426070.12	427259.21	430525.39	471279.78	
ERAV	266.70	266.48	266.85	267.87	280.26	
HYBRID	2142.09	2146.20	2129.67	2128.75	2292.37	
MPSD	462.83	463.27	461.48	461.38	478.79	
EABS	1448.36	1443.91	1452.66	1456.65	1448.31	
(SNE) <sup>7</sup>	4.753	4.750	<b>4.748</b>	4.762	4.994	

<sup>1</sup>LTFM: Linear transform

<sup>2</sup>ERRSQ: Error of the sum of squares, (eq. [4.15])

<sup>3</sup>ERAV: Sum of square of the average squares of the errors, (eq. [4.16])

<sup>4</sup>HYBRID: Hybrid fraction error function, (eq. [4.17])

<sup>5</sup>MPSD: Marquardt's percent standard deviation, (eq. [4.18])

<sup>6</sup>EABS: Sum of the absolute errors, (eq. [4.19])

<sup>7</sup>Sum of normalized error

The parameters of linear, Langmuir, Freundlich and Temkin isotherms obtained using the error functions are close to linear transformation (Table 4-18), indicating that these isotherms provided good fit ammonium adsorption on broiler cake. Based on the error values, the quality of the isotherm fit can be arranged in order of increasing error values as: linear < Freundlich < Temkin < Langmuir (Table 4-18). Hence, the parameters of the linear isotherm obtained through non-linear provided the best fit and the results are very similar to linear regression (Table 4-18).

The parameters of the six isotherms for modeling ammonium adsorption on broiler cake at pH of 7 using non-linear regression (five error functions) are presented in Table 4-16. The non-linear regression are similar to one-another and to the LTFM (Table 4-19). Based on the error values, the quality of the isotherm fit can be arranged in order of increasing error values: linear < Freundlich  $\approx$  Redlich < Toth < Temkin < Langmuir. The linear isotherm parameters calculated by ERRSQ and ERAV were identical or nearly identical to those calculated by linear regression and provided the best fit of ammonium adsorption on broiler at pH of 7.

Table 4-19 Linear and non-linear isotherm parameters and errors calculated using different error functions for broiler cake at pH 7

Linear isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
K <sub>L</sub>	6.34	6.34	6.34	6.28	6.28	6.38
b	2224.10	2224.14	2224.14	2251.52	2251.51	2224.25
R <sup>2</sup>	0.96					
ERRSQ	91545.41	91545.41	91545.41	91767.41	91767.35	93843.47
ERAV	123.52	123.52	123.52	123.67	123.67	125.06
HYBRID	402.83	402.83	402.83	401.88	401.88	416.24
MPSD	200.71	200.71	200.71	200.47	200.47	204.02
EABS	616.54	616.52	616.52	619.26	619.27	579.66
(SNE) <sup>7</sup>	<b>4.910</b>	<b>4.910</b>	<b>4.910</b>	4.915	4.915	4.936
Langmuir isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
Q <sub>0</sub>	12500.00	13230.23	13999.97	12918.72	12917.99	12801.67
b	1.49E-03	1.40E-03	1.25E-03	1.44E-03	1.44E-03	1.47E-03
R <sup>2</sup>	0.90					
ERRSQ	206768.42	125292.57	136495.58	134866.47	134869.94	129785.95
ERAV	185.64	144.51	150.83	149.93	149.93	147.07
HYBRID	899.17	566.56	631.44	598.79	598.79	575.26
MPSD	299.86	238.03	251.29	244.70	244.70	239.85
EABS	988.06	775.32	855.36	847.21	847.20	817.35
(SNE)	5.000	<b>3.593</b>	3.879	3.799	3.799	3.687

Table 4-19 continued

Freundlich						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
K <sub>f</sub>	156.23	141.49	141.26	147.99	150.54	150.54
n	1.75	1.70	1.70	1.73	1.73	1.73
R <sup>2</sup>	0.96					
ERRSQ	106984.12	105507.75	105508.45	105887.99	105900.02	125321.28
ERAV	133.53	132.61	132.61	132.85	132.85	144.52
HYBRID	470.54	470.33	470.40	468.52	468.52	567.39
MPSD	216.92	216.87	216.89	216.45	216.45	238.20
EABS	688.81	695.05	695.65	697.34	697.64	631.58
(SNE)	4.505	<b>4.495</b>	4.496	4.498	4.499	4.905
Temkin isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
b	0.80	0.80	0.80	0.81	0.81	0.79
A	1.17E-02	1.16E-02	1.16E-02	1.19E-02	1.19E-02	1.17E-02
R <sup>2</sup>	0.94					
ERRSQ	135009.21	134939.24	134939.16	135727.20	135739.04	196614.46
ERAV	150.01	149.97	149.97	150.40	150.41	181.02
HYBRID	604.11	605.23	605.16	601.61	601.61	904.77
MPSD	245.79	246.01	246.00	245.28	245.28	300.79
EABS	789.27	794.65	794.55	794.31	794.38	783.86
(SNE)	<b>3.993</b>	4.002	4.001	4.001	4.001	4.986
Redlich-Peterson isotherm						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>

