CHAPTER 8

Use of Functionalized Filter Media for Nutrient Removal in Stormwater Ponds

Ni-Bin Chang, Ph.D., P.E., F.ASCE, M.EAS
Professor, Department of Civil, Environmental and Construction Engineering
University of Central Florida, Orlando, Florida, USA

Marty Wanielista, Ph.D., P.E., D.WRE
Director, Stormwater Management Academy
University of Central Florida, Orlando, Florida, USA

Mikhal Moberg, Fahim Hossain, and Ammarin Daranpob
Former Graduate Students, Department of Civil, Environmental and Construction Engineering
University of Central Florida, Orlando, Florida, USA

ABSTRACT: Many best-management practices (BMPs) currently used in urban regions have been developed to minimize flood risk, sustain downstream ecosystems, and secure the quality of groundwater sources either directly or indirectly. One such BMP is the reuse of stormwater by removing nutrients from the nutrient-laden "first flush" water collected in wet or dry ponds; this practice has led to the development of multifunctional sorption materials. In the interests of sustainable infrastructure, this chapter describes a design philosophy for proper use of functionalized green sorption or filter media placed in stormwater ponds for nutrient removal. The chapter includes a thorough literature review of past uses of green sorption media and also describes the results of a laboratory column test conducted to mimic a field environment and evaluate the feasibility of the design philosophy. This approach to stormwater treatment has "green" implications because it includes recycled material in the sorption media to promote treatment efficiency and effectiveness. Such design strategies may be extended to enhance the sustainability of low-impact developments such as rain gardens, bioswales, and green roofs where plants, sorption media, and soils naturally filter nutrients and other pollutants from stormwater.

8.1 INTRODUCTION

Nutrients such as ammonia, nitrite, nitrate, and phosphorus are common contaminants in water bodies worldwide. Directly or indirectly, these nutrients have acute and chronic harmful effects on humans and ecosystems. Ammonia can exist in aqueous solution in the form of ammonium ions or ammonia gas. Ammonium ions (NH_4^+) are much more toxic than ammonia gas (NH_3); however, the form present depends on the pH (Crites and Tchobanoglous, 1998). According to the United States Environmental Protection Agency (USEPA), unionized ammonia is extremely toxic for salmonid and nonsalmonid fish species (USEPA, 1993). The presence of 0.10–10.00 mg/L of ammonia can cause fish mortality and negatively affect fish health and reproduction

(USEPA, 1993). Nitrate is more toxic than nitrite and can cause human health problems such as liver damage and even cancer (Gabel et al., 1982; Huang et al., 1998). Nitrate can also bind with hemoglobin and create an oxygen deficiency called methemoglobinemia in warm-blooded animals, especially in the young babies (WEF, 2005). Meanwhile, nitrite has been associated with "brown blood diseases" in warm-water fish (Kentucky Water Watch, 2008), and is carcinogenic when involved in chemical and enzymatic reactions with amines (Sawyer et al., 2003). In addition, both phosphorus and nitrogen species can trigger eutrophication, which occurs when excessive nutrients in a water body encourage the excess growth of plants such as algae and weeds. These plants consume available oxygen in the water, leaving less available for fish and other aquatic species. Ultimately this condition degrades both the aesthetics and ecosystem health of rivers, springs, and lakes.

Compounds containing nitrogen and phosphorus are found in stormwater runoff. While highways are a main source of these nutrients in stormwater runoff (USEPA, 1999a), many other sources are also contributing to increased nutrient contents in stormwater and groundwater. These sources include agricultural fertilizers, untreated wastewater, insufficiently treated wastewater from septic tanks, and animal urine and droppings. Phosphorus is released from fertilizer, dead plants, animal waste, detergents, forest fires, synthetic materials, and decaying animal bones. Most phosphorus exists in the form of orthophosphate (PO_4^{3-}, OP) (Crites and Tchobanoglous, 1998). As populations increase and various regions worldwide face water scarcity, obtaining high-quality clean drinking water is increasingly important, especially when the groundwater becomes the major source of drinking water. Treating stormwater in a way that is both cost effective and meets drinking-water regulatory standards is challenging.To meet the goal of sustainable development, stormwater may also be needed to recharge and sustain groundwater supplies. If the nutrient-laden "first flush" runoff water collected in wet or dry ponds cannot be properly treated, it will eventually percolate through the soil and contaminate the groundwater. According to the USEPA maximum contaminant levels (MCLs), nitrate and nitrite levels in water bodies should not exceed 10.00 mg/L $N0_3^-$–N and 1.00 mg/L NO_2^-–N, respectively (USEPA, 1988). Nutrient removal from stormwater runoff is therefore important for sustaining human society and aquatic ecosystems.

Under existing hydrologic systems, the high nitrogen and phosphorus concentrations in stormwater runoff, contaminated groundwater, landfill leachate, and domestic and industrial wastewater effluents will continue to increase surface and groundwater contamination and reduce the potential for water reuse. In water management, best-management practices (BMPs) include maintenance procedures and management practices aimed at preventing or reducing water pollution. As both quantity and quality of stormwater runoff are taken into account in the U.S., low-impact development (LID), applying a suite of landscape architecture practices in urban ecology to minimize the hydrological effects of urban development, has been emphasized and assessed by comparing pre- and post-development hydrology as an integral part of BMPs. Relevant concepts associated with LID worldwide include the sustainable urban drainage system (SUDS) in the United Kingdom and water-sensitive urban design (WSUD) in Australia. In an effort to promote these engineering BMP practices, engineered, functionalized, and natural sorption media can be used to remove nutrients in stormwater runoff, wastewater effluent, groundwater flows, landfill leachates, and drinking-water sources via both physicochemical and microbiological processes embedded in most of the BMPs, such as bioswale, biofiltration, permeable reactive barriers, and pervious pavement (Chang et al., 2008a).

Synthesis of the literature on the relationships of urban development and the hydrological cycle is an important step in developing more advanced and adaptive materials, biomaterials, and multifunctional engineering materials with co-treatment capacities and in creating sustainable neighborhoods and responding to rapid changes in land use and stormwater runoff. Recent studies have reported that removal of ammonia, nitrite, nitrate, and phosphorus can be enhanced by the inclusion of various sorption media such as sawdust, tire crumb, sand, clay, zeolite, sulfur, and/or limestone in natural soil (Kim et al., 2000; Clark et al., 2001; Jokela et al., 2002; Hsieh and Davis, 2005). A number of devices, collectively known as structural BMPs, which can be an effective integrative concept for examining urban carrying capacity, may be used in combination with green sorption media to treat contaminated stormwater based on both physicochemical and microbiological principles (Chang et al., 2008a; Ray et al., 2006). Examples of such devices are rain barrels and bioswales filled with green sorption media, rain gardens with retention/detention ponds and green sorption media, bioswales in front of constructed wetlands filled with green sorption media, green roofs integrated with green sorption media and stormwater reuse, permeable pavement that includes a mixture of coarse sand and green sorption media, level spreaders with green sorption media, and vegetative filter strips with soil and green sorption media mixture.

