

SORPTION OF AMMONIUM DERIVED FROM MEMBRANE TREATED LANDFILL  
LEACHATE TO WOODY BIOMASS

By

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To my mother, father, and sister

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## LIST OF ABBREVIATIONS

ACSWL	Alachua County Southwest Landfill
CEC	Cation Exchange Capacity
DI	Deionized
FDEP	Florida Department of Environmental Protection
GWCTL	Groundwater Cleanup Target Level
HDPE	High Density Polyethylene
MAPE	Mean Absolute Percentage Error
MSW	Municipal Solid Waste
NMC	New Mulch Coarse
NMF	New Mulch Fine
OMC	Old Mulch Coarse
OMF	Old Mulch Fine
RO	Reverse Osmosis
SSE	Sum of Square Error

Abstract of Thesis Presented to the Graduate School  
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SORPTION OF AMMONIUM DERIVED FROM MEMBRANE TREATED LANDFILL  
LEACHATE TO WOODY BIOMASS

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Treatment of municipal solid waste (MSW) landfill leachate is challenging because of its potential to contain a wide range of pollutants. Operators will often employ a combination of different treatment techniques to address these various pollutants. Reverse osmosis (RO) is one treatment method that can achieve full purification (rejection rates of 98-99%) of most leachate pollutants (Renou, 2008); however, ammonia-nitrogen is one pollutant that is difficult to remove using RO and still requires additional treatment. At the Alachua County Southwest Landfill (ACSWL), a research site located in Florida, a RO system is used to treat leachate from a closed MSW landfill. The system produces an effluent that meets state requirements for land application with the exception of ammonia-nitrogen concentrations exceeding the 2.8 mg/L threshold. A landfill operator could land apply the RO effluent to terrestrial crops; in this scenario the plants would uptake the remaining ammonia-nitrogen. An alternative approach would be to capture the nitrogen for beneficial use off-site. Landfill operators produce a large amount of woody biomass from yard waste collection; such material is typically low in nitrogen and high in carbon content. Research was conducted to evaluate whether the nitrogen content in the RO effluent could be adsorbed onto the

woody biomass, thus forming a value-added product; a nitrogen-enriched mulch or compost.

Chapter 2 of this thesis details a laboratory isotherm experiment evaluating the adsorption capacities of the woody biomass. The Freundlich isotherm was determined to be the best fit isotherm model to the experimental data. In comparison to other adsorbent materials, popular zeolites such as Clinoptilolite outperform the mulch; however, the mulch is comparable to other adsorbent materials such as soils. A theoretical ammonia-woody biomass adsorption system was developed from the experimental data. The results suggest a nitrogen-enriched mulch product could be produced from the adsorption system, yielding a fertilizer or compost product; however, in terms of ammonia-nitrogen removal, the woody biomass is better suited for a low volume system wherein the system produces low amounts of ammonia-nitrogen that need to be treated.

Chapter 3 consists of passing the ACSWL RO system permeates through fixed bed columns containing the mulch. A high ammonia removal rate (>99%) was achieved through a two-step process of adsorption and nitrification. Degradation and composting were evaluated, in terms of percent carbon and nitrogen composition, dry weights, and carbon-to-nitrogen ratios, to determine the nutrient value of the mulch after the experimental period. Degradation and composting did occur within the mulch substrate because of a decrease in both mulch dry weights and C/N ratios; however, if the total amount of nitrogen added during the experiment period adsorbed onto the mulch substrate, the C/N ratios would not significantly reduce to optimal composting

conditions. Further studies must be conducted to demonstrate the full effect of adding nitrogen to the mulch with the goal of decreasing the C/N ratio to composting conditions.

## CHAPTER 1 INTRODUCTION

### 1.1 Background and Problem Statement

Municipal solid waste (MSW) management today constitutes a major environmental, economical, and social problem worldwide (Renou et al., 2008). Landfilling continues to be the most effective and popular method for disposal of MSW - in 2010, approximately 54% of MSW generated in the United States was landfilled (EPA, 2010). As landfilling continues to be implemented, leachate generated from landfill cells will continue to be a problem. Landfill leachate is the aqueous effluent produced from rainwater percolation through the waste layers. Leachate can also stem from inherent moisture within the waste contained in the landfill cell. It is characterized as a complex wastewater and can contain many different types of pollutants including organic matter, ammonia-nitrogen, heavy metals, and chlorinated organic and inorganic salts (Zouboulis and Petala, 2008; Renou et al., 2008). These pollutants can make it difficult to implement treatment techniques to meet groundwater quality regulatory thresholds.

Reverse osmosis (RO) treatment is one technique that can remove a majority of these pollutants; however, ammonia-nitrogen is one pollutant that is difficult to remove from leachate using RO techniques. This is observed with the RO leachate treatment system at the Alachua County Southwest Landfill (ACSWL). The RO system at the ACSWL is a two-stage system that produces a clean effluent (permeate) and a rejected, more contaminated, effluent (concentrate). The permeate meets groundwater quality regulatory thresholds except for ammonia-nitrogen. Table 1-1 shows the water quality for both stages of the system along with the influent (raw leachate). Currently, the

second stage permeate is spray irrigated onto the ACSWL's vegetative cover wherein the vegetation consumes the remaining ammonia-nitrogen; however, researchers in the current study evaluated methods to capture this residual nitrogen as a value-added nutrient. In the current study, a method is explored to transfer the nitrogen found in the ACSWL RO system's permeate onto woody biomass, another waste product often managed by landfill and waste station operators, aiming to create a value-added biomass product that can be used as a fertilizer or compost.

## **1.2 Research Approach**

### **1.2.1 Sorbate and Sorbent**

The current study evaluates the feasibility of transferring the nitrogen in the ACSWL RO system's permeate (the sorbate) to woody biomass (the sorbent). The sorbate originates from the ACSWL site, located in the city of Alachua, Florida. The landfill began receiving waste in the 1970s and closed in 1999. During operation, approximately 300 tons per day of MSW was disposed in the landfill. The ACSWL contains a 27 acre, class I, lined solid waste cell that operates as a bioreactor (leachate is recirculated to promote waste stabilization). As part of bioreactor operations, a RO system is used to partially treat the leachate produced from the lined cell. The RO system produces a clean effluent (permeate) and a more contaminated effluent (concentrate) wherein intermediate effluents (first stage concentrate, first stage permeate) and final effluents (second stage concentrate, second stage permeate) are produced. Table 1-1 provides the water quality of the first and second stage permeates as well as the raw leachate from the landfill waste cell averaged during the first quarter of 2012. As seen in Table 1-1, both permeate effluents exceed the Florida Department of Environmental Protection (FDEP) ammonia-nitrogen groundwater cleanup target

level (GWCTL) of 2.8 mg/L with first stage and second stage permeate containing an ammonia-nitrogen concentration of 131 mg/L and 5.3 mg/L, respectively.

The sorbent originates from the Alachua County solid waste transfer station located in the Leveda Brown Environmental Park in Gainesville, Florida. Biomass waste (consisting of wood and yard biomass materials) is accepted through a yard waste and wood debris refuse service. The biomass waste consists of tree branches, twigs, leaves, pine needles, and other typical constituents of yard waste and wood debris. The woody biomass (mulch) is ground into a mulch product that is available for local residents to pick up. Two mulch types were obtained from the collection facility, new and old mulch. New mulch refers to mulch that was stored at the transfer station for one month; old mulch was stored at the transfer station for one year. Each mulch type was processed separately through a high volume screener. Four mulch types were examined in this experiment: new fine mulch, new coarse mulch, old fine mulch, and old coarse mulch. Table 1-2 depicts the four mulch types, abbreviations, ages, and particle size ranges.

### **1.2.2 Experimental Approach**

The approach to the current study begins with a laboratory isotherm experiment (Chapter 2). In this experiment the mulch is contacted with ammoniated solutions that vary in ammonia-nitrogen concentrations. Results will help determine the ability of the various mulch types to adsorb the ammoniated species from the solutions. The experimental data can be interpreted into an isotherm model that can then be used to predict adsorption at varying ammonia-nitrogen concentrations, particularly in field applications. Results determined in Chapter 2 will be the foundation for the field experiment conducted in Chapter 3. This experiment consists of passing the ACSWL

RO system permeates through fixed bed columns containing the mulch. Results of this experiment will help determine the amount of nitrogen (in the form of ammoniated species) that can be captured onto the mulch's surface. Results will also determine the feasibility of using the mulch as a compost and/or fertilizer product. Comparisons will be made between both experiments to evaluate the ability to predict ammonia adsorption in field settings by models determined in the laboratory.

### **1.3 Research Objectives**

Objectives for the laboratory isotherm experiments (Chapter 2) are:

- Determine maximum adsorption capacities of the mulch.
- Compare adsorption capacities of different mulch types (fine vs. coarse and new vs. old)
- Compare mulch adsorption behaviors to isotherm models, Langmuir and Freundlich, and determine which model best fits the experimental data.
- Compare mulch to other adsorbent materials in literature to evaluate relative adsorption performance.
- Evaluate the ACSWL RO system permeate under the laboratory isotherm experiments and compare to theoretical isotherm models.
- Develop an adsorption model to predict ammonia adsorption concentrations per mass of mulch.

Objectives for the fixed bed column experiments (Chapter 3) are:

- Determine if the mulch (carbon rich source) can be used as compost after contact with ACSWL RO permeate (nitrogen rich source).
- Compare mulch (post experiment) with commercial fertilizer.
- Compare the adsorption behavior of different mulch types (fine vs. coarse and new vs. old).
- Determine if isotherm models, developed in Chapter 2, are able to predict ammonia-nitrogen adsorption in the Chapter 3 experiment.

## **1.4 Organization of Thesis**

Chapter 2 of this thesis consists of laboratory isotherm experiments. Chapter 3 examines fixed bed column experiments, expanding upon Chapter 2 results. The thesis ends with a summary and conclusions in Chapter 4. Appendices are presented at the end.

Table 1-1. Average Influent and effluent water quality of the RO leachate treatment system at the ACSWL during the first quarter of 2012

Parameter	Units	Raw Leachate	First Stage	Second Stage
pH	SU	7.41	6.67	5.31
Conductivity	µmho/cm	12520	2016	48
COD	mg/L	1960	51	1
NH <sub>3</sub> -N	mg/L	980	131	5.3
Cl <sup>-</sup>	mg/L	1405	151	2.3

Table 1-2. Brief description of the four mulch types used in the current study

Sample Type	Abbreviation	Age	Size
New, Fine	NMF	One month old	12.7mm – 6.35mm
New, Coarse	NMC	One month old	12.7mm – 6.35mm
Old, Fine	OMF	One year old	6.35 mm-.42mm
Old, Coarse	OMC	One year old	6.35 mm-.42mm

## CHAPTER 2 AMMONIUM SORPTION TO WOODY BIOMASS USING LABORATORY BENCH SCALE ISOTHERM EXPERIMENTS

### **2.1 Background and Problem Statement**

Treatment of municipal solid waste (MSW) landfill leachate is challenging because of its complex chemistry and its potential to contain a wide range of pollutants. Operators will often employ a combination of different treatment techniques to meet strict water regulatory standards (Ahmed and Lan, 2012; Li et al., 2009). Reverse osmosis (RO) is a treatment technique that can achieve full purification (rejection rates of 98-99%) of most leachate pollutants (Renou, 2008); however, ammonia-nitrogen is one pollutant that is difficult to remove using RO and still requires additional treatment. Ammonia-nitrogen occurs in relatively high concentrations in MSW leachate (500-2000 mg/L, Kjeldsen et al., 2002), which makes it difficult to remove using RO membranes when meeting drinking water regulatory standards is required.

At the Alachua County Southwest Landfill (ACSWL), a research site located in Florida, a RO system is used to treat leachate from a closed MSW landfill. The system produces an effluent that meets state requirements for land application with the exception of ammonia-nitrogen concentrations exceeding the 2.8 mg/L threshold. In one treatment scenario, a landfill operator could land apply the RO effluent to terrestrial crops in which the crops would uptake the remaining ammonia-nitrogen; however, the capture of this nitrogen could be used more beneficially off-site for more innovative applications. Landfill operators also produce a large amount of woody biomass from yard waste collection; such material is typically low in nitrogen and high in carbon content. Research was conducted to evaluate whether the nitrogen content in the RO effluent could be adsorbed onto the woody biomass, thus forming a value-added

product - a nitrogen enriched mulch or compost. Results of this study will determine the maximum amount of nitrogen (in the form of ammonia and ammonium) that is able to adsorb onto woody biomass. These data will be interpreted into an adsorption model that can be used to develop an ammonia-woody biomass adsorption system and ultimately provide insight on the feasibility of creating a fertilizer or compost product.

The objectives of this study are as follows:

- Observe the nature of ammonia adsorption onto woody biomass by comparing isotherm adsorption models (Langmuir and Freundlich) and determining which model best fits the observed data.
- Determine the maximum adsorption capacities of the woody biomass.
- Compare different woody biomass types (e.g. ranges in particle sizes) and determine which is best for ammonia adsorption.
- Compare woody biomass to other adsorbent materials in literature to evaluate relative adsorption performance.
- Develop an adsorption model equation to predict the adsorption of ammonia species to woody biomass.

## **2.2 Materials and Methods**

**Woody Biomass Characterization.** Experiments were conducted using woody biomass obtained from a wood debris and yard waste refuse service located in a municipal solid waste collection facility in Gainesville, Florida. The facility grinds the yard and wood debris into a mulch product. The specific species of the woody biomass (mulch) are not known; Appendix A provides materials that closely identify the mulch used in this study. Carbon, tannin, and lignin contents are also provided in Appendix A; phenolic compounds such as tannin and lignin can increase ammonium adsorption via ion exchange and hydrogen bonding (Wahab et al., 2010). The mulch is stored in piles at the collection facility, exposed to the surrounding environment with the absence of

any covering; it is free of cost and abundant. The mulch was collected from specific piles using large plastic bags. Table 2-1 depicts the four mulch types, abbreviations, ages, and particle size ranges. Samples of new, old, fine, and coarse mulch were collected. New mulch refers to mulch that was stored in piles for one month. Old mulch was stored in piles in for one year. The new and old mulch were processed separately through a high volume screener to create fine and coarse categories. The different mulch types were stored in buckets at 4 °C. The mulch was analyzed for its particle size distribution, moisture, volatile solids, ash, and total carbon and nitrogen contents. Tables 2-2 and 2-3 show the data for each sample type. A description of the analytical methods and instrumentation used in the current study are provided in Appendix B.

