

## Ammonia removal from air for Foulum soil and saw dust as biofilters: The material properties importance.



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## Preface

This project has been worked in the period 1 February 2007 and April 2008, during this time I have taken a break as maternity leave; at Aalborg University, at the

Faculty of Civil Engineering. The main theme for the project is the ammonia removal in the biofilter.

This report is the result of hard work during the first 4<sup>th</sup> months at the laboratory and no less afterwards trying to find time between my daughter and the project to made the final written. Therefore I would like to thanks my husband for his big help, during the weekends so I could have free time. And I would like also to thanks my supervisor, Tjalfe Poulsen, for his enormous patience and of course help with the scientific and methodical part of the project. He has been an excellent guidance.

Aalborg University, Denmark, April 2008

Maria D. Gomez Cortina

## Resume

The Danish agriculture has changed in the last 100 years; it has developed from an intensive agriculture to a more moderated one that takes care of the environment. The agriculture has changed, because of fluctuating prices has required farmers to increase the production to maintain or get a higher profit. This has contributed to an increase in the number of specialized farms. The main environmental impacts caused by animal production are emissions to the atmosphere and emissions to ground and surfacewater originating from the animal manure. Odor making from pig production is one of the biggest barriers for expanding pig production units in Denmark. The odor produces discomfort in the neighboring environment, nature and landscape. For this reason have been developed new methods to help the farmers maintain a good environment.

It has been developed different techniques for cleaning the air from animal farms and for control the odor produced by manure, slurry and animal waste. Biofiltration is one of these techniques that have gained most interest in the past years.

The goal of this project is therefore to study how the physical characteristics of the biofilters influence the filter efficiency. It is therefore decided to study two different biofilter materials (soil and saw dust) with respect to ammonia removal capacity as a function of physical characteristics. The study will be carried out using laboratory scale biofilters supplied with an artificially made ammonia-air mixture. The experiments will determine both the physical (air permeability, bulk density and water content) and the biological (ammonia removal kinetics) properties of the selected biofilter materials.

The analyses demonstrate that both materials are effective for removing ammonia from air. The results show also that the water content has influence in the ammonia concentration in the material biofilter after the experiments.

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## **1** Introduction

## 1.1 Background

The Danish agriculture has changed over the last 100 years due to a developing market. In the recent years the agricultural change because of fluctuating prices has required farmers to increase the production to maintain or get a higher profit. This has contributed to an increase in the number of specialized farms. Denmark is a country with a high density of pigs, producing 25 million pigs per year (Lyngbye, et al., 2006).

Agriculture, extensive as well as intensive, potentially produces environmental contamination. This takes place by use of pesticides, manure or fertilizer in the fields that will move to the groundwater and surfacewater. Also the animal production will produce contamination in the form of nutrients present in the large quantities of manure produced. Pesticides and nutrients are the main problem components that may potentially generate contamination problems.

# **1.2 Environmental problems associated with animal production in agriculture**

The main environmental impacts caused by animal production are emissions to the atmosphere and emissions to ground and surfacewater originating from the animal manure. According to Matthews (2006) the animal production is responsible of the 9% of  $CO_2$  and 37% of  $CH_4$  produced by human activities, and of the production of other gases that contribute to the global warming potential (GWP) such as  $NO_x$ . This contamination contributes also to acid rain and eutrophication, due to the  $NH_3/NH_4$  released from the manure.

Odor production from pig production is one of the biggest barriers for expanding pig production units in Denmark. The odor produces discomfort in the neighboring environment. Seventy percent of the odor from an integrated production facility comes from the finishing unit (Lyngbye et al, 2006). In recent years there has been a growing interest in reducing ammonia emissions and odor from pig production. In Denmark, the main research areas are reduction at the source, which means slurry and wet surfaces in the pig production unit and chemical and biological cleaning of air. Due to the odor problem the pig production in Denmark cannot develop much more, because increasing the density of pig units will increase both odor and eutrophication problems. To fight these problems pig farms must be competitive; they must get a solution that does not increase the price of the meat.

Odor is produced by emissions of odorous compounds present in the manure. Degradation of the manure can also produce further odorous compounds. Manure that is under anaerobic conditions produces a wide range of compounds such as sulfur compounds, volatile fatty acids, aromatic compounds and amines. Ammonia is one of the main compounds formed under anaerobic conditions.

Besides the odor problems exists other problems related to the animal production. One of them is eutrophication of surface water due to extra input of nutrients (primarily nitrogen). Surface water pollution threatens aquatic ecosystems and the quality of drinking water taken from streams. There are also problems caused by leaching of nitrate and possible pathogens transfer to the groundwater from manure storage facilities or from fields where high doses of manure have been applied. This can also produce soil infertility.

As mentioned in the background the agriculture has become more intensive and the pig units have increased in both number and size, this is shown in table 1.1., producing also the increment of the problems mentioned above.

Development in pig	production	II.						
Year	1999	2000	2001	2002	2003***	2004	2005*	2006*
Sows, 1000	1080	1070	1130	1128	1141	1144	1150	110
Prod. million**	22,5	22,4	22,9	24	24,3	24,7	25,3	25,5
Slaughter weight, kg	76,6	77,1	77,9	78,1	77,7	78,5	80	81,5

Development in pig production

\* Projection

\*\* Incl.export of live animals, and sows, boars, young sows, etc.

\*\*\* 53 weeks

Table 1.1 Development in pig production (The National Committee for Pig Production, 2006)

However in the last years the agricultural systems has been concerned about the environment and as the report Facts on Environmental Impact and Odor (2006) shows there has been an improvement in ammonia emissions due to:

From 1985 to 2000, the production of pork has increased by 54% and in that same period, the nitrogen supply from pig manure to fields has increased only by 2%. This is due to a significant reduction in the environmental impact of the individual animal.

• The nitrogen excretion per produced finisher (including sows and weaners) has decreased by 34% since 1985. This is a consequence of changed feeding, the use of enzymes, improved breeding, etc.

In 1985 the Danish Parliament introduced a plan to reduce nitrogen and phosphorous leaked to the water medium due high problems with these compounds in the water. At that time a direct spill of manure from the farms to surface waters (streams and lakes) became prohibited and at the same time the maximum number of animals allowed on each farm was regulated according to the amount of land the farmer had access to. This was done to prevent excess manure application and subsequent groundwater and surface water contamination by nutrients. Water quality plans were put forth in1987 and 1998 aiming for reducing the N and P loading from farmland sources to the surface and groundwater. As a result of the failure of the water quality plans from 1987 and 1998 to achieve satisfactory results a third water quality plan (VMP III) was approved by the Danish government in 2004. This plan aims at further reducing N and P loadings from the agriculture through improved manure management. And for the first time have been introduced requirements for reduction in P loadings and odor emissions (Miljøministeriet, 2004). January 1, 2007, the limit for environmental approval was lowered to 75 livestock units per ha. (Kjaer, 2007). At the same time, it became possible for the authorities to require that technology be used to reduce odor nuisances and ammonia emissions from the farms. Establishment of new environmentally friendly facilities together with good management alone can contribute to a significant reduction of odor and ammonia emissions.

## 1.3 Control of gaseous emissions from animal farms

Gaseous emissions from the agricultural sector include emission of nitrogen compounds, consisting of ammonia (NH<sub>3</sub>), greenhouse gases methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>). The ammonia emission from 1985 to 2002 has decreased from 138.400 tons of NH<sub>3</sub> to 98.300 tons NH<sub>3</sub> (Mikkelsen, et al, 2005), corresponding to an approximately 30% reduction. The main part of the ammonia emission is related to the livestock manure. In 2002 the emission from swine and cattle contributed to the total ammonia emission with 53% and 33% respectively (Mikkelsen, et al, 2005). The ammonia emission from pig production contributes to about half the overall ammonia

emission from animal manure. Despite the relatively high increase in pig production, the emission from the production of pigs has been reduced over the same period. One of the most important reasons for this is the associated marked improvement in feed efficiency.





