

# **NUTRIENT REMOVAL FROM STORMWATER BY USING GREEN SORPTION MEDIA**

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A thesis submitted for the partial fulfillment of the requirements  
for the degree of Master of Science  
in the Department of Civil, Environmental and Construction Engineering  
in the College of Engineering and Computer Science  
at the University of Central Florida  
Orlando, Florida

Fall Term  
2008

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## **ABSTRACT**

High nitrogen and phosphorus content in storm water runoff has affected groundwater, springs and surface water by impacting ecosystem integrity and human health. Nitrate may be toxic and can cause human health problem such as methemoglobinemia, liver damage and even cancers. Phosphorus may trigger the eutrophication issues in fresh water bodies, which could result in toxic algae and eventually endanger the source of drinking waters.

Sorption media with mixes of some recycled materials, such as sawdust and tire crumb, combined with sand/silt and limestone, becomes appealing for nutrient removal in environmental management. This paper presented is a specific type of functionalized filtration media, Langmuir and Freundlich isotherms with reaction kinetics for nutrient removal using a suite of batch tests represented.

Pollutants of concern include ammonia, nitrite, nitrate, orthophosphate and total dissolved phosphorus. Application potential in storm water management facilities, such as dry ponds, is emphasized in terms of life expectancy and reaction kinetics. As compared to the natural soil that is selected as the control case in the column test, our green sorption media mixture is proved relatively effective in terms of removing most of the target pollutants under various influent waste loads.

## **ACKNOWLEDGMENTS**

It is difficult to express my gratitude to my M.Sc supervisor Dr. Ni Bin Chang, professor of Department of Civil, Environmental and Construction engineering. With his great efforts and inspiration, he helps me to explain everything in a simple and understandable way.

I am grateful to Dr. Marty Wanielista for his valuable advice and help for this thesis. His experience helped me to understand the project work well. I am thankful to all my course instructors for their valuable lectures and information. I greatly appreciate for the knowledge they give to me during the course work.

I am indebted to all my friends at the UCF. They give me a stimulating and fun environment to learn and grow. I am especially grateful to all who work in this project.

Lastly and most importantly, I am grateful to my parents. They supported me, taught me and loved me. From my childhood to now, they are encouraging me to gain knowledge and use that for the well of mankind. I am also grateful to my wife for her sacrifice in the last two years.

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# CHAPTER 1: INTRODUCTION

## Introduction

Nutrients such as ammonia, nitrate, nitrite and phosphorus are common contaminants in the water bodies all over the world. Nutrient removal is very important for the sustainability of the aquatic ecosystem and environment. All these nutrients have acute and chronic harmful outcome for human beings and ecosystems directly or indirectly. According to USEPA, unionized ammonia is very toxic for salmonid and nonsalmonid fish species (1). Fish mortality, health and reproduction can be hampered by the presence of 0.100 mg/L to 10.00 mg/L of ammonia (1). Nitrate is more toxic than nitrite and can cause human health problems such as liver damage and even cancers (2, 3). Nitrate can also bind with hemoglobin and create a situation of oxygen deficiency in infant's body called methemoglobinemia (4). Nitrite, however, can react with amines chemically or enzymatically to form nitrosamines that are very strong carcinogens (5).

Nitrogen and phosphorus compounds are the most frequent measurements to indicate nutrient loadings. Nitrogen and phosphorous-containing compounds are found in urban storm water runoff primarily from highways (6). Nitrates normally result from vehicular exhaust on the road itself and adjacent soils from fertilization of landscaped areas beside the roads and the neighboring residential areas (7, 8). On the other hand, when urban regions gradually expand due to regional development, centralized sewage collection, treatment, and disposal is often unavailable for both geographic and economic reasons. Thus, decentralized or on-site wastewater treatment systems (OWTS) may be necessary to protect public health.



Nationwide, wastewater effluent from OWTS can represent a large fraction of nutrient loads to groundwater aquifers, however.

Nitrogen, particularly nitrate-N, easily moves from terrestrial ecosystems into surface and ground waters, including lakes, streams, rivers, and estuaries (9, 10, and 11). According to USEPA, nitrate and nitrite levels in the water bodies should not be above 10.00 mg/L  $\text{NO}_3^-$ -N and 1.000 mg/L  $\text{NO}_2$ -N, respectively (12). For effective storm water management, bioretention or bioinfiltration pond is a relatively new urban storm water best management practice (BMP) (13). Yet the use of differing filter media in wet and dry bioretention ponds turns out to be an appealing engineering approach in dealing with the increasing trend of higher nutrient concentrations that is expected to continue in the surface and groundwater systems. Large-scale implementation with different filter media to remove nutrients will be popular in the future (14, 15). The main purpose of this research is to examine the sorption capacity and reaction kinetics of selected mixes of filter media for nutrient removal using isotherm and column tests. Pollutants of concern mainly include ammonia, nitrate, nitrate, and orthophosphate (OP), total dissolved phosphorus (TDP), etc. Filter media that were reviewed include but are not limited to tire crumb, sawdust, activated carbon, iron amended resins, orange peel, peat, leaf compost, naturally occurring sands, zeolites, coconut husks, polymers, soy bean hulls, etc.

## **Objectives**

The objectives of this study are thus to:

- 1) present a specific functionalized filtration media for nutrient removal via a systematic literature review,

- 2) determine the absorption/adsorption isotherm for different nitrogen and phosphorus species,
- 3) estimate the life expectancy of selected filter media in the field,
- 4) investigate the removal efficiency of nutrient from storm water,
- 5) understand the kinetics of selected filter media mixture, and
- 6) discuss the field implementation potential.

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## CHAPTER 2: LITERATURE REVIEW

### **Nutrient Concentrations in Stormwater, Groundwater and wastewater in Florida**

Both the Florida Department of Environmental Protection (FDEP) and St. Johns River Water Management District (SJRWMD) found that maximum total phosphorus (TP), orthophosphate, total nitrogen (TN), ammonia-nitrogen (NH<sub>3</sub>-N) and nitrate-nitrogen (NO<sub>3</sub>-N) and nitrite-nitrogen (NO<sub>2</sub>-N) was 0.329 mg/L, 0.265 mg/L, 1.300 mg/L, 0.046 mg/L, and 0.048 mg/L, respectively in stormwater runoff (1). Stormwater runoff is one possible source of nitrogen, among others such as septic tanks and land-based application of reclaimed wastewater or fertilizer, which can contribute to elevated nitrate and nitrite concentrations in the Upper Floridian aquifer. It was evidenced that nitrate concentrations have increased in many Upper Floridian aquifer springs since the 1950s. Phelps (2004) reported that nitrate concentrations ranged from less than 0.020 to 12.00 mg/L, with a median of 1.200 mg/L, for 56 Upper Floridian aquifer wells sampled in Marion County during 2000-2001 (2). It is known that nitrate concentrations have exceeded 1.000 mg/L in recent years at some springs in Lake, Marion, Orange, Seminole, and Volusia Counties according to Phelps et al. (2006) and St. Johns River Water Management District (2008) (3, 4). Increasing trends in nitrate concentration were documented in Volusia County springs, such as DeLeon and Gemini Springs (3) and Blue Spring (4). The nutrient concentration in a medium strength (i.e. 460.0 L/capita.d) wastewater is 40.00 mg/L of TN and 7.000 mg/L TP (5).

## **Technologies used for treatment of stormwater, wastewater, groundwater and drinking water**

A number of devices, collectively known as structural Best Management Practice (BMP) and low impact development (LID) were employed to treat contaminated water with respect to either physicochemical or microbiological principles (6). Nutrient in stormwater, groundwater and wastewater can be removed by using physicochemical processes, such as activated carbon absorption, ion exchange with synthetic resins, reverse osmosis, and electro dialysis. Bioinfiltration process with different filter media has been gaining popularity due to its cost-effectiveness. Within the context of bioinfiltration, two important processes that result in the transformation of ammonia to nitrogen gas are nitrification by autotrophic bacteria and denitrification by either autotrophic or heterotrophic bacteria. In nitrification, there are two steps: Ammonia is transformed to nitrite with the help of *nitrosomonas* bacteria and nitrite is transformed to nitrate with the help of *nitrobactor* in an aerobic environment. In denitrification, nitrate is transformed to nitrogen gas by heterotrophic or autotrophic bacteria in an anoxic condition (5). Although nitrification and denitrification are popular for wastewater treatment, it is now used for drinking water treatment in Europe. Denitrification needs an external carbon source and presently ethanol, methanol and acetate are used as a carbon source. Additional treatment may be required for the effluent for those chemicals. Filter media can act as a harmless carbon source and supporting element for microbial colony development. Anaerobic ammonia oxidation (ANAMMOX) process is another biological autotrophic process in which partial nitrification and ammonia is converted to nitrogen gas in the presence of nitrite in an anoxic condition. Here nitrite is acting as an electron acceptor and no external carbon source is needed for denitrification as the bacteria are autotrophs (7). Phosphorus can also be removed by PAO (i.e. Phosphorus accumulating organisms) in

biological process in anaerobic and aerobic stage (7). Most of the filter media may improve solid-liquid contact and prevent channeling via physicochemical processes too with a more efficient way. In general, higher surface area of clay in natural soil might be able to provide more contact area for the solid to absorb and more space for bacteria to develop the colony. But functionalized filter media might have a better ion exchange capacity to support absorption/adsorption, better retaining capability for adsorbed nutrient and more surface area for the bacteria colony to develop.

Riverbank filtration (BF) is another innovative process used in Europe for centuries to remove microorganisms from surface water (8). There are different technologies to remove phosphorus including: 1) chemical precipitation, 2) biological treatment, 3) crystallization, 4) ion exchange, 5) magnetic separation, 6) adsorption/absorption, 7) tertiary filtration and 8) sludge treatment (9). Phosphorus removal from storm water may be achieved mostly by both precipitation and absorption processes.

Some functionalized sorption media used by different researchers for phosphorus removal are sand rich with Fe, Ca or Mg, gravel, limestone (a sedimentary rock largely composed of calcium carbonate,  $\text{CaCO}_3$ ), shale (fine grained sedimentary rock mostly clay minerals), light weight aggregates (LWA), zeolite (natural mineral or artificially produced alumino silicates), pelleted clay (along or in combination with soils), opaka (a siliceous sedimentary rock), pumice (a volcanic rock and natural porous mineral), wollastonite (a mineral containing calcium and ferrous metasilicate), fly ash (a residue generated from the combustion of coal), blast furnace slag (BFGS – a porous non-metallic co-product in iron and steel industry), alum (a hydrated aluminum potassium sulfate), goethite (a hydrous ferric oxide), hematite (a mineral form of iron(III) oxide,  $\text{Fe}_2\text{O}_3$ ), dolomite (a sedimentary carbonate rock or mineral

composed of calcium magnesium carbonate,  $\text{CaMg}(\text{CO}_3)_2$ , and calcite (a carbonate mineral)

(10). Table 2.1 to 2.5 shows the sorption media used to treat stormwater, wastewater, groundwater, land fill leachate and drinking water.



**Table 1: Sorption media used by different researchers to treat storm water**

No.	Sorption media	Additional environmental benefits	Physical/Chemical Properties	References
1	Sandy Coastal soil			11
2	Compost	Oil & greases, heavy metals,	Maple & elm leaf compost	12
3	Peat	Cu, Cd, Ni,		13
	Wollastonite			
	Limerock			
	Sand with quartz			
4	Alfalfa		D<4.000mm	14
	Leaf mulch compost		D<2.000mm	
	Sawdust		D<2.000mm	
	Wheat straw		D<4.000mm	
	Wood chips		D<2.000mm	
	Newspaper		D (average)<4.000mm	
	Sulfur		Large particles 2.000 to 2.360 mm and small particles 0.600 to 1.180 mm	
Limestone		D= 0.600 to 1.180 mm		
5	Crushed piping materials	Organics		15
6	Iron Sulfide			16
7	Peat	Cu, Fe, Pb, Zn		17
	Carbon sand, enretech sand or sand			
	Zeolites			
	Activated carbon			
8	Natural sand (Bank filtration)			8
10	Lignocellulosic material		Basically pine bark chips,	18
11	Clay	Cd, Pb, Ni		9
12	Zeolites			19
13	Opoka	Microorganisms		20
14	Waste medium density fiberboard (MDS) sawdust			21
9	Wood fibers	Polynuclear Aromatic Hydrocarbons	Aspen wood fibers composed of 51.00% cellulose, 26.00% hemicellulose, 21.00% lignin, and 1.000% ash	22
15	Mulch	Lead, TSS, oil and grease		23
	Soil		Sandy loam	
	Sand		Sand	
16	Zeolites	Cu, Pb, Zn		24
	Pure quartzitic sand			
17	Allophane			25

No.	Sorption media	Additional environmental benefits	Physical/Chemical Properties	References
17	Chitin		iron (18.20%) , aluminium (13.70%), calcium (12.70%) and magnesium (7.300%) and other. 4.000%-8.000% calcium carbonate	25
	Pumice			
	Bentonite			
	Steel slag			
	Lime stone			
	Zeolites			
18	Hard wood Mulch	Cu, Cd, Cr, Zn, Pb, dichlorobenzene, naphthalene, fluoranthene, benzopyrene	Silver maple, Norway maple, Red oak and Cherry mulch, size 4760 micron,	6
19	Wood fibers	Zn, Cu	D = 4.000 mm	26
	sand			
	Zeolites			
	Glass		D= 4.000 mm	
	Ash			
20	Compost			26
20	Iron Sulfide			27
21	Metallic iron		D=0.006 to 0.010 mm; Surface area 0.3125 m <sup>2</sup> /g	28
	Clinoptilolite	Fe	D=0.177-4.000 mm	

**Table 2: Sorption media used by different researchers to treat wastewater**

No.	Sorption media	Additional environmental benefits	Physical/Chemical Properties	References
1	Sand filter			29
2	Tire crumb/Tire chips	2,4-dichlorophenol (DCP), 4-chlorophenol (CP)	20.00 to 40.00 mm,	30
3	Zeolite+ Expanded Clay		2.500-5.000 mm	31
4	Polyurethane porous media		Porous structure, Average diameter 3.000-5.000 mm, External pore diameter 300.0 micron.	32
5	Limestone		D= 2.380 to 4.760 mm	33
	Sulfur		D= 2.380 to 4.760 mm	
6	Sand granules			34
7	Clay			35
8	High density module			36
9	Sandy clay loam (SCL)		Sand (53.28%), Silt (24.00%), Clay (22.72%)	37
	Loamy sand (LS)		Sand (78.28%), Silt (10.64%), Clay (11.08%)	
	Sandy loam (SL)		Sand (70.28%), Silt (14.64%), Clay (15.08%)	
10	Masonry sand		Bulk density of masonry sand is 1670 kg/m <sup>3</sup> ; Porosity of masonry sand is 0.304.	38
	Expanded shale		Expanded shale (SiO <sub>2</sub> 62.06%, Al <sub>2</sub> O <sub>3</sub> 15.86%, Fe <sub>2</sub> O <sub>3</sub> 5.800%, CaO 1.440%, MgO 1.680%); Bulk density of expanded shale is 728.0 kg/m <sup>3</sup> ; Porosity of expanded shale is 0.594;	
11	Oyster shell powder		Powder form, 28.00% Calcium, Average particle size 200.0 μm, Surface area 237.0 m <sup>2</sup> /g,	39
12	Limestone		D =2.380 to 4.760 mm	40
	Oyster shell			
	Marble chips		Mg(OH) <sub>2</sub> and CaCO <sub>3</sub>	

No.	Sorption media	Additional environmental benefits	Physical/Chemical Properties	References
13	Soy meal hull	Direct and acid dye	<0.1250 mm	41
14	Clinoptilolite			42
	Blast furnace slag		Composed of melilite, merwinite, anorthite, gehlenite	
15	Perlite			43
16	Clinoptilolite		0.300 -4.760 mm	44
	Expanded clay		0.400-5.000 mm	
	Tire crumb		0.300-5.000 mm	
	Sulfur		2.000-5.000 mm	
	Crushed oyster shell		3.000-15.00 mm	
	Utelite (expanded shale)		0.400-4.500 mm	

**Table 3: Sorption media used by different researchers to treat groundwater**

No.	Sorption media	Additional environmental benefits	Physical/Chemical Properties	References
1	Waste foundry sand	TCE, Zn, Metolachlor, Alachlor, Hearbicides		45
2	Sawdust		Monterey pine (Pinus Radiata D. Don) sawdust,	46

**Table 4: Sorption media used by different researchers to treat land fill leachate**

No.	Sorption media	Additional environmental benefits	Physical/Chemical Properties	References
1	Wood chips compost with household waste			47
	Crushed bricks			
2	Tire crumb	VOC		48
3	Wood chips			49
	Oversized pulverized brick			
	Polystyrene packing			
4	Peat	Zn, Ni, Co, Ti, Cu, Ba,		50
	Polonite		Manufactured from cretaceous rock Opoka (SiO <sub>2</sub> 39.40%, CaO 42.00%, Al <sub>2</sub> O <sub>3</sub> 4.300%, Fe <sub>2</sub> O <sub>3</sub> 2.000%)	
	Blast furnace slag		SiO <sub>2</sub> 36.20%, CaO 35.00%, MgO 13.40%, Al <sub>2</sub> O <sub>3</sub> 10.60%,	

**Table 5: Sorption media used by different researchers to treat drinking water**

No.	Sorption media	Additional environmental benefits	Physical/Chemical Properties	References
1	Newspaper		0.400 cm width ribbons, (25.49% extractives, 43.11% cellulose, 29.59% lignin, 2.590% ash)	51
2	Sulfur		D =2.380 to 4.760 mm	52, 53
	Limestone		D =2.380 to 4.760 mm	
3	Cotton waste			54

## **Stormwater treatment by sorption media**

Many researchers had tried to remove nutrients from stormwater by using different sorption media. Before 1995, researchers tried to remove nutrients mostly by sand filter method. For this reason, different types of sand filter methods had developed like: 1) Washington D.C. sand filter method around 1989, 2) Delaware sand filter design and 3) Austin sand filter (55). The removal efficiency of Delaware sand filter is solids 70.20%, TP 71.10%, NH<sub>3</sub>-N 6.700% and Total Kjeldahl nitrogen (TKN) 59.90% (29). These filter methods gave promising result but these methods can not remove all nutrients. So scholars had started to search new concepts to remove all nutrients from water. They found out that use of sorption media can be very good for nutrient removal from water bodies.