**Isotherm experiments.** The adsorption of ammonium onto mulch is examined through a series of isotherm experiments. The isotherm data help determine the adsorption capacity and characteristics of the mulch and provide comparisons to other adsorbents in literature studies. Stock solutions of 1000 mg/L total ammonia-nitrogen were prepared by dissolving ammonium chloride ( $\text{NH}_4\text{Cl}$ ) salts into 1 liter of deionized (DI) water; 3.817 grams of  $\text{NH}_4\text{Cl}$  was weighed on a digital scale. Approximately half of the weighed crystals were transferred to a 100 mL beaker; the beaker was filled with 50 mL of DI water and stirred until the salts dissolved into an aqueous solution. The solution was poured into a 1000 mL volumetric flask. This step was repeated with the remaining half of the weighed crystals. The 100 mL beaker was rinsed with DI water and poured into the 1000 mL volumetric flask to ensure that all  $\text{NH}_4\text{Cl}$  salts were dissolved into the stock solution. This step was performed three times. The poured solution in the volumetric flask was diluted up to the 1000 mL mark with DI water. All

stock solutions were prepared on the day of the isotherm experiments. The pH of the solutions ranged from 8.0 to 8.5.

Experiments were conducted to determine the appropriate contact time when the mulch reached an equilibrium adsorption capacity. 100 grams of NMF were added to three 2 liter HDPE containers (50 g/L dosage). The stock solution was then diluted to 500 mg/L  $\text{NH}_3\text{-N}$  and added to each container with the NMF. The containers were tumbled for 240 minutes. 1 mL samples were extracted using pipettes and analyzed at 5, 15, 30, 45, 60, 120, 180, and 240 minute time marks. The dependence of contact time on percent ammonia removed is shown in Figure 2-1. Equilibrium adsorption capacities were reached at the 45 minute time mark with a maximum total ammonia-nitrogen adsorption of 11%. Between the 60 and 240 minute time marks, the total  $\text{NH}_3\text{-N}$  concentrations stabilized at 11%. A total contact time of 60 minutes was used (instead of 45 minutes) to ensure equilibrium adsorption capacities were met during the batch experiments.

The initial total  $\text{NH}_3\text{-N}$  concentrations used in the experiment ranged from 0 to 500 mg/L. In addition to these concentrations, other ammoniated aqueous solutions were tested. The additional solutions were obtained from the RO system at the ACSWL. The RO system produces two effluents, first stage permeate and second stage permeate, that contain an  $\text{NH}_3\text{-N}$  concentration of 131 and 5.3 mg/L, respectively. A contact time of 60 minutes, established in the sorption rate study, was utilized in the batch experiments. Isotherm experiments were conducted on different days for each initial  $\text{NH}_3\text{-N}$  concentration for a total of five days of elapsed experiment time. For each day, twelve 2 liter HDPE containers were washed with DI water. The 12 containers consist of

one container per mulch type (NMF, NMC, OMF, and OMC) measured in triplicate. Each container was washed three times with a solution of laboratory grade detergent and DI water. After cleaning with the detergent, the containers were rinsed thoroughly six times to ensure no residual chemicals remained. The 1000 mg/L NH<sub>3</sub>-N stock solution was then diluted to the prescribed initial concentration for that day. Each prescribed solution was sampled; 2 mL of solution was extracted with an automatic pipette. The samples were stored in small cuvettes, and pH and temperature were measured in each solution before any contact with mulch; 200 grams of each mulch type was weighed using a digital scale. The mulch samples were transferred into their corresponding containers and the NH<sub>3</sub>-N solutions were poured into each container. The containers were tumbled for 60 minutes; after 60 minutes, 5 mL samples were extracted using an automatic pipette and then stored in small cuvettes. The samples were analyzed for total NH<sub>3</sub>-N and pH within 10 minutes of sample extraction.

## **2.3 Results and Discussion**

### **2.3.1 pH, Temperature, and Ionic Strength Effect on Ammoniated Solutions**

Total ammonia in an aqueous solution consists of two principal forms, the ammonium ion (NH<sub>4</sub><sup>+</sup>) and un-ionized ammonia (NH<sub>3</sub>), with relative concentrations being pH, temperature, and ionic strength dependent. The adsorption behavior of the mulch can be affected by the relative concentrations of NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub> in the solution. The two species of total ammonia, NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>, establish an equilibrium following the equation:



The equilibrium relationship with relative activities is given by the following equation:

$$K = \frac{\{NH_3\}\{H^+\}}{\{NH_4^+\}} \quad (2-2)$$

Equation 2-2 can be transformed to give the ratio of  $NH_3$  and  $NH_4^+$  in a particular solution:

$$\frac{[NH_3]}{[NH_4^+]} = \frac{\gamma_{NH_4^+} K_a}{\{H^+\}} \quad (2-3)$$

Where  $\gamma_{NH_4^+}$  is the activity coefficient of  $NH_4^+$ ,  $K_a$  is the acid dissociation constant, and  $\{H^+\}$  is the hydrogen ion activity. The pH range for the isotherm solutions before mulch contact was between 8.0 and 8.5. Solution temperatures were at  $21 \pm 1$  °C for the experiment. By using equation 2-3, the ammonium ion percentage range was calculated at 86% to 96%. This indicates that before the mulch was contacted, the ammonia species within the solution existed primarily as the ammonium ion. The dominance of ammonium ions along with a pH of 8.0 to 8.5 suggests favorable conditions for adsorption, wherein significant biosorption can occur under high pH and alkaline conditions by polar groups of lignin within the mulch. Biopolymers, mainly lignin and cellulose chains, may become negatively charged, which enhances binding of the positively charged ammonium cations (Wahab et al., 2010).

After the isotherm experiments were conducted, pH values were measured again. The solution pH values ranged between 6.5 and 7.5 for all mulch types. The ionized ammonia percentage range was then calculated at 99% to >99% using equation 2-3. The pH decreased approximately 15% after the solutions came into contact with the mulch. This suggests that the pH of the mulch is less than the pH of the aqueous solution. At a lower pH solution, ammonium has greater competition with  $H^+$  ions. As

more cations are adsorbed, the surface of the mulch becomes positively charged which contributes to the decreasing adsorption capacity (Jang et al., 2005).

### 2.3.2 Overall Sorption Capacities of Mulch

In order to investigate the effect of total  $\text{NH}_3\text{-N}$  concentration on the adsorption capacity of mulch, an equilibrium experiment was performed using a dosage of mulch (100 g/L) that was subjected to various concentrations of total  $\text{NH}_3\text{-N}$  ranging from 0 to 500 mg/L. A comparison of the maximum adsorption capacities of the four mulch types to various  $\text{NH}_3\text{-N}$  concentrations in solution is shown in Figure 2-2, where  $C_e$  (mg/L) is the equilibrium total  $\text{NH}_3\text{-N}$  concentration and  $Q_e$  (mg/g) is the maximum adsorption capacity. Standard deviations show the error range in the results and are represented by error bars for individual data points. As seen in Figure 2-2, fine mulch exhibited greater adsorption capacity than coarse mulch. This is likely attributed to the fine mulch containing smaller particle sizes; due to a higher surface area, more ammonium adsorption sites are available. To determine relative adsorption capacities between individual fine (NMF and OMF) and coarse mulches (NMC and OMC) further data evaluation was conducted. The sum of square error (SSE) was calculated for the experimental data. SSE is calculated by the following equation:

$$SSE = \sum_{i=0}^n (y_i - \bar{y}_i)^2 \quad (2-4)$$

Where  $y_i$  represents the observed data values and  $\bar{y}_i$  represents the predicted data values.

SSE calculations, as shown in Table 2-4, distinguish adsorption capacities between fine and coarse mulch types. A higher SSE, relative to the other mulch types, indicates that the data points for individual equilibrium concentrations are farther apart and relative adsorption capacities are easier to determine. SSE values were high for

NMF and OMF relative to NMC and OMC. This suggests favorable determination, coupled with Figure 2-2 observations, that OMF exhibits a greater adsorption capacity than NMF. This is likely attributed to various physical characteristics:

- OMF contains smaller particles, as seen in Table 2-2, which indicates greater surface area for ammonium ions to be adsorbed; more pore spaces are also present which allows ammonium ions to be trapped.
- OMF contained the largest percentages of mulch in the mesh sizes of 20, 40, and the bottom pan (Table 2-3). The mulch in the bottom pan consists of the finest mulch constituents in the sample along with the inherent soil particles; soil clay content and soil organic matter content can provide high surface areas and active adsorption sites (Cox et al., 1993).
- Old mulch was exposed to the surrounding environment 11 months more than new mulch. Processes such as physical and chemical weathering can affect the surface characteristics of the mulch. Both processes promote the degradation of the mulch's physical and chemical makeup thus old mulch contains more pore spaces, more surface area.
- Biodegradation (composting) can also occur when microorganisms break down the mulch's organic matter. Mulch exposure to rain and atmospheric oxygen promote this process. In the current study, old mulch was found (by researcher observations) to contain fewer leaves and less grassy material, which is indicative of biodegradation. This degradation can lead to increased pore spaces and greater mulch surface area.

Coarse mulches (NMC and OMC) exhibited almost equal adsorption capacities. A majority of the error bars for both mulch types overlapped, indicating ambiguity between relative adsorption capacities. In addition, SSE values for NMC and OMC were small compared to NMF and OMF; orders of magnitude ranged from -3 to -6, with three of the equilibrium concentrations containing an order of magnitude of -4. As seen in the particle size distribution (table 2-3), OMC contains smaller mulch particles thus a higher surface area which suggests a higher adsorption potential; however, this higher surface area did not positively contribute to OMC adsorption capacities. In addition, factors affecting adsorption capacities as listed above (i.e. physical/chemical weathering and

biodegradation) did not seem to significantly influence adsorption between old and new coarse mulch. The coarse mulches also contain minimal soil particles that can minimize active cation adsorption sites. Overall adsorption capacities observed for all mulch types decreased in the order: OMF>NMF>NMC≈OMC.

### 2.3.3 Isotherm Experiments

An adsorption isotherm is any equation that relates the amount of adsorbate at the surface to the amount of adsorbate in solution when the system has reached equilibrium. Equilibrium adsorption isotherms are fundamentally important in the design of adsorption systems because they can predict the ability of a certain adsorbent to remove a pollutant down to a specific discharge value. Langmuir and Freundlich isotherm models are used to describe the experimental results of adsorption isotherms, specify the parameters that can be determined, compare the ammonium ion behavior, and determine the theoretical adsorption isotherms. The isotherms are expressed by plotting the amount of ammonium ions held by the mulch versus the equilibrium concentrations of total NH<sub>3</sub>-N left in the solution. Equations 2-5 and 2-6 show the Langmuir and Freundlich isotherm models where Q<sub>e</sub> (mg/g) is the amount of adsorbed ammonia per kilogram of woody biomass, C<sub>e</sub> (mg/L) is the equilibrium concentration of ammonia, b (L/mg) is the Langmuir isotherm constant, S<sub>m</sub> (mg/g) is the maximum adsorption capacity, K<sub>f</sub> (L/g) is the Freundlich empirical constant, and n is related to the sorption intensity.

The Langmuir isotherm:

$$Q_e = \frac{S_m b C_e}{1 + b C_e} \quad (2-5)$$

The Freundlich isotherm:

$$Q_e = K_f C_e^{\frac{1}{n}} \quad (2-6)$$

Both the Langmuir and Freundlich isotherm models were linearized to determine the models' parameters:

Langmuir model (one possible linearization):

$$\frac{C_e}{Q_e} = \frac{1}{bS_m} + \frac{C_e}{S_m} \quad (2-7)$$

Freundlich model:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (2-8)$$

The linearized forms were plotted. Linear regressions were conducted to determine the y-intercepts and slopes. The y-intercepts and slopes were then calculated into the isotherm constants. Table 2-5 shows the isotherm constants ( $S_m$ ,  $b$ ,  $n$ , and  $K_f$ ) derived from the linearized forms of the isotherm models. SSE values were calculated between experimental and predicted values. Mean absolute percentage errors (MAPE) were also calculated, which indicates the fit between the experimental and predicted values of adsorption capacity. MAPE is determined by the following equation:

$$\text{MAPE}(\%) = \sum_{i=1}^n \frac{|(q_e)_{\text{experimental}} - (q_e)_{\text{predicted}}|}{(q_e)_{\text{experimental}}} \times 100\% \quad (2-9)$$

Where  $n$  is the number of experimental data.

Figure 2-3 shows the superposition of experimental results (points) and the predicted calculated points (lines). The predicted solid phase loadings (adsorption densities) for all mulch types are higher than the Freundlich lines between equilibrium concentrations of 0 to 250 mg/L. After 250 mg/L, both lines intersect, at which point the maximum adsorption capacities for both models are equal. After this intersection,

Langmuir lines stabilize to their respective maximum adsorption capacities while Freundlich lines continue to increase. Both isotherm models follow their respective principles: Langmuir stabilizes due to monolayer adsorption while Freundlich increases due to multilayer adsorption.

The ammonium adsorption onto the mulch best fits the Freundlich model. As previously seen in Figure 2-2, the experimental data for all mulch types follow the same pattern – high slope at low  $C_e$  values and a lower slope at higher  $C_e$  values (average slope between  $C_e$  values of 0 to 100 mg/L is 0.0033 L/g and between 100 and 450 mg/L is 0.0014, a 57% decrease). This decrease follows the isotherm behavior of the ammonium ions as they reach adsorption equilibrium with the mulch (e.g., as seen in Jang et al., 2005 or Hamdaoui, 2007); however, the experimental data show that as equilibrium concentrations increase, the adsorption capacities continue to increase with minimal decline in adsorption rates; this suggests the experimental data could follow the Freundlich line.

Freundlich SSE values for NMF, NMC, and OMC are less than the Langmuir values, which suggests a better fit for the Freundlich model, while SSE values for Langmuir are smaller for OMC, suggesting a better fit for Langmuir for that mulch type. MAPE percentages indicate favorable fits to Freundlich for NMF and OMC, while Langmuir provides a better fit for NMC and OMF. The SSE and MAPE data suggest ambiguity for distinguishing the best isotherm fit for predicting overall mulch adsorption behavior. This ambiguity is likely attributed to the initial separation of the Langmuir and Freundlich predicted lines. Between equilibrium concentrations of 0 to 250 mg/L, Langmuir and Freundlich lines are relatively close to each other. Difference calculations

between the Langmuir and Freundlich predicted lines, for equilibrium concentrations of 0 to 250 mg/L, were conducted by subtracting the Langmuir predicted value from the Freundlich predicted value for that specific  $C_e$  value. The maximum distances observed for NMF, NMC, OMF, and OMC are 0.071, 0.033, 0.063, and 0.042 mg/g, respectively. This indicates that experimental values with higher standard deviation that are between both predicted lines can be assigned to either isotherm model. For example, in Figure 2-3, the average adsorption capacity for NMF at 239 mg/L is  $0.5817 \text{ mg/g} \pm 0.0503$ . The standard deviation range contains both Langmuir and Freundlich predicted lines. Average adsorption capacities were used in SSE and MAPE calculations excluding standard deviations; this exclusion can influence the SSE and MAPE values.