In this study, we deemed an appropriate media mix to be any kind of multifunctional material or functionalized sorption media that may be used in both natural and built environments to improve the existing physicochemical and microbiological processes for nutrient removal (Chang et al., 2008a). Such a media mix can be made "green" by including recycled materials, such as tire crumb or sawdust, to increase the treatment efficiency and effectiveness (Chang et al., 2008a). The use of these filtering media in stormwater treatment could also resolve solid waste management problems. However, the inclusion of recycled materials in the mixture may raise concerns about toxicity. To answer such questions, Birkholz et al. (2003) conducted toxicological tests on tire crumb and found no DNA- or chromosome-damaging chemicals. From an engineering standpoint, by the use of such green sorption media, nutrients in water bodies can be reduced or even mostly removed by enhanced absorption/adsorption, nitrification/denitrification, and other chemical reactions such as precipitation and ion exchange (Chang et al., 2008b).

8.2 DESIGN PHILOSOPHY

Most filter media improve solid-liquid contact, prevent channeling, and enhance physicochemical processes. In general, the calcium/iron minerals and larger surface areas of clay in natural soil provide more contact areas where solids can be absorbed and more space for bacteria colonies to develop. Soil with fewer clay particles can present problems in regard to the removal of stormwater nutrients. In comparison, functionalized filter media have better ion exchange capacities to support absorption/adsorption, greater capabilities to retain adsorbed nutrients, and larger surface areas for bacterial colony development possibly. Riverbank filtration is an innovative process of this kind that has been widely used for centuries in Europe to remove pollutants, including microorganisms, from surface water (Tufenkji et al., 2002).

Proper deployment of green sorption media may be challenging in structured BMPs. Figures 8.1 and 8.2 show typical detention (wet) ponds and retention (dry) ponds, respectively. The filter media operate as a four-phase system (solid media, water, gas phase, and attached biofilm) designed to remove nutrients and other pollutants, such as heavy metals, pesticides, and bacteria, when stormwater infiltrates into the underlying vadose zone. Isotherm tests can help understand the necessary periodic maintenance and replacement of the filter media. However, laboratory-scale isotherm tests of the filter media can only reveal the physicochemical characteristics of adsorption, which are unrelated to the microbiological activities (i.e., nitrification and denitrification); additional laboratory and field studies are required. This type of system may be also used for groundwater remediation (Schipper et al., 2005).

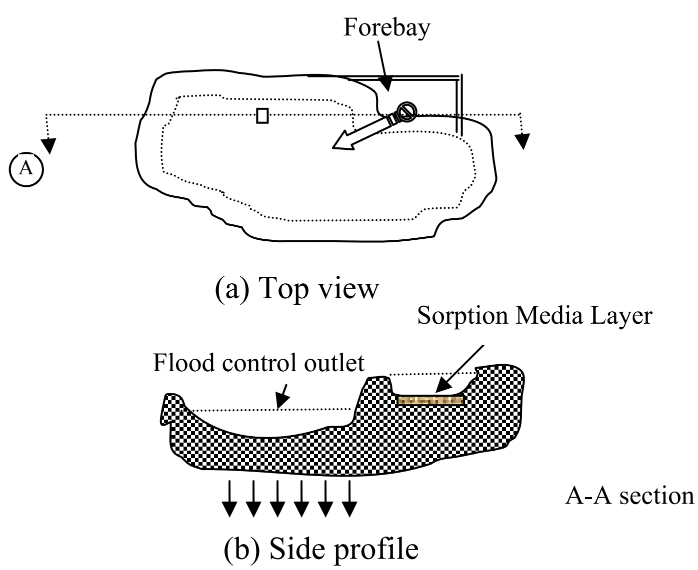

Figure 8.1: Detention (wet) pond with *in situ* treatment units and low infiltration

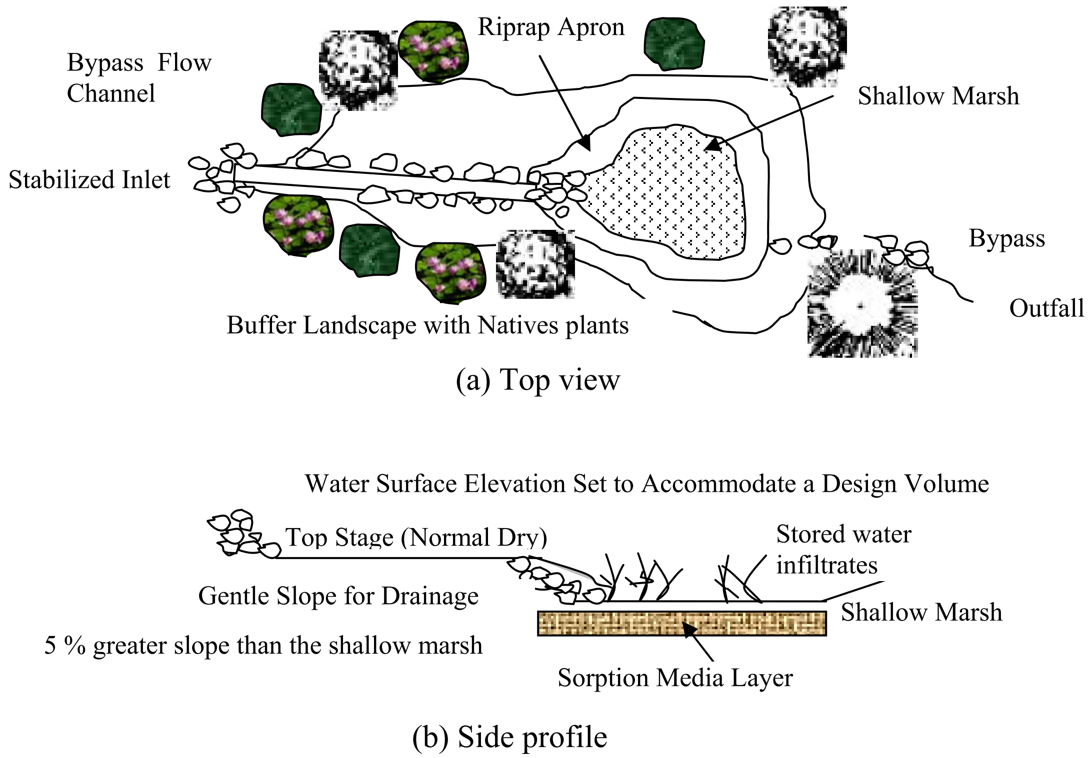

Figure 8.2: Retention (dry) pond with *in situ* treatment

8.3 LITERATURE REVIEW

This section presents examples of increased nutrient concentrations in stormwater runoff in Florida, followed by technologies currently available to remove nutrients, and the use of green sorption media to remove nutrients from stormwater runoff. There are several benefits to using sorption media for nutrient removal. They decrease the cost of treatment without compromising public health, on one hand. They eliminate the cost of chemicals used for nutrient removal, on the other hand. In addition, they solve problems related to the management and disposal of sludge. The conventional use of aluminum sulfate to form the coagulation floc for fine-particle removal produces tremendous amounts of chemical sludge; sorption media achieve the same treatment efficiency without the problem of chemical sludge. Furthermore, sorption media reduce some solid-waste management and disposal problems by including media that would otherwise have no recycle value or reuse potential. For example, scrap tires cannot be used to make more tires (Lisi et al., 2004). The use of sorption media also reduce dependence on bacteria and do not require aerobic or anaerobic conditions.

