ABSTRACT

Title of Dissertation: BIORETENTION MEDIA FOR ENHANCED PERMEABILITY AND PHOSPHORUS SORPTION FROM SYNTHETIC URBAN STORMWATER

Qi Yan, Doctor of Philosophy, 2017

Directed by: Dr. Allen P. Davis, Civil and Environmental Engineering

Bioretention systems are commonly used to improve both quantity and quality (pollutant removal) aspects of urban runoff. A promising media modification process is developed to simultaneously achieve both high infiltration rate and improved P removal in bioretention systems, Bioretention soil media (BSM) and a sandy ‘high flow medium’ (HFM) were modified with three Al-based amendments: water treatment residual (WTR), alum, and partially hydrolyzed aluminum (PHA), 10% by dry mass, respectively. The sorption of adenosine monophosphate (AMP) and myo-Inositol hexakisphosphate (IHP), two forms of organic phosphorus, and inorganic phosphate by modified media mixtures were studied. Compared with unmodified BSM and HFM, the sorption of AMP was increased by a factor of 26 and 80 for media with alum and PHA, respectively. Similarly, the IHP removal capacity were increased by factors of 7 and 8, respectively. Alum and PHA modified media mixtures can reduce P concentrations to <0.01 mg P/L within a contact time < 1 min. Adsorption and chemical precipitation are two predominated mechanisms for P removal using modified media mixtures. HFM modified with HFM and WTR showed high permeability and excellent P removal relative to other media mixtures and most importantly, it requires simplified modification conditions and is recommended for use in bioretention and related SCMs.

BIORETENTION MEDIA FOR ENHANCED PERMEABILITY AND PHOSPHORUS SORPTION FROM SYNTHETIC URBAN STORMWATER

By

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Chapter 1. Introduction

1.1 Research Background

Booming urbanization has increased the amount of impervious surfaces in developed areas. In fact, the rate of increase in impervious surfaces has exceeded the rate of population growth by 5 times over the last 40 years in the U.S. (Luoni et al., 2010). In undeveloped areas with natural ground covers (e.g., forest, meadow), the majority of rainfall can be transported through infiltration and evapotranspiration by soils and vegetation, resulting in a small fraction (~10%) of the incoming rainfall becoming surface runoff. However, surface runoff can be dramatically increased to more than 50% in urbanized lands with 75% - 100% impervious areas, contributing to many problems in the water environment (Luoni et al., 2010).

Impervious surfaces prevent rain from naturally infiltrating into the ground and as a result, large volumes of runoff form and run rapidly into storm drains, sewer systems, and drainage ditches, which can cause flooding problems. For those storm drains directly connected to open discharges, stormwater runoff can impair water quality in receiving water bodies as it concentrates hydrocarbon residues from household and lawn care chemicals, oil, gasoline, brake fluid, nutrients (N and P), and heavy metals (Luoni et al., 2010). In fact, urban stormwater runoff discharge is classified as a significant source of water quality impairment in receiving water bodies (USEPA 1996, 1999; U.S. National Research Council 2008).

Management strategies for stormwater runoff have evolved considerably in the past few decades in order to mitigate the deleterious impacts of urbanization on the environment. Low Impact Development (LID) is an ecologically-based approach that utilizes land planning and engineering design to manage stormwater runoff on site through a vegetated treatment network (Luoni et al., 2010). Developed from the LID ideology, bioretention systems (also known as rain gardens) have been proven as effective on-site stormwater management practices (Hunt et al., 2006; Davis, 2007; Bratieres et al., 2008; Li and Davis 2008; Li and Davis, 2009; Trowsdale and Simcock, 2011). Bioretention generally consists of a shallow ponding area and a porous soil media layer covered with a thin layer of plants or mulch. During rainfall events, runoff enters the facility; planting soil and plants help to infiltrate and evapotranspirate the runoff, and pollutants can be removed by fill media (typically mixes of soil, sand, and organic matter) through mechanisms including filtration, sorption, ion exchange, precipitation and biodegradation.

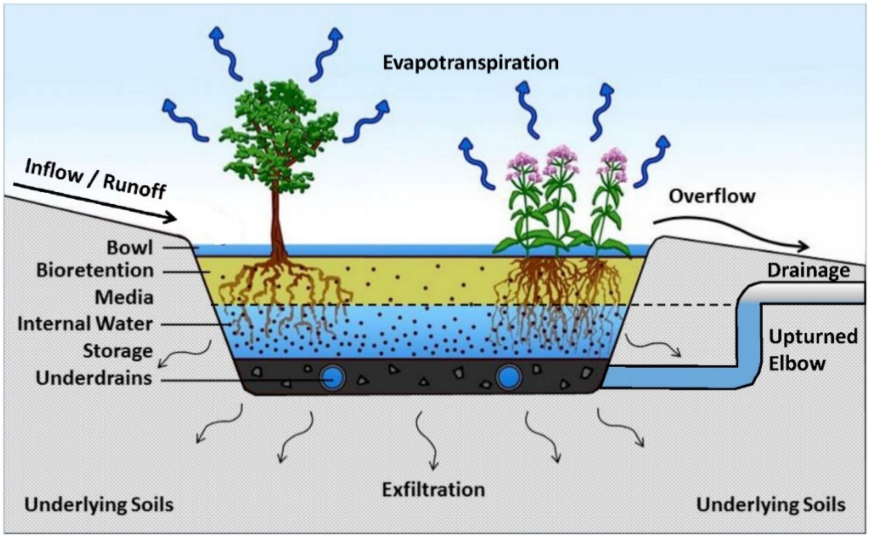

Figure 1-1. Schematic of a bioretention cell (from Winston et al., 2016)

Effective removal of suspended solids, oil and grease, and particulate metal species in bioretention systems have been observed in previous studies (e.g., Davis et al., 2001; Bratieres et al., 2008). However, the removal of dissolved nitrogen (N) and phosphorous (P) were found to be highly variable. Nutrient overloading from N and P used in industrialized landscaping practices (lawn fertilizers, insecticides, and herbicides), as well as animal wastes, can result in heavy algae growth, which lowers dissolved oxygen levels and, leading to eutrophic conditions in receiving lakes and rivers (Stumm and Morgan 1996; U.S. EPA 1999). Therefore, opportunities exist to improve N and P removal in bioretention systems.