Figure 1.2 shows the sources of nitrogen deposited on Danish area. It is seen that the nitrogen content in manure and the ammonia emissions from pig facilities have decreased from 1985 to 2002 and is expected to continue decreasing until 2015.



Figure 1.2. Average fallout of atmospheric ammonia over the Danish rural areas in 2002 (The National Committee for pig production, 2005)

More and more pig producers are required to reduce ammonia emissions or odor or both. The emissions can be controlled by improved manure management combined with technical solutions for air and manure treatment. The necessity of decreasing the emissions has sped up the development of air purification systems. These systems for pig facilities can be divided into three main groups in terms of function: Air cleaners, acid purifiers and biofilters.

## 1.3.1 Different types of technologies for air cleaning

Different techniques for cleaning the air from animal farms and for control the odor produced by manure, slurry and animal waste have been developed. Some of these are; improved farm management, biological air cleaners, acid purifiers, and biofilters.

#### 1.3.1.1 Pig farm management

A good quality pig organization at the farms can decrease the emissions. Improving the food, breeding and manure management reduces the odor release. Housing has also a high significance in the emissions reduction. First, the pig's units management, changing the finishers to an appropriate stable with a correct manure management will contribute to reduce the emissions. And second, keeping the facilities clean and dry and avoiding over-ventilation. The odor emission from finishing units with slurry systems is 3-5 times higher during the summer than during the winter. The odor emission can be reduced by cooling the inlet air (Lyngbye, et al, 2006). A high rate of ventilation in a facility increases odor emissions to the surrounding environment. It is therefore important not to over-ventilate the housing facility in the summer.

#### 1.3.1.2 Biological air cleaners (bioscrubbers)

In this technique the outlet air passes through a set of lamellas that are sprinkled with water. This can take place either in one time or in several steps.

Dust, ammonia and odorous compounds from the housing air are absorbed whereby a bacteria film is formed on the lamellas. It is a biologically open system, and the bacteria culture will adapt to what performs best under the given circumstances. The bacteria culture can be controlled on the basis of growth conditions, for instance temperature, pH, concentration of mineral nutrients in sprinkling liquid, etc. It will in addition be possible to control the culture by adding nutrients or other elements that enhance certain cultures (The National Committee for pig production, 2005).

Management of water and nutrient supply is essential for the efficiency of the purifiers. This applies to both odor and ammonia. Odor measurements have shown that odor reductions of 60-70% are possible (The National Committee for pig production, 2005), but that there are many more or less unknown conditions that for periods of time result in poorer effect of the filters.

#### 1.3.1.3 Acid purifiers

When acid purifiers are used, the outlet air passes through a set of lamellas that are sprinkled with diluted acid, typically sulphuric acid with a pH of 2-4. The acidified liquid very efficiently transforms ammonia into ammonium. There are currently several systems that remove more than 90% of the ammonia. This ammonia is then stored in separate tanks as ammonium sulphate with an N concentration of typically 5-10% (The National Committee for pig production, 2005).

Acid purifiers are not suitable for reducing odor measured by olfactometry. Analyses of individual substances show that the purifier reduces most of the odorants, but it is not capable of eliminating the most significant odorants.

## 1.3.1.4 Biofilters

In biofilters, contaminated air passes through a moist, material such as compost, soil, straw and/or wood chips in which the odorants are absorbed and decomposed by bacteria growing on the surfaces of the material. The material must facilitate growth of microorganisms that are able to degrade the contamination compounds, such as for instance denitrifying bacteria that will degrade ammonia. It is essential that the filters are moist and are routinely maintained by adding or replacing the biological material.

Biofiltration has a high efficiency (it is named as a 90% of efficiency by Anit 2007) in both odor and ammonia removal.

### 1.3.1.5 Comparison of purification systems

Based on the above presentation a comparison in terms of cleaning effect of the different systems can be made. The performance of the systems is illustrated in table 1.2.

Typical characteristics of different types of air purification systems							
	Acid purifier	Air cleaner	Biofilter				
Cleaning effect							
Ammonia	++	+	++				
Odor	%	+ [+]	++				
Impact. M3/h per m2	5.000-10.000	5.000-10.000	← 300				

++ Very good, + Good, % Unsuitable

Table 1.2. (Modified from The National Committee for pig production, 2005)

It is seen that biofiltration is one of the systems with a higher cleaning effect in terms of both odor and ammonia.

## 1.4 Biofiltration for air cleaning

Biofiltration has in recent years gained increased interest for removing odor and unwanted compounds in exhaust air from facilities such as animal farms, biogas plants and composting plants. Biofiltration is a quite new technology that uses a support medium for microbial growth to remove odors and organic contaminants from air streams. The support medium is wet, often organic materials that adsorb the contaminants and allows for biological degradation of the compounds by bacteria present on the surface of the support medium. Often used materials are soil, compost, straw, wood chips, etc. that sometimes are blended with other materials to obtain the optimal porosity. Biofilters have demonstrated a high efficiency for treating odors associated with composting, including ammonia. The principle design criteria are air flow and water content.

The filter typically consists of a chamber that encloses degrading microorganisms and absorbed water suspended in the medium. The filter material should be designed with a high capacity for water uptake, long working life, and low pressure drop for the gases passing through the media. In the biofiltration process, contaminated air is pumped through the filter medium. While the air flows through the filter media, the contaminants in the air stream are absorbed and metabolized. The purified air passes out of the top of the biofilter and into the atmosphere. Most biofilters that are in operation today can treat odor with efficiencies greater than 90% (Anit, 2007).

## 1.4.1 Advantages and disadvantages of using biofiltration:

Advantages of biofiltration:

- Lower capita costs, operating costs, low chemical usage and no combustion source
- The biofiltration unit can be designed in any shape or size
- The treatment efficiency for odors, toxic compound and volatile organic compounds (VOCs) are above 90% (Anit, 2007)
- Different media and microorganisms can be used
- Disadvantages of biofiltration:
- Contaminant sources with high chemical emissions will need a large biofilter unit
- Sources of emissions that fluctuate severely can be a problem for the biofilter efficiency due to the fluctuation of the population and its performance.

The efficiency of the biofilter depends on the material used. To be effective it is necessary that the biofilter has a large internal surface area and that a large number of microorganisms are present. The most important physical characteristics of the filter material are the volumetric water content, volumetric air content, the air permeability and the specific surface area. The most important biological parameter is the biological contaminant removal rate. A main factor to take in account is the air permeability of the material; this has to be large so the pressure drop across the filter can be kept small to reduce operation costs. A large specific surface area supports increased water retention, nutrient retention and microbial biomass.

Examples of materials that have been utilized in biofilters are compost (Das and Keener, 1997; Richard et al. 2004; Poulsen et al. 2006), coconut fibre and fibre peat (Martinec Milos, et. al, 2000; Roth-gmbh, 2007), bark and chopped wood (Martinec Milos, et. al, 2000), root wood (Roth-gmbh, 2007) between others. Soil can be considered as a good biofilter because is a suitable environment to microbial

growth, has a good moisture capacity and a useful life, might be supply with some other material as compost to supply microorganisms and maintain adequate porosity.

Even though the number of studies focusing on biofiltration is large the number of studies focusing on the use of compost as filter materials is limited. Moreover most of the studies have been focused on measurement of influent and effluent gaseous ammonia concentrations to and from the filter. This data will not provide sufficient information to determine the type of ammonia conversion kinetics in the filter materials. For other filter materials the studies have been even more limited. Although there have been some experiments done for porous pellets and wood chips (Morgan-Sagastume et al, 2001).

Few studies have investigated the influence of water content in the biofilter on filter performance (Boswell (2002) found that the bed of biomass must be neither too dry nor too wet (flooded). The correct moisture for the biofilter to work will be around 40 and 60% (Richard, T, 2005)

If the bed is excessively dry, the biomass will die, or too much contaminated air will move very rapidly through the system not allowing the treatment to be completed. On the other hand, if the bed contains too much moisture, the biomass may be drained, which can result in the loss of treatment capacity, and/or the airflow may be restricted, which increases pressure drop and result in increased power consumption (Boswell, 2002).