Table 4-19 continued

$K_R$	368.28	341.30	341.33	342.33	335.02	
b	2.34	2.15	2.05	2.05	2.13	
$\beta$	0.43	0.43	0.43	0.42	0.42	
$R^2$						
ERRSQ	105872.93	105902.79	106309.49	106315.72	115467.21	
ERAV	132.84	132.86	133.11	133.11	138.72	
HYBRID	472.19	472.32	470.46	470.46	521.80	
MPSD	217.30	217.33	216.90	216.90	228.43	
EABS	696.93	697.04	698.99	699.13	622.45	
(SNE)	<b>4.727</b>	4.728	4.731	4.731	4.890	
<b>Toth isotherm</b>						
	LTFM <sup>1</sup>	ERRSQ <sup>2</sup>	ERAV <sup>3</sup>	HYBRID <sup>4</sup>	MPSD <sup>5</sup>	EABS <sup>6</sup>
t	0.61	0.62	0.62	0.60	0.58	
$K_T$	23116.11	22354.45	22353.47	22353.64	22321.04	
a	60.34	65.21	65.40	57.16	46.64	
$R^2$						
ERRSQ	116863.30	117160.05	117159.07	117801.48	141925.63	
ERAV	139.56	139.74	139.74	140.12	153.80	
HYBRID	523.64	524.67	524.76	522.47	643.51	
MPSD	228.83	229.06	229.08	228.58	253.68	
EABS	741.73	742.35	742.47	743.68	717.78	
(SNE)	<b>4.444</b>	4.451	4.451	4.454	4.965	

<sup>1</sup>LTFM: Linear transform

<sup>2</sup>ERRSQ: Error of the sum of squares, (eq. [4.15])

<sup>3</sup>ERAV: Sum of square of the average squares of the errors, (eq. [4.16])

<sup>4</sup>HYBRID: Hybrid fraction error function, (eq. [4.17])

<sup>5</sup>MPSD: Marquardt's percent standard deviation, (eq. [4.18])

<sup>6</sup>EABS: Sum of the absolute errors, (eq. [4.19])

<sup>7</sup>Sum of normalized error

Ammonium adsorption on cake was greater than on litter at all three pH values (Figure 4-15). The concentration of ammonium adsorbed at pH of 4 on cake is close to that adsorbed at pH of 7 on litter. Greater ammonium adsorption on cake vs. litter could be due to higher specific surface area ( $2.71 \text{ m}^2/\text{g}$  vs.  $1.99 \text{ m}^2/\text{g}$ ) as well as greater concentrations of carboxyl groups. Since adsorption is correlated to specific surface area, higher ammonium adsorption capacity on cake was expected.

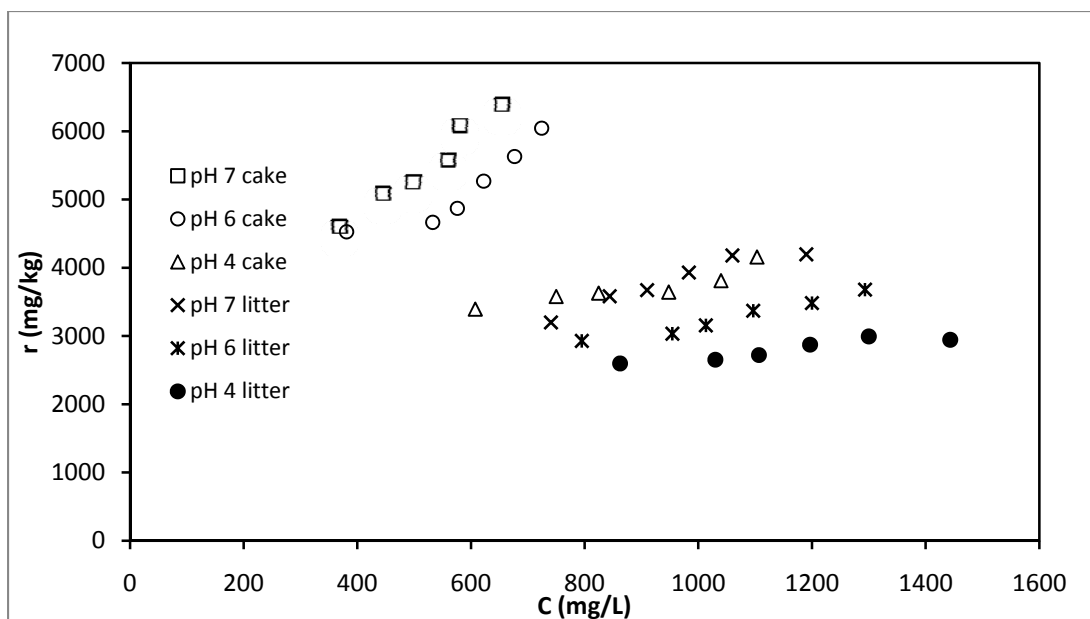


Figure 4-15. Dissolved (C) vs. adsorbed (r) on broiler cake and litter at three pH values

In soil, organic matter particles and clay have negative charges due to presence of carboxyl group ( $R-COO^-$ ), phenolic groups (phenolic-OH) that can hold cations, such as ammonium by chemical adsorption (Cornell University Cooperative Extension). Broiler litter also contains some functional group, such as carboxyl ( $R-COO^-$ ), phenolic groups (phenolic-OH) (Prasad and Sinha, 1981). Broiler cake contains more fecal material and feed than litter. Undigested proteins in feces and feed can be broken down by bacteria and fungi into amino acid and amines. Amino acid contains carboxyl group and amino group. Hence, broiler cake may have higher concentration of carboxyl functional groups than litter. This may also explain greater ammonium adsorption on cake vs. litter. Therefore, the adsorption of ammonium occurs by not only physical adsorption (i.e., Van der Waal's force) but also chemical adsorption with the carboxyl groups in broiler litter and cake.