Richman (1997) found that compost had good removal for 90.00% solids, 85.00% oil and greases and 90.00% heavy metals (12). DeBusk et al. (1997) used sand (with quartz), fresh organic (peat) soil, crushed lime rock (2.500 cm nominal size) and wollastonite to remove TP, copper (Cu), nickel (Ni) and cadmium (Cd) from storm water. They found that wollastonite had very good removal efficiency for their targeted contaminants. Wallastonite could remove about 87.80% P, 97.70% Cd, 81.40% Cu and 80.30% Ni. On the other hand, Limerock, peat and sand could remove 41.40%, 44.00%, and 41.40% of P, respectively. It can be concluded that wallastonite is very effective in phosphorus removal because it contains calcium and ferrous ions (13). Calcium and ferrous ions can remove phosphorus by precipitation reaction or adsorption. It is assumed that limerock will remove P by adsorption and precipitation but a lower removal of P is observed in the above experiment. pH is also an important factor for phosphorus removal.

Kim et al., (2000) used different kinds of filter media, such as alfalfa, mulch compost, newspaper, sawdust, wheat straw, wood chips for nitrate removal from stormwater runoff in biological process. They found that alfalfa and newspaper had 100.0% nitrate removal efficiency but mulch compost had 60.00% removal efficiency. They also found that sawdust, wheat straw and wood chips had good removal efficiency (>95.00%), but wood chips showed consistently better performance than sawdust for nitrate removal. It could be concluded that all of these were electron donors and good carbon sources for promoting denitrification. They suggested that increasing the hydraulic retention time (HRT) may gain better removal. They also found that soil could only remove 7.000% to 10.00% of nitrate due to its anionic form (14). The nitrate removal is also done by other processes rather than only biological process. If the nitrate removal is only by biological process, all the media should get almost same removal but different media get different removal. So it might be a combined effect of adsorption and biological process. Bacterial growth may not be same in all media as bacteria may have preference for certain types of media.

Clark et al. (2001) conducted an experiment to improve the quality of stormwater runoff by using activated carbon, peat moss, compost and sand in aerobic and anaerobic conditions. They observed that adsorbed ammonia and nitrate was released from compost and peat moss respectively in anaerobic conditions. They found good phosphorus removal efficiency by all four media in both conditions and found no desorption condition in their system for phosphorus. But they observed that sorption was better and leaching was lesser in aerobic condition for compost. They also tried to remove heavy metals (i.e. Cu, iron (Fe), lead (Pb), and zinc (Zn)) from storm water runoff by using the same filter media and found that the removal was permanent by the media. They suggest that sorption media might not be

comfortable to retain the sorbed materials under anaerobic conditions (17). There might be other reasons for desorption. Retention time and amount of media may be responsible for desorption. If anaerobic condition is only responsible for desorption, there should not be any leachate from landfill.

Tufenkji et al. (2002) used BF method to remove pathogenic microbes from surface water. River BF method is also a very effective method for the removal of natural organic matter (i.e. NOM-dissolved and particulate humic and non-humic organic substances), odorous compounds (i.e. geosmin), fragrance compounds (i.e. menthol, limonene,  $\alpha$ -terpineol) and aromatic hydrocarbons. BF removes the pollutants by sorption, precipitation, redox reactions, complexation with organic matter, microbial degradation and dilution. According to this article, the success of BF is depending on raw water quality, characteristics of the bed sediments and retention time. So each site should be considered separately and success in one site will not indicate that it will be helpful for other sites. It is also mentioned that EPA is giving importance on bank filtration for the removal of *Cryptosporidium*. The *Cryptosporidium* oocysts (4.000-6.000  $\mu\text{m}$ ) and *Giardia* cysts (9.000-12.00  $\mu\text{m}$ ) can be removed by interception (i.e. the microbe's will encounter a collector grain due to its size and moving path) and gravitational sedimentation (i.e. the microbe's will be settled on a collector grain due to gravitational force) (8). It is not monitored that if the BF process is good for nutrient removal. If the surrounding soil has clay with mineral content, it should be an effective process for phosphorus removal. Again, soil can support the growth of nitrifiers so it will work for the removal of ammonium and nitrite. But it may not work for nitrate removal as it is proved that soil particles have little affinity for nitrate. The BF process and sorption media can be used together. In a bank filtration, if filter media is placed around the well, then



it will help to remove nutrients. Tshabalala (2002) also tried to remove pesticides by lignocellulosic materials and the media was removed about 82.00% of dichlobenil (DBN), 92.00% of chlorothalonil (CTL) and 96.00% of chlorpyrifos (CPS) (18).

Boving and Zhang (2004) used aspen wood (*Populus tremula*) fibers to remove aqueous phase polynuclear aromatic hydrocarbons (i.e. PAH such as naphthalene, pyrene, anthracene and fluorene) from stormwater runoff by column study. The ultimate removal of anthracene was 60.00%, pyrene was 89.00%, fluorene was 36.00% and naphthalene was not that much attracted by wood fibers. The research data implied that the sorption of PAH by aspen wood was related with hydrophobicity and molecular weight of the PAH. They observed some desorption but the desorption was slower than the adsorption. They also observed that the sorption rate was slow with time and smaller particles had more sorption capability (22).

Hsieh and Davis (2005) did their experiment on urban stormwater runoff in 18 columns filled with different media mixtures composed of mulch, soil and sand. Mulch was very effective in removing nitrate (about 43.00% of nitrate was removed by a mulch and sand mixture) and sand was not very effective in nitrate removal. But they had not received good ammonium and TP (only 4.000% TP removed) removal by mulch and no reason was given by the research group for the lower ammonium removal. The ammonium removal was between 2.000-26.00% and nitrate removal was 1.000-43.00% in different columns. They concluded that soil with higher silt/clay contents, higher cation (Mg/Ca/K) contents, organic matter (OM) and cation exchange capacity (CEC) might be very effective in nutrient removal and coarse media might not be able to retain the nutrient in repetitive loading due to small surface area. Good TP removal (i.e. about 41.00% to 48.00%) was observed by three types of sandy loam soils and concluded that it might happen due to simple adsorption or complex

sorption/precipitation processes (23, 56). All types had significant portion of sand (i.e. 66.00-79.00%), clay (i.e. 12.00-19.00%) and silt (i.e. 9.000-15.00%). This research group concluded that TP removal was highly variable (i.e. from 4.000% to 85.00% in different columns) and it might be related to properties of sorption media used and flow pattern of nutrient laden water. Again, OM could also accelerate TP removal (about 93.00% TP removal) and a good correlation between OM and TP removal was established by the research group. They also tried to remove other chemicals like oil and grease, Pb and total suspended solids (TSS) by sand and found above 96.00% removal of all targeted compounds by sand. Different mixtures of mulch, soil and sand was used to remove those compounds and achieved noticeable removal. They suggested that TSS removal at the upper layer or first stage of the bioretention system is very important to protect the system from clogging (23). Either mulch is not good for the growth of nitrifiers or to adsorb the ammonium. Again, sometime the manufacturers add fertilizers with the mulch, as mulch is used for gardening and those fertilizers will contribute nitrate and ammonium. Significant amount of clay particles are helpful for TP removal as clay particle has a tendency to adsorb P due to their huge surface area.

Birch et al. (2005) did an experiment to remove nitrogen species by using a stormwater filtration basin (SIB) and flow through the filtration media of 1:6 mixture of zeolite (have clinoptilolite) and coarse, pure quartzitic sand. Their analysis gave importance to removal by SIB. TKN removal was about 47.00-74.00% and TN removal was about 33.00-40.00% (also some negative removal was observed). They found negative removal of  $\text{NO}_x$  by the system. It was suggested that sand was not effective in removing nitrate +nitrite and denitrifiers were not enough to support the removal system. On the other hand, nitrifiers might be worked well to convert ammonia into nitrate and the ultimate nitrate concentration in the effluent was

increased. TP removal was about 37.00-67.00% by SIB. The removal of some metals was also observed by the SIB system. They found good removal for Cu (49.00-81.00%), Pb (88.00-98.00%), and Zn (-1.000-77.00%). Other metals like chromium (Cr), Fe, Ni had substantially variable removal efficiency with some negative removal. They concluded that the SIB might be effective in removing Cr, Fe and Ni, but leachate from sand might increase the effluent concentration of those metals (24). Clinoptilolite has attraction for ammonium and it removes TN and TKN in an ion exchange process. So biological process is not solely responsible for TN and TKN removal. Clinoptilolite may be acting as inhibitor for denitrifiers by producing a less anaerobic condition. The pH should be  $>7.000$  for the best removal of metals by sorption media, otherwise the adsorbed metal ions will be released soon.

Analytical & Environmental Consultants (AEC, 2005) accomplished an investigation for selecting locally available adsorption materials to remove nutrient from surface and ground water. Basically they worked on some materials that have strong potential to remove nutrients. Those materials are, 1) Allophane (an amorphous hydrous aluminum silicate clay mineral have affinity for  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ ), 2) Bentonite (generally impure clay mostly montmorillonite have affinity for  $\text{PO}_4^{3-}$ ), 3) Chitin (a long chain polymer and a derivative of glucose with affinity for  $\text{NH}_4^+$ ), 4) Pumice (have affinity for  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ ), 5) Zeolite (have affinity for  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ ), 6) steel slag (have attraction for  $\text{PO}_4^{3-}$ ) and 7) limestone. After their investigation based on local availability, cost, nutrient removal capability, environmental impact and applicability, they narrow down the list by including Allophane, Zeolite, Bentonite, steel slag and limestone (25). These minerals will basically remove nutrient in an ion exchange and adsorption process.

Ray et al. (2006) used hardwood mulch to remove some metals (i.e. Cu, Cd, Cr, Pb and Zn) and organics (i.e. dichlorobenzene, naphthalene, fluoranthene, butybenzylphthalate, and benzopyrene) from urban stormwater runoff. They found significant removal efficiency (i.e. 85.00% Cu, 86.00% Cd, 68.00% Cr, 92.00% Pb, 72.00% Zn, 100.0% dichlorobenzene, 88.00% naphthalene, 93.00% fluoranthene, 77.00% butybenzylphthalate, 92.00% benzopyrene) of those chemicals by hardwood mulch after 72 hours. The removal of  $\text{Cr}^{6+}$  was very slow as the actual removal process was two steps: conversion of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  (a very slow process) by mulch and sorption of  $\text{Cr}^{3+}$  by mulch. Chromium had also some desorption tendency that was higher than other species. The research group suggested that 1) sorption capacity might be correlated with the ionic radii and molecular weight of metals and organics 2) sorption by mulch was varied with concentration and species (6). From the above experiment it is proved that sorption media is also very effective in metals removal. Metal removal will be effected by pH: 1) metals ions will be dispersed in solution under acidic pH and 2) ions will engage in precipitation reaction or adsorption under alkaline pH. It will be completely an adsorption or ion exchange process because there is little possibility that metals will be removed by biological process.

Seelsaen et al. (2006) used fine glass, sand, course glass, ash, zeolite, compost and packing wood to remove heavy metals from storm water. They found that all these media were removing considerable amount of Zn and Cu (i.e. above 20.00%). In their experiment, about 95.00% Zn was removed by compost and 96.00% Cu was removed by ash (26).

Huang et al. (2006) executed an experiment to remove nitrate by metallic iron and removal of ammonium ( $\text{NH}_4^+ + \text{NH}_3$ ) and ferrous ions (Fe (II)) by clinoptilolite. The research group reported that acidic pH (i.e.  $2.000 < \text{pH} < 4.500$ ) was an important factor for the removal

of nitrate by  $\text{Fe}^0$  and  $\text{Fe}^0$  was very active to remove nitrate within a very short time (i.e. about 30 min.) in lower pH. The pH value and nitrate removal was inversely related. The nitrate removal was also related with nitrate loading and these two terms were inversely related. The research group explained that when the nitrate loading was higher, there were not enough surfaces on iron to attract more nitrates and ultimately the removal efficiency was hampered. They also observed the appearance of ammonium when the nitrate was reducing. The removal of ammonium and Fe (II) by clinoptilolite was examined. It was observed that this removal process was depending on pH and F/N ratio (i.e. Fe (II) to  $[\text{NH}_4^+] + [\text{NH}_3]$ ). When the F/N ratio was lower in the system, the ammonium removal was higher. The removal efficiency of Fe (II) was about 100.0% at 4.000 pH and the critical F/N ratio was  $<2.000$ . This critical value is very important for a system otherwise the ion exchanger will prefer to remove ferrous ions (28). Nitrate has a tendency to produce ammonium in the presence of Fe and the produced ammonium can be removed by clinoptilolite. Clinoptilolite is already well known for its ammonium removal capability but it is too costly to use as a sorption media in a small scale facility.

### **Wastewater treatment by sorption media**

Nutrient removal from wastewater is basically depending on adsorption and biological process. The filter media acts as a growth chamber for the microorganisms and the microorganisms are inoculated in the reactors. The removal of nutrient may not be accelerated by these dual effects. As the microorganisms are attached on the surface of the media, they will reduce the surface area for adsorption. So the growth of microorganisms is a benefit for

the system and it is also a problem on the other hand. The adsorption will be dominated by biological process, if too much bacteria grow in the system.

Shin et al. (1999) found that tire chips could adsorb volatile organic carbon (VOC) from wastewater and proved that it would be a good filter media (30). Han et al. (2001) used polyurethane based porous media in an up flow biological aerated filter (BAF) to treat wastewater at 18.00 to 22.00°C. The BAF consisted of a sludge drain, wastewater and air inlets, sampling ports and effluent outlet. The porous media (about 70.00% of the reactor volume was filled) was used for the growth of autotrophic nitrifiers and denitrifiers. The nitrification was about almost 100.0% and they observed significant nitrogen loss from the BAF. The heterotrophic denitrifiers were not responsible for this loss because total organic carbon available in the system could not serve as electron donor. *Nitrosomonas* were capable of denitrification by using hydrogen and ammonium as electron donor in the absence of oxygen. But the system was very slow and it was not solely possible for the denitrification in this BAF. At last the research group reached a conclusion that the denitrification was completed by autotrophic nitrifiers and Anammox reaction in anaerobic zone (32). The maintenance of this kind of system and the growth of the anammox bacteria are critical.

Zhang (2002) performed an experiment to remove nitrate from wastewater by using sulfur: limestone autotrophic denitrification (SLAD) pond reactor with three conditions: 1) aerobic (mixed) and anoxic (unmixed) condition, 2) effect of temperature and 3) influence of COD/N ratios in feed to nitrate removal. All the reactors were containing sediment from a rural cattle pond and the sulfur and limestone were not covered by sediment. There were four types of reactors: 1) a reactor of granular sulfur and limestone on sediment 2) same as reactor 1 but seeded with sulfur based autotrophic denitrifiers (i.e. *Thiobacillus denitrificans*), 3) a

control case with only the sediment and 4) same as reactor 1 but 1/3 less sulfur and limestone by volume. In this research, it was observed that the nitrate removal was about 90.00-100.0% with alkalinity control and mixing, about 80.00-85.00% without alkalinity control and mixing and the control case had very low nitrate removal with wide fluctuation. The reactor 2 was not used for temperature condition. In the research, it was established that the removal of nitrate in reactor 1 and 4 would increase with increasing temperature but removal of nitrate decreased with increasing temperature in control case. The COD/N ratio had great influence on nitrate removal. It was found that if the COD/N ratio was below 1.200, the nitrate removal efficiency was 85.00%. On the other hand, if the ratio was above 3.000, the removal was only 30.00% (33). High concentration of organics can help rapid growth of heterotrophic in the system and heterotrophic will consume the organic carbon. This may affect the activity of autotrophic bacteria and ultimately the nitrate removal is hampered.

Espino-valdés et al. (2003) did an experiment to remove nitrogen species from wastewater by biological process in reactors. There was an up flow bioreactor (R1) followed by a clarifier (C1). This reactor was used as a nitrification chamber and required air was supplied from the bottom of the reactor. The C1 is connected with the second up flow bioreactor (R2) followed by a clarifier (C2). R2 was used a denitrification chamber and methanol was supplied from the bottom of the reactor. They used sand to support the growth of biomass and the reactor was inoculated by secondary sludge. About 81.30% of ammonia-nitrogen was removed at 26.60°C in 2.700 hours and the final concentration was 4.200 mg/L. Nitrate and nitrite removal was also very significant in the reactor. At 28.70°C, 86.20% nitrate+nitrite were removed in 2 hours and the final concentration was 4.900 mg/L (34). Both the ammonia and nitrate concentration is within the acceptable range.

Gálvez et al. (2003) tried to use a submerged fixed film reactor to remove nitrogen from urban wastewater. There were two columns in the system. The first column was a down flow nitrification reactor with aerobic condition and the second one was an up flow denitrification reactor with anoxic condition. Air was added in the first column and methanol was added in the second column from bottom. The reactor was filled with clay schists from recycled construction materials and the research basically emphasized on the influence of hydraulic loading and air flow rate on nitrogen removal. They found that when the methanol concentration was decreased, the nitrate removal efficiency was also decreased and there was a good correlation between nitrogen removal and methanol concentration. Excess methanol or carbon source was required to fully complete the denitrification. It was observed that high hydraulic loading had higher organic loadings that would help for the growth of heterotrophic bacteria and high air flow rate had a tendency to increase total nitrogen removal efficiency. Direct competition between heterotrophic and autotrophic bacteria for substrate can reduce the amount of nitrification. The nitrification in the system can be increased by decreasing the organic loadings. The research group concluded that the system could do about 95.00% denitrification and about 75.00% COD was removed (35). When denitrifies has less methanol to consume with time, the nitrate removal has decreased. Again high organic loading can hamper the nitrogen removal process in the system.

Rodgers and Zhan (2004) used a vertically moving biofilm system (VMBS) to remove nitrogen species from wastewater by biological process. This small biological nitrogen removal (BNR) process was operated at 11.00°C and was consisted of six polypropylene tanks (dimension of 0.400 m\* 0.400 m\* 0.600 m) in series; six biofilm modules- one for each tank with a specific surface of 6.480 m<sup>2</sup>; a wastewater feed mixing tank; three peristaltic



pumps- one for feed mixing tank, another one for tap water and the other one for recirculation of nitrified wastewater and a pneumatic system complete with limit switches and delay controllers. The delay controllers had the capability to lift and lower the biofilm modules. The first two tanks were anoxic for denitrification and the other four tanks were aerobic for nitrification. The research group found an overall COD removal of 94.00%, TN removal of 82.00% and NO<sub>3</sub>-N removal of 95.00% in tank 1 without any clogging. They concluded that nitrification might be inhibited for DO competition between nitrifiers and heterotrophs (36). The modules should be slow enough so that they have sufficient contact time with the liquid. If the modules are too fast, the biofilm layers may be washed out. So it is a very critical issue to operate this system.

