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BIOFILTER MATERIAL SELECTION FOR ODOR REMOVAL

Master of Science thesis

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ABSTRACT

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A possible way to arrange sanitation in developing countries and economize on sanitation in the industrialized countries is dry sanitation. In order to become general in industrial countries, the dry toilets should be pleasant to use. In dry toilets unpleasant odors are possible. The odors can be removed from the toilet with proper ventilation. However, when the odors are conveyed outside it is possible that the surroundings of the building have unpleasant odors. In that case the exhaust gases of dry toilet must be treated.

Possible way to treat the exhaust gases is biofiltration. In biofiltration gas flows through porous bed and the contaminants of the gas transfer to water phase of the filter bed. In water phase the micro-organisms of the biofilter degrade the contaminants biologically.

The aim of this study is to find a good material for biofilter treating exhaust gases of dry toilet. In two experiments five materials were tested in laboratory scale biofilters. Tested materials were Langfaserfiltergranulat (UGN Umwelttechnik GmbH), UgnCleanPellets © B (UGN Umwelttechnik GmbH), UgnCleanPellets © N (UGN Umwelttechnik GmbH), vermiculite (Nelson Garden PLC) and activated carbon (PICA).

First experiment was done with dry air and in the second experiment the inlet gas was humidified. Real stored urine was used as a source of odorous compounds. Performance of the biofilters was determined by measuring ammonia and total organic carbon removal in the biofilters. Also water-holding capacity, pressure drop, nitrate concentration and microbial growth in the filter beds were determined. With data collected during the experiment it was also possible to calculate a mass transfer coefficient for ammonia from urine to air.

All tested materials were able to remove ammonia and organic compounds from air. Because of drying none of them was able to perform efficiently through the whole experiment. Vermiculite and Langfaserfiltergranulat maintained best moisture conditions in the filter bed. Ammonia and organic compounds were significantly biodegraded only in UgnCleanPellets © B and UgnCleanPellets © N biofilters.

According to results it was possible to recommend that combination of UgnCleanPellets © B and vermiculite would be good material for biofilter treating exhaust gases of dry toilet. It would be a good growth medium for micro-organisms and it would have high water-holding capacity. Also its pressure drop would be relatively small. However, further laboratory experiments in slightly larger scale are recommended before the new material is used in full scale applications.

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Kehitysmaissa sanitaation tasoa voitaisiin parantaa ja teollisuusmaissa sanitaatio aiheuttamaa luonnonvarojen ja rahan kulutusta voitaisiin pienentää käyttämällä kuivakäymälöitä. Jotta kuivakäymälät yleistyisivät teollisuusmaissa, niiden käytön pitäisi olla miellyttävää. Epämiellyttävät hajut ovat kuitenkin mahdollisia kuivakäymälöissä, mikä vähentää halua käyttää niitä. Hajut voidaan poistaa käymälästä järjestämällä käymälän ilmastointi oikein. Tämä kuitenkin saattaa aiheuttaa hajuhaittoja käymälärakennuksen ympäristössä. Tällöin käymälän tuuletusilma tulee käsitellä.

Kuivakäymälän tuuletusilma on mahdollista käsitellä biosuodattamalla. Biosuodatuksessa ilma johdetaan huokoisen pedin läpi ja ilman epäpuhtaudet siirtyvät suodatinpedissä vesifaasiin. Vesifaasissa biosuodattimen mikro-organismit hajottavat ilmassa olleet epäpuhtaudet biologisesti.

Tämän työn tarkoituksena oli löytää kuivakäymälän tuuletusilman biosuodatukseen sopiva suodatinmateriaali. Tätä varten viittä materiaalia testattiin biosuodatinmateriaalina laboratoriomittakaavassa kahdessa eri kokeessa. Testatut materiaalit olivat Langfaserfiltergranulat (UGN Umwelttechnik GmbH), UgnCleanPellets © B (UGN Umwelttechnik GmbH), UgnCleanPellets © N (UGN Umwelttechnik GmbH), vermikuliitti (Nelson Garden Oy) ja aktiivihilli (PICA).

Ensimmäisessä kokeessa käytettiin kuivaa ilmaa ja toisessa kokeessa sisäänmenoilmaa kostutettiin. Kokeissa käytettiin säilöttyä virtsaa haisevien yhdisteiden lähteenä. Suodattimien toimintakyky määritettiin mittaamalla ammoniakin ja kokonaisorganisen hiilen poistumista suodattimissa. Tämän lisäksi määritettiin suodatinpetien vedensitomiskyky, painehäviö ja nitraattikonsentraatio sekä mikrobien kasvu suodattimissa. Kerätyn datan perusteella oli myös mahdollista laskea ammoniakille massansiirtokerroin virtsasta ilmaan.

Kaikilla testatuilla materiaaleilla oli mahdollista poistaa ammoniakkaa ja orgaanisia yhdisteitä ilmasta. Kuivumisesta johtuen yksikään biosuodatin ei toiminut tehokkaasti koko kokeen ajan. Vermikuliitti ja Langfaserfiltergranulat säilyttivät kosteuden parhaiten. Huomattavaa ammoniakin ja orgaanisten yhdisteiden biohajoamista tapahtui vain UgnCleanPellets © B ja UgnCleanPellets © N biosuodattimissa.

Kokeissa saatujen tulosten perusteella voitiin suositella uuden materiaalin valmistamista UgnCleanPellets © B:stä ja vermikuliitista. Uusi materiaali olisi hyvä kasvualusta mikro-organismeille ja sillä olisi suuri vedensitomiskyky. Lisäksi kyseisen materiaalin aiheuttama painehäviö olisi pieni. On kuitenkin suositeltavaa, että laboratorioskokeita jatketaan hieman suuremmassa mittakaavassa ennen kuin uutta materiaalia aletaan käyttää täyden mittakaavan sovelluksissa.

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SYMBOLS AND ABBREVIATIONS

a	experimental constant
α_a	partial mass transfer coefficient from air side of the liquid-air interface
α_{aw}	combined mass transfer coefficient from liquid to air
α_w	partial mass transfer coefficient from liquid side of the liquid-air interface
a_v	specific surface (total particle surface/volume of the particle)
b	saturation constant
A	surface area
C	concentration
D	equivalent diameter
d	diameter
ΔG^0	free-energy change under standard conditions at pH 7
F	dimensionless form drag constant
h	height
J_{NH_3}	ammonia flow from water to air
k	Henry's law constant
K	specific permeability
K_f	Freundlich adsorption isotherm
K_M	Michaelis constant
m	mass
M	molar mass
μ	dynamic viscosity
n	empirical constant
ω	specific humidity
p	partial pressure
P	pressure
φ	porosity
ϕ	relative humidity
Q	flow rate
R	gas constant
ρ	density
t	time
T	temperature
θ	percentage of unionized ammonia from total ammonia concentration
v	velocity
V	volume
w	width
x	distance
x/m	mass of adsorbed compound per mass unit of adsorbent

AC	activated carbon
AL	area loading
B	UgnCleanPellets © B
CMP	chemical manufacturing plant
CoA	coenzyme-A
FAD	flavinadine dinucleotide
FADH ₂	reduced form of flavinadine dinucleotide
EBRT	empty bed residence time
EC	elimination capacity
GTZ	Deutsche Gesellschaft für Technische Zusammenarbeit GmbH (German technical cooperation)
IC	inorganic carbon
Langfaser	Langfaserfiltergranulat
LR	loading rate
MC	moisture content
MCP	manure composting plant
MWTP	municipal waste treatment plant
N	UgnCleanPellets © N
NAD ⁺	nicotinamide-adenine dinucleotide
NADH	reduced form of nicotinamide-adenine dinucleotide
OWCP	organic waste composting plant
ppb	parts per billion
ppm	parts per million
RE	removal efficiency
SL	surface loading
TC	total carbon
TOC	total organic carbon
UK	unknown
Verm	vermiculite
VOC	volatile organic compound
WHO	World Health Organization
WECF	Women in Europe for a Common Future
WWTP	waste water treatment plant

1 INTRODUCTION

Water supply and sanitation are essential needs and human rights. Lack of clean drinking water, sanitation and hygiene is cause for approximately four billions of diarrhea cases per year. 2.2 million of these cases lead up to the death, mostly among children under the age of five years. Lack of clean drinking water forces people to use dirty water as drinking water which causes cholera epidemics. Risk of the epidemic arises in areas where population density is high and hygiene is poor. Especially in refugee camps the conditions are favorable for health risks. In the year 2000 it was estimated that 1.1 billion people did not have access to improved water supply and 2.4 billion people were without improved sanitation, mostly in developing countries. (WHO/UNICEF 2000.)

Besides developing countries, also industrial countries have problems with sanitation. Water systems started to get contaminated in 1800's because of the high popularity of water closets. The relationship between contaminated drinking water and for example cholera epidemic was found and it was realized that waste waters need to be treated somehow. At first waste waters were treated to prevent the transmission of diseases. Nowadays also the reduction of environmental impacts is an important aspect in waste water treatment. (Cooper 2001.)

Nowadays the main purpose of sewer systems is to move waste water to a suitable waste water treatment plant where pathogens, organic matter, nutrients, pharmaceuticals and solid wastes are removed from the waste water. Mainly activated sludge process is used for that. (Heip et al. 2001.) Waste water treatment and maintenance of the sewer system is very expensive. For example in Tampere in four waste water treatment plants 23.9 million m³ of waste water was treated in year 2010. Tampereen Vesi which maintains sewer network and waste water treatment plants in Tampere charged their costumers 23.3 million euro in 2010. (Tampereen vesi 2010.)

There is also a big concern of how much longer there are nutrients available, especially phosphorus. Nutrients that are used in farms end up to food. After eating and digesting the food people excrete the nutrients through urine and faeces. In waterborne sanitation the nutrients are finally after waste water treatment discharged as waste. This leads us to a situation where shortage of fertilizers is universal. (Vinnerås 2002.) Production of fertilizers is also energy-intensive. For example worldwide annual production capacity of nitrogen fertilizers is over 100 Mtonnes N. It is estimated that nitrogen fertilizer industry consumes 1 % of global primary energy use in fertilizer production. (Worrel et al. 2000.)

To arrange sanitation in developing countries or economize on waste water treatment costs in industrial countries the solution could be the same. Dry toilets can be

used in poor areas as a way to safely manage human excreta. Dry toilets also have a great potential to reduce costs in waste water treatment in areas where waterborne sanitation is used. Advantage of the dry toilets is also that nutrients can be recirculated by making human excreta available for re-use.

It is possible that problems can occur in dry toilet. Odors can be formed in excreta container. In stored urine large amount of ammonia is formed (Udert et al. 2006). Also sulfuric compounds (Storer et al. 2011) and volatile organic compounds (VOC), such as alcohols, ketones and alcohols (Zlatkis et al. 1981) are found from stored urine. When the ventilation of the toilet is arranged correctly, these malodorous compounds are sucked from the excreta container outside the building (Winbland 2004). If the amounts of the odorous compounds are high enough the surround of the building might have unpleasant odors and in that case the exhaust gases need to be treated.

A possible way to treat malodorous gases efficiently and economically is biofiltration. In biofiltration the contaminated gas flows through a porous bed and the contaminants of the gas absorb to the water phase of the bed. From the water phase the contaminants can adsorb to the filter material or the micro-organisms of the biofilter biologically degrade the contaminants. (Devinny et al. 1999.)

Many different materials can be used as a carrier material in biofiltration. Use of materials such as compost (Jun & Wenfeng 2009), coconut fiber (Gabriel et al. 2007), polyurethane foam (Filho et al. 2010) and activated carbon (Babbitt et al. 2009) has been reported. There are few requirements for material used in biofilter. Micro-organisms must be able to grow on the surface of the material. The material should also have high water-holding capacity so the conditions in the biofilter will be moisture. Micro-organisms cannot be active in dry conditions and the treatment of the gas will not be efficient. The filter material should also cause small pressure drop in the filter bed. That way the operational costs of the biofiltration will be smaller. (Devinny et al. 1999).

This work is part of DryCloset project financed by European Union. Aim of the DryCloset project is to develop technical innovations which will minimize the impact of the shortcomings in dry toilets, such as unpleasant odors and struvite formation in pipe connections. The technical innovations will be compact and gas specific biofilter and struvite prevention system.

In this work five different materials were used in laboratory scale biofiltration to find out which of them would be the most suitable material for biofiltration of exhaust gases of dry toilet. The studied materials were Langfaserfiltergranulat (UGN Umwelttechnik GmbH), UgnCleanPellets © B (UGN Umwelttechnik GmbH), UgnCleanPellets © N (UGN Umwelttechnik GmbH), vermiculite (Nelson Garden PLC) and activated carbon (PICA). Real stored urine was used as odor source in the experiment.

In the laboratory two separate experiments were done. The first experiment was done with one biofilter with a view to find out if there is something to improve in experimental setup or analytical method. In the second experiment five biofilters were used parallel to treat volatile compounds of urine and the performance of the biofilters was monitored. The performance of the biofilters was determined by measuring ammonia

and total organic compound (TOC) removal in the biofilters. Other measured variables were the moisture content (MC) and nitrate concentration of the filter beds and growth of heterotrophs, yeasts, sulphate oxidizing bacteria, *Nitrosomonas* and *Nitrobacter*. Pressure drop in the filter beds was calculated with Ergun's equation. With the collected data it was possible to give suggestion for the best biofilter material.

VOCs in headspace of stored urine were determined qualitatively. It was also possible to calculate mass transfer coefficient for ammonia from urine to air by using the collected data. The mass transfer coefficient can be used to estimate ammonia flow rate from urine to air.

This work divides into five Chapters. Chapter 2 is a literature survey covering the theoretical background of the experimental part of the study. It describes the use of dry toilets around the world, what kind of odorous compounds can be formed in dry toilet and how they can be treated. The main subject of Chapter 2 is biofiltration and theory of it.

Chapters 3 and 4 cover the experimental part of the work. In Chapter 3 the used materials and methods are covered in detail. In Chapter 4 the results of the laboratory tests are presented and discussed. Also sources of error are discussed in this Chapter. In Chapter 5 the results are concluded and recommendations for further studies are suggested.

2 BACKGROUND

2.1 Use of dry toilets around the world

Dry toilets are successfully used in both developing and industrialized countries in rural and urban areas. Used techniques vary from simple dry toilets to sophisticated high-tech concepts. (Langergraber et al. 2005.) Dry toilet is a toilet concept that uses no water to flush the toilet. Ecological sanitation aspires to save water, prevent water pollution and recycle the nutrients in human urine and faeces (Winbland et al. 2004). Both dry toilets and ecological sanitation have been used for hundreds of years. They are still widely used in parts of East and Southeast Asia. In Western countries these kinds of techniques have not been used widely after waterborne sanitation become common. In recent years there has been interest in dry toilets and ecological sanitation also in Western countries.

There are many projects which purpose is to arrange sanitation and give information of dry toilets in developing countries. Women in Europe for a Common Future (WECF) have these kinds of projects for example in Moldova, Kyrgyzstan, Tajikistan and Azerbaijan. (Women in Europe for a Common Future 2011.) World Health Organization (WHO) has also sanitation involved projects in areas where hygienic situation and knowledge of sanitation are poor. (WHO 2011.)

Global Dry Toilet Association of Finland (Käymäläseura Huussi ry) is as well involved in many projects which aim is to improve the sanitation, hygiene and welfare of the local people. At the moment, Global Dry Toilet Association of Finland is working in Zambia, Swaziland and Karelia. They have also promoted to get a standard and CE-marking for dry toilets in European Union. (Global Dry Toilet Association of Finland)

In Finland a large project with relation to ecological sanitation and dry toilets was the renovation of I-building in Tampere University of Applied Science. When the building was renovated at the same time wind farms, solar panels and a geothermal power plant were installed. (Tampere University of Applied Science 2011.) In the building composting dry toilets and urine separating dry toilets were installed. Also very water sparing vacuum toilets and urine separating Eco Flush toilets was installed. Toilets are in everyday use and experiences of using them are examined. (Valtonen 2011.) Experiences of ecological sanitation have been got for example from Germany, Denmark and Sweden (Langergraber 2005, Druitt et al. 2009).

2.1.1 Available dry toilet techniques

Dry toilets can be built with very different concepts and equipped with various techniques. The simplest construction can be just a hole on the floor or ground but the most sophisticated toilets can use electrical ventilation and burn or freeze excreta. Liquids and solids can be separated in three different ways: keep them separate, mix them and somehow collect liquids from the excreta container, or mix them and evaporate liquids.

In developing countries built toilets are simple and often quite robust. There is a small shelter above the ground. In the shelter there are two holes on the floor, the bigger and the smaller. The idea is that people takes squatting position on the holes and relieves themselves. The liquids end up to the smaller hole and the solids go to the bigger hole which leads to containers under the floor. There might be two pairs of the holes on the floor. In that case at first only other pair of holes is used. When the containers of these holes get full people begin to use other pair of holes and the faeces in the full container are composted until the other containers are full. The toilet can also be equipped with a squatting pan on the floor. (Winblad et al. 2004.)

Somewhat an advanced version of toilet in developing countries is an outhouse used commonly for example in Finnish summer cottages. Difference between this and previous solution is that there is a seat in the toilet. These outhouses can compost the excreta, separate urine and faeces or urine can vaporize from the excreta container. These solutions have to be emptied approximately once per year.

Outhouses can also have sophisticated technology for urine separation and excreta treatment. Example of that is a dry toilet invented and made by Ecosphere Technologies. In toilet, urine and faeces drop on sloping conveyor belt. From the belt urine flows downwards to a pipe from which urine infiltrates to soil and the conveyor belt delivers faeces to treatment area. Users of the toilet rotate the conveyor belt by pressing a pedal next to the toilet seat. In the treatment area of faeces worms accelerate the composting process of the faeces. (Pat. US 6,601,243 B2 2003.) In Figure 1 there is a schematic view of Ecosphere Technologies dry toilet.

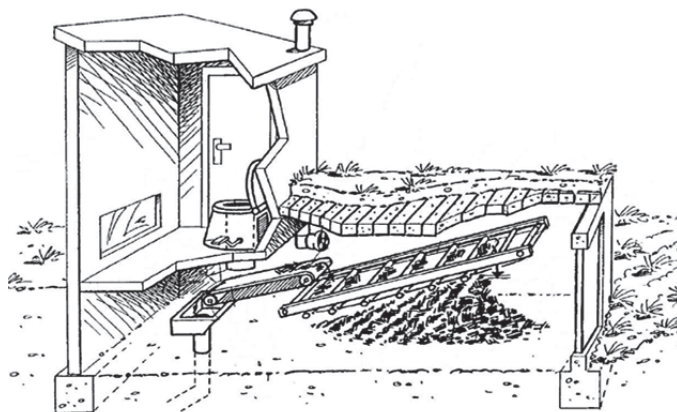


Figure 1: Schematic view of dry toilet invented and produced by Ecosphere Technologies (Pat. US 6,601,243 B2 2003).

There are plenty of different dry toilet techniques available for households. In these cases it is important that the toilets are comfortable to use. For example odors should be minimized in the toilet. For detached houses, a very simple and popular solution is the Norwegian “carousel”. In a vault below the floor of the toilet there is a four sectional tank which is able to rotate. The idea is that one of the sections is used and when it gets full the carousel is rotated and the next section is introduced. Material in the oldest section is emptied. The toilet seat can be either urine diverting or non-diverting. Another good solution for detached houses is a classic model of the composting toilet called Clivus. In Clivus, there is a container in a vault with an inclined floor. The principle is that contents slide very slowly from the upper end down to the storage part of the container. At the same time contents decompose similarly to garden composting. Advantage in Clivus is that it is possible to connect a pipe from kitchen to it and compostable waste can also be dumped into Clivus. (Winbland 2004.)

Dry toilet in a detached house does not have to have equipment under the floor. There are plenty of solutions where the excrement container is inside the toilet seat. Of course in these cases container is smaller and it has to be emptied more often. Also there must be good ventilation in the toilet seat to control odors in the toilet. Separett Villa 9000 is a good example of introduced technology. It has 23 liter container inside and uses electrical fans to remove the odors. (Separett 2008.) Biolan also has techniques that have excrement container inside the seat. Icelett freezes the excreta so that microbial activity stops. Naturum composts excreta inside the seat. (Biolan 2011.)

In apartment buildings and other bigger buildings arranging of dry sanitation might be more complicated than in detached houses. In apartment buildings the toilets or at least the toilet seats need to be located so that the faeces can freely drop in the container in vault or first floor. Of course toilet seats with own container for the faeces could be used but that would not be practical at all. An example of how the dry toilet could be stationed in apartment building is shown in Figure 2. (Windbland 2004.)

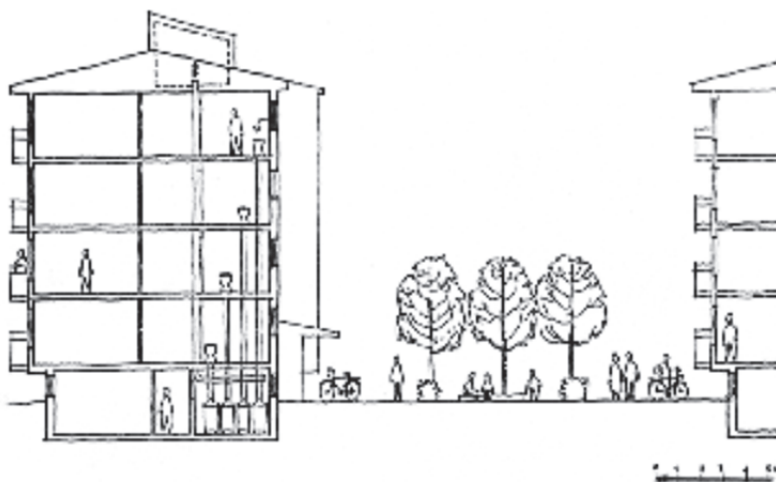


Figure 2: A way to situate dry toilets in apartment building (Winbland 2004).

2.1.2 Ventilation in toilets

Comfortable use of toilet requires that the ventilation is decent. If toilet has lot of odors inside, the toilet is unpleasant to use and it gives impression of dirtiness. Many people in industrialized countries are used to use water closet and they might have lot of prejudices against dry toilet. In these cases if dry toilet has bad odors inside, people might even refuse to use it.

In Finland, Ministry of the Environment has enacted the collection of the building regulations. This The National Building Code of Finland determines the right methods of construction, construction planning and used techniques and equipment in buildings. In part D there are regulations of heating, plumbing and air-conditioning (HPAC) and energy economy and part D2 covers ventilation in buildings. It is said that building needs to be constructed in a certain way that there are not insanitary amounts of gases, particles, microbes or odors that reduce habitability. (Ministry of the Environment 2008.)

The National Building Code of Finland does not specify how many times air should be changed per hour in a toilet. Instead it says that outgoing air flow from the toilet has to be at least 10 l/s (36 m³/h) in residential buildings. In hospitals the outgoing air flow from the toilet has to be much larger, 30 ((l/s)/m²)/seat (108 ((m³/h)/m²)/seat). In other buildings the outgoing air flow from the toilet needs to be at least 20 or 30 ((l/s)/m²)/seat depending on what kind of usage the building has. (Ministry of the Environment 2008.)

In water closets the input air comes from the other rooms of the building and outgoing air is removed outside from the toilet. Outgoing air is often removed through a ventilating tube from ceiling or top of the wall. This is not a proper way to arrange ventilation in a dry toilet. In the dry toilet the air must be sucked from the toilet through the toilet seat to the excreta container and from that through the ventilation pipe outside the building. (Winbland et al. 2004.) Figure 3 shows the direction of the air flow in the dry toilet.

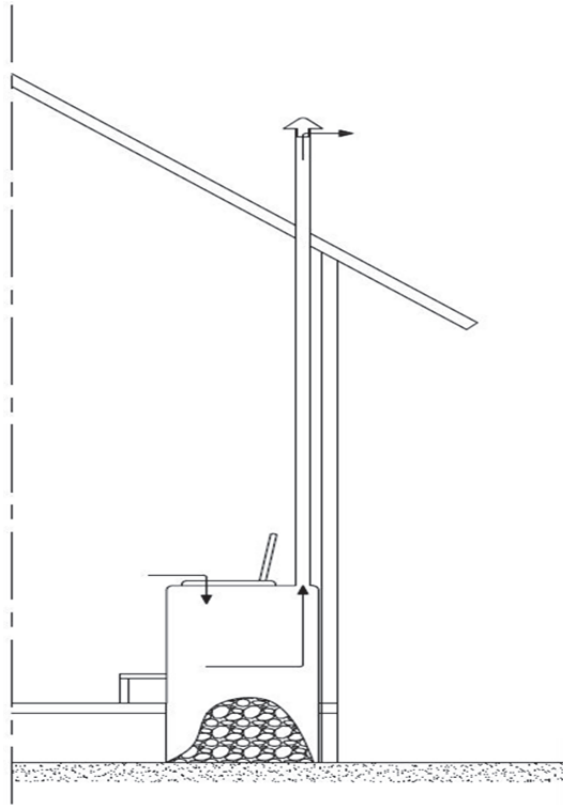


Figure 3: Scheme of the ventilation in dry toilet. Direction of the air flow is shown with arrows.

If toilet is inside of the building, it is recommended to use an electrical fan. With the direction of the air flow shown in Figure 3 it can be secured that none of the bad odors of the excreta can escape from the excreta container to the indoor air of the toilet. If the concentrations of malodorous compounds are high, the surroundings of the building might have unpleasant odors and treatment of exhaust gas is needed.

In a composting toilet, preventing odors is not the only reason for ventilation. Composting is an aerobic process and many micro-organisms decomposing the excreta need oxygen. With sufficient ventilation, enough oxygen can be brought to the excreta container. (Winbland et al. 2004.)

2.1.3 Occurring problems with dry toilets

Dry toilets are often claimed to be smelly, dirty and provide a fortunate habitat for flies to live. If the dry toilet is not properly designed and operated, these beliefs can become true. (Winblad et al. 2004.)

In waterborne sanitation flush and forget mentality is possible but dry sanitation requires maintenance. In households, occupants have to take care of the whole sanitation system including weekly/monthly emptying of the urine tank, recycling of urine, monitoring of the processing chamber, emptying of the processing chamber, secondary processing of the chamber content and finally use of the sanitized material. All this needs time and interest, and if occupants do not have them, problems will occur. In

larger projects in urban areas, the workload of the toilet users is smaller because the operation of the dry toilet can be carried out by municipal or private organization. (Winblad et al. 2004.)

It is possible to have unpleasant odors in a dry toilet. If the ventilation does not work properly, odors from the urine and excrement tank might get into the toilet. In urine separating toilet, deposits might form in urine collectors and pipes. These deposits need to be removed. Otherwise they can cause blockages in pipes and bad odors in toilet. (Winblad et al. 2004.) Problems of this kind have been encountered in Eschborn, Germany where is the main office building of the Deutsche Gesellschaft für Technische Zusammenarbeit GmbH (GTZ, German technical cooperation). Urine diverting toilets and waterless urinals has been installed in the main building. Both toilets and urinals had precipitation problems which were caused by insufficient cleaning of the urine valves and pipes. This resulted blocks in pipes and bad odors in toilets. (Blume & Winker 2011.)

A possible source of problems in dry toilets is bad design. It can be reason for excrement tanks filling up more often than was expected. Often the tanks are emptied manually. That increases the need for the maintenance which might decrease the motivation of the dry toilet users. (Bhagwan et al. 2008.)

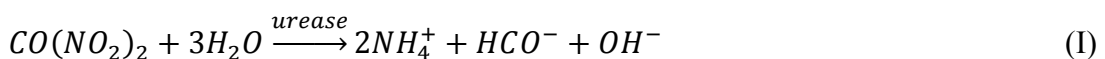
2.2 Odorous compounds in dry toilets

As described odors can be a problem in dry toilet especially if the ventilation is poor. In those cases the odorous compounds might end into the toilet from the excreta container and it will be uncomfortable to use the toilet. Next three Chapters describe what kind of odors might occur in toilet and how they are generated.

2.2.1 Ammonia

Human excretes about 4.5 kg nitrogen in urine and faeces annually. Majority of the nitrogen, approximately 89 % is in urine. (Weckman 2005.) 75 – 90 % of the nitrogen in urine is in form of urea ($\text{CO}(\text{NH}_2)_2$) and the rest of the nitrogen is in creatinine, amino acids and uric acids (Karak & Bhattacharyya 2011). Fresh urine also contains small amounts of ammonia (NH_3) and ammonium ions (NH_4^+). During the storage of the urine urea hydrolyses and lots of ammonia is formed (Udert et al. 2006).

Urea hydrolysis (ureolysis) is a reaction where urea decomposes to ammonium, bicarbonate and hydroxide ions. The hydrolysis reaction is presented in reaction Equation I.



Ammonium ion is in equilibrium with unionized ammonia according to reaction Equation II. (Hellström et al. 1999.)



In watery solutions, the ratio of ammonia and ammonium concentration depends on the temperature, pH and ionic strength of the solution. The percentage of the unionized ammonia increases with the increase of temperature and pH, but decreases when ionic strength is increased. (Thurston et al. 1979.) Dissolved unionized ammonia is in equilibrium with gaseous ammonia as shown in reaction Equation III (Hellström et al. 1999).



Urea hydrolysis is catalyzed by enzyme urease which is synthesized in plants, bacteria, algae and fungi. Ureolysis typically follows Michaelis-Menten kinetics, but the kinetic characteristics such as Michaelis constant K_M , activities, optimum pHs and isoelectric points vary depending on which organisms discussed. (Krajewska 2009.)