The Temkin isotherm adsorption energy (b) parameter for both litter (Table 4-7) and cake (Table 4-16) are positive for all pH values indicating that adsorption is exothermic (Hamdaoui and Naffrechoux, 2007) in both litter and cake. The adsorption energy of ammonium on cake (Table 4-16) is greater than litter (Table 4-7), indicating that adsorbed ammonium on broiler cake is more stable than litter.

### **Ammonia sorption on litter**

Figure 4-16 shows that ammonia/um absorption and adsorption by the broiler litter increased linearly with moisture content. As the litter moisture content increased, the amount of  $\text{NH}_4\text{Cl}$  solution required to be added to  $\text{NaOH}_{(\text{aq})}$  to maintain an equilibrium ammonia gas concentration of  $\sim 480 \pm 24 \text{ mg/m}^3$  increased (Appendix A).



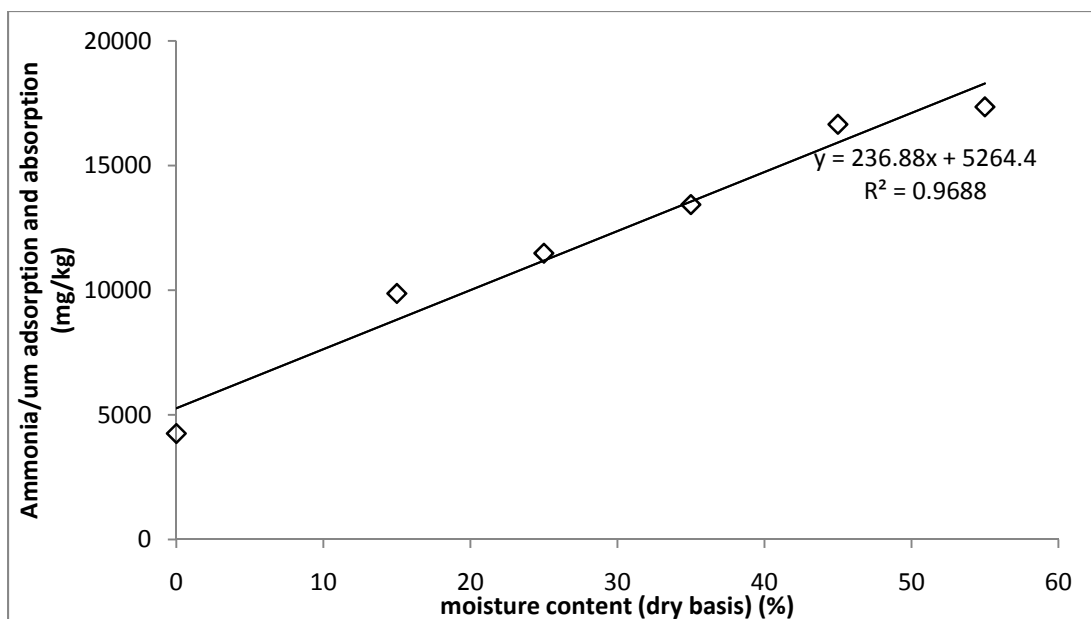


Figure 4-16. Ammonia/um adsorption and absorption on broiler litter at different moisture contents (dry basis).

Ammonia adsorption on oven-dry litter (eq. [4.20]) is shown in Table 4-20. Ammonia adsorbed on litter at 0% moisture content was due to physical adsorption - Van der Waals force, which arises from the interaction between the ammonia gas and charges on the litter surface and within the pores.

Table 4-20 Ammonia adsorption on broiler litter at 0% moisture content (n=3)

MC (%)	pH <sup>1</sup>	TAN <sub>back</sub> (mg) <sup>2</sup>	NH <sub>3</sub> -N <sub>add</sub> (mg) <sup>2</sup>	NH <sub>3</sub> -N <sub>head</sub> (mg) <sup>3</sup>	TAN <sub>meas</sub> (mg) <sup>2</sup>	NH <sub>3</sub> -N <sub>ads</sub> (mg) <sup>2</sup>	NH <sub>3</sub> -N <sub>ads</sub> (mg/kg)
0	7.27	37.93	26.56	2.66	33.18±1.52	28.62±1.46	2862±146

<sup>1</sup>pH was determined in 1: 3 (litter : water and 3 M KCl<sub>(aq)</sub>) suspension.

<sup>2</sup> Mass for ~10-g oven-dry litter sample

<sup>3</sup> One- third mass in the headspace of container with three 10-g oven-dry litter replicates

Ammonia adsorption and absorption, collectively referred to as sorption, on broiler litter at moisture content ranging from 15 to 55% (dry basis) is shown in Table 4-21 (eq. [4.25]). Ammonia sorption on broiler litter increased with moisture content from 0% to 25 %, reaching a maximum of 4,230 mg/kg at 25% and then decreased with increasing moisture content from 35% to 55% (Figure 4-17). Li et al. (2010) studied ammonia adsorption capacity on clinoptilolite at 140-142 mg/m<sup>3</sup> ammonia gas concentrations under different moisture content (20%, 30%, 40%, 50%, 60% (dry basis)). The greatest ammonia adsorption was at 40% moisture content, followed by 50%, 30%, 20%, 60%. Ammonia adsorption on clinoptilolite reached equilibrium in less than 3 h and the maximum adsorption capacity was 97 mg/kg at original ammonia gas concentration between 36.4-40.0 mg/m<sup>3</sup> (Li et al., 2010). Hence, the findings of this study were similar to that of Li et al. (2010).