Güngör and Ünlü (2005) conducted nitrate and nitrite removal from wastewater by laboratory column experiment by using only three types of soils. They used sandy clay loam (SCL), loamy sand (LS) and sandy loam (SM) and found significant result in nitrate and nitrite removal (i.e., over 90.00%) (37). This experiment is very important for nitrate removal by soil. It proves that some soils have affinity for nitrate. Nitrate removal by soil will vary from one kind of soil to another. Forbes et al. (2005) used lightweight expanded shale and masonry sand for the removal of phosphorus from secondarily treated municipal effluent. The system contained three cells filled with expanded shale and three cells filled with masonry sand. They summarized that sand was a poor candidate for retaining phosphorus and expanded shale had greater removal efficiency due to its larger surface area. The chemical composition (i.e. Fe+Al) and excellent hydraulic efficiency of shale were also responsible for the removal of phosphorus (38). Sand can remove phosphorus by adsorption if it is rich in clay and silt particles or rich in minerals. Both of these may be absent in this masonry sand.

Namasivayam et al. (2005) used oyster shell powder (OSP) to remove phosphorus from wastewater at 24.00°C. They found that raw oyster shell had no affinity for phosphorus but about 45.00% of phosphorus in batch mode and 85.00% of phosphorus in continuous mode was removed by OSP. They reached in a conclusion that the phosphorus was removed by sorption as amorphous calcium phosphate on OSP surface and then slowly transformed into more stable hydroxyapatite (39).

Sengupta and Ergas (2006) did an experiment to remove nitrate from wastewater by using marble chips, limestone, and oyster shell. Their experiment gave some significant outcomes about using those solids as sorption media. They found that oyster shell (almost 98.00% CaCO<sub>3</sub>) could remove 80.00% nitrate and limestone could remove 56.00% of nitrate. The pH and alkalinity were higher for oyster shell rather than limestone and marble chips. Oyster shell was very much efficient to reduce nitrite accumulation and DO did not work as a denitrification inhibitor when oyster shell was used as a filter media. It can be concluded that oyster shell is much more effective than limestone or marble chips for removing nitrate. Oyster shell can be a good candidate for controlling the pH that is a controlling factor for denitrification (40).

Arami et al. (2006) did the adsorption study of direct (i.e. DR80 and DR81) and acid (i.e. AB92 and AR14) dyes by using soy meal hull (SMH). In all cases, the higher the initial dye concentration, the lower the dye adsorption. They observed that with an initial concentration of 50.00 mg/L and a pH of 2.000, DR80 removal efficiency was 98.00%, DR81 removal efficiency was 97.00%, AR14 removal efficiency was 86.00% and AB92 removal efficiency was 98.00% after 120 minutes. They found that pH and dye removal was inversely related.

The research group concluded that electrostatic attraction, organic property and structure of dye molecules might influence the adsorption process (41).

Smith et al. (2008) did an experiment on passive (i.e. not depending on pumping and external aeration) nitrogen removal from septic tank wastewater in Florida. There were three filter systems with the same structure. In each system, there was two columns: one was vertical filled with stage 1 media (i.e. saturated condition, aerobic) and the other one was horizontal filled with stage 2 media (i.e. unsaturated condition, anoxic). The stage 1 media was clinoptilolite (have ion exchange properties), expanded clay (will increase the retention time and have adsorption properties) and tire crumb (have adsorption properties) and stage 2 media was elemental sulfur (electron donor media for denitrifiers), crushed oyster shell (used as alkalinity source) and Utelite (i.e. expanded shale have anion exchange properties). In system one, the vertical column (1A) was filled with clinoptilolite and horizontal column (2A) was filled with 75.00% sulfur and 25.00% oyster shell. In system two, the vertical column (1B) was filled with expanded clay and horizontal one (2B) was filled with 60.00% sulfur, 20.00% oyster shell and 20.00% expanded shale. In third system, the vertical column (1C) was filled with tire crumb and horizontal one (2C) was filled with 45.00% sulfur, 15.00% oyster shell and 40.00% expanded shale. The research group found very noticeable result for nitrogen species removal. TN removal was about 97.10% for [1A+2A], 97.70% for [1B+2B] and 33.00% for [1C+2C]. Total inorganic nitrogen (TIN) removal was about 99.80% for [1A+2A], 98.10% for [1B+2B] and 34.40% for [1C+2C]. TN removal was about 50.60% for 1A, 26.10% for 1B and 13.00% for 1C. NH<sub>3</sub>-N removal was about 99.90% for 1A, 99.90% for 1B and 60.50% for 1C. The denitrification process in the system was also good and denitrification rate in 2C column was the lowest. They gave two possible explanations for

this: 1) amount of sulfur was lowest so not enough electron donors for denitrification and 2) harmful leachate from tire crumb. The DO concentration was 7.210 mg/L in average in stage 1 columns and 0.340 mg/L in average in stage 2 columns (44).

### **Groundwater treatment by sorption media**

Ground water treatment is most expensive and difficult among all types of water bodies. Most of the researches are done in shallow ground water. The main problem in working with groundwater is that water may change its flow path way during the test. Benson and lee (2001) used waste foundry sand to treat the groundwater (45).

Schipper et al. (2005) did an experiment by using sawdust denitrification wall to remove nitrate in shallow groundwater with a HRT of 5 days. They dug a trench (about 35.00 m long, 1.500 m deep and 1.500 m wide) and used 30.00% Monterey pine sawdust (*Pinus Radiata D. Don*) by volume mixed with the excavated soil to place in the trench. The research group suggested that the nitrate concentration was a limiting factor rather than carbon for denitrification because when they added additional nitrate in soil, it increased the denitrification rate. No nitrate accumulation was observed in organic matter in soil or nitrate transformed into ammonia. They found a nitrate N removal rate of  $1.400 \text{ g N m}^{-3}$  of wall  $\text{d}^{-1}$  that is about 97.20% of nitrate removal (46).

### **Land fill leachate treatment by sorption media**

Groundwater is also contaminated by landfill leachate. Some protective measures are taken during landfill but the condition of the system may deteriorate with time and start to

pollute the groundwater. For this reason, sometimes it is necessary to treat the landfill leachate.

Jokela et al. (2002) conducted an experiment to eliminate nitrogen from a municipal landfill leachate by biological process. Nitrification was tested in three types of reactors: 1) up flow (UF) nitrification filter with crushed brick as a filter medium, 2) down flow (DF) nitrification filter with wood chips and 3) nitrification in suspended carrier biofilm process (SCBP). All the nitrification reactors were inoculated by nitrifying activated sludge collected from a sewage treatment plant. In the UF filter, nitrification efficiency was about 60.00% to 88.00% in 60 days and after 60 days it was above 90.00%. COD removal efficiency was ranged from 26.00% to 62.00%. In DF filter, the nitrification efficiency was about 90.00% and no COD removal was detected. In SCBP, the nitrification efficiency was 75.00% to 99.00% and COD removal was 53.00% to 63.00%. They suggested that the UF nitrification mode is more efficient due to the higher HRT. Denitrification was tested in a landfill waste column and feeding was received from nitrified sample from SCBP. They concluded that leachate with high COD value might inhibit the denitrification due to the growth advantage of heterotrophs over nitrifiers (47).

Lisi et al. (2004) used granulated tire for the removal of nitrate. They found 48000 g of tire crumb can remove 16.20 g of  $\text{NO}_3^-$ -N (48). Savage and Tyrrel (2005) used wood mulch, compost, soil, broken brick and polystyrene packaging for removal of  $\text{NH}_3$ -N and  $\text{BOD}_5$  from compost leachate. They reached a conclusion that wood mulch (75.00% removal) and compost (55.00% removal) had better removal efficiency and polystyrene (31.00% removal) was the least capable one to remove  $\text{NH}_3$ -N. Again for  $\text{BOD}_5$ , compost had better removal efficiency (i.e. about 78.00%) and polystyrene had least removal efficiency (i.e. about

34.00%). The research group found that compost and wood mulch had a tendency to increase the pH and concluded that specific surface area, void space, permeability, media durability and strength, absorption capacity and adsorption capacity might influence removal efficiency (49).

Kietlińska and Renman (2005) applied sand, blast furnace slag (BFS) and Polonite to remove nitrogen species and heavy metals from landfill leachate by a column study. Polonite is a product manufactured from cretaceous rock opoka with high sorption capability. TIN could be removed by sand (about 4.000%), Polonite (18.00%) and BFS (8.000%). They inferred that wollastonite in Polonite might be responsible for the removal of nitrogen species as wollastonite has some preference for nitrogen species spatially ammonia. Polonite could also remove 93.00% Fe, 86.00% Zn, 86.00% zirconium (Zr), 85.00% barium (Ba), 67.00% Cu, 77.00% titanium (Ti), 60.00% yttrium (Y), 30.00% cobalt (Co), BFS could remove 20.00% Fe, 62.00% Zn, 63.00% Zr, 31.00% Ba, 66.00% Cu, 33.00% Co, 19.00% Ni and sand could remove 25.00% Cu and 15.00% molybdenum. They concluded that pH can affect the removal of heavy metals by Polonite and hydroxide precipitation is responsible for the high removal of metals by forming insoluble precipitate. But ion exchange and adsorption can also influence the removal process (50).

### **Drinking water treatment by sorption media**

Application of biological process in drinking water treatment is not very popular. There is a risk of bacterial contamination in drinking water. Disinfectant should be used to reduce possible bacterial contamination. But nutrient and heavy metals can be removed by adsorption and ion exchange process by using sorption media. In drinking water treatment, the use of sorption media is much more attractive than biological process. As sorption media is good

support for the bacterial growth, the sorption media should be change frequently to treat drinking water.

Volokita et al. (1996) used shredded newspaper for denitrification in drinking water by column study. Newspaper is a good source of carbon and support for microbial population. They found that the system could remove about 77.78% of nitrate after 30 days and 38.90% of nitrate after 120 days. This longer time was taken due to the growth of denitrifying bacteria in the system. The group suggested that temperature and retention time has a marked effect on the cellulose based denitrification. The detention time can be increased by decreasing the flow or by increasing the length of the system. The ink on paper also effected the growth on microbial in the system but not a limiting factor for the system. The research group observed that the temperature should be 25.00-32.00°C and unprinted newspaper was better to achieve higher denitrification rate (51).

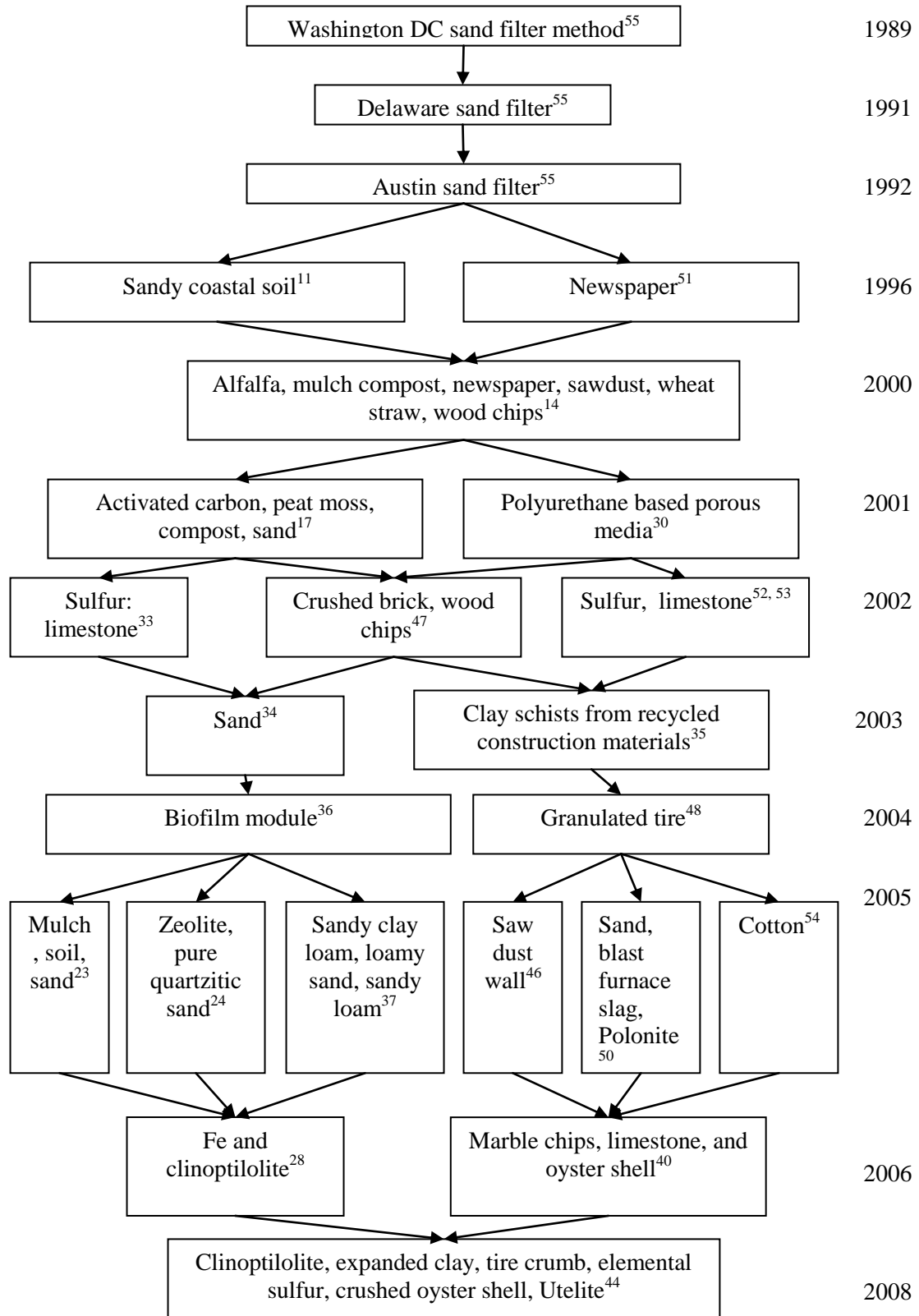
Darbi et al., (2002) used sulfur and limestone for nitrate removal from potable water in a batch study. In this experiment, sulfur was used as an electron donor and limestone was used to maintain the pH. They found that the optimum mixing ratio of sulfur and limestone is 1:1 (i.e., about 98.00% nitrate removal was observed) and sulphate production was lower. The sulphate production was decreased when the nitrate removal was increased. This research group suggested that increasing the retention time may obtain higher removal efficiency (52). The same research group did the column test for nitrate removal from potable water and the result was published in 2003. There were three up flow columns filled by elemental sulfur and limestone with ratios of 1/1, 2/1 and 3/1. All the columns were inoculated by *Thiobacillus denitrificans*. With 26 h HRT, the nitrate removal was about 95.00-100.0% and nitrite concentration was below 1.000 mg NO<sub>2</sub><sup>-</sup>-N/L in all columns. The nitrate removal and sulfate

production was higher when the S/L ratio was 2/1. It was noticed that the sulfate ( $\text{SO}_4^{2-}$ ) production was increased with increasing volumetric loading rate. It was also noticed that the  $\text{SO}_4^{2-}$  production was increased when the nitrate removal was increased and about 6.000 mg  $\text{SO}_4^{2-}$  was produced for 1.000 mg  $\text{NO}_3^-$ -N removal (53).

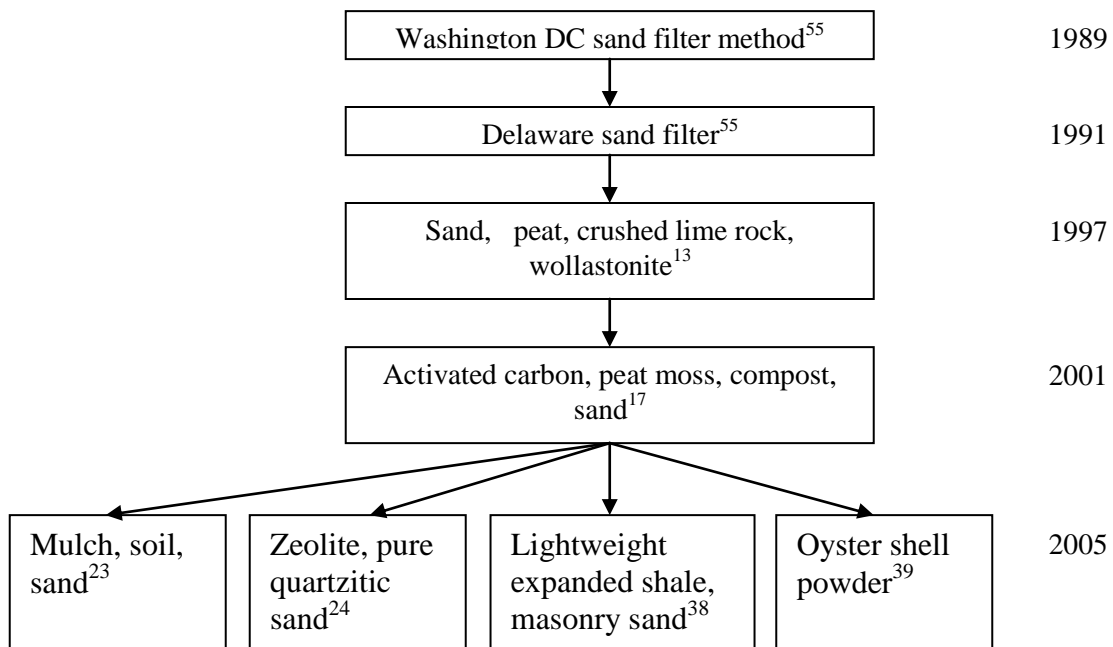
Rocca et al. (2005) used cotton supported heterotrophic denitrification (HD) for the removal of nitrate from drinking water. There were two reactors: a HD reactor followed by a trickling sand filter (TSF). Cotton (it is the purest form of naturally occurring cellulose) was used as an organic carbon source and supporting material for the growth of denitrifiers. Nitrate removal was about 91.50% with a system temperature of 28.00°C. The research group found that nitrate removal was decreased with an increasing temperature and nitrate removal was increased with an increasing velocity of water (54).

Figure 2.1 and 2.2 show the flow chart of sorption media used to remove nutrient.





**Figure 1: Flow chart showing the use of filter media for nitrogen species removal in chronological order**



**Figure 2: Flow chart showing use of filter media as phosphorus species removal in chronological order**

## Discussion on literature review

It is already proved that filter media can be used extensively to remove nutrient from storm water, groundwater and wastewater. There are some findings from the above discussion:

- Filter media can remove the nutrient from water basically by adsorption, precipitation and nitrification/denitrification. Adsorption is taking place for high surface area and some media have special affinity for specific species of nitrogen, phosphorus and heavy metals. Chemical reaction may be only possible for phosphorus removal because phosphorus has precipitation reaction with some chemicals.
- Noticeable amount of solid particles can also be removed by the filter media.