1.2 Research Goals

Among the substances conveyed by stormwater, phosphorus (P) is the leading nutrient that can generate eutrophic conditions in receiving lakes and rivers (U.S. EPA, 1998). Effectiveness of bioretention systems as a stormwater management practice for P capture has been investigated (Hunt et al., 2006; Bratieres et al., 2008; Hsieh et al., 2007; Li and Davis, 2009). Total phosphorus (TP) carried by stormwater runoff comprises particulate phosphorus (70-80%, PP) and dissolved phosphorus (20-30%, DP). DP includes soluble reactive phosphorus (SRP, commonly assumed to be inorganic phosphate) and dissolved organic phosphorus (DOP).

As an effective filtration/infiltration practice, bioretention treats runoff by physically sieving suspended solids and the associated pollutants from the water. Previous field studies demonstrated that most of the P mass removal usually results from volume attenuation and PP reduction (Li and Davis, 2009, Liu and Davis, 2014). While this process may capture PP effectively, it exhibited low removal potential for DP. The abiotic stabilization of DP is predominantly determined by media selection. It is generally acknowledged that the processes responsible for P removal typically include fast P sorption reactions onto charged, media surface sites (Fe and Al hydr(oxides), and the slow precipitation of P with Ca^{2+}, Al(III) and Fe(III) ions (Barrow, 1985; McGechan and Lewis, 2002). Therefore, many laboratory studies have investigated the removal of SRP, focusing on media selection and geometry of the flow system (Davis et al., 2001; Erickson et al. 2007; Hsieh et al. 2007; O’Neill and Davis 2012a, b).

However, these studies have only focused on the removal of PP and SRP, ignoring the importance of DOP. Excessive amounts of DOP in urban stormwater runoff, which results from pesticides, animal wastes, and organic matter decomposition, can be a major component of TP. From a field study by Liu and Davis (2014), DOP accounts for 10-15% of stormwater TP concentration and remained basically unchanged through the bioretention treatment. Therefore, a media mixture is desired to provide effective removal for not only SRP, but also DOP.

In acidic soils, P mobility is strongly affected by Al and Fe species (McGechan and Lewis, 2002). Both SRP and DOP can be strongly adsorbed on amorphous (poorly crystalline) Al(hydro)xide adsorbents (Shang et al. 1990; Elliott et al. 2002; Erikson et al. 2007). Al-based water treatment residual (WTR), which has high aluminum contents, is produced as by-products during the coagulation process in water treatment plants. In both previous field and lab-scale studies, WTR-amended bioretention media have been shown to be effective in removing SRP from urban stormwater runoff (Lucas and Greenway 2011; O’Neill and Davis 2012; Liu and Davis 2014). Moreover, montmorillonite is a clay mineral that can strongly adsorb DOP (Anderson and Arlidge 1962; Sanchez-Camizano and Sanchez-Martin 1983). Therefore, WTR and montmorillonite were selected as two initial amendments to bioretention media for enhanced P sorption from stormwater runoff.

In order to further optimize the P (especially DOP) sorption capacity of the media, two modification processes were proposed using two additional amendments: alum and partially hydrolyzed aluminum (PHA). Alum (aluminum sulfate) has been suggested as an effective amendment for P removal from wastewater; enhanced removal was attributed to the extra active sites provided by complex aluminum species on adsorbent surfaces (Urano and Tachikawa 1991; Hano et al. 1997). Alkalinity was provided during the alum addition process to assists in the formation of $Al(OH)_3$ precipitates, which is hypothesized to be an effective adsorbent for both SRP and DOP.

Aluminum chlorohydrate is a partially neutralized aluminum salt with a high basicity (~83%); it can hydrolyze to highly positively-charged cationic polynuclear species, which can be used for coagulation of negatively charged particles through adsorption and particle surface-charge neutralization (Letterman, 1999). The incorporation of aluminum chlorohydrate as a PHA to bioretention media is hypothesized to consume less alkalinity to form $Al(OH)_3$ and, requires less labor input compared with alum. Therefore, PHA was studied as an alternative Al amendment and compared with alum for: (1) media performances for P removal; (2) feasibility of the media preparation process; (3) underlying sorption mechanisms for the enhanced P removal.

Furthermore, the hydraulic characteristics of bioretention media are critical since they determine the quantity management of stormwater runoff. Generally, a very sandy bioretention media with high hydraulic conductivity may be desired because it can mitigate peak flow by promoting the infiltration of runoff, especially from infrequent storm events (Hartsig and Szatko, 2012). Therefore, the ideal media mixture should not only possess a high sorption capacity for P, but also a high permeability to promote rapid runoff infiltration.