## **1.5 Purpose of the project**

The content of the introduction points at ammonia emissions and consequently odor problems are some of the main problems in farming nowadays. As has been emphasized biofiltration is one of the methods with highest efficiency in removing odor and ammonia emissions in the air. There have been many studies on biofilter efficiency but few about the impact of biofilter material characteristics on filter performance. The goal of this project is therefore to study how the physical characteristics of the biofilters influence the filter efficiency. It is therefore decided to study of two different biofilter materials (soil and saw dust) with respect to ammonia removal capacity as a function of physical characteristics. These two materials have been selected because there are easy to obtain at low cost and soil has in itself the microorganisms necessary for degradation. For the saw dust it is necessary to add of sludge compost to improve the removal rate.

The purpose of the project is to study the ammonia removal efficiency of the two filter materials at different water contents to determine the optimal water content for biofiltration.

The study will be carried out using laboratory scale biofilters supplied with an artificially made ammonia-air mixture. The experiments will determine both the physical (air permeability, bulk density and water content) and the biological (ammonia removal kinetics) properties of the selected biofilter materials.

### **1.6 Structure of the project**

This report consists of 5 chapters followed by References. The appendixes can be found in the attached CD.

Chapter 2, Theory, introduces the processes and mechanism that are involved in the biofiltration system. First the general physical characteristics of the biofilter are explained and afterwards the process associated with the transport of air-borne contaminants.

Chapter 3, Material and methods, describes how the experiments were performed, how the characteristics were chosen for the biofilters, the measurements of ammonia removal in the laboratory scale experiment and the measurements of the material characteristics at the end of the filtration experiment.

Chapter 4, Results, describes the results obtained after doing the analyses in the laboratory.

Chapter 5, Conclusions, presents the finale observations obtained after the project results and formulates recommendations form the findings of the study.

## 2 Theory

The following chapter introduces the processes and mechanism that are involved in the biofiltration system. First the general physical characteristics of the biofilter are explained to understand which parameters are important for the selection of optimal materials and conditions in the biofilter. Afterwards the process associated with the transport of air-borne contaminants in the biofilter material and their biological removals are described.

## 2.1. Biofilter media as a three phase system

The biofilter material, in this case, saw dust and soil, can be characterized as three phase medium composed of a solid phase (mineral and organic matter), a liquid phase (water containing dissolved matter and colloid particles) and a gaseous phase (air containing gases and volatile compounds). Bacteria are located in a biofilm resting on the solid phase in contact with the water phase. Air flow in the biofilter media is controlled by the permeability of the media and the gas pressure difference applied over the filter.

The following parameters are used to characterize the biofilter material:

The <u>mean density of solids</u>  $(\rho s)$  that is described as

$$\rho s = \frac{Ms}{Vs} = \frac{Msolids}{L^3}$$
(Eq. 2.1)

Where Ms is the solid mass Vs is the solid volume

<u>Dry bulk density</u> (pb) that expresses the ratio of the mass of dry matter (DM) in relation with the total volume and is described as

$$\rho b = \frac{Ms}{Vt} = \frac{MDM}{L^3}$$
(Eq. 2.2)

Where

 $\rho b < \rho s$ 

Bulk density is affected by the structure of the filter material and it increases relatively with the increment of the compactness.

<u>Gravimetric water content</u> (w) represents the material wetness expressed as the mass of water relative to the mass of solids and is described as

$$w = \frac{Mw}{Ms} = \frac{MH_2O}{Msolids}$$
(Eq. 2.3)

Normally the gravimetric water content is expressed as a fraction, in percentage and depends on the bulk density.

<u>Air filled porosity</u> ( $\epsilon$ ) expresses the volumetric air content of the material and is described as

$$\varepsilon = \frac{Va}{Vt} = \frac{L^3 air}{L^3 soil}$$
(Eq. 2.4)

Where

Va = volume of air Vt = total volume

<u>Pressure Drop</u> (Unit in Pa) is an important factor in a biofilter design; this should be minimized since an increase in pressure drop requires more blowing power. The pressure drop generally depends on water content and the material pore size (Anit, 2006).

<u>Air permeability</u> (Ka) (Unit in  $L^2 M^{-1}$ ). Air permeability, is a function of the air content, which controls air flow through the biofilters together with the pressure difference applied. Therefore is important characteristic of the biofilter material. Air transport in the biofilter is governed by advection flow created by difference of pressure generated passively or actively.

### 2.2. Relation between physical properties

Generally air permeability in soils is very dependent on both soil air filled porosity ( $\epsilon$ ) and soil dry bulk density ( $\rho$ b) and this can be also applicable to compost (in our case saw dust + sludge) (Poulsen and Moldrup, 2006).

The basic physical properties of porous media are their dry bulk density ( $\rho$ b), gravimetric water content (w), and air filled porosity ( $\epsilon$ ). The relation between these 3 properties is expressed as Eq. 2.5

$$\varepsilon = 1 - \rho b \cdot \left(\frac{1}{\rho s} + \frac{w}{\rho w}\right)$$
 (Eq. 2.5)

Where  $\rho w =$  water density (ML<sup>-3</sup>)  $\rho s =$  material density (ML<sup>-3</sup>)

#### **2.3. Solute transport**

The transport of the solutes in the biofilter takes place in two different phases, the gas phase and the water phase.

#### 2.3.1 Transport in the water phase

Water flow can occur in a biofilter meant only for air transport. Water flow can be induced by gradients in the water tension caused for instance by evaporation or condensation of water in different parts of the filter. According to Loll og Moldrup (2000) the transport of water in a biofilter intended for gas transport and cleaning is much slower than the air transport. The water phase can be in that case considered stationary.

#### 2.3.2 Transport in the gas phase

The substance that can be found in the gas phase (in this case ammonia) can spread, via convective, dispersive and diffusive transport. The convective transport refers to the passive movement of the substance and depends on the air velocity through the filter. Dispersive transport, in the other hand, depends on both the overall air velocity as well as differences in air velocity at different points in the filter material Diffusive transport happens when there are gradients in the concentrations of the substance within the filter causing mass to move from regions of higher concentrations to regions with lower concentrations. In air cleaning biofilters under normal circumstances advective transport will be the most important transport mechanism.

The advective flow is described by Darcy's law (Eq.2.6), when the flux is laminar.

$$v_a = -K_A \cdot \frac{\partial h_a}{\partial z} \tag{Eq. 2.6}$$

Where  $v_a$  = Darcy flux in the air (L T<sup>-1</sup>)  $K_A$  = air conductivity (L T<sup>-1</sup>) ha = Air pressure (L air) z = Depth of the filter (L)

Air conductivity can be determined from the air permeability (Eq. 2.7)

$$K_{A} = \frac{(Ka \cdot \rho_{a} \cdot g)}{\eta_{a}}$$
(Eq. 2.7)

Where Ka = air permeability (cm<sup>2</sup>)

 $\rho_a$  = density of air (aprox. 0,00219 g/cm3)

g = gravitational acceleration constant (7,58  $10^{-5}$  cm or 98,2 Pa cm<sup>2</sup> g<sup>-1</sup>)

 $\eta_a$  = air viscosity (0,652 g cm<sup>-1</sup> h<sup>-1</sup>)

## 2.3.3 Relation transport water and gas phase

The mechanism describing the distribution between the gas phase and the liquid phase is known as Henry's law and is described as

$$C_a = K_H \cdot C_1 \tag{Eq. 2.8}$$

Where  $K_H$  = Henry's constant (-)

 $C_a$  = the chemical concentration in the air phase (M L<sup>-3</sup>)

 $C_1$  = chemical concentration in the water phase (M L<sup>-3</sup>)

### 2.3.4 Sorption

Sorption is a process that influences the transport of substances in porous media. The term sorption actually covers two processes, adsorption and absorption. Adsorption is the process where a compound adheres or attaches itself to a surface of a medium particle; it depends on the concentration of substances in the gas phase and the properties of the particle surfaces. Absorption is when a compound binds itself chemically within a soil particle. Where adsorption is a largely reversible process, absorption is often non-reversible Sorption can happen as a result of ion exchange as the surface of the organic matter present in the biofilter material often is negatively charged. This means that positively charged ions and molecules will attached to the particles. Therefore sorption is especially important in inorganic materials. Sorption is often described as a linear isotherm as:

$$C_s = K_d \cdot C_1 \tag{Eq. 2.9}$$

Where Cs = the sorbed concentration (M M<sup>-1</sup>) Kd = the linear distribution coefficient (L M<sup>-1</sup>) Cl = the liquid concentration (M L<sup>-1</sup>)

## 2.3.5 Biofiltration mechanisms

The removal of contaminants in a biofilter begins with the advective transport of the substances into the biofilter. Here transfers of substances from the air to the water phase governed by Henry's law occur. The substances then move by diffusion in the water phase to the biofilm or solid particle surfaces. The contaminants can be absorbed to the biofilm or solid particle surfaces (see figure 2.1) or they may be transported into the biofilm where they are degraded.