8.3.1 Nutrient Concentrations in Stormwater and Groundwater in Florida

Sources of nitrogen include stormwater runoff, as well as septic tanks and land-based applications of reclaimed wastewater and fertilizer. Such sources have contributed to elevated nitrate and nitrite concentrations in the Upper Floridian aquifer. Nitrate concentrations have increased in many springs of the Upper Floridian aquifer since the 1950s. Phelps (2004) reported that nitrate concentrations ranged from less than 0.02 to 12.00 mg/L, with a median of 1.20 mg/L, for 56 Upper Floridian aquifer wells sampled in Marion County during 2000 and 2001. Nitrate concentrations have exceeded 1.00 mg/L in recent years at a number of springs in Lake, Marion, Orange, Seminole, and Volusia counties, according to Phelps et al. (2006) and researchers from the St. Johns River Water Management District (SJRWMD, 2008). Increasing trends in nitrate concentration have also been documented at springs in Volusia County, such as DeLeon and Gemini springs (Phelps et al., 2006) as well as Blue Spring (SJRWMD, 2008).

8.3.2 Multifunctional Sorption Media for Nutrient Removal

Much work prior to 1995 focused on removing nutrients by the sand filter method. Various types of sand filter methods were developed, including the Washington D.C. sand filter method, the Delaware sand filter design, and the Austin sand filter (USEPA, 1999a). Removal efficiency of the Delaware sand filter is 70.20% for total suspended solids (TSS), 71.10% for total phosphorus (TP), 67.00% for ammonia nitrogen (NH_3-N), and 59.90% for total Kjeldahl nitrogen (TKN) (Bell et al., 1995). Later on, more advanced physicochemical technologies were considered. Nutrients in stormwater, groundwater, and wastewater can be removed using physicochemical processes, such as activated carbon absorption, ion exchange with synthetic resins, reverse osmosis, and electrodialysis (ED). Absorption is a physical or chemical process in which ions enter into the bulk phase, either a solid or liquid material. This is a different process than adsorption. Ions are taken by bulk volume in absorption, whereas ions accumulate on the surface of solids in adsorption. In the process of sorption, adsorption and absorption take place simultaneously. Ion exchange is a process of purification, demineralization, or decontamination of aqueous solutions or drinking water by polymer or mineral ion exchange (i.e., exchange of an ion in liquid phase for an ion in solid phase). Reverse osmosis uses pressure to pass contaminated solution through a membrane; the pure solution reaches the far side of the membrane while the contaminants collect on the near side of the membrane. In ED, used for desalination or deionization, ions in the solution pass through an ion exchange membrane to another solution under the influence of an electric potential difference. However, most of these technologies are not cost effective for treating stormwater, which is characterized by large volume flow rates and low concentrations over short time periods. In this study, we deemed an appropriate media mix to be any kind of multifunctional material or functionalized sorption media that could be used cost effectively in both natural and built environments to improve physicochemical and microbiological processes for nutrient removal (Chang et al., 2008).

The ability of bioinfiltration to remove nutrients from stormwater depends on a combination of vegetation and soil effects and is influenced by soil adsorption and uptake in vegetative root zones. After treatment, the treated stormwater percolates to the ground through the vadose zone. Bioinfiltration with different filter media has been gaining popularity due to its cost effectiveness. In bioinfiltration, two important processes that transform ammonia to nitrogen gas are nitrification by autotrophic bacteria and denitrification by either autotrophic or heterotrophic bacteria. Carbon is generally used as a cell building block in both autotrophic and heterotrophic bacteria. Autotrophic bacteria generally derive their cell carbon from carbon dioxide (i.e., inorganic carbon sources), whereas heterotrophic bacteria derive cell carbon from organic carbon sources.

Nitrification involves two steps: ammonia is transformed to nitrite with the help of *Nitrosomonas* bacteria, and nitrite is transformed to nitrate with the help of *Nitrobactor* bacteria in an aerobic environment. In nitrification, ammonium and nitrite are electron donors and oxygen is an electron acceptor. In denitrification, nitrate is transformed to nitrogen gas by heterotrophic or autotrophic bacteria under anoxic conditions. If heterotrophic bacteria are prevalent, organic compounds that exhibit carbonaceous biochemical oxygen demand (CBOD) are electron donors and nitrate is an electron acceptor. BOD is the amount of oxygen required for the biological decomposition (i.e., chemical or biological transformation) of organic waste. The term “biochemical” in this context means biological actions that cause chemical change. This process creates CO_2 and NH_3 through chemical reaction. To determine CBOD, a nitrification inhibitor such as thiourea or allylthiourea is added to represent the amount of oxygen required for biological conversion of only carbonaceous organic matter into cell tissue. As the denitrification system requires anoxic conditions, the oxygen acts as an inhibitor in the process. Skerman and MacRae (1972), Terai and Mori (1975), Nelson and Knowles (1978), and Dawson and Murphy (1972) investigated this issue (Metcalf & Eddy, Inc., et al., 2002). All of these researchers noted that a dissolved oxygen (DO) level greater than 0.2 mg/L can halt the denitrification process. Thus denitrification is very sensitive to DO.

Nutrient removal treatment using sorption media in stormwater retention and detention ponds normally occurs in natural or semi-built environments. Ammonification and nitrification occur simultaneously in the filter media when stormwater containing ammonium and biodegradable carbon contacts aerobic soil or media. Denitrification is then achieved by cycling between oxic and anoxic conditions. Either autotrophic denitrification or heterotrophic denitrification may occur depending on the type of sorption media. Some attention was given to autotrophic denitrification systems involving elemental sulfur-based media filters (Zhang, 2002). Sulfur-based denitrification filters may include limestone or oyster shell as a solid-phase alkalinity source to buffer the alkalinity consumption during biochemical denitrification (Zhang, 2002). On the other hand, heterotrophic denitrification systems use solid-phase carbon sources including woodchips (Kim et al., 2003), sawdust (Kim et al., 2003), cardboard (Greenan et al., 2006), paper (Kim et al., 2003), and agricultural residue (Kim et al., 2003; Greenan et al., 2006; Della Rocca et al., 2005). Some proprietary media mixes containing woodchips and other materials have also been developed (Lombardo, 2005; Chang et al., 2008c).

Cellulose-based systems using palm tree or coconut shell and lignin-based systems using wood chips or sawdust are the most common heterotrophic denitrification filter technology, although elemental sulfur (autotrophic denitrification) may also be used as an electron donor. In lignocellulosic materials such as wood chips and sawdust, facultative heterotrophs may quickly degrade the organic carbon and deplete the oxygen. However, this simultaneous process with intermittent cycling between oxic and anoxic conditions may be sustainable for denitrification as it maintains lower oxygen requirements. It also recycles the alkalinity in denitrification required for nitrification. During this stage, ammonia may be retained in the filter media depending on the cation exchange capacity because ammonium cannot be nitrified under anoxic conditions. The adsorbed ammonia will be nitrified when the next storm event raises the DO level, changing conditions in the soil or media from anoxic to oxic. Ultimately the amount of denitrification may be limited by the frequency and duration of the oxic/anoxic fluctuations within the filter with respect to the reaction rates or dosing conditions in the treatment during intermittent storm events.