Pure urea is very stable and decomposes extremely slow with a half-life of 3.6 years at 38 °C (Andrews et al. 1984, according to Hotta & Funamizu 2008). If there are urease producing bacteria in urine, urea hydrolysis will happen much faster. The urease producing bacteria can end up in urine for example through faecal contamination. If the urine was collected in patches, the urea hydrolysis would begin with a high rate and after few days the rate of the urea hydrolysis will begin to decrease. The maximum ammonia concentration would be reached in approximately one month. (Hotta & Funamizu 2008.) In dry toilet new urine is brought to urine storage tank daily and urea hydrolysis can occur constantly.

In urine, the ammonia produced through urea hydrolysis is in equilibrium with gaseous ammonia as described earlier. Ammonia is highly soluble in water which prevents large amounts of ammonia to volatilize to air. Thus the concentration of the ammonia is higher in the urine than in the head space of the urine storage tank. Nevertheless the ammonia concentration of the head space can increase high enough to cause odor problems and even be insanitary. (Udert et al. 2006.)

The volatilization rate of ammonia from water can be estimated by a mathematical model demonstrated by Whelan et al. (2010). In the model it is assumed that only unionized ammonia volatilizes. When ammonia concentration in water and air is known, the ammonia flow to air can be calculated with Equation 1

$$J_{NH_3} = A \cdot \alpha_{aw} \cdot \left(C_{NH_3}^w - \frac{C_{NH_3}^a}{k_{AW}} \right), \quad (1)$$

where A = is the surface area of the air water interface (m^2), $C_{NH_3}^w$ = ammonia concentration in water (mol/m^3), $C_{NH_3}^a$ = ammonia concentration in air (mol/m^3), k_{AW} = the

air:water partition coefficient for NH_3 (dimensionless Henry's law constant) and α_{aw} = a combined mass transfer coefficient (m/h). α_{aw} can be calculated with Equation 2

$$\frac{1}{\alpha_{aw}} = \frac{1}{\alpha_w} + \frac{1}{\alpha_a \cdot k_{AW}} \quad (2)$$

where α_w = partial mass transfer coefficient for the water side of the liquid-air interface (m/h) and α_a = partial mass transfer coefficient for the air side of the liquid-air interface (m/h). (Whelan et al. 2010.)

2.2.2 Organic compounds

Detection of VOCs in human urine has been used as a method to diagnose diseases. Micro-organisms in urine produce organic compounds that can be identified with gas chromatography-mass spectrometry or very sensitive selected ion flow tube-mass spectrometry technology. With the latter method, VOCs are measured from the headspace of the urine. Storer et al. (2011) used selected ion flow tube-mass spectrometry technology to determine selected VOCs in urine after inoculation with common urinary tract infection –causing micro-organisms *Echerichia coli*, *Proteus vulgaris*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Staphylococcus epidermidis*, *Klebsiella pneumoniae*, *Enterococcus faecalis* and *Candida albicans*. The amount of VOCs in the headspace of the urine increased significantly during the inoculation. VOC concentrations varied between few ppb to nearly 30 000 ppb depending on which micro-organism was used. Five VOCs of the selected ones that were detected in the largest concentrations were formaldehyde, methyl mercaptan, trimethyl amine, methanol and acetone. (Storer et al. 2011.)

Pysanenko et al. (2009) used selected ion flow tube-mass spectrometry to identify ketones in the headspace of urine from a healthy person. Acetone, butanone, pentanone and hexanone were detected. Also heptanone was detected when the urine was acidified to pH 3. (Pysanenko et al. 2009.)

In addition to previous compounds, Zlatkis et al. (1981) reported several VOCs that can be detected from urine. Compounds included alcohols, ketones, aldehydes, hetero-cyclic compounds and organic compounds that include sulfur. (Zlatkis et al. 1981.) Also many organic acids are found in human urine (Gates et al. 1978).

Each VOC detected from urine has different specific odor and odor threshold. People experience odors variously. Someone might think one odor pleasant and at the same time other might consider it unappealing. People also notice odors in different contents depending on for example health condition and age. The mixture of different odorous compounds might have different odor than single compounds. (Stuetz & Frechen 2001.) Therefore it is difficult to describe the odor of urine with the odors of single compounds.

2.2.3 Sulfuric compounds

Many sulfuric compounds are described being malodorous. Used odor descriptions are for example rotten egg, decayed cabbage, decayed vegetables, putrefaction and skunk. These compounds have low odor threshold varying between 0.00014 ppb and 18 ppb. Odorous sulfuric compounds include hydrogen sulphide, methyl mercaptan, ethyl mercaptan, sulfur dioxide, dimethyl sulphide, dimethyl disulphide and thiocresol. (Stuetz & Frechen 2001.)

Only two reports including information about sulfuric compounds in urine were available. Zlatkis et al. (1981) detected with gas chromatography-mass spectrometry ten different sulfuric compounds in urine including dimethyl sulfone, propylene sulfide, thiophene, butylisothiocyanate, dimethyl disulfide, allylisothiocyanate, 2,3-diathiabutane and thiolan-2-one. Storer et al. (2011) investigated volatile compounds from headspace of urine. Four sulfuric compounds were reported including hydrogen sulfide, dimethyl disulfide, dimethyl sulfide and methyl mercaptan. From above mentioned compounds at least dimethyl disulfide, hydrogen sulfide, dimethyl sulfide and methyl mercaptan have been reported being malodorous (Stuetz & Frechen 2001).

2.3 Removal technologies of odorous compounds

In Chapters 2.3.1 and 2.3.2, technologies to remove odorous compounds from air are briefly introduced. Introduced technologies are selected because they are well known but of course there are also many other technologies available to remove odors. Biofiltration is introduced broadly in Chapter 2.4.

2.3.1 Activated carbon

Activated carbon has been widely used to remove hazardous or destructive compounds from gas streams. With activated carbon it is possible to separate gas mixtures, recover useful and valuable compounds from industrial exhaust gases and remove undesirable contaminants, such as odors, from process gases. (Bansal & Goyal 2005.) Treated gases can be contaminated with very different compounds such as VOCs, sulfuric compounds or ammonia.

Removal of variety of VOCs with activated carbon has been studied previously. Lillo-Ródenas et al. (2005) used activated carbon to remove toluene and benzene from air in laboratory scale. They noticed that the content of molecules that include oxygen and the porosity of the activated carbon have remarkable influence on adsorption of toluene and benzene. The adsorption capacity increases with increase of the porosity. When content of molecules that include oxygen in activated carbon is decreased with thermal treatment the adsorption capacity increases. (Lillo-Ródenas et al. 2005.) Examples of other VOCs that have been removed with activated carbon are methanol (Tao et al. 2006), ethanol (Silvestre-Albero et al. 2009) and phenol (Stravropoulos et al. 2008).

Activated carbon filters can be used in waste water treatment plants to remove odors. In New York City's waste water treatment plant the odors has been controlled with 44 large filter towers (Turk et al. 1993). Odorous compounds in waste water often contain sulfur or nitrogen. Compounds of this kind are for example carbon disulfide, dimethyl sulfide, dimethyl disulfide, trimethylamine, dimethylamine and n-propylamine. According to Hwang et al. (1994) these compounds can be adsorbed with activated carbon.

In waste water treatment plant activated carbon does not only remove odors from air. It can also adsorb efficiently airborne micro-organisms emitted from waste water treatment processes. Most of those micro-organisms have particle size 0.65 – 4.7 μm . Small macropores of activated carbon are suitable to capture particles that size. (Li et al. 2011.)

Drawback in removal of odorous compounds from air with activated carbon is that activated carbon saturates with the contaminant in time. Breakthrough time is the time that activated carbon filter can work properly before it is saturated and begins to leak. The breakthrough time depends on the contaminant and its concentration, the degree of the air stream and the size of the filter. After breakthrough time activated carbon cannot remove contaminants from air. When activated carbon filter is saturated it needs to be regenerated. There are several regeneration methods available such as steam or hot inert gas injection, chemical or solvent washing, induction heating and biological oxidation. (Smet & Van Langenhove 1998.)

2.3.2 Ozonation

Removal of odors with ozonation is based on high oxidizing power of ozone. Ozone can react with contaminants either by direct reaction with molecular ozone or by indirect reaction with the radical species that are formed when ozone decomposes. Reactions with molecular ozone are highly selective and appear only with unsaturated aromatic and aliphatic compounds and with specific functional groups. Presence of hydroxyl ions, hydroperoxide ions, hydrogen peroxide or UV radiation at 253.7 nm can cause the decomposition of ozone and production of free-radicals. These radicals are able to react rapidly and unselectively with the contaminants. (Langlais et al. 1991.)

Many odors such as hydrogen sulfide, odors caused by cigars and cigarettes, many VOCs, perspiration odors, odors of manure etc. can be destroyed with ozone. The problem in ozonation of odors is that ozone is hazardous to health and it needs to be secured that no human is exposed to ozone. In practice the contaminated air needs to be conveyed to enclosed contactor where the air is ozonated. That way it is also possible to ensure that sufficient amount of ozone and sufficient contact time are provided for complete oxidation of odorous compounds. After ozonation the excess ozone needs to be destroyed before the treated air is discharged to atmosphere. (Rice 2002.)

In Renton, Washington, USA is a bingo hall which customers and employees complained about strong odors and physical discomfort associated with high levels of

tobacco smoke, in other words high levels of VOCs. Addition of fans to ventilation system did not solve the odor problem. The final solution for the problems was to add ozone generators to air conditioning system which produced small amount of ozone to the indoor air. The ozone levels (0.01 – 0.04 ppm) were below local 24-hour, seven-day exposure limit, but there was still enough ozone to reduce the VOCs in the indoor air. The solution was economic with cost of 22 000 \$ compared to recommended activated carbon system with annual costs of 25 000 \$. (Kilham & Dodd 1999.)

In rubber industry removal of odors by ozonation has also been investigated. Perng et al. (2011) heated rubber in oven with a view to produce odors and VOCs similar in rubber processing. Produced gas was conveyed to contactor where it reacted with ozone. Conclusion of the research was that the odors and VOCs can be removed by oxidizing them with ozone. The process can still be accelerated by letting odors, VOCs and ozone react in aqueous phase. (Perng et al. 2011.)

In animal husbandry odors might be unpleasant especially in barns and piggeries. Within poultry industry there has been interest to use ozonation in intensive animal production units to improve air quality: reduce odorous compounds, ammonia levels and bacterial load in air. Schwean-Lardner et al. (2009) investigated how the ozonation of the indoor air in broiler house effects on the broilers. The ozone concentration of the air was kept at average 0.03 ppm. During the test period growth rate decreased, mortality increased and incidence of heart-related condemnations and deaths of broilers increased. Used low ozone level was not able to reduce ammonia or aerosol bacteria from air. (Schwean-Lardner et al. 2009.) Described results show that ozonation is not the right solution everywhere to treat odorous air. Safety of humans and animals near ozonation plant needs to be taken seriously.

2.4 Biofilters

Biofilters have been successfully used to remove various odorous compounds from air. Applications include for example waste water treatment plants, waste water pumping stations and toilets. In recent decades many laboratory researches of biofiltration have also been done. Removed compounds can be hydrogen sulfide, ammonia, VOCs or something else biodegradable.

2.4.1 Operational parameters in biofiltration

In this Chapter widely used operational parameters in biofiltration are introduced. Empty bed residence time (EBRT) is the time that flowing air stays in empty filter column. EBRT can be calculated with Equation 3

$$EBRT = \frac{V_f}{Q}, \quad (3)$$

where V_f = filter bed volume (m^3 , l, etc.) and Q = air flow rate (m^3/h , l/min, etc.). Removal efficiency (RE) tells the percentage of the contaminant that is removed in biofilter and it can be calculated with Equation 4

$$RE = \left(\frac{C_{Gi} - C_{Go}}{C_{Gi}} \right) \cdot 100, \quad (4)$$

where C_{Gi} = contaminant concentration in inlet gas (mg/m^3 , ppm, mol/m^3 , etc.) and C_{Go} = contaminant concentration in outlet gas (mg/m^3 , ppm, mol/m^3 , etc.). Loading rate (LR) shows the mass of the contaminant that enters every volume unit of the biofilter in time unit. Equation 5 gives LR as a result.

$$LR = \frac{C_{Gi} \cdot Q}{V_f} \quad (5)$$

Elimination capacity (EC) is the mass of contaminant that is degraded in volume unit of the filter in time unit. EC can be calculated with Equation 6.

$$EC = \frac{(C_{Gi} - C_{Go}) \cdot Q}{V_f} \quad (6)$$

RE, LR and EC correlates as shown in Equation 7. (Deviny et al. 1999.)

$$EC = LR \cdot RE \quad (7)$$

Moisture content (MC) is the percentage of water in biofilter and it can be calculated either on wet basis or on dry basis. Equations 8 and 9 show how these values can be calculated.

$$MC_w = \left(\frac{m_w - m_d}{m_w} \right) \cdot 100 \quad (8)$$

$$MC_d = \left(\frac{m_w - m_d}{m_d} \right) \cdot 100 \quad (9)$$

In Equation 8 MC_w = moisture content calculated on wet basis (%), m_w = wet mass of filter material sample (kg, g, etc.) and m_d = dry mass of filter material sample (kg, g, etc.). In Equation 9 MC_d = moisture content calculated on dry basis (%). (Kennes & Veiga 2001.)

2.4.2 Biofilter materials

Many organic and inorganic materials have been used as biofilter support materials. Examples of organic support materials are compost, coconut fiber, peat and soil, and

examples of used inorganic materials are polyurethane foam, perlite and lava rocks. Filter materials should maintain favorable conditions for micro-organisms to grow and treat efficiently the waste gas. Good filter material has to be replaced seldom and it causes only a small pressure drop in the filter. That way the operating costs of biofiltration will be smaller. (Devinny et al. 1999.)

Compost has been successfully used as a filter material in many studies. The group of treated contaminants is diverse including hydrogen sulfide (Morgan-Sagastume & Noyola 2006), toluene (Rene et al. 2005, Znad et al. 2007), ammonia (Jun & Wenfeng 2009, Chen et al. 2005) and VOC (Liu et al. 2005). Compost biofilters were able to remove the mentioned contaminants with RE varying between 40 % and 100 % depending on the LR. However, in all studies REs above 95 % was reached. Downside of using compost as filter material in biofilter is that some compost may become hydrophobic when dried (Devinny et al. 1999). After that it might be extremely difficult to wet the filter again and the RE will decrease. In full scale, compost has been used as a filter material at least in waste water treatment plant to remove odors (Zhuang et al. 2001) and in chemical industry to remove VOCs (Gárdenez-González et al. 1999).

Gabriel et al. (2007) studied coconut fiber as a filter material in a full scale biofilter. The biofilter was located in municipal solid waste treatment facility and its performance was evaluated in terms of ammonia removal. Right after start-up the biofilter was able to remove 80 % of ammonia. With stronger irrigation and better water distribution it was possible to increase the RE to 100%. Coconut showed high water-holding capacity and balanced C/N/P ratio which are good properties for carrier material of biofilter. (Gabriel et al. 2007.) Baquerizo et al. (2009) used the same material in laboratory scale tests as was used in by Gabriel et al. (2007). Baquerizo et al. (2009) wanted to test how coconut fiber can remove ammonia from air in steady state and transient conditions. In steady state conditions almost complete ammonia degradation was achieved and the RE was above 97 %. In transient conditions the RE decreased but still the minimum RE was 88 %. (Baquerizo et al. 2009.) Treatment of hydrogen sulfide (Filho et al. 2010) and toluene (Maestre et al. 2007) with coconut biofilter has also been reported.

Peat has been used as carrier material in biofilters because of its low pressure drop. However, peat has many disadvantages when it is used in biofilter. Peat is naturally hydrophobic and moisture control of peat biofilter can be difficult. Peat does not contain large populations of micro-organisms so inoculation will be needed. Also nutrient addition might be needed as peat has much less nutrients than compost for example. (Devinny et al. 1999.) However, peat can be used as a filter material if conditions are favorable. Sorial et al. (1997) were able to remove 99 % of toluene with peat-styrofoam biofilter, but it needs to be noticed that the EBRT was very long, 12 min (Sorial et al. 1997).

Soil has been used as a filter material because it is cheap and it contains a large population of micro-organisms. Soils are naturally hydrophilic so it is easy to maintain enough moisture in filter bed. A drawback with soil as a filter material is that it has low permeability which causes high pressure drop in filter bed. (Devinny et al. 1999.)

Polyurethane foam has been used as a filter material to treat hydrogen sulfide, toluene and benzene. Filho et al. (2010) treated air contaminated with hydrogen sulfide with polyurethane foam biofilter. The RE was above 98 % during whole 100-day experimental period. In the experiment polyurethane foam was found to have low pressure drop. With air velocity of 0.017 m/s the pressure drop was 94 Pa/m. (Filho et al. 2010.) Singh et al. (2010) were able to remove toluene from air with polyurethane foam biofilter with REs above 80 %, maximum 99 %. Ryu et al. (2010) experimented biodegradation of benzene in polyurethane foam biofilter. At the beginning the biofilter removed more than 90 % of benzene, but after 27 days the RE decreased to approximately 75 %. At the same time the pressure drop in the biofilter increased. Reason for that was the excess growth of the biomass. After removing the excess biomass the filter was again able to remove benzene efficiently. (Ryu et al. 2010.)

Perlite has been used as a filter material in biofilter to remove styrene. Rene et al. (2009) were able to remove 100 % of styrene with 150 g/m³·h LR. They also found that pressure drop in the filter was low varying between 0.5 and 4.2 cm H₂O/m depending on the gas velocity. (Rene et al. 2009.) Paca et al. (2001) had similar results when they removed styrene with perlite biofilter in laboratory scale. With LR 140 g/m³·h they were able to remove more than 90 % of styrene. In this experiment the pressure drop varied between 139 and 278 Pa/m (= 14 – 28 cm H₂O/m). (Paca et al. 2001.)

Activated carbon is also a possible carrier material for biofilter. It has good water-holding capacity and it provides good surface for microbial attachment. Activated carbon resists well crushing and it is possible to get activated carbon with homogenous particle size. Disadvantages with activated carbon are that it does not include microorganisms and nutrients. Therefore they need to be inoculated. Activated carbon is also very expensive. (Devinny et al. 1999.) Activated carbon has been used in biofilters to remove VOCs such as methanol, toluene, benzene, ethylbenzene and xylene. Babbitt et al. (2009) used activated carbon in biofilter to remove methanol from air. They reached 100 % RE while LR varied between 1 and 17 g/m³·h. (Babbitt et al. 2009.) Kwon & Cho (2009) experimented biodegradation of benzene, toluene, ethylbenzene and xylene in biofilters packed with cork and activated carbon. Cork was found to be better carrier material than activated carbon in biofilter. With LR 94 g/m³·h the cork biofilter had maximum EC 86 g/m³·h while EC of the activated carbon was 67 g/m³·h. Maximum EC of cork was higher because cork had more adequate pore size and void space for bacterial accumulation than activated carbon. (Kwon & Cho 2009.)

2.4.3 Removal processes

The biofiltration process consists of a series of steps beginning with the transfer of contaminants to the water phase. From the water phase the contaminants can adsorb to the filter material or they can be biodegraded within biofilm. In this Chapter, removal processes of contaminants are presented.

Absorption and adsorption

In biofiltration the contaminants must absorb from gas phase to water phase. After that the micro-organisms of the biofilter are able to degrade the contaminants and release the products back to the water phase. If the contaminants are not able to absorb to the water phase, biodegradation of the contaminants is not possible. (Deviny et al. 1999.)

The ability of a gas to absorb to water depends on the chemical compatibility of the gas. Polar molecules absorb in water much more efficiently than non-polar molecules. For example nitrogen, which is inert and non-polar molecule, absorbs in water very slightly, but polar carbon dioxide absorbs in water much faster. Carbon dioxide also reacts with water, which makes the transfer rate of carbon dioxide even higher. (Downie 1996.)

The absorption of gases in water can be modelled with Henry's law. Many gases follow Henry's law up to 100 bars. Henry's law states that the partial pressure of the gas in equilibrium with water is proportional to the concentration of the gas in water. Henry's law is introduced in Equation 10,

$$p = k \cdot C, \quad (10)$$

where p = partial pressure, k = Henry's law constant and C = concentration. (Downie 1996.) Henry's law constant is specific for all compounds and it depends on temperature. The smaller the Henry's law constant is the more compound will absorb to water phase. Henry's law constants of compounds that can be found in stored urine are introduced in Table 1. If a compound reacts with water, Henry's law gives only approximate results of its absorption. An example of compound this kind is ammonia.

Table 1: Henry's law constants for example compounds that can be found in stored urine (Hazardous Substances Data Bank).

Compound	Henry's law constant (25°C)
Acetone ((CH ₃) ₂ CO)	$3.97 \cdot 10^{-5} \text{ atm} \cdot \text{m}^2/\text{mol}$
Ammonia (NH ₃)	$1.61 \cdot 10^{-5} \text{ atm} \cdot \text{m}^2/\text{mol}$
Dimethyl sulphide ((CH ₃) ₂ S)	$1,61 \cdot 10^{-3} \text{ atm} \cdot \text{m}^2/\text{mol}$
Formaldehyde (CH ₂ O)	$3.37 \cdot 10^{-7} \text{ atm} \cdot \text{m}^2/\text{mol}$
Methanol (CH ₃ OH)	$4.55 \cdot 10^{-6} \text{ atm} \cdot \text{m}^2/\text{mol}$
Sulfur dioxide (SO ₂)	$8.10 \cdot 10^{-4} \text{ atm} \cdot \text{m}^2/\text{mol}$
Trimethylamine (N(CH ₃) ₃)	$1.04 \cdot 10^{-4} \text{ atm} \cdot \text{m}^2/\text{mol}$

The absorbed contaminant can be degraded by the micro-organisms but it is also possible that the contaminant adsorbs on the filter material. Adsorption is possible also from the gas phase. Adsorption is a process where atoms, ions or molecules of gas or liquid attach to a surface. Contaminants can attach onto surface of the filter material as physical or chemical adsorption. A driving force in physical adsorption is the van der

Waals attraction between the contaminant and the surface. In chemical adsorption the contaminant forms chemical bond with the surface. (Fink 2009.)

The two most commonly known ways to model adsorption in constant temperature are called Langmuir and Freundlich isotherms. Langmuir isotherm assumes that there is certain amount of points where compound (adsorbate) can reversibly attach. In equilibrium adsorption and desorption are equal. The rate of adsorption depends on the amount of adsorbed compound at time t and maximum amount of compound that can be adsorbed on the surface of the material (adsorbent). If the difference between them is zero the system is in equilibrium state. The equation of Langmuir isotherm is introduced in Equation 11

$$\frac{x}{m} = \frac{a \cdot b \cdot C}{1 + b \cdot C}, \quad (11)$$

where x/m = mass of adsorbed compound per mass unit of adsorbent (mg/g), a = experimental constant, b = saturation constant (l/g) and C = concentration of the adsorbate in equilibrium (mg/l). (Karttunen et al. 2004.)

A drawback in Langmuir isotherm is that it does not give reliable results in situations where adsorbate forms several layers on adsorbent. However, often several layers are formed. To achieve more reliable results Freundlich created equation introduced in Equation 12

$$\frac{x}{m} = K_f \cdot C_e^{1/n}, \quad (12)$$

where K_f = Freundlich adsorption isotherm and n = empirical constant. Freundlich isotherm is an empirical equation but still it is commonly used to estimate the adsorption capacity of different adsorbents. (Karttunen et al. 2004.)

Nitrification

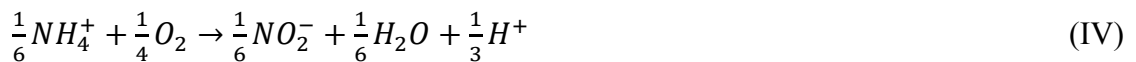
Nitrification is a biological process where ammonium ions are oxidized to nitrite and nitrate. It is commonly used and often required process in waste water treatment plants.

Nitrifying bacteria are autotrophs, chemolithotrophs and obligate aerobes. Being autotrophs mean that nitrifying bacteria adsorb and reduce inorganic carbon. In biofilters the source of inorganic carbon is the carbon dioxide of the air that flows to filter. Using carbon dioxide as the source of carbon is an energy-expensive process that causes the small growth rate of the nitrifiers. (Rittmann et al. 2001.)

Chemolithotrophic bacteria use inorganic compounds as electron donors. In case of nitrifying bacteria the electron donor is ammonium ion. The chemolithotrophic nature of the nitrifying bacteria makes the growth rate even smaller because ammonium ions release less energy per electron equivalent than organic compounds, hydrogen atoms or reduced sulfur. (Rittmann et al. 2001.)

Obligate aerobes use oxygen for respiration. In nitrification process oxygen is a direct reactant for the initial mono-oxygenation of ammonium ion to hydroxylamine (NH_2OH). The above-mentioned use of oxygen may be the reason why nitrifiers are relatively intolerant of low dissolved oxygen concentration. The catabolism of nitrifying bacteria is slowed by oxygen limitation at concentrations that have no effect on many bacteria that use organic carbon as carbon source. (Rittmann et al. 2001.)

Nitrification is a two-step process. There is no micro-organism that is known to be able to carry out the both steps and completely oxidize ammonia to nitrate. (Madigan & Martinko 2006.) In the first step of the nitrification, ammonium is oxidized to nitrite as shown in the reaction Equation IV.



The reaction yields energy and its free-energy change under standard conditions at pH 7 ($\Delta\text{G}^{0'}$) is -45.79 kJ per e^- eq. The most commonly known genus of bacteria that is able to oxidize ammonium to nitrite is *Nitrosomonas*. However *Nitrosococcus*, *Nitrosopira*, *Nitrosovibrio* and *Nitrosolobus* can also carry out the first step of nitrification. (Rittmann et al. 2001.)

In the second step of the nitrification, nitrite is oxidized to nitrate as shown in the reaction Equation V.

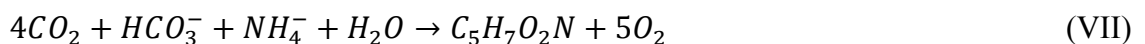


Also this is an energy-yielding reaction and its $\Delta\text{G}^{0'} = -37.07$ per e^- eq. *Nitrospira*, *Nitrospina*, *Nitrococcus*, and *Nitrocystis* are known to be able to sustain the nitrification in the second step. The most famous genus of NO_2^- oxidizer is *Nitrobacter*. Nevertheless it has been found out that *Nitrobacter* is not the most important nitrite-oxidizing genus in most waste water treatment processes. *Nitrospira* is more often identified as the dominant NO_2^- oxidizer. (Rittmann et al. 2001.)

The overall conversion of ammonia to nitrate is presented in Equation VI.

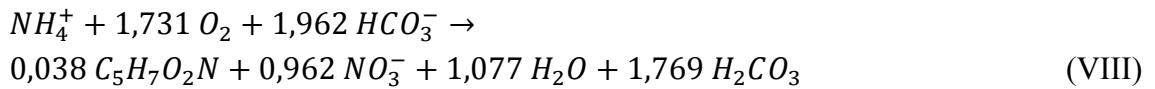


A portion of the ammonium ion assimilates into cell tissue along with obtaining energy. The reaction of biomass synthesis can be presented as follows:



In reaction Equation VII chemical formula $\text{C}_5\text{H}_7\text{O}_2\text{N}$ represents the synthesized bacterial cells. Half reactions for cell synthesis, oxidation of ammonia to nitrate, and reduction

of oxygen to water can be combined to create Equation VIII which is the overall reaction of nitrification. (Crites & Tchobanoglous 1998.)



From reaction Equation VIII can be seen that for each milligram of ammonia nitrogen oxidized, 3.96 mg of oxygen is utilized, 0.31 mg of new cell is formed, 7.01 mg of alkalinity is removed and 0.16 mg of inorganic carbon is utilized. From reaction Equation (VI) can be calculated that theoretically oxidation of 1 mg of ammonia consumes 4.57 mg oxygen. Utilized 3.96 mg of oxygen is less because the ammonia for cell synthesis is not considered in Equation VI. (Crites & Tchobanoglous 1998.)

Nitrifiers are reputed to be highly sensitive to chemical inhibition. This assumption is partly true. The very slow growth rate of nitrifying bacteria increases the negative effects of inhibition and in part that is why it appears that nitrifiers are more sensitive than faster growing bacteria. However, many organic and inorganic compounds can inhibit nitrifying bacteria. The most relevant ones are unionized NH_3 , undissociated HNO_2 , anionic surfactants, heavy metals, chlorinated organic chemicals and low pH. (Rittmann et al. 2001.)

Because all removal processes in biofilter happen in water phase it is possible to use studies related to nitrification in water as reference material. Grundizt & Dalhammar (2001) studied the effect of temperature, pH and cell concentration on oxidation rate of ammonium and nitrite. In experiments they used pure cultures of *Nitrosomonas* and *Nitrobacter*. In Figure 4 the cell activity of *Nitrosomonas* and *Nitrobacter* are presented as function of temperature, pH and cell concentration.