- The research papers mentioned that bacteria can grow very well in filter media due to the high surface area and porous structure of the filter media. In traditional biological process, different types of plastic media are used. Filter media can be used as a substitute of those plastic media. The filter media is easily available and may be cheaper than those plastic media. The traditional plastic media can only support microorganisms. But filter media can not only support organisms but also adsorb the nutrients.
- Cellulose based sorption media is very good for the growth of microorganisms.
- Filter media like tire crumb, sawdust, compost, wood chips, newspaper, cotton waste can act as electron donor and can help the denitrification process as excellent source of carbon. So filter media can save the cost of chemicals used as carbon source in traditional biological process.
- Dual process in a single system may not accelerate the removal process. Such as, growth of microorganisms on filter media may reduce the surface area for adsorption. Again, if more particles are involved in adsorption, there will be fewer filter media particles to take part in chemical reaction. But still there is an advantage of using filter media. The dual effect of adsorption and biological process can be expected. As bacteria will need some time to grow fully in the media, it can be assumed that adsorption will occur first and biological process will occur second in a system.
- Biological nutrient removal (BNR) process has been used to treat wastewater for many years but now scientists are suggesting biological process for potable water treatment. Care must be taken for possible negative effect (if any) of nitrifiers, denitrifiers and

PAOs on human health (53). For this reason, research should be conducted to determine the possible harmful effect of those bacteria on human health.

- Filter media has a propensity to remove heavy metals from water but in that case pH may be an important factor. Acidic pH will release the metals ions from the media surface rather than retaining them or will dissolve the precipitation. So pH>7.000 is good for metal removal by filter media.
- Filter media is also very important for increasing the HRT in a reactor because it is observed that higher HRT is required to obtain higher removal efficiency.

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## CHAPTER 3: MATERIAL CHARACTERIZATION

### Introduction

The sorption media is used to remove nutrient from stormwater, wastewater and ground water. Most of the research papers focus on the removal of nutrients by sorption media. Most of them ignored the properties of sorption media. But removal is depending on some physiochemical properties such as surface area, porosity, and permeability. These properties are very important to understand the nutrient removal process.

Kietlińska and Renman determined the dry density, porosity and permeability of sand, blast furnace slag (BFS) and polonite (1). Forbes et al. (2005) determined the density, porosity, effective size, uniformity coefficient, surface area and hydraulic conductivity of masonry sand and expanded shale (2). Güngör and Ünlü (2005) measured the porosity of sand used as sorption media (3). Dispersion phenomenon is very important in the field of environmental engineering. Dispersion of pollutants occurs in many ground waters and river streams. It is very important to control the pollutants distribution in ground waters and river streams. The dispersion coefficient can be determined by using breakthrough curve (BTC) obtained by a tracer test (4). Many researchers have given different ways to determine the dispersion coefficient (5, 6, and 7) but this one is the simplest one. Only enough points are required to identify the peak. It saves time to do a lengthy experiment and the calculation is very simple. This procedure does not require flow rate, cross sectional area of specimen and porosity of the sample. Other procedures are difficult to understand by people who have no background in advanced mathematics and those methods are not applicable in field. This dispersion coefficient is also known as coefficient of hydrodynamic dispersion.

The objective of this chapter is to determine the physical and chemical properties of sorption media. The properties such as particle size distribution curve, density, porosity, surface area, hydraulic conductivity, dispersion coefficient and void ratio of filter media are determined. Particle size distribution curve can give some ideas about the grain size of soil or sorption media and type of distribution of particles in a certain soil or sorption media sample. Porosity helps to get idea about volume of voids in a sorption media sample and how much water actually come in contact with the sorption media or soil can be determined from volume of voids. Porosity is calculated from specific gravity and void ratio. These properties can also influence the dispersion phenomena in soil or filter media column test.

## **Methodology**

### **Material Preparation and Characterization**

It is very important to understand the physical properties (i.e. density, void ratio, porosity, specific gravity, surface area and conductivity) of the filter media. These properties are used to determine the hydraulic residence time and adsorption area available for the nutrient. The research team at UCF decided to follow six criteria to screen those possible filter media: 1) the relevance of nitrification or denitrification process or both, 2) the hydraulic conductivity or conductivity, 3) the cost level, 4) the removal efficiency as evidenced in the literature with regard to adsorption, precipitation, and filtration capacity, 5) the availability in Florida, and 6) additional environmental benefits. Eight filter media were eventually selected for final consideration according to a multi-criteria decision making process. They include 1) peat, 2) sandy loam, 3) sawdust/wood chip, 4) paper/newspaper, 5) tire crumb, 6) limestone/sulfur, 7) crusted oyster and 8) compost. In the end, sand (citrus grove sand), tire crumb, saw dust, and

limestone are used as the proposed filter media in this study. The composition of filter media mixture was 50.00% sand (citrus grove sand), 15.00% tire crumb, 15.00% saw dust and 20.00% limestone. All the filter media were purchased commercially. Both Tire crumb and sawdust are lighter than water. Tire regeneration from scrap tire is not economically possible due to the vulcanization process in tire production (8). Blrkholz et al. (2003) did toxicological test on tire crumb and found that no DNA and chromosome damaging chemicals are present in the tire crumb (9). Hence, the inclusion of tire crumb and sawdust is viewed as part of the resources recovery with sustainable implication in this study. Limestone was crushed by Universal Testing Machine (UTM) and particle size was about 250.0 micron. The natural soil was collected from a dry pond (Hunter Trace) in Ocala, Marion County, Florida as control case in column test. This soil showed significant difference in hydraulic conductivity in both wet and dry condition. For this reason, physical properties of both wet and dry natural soil were determined.

The ASTM procedures were followed to determine the properties of filter media. The specific gravity was determined by following the standard test method for specific gravity of soils (10). The procedure follows the Method A (Procedure for oven dry specimen). The pycnometer was a volumetric flask having a capacity of 500.0 mL and 100.0 g of sample was taken for the experiment. The value of void ratio and porosity is determined from specific gravity by using the following two equations.

$$\text{Void ratio of filter media mixture (E)} = \frac{G_s * \rho_w}{\rho_d} - 1 \quad (3.1)$$

$$\text{Porosity of filter media mixture (N)} = \frac{E}{1 + E} \quad (3.2)$$

Here,

$G_s$  = Specific gravity of filter media mixture

$\rho_w$  = Density of water

$\rho_d$  = Density of filter media mixture

$E$  = Void ratio

$N$  = Porosity

The hydraulic conductivity test was conducted by following the standard test method for conductivity of granular soils (Constant head) (11). Several trials were run and averaged. Then the conductivity was converted to a test temperature of water at 20.00 °C. The particle size was determined by following the standard practice for dry preparation of soil samples for particle size analysis and determination of soil constants (12). The sample size was 1.000 kg for this analysis. The surface area of sorption media mixture was determined by using Multipoint BET with nitrogen adsorption at 77K (Vacuum volumetric method) conducted by the Quanta Chrome Instruments, Boynton Beach, Florida. About 3.500 g of sample was used to determine the surface area of the proposed sorption media mixture. Effective size ( $D_{10}$ ) is the diameter of the particles in mm corresponding to 10.00% finer. Uniformity coefficient ( $U$ ) is the ratio of  $D_{60}$  to  $D_{10}$ .  $D_{60}$  is the diameter of the particles in mm corresponding to 60.00% finer. Surface area is very important for the removal of nutrients by sorption media. The more the surface area, the more will be the removal efficiency of nutrient.

### **Preparation for determination of dispersion co-efficient**

Two Plexiglas columns with a diameter of 14.80 cm and height about 190.0 cm were prepared in the laboratory for this experiment. The two columns were placed in a wooden frame. Both columns had screw cap in top and bottom to fill the column with filter media from the top and remove the media from the bottom of the column. All the joints were making water tight by using Silicone II (100.0% silicone sealant, GE sealants and adhesives). One column was filled with proposed filter media mixture and the other column was filled with natural soil (Hunter trace soil from Ocala, Marion County, Florida) up to a height of 90.00 cm. There were about 2 outlets to collect samples from each column. A T was connected at the point where the liquid is entering the column. This T would be used to inject the tracer in to the column. Peristaltic pumps (Cole-Parmer) were used to control the inflow into the columns. Potassium Bromide (KBr, from Fisher Scientific) that was proved harmless for the environment was a good inorganic conservative tracer. The chemical analysis was done by following the phenol red colorimetric method (standard method, bromide, 4500, 13).

In a column, the effluent concentration was determined at various time periods. (Sample was collected in every 5.000 minutes or any other regular interval). Then a graph was plotted between  $C$  VS  $t$  and this graph was known as breakthrough curve (BTC) (Here  $C$  is the fraction of influent concentration in effluent and  $t$  is the time interval for collecting sample). The values of  $t_0$  and  $m_0$  were determined from the graph. The  $t_0$  was the value when  $C$  was equal to 50.00% of influent concentration and  $m_0$  was the slope at that point. The value of  $D$  (Dispersion co-efficient) could be calculated from the following equation 3.3. Figure 3.1 and 3.2 shows the schematic diagram of the column setup for kinetic study and dispersion coefficient respectively.



$$D = \frac{x^2}{4\pi m_0^2 t_0^3} \quad (3.3)$$

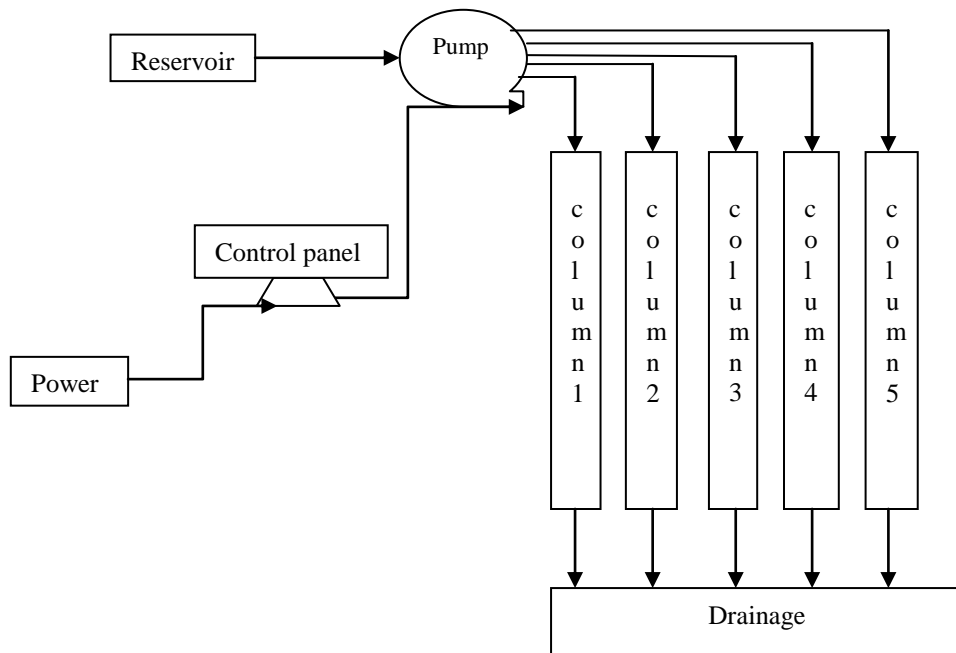
Here,

$x$ = Height of soil or filter media in the column

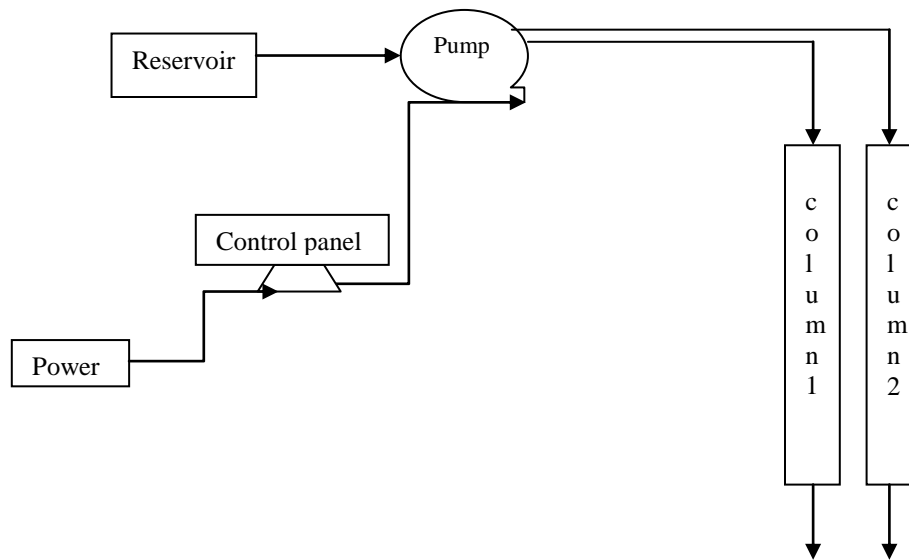
$t_0$ = the value when  $C$  is equal to 50.00% of influent concentration

$m_0$ = the slope at that point

$\pi$ = 3.141



**Figure 3: Schematic diagram of the column setup for kinetic study**



**Figure 4: Schematic diagram of the column setup for dispersion coefficient**

## **Results and Discussion**

### **Material Characterization**

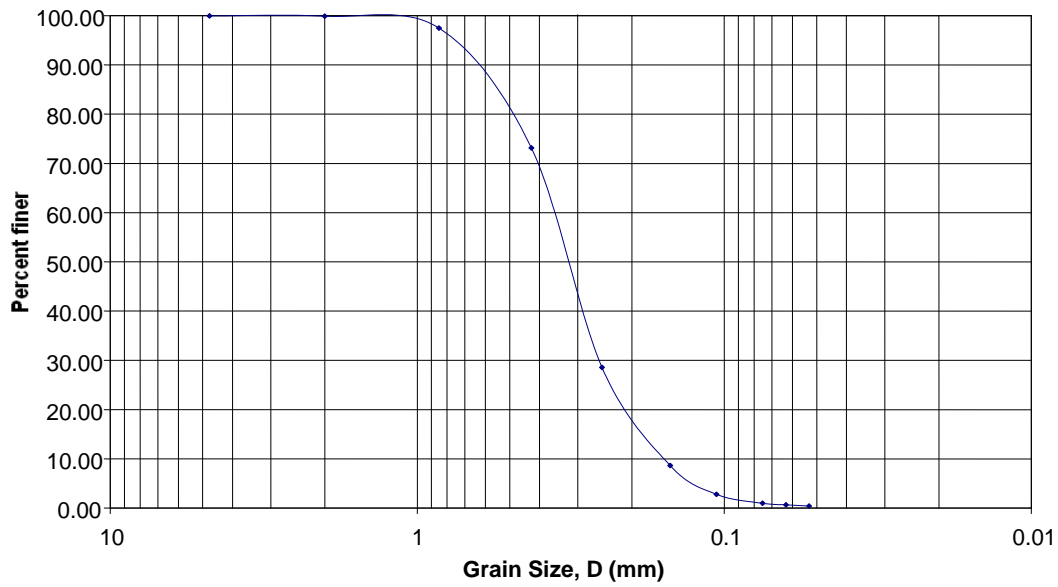
Table 3.1 shows the physical properties of natural soil and filter media used in the experiment. Filter media proposed in this study has larger porosity and void ratio than natural soil at Hunter's Trace pond. The soil packed into the columns might not be oven dried, so the conductivity was also tested using a moist sample. The conductivity of the moist sample of Hunter's Trace soil and sorption media are measured to be 4.470 cm/hr (1.759 in/hr) and 3.580 cm/hr (1.410 in/hr). As the Hunter Trace soil contains clay particles and clay particles are small, the larger surface area was observed. The situation that sorption media has larger particles, like saw dust and tire crumb, makes the surface area smaller than that of Hunter Trace soil. If the surface area is larger, the removal efficiency should also be larger as there will be more space on the solid phase to adsorb more nutrients.

**Table 6: Data showing the physical properties of natural sand and sorption media.**

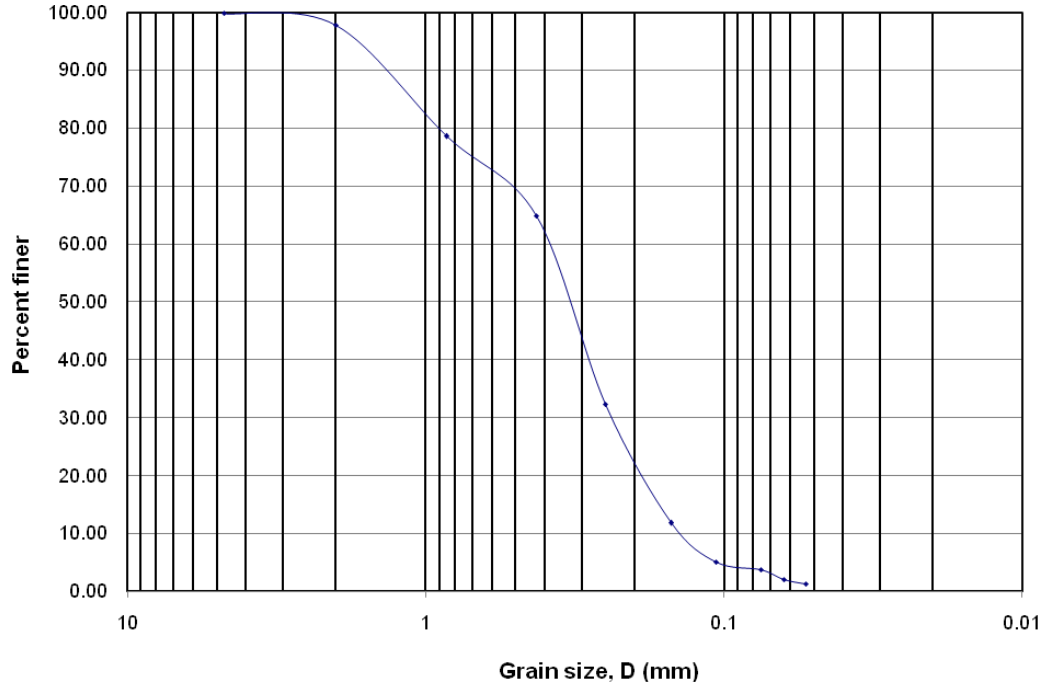
	Hunter's Trace (dry sample)	Hunter's Trace (moist sample)	Sorption media
Dry density (g/cm <sup>3</sup> )	1.560	1.730	1.210
Void Ratio (unit less)	0.670	0.510	0.740
Porosity (unit less)	0.400	0.340	0.420
Specific Gravity (Gs)	2.620	2.620	2.110
Surface Area (m <sup>2</sup> /g)	3.111	3.111	0.604
Intrinsic conductivity (cm/hr)	62.48	4.470	3.580

To determine the particle-size distribution a sieve analysis was performed. Figures 3.3 and 3.4 present the gradation curves of natural soil at Hunter's Trace site and sorption media comparatively. The Hunter's Trace pond soil had a larger fraction retained on various sieve sizes as compared to the others. For example, approximately 91.00% was retained on the 100 U.S. Standard size sieve for the Hunter's Trace location whereas only approximately 75.00% was retained for the media mix proposed. The particle-size distribution of media mix is well graded. The percentage of finer grained particles can be determined from particle size distribution curve. Fine grains can improve the retention time (i.e. contact time between media and water) and amount of solids in the effluent. The effective sizes ( $D_{10}$ ) of natural soil and sorption media are 0.165 mm and 0.150 mm, respectively. This  $D_{10}$  may be used to determine the hydraulic conductivity by using an empirical equation (i.e.  $k=1.0D_{10}^2$ , 14). Ammonia removal is a function of effective size. The lower the effective size, it is easier to remove ammonia.  $D_{60}$  of natural soil and sorption media are 0.360 mm and 0.390 mm, respectively. The uniformity coefficient (U) of natural soil and sorption media is 2.182 and 2.600 respectively. It can be said that both natural soil and sorption media have non-uniform particle size.  $U=1.0$  means all the particles are nearly same size and  $U>1.000$  means the

particles are not in the same size. From porosity, amount of storm water come in contact with media or natural soil can be determined. Amount of storm water that come in contact with the media is about 200.0 mL and 236.0 mL for natural soil and sorption media respectively.