Simultaneous nitrification and denitrification processes in cellulose-based systems of stormwater ponds may occur intermittently. The two steps in the oxidation of ammonia can be summarized in Eqs. (1)–(3) (Metcalf and Eddy, 2003):

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O \quad (1)$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \quad (2)$$

The overall nitrification reaction is

$$NH^+{}_4 + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \quad (3)$$

and the denitrification of wastewater is shown in Eq. (4) (Metcalf and Eddy, 2003):

$$C_{10}H_{19}O_3N + 10NO_3^- \rightarrow 5N_2 + 10CO_2 + 3H_2O + NH_3 + 10OH^- \quad (4)$$

Both pH and temperature also have important impacts on these two biological processes. A pH range of 7.00–8.00 is considered good for both nitrification and denitrification (Metcalf and Eddy, 2003). Nitrifiers can grow best in a temperature range of 35–42°C, while denitrifiers work well in the range of 10–25°C (Rittmann, 2000; USEPA, 1993).

Technologies to remove phosphorus include chemical precipitation, biological treatment, crystallization, ion exchange, magnetic separation, adsorption/absorption, tertiary filtration, and sludge treatment (Lazaridis, 2003). Most phosphorus can be removed from stormwater by both precipitation and absorption processes. Precipitation is the formation of a solid in a solution as the result of a chemical reaction; the solid settles to the bottom for pH > 7.00. The precipitation reactions of phosphorus with calcium, iron, and aluminum are given below in Eqs. (5)–(7). The end product in a calcium reaction is hydroxylapatite, and the end product in an iron reaction is insoluble ferric phosphate (Metcalf and Eddy, Inc., 2002).

$$10Ca^{2+}+6PO_4^{3-}+2OH^- \leftrightarrow Ca_{10}(PO_4)_6(OH)_2 \quad (5)$$

$$Fe^{3+}+H_nPO_4^{3-n} \leftrightarrow FePO_4+nH^+ \quad (6)$$

$$Al^{3+}+H_nPO_4^{3-n} \leftrightarrow AlPO_4+ nH^+ \quad (7)$$

The geochemical process of crystallization converts the thickened concentration into crystals, which is followed by dewatering in a centrifuge. Tertiary filtration is a physicochemical process that involves removing solids from the secondary treated effluent. Sludge treatment refers to the management and disposal of the sludge produced during the wastewater treatment process. Some functionalized sorption media used for phosphorus removal are sand rich in Fe, Ca, or Mg, as well as gravel, limestone (sedimentary rock largely composed of calcium carbonate, $CaCO_3$), shale (fine-grained sedimentary rock composed mostly of clay minerals), light-weight aggregates, zeolite (natural mineral or artificially produced hydrated aluminosilicates with a microporous structure), pelleted clay (alone or in combination with soil), opaka (siliceous sedimentary rock), pumice (natural porous volcanic rock with an average porosity of 90% that generally floats on water), wollastonite (white mineral containing calcium and ferrous metasilicate produced from impure limestone under high temperature and pressure), fly ash (residue generated from coal combustion), blast furnace slag (porous non-metallic byproduct of the iron and steel industry), alum (hydrated aluminum potassium sulfate, $KAl(SO_4)_2 \cdot 12H_2O$), goethite (hydrous ferric oxide found in soil), hematite (black or reddish-brown mineral form of iron(III) oxide, Fe_2O_3), dolomite (sedimentary carbonate rock or mineral composed of calcium magnesium carbonate, $CaMg(CO_3)_2$), and calcite (carbonate mineral) (Korkusuz et al., 2007).

8.3.3 Nutrient Removal in Stormwater Runoff by Sorption Media

Various types of sorption media may be used to treat stormwater, wastewater, groundwater, landfill leachate, and drinking water sources. Key studies by Richman (1997), DeBusk et al. (1997), Kim et al. (2000), Clark et al. (2001), Tshabalala (2002), Boving and Zhang (2004), Hsieh and Davis (2005), Birch et al. (2005), Analytical and Environmental Consultants (AEC, 2005), Ray et al. (2006), and Seelsaen et al. (2006) demonstrated successful uses of sorption media to remove nutrients. These tests found that nutrients can be removed by adsorption and biological nitrification/denitrification processes. The sorption materials involved included compost, peat, sand, wollastonite, limerock, alfalfa, sawdust, newspaper, wheat straw, wood chips, lignocellolosic materials, aspen wood fibers, mulch, hardwood mulch, fine and coarse glass, and clinoptilolite. In addition to nutrients, sorption media can also remove significant amounts of solids, BOD material, and heavy metals from stormwater runoff. Table 1 summarizes the removal efficiency of nutrients from stormwater using sorption media.

In Table 8.1, TP (i.e., 70%–90% OP) is the sum of all phosphorus types, both dissolved and particulate (suspended). The dissolved and particulate portion can be separated using a filter with a nominal pore size of 2.0 μm (APHA, 1995). The dissolved portion passes through the filter, and the particulate portion is retained on the filter. OP can exist in the form of PO_4^{3-}, hydrogenophosphate (HPO_4^{2-}), dihydrogen phosphate ($H_2PO_4^-$), or phosphoric acid (H_3PO_4) (Metcalf and Eddy, 2003). OP is also known as soluble reactive phosphorus. TKN is the sum of the organic nitrogen, ammonia in gaseous form, and ammonium ions. Total nitrogen (TN) is the sum of all organic and inorganic nitrogen species. Organic nitrogen includes proteins, urea, amino acids, and the nitrogen found in decayed plant and animal tissues. Inorganic nitrogen is NH_3, NH_4^+, NO_3-, and NO_2^-.

Table 8.1: Nutrient removal efficiency from stormwater by various sorption media

Year	Researcher	Sorption media	Mechanism	Removal efficiency
1997	Richman	compost	adsorption	90.00% solids, 85.00% oils and greases (O/G), and 82.00–98.00% heavy metals
1997	Debusk et al.	wollastonite	adsorption	87.80% TP, 81.40% Cu, 97.70% Cd, and 80.30% Ni
		limerock		41.50% TP, 32.20% Cu, 81.34% Cd, and 31.30% Ni
		peat		44.00% TP, 41.20% Cu, 97.80% Cd, and 92.30% Ni
		sand		41.50% TP, 76.95% Cu, 94.40% Cd, and 77.67% Ni
2000	Kim et al.	sulfur	nitrification and denitrification	
		alfalfa		100.00% nitrate
		leaf mulch compost		60.00% nitrate
		newspaper		100.00% nitrate
		sawdust		>95.00% nitrate
		wheat straw		>95.00% nitrate
		wood chips		>95.00% nitrate
2002	Tshabalala	lignocellulo-sic materials	adsorption	82.00% dichlobenil (DBN)
				92.00% chlorothalonil (CTL)
				96.00% chlorpyrifos (CPS)
2004	Boving and Zhang	aspen wood fibers	adsorption	60.00% anthracene
				89.00% pyrene
				36.00% fluorene