Table 2-6 compares the results of the current study to other adsorbents found in literature. The source of the study and type of adsorbent are given in the first and second columns. The reported maximum adsorption capacities ( $S_m$ ) are given in the third column, which compares the maximum amount of adsorbate (ammonium) that is able to adsorb onto that particular adsorbent. The fourth and fifth columns (Scenario 1 and Scenario 2) give a detailed comparison of the various adsorbents. Scenario 2 uses the Langmuir model (equation 2-5) to determine  $Q_e$  values for comparison. Scenario 1 transforms equation 2-5 to calculate the required dosages for comparison:

$$\frac{C_o - C_e}{D} = \frac{S_m b C_e}{1 + b C_e} \quad (2-10)$$

Where  $C_o$  is the initial total ammonia-nitrogen concentration (mg/L),  $C_e$  is the equilibrium total ammonia-nitrogen concentration (mg/L), and  $D$  is the dosage (g/L). The effluent produced from the RO system at the ACSWL is used as a case study to set baseline parameters in both Scenario 1 and Scenario 2. The effluent from the RO system has an

ammonia-nitrogen concentration of 5.3 mg/L that exceeds the treatment target concentration of 2.8 mg/L, the Florida Department of Environmental Protection (FDEP) Groundwater Cleanup Target Level (GWTCL).

Scenario 1 compares the required dosages, calculated using equation 2-10, for the various adsorbents; a lower dosage is optimal because less mass of the adsorbent is required. It specifies  $C_o$  and  $C_e$  where  $C_o$  is 5.3 mg/L and  $C_e$  is 2.8 mg/L. As seen in table 2-6, zeolite adsorbents require the least adsorbent mass. Natural zeolites such as clinoptilolite have been found very effective in removing ammonia from water by means of its excellent adsorption capacity (Du et al., 2003). Sawdust, an inexpensive biosorbent that is abundant in nature, requires a dosage amount of 9.6 g/L which is comparable to the zeolite materials. Sawdust, like the mulch used in this experiment, is high in polymeric materials such as lignin and tannins that can become negatively charged to adsorb ammonium cations. NMF and OMF were the most comparable to the other adsorbents with dosages at 160 and 177 g/L, respectively. Both NMF and OMF were closest to the Haynie soil, as reported by Fernando et al (2005). Scenario 2 compares  $Q_e$  values, the amount of ammonium able to adsorb per gram of adsorbent, with  $C_e$  being specified at 2.8 mg/L. The three types of Clinoptilolites were the materials able to adsorb the most amount of ammonium per gram of Clinoptilolite. NMF and OMF were most comparable to other adsorbents such as Sepiolite, reported by Bernal and Lopez Real (1993), and Kennebec and Haynie soil, reported by Fernando et al., 2005.

Isotherm experiments were conducted mixing the mulch with two ammoniated effluents from a membrane filtration system that treats landfill leachate. The treatment system produces two effluents, first stage permeate and second stage permeate,

containing total ammonia-nitrogen concentrations of 131 and 5 mg/L, respectively. The experiments yielded isotherm data that compare the theoretical models with the experimental data of both permeates. Table 2-7 compares the predicted adsorption capacity values to the adsorption capacities of the permeates, along with MAPE and SSE data. As seen in Table 2-7, Langmuir is more suitable for predicting the first and second stage permeate adsorption capacities. For first stage permeate, MAPE and SSE are lower for all mulch types for the Langmuir model. For second stage permeate, MAPE for Langmuir is lower than Freundlich for all mulch types except NMC. Langmuir SSE values are also lower than Freundlich for all mulch types. These data suggest that Langmuir is better suited to predict field related adsorption capacities.

The theoretical versus experimental values for first and second stage permeate are represented graphically in Figure 2-4. NMF and OMF yielded the closest capacities for Langmuir in which the predicted values are within the standard deviation ranges for the experimental data. NMC adsorption capacities for Langmuir are also within the standard deviation range; however, the Freundlich predicted value is 2.9 mg/g below the standard deviation range. This suggests that the experimental data for NMC can follow either isotherm model. The OMC experimental data point for first stage permeate shows the greatest gap between the Langmuir and Freundlich models. Further experiments have to be conducted to determine if the experimental data follow a Langmuir or Freundlich model for all mulch types over larger equilibrium concentrations. Overall, Langmuir provided a better fit for both first and second stage permeate.

The comparison of the theoretical values of the isotherm models to the experimental adsorption capacities provides insight into the design of a mulch-

ammonium adsorption system. The effluents from the RO system contain other chemical constituents; in contrast to the laboratory batch experiments which used aqueous solutions consisting of ammonium and chloride ions along with ammonia gas. In Figure 2-4, the first stage adsorption capacities for OMC were greater than the theoretical isotherm models. This could indicate that the other constituents contained within the first stage permeate could positively influence the sorption mechanisms. NMF, NMC, and OMF stayed relatively close to the theoretical isotherm models, which indicate that if a mulch-ammonia adsorption system were designed, the adsorption capacities could be predicted by the theoretical isotherm models determined in this study.

## **2.4 Summary and Discussion**

The objectives set forth in the current study were met. The Freundlich isotherm was determined to be the best fit adsorption model. The mulch was compared to other adsorbents. NMF and OMF were the most comparable to the other adsorbents such as Haynie soil. Comparisons between different mulch types were made; mulches primarily consisting of fine particles can yield better adsorption capacities compared coarse mulches due to the fine mulches contained greater surface areas. In addition, RO system effluents were contacted with the mulch; results suggested Langmuir was the best fit; however, further experiments must be conducted with varying concentrations to support this finding.

The results of the current study show that nitrogen (in the form of ammonia and ammonium) can adsorb onto the mulch thus suggesting a potential fertilizer or compost product; however, further analysis must be conducted to determine the practical use of mulch as a viable treatment option to remove high levels of nitrogen in a particular

solution. The following is an example of an ammonia-mulch adsorption system derived from the results of the current study. The RO system at the ACSWL produces a second stage permeate that contains a total ammonia-nitrogen concentration of 5.3 mg/L. The Freundlich adsorption model for NMF, as determined in the current study, will be used to calculate the required amount of mulch needed per day to treat the ammonia to levels acceptable for discharge to groundwater per Florida requirements:

$$Q_e = (0.0126)C_e^{\frac{1}{1.458}} \quad (2-11)$$

The desired ammonia-nitrogen equilibrium concentration ( $C_e$ ) for this example is 2.8 milligrams/liter (the FDEP groundwater cleanup target level); this yields a  $Q_e$  value of 0.0255 milligrams/gram. The second stage ammonia-nitrogen concentration of 5.3 milligrams/liter is divided by 0.0255 milligrams/gram to yield a mulch dosage of approximately 208 grams of mulch per liter of second stage permeate produced from the RO system. The system produces approximately 22,680 liters/day of second stage permeate. This rate is multiplied by 208 grams/liter to yield a daily amount of mulch required of 4,717 kilograms which is the amount of mulch needed daily for treatment of the second stage permeate (5.3 mg/L ammonia-nitrogen) to meet the FDEP groundwater cleanup target level of 2.8 mg/L. This suggests the mulch is not a viable treatment option for high flow rates; however, the mulch could be favorable for lower volume systems. In addition, the adsorbed nitrogen can still increase the nutrient value of the mulch. In this case, the mulch can be used to intermittently to capture the nitrogen in the second stage permeate and then used as a slow release fertilizer or composting product.

To date, there is little research on ammonium sorption onto mulch; further investigation is needed to examine the total adsorption effectiveness of ammoniated species to mulch. In addition, the mulch used in the current study consisted of various materials, making the adsorbent surface more heterogeneous than in previous literature studies. For example, Jang et al. (2005) determined that heavy metal adsorption onto hardwood bark was best described as a Langmuir behavior. Wahab (2010) described ammonium adsorption onto sawdust that also followed the Langmuir isotherm. In both cases, the researchers used a material that was more uniform than the mulch in the current study; both researchers also used a material comprised of a single constituent (i.e. hardwood bark and sawdust, respectively). The current study presents an alternative use for two waste products generated by landfill operators: ammoniated effluent from leachate treatment and woody biomass from yard waste collection. Although the mulch does not present a viable option for ammonia-nitrogen removal at higher flow rates, the mulch can be used intermittently to capture nitrogen from ammoniated solutions; in turn using the nutrient rich mulch as a slow release fertilizer or compost product.

Table 2-1. Brief description of the four mulch types used the current study

Sample Type	Abbreviation	Age	Size
New, Fine	NMF	One month old	12.7mm – 6.35mm
New, Coarse	NMC	One month old	12.7mm – 6.35mm
Old, Fine	OMF	One year old	6.35 mm-.42mm
Old, Coarse	OMC	One year old	6.35 mm-.42mm

Table 2-2. Moisture, volatile solids, and elemental carbon and nitrogen content of the four mulch types

Sample Type	% Moisture Content 70° C	% Volatile Solids 550° C	% Ash	%Carbon	%Nitrogen
NMF	41.2	77.5	16.4	41.3	0.63
NMC	38.7	81.2	6.5	45.8	0.51
OMF	36.5	66.4	25.0	37.2	0.73
OMC	43.1	72.3	17.7	40.4	0.48

Table 2-3. Particle size distribution analysis of the four mulch types (dried at 70°C)

Mesh size	Opening size (mm)	% Retained			
		NMF	NMC	OMF	OMC
1/2"	12.7	0	15	0	15
1/4"	6.35	3	62	8	54
4	4.76	21	8	11	9
10	2.00	46	9	46	12
20	0.841	16	1	18	2
40	0.420	5	1	6	1
Pan	<0.420	9	5	12	8

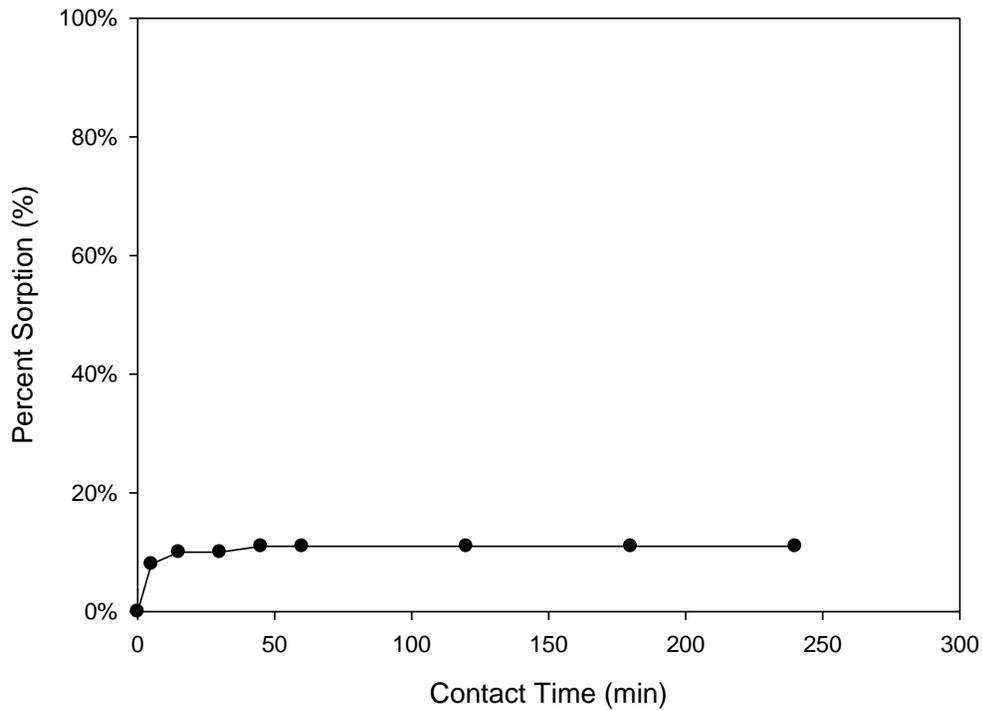


Figure 2-1. Determination of appropriate contact time by evaluating percent of ammonia adsorbed versus contact time

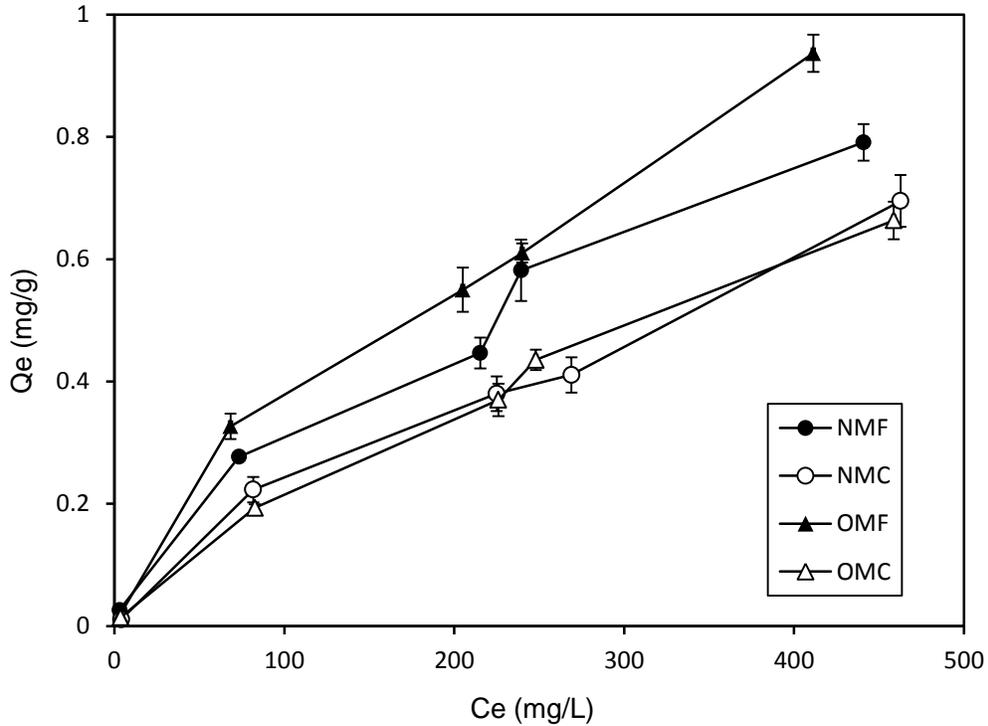


Figure 2-2. Maximum adsorption capacities of the four mulch types after conducting isotherm experiments

Table 2-4. SSE values comparing NMF and OMF mulch types and NMC and OMC mulch types for determination of overall adsorption capacity order