Figure 2.1. Mechanisms of biofiltration (Modified from Jensen, Ann, 2006).

## 2.4 Ammonia removal in biofilters

Nitrification is the biological oxidation of ammonia with oxygen into nitrite followed by the oxidation of nitrite into nitrate. The bacteria that perform this process are autotrophic. The process occurs in two steps, ammonium oxidized to nitrite frequently by Nitrosomonas. Subsequently nitrite is oxidized to nitrate mainly by Nitrobacter. (Henze et. al., 2002)

The process for the ammonium oxidizing bacteria is

$$NH_4^+ + 3/2 O_2 \rightarrow NO_2^- + H_2O + 2H^+$$
 (Eq.2.10)

The process for the nitrite oxidizing bacteria is

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^-$$
 (Eq. 2.11)

Besides of nitrification, denitrification can also occur in the biofilter. Denitrification is the process of reducing nitrate and nitrite into free nitrogen and it takes place under anoxic conditions. The process is performed by heterotrophic bacteria. Denitrification occurs when the oxygen concentration is at a low level, and bacteria turn nitrate into nitrite by using organic matter.

The process for denitrification is (Henze et. al., 2002)

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$
 (Eq. 2.12)  
Organic matter +  $NO_3^- + H^+ \rightarrow Biomass + N_2 + CO_2 + H_2O$  (Eq. 2.13)

The ideal biofilter should have an optimal microbial environmental, with availability of nitrogen, water and nutrients. The right biofilter conditions can be provided or can be found naturally in the biofilter material.

Conversion of contaminants (including ammonia) in compost biofilters can be model using Monod kinetics. If local equilibrium between water and air phase is assumed, the change in air phase contaminant concentration, with time in a batch reactor is described by eq. 14. (Poulsen and Moldrup\*, 2006).

$$\frac{dC_a}{dt} = -r_m \cdot \frac{C_a}{Ks + C_a} \tag{Eq. 2.14}$$

Where  $C_a$  = concentration of contaminant in the air phase (M L<sup>-3</sup>)

t = time (min)  $r_m$  = maximum contaminant removal rate (M L<sup>-3</sup> · T) Ks = half saturation constant (M L<sup>3</sup>)

A biofilter can be considered a plug reactor for constant flow conditions, constant inlet of ammonia concentration through the biofilter columns and uniform material properties if the gas phase diffusion and dispersion is neglected. At steady state the amount of time a gas particle has spent inside the filter to reach a given depth, z, is given as eq. 15. This is also the time of exposure that the gas has experienced when it arrives at any given depth in the filter.

$$t = \frac{z \cdot A \cdot \varepsilon}{Q} \tag{Eq.2.15}$$

Where  $Q = gas flow (L^3 T^{-1})$ 

z = the filter depth (L) A = the filter unit cross sectional area (L<sup>2</sup>)  $\epsilon =$  the air-filled porosity of the filter material (L<sup>3</sup>L<sup>-3</sup>).

Combining Eq. 2.13 and Eq. 2.15;

$$\frac{dC_a}{dz} = -r_m \cdot \frac{A \cdot \varepsilon \cdot C_a}{Ks + C_a} \cdot Q$$
 (Eq. 2.16)

Knowing the contaminant removal kinetics, filter physical characteristics and gas flow rate, the concentration of ammonia in the gas phase as a function of filter depth can be calculated from Eq. 2.17.

$$C_{a,z+\Delta z} = C_{a,z} - r_m \cdot \frac{\Delta z \cdot A \cdot \varepsilon \cdot C_{a,z}}{Ks + C_{a,z}} \cdot Q$$
(Eq. 2.17)

Where  $\Delta z = \text{depth step } (L)$ 

Equation 2.17 requires knowledge of the steady state phase contaminant concentration in the inlet of the filter.

Measured values of  $C_{a,z}$  from biofiltration experiments can be fitted at Eq. 18 to obtain  $r_m$  and Ks. The optimal values of  $r_m$  and Ks can be fitted by minimizing the average square error between measured and predicted concentrations. This can be done by minimizing the Root Mean Square Error (RMSE) given as

$$RMSE = \sqrt{\frac{1}{N}} \Sigma_{i=1}^{N} (C_{i,measured} - C_{i,predicted})^{2}$$
(Eq. 18)

Where N = number of measured points used in the estimation

The concentration in the air as a function of filter depth can be estimated from measurements of the concentration in the biofilter material, assuming local equilibrium and a linear relationship between the concentration in the air phase and the concentration in the biofilter material as given in Eq. 2.18

$$C_a = C \cdot Kd \tag{Eq. 2.18}$$

Where C = concentrate

Kd = distribution coefficient (estimated from measured values of inlet air phase ammonia concentration and  $NH_3/NH_4^+$  concentration at the filter inlet)

## 3 Materials and methods

In this section it will be described how the experiments were performed, including the different analyses done to obtain the characteristics of the samples, how the characteristics chosen for the biofilters, measurements of ammonia removal in the laboratory scale experiment and measurements of the material characteristics at the end of the filtration experiment.

## **3.1.** Overview of the project experiment work

Figure 3.1 describes the processes that have been followed in the experimental work to obtain the effectiveness of the biofilter material given an overview of the procedure.



Figure 3.1. Overview of the measurements carried out during the experimental work.

The first experiments are made to characterize the biofilter materials, in order to obtain the water content, air permeability and bulk density necessary to determine the optimal packing characteristics for both materials when used for biofiltration. Once selected, biofilters will be packed to those specifications and an artificial ammonia air-mixture will be supplied to the filters for duration of 15 days. Upon completion of the experiments the filter columns will be analyzed for the concentrations of nitrogen fractions and the material physical properties.

## **3.2.** Characteristics of the biofilter materials

Two materials were selected as biofilter materials for the experiments. These materials were a loamy soil and fresh elm wood saw dust. The soil was obtained from top 10 cm at an agricultural field at the agricultural research station Foulum near Viborg and the saw dust was collected at a woodworking shop where wood sculptures were made using a chainsaw. For analysis of the material characteristics duplicate samples of each material were weighed and dried in an oven at 105°C until the weight is stable (ca. 24 hours) to obtain the water content. The samples were then combusted in an oven at 505°C to determine the organic matter content. A mean solids density for the two materials was determined assuming a solids density of 2.65 and 1.2 g/cm3 for inorganic matter and organic matter, respectively.

After physical analyses of the soil and saw dust the parameters in table 3.1 are obtained.

	Water content	Organic matter content	Density of solids
	gH2O/gDM	gOM/gDM	g/cm3
Soil	0,153	0,035	2,259
Saw dust	0,321	3,034	1,241

Table 3.1. Physical characteristics of biofilter materials

The type of soil used is sandy and the organic matter content is quite low. Soil contains natural microorganisms in itself that is a required characteristic for the biofilter to work.