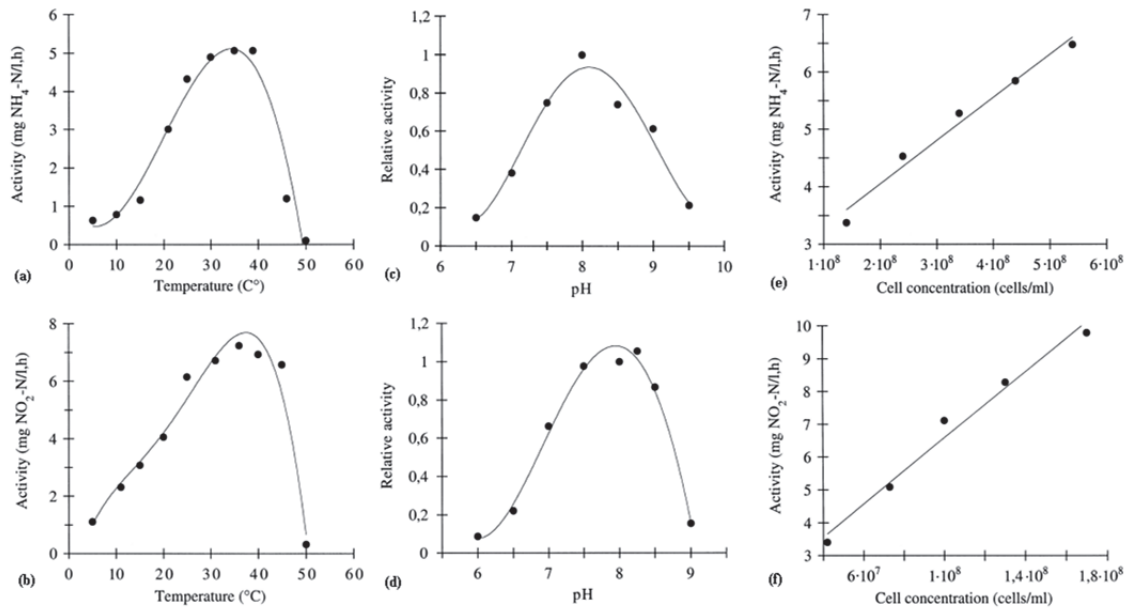


Figure 4: (a) Effect of temperature on the oxidation rate of ammonia by *Nitrosomonas*. (b) Effect of temperature on the oxidation rate of ammonia by *Nitrobacter*. (c) Effect of pH on the oxidation rate of ammonia by *Nitrosomonas*. (d) Effect of pH on the oxidation rate of ammonia by *Nitrobacter*. (e) Effect of cell concentration on the oxidation rate of ammonia by *Nitrosomonas*. (f) Effect of cell concentration on the oxidation rate of ammonia by *Nitrobacter*. (Grunditz & Dalhammar 2001.)

In Figures 4 (c) and (d) the activity at pH 8 is used as the reference activity. As can be seen from Figure 4 temperature, pH and cell concentration has a significant effect on the oxidation rates of ammonia and nitrite. In the experiments the optimal values of temperature and pH for *Nitrosomonas* and *Nitrobacter* were found to be 35 °C, 38 °C, 8.1 and 7.9. (Grunditz & Dalhammar 2001.)

Andersson et al. (2001) had similar results about the effect of temperature on nitrification as Grunditz & Dalhammar (2001) when they studied nitrification in biological activated carbon in water treatment plant. With pilot scale filters nitrification efficiency was clearly above 70 % when the water temperature was near 20 °C. The nitrification efficiency decreased simultaneously with the water temperature reaching the minimum of 10 % at temperature 3 °C. When water temperature increased again the ammonia removal increased to the same level as it was before the cold period. (Andersson et al. 2001.)

Sudarno et al. (2011) studied the effect of different ammonia and nitrite concentrations on nitrification in saline waste water. Both high concentration of ammonia and nitrite can inhibit nitrification. Ammonia oxidation was inhibited by 50 % in concentration 1 g ammonia-N/l. Nitrite oxidation was inhibited by 50 % in much higher concentration, 5 g ammonia-N/l. The effect of nitrite concentration on ammonia oxidation was more significant. 50 % inhibition of ammonia oxidation was reached at the concentration of 24 mg nitrite-N/l. High nitrite concentration did not have effect on nitrite oxidation. (Sudarno et al. 2011.)

Biodegradation of sulfuric compounds

Proteobacteria is a large phylum of bacteria that includes many commonly known gram-negative bacteria, for example *Escherichia coli*. A diverse group of Proteobacteria is able to oxidize sulfur compounds chemolithotrophically. There are two ecological classes of sulfur-oxidizing bacteria. One lives in neutral pH and another one lives in acidic pH. (Madigan & Martinko 2006.)

One genus that can oxidize sulfur is called *Thiobacillus*, which is the most studied sulfur chemolithotroph. In the chemolithotrophic metabolism of *Thiobacillus* the most common sulfur compounds used as an electron donor are hydrogen sulfide (H_2S), elemental sulfur (S^0) and thiosulfate ($S_2O_3^{2-}$). The oxidation reactions of the foregoing compounds are presented in reaction Equations IX – XI.



As can be seen from the reaction Equations, large amount of protons is generated in these reactions, which decreases the pH. That is why some sulfur oxidizing bacteria live in acidic pH. (Madigan & Martinko 2006.)

Oh et al. (1998) studied the oxidation of hydrogen sulfide from gas in fluidized bed bioreactor by *Thiobacillus* sp. IW. They found the optimum pH for hydrogen sulfide oxidation at 7 and temperature between 30 and 40 °C. Park et al. (2002) had similar experiments of hydrogen sulfide oxidation with *Thiobacillus* sp. IW. The results were more or less similar. In Figure 5, the effect of pH and temperature on hydrogen sulfide oxidation are presented.

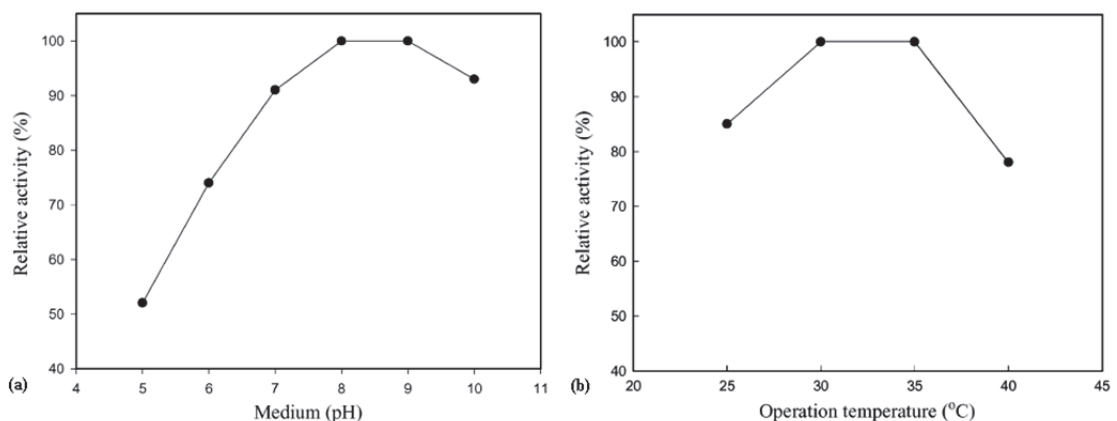


Figure 5: (a) Effect of pH on the relative activity of the hydrogen sulfide oxidizing bacteria. (b) Effect of temperature on the relative activity of the hydrogen sulfide oxidizing bacteria. (Park et al. 2002.)

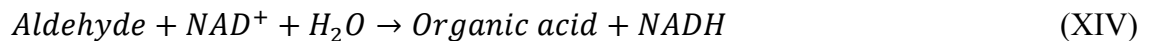
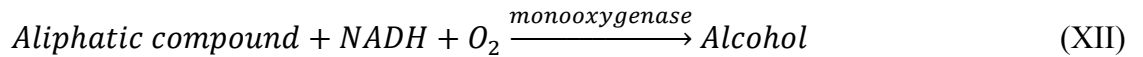
The optimal temperature for their reactor was found to be at 30 °C and pH 8. In these experiments the 600 ppm was a kind of limiting value of the hydrogen sulfide concentration in the inlet gas. In smaller concentrations all the hydrogen sulfide was reduced. When the concentration was increased hydrogen sulfide was detected in the outlet gas. (Park et al. 2002.)

Also organic sulfur compounds can be biologically degraded. Many of these compounds are highly volatile and they often smell foul. The most common organic sulfur compound in environment is dimethyl sulfide ($S(CH_3)_2$). In atmosphere dimethyl sulfide oxidizes photochemically to methane sulfonate ($CH_3SO_3^-$), sulfur dioxide (SO_2) and sulfate (SO_4^{2-}). In anoxic environment dimethyl sulfide can be microbially transformed at least in three ways. In methanogenesis dimethyl sulfide is transformed to methane (CH_4) and hydrogen sulfide (H_2S). Dimethyl sulfide can be an electron donor for photosynthetic CO_2 fixation yielding dimethyl sulfoxide ($(CH_3)_2SO$). Dimethyl sulfide can also be an electron donor in energy metabolism in certain chemo-organotrophs and chemolithotrophs. In those reactions dimethyl sulfoxide is also produced. (Madigan & Martinko 2006.)

Many studies have been conducted about biodegradation of dimethyl sulfide with a membrane bioreactor. In the membrane biofilter the biomass and contaminated gas are separated with a membrane. Bo et al. (2002) found this technique to be promising for the treatment of gases contaminated with dimethyl sulfide. Both the gas residence time and initial dimethyl sulfide concentration of inlet gas affected dimethyl sulfide RE. At gas residence time 24 s and average inlet gas concentration 33 mg/m^3 the RE was 99 %. When gas residence time was decreased to 12 s the RE was 90 % and with 8 s gas residence time the RE reduced to 85 %. Similar trend was found when gas residence time was kept at 24 s and dimethyl sulfide concentration of inlet gas was increased from 33 mg/m^3 to 116 mg/m^3 and 375 mg/m^3 . With those concentrations, the REs were 93 % and 87 % respectively. (Bo et al. 2002.) Kumar et al. (2010) and Luvsanjamba et al. (2007) found the similar effects of the gas residence time and dimethyl sulfide concentration in inlet gas on the RE of dimethyl sulfide in membrane biofilter. Luvsanjamba et al. (2007) also discovered that membrane biofilter worked better at 22 °C than at 52 °C.

Biodegradation of organic compounds

Several bacteria, molds and yeasts are able to use hydrocarbons as electron donors to maintain growth. When straight-chain (aliphatic) compounds are biodegraded, in first step molecular oxygen reacts with the organic compound producing alcohol. After that one hydrogen atom is removed from the alcohol and aldehyde is produced. From aldehyde again one hydrogen atom is removed and the organic compound transforms to organic acid. After that organic acid is oxidized by a process called β -oxidation. In reaction Equations XII – XIV the pathway from aliphatic organic compound to organic acid is presented.



As can be seen from Equations XII – XIV also alcohols and aldehydes can be biodegraded through this process. In Equations XII – XIV NAD^+ = nicotinamide-adenine dinucleotide and NADH = reduced form of NAD^+ which are coenzymes that catalyze the reactions in biochemistry. (Madigan & Martinko 2006.)

In β -oxidation organic acid is oxidized to acetyl-CoA in five steps. In first step organic acid is activated with coenzyme-A (CoA). In second step a double bond is formed between second and third carbon atoms. In third step a hydroxyl ion is added to the third carbon atom. In the fourth step the hydroxyl group is oxidized to keto group. In the final step the molecule is divided into acetyl-CoA and CoA-activated organic acid. In Figure 6 is presented the β -oxidation process.

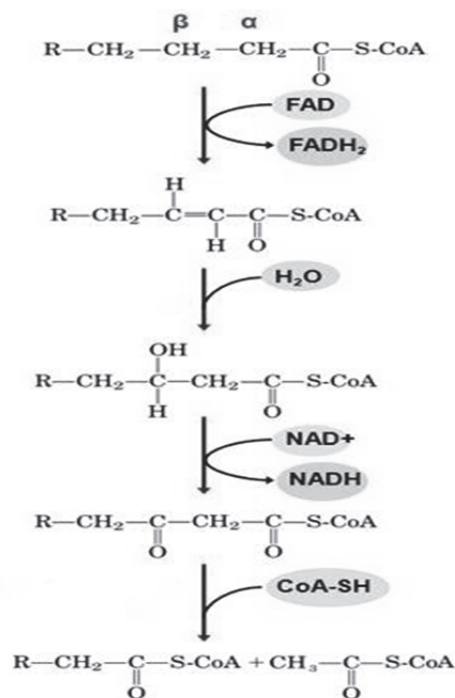


Figure 6: Beta oxidation process of CoA-activated organic acid. CoA = coenzyme-A, FAD = flavinadenine dinucleotide, FADH_2 = reduced for of FAD, NAD^+ = nicotina-mide adenine dinucleotide and NADH = reduced form of NAD^+ . (Scitable 2010.)

The circle of β -oxidation is repeated until two acetyl-CoAs are produced. After β -oxidation acetyl-CoAs are oxidized by citric acid cycle or they are converted to hexose and other cell constituents. (Madigan & Martinko 2006.)

2.4.4 Effect of moisture content on biofilter performance

As described earlier, contaminants absorb to water phase from air before they can be degraded in biofilter. Therefore it is essential to have water on the filter material. The water phase in biofilter is considered stationary. If wetting is too heavy or a lot of condensation occurs in filter there might be downward movement of water in the filter but the flow is very slow. Normally water flow is minimized to avoid leachate. If some flow occurs, it is always laminar rather than turbulent and under these conditions diffusion will be the dominant way which contaminants move from place to another in the water. (Devinny et al. 1999.)

In the water phase the contaminant concentration is the highest near the surface where the transfer from air to water occurs. Part of the contaminants is biodegraded by microbial cells in the water and biofilm. Part of the contaminants is adsorbed to the filter media. The products of the biodegradation are released to the water phase and from that they evaporate to the air. (Devinny et al. 1999.)

To maintain MC high enough in biofilter the filter needs to be wetted somehow. Possible ways to wet the filter material are to humidify the inlet gas or to wet the filter material. Humidification of the inlet gas is possible by passing it through pre-humidification chamber before the gas flows to the filter. Ideally relative humidity of the inlet gas should be higher than 99 % and be as close as possible to 100 %. In that case the air is not able to adsorb any water from the filter bed. (Kennes & Veiga 2001.) The situation changes if the air temperature increases in filter bed. Reason for that is that in warmer temperature the partial pressure of saturated vapour is higher (Seppänen et al. 1991).

In real life relative humidity only near 95 % is reached in pre-humidification. That is not enough to maintain sufficient MC in filter bed and water needs to be sprinkled on the top of the filter. Too strong wetting needs to be prevented because it can cause anaerobic zones and increase in the pressure drop in the filter. (Kennes & Veiga 2001.) The excess water needs also to be discharged which requires arranging of suitable drainage (Verein Deutcher Ingenieure 2004).

The medium used as filter material should have characteristic to keep the water content high enough to support the micro-organisms because the micro-organisms cannot be active in environments where water exists only in low content. The material should be able to store large amounts of water and the water should be easily available when the filter is drying. In the other words it is desirable to have a material with a high water-holding capacity. A typical value of MC in saturated organic materials may be between 40 % and 80 %. If the water content in the filter is too low, the system will be dominated by xerophytic fungi. (Devinny et al. 1999.)

Elias et al. (2009) investigated biofiltration in dry conditions. The aim was to remove p-xylene from air with biofilter. In their experiment the filter was operated without any humidification in the first 259 days. In the period from day 260 to 450 the

filter was wetted with 400 ml of nutrient solution in every 25 days. The inlet load of *p*-xylene and RE are presented as function of time in Figure 7.

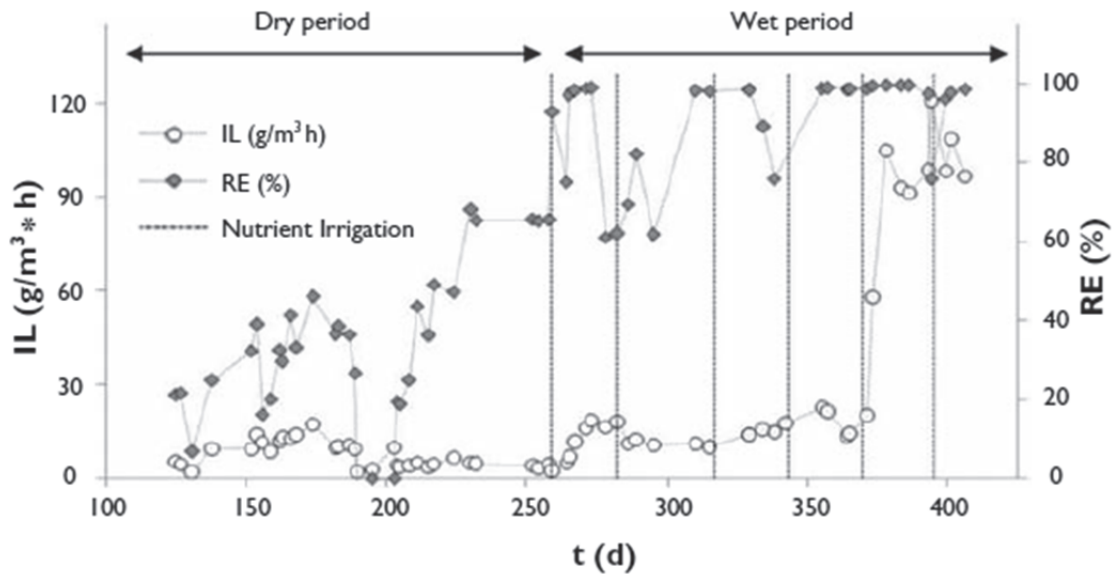


Figure 7: The inlet load of *p*-xylene and removal efficiency of the biofilter as function of time in dry and wet conditions. IL = inlet load, RE = removal efficiency. (Elias et al. 2009).

As can be seen from Figure 7 the RE was lower than 70 % during the first 259 days. When the irrigation was started, the RE increased to 95 % and stayed stable even when the inlet load was suddenly increased from 20 g·m³/h to 90 g·m³/h at the end of the test period. (Elias et al. 2009.)

Sun et al. (2002) degraded toluene from air in biofilters with different initial MCs. They clearly indicated that MC had significant effect on the performance of biofilter. With the initial MCs of 30 % and 40 % the toluene RE was at the beginning of the experiment 2 % and at the end of the experiment 60 %. Filters with 60 % and 70 % initial MC were able to remove more than 70 % of the toluene at the beginning of the experiment and RE increased to about 100 % at 75 hour operation. It was also found that the number of bacteria increased with the increase in the initial MC of the filter. At the same time the number of moulds and actinomycetes decreased with the increase in initial MC. In this study the optimal initial MC of the filter material was discovered to be approximately 60 %. (Sun et al. 2002.)

The aim of the study of Prado et al. (2005) was not to investigate the effect of MC in biofilter on the RE of the filter but they experienced that by accident. In their study the relative humidity of the inlet gas was above 90 % but in the middle of the test period the humidification system failed. The humidification system was out of order for 7 days and for that time the relative humidity of the inlet gas was below 1 %. The lack of moisture led to a fast decrease of the RE. After repairing the humidification system,

the RE recovered in a week to a value that was obtained before the failure. (Prado et al. 2005.)

2.4.5 Effect of the temperature in the filter bed

The temperature has a significant influence on the function of the biofilter. Reactions in cells run faster as the temperature increases. In general the warmer the biofilter is, the rapidly it will treat the contaminants. (Devinny et al. 1999.)

However, microbes cannot live in whatever temperature. Each enzyme has a temperature limit that cannot be exceeded without denaturation. Above that limit temperature the enzyme is no longer effective. Also other parts of the cell like the structural lipids of the membranes can be decomposed by high temperatures. (Devinny et al. 1999.)

Every organism has minimum, optimum and maximum temperatures that limit the habitat they can live. These three temperatures are called cardinal temperatures. Below the minimum temperature growth no longer occurs. At the optimum temperature growth is the most rapid. Above the maximum temperature growth is no longer possible. According to cardinal temperatures, micro-organisms can broadly be separated in four groups: psychrophiles, mesophiles, thermophiles and hyperthermophiles. Psychrophiles have low optimum temperature, mesophiles have midrange optimum temperature, thermophiles have high optimum temperature and hyperthermophiles have very high optimum temperature. The active temperature ranges and optimum temperatures of typical psychrophile, mesophile, thermophile and two different hyperthermophiles are presented in Table 2. (Madigan & Martinko 2006.)

Table 2: Active temperature ranges and optimum temperatures of typical psychrophile, mesophile, thermophile and two different hyperthermophiles

Group name	Psychrophile	Mesophile	Thermophile	Hyperthermophile	Hyperthermophile
Active temperature range (°C)	-5 – 13	9 – 47	41 – 68	65 – 96	90 – 114
Optimum temperature (°C)	4	39	60	88	106

If there was only one species of micro-organisms in the biofilter, the temperature could be optimized to the optimum temperature of that certain species. However, a concrete biofilter contains hundreds or thousands of species of micro-organisms and therefore that kind of optimization of the temperature is not practical. Biofilters can work and have good efficiency in very different temperatures. The important thing is that the temperature does not fluctuate. A rapid change to cold air in a thermophilic filter can reduce the RE even to zero. On the other hand, a sudden burst of hot air to psychrophilic filter can destroy the microbial ecosystem. (Devinny et al. 1999.)

The temperature does not only effect on the micro-organisms in the biofilter but also to the physico-chemical properties of the contaminant. In higher temperatures contaminants often dissolve into the water phase more poorly than in colder temperatures. Sorption of the contaminants might also be reduced. (Devinny et al. 1999.) Increase of temperature has also effect on the MC of the filter bed. In higher temperatures evaporation of water is stronger and filter material will dry faster. (Kennes & Veiga 2001.) Still, it is believed that the biological effect is more important than the physical effects and warm filters will work better. However, the physical effects should be considered especially if the contaminant is poorly soluble in water. (Devinny et al. 1999.)

Biodegradation reactions are exothermic which means that they produce heat and therefore temperature will increase in biofilter. Often higher biological activity is found near the inlet of the biofilter where the substrate concentration is highest. Therefore, the filter bed will dry rather near the inlet of the biofilter. Biofilters are always wetted from the top of the bed and that is why downflow operation is more indicated in enclosed biofilters. (Kennes & Veiga 2001.)

Sorial et al. (1997) found out that the performance of biofilter is highly dependent of the operational temperature. When they studied degradation of toluene from air with a biofilter with EBRT of 2 min and at the temperature 11 °C the RE was only 58 %. The RE increased simultaneously with the increase in the operational temperature and the highest RE was achieved in temperature 32.2 °C. The REs in different temperatures are presented in Table 3. (Sorial et al. 1997.)

Table 3: Toluene removal efficiencies of biofilter at different operational temperatures with 2 min empty bead residence time (Sorial et al. 1997).

Temperature (°C)	11.1	15.6	21.1	26.7	32.2
Removal efficiency (%)	58	63-77	75	83-87	96

Also in Yoon et al. (2002) found that the best operational temperature was 32 °C. They studied biofiltration of VOCs (isoprene, dimethyl sulfide, chloroform, benzene, trichloroethylene, toluene, m-xylene, o-xylene and styrene) in three different temperatures. The temperatures, EBRTs, VOC concentrations and REs during the experiment are introduced in Table 4.

Table 4: Temperatures (T), empty bed residence times (EBRT), Volatile organic compound concentrations (C) and removal efficiencies (RE) during the biofiltration of volatile organic compounds (Yoon et al. 2002).

	Stage 1, C = 83 g/m ³ , EBRT = 3 min		Stage 2, C = 92 g/m ³ , EBRT = 1.5 min		Stage 3, C = 83 g/m ³ , EBRT = 1 min	
	T (°C)	RE (%)	T (°C)	RE (%)	T (°C)	RE (%)
Biofilter 1	25	93	25	91	25	68
Biofilter 2	42	74	32	94	32	81

Besides showing the optimal operational temperature to be 32 °C, the study showed that the RE cannot be increased infinitely by increasing temperature. (Yoon et al. 2002.)

The operational temperature has been near the room temperature varying between 20 °C and 35 °C in several studies that have covered biofiltration of ammonia (Baquerizo et al. 2009, Chen et al. 2005, Galera et al. 2008, Kim et al. 2000, Ryu et al. 2011).

2.4.6 Effect of the pH in the filter material

Besides temperature range, each micro-organism has a pH range within which growth is possible. The pH range is generally 2 – 3 units. (Madigan & Martinko 2006.) Outside this range the micro-organism will be inhibited or killed (Devinny et al. 1999). Usually, micro-organisms also have a well-known specific pH optimum. In the most natural environments, the pH values are between 5 and 9 and the micro-organisms with pH optimum in this range are the most common. (Madigan & Martinko 2006.)

Most biofilters are designed to operate near pH 7. Often it is put aside that many micro-organisms can live and be active in lower or higher pH than 7. In ideal situation the removal of a certain contaminant should be tested in many pH values in order to find an optimal pH for biofilter operation. This is of course expensive and therefore it is often skipped. (Devinny et al. 1999.)

In biofilter the pH may change during the operation. The biodegradation products and intermediates are often acidic compounds. In case of acidic end-products the pH of biofilter will decrease and can fall to value where the microbial ecosystem is inhibited. With the intermediates the situation is better because these compounds can be further biodegraded. (Devinny et al. 1999.) When mixed waste gases are treated with biofilter the nature of different contaminants or their degradation products may present neutralizing effect and the pH maintains quite constant (Kennes & Veiga 2001).

The ability of filter material to resist pH changes is called buffer capacity. Different filter materials have very different buffer capacities: inorganic materials may have very low buffer capacities as against compost may have at least moderate buffer capacity. High buffer capacity will make biofilter resistant to pH changes caused by acidic biodegradation products and intermediates. Buffer capacity can be increased for example by mixing calcium carbonate in filter material. (Devinny et al. 1999.)

Lu et al. (2002) studied the effects of pH on the RE of benzene, toluene, ethylbenzene and o-xylene in a trickle-bed air filter. In the experiment the pH of the nutrient solution fed into filter column was controlled. It was seen that the pH of the nutrient solution had a significant impact on the RE of the filter. When the pH increased in the range 5 – 8 the RE increased simultaneously. Between pH values 8 and 8.5 the correlation was opposite. (Lu et al. 2002.)

In biofilters that are meant to treat gases contaminated with ammonia, it is important to make sure that the pH of the filter material does not increase too high. The

increase of pH increases the amount of unionized ammonia in the water phase (Thurston et al. 1979). According to Rittman et al. (2001) unionized ammonia can inhibit nitrifying bacteria. Baquerizo et al. (2009) discovered in their study that with high ammonia loads pH might increase and unionized ammonia can accumulate in biofilter which can reduce the nitrification of ammonia. They suggested that the pH regulation might be an essential factor to improve the nitrification rate. They also mentioned that if too high amount of unionized ammonia is accumulated in the filter, an acidification agent might be an opportunity to decrease the effect of the unionized ammonia. (Baquerizo et al 2009.)

2.4.7 Designing the biofilter

The designing of a biofilter is a process that begins with the characterization of air to be treated and small scale tests. It is also important to find out if there are previous studies available about biofiltration of concerned contaminants. After that it is possible to do pilot scale tests and with all collected information to design a full scale biofilter. A decision-making process to design a full scale biofilter is presented in Figure 8.

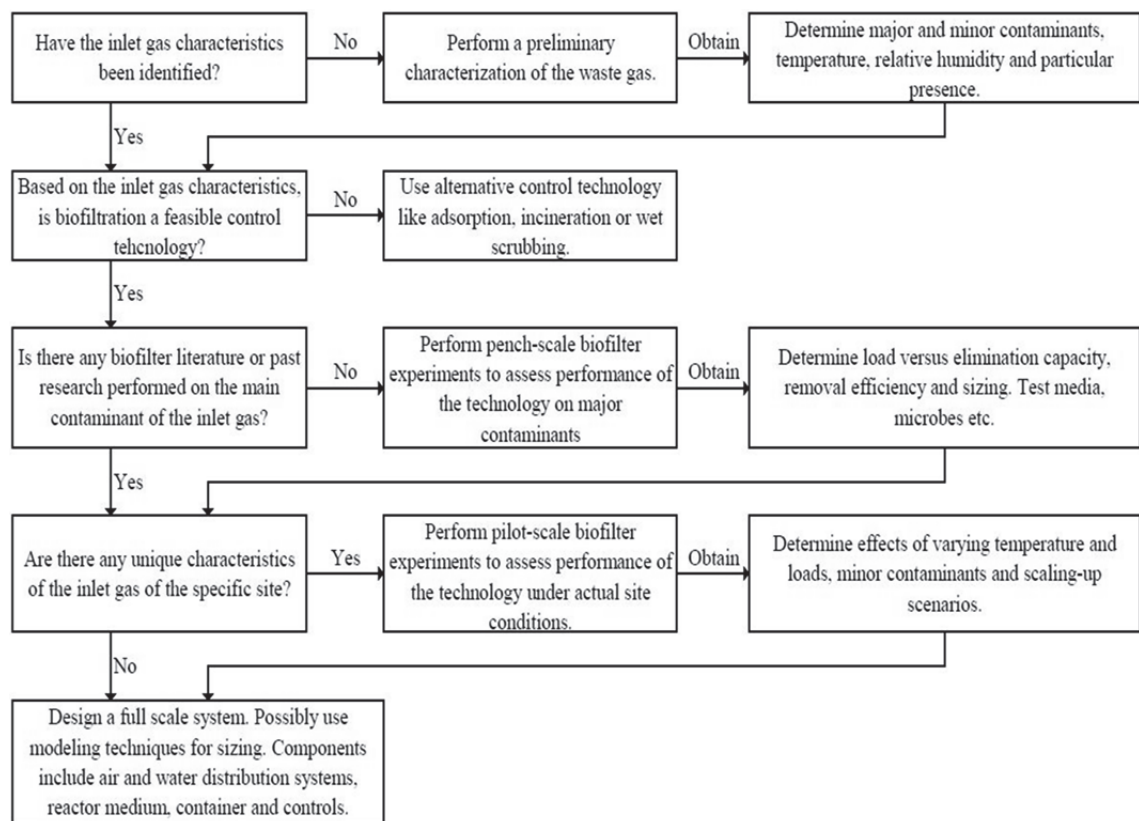


Figure 8: Decision-making process in designing a full scale biofilter (Deviny et al. 1999).