High flow media (HFM), which is an engineered sandy material, was investigated for enhanced P sorption in bioretention systems. In general, fine fractions (such as clay) are chemically active for P sorption, and sustain plant growth (Hunt et al 2012, Shanstrom, 2015). Therefore, HFM alone may has limited potential to provide effective P removal because of its limited fines content. Sorption of P is also dependent on solid/water contact time; systems utilizing a highly permeable media may compromise the P removal since the contact time can be shortened when runoff quickly moves through the media (Ayoub et al., 2001; Riahi et al., 2009; Rout et al., 2014). Therefore, there is a trade-off between the permeability of the media and P removal characteristics. Considering all these goals, a HFM was synthesized and modified with different amendments as mentioned above, to simultaneously achieve both high runoff infiltration rate and effective P removal in bioretention systems. The overall research objectives of this study include:

1) Achieve effective removal for both SRP and DOP from urban stormwater using different amendments: WTR, montmorillonite, alum, and PHA;

2) Examine P sorption using a highly permeable sandy media to provide both rapid runoff infiltration and improved P treatment;

3) Determine the contact time required for P sorption, and examine the faster P sorption process by using modified media mixtures;

4) Investigate media performance when competitive sorption reactions are presented between different P compounds and, explore underlying sorption mechanisms;

5) Significantly simplify the P-enhancement processes by using PHA, and propose an optimal media modification recipe, with application to stormwater control facilities for effective and efficient P capture.

Development of the ideal media mixture to achieve enhanced dissolved P (both DOP and SRP) sorption and high runoff infiltration progressed in three phases. Initially, batch-scale adsorption isotherm experiments were employed to determine P removal performances of less permeable bioretention media mixtures containing different amendments (WTR, montmorillonite and alum). Building on the results of the batch studies, selected media mixtures were further investigated in small (15 cm) upflow columns undergoing continuous flow patterns to simulate the P flux conditions experienced in bioretention system. The final phase evaluated P removal using HFM modified with PHA in order to promote rapid runoff infiltration. Kinetics experiments of P sorption under varied superficial flow velocities were performed through the study to estimate the contact time required to reduce P concentrations to < 0.01 mg P/L. Possible adsorption competitions between different P species were also investigated. Most importantly, PHA was compared with alum in an effort to develop a practical and effective media preparation recipe for use in bioretention systems.

Chapter 2. Batch Adsorption Isotherm Studies

Abstract

Dissolved organic phosphorus (DOP) has been found to be a significant fraction of the urban runoff phosphorus load. To achieve enhanced DOP removal, bioretention soil media (BSM) amended with an aluminum-based water treatment residual (WTR) and montmorillonite (both 10% by mass) were additionally treated with aluminum sulfate (10% by mass) to improve sorption capacities. The sorption of myo-Inositol hexakisphosphate (IHP) and adenosine monophosphate (AMP), two forms of organic phosphorus, by modified BSM were studied using batch experiments. The sorption of AMP was increased by a factor of 17 and 21 for WTR- and montmorillonite-amended BSM with 10% alum, respectively. Similarly, the IHP removal capacity of these two modified media mixtures were increased by factors of 4 and 5, respectively. Scanning electron microscopy (SEM) and Brunauer, Emmett, and Teller (BET) surface area analyses were used to provide support for underlying sorption mechanisms for the enhanced DOP removal. The oxalate ratio (OR) was employed to provide an index for DOP sorption onto BSM. Generally, greater DOP sorption was observed with higher oxalate ratios.

Keywords: Bioretention, Water Treatment Residual (WTR), Montmorillonite, Alum, Dissolved Organic Phosphorus

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2.1 Introduction

Excessive phosphorus and nitrogen in urban stormwaters contribute to receiving water eutrophication by stimulating algal growth, which threatens water quality and limits human use of water resources (U.S. EPA 1999). In order to reduce nutrient concentrations in surface waters, management strategies have evolved considerably in the past few decades. Bioretention systems have been proven as effective urban stormwater control measures (SCMs) (Davis 2007; Bratieres et al. 2008; Li and Davis 2009; Trowsdale and Simcock 2011). During rainfall events, runoff enters the SCMs, and pollutants can be removed by mechanisms including filtration, sorption, ion exchange, chemical precipitation, and biodegradation.

Total phosphorus (TP) carried by stormwater runoff comprises particulate phosphorus (PP) and dissolved phosphorus (DP). DP includes soluble reactive phosphorus (SRP), commonly assumed to be inorganic phosphate, and dissolved organic phosphorus (DOP). Sorption and/or chemical precipitation have been demonstrated as the two primary mechanisms for the retention of SRP in bioretention and similar SCMs (Erickson et al. 2007; Hsieh et al. 2007).

Water treatment residuals (WTRs), which have high aluminum and iron contents, are produced as by-products during the coagulation process in water treatment plants. WTR-amended media have been shown to be effective in removing SRP from urban stormwater runoff (Lucas and Greenway 2011; O'Neill and Davis 2012a, b). The performance of a field bioretention cell incorporated with 5% WTR showed significant reduction for TP and PP (84 and 91% mass reduction, respectively) through filtration and enhanced sorption (Liu and Davis, 2014).