2005	Hsieh and Davis	100% sand	adsorption	96.00% TSS, 96.00% O/G, 98.00% lead, 85.00% TP, 11.00% nitrate, and 8.00% ammonia
		100% sand		96.00% TSS, 96.00% O/G, 96.00% lead, 10.00% TP, 1.00% nitrate, and 15.00% ammonia
		2% mulch, 93% soil, 5% sand		29.00% TSS, 96.00% O/G, 98.00% lead, 47.00% TP, 1.00% nitrate, and 6.00% ammonia
		2% mulch, 93% soil, 5% sand		88.00% TSS, 96.00% O/G, 98.00% lead, 41.00% TP, 14.00% nitrate, and 24.00% ammonia
		2% mulch, 93% soil, 5% sand		91.00% TSS, 96.00% O/G, 98.00% lead, 48.00% TP, 8.00% nitrate, and 16.00% ammonia
		91% mulch, 9% sand		86.00% TSS, 96.00% O/G, 75.00% lead, 4.00% TP, 43.00% nitrate, and 16.00% ammonia
		100% sand		96.00% O/G, 66.00% lead, 84.00% TP, 13.00% nitrate, and 5.00% ammonia
		3% mulch, 97% sand		96.00% TSS, 96.00% O/G, 98.00% lead, 61.00% TP, 9.00% nitrate, and 9.00% ammonia
		2% mulch, 21% soil, 77% sand		66.00% TSS, 96.00% O/G, 98.00% lead, 47.00% TP, 3.00% nitrate, and 2.00% ammonia
		8% mulch, 26% soil, 66% sand		94.00% TSS, 96.00% O/G, 98.00% lead, 50.00% TP, 4.00% nitrate, and 7.00% ammonia
		6% mulch, 32% soil, 62% sand		93.00% TSS, 96.00% O/G, 98.00% lead, 39.00% TP, 4.00% nitrate, and 7.00% ammonia

		24% soil, 76% sand		93.00% TSS, 96.00% O/G, 98.00% lead, 39.00% TP, 2.00% nitrate, and 5.00% ammonia
		3% mulch, 43% soil, 54% sand		96.00% TSS, 96.00% O/G, 98.00% lead, 83.00% TP, 13.00% nitrate, and 26.00% ammonia
		3% mulch, 24% soil, 73% sand		96.00% TSS, 96.00% O/G, 98.00% lead, 57.00% TP, 24.00% nitrate, and 17.00% ammonia
		11% mulch, 19% soil, 70% sand		96.00% TSS, 96.00% O/G, 98.00% lead, 54.00% TP, 27.00% nitrate, and 20.00% ammonia
		2% mulch, 17% soil, 81% sand		96.00% TSS, 96.00% O/G, 97.00% lead, 24.00% TP, 6.00% nitrate, and 11.00% ammonia
		2% mulch, 72% soil, 26% sand		92.00% TSS, 96.00% O/G, 98.00% lead, 72.00% TP, 9.00% nitrate, and 19.00% ammonia
		2% mulch, 49% soil, 49% sand		92.00% TSS, 96.00% O/G, 98.00% lead, 71.00% TP, 9.00% nitrate, and 19.00% ammonia
2005	Birch et al.	1:6 mixture of zeolite (clinoptilolite) and coarse, pure quartzitic sand	adsorption	47.00–74.00% TKN, 33.00–40.00% TN, 37.00–67.00% TP, 49.00–81.00% Cu, 88.00–98.00% Pb, −1.00–77.00% Zn, 10.00% Cr, −213.00–38.00% Fe, and 20.00–88.00% TSS
2006	Ray et al.	hardwood mulch	adsorption (2 hour HRT)	85.00% Cu, 75.00% Cd, 21.00% Cr, 90.00% Pb, 60.00% Zn, 63.00% dichlorobenzene, 63.00% naphthalene, 89.00% fluoranthene, 90.00% butybenzylphthalate, and 80.00% benzopyrene

			adsorption (4 hour HRT)	85.00% Cu, 83.00% Cd, 26.00% Cr, 85.00% Pb, 72.00% Zn, 71.00% dichlorobenzene, 65.00% naphthalene, 95.00% fluoranthene, 95.00% butybenzylphthalate, and 84.00% benzopyrene
			adsorption (72 hour HRT)	85.00% Cu, 86.00% Cd, 68.00% Cr, 92.00% Pb, 72.00% Zn, 100.00% dichlorobenzene, 88.00% naphthalene, 93.00% fluoranthene, 77.00% butybenzylphthalate, and 92.00% benzopyrene
2006	Seelsaen et al.	fine glass	adsorption	68.00% Zn and 40.00% Cu
		sand		15.00% Zn and 30.00% Cu
		coarse glass		15.00% Zn and 28.00% Cu
		ash		50.00% Zn and 97.00% Cu
		zeolite		97.00% Zn and 50.00% Cu
		compost		97.00% Zn and 90.00% Cu
		packing wood		88.00% Zn and 84.00% Cu
2006	Huang et al.	clinoptilolite	ion exchange	100.00% Fe

8.4 MATERIALS AND METHODS

8.4.1 Physical Properties of Sorption Media

The following six criteria were often considered to screen possible filter media to be used in BMPs: 1) the relevance of nitrification and/or denitrification processes; 2) the hydraulic conductivity or permeability; 3) the cost; 4) the removal efficiency reflected in the literature with regard to adsorption, precipitation, and filtration capacity; 5) the availability in Florida; and 6) additional environmental benefits. Sand, tire crumb, and sawdust were selected for this study based on these criteria. The final composition of the filter media mixture for this demonstration was 50% sand (masonry sand in natural soil, 25% retained on a number 140 sieve and 25% retained on a number 200 sieve), 30% tire crumb, and 20% sawdust by weight. The natural soil was collected from a stormwater dry pond (Hunter's Trace) in Ocala, Marion County, Florida, located at coordinates 29°11'49.42"N, 82°3'52.83"W, as shown in Figure 8.3.