Equilibrium Concentration	NMF and OMF	NMC and OMC
3	$5.78 \times 10^{-5}$	$9.00 \times 10^{-6}$
73	$2.50 \times 10^{-3}$	$9.00 \times 10^{-4}$
215	$1.07 \times 10^{-2}$	$1.00 \times 10^{-4}$
239	$8.18 \times 10^{-4}$	$6.05 \times 10^{-4}$
440	$2.12 \times 10^{-2}$	$1.00 \times 10^{-3}$

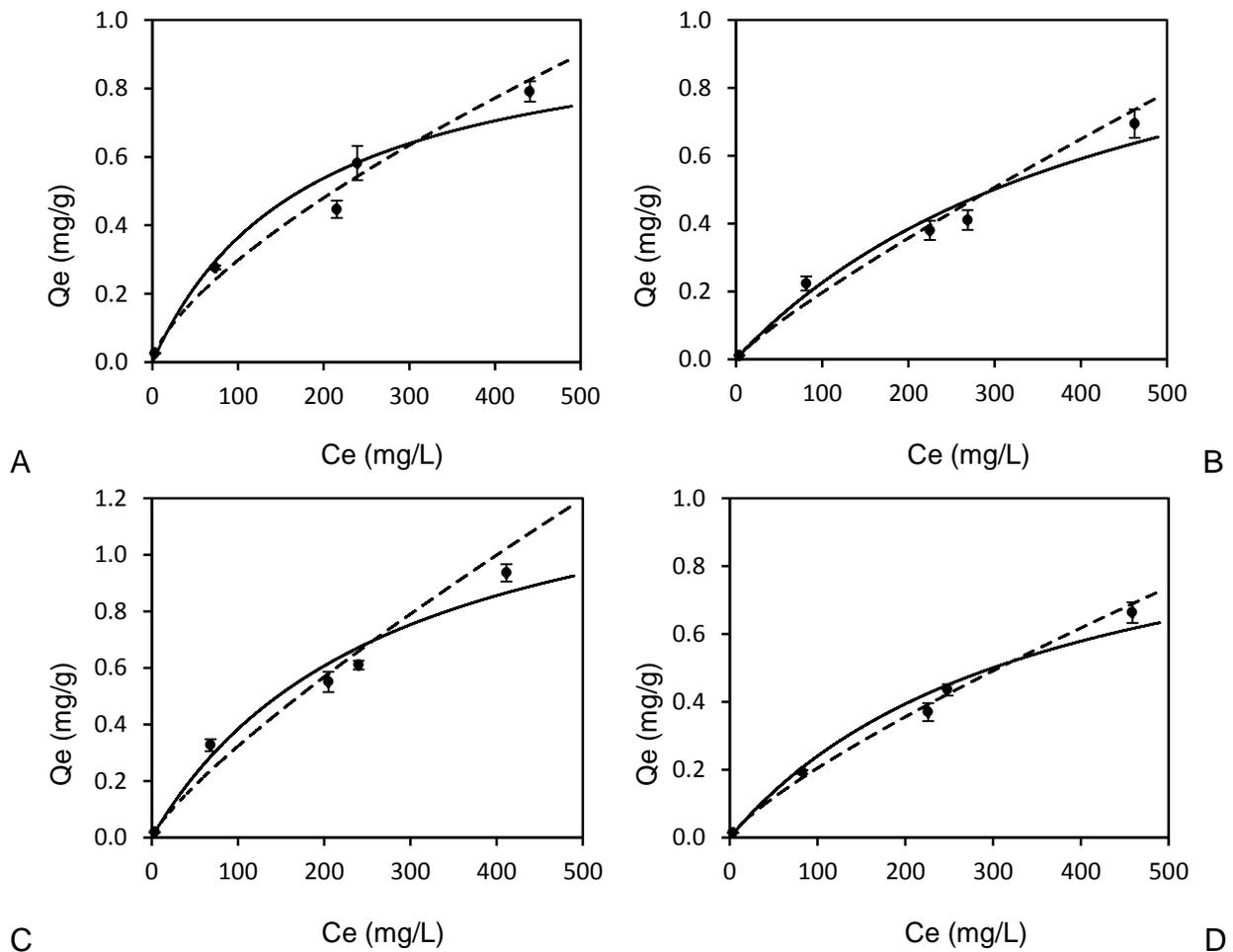


Figure 2-3. Isotherm experimental results (●) of the four mulch types along with Langmuir (—), and Freundlich (- - -) theoretical adsorption models based on experimental data A) NMF, B) NMC, C) OMF, D) OMC

Table 2-5. Comparison of Langmuir and Freundlich constants, correction coefficients ( $R^2$  values) and MAPE and SSE values for the adsorption of ammoniated species to mulch

Mulch Type	Langmuir				$K_f$	Freundlich		
	$S_m$ $\text{mg g}^{-1}$	$b$ $\text{L mg}^{-1}$	MAPE %	SSE		$n$	MAPE %	SSE
NMF	1.026	0.0055	16.33	0.0033	0.0126	1.458	8.58	0.0014
NMC	1.281	0.0021	10.89	0.0018	0.0036	1.159	13.01	0.0015
OMF	1.451	0.0035	9.46	0.0029	0.0076	1.228	12.74	0.0037
OMC	1.092	0.0028	11.02	0.0011	0.0052	1.255	6.10	0.0003

Table 2-6. Comparison of the mulch used in the current study to other adsorbent materials found in literature

Source	Adsorbent	Maximum Adsorption Capacity, $S_m$ (mg/g)	Scenario 1 <sup>a</sup> Dosage (g/L)	Scenario 2 <sup>b</sup> $Q_e$ (mg/g)
Bernal and Lopez-Real, 1993	Zeolite 1	8.149	4.9	0.513
Bernal and Lopez-Real, 1993	Zeolite 2	10.616	60	0.041
Bernal and Lopez-Real, 1993	Sepiolite	1.47	157	0.016
Current Study	NMF	1.026	160	0.016
Current Study	NMC	1.281	333	0.007
Current Study	OMF	1.451	177	0.014
Current Study	OMC	1.092	294	0.008
Fernando et al., 2005	Kennebec soil	0.909	231	0.011
Fernando et al., 2005	Haynie soil	0.217	190	0.013
Wahab et al., 2010	Sawdust	1.7	9.6	0.262
Wang et al., 2006	Clinoptilolite-1	2.128	3.5	0.718
Wang et al., 2006	Clinoptilolite-2	2.375	3.1	0.813
Wang et al., 2006	Clinoptilolite-3	2.469	3.2	0.787

<sup>a</sup> Scenario 1 calculates the dosage, the amount of adsorbent needed per liter of solution, with a specified initial total ammonia-nitrogen concentration ( $C_o$ ) of 5.3 mg/L and an equilibrium ammonia-nitrogen concentration ( $C_e$ ) of 2.8 mg/L.

<sup>b</sup> Scenario 2 calculates the  $Q_e$  value, the amount of ammonium (mg) adsorbed per gram of adsorbent with a specified equilibrium concentration ( $C_e$ ) of 2.8 mg/L.

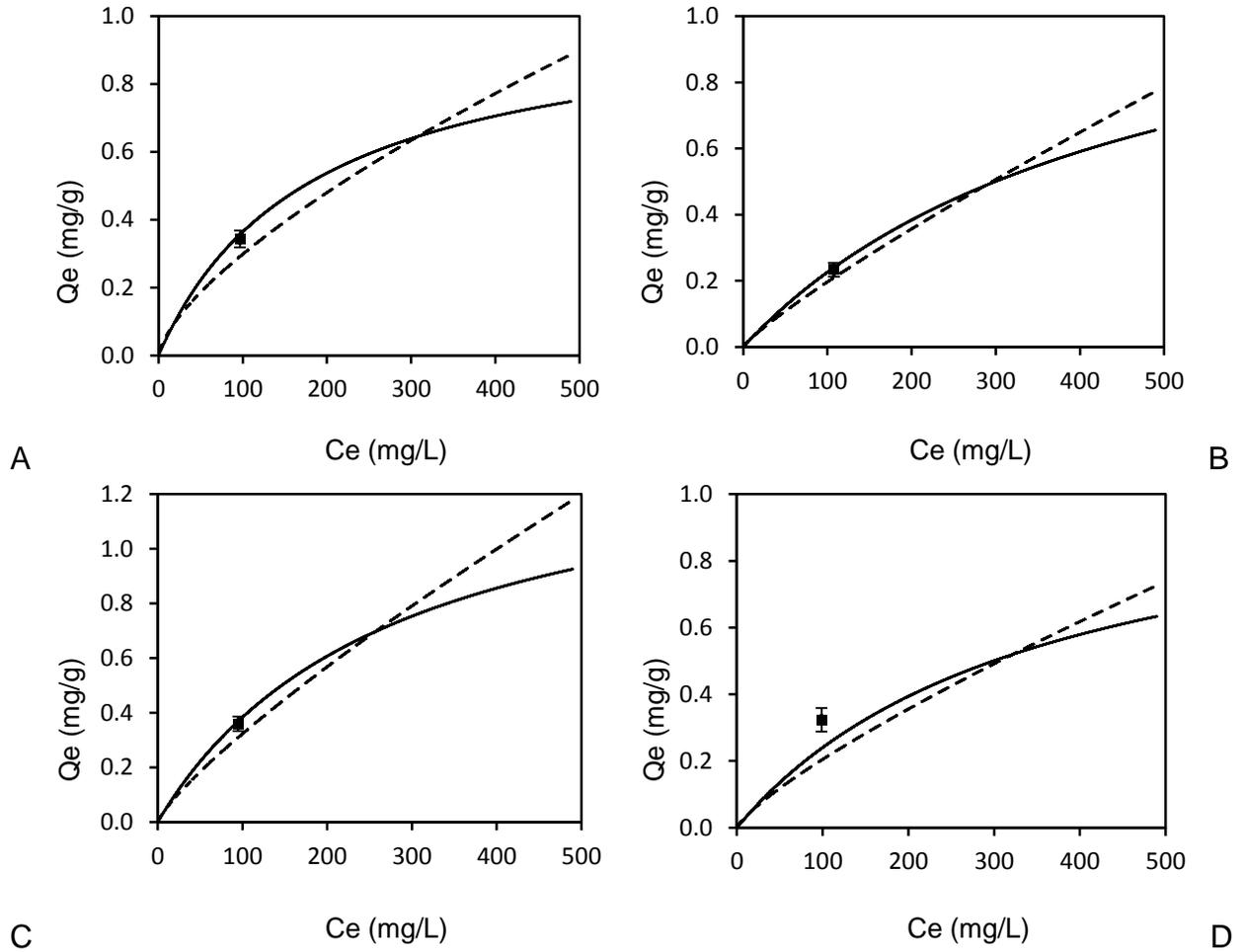


Figure 2-4. Experimental data (■) for RO system effluents (first stage permeate) compared to the theoretical isotherm models, Langmuir (—) and Freundlich (- -) A) NMF, B) NMC, C) OMF, D) OMC

Table 2-7. Theoretical maximum adsorption capacities for the RO system effluents (first stage and second stage permeate) along with the observed (experimental) data for the RO system effluents with MAPE and SSE calculations

Mulch Type	Theoretical		Observed	MAPE (%)		SSE	
	Langmuir	Freundlich		Langmuir	Freundlich	Langmuir	Freundlich
First Stage							
NMF	0.3563	0.2916	0.343 ± 0.025	7.87	14.69	1.71 x 10 <sup>-4</sup>	2.66 x 10 <sup>-3</sup>
NMC	0.2398	0.2091	0.233 ± 0.021	7.36	10.74	4.23 x 10 <sup>-5</sup>	5.81 x 10 <sup>-4</sup>
OMF	0.3694	0.3099	0.360 ± 0.027	6.60	13.49	8.93 x 10 <sup>-5</sup>	2.5 x 10 <sup>-3</sup>
OMC	0.2377	0.2026	0.323 ± 0.035	25.74	36.71	7.31 x 10 <sup>-3</sup>	1.45 x 10 <sup>-2</sup>
Second Stage							
NMF	0.0244	0.0352	0.0137 ± 0.0012	79.94	159.3	1.15 x 10 <sup>-4</sup>	4.64 x 10 <sup>-4</sup>
NMC	0.0116	0.013	0.0150 ± 0.0017	21.28	12.39	1.1 x 10 <sup>-5</sup>	3.99 x 10 <sup>-6</sup>
OMF	0.0214	0.0242	0.0163 ± 0.0006	31.27	48.90	2.61 x 10 <sup>-5</sup>	6.39 x 10 <sup>-5</sup>
OMC	0.0138	0.0175	0.0123 ± 0.0012	13.52	43.20	2.53 x 10 <sup>-6</sup>	2.73 x 10 <sup>-5</sup>

## CHAPTER 3 AMMONIUM SORPTION TO WOODY BIOMASS USING FIXED BED COLUMNS

### 3.1 Background and Problem Statement

Ammonia-nitrogen is a common aquatic pollutant that can be found in lakes, rivers, and drinking water reservoirs; it can stem from a variety of man-made and natural sources. Ammonia levels exceeding 0.3 – 0.5 mg/L (AWWA, 1990) can cause eutrophication - growth of simple algae and plankton in bodies of water which decreases dissolved oxygen concentrations. The removal of ammonia from these waters is important to meet environmental regulatory standards, and minimize groundwater contamination and eutrophication. In the current study, ammonia contained in an effluent from a landfill leachate treatment system is examined. Landfill leachate is a wastewater produced mostly from rainfall percolation through a landfill waste mass. Ammonia concentrations within landfill leachate can range from 500 – 2000 mg/L, and concentrations within the waste mass do not decrease with time (Kjeldsen, 2002). Several researchers have identified ammonia as the most significant component of leachate for the long-term (Robinson, 1995; Krumpelbeck and Ehrig, 1999; Christensen et al., 1994; Christensen et al., 1999). Adsorption processes for ammonia removal typically use activated carbon and zeolites as the adsorbent; although these materials are effective, they are expensive compared to other adsorbents and the cost for regeneration processes can be expensive (Wahab, 2010). The current study examines woody biomass (mulch) as an alternative adsorbent for ammonia removal. The mulch is renewable, low cost, and can be used as a slow release fertilizer (the adsorbed ammonium as the nutrient) eliminating the need for regeneration processes.

The previous study on ammonia adsorption onto mulch (chapter 2 of this thesis) showed that the experimental mulch can adsorb nitrogen within a particular solution; thus, a slow release fertilizer or compost can potentially be produced. The goal of the current study is to apply the laboratory batch experiments in a field setting using fixed bed columns. The focus of the experiment is to examine the mulch's ability to adsorb the ammonium and the compost-ability and degradation of the mulch to further determine the use of the mulch as a nutrient product. The results of this experiment can provide a case study for ammonia adsorption onto the mulch; in such a case study, an adsorption system is developed that uses a material (mulch) that is low cost, renewable, and beneficial for use as a fertilizer. The objectives of this study are as follows:

- Determine if the mulch (carbon rich source) can be used as compost after contact with ACSWL RO permeate (nitrogen rich source).
- Compare mulch (post experiment) with commercial fertilizer.
- Compare the adsorption behavior of different mulch types (fine vs. coarse and new vs. old).
- Determine if isotherm models, developed in Chapter 2, are able to predict ammonia-nitrogen adsorption in Chapter 3 experiment.