These studies only focused on the removal of PP and SRP, ignoring the importance of DOP. Excessive amounts of DOP in urban stormwater runoff, which results from pesticides, animal wastes, and organic matter decomposition, can be a major component of total runoff P. DOP has been found to be a significant part of the urban runoff TP load and remained basically unchanged through the bioretention treatment (mean concentration of 0.03 mg P/L, 10% of the TP; Liu and Davis, 2014). With high surface charge and large specific surface area (SSA), amorphous aluminum-hydroxide adsorbents are promising materials for both SRP and DOP removal (Shang et al. 1990; Elliott et al. 2002; Erikson et al. 2007). Alum has been suggested as an effective amendment for P removal from wastewater; enhanced removal was attributed to the extra active sites provided by complex aluminum species on adsorbent surfaces (Urano and Tachikawa 1991; Hano et al. 1997). The high SSA and large pore structure of adsorbents have been found to contribute to enhanced SRP and DOP sorption (Urano and Tachikawa 1991; McGechan and Lewis 2002; Celi et al. 2003; Wu and Sansalone 2013). Additionally, montmorillonite is a clay mineral that can strongly adsorb DOP (Anderson and Arlidge 1962; Sanchez-Camizano and Sanchez-Martin 1983). Therefore, alum addition to WTR- and montmorillonite-amended bioretention soil media (BSM) was evaluated to develop a new removal pathway for low concentrations of DOP in urban stormwater runoff. The objectives of this study were:

1) To perform batch sorption isotherms to analyze both DOP and SRP removal at low concentrations from synthetic stormwater runoff through BSM and BSM amended with WTR, montmorillonite, and alum. Myo-inositol hexakisphosphate (IHP, also known as phytic acid) and adenosine monophosphate (AMP) are two important forms of organic P in aquatic environments and were selected as DOP substances (Leytem et al. 2002; Celi and Barberis 2005). IHP is the most common form of organic P found in the environment (Celi and Barberis 2007). AMP was chosen to provide comparison with IHP for DOP sorption in this study to investigate how the extent of sorption of organic P changes with the structure of the organic P compound, especially in terms of the number of phosphate groups.

2) To correlate the oxalate extraction ratio, which is a simple metric, with media DOP sorption capacity, and provide prediction of media removal performances.

3) To examine the mechanisms for enhanced DOP removal by alum modification, incorporating supporting information of pore structures provided by scanning electron microscopy (SEM) and Brunauer, Emmett, and Teller (BET) surface area characterizations.

4) To recommend an optimal media mixture for use in bioretention and related stormwater control facilities.

2.2 Materials and Methods

2.2.1 Preparation of Media Mixtures

BSM with a textural profile of 85% sand, 10% silt, and 5% clay, classified as a loamy sand soil, was obtained from a Maryland local supplier (NutriGrown, Columbia, Maryland). Aluminum-based WTR was obtained from the Rockville Drinking Water Treatment Plant in Potomac, Maryland. Montmorillonite (AGSORB, Oil-Dri, Ripley, Mississippi) was washed with deionized water (DI water), then air-dried for at least 1 week. BSM, WTR, and montmorillonite were all stored in a watertight container and not exposed to light in order to minimize media changes with time. All media were sieved through a 2-mm sieve. Three media mixtures were prepared: BSM, 10% (by mass) WTR-amended BSM, and 10% (by mass) montmorillonite- amended BSM; labeled as: BSM, WTR-BFM and montmorillonite-BSM. These three control media mixtures were additionally modified with 10% (by mass) alum, respectively; labeled as: A-BSM, A-WTR-BSM and A-montmorillonite-BSM.

The mass of alum added (10% by mass, 2% as Al) was determined by preliminary sorption experiments (not presented), which suggested alum amendments of 10% should yield meaningful results. Urano and Tachikawa (1991) reported that activated alumina combined with 10% alum demonstrated SRP sorption capacity as high as 0.02 g/g. This is consistent with the mass ratio of alum investigated in this study. Alum modification was performed as follows: 10 g of the media mixtures (BSM, WTR-BSM, and montmorillonite-BSM) were added to 0.03 M aqueous aluminum sulfate solutions ($Al_2(SO_4)_3 \cdot 14H_2O$, Alfa Aesar, Ward Hill, Massachusetts) at a solid: liquid ratio of 1:10, resulting in mass of alum equal to 10% (2% as Al) for each media mixture. Crushed limestone from a local landscape supply store was sieved through a 2-mm sieve and was added (20% of the media mass) to increase the pH above 6 and to assist in the formation of aluminum hydroxide precipitate. Media were shaken with the alum solution at room temperature (~298 K) for 48 h. After that, all media were washed by sufficient deionized water (DI water) water to remove the residual salts (Hano et al. 1997), then dried at 378 K until the mass was constant. Formation of aluminum precipitate during the alum modification processes was verified by calculating the decrease of the aluminum concentration, which was measured by graphite furnace atomic absorption spectrophotometry (Perkin Elmer Model 5100 ZL, Waltham, Massachusetts) following Standard Method 3111 (APHA 2005).

Aluminum hydroxide ($Al(OH)_3$) and calcium sulfate ($CaSO_4$), which are the two primary precipitates expected during the alum modification process, were synthesized to provide comparison for DOP sorption with other mixtures. $Al(OH)_3$ precipitate was obtained by titrating 0.17 M $Al_2(SO_4)_3 \cdot 14H_2O$ solution with 0.5M NaOH (Fisher Scientific, Waltham, MA, American Chemical Society) to pH 6.5 (Shang, 1992). CaSO4 was precipitated from aqueous solutions at room temperature by combining equimolar solutions of $CaCl_2 \cdot 2H_2O$ and Na_2SO_4 (Fisher Scientific, Waltham, MA) (Luo, 2012). The precipitates were washed with DI water and oven-dried. A total of 10% $Al(OH)_3$ and 10% $CaSO_4$ (by mass) were mixed into BSM, respectively.