It is important to remember that contaminants of all kind cannot be treated by biofiltration. (Devinny et al. 1999.) In those cases, some other removal technique needs to be chosen. Also operational conditions impact on the choice of the treatment method.

The next three Chapters describe the characterization of contaminated air, small scale testing and designing of the full scale biofilter.

Characterization of the air to be treated

When the air that is going to be treated is characterized, at least the following six variables should be defined: major and minor contaminants and their concentrations, flow rate of the air, MC of the air, temperature and particulate concentration (Devinny et al. 1999). If this background information is not determined and the designing is done on the basis of data available from existing plants, it is possible that crucial mistakes are made in designing (Verein Deutcher Ingenieure 2004). For mentioned variables a minimum, maximum and average value should be measured. That is important because a biofilter should be designed by using the average value. Under- or overdesigned biofilter would not operate as efficiently as a filter designed by using average value. (Devinny et al. 1999.)

A literature survey about biofiltration research might give information about the REs and ECs of certain contaminant. It needs to remember that those values are accurate only in the conditions of the experiments. That is why it is recommended to do small scale tests in concrete conditions. (Devinny et al. 1999, Verein Deutcher Ingenieure 2004)

Laboratory and pilot scale tests

Laboratory scale tests are a good way to determine favorable conditions for biofiltration of the major contaminants if the tests are ran with air stream similar to the actual contaminated gas stream. Also different filter materials can be tested at the same time to find the best material. Laboratory tests give information about RE and EC of the biofilter. (Devinny et al. 1999.)

In laboratory scale tests the loading conditions can be altered by two ways. When the flow rate is increased, LR increases simultaneously and residence time decreases. Now contaminants have less time to diffuse into biofilm and reduce and the increased flow rate may limit the removal of the contaminant. By using the results of the test it is possible to determine a maximum LR that can still be reduced with desired RE. Tests of this kind should be done if it can be assumed that the contaminant concentrations of the actual gas will be stable. (Devinny et al. 1999.)

Other way to do loading tests for biofilter is to keep EBRT constant and to increase the contaminant concentration. The higher concentration will increase the contaminant diffusion into biofilm and enable faster degradation. However, there is a limiting concentration above which concentrations may be toxic for microbes. If it is ex-

pected that the contaminant concentrations will fluctuate in the actual waste gas, both test methods should be used. (Deviny et al. 1999.)

Laboratory tests give information for designing a larger scale filter. EBRT, LR, RE and EC can be calculated as shown in Chapter 2.4.1. Examples of used EBRT and LR values and achieved RE and EC values in previous studies done in laboratory scale are presented in Table 5.

Table 5: Examples of used empty bed residence time (EBRT) and loading rate (LR) and achieved removal efficiency (RE) and elimination capacity (EC) values in biofiltration studies. UK = unknown.

Contaminant	EBRT (min)	LR (g/m ³ ·h)	RE (%)	EC (g/m ³ ·h)	Reference
Ammonia	0.3 - 1	1 - 11.8	95 - 99	226 - 276	Jun & Wenfeng 2009
	0.3 - 0.6	5.4 - 22.5	97.8 - 99.1	70.8 (max)	Baquerizo et al. 2009
	1.3	15.9 - 32.3	71.8 - 89.9	14.0 - 23.9	Kaosol & Pongpat 2011
	1.4	0.8 - 67.1	89.5-99.4	0.829 - 61.3	Pagans et al. 2005
	0.5 - 1.4	0.05 - 7.5	60 - 100	5.5 (max)	Kim et al. 2007
Hydrogen sulfide	0.8	80 (max)	97.6 - 100	66 - 79	Filho et al. 2010
	0.5 - 0.85	0.1 - 13.9	52 - 99	8 (max)	Kim et al. 2008
	1.3 - 5.2	UK	97.8 - 24.7	220 (max)	Chaiprapat et al. 2011
	0.4 - 0.6	9.7 - 26.7	> 99	UK	Wani et al. 1998
Toluene	1.1 - 2.8	126.3 (max)	83.3 - 99.2	90,5 (max)	Singh et al. 2010
	3.1 - 4.3	117 (crit.)	70 - 100	120 (max)	Znad et al. 2007

The critical LR is a value that above RE begins to decrease.

With results of the laboratory scale tests it is possible to design larger biofilters. Laboratory tests give a maximum LR that can still be treated with desired RE. By knowing the initial concentration and gas flow rate in larger scale it is possible to calculate the needed minimum filter volume with Equation 12.

$$V_f = \frac{c_{Gi} \cdot Q}{LR} \quad (12)$$

If greater RE is required, the volume of the filter bed needs to be increased to decrease the LR. (Verein Deutcher Ingenieure 2004.)

Often the operation of the biofilter is not the same in the laboratory and in the full scale. In the laboratory, the conditions (temperature, humidity, etc.) are optimal but in the actual filter they might be different. Therefore it is recommended to do pilot scale tests at the site with a side stream of the actual waste gas. Pilot scale tests should include experiments of the same kind as the laboratory scale tests. That way encountered problems can be identified and solved. (Deviny et al. 1999, Verein Deutcher Ingenieure 2004.)

Designing a full scale biofilter

The designing of a full scale biofilter is based on the information from laboratory and pilot scale tests and literature survey. With this information it is possible to estimate the effectiveness of the biofiltration in particular conditions and it gives necessary sizing information. However, many things need to be planned specially for the full scale system like the bioreactor configuration, air distribution system, pretreatment system and moisture control system. (Deviny et al. 1999.)

Biofilter sizing can base on area and space loading or on LR (Verein Deutcher Ingenieure 2004). Area and space loading can be calculated with Equations 13 and 14

$$AL = \frac{Q \cdot C_{Gi}}{A_f} \quad (13)$$

$$SL = \frac{Q \cdot C_{Gi}}{V_f} \quad (14)$$

where AL = area loading, A_f = are of the filter bed and SL = space loading (Deviny et al. 1999). These values should only be used as a basis for biofilter sizing when comprehensive experience from similar operational environments is available. Applications of this kind often treat odorous waste gas for example in waste water treatment plants or composting facilities. (Verein Deutcher Ingenieure 2004.)

Biofilters treating industrial waste gases should be sized based on the LR. When the degradation rates of micro-organisms for the specific waste gas mixture are determined, the needed size of the filter bed can be calculated with Equation 12. (Verein Deutcher Ingenieure 2004.) When biofilter operates properly it can remove contaminants completely or nearly completely from the waste gas up to a certain LR. With larger LRs the RE will gradually decrease. That still does not mean that the EC will decrease but it can still increase. Decrease of RE just means that some of the contaminants can be found from the outlet gas. (Kennes & Veiga 2001.)

There are two common biofilter designs, open bed and enclosed biofilter. In the open bed biofilter the filter media is placed in a supporting system and the top surface of the filter is exposed to the atmosphere. Open bed biofilters are often used as low cost

and low performance biofilters to remove odors. Heavy rain and cold weather may reduce the operational performance of the open bed biofilter. (Devinny et al. 1999.) In typical full scale open bed biofilter the area varies between 250 m² and 3000 m² while bed depth is between 1.5 m and 2.5 m. Open bed biofilter is always a bottom-loaded system. (Verein Deutcher Ingenieure 2004.)

In enclosed biofilter the whole filter is covered and it makes possible to control conditions such as temperature, water content and pH better than in open bed system. This allows a more favorable environment to be maintained for micro-organisms. (Devinny et al. 1999.) Either top- or bottom-loaded system is feasible in the enclosed biofilter. It is also possible to have several filter layers on top of the other. The depth of the filter media ranges between 1.2 m and 1.75 m. In enclosed biofilter it is possible to collect and discharge controlled the treated gas. On the other hand, the enclosed structure restricts access for maintenance. (Verein Deutcher Ingenieure 2004.)

Sometimes the inlet gas needs to be pretreated before supplying it in the biofilter. In general, biofilters operate in mesophilic temperature range (20 – 45 °C) and if the temperature of the inlet gas is significantly lower or higher it needs to be warmed or cooled. Particles and aerosols need to be removed from the inlet gas to prevent clogging of the filter bed. (Devinny et al. 1999, Verein Deutcher Ingenieure 2004.) Humidification of the inlet gas is also possible to prevent adequate MC in the filter bed. If that is not enough to secure moisture conditions in the filter bed, water must be sprinkled on the filter bed. (Devinny et al. 1999.)

Few examples of full scale biofilters, treated contaminants and designing parameters are introduced in Table 6.

Table 6: Examples of full scale biofilters, contaminants they are treating and parameters of design. MWTP = Municipal waste treatment plant, WWTP = waste water treatment plant, MCP = manure composting plant, CMP = chemical manufacturing plant, OWCP = organic waste treatment plant, Q = air flow rate, EBRT = empty bed residence time, EC = elimination capacity and UK = unknown.

Application	Contaminant(s)	Q (m ³ /h)	Moisture control method	EBRT (min)	EC (g/m ³ ·h)	Reference
MWTP	NH ₃	345 000	Wetting	0.4 – 1.5	0.1 - 3	Gabriel et al. 2007
WWTP	Odors, VOC	828	Wetting	0.5	UK	Liu & Ma 2011
WWTP	H ₂ S	10 700	Wetting & Humidification of the air	0.9	0.17 – 18.09	Zhunag et al. 2004
MCP	NH ₃	3 600	Wetting	1.7 – 3.3	UK	Yasuda et al. 2009
CMP	VOC	24 000	Humidification of the air	1.7	2 - 10	Gárdenas-González et al. 1999
OWCP	NH ₃ , VOC	3 950 – 15 800	Wetting	0.4 – 1.6	1.1 – 2 (NH ₃), 11 – 17.1 (VOC)	Colón et al. 2009

As can be seen from Tables 5 and 6 the EBRTs are in the same magnitude. Achieved ECs are much smaller in the full scale than in the laboratory scale which shows that the laboratory scale results cannot directly be extrapolated to the full scale. In full-scale biofilter the EC should be as high as possible because this allows using smaller filter bed volumes and thus reduces investment costs (Kennes & Veiga 2001).

2.4.8 Pressure drop in biofilter

In literature, commonly used equation to calculate pressure drop in porous media is called Ergun's law. Ergun's law is presented in Equation 15

$$\frac{\Delta P}{\Delta x} = - \frac{150\mu(1-\phi)^2 v}{d_p^2 \phi^3} - \frac{1,75\rho_f(1-\phi)v^2}{d_p \phi^3}, \quad (15)$$

where P = pressure, x = distance, μ = dynamic viscosity of the fluid, ϕ = porosity of the media, v = velocity of the fluid, d_p = mean particle diameter and ρ_f = density of the fluid. (Nield & Bejan 2006.) First part of Ergun's law is also known as Blake-Kozeny equation. It gives generally good results for the pressure drop when the porosity of the media is less than 0.5 and the flow is laminar. The second part of Ergun's law is known

as Burke-Plummer equation which can be used to calculate the pressure drop when the flow is turbulent. (Bird et al. 1960.)

Another Equation that can be used to the calculate pressure drop in porous media is called Forchheimer's equation. It is presented in Equation 16

$$\frac{\Delta P}{\Delta x} = -\frac{\mu v}{K} - \frac{F \rho_f v^2}{\sqrt{K}}, \quad (16)$$

where F = is a dimensionless form drag constant and K = specific permeability of the media. For spheres the constant F can be calculated with Equation 17

$$F = 0,55 \left(1 - 5,5 \frac{d}{D_e} \right), \quad (17)$$

where d = diameter of the spheres and D_e is the equivalent diameter of the bed, which can be calculated with Equation 18 by using bed height h and width w . (Nield & Bejan 2006.)

$$D_e = \frac{2wh}{w+h} \quad (18)$$

Mayerhofer et al. (2011) used both Ergun's law and Forchheimer's equation to model pressure drop in bed of crushed wood particles. Experiments were done with different distribution of large, medium and small size wood particles. As can be seen from Figure 9 both equations gave very good results of the pressure drop in the bed. (Mayerhofer et al. 2011.)

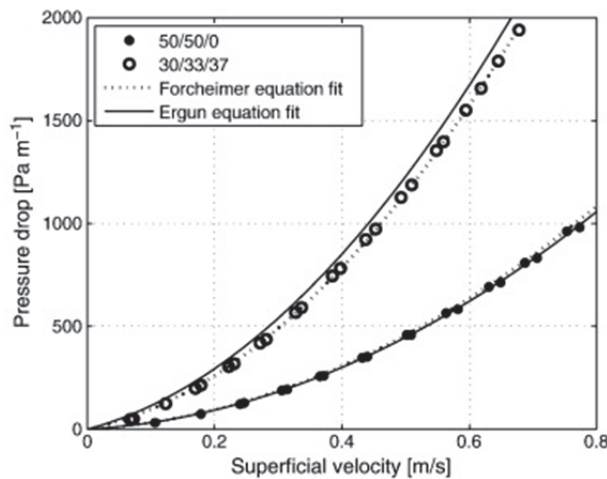


Figure 9: Measured pressure drop, Ergun's law fit and Forchheimer's equation fit as function of superficial velocity of the air. Used mixture of large/medium/small particles were 50/50/0 and 30/33/37. (Mayerhofer et al. 2011.)

Filho et al. (2010) investigated the effect of the filter material on the pressure drop. They measured the pressure drop in polyurethane foam, sugarcane bagasse and coconut fiber beds. With the air velocity of 0.064 m/s, the pressure drop in coconut fiber bed was 550 Pa/m while it was 510 Pa/m in polyurethane foam and sugarcane bagasse beds. (Filho et al. 2010.) However, the pressure drop depends on the particle size and if larger coconut fiber particles had been used, the pressure drop would be smaller.

From Equations 15 and 16 can be seen that characteristics of the fluid flow and porous media have effect on the pressure drop in the bed. In biofilters MC and bacterial growth also have effect on the pressure drop. If the MC of the filter bed is too high, the pressure drop will increase. The extensive growth of micro-organisms in filter bed increases the pressure drop and might cause clogging. (Kennes & Veiga 2001.)

The aim of the study of Ryu et al. (2010) was to investigate the relationship between biofilter performance, biomass concentration and pressure drop. In the experiments, they used polyurethane foam as filter material. The experiments showed that excess biomass can dramatically increase the pressure drop in biofilter and simultaneously decrease biofilter performance. The excess biomass can be removed by backwashing or agitation. These actions decreased the pressure drop and increased the biofilter performance. (Ryu et al. 2010.)

Morgan-Sagastume et al. (2001) have also investigated the relationship between biomass concentration and pressure drop in biofilters. They noticed that increase in biomass concentration causes an exponential increase in the pressure drop. During the experiment the filter bed was agitated. After agitation, the pressure drop decreased significantly, almost to the initial value. It indicates that localized high biomass concentration causes local clogging or local void space reduction or both which is the main reason for the increase in pressure drop in the biofilter. (Morgan-Sagastume 2001.)

In full scale biofilters the pressure drop is an important parameter and it can be used to measure indirectly the permeability of the bed. When records of the pressure drop and air velocity are kept, it is possible to notice increases in the pressure drop and decreases in air velocity. These changes might be signals that the filter material should be reworked or replaced. (Devinny et al. 1999.)

Continuous pressure drop measuring has been used in a pilot scale biofilter in food waste composting facility. The biofilter was used to remove ammonia and VOCs. When the pressure drop increased above 50 mm H₂O/m, the filter bed was automatically agitated and washed with water to remove excess biomass. Results of that experiment were very good. Agitation was carried out four times in 125-day period. It was enough to keep the pressure drop in desired range. RE was high, 97 – 99 % through the whole experimental period. (Ryu et al. 2011.)

3 MATERIALS AND METHODS

3.1 Used urine in experiments

In this study real urine was used as a source of odorous compounds. Employees of the DryCloset project collected urine at home and at work. The employees brought urine in small batches to a canister which was used as a urine container in laboratory. In the beginning urine was collected only in the morning. When the total urine volume needed daily increased also day urine was used.

The collected urine was stored in the canister several weeks to get the pH of urine near 9. The increase of pH shows that urea has hydrolyzed and ammonia is produced into urine. The increase of pH also moves equilibrium between ammonia and ammonium ion towards ammonia.

In the beginning, the urea hydrolysis was accelerated by adding plant urease, jack bean urease (lyophilized urease 5 U/mg EC 3.5.1.5, Merck KGaA, Darmstadt Germany) to urine. With jack bean urease it was possible to get the pH of urine high enough in short time, even in few days. Jack bean urease was assumed to have effect on the amount of VOCs in urine so it was not used when actual filter experiments began. During the filter experiments human faeces were added to urine to accelerate urea hydrolysis.

3.2 Ammonia recovery from urine container

Before starting the actual filter experiments, it was extremely important to investigate how much ammonia it is possible to get in air which flows through headspace of urine. The experiment was done by adding 250 ml of stored urine in 1000 ml Woufff bottle and conveying air into it. Rotameter was used to regulate the flow rate of the inlet air. Used air flows were 1 l/min and 6 l/min. From the Woufff bottle the outlet gas flowed to a gas washing bottle which contained dilute sulfuric acid. The ammonia that had evaporated to air reacted in gas washing bottle with the acid and transformed to ammonium which could be measured potentiometrically. A schematic view of used equipment is presented in Figure 10.

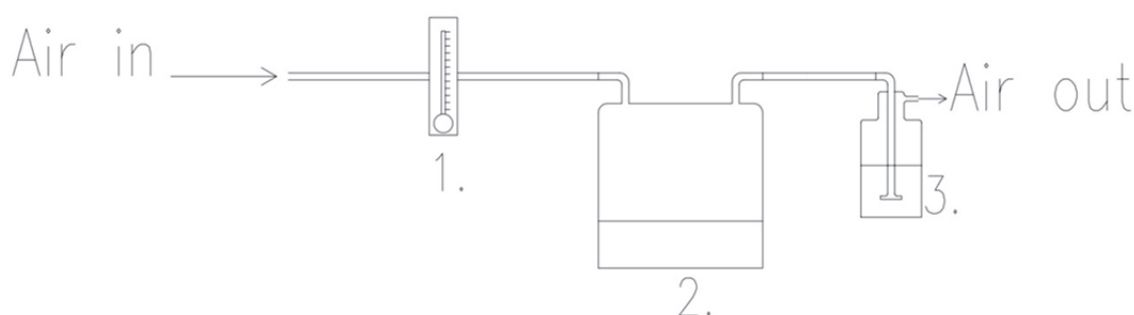


Figure 10: Used equipment in ammonia recovery test. 1. = rotameter, 2. = Woufff bottle including urine, 3. = gas washing bottle including dilute sulfuric acid.

Before starting the experiment the pH of urine and acid was measured. That way it was possible to make sure that the urea had hydrolyzed and that ammonia was formed. Also the amount of ammonia that ended up in acid could be roughly estimated with the change of the pH.

In the first experiment 0.05 M sulfuric acid (H_2SO_4 , Merck KGaA, Darmstadt Germany) was used in gas washing bottle. In so concentrated acid, the pH increased only few decimals during the experiment. Therefore in later experiments 0.005 M H_2SO_4 could be used in gas washing bottle. To make sure that the pH does not get too high in the gas washing bottle, 375 μl of indicator was added in acid. Used indicator was phenolphthalein diluted in ethanol (Merck KGaA, Darmstadt Germany). Phenolphthalein was used because it changes color at pH 8.2 – 10.

Ammonia recovery experiments were done with three different methods. First only one gas washing bottle was used to collect the evaporated ammonia. Then two gas washing bottles were used in series to see if any of the ammonia leaks through the first gas washing bottle. Experiment was also run overnight to see how much ammonia is evaporated in a long time period. In this experiment two gas washing bottles in series were also used.

3.3 Preparing of the filter column

Filter columns were made out of plastic cylinders. Their total volume was 2.7 l, diameter was 13 cm and height was 24 cm. The cylinder was transparent and it had separable cover. The filter column was bottom loaded.

A modified funnel was placed at the bottom of the cylinder to ensure regular air distribution in the filter column. The funnel had plastic and flexible net attached to it. Used filter materials were placed on that. Some of the filter materials had so small particle size that they would have gone through the net. Therefore a thin layer of foamed plastic was used on the net. The bottom of the filter bed was at height of 8.5 cm.

Holes were drilled for hose connection on the bottom and on the top of the column. Used connectors were air proof and destined for air hoses. For all hosing ToppTube™ PA12PA40 was used. It had 10 mm outside diameter and 8 mm inside diameter. Also rubber hose was used to connect ToppTube™ to Woulff and gas washing bottles. A schematic view of the filter column is presented in Figure 11.

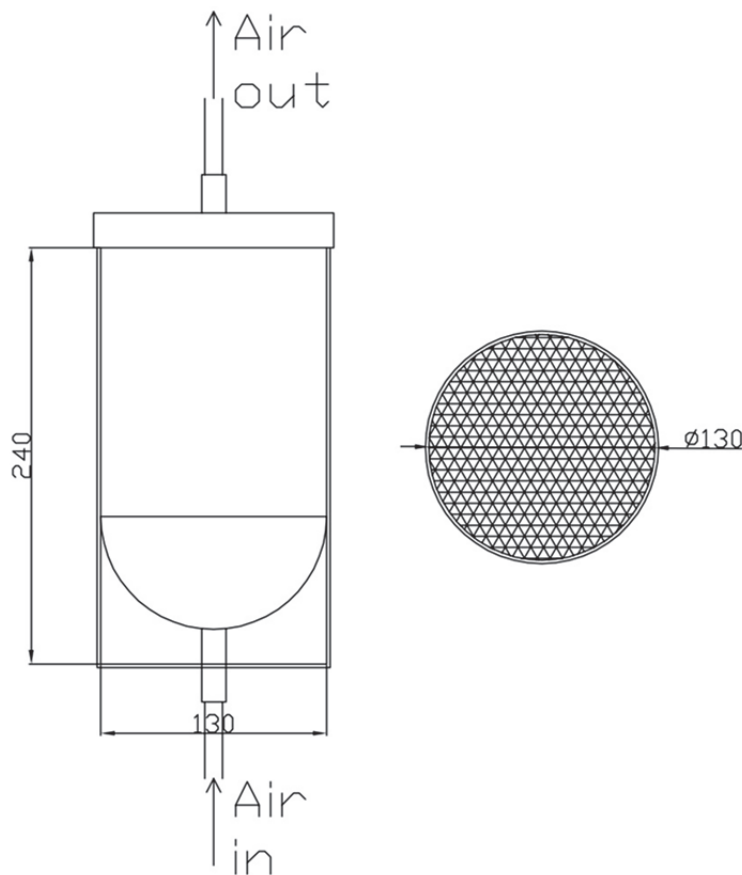


Figure 11: Schematic view of the filter column. Used unit of length is mm.

Filter columns were sealed with SikaBond-500 installation glue, Sikaflex-11FC⁺ polyurethane sealant/adhesive, Bostik professional universal silicon and ventilation duct tape. To find leaks the filter columns were sunk in water. Also AGA TL4 leak detection

spray was used. However, the leak detection spray spoiled the glue of the duct tape so the use of it had to be stopped. After sealing all leaks, filter columns were ready to use.

3.4 First experiments with one filter column

Before starting experiments with five different filter materials, experiment with one filter was carried out. That was done with a view to see if there is something to improve on the filter column, on experimental setup or on analytical methods.

3.4.1 Filter material

In this experiment used filter material was UgnCleanPellets © N produced by UGN Umwelttechnik GmbH. UgnCleanPellets © N has been used in full scale biofilters manufactured by UGN Umwelttechnik GmbH. UgnCleanPellets © N pellets are cylindrical with diameter approximately 4 mm and length 10 – 30 mm. The surface of the pellets is porous and the particles have a rusty color. Bulk density of the pellets is approximately 450 g/l.

3.4.2 Inoculation of filter material

Before starting the filtration experiments UgnCleanPellets © N was inoculated with activated sludge. The aim of the inoculation was to get the micro-organisms of activated sludge to filter material. Especially nitrifying bacteria were desired to get in filter material. With inoculation, also the MC of the filter material was increased to desired range.

Used activated sludge was collected on 11th July 2011 from Viinikanlahti waste water treatment plant in Tampere, Finland. It was known that there are nitrifying bacteria in activated sludge of Viinikanlahti waste water treatment plant. The aeration line from which activated sludge was collected had performed well and no service operations were done in past few months. Aeration of activated sludge was started immediately after the sludge was brought to laboratory. The activated sludge was without aeration approximately 30 min. In the laboratory the activated sludge was aerated for two days before inoculation.

Before the inoculation of filter material, 1.2 l of activated sludge was filtered with Macherey-Nagel MN 615¼ filters. Filters had thickness of 0.16 mm. Filtration was done to prevent clogging in filter caused by suspended matter in activated sludge.

One liter of UgnCleanPellets © N was immersed in the filtered activated sludge. UgnCleanPellets © N particles were in activated sludge for six minutes. After that the excess sludge was removed with a colander. MC, pH and ammonia concentration of wet UgnCleanPellets © N was determined and one liter was measured to the filter column.

3.4.3 Experimental setup

After adding one liter of filter material and sealing the column, it was ready to be used in experiment. A schematic view of experimental setup is presented in Figure 12.

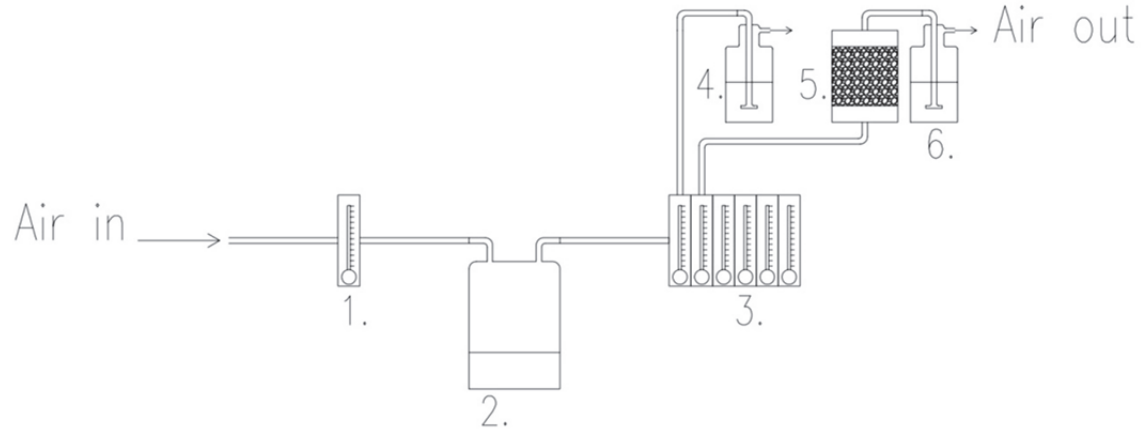


Figure 12: Schematic view of the experimental setup. 1. = rotameter, 2. = Woulff bottle used as a urine container, 3. = rotameter, 4. = gas washing bottle for inlet gas measurements, 5. = biofilter, 6. = gas washing bottle for outlet gas measurements.

In experiment air flowed to 1000 ml Woulff bottle where was 500 ml urine. Urine was changed daily. Total ammonia ($\text{NH}_3 + \text{NH}_4^+$) concentration and pH of urine were measured. Air flow of 2 l/min was regulated with rotameter. After Woulff bottle the air flow was separated in two lines. Regulation of air flow in these two air lines was needed to maintain 1 l/min air flow in both lines.

The ammonia concentration of inlet and outlet gas was determined daily except weekends. The first air line after separation was used to measure the ammonia concentration of inlet gas. Air flowed for a known time to a gas washing bottle where was 100 ml of 0.005 M H_2SO_4 . The ammonia in air reacted with acid and after sampling the ammonia concentration of acid was measured. TOC in air was also determined by measuring TOC in bubbled acid.

From the second air line after separation, air flowed through biofilter to a gas washing bottle where was 100 ml of 0.005 M H_2SO_4 . The ammonia concentration of outlet gas was determined by measuring the ammonia concentration in acid. TOC of outlet gas was also determined.

At the beginning of the experiment, in both gas washing bottles phenolphthalein diluted in ethanol was used to indicate the pH change. That way the pH in acid did not increase too high during the test runs. Ethanol naturally effected on TOC results in acids. Therefore the use of indicator was ended. During the experiment, an idea that UV-radiation might degrade VOCs in urine arose. That is why the Woulff bottle, biofilter and gas washing bottles were covered with aluminium foil.

After the experiment the MC, pH, TOC and ammonia concentration of used Ammonganulat 1.0 was measured.

3.5 Experiments with five different filter materials

After running experiment with one biofilter it was time to do parallel tests with five different filter materials. The aim of this experiment was to test which filter material would be the most suitable for biofiltration of exhaust gases of dry toilet. A good filter material is good growth medium for micro-organisms, has high water-holding capacity and causes low pressure drop.

3.5.1 Filter materials

In this experiment five different filter materials were used. Filter materials were Langfaserfiltergranulat, UgnCleanPellets © B, UgnCleanPellets © N, vermiculite and activated carbon.

Langfaserfiltergranulat is produced by UGN Umwelttechnik GmbH. Langfaserfiltergranulat was chosen to the experiment because it was known to be able to absorb water from air and it is suspected that the water-holding capacity of Langfaserfiltergranulat is high. Langfaserfiltergranulat has cylindrical particles with a diameter of approximately 5 mm and length of approximately 20 mm and its color is white.

UgnCleanPellets © B is also produced by UGN Umwelttechnik GmbH and it has been used in full scale biofilters manufactured by UGN Umwelttechnik GmbH. UgnCleanPellets © B has the same particle shape and size as UgnCleanPellets © N. UgnCleanPellets © B has grey color. The main components of UgnCleanPellets © B are cellulose and calcium carbonate. Because of calcium carbonate UgnCleanPellets © B can buffer pH change. UgnCleanPellets © B also has trace elements and nutrients for biological growth.

UgnCleanPellets © N is introduced in Chapter 3.4.1.

