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Modeling Kinetics and Isotherms of Functionalized Filter Media for Nutrient Removal from Stormwater Dry Ponds

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Sorption media with mixes of some recycled materials, such as sawdust and tire crumbs, combined with sand/silt and limestone, become appealing in nutrient removal for promoting urban stormwater management with sustainability implications. This article aims to present a specific type of functionalized filter medium and examine its physicochemical process for nutrient removal with the aid of Langmuir and Freundlich isotherms and isolated filtration kinetics. Within a suite of batch tests, pollutants of concern include ammonia, nitrite, nitrate, orthophosphate, total dissolved phosphorus, etc. The potential for application in stormwater management facilities, such as dry ponds, was emphasized in terms of life expectancy and removal efficiency. When compared with the natural soil that was selected as the control case in the column tests, our "green sorption media mixture" with respect to three types of sorption, including adsorption, absorption, and ion exchange, proved relatively effective in terms of removing most of the target pollutants under various influent waste loads. Sensitivity analysis with respect to the pH values and initial concentrations simultaneously or separately was presented in the end to enhance the engineering reliability analysis. It shows that with the inclusion of limestone, drastic changes of pH values can be buffered well, so that the impacts on the ultimate removal efficiency of ammonia and nitrates can be isolated solely to the changes of initial concentrations. © 2009 American Institute of Chemical Engineers Environ Prog, 29: 319–333, 2010

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INTRODUCTION

Nutrients such as ammonia, nitrite, nitrate, and phosphorus are common contaminants in water bodies all over the world. High nitrogen and phosphorus contents in stormwater runoff have impeded the reuse potential and impacted ecosystem integrity and human health. Nitrate may be toxic and can cause human health problems such as methemoglobinemia, liver damage, and even cancers. Phosphorus may trigger eutrophication issues in fresh water bodies, which could result in toxic algae and eventually endanger the source of drinking waters. Nutrient removal is very important for the sustainability of the aquatic ecosystem and environment. All these nutrients have acute and chronic harmful outcomes for human beings and ecosystems directly or

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indirectly. According to the United States Environmental Protection Agency (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 0.10–10.00 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 result in oxygen deficiency in an 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 most frequently measured to indicate nutrient loadings in natural and built systems. They are found in urban stormwater 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 onsite 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, wastewater effluents reclaimed from secondary wastewater treatment plants and reused as irrigation water may result in the same level of environmental impact.

Nitrogen, particularly nitrate–N, easily moves from terrestrial ecosystems into surface and ground waters, including lakes, streams, rivers, and estuaries [9–11]. According to USEPA, the maximum contaminant level of nitrate and nitrite levels in drinking water should not be >10.00 mg/L nitrate—nitrogen (NO_3^-—N) and 1.00 mg/L nitrite—nitrogen (NO_2—N), respectively [12]. For effective stormwater management, a bioretention or bioinfiltration pond is a relatively new urban stormwater best management practice (BMP) [13]. The use of differing filter media in wet and dry bioretention ponds to help promote nutrient removal is an appealing engineering approach to deal with the increasing trend of higher nutrient concentrations. 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 model the isolated filtration kinetics of selected mixes of filter media for nutrient removal using Langmuir and Freundlich isotherms and column tests. Pollutants of concern mainly include ammonia, nitrite, nitrate and orthophosphate (OP), total dissolved phosphorus (TDP), etc. Filter media 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. The goals of this study are thus to: (1) present specific functionalized filter media for nutrient removal via a systematic literature review, (2) examine the adsorption, absorption, and ion exchange capacity for nutrient removal separately as a function of the physicochemical conditions, (3) estimate the life expectancy of the selected filter media which we denote as "green sorption media," (4) understand the isolated filtration kinetics of selected filter media mixtures in the physicochemical process, and (5) discuss the field implementation potential. These efforts should collectively demonstrate the trend and potential for application of green sorption media leading to the promotion of sustainable civil infrastructure systems in urban regions.

LITERATURE REVIEW

Nutrient Concentrations in Stormwater and Groundwater in Florida

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. 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_3—N), and nitrate—nitrogen (NO_3—N) + nitrite—nitrogen (NO_2—N) were 0.30 mg/L, 0.27 mg/L, 1.30 mg/L, 0.05 mg/L, and 0.05 mg/L, respectively, in stormwater runoff [16]. Because of the collective impacts of stormwater runoff from both urban and agricultural areas and onsite wastewater treatment plants, this result clearly demonstrated that nitrate concentrations have increased in many Upper Floridian aquifer springs since the 1950s. Phelps [17] reported that nitrate concentrations ranged from less than 0.02–12.00 mg/L, with a median of 1.20 mg/L, based on 56 Upper Floridian aquifer wells sampled in Marion County during 2000–2001 [17]. It is known that nitrate concentrations have exceeded 1.00 mg/L in recent years at some springs in Lake, Marion, Orange, Seminole and Volusia Counties according to Phelps et al. [18] and St. Johns River Water Management District [19]. Increasing trends in nitrate concentrations were documented in Volusia County springs, such as DeLeon and Gemini Springs [18] and Blue Spring [19].

Stormwater Best Management Practices

A number of devices, collectively known as structural BMP, were employed to treat contaminated stormwater [20]. Nutrient in stormwater, groundwater, and wastewater can be removed by using physicochemical and microbiological processes. The former include activated carbon absorption, ion exchange with synthetic resins, reverse osmosis, and electrodialysis, whereas the latter consists of nitrification and denitrification triggered by either autotrophs or heterotrophs. Bioinfiltration processes with differing sorption media have been gaining popularity due to their cost-effectiveness [21]. Within the context of bioinfiltration, including stormwater trench, ponds, infiltration biowells in low-impact development (LID), and exfiltration facilities, three types of physicochemical processes are of interest. They are adsorption, absorption, and ion exchange. Besides, two important processes that result in the transformation of nitrate are nitrification and denitrification in the microbiological process. Although both may contribute to nutrient removal, most of the filter media are expected to improve solid–liquid contact and prevent channeling during physicochemical and microbiological processes. In general, the higher surface area of clay/silt in natural soil might provide more contact area for the solid to absorb and more space for bacteria to grow. As a consequence, the hypothesis in this study is that the functionalized filter media using a proper mixture of recycled materials, such as tire crumb, sawdust, fine sand, clay, or silt might have a higher capacity for nutrient removal. Comparative studies for a quantitative process-based understanding of the filtration kinetics with respect to differing material mixes in both physicochemical and microbiological processes would help to sustain the renewed interest for the bioinfiltration BMP in stormwater management. However, the interesting and challenging research question is how to examine the adsorption, absorption, and ion exchange capacity for nutrient removal restricted to the physicochemical conditions solely in the case of the hydraulic retention time (HRT) not being sufficiently long to bring about complete microbiological transformation during the storm events in the BMP facilities.