### **3.2 Materials**

**Sorbent and Sorbate.** Experiments were conducted using woody biomass obtained from a wood debris and yard waste refuse service located in a municipal solid waste collection facility in Gainesville, Florida. The facility grinds the yard and wood debris into a mulch product. The specific species of the mulch are not known; Appendix A provides materials that closely resemble to the mulch used in this study. Carbon, tannin, and lignin contents are also provided in Appendix A; phenolic compounds such as tannin and lignin can increase ammonium adsorption via ion exchange and hydrogen

bonding (Wahab et al., 2010). The mulch is stored in piles at the collection facility, exposed to the surrounding environment with the absence of any covering; it is free of cost and abundant. The mulch was collected from specific piles using large plastic bags. Table 2-1 depicts the four mulch types, abbreviations, ages, and particle size ranges. Samples of new, old, fine, and coarse mulch were collected. New mulch refers to mulch that was stored in piles for one month. Old mulch was stored in piles in for one year. The new and old mulch were processed separately through a high volume screener to create fine and coarse categories. The different mulch types were stored in buckets at 4 °C. The mulch was analyzed for its particle size distribution, moisture, volatile solids, ash, and total carbon and nitrogen contents. Tables 3-3 and 3-4 show the data for each sample type. A description of the analytical methods and instrumentation used in the current study is provided in Appendix B.

The sorbate (ammonium) originates from the Alachua County Southwest landfill (ACSWL) site located in the city of Alachua, Florida. The leachate from the landfill is treated by a two stage reverse osmosis (RO) system. The RO system produces a clean effluent (permeate) and a more contaminated effluent (concentrate) wherein intermediate effluents (first stage concentrate, first stage permeate) and final effluents (second stage concentrate, second stage permeate) are produced. Table 1 provides the water quality of the first and second stage permeates as well as the raw leachate from the landfill waste cell. According to the Florida Department of Environmental Protection (FDEP), the groundwater cleanup target level for ammonia-nitrogen is 2.8 mg/L. As seen in Table 3-1, both permeate effluents exceed this discharge standard with first stage and second stage permeate containing an ammonia-nitrogen concentration of

131 mg/L and 5.3 mg/L, respectively. Both first and second stage permeates are used as the sorbates in the current study; deionized water is also used as the experiment blank. The mulch types and permeate effluents were combined to create a total of 12 sample types. Table 3-2 shows these sample types along with the associated abbreviations, age of the mulch, and particle size range.

### 3.3 Methods

**Fixed Bed Column Experiments.** The fixed bed columns were in the form of buckets; Table 3-5 provides specific dimensions of the buckets and related experimental parameters. Buckets used in this study were purchased from a local hardware store. A bucket was assigned to each of the 12 sample types listed in Table 3-2. Each sample type was measured in duplicate, equaling a total of 24 mulch buckets. Bucket configurations were assembled into arrays on a concrete pad. A picture of the array configuration is shown in Figure 3-1. The bucket arrays were covered by a metal roof to shield them from rainfall. When the site was vacant, a tarp was placed over the buckets as additional coverage to protect against strong winds and storms. Figure 3-2 shows a schematic of the mulch bucket configuration. Holes were drilled to perforate the bottom of each bucket. The mulch buckets were placed into another bucket labeled as the bottom bucket, as seen in Figure 3-2. The bottom bucket collects leachate effluent after the liquid percolates through the mulch and drains through the perforated bottom. Each collected mulch type was mixed thoroughly with a shovel for 5 minutes before being placed into the individual mulch buckets. After each sample was mixed, the mulch was transferred to the assigned buckets. The buckets were shaken to make sure settling occurred within the mulch bed. The mulch was filled in the buckets until a depth of 3 inches from the top of the bucket to the top of the mulch bed was achieved. Lids

were kept on the mulch buckets at all times except during a watering event. The lid was perforated by drilling holes into it, which allowed oxygen to enter the bucket to maintain an aerobic environment.

The 24 mulch buckets were watered every week for nine weeks and during weeks 11, 15, and 19. At the beginning of each watering event, each bucket was weighed on a digital scale; the weight of each bucket was recorded. The depth from the surface of the mulch to the top of the bucket was then measured and recorded. The depth was determined with measuring tape at four equidistant points on the bucket. The distances were averaged to determine the average depth of the mulch bed. The leachate effluent collected in the bottom bucket was then poured into a graduated cylinder and the volume was recorded. Then 250 mL samples were taken of the leachate effluent and pH measurements were conducted. The samples were stored at 4 °C.

After the leachate sample was collected, the mulch bucket was shaken for 2 minutes for aeration. Between 1900 and 1925 mL of liquid influent per assigned bucket (either first or second stage permeate, or DI water) was measured and poured into a watering can. A watering can was used to water the mulch, distributing the liquid equally throughout the bucket area. A specific watering can was selected with a large spout to cover the area of the bucket equally when watering took place; the perforated lid was then placed back onto the bucket. This process was carried out for each mulch bucket during every watering event. The leachate samples were analyzed within 48 hours of collection. Total ammonia-nitrogen analysis was performed every week for the collected samples. A colorimetric method was used when analyzing the sample in a

spectrophotometer. Nitrate analysis was also performed in weeks 6, 11, and 15. A colorimetric method was also used for nitrate analysis using a spectrophotometer.

### **3.4 Results and Discussion**

#### **3.4.1 Fixed Bed Column Experiments**

Figure 3-3 shows a nitrogen mass balance for the mulch bucket experiments. Ammonium ions contained in the influent enter into the mulch buckets. The nitrogen species in the influent exist only as total ammonia-nitrogen; the influent does not contain nitrite or nitrate concentrations. It should be noted that the ammonia species exists mostly as the ammonium ion due to the low pH ( $\approx 5.5-6.5$ ). In addition, concentrations or references to ammonia, ammonium, nitrite, and nitrate refer to the species as only nitrogen mass and not the total mass of the molecule. Once the ammonium enters the bucket, it follows one of two paths; it either adsorbs to the mulch or stays in solution residing in the leachate effluent. If the ammonium is adsorbed onto the mulch, it can remain unchanged or undergo nitrification. In the case of nitrification, the nitrate species can desorb mainly because of the anionic character of the nitrates thus draining it to the leachate effluent collected in the bottom bucket. The nitrate species can also stay adsorbed onto the mulch, or the nitrate can be denitrified into elemental nitrogen gas and dissipate into the atmosphere. If the ammonium does not adsorb onto the mulch, thus residing in the leachate effluent, the ammonium can either remain as ammonium in solution or undergo nitrification. If nitrification occurs, the nitrite and nitrate species can remain in solution or denitrify into elemental nitrogen gas and dissipate into the atmosphere. Due to the experimental methods, an exact measure of the total nitrogen mass balance will not be known; however, many conclusions can be drawn from the results.

### 3.4.2 Overall Ammonia Removal Rates

Figure 3-4 shows the total ammonia-nitrogen concentrations in the leachate effluent over time for new mulch. First stage permeate contained an influent concentration of approximately 130 mg/L. During weeks 1 through 9, ammonia concentrations in the first stage leachate decreased with NMF decreasing faster than NMC. NMF contained smaller mulch particles that, compared to NMC, had more surface area and acted more as a filter bed, trapping liquid within the column. Between weeks 9 and 19, ammonia concentrations were almost completely removed, which reduced concentrations in the leachate to below 0.5 mg/L. The second stage permeate contained approximately 5 mg/L ammonia in the influent. Between weeks 1 and 6, concentrations for the second stage permeate and DI water stabilized between 1 and 10 mg/L ammonia-nitrogen. During this time, ammonia concentrations in the second stage permeate did not reach significant removal. Between weeks 11 and 19, ammonia concentrations in second stage permeate and DI water achieved an ammonia removal rate of 90%; ammonia concentrations below 0.5 mg/L were achieved.

Figure 3-5 shows the total ammonia-nitrogen concentrations in the leachate effluent over time for old mulch. In weeks 1 through 9, ammonia concentrations in the first stage leachate decreased, with OMF decreasing faster than OMC. Old mulch adsorption of first stage permeate was similar to new mulch in that the fines exhibited better adsorption. This is likely attributed to the increased surface area of the mulch and the fine mulch acting more as a filter bed compared to OMC. From weeks 9 to 19, ammonia concentrations were almost completely removed, which reduced concentrations in the leachate to below 0.5 mg/L. During weeks 1 to 9, second stage permeate and DI water bucket leachates remained between 1 and 10 mg/L. Significant

ammonia removal was not achieved during this time. Between weeks 11 and 19, second stage and DI effluents achieved an ammonia removal rate of 90% with concentrations below 0.5 mg/L, with the exception of OMC-DI, which contained approximately 2 mg/L ammonia-nitrogen at week 11. For all bucket types, approximately 100% ammonia removal was achieved during the later weeks of bucket watering (i.e., weeks 11 to 19).

Ammonia removal was slower in the coarse mulches compared to the fine mulches. Although 100 % ammonia removal was achieved for fine mulches at week 7; 100% ammonia removal was not achieved for the coarse mulches until week 11. In addition, between weeks 3 and 7, the ammonia-nitrogen concentrations for fine mulches measured below 20 mg/L, which indicates that the fine mulch adsorbs ammonium faster than the coarse mulch. This can be attributed to the fine mulch acting more as a filter for the influent. In addition, the fine mulch contains smaller mulch particles that indicate a greater surface area.

### **3.4.3 Occurrence of Nitrite and Nitrate**

Figure 3-6 shows total ammonia-nitrogen and nitrate-nitrogen versus time for the first stage permeate. The occurrence of nitrification, as indicated by nitrite and nitrate concentrations, is important to observe. Autotrophic nitrification is associated with the bacteria of the family Nitrobacteraceae. These nitrifiers are bacteria that grow by consuming inorganic nitrogen compounds. Nitrifiers have a very limited range of substrates, either ammonium or nitrite (Belser, 1979). In this study, nitrite is not present within the influent; therefore, the source of nitrogen is solely in the ammonia species. Populations and in situ activities of nitrifiers may commonly be limited by the production rate of ammonium. This limitation occurs because the potential rate of ammonium

oxidation can greatly exceed the rate of ammonification. This is commonly tested by adding ammonium to soils and observing stimulation in the growth of the nitrifier population; this is observed in the current study - ammonium, the source of nitrogen, is added to the mulch substrate and, as a result, nitrification rates increase.

Belser (1979) examined the change in ammonia concentration as a function of ammonification and ammonium oxidation rate over a nitrifier growth population, as seen in Equation 3-1:

$$\frac{dS}{dt} = A - r \quad (3-1)$$

where  $dS/dT$  is the change in the ammonium concentration with time ( $t$ ),  $A$  is the constant rate of ammonium production due to ammonification, and  $r$  is the ammonium oxidation rate. Ammonification is the process of organic nitrogen, in the form of dead organic matter, converted to inorganic nitrogen, in the form of ammonium. For this study, ammonification was assumed to not occur within the mulch because of the composition - organic nitrogen is not readily available in mulch and the mulch contains minimal amounts of total nitrogen content (Appendix A). Belser's equation is modified so that  $A$  represents the constant rate of inorganic ammonium added on a weekly basis to the mulch buckets. Belser explains that when the initial nitrifier population is low,  $r$  will be much less than  $A$ ; therefore, the ammonium oxidation rate is much less than the constant amount of nitrogen added per week to the mulch buckets. As seen in Figure 6, total ammonia-nitrogen concentrations in the leachate effluent were relatively high between weeks 1 and 4. The nitrifier populations were low at this point. Belser noted that as bacteria populations increased,  $r$  increased and at some point would be equal to  $A$ . At this point,  $dS/dT$  was 0 and the substrate concentration was at maximum. In this

study, the nitrifier population never reached this point where  $r$  equaled  $A$ . The growth of the nitrifier population was observed between weeks 6 and 11; however, nitrate concentrations reached a maximum of approximately 60 mg/L in week 15. The ammonia-nitrogen in the influent was never totally converted to nitrite and nitrate; therefore other factors might have inhibited the nitrifier population growth.

Belser (1979) stated that physical parameters could produce enough stress to kill a portion of the nitrifier population. Such conditions would cause declines in the populations obtained during conditions of good growth and survival. If such adverse conditions were persistent, they would prevent the populations from ever reaching their theoretical maxima. The two physical factors that seem to influence nitrifier populations the most are moisture and temperature. Keeney and Bremner (1967) observed nitrification inhibition when soils reached 40 °C. In the current study, temperatures never reached 40 °C; thus, temperature was not a factor in probable inhibition of the population growth. Dommergues (1998) found that nitrification is inhibited under high moisture stress; other studies have shown that high moisture contents can decrease nitrification rates exponentially. This could influence the experimental results because the mulch had reached maximum moisture uptake. Lastly, the mulch buckets could produce anaerobic environments that inhibit nitrite oxidation (Belser, 1979). All these factors could explain why total conversion of ammonium to nitrate did not occur.

Table 3-6 shows the fate of the nitrogen in the mulch buckets as percent mass. The nitrogen fate was only determined in weeks 6, 11, and 15 because the nitrite and nitrate concentrations were analyzed at that time. In comparison to Figure 3-3 (nitrogen mass balance diagram), Table 3-6 does not take into account the amount of nitrate

denitrified from both the leachate effluent and mulch substrate. The nitrogen fate was divided into mass percentages of percent adsorbed on the mulch, the percent nitrified, and the percent of ammonia-nitrogen that remained in the leachate effluent. As seen in week 6, a majority of the ammonium-nitrogen was adsorbed onto the mulch. This data was consistent with Figure 3-6, which shows that adsorption occurred in the beginning weeks. In addition, at week 6, NMC and OMC leachate effluents contained 23 and 56% residual ammonia, respectively. The fine mulch leachate effluents contained 1 and 5.5% residual ammonia. This is consistent with the determination that coarse mulch is a less effective adsorbent than fine mulch (see Figure 3-6). In week 11, the percent of ammonium nitrified increased and the percent residual ammonia decreased dramatically. This is consistent with the population growth of the nitrifiers and is consistent with Figure 3-6. In week 15, nitrification percentages were greater than adsorption for the removal of ammonia-nitrogen. This indicates that the nitrifier population grew, which resulted in greater rates of ammonium oxidization. At week 15, the percent of residual ammonia-nitrogen for all mulch types was zero.