Table 4-21 Ammonia adsorption and absorption on broiler litter at different moisture content (n=3 for each moisture content)

MC (%)	pH <sup>1</sup>	TAN <sub>back</sub> (mg) <sup>2</sup>	NH <sub>3</sub> -N <sub>add</sub> (mg) <sup>2</sup>	NH <sub>3</sub> -N <sub>head</sub> (mg) <sup>3</sup>	NH <sub>3</sub> -N <sub>aq</sub> (mg) <sup>2</sup>	NH <sub>4</sub> -N <sub>aq</sub> (mg) <sup>2</sup>	NH <sub>4</sub> -N <sub>ads</sub> (mg) <sup>2</sup>	NH <sub>3</sub> -N <sub>ads</sub> (mg) <sup>2</sup>	NH <sub>3</sub> -N <sub>ads</sub> (mg/kg)
15	7.24	37.79	63.61	2.72	0.05±0.00	30.11±0.95	39.37±0.73	29.15±1.68	2915±168
25	7.27	37.79	79.69	2.66	0.06±0.00	32.23±1.06	40.23±0.77	42.30±1.83	4230±183
35	7.41	37.79	99.27	2.73	0.12±0.00	46.55±0.73	48.56±0.40	39.10±1.12	3910±112
45	7.68	37.79	131.42	2.68	0.40±0.04	80.63±0.33	61.37±0.10	24.12±0.38	2412±38
55	8.00	37.79	138.41	2.67	0.89±0.06	87.78±3.57	62.69±0.94	22.18±4.58	2218±458

<sup>1</sup>pH was determined in 1: 3 (litter : water and 3 M KCl<sub>(aq)</sub>) suspension.

<sup>2</sup>Mass for ~10-g oven-dry litter sample

<sup>3</sup> One- third mass in the headspace of container with three 10-g oven-dry litter replicates

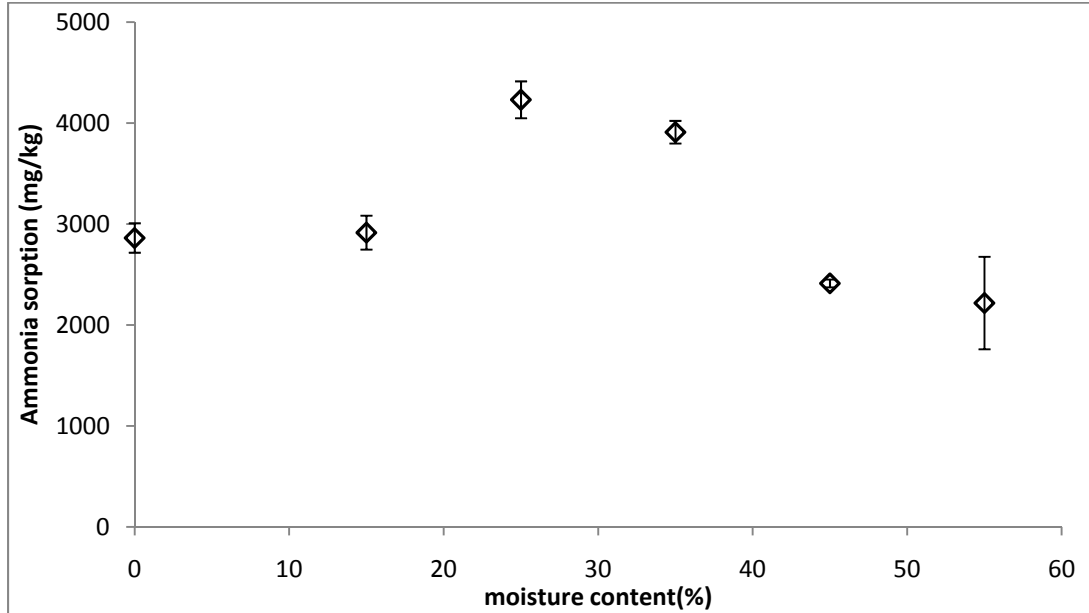


Figure 4-17. Ammonia sorption on broiler litter at different moisture contents. Each data point is the mean of three values. The error bars indicate the spread of the data.

Ammonia adsorbed on litter at 0% moisture content was due to Van der Waals force between ammonia gas and litter surface. In moist litter, in addition to physical adsorption on surface not covered with water molecules, ammonia sorption could be due to chemical adsorption. Examples of H bonding include the interaction between ammonia and water, complexation by dissolved metals ( $\text{Cu}(\text{NH}_3)_4^{2+}$ ,  $\text{Zn}(\text{NH}_3)_2^{2+}$ ) (Kotz et al., 2006) and acid base reaction (eq. [4.2]). Ammonia sorption will be discussed in the following paragraphs in the context of chemical reaction and thermodynamics.

Biologically, pH between 7 and 8 and 45% to 75% moisture content (dry basis) was adequate for nitrification process (Weaver and Meijerhof, 1991). However, the litter had been dried at 70°C for 16 h, stored in a freezer (-18°C), and the experiment was

conducted for 11 h only. Since the microbial population in the litter had probably been destroyed to the high temperature of drying, the effect of nitrification was neglected.