Sorption Media Used for Nutrient Removal

In water chemistry, sorption is brought about by physical van der Waals forces and/or binding between the pollutant chemical complexes on the surface of the media. Adsorption occurs normally at the media surface, either its interior or immediate exterior surfaces within a porous media. Yet absorption takes place when the pollutant penetrates to the molecular level of the sorption media. Within the sorption process, the pollutant and media become homogenous in structure although no chemical reactions occur resulting in alteration of the media's chemical structure. However, ion exchange is not strictly a sorptive process as it involves the replacement of ions. For example, potassium or sodium in the media may be commonly replaced by various metals, making the flow to receiving waters less harmful or harmless. Some nutrients, such as phosphorus, removed by inorganic media are likely to be in the form of sorption/precipitation complexes. The distinction between adsorption and precipitation is the nature of the chemical bond forming between the pollutant and sorption media. Yet the attraction of sorption surface between the pollutant and the sorption media causes the pollutants to leave the aqueous solution and simply adhere to the sorption media. In the context of using various green sorption media for nutrient removal, it might appear that sorption is followed by precipitation or occurs at the same time in the same physicochemical process. For example, the initial reaction of phosphorus removal by sorption media appears to be adsorption with slow alteration of the complex to a precipitate. When limestone is present, however, removal of phosphorus by calcium compounds such as calcium carbonate may involve sorption followed by precipitation. These processes also occur in natural soils though with different degrees. Most pollutants, including bacteria and viruses, in stormwater runoff are likely to be hydrophobic. Therefore, significant shifts in any one of four chemical conditions, including the background concentration of the pollutant, dissolved oxygen concentration, pH values, and salinity, may cause a change of thermodynamic equilibrium between sorption media and aqueous solution.

As long as the HRT is long enough, a microbe-mineral interface can be initiated for either or both nitrification and denitrification. Nitrification which changes ammonia to nitrite and later nitrate may be triggered by some nitrifiers in an aerobic environment. The nitrate would be eventually lost from the stormwater treatment system after being converted by denitrifiers to nitrogen gas in an anaerobic environment. Still, the denitrification process must count on the presence of organic matter, such as a carbon source (i.e., electron donors). Pollutants removed by the adsorption process in green sorption media may subsequently desorb. The adsorption, absorption, ion exchange, and precipitation processes are actually intertwined and dynamic. For example, ammonia maybe sorbed by clay in bioretention filters filled with sorption media. However, the nitrate that is quite soluble may be sorbed first and then leached from the clay during subsequent storm events rejuvenating the sorptive sites for incoming nutrients such as ammonia. During this stage, absorption/adsorption capacity would, in turn, become available, which is limited in each type of media. There might be competition for N, P and metal removal simultaneously when they sorb onto the same sites. They each prefer different or even mutually exclusive conditions (e.g., pH, dissolved oxygen, temperature, etc.). Besides, some of the nutrient removal mechanisms are either reversed or promoted by anaerobic conditions. For example, adsorption/precipitation of dissolved phosphorus with ferric/ferric oxide embedded in the sorption media can occur only in an aerobic environment and the complex dissolves under anaerorobic conditions. When the sorption media is saturated, an aerobic environment is most likely to be maintained for quite a while in the wet ponds. However, both anaerobic and aerobic conditions would appear alternately in the dry ponds so that the denitrification process returns after storm events affecting the sorptive process. This would complicate the nutrient removal process in the sense that we cannot count on the denitrification process as the major nutrient removal mechanism. Consequently, a more profound study with respect to the physiochemical processes, such as adsorption, absorption, and ion exchange, would become of interest.

Removal of ammonia, nitrite, nitrate, and phosphorus by sawdust, tire crumb, sand, clay, and other organic media can be achieved using natural, functionalized, and/or engineered filter media. Using sorption media for the removal of both nitrogen and phosphorus species has been well documented [22]. In recent years, Debusk et al. [23], Kim et al. [24], Clark et al. [25], Boving and Zhang [26], Hsieh and Davis [13], Ray et al. [20], and Seelsaen et al. [27] carried out experiments to remove nutrients from stormwater runoff using a suite of sorption media. They include but are not limited to sawdust, peat, compost, zeolite, wheat straw, newspaper, sand, limestone, expanded clay, wood chips, wood fibers, mulch, glass, ash, pumice, bentonite, tire crumbs, expanded shale, oyster shell, and soy meal hull. Table 1 presents a list of sorption media used in previous work to remove nutrients from stormwater.

METHODOLOGY

The overall evaluation of sorptive processes is commonly comprised of two aspects: performance and capacity. Performance in terms of filtration kinetics refers to the efficiency of the process and the concentration of the resulting effluent. Capacity refers to how much of the pollutant can be removed before the green sorption media must be replaced, which is related to the isotherm tests.

Isotherm Study for the Sorption Media Mixture

An adsorption isotherm can be produced by exposing a known quantity of adsorbate to various dosage of adsorbent in a batch test. The isotherm gives us am 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. The adsorption strength is inversely proportional to solubility [41]. In our experiment, about 800.00 g filter media mixture was prepared by using 50.00% sand, 20.00% limestone, 15.00% sawdust, and 15.00% tire crumb. A known concentration of adsorbate solution (i.e., 1.00 mg/L) was prepared from stock solution. Three hundred milliliter of that solution was transferred into each Erlenmeyer flask and five flasks were used. Then 50.00 g of media mixture was taken in flask 1, 100.00 g in flask 2150.00 g in flask 3, 200.00 g in flask 4, and 250.00 g in flask 5 simultaneously. The top of the each flask was covered by parafilm to minimize outside disturbance during the waiting period. All the flasks were kept on a shaking platform (Innova 2000, New Brunswick Scientific) with 50 rpm for a certain time (variable for each different adsorbate). After the waiting period, the flasks were removed from the shaking platform and samples were collected from the flasks. The test temperature was in between 22 and 23°C (i.e., in room temperature). Isotherm curves for ammonia, nitrate, nitrite, OP, and TDP were created via this procedure.

Ammonia—nitrogen (NH_3—N; Fisher Scientific) solution was prepared from anhydrous NH_4Cl (dried at 100°C), nitrate (NO_3—N) solution was prepared from KNO_3 (dried at 105°C for 24 h) and nitrite (NO_2—N) solution was prepared from $NaNO_2$ from Fisher Scientific. All solutions were freshly prepared to avoid possible contamination. In some cases ammonia (100.00 mg/L), nitrate (10.00 mg/L), and standard phosphorus stock solutions (50.00 mg/L) were purchased commercially from HACH (Loveland, CO). All the glassware was washed with HCl (i.e., 1:1 solution) before starting the experiments.