2.2.2 Media Characterization

pH Measurement and Loss on Ignition

The pH values of the media were measured by a glass electrode probe and pH meter (Mettler Toledo MA235, Greifensee, Switzerland) with a Ag/AgCl reference, using an air-dried soil:water ratio of 1:2 (weight: volume). Loss-on-ignition (LOI) measurements were initially conducted for all media mixtures at 550°C. However, WTR exhibits high LOI (35%), which can be attributed to the loss of chemically-bound water from hydrous oxides of WTR during the ignition (Elliott et al., 2002). Therefore, LOI measurements were performed at 350°C for WTR-BSM and alum-modified WTR-BSM, which is a more defensible measurement, minimizing the dehydroxylation of WTR (Pansu and Gautheyrou, 2006).

Extractions

The P sorption and leaching potential of a media has been shown to be affected by its oxalate extractable Al, Fe and P content (Elliott et al., 2002; Maguire and Sims, 2002; Agyin-Birikorang and O'Connor, 2009). Therefore, oxalate extractions were performed on all mixtures to estimate their P sorption capacities. A 0.275 M acid ammonium oxalate (0.175 M ammonium oxalate + 0.1 M oxalic acid) extractant was used to determine the amorphous fractions of Al and Fe hydroxides of all media mixtures. The extraction experiments were performed with a 1:40 media: solution (weight: volume, w/v) ratio and pH controlled at 3.0 (McKeague and Day 1966, 1993). Mixtures with high Al content (WTR and alum) used a 1:100 (w/v) ratio during the extraction as recommended by Dayton and Basta (2005). Samples were shaken on an orbital shaker for 2 h in the dark, centrifuged for 13 min at 1610 *g* and filtered through a 0.22 μm polyethersulfone membrane (Fisher Science, Waltham, MA). Oxalate extractable P was measured using the method of Wolf and Baker (1990). The Fe and Al concentrations in all extraction solutions were determined using inductively coupled plasma-atomic emission spectroscopy (ICPE-9000, Shimadzu Scientific Instruments, Columbia, MD).

The oxalate ratio (OR), is defined as:

$$\mathrm{OR} = \frac{\mathrm{Al_{ox}} + \mathrm{Fe_{ox}}}{\mathrm{P_{ox}}} \tag{2-1}$$

where Al_{ox}, Fe_{ox} and P_{ox} are oxalate-extractable Al, Fe and P measured in mmol/kg, respectively.

SEM and BET Characterization

SEM and BET surface area analyses were performed for BSM, A-BSM, $Al(OH)_3$ and $CaSO_4$. The morphology of all the samples was observed on an SU-70 field emission scanning electron microscope (SU-70, Hitachi High Technologies America, Gaithersburg, MD) at an accelerating voltage of 10 kV.

The media specific surface area was determined by N_2 adsorption and desorption, using the BET equation (Accelerated Surface Area and Porosimetry System, ASAP 2020, Micromeritics Instrument Corporation, Norcross, GA) (Foo and Hameed, 2010). The microporosity of each media was measured by the t-plot method based on the N_2 adsorption data (Gregg and Singh, 1982). Adsorption branches of the isotherms were used to determine the pore-size distributions for the samples studied via the

Barrett−Joyner−Halenda (BJH) method (Lowell et al., 2004). All samples were degassed at 150 °C prior to N_2 adsorption measurements.

2.2.3 P Sorption Isotherms

IHP (Sigma-Aldrich, St. Louis, MO), AMP (Acros-Organics, New Jersey) and NaH_2PO_4 (Fisher Scientific, Waltham, MA) were used to prepare 0.5, 1.0, 1.5 and 2.0 mg/L P (as DP) solutions with a 0.01 M KCl background electrolyte concentration, resulting in a typical background concentration of urban runoff (Dean et al. 2005). IHP contains 6 phosphate groups and is characterized by wide range of acidity constants (pK_1=1.1, pK_{2-3}=1.5, pK_{4-6}=1.8, pK_7=5.7, pK_8=6.9, pK_9=7.6, pK_{10-11}=10.0, pK_{12}=12.0; Costello et al., 1976) and high charge density in the normal pH range of urban stormwater runoff. AMP, also known as 5'-adenylic acid, is also negatively charged in the normal pH range of stormwater runoff (pK_1=6.0, pK_2=9.8; Kiss et al., 1991).

Isotherms were obtained using 0.5 g of media mixture placed in centrifuge tubes, with 50 mL solution added. A fifth centrifuge tube containing DI water and media was carried through all procedures with the samples. The pH of each suspension was adjusted to 7.0 using 0.1 M NaOH and 0.1 M HCl. In addition, IHP sorption isotherms were performed with a wider range of P initial concentrations (up to 7.0 mg/L P) in order to allow for comparison of all treatments. Isotherm experiments were initially determined for three mixtures with 10% alum addition: A-BSM, A-WTR-BFM and A-montmorillonite-BSM; their native substrates (without alum addition) serve as control media: BSM, WTR-BFM, and montmorillonite-BSM. Additional sorption experiments (as described before) were conducted for 10% $Al(OH)_3$-amended BSM and 10% $CaSO_4$-amended BSM for comparison; labeled as $Al(OH)_3$-BSM and $CaSO_4$-BSM.

Samples were shaken on an end-over-end shaker for 24 h, after which they were centrifuged at 2862 *g* for 15 min and the supernatant liquid was filtered through a 0.22 μm polyethersulfone membrane filter (Fisher Science, Waltham, MA). Final pH was measured and then the samples were digested and analyzed for TDP using potassium persulfate digestion (4500-P B.5) and colorimetric determination by the ascorbic acid molybdenum blue method (4500-P E) at 880 nm (Shimadzu UV-160, Kyoto, Japan) as described in Standard Methods (APHA, 1992). A 5-cm path length cuvette was employed to provide a detection limit of 0.01 mg/L. Sorbed DP was calculated from the difference between the initial and equilibrium DP concentrations.