Saw dust has a high content of organic matter, but it contains only few microorganisms. To function as a biofilter it is therefore mixed with sludge compost that contains a high number of nitrifying bacteria introduced during waste water treatment.

## **3.3.** Preparation of samples for air permeability measurements

In order to decide on the water content ( $\omega$ ) and dry bulk density ( $\rho$ b) to use in the bioifilters, it is necessary to determine the air permeability of the filter materials as a function of water content and bulk density ( $\rho$ b).

The first step is to check the possible ranges of water content and bulk density that can be achieved for the two materials. For this process samples from each material were prepare during materials at air dry and field capacity conditions. The water contents of the materials were measured using a halogen moisture analyzer (Mettler Toledo). At each of these two water contents samples were packed as loose and as hard as possible into 100 cm3 steel sample rings and the dry bulk densities of the samples were determined. Once the upper and lower limits for water content and bulk densities were selected within this range with the aim of measuring the air permeability at these combinations. Table 3.3 shows the combinations selected for measuring the air permeability.

Duplicate 100 cm3 samples for both materials at the selected water contents and bulk densities were prepared using materials adjusted to the desired water contents. The procedure used for adjusting the water contents is presented in appendix A and B.

Saw dust									
Bulk density									
(g DM/cm3)	0,13	0,14	0,17	0,2	0,23	0,26			
Water content									
(g H2O/g DM)	0,08	0,5	1	2	2,5	3	3,38		
Soil									
Bulk density									
(g DM/cm3)	1,20	1,25	1,30	1,35	1,40				
Water content									
(g H2O/g DM)	0,020	0,080	0,150	0,200	0,280	0,350	0,420		

Table 3.3. Combinations of water content and dry bulk density for samples used in air permeability measurements.

## 3.4. Air permeability measurements

The air permeability was measured using an air permeameter that measures the flow and pressure drop across the sample. Once these parameters are known it is possible to obtain the air permeability. Darcy (1856) reported a linear relationship between pressure drop ( $\Delta P$ ) and water flow rate in sand filters. Through the years this relation has been developed from the Darcy equation (3.1) to the quadratic Fochheimer equation (3.2) (Gostomski and Liaw, 2001).

$$\frac{\Delta P}{L} = \frac{\mu}{K} \cdot V \tag{Eq. 3.1}$$

$$\frac{\Delta P}{L} = \frac{\mu}{Ka} \cdot V + C \cdot \rho \cdot V^2 \qquad (Eq. 3.2)$$

Where	$\Delta P = pressure drop (Pa)$	V = Darcy velocity (m/sec)
	L = bed length (m)	$C = form coefficient (m^{-1})$
	$\mu = viscosity (Pa \cdot sec)$	$\rho = \text{density} (\text{kg/m}^3)$
	Ka = air permeability $(m^2)$	K = unsaturated hydraulic conductivity (cm $h^{-1}$ )

The measurements of air flow and pressure drop obtained by laboratory analysis in this project revealed that that their relationship was not linear. Therefore the quadratic Forcheimer equation was used for calculating the air permeability in both materials. The reason for the non-linearity is the occurrence of turbulence in the air flow through the material especially at the higher air flows. The linear Darcy law neglects the effects of turbulence whereas the Forcheimer equation takes turbulence into account. The Forcheimer equation can be simplified as equation 3.3:

$$AP = K_1 \cdot Q + K_2 \cdot Q^2 \tag{Eq. 3.3}$$

Where A = cross sectional area (m<sup>2</sup>)Q = air flow (m<sup>3</sup>/sec)

Fitting a second order polynomium to a plot of  $\Delta P$  versus air flow yields the value of K<sub>1</sub> and substituting this value in Eq. 3.5 the air permeability (ka) is obtained.

$$K_1 = \frac{\mu L}{kaA} \tag{Eq 3.4}$$

$$Ka = \frac{K_1}{\mu} \cdot \frac{A}{L} \tag{Eq. 3.5}$$

Where  $K_1$  is obtained by plotting  $\Delta P$  versus air flow (appendix A and B)  $\mu = 1,74 \cdot 10^{-5}$  Pa  $\cdot$  sec A = 19,63 cm L = 5 cm

### **3.4.** Packing and biofilter setup for ammonia removal.

Based on the air permeability measurements it was decided to carry out the biofiltration experiments at four different water contents for a fixed value bulk density. The selected water contents and bulk densities for each of the two materials are shown in Table 3.4.

Sample number	1	1'	2	2'	3	3'	4	4'
Saw dust								
bulk density (g DM/cm3 soil)	0,25	0,25	0,25	0,25	0,25	0,25	0,25	0,25
water content (g water/g DM)	0,50	0,50	1,20	1,20	1,80	1,80	2,50	2,50
Soil								
bulk density (g DM/cm3 soil)	1,375	1,375	1,375	1,375	1,375	1,375	1,375	1,375
water content (g water/g DM)	0,025	0,025	0,050	0,050	0,100	0,100	0,125	0,125

Table 3.4. Conditions used in the biofiltration experiments.

To evaluate the ammonia removal capacity of the two biofilter materials under the conditions specified in Table 3.4, the materials adjusted to the desired water contents using were packed into columns with the same dimensions (3,4 cm of diameter and 29,8 cm of length) to the desired dry bulk densities. The material was packed into the columns in 4 portions to get the packing as homogeneous as possible. Between packing of each portion, the surface of the previous portion is scraped to ensure good contact between the portions. The columns were supplied with an ammonia-air mixture which was produced by bubbling air through 6-liter reservoirs containing an aqueous solution of 2,67 g/l NH<sub>4</sub>Cl, 0,434 g/l NaOH and 1,36 g/l KH<sub>2</sub>PO<sub>4</sub>. Each column was connected to a separate reservoir. The effluent air from the columns is bubbled through an outlet trap (250 ml BlueCap bottle) that contains 200 ml of 0,1 M HCl for collection of effluent ammonia. The outlet trap is changed every second day (Monday, Wednesday and Friday), except for the weekends and analyzed for NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub> on a TRAACS-800 analyzer.



Figure 3.3 shows a schematic of the experimental biofilter set-up.

Figure 3.3. Biofilter setup for ammonia removal (Modified from Jensen, A., 2006).

The influent ammonia concentration was measured once every second day (Monday, Wednesday and Friday) during 1 hour. This is measured bubbling the air coming from the ammonia reservoir directly through an inlet trap, containing 200 ml 0,1 M HCl as shown in figure 3.4.



Figure 3.4. Measurement of inlet ammonia concentration. (Modified from Jensen, A., 2006).

The experiments were run for 2 weeks. The air flow applied to the columns was 0,5 l/min for the dust saw samples and 0,2 l/min for the soil samples.

The filter effectiveness that is the capacity of the biofilter to remove ammonia from the air and is calculated as the difference between the outlet and inlet ammonia concentrations (( $CNH_4$ -N,in –  $CNH_4$ -N,out)/ $CNH_4$ -N,in ).

# **3.5. Measurement of filter material characteristics at the end of the experiments**

After finishing the filtration experiments the columns were divided into 2 cm sections to measure the final physical properties and the concentrations of the N fractions as a function of filter depth. From each slice 2,5 g of material were taken for N fraction analyses and the rest was used to measure the organic matter, dry bulk density and water content of each slice. The measurements were carried out as discussed earlier in section 3.2, however, due to the limited amount of material available measurements were only carried out once per slice.

The N fractions measured were  $NH_4^+$ ,  $NO_3^-$  and  $NO_2^-$ . The measurements were carried out as follows: From each slice 2,5 g were introduced into a 100 ml BlueCap bottle containing 25 ml of 1M KCl solution. The bottles were shaken for 2 hours, the samples were then centrifuged for 10 min at 4000 rpm and the supernatant filtered. The filtrate was then analyzed for the above N fractions on a TRAACS-800 analyzer.