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

- Freundlich isotherm equation [5],

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

- Langmuir isotherm equation [5],

$$\frac{1}{q} = \frac{1}{q_{\mathrm{m}}K_{\mathrm{ads}}}\left(\frac{1}{C}\right) + \frac{1}{q_{\mathrm{m}}} \qquad (2)$$

where q is the sorbed concentration (mass adsorbate/mass adsorbent), q_{m} is the maximum capacity of adsorbent for absorbate (mass adsorbate/mass adsorbent), C is the aqueous concentration of adsorbate (mass/volume), K_{ads} is the measure of affinity of adsorbate for adsorbent (unitless), and K is the Measure of the capacity of the adsorbent (unitless).

Life Expectancy of the Sorption Media

The isotherm testing 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. First, 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 the amount of media used in a specific system, the concentration of nutrient in stormwater and flow rate of stormwater. If we know the concentration of nutrient in and flow rate of stormwater, the amount of nutrient per year in stormwater can be calculated, and thus the life expectancy of media may be easily deduced.

Removal Efficiency, Kinetics, and Head Loss

A laboratory column test method is a physical model which attempts to simulate a portion of the real world subsurface environment under a controlled set of experimental conditions. Five Plexiglas columns with a diameter of 5.00 cm (2.00 inches) and length of 30.00 cm (1.00 foot) were prepared. All the five columns were tied with a wooden frame. All joints of the columns were made leak proof using pipe thread sealant. The top and bottom of the column were closed but removable screw caps were used to enable addition and removal of media. A filter with glass beads (diameter of 4.00 mm) was placed at the bottom to prevent the outward flow of finer particles from the column during the collection of samples. Although the column is 30.00 cm long, the media was only filled up to about 22.50 cm (9.00

Table 1. Sorption media used by different researchers to treat stormwater.

No.	Sorption media	Additional environmental benefits via other pollutant removal	Physical/chemical properties	References
1	Sandy coastal soil			[28]
2	Compost	Oil and greases, heavy metals	Maple and elm leaf compost	[29]
3	Peat Wollastonite Limerock Sand with quartz	Cu, Cd, Ni		[23]
4	Alfalfa		$D < 4.00$ mm	[24]
	Leaf mulch compost		$D < 2.00$ mm	
	Sawdust		$D < 2.00$ mm	
	Wheat straw		$D < 4.00$ mm	
	Wood chips		$D < 2.00$ mm	
	Newspaper		D (average) < 4.00 mm	
	Sulfur		For large particles, $D = 2.00$–2.36 mm and for small particles, $D = 0.60$–1.18 mm	
	Limestone		$D = 0.60$–1.18 mm	
5	Crushed piping materials	Organics		[30]
6	Iron sulfide			[31]
7	Peat Carbon sand, enretech sand, or sand Zeolites Activated carbon	Cu, Fe, Pb, Zn		[25]
8	Natural sand (bank filtration)			[32]
9	Lignocellulosic material		Basically pine bark chips	[33]
10	Clay	Cd, Pb, Ni		[34]
11	Zeolites			[35]
12	Opoka	Microorganisms		[36]
13	Waste medium density fiberboard (MDS) sawdust			[37]
14	Wood fibers	Polynuclear aromatic hydrocarbons	Aspen wood fibers composed of 51.00% cellulose, 26.00% hemicellulose, 21.00% lignin, and 1.00% ash	[26]
15	Mulch	Lead, TSS, oil, and grease		[13]
	Soil		Sandy loam	
	Sand		Sand	
16	Zeolites Pure quartzitic sand	Cu, Pb, Zn		[15]
17	Allophane Chitin			[38]
	Pumice		Iron (18.20%), aluminum (13.70%), calcium (12.70%), magnesium (7.30%), and others	
	Bentonite		4.00–8.00% calcium carbonate	

Table 1. (Continued).

No.	Sorption media	Additional environmental benefits via other pollutant removal	Physical/chemical properties	References
	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,	[20]
19	Wood fibers	Zn, Cu	D = 4.00 mm	[27]
	Sand			
	Zeolites			
	Glass		D = 4.00 mm	
	Ash			
	Compost			
20	Iron sulfide			[39]
21	Metallic iron		D = 0.006–0.01 mm; surface area 0.31 m^2/g	[40]
	Clinoptilolite	Fe	D = 0.18–4.00 mm	

D is the diameter of the media.

inches) from the bottom. Tygon (Saint-Gobain, no. 16) tubes were added to both the top and bottom of the column for delivering the flow of influent and effluent. Influent was flowed to the column from a reservoir by using a peristaltic pump (Master flex L/S, Cole-Parmer instrument).

The kinetics for nitrate, nitrite, OP, TP, and TDP were derived from the column study. Kinetics was derived for each species with different influent concentrations that mimic the actual fluctuations in stormwater dry ponds. Filtration kinetics gives an idea about the velocity of a chemical reaction and helps us to estimate the duration of the nutrient removal process by sorption media. It provides us with an estimate of the residence time and volume of a reactor. For example, it is expected that limestone ($CaCO_3$), as calcium (Ca^{2+}) ion, will help to remove phosphorus in the form of hydroxyapatite ($Ca_5(OH)\ (PO_4)_3$). The approximate chemical reaction is shown as follows [42],

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^- \tag{3}$$

$$3HPO_4^{2-} + 5Ca^{2+} + 4OH^- \rightarrow Ca_5(OH)(PO_4)_3 + 3H_2O \tag{4}$$

A schematic diagram of the columns setup is given in Figure 1. Four columns were loaded with 580.00 g of media mixture and the fifth one, the control, was loaded with natural soil collected from the Hunter's Trace pond in Marion County, Florida. The reason for such separation of testing in different columns with respect to different chemical species is to avoid the crosscontamination by the different chemical species of interest. The surface areas of sorption media would play an important role for the adsorption, absorption, and the growth of microbes for nitrification/denitrification. Yet this testing would not consider the impact of the growth of microbes for nitrification/denitrification. It was expected that sorption processes may dominate the system in the first few hours allowing us retrieve the kinetics information without interference. The subsequent abiotic test ensured that this assumption held throughout the tests.