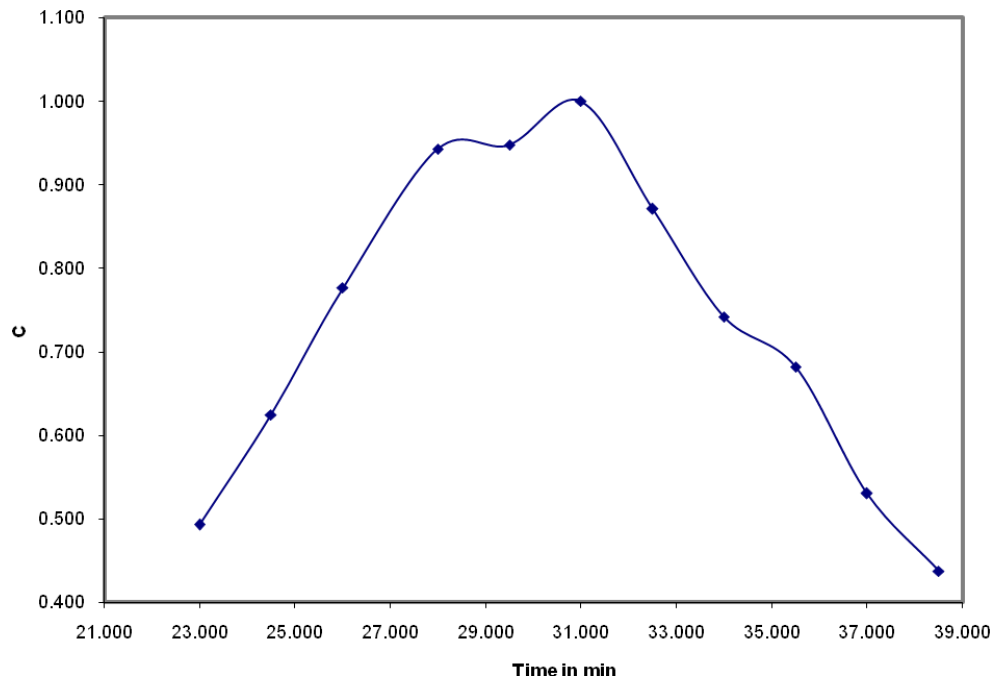
**Figure 5: Particle size distribution of natural soil collected from Hunter's Trace pond**



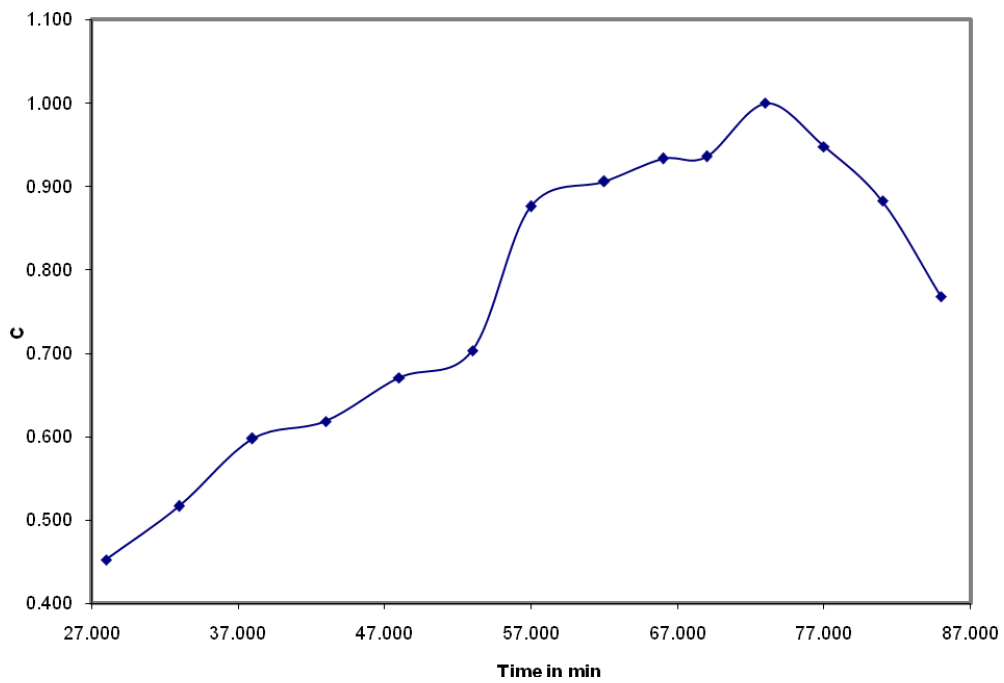
**Figure 6: Particle size distribution of filter media mixture**

**Dispersion coefficient**

Dispersion coefficient of natural soil and sorption media is determined about 6.830 cm<sup>2</sup>/min and 119.617 cm<sup>2</sup>/min respectively. It is found that dispersion through sorption media is much faster than natural soil. It is possible due to the more pore space in sorption media and solution is passing very slowly through the sorption media. So solution has enough time to disperse into the sorption media. The graphs between C vs. time are shown in figure 3.5 and 3.6.



**Figure 7: Dispersion coefficient graph for natural soil**



**Figure 8: Dispersion coefficient graph for sorption media**

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## CHAPTER 4: ISOTHERM AND KINETICS ANALYSIS

### Isotherm Study for the Sorption Media Mixture

Adsorption isotherm can be produced by exposing a known quantity of adsorbate to various dosage of adsorbent. The isotherm gives us the idea about when a certain amount of adsorbent reaches the equilibrium condition with a fixed mass of adsorbate. Adsorption also depends on the solubility of adsorbent. Adsorption strength is inversely proportional to solubility (1). In this experiment, about 800.0 g filter media mixture was prepared by using 50.00% sand (citrus grove sand), 20.00% limestone, 15.00% sawdust and 15.00% tire crumb. A known concentration of adsorbate solution (i.e. 1.000 mg/L) was prepared from stock solution. 300.0 mL of that solution was transferred into each Erlenmeyer flask and five flasks were used. Now 50.00 g of media mixture was taken in flask 1, 100.0 g in flask 2, 150.0 g in flask 3, 200.0 g in flask 4 and 250.0 g in flask 5 simultaneously. The top of the each flask was covered by parafilm so that it will be free from outside disturbance during the waiting period. All the flasks were kept on a shacking platform (Innova 2000, New Brunswick Scientific) with 50 rpm for a certain time (time varies for different adsorbate to remove). After waiting period, the flasks were removed from shacking platform and samples were collected from the flasks. The test temperature was in between 22.00<sup>0</sup>C and 23.00<sup>0</sup>C (i.e. in room temperature). Isotherm curves for ammonia, nitrate, nitrite, OP, and TDP were created via this procedure finally.

Ordered from Fisher Scientific, Ammonia nitrogen (NH<sub>3</sub>-N) solution was prepared from anhydrous NH<sub>4</sub>Cl (dried at 100.0<sup>0</sup>C), nitrate (NO<sub>3</sub>-N) solution was prepared from KNO<sub>3</sub> (dried at 105.0<sup>0</sup>C for 24 hours) and nitrite (NO<sub>2</sub>-N) solution was prepared from NaNO<sub>2</sub> from

Fisher Scientific. All solutions were freshly prepared to avoid possible contamination. Sometimes ammonia (100.0 mg/L) and nitrate (10.00 mg/L) stock solutions were purchased commercially from HACH (Loveland, CO). Standard phosphorus solution (50.00 mg/L) was purchased commercially from HACH too. All the glass wares were washed by HCl (i.e. 1:1 solution) before starting every experiment.

The Freundlich and Langmuir isotherm equations were used to draw the isotherm curves. The Langmuir isotherm is determined by plotting a graph between  $1/q$  and  $1/C$  and Freundlich isotherm is determined by plotting between  $\log q$  and  $\log C$ . Overall, the following two equations were applied in this study.

- Freundlich isotherm equation is (2),

$$\log q = \log K + \frac{1}{n} \log C \quad (4.1)$$

- Langmuir isotherm equation is (2),

$$\frac{1}{q} = \frac{1}{q_m K_{ads}} \left( \frac{1}{C} \right) + \frac{1}{q_m} \quad (4.2)$$

Where,

$q$  = Sorbed concentration (mass adsorbate/mass adsorbent)

$q_m$  = Maximum capacity of adsorbent for adsorbate (mass adsorbate/mass adsorbent)

$C$  = Aqueous concentration of adsorbate (mass/volume)

$K_{ads}$  = Measure of affinity of adsorbate for adsorbent

$K$  = Measure of the capacity of the adsorbent

## **Life Expectancy of the Sorption Media**

With the isotherm testing, it enables us to determine the life expectancy of filter media in BMP operation. This life expectancy can be determined with respect to each type of pollutant of concern in the study. Firstly, the maximum capacity of adsorbent for a particular type of adsorbate may be retrieved from the corresponding isotherm plot. The life expectancy of filter media depends on amount of media used in a specific system, concentration of nutrient in storm water and flow rate of storm water. In case we know the concentration of nutrient in and flow rate of storm water, the amount of nutrient per year in storm water can be calculated, and then the life expectancy of media may be easily inducted.

## **Removal Efficiency, Kinetics, and Head Loss**

A laboratory column test method is a physical model, or microcosm, which attempts to simulate, on a small scale, a portion of the real world subsurface environment under a controlled set of experimental conditions. Five Plexiglas columns with a diameter of 5.000 cm (2.000 inch) and length of 30.00 cm (1.000 foot) were prepared. All the five columns were tied with a wooden frame. All joints of the columns are leak proof by using pipe threat sealant. The top and bottom of the column were closed but there is removable screw cap to add media from the top and remove the media from the bottom. A filter with glass beads (diameter of 4.000 mm) was placed at the bottom to prevent the outward flow of finer particles from column during the collection of samples. Although the column is 30.00 cm long, the media was filled up to about 22.50 cm (9.000 inch) from the bottom. Tygon (Saint-Gobain, no. 16) tubes are added both top and bottom of the column for the flow of influent

and effluent. Influent is flowed to the column from a reservoir by using a peristaltic pump (Master flex L/S, Cole-Parmer instrument).

Kinetics for nitrate, nitrite, OP, TP, and TDP were derived from column study. Kinetics gives idea about velocity of a chemical reaction. Kinetics will help us to understand how long it will take to finish the nutrient removal process by sorption media. It will give us idea about residence time and volume of a reactor. The limestone ( $\text{CaCO}_3$ ) as calcium ( $\text{Ca}^{2+}$ ) ion will help to remove phosphorus in the form of hydroxyapatite ( $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$ ). The approximate chemical reaction can be shown below (3),



Kinetics was derived for each species with different influent concentrations that mimic the actual fluctuations in storm water wet and dry ponds. Four columns were loaded with 580.0 g of media mixture and the fifth column was loaded with natural soil collected from the Hunter's Trace pond in Marion County, Florida that was used as the control case. The reason for such separation of testing in different columns with respect to different chemical species is to avoid the cross contamination by different chemical species of interest. The surfaces area of sorption media would play an important role for the adsorption, adsorption, and the growth of microbes for nitrification/denitrification. It was expected that sorption processes may dominate the system in the first few hours that allows us to retrieve the kinetics information solely.

No pretreatment of the sorption media and natural soil was done because those pretreatment cannot be applicable in practical situations. The storm water was collected from UCF campus. The influent concentration of the storm water was then controlled by spiking

from stock solution (i.e., augmentation). The influent concentration portfolio for all testing species is comprised of 5.000 mg/L, 2.500 mg/L and 0.500 mg/L although it might vary by  $\pm 5.000\%$  in actual testing due to the instability of augmentation. The experiment was done in a batch mode. The five columns were flushed for three times upfront by the same solution that was to be used in the actual experiment. Flushing will remove the possible contaminants from sorption media mixture before starting the experiment. After flushing, the valve at the bottom of each column was closed to retain the nutrient laden solution into the media. The samples were collected after 1 hour, 3 hours and 5 hours generally by opening the valve at the bottom except for ammonia and TN. For ammonia and TN, the sample collection time was 0.5 hour, 1 hour and 1.5 hour. Each time, about 60.00 mL sample was collected from each column for kinetics study. The samples were diluted in case of higher concentration during the chemical analysis.

A list of methods used in the chemical analysis is shown in Table 4.1. A HACH 2800 spectrophotometer is used to determine the effluent concentration of nutrients by using Powder pillows (purchased from HACH Company, Loveland, CO). The pH values were measured by using an Accumet research (AR 50- dual channel pH meter) equipment. In these columns, however, both nitrification/denitrification and sorption mechanism may work together in the removal process.

**Table 7: Method used to determine effluent concentration for each chemical species**

<b>Chemical Species</b>	<b>Title of Method</b>	<b>Method No.</b>
Ammonia as nitrogen	Salicylate method	Method 8155
Nitrate as nitrogen	Cadmium reduction method	Method 8192, 8171
Nitrite as nitrogen	Diazotization method	Method 8507
Total nitrogen	Persulfate digestion method	Method 10071
Total dissolved phosphorus	Acid persulfate digestion method	Method 8190
Total phosphorus	Acid persulfate digestion method	Method 8190
Orthophosphate	PhosVer 3 (Ascorbic acid) method	Method 8048

Kinetic studies have a significant role for the design of a proper reactor to produce the desired product. In most studies, it is common to first assume reaction order as a first-order (see Equation 4.5), and rate constant  $k$  ( $\text{hr}^{-1}$ ) is calculated from the slope of the line for  $\ln [C_0/C]$  vs. reaction time. Integration of equation results in

$$-dC/dt = k [C] \quad \text{and} \quad \ln [C_0/C] = kt \quad (4.5)$$

Where,  $C_0$  is the influent concentration (i.e., nutrient at here).

Rates of the reaction orders may be calculated from liner regression of  $\ln [C_0/C]$  vs. reaction time for the reduction of ammonia, nitrite, nitrate, OP etc. if in the first-order kinetics works well. If first-order reaction is not a good fit, a second-order reaction may be assumed as the kinetics by a similar approach in which graphs between  $1/C$  vs. time for each species may be plotted for identification (see Equation 4.5).

$$-dC/dt = k [C] [H^+] \quad \text{and} \quad 1/[C] = 1/[C_0] + kt \quad (4.5)$$

The head loss of the column was also measured. For this reason, two new columns with the same size as column test were built. Each column has three holes: one is at the top, another one is at the bottom and the other one is in the middle. The distance between top and bottom holes is about 22.86 cm and the middle hole is about 11.43 cm below the top one. A tube with an inner diameter of 5.000 cm was connected with each hole by glue as piezometric tube. The water was directed to flow continuously into the column from a reservoir that is about 120.0 cm above the floor of the room and column bottom is about 10.16 cm above the floor. The reading was taken after 15 minutes of water flow got started.

## **Abiotic test**

It is a major concern during the experiment as to whether the removal process of nutrients from stormwater is due to either the physicochemical or microbiological process. An abiotic test is conducted to confirm the removal process. A stock solution of 2000 mg/L of  $\text{HgCl}_2$  was prepared for abiotic control. 9.000 ml of  $\text{HgCl}_2$  was added into every 1.000 L of influent. The retention time was 5 hours for nitrate and OP and 1 hours for ammonia, respectively. The abiotic test was conducted for ammonia in response to the presence of nitrifiers, whereas it is conducted for nitrate and phosphorus in response to the presence of denitrifiers and and Phosphorus Accumulating Bacteria (PAB), respectively. All other things was remain same (i.e. like kinetic analysis). Extreme care was taken to use  $\text{HgCl}_2$  during the experiment.

## **Results and Discussion**

### **Isotherm Study for the Sorption Media Mixture**

From the Tables 4.2 and 4.3, it is observed that value of  $n$  is above 1 for nitrate and TDP. When the  $n=1$  or less, it indicates that all cases of adsorbent have equal affinity for the adsorbate. When  $n>1$ , it means affinity decrease with increasing adsorption density (2). The value of maximum capacity of adsorbent for adsorbate is also shown by  $q_m$ . The isotherm graphs (Figures 4.1-4.5) are shown below to take an idea about the whole scenario.