Table 3-6 shows the ammonia-nitrogen concentrations for the leachate effluent. In week 6, NMF was the only leachate effluent to meet the FDEP groundwater cleanup target level of 2.8 mg/L ammonia-nitrogen. In weeks 11 and 15, the ammonia-nitrogen concentrations were completely removed from the influent, which indicated that the effluent from the mulch buckets met the FDEP ammonia-nitrogen limit. These results were consistent with a previous study of ammonium adsorption onto peat. Heavey (2003) used columns containing peat as a treatment medium. In the experiment, landfill leachate was filtered through the peat columns to measure pre and post nitrogen

species including ammonia-nitrogen, nitrite, and nitrate. Heavey (2003) observed that the ammonium was removed from the leachate through a two-step physicochemical process of adsorption and nitrification. The ammonium would adsorb to the surface of the peat. Nitrifying bacteria located on the peat surface would then oxidize the ammonium to nitrite and nitrate. Heavey (2003) concluded that almost 100% of total ammonia-nitrogen was removed from the leachate. The current study resulted in adsorption and nitrification yielding 100% ammonia removal. This removal of ammonia-nitrogen indicates a potential treatment method by adsorption and nitrification in fixed bed reactors.

#### **3.4.4 Compost and Degradation of the Mulch**

Physical characteristics of the mulch were examined to determine if degradation and composting had occurred during the experimental period. As seen in Figure 3-7, each mulch bucket weighed between 5.5 and 6 kg wet weight at the start of the experiment. Between weeks 1 and 7, the mulch's wet weight continued to increase due to water retention. After seven watering events, the mulch's moisture capacity was reached and its weight stabilized for the remainder of the experiment. The stabilization of wet weight with no decline over the experimental period indicates significant degradation did not occur; however dry weights, before and after the experimental period suggest that degradation did occur. Average dry weights for NMF, NMC, OMF, and OMC at week 1 were 3.2, 3.1, 3.4, and 3.0 kilograms, respectively; for week 19 the dry weights were 2.8, 2.5, 2.8, and 2.6 kilograms, respectively. Dry weight percentage reductions for NMF, NMC, OMF, and OMC were 12.5, 19.3, 17.6, and 13.3%, respectively over the experimental period. The decline in dry weight over the experimental period suggests degradation did occur within the buckets.

Figure 3-8 shows the depth of the new and old mulch contained in the buckets. The depth is measured from the top of the bucket to the surface of the mulch. As seen in Figure 3-8, new and old mulch exhibited almost the same behavior. The mulch depths for the various sample types started at approximately 3 inches and increased each week up to week 10. After week 10, the depths stabilized for the remainder of the experiment. The bucket depth for all mulch types increased about 1.5 inches (from 3 to approximately 4.5 inches). The increase in depth can be attributed to mulch compaction within the buckets. During each watering event, the buckets were shaken to promote settling within the mulch particles. The depth increase can also be attributed to degradation of the mulch. Fungi growth within the mulch medium was observed during the experiment period, as seen in Figure 3-9. Fungi, like bacteria, secrete enzymes to break down organic compounds that can aid in composting; however, fungi presence was minimal, which did not significantly contribute to the degradation of the mulch.

Table 3-7 shows the mulch composition after the experiment period. Carbon and nitrogen composition percentages are given in the table along with the respective carbon/nitrogen (C/N) ratios before and after the experimental period. The change in C/N ratios ( $\Delta$ C/N) is also provided wherein a negative number indicates a decrease in C/N from before to after the experimental period. C/N ratios decreased for all mulch types. A typical C/N ratio for optimal composting conditions is 25 – 40 (Golueke, 1991); this ratio was not achieved for NMC or OMC after the experimental period. NMF and OMF achieved C/N ratios closest to 40, indicating the best potential for composting conditions. An optimal C/N ratio at the end of a composting period is 10-15:1 (Cornell Waste Management Institute, 1996) which was not achieved in the current study;

however, the decrease in both the mulch's dry weight and the C/N ratios suggest composting occurred wherein carbon is lost via CO<sub>2</sub> emission during organic matter breakdown and nitrogen is increased due to the adsorption of nitrogen and the breakdown of organic matter. C/N ratios of both fine mulches (NMF and OMF) are significantly lower than the coarse mulches. This can be attributed to the varying surface area between the fine and coarse mulches. Most microbial activity occurs on the surface of the organic particles. Fine mulch contains smaller particle sizes as seen in the particle size distribution analysis (table 3-4) which encourage microbial activity and increase the rate of decomposition. Decreasing particle size also increases the availability of carbon and nitrogen within the mulch substrate.

The relatively small decrease of the C/N ratios within each mulch type could have been predicted by analyzing the nitrogen mass within the first and second stage permeate. The total amount of nitrogen added to the first stage and second stage permeate buckets over the experimental period was 2,502 mg and 120 mg total ammonia-nitrogen. The theoretical nitrogen composition, if all the nitrogen added was adsorbed to the mulch, for first stage permeate buckets for NMF, NMC, OMF, and OMC is 0.68, 0.57, 0.78, 0.53, respectively; compared to the original nitrogen composition at 0.63, 0.51, 0.73, and 0.48%, respectively. In addition, C/N ratios, if all the nitrogen added was adsorbed to the mulch for the first stage permeate buckets, would be 57, 76, 49, and 81, respectively; compared to the original C/N ratios of 66, 91, 51, and 85. The theoretical values suggest that the minimal decrease in C/N ratios, observed in the experimental data, could have been predicted. The amount of nitrogen applied to each bucket was relatively minimal compared to the amount of mulch present.

Table 3-8 compares the nitrogen enriched mulch to commercial fertilizers. The mulch contains minimal nutrient value relative to the other fertilizer products; this is likely due to the small amount of nitrogen added to the mulch substrate during the experimental period. However, the benefits of using the mulch include it being free of cost and can also be used in an adsorption system which helps reduce ammonia-nitrogen levels in solution. In order to fully realize the benefits of the mulch, future studies must be conducted to demonstrate the full effect of adding nitrogen to the mulch with the goal of decreasing the C/N ratio to composting conditions. In such studies, an influent containing a higher ammonia-nitrogen concentration, than the influent used the current study (131 mg/L and 5.3 mg/L  $\text{NH}_3\text{-N}$ ), should be used. Results of such studies should then compare before and after C/N ratios and nitrogen composition of the mulch to evaluate the amount of nitrogen adsorbed. In addition, the mulch could then be compared to commercial fertilizers with the intention of the mulch being comparable in nitrogen composition, in addition to the benefits of it being free of cost and reducing ammonia-nitrogen levels in solution.

### **3.5 Summary and Discussion**

Fixed bed column studies were performed to study the adsorption of ammonium to mulch. An ammoniated effluent generated from a leachate treatment system was passed through buckets (acting as the fixed bed columns) containing various mulch types. The main objectives of this study were to examine the adsorption capacities and behaviors of the ammonia to the mulch and to determine if the mulch can be promoted as compost and fertilizer after it is contacted with a nitrogen source. A high ammonia-nitrogen removal rate (>99%) was achieved through a two-step process of adsorption and nitrification. This process was consistent with the findings of Heavey (2003),

wherein peat was contacted with ammonia. Complete nitrification of ammonia-nitrogen to nitrate-nitrogen was not observed during the experimental period. In addition, nitrifying bacteria colonies were fully established at week 15 of the experimental period. Fine mulch exhibited greater adsorption capacity than coarse mulch. The fine mulch acted as a more effective filter than coarse mulch and also contained greater surface area due to its smaller particle size.

Degradation and composting did occur because of a decrease in both mulch dry weights and C/N ratios. C/N ratios moderately decreased throughout the experimental period. The inhibition of achieving optimal C/N ratios within the mulch substrate could be due to the high mulch water capacities, varying particle sizes, and low nitrogen availability. If all the nitrogen applied to the mulch buckets adsorbed onto the mulch, the amount of nitrogen would still be very minimal and would not cause a significant decrease in C/N ratios. The use of mulch as a media to remove total ammonia-nitrogen from an aqueous solution through a two-step mechanism of adsorption and nitrification is a feasible, inexpensive option. Water quality issues can arise in the contacted effluent, including an increase in turbidity and suspended solids. Future research needs to be conducted to determine the de-adsorption capacities of the ammoniated mulch surface. Studies could be performed to attempt to quantify the amount of nitrogen that would de-adsorb from the mulch. This would aid in determining if the mulch (with nitrogen adsorbed onto its surface) can act as a slow release nitrogen fertilizer.

Table 3-1. Effluent and influent water quality of the RO system at the ACSWL

Parameter	Units	Raw Leachate	First Stage	Second Stage
pH	SU	7.41	6.67	5.31
Conductivity	µmho/cm	12520	2016	48
COD	mg/L	1960	51	1
NH <sub>3</sub> -N	mg/L	980	131	5.3
Cl <sup>-</sup>	mg/L	1405	151	2.3

Table 3-2. Summary of the twelve mulch types used in the current study

Sample Type	Effluent	Abbreviation	Age	Size
New, Fine	1 <sup>st</sup> Stage	NMF-1	One month	6.35 mm-.42mm
	2 <sup>nd</sup> Stage	NMF-2	One month	6.35 mm-.42mm
	Deionized Water	NMF-DI	One month	6.35 mm-.42mm
New, Coarse	1 <sup>st</sup> Stage	NMC-1	One month	12.7mm – 6.35mm
	2 <sup>nd</sup> Stage	NMC-2	One month	12.7mm – 6.35mm
	Deionized Water	NMC-DI	One month	12.7mm – 6.35mm
Old, Fine	1 <sup>st</sup> Stage	OMF-1	One year	6.35 mm-.42mm
	2 <sup>nd</sup> Stage	OMF-2	One year	6.35 mm-.42mm
	Deionized Water	OMF-DI	One year	6.35 mm-.42mm
Old, Coarse	1 <sup>st</sup> Stage	OMC-1	One year	12.7mm – 6.35mm
	2 <sup>nd</sup> Stage	OMC-2	One year	12.7mm – 6.35mm
	Deionized Water	OMC-DI	One year	12.7mm – 6.35mm

Table 3-3. Moisture, volatile solids, ash, carbon, and nitrogen content of the mulch used in the current study

Sample Type	% Moisture Content 70° C	% Volatile Solids 550° C	% Ash	%Carbon	%Nitrogen	C/N Ratio
NMF	41.2	77.5	16.4	41.3	0.63	66
NMC	38.7	81.2	6.5	45.8	0.51	91
OMF	36.5	66.4	25.0	37.2	0.73	51
OMC	43.1	72.3	17.7	40.4	0.48	85

Table 3-4. Particle size distribution analysis of the four mulch types (dried at 70°C)

Mesh size	Opening size (mm)	% Retained			
		NMF	NMC	OMF	OMC
1/2"	12.7	0	15	0	15
1/4"	6.35	3	62	8	54
4	4.76	21	8	11	9
10	2.00	46	9	46	12
20	0.841	16	1	18	2
40	0.420	5	1	6	1
Pan	<0.420	9	5	12	8

Table 3-5. Dimensions of the fixed bed columns (in the form of buckets) used to hold the mulch during the experimental period

Parameter	Units	
Bucket Diameter	inches	11.5
Bucket Height	inches	17.5
Weight of bucket	kg	0.8
Mulch mass	kg	5.3 - 6.1
Mulch height in bucket	inches	14.5
Empty bucket volume	ft <sup>3</sup>	1.05
Mulch volume in bucket	ft <sup>3</sup>	0.87
Mulch density	lb/3ft	13.4-15.5



Figure 3-1. Fixed bed column (bucket) arrays at the experimental site

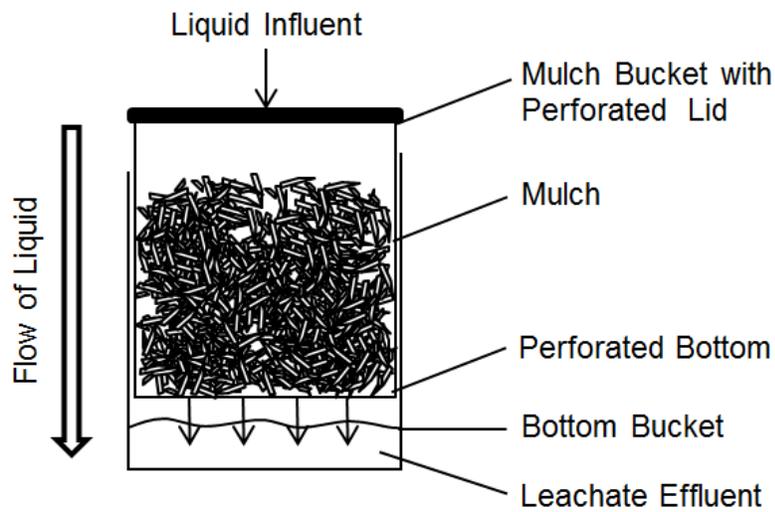
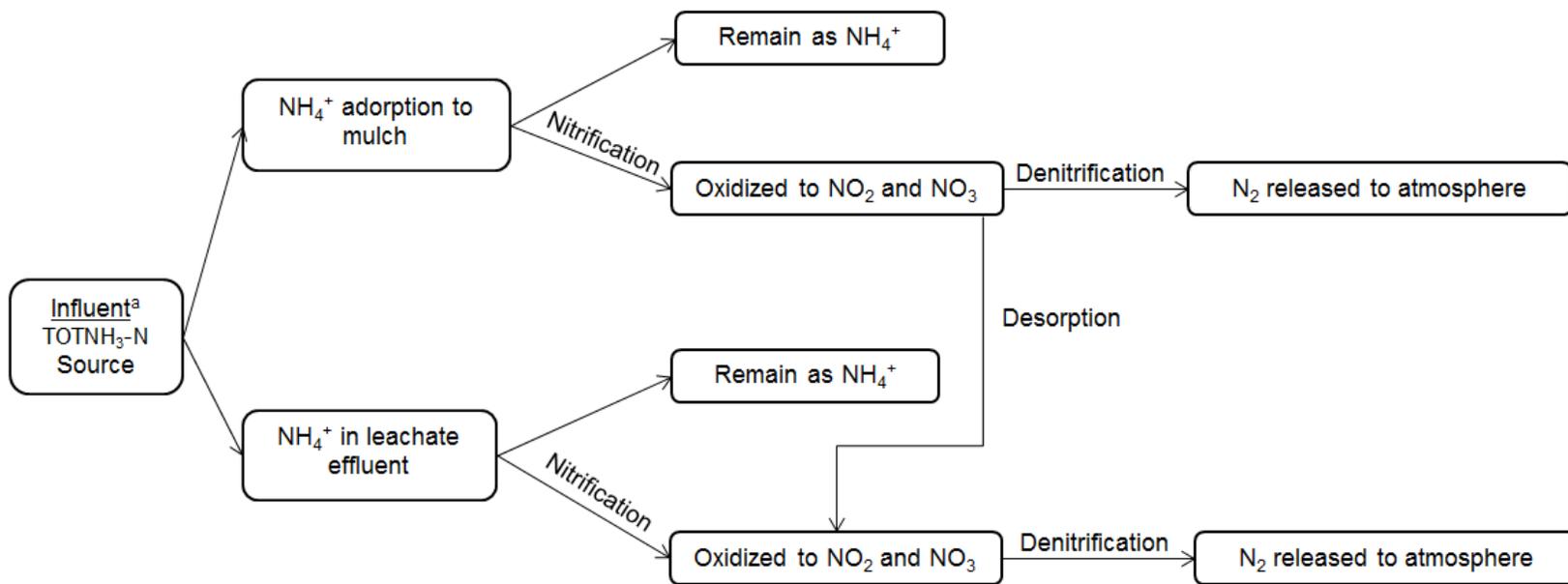