To simulate practical conditions as far as possible, no pretreatment of the sorption media and natural soil was carried out. The stormwater was collected from UCF campus. The influent concentration of the stormwater was then controlled by spiking from stock solution (i.e., augmentation). The influent concentration portfolio for all testing species comprised 5.00 mg/L, 2.50 mg/L, and 0.50 mg/L although it might vary by ±5.00% in actual testing due to the instability of augmentation. The experiment was done in a batch mode. The five columns were flushed three times by the experimental solution prior to the beginning of the experiment to maintain a consistent working environment. Flushing is expected to remove some off 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. Samples, except for ammonia and TN, were collected after 1.00, 3.00, and 5.00 h generally by opening the valve at the bottom of the column. For ammonia and TN, the sample collection time was 0.50, 1.00, and 1.50 h. Each time, about 60.00 mL of sample was collected from each column for study of the kinetics. The samples were diluted in

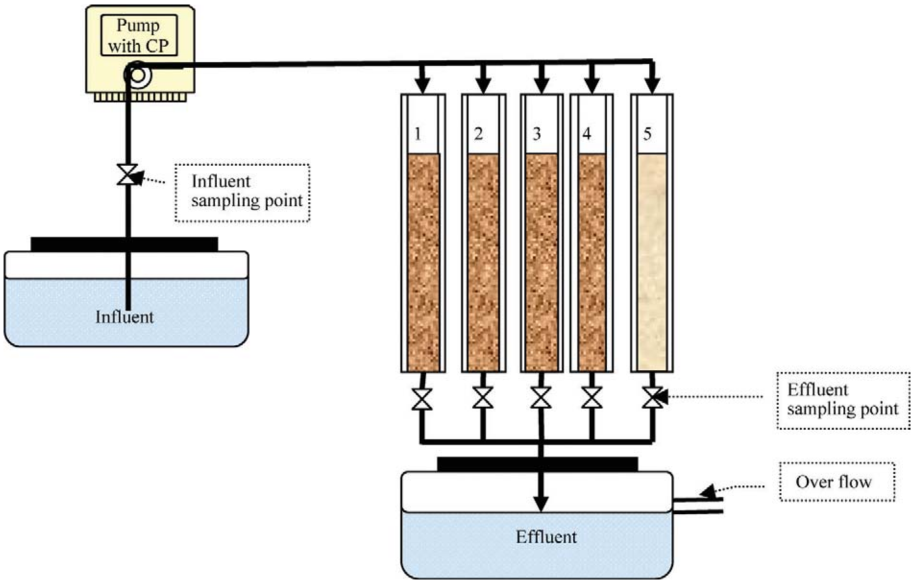


Figure 1. Schematic diagram of the column setup (Here CP = control panel; columns 1–4 are filled with the proposed media mixture and column 5 is filled with soil collected from Hunter Trace pond as control). [Color figure can be viewed in the online issue, which is available at **wileyonlinelibrary.com**.]

Table 2. Analytical methods for the determination of chemical species in effluent.

Chemical species	Title of method	Method no.
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

case of higher concentration during the chemical analysis to avoid exceeding the detection limit.

Kinetics studies play a significant role in the design of an optimized reactor to produce the desired product. In most studies, it is common to initially assume first-order reactions (see Eq. 5a), and the rate constant k (h^{-1}) is calculated from the slope of the line of $\ln[C_0]/[C]$ versus reaction time. Integration of equation results in

$$-dC/dt = k[C] \quad \text{and} \quad \ln[C_0]/[C] = kt \tag{5a}$$

where C_0 is the influent concentration (ie., nutrient in this case).

The rates may be calculated from a linear regression of $\ln[C_0]/[C]$ versus reaction time for the reduction of ammonia, nitrite, nitrate, OP etc. if first-order kinetics is fairly well followed. 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 $1/C$ versus time for each species may be plotted for identification (see Eq. 5b).

$$-dC/dt = k[C][H^+] \quad \text{and} \quad 1/[C] = 1/[C_0] + kt \tag{5b}$$

A list of methods used in the chemical analysis is shown in Table 2. 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 using an Accumet research pH meter (type AR 50-duel channel). In these columns, however, both nitrification/denitrification and sorption mechanism may participate in the removal process.

A sensitivity analysis with respect to the pH values in the water bodies and initial concentrations of ammonia and nitrates was conducted to observe the effect of varying pH values on different nutrients given that the limestone may behave as a buffer. It is expected that the change of pH values will play an important role, especially in adsorption process.

Table 3. Parameters of the Langmuir isotherm for different species.

Species	Isotherm equation for Langmuir	*R*-square value	$1/(q_m K_{ads})$	$1/q_m$ (mg/mg)
NH_3—N	$y = 10{,}233.000x - 8880.700$	0.94	10,233.00	−8880.70
OP	$y = 272.850x - 129.740$	0.97	272.85	−129.74
NO_3—N	$y = 128.740x + 1030.000$	0.80	128.74	1030.00
NO_2—N	$y = 229{,}620.000x - 229{,}133.000$	0.84	229,620.00	−229,133.00
TDP	$y = 101.120x + 137.000$	0.74	101.12	137.00

$y = 1/q$; $x = 1/C$.

Table 4. Parameters of the Freundlich isotherm for different species.

Species	Isotherm equation for Freundlich	*R*-square value	$1/n$	log *K*	*K* (mg/mg)
NH_3—N	$y = 3.951x - 3.213$	0.95	3.95	−3.21	0.001
OP	$y = 1.293x - 2.215$	0.96	1.29	−2.22	0.006
NO_3—N	$y = 0.231x - 3.043$	0.85	0.23	−3.04	0.001
NO_2—N	$y = 34.571x - 3.389$	0.75	34.57	−3.39	0.00041*
TDP	$y = 0.771x - 2.268$	0.75	0.77	−2.27	0.005

$y = \log q$; $x = \log C$.
*Very small number that might be ignored.

Initial pH values were adjusted from 3.00 to 5.00, 7.00, and 9.00 and the initial concentrations from 0.50 to 2.50 and 5.00 mg/L in the sensitivity test. The HRT was 5.00 h for nitrate and OP and 45.00 min for ammonia.

It was a major concern during the experiment to elucidate whether the removal process of nutrients from stormwater is mainly a physicochemical or a microbiological process. An abiotic test was conducted to confirm the type of process that would prove that sorption mechanism is the dominant one. A stock solution of 2,000.00 mg/L of $HgCl_2$ was prepared for abiotic control. Nine milliliters of $HgCl_2$ was added to every 1.00 L of influent. The HRT was 5.00 h for nitrate and OP and 1 h 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 phosphorus accumulating bacteria, respectively. All other conditions remained identical (i.e., as in the kinetic analysis). Extreme care was taken to use $HgCl_2$ during the experiment since it is a hazardous substance.

The head loss of the column was also measured as a critical engineering design parameter. For this reason, two new columns with the same size as those in the column test were built. Each column has three holes: One is at the top, another one is at the bottom, and the other 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 (inner diameter of 5.00 cm) as piezometric tube was connected with each hole using glue. The water was directed to flow continuously into the column from a reservoir about 120.00 cm above the floor of the room and column bottom is about 10.16 cm above the floor. The reading was taken 15.00 min after commencement of water flow.