**Table 8: Data showing the properties of Langmuir isotherm for different species.**

Species	Isotherm equation for Langmuir	R-square value	$1/(q_m K_{ads})$	$q_m K_{ads}$	$1/q_m$ in mg/mg	$q_m$ in mg/mg
NH <sub>3</sub> -N	$y=10233.000x-8880.700$	0.941	10233.000	0.000098*	-8880.700	-0.000
OP	$y=272.850x-129.740$	0.970	272.850	0.004	-129.740	-0.008
NO <sub>3</sub> -N	$y=128.740x+1030.000$	0.801	128.740	0.008	1030.000	0.001
NO <sub>2</sub> -N	$y=229620.000x-229133.000$	0.844	229620.000	0.000004*	-229133.000	-0.000004*
TDP	$y=101.120x+137.000$	0.741	101.120	0.010	137.000	0.007

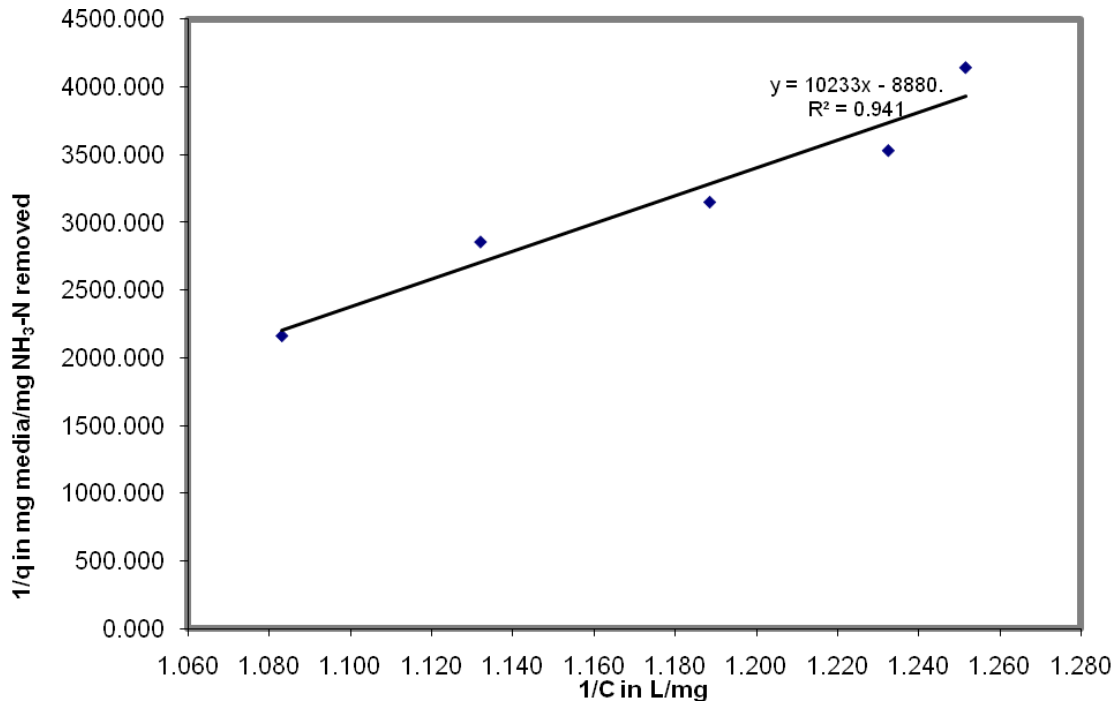
Note:  $y= 1/q$  and  $x=1/C$ ; The asterisk represents very small number.

**Table 9: Data showing the properties of Freundlich isotherm for different species.**

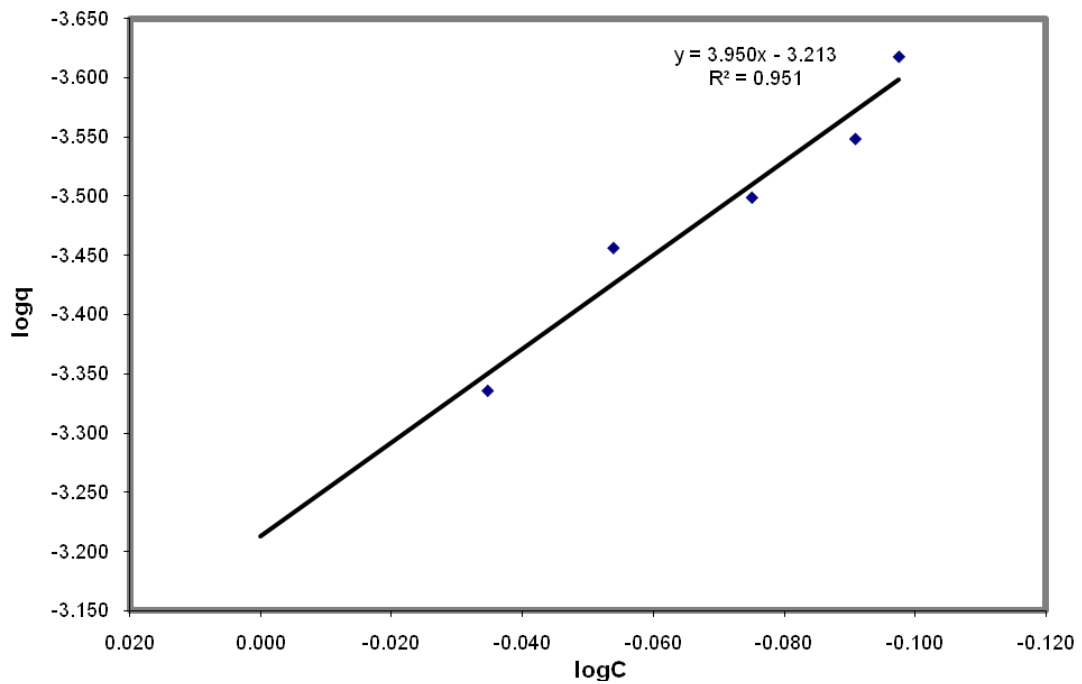
Species	Isotherm equation for Freundlich	R-square value	$1/n$	$n$	LogK	K in mg/mg
NH <sub>3</sub> -N	$y=3.951x-3.213$	0.951	3.951	0.253	-3.213	0.001
OP	$y=1.293x-2.215$	0.955	1.293	0.774	-2.215	0.006
NO <sub>3</sub> -N	$y=0.231x-3.043$	0.847	0.231	4.331	-3.043	0.001
NO <sub>2</sub> -N	$y=34.571x-3.389$	0.754	34.571	0.029	-3.389	0.00041*
TDP	$y=0.771x-2.268$	0.747	0.771	1.298	-2.268	0.005

Note:  $y=\log q$  and  $x=\log C$ ; The asterisk represents very small number.



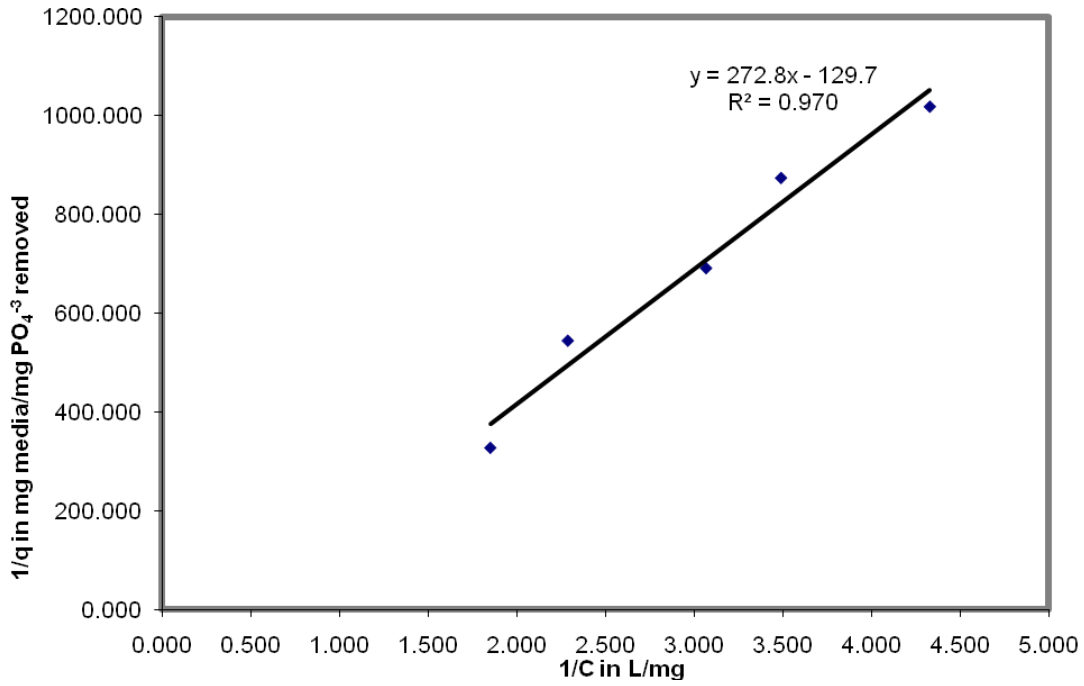


(a)

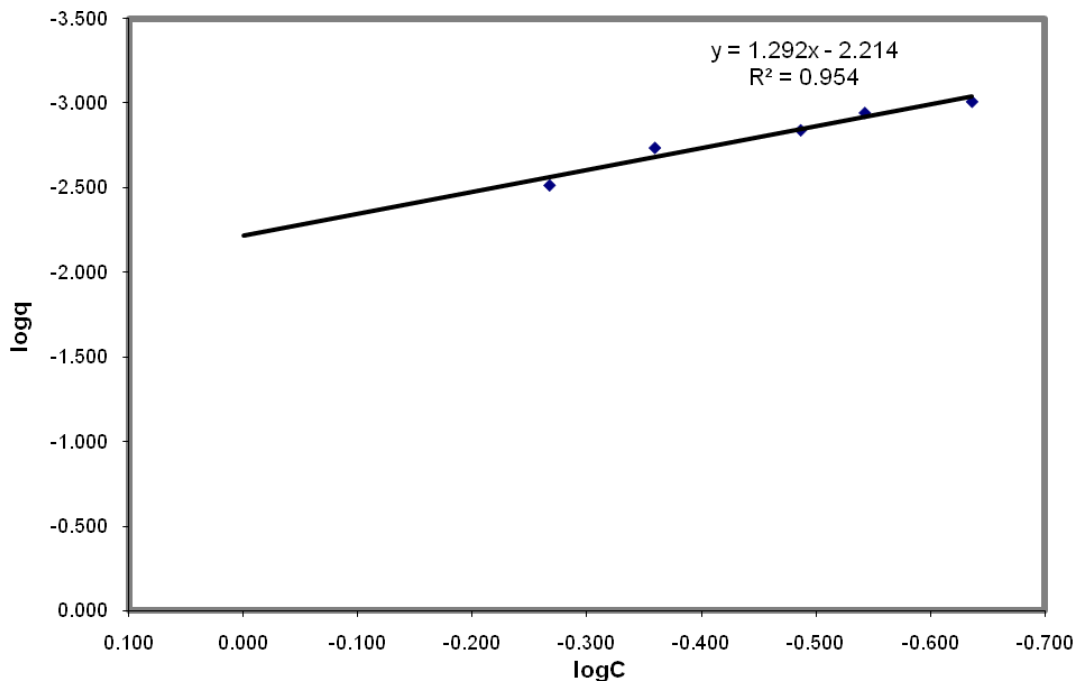


(b)

**Figure 9: The isotherm study for ammonia. (a) is Langmuir isotherm plot and (b) is Freundlich isotherm plot**

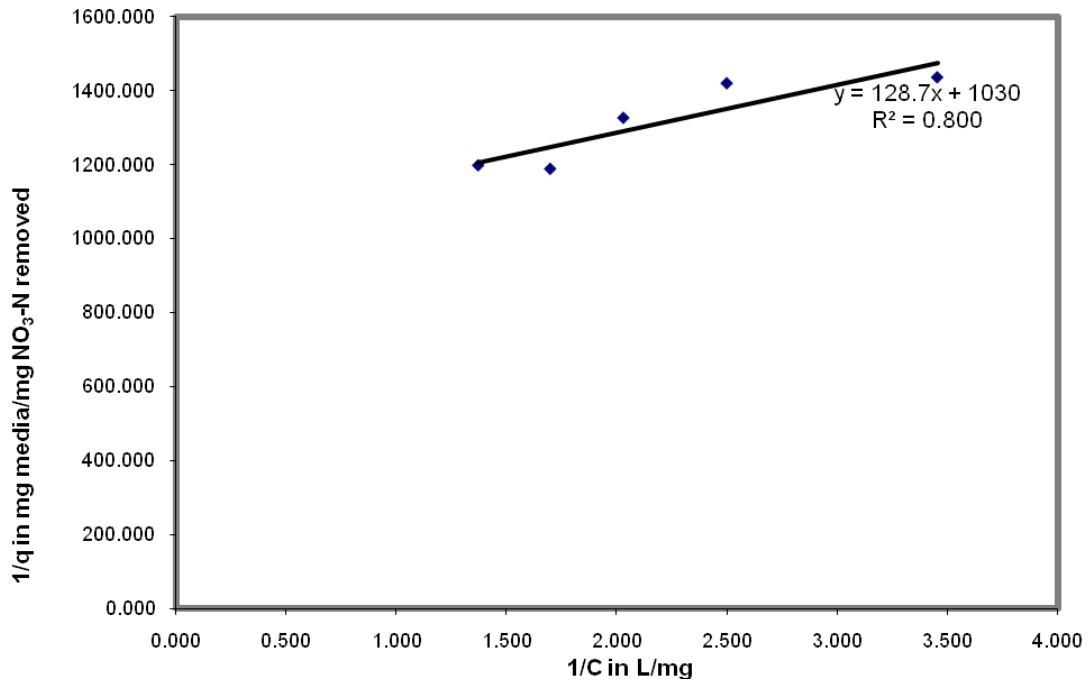


(a)

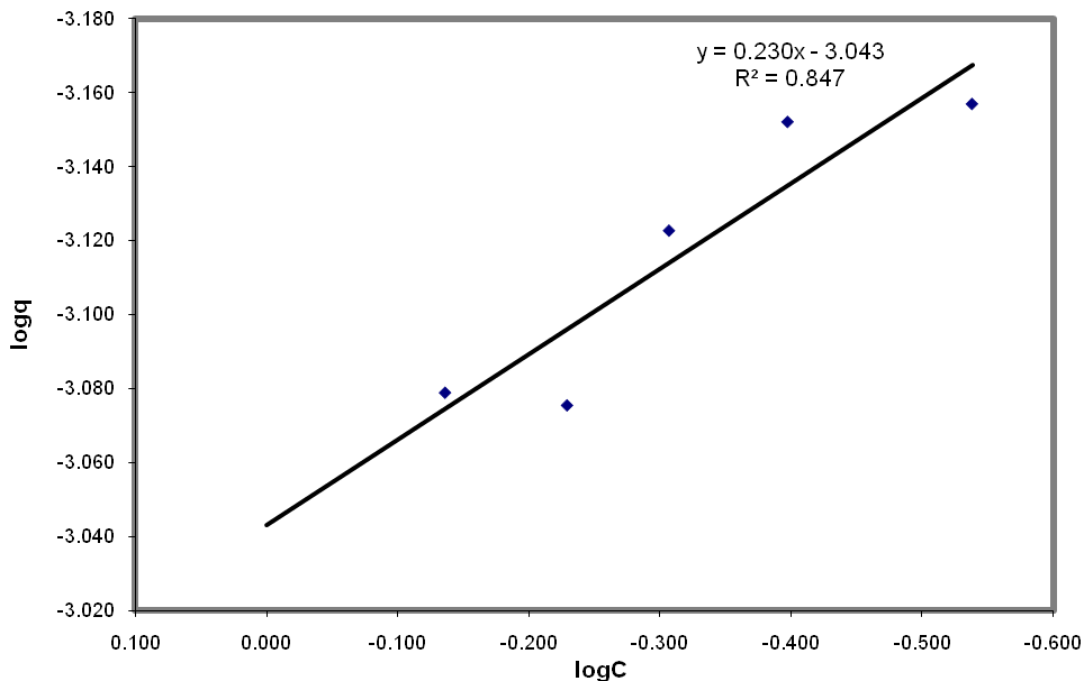


(b)

**Figure 10: The isotherm study for orthophosphate. (a) is Langmuir isotherm plot and (b) is Freundlich isotherm plot**

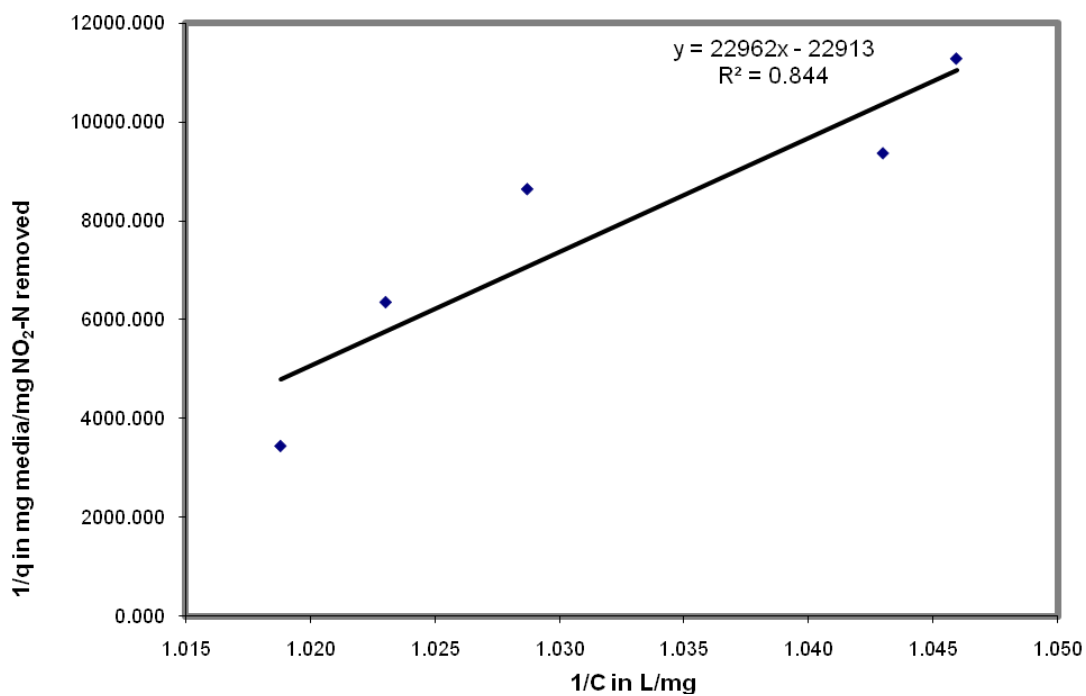


(a)