Sorption of DOP and SRP onto Al- and Fe-based materials and clays has been found to be widely described by the Freundlich isotherm model (Barrow, 1983; Colombo *et al*., 1994; O'Neill and Davis, 2012). Therefore, DOP sorption in this work was described by the Freundlich model.

2.3 Results and Discussions

2.3.1 Media Performance Benchmark

Bioretention media performance was determined against a DOP sorption benchmark. The DOP sorption benchmark (q_{goal}) was calculated as:

$$q_{goal} = \frac{D \times C \times T}{5\% \times D_m \times \rho_{media}} \quad (2\text{-}2)$$

where D_m is the depth of the bioretention media with enhanced DOP sorption capacity (selected as 50 cm), and ρ is the bioretention media bulk density (1 kg/L). The bioretention facility sized at 5% of the impervious catchment area and requires 30 years (T) of DOP sorption capacity. The Washington DC Metropolitan Area receives approximately 100 cm (40 in.) of rainfall per year (D), and the average stormwater DOP concentration, C is 0.2 mg P/L (the mean concentration of DOP reported by Liu and Davis (2014) is 0.03 mg P/L, which is close to the 0.01 mg P/L P detection limit; a higher concentration level was selected in order to better quantify the P measurements). The q_{goal} was calculated as 240 mg P/kg at 0.2 mg/L soluble DOP to provide the effective stormwater treatment for 30 years.

2.3.2 Media P Sorption Isotherms

Equilibrium pH values for all DP studies ranged from 6.5-7.5; most were between 7.0 and 7.5. Solution pH may change the amount of adsorbed P in two ways: (1) affecting the charge of the reacting surfaces of adsorbents (Barrow et al., 1983; Bolan et al., 1986); (2) influencing the relative concentration of the anionic forms of adsorbates (Shang et al., 1992). In general, less sorption of DP has been found at higher pH (> 6.0, Anderson and Arlidge, 1962; Greaves and Wilson, 1969; Celi et al., 2001), due to the formation of repulsive forces between the highly-negative P compound and the more negative surfaces (Celi and Barberis, 2005). However, the pH differences found in this study were relatively small and all values are near neutral. Therefore, the small variations in pH are not considered to significantly impact the results.

Sorption of AMP

AMP sorption isotherms for unmodified and alum-modified media are presented in Figure 2-1. These isotherm points were all duplicated to evaluate experimental variability of the AMP sorption; as shown by the error bars, reproducibility was very good. The lines in the figure are fitted Freundlich isotherms. The isotherm for media without alum addition has a flat and nearly linear slope, indicating low AMP sorption capacity. However, the removal of AMP is remarkably increased with 10% alum addition, as indicated by the steep isotherm slope of all three alum-modified mixtures. Figure 2-1 shows that A-BSM sorbed 190 mg/kg AMP at an equilibrium concentration of 0.2 mg P/L, which is approximately 19 times higher than that removed by unmodified BSM (10 mg P/kg). Furthermore, A-WTR-BSM and A-montmorillonite-BSM both showed greater

AMP sorption compared with their native substrates, increased by a factor of 17 and 21 (at C_e=0.2 mg P/L).

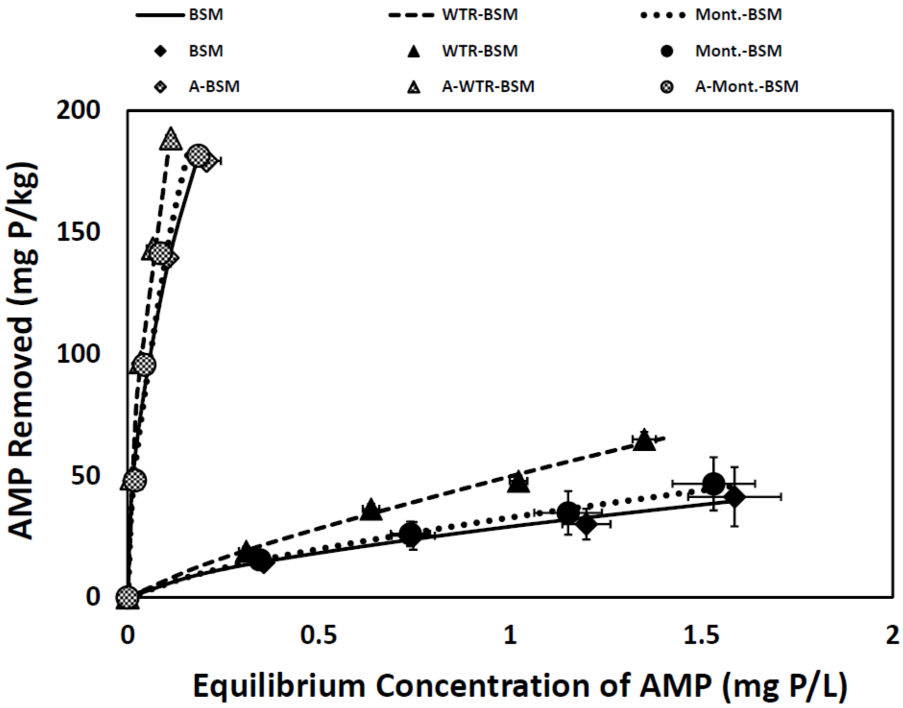


Figure 2-1. Sorption isotherms of AMP by BSM, WTR- and Montmorillonite-BSM with 10% alum addition (Equilibrium pH values for all AMP studies ranged from 7.01-7.46; Mont. indicates montmorillonite; Lines are fitted Freundlich isotherms).