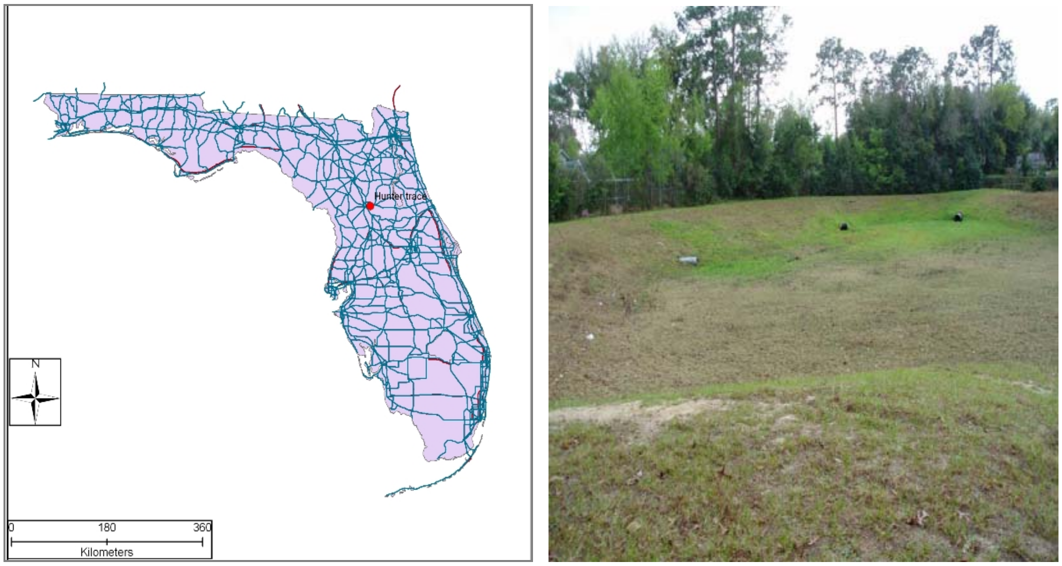

Figure 8.3: Location and photograph of the Hunter's Trace pond

It is important to understand the physical properties of the filter media, including the particle-size distribution, density, void ratio, porosity, specific gravity, surface area, and hydraulic conductivity. American Society for Testing and Materials (ASTM) procedures were used to determine the particle-size distribution, specific gravity, and hydraulic conductivity (ASTM, D421-85, D854-92, D2434-68). The surface area of the sorption media mixture was determined using the multipoint Brunauer, Emmett, and Teller (BET) method with nitrogen adsorption at 77 K, determined using the vacuum volumetric method of Quanta Chrome Instruments, Boynton Beach, Florida. The void ratio is the volume of the voids divided by the volume of the solid. The porosity is the volume of the voids divided by the total volume. These properties are used to determine the hydraulic residence or retention time (HRT) and the adsorption area available for the nutrients. The particle-size distribution curve can suggest the grain size and type of distribution of particles in a certain soil or sorption media sample. The effective size (D_{10}) is calculated from the particle-size distribution as the diameter in millimeters at which 10.00% of particles are finer. The porosity gives some idea about the volume of voids in a sorption media sample, and the amount of water that actually comes in contact with the media can be determined from the void volume. The porosity is calculated from the specific gravity and void ratio. These properties can influence dispersion phenomena in the soil or the filter media column test. The surface area is also important for nutrient removal as greater surface area will remove more nutrients from the stormwater. The void ratio and porosity can be calculated by Eqs. (8) and (9):

$$\text{Void ratio of filter media mixture (E)} = \frac{G_S * \rho_W}{\rho_d} - 1 \qquad (8)$$

$$\text{Porosity of filter media mixture (N)} = \frac{E}{1 + E} \qquad (9)$$

where G_s is the specific gravity of the filter media mixture, ρ_w is the density of water, ρ_d is the density of the filter media mixture, E is the void ratio, and N is the porosity.

8.4.2 Experimental Setup of the Column Study

The column test was designed to determine the nutrient removal performance of the selected green sorption media in saturated and unsaturated conditions that mimic the field condition of stormwater dry ponds. Figure 8.4 shows the two pairs of plexiglass columns that were prepared in the University of Central Florida laboratory to represent the two-stage flow pathway by which pond water infiltrates into the vadose zone (stage 1, unsaturated) and then percolates into the sorption media layer placed between the groundwater table and the capillary zone (stage 2, saturated) to mimic th egepphysical environment beneath the pond as shown in Figure 2(b). The columns were 182.88 cm (6 ft) long, with an inner diameter of 14.73 cm (5.8 in) and a wall thickness of 0.51 cm (0.2 in). All four columns were attached to wooden frames with fabric straps. The wooden frames were attached to a steel rack in the laboratory. Each column had three sampling ports. The first port was 39.37 cm (15.50 in) from the bottom of the column, the second port was 44.45 cm (17.5 in) above the first, and the third port was 38.10 cm (15.00 in) above the second. Pipe thread sealant was used to make all the joints in the columns leak proof. The top and bottom of each column were closed but had removable screw caps through which to add and remove media.

A plastic mesh filter with gravel was placed at the bottom of each column to prevent the outward flow of finer particles from the columns during sample collection. All the columns were filled with sand or sorption media to a height of 121.92 cm (48 in). The fill line was slightly below the first port and 38.10 cm (15 in) above the second port. The first pair of columns was filled with natural soil collected at the Hunter's Trace pond as a control case. In the second pair, the first column was filled with natural soil, and the second column was filled with the sorption media mixture. The natural soil was sun dried, and impurities were removed with a number 10 sieve. The control case natural soil was compacted to a density of 516.00 kg/m^3 (106.00 lb/ft^3), and the media mixture was compacted to a density of 204.45 kg/m^3 (42.00 lb/ft^3). In each pair, the first column was considered to be the unsaturated (vadose) zone, and the second column was considered to be the saturated zone.

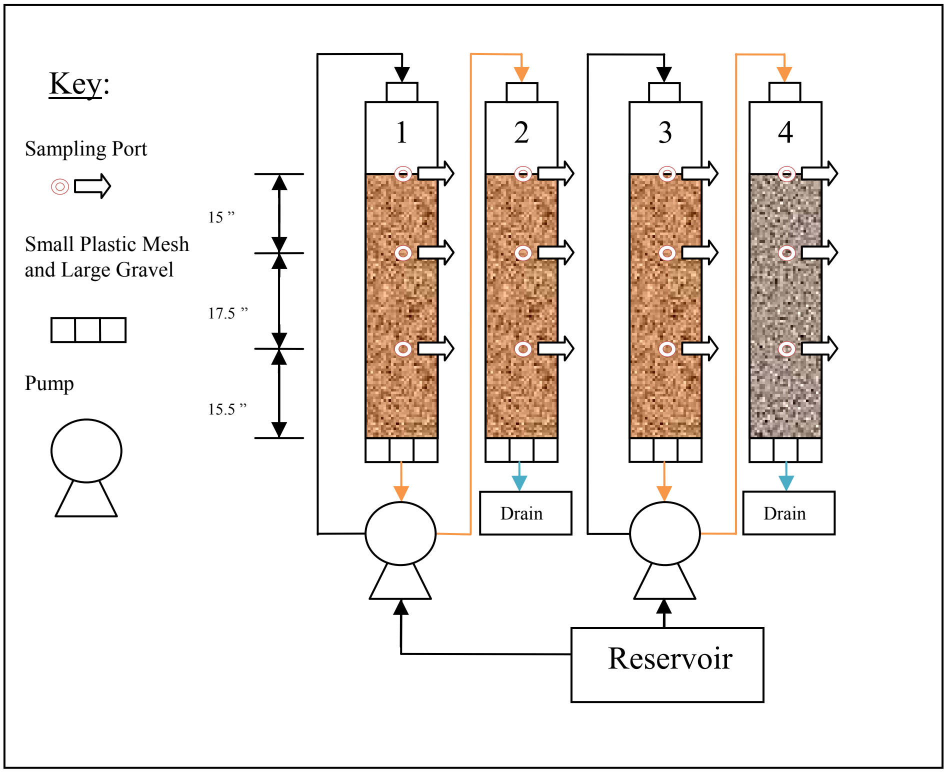

Figure 8.4: Schematic diagram of the column setup for the laboratory experiment

Water was pumped from the unsaturated column using a peristaltic pump. The flow rate in all the columns was 10 mL/min, equivalent to 1.38 in/hr. Typically, detention pond infiltration ranges from 2.54–5.08 cm/hr (1–2 in/hr). Stormwater was supplied from a 25-gallon reservoir. The initial nitrate concentration in the stormwater was set to 0.40, 1.25, and 2.50 mg/L in three successive experiments, and the initial orthophosphate concentration was set to 0.13, 0.36, and 0.79 mg/L. These nitrate and phosphorus concentrations were higher than the actual concentrations given in the above literature review section. The stock solutions of nitrate and phosphorus were prepared from potassium nitrate and potassium phosphate according to standard methods (APHA, 1995). The removal efficiencies of TN, nitrate, nitrite, ammonia, and OP by the sorption media were measured by the Hach methods listed in Table 8.2 below. The detention time was calculated by

$$T_d = V/Q \tag{10}$$

where T_d is the HRT, V is $(3.14\ n)(d_{inside}^2)/4$, d_{inside} is the inside diameter of column, n is the porosity; and Q is the flow rate.