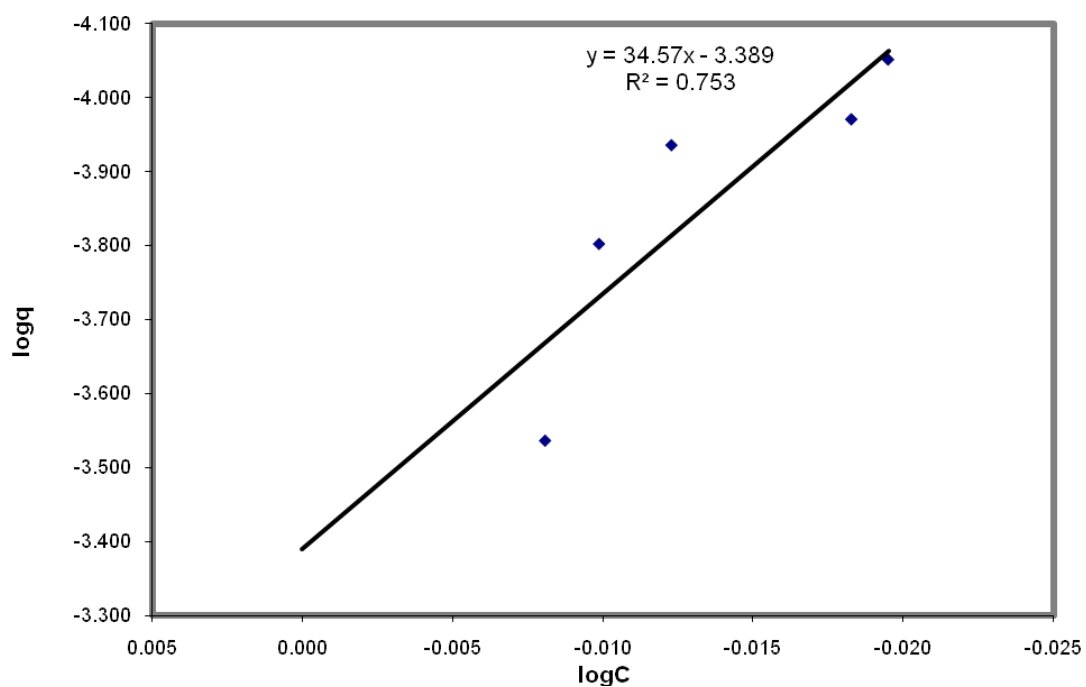


(b)

**Figure 11: The isotherm study for nitrate. (a) is Langmuir isotherm plot and (b) is Freundlich isotherm plot**

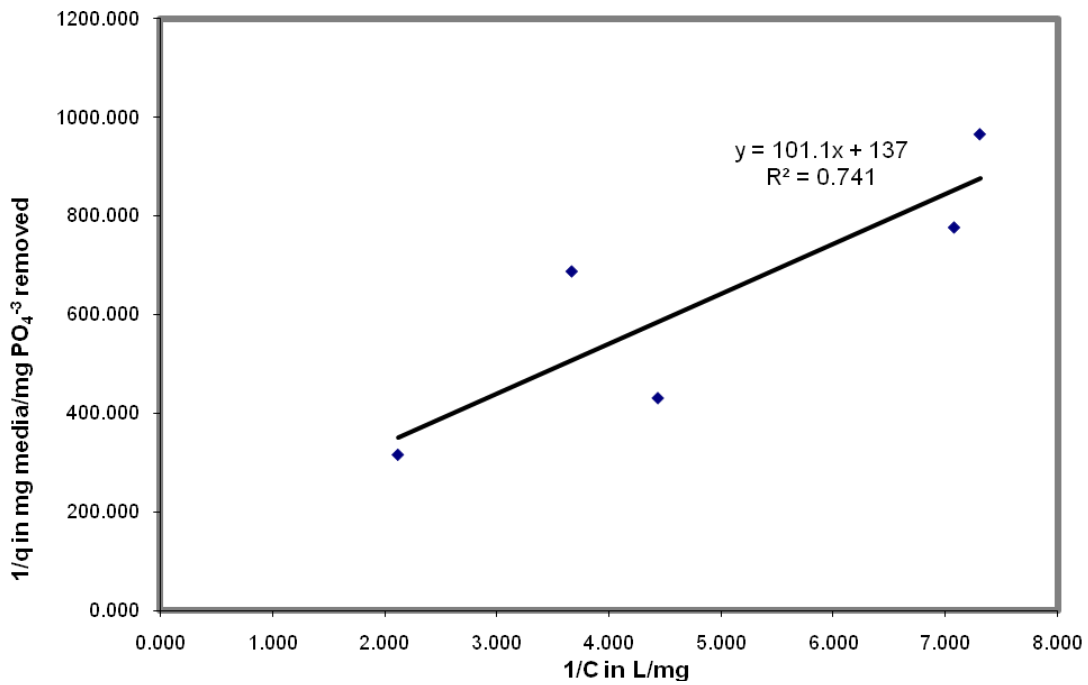


(a)

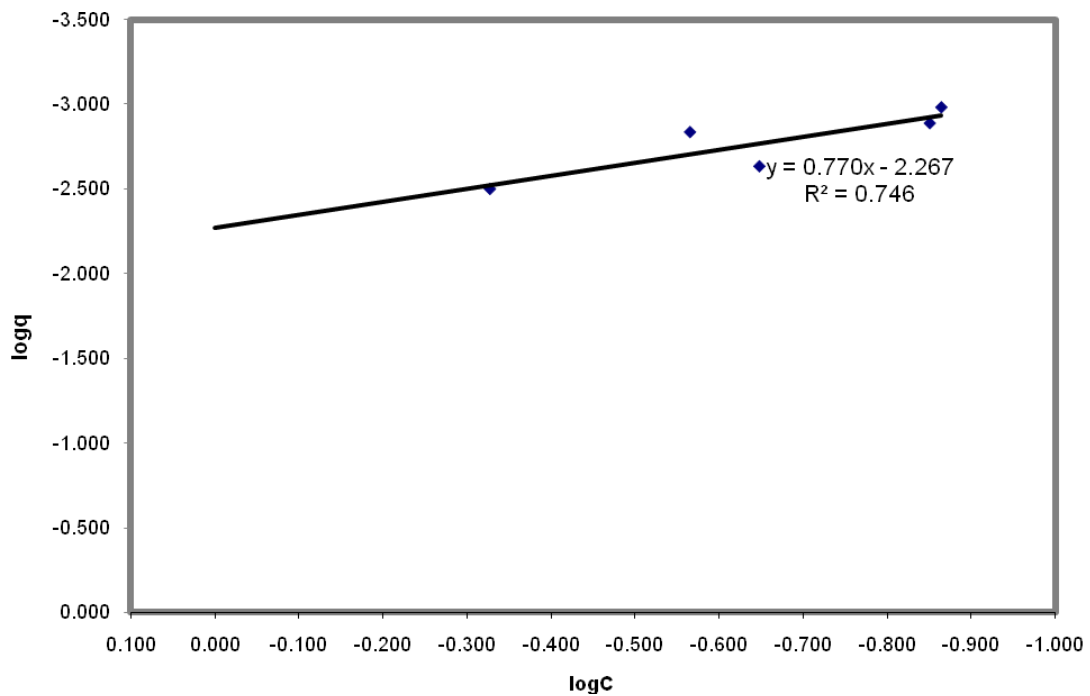


(b)

**Figure 12: The isotherm study for nitrite. (a) is Langmuir isotherm plot and (b) is Freundlich isotherm plot**



(a)



(b)

**Figure 13: The isotherm study for total dissolved phosphorus. (a) is Langmuir isotherm plot and (b) is Freundlich isotherm plot**

### **Life Expectancy of the Media**

Suppose that 300,000.000 g of media is used in a BMP system to remove OP in the runoff. Based on our isotherm test of OP, the maximum waste load is 0.008 mg nutrient/mg filter media. So the maximum amount of OP that can be adsorbed is 2,310.000 g (0.008 mg/mg \*300,000.000 g). Assume that stormwater has an OP concentration of 1.0000 mg/L on average and average stormwater flow is about 378.500 L per day (100.000 gal per day), then the total amount of OP is about 138.153 g/year (i.e., (100.000\*365\*3.785\*1.000)/1000). As a result, the life expectancy of the media mixture for OP removal would be about 16.740 years (2,310.000/138.153). This life expectancy may vary according to the type of media used, the waste loads in stormwater, and the intensity, frequency and duration of the stormwater in the study area. Based on the same rationale, Table 4.4 summarizes all the relevant life expectancy of media with respect to each pollutant of concern in this study. It appears that the effective removal of nitrogen species would lean to be more microbiological than physicalchemical process.

**Table 10: Life expectancy of sorption media mixture for different nutrient**

<b>Species</b>	<b>Life expectancy in year</b>
Ammonia as Nitrogen	0.2445
Orthophosphate	16.737
Nitrate as Nitrogen	2.1083
Nitrite as Nitrogen	0.0095
Total Dissolved Phosphorus	15.850

## **Reaction Kinetics**

A great difference of removal efficiency was observed between the column test and the isotherm study. Nutrients could not flow through the flask used in the isotherm test as there was no inflow or outflow in the flask. In the column test, however, the media might contribute to release (i.e., desorption) some nutrients being absorbed in the early stage which could ultimately impact the total removal efficiency. In the column, this was the test is conducted so that the media are flushed three times in the beginning of each run to wash out the contributed nutrients possibly. The sorption media is freshly loaded into the column. No seed or sludge was added into the column. Moreover the natural sand and citrus grove sand was oven dried at 105.0°C. It is not possible for bacteria to grow itself in a short time in the media. Again, it is not possible to ensure aerobic and anaerobic condition at the same time in a 30.00 cm column. Aerobic and anaerobic condition is very important to trigger biological nitrification/denitrification.

Findings in reaction kinetics analysis showed that if the influent concentration is lower in the case of ammonia, the sorption media can remove ammonia in a relatively greater efficiency. Our records showed that the removal may even reach 100.0% with waste load concentration of 0.500 mg/L and 2.500 mg/L after 1 hour and 1.5 hours of hydraulic retention time (HRT), respectively. When the ammonia concentration was up to 5.000 mg/L, the removal was about 64.00% after 1.5 hours of HRT. Given that the ammonia concentration is normally not very high in storm water, this media mixture should work well in terms of removing ammonia from storm water runoff. The removal of nitrate was about 95.36%, 81.34% and 65.68% after 5 hours of HRT when the influent waste loads were 0.500 mg/L, 2.500 mg/L and 5.000 mg/L, respectively. The removal of nitrite was promising when its

influent concentration was lower. Our record showed that the removal efficiency was about 94.14% and 98.72% when the influent waste loads were 0.500 mg/L and 2.500 mg/L, respectively. But it went down to 65.40% when the influent waste load was as high as 5.000 mg/L. Higher concentration means the solution has more ammonia ions and may be the sorption media has not enough surface to attract the additional ions due to higher concentration. With this observation, it can be concluded that filter media is efficient and effective for the removal of both nitrate and nitrite at lower influent concentrations (i.e., 0.500 mg/L and 2.500 mg/L) that covers most of the cases in real world systems. From the above analysis, it is certain that the proposed media can remove TN too. To prove this hypothesis, some TN removal test is conducted in the laboratory for confirmation. During the chemical analysis, conversion from ammonia to nitrite and nitrite to nitrate was tested to identify possible bacterial activity. No such conversion was detected during the test. So it could be concluded that the nutrient was removed by adsorption/absorption or physiochemical process. No biochemical process was present in the system.

OP is the main component of TP and it is about 70.00% to 90.00% of TP. The removal of OP was 79.50%, 94.39% and 97.50% after 5 hours HRT when the influent concentrations were 0.500 mg/L, 2.500 mg/L and 5.000 mg/L, respectively. The removal of OP went up with increasing influent concentrations in the sense that the proposed media may perform well if the storm water has higher phosphorus concentration. The same tendency was observed for the cases of TDP and TP removal. The removal of TDP was 86.30%, 96.06%, and 98.17% when the influent concentrations were 0.500 mg/L, 2.500 mg/L, and 5.000 mg/L after 5 hours HRT. The removal of TP was even above 99.00% no matter what influent concentrations



occurred. Hence, it can be confirmed that the proposed media should be effective in removing other forms of phosphorus.

The removal of nutrient from the natural soil is also observed for the purpose of comparison. Findings confirmed that natural soil is not capable of removing nitrate (only 19.20% nitrate removed in 5 hours HRT with influent concentration of 0.500 mg/L). But natural soil seems to be quite effective in removing ammonia though. The removal of ammonia was about 98.68% and 96.20% within 1.5 hours HRT when the influent concentration was 0.500 and 5.000 mg/L respectively. But natural soil cannot adsorb the ammonia and nitrate for a long time and some desorption phenomenon was observed every time. Natural soil can adsorb some nitrite at lower influent concentration but it is not the case at higher influent concentration. The removal of OP by natural soil was not well at lower influent concentration. Findings indicated that it can only remove 19.40% of OP at an influent concentration of 0.500 mg/L. But it may perform well in removing both TP and TDP. Both species had a removal efficiency of above 75.00% in our test.

### **Abiotic test**

Finally, the chemical analysis for the abiotic test confirmed that the nutrients removal process in our analysis was mainly a physicochemical process. After 5 hours of hydraulic retention time, the removal efficiency of nitrate and OP was about 83.32% and 92.20%, respectively with an initial concentration of 0.500 mg/L. The ammonia removal efficiency was about 100.0% after 1.500 hours of hydraulic retention time and the same initial concentration. All of the removal efficiencies remain almost same as what we had observed in the kinetics analysis. Since we did not seed or add sludge into the column to foster any amenable microbial environment and the natural and citrus grove sand was heated up to

105.0<sup>0</sup>C up front, it is not possible for bacteria to grow in such a short hydraulic retention time in the media. In other word, no nitrification/denitrification process was triggered in our test. Aerobic and anaerobic condition is very important to trigger biological nitrification/denitrification. The pH of the effluent was 6.500 to 8.000.

### **pH value**

The pH value of effluent varied in between 7.000 to 8.000 from these media columns and 6.000 to 7.500 in the natural soil column (i.e., the control case) at room temperature. The room temperature was in between 22.00 <sup>0</sup>C to 24.00 <sup>0</sup>C. This pH has important effect on reaction kinetics. If the pH is acidic, the media cannot retain the nutrients for a long time and desorption will start very fast. On the other hand, sorption media can retain the nutrient in basic pH. Again, basic pH is favorable for the precipitation reaction between phosphorus and limestone. In summary, the proposed media can quickly remove the nutrient from storm water runoff whereas the natural soil can remove part of the nutrient if the HRT is big enough. But it is not possible because the storm water would reach groundwater quickly via seepage flow if the vadose zone is shallow. For this reason, it is better to use sorption media to remove nutrient from storm water runoff before it reaches groundwater aquifer.

Assume that the proposed filter media in this experiment may follow either the first-order or second-order reaction kinetics. The regression equations, R-square values, and rate constants may be determined from the graphs plotted. We found out that it is very difficult to determine the kinetics for ammonia as it is removed very quickly by the media. Overall, the OP, nitrate and nitrite follow the second-order reaction kinetics. In the case of OP testing, the second-order reaction kinetics may be derived with respect to a good R-square value of 0.700

to 0.940. The removal of OP by natural soil also confirmed that the same kinetics works well like the others. The minimum R-square value for nitrate was 0.880 and for nitrite was 0.810.

Tables 4.5 and 4.6 summarize all of reaction kinetic analysis of the sorption media and natural soil. Based on R-square value, it can be concluded that all the species follow the second-order reaction kinetics more closely. This is mainly due to the collective impact of both the influent concentration and the pH value. Apparently, the proposed media exhibits better removal efficiency in terms of all chemical species of concern (i.e. ammonia, nitrate, nitrite, TN, TP, TDP and OP). Our justification is that ammonia, nitrate, nitrite, and TN were mainly removed by saw dust and tire crumb via adsorption whereas TP, TDP and OP were mainly removed by tire crumb and limestone via adsorption. Phosphorus species may also be removed by other chemical precipitation reactions.

**Table 11: Summary table of kinetics for the sorption media mixture**

Species	Initial concentration in mg/L	first order equation	R-square value for first order equation	K value for first order equation in hr <sup>-1</sup>	second order equation	R-square value for second order equation	K value for second order equation in L/mg.hr
Nitrate	5.000	y=0.230x	0.943	0.230	y=0.074x+0.193	0.996	0.074
	2.500	y=0.330x	0.998	0.330	y=0.302x+0.391	0.920	0.302
	0.500	y=0.749x	0.654	0.749	y=9.516x+2.000	0.880	9.516
Ortho-Phosphate	5.000	y=0.887x	0.381	0.887	y=1.637x+0.201	0.859	1.637
	2.500	y=0.712x	0.334	0.712	y=1.511x+0.389	0.698	1.511
	0.500	y=0.345x	0.780	0.345	y=1.340x+1.754	0.940	1.340
Nitrite	5.000	y=0.222x	0.831	0.222	y=0.072x+0.198	0.919	0.072
	2.500	y=0.897x	0.990	0.897	y=5.088x+0.402	0.818	5.088
	0.500	y=0.683x	0.649	0.683	y=6.736x+1.879	0.929	6.736
TP	5.000	y=1.328x	0.781	1.328	y=11.275+0.202	0.961	11.28
	2.500	y=1.314x	0.523	1.314	y=19.46x+0.413	0.725	19.46
	0.500	y=0.954x	0.935	0.954	y=27.53x+1.68	0.751	27.53
TDP	5.000	y=0.942x	0.443	0.942	y=2.089x+0.199	0.912	2.089
	2.500	y=0.692x	0.738	0.692	y=1.715x+0.405	0.862	1.715
	0.500	y=0.519x	0.231	0.519	y=3.454x+2.045	0.358	3.454

Note: for first order  $y=\ln(C_0/C)$  and  $x=t$ ; for second order  $y=1/C$  and  $x=t$

**Table 12: Summary table of kinetics for the natural soil (Hunter's Trace soil)**

Species	Initial concentration in mg/L	First order Equation	R-square value for first order equation	K value for first order equation in hr <sup>-1</sup>	Second order Equation	R-square value for second order equation	K value for second order equation in L/mg.hr
Nitrate	5.000	y=0.230x	0.653	0.230	y=0.074x+0.19	0.996	0.074
	0.500	y=0.066x	0.222	0.066	y=1.635x+2.14	0.213	1.635
Ortho-Phosphate	5.000	y=0.577x	0.388	0.577	y=0.443x+0.20	0.705	0.443
	0.500	y=0.036x	0.836	0.036	y=0.065x+1.65	0.820	0.065
Nitrite	5.000	y=0.146x	0.254	0.146	y=0.039x+0.19	0.305	0.039
	0.500	y=0.652x	0.881	0.652	y=6.101x+1.82	0.964	6.101
TP	5.000	y=1.003x	0.745	1.003	y=3.344x+0.22	0.912	2.090
	0.500	y=0.336x	0.846	0.336	y=1.425x+1.98	0.971	1.425
TDP	5.000	y=0.953x	0.412	0.953	y=1.946x+0.17	0.460	1.946
	0.500	y=0.620x	0.334	0.620	y=5.502x+2.08 3	0.663	5.502

Note: for first order  $y=\ln(C_0/C)$  and  $x=t$ ; for second order  $y=1/C$  and  $x=t$

## **Application Potential Head Loss**

The head loss is calculated based on the aforementioned procedure in a batch run. It implies the permeability rate in the system. Within the natural soil column, the head loss is about 57.15 cm of water (22.50 inches of water) and in filter media column the head loss was about 83.82 cm in water (34.00 inches of water). Stormwater detention ponds or dry ponds are areas that are normally dry, but function as detention reservoirs during storm events. The head loss information may be used to design the essential depth of the dry pond so as to help the stormwater get through the pond via infiltration before overflow. The volume of the pond should at least be equal to the average runoff event during the year. The removal of nutrients in these ponds could be worse than that in wet ponds.