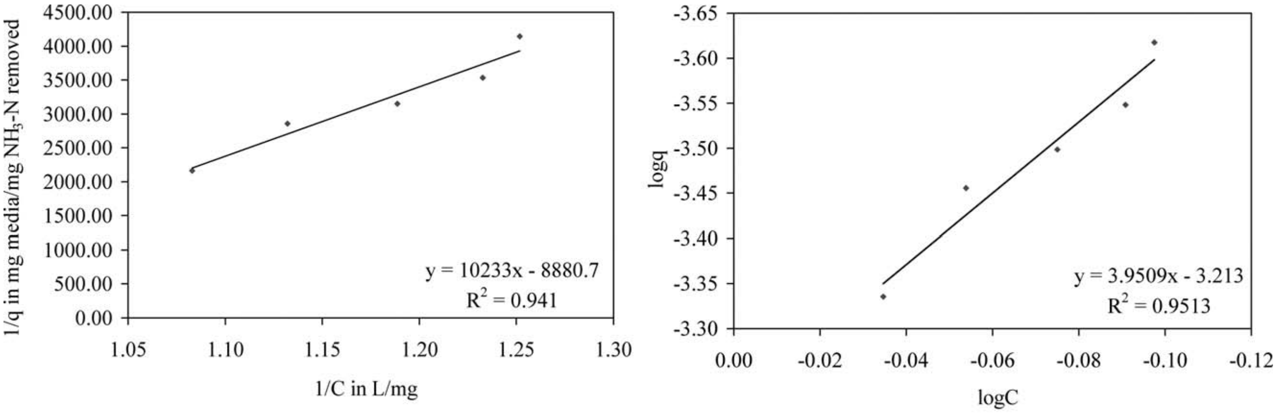
RESULTS AND DISCUSSION

Isotherm Study for the Sorption Media Mixture

From Tables 3 and 4, it can be seen that the value of *n* is >1 for nitrate and TDP. When $n = 1$ or lower, it indicates that all types of adsorbent have an equal affinity for the adsorbate. When $n > 1$, the affinity decreases with increasing adsorption density [5]. The maximal capacity of adsorbent for adsorbate is also shown by q_m. The isotherm plots (Figures 2–6) are shown later to provide an idea of the overall scenario.

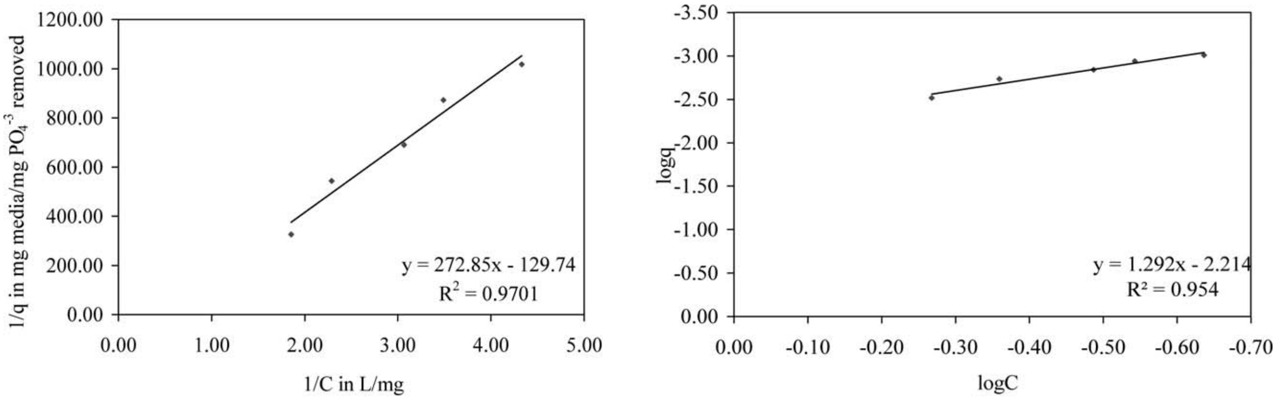
Life Expectancy of the Media

Suppose that 300,000.00 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 0.01 mg nutrient/mg filter media. So the maximum amount of OP that can be adsorbed is 2310.00 g (0.01 mg/mg × 300,000.00 g). Assuming that storm water has an average OP concentration of 1.00 mg/L and the average storm water flow is about 378.50 L per day (100.00 gal per day), then the total amount of OP will be about 138.15 g/yr [i.e., (100 × 365 × 3.78 × 1.00)/1000]. As a result, the life expectancy of the media mixture for OP removal would be about 16.74 yr (2,310.00/138.15). This life expectancy may vary according to the type of media used, the waste loads in stormwater, and the intensity, frequency and



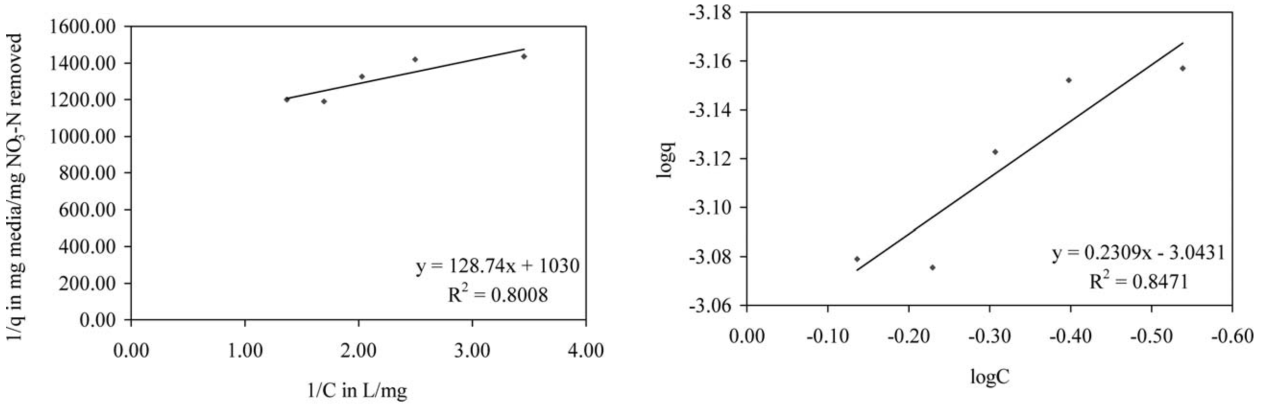
(a) (b)

Figure 2. The isotherm study for ammonia. (a) The Langmuir isotherm plot and (b) the Freundlich isotherm plot.



(a) (b)

Figure 3. The isotherm study for orthophosphate. (a) The Langmuir isotherm plot and (b) the Freundlich isotherm plot.



(a) (b)

Figure 4. The isotherm study for nitrate. (a) The Langmuir isotherm plot and (b) the Freundlich isotherm plot.