When moisture content was between 15% and 25%, water film may have formed on the litter surface where ammonia may have adsorbed due to Van der Waals force and hydrogen bonding between water and ammonia. However, as moisture content increased above 25%, ammonia sorption decreased (Table 4-21). When moisture content exceeded 25%, water may fill up the pores in broiler litter and ammonia may dissolve ( $\text{NH}_3\text{-N}_{(\text{aq})}$ ) due to its high water solubility (Table 4-21). The characteristics of ammonia and water are similar in that both exhibit polarity and form hydrogen bonds, which explains the high solubility of ammonia in water (Krasnopoler et al., 1996). However, the surface area available for physical (van der Waals forces) and chemical adsorption (H bonding) may have decreased when moisture content exceeded 25%.

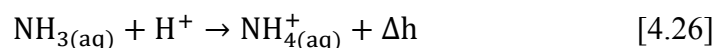
A fraction of the dissolved ammonia also participates in acid-base reaction to form ammonium ions. Dissolved ammonium ( $\text{NH}_4\text{-N}_{\text{aq}}$ ) concentration increased 44% between 25% and 35 % moisture content and 73% between 35% and 45 % moisture content (Table 4-21). However, ammonium formation depends on the pH of the system and only a small fraction of the dissolved ammonia will participate in ammonium fraction.

Increased moisture content may result in increased dissociation of carboxyl functional group in broiler litter, which may increase ammonium adsorption. Adsorbed ammonium concentration increased 20% between 25% and 35% moisture content and 27% between 35% and 45% moisture content (Table 4-21). Broiler litter contains copper ( $\text{Cu}^{2+}$ ) and zinc ( $\text{Zn}^{2+}$ ) from common dietary mineral additives (Kim and Patterson, 2002). Besides ammonia/um reaction, dissolved  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  may complex  $\text{NH}_3(\text{aq})$ ,

resulting in the formation of  $(\text{Cu}(\text{NH}_3)_4)^{2+}$  and  $\text{Zn}(\text{NH}_3)_2^{2+}$  respectively, in liquid phase. Complexation may play small role in ammonia sorption in poultry litter.

The other way to explain why ammonia adsorption decreases over 25% moisture content is thermodynamics. Adsorption is an exothermic process (Dutta, 2007). Chemical reactions tend to move toward states of lower potential energy. Chemical reaction generally produces or requires more energy than physical reaction. Ionic bonding usually produces the greatest energy, followed by covalent bonding, hydrogen bonding and finally, Van der Waals force. Ammonia adsorbed on litter would make ammonia gas move toward a lower energy at 0% moisture content. As moisture content increases, chemical reaction, such as acid-base reaction, dissociation, complexation would occur more easily than physical reaction to reach the configuration with the lowest energy.

Equation [4. 26] shows that  $\text{NH}_{3(\text{aq})}$  would obtain hydrogen ion from water and the energy of chemical reaction is negative (the enthalpy  $h = -12.42$  kcal/mole) (Snoeyink and Jenkins, 1982), and releases more energy than adsorption, which indicates that  $\text{NH}_{3(\text{aq})}$  tends to move toward  $\text{NH}_{4(\text{aq})}^+$  instead of being adsorbed on litter. Because the pH of moist litter was between 7-8 (Table 4-21) and dissociation constant ( $K_d$ ) of ammonium in broiler litter was 20% of that in dilute aqueous solution (Chapter 4), ammonium concentration ( $\text{NH}_4\text{-N}_{(\text{aq})}$ ) was a larger proportion compared to  $\text{NH}_3\text{-N}_{(\text{aq})}$  concentration. Therefore, when moisture content was above 25%, ammonia sorption decreased but ammonium concentration and adsorption increased.



Complexation includes some ionic bonding and covalent bonding and ammonia/ammonium transformation is covalent bonding. Both processes may produce more

energy and take the products to a lower energy state than ammonia adsorbed on broiler litter. Therefore, thermodynamics may also explain why when moisture content increased above 25%, ammonia sorbed on broiler litter decreased reaching the minimum at 55% moisture content vs. all other moisture content (Table 4-21).

## Conclusions

1. Linear regression analysis may not be appropriate to determine the best-fit of ammonium adsorption isotherm to the experimental data because it may introduce an offset.
2. In broiler litter, Freundlich, linear, and Temkin isotherm provided the best fit at pH of 4, 6, and 7, respectively. In broiler cake, linear isotherm provided the best fit at pH 4, 6, and 7. Overall, it may be preferable to use the linear isotherm for both cake and litter for the pH range studied because of its simplicity.
3. Ammonium adsorbed on broiler cake at pH 4, 6 and 7 but ammonium desorbed on broiler litter at pH 4, 6 and 7 (below ammonium equilibrium concentration 850 mg/L) because broiler cake has greater surface area and carboxyl groups than broiler litter.
4. Concentration of ammonia sorption increased with moisture content from 0% to 25%. The concentration of ammonia sorption was maximum (4230 mg/kg) at 25% moisture content and then decreased with increasing moisture content from 35% to 55%.
5. As moisture content increases above 25%, water may fill up the pores in broiler litter and ammonia dissolves in liquid phase, more ammonium ions form due to low value of dissociation constant and more ammonium adsorbed on broiler litter. This may explain the reduction of ammonia sorption above 25% moisture content.