## 4. Results

This chapter describes the results obtained after doing the analyses in the laboratory. Initially the relationships between water content, dry bulk density and air permeability for the two materials are presented. Here after the ammonia removal effectiveness of the columns and finally the physical properties and N fractions of the filter material after the experiment are presented and discussed.

## 4.1 Air permeability as a function of water content and dry bulk density

To select the optimal water content and dry bulk density to be used in the biofilters to ensure adequate air permeability, the air permeability is plotted as a function of water content and bulk density on a contour plot with the bulk density, water content and the logarithm of the air permeability in Figure 4.1. The air permeability typically decreases with increasing bulk density and water content due to a decrease in the air filled porosity of the material. There is a difference between the two materials in dry bulk density,  $\rho_{\rm b}$ , (g DM/cm<sup>3</sup> material); the soil has a higher bulk density than the saw dust. Therefore the water content accepted by the saw dust is higher than for the soil.





In the next figures, 4.2 and 4.3, is plotted Log Ka (log permeability) in function of dry bulk density for constant water content.



Figures 4.2 Log permeability/ dry bulk density for constant water content for soil samples.



Figures 4.3 Log permeability/ dry bulk density for constant water content saw dust samples.

In figures 4.2 and 4.3 the relation between dry bulk density and log(air permeability). When dry bulk density decreases permeability increases. This phenomenon is more visible within the saw dust material, because for this material the air-filled porosity is higher than the one for the soil material. The soil is more compact than the saw dust therefore the permeability range is lower, accepts less water intake. Looking at identical bulk densities in the graphs it can be observed that permeability varies in a small scale for the same bulk density, lower for soil than for

saw dust. The relationship between air permeability and the water content is less clear. The permeability is more variable for the same water content

The conclusion is that the air permeability depends most on the dry bulk density, if the water content is high but the pores are not filled, the air can still go through.

## 4.2. Ammonia removal efficiency in sawdust and soil biofilters.

Figures 4.4 and 4.5 show the ammonia removal efficiency defined as the relative decrease in concentration from inlet to outlet divided by the inlet concentration as a function of operation time for saw dust and soil, respectively. For the saw dust (Figure 4.4) it can be observed that the removal efficiency is very high, for the columns with water contents between 0,5 and 1,8 g/g the removal efficiency is more or less stable at 99% efficiency in average. At a water content of 2,5 g/g the efficiency removal is slightly lower at 96% in average. It is seen that it is almost 99% during the first days after which it decreases somewhat. For the 2 lower water contents (0,5 and 1,2 g/g) it is observed that the efficiency remains high at the end of the 2 weeks, whereas for water contents of 1,8 and 2,5 g/g the efficiency decreases somewhat after 12 days.



Figure 4.4. Ammonia removal efficiency using saw dust as biofilter material.

During the first week of operation all the filters showed a more variable ammonia removal efficiency indicating that it takes at least one week for the filter to reach a stable condition. The removal efficiency is generally high for all four columns even thought it can be seen that the wettest column exhibits slightly lower removal rates toward the end of the experiment. The reason why the samples with lower water content have a higher efficiency is likely that the air flow through these columns is better distributed ensuring faster ammonia removal.

Figure 4.5 shows the ammonia removal efficiency for the soil filter columns. It is seen that the removal efficiency is very high for all columns regardless of the water contents investigated. The efficiency is generally above 98 % all the time and remains almost constant at an average of 99% during the 15 days of filtration.



Figure 4.5. Ammonia removal efficiency as a function of time for columns with soil as biofilter material.

The results in Figs 4.4 and 4.5 suggest that both saw dust mixed with sludge compost and soil are good materials to use as biofilter in order to remove ammonia. This was also observed for other materials such as sewage sludge and yard waste compost (Poulsen, 2006) and for peat soil (Redinova, et al, 2006).

The fraction removed is very high for both of the studied materials. There is a bit more variability in the removal efficiency for the saw dust, as a result of higher differences in water content for this material. Both materials are a good selection speaking in terms of ammonia removal.

## 4.3. Physical properties of the biofilter material at the end of the filtration experiments

This section presents the distribution of physical properties in the filter columns; such as organic matter content, dry bulk density, water content, and air filled porosity measured at the end of the filtration experiments.

#### **4.3.1 Organic matter content distribution in the filter columns**

Figure 4.6 and 4.7 show the organic content matter distribution of the filter columns once the experiment was done, after the 15 days. The data for the different water contents is data obtained from the average of two experimental columns.

As expected for saw dust the organic matter content is very high, and close to one grams of organic matter (OM) per grams of dry matter (DM), it can be said that almost all the saw dust is OM. The 4 samples have an organic matter average around the 91%.



Figure 4.6. Organic matter content distribution for columns with saw dust as a biofilter material. Where the red line is organic matter 0,91 g OM/g DM (average of all the samples).

The organic matter content average after the experiment compared with the organic matter content of the saw dust before packing it into the columns has not changed. The organic matters content, however, exhibit some variation along the column. This is likely due to difficulties in cutting the column into exactly 2 cm slices as the material is somewhat difficult to cut.

Figure 4.7 shows the organic matter content distribution of the soil in the filter columns after the experiment. All the data are averages of two experimental columns in the same conditions. The organic matter content for the soil is much lower than for the saw dust although it is still high compared to most other agricultural soils. If the average value 0,057 gOM/gDM obtained from the columns after the experiments is compared with the initial value 0,0034 gOM/gDM can be seen this has increased slightly except for a water content of 0,025 gOM/gDM where the organic matter content is somewhat lower than the initial value.



Figure 4.7. Organic content matter distribution for filter columns with soil as a biofilter material. The red line is indicates the initial organic matter content.

For the soil columns the organic matter content is generally almost constant along the column. The only column that has a higher variation is the columns with water content 0,025 g H<sub>2</sub>O/ g DM.

## 4.3.2 Dry bulk density

All the columns were packed to the same bulk density  $(0.25 \text{ gDM/cm}^3 \text{ sample})$ for the saw dust columns and 1,375g DM/cm<sup>3</sup> sample for the soil columns) to be able to observe the differences in ammonia removal efficiency due to changes in the water content. After the 2 weeks of filtration it was observed that the bulk density did not change significantly, indicating that the bulk density used will produce a physically stable filter material. Bulk densities as a function of column depth are given for the two materials in figures 4.8 and 4.9, respectively. All the values of the figures are average between to columns with the same characteristics. The slight variability in bulk density with depth is likely due to non exact division of the columns in exactly 2 cm as it was very difficult to do this accurately. It can be also observed for the saw dust columns that there is a slight tendency for increased bulk density at the bottom of the column (first 5 cm) for all water contents with the exception of the 1.2 g/g water content where the bulk density is somewhat lower. The increase could be due to a slight settling of the material. The bulk density average for the 4 columns after the experiment is 0.21 g DM/cm<sup>3</sup> sample, very similar to the 0.25 g DM/cm<sup>3</sup> sample from the packing. For the column packed at water content 1,2 the bulk density has decreased to an average value of 0,21 g DM/cm3 which can be explained by a water intrusion during the management of the columns. This is produced by an intrusion of water together with the air introduced in the bottom of the column as the water in the inlet air is likely saturated with water which may condense as the air pressure decreases within the column.



Figure 4.8. Bulk density as a function of depth for columns with saw dust as a biofilter material. The red line is bulk density used at the packing (0,25 g DM/ cm<sup>3</sup> sample).

The same fact occurs for soil, the bulk density remains more or less constant around the initial value to which the columns were packed. The slight differences in bulk density along the column length are also probably due to a non accurate division of the columns in exactly 2 cm slices. The initial packing value was 1,375 and the average value from all the columns after the experiment is 1,34 g DM/cm3 sample.



Figure 4.9. Bulk density for columns with soil as a biofilter material. The red line is bulk density used at the packing (1,375 g DM  $\cdot$  cm<sup>-3</sup> sample).

## 4.3.3 Water content

Figures 4.10 and 4.11 show the final water contents after the 15 days of the experiments for saw dust and soil respectively. All data are averages of two experimental columns in the same conditions.