Table 2-1 presents the Freundlich model constants describing the sorption of AMP. The Freundlich K and n determine the isotherm steepness and curvature and provide comparisons for DOP removal by modifying BSM with amendments. K values of BSM, WTR-BSM and montmorillonite-BSM were increased from 29, 50 and 33 to 430, 647 and 544, respectively, with alum addition, demonstrating higher equilibrium sorption capacity with alum addition compared to their native substrates.

The AMP sorption capacities in equilibrium with a 0.2 mg P/L DOP solution, as calculated from the isotherm equation, are also summarized in Table 2-1. The unmodified materials have low sorption capacities and solving for design life in equation 2 yields only 2 years of effective DOP sorption. However, the sorption capacities of unmodified materials were all increased by an approximate factor of 20, approaching the benchmark value of 240 mg P/kg with alum addition, indicating enhanced DOP retention with extended treatment lifetime for the media.

Table 2-1. Freundlich model constants for the investigated BSM mixtures for AMP, IHP and SRP sorption.

	AMP				IHP				SRP			
	K	1/n	R^2	q^* (mg/kg)	K	1/n	R^2	q^* (mg/kg)	K	1/n	R^2	q^* (mg/kg)
BSM	29.1	0.67	0.97	10	550	0.35	0.95	313	30	1.23	0.80	4.14
WTR-BSM	49.8	0.81	0.99	15	1050	0.53	0.88	447	389	0.66	0.92	134
M-BSM	32.8	0.72	0.99	10	501	0.65	0.76	176	40	2.01	0.84	1.57
A-BSM	430	0.51	0.96	190	6023	0.84	0.98	1558	1070	1.13	0.99	174
A-WTR-BSM	647	0.56	0.98	263	5140	0.59	0.91	1988	6093	0.98	0.98	1258
A-M-BSM	544	0.59	0.98	210	2818	0.59	0.99	1090	984	0.54	0.90	412

Note: BSM: bioretention soil media; WTR-BSM: BSM + 10% WTR; M-BSM: BSM + 10% Montmorillonite; A-BSM: BSM + Alum; A-WTR-BSM: BSM + 10% WTR + Alum; A-M-BSM: BSM + 10% Montmorillonite + Alum;

* Calculated P sorption capacity equilibrium at 0.2 mg P/L.

Sorption of IHP

All media mixtures with alum addition removed IHP to less than 0.1 mg P/L even from the highest initial concentration (7 mg P/L), which makes it hard to compare their sorption capacities at Ce of 0.2 mg P/L. Therefore, IHP sorption is discussed at equilibrium concentration of 0.02 mg P/L in order to allow for comparison. Unmodified BSM removed as high as 135 mg P/kg IHP, demonstrating high potential for IHP sorption (at C_e=0.02 mg P/L). Amending BSM with WTR increased the IHP sorption to 148 mg P/kg (at C_e=0.02 mg P/L). The addition of alum to WTR-BSM and montmorillonite-BSM resulted in pronounced increases in IHP removal as well, increased by factors of 4 and 5, respectively (Figure 2-2).

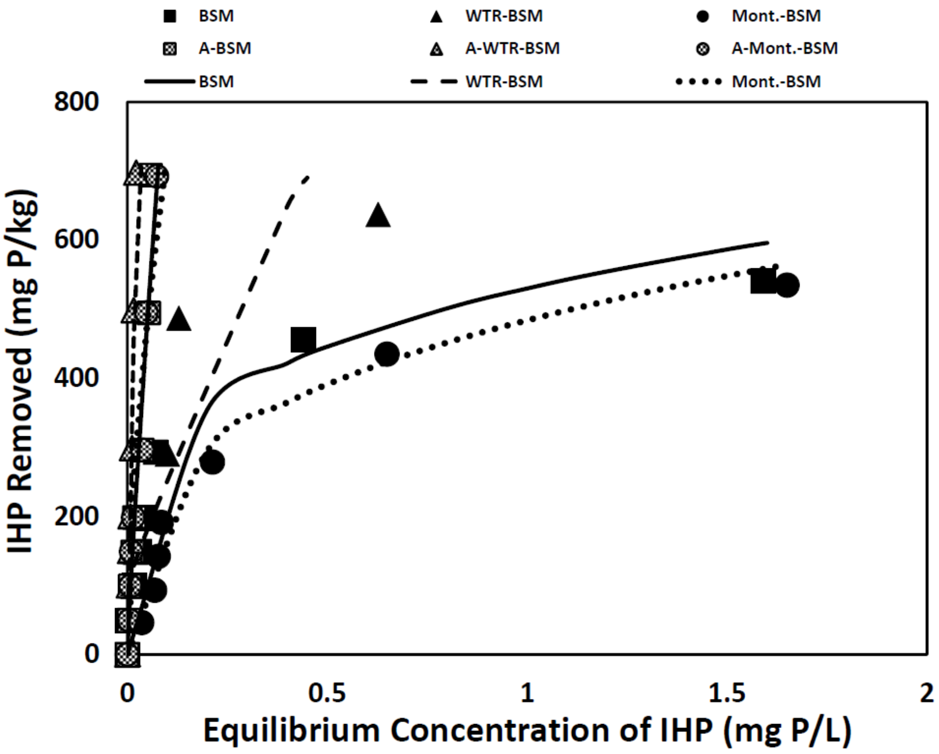


Figure 2-2. Sorption isotherms of IHP by BSM, WTR- and Montmorillonite-BSM with 10% alum addition (Equilibrium pH values for all IHP studies ranged from 6.53-7.66; Mont. indicates montmorillonite; Lines are fitted Freundlich isotherms).