Table 8.2: Column study water quality parameters and methods

Parameter	Method	Range*
nitrates and nitrites	Hach method 8192	0.01–0.50 mg/L NO_3–N
nitrites	Hach method 8507	0.002–0.30 mg/L NO_2–N
ammonia	Hach method 8155	0.01–0.50 mg/L NH_3–N
total nitrogen	Hach Method 10071	0.50–25.00 mg/L N
reactive/orthophosphate	Hach method 8048	0.02–2.50 mg/L PO_4^{3-}
total phosphorus	Hach method 8190	0.06–3.50 mg/L PO_4^{3-}

*Note: In some cases, samples were diluted with deionized water to fall within this range.

8.5 RESULTS AND DISUCSSION

8.5.1 Physical Properties of Sorption Media

Table 8.3 shows the physical properties of the natural soil and sorption media mixture. The hydraulic conductivity of the moist sample of Hunter's Trace soil and the sorption media were measured as 4.470 cm/hr (1.759 in/hr) and 4.380 cm/hr (1.724 in/hr), respectively. The Hunter's Trace soil contained small clay particles, which created a surface area larger than that in the sorption media with larger particles such as sawdust and tire crumb. A larger surface area means greater removal efficiency because there is more solid-phase area to adsorb nutrients. As noted above, finer particles may increase the HRT and decrease the amount of solids in the effluent. The porosity of the sorption media was greater than that of the natural soil.

Figures 8.5 and 8.6 give particle-size distribution curves for the natural soil and the sorption media. The control sample (natural soil) was well graded, but the sorption media mixture was not. The effective sizes (D_{10}) of the natural soil and sorption media were 0.17 mm and 0.08 mm, respectively, as calculated from the particle-size distribution curve. These D_{10} values can be used to determine the hydraulic conductivity using an empirical equation (i.e., $k = 1.0 \times D_{10}^2$; Das, 2002).

Table 8.3: Physical properties of natural sand and sorption media.

	Hunter's Trace (dry sample)	Hunter's Trace (moist sample)	Sorption media
dry density (g/cm^3)	1.560	1.730	1.41
void ratio	0.670	0.510	0.56
Porosity	0.400	0.340	0.36
specific gravity	2.620	2.620	2.19
surface area (m^2/g)	3.111	3.111	0.129
intrinsic conductivity (cm/hr)	62.48	4.470	4.38

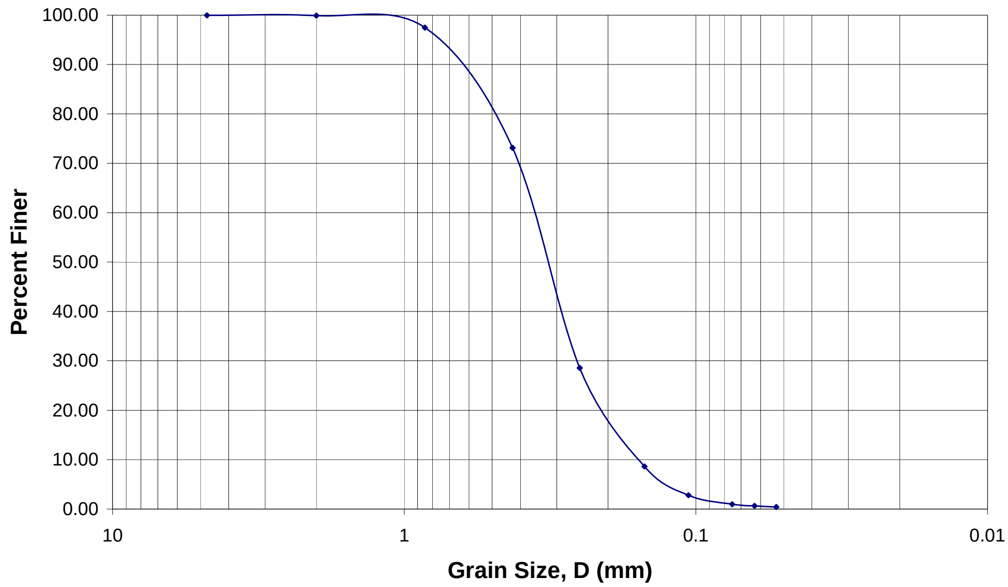

Figure 8.5: Particle-size distribution of natural soil collected from Hunter's Trace pond

8.5.2 Experimental Results of the Column Study

At the beginning of the experiment, the sorption media mixture contributed some nutrient (ammonia) and color in the effluent stormwater from the column due to the inclusion of sawdust. But with time, both the color and contributed ammonia diminished and the sorption media started to remove all the nutrients. The pH of the effluent was in the range of 7.00–8.00, and the temperature was maintained at 22.0–23.0°C throughout the experiment.