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## APPENDICES

## Appendix A Ammonia sorption study

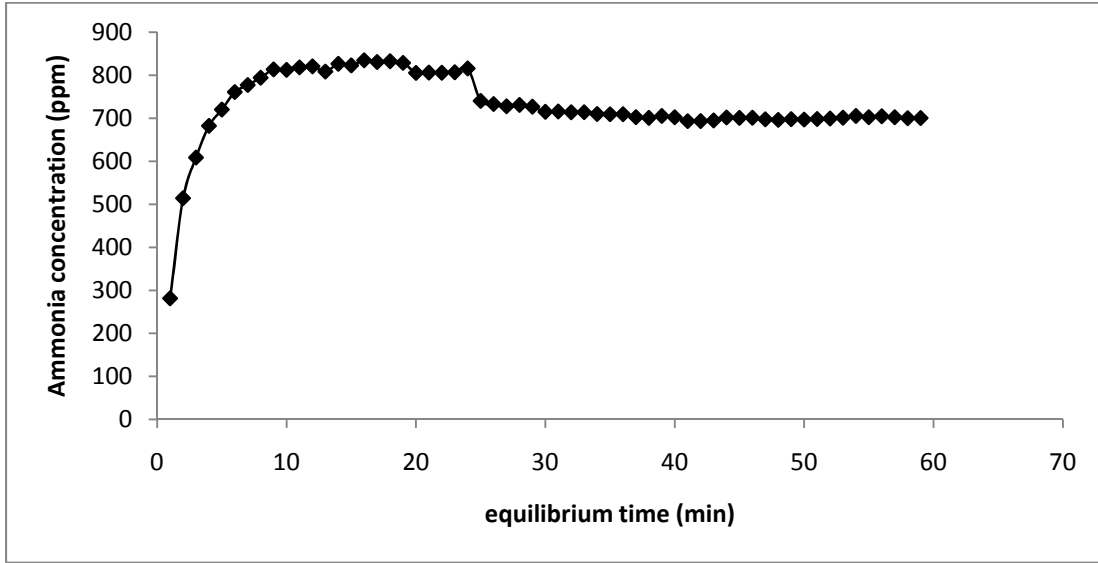


Figure C-0-1 Ammonia equilibrium concentration at 0% moisture content in the container headspace. Readings were taken every 1 min.

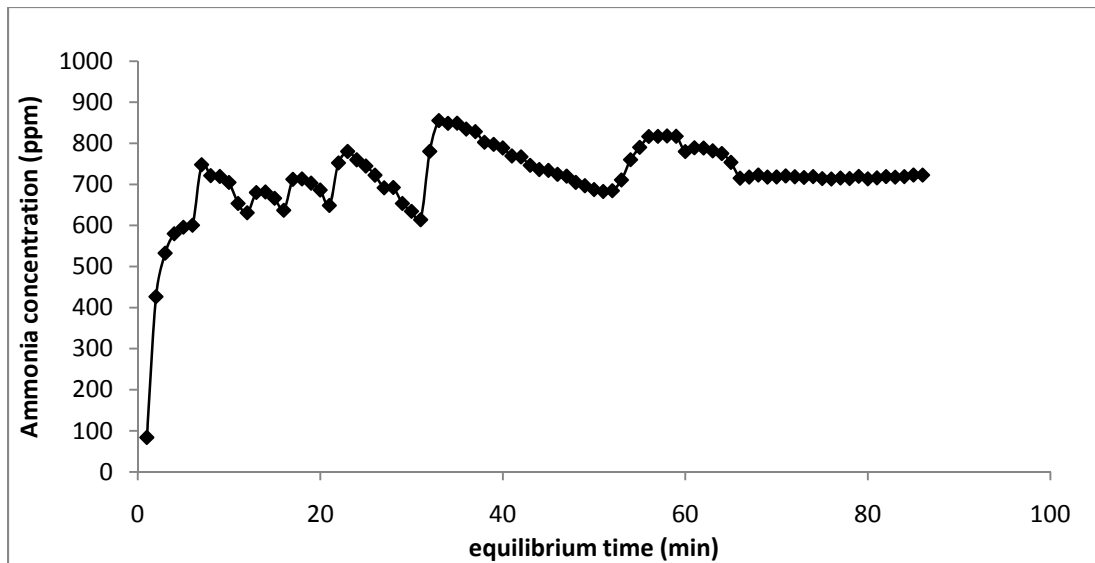


Figure C-0-2 Ammonia equilibrium concentration at 15% moisture content in the container headspace. Readings were taken every 1 min.

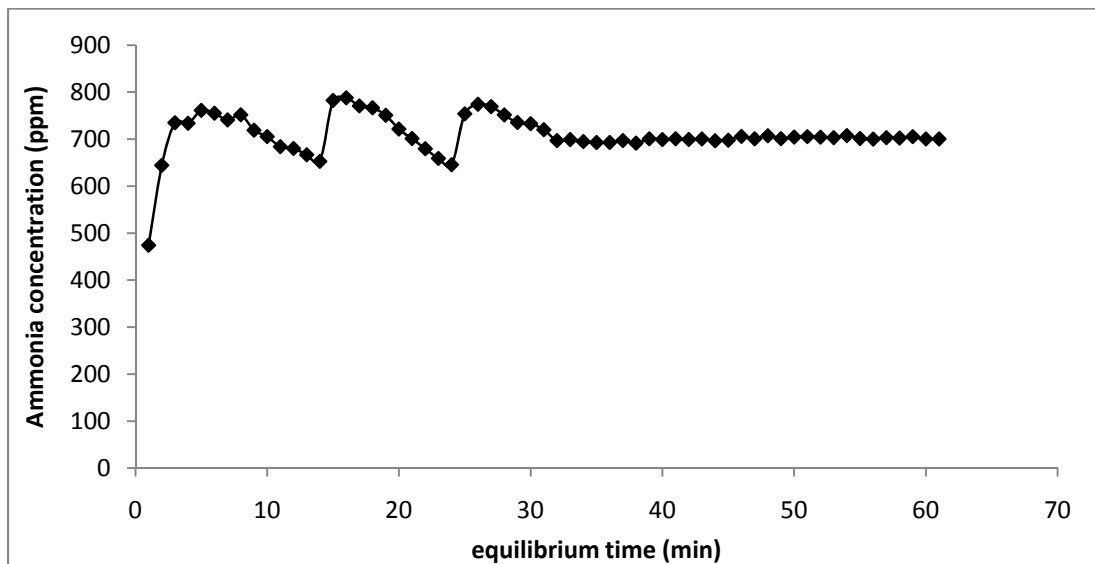


Figure C-0-3 Ammonia equilibrium concentration at 25% moisture content in the container headspace. Readings were taken every 1 min.