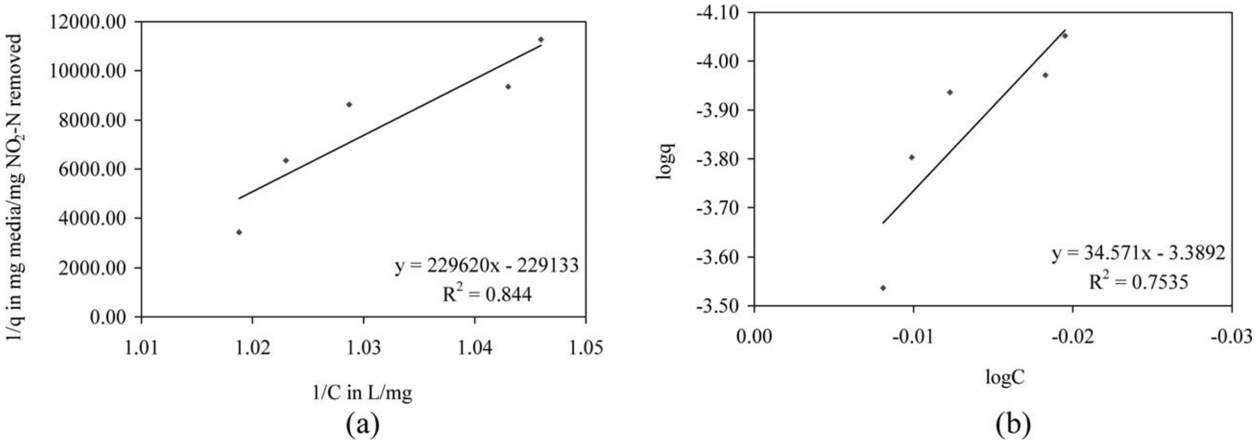


Figure 5. The isotherm study for nitrite. (a) The Langmuir isotherm plot and (b) the Freundlich isotherm plot.

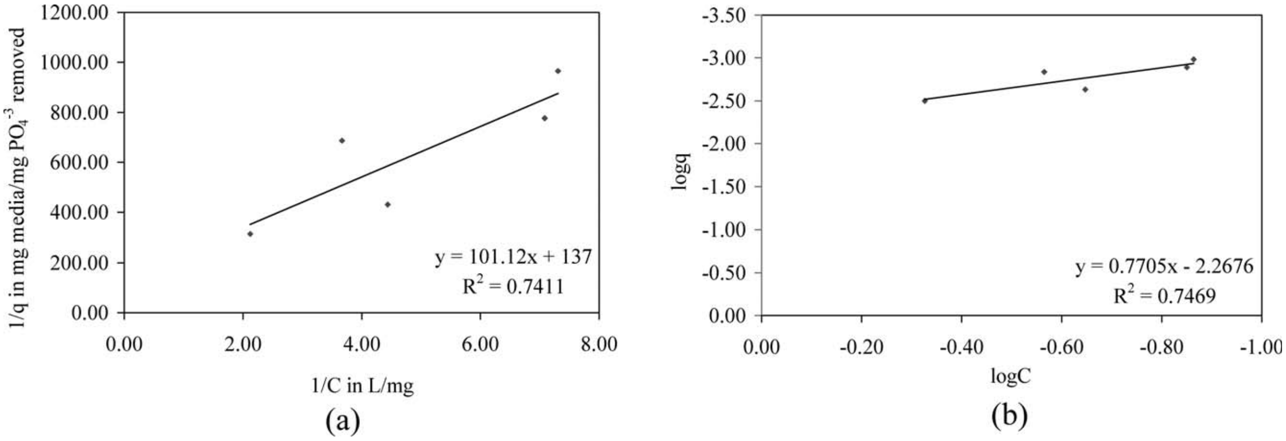


Figure 6. Isotherms for total dissolved phosphorus (TDP). (a) The Langmuir isotherm plot and (b) the Freundlich isotherm plot.

Table 5. Isotherm test of sorption media mixture for different nutrient species.

Species	Life expectancy (yr)
Ammonia as nitrogen	0.244
Orthophosphate	16.737
Nitrate as nitrogen	2.108
Nitrite as nitrogen	0.009
Total dissolved phosphorus	15.851

duration of the stormwater in the study area. Based on the same rationale, Table 5 summarizes all the relevant life expectancies of the functionalized filter media with respect to each type of pollutant of concern in this study. It appears that the effective removal of nitrogen species will probably be more a microbiological than physicochemical process.

Filtration Kinetics

A great difference of removal efficiency was observed across differing column tests and the isotherm studies. Nutrients cannot flow through the flask in the isotherm test as there is no inflow or outflow in the flask setup. In the column tests, however, the media, such as sawdust, may release (i.e., desorption) some nutrients absorbed in the early stage, which could ultimately impact the total removal efficiency. For this reason, we conducted the test by flushing the column three times at the beginning of each run to wash out the contributed nutrients possibly from sawdust in previous testing. Findings in the filtration kinetics analysis showed that if the influent concentration is lower ammonia, the sorption media can remove it in a relatively more efficient way. The removal efficiency may even reach 100.00% with waste load concentrations of 0.50 and 2.50 mg/L after 1.00 and 1.50 h of HRT, respectively. When the ammonia concentration was up to 5.00 mg/L, the removal efficiency was about 64.00% after 1.50 h of HRT. Given that the ammonia concentration is normally not very high in stormwater, the proposed sorption media mixture should work well in terms of removing ammonia from stormwater runoff. The removal efficiency of nitrate was about 95.36%, 81.34%, and 65.68% after 5.00 h of HRT when the

Table 6. Summary of kinetics for the proposed sorption media mixture.