Vermiculite was bought from a local hardware shop and it is produced by Nelson Garden PLC, Turku Finland. Vermiculite was chosen because the recycling of vermiculite after using in biofilter is easy. It can be disposed of for example in garden. Vermiculite is a natural mineral that forms as an alteration product of biotite or phlogopite. It is used as an insulation material but it can also be used for example as a soil conditioner. Vermiculite has a brownish color and its average particle size is 2 mm.

Activated carbon was wood-based PICABIOL granulated activated carbon produced and supplied by PICA, France. The characteristics of the activated carbon are presented in Table 7.

Table 7: Characteristics of PICABIOL granulated activated carbon produced by PICA.

Parameter	PICABIOL GAC
Apparent density (g/cc)	0.202
Humidity (%)	2.9
Ash content (%)	3.5
CCl ₄ adsorption (%)	111.7
Iodine number (mg/g)	1082
Uniformity coefficient	1.35
BET surface area (m ² /g)	1500
Median diameter (mm)	1.4

PICABIOL has been developed to serve as microbial support and it has been used as a filter material in Rusko water treatment plant in Tampere, Finland.

3.5.2 Inoculation of filter materials

Also in this experiment the filter materials were inoculated with activated sludge. Activated sludge was collected 28th July 2011 from Viinikanlahti waste water treatment plant in Tampere, Finland. Aeration of the sludge was started immediately after the sludge was brought to the laboratory. The sludge was approximately half an hour without the aeration. The sludge was aerated for one day before inoculation.

Before the inoculation, the sludge was filtered with Macherey-Nagel MN 615µ filters. That was done to prevent clogging in filter bed caused by suspended matter in activated sludge.

One liter of each filter material was immersed in filtered activated sludge for 20 minutes except Langfaserfiltergranulat which was in filtered activated sludge only for ten minutes. Reason for shorter time with Langfaserfiltergranulat was that there was a possibility that Langfaserfiltergranulat particles might fall apart if they are too long in sludge. After the inoculation, the excess sludge was removed with a colander. MC, pH, alkalinity, ammonia concentration, TOC and nitrate concentration of the wet filter materials were measured and one liter of each material was measured to filter columns.

3.5.3 Experimental setup

After adding the filter materials and sealing the filter columns they were ready for the experiment. A schematic view of the experimental setup is presented in Figure 13.

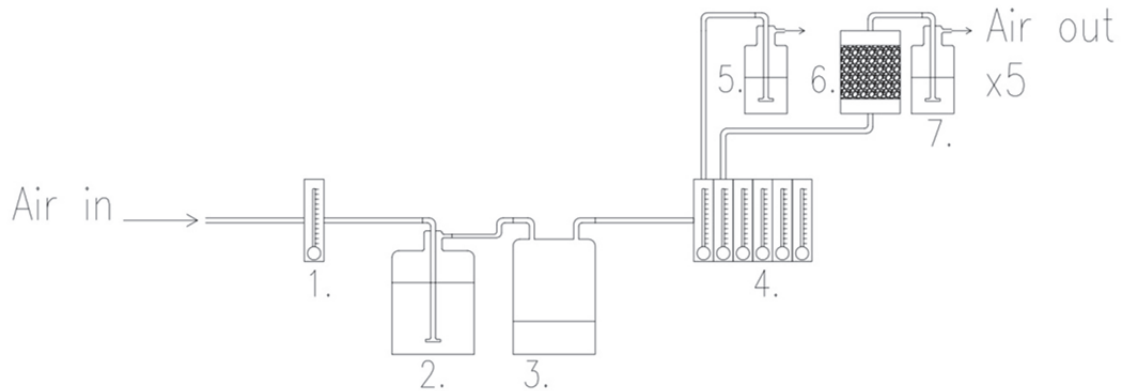


Figure 13: Schematic view of the experimental setup with five different filter materials. 1. = rotameter, 2. = humidifying column, 3. = Woulff bottle used as an urine container 4. = rotameter, 5. = gas washing bottle for inlet gas measurements, 6. = biofilter, 7. = gas washing bottle for outlet gas measurements.

As can be seen from Figure 13 in this experimental setup inlet gas was humidified. The inlet gas flowed through 1000 ml gas washing bottle filled with deionized water (Milli-Q system, Millipore). Deionized water adsorbed to air. Deionized water was added to the gas washing bottle when needed, approximately once per four days.

At the beginning of the experiment 500 ml of urine was used in 1000 ml Woulff bottle. Urine was changed daily. Total ammonia concentration and pH of the urine were measured. If the total ammonia concentration of the urine was higher than 3700 mg/l, the urine was diluted. That was done with a view to prevent too high ammonia concentrations in inlet gas. After 14 days of experiment, the Woulff bottle was changed to a larger 2000 ml Woulff bottle and the volume of the urine was increased to 1000 ml.

Air flow to Woulff bottle was regulated with rotameter to the value of 6 l/min. After Woulff bottle the air flow divided in six air lines. The air flow in each airline was regulated with rotameter to the value of 1 l/min.

Ammonia concentration and TOC of the inlet and outlet gas was determined with the same method as was done in experiment with one filter. The used method is introduced in Chapter 3.4.3. Also in this experiment Woulff bottle and all five biofilters and six gas washing bottles were covered with aluminium foil.

During the experiment, it was noticed that TOC in inlet and outlet gases is very low. That is why the gas washing bottles were acid and ethanol washed before collecting samples. Acid and ethanol wash was started after 15 days of experimenting. Acid wash was done with 1 M hydrogen chloride (HCl). Denatured ethanol (ETAX A12, Altia PLC, Riihimäki Finland) was used for ethanol wash. After ethanol wash the gas washing bottles were dried in oven to ensure that there is no ethanol residue in bottles.

After 29 days of experimenting the filter columns were opened and samples of filter materials were collected. MC, pH, alkalinity, ammonia concentration, TOC and nitrate concentration were measured from filter material samples. At the same time MSR 145W data loggers were installed in each filter column. The loggers measured temperature and relative humidity in filter beds. The loggers took samples once per 30

min. After experiment, the loggers were connected to a computer and data of temperature and relative humidity were downloaded. Also MC, pH alkalinity, ammonia concentration, TOC and nitrate concentration were measured from filter material samples after the experiment.

3.5.4 Humidity of the inlet gas

The humidity of the inlet gas was measured by monitoring the weight of the gas washing bottle used as humidifying column. In that way it was possible to calculate how much water had adsorbed to the air in a certain time period. Specific humidity of air is the mass of water in a unit mass of dry air and it can be calculated with Equation 19

$$\omega = \frac{m_w}{m_a}, \quad (19)$$

where ω = specific humidity (kg H₂O/kg dry air), m_w = mass of water and m_a = mass of air. (Çengel & Boles 2011.) When the volume of the air is known, the mass of it can be calculated with ideal gas law as shown in Equation 20

$$m_a = \frac{PV_a M_a}{RT}, \quad (20)$$

where P = pressure (Pa), V_a = volume of air (m³), M_a = molar mass of air (kg/mol), R = universal gas constant (J/mol·K) and T = temperature (K).

Relative humidity of air is a ratio between the partial pressure of moisture in air and saturated vapor pressure in certain temperature. The relative humidity can be calculated with Equation 21

$$\phi = \frac{p_w}{p_s} \cdot 100, \quad (21)$$

where ϕ = relative humidity of air (%), p_w = partial pressure of moisture in air (Pa) and p_s = saturated vapor pressure (Pa). (Çengel & Boles 2011.) The partial pressure of moisture can be calculated with ideal gas law as shown in Equation 22

$$p_w = \frac{m_w RT}{M_w V_w}, \quad (22)$$

where M_w = molar mass of water (kg/mol) and V_w = volume of water (m³). Saturated vapor pressure is temperature dependent tabular value and needs to be checked separately for all temperatures.

3.6 Analyses

3.6.1 Filter material analyses

Filter material analyses were done according to modified standard SFS-EN 12176. 10 g of filter material and 190 g of deionized water was weighted to Erlenmeyer. Erlenmeyer was mixed for 15 min with 150 rpm. After that the pH of the solution was measured. After measuring the pH, the liquid was filtered with Macherey-Nagel MN 615¼ filter. From the filtered liquid TOC, alkalinity, ammonia concentration and ions were measured. Prior to TOC measurement the samples were filtered through prewashed syringe filters with a pore size 0.45 µm.

To make results comparable they were calculated to unit mg/kg dry matter. That can be done with Equation 23

$$C_{mg/kg} = \frac{C_{mg/l} \cdot V}{m_w \cdot \left(1 - \frac{MC}{100}\right)}, \quad (23)$$

where $C_{mg/kg}$ = content in unit mg/kg dry matter, $C_{mg/l}$ = concentration in liquid, V = volume of the sample, m_w = mass of wet sample and MC = moisture content of the sample.

3.6.2 Bacterial growth in biofilters

The viable counts of bacteria and fungi were determined with R2A agar for heterotrophic bacteria (Reasoner & Geldreich 1985), with agar for sulphate oxidizing bacteria (Cote & Ghema 1994) and with carrot potato agar (Hunter-Cevera et al. 1986) supplemented with antibiotics for fungi (Hernandez et al. 2010). The sampling method developed by Friedrich et al. (1999) was slightly modified for this purpose. For direct counts, 10 g of filter material was diluted with Ringer solution (0.9% NaCl, 0.042% KCl, 0.024% NaHCO₃) to a ratio 1:9. The tubes were mixed in horizontal shaker (250 rpm) for 30 min. After that 1 ml of solution was diluted in 9 ml of 0.9 % NaCl and dilution series was done. The micro-organisms were cultured by spread plate method. Heterotrophic bacteria, sulphate oxidizing bacteria and fungi were incubated in 35 °C and incubation times were 2, 7 and 3 days respectively. *Nitrosomonas* and *Nitrobacter* were incubated in 30 °C for 4 days.

Viable counts of heterotrophic bacteria, sulphate oxidizing bacteria and yeasts were measured on 26th August 2011 and at the end of the experiment. Viable counts of *Nitrosomonas* and *Nitrobacter* were measured only at the end of the experiment.

3.6.3 pH

Hanna HI72911 pH-electrode and Hanna HI98184 pH/ORP/ISE meter was used for pH measurements.

3.6.4 NH₃-concentration in inlet and outlet gases

Oxonium ions form to dilute H₂SO₄ through reaction Equations XV and XVI.



When air that includes ammonia is bubbled through acid, ammonia reacts with oxonium ions. That reaction produces ammonium ions as shown in reaction Equation XVII.



Produced ammonium ions stays in solution and concentration of ammonium ion can be measured potentiometrically with ion selective electrode (ISE). This method has also been used by Baquerizo et al. (2009).

Orion 9512HPBNWB ammonia electrode attached to Orion 290A ISE meter was used to measure ammonium concentrations. It measures total ammonia concentration which includes both unionized ammonia and ammonium ions. The electrode was calibrated before each measurement with 1, 10, 100 and 1000 mg NH₃-N/l. In all samples and standards Orion 951211 ammonia pH adjusting ISA was added before measuring the ammonia concentration.

With total ammonium concentration in acid it was possible to calculate the ammonia concentration in inlet and outlet gas of the biofilter (mg/m³) with Equation 24

$$C_a = \frac{m_{ammonia}}{V_{air}} = \frac{C_{ta,acid} \cdot 17,024g/mol}{14g/mol} \cdot V_{acid} = \frac{1,216 \cdot C_{ta,acid} \cdot V_{acid}}{t \cdot \frac{Q_{air}}{1000}}, \quad (24)$$

where C_a = ammonia concentration in air (mg/m³), $m_{ammonia}$ = mass of ammonia in air (mg), V_{air} = volume of air (m³), $C_{ta,acid}$ = total ammonia concentration in acid (mg NH₃-N/l), V_{acid} = volume of acid (l), t = sampling time (min) and Q_{air} = air flow (l/min).

3.6.5 NH₃-concentration in urine

Ammonia concentration of stored urine was also measured with Orion 9512HPBNWB ammonia electrode attached to Orion 290A ISE meter. Ammonia concentration of urine can be calculated with Equation 25

$$C_u = 1,216 \cdot C_{ta,urine} \cdot \theta, \quad (25)$$

where C_u = ammonia concentration in urine (mg/l), $C_{ta,urine}$ = total ammonia concentration in urine (mg NH₃-N/l) and θ = percentage of unionized ammonia from total ammonia. Thurston et al. (1979) has listed θ values as function of temperature and pH.

3.6.6 Sensitivity of ammonia electrode

4th October 2011 ammonia concentrations in inlet and outlet gases were measured with both Orion 9512HPBNWB ammonia electrode and according to standard method SFS 3032. That was done with a view to determine how much error there is in results measured with ammonia electrode. Principle of the method is that ammonium ion reacts with hypochlorite which produces monochloramine. When phenol and excess hypochlorite attend, monochloramine transforms to indophenols. Absorbance of indophenol blue can be measured with a wavelength of 630 nm. Shimadzu UV-1601 UV-visible spectrophotometer was used to measure absorbance.

11th October 2011 the sensitivity of SFS 3032 method was determined. From acids collecting ammonia from UgnCleanPellets © B filter and activated carbon filter three parallel samples were taken. These samples were analyzed according to SFS 3032 method.

3.6.7 Total organic carbon

TOC in inlet and outlet gas of the biofilters were determined by measuring TOC from bubbled acids. Used equipment was Shimadzu TOC-5000 with Shimadzu ASI-5000 autosampler.

For total carbon (TC) and inorganic carbon (IC) standards of 0-10-20-30 mg/l and 30-100-200-300 mg/l were used. All standards were prepared from 1000 mg/l stock solutions. TC-standard stock solution was made by diluting 2.125 g of potassium hydrogen ftalate ($C_8H_5KO_4$, dried 2 h in 120 °C) to 1000 ml of deionized water. IC-standard was made by diluting 4.41 g of sodium carbonate (Na_2CO_3 , dried 1 h in 285 °C) to 500 ml of deionized water. After that 3.50 g of sodium hydrogen carbonate ($NaHCO_3$, dried in exsiccator) was added in solution and solution was diluted with deionized water to 1000 ml.

With TOC in acid it was possible to calculate TOC in air with Equation 26

$$TOC_{air} = \frac{TOC_{acid} \cdot V_{acid}}{t \cdot \frac{Q_{air}}{1000}}, \quad (26)$$

where TOC_{air} = TOC in air (mg/m^3) and TOC_{acid} = TOC in acid (mg/l).

3.6.8 Alkalinity

Alkalinity was measured according to standard method SFS-EN ISO 9963-1. Analysis was done potentiometrically. Used pH-meter is introduced in Chapter 3.6.2. Sample volume was 50 ml. 0.02 M hydrogen chloride was used because in every sample the alkalinity was lower than 4 mmol/l.

3.6.9 Moisture content

The MC of the filter materials were determined by oven drying materials at 105 °C according to standard method SFS-EN 14346.

3.6.10 Ion chromatography

Nitrate concentrations were measured with Dionex DX-12 ion chromatograph equipped with Dionex AS40 autosampler. Used column was Dionex 064149, IonPac® AS23, 4.250 mm. Eluent and standard solutions were prepared according to SFS-EN ISO 10304-1.

3.6.11 Pressure drop in biofilters

Pressure drop in biofilters was estimated with Ergun's equation. Ergun's equation is introduced in Chapter 2.4.8. In Ergun's equation there are velocity of the fluid v and mean particle diameter d_p that can be calculated with Equations 27 and 28.

$$v = \frac{Q}{A} \quad (27)$$

$$d_p = \frac{6}{a_v} \quad (28)$$

In Equation 27, Q = air flow rate and A = area of the filter bed. In Equation 28, a_v = specific surface (the total particle surface/the volume of the particle). (Bird et al. 1960.) Langfaserfiltergranulat, UgnCleanPellets © B and UgnCleanPellets © N pellets were assumed to have cylindrical shape. Vermiculite and activated carbon particles were assumed to be spheres. The needed total particle surface and volume of the particle were calculated by taking 25 particles of each filter material and measuring their dimensions.

In calculations it is assumed that dry air in temperature 300 K flows through filter material. In 300 K dynamic viscosity of air is $1.846 \cdot 10^{-5}$ kg/m·s and density is 1.177 kg/m³ (The Engineering Toolbox).

3.6.12 Volatile organic compounds in headspace of urine

Analysis of VOCs in headspace of urine was ordered from accredited company specialized in air quality analysis (Ositum Oy). The samples were analyzed according to methods which are modified from standards SFS-EN ISO 16017 and SFS-EN ISO 16000. Briefly, air was pumped from the headspace of the stored urine into sampling tube containing Tenax TA/Carbograph 1TD/Carboxen absorbent. Pump was operated for 1 min or 10 min to obtain sample from headspace of stored urine. As a control, laboratory air was also analysed to identify impurities deriving from other sources of contamination. It was pumped for 25 min corresponding to air volume of 3.5 litres. Compounds accumu-

lated in the absorbent were analysed using thermal desorption with gas chromatograph equipped with mass selective detector (Agilent Technologies). Compounds were identified from Wiley and NIST mass spectral libraries with the help of Chem Diag Wizard.

3.6.13 Volatilization of ammonia from stored urine

With collected data it is possible to model volatilization of ammonia from stored urine. That can be done with theory introduced by Whelan et al. (2010) (see Chapter 2.2.1). A mass transfer coefficient for ammonia from urine to air is calculated from Equation 1.

4 RESULTS AND DISCUSSION

4.1 Ammonia collection from stored urine

Ammonia collection from stored urine was a success. The equipment introduced in Chapter 3.2 worked well. With different air flow rates it was possible to get different ammonia concentrations into air. In the experiment with flow rate 1 l/min the average ammonia concentration of the air was 893 mg/m³. When the flow rate was increased to 6 l/min the average ammonia concentration of the air was 303 mg/m³.

The amount of ammonia that flows through the gas washing bottle was also measured. With air flow 1 l/min the amount of the escaped ammonia was less than 2 ‰. With air flow 6 l/min less than 6 ‰ escaped from the gas washing bottle. These results showed that the amount of the ammonia that flows through the gas washing bottle is negligible.

In the experiment that was done overnight the average ammonia concentration of the air was only 24 mg/m³. It showed that the amount of the ammonia that can be collected from urine decreases significantly during a long time period. Therefore the urine had to be changed daily in further experiments.

4.2 Results with one biofilter

Experiment with one biofilter was made to see if there is something to improve in filter column, experimental setup or analytical methods. Some things were found to work poorly and improvements needed to be done. At the beginning of the experiment, the biofilter performance was good and it managed to remove ammonia from the air. However, the biofilter performance decreased rapidly and the experiment was finished after 16 days. Results of experiment with one biofilter are introduced in next Chapters. Also done improvements are introduced.

4.2.1 Moisture content in filter material

When biofilter experiment was started, the initial MC of the filter material was measured. After the inoculation with activated sludge, the MC was 40.6 %. It was barely in the desired range between 40 and 60 % (Verein Deutscher Ingenieure 2004), but the experiment was still decided to begin.

During the experiment, there was no humidification of the inlet air or wetting of the filter bed. That caused a very rapid drying of the filter material. After only 16 days of experimenting the MC of the filter material had decreased to value 13.7 %. During

the experiment 66.3 % of the water in filter bed had humidified. It shows that it is extremely important to humidify the inlet air or wet the filter bed to keep the MC of the filter material in the desired range.

The MC measurement after the experiment was done from three different heights of the filter bed: one from the top, one from the middle and one from the bottom of the filter bed. There was a significant difference in MC in different heights. On the top of the filter bed, the MC was 19.5 %. In the middle part of the filter bed, the MC was 12.6 %. At the bottom of the filter bed, the MC was only 8.9 %. That is not a surprising result because when air flows through the filter bed it adsorbs water from the filter material and moisturizes. At the bottom of the filter bed, the air is driest and the adsorption rate of water is highest. In the higher parts of the filter bed, the air is already little moist, the adsorption rate of the water is lower and less water is adsorbed.

4.2.2 Performance of the biofilter

The height of the filter bed was 7.5 cm which causes 1 min EBRT. During the 16 days of experiment the ammonia concentration in inlet gas varied between 39.5 and 280.4 mg/m^3 . At the same time, the ammonia concentration in outlet gas varied between 0.2 and 150 mg/m^3 . Variation of ammonia concentration in inlet and outlet gas is introduced in Figure 14. LR of the filter varied between 2.37 and 16.83 $\text{g}/\text{h}\cdot\text{m}^3$ while reached EC varied between -6.63 and 14.32 $\text{g}/\text{h}\cdot\text{m}^3$. LR and EC values are introduced in Figure 15.

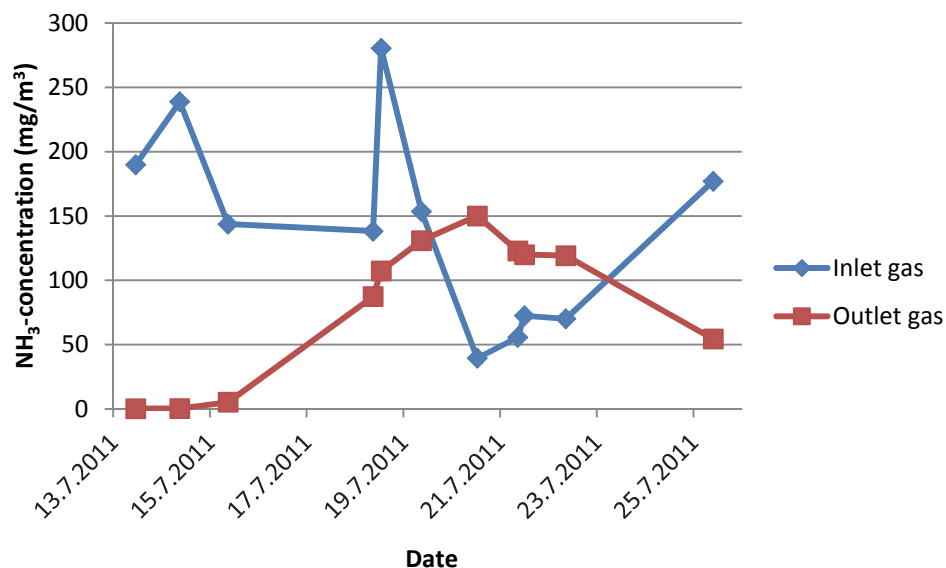


Figure 14: Ammonia concentration in inlet and outlet gas during the experiment with one filter.

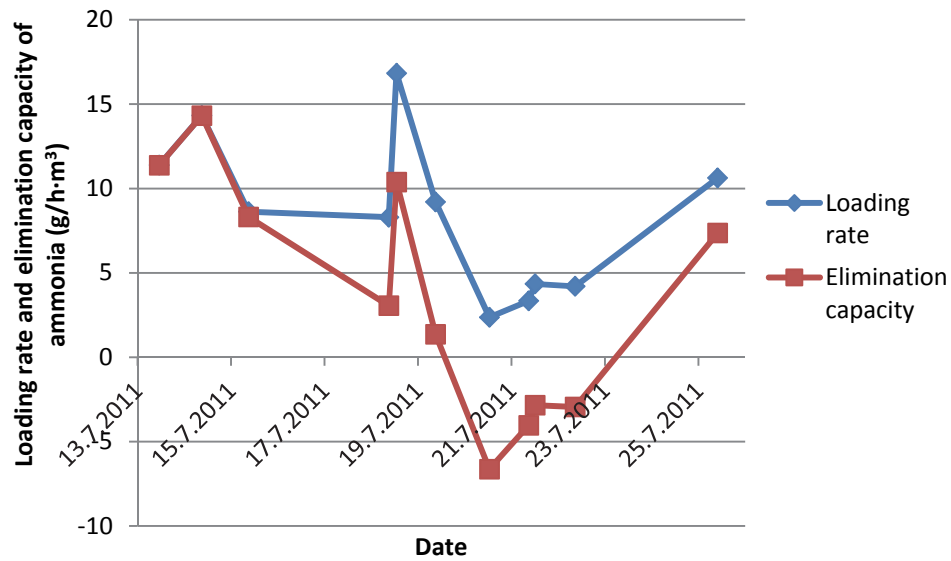


Figure 15: Loading rate of ammonia and elimination capacity of biofilter during the experiment with one biofilter.

From Figures 14 and 15 can be seen that the biofilter performance was very good at the beginning of the experimental period. Almost all ammonia was removed from the air. After only three days of experimenting the ammonia concentration in outlet gas started to increase and simultaneously the EC started to decrease.

At the eighth day of experiment, the ammonia concentration in outlet gas was even higher than the ammonia concentration in inlet gas. That naturally causes negative value for EC. The ammonia concentration was larger in outlet gas than in inlet gas for four days. After that clean air was fed in biofilter over weekend and better results were reached. The same trend can also be seen from Figure 16 where RE of the biofilter is introduced.

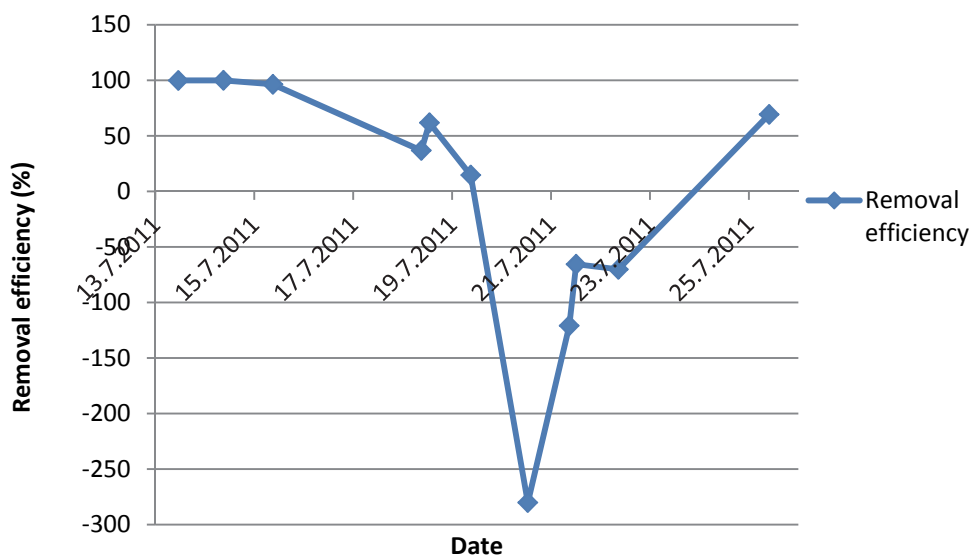


Figure 16: Removal efficiency of the biofilter during the experiment with one biofilter.

The main reason for dramatic drop in EC and RE is that the filter bed dried. The micro-organisms were unable to degrade the ammonia because it could not absorb to the water phase. The drying of the filter bed did not only cause small ECs and REs. When the filter bed dried, the ammonia that had absorbed to the water phase, volatilized with the water and caused negative EC and RE values.

4.2.3 Filter bed characteristics after the experiment

When the filter column was opened, three 10 g samples of the filter material were taken. Samples were taken from three different heights of the filter bed: one from the top, one from the middle and one from the bottom of the filter bed. TOC, pH and ammonia concentration of the samples were measured. Average pH, TOC and ammonia concentration of the filter bed were 8.11, 974.4 mg/kg dry matter and 1680.0 mg/kg dry matter respectively. The pHs, TOCs and ammonia concentrations varied depending on the height of the filter bed. In Figure 17 pHs, TOCs and ammonia concentrations on different heights are introduced.

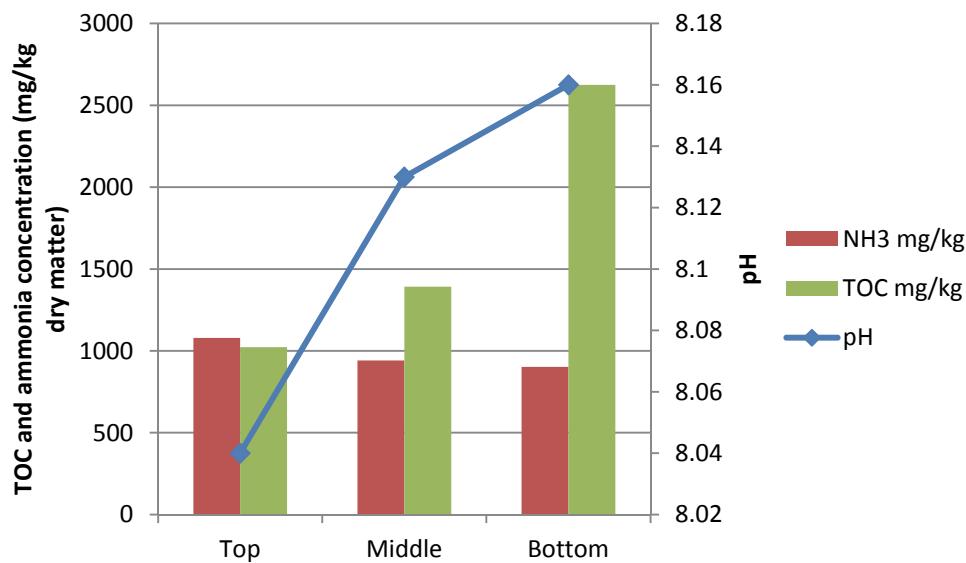


Figure 17: pH, TOC and ammonia concentration in different heights of the filter bed.

The highest ammonia concentration is on the top of the filter bed and the lowest at the bottom of the bed. Order of the ammonia concentrations is the same with the order of MCs. Assumption is that when the filter bed dried the solute ammonia vaporized at the same time with water. If the reason for the decrease of the ammonia concentration was nitrification, the pH should also decrease from the top to the bottom of the bed.

TOC increases from the top to the bottom of the filter bed. The highest TOC in the gas is at the bottom of the filter bed. TOC begins to adsorb to the filter bed when the gas flows in it. Naturally there is less TOC to adsorb on the top of the filter bed. There-

fore the TOC of the filter material is higher at the bottom of the filter bed than on the top of it.