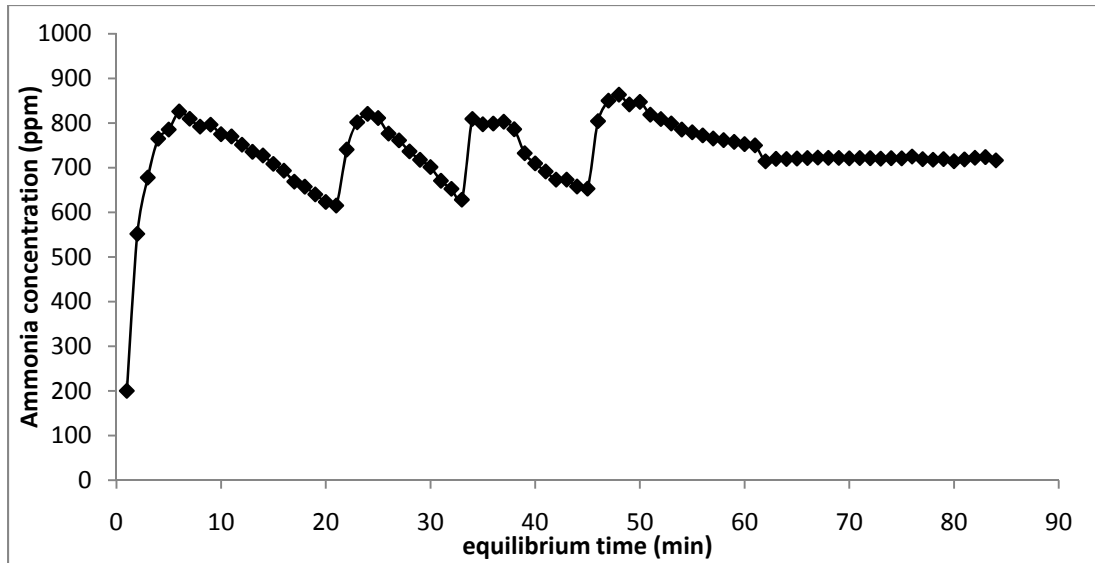


Figure C-0-4 Ammonia equilibrium concentration at 35% moisture content in the container headspace. Readings were taken every 1 min.

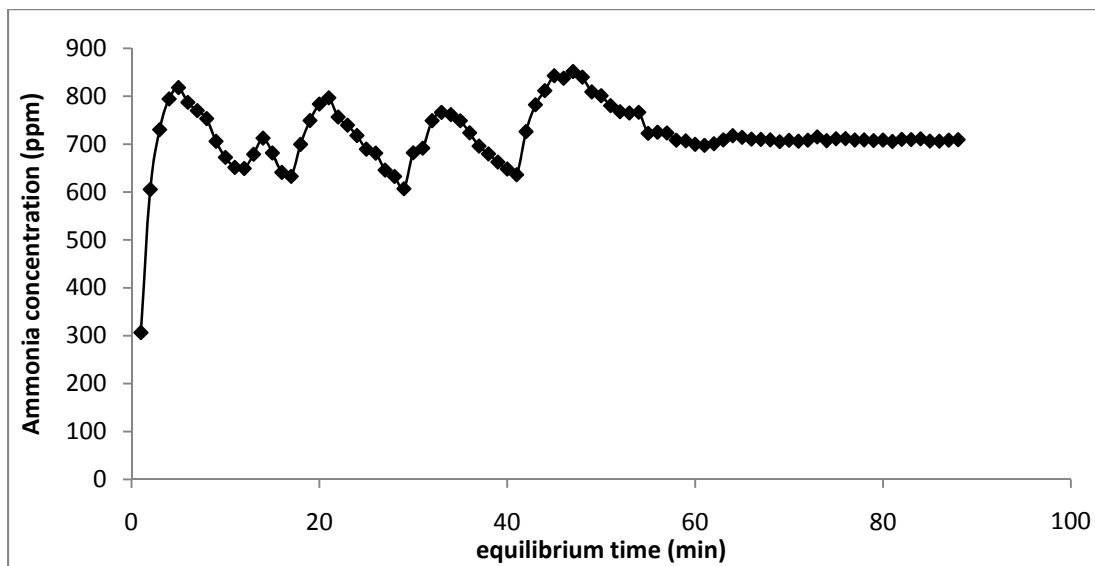


Figure C-0-5 Ammonia equilibrium concentration at 45% moisture content in the container headspace. Readings were taken every 1 min.