Figure 3-2. Schematic of the fixed bed column (bucket) used to hold the mulch samples



<sup>a</sup> Influent contains nitrogen only in the form of total NH<sub>3</sub>-N (TOTNH<sub>3</sub>-N). Influent does not contain NO<sub>2</sub>-N and NO<sub>3</sub>-N species

Figure 3-3. Nitrogen mass balance chart showing the fate of nitrogen throughout the fixed bed columns (buckets)

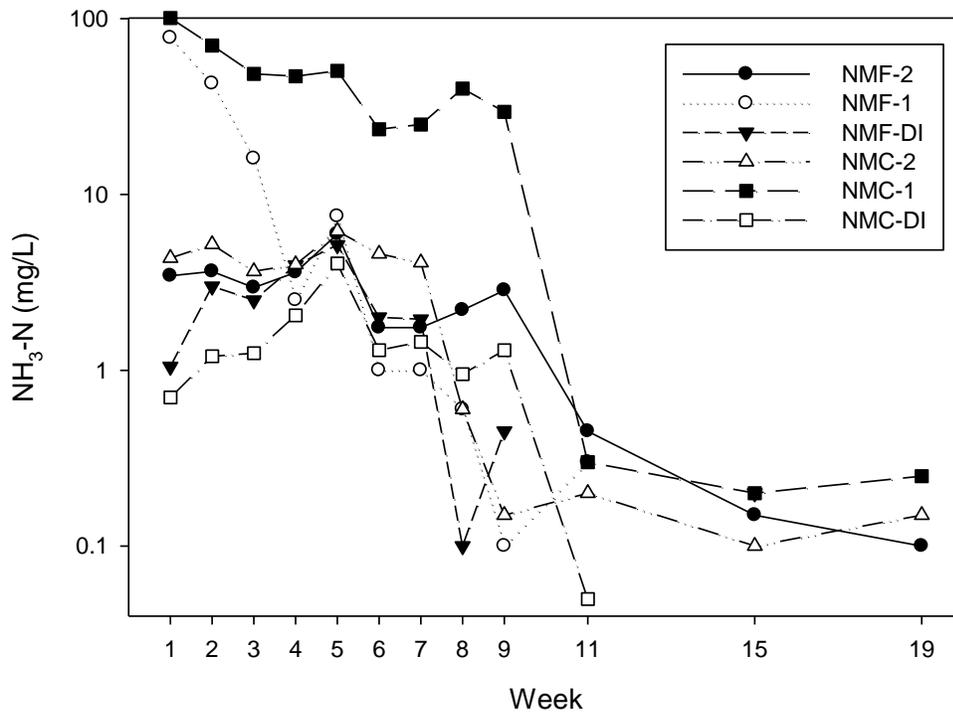


Figure 3-4. Total ammonia-nitrogen concentrations in the bottom bucket leachate for new mulch

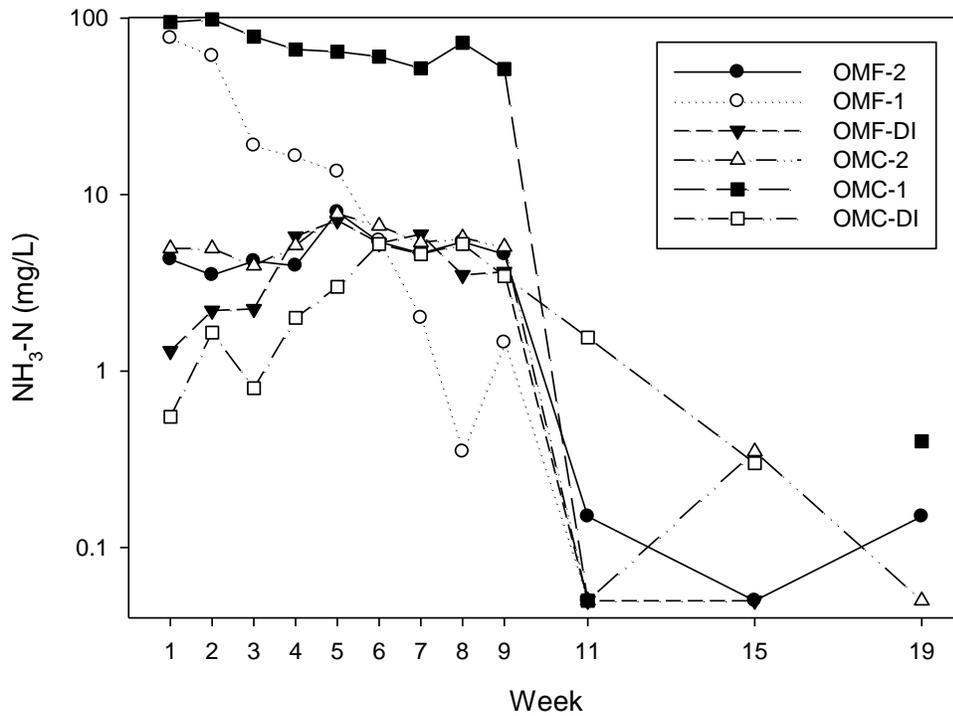


Figure 3-5. Total ammonia-nitrogen concentrations in the bottom bucket leachate for old mulch

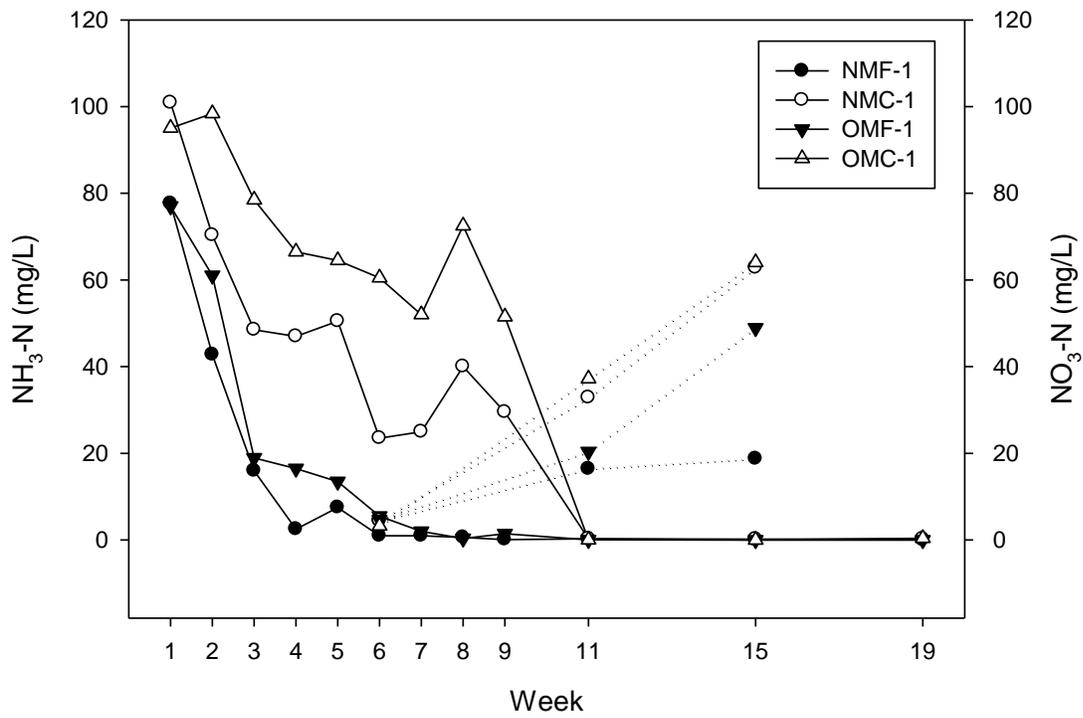


Figure 3-6. Total ammonia-nitrogen (left y-axis) and nitrate-nitrogen (right y-axis) concentrations over time in the bottom bucket leachate for first stage permeate

Table 3-6. Nitrogen fate (as percent mass) in the fixed bed columns for weeks 6, 11, 15

Sample Type	Week 6				Week 11				Week 15			
	% Adsorb	% Nitrify	% NH <sub>3</sub> -N	NH <sub>3</sub> -N (mg/L)	% Adsorb	% Nitrify	% NH <sub>3</sub> -N	NH <sub>3</sub> -N (mg/L)	% Adsorb	% Nitrify	% NH <sub>3</sub> -N	NH <sub>3</sub> -N (mg/L)
NMF-8"	81	19	1	1	75	25	0	0	79	21	0	0
NMC-8"	57	20	23	23.5	61	39	0	0	36	64	0	0
OMF-8"	77	18	5	5.5	77	23	0	0	52	48	0	0
OMC-8"	40	5	56	60.5	52	48	0	0	36	64	0	0

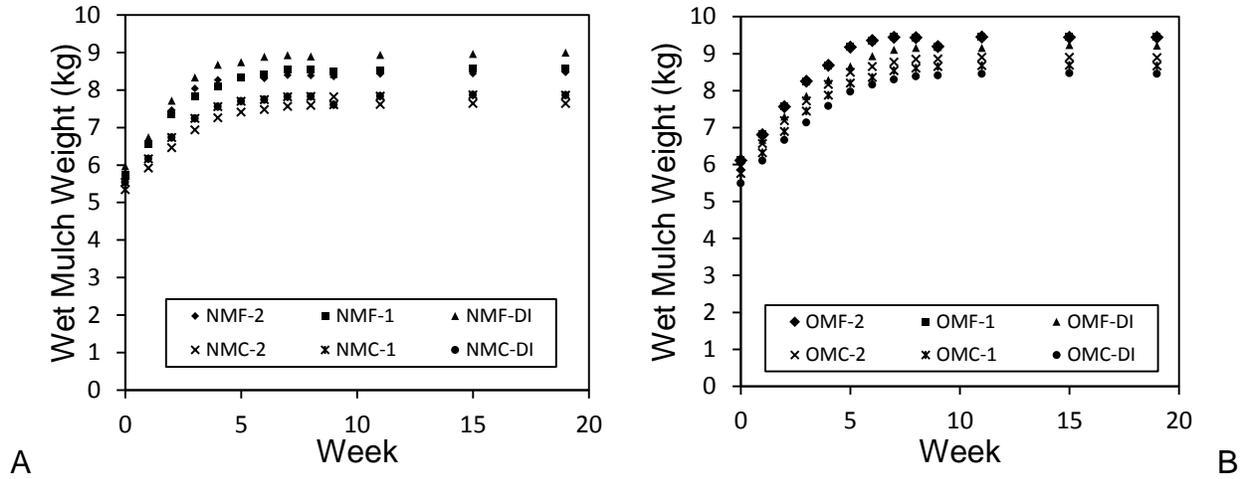


Figure 3-7. New mulch and old mulch wet weight over experimental period A) New mulch B) Old mulch

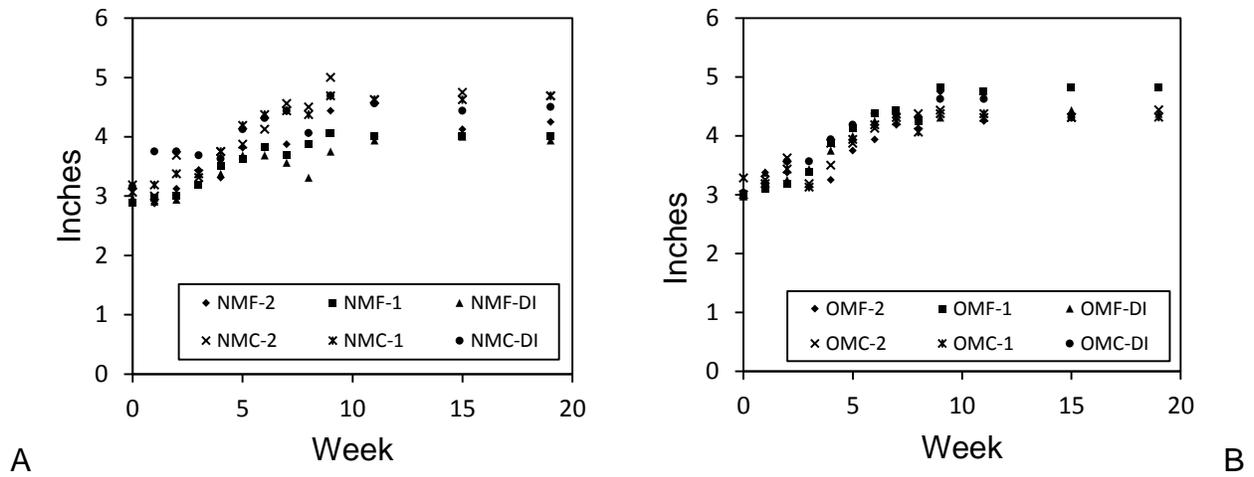


Figure 3-8. New mulch and old mulch depth (as measured from the top of the bucket to the surface of the mulch) over the experimental period



A  
Figure 3-9. Example of fungi growth within the fixed bed columns A) Mulch substrate B)  
Magnified view

Table 3-7. Moisture, volatile solids, ash, carbon, and nitrogen content along with C/N ratios before and after the experimental period for the twelve mulch types

Sample Type	% Moisture Content 70°C	% Volatile Solids 550° C	% Ash	%Carbon	%Nitrogen	C/N Before	C/N After	$\Delta$ C/N <sup>a</sup>
NMF								
4"	64	29	7	40	0.75	66	53	-13
8"	66	26	8	39.2	0.8	66	49	-17
DI	66	27	7	38.8	0.87	66	44	-22
NMC								
4"	66	29	6	43.3	0.54	91	81	-10
8"	66	30	4	44	0.53	91	83	-8
DI	65	32	3	44.7	0.56	91	80	-11
OMF								
4"	66	27	7	38.5	0.93	51	41	-10
8"	69	23	8	38.8	0.95	51	41	-10
DI	69	23	9	36.1	0.9	51	40	-11
OMC								
4"	68	26	6	43.2	0.58	85	69	-16
8"	69	28	3	44.4	0.71	85	63	-22
DI	70	27	4	43.1	0.57	85	76	-9

<sup>a</sup> The change in C/N ratio before to after the experimental period. A negative number indicates a decrease in C/N from the start of the experiment.