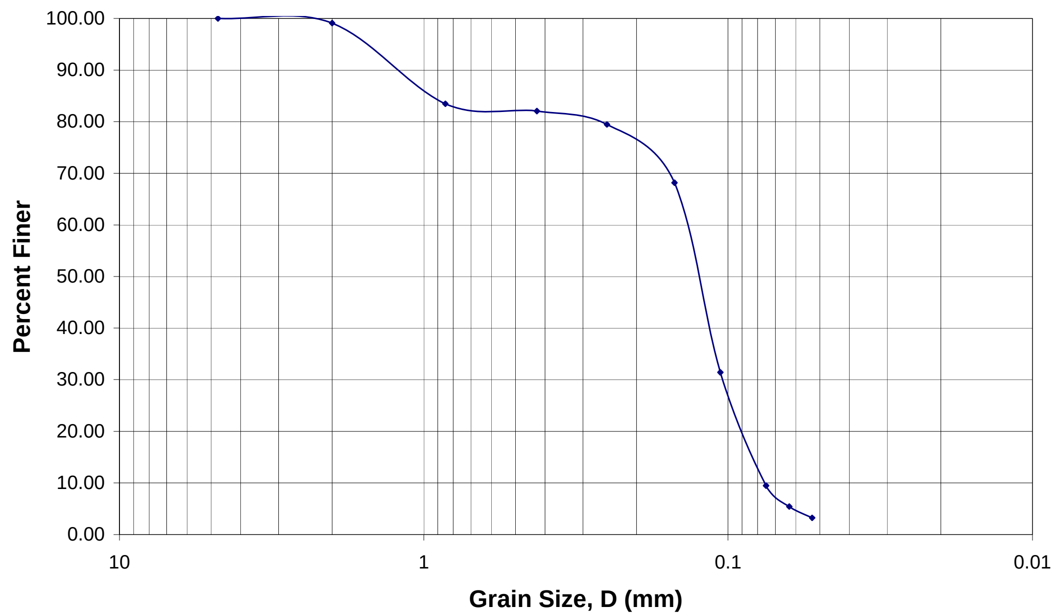

Figure 8.6: Particle-size distribution of filter media mixture

Nitrate removal

Table 8.4 presents the nitrate removal efficiencies with initial nitrate concentrations of 0.4, 1.25, and 2.53 mg/L in both the saturated and unsaturated columns. In particular, the media mixture with an initial concentration of 2.53 mg/L removed approximately 99.20% of the NO_3-N compared to the natural soil that removed only 39.50% of the NO_3^--N with an HRT of 4.00 hours. This result was very similar to a previous study of batch-fed augmented stormwater with an initial nitrate concentration of 2.5 mg/L in a 30.48-cm (12-in) column. In that experiment, the nitrate removal efficiency was 90.28% and 90.83% with HRTs of 3 and 5 hours, respectively (Chang et al., 2008b).

A possible explanation for the lower removal of nitrate in the control case is as follows. Both soil and nitrate are negatively charged (Kim et al., 2000) and may repel each other when soil and stormwater come in contact. During the adsorption process, the surface charge may change with the pH; thus, in some cases, the surface charges of the soil particles change and adsorb some of the nitrate ions. As noted, the removal efficiency also depends on the porosity of the sorption media. Both sawdust and tire crumb have larger porosities, and these two media can accelerate the removal efficiency via absorption. In summary, the effluent nitrate concentration (0.021 mg/L) from the sorption media column met the USEPA MCL requirement, although that from the natural soil column (Hunter's Trace soil) did not.

Table 8.4(a): Nitrate removal efficiency in the two-stage system with approximate nitrate influent concentration of 0.40 mg/L NO_3^--N

Control Run	Initial Concentration (mg/L NO_3-N)	Final Concentration (mg/L NO_3-N)	Removal Efficiency (%)
1	0.382	0.294	23.0
2	0.382	0.266	30.2
3	0.382	0.139	63.6
Average	0.382	0.233	38.9
Media Run	Initial Concentration (mg/L NO_3-N)	Final Concentration (mg/L NO_3-N)	Removal Efficiency (%)
1	0.382	0.021	94.5
2	0.382	0.022	94.1
3	0.382	0.023	94.0
Average	0.382	0.022	94.2

Table 8.4(b): Nitrate removal efficiency in the two-stage system with approximate nitrate influent concentration of 1.25 mg/L NO_3^--N

Control Run	Initial Concentration (mg/L NO_3-N)	Final Concentration (mg/L NO_3-N)	Removal Efficiency (%)
1	1.269	0.312	75.4
2	1.269	0.391	69.2
3	1.269	0.438	65.4
Average	1.269	0.380	70.0
Media Run	Initial Concentration (mg/L NO_3-N)	Final Concentration (mg/L NO_3-N)	Removal Efficiency (%)
1	1.269	0.023	98.2
2	1.269	0.022	98.2
3	1.269	0.023	98.2
Average	1.269	0.023	98.2

Table 8.4(c): Nitrate removal efficiency in the two-stage system with approximate nitrate influent concentration of 2.50 mg/L NO_3^--N

Control Run	Initial Concentration (mg/L NO_3-N)	Final Concentration (mg/L NO_3-N)	Removal Efficiency (%)
1	2.529	1.615	36.1
2	2.529	1.508	40.4
3	2.529	1.463	42.1
Average	2.529	1.529	39.5
Media Run	Initial Concentration (mg/L NO_3-N)	Final Concentration (mg/L NO_3-N)	Removal Efficiency (%)
1	2.529	0.021	99.2
2	2.529	0.021	99.2
3	2.529	0.021	99.2
Average	2.529	0.021	99.2

Orthophosphate (OP) removal

Table 8.5 shows the total OP removal efficiency for initial concentrations of 0.36 and 0.79 mg/L PO_4-P. In the latter case, the OP removal efficiency was about 55.20% by the soil and 91.40% by the sorption media. In the former case, the performance of natural soil was relatively lower. In general, natural soil performs better for OP removal than for nitrate removal. Clay particles have some affinity for phosphorus ions (Gisvold et al., 2000), and the particle-size distribution curve in Fig. 3 reveals that the Hunter's Trace soil had some clay particles. These clay particles undoubtedly contributed to the phosphorus removal from stormwater. The final effluent concentrations of phosphorus met the USEPA requirements of less than 0.1 mg/L after passing through the two-stage treatment, but not after passing through the natural soil column. This finding confirms the necessity of an underground sorption media layer. According to Table 2, a larger surface area (as in natural soil) resulted in a smaller amount of nutrients being removed. This negative relationship also strongly supports the use of sorption media for nutrient removal.

Table 8.5(a): Orthophosphate removal efficiency in the two-stage system with approximate PO_4-P influent concentration of 0.36 mg/L PO_4-P

Control Run	Initial Concentration (mg/L PO_4-P)	Final Concentration (mg/L PO_4-P)	Removal Efficiency (%)
1	0.361	0.293	18.8
2	0.361	0.285	21.0
3	0.361	0.302	16.3
Average	0.361	0.294	18.7
Media Run	Initial Concentration (mg/L PO_4-P)	Final Concentration (mg/L PO_4-P)	Removal Efficiency (%)
1	0.361	0.043	88.2
2	0.361	0.077	78.8
3	0.361	0.031	91.4
Average	0.361	0.050	86.1

Table 8.5(b): Orthophosphate removal efficiency in the two-stage system with approximate PO_4-P influent concentration of 0.79 mg/L PO_4-P

Control Run	Initial Concentration (mg/L PO_4-P)	Final Concentration (mg/L PO_4-P)	Removal Efficiency (%)
1	0.785	0.339	56.8
2	0.785	0.358	54.3
3	0.785	0.357	54.5
Average	0.785	0.351	55.2
Media Run	Initial Concentration (mg/L PO_4-P)	Final Concentration (mg/L PO_4-P)	Removal Efficiency (%)
1	0.785	0.099	87.4
2	0.785	0.048	93.9
3	0.785	0.057	92.7
Average	0.785	0.068	91.4

8.6 CONCLUSIONS

Stormwater retention and detention ponds are designed to store water during a wet season and to maintain an artificial hydrologic balance to meet groundwater recharge during a dry season. As clearly demonstrated above, the use of sorption media is a promising way to remove nutrients from stormwater runoff through various design strategies. The life expectancy of the sorption media and practical installation can be a challenging task for engineers attempting to integrate sorption media with other system components. Even so, use of sorption media to clean stormwater runoff offers cost-effective option and will play a vital role in urban water resources management and sustainability.

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