Species	Initial concentration (mg/L)	First-order equation	*R*-square value for first-order equation	*K* value for first-order equation (h^{-1})	Second-order equation	*R*-square value for second-order equation	*K* value for second-order equation (L/mg h)
Nitrate	5.00	$y = 0.230x$	0.65	0.75	$y = 0.074x + 0.193$	0.99	0.07
	2.50	$y = 0.330x$	0.99	0.33	$y = 0.302x + 0.391$	0.92	0.30
	0.50	$y = 0.749x$	0.26	0.25	$y = 9.516x + 2.000$	0.88	9.52
Orthophosphate	5.00	$y = 0.521x$	0.28	0.52	$y = 1.637x + 0.201$	0.86	1.64
	2.50	$y = 0.420x$	0.11	0.42	$y = 1.511x + 0.389$	0.69	1.51
	0.50	$y = 0.105x$	0.78	0.11	$y = 1.340x + 1.754$	0.94	1.34
Nitrite	5.00	$y = 0.222x$	0.83	0.22	$y = 0.072x + 0.198$	0.92	0.07
	2.50	$y = 0.897x$	0.99	0.89	$y = 5.088x + 0.402$	0.82	5.09
	0.50	$y = 0.683x$	0.65	0.68	$y = 6.736x + 1.879$	0.93	6.74
TP	5.00	$y = 1.328x$	0.78	1.33	$y = 11.275x + 0.202$	0.96	11.28
	2.50	$y = 1.314x$	0.52	1.31	$y = 19.46x + 0.413$	0.73	19.46
	0.50	$y = 0.954x$	0.94	0.95	$y = 27.53x + 1.68$	0.75	27.53
TDP	5.00	$y = 0.942x$	0.44	0.94	$y = 2.089x + 0.199$	0.91	2.09
	2.50	$y = 0.692x$	0.74	0.69	$y = 1.715x + 0.405$	0.86	1.72
	0.50	$y = 0.519x$	0.23	0.52	$y = 3.454x + 2.045$	0.36	3.45

For the first-order equation, $y = \ln[C_0]/[C]$ and $x = t$; for the second-order equation, $y = 1/[C]$ and $x = t$.

influent waste loads were 0.50, 2.50, and 5.00 mg/L, respectively. Results indicated that the removal efficiency was about 94.14% and 98.72% when the influent waste loads were 0.50 and 2.50 mg/L, respectively. However, it was reduced to 65.40% when the influent waste load was as high as 5.00 mg/L. With this observation, we conclude that the filter media mixture is efficient and effective for the removal of both nitrate and nitrite at lower influent concentrations (i.e., 0.50 and 2.50 mg/L) that covers most of the cases in real world stormwater management systems. With such an analysis, it is certain that the proposed sorption media mixture can remove TN.

OP (70.00–90.00%) is the main component of TP. The removal of OP was 79.50, 94.39, and 97.50% after 5.00 h HRT, when the influent concentrations were 0.50, 2.50, and 5.00 mg/L, respectively. The removal of OP increased with increasing influent concentrations indicating that the proposed media mixture may perform well if the stormwater 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 0.50, 2.50, and 5.00 mg/L after 5.00 h HRT. The removal of TP was >99.00% independent of the magnitude of influent concentrations. Hence, it is confirmed that the proposed media mixture will be effective in removing other forms of phosphorus.

The removal efficiency of nutrients of the natural soil was also observed for comparison. The results confirmed that natural soil is not capable of removing nitrate given—only 19.20% nitrate was removed within 5.00 h HRT with influent concentration of 0.50 mg/L. But natural soil seems to be quite effective in removing ammonia. The removal efficiency of ammonia was about 98.68% and 96.20% within 1.50 h HRT when the influent concentration was 0.50 and 5.00 mg/L, respectively. However, natural soil cannot adsorb the ammonia and nitrate for a long time and some desorption was frequently observed. Natural soil can adsorb some nitrite at lower influent concentration. The removal efficiency of OP by natural soil was not good enough at lower influent concentration. The results showed that it can only remove 19.40% of OP at an influent concentration of 0.50 mg/L. But both TP and TDP had a removal efficiency of >75.00% in our tests.

Modeling the filtration kinetics would help the engineering design. We assume that the proposed filter media in these experiments may follow either first-order or second-order filtration kinetics. The regression equations, *R*-square values, and rate constants may be determined from the appropriate plots. 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 filtration kinetics. In the case of OP testing, second-order filtration kinetics may be derived with respect to a good *R*-square value of 0.70–0.94. The minimum *R*-square value for nitrate is 0.88 and for nitrite is 0.81.

Tables 6 and 7 summarize all kinetic analyses based on the proposed sorption media and natural soil. With these *R*-square values, it can be concluded that all the water quality constituents follow second-order filtration kinetics more closely. This is mainly due to the collective impact of both the influent con-

Table 7. Summary of kinetics for the natural soil (Hunter's trace soil).

Species	Initial concentration (mg/L)	First-order equation	*R*-square value for first-order equation	*K* value for first-order equation (h^{-1})	Second-order equation	*R*-square value for second-order equation	*K* value for second-order equation (L/mg h)
Nitrate	5.00	$y = 0.230x$	0.65	0.75	$y = 0.074x + 0.1903$	0.99	0.07
	0.50	$y = 0.066x$	0.22	0.07	$y = 1.635x + 2.146$	0.21	1.64
Orthophosphate	5.00	$y = 0.577x$	0.39	0.58	$y = 0.443x + 0.202$	0.71	0.44
	0.50	$y = 0.036x$	0.84	0.04	$y = 0.065x + 1.650$	0.82	0.07
Nitrite	5.00	$y = 0.146x$	0.25	0.15	$y = 0.039x + 0.197$	0.31	0.04
	0.50	$y = 0.652x$	0.88	0.65	$y = 6.101x + 1.820$	0.96	6.10
TP	5.00	$y = 1.003x$	0.75	1.00	$y = 3.344x + 0.221$	0.91	2.09
	0.50	$y = 0.336x$	0.85	0.34	$y = 1.425x + 1.981$	0.97	1.43
TDP	5.00	$y = 0.953x$	0.41	0.95	$y = 1.946x + 0.176$	0.46	1.95
	0.50	$y = 0.620x$	0.33	0.62	$y = 5.502x + 2.083$	0.66	5.50

For the first-order equation, $y = \ln[C_0]/[C]$ and $x = t$; for the second-order equation, $y = 1/[C]$ and $x = t$.

centrations and the pH values. Apparently, the proposed media mixture 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 sawdust and tire crumb via adsorption and/or some ion exchange whereas TP, TDP, and OP were mainly removed by tire crumb and limestone via absorption and precipitation.

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 5.00 h of HRT, the removal efficiency of nitrate and OP was about 83.32 and 92.20%, respectively, with an initial concentration of 0.50 mg/L. The ammonia removal efficiency was about 100.00% after 1.50 h of HRT and the same initial concentration. All of the removal efficiencies remain almost to those we 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°C prior to use, it is not possible for bacteria to grow in such a short HRT in the media. In other words, no nitrification/denitrification process was triggered in our test. Aerobic and anaerobic conditions are very important to trigger biological nitrification/denitrification. The pH of the effluent was 6.50–8.00.

pH Values and Sensitivity Analysis

The pH of effluent varied between 7.00 and 8.00 in the media columns, and 6.00 and 7.50 in the natural soil column (i.e., the control case) at room temperature. Room temperature was between 22 and 24°C. These pH values have important effect on filtration kinetics. If the medium is acidic, it cannot retain the nutrients sufficiently long and desorption starts very soon after adsorption. On the other hand, some sorption media can retain the nutrient well even in basic pH environments. Again, basic pH is favorable for the precipitation reactions between phosphorus and limestone. In summary, the proposed sorption media can quickly remove the nutrient from stormwater runoff whereas the natural soil can remove part of the nutrient if the HRT is long enough. However, the latter is not practicable because the stormwater 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 stormwater runoff before it reaches groundwater aquifers.