Table 3-8. Commercial fertilizer product comparison to nitrogen enriched mulch

Fertilizer Product	N-P-K Ratio	Price
Bat Guano	1-10-0.2	\$8.50
Roots Organic Uprising Grow	6-0.5-1.5	\$14.95
Milorganite Lawn Fertilizer	5-2-0	\$12.95
Nitrogen Enriched Mulch (current study)	1 <sup>a</sup> -0-0	\$0

<sup>a</sup> Nitrogen composition after the experimental period ranged from 0.53 – 0.95%

## CHAPTER 4 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

### 4.1 Summary of Results

Ammonia-nitrogen is one of the major long term pollutants found in landfill leachate (Kjeldsen, et al, 2002). Ammonia is also problematic in other water sources such as potable water, wastewater, and general aqueous solutions. The removal of ammonia within these waters is important to minimize adverse impacts to the environment. In the current study, mulch (chipped woody biomass product) was used as a low cost adsorbent. The use of mulch as an adsorbent was hypothesized to remove ammonia-nitrogen molecules from the wastewater thus decreasing the water toxicity. In addition, the transferred ammonia-nitrogen, paired with the biodegradability of the mulch, would allow the mulch to be used as a compost and fertilizer product.

The present work demonstrates that mulch shows promise as a material to remove ammonium ions from an aqueous solution. Different mulch types yield varying adsorption results; mulches primarily consisting of fine particles can yield better adsorption capacities compared to mulches primarily consisting of coarse particles. The fine particles contain greater surface area increasing the amount of adsorption sites. Langmuir and Freundlich theoretical models were developed; the Freundlich theoretical model was best in describing ammonium adsorption onto the mulch. The models can be used to develop a mulch-ammonia adsorption system; however, high flow rates would be problematic as a large amount of mulch would be needed. The mulch is ideal for low volume systems where ammonia is removed from the polluted water and the captured nitrogen could be used as a fertilizer.

Fixed bed column studies were performed to study the adsorption of ammonium to mulch. An ammoniated effluent generated from a leachate treatment system was passed through buckets (acting as the fixed bed columns) containing various mulch types. A high removal rate was achieved through a two-step process of adsorption and nitrification. This process was consistent with the findings of Heavey et al. (2003) wherein ammonia from landfill leachate was contacted with peat beds. Heavey et al. (2003) observed high ammonia-nitrogen removal rates after initial adsorption and then eventual nitrification of the adsorbed ammonium ions on the peat surface. Complete nitrification of ammonia-nitrogen to nitrate-nitrogen was not observed during the experimental period. In addition, nitrifying bacteria colonies were fully established at week 15 of the experimental period. Fine mulch, compared to coarse mulch, exhibited faster adsorption rates. The fine mulch acts more as a filter than coarse and also contains greater surface area due to smaller particle size. Degradation and composting was observed by a decrease in dry weight composition and C/N ratios. The inhibition of composting within the mulch substrate is likely due to high mulch water capacities, varying particle sizes, and low nitrogen availability. The use of mulch as a media to remove total ammonia-nitrogen from an aqueous solution through a two-step mechanism of adsorption and nitrification is a feasible, in-expensive option. Water quality issues can arise in the contacted effluent such as an increase in turbidity and suspended solids.

#### **4.2 Integration and Conclusion**

Below is an example of a pilot scale system, incorporating the results from chapter 2 and chapter 3 of this thesis, which could be implemented at the ACSWL for the RO system permeate. Figure 4-1 shows a flow chart detailing the process of the adsorption

system. The operator would extract the mulch from the yard waste collection area using an excavator or shovel. The mulch would then be processed into a high volume screener that would separate the mulch into fine and coarse categories. Mulch fines would be the most optimal to use in the adsorption system because of the results determined in both chapter 2 and 3 of this thesis. Next, the appropriate amount of mulch has to be calculated based on the permeate production rate for the RO system and the concentration of the ammonia in the RO permeate. The RO system at the ACSWL produces a second stage permeate that contains a total ammonia-nitrogen concentration of 5.3 mg/L. The Freundlich adsorption model for NMF, as determined in the current study, will be used to calculate the required amount of mulch needed per day to treat the ammonia to levels acceptable for discharge to groundwater per Florida requirements:

$$Q_e = (0.0126)C_e^{\frac{1}{1.458}} \quad (2-8)$$

The desired ammonia-nitrogen equilibrium concentration ( $C_e$ ) for this example is 2.8 milligrams/liter (the FDEP groundwater cleanup target level); this yields a  $Q_e$  value of 0.0255 milligrams/gram. The second stage ammonia-nitrogen concentration of 5.3 milligrams/liter is divided by 0.0255 milligrams/gram to yield a mulch dosage of approximately 208 grams of mulch per liter of second stage permeate produced from the RO system. The system produces approximately 22,680 liters/day of second stage permeate. This rate is multiplied by 208 grams/liter to yield a daily amount of mulch required of 4,717 kilograms, which is the amount of mulch needed daily for treatment of the second stage permeate (5.3 mg/L ammonia-nitrogen) to meet the FDEP groundwater cleanup target level of 2.8 mg/L. This amount of mulch would be placed

inside a mulch flow reactor, as seen in Figure 4-1. The permeate would passively flow through the reactor using gravity and the residual pressure from the permeate pipeline. The size of the reactor would be calculated so that the total time of the permeate spent in the reactor is 45 to 60 minutes. The effluent from the reactor would be analyzed for ammonia-nitrogen; then, if it meets the Florida groundwater discharge requirement, the effluent would be discharged to groundwater. The mulch inside the reactor will be replaced every day. The extracted mulch from the reactor could then be used as mulch around the city landscape. The mulch could be marketed to citizens and entities as a nutrient-enriched fertilizer produced from the combination of two waste materials: treated leachate and woody biomass from yard waste collection.

The amount of mulch needed to fill the reactor per day at the ACSWL RO system is impractical at 4,717 kilograms per day. This suggests the mulch is not a viable treatment option for high flow rates; however, the mulch could be favorable for lower volume systems. In addition, the adsorbed nitrogen can still increase the nutrient value of the mulch. In this case, the mulch can be used intermittently to capture the nitrogen in the second stage permeate and then used as a fertilizer or composting product. The second stage permeate can also be directly sprayed onto the mulch piles, either at the yard waste collection facility or a transported mulch pile placed at the ACSWL where the RO system is located. In this scenario, the ammonia-nitrogen-woody biomass adsorption system process is simpler by direct discharge of permeate onto the mulch; however, target equilibrium concentrations might not be achieved because of minimal contact time between the permeate and the mulch.

### 4.3 Opportunities for Future Work

To date, there is little research on ammonium sorption onto mulch. Ammonia-nitrogen is not a limited resource; alternatively, nutrients such as phosphorus, are scarcer and more widely researched. However, high levels of nitrogen in water bodies can cause toxic conditions; therefore, cheap, renewable methods to remove nitrogen from these waters could be desirable. In addition, further research must be conducted to evaluate lower equilibrium ammonia-nitrogen concentrations (e.g. 0 to 10 mg/L). For instance, in the case of the RO system at the ACSWL, the effluent contains 5.3 mg/L ammonia-nitrogen. In the current study, equilibrium ammonia-nitrogen concentrations between 0 to 500 mg/L were studied; this range is large compared to the smaller range needed to study the RO effluent case study. Lastly, chapter 3 results showed that the permeate added to the mulch buckets was insignificant and did not demonstrate the mulch's compost ability; therefore, more studies need to be conducted, using higher nitrogen concentrations applied to the mulch substrate, to demonstrate the compost and degradation ability of the mulch. Overall, the results of this study prove that mulch can adsorb nitrogen; further case studies must be conducted to determine this would be applied in field applications.

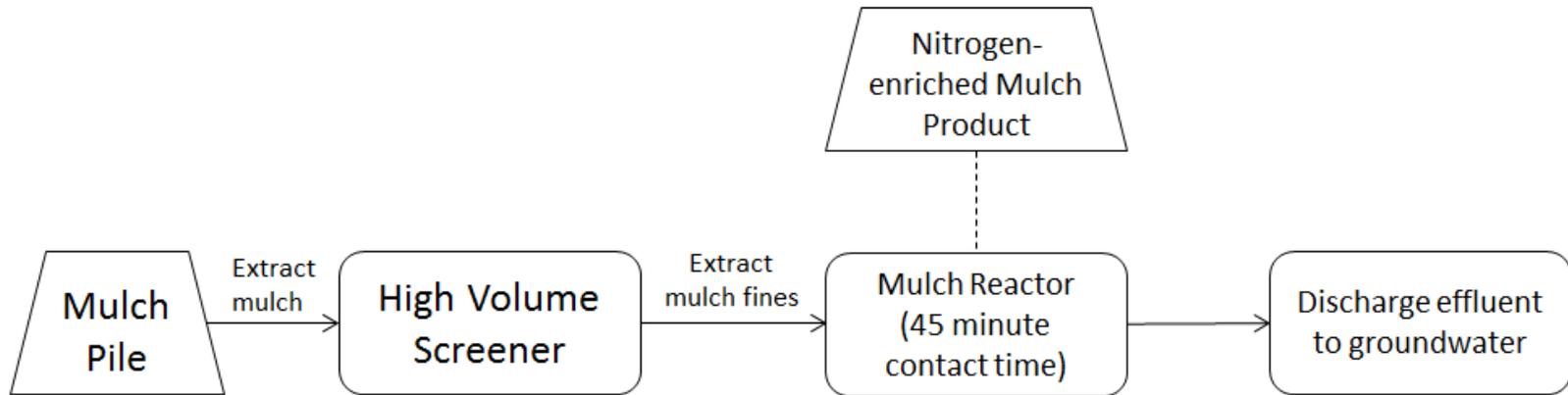


Figure 4-1. Example of ammonia-woody biomass adsorption system using the ACSWL RO permeate effluent as an example

APPENDIX A  
DETAILED MULCH COMPOSITION

Table A-1. Carbon (C), Nitrogen (N), cellulose/hemicellulose (C<sub>as</sub>), tannin (C<sub>sst</sub>), and lignin (C<sub>l</sub>), contents for various woody biomass materials (Valenzuela-Solano et al., 2006)

Woody Biomass Materials	Type	% Composition				
		C	N	C <sub>as</sub>	C <sub>l</sub>	C <sub>sst</sub>
Shredded redwood	Shredded timber	48.5	0.3	51.8	42.7	5.1
Grass clippings	Fescue mowing residuals	42.2	3.9	58.6	11.1	26
Oleander yardwaste	Leaves and branch pieces	46.9	0.8	64.3	15.6	14.7
Eucalyptus yardwaste	Leaves and branch pieces	47.5	1.3	55.0	21.9	18.4
Pine yardwaste	Needles and branch pieces	49.2	0.7	46.9	24.5	17.4
Compost	Commercially composted forest residuals	47.5	0.6	67.7	28.3	3.6

## APPENDIX B ANALYTICAL METHODS

Moisture content was determined by oven drying the mulch for 24 hours at 70 °C. Moisture content for the various types ranged from 6 to 12%. The oven dried mulch was ignited in an oven at 550 °C for 30 minutes per sample to determine the volatile solids content, which ranged from 66 to 82%. After the samples were ignited at 550 °C, the leftover material was designated as the ash content. Ash content percentages varied from 6 to 25%. Oven dried mulch was also analyzed for total carbon and nitrogen content. Carbon content was in the range of 37 to 46%.

Particle size distribution analysis was performed on the oven dried mulch. Mesh sizes of 12.7 millimeters (mm) to 0.420 mm (bottom pan collected residuals) were selected for particle size distribution analysis. Coarse mulch size ranges between 6.35 mm to 12.7 mm. The majority of coarse mulch was retained at the 6.35 mm sieve size with NMC and OMC at 62 and 54% retained, respectively. Fine mulch size ranges from 0.42 to 6.35 mm including a pan catching the residual mulch. The majority of fine mulch reported at 2.00 mm sieve size with both NMF and OMF reporting 46% retained. The percentages of material retained in the bottom pan ranges from 5 to 12% across the various mulch types. These percentages are significant because this portion represents the mulch particles smaller than 0.42 mm. They also represent part of the soil content contained in samples. The various mulch samples inherently contained soil particles adhered to the mulch chips. After the mulch is oven dried, the soil particles are detached from individual mulch chips then sieved through the particle size distribution analysis where the soil particles were collected in the bottom pan.

Table B-1. Analytical methods for experimental parameters

Measurement	Instrumentation
pH	pH electrode
Temperature	Digital probe
Moisture content	Oven
Volatile solids	Oven
Particle size distribution	Mechanical screener
Carbon, nitrogen content	Carlo Erba NA1500 CNHS Analyzer
Ammonia-nitrogen	HACH DR/4000 Spectrophotometer

## APPENDIX C COMPOSTING AND DEGRADATION CONDITIONS

In this study, it was hypothesized that composting would be favorable due to the following:

- The mulch contains high carbon content, which serves as an energy source for the microorganisms. A small fraction of the carbon is incorporated into the microbe's cells; some of the energy formed is used for microbial metabolism, and the rest is released as heat.
  - The permeate adds nitrogen in the form of ammonia to the mulch every week during a watering event. The nitrogen is a critical element for microorganisms because it is a component of the proteins, nucleic acids, amino acids, enzymes, and co-enzymes necessary for cell growth and functioning (Tuomela et al., 2000).
  - The shaking of the buckets adds oxygen to the mulch substrate. Oxygen is needed for degradation; microbes advance the degradation process by breaking down organic matter, utilizing the carbon as an energy source wherein oxygen acts as the electron acceptor.
  - The permeate added each week to the mulch was the source of water, which was critical to maintaining optimal composting conditions.
- Areas of this experiment that could inhibit the composting of the mulch are as

follows:

- The optimal carbon/nitrogen ratio for composting is 25 - 40 (Golueke, 1991). The mulch inherently has a large carbon content, but has minimal nitrogen content as seen in Table 4. Carbon/nitrogen (C/N) ratios for the collected mulch for NMF, NMC, OMF, and NMC are 66, 91, 51, and 85, respectively.
- The high moisture content of the mulch can cause a lack of aeration and leaching of the nutrients.
- Anaerobic conditions can be created that decrease the decomposition rate (Golueke, 1991).
- The mulch contains high lignin and cellulose contents that make degrading the material difficult for microorganisms.

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## BIOGRAPHICAL SKETCH

James Lloyd earned his Bachelor of Science degree in Building Construction from the University of Florida in 2010. He decided to follow his engineering passion and enrolled in graduate school in the Environmental Engineering Sciences Department in fall 2010.