## **Engineering Feasibility Study**

In any cases, dry ponds have dual purpose in both quality and quantity control. Without having specific filter media, typical removal rates in dry detention ponds would be between 10.00%-20.00% (4). This study proved that the functionalized green media effectively and efficiently remove most of the nutrient species within an appropriate retention time via the adsorption and absorption processes in which the later one dominates the system. The life expectancy of the proposed media is reasonably long for removing phosphorus species that ensures the system reliability in green infrastructures. The column test was set up by such a way that may prove its credibility to the application in dry ponds where storm water impact is in a batch mode. The assurance of HRT would be a major challenge in applying this concept because the time for the intermittent flow (i.e., infiltrate) to pass through the media layer

constitutes the legitimate HRT. The design of thickness of the media layer at the bottom of the dry ponds may be examined further with regard to the reaction kinetics data. The proposed media can be wrapped up by geotextile and laid down at the bottom of the riprap apron area.

## References

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## **CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS**

### **Conclusions and Recommendations**

As physiochemical properties are influencing the removal efficiency, it is very important to determine the properties of sorption media. From the above analysis, it is found that the dispersion coefficient is higher when there is more pore space and lower hydraulic conductivity. The lower hydraulic conductivity will increase the hydraulic retention time and the tracer has more time to disperse into the sorption media. These three terms (i.e. hydraulic conductivity, HRT and dispersion coefficient) will influence the removal efficiency of nutrients. Kinetics gives us idea about the completion time of nutrient removal process.

From the above analysis, it is found that sorption media is very effective to remove nutrients from storm water. The concentration of the species was much higher than the average concentration of species in the storm water. The hydraulic retention time (HRT) is playing a very important role in the removal process. Higher nutrient removal can be expected for higher HRT. Again, pH is also very important as acidic pH will accelerate the desorption process. So neutral or basic pH is most favorable for the adsorption process by sorption media. Sorption media can easily remove nitrogen species with removal efficiency above 80.00% in most of the cases. On the other hand, it can remove phosphorus species with higher concentration. This tendency is observed in the analysis of OP, TP and TDP. From isotherm test, it is found that sorption media may contribute some ammonia and nitrite at the beginning of the experiment. But ultimately these two species are adsorbed by media. Isotherm test helps to determine the life expectancy of sorption media and kinetics helps to determine the time required to complete a removal process.

## **Future research**

Sorption media should be tested in practical application to determine the long term performance of the sorption media and life expectancy of the media. Media can also be tested to remove heavy metals and organics from storm water, wastewater and groundwater. Optimum hydraulic retention time can be determined by a long term experiment.

Nowadays wetland treatment process for wastewater treatment is very well known. If it is possible to grow the native plants on sorption media without any sand, then it is possible to enjoy the dual effect of sorption media and native plants for nutrient removal.



**APPENDIX**  
**NUTRIENT REMOVAL EFFICIENCY BY SORPTION MEDIA**  
**MIXTURE**

Table A1: Removal efficiency of ammonia by sorption media

Time in hour	Ammonia			
	Initial conc. In mg/L NH <sub>3</sub> -N	Conc. In mg/L NH <sub>3</sub> -N	Removal	ln(C <sub>0</sub> /C)
0.000				0.000
0.500	0.526	0.004	99.154	4.773
1.000	0.526	0.000	100.000	-
1.500	0.526	0.000	100.000	-
pH	7.000			
Temperature	23.500 degree C			

Table A2: Removal efficiency of ammonia by sorption media

Time in hour	Ammonia			
	Initial conc. In mg/L NH <sub>3</sub> -N	Conc. In mg/L NH <sub>3</sub> -N	Removal	1/C
0.000				1.901
0.500	0.526	0.004	99.154	224.785
1.000	0.526	0.000	100.000	-
1.500	0.526	0.000	100.000	-
pH	7.000			

Table A3: Removal efficiency of ammonia by sorption media

Time in hour	Ammonia			
	Initial conc. In mg/L NH <sub>3</sub> -N	Conc. In mg/L NH <sub>3</sub> -N	Removal	ln(C <sub>0</sub> /C)
0.000				0.000
0.500	2.560	0.034	98.681	4.329
1.000	2.560	0.020	99.234	4.871
1.500	2.560	0.000	100.000	0.000

Table A4: Removal efficiency of ammonia by sorption media

Time in hour	Ammonia			
	Initial conc. In mg/L NH <sub>3</sub> -N	Conc. In mg/L NH <sub>3</sub> -N	Removal	1/C
<b>0.000</b>				<b>0.391</b>
0.500	2.560	0.034	98.681	29.621
1.000	2.560	0.020	99.234	50.958
1.500	2.560	0.000	100.000	-
pH	7.000			

Table A5: Removal efficiency of ammonia by sorption media

Time in hour	Ammonia			
	Initial conc. In mg/L NH <sub>3</sub> -N	Conc. In mg/L NH <sub>3</sub> -N	Removal	ln(C <sub>0</sub> /C)
0.000				0.000
0.500	5.317	1.585	70.198	1.211
1.000	5.317	1.774	66.632	1.098
1.500	5.317	1.879	64.661	1.040

Table A6: Removal efficiency of ammonia by sorption media

Time in hour	Ammonia			
	Initial conc. In mg/L NH <sub>3</sub> -N	Conc. In mg/L NH <sub>3</sub> -N	Removal	1/C
<b>0</b>				<b>0.188</b>
0.500	5.317	1.585	70.198	0.631
1.000	5.317	1.774	66.632	0.564
1.500	5.317	1.879	64.661	0.532

Table A7: Removal efficiency of nitrate by sorption media

Time in hour	Nitrate			
	Initial conc. In mg/L NO <sub>3</sub> -N	Conc. In mg/L NO <sub>3</sub> -N	Removal	ln(C <sub>0</sub> /C)
0.000				0.000
1.000	0.500	0.083	83.430	1.798
3.000	0.500	0.024	95.137	3.024
5.000	0.500	0.023	95.362	3.071

Table A8: Removal efficiency of nitrate by sorption media

Time in hour	Nitrate			
	Initial conc. In mg/L NO <sub>3</sub> -N	Conc. In mg/L NO <sub>3</sub> -N	Removal	1/C
<b>0</b>				<b>2</b>
1.000	0.500	0.083	83.430	12.070
3.000	0.500	0.024	95.137	41.128
5.000	0.500	0.023	95.362	43.124

Table A9: Removal efficiency of nitrate by sorption media

Time in hour	Nitrate			
	Initial conc. In mg/L NO <sub>3</sub> -N	Conc. In mg/L NO <sub>3</sub> -N	Removal	ln(C <sub>0</sub> /C)
0.000				0.000
1.000	2.549	1.804	29.240	0.346
3.000	2.549	0.990	61.179	0.946
5.000	2.549	0.476	81.347	1.679

Table A10: Removal efficiency of nitrate by sorption media

Time in hour	Nitrate			
	Initial conc. In mg/L NO <sub>3</sub> -N	Conc. In mg/L NO <sub>3</sub> -N	Removal	1/C
<b>0.000</b>				<b>0.392</b>
1.000	2.549	1.804	29.240	0.554
3.000	2.549	0.990	61.179	1.010
5.000	2.549	0.476	81.347	2.103

Table A11: Removal efficiency of nitrate by sorption media

Time in hour	Nitrate			
	Initial conc. In mg/L NO <sub>3</sub> -N	Conc. In mg/L NO <sub>3</sub> -N	Removal	ln(C <sub>0</sub> /C)
0.000				0.000
1.000	5.172	3.526	31.821	0.383
3.000	5.172	2.385	53.884	0.774
5.000	5.172	1.775	65.674	1.069

Table A12: Removal efficiency of nitrate by sorption media

Time in hour	Nitrate			
	Initial conc. In mg/L NO <sub>3</sub> -N	Conc. In mg/L NO <sub>3</sub> -N	Removal	1/C
<b>0.000</b>				<b>0.193</b>
1.000	5.172	3.526	31.821	0.284
3.000	5.172	2.385	53.884	0.419
5.000	5.172	1.775	65.674	0.563

Table A13: Removal efficiency of nitrite by sorption media

Time in hour	Nitrite			
	Initial conc. In mg/L NO <sub>2</sub> -N	Conc. In mg/L NO <sub>2</sub> -N	Removal	ln(C <sub>0</sub> /C)
0.000				0.000
1.000	0.532	0.096	81.963	1.713
3.000	0.532	0.037	93.111	2.675
5.000	0.532	0.031	94.144	2.838

Table A14: Removal efficiency of nitrite by sorption media

Time in hour	Nitrite			
	Initial conc. In mg/L NO <sub>2</sub> -N	Conc. In mg/L NO <sub>2</sub> -N	Removal	1/C
0.000				1.879
1.000	0.532	0.096	81.963	10.418
3.000	0.532	0.037	93.111	27.279
5.000	0.532	0.031	94.144	32.088

Table A15: Removal efficiency of nitrite by sorption media

Time in hour	Nitrite			
	Initial conc. In mg/L NO <sub>2</sub> -N	Conc. In mg/L NO <sub>2</sub> -N	Removal	ln(C <sub>0</sub> /C)
0.000				0.000
1.000	2.490	1.203	51.698	0.728
3.000	2.490	0.129	94.814	2.959
5.000	2.490	0.032	98.726	4.363

Table A16: Removal efficiency of nitrite by sorption media

Time in hour	Nitrite			
	Initial conc. In mg/L NO <sub>2</sub> -N	Conc. In mg/L NO <sub>2</sub> -N	Removal	1/C
0.000				0.402
1.000	2.490	1.203	51.698	0.831
3.000	2.490	0.129	94.814	7.744
5.000	2.490	0.032	98.726	31.532

Table A17: Removal efficiency of nitrite by sorption media

Time in hour	Nitrite			
	Initial conc. In mg/L NO <sub>2</sub> -N	Conc. In mg/L NO <sub>2</sub> -N	Removal	ln(C <sub>0</sub> /C)
0.000				0.000
1.000	5.059	2.982	41.054	0.529
3.000	5.059	2.646	47.696	0.648
5.000	5.059	1.751	65.395	1.061

Table A18: Removal efficiency of nitrite by sorption media

Time in hour	Nitrite			
	Initial conc. In mg/L NO <sub>2</sub> -N	Conc. In mg/L NO <sub>2</sub> -N	Removal	1/C
0.000				0.198
1.000	5.059	2.982	41.054	0.335
3.000	5.059	2.646	47.696	0.378
5.000	5.059	1.751	65.395	0.571

Table A19: Removal efficiency of OP by sorption media

<b>Time in hour</b>	<b>OP</b>			
	<b>Initial conc. In mg/L</b>	<b>Conc. In mg/L</b>	<b>Removal</b>	<b>ln(C<sub>0</sub>/C)</b>
0.000				0.000
1.000	0.570	0.241	57.777	0.862
3.000	0.570	0.191	66.527	1.094
5.000	0.570	0.117	79.510	1.585
pH	7.600			
Temperature	23.000 degree C			

Table A20: Removal efficiency of OP by sorption media

<b>Time in hour</b>	<b>OP</b>			
	<b>Initial conc. In mg/L</b>	<b>Conc. In mg/L</b>	<b>Removal</b>	<b>1/C</b>
<b>0.000</b>				<b>1.754</b>
1.000	0.570	0.241	57.777	4.155
3.000	0.570	0.191	66.527	5.241
5.000	0.570	0.117	79.510	8.562
pH	7.600			

Table A21: Removal efficiency of OP by sorption media

<b>Time in hour</b>	<b>OP</b>			
	<b>Initial conc. In mg/L</b>	<b>Conc. In mg/L</b>	<b>Removal</b>	<b>ln(C<sub>0</sub>/C)</b>
0.000				0.000
1.000	2.569	0.234	90.875	2.394
3.000	2.569	0.172	93.309	2.704
5.000	2.569	0.144	94.390	2.881
pH	7.440			
Temperature	23.000 degree C			

Table A22: Removal efficiency of OP by sorption media

<b>Time in hour</b>	<b>OP</b>			
	<b>Initial conc. In mg/L</b>	<b>Conc. In mg/L</b>	<b>Removal</b>	<b>1/C</b>
0.000				0.389
1.000	2.569	0.234	90.875	4.266
3.000	2.569	0.172	93.309	5.817
5.000	2.569	0.144	94.390	6.939
pH	7.440			

Table A23: Removal efficiency of OP by sorption media

Time in hour	OP			
	Initial conc. In mg/L	Conc. In mg/L	Removal	ln(C <sub>0</sub> /C)
0.000				0.000
1.000	4.980	0.256	94.867	2.969
3.000	4.980	0.201	95.971	3.212
5.000	4.980	0.124	97.506	3.691
pH	7.050			
Temperature	24.000 degree C			

Table A24: Removal efficiency of OP by sorption media

Time in hour	OP			
	Initial conc. In mg/L	Conc. In mg/L	Removal	1/C
<b>0.000</b>				<b>0.201</b>
1.000	4.980	0.256	94.867	3.912
3.000	4.980	0.201	95.971	4.984
5.000	4.980	0.124	97.506	8.051
pH	7.050			

Table A25: Removal efficiency of TDP by sorption media

Time in hour	TDP			
	Initial conc. In mg/L PO <sub>4</sub> <sup>-3</sup>	Conc. In mg/L PO <sub>4</sub> <sup>-3</sup>	Removal	ln(C <sub>0</sub> /C)
0.000				0.000
1.000	0.489	0.083	83.027	1.774
3.000	0.489	0.057	88.344	2.149
5.000	0.489	0.067	86.299	1.988

Table A26: Removal efficiency of TDP by sorption media

Time in hour	TDP			
	Initial conc. In mg/L PO <sub>4</sub>	Conc. In mg/L PO <sub>4</sub>	Removal	1/C
0.000				2.045
1.000	0.489	0.083	83.027	12.048
3.000	0.489	0.057	88.344	17.544
5.000	0.489	0.067	86.299	14.925

Table A27: Removal efficiency of TDP by sorption media

Time in hour	TDP			
	Initial conc. In mg/L PO <sub>4</sub> <sup>-3</sup>	Conc. In mg/L PO <sub>4</sub> <sup>-3</sup>	Removal	ln(C <sub>0</sub> /C)
0.000				0.000
1.000	2.467	0.385	84.394	1.858
3.000	2.467	0.315	87.231	2.058
5.000	2.467	0.097	96.068	3.236

Table A28: Removal efficiency of TDP by sorption media

Time in hour	TDP			
	Initial conc. In mg/L PO <sub>4</sub>	Conc. In mg/L PO <sub>4</sub>	Removal	1/C
0.000				0.405
1.000	2.467	0.385	84.394	2.597
3.000	2.467	0.315	87.231	3.175
5.000	2.467	0.097	96.068	10.309

Table A29: Removal efficiency of TDP by sorption media

Time in hour	TDP			
	Initial conc. In mg/L PO <sub>4</sub> <sup>-3</sup>	Conc. In mg/L PO <sub>4</sub> <sup>-3</sup>	Removal	ln(C <sub>0</sub> /C)
0.000				0.000
1.000	5.014	0.233	95.350	3.068
3.000	5.014	0.184	96.326	3.304
5.000	5.014	0.092	98.165	3.998

Table A30: Removal efficiency of TDP by sorption media

Time in hour	TDP			
	Initial conc. In mg/L PO <sub>4</sub>	Conc. In mg/L PO <sub>4</sub>	Removal	1/C
0.000				0.199
1.000	5.014	0.233	95.350	4.289
3.000	5.014	0.184	96.326	5.428
5.000	5.014	0.092	98.165	10.870

Table A31: Removal efficiency of TP by sorption media

Time in hour	TP			
	Initial conc. In mg/L PO <sub>4</sub> <sup>-3</sup>	Conc. In mg/L PO <sub>4</sub> <sup>-3</sup>	Removal	ln(C <sub>0</sub> /C)
0.000				0.000
1.000	0.595	0.099	83.436	1.798
3.000	0.595	0.037	93.711	2.766
5.000	0.595	0.006	99.055	4.661

Table A32: Removal efficiency of TP by sorption media

Time in hour	TP			
	Initial conc. In mg/L PO <sub>4</sub>	Conc. In mg/L PO <sub>4</sub>	Removal	1/C
0.000				1.680
1.000	0.595	0.099	83.436	10.141
3.000	0.595	0.037	93.711	26.712
5.000	0.595	0.006	99.055	177.696



Table A33: Removal efficiency of TP by sorption media

Time in hour	TP			
	Initial conc. In mg/L PO <sub>4</sub> <sup>-3</sup>	Conc. In mg/L PO <sub>4</sub> <sup>-3</sup>	Removal	ln(C <sub>0</sub> /C)
0.000				0.000
1.000	2.421	0.069	97.139	3.554
3.000	2.421	0.011	99.565	5.438
5.000	2.421	0.013	99.464	5.229

Table A34: Removal efficiency of TP by sorption media

Time in hour	TP			
	Initial conc. In mg/L PO <sub>4</sub>	Conc. In mg/L PO <sub>4</sub>	Removal	1/C
0.000				0.413
1.000	2.421	0.069	97.139	14.442
3.000	2.421	0.011	99.565	95.047
5.000	2.421	0.013	99.464	77.113

Table A35: Removal efficiency of TP by sorption media

Time in hour	TP			
	Initial conc. In mg/L PO <sub>4</sub> <sup>-3</sup>	Conc. In mg/L PO <sub>4</sub> <sup>-3</sup>	Removal	ln(C <sub>0</sub> /C)
0.000				0.000
1.000	4.941	0.336	93.201	2.688
3.000	4.941	0.026	99.465	5.231
5.000	4.941	0.018	99.638	5.623

Table A36: Removal efficiency of TP by sorption media

Time in hour	TP			
	Initial conc. In mg/L PO <sub>4</sub>	Conc. In mg/L PO <sub>4</sub>	Removal	1/C
0.000				0.202
1.000	4.941	0.336	93.201	2.977
3.000	4.941	0.026	99.465	37.843
5.000	4.941	0.018	99.638	55.986