For the saw dust the column packed to 0,5 g/g the final water content is close to the initial water content to which the column was packed. The column with a water content of 1,2 g/g has changed to an average value of 1,5 g water/g DM. The other two columns with initial values of 1,8 and 2,5 g/g have a loss of water in the top of the column which is about 50 % of the initial values. It can be seen that the water content has decreased near the outlet and increased near the inlet compared to the initial condition and the changes are largest for the columns. It could be observed when the ammonia trap bottles were disconnected from the bottom of the columns that the columns had been dripping a little bit. Another explanation for the increase in the water in the inlet air which is saturated with water, condenses as the air pressure decreases during passage through the filter media. A third mechanism that changes the water content could be evaporation near the column outlet caused by small temperature variations along the column.



Figure 4.10. Water content for columns with saw dust as a biofilter material. The straight lines represent the initial water content at which the column was packed for the experiments.

One of the columns with a water content 1,2 g  $H_2O/g$  DM had water intrusion from the reservoir due to an accidental pressure drop.

For the soil columns the final water content has change in relation to the initial water content to which the columns were packed. The column with initial water content 0,025 g H<sub>2</sub>O/g DM has almost not changed its water content, likely because the water content is very small and draining, therefore, is not likely. On the other hand the columns with the higher water content have lost water in the top of the column likely due to draining and evaporation. In the columns with initial water contents of 0,100 and 0,150 g/g the loss is around 45 % of the initial water.



Figure 4.11. Water content for columns with soil as a biofilter material. The straight lines represents the water content at which the column was packed for the experiments.

## 4.3.4 Air filled porosity

Figure 4.12 shows the final air filled porosity as a function of column depth for the saw dust columns. Here also all the data are averages of 2 experimental columns with the same conditions. As expected the air-filled porosity is lower when the water content is higher. It can be also observed at the inlet of some of the columns that the air-filled porosity is a bit lower than the rest of the column which is a result of the water content increase in this region.



Figure 4.12. Air filled porosity for columns with saw dust as a biofilter material. All the data are obtained as the average of two experimental columns packed with the same initial data values.

An overview of initial and final average values of air filled porosity for the 4 columns with different initial water contents is given in Table 4.1

In figure 4.13 can be seen that for the soil is material the differences in airfilled porosity between the columns are very small, because the water contents are all quite small compared to the total porosity. All the data are averages of 2 experimental columns with the same initial conditions.



Figure 4.13. Air filled porosity for columns with soil as a biofilter material. All the data is obtained by average of two experimental columns packed with the same data values.

An overview of the initial and final average values of air filled for the columns packed to 4 different initial water contents is given in table 4.1

Saw dust				
Water content (g H2O/g DM)	0,5	1,2	1,8	2,5
Air filled porosity before the experiment	0,67	0,5	0,34	0,16
Air filled porosity after the experiment	0,67	0,5	0,38	0,27
Soil				
Water content (g H2O/g DM)	0,025	0,05	0,1	0,125
Air filled porosity before the experiment	0,46	0,43	0,36	0,33
Air filled porosity after the experiment	0,44	0,44	0,43	0,42

Table 4.1. Difference of air filled porosity (cm<sup>3</sup> air/cm<sup>3</sup> sample) before and after the experiment.

The air filled porosity appears to be rather constant for the columns with the lower water contents even though the water contents do change significantly over time. At the higher water contents, the air-filled porosity exhibits larger changes over time. Again the variations in air-filled porosity are largely controlled by the ratio of the water content to total porosity.

## 4.4. Analyses of the nitrogen fractions in the filter columns after the experiments.

This section presents the distribution of the nitrogen fractions in the columns after the filtration experiment. Every column has been analyzed for ammonia,  $NO_3^-$  and  $NO_2^-$  concentrations. This data will show the distribution in the columns of the different fractions and where the removal or production of these fractions is taking place. A comparison between both filter materials used in this project is also presented.

## 4.4.1 Ammonia concentration distribution in the columns

Figure 4.14 shows the ammonia concentration in the saw dust columns after the 15 days experiment. All the data are averages of two columns with the same initial characteristics. Looking at figure 4.14 it can be observed that the concentrations of ammonia after the first centimeters of filter material are very low indicating that, ammonia removal in the columns happens near the inlet. For the columns with a water content of 0,5 g H<sub>2</sub>O/g DM the ammonia removal happens within the first 15 cm, for



water content 1,2 g H<sub>2</sub>O/g DM within the first 12 cm and for 1,8 and 2,5 g H<sub>2</sub>O/g DM within the first 5 cm.

Figure 4.14. Final ammonia concentrations as a function of column depth for columns with saw dust as a biofilter material. Data are averages of two columns with the same initial conditions.

In figure 4.15 is shown the ammonia concentrations in the soil columns after the 15 days experiment. The concentrations of ammonia after the first centimeters are very low indicating that, ammonia removal in the columns happens in the initial centimeters of the columns. For the columns with water content 0,025, 0,050 and 0,100 g H2O/g DM the removal happens within the first 10 cm, for water content 0,125 g H2O/g DM within the first 5 cm.



Figure 4.15. Final ammonia concentration as a function of column depth for columns with soil as a biofilter material. Data are averages of two columns with identical initial conditions

Looking at the two figures, 4.14 and 4.15, it seems that the soil has a high capacity for ammonia removal, so the saw dust. For all the columns the ammonia is removed within the first 10 cm and it takes 15 cm for the saw dust. It is also observed that the ammonia concentrations are higher in the bottom of the soil columns, the maximum ammonia concentration for saw dust are 0,125 mg NH<sub>4</sub>-N/ g DM at the column with a water content 0,5 g H<sub>2</sub>O/g DM and 0,22 NH<sub>4</sub>-N/ g DM for the 0,025 H<sub>2</sub>O/g DM soil column, both of them columns with a low water content.

## 4.4.2 NO3<sup>-</sup> concentration distribution in the columns

In figure 4.16 can be observed the  $NO_3^-$  concentration in the saw dust experimental columns, again being an average of 2 columns with the same characteristics.  $NO_3^-$  is also higher at the inlet due to nitrification of the ammonia in this region. The presence of nitrate proves that nitrification does occur, meaning that the bacteria at the columns are working.



Figure 4.16. Final nitrate concentration as a function of depth for columns with saw dust as a biofilter material. Data are averages of two columns with identical initial conditions.

Figure 4.17 shows  $NO_3^-$  removal for the soil material (data are averages of two columns with the same characteristics) and it can be seen that  $NO_3^-$  is higher at the inlet of the column as was also the case for  $NH^4$ -N. Concentrations of  $NO^{3-}$  are higher near the inlet due nitrification of the ammonia removed in this region.



Figure 4.17. Nitrate concentration for columns with soil as a biofilter material. Data are averages of two columns with identical initial conditions.

Looking at the two figures, 4.16 and 4.17, it can be observed that the NO<sub>3</sub>-N concentrations are higher at the inlet of the saw dust columns compared to the soil

columns. Also nitrate is detected in all the columns at all depths because the last small fraction is very difficult to remove.

## 4.4.3. NO2<sup>-</sup> concentration distribution in the filter columns

In figures 4.18 and 4.19 the distribution of  $NO_2^-$  in the columns is shown. All the data are averages of two experimental columns treated under the same conditions. The concentrations of  $NO_2^-$  are generally very low, but  $NO_2^-$  is detected throughout the entire column, but concentrations are especially high in the inlet.





For the soil columns the concentrations of  $NO_2^-$  are also very low, but again  $NO2^-$  is detected in the entire column, with the highest concentrations near the inlet.



Figure 4.19. Nitrite concentration for columns with soil as a biofilter material. Data are averages of two columns with identical initial conditions.

Figures 4.18 and 4.19 show that the NO2- concentration in the columns has the same distribution in both soil and saw dust. But the concentrations are lower for the soil columns.