The pH of the filter bed behaves similarly with TOC. It increases from the top to the bottom of the filter bed. Therefore the adsorbed organic compounds must have increasing effect on pH. Still the effect on pH is very small and the change of the pH was only 0.12.

4.2.4 Improvements in experimental setup

In the experiment with one biofilter few things came up that needed to be improved before starting the experiment with five biofilter. Those problems and solutions for them are introduced in this Chapter.

The biggest reason for a rapid decrease in biofilter performance was the drying of the filter bed. In 16 days, 66.3 % of the moisture in the filter bed humidified. Final MC was 13.7 % which is not enough. The contaminants of the air were not able to absorb to the water phase and micro-organisms could not be active in dry environments. Therefore, the humidification of the inlet gas needs to be started in the experiment with five biofilters.

The water-holding capacity of the filter material is an important property when deciding the best biofilter material. Therefore, information on the behavior of the MC in the filter bed during the experiment would be very useful. The MC of the filter bed could be measured continuously with a data logger that is in the middle of the filter bed. With the results of the data logger it could be seen which filter material can best maintain moisture environment in the bed.

In this experiment, phenolphthalein was used to indicate the pH increase in acid of the gas washing bottles. In that way too high pHs and ammonia concentrations in the acids were prevented. The phenolphthalein was diluted in ethanol. Ethanol addition definitely caused error to the TOC measurements of the acid. In the experiment of five biofilters the use of the phenolphthalein must stop and adequate sampling time needs to be decided.

Amounts of TOC that ended up in acid in gas washing bottle during the sampling were assumed to be small. To prevent error in TOC measurements the gas washing bottles and gas washing bottle heads with filter disc should be washed with hydrochloric acid (HCl) and ethanol. Drying of the gas washing bottles and gas washing bottle heads with filter disc is also essential to ensure that there are no ethanol residues in equipment. The drying is best to do in oven.

4.3 Results with five biofilter

When experiment with one biofilter and improvements in experimental setup were done, it was possible to begin the experiment with five biofilters. Langfaserfiltergranulat, UgnCleanPellets © B, UgnCleanPellets © N, vermiculite and activated carbon were used as filtermaterials. Experimental setup in laboratory is introduced in Figure 18.



Figure 18: *Experimental setup in laboratory in five filter experiment.*

In this experiment humidification of the inlet gas was used and the use of pH indicator was stopped. Increase in specific humidity of the inlet gas was 0.0084 kg H₂O/kg dry air. In temperature 20 °C that is equal to 86.7 % relative humidity, if it is assumed that the relative humidity of the air is 0 % before humidification (Seppänen et al. 1991). During the experiment all bottles and filter columns were covered with aluminum foil to prevent UV-degradation of VOCs of urine. Also data loggers were used to measure temperature and humidity of the gas inside the filter beds. The experiment took 77 days.

4.3.1 Performance of the biofilters

At the beginning of the experiment the bed height was 7.5 cm in all biofilters except in UgnCleanPellets © B biofilter. In UgnCleanPellets © B biofilter the bed height was 8.0 cm and it caused 1.06 min EBRT. In other biofilters the EBRT was 1 min at the beginning of the experiment. Filtration results of ammonia and TOC are introduced in this Chapter.

Ammonia removal

In this experiment the urine was diluted with a view to keep the ammonia concentration of the inlet gas smaller than in the experiment with one filter. The ammonia concentration of the inlet gas varied between 15.6 and 73.0 mg/m³. The ammonia concentrations in the inlet and outlet gases of the biofilters are introduced in Figure 19.

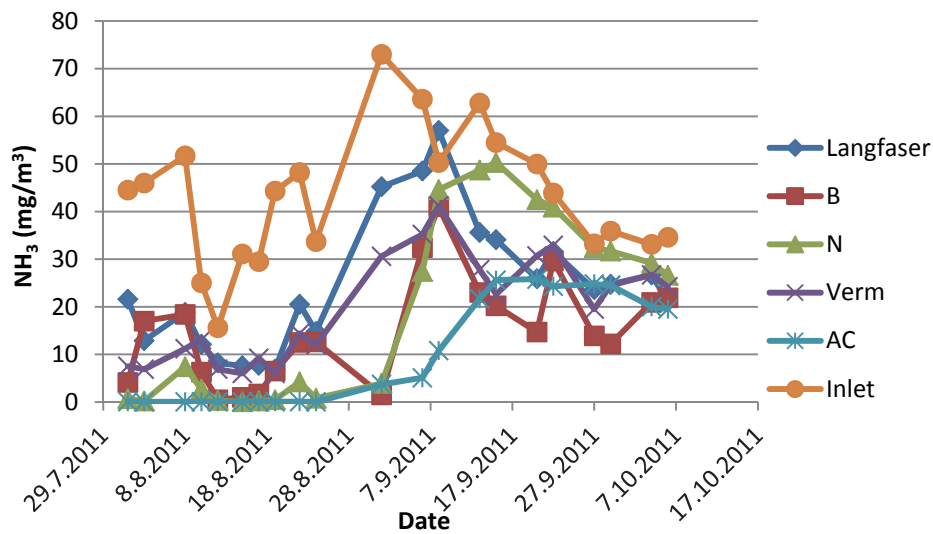


Figure 19: Ammonia concentrations of the inlet gas and outlet gases of the biofilters during the experiment with five biofilters. Langfaser = Langfaserfiltergranulat, B = UgnCleanPellets © B, N = UgnCleanPellets © N, Verm = vermiculite and AC = activated carbon.

At the beginning of the experiment very good ammonia removal results were reached. With UgnCleanPellets © B, UgnCleanPellets © N and activated carbon it was possible to remove more than 90 % of the ammonia. Activated carbon had immediately 99.9 % RE. The RE of activated carbon was more than 90 % for 40 days. After that the performance of the activated carbon decreased constantly. During the last 28 days the RE of activated carbon varied between 25.2 and 48.4 %.

UgnCleanPellets © N performed well for 35 days reaching REs above 85.7 %. The maximum RE during the first 35 days of experiment was 99.9 % and average RE was 95.7 %. After 6th September 2011, the performance of UgnCleanPellets © N decreased rapidly. In worst cases UgnCleanPellets © N was not able to remove ammonia from air practically at all. The minimum RE was 2.4 % and average RE during the last 42 days was 16.9 %.

At the first measurement UgnCleanPellets © B was able to remove 90.8 % of ammonia from the air. Next three measurements were worse and REs varied between 63.1 and 74.7 %. After that UgnCleanPellets © B was able to remove more than 90 % of the ammonia with maximum RE of 98.0 %. The performance of UgnCleanPellets © B also decreased after 35 days but UgnCleanPellets © B had still the best RE in last 42 days. The average RE of UgnCleanPellets © B during the last 42 days was 49.5 %.

During the 77 days of experimenting, vermiculite was not able to remove over 90 % of the ammonia. REs of vermiculite varied between 18.1 % and 84.9 % and the average RE was 54.4 %. With vermiculite there was no clear decrease in performance like activated carbon, UgnCleanPellets © N and UgnCleanPellets © B had. The results of vermiculite varied a lot between the measurements.

Also Langfaserfiltergranulat did not reach over 90 % RE during the experiment. The maximum RE of Langfaserfiltergranulat was 84.5 %. Langfaserfiltergranulat was only material that had negative RE when the ammonia concentration in outlet gas was larger than in inlet gas (see Figure 19). REs of all biofilters are introduced in Figure 20.

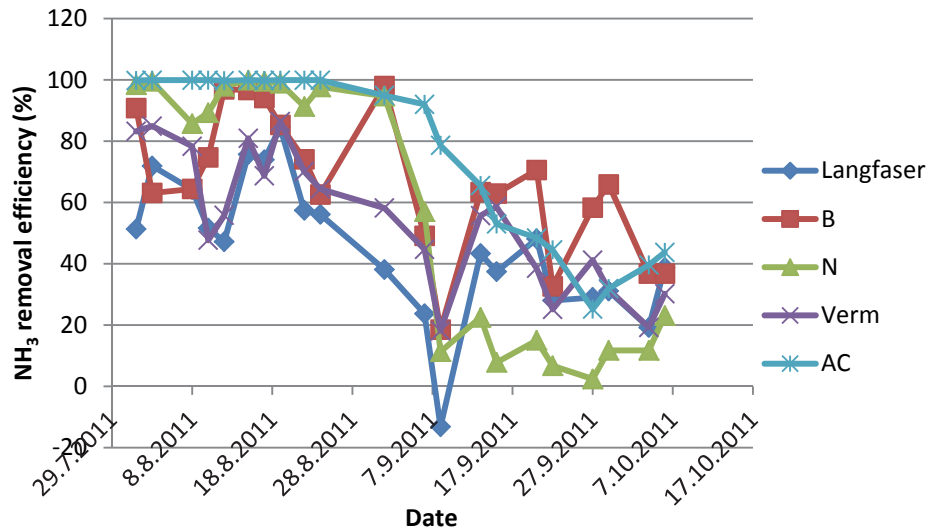


Figure 20: Removal efficiencies of the biofilters during the experiment with five biofilters. Langfaser = Langfaserfiltergranulat, B = UgnCleanPellets © B, N = UgnCleanPellets © N, Verm = vermiculite and AC = activated carbon.

LR of ammonia varied between 0.936 and 4.38 g/h·m³ which are in same magnitude but smaller than in previous laboratory scale studies (see Table 5). During the first 35 days of the experiment, activated carbon, UgnCleanPellets © N and UgnCleanPellets © B were able to reach ECs nearly as high as the LR was. After 35 days the EC of every biofilter started to decrease. LRs and ECs of each biofilters are introduced in Figure 21.

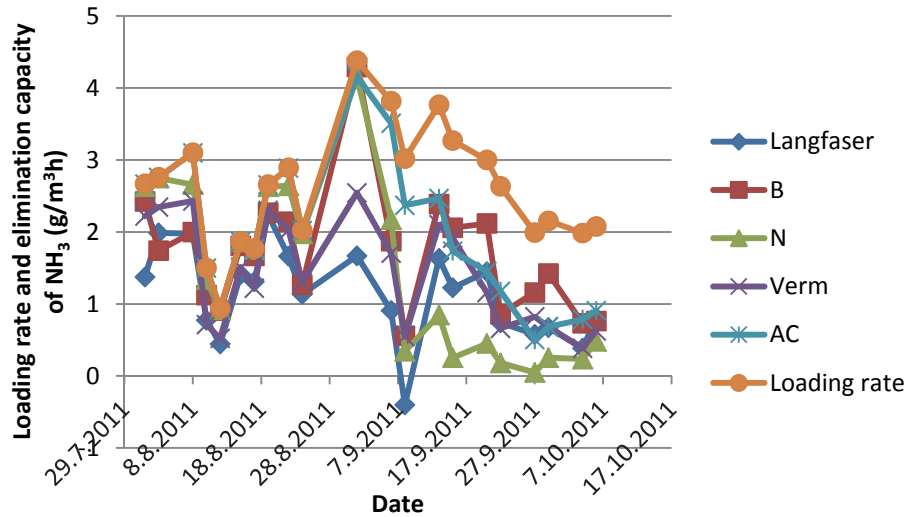


Figure 21: Loading rate of ammonia and elimination capacities of the biofilters during the experiment with five biofilters. Langfaser = Langfaserfiltergranulat, B = Ugn-CleanPellets © B, N = UgnCleanPellets © N, Verm = vermiculite and AC = activated carbon.

The negative EC of Langfaserfiltergranulat is caused by the higher ammonia concentration in outlet gas than in inlet gas. From Figure 21 it can be seen that in the first 35 days the EC curves followed the LR curve but at the end of the experiment the curves were very separate.

Total organic carbon removal

TOC concentrations in the inlet gas were much smaller than the ammonia concentrations and TOC in inlet gas varied between 0.82 and 5.79 mg/m³. Only vermiculite was able to reach over 90 % TOC RE. It had maximum RE 90.6 % on 1st September 2011. REs, LRs and ECs of all biofilters are introduced in Figures 22 and 23.

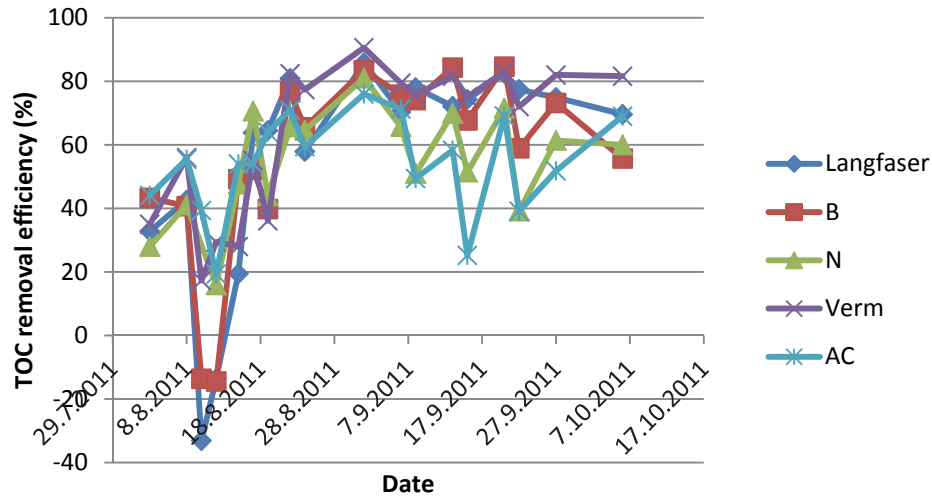


Figure 22: Total organic carbon (TOC) removal efficiencies of the biofilters during the experiment with five biofilters. Langfaser = Langfaserfiltergranulat, B = UgnCleanPellets © B, N = UgnCleanPellets © N, Verm = vermiculite and AC = activated carbon.

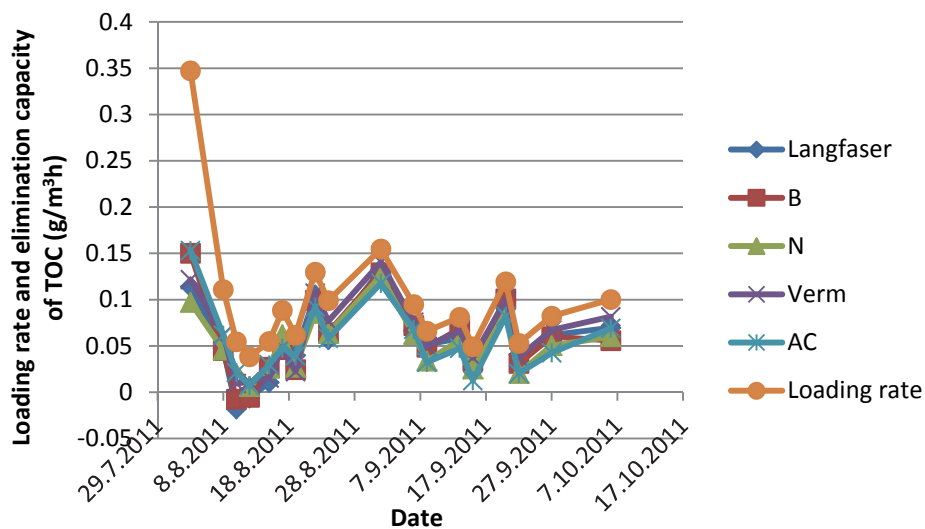


Figure 23: Loading rate of total organic carbon (TOC) and elimination capacities of the biofilters during the experiment with five biofilters. Langfaser = Langfaserfiltergranulat, B = UgnCleanPellets © B, N = UgnCleanPellets © N, Verm = vermiculite and AC = activated carbon.

As can be seen from the Figure 22 the REs were small at the beginning of the experiment. Even negative REs existed with Langfaserfiltergranulat, UgnCleanPellets © B and UgnCleanPellets © N. After two weeks the REs started to increase. With Langfaserfiltergranulat, UgnCleanPellets © B, UgnCleanPellets © N and vermiculite the majority of the reached REs were between 60 and 90 %. Activated carbon had most REs between 50 and 70 %. Average removal efficiencies during the last 56 days for Langfaserfiltergranulat, UgnCleanPellets © B, UgnCleanPellets © N, vermiculite and activated carbon were 74.0, 70.0, 60.4, 76.4 and 58.6 % respectively.

From Figure 23 it is easy to see that the TOC REs have been quite constant. When the LR of TOC has increased the ECs has simultaneously increased. On the other hand when the LR decreased the ECs also decreased. It shows that it was impossible to remove TOC more efficiently when the LR decreased.

4.3.2 Conditions in filter beds during the experiment

Amount of micro-organisms, MC, pH, alkalinity, TOC, ammonia concentration and nitrate concentrations of the filter materials were measured three times during the experiment. Measurements were done at the beginning of the experiment, after 29 days and at the end of the experiment. Results of these measurements are introduced in this Chapter.

Moisture content

MCs of filter beds in each biofilter are introduced in Figure 24.

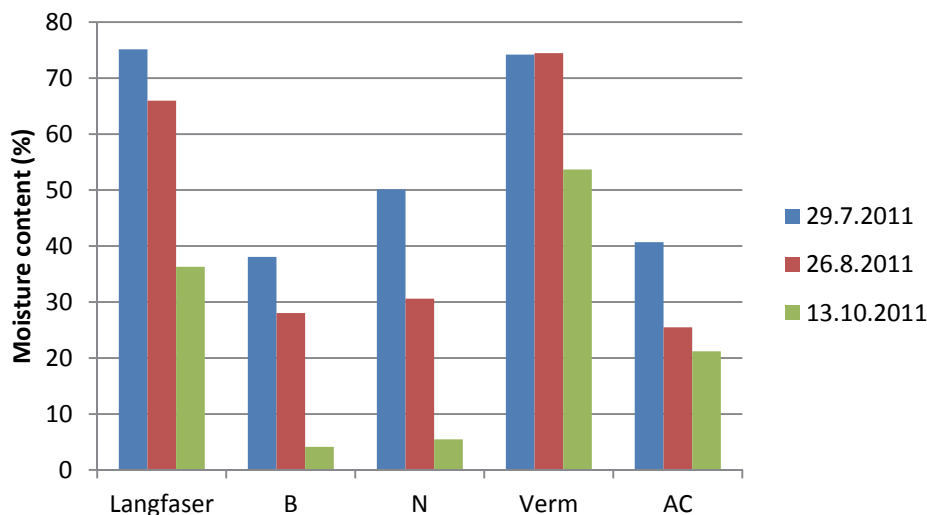


Figure 24: Moisture contents of the filter beds in each biofilter during the experiment with five biofilters. Langfaser = Langfaserfiltergranulat, B = UgnCleanPellets © B, N = UgnCleanPellets © N, Verm = vermiculite and AC = activated carbon.

At the beginning of the experiment Langfaserfiltergranulat and vermiculite had the highest MCs. Their MCs were 75.1 % and 74.2 % respectively. The MC of UgnCleanPellets © N was 50.1 % and the MC of activated carbon was 40.7 %. UgnCleanPellets © B had the lowest MC at the beginning of the experiment, only 38.1 %.

In spite of humidification of the inlet gas all filter materials dried during the experiment. That caused decrease in filter performance and REs after 35 – 40 days. Drying was most intense in UgnCleanPellets © B and UgnCleanPellets © N. Their MCs at the end of the experiment were only 4.1 and 5.5 % respectively, which are significantly lower than the MCs that are reported to be sufficient. For example, Cox et al. (1996) investigated biofiltration of styrene in with different filter bed MCs. In their study it was

possible to increase the EC from 14 g/m³·h to 48 g/m³·h by increasing the MC from 22 % to 55 %. Cox et al. (1996) also discovered that drying of the filter bed is very fast if the relative humidity of the inlet gas is not high enough. With relative humidity of 91 % the MC of the filter bed decreased from 66 % to near 0 % only in approximately 20 days. (Cox et al. 1996.)

In this experiment drying of the filter beds was not quite that fast, but however the relative humidity of the inlet gas should have been higher to prevent drying. The drying rate was also different depending on the filter material.

At the end of the experiment vermiculite was only filter material that had MC above 40 %. Its MC had decreased only to value 53.7 %. Langfaserfiltergranulat had also good MC at the end of the experiment, 36.3 %. Despite of relatively high MCs Langfaserfiltergranulat and vermiculite were not able to remove efficiently ammonia from air.

Amount of micro-organisms

Numbers of heterotrophic bacteria, yeasts, sulphate oxidizing bacteria, *Nitrosomonas* and *Nitrobacter* were determined twice during the experiment, on 26th August 2011 and 13th October 2011. The results are presented in Figures 25 – 28.

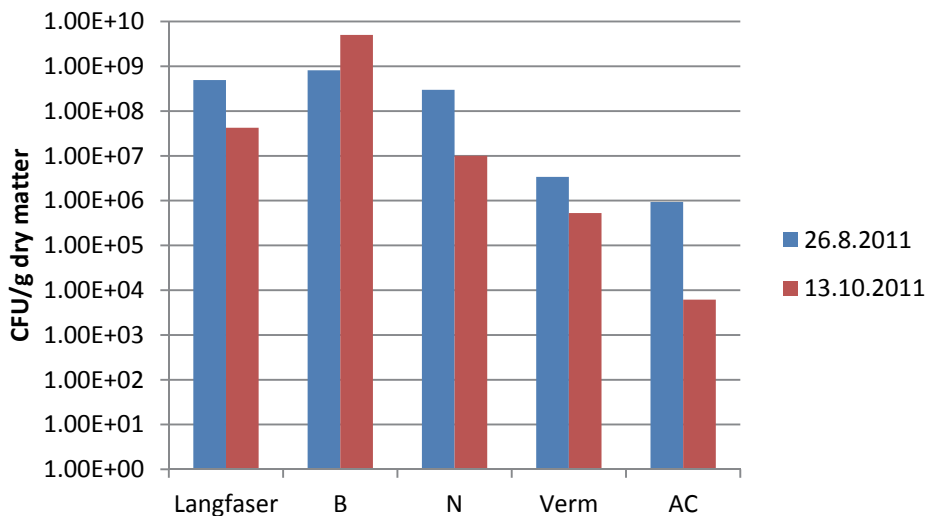


Figure 25: Viable count of heterotrophic bacteria (CFU/g dry matter) in different filter materials. Langfaser = Langfaserfiltergranulat, B = UgnCleanPellets © B, N = Ugn-CleanPellets © N, Verm = vermiculite and AC = activated carbon.

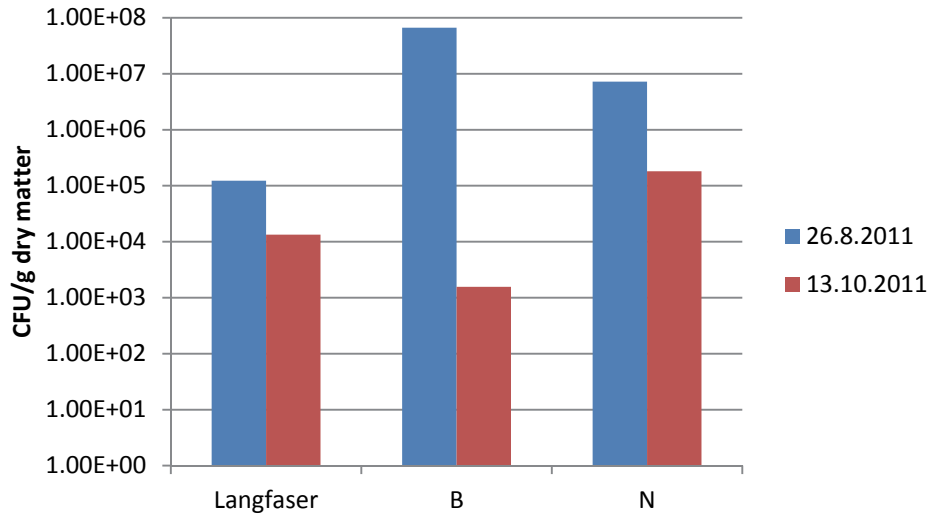


Figure 26: Viable count of yeasts (CFU/g dry matter) in different filter materials. Langfaser = Langfaserfiltergranulat, B = UgnCleanPellets © B and N = UgnCleanPellets © N.

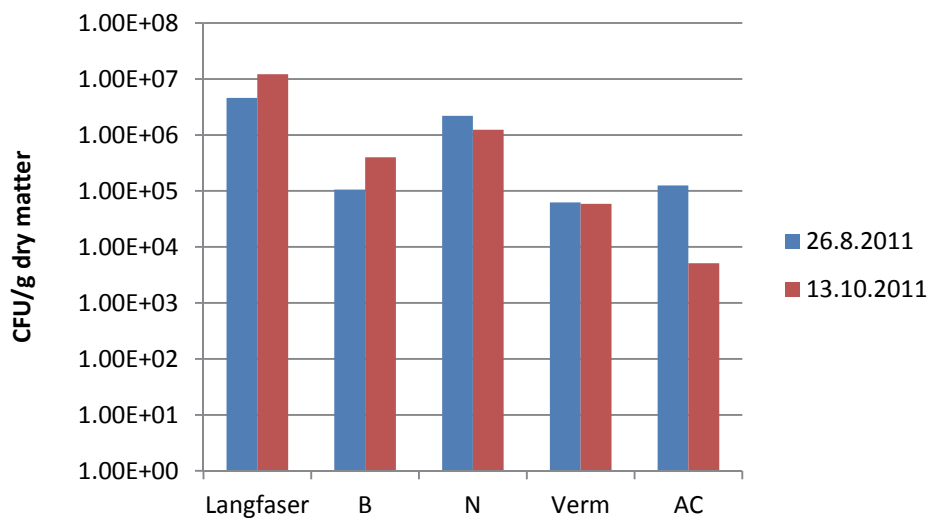


Figure 27: Viable count of sulphate oxidizing bacteria (CFU/g dry matter) in different filter materials. Langfaser = Langfaserfiltergranulat, B = UgnCleanPellets © B, N = UgnCleanPellets © N, Verm = vermiculite and AC = activated carbon.

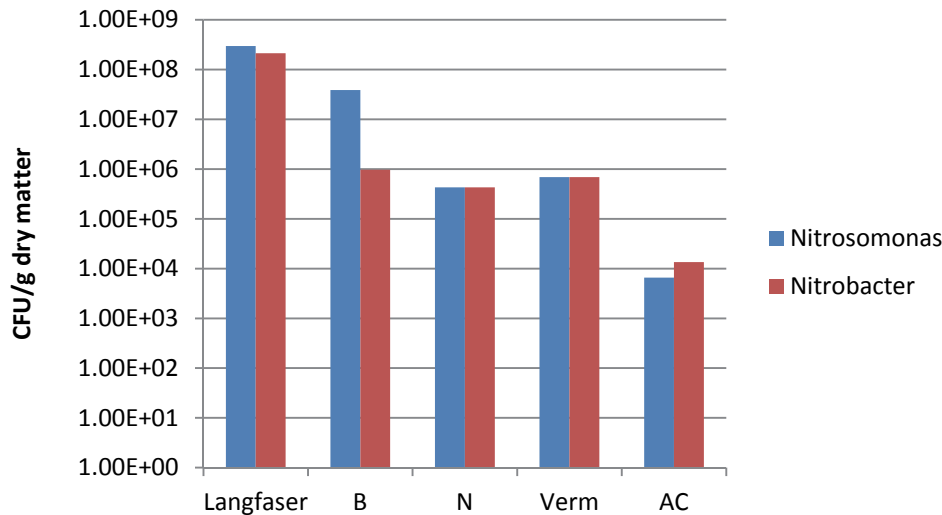


Figure 28: Viable count of *Nitrosomonas* and *Nitrobacter* (CFU/g dry matter) in different filter materials. Langfaser = Langfaserfiltergranulat, B = UgnCleanPellets © B, N = UgnCleanPellets © N, Verm = vermiculite and AC = activated carbon.

Heterotrophic bacteria were detected from all five biofilters. The number of heterotrophic bacteria was largest in UgnCleanPellets © B biofilter and it even increased during the experiment. In other biofilters the number of heterotrophic bacteria was smaller and it decreased after the first determination.

Yeasts were detected only from Langfaserfiltergranulat, UgnCleanPellets © B and UgnCleanPellets © N biofilters. The number of yeasts was particularly high in UgnCleanPellets © B and UgnCleanPellets © N biofilters. That is not a surprise because fungal populations are known to be dominant in dry biofilters (Devinny et al. 1999). It was also possible to see fungi in UgnCleanPellets © B and UgnCleanPellets © N biofilters without microscope (see Chapter 4.3.4).

Sulphate oxidizing bacteria, *Nitrosomonas* and *Nitrobacter* were detected from all five biofilters. Number of these bacteria was highest in Langfaserfiltergranulat biofilter. In UgnCleanPellets © B, UgnCleanPellets © N and vermiculite sulphate oxidizing bacteria, *Nitrosomonas* and *Nitrobacter* were found in smaller quantities and number of these bacteria was smallest in activated carbon biofilter. Detection of sulphate oxidizing bacteria shows that sulphuric compounds had evaporated from the stored urine.

Langfaserfiltergranulat biofilter had the highest amount sulfur oxidizing bacteria, *Nitrosomonas* and *Nitrobacter* and second-highest amount of heterotrophic bacteria. However, the performance of Langfaserfiltergranulat biofilter was not the best in terms of ammonia and TOC removal. It shows that the high amount of micro-organisms in biofilter does not always lead to high RE.

pH and alkalinity

The monitoring of the pH in filter beds gave information of biological activity in biofilters. In Figure 29, pH of each filter bed during the experiment is introduced.