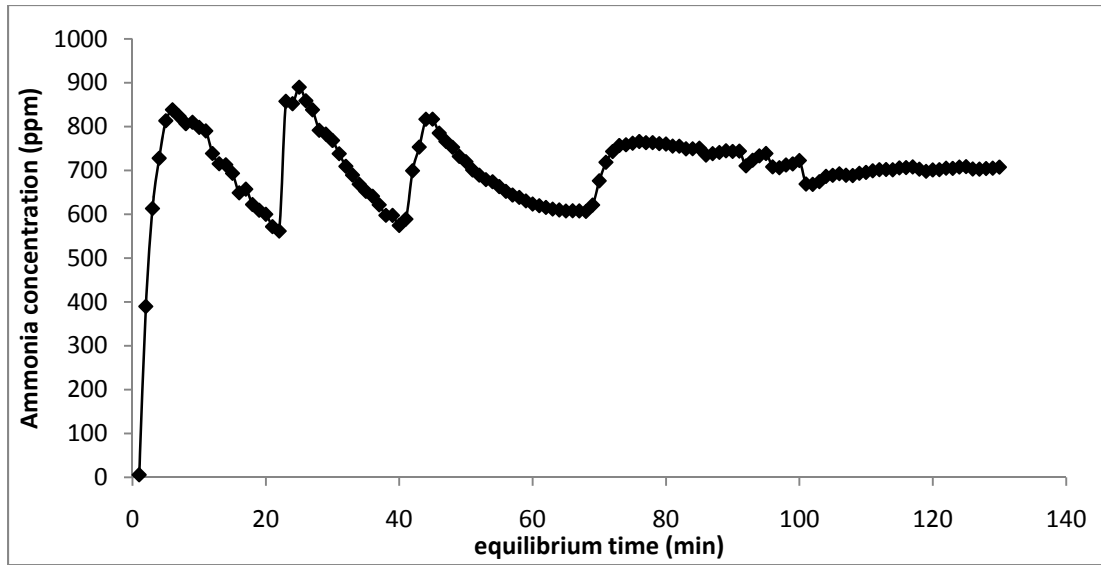


Figure C-0-6 Ammonia equilibrium concentration at 55% moisture content in the container headspace. Readings were taken every 1 min.

## 5 Conclusion and Future Work

The ability to accurately simulate nitrogen dynamics in broiler litter, an important source of ammonia that affects farm productivity and the environment, is hampered by the lack of information on mechanisms controlling ammonia/um dynamics in broiler litter. This research evaluated the drying temperature-time impacts of drying litter on C and N losses, determined the dissociation constant for ammonium-ammonia and Henry's constant of ammonia, and studied ammonium and ammonia sorption in broiler litter. Temperature-time impacts on C and N losses was determined by drying the litter at 70°C for 16 h, 50 °C for 24 h, or 25 °C (or room temperature) for 48 h. Dissociation constant for ammonium and Henry's Law constant for ammonia in broiler litter slurry were determined at room temperature (~22°C). Ammonium adsorption on broiler litter and cake were modeled at three different pH values and ammonium concentrations. Ammonia sorption on broiler litter was measured at moisture contents ranging from 0 to 55%. The findings of the study are listed below.

1. Drying broiler litter at 70 °C for 16 h resulted in complete moisture removal with a small loss of C and moderate loss of TAN. Drying at 25 °C and 50 °C resulted in incomplete moisture removal.
2. Total losses of C and N were 0.7 to 3.1% and 6.9% to 13.8%, respectively, during the drying experiment. While C losses increased with temperature, significant difference in N losses was only observed between the high and low temperature treatments.
3. Adjusted for C and N losses, moisture contents of the litter was reduced by nearly 4% resulting in actual dry basis chemical concentrations being increased by the same amount.

4. Dissociation constant for ammonium in litter slurry was  $1.02 \times 10^{-10}$ , which was 20% of  $K_d$  in aqueous solution probably due to ammonia/um adsorption and reduced activity coefficient.
5. Henry's Law constant measured in litter slurry was 0.0158 atm/M, which was close to  $K_h$  (0.0164 atm/M) in aqueous solution.
6. Ammonium adsorption occurred on broiler cake at pH of 4, 6 and 7, but desorbed from broiler litter at pH of 4, 6 and 7 when equilibrium ammonium concentration  $\leq 850$  mg/L. Ammonium adsorption on broiler cake was higher than broiler litter, probably due to higher specific surface area of broiler cake.
7. The Freundlich, linear and Temkin isotherms provided the best fits for ammonium adsorption at pH of 4, 6, and 7, respectively, on broiler litter. In broiler cake, the linear isotherm provided the best fit for ammonium adsorption at the three pH values. Overall, the linear isotherm seemed to be the most appropriate for broiler litter and cake for those pH values because of its suitability and simplicity.
8. Under the test conditions, ammonia sorption increased with moisture content from 0% to 25% and maximum of ammonia sorption was 4,230 mg/kg at 25% moisture content and then decreased with increasing moisture content from 35% to 55%. Litter at 0% moisture content adsorbed  $>2,800$  mg/kg of ammonia, more than by litter with moisture content  $\geq 45\%$ .

Based on the results of this research, following are some recommendations for future study.

1. Based on the assumption in isotherms, it may important to analyze and discuss using

thermodynamics of adsorption and desorption in broiler litter.

2. Broiler litter and cake has enough oxygen due to ventilation, adequate moisture content for microbes, and neutral pH values. Based on the environment, it would seem that nitrification should occur; however, nitrate concentrations were very low. This is probably due to ammonium substrate inhibition or other chemical compounds, which reduced the nitrate concentration in broiler litter. There is need to confirm if substrate or other chemical inhibition prevented nitrification.