## 4.5. Mass balances for ammonia, nitrite and nitrate.

The knowledge of the amount of much ammonia supplied to the inlet and emitted via the outlet of the filter (columns) together with information about the amount of ammonia present in the filters before and after the filtration of experiment makes it possible to obtain a mass balance for ammonia and for total inorganic nitrogen. The mass balance is represented in table 4.2.

$$\Delta m_{\text{TOT,UORG}} = \Delta m_{\text{NH4}}^{+} + \Delta m_{\text{N03}}^{-} + \Delta m_{\text{N02}}^{-}$$

$$\Delta m_{\text{NH4}}^{+} = m_{\text{NH4}}^{+}, \text{ final} - m_{\text{NH4}}^{+}, \text{ start} - m_{\text{NH4}}^{+}, \text{ flow} \qquad (4.1)$$

$$\Delta m_{\text{N03}}^{-} = m_{\text{N03}}^{-}, \text{ final} - m_{\text{N03}}^{-}, \text{ start}$$

$$\Delta m_{\text{N02}}^{-} = m_{\text{N02}}^{-}, \text{ final} - m_{\text{N02}}^{-}, \text{ start}$$

Where

m <sub>TOT,UORG</sub>	Total mass of inorganic ammonia (mg N)
$m_{\rm NH4}^{+}$	Mass of $NH_4^+$ (mg N)
m <sub>N03</sub>	Mass of NO <sub>3</sub> <sup>-</sup> (mg N)
m <sub>N02</sub>	Mass of $NO_2^-$ (mg N)

The quantity of  $NH_4^+$  removed is calculated as a result of the differences between flow and the inlet and outlet from the beginning and end of the experiments. It can be seen that even with the different materials and different water contents used, the  $NH_4^+$  removal in the columns is around 97% (of the ammonia that comes in trough the air) for all the columns. The percentage of the total N-compounds (ammonia, nitrite and nitrate) removed is in the order of 290% for all the columns. The high percentage of the inorganic N-compounds removal can be explained by a change of the inlet-outlet concentrations as a result of biological processes, like mineralization of organic nitrogen, possible working together with the nitrification process. In addition, the growth of biomass and the denitrification benefits the increment of inorganic N-compounds in the biofilter, for this reason it is removed more than it is supply.

Saw dust									
		%∆M NH4		% ΔmTOT,uorg					
Water content (g H20/g DM)	∆mNH4+	(in + initial)	∆mTOT,uorg	(in + initial)					
0,5	21,667	97,667	65,250	293,351					
1,2	20,726	96,983	62,354	291,672					
1,8	14,088	97,558	42,274	292,466					
2,5	25,821	96,896	77,726	290,839					
		Soil							
Water content									
0,025	30,229	97,624	91,198	294,492					
0,5	25,528	97,426	76,817	291,855					
0,1	20,199	97,215	60,747	289,093					
0,125	19,014	97,247	57,233	292,589					

Table 4.2. Mass balances for every experimental column for saw dust and soil. The data is obtained by averages of 2 experimental columns with the same conditions.

The high percentage removal of the inorganic nitrogen compounds proves that the filters do remove ammonia from the air by nitrification and incorporation in the biomass and not only by adsorption. This fact has also been described in other papers, (Poulsen and Moldrup, 2006 and Jensen, 2006).

# 4.6. Estimation of the nitrification rate based on Monod kinetics

Monod kinetics was used to estimate ammonia removal rates inside the filters (give equation numbers from theory section) (point 2.4). A simple numerical solution of the equations was fitted to data for the ammonia concentration profile in the air phase as a function of the filter depth (Appendix C). The values of maximum removal rate,  $r_m$  and half saturation constant,  $K_s$ , were estimated by minimizing the error between the experimental data and the numerical ammonia degradation model. The results are presented in table 4.3.

Parameters	Saw dust Soil							
Water content (q water/q DM)	0.5000	1.2000	1.8000	2.5000	0.0250	0.0500	0.1000	0.1250
Average air filled porosity	0,0000	.,	.,	_,	0,0200	0,0000	0,1000	0,1200
(cm3. cm-3)	0,670	0,510	0,380	0,270	0,440	0,440	0,440	0,420
Distance from Inlet								
(cm)	15,000	12,000	5,000	5,000	15,000	10,000	10,000	5,000
Minimum residence time								
(sec)	21,889	16,402	12,214	8,902	36,048	36,265	35,352	34,157
r <sub>m</sub> (mg N/cm3. min)	4,00E-05	3,05E-04	7,47E-04	9,45E-04	5,00E-05	1,52E-05	1,45E-04	6,80E-05
K <sub>s</sub> (mg. cm-3)	1,00E-06	1,00E-06	1,00E-06	1,00E-06	1,88E-06	1,00E-06	1,00E-06	1,00E-06
Full residence time (sec)	21,889	16,402	12,214	8,902	36,048	36,265	35,352	34,157

Table 4.3. Results of ammonia removal efficiency derived from Monod kinetics conversion (see parameters definition in section 2.4).

The Ks values were assumed to be on the order of  $1,00E^{-6}$  mg  $\cdot$  cm<sup>3</sup> as this was the value found in Poulsen and Mouldrup, 2006,

In figures 4.20.a and b is shown the nitrification rate as function of the water content.



Figures 4.20. Estimated values of the nitrification rate  $(r_m)$  as a function of water content. a) Nitrification rate for the saw dust filter and b) nitrification rate for the soil filter.

Figure 4.20.a shows that the nitrification rate for the saw dust material increases with increasing water content where as the nitrification rate is variable and does not show a consistent trend with the water content for the soil filters (figure 4.20b). It has to take into consideration that the water content difference between the saw dust samples are higher than the difference in water content for the soil samples.

## **5** Conclusions

The goal of this project is to study how the physical characteristics of the biofilters influence the filter efficiency. Therefore will be studied the ammonia removal efficiency of the two filter materials at different water contents to determine the optimal water content for biofiltration.

There is a difference between the two materials in dry bulk density,  $\rho_b$ , (g DM/cm<sup>3</sup> material); the soil has a higher bulk density than the saw dust. Therefore the water content accepted by the saw dust is higher than for the soil. A conclusion obtained here is that the air permeability depends most on the dry bulk density, if the water content is high but the pores are not filled, the air can still go through. The results show also than even if the experiments were running for a short time (15 days) the biofilter material characteristics changed, especially in water content and organic matter. It is shown in the results that water content in the biofilter samples falls down a slightly for both materials, especially for the samples with a higher water content, and the organic matter in the material is maintained stable for saw dust and it is a little bit higher for soil.

In the project is estimated the accumulation, in- and out N-concentration, showing that for the two materials the removal efficiency is high. And is also studied the nitrification rate by the Monod kinetic method, where it shows that the higher the water content, the higher the N removal for the saw dust material. It cannot be appreciated for the soil material the differences in relation with the water content because the differences in the samples in terms of water content were very small. The removal efficiency is generally high for all four columns even thought it can be seen that the wettest column exhibits slightly higher removal rates toward the end of the experiment. The reason why the samples with lower water content have a lower efficiency is likely that the air flow through these columns is not distributed regular ensuring slower ammonia removal. The fraction removed is very high for both of the studied materials. There is a bit more variability in the removal efficiency for the saw dust, as a result of higher differences in water content for this material, meaning that the water content in the biofilter influence in the results. Both materials are a good selection speaking in terms of ammonia removal.

## 5.1 Recommendation to next experiments

The Laboratory analyses with the biofilters panel for removing ammonia shows that the biofiletrs work effectively.

As this method is effective and economic is interesting to analyze samples in laboratory and get the best materials with the best characteristics to use in the pilot experiments. This project studies the organic matter, water content and bulk density variations and how do they influence in the nitrogen removal. There have been few analyses in this area, therefore is important to make analyses of other different materials to study their characteristics and the influence of them.

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## 7 Appendixes

- 7.A. Appendix A-Water content and bulk density selection for soil
- 7.B. Appendix B-Water content and bulk density selection for saw dust
- 7.C. Appendix C-Nitrification rate