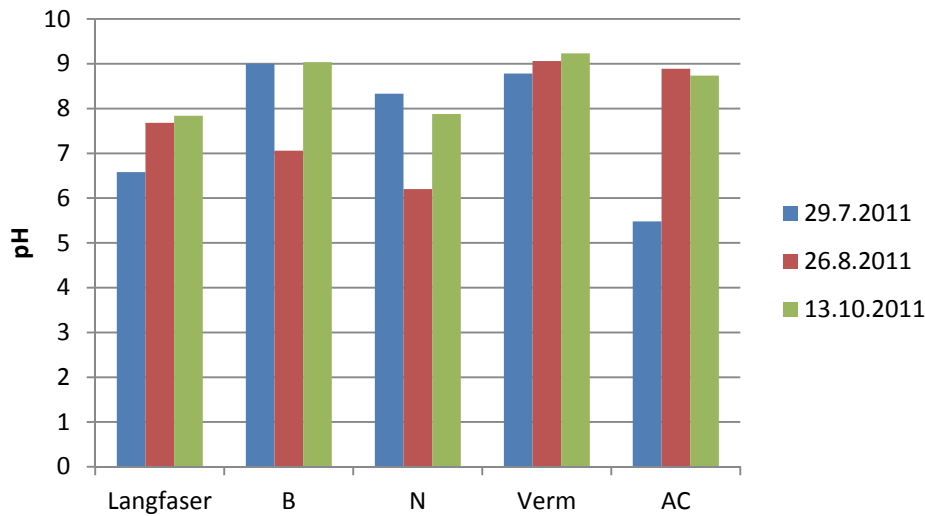


Figure 29: pHs of the filter beds in each biofilter during the experiment with five biofilters. Langfaser = Langfaserfiltergranulat, B = UgnCleanPellets © B, N = UgnCleanPellets © N, Verm = vermiculite and AC = activated carbon.

As can be seen from Figure 29, in UgnCleanPellets © B and UgnCleanPellets © N biofilters pH decreased during the first 29 days of experiment. As described earlier biodegradation of ammonia, organic compounds and sulphur compounds produces acidic compounds (Crites & Tchobanoglous 1998, Madigan & Martinko 2006). The decrease in pH proves that the micro-organisms detected from UgnCleanPellets © B and UgnCleanPellets © N biofilters have been able to biologically degrade ammonia and other volatilized compounds.

In last measurement the pH of UgnCleanPellets © B and UgnCleanPellets © N biofilters had increased. When the filter beds started to dry, the biological activity in the filter beds reduced and ammonia started to adsorb to biofilter which caused the increase in pH.

In Langfaserfiltergranulat, vermiculite and activated carbon biofilter pH has increased during the experiment. It is possible that the micro-organisms in the biofilters have biodegraded part of the ammonia but ammonia has also adsorbed to filter bed and therefore pH has increased.

Alkalinity of the filter beds behaved similarly with pHs. Alkalinities of the filter beds during the experiment are introduced in Figure 30.

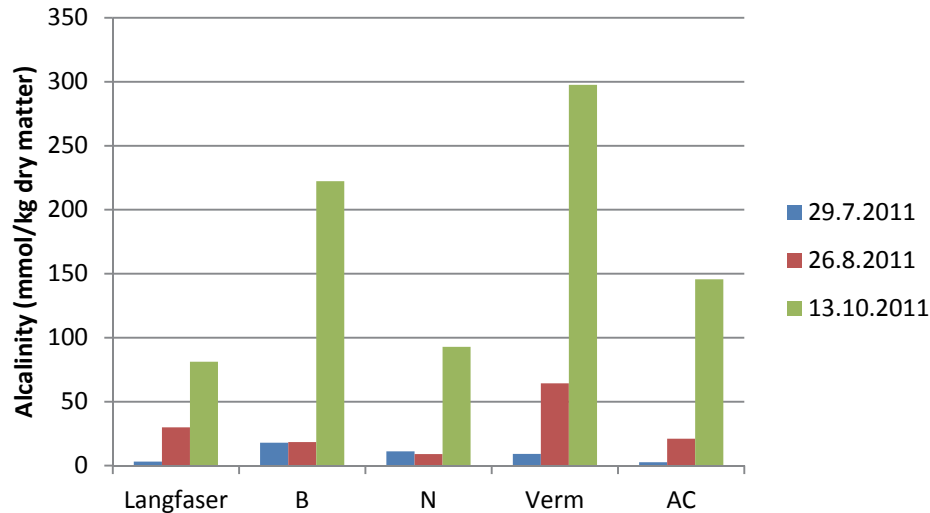


Figure 30: Alkalinity of the filter bed in each biofilter during the experiment with five biofilters. Langfaser = Langfaserfiltergranulat, B = UgnCleanPellets © B, N = UgnCleanPellets © N, Verm = vermiculite and AC = activated carbon.

In Langfaserfiltergranulat, vermiculite and activated carbon biofilters alkalinity increased during whole experiment. It shows that the ammonia has at least partly adsorbed to the filter bed. The adsorbed ammonia reacted with the hydrochloric acid in alkalinity measurement and increased the alkalinity.

The biodegradation of ammonia is known to reduce alkalinity (Crites & Tchobanoglous 1998). In UgnCleanPellets © B and UgnCleanPellets © N biofilters the alkalinity did not change or decreased slightly during the first 29 days of experiment. It can be perceived as an evidence of biological activity. The increase in alkalinity at the end of the experiment is caused by the same reason as the increase in the pH.

Ammonia concentration

The ammonia concentration of the filter bed in each biofilter verifies what could have been concluded from the behavior of pH and alkalinity in the filter beds. In UgnCleanPellets © B and UgnCleanPellets © N biofilters ammonia was partly degraded biologically. In other biofilters most of the ammonia has been removed physically. Ammonia concentrations of each filter bed are introduced in Figure 31.

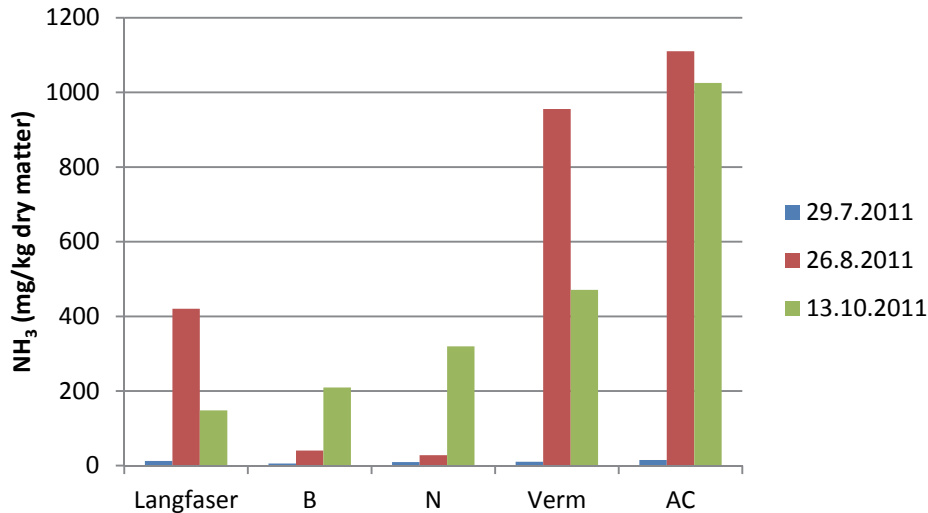


Figure 31: Ammonia concentrations of the filter beds in each biofilter during the experiment with five biofilters. Langfaser = Langfaserfiltergranulat, B = UgnCleanPellets © B, N = UgnCleanPellets © N, Verm = vermiculite and AC = activated carbon.

At the beginning of the experiment ammonia concentration was very small in all filter beds. During the first 29 days of experiment the ammonia concentration increased only slightly in UgnCleanPellets © B and UgnCleanPellets © N biofilters. If the removal of ammonia in those biofilters was only physical the ammonia concentration would be much higher. It shows that ammonia was degraded biologically in UgnCleanPellets © B and UgnCleanPellets © N biofilters. During the later period the UgnCleanPellets © B and UgnCleanPellets © N biofilters started to dry. Therefore the biological activity reduced and ammonia concentration increased.

In Langfaserfiltergranulat, vermiculite and activated carbon biofilters the ammonia concentration increased during the first 29 days. It shows that the ammonia in the inlet gas had been mostly removed through adsorption to the water phase and filter material. During the later period of the experiment the ammonia concentration in Langfaserfiltergranulat, vermiculite and activated carbon biofilters decreased. Assumption is that when the filter beds dried the solute ammonia vaporized at the same time with water and caused the decrease in ammonia concentration.

In activated carbon biofilter the ammonia concentration decreased only less than 10 % during the last 48 days. It indicates that most of the ammonia had adsorbed on the surface of activated carbon, not only to the water phase.

Total organic carbon

TOC measurements during the experiment also gave evidence that there has been biological activity at least in UgnCleanPellets © B and UgnCleanPellets © N biofilters. TOCs in each biofilter during the experiment are introduced in Figure 32.

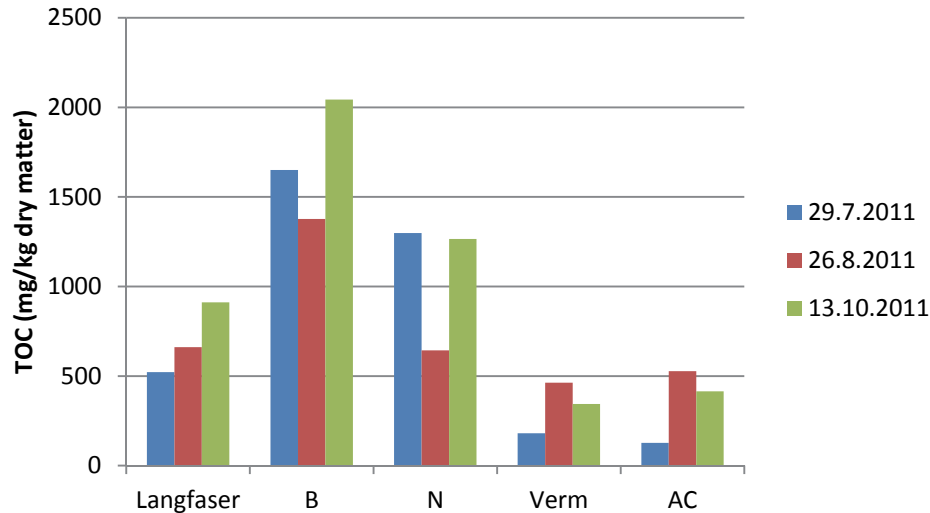


Figure 32: Total organic carbon (TOC) of the filter beds in each biofilter during the experiment with five biofilters. Langfaser = Langfaserfiltergranulat, B = UgnCleanPellets © B, N = UgnCleanPellets © N, Verm = vermiculite and AC = activated carbon.

As can be seen from Figure 32 the amount of TOC has decreased during the first 29 days in UgnCleanPellets © B and UgnCleanPellets © N biofilters. However, UgnCleanPellets © B and UgnCleanPellets © N biofilters were able to reduce TOC in the air. If the TOC had removed only through adsorption, the TOC would have increased during the first 29 days. Therefore biological degradation of organic compounds must have occurred in UgnCleanPellets © B and UgnCleanPellets © N biofilters. During the last 48 days of experiment biological activity has reduced in UgnCleanPellets © B and UgnCleanPellets © N biofilters and TOC has adsorbed into them. In Langfaserfiltergranulat, vermiculite and activated carbon biofilters the TOC in the inlet gas has been removed mostly by adsorption.

Nitrate concentration

Samples of filter materials for ion chromatograph were taken on 29th July 2011, 26th August 2011 and 13th October 2011. Because of hardware failure the samples taken on 26th August 2011 could not be analyzed. If in those samples UgnCleanPellets © B and UgnCleanPellets © N biofilters had nitrite or nitrate, it would have been a final evidence of ammonia biodegradation in those biofilters. The nitrate concentrations in each biofilter are introduced in Figure 33.

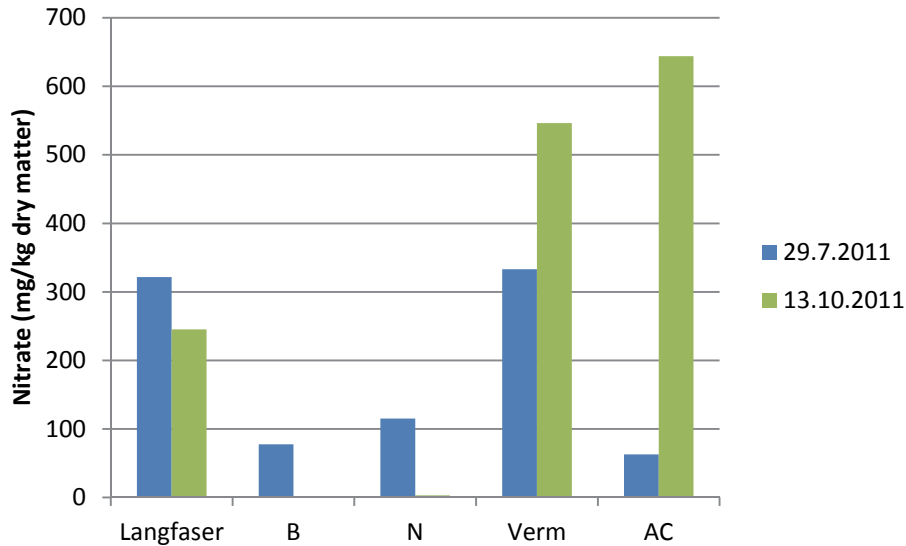


Figure 33: Nitrate concentrations of the filter beds in each biofilter at the beginning and at the end of the experiment with five biofilters. Langfaser = Langfaserfiltergranulat, B = UgnCleanPellets © B, N = UgnCleanPellets © N, Verm = vermiculite and AC = activated carbon.

As can be seen from the Figure 33, nitrate has been detected from all biofilters. When ammonia is biologically degraded, nitrate can be formed. Therefore it can be said that biodegradation of ammonia has occurred also in Langfaserfiltergranulat, vermiculite and activated carbon biofilters. However, the other analyses show that the biodegradation has not been the major removal process of ammonia in those biofilters. Also the nitrate concentration in Langfaserfiltergranulat, vermiculite and activated carbon biofilters is significantly smaller than the concentration around 2 g/kg dry matter reported in literature (Chen et al. 2005).

Nitrate was not detected from UgnCleanPellets © B and UgnCleanPellets © N biofilters at the end of the experiment. However, ammonia has been biologically oxidized in those biofilters. There are two possible explanations for the absence of nitrate. UgnCleanPellets © B and UgnCleanPellets © N biofilters dried heavily during the experiment. It is possible that the formed nitrate has been in water phase and evaporated with the water. On the other hand, it is possible that the ammonia has been oxidized only to nitrite and not further to nitrate. Unfortunately nitrite concentration was not determined during the experiment so destiny of oxidized ammonia could not be defined.

4.3.3 Temperature and humidity of the gas inside the filter bed

The temperature and humidity of the gas inside the biofilter were monitored with data loggers. Data loggers were installed to every biofilter on 26th August 2011 when the filter columns were opened. Data loggers were installed in the middle of the filter bed and they were inside the filter bed for rest of the experiment. They measured tempera-

ture and humidity of the air inside the filter bed once per 30 min. When the experiment was ended, the data loggers were connected to the computer and the data was collected.

The data collected by data loggers shows that all five biofilters operated in room temperature. The temperature varied between 19 – 25 °C depending on what time it was. From the temperature data it was impossible to find any signs of increase in temperature caused by exothermic biological reactions. Even UgnCleanPellets © B and UgnCleanPellets © N did not have any signs of that.

The drying of the filter beds can be clearly seen from the humidity data collected by the data loggers. When the data loggers were installed into filter columns the humidity of the air was in all columns nearly 100 %. The humidity of the air started to decrease immediately in Langfaserfiltergranulat and UgnCleanPellets © N biofilters ending up to values 67.0 and 53.0 % respectively. It shows that at the end of the experiment the filter materials were so dry that they could not maintain humid circumstances even in the gas phase.

Assumption is that there should have been similar trend in the humidity of the gas in UgnCleanPellets © B and activated carbon biofilters because they also dried significantly during the experiment. For some reason the humidity data collected from UgnCleanPellets © B and activated carbon biofilters shows humidity near 100 % for whole experiment. Reason for that is unknown.

In vermiculite biofilter the humidity of the air inside the filter column was near 100 % for whole experimental period. That seems plausible because vermiculite did not dry as much as other biofilters. MC of the vermiculite was 53.7 % at the end of the experiment. Consequently it had plenty of water to keep the humidity of the air constant. All data collected with data loggers is introduced in Appendix 1.

4.3.4 Observations in filter materials after experimental period

When the filter columns were opened after 77 days of experiment, it was possible to see changes in the filter materials. All filter materials had compacted and in some filter columns it was possible to see signs of microbial activity. Observations in filter materials are described in this Chapter.

Height of the filter beds

In all five filter columns the height of the filter bed had decreased. Decrease in bed height was not the same in all columns, but it varied depending on the filter material. Material decomposition, bed compaction and water condensation are possible reasons for decrease in bed height. The decrease in the bed height naturally decreases EBRT. The initial and final bed heights and EBRTs of each biofilter are introduced in Table 8.

Table 8: Initial and final bed heights and empty bed residence times (EBRT) of each biofilter used in experiment with five biofilters. Langfaser = Langfaserfiltergranulat, B = UgnCleanPellets © B, N = UgnCleanPellets © N, Verm = vermiculite, AC = activated carbon

Biofilter	Langfaser	B	N	Verm	AC
Initial bed height (cm)	7.5	8	7.5	7.5	7.5
Initial EBRT (min)	1.00	1.06	1.00	1.00	1.00
Final bed height (cm)	6.5	5.5	6	4.5	5
Final EBRT (min)	0.86	0.73	0.80	0.60	0.66

Reason for decrease in bed height in Langfaserfiltergranulat, UgnCleanPellets © B and UgnCleanPellets © N biofilters was shrinking of the particles. In inoculation filtered activated sludge absorbed into filter materials which made the particles swell. During the experiment the filter materials dried and particle size of Langfaserfiltergranulat, UgnCleanPellets © B and UgnCleanPellets © N returned to size of dry material.

Decrease in particle size caused by drying cannot be the only reason for decrease in bed height in vermiculite biofilter. MC of vermiculite decreased 20.5 % during the experiment while the bed height decreased 40 %. Vermiculite particles were very weak and they broke very easily. It is possible that weight of the upper layers in the filter bed have crushed the particles in lower layers. The particles might have also resettled in tighter order.

Activated carbon particles did not swell during the inoculation. Also they resist well breakage. Therefore the reason for decrease in bed height in activated carbon filter is the resettling of the particles.

Microbial growth in filter beds

It was possible to see signs of microbial activity in UgnCleanPellets © B and UgnCleanPellets © N biofilters when the filter columns were opened after 29 and 77 days of experiment. During the first 29 days something brown had appeared to lower part of UgnCleanPellets © B and UgnCleanPellets © N biofilters. The formations were so large that they were easy to see without microscope. There were also large hyphae of fungi in UgnCleanPellets © B and UgnCleanPellets © N biofilters. The color of Langfaserfiltergranulat had changed from white to yellowish brown during the first 29 days. It might be caused by microbial growth. There was no noticeable microbial growth in vermiculite and activated carbon biofilters. The brown formations and fungi populations of UgnCleanPellets © B and UgnCleanPellets © N biofilters and yellow color of Langfaserfiltergranulat biofilter are introduced in Figures 34 – 36.



Figure 34: Brown formations in UgnCleanPellets © B and UgnCleanPellets © N biofilters during the experiment with five biofilters. UgnCleanPellets © B biofilter is on left and UgnCleanPellets © N biofilter is on right.



Figure 35: Fungal growth in UgnCleanPellets © B and UgnCleanPellets © N biofilters in the experiment with five biofilters. UgnCleanPellets © B biofilter is on left and UgnCleanPellets © N is on right.



Figure 36: Yellowish brown color of Langfaserfiltergranulat in the experiment with five biofilters.

When the filter columns were opened after 77 days the filter columns looked similar as 48 days before. Fungal growth was dominant in UgnCleanPellets © B and UgnCleanPellets © N biofilters. Color of Langfaserfiltergranulat had stayed yellowish brown and there was no noticeable microbial growth in vermiculite and activated carbon biofilters.

It is possible that the brown formations in UgnCleanPellets © B and UgnCleanPellets © N biofilters included nitrifying bacteria. Activated sludge that was used for inoculation included nitrifying bacteria, *Nitrosomonas* and *Nitrobacter* were detected from UgnCleanPellets © B and UgnCleanPellets © N biofilters and the major contaminant of the treated gas was ammonia. Growth of nitrifying bacteria needs hydrogen carbonate (Crites & Tchobanoglous 1998). UgnCleanPellets © B and UgnCleanPellets © N were only filter materials which had source of hydrogen carbonate and the brown formations were found only from these biofilters.

When the filter beds started to dry the bacterial growth in UgnCleanPellets © B and UgnCleanPellets © N biofilters stopped. In dry conditions fungi began to dominate in the filter bed. Occurrence of fungi in those filter beds is not surprising because xerophilic fungi are known to be able to grow in dry biofilters (Devinny et al. 1999). Elias et al. (2009) also found fungal populations in their laboratory scale biofilter when they operated a biofilter in dry conditions. When Sun et al. (2002) operated biofilters with different MCs, they noticed that moulds and actinomyces grow faster in drier conditions than in moist conditions.

4.3.5 Pressure drop in biofilters

Pressure drop of each filter material was calculated by using Ergun's equation. UGN Umwelttechnik GmbH has used porosity of 0.5 for UgnCleanPellets © B and UgnCleanPellets © N in their calculations, which is also used in this work. Porosities of Langfaserfiltergranulat, vermiculite and activated carbon needed to be estimated. The calculated average particle diameters and estimated porosities are introduced in Table 9.

Table 9: Calculated average particle diameters and estimated porosities of studied filter material

Material	Average particle diameter (mm)	Porosity
Langfaserfiltergranulat	8.6	0.65
UgnCleanPellets © B	5.2	0.5
UgnCleanPellets © N	5.3	0.5
Vermiculite	1.6	0.25
Activated carbon	2.2	0.25

With the introduced constants it is possible to calculate pressure drop in porous bed with Equation 15. Pressure drops in Langfaserfiltergranulat, UgnCleanPellets © B

and UgnCleanPellets © N filter beds are introduced as function of air velocity in Figure 37. Pressure drops in vermiculite and activated carbon filter beds are introduced as function of air velocity in Figure 38.

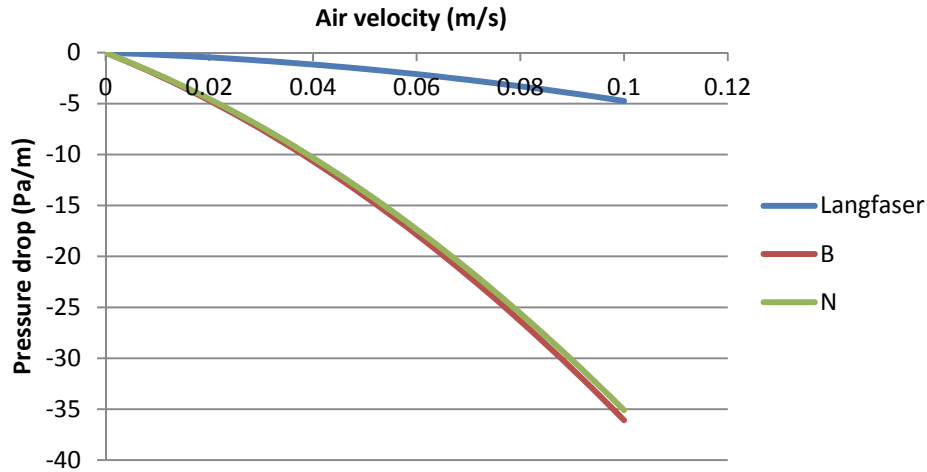


Figure 37: Pressure drops in Langfaserfiltergranulat (Langfaser), UgnCleanPellets © B (B) and UgnCleanPellets © N (N) filter beds as function of air velocity. Pressure drops are calculated with Ergun's equation.

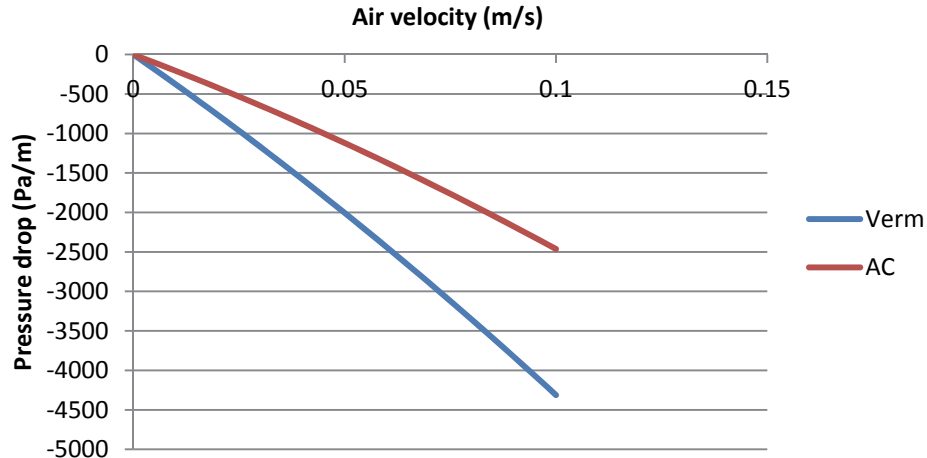


Figure 38: Pressure drops in vermiculite (Verm) and activated carbon (AC) filter beds as function of air velocity. Pressure drops are calculated with Ergun's equation.

As can be seen from Figures 37 and 38, pressure drop is the lowest in Langfaserfiltergranulat filter bed. Reason for that is the largest particle size of Langfaserfiltergranulat. Vermiculite has the smallest particle size which causes the highest pressure drop in vermiculite filter bed. The pressure drop is very high also in activated carbon filter bed. Pressure drops in UgnCleanPellets © B and UgnCleanPellets © N filter beds are almost identical caused by the similar properties of the materials.

In biofilters, low pressure drop is always desired. With low pressure drop the operational costs decrease. (Deviny et al. 1998.) In this perspective Langfaserfiltergranulat would be the best of studied materials for biofilter material. The pressure drop in Langfaserfiltergranulat bed is much lower than reported pressure drop in coconut fiber, polyurethane foam or perlite bed (Filho et al. 2010, Paca et al. 2001, Rene et al 2009). However it must remember that growth of biomass significantly increases the pressure drop in biofilter (Kennes & Veiga 2001, Ryu et al. 2010, Morgan-Sagastume 2001). Therefore the calculated results are valid only when biofilter is started.

4.3.6 Selection of the best biofilter material

Aim of this work was to find a good material for biofilter treating exhaust gases of dry toilet. According to filter performance results it is fairly difficult to choose the best biofilter material, because there was no biofilter that was able to degrade ammonia efficiently from air through whole experiment. On the other hand it was assumed that reason for bad performance in biofilters was too low humidity of the inlet gas and drying of the filter bed. Therefore it is possible that by using decent humidifying or wetting equipment the biofilters would have performed significantly better.

At the beginning of the experiment activated carbon biofilter removed ammonia from air more efficiently than other biofilters. However, nitrifying bacteria were not able to be active on activated carbon and ammonia was mainly removed through adsorption. Because of that activated carbon saturated with ammonia and RE decreased.

Only biofilters that were able to remove significant amounts of ammonia micro-biologically during the experiment were UgnCleanPellets © B and UgnCleanPellets © N. At the beginning of the experiment both biofilters were able to remove ammonia efficiently from air, but RE of UgnCleanPellets © N was slightly larger than RE of UgnCleanPellets © B. On the other hand, at the end of the experiment when the biofilters had dried, UgnCleanPellets © B had larger RE than UgnCleanPellets © N.

Biofilter material should have low pressure drop as described earlier. Within this frame Langfaserfiltergranulat would definitely be the best filter material. It has the lowest pressure drop. UgnCleanPellets © B and UgnCleanPellets © N have also fairly small pressure drop, less than 40 Pa/m with air velocity 0.1 m/s. In vermiculite and activated carbon the pressure drop is remarkably high.

High water-holding capacity is a desired characteristic for biofilter material. With that it is possible to maintain sufficient MC for microbial activity. In this experiment vermiculite was discovered to have very good water-holding capacity. At the end of the experiment the MC of vermiculite was still 53.7 %. Activated carbon and Langfaserfiltergranulat had also capability to maintain moisture conditions inside the filter bed. Lowest water-holding capacity was in UgnCleanPellets © B and UgnCleanPellets © N.

For the foregoing reasons it is impossible to decide one best biofilter material. One material removed ammonia efficiently at the beginning of the experiment and an-

other at the end of it. One material has high water-holding capacity but cannot maintain microbial activity. Therefore a new biofilter material could be developed by combining different filter materials. Probably the best combination is UgnCleanPellets © B and vermiculite. UgnCleanPellets © B is able to maintain microbial activity and remove ammonia efficiently from air. By adding vermiculite to UgnCleanPellets © B the water-holding capacity of the material would improve and the material would dry slower. In that way it is possible to maintain microbial activity in biofilter longer in dry conditions. With particle size of UgnCleanPellets © B the pressure drop in biofilter will be small. UGN Umwelttechnik GmbH has produced filter material that includes UgnCleanPellets © B and vermiculite and experiments with that in larger scale will be done in DryCloset project.

4.3.7 Suggestions for larger scale experiment

Experiments with biofilter are going to be continued with new filter material described in Chapter 4.3.6. The future experiments are done in larger scale but still in laboratory. Aim of the experiments is to find out the characteristics of the new filter material. Suggestions for easier and more reliable larger scale experimental setup are introduced in this Chapter.