OP can be removed through the precipitation reaction by calcium ions. This precipitated portion may settle on the surface of sorption media and restrict the further adsorption process. It can be assumed that neutral pH will be best for nutrient removal by sorption media. With the aid of sensitivity analysis as shown in Figures 7–9, it was observed that the removal efficiency increased with increasing pH for nitrate and ammonia. In Figures 7–9, the plots reveal that when the pH value is close to 5–7, the removal efficiency of OP reaches its maximum. Overall, the removal efficiency showed a decreasing trend with increasing pH values for OP if the pH values were >7. Our evidence clearly showed that OP removal was well-established at pH ≤ 7.00 and started to decrease after pH $= 7.00$. The results in Figure 7 particularly confirm that basic pH values are not always favorable for the precipitation reactions between phosphorus and limestone since additional factors, such as initial concentrations, might also be influential.

Both nitrate and ammonia are soluble in water. Nutrients may be dissolved in water at acidic pH and adsorbed on solid surface at higher pH. The

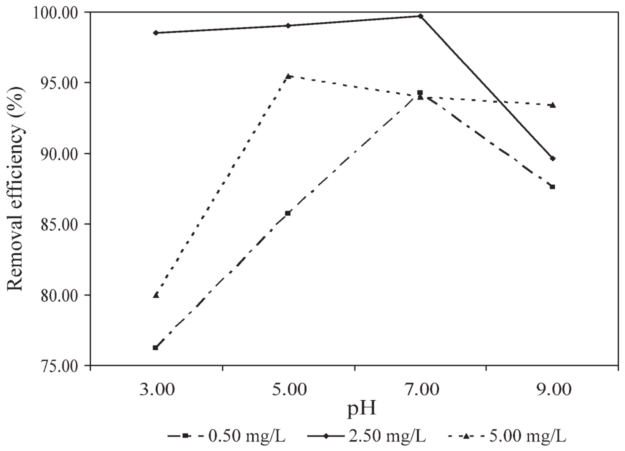


Figure 7. Variation of removal efficiency of OP with the varying pH values and initial concentrations.

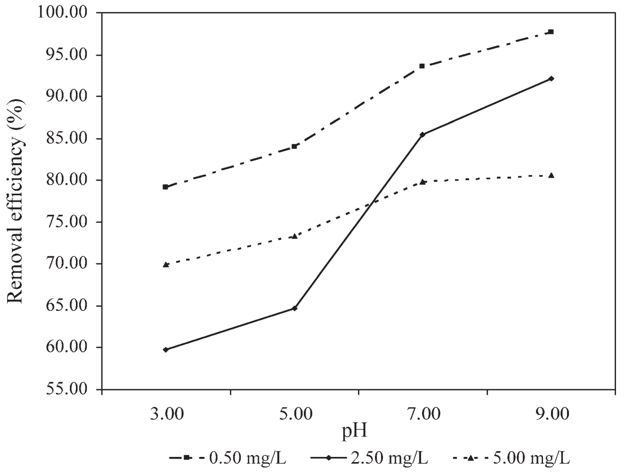


Figure 8. Variations of removal efficiency of nitrate with the varying pH values and initial concentrations.

adsorption/absorption of ammonia and nitrate in the filter media depends on both pH values and initial concentrations. The pH values would normally vary from 7.00 to 8.00. In general, the acidic pH should promote desorption whereas the basic pH should favor the adsorption. There might be competition between adsorption and desorption process in the system at acidic pH. It is expected that the adsorption process would prevail facing increasing pH and ultimately show the higher removal efficiency. In any instance, with the inclusion of limestone as one of the ingredients in the filter media, the pH values are buffered to the maximum so that the nutrient removal remains almost same over all pH levels tested in the sensitivity analysis.

Head Loss

The head loss was calculated based on the aforementioned procedure in a batch run. It presents the permeability rate in the system. Within the natural soil column, the head loss was 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). Storm water 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 ponds so as to help the storm water pass through the pond via infiltration before overflow. Their volume should at least be equal to the average runoff event during the year. The removal of nutrients in these dry ponds could be worse than that in wet ponds.

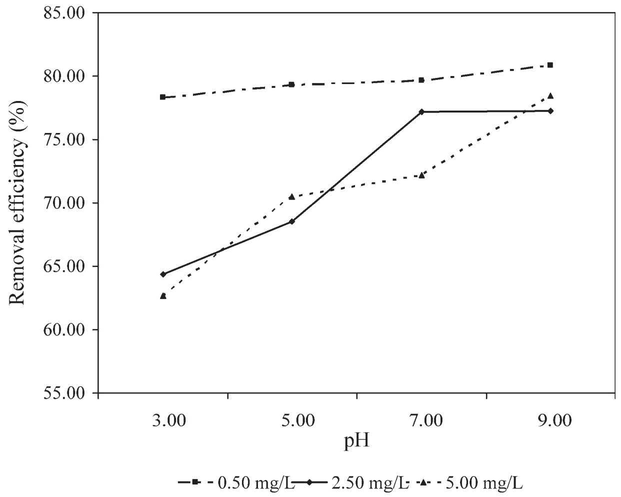


Figure 9. Variations of removal efficiency of ammonia as a function of varying pH values and initial concentrations.

CONCLUSIONS

In stormwater management, dry ponds have dual purposes in both quality and quantity control. Without having specific filter media, typical removal efficiencies in dry ponds would vary between 10.00 and 20.00% [43]. This study proved that the functionalized filter media may effectively and efficiently remove most of the nutrient species within an appropriate HRT via both adsorption and the more dominant absorption processes. The life expectancy of the proposed media is reasonably long for removing phosphorus species thus ensuring system reliability in green infrastructures. However, this is not the case for nitrogen removal. Microbiological effects (i.e., nitrification and denitrification effects) need to be carefully considered to complete the design goal. The column test in this study was set up to test its potential for nutrient removal in dry ponds where stormwater impact is in a batch mode. During field application, the proposed sorption media mixture can be wrapped in geotextile and laid at the bottom of the riprap apron area in dry pond systems or placed as part of the fore bay. In any circumstance, the assurance of HRT would be a major challenge in field application because the time for the intermittent flow (i.e., infiltrate) to pass through the media layer must constitute the legitimate HRT. Otherwise, the removal mechanism would be limited as a physicochemical process. In field applications, the design of thickness of the media layer at the bottom of the dry ponds may be examined further with regard to the treatment efficiency data.

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