A new biofilter column needs to be built for larger scale experiment. A schematic view of larger biofilter column is introduced in Figure 39.

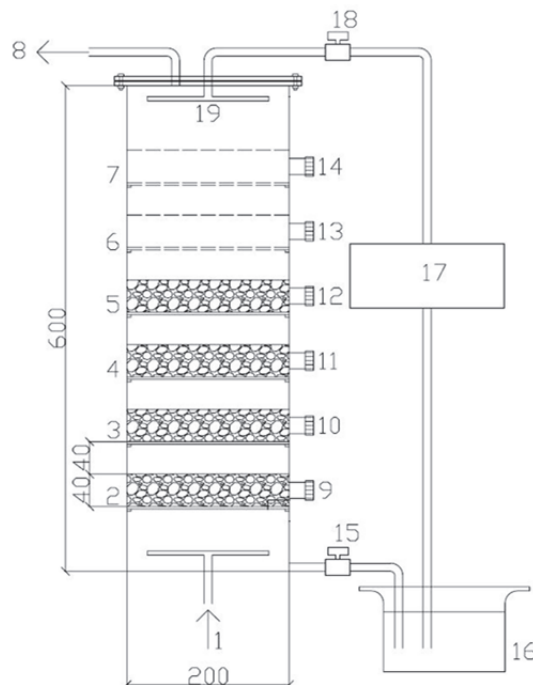


Figure 39: Schematic view of larger scale biofilter. 1 = Inlet gas, 2 - 5 = Filter bed layers, 6 - 7 = Opportunity to increase the volume of the filter bed with two extra layers, 8 = Outlet gas, 9 - 14 = Filter material sampling ports, 15 = drain for excess water and air proof valve, 16 = water container for wetting, 17 = water pump, 18 = air proof valve, 19 = wetting.

The volume of the filter bed in the new column is 5 l. In laboratory the maximum air flow that can be used is 10 l/min. With air flow of 5 l/min the EBRT of the column is 1 min. By increasing the air flow to 10 l/min the EBRT will decrease to 0.5 min and LR increases. With increase in LR it is possible to find a critical LR that cannot anymore be treated with 100 % RE.

The filter bed is divided in four layers to prevent compaction of the filter bed. With four layers it is also possible to collect more detailed data of temperature and humidity in filter bed by using data loggers in all layers. There is also opportunity to add two more filter bed layers in filter column.

As was discovered in this work, it is essential to have sufficient MC in biofilter. If the filter bed dries too much the biological activity will reduce and filter performance will decrease. Therefore there is possibility to wet the filter bed in the new filter column. That can be done by sprinkling water on the top of the filter bed. In the filter column there is also a drain for possible excess water.

The filter column is also equipped with six test ports. If biofilter does not perform with desired RE, it is possible to take sample of the filter material. From the sample the MC of filter bed and existence micro-organisms can be determined. That way it is possible to try to increase the filter performance by for example wetting the filter bed more.

4.3.8 Sources of error

In this Chapter the most significant sources of error are described. Leakages in filter columns, difficulty in regulation of air flow, compaction of the filter beds and inaccuracy of the ammonia electrode caused error to results. In the experiments, collection of air samples was very time consuming and therefore it was impossible to take parallel samples. Because of that actual error in one measurement could not be calculated. In addition to introduced sources of error, all used instruments have error in the results they give, but those errors are assumed to be negligible compared to the introduced ones.

Leakages in filter columns

During the experiment there were a few leakages in Langfaserfiltergranulat, UgnCleanPellets © B, UgnCleanPellets © N and vermiculite filter columns. Leakages were located and sealed immediately when they appeared. After sealing compound had dried the filter column was used again in the experiment. Maintenance periods of each filter column are introduced in Table 10.

Table 10: Maintenance periods of each biofilter during the experiment with five biofilters. Biofilters were maintained only when there was leakage in filter column.

Biofilter	Period of maintenance
UgnCleanPellets © B	2.8.2011 9:30 - 2.8.2011 15:15
UgnCleanPellets © N	2.8.2011 9:30 - 3.8.2011 8:00
Vermiculite	2.8.2011 9:30 - 3.8.2011 8:00
Langfaserfiltergranulat	9.8.2011 14:15 - 10.8.2011 9:50
Vermiculite	9.8.:2011 14:15 - 10.8.2011 9:50
Langfaserfiltergranulat	28.8.2011 14:15 - 14.8.2011 12:10
Vermiculite	28.8.2011 14:15 - 14.8.2011 12:10
Vermiculite	19.9.2011 9:30 - 20.9.2011 8:10
UgnCleanPellets © B	21.9.2011 12:30 - 22.9.2011 8:50
UgnCleanPellets © B	3.10.2011 9:30 - 4.10.2011 8:20

Leakages in filter columns have had effect on single results before sealing the leakages. Naturally, when part of the inlet gas escapes from the filter column and does not flow through the gas washing bottle, the ammonia concentration in acid decreases. That causes increase in RE.

Amount of leaking gas was impossible to measure. Therefore it is impossible to calculate how much error leakages have caused to the results. If it is estimated that 10 % of the inlet gas escapes from filter column, the calculated ammonia concentration in outlet gas is 10 % smaller than without leakage. On the other hand the ammonia concentration in outlet gas without leakage would be 11.14 % larger than the calculated ammonia concentration with leakage. The effect of 10 % leakage on RE depends on the ammonia concentration in outlet gas and it should be calculated for each result separately.

Regulation of air flow in all six lines

During the experiment there were difficulties to have exactly 1 l/min air flow in all six air lines. The challenge was that the used urine container (Woulff bottle) could not stand pressure. Therefore the inlet gas flow to Woulff bottle had to be regulated to value of 6 l/min. Without any excess air flow it was difficult to have 1 l/min air flow in all air lines. It also caused variation in air flows during sampling. However, the air flows were regulated to 1 l/min as precisely as it was possible. Degree of error caused by variation in air flows behaves similarly with error caused by leakages.

Compaction of the filter beds

During the experiment the height of all filter beds decreased. That decreases the volume of the filter bed. As can be seen from Equations 5 and 6 (see Chapter 2.4.1) LR and EC of the filter are inversely proportional to bed volume. When the filter bed volume decreases, LR and EC increases.

LR and EC results are calculated with filter bed volume 1 l for all five biofilter. This could have been done because in this way the comparability of the results remains and selection of best filter material has been easier. Decrease in bed height does not effect on RE values.

Accuracy of the ammonia electrode

In ammonia concentration measurements with ammonia electrode Orion 9512HPBNWB, standard solutions of 1, 10, 100 and 1000 mg NH₃-N/l were used. To get accurate results the measured ammonia concentrations should be inside this range. At the beginning of the experiment when the biofilters performed well concentrations below 1 mg NH₃-N/l were measured (smallest 0.055 mg NH₃-N/l). In all those cases the RE has been more than 96 %. If in the RE calculations the ammonia concentrations below 1 mg NH₃-N/l are changed to value 1 mg NH₃-N/l, the REs would still be more than 95 %. Therefore it can be said that error caused by too low ammonia concentration is negligible.

Standard method SFS 3032 was used to determine the error in ammonia concentrations measured with ammonia electrode. 3rd October 2011 the ammonia concentrations were measured with ammonia electrode and spectrophotometrically according to standard method. Results of ammonia electrode were on average 9.2 % smaller than results of standard method. Standard deviation in difference between ammonia electrode and standard method was 1.1 %.

Repeatability of standard method was also determined. Ammonia concentration of parallel samples was measured spectrophotometrically. Difference between the parallel measurements was less than 0.2 %.

Ammonia electrode was used instead of standard method because the ammonia electrode was relatively quick to use. On the other hand the standard method would have been very time consuming. With standard method it would have been possible to do measurements maximum twice per week. The error in results of ammonia electrode was very constant. Therefore the results measured with ammonia electrode are comparable with each other.

4.4 Volatile organic compounds in urine

VOCs in headspace of urine were determined qualitatively by pumping air from the headspace to a sampling tube. Sampling times 1 and 10 min were used. Also a sample from laboratory air was analyzed. The analysis was not quantitative and surprisingly more peaks were found in sampling tube in which air was pumped for 1 min than in tube where air was pumped for 10 min. The results of VOC analysis are introduced in Table 11.

Table 11: Volatile organic compounds determined by GC/MS from absorbent tube in which air from above stored urine was pumped for 1 or 10 min. Sampling time for laboratory air was 25 min.

Compound group	Laboratory air ($\mu\text{g}/\text{m}^3$)	1 min ($\mu\text{g}/\text{m}^3$)	10 min ($\mu\text{g}/\text{m}^3$)
Aldehydes	4	45	4
Alkanes	7	-	28
Alkenes	6	35	6
Alcohols	49	167	44
Amines	-	29	13
Aromatic compounds	5	4	42
Esters	2	-	-
Halogenated compounds	4	5	1
Ketones	14	67	19
Organic acids	13	127	10
Unidentified	4	168	40
Total	107	647	207

As can be seen from Table 11, aldehydes, alkanes, alkenes, alcohols, amines, aromatic compounds, halogenated compounds, ketones and organic acids were found in higher concentrations in the headspace of urine than in laboratory air. Presence of alcohols, aldehydes, amines, hetero cyclic compounds and ketones in urine has been reported previously in literature (Zlatkis et al. 1981, Pysanenko et al. 2009, Storer et al. 2011). Also presence of sulfur containing organic compounds in urine has been reported (Storer et al. 2011). In this analysis sulfuric compounds were not found.

Challenge in this analysis was that the sampling was done in laboratory. The laboratory air had VOCs and contamination was probable. The accuracy of the analysis could have been improved by doing the sampling in clean environment and taking more parallel samples. Also the sampling time for the headspace and laboratory air samples could have been the same.

4.5 Volatilization of ammonia from stored urine

During the study it was possible to collect fairly large amount data of volatilization of ammonia from stored urine. A mass transfer coefficient for ammonia from urine to air was calculated from Equation 1 (see Chapter 2.2.1).

In calculations data from experiment with five biofilters was used. In that experiment 2000 ml Woulff bottle was used as a urine container. Used urine volume was 1000 ml and air flow to Woulff bottle was 6 l/min. Hence the air in Woulff bottle changes completely six times per minute. Therefore in calculations it was assumed that ammonia concentration in air was zero. With that assumption the value of the mass transfer coefficient is 0.00145 ± 0.000132 m/h.

Whelan et al. (2010) investigated ammonia volatilization from food waste anaerobic digestate. They calculated a mass transfer coefficient for ammonia by using same model as is used in this work. The value of the mass transfer coefficient was 0.000125 which is order of magnitude smaller than value calculated in this work. (Whelan et al. 2010.) In this work turbulent conditions prevailed in Woulff bottle but in study of Whelan et al. (2010) the conditions were laminar and therefore they got smaller mass transfer coefficient. Values of mass transfer coefficient for ammonia from liquid manure to air are also reported. The values of mass transfer coefficient vary between 0.00468 and 0.684 m/h. (Ni 1999.) The value of mass transfer coefficient depends on speed of air flowing above urine or manure, temperature, air density and air viscosity. Therefore the values of the reported mass transfer coefficients vary significantly.

By using the calculated mass transfer coefficient it is possible to model ammonia volatilization in urine tank. Dependence of ammonia flow from urine to air, ammonia concentration in urine and area of the air urine interface is introduced in Figure 40.

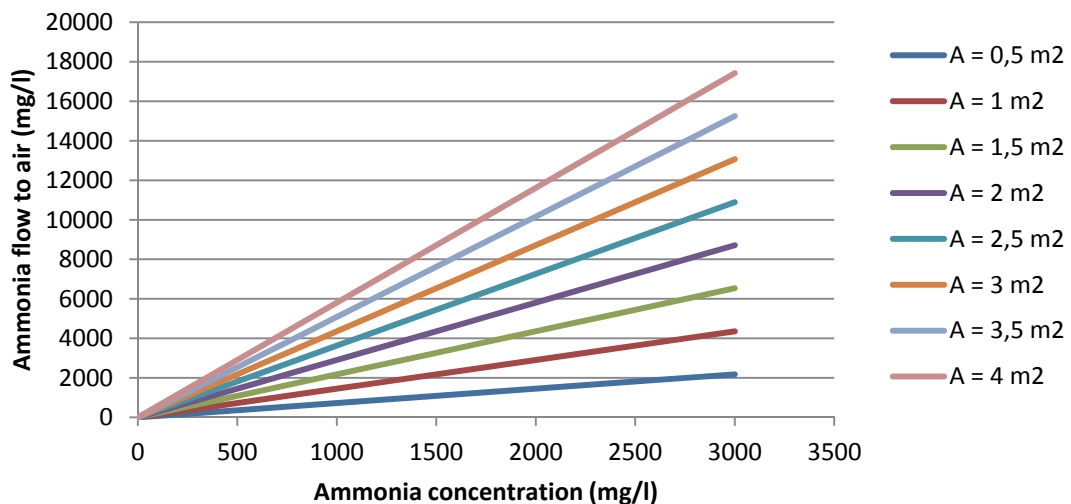


Figure 40: Dependence of ammonia flow from urine to air, ammonia concentration in urine and area of the air urine interface.

As can be seen from Figure 40, ammonia concentration of urine and surface area of air urine interface have significant effect on the ammonia flow from urine to air. When ammonia concentration in urine or the area of the air urine interface increases, ammonia flow from urine to air increases. In dry toilet, it is difficult to decrease the ammonia concentration in urine without chemical addition. On the other hand, with designing it is possible to decrease the surface area of the air urine interface and that way decrease the ammonia flow from urine to air. With smaller ammonia flow the odors will be lower and if the odors are treated with biofilter, the LR of the biofilter will be smaller. In that way the volume of the biofilter can be decreased. If more accurate estimations of ammonia flow rate from urine to air in dry toilet are desired, the mass transfer coefficient should be determined in conditions similar as in the dry toilet.

5 CONCLUSIONS

Dry toilets are a possible way to arrange sanitation in developing countries and economize on waste water treatment costs in industrialized countries. With decent ventilation unpleasant odors can be prevented in dry toilet. However, it is possible that the odorous compounds become a problem outside of the building and in that case the exhaust gases of dry toilet need to be treated. A possible way to treat the exhaust gases is biofiltration.

The aim of this study was to find a good material that can be used in the biofiltration of the exhaust gases of dry toilet and two different experiments were done with that purpose. In both experiments real urine was used as a source of malodorous compounds. Five different filter materials were tested. Performance of the biofilters was determined by measuring ammonia and TOC removal.

First experiment was done with one biofilter. The aim of this experiment was to see if there was something to improve in experimental setup or analytical methods. The experiment clearly showed that biofilter cannot remove ammonia and organic compounds efficiently from air in dry conditions. It was obvious that the inlet air of the biofilter must be humidified in the experiment with five biofilters.

The aim of the experiment with five biofilters was to find out which material is the best for the biofiltration of the exhaust gases of dry toilet. At the beginning of the experiment, the best removal efficiencies above 95 % were achieved with UgnCleanPellets © B, UgnCleanPellets © N and activated carbon biofilters. However, in spite of the humidification of the inlet gas all biofilter beds dried during the experiment and the performance of the biofilters decreased. Drying also caused fungal growth in Langfaserfiltergranulat, UgnCleanPellets © B and UgnCleanPellets © N biofilters. The TOC removal efficiency of all biofilters was lower than the ammonia removal efficiency during the whole experiment.

During the experiment nitrate concentration and the amount of micro-organisms in the filter beds were determined twice. Increase in nitrate concentration during the experiment shows that part of ammonia was degraded biologically in Langfaserfiltergranulat, vermiculite and activated carbon biofilters. However, the removal of ammonia and TOC was mainly physical in these biofilters. Biodegradation of ammonia and TOC in UgnCleanPellets © B and UgnCleanPellets © N biofilters was significant. Heterotrophic bacteria, sulphate oxidizing bacteria, *Nitrosomonas* and *Nitrobacter* were detected from all biofilters. Yeasts were found only from Langfaserfiltergranulat, UgnCleanPellets © B and UgnCleanPellets © N biofilters. The amount of micro-organisms was the highest in Langfaserfiltergranulat biofilter. However, the performance of the Langfaserfiltergranulat biofilter was not the best.

High water-holding capacity and low pressure drop are desired characteristics of biofilter material. Vermiculite and Langfaserfiltergranulat had the best water-holding capacities. Other filter materials dried significantly during the experiment. Drying was the most intense in UgnCleanPellets © B and UgnCleanPellets © N biofilters. The pressure drop in the filter beds was calculated with Ergun's equation. The pressure drop was the lowest in Langfaserfiltergranulat. Also UgnCleanPellets © B and UgnCleanPellets © N had a low pressure drop. In vermiculite and activated carbon the pressure drop was a hundred times higher than in the other filter materials.

The experiment showed that ammonia and volatile organic compounds formed in stored urine can be removed from air with biofiltration. However, the biofiltration of these compounds is efficient only if moisture conditions are maintained in the filter bed. Humidification equipment used in this experiment is not sufficient to keep filter bed moisture. In further experiments and full scale applications wetting of the filter bed is needed. The experiment also showed that high amount of micro-organisms does not guarantee high biofilter performance and therefore the amount of micro-organisms is not the most important criterion for the selection of the best biofilter material.

According to the results of the experiment with five biofilters, it was impossible to decide which material is the best for the biofiltration of the exhaust gases of dry toilet. None of the biofilters were able to remove ammonia and TOC from the air efficiently through the whole experiment. Suggestion is that a new biofilter material is developed by combining UgnCleanPellets © B and vermiculite. UgnCleanPellets © B is a good growth medium for micro-organisms. By adding vermiculite to UgnCleanPellets © B the water-holding capacity of UgnCleanPellets © B can be improved. If the particle size of the new material is similar with the particle size of UgnCleanPellets © B, the pressure drop in the filter bed will be low. UGN Umwelttechnik GmbH has produced new biofilter material and laboratory experiments will be done with that in DryCloset project. Those experiments are done in a larger scale but still in laboratory. In those experiments regulation of loading rate should be done to see if there is a critical loading rate that cannot be anymore treated with 100 % removal efficiency. Also the regulation of the moisture content in the filter bed should be better.

Volatile organic compounds in the head space of stored urine were also determined qualitatively in this experiment. The same compounds that have been reported in the literature were detected. Also it was possible to calculate a mass transfer coefficient for ammonia from urine to air with the data collected during the experiment. The calculated mass transfer coefficient was in the same range as the values that have been reported in the literature. However the mass transfer coefficient depends on the circumstances and the results calculated with it give only approximate results of reality situation.

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APPENDIX 1: DATA COLLECTED WITH DATA LOGGERS

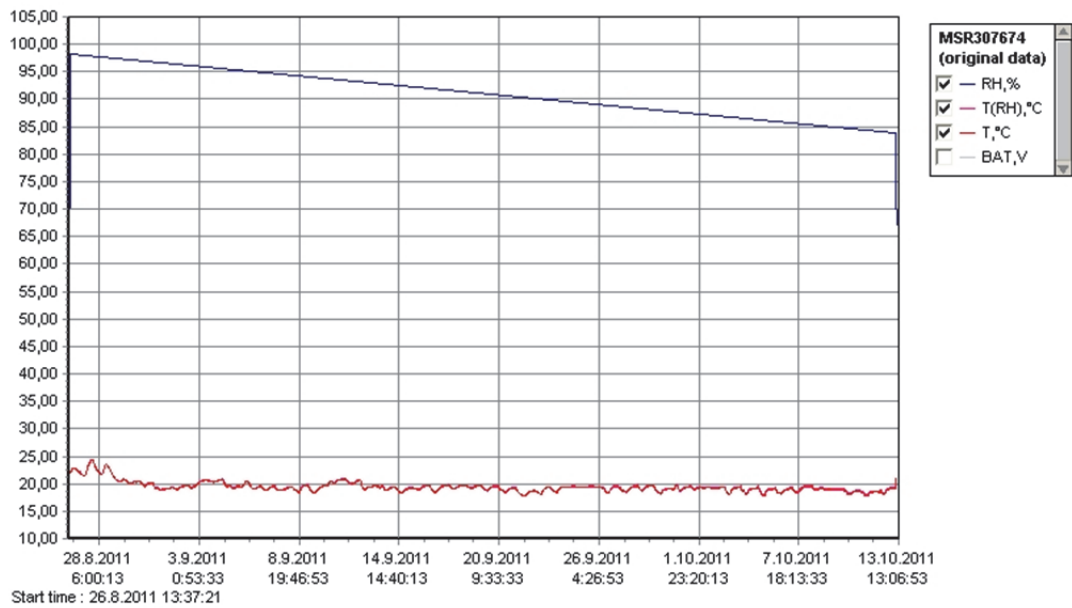


Figure 41: Humidity and temperature data collected from Langfaserfiltergranulat biofilter during the experiment with five biofilters. RH = Relative humidity (%), T = Temperature (°C)

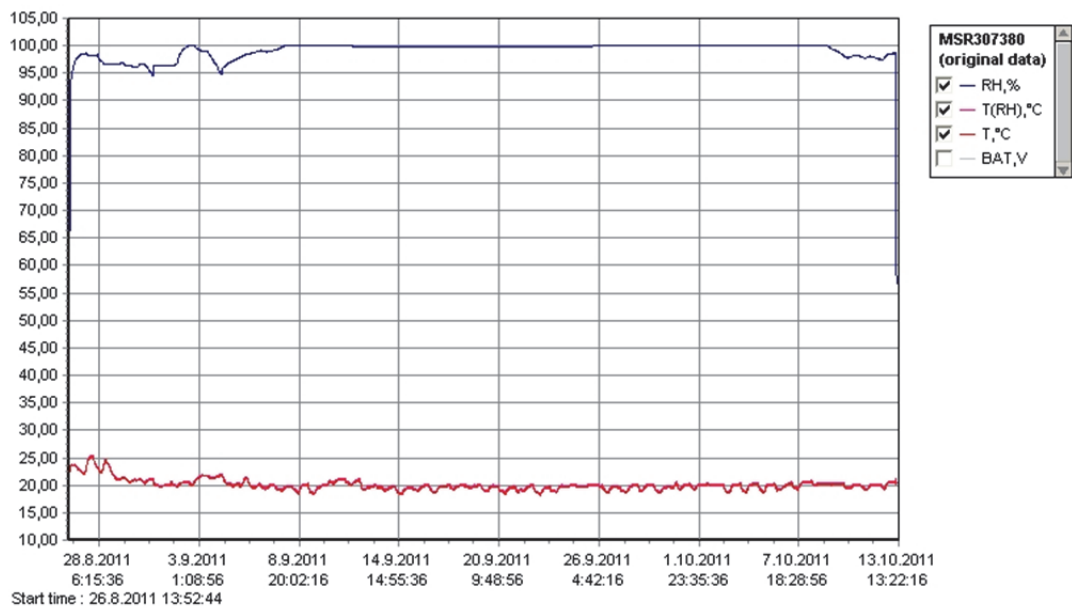


Figure 42: Humidity and temperature data collected from UgnCleanPellets © B biofilter during the experiment with five biofilters. RH = Relative humidity (%), T = Temperature (°C)

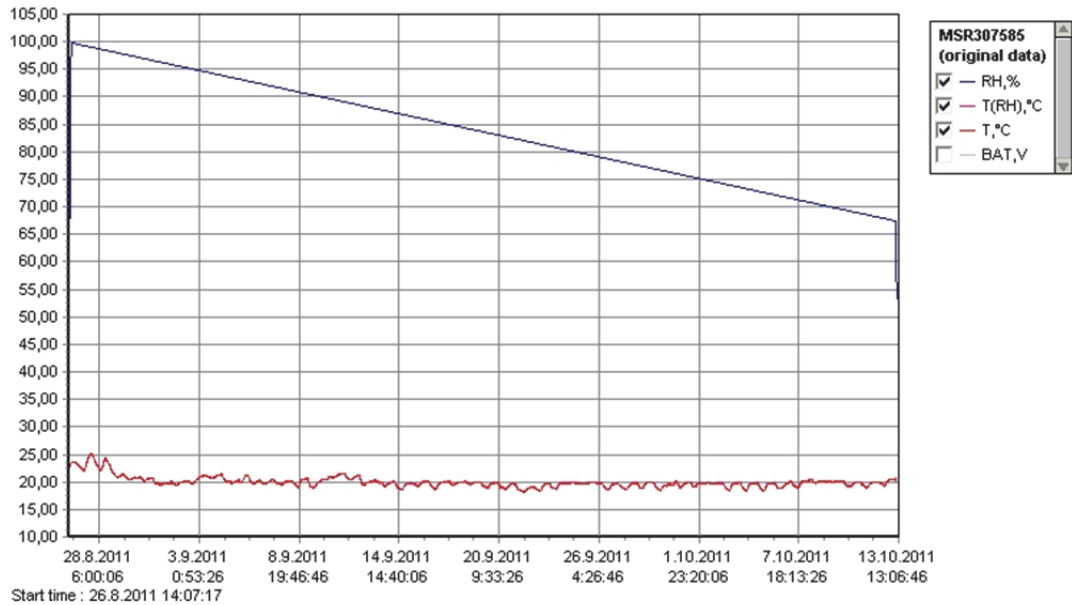


Figure 43: Humidity and temperature data collected from UgnCleanPellets © N biofilter during the experiment with five biofilters. RH = Relative humidity (%), T = Temperature (°C)

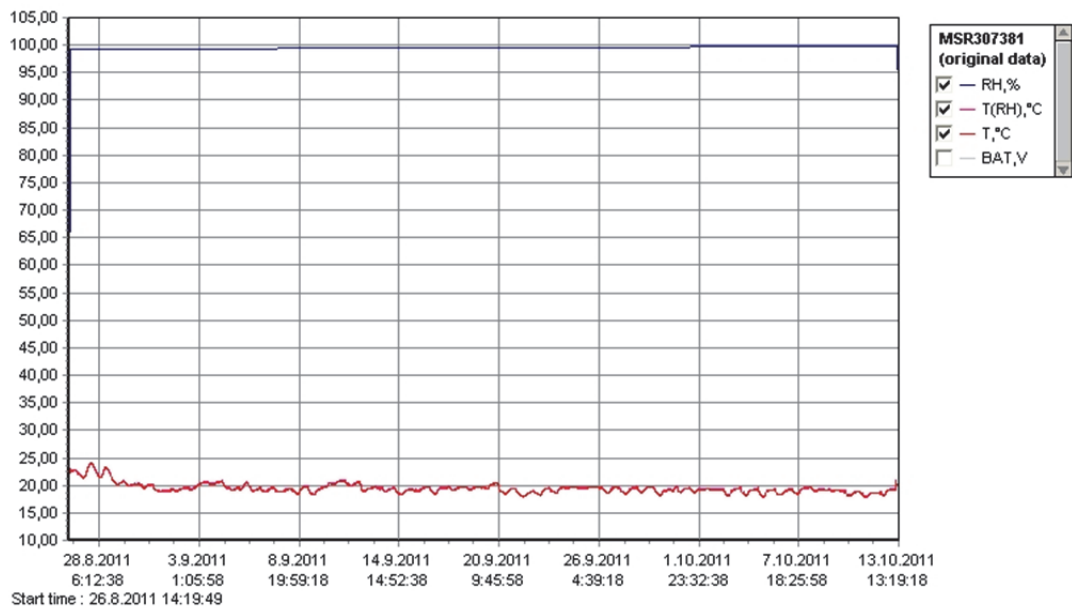


Figure 44: Humidity and temperature data collected from vermiculite biofilter during the experiment with five biofilters. RH = Relative humidity (%), T = Temperature (°C)

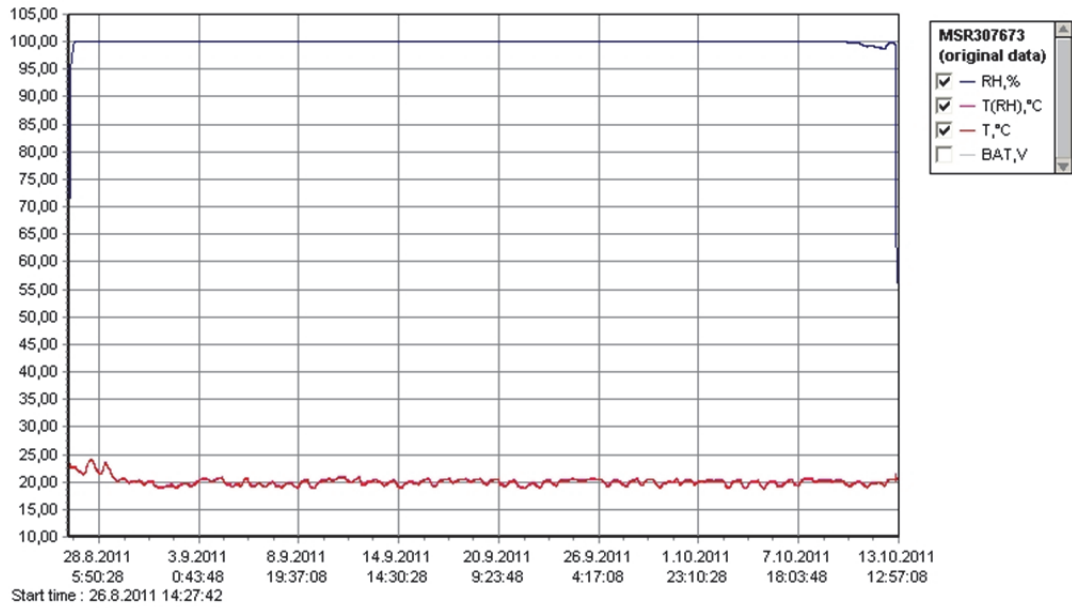


Figure 45: Humidity and temperature data collected from activated carbon biofilter during the experiment with five biofilters. RH = Relative humidity (%), T = Temperature (°C)