The Freundlich model was used to describe the sorption of IHP as well (Table 2-1). The K value of unmodified BSM is 550, which is significantly increased (by a factor of 11) by alum modification. The same improvements were also observed with WTR-BSM and montmorillonite-BSM, for which K values were increased by factors of 5 and 6, respectively. As expected, higher sorption capacities at equilibrium with a 0.2 mg P/L P solution of these three media were calculated. A-WTR-BSM demonstrated the best performance for both AMP and IHP removal. This media mixture reduced IHP concentration to less than 0.01 mg P/L, a stringent goal for DOP discharge in stormwater runoff.

The amount of IHP sorbed by WTR-BSM was 148 mg/kg (at C_e=0.02 mg P/L). However, Lucas and Greenway (2011) observed a higher DOP sorption by WTR at a slightly higher C_e (475 mg P/kg at C_e=0.025 mg P/L). This wide variability in WTR retention of P can be attributed to the variability in WTR properties, which can result from difference in operating conditions during the water treatment processes. For example, sorption capacities of WTR can be affected by the amount of alum added in the flocculation processes and treatment of water with different sources will produce WTR with variable compositions (Makris et al., 2005).

Sorption of SRP

Mixtures without alum addition generally showed low SRP sorption capacities, except for WTR-BSM (Figure 2-3). While the SRP sorption isotherm is steep for WTR-BSM, the BSM and montmorillonite-BSM both have very flat slopes. The sorption of SRP by BSM is enhanced from 4 mg P/kg to 134 mg P/kg (at C_e=0.2 mg P/L) by WTR addition. The most pronounced increase of SRP sorption was observed for A-montmorillonite-BSM (by a factor of 400).

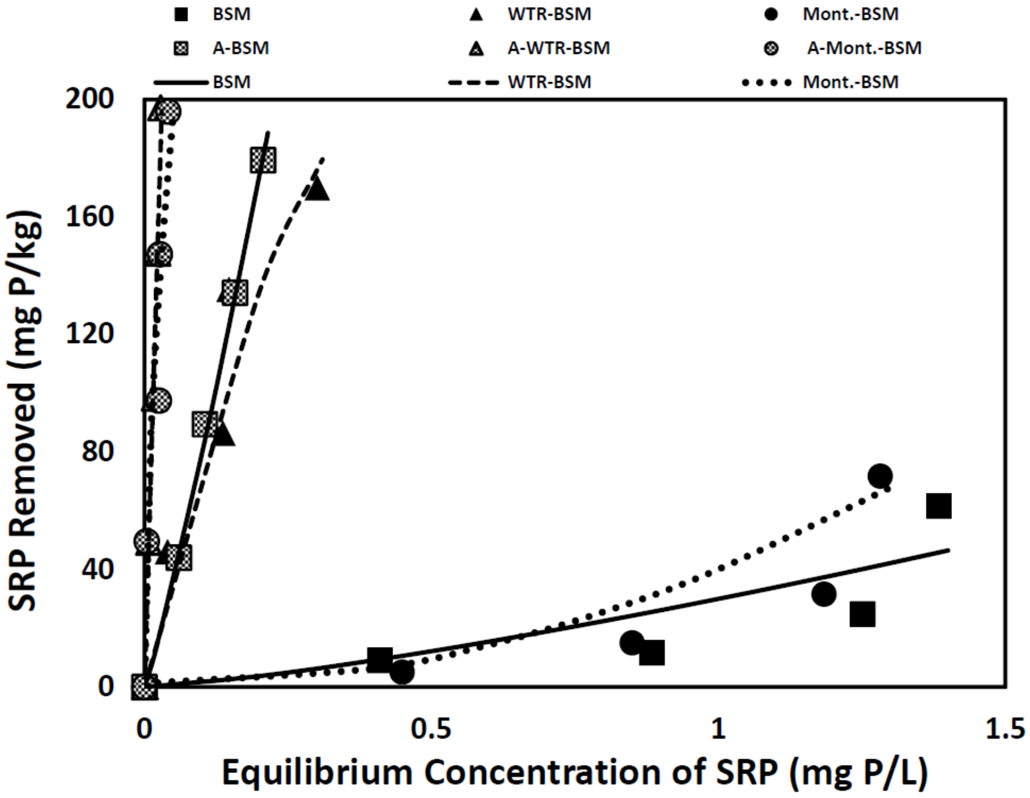


Figure 2-3. Sorption isotherms of SRP by BSM, WTR- and Montmorillonite-BSM with 10% alum addition (Equilibrium pH values for all SRP studies ranged from 6.50-7.52; Mont. indicates montmorillonite; Lines are fitted Freundlich isotherms).

The Freundlich K values for SRP sorption by unmodified BSM and WTR-BSM were observed as 30 and 389, which increased to 1070 and 6093 with alum modification, respectively (Table 2-1). O'Neill and Davis (2012) reported a similar Freundlich K value of 21 for unmodified BSM. They also presented a K of 1786 and 1/n of 0.978 at C_e of 0.12 mg P/L for 10% WTR-BSM (q=367 mg P/kg at C_e=0.2 mg P/L-calculated from the K and 1/n values). This value is higher than what was observed in this study (q=134 mg P/kg at C_e=0.2 mg P/L) and again can be attributed to variability of WTR. As expected, the K value of montmorillonite-BSM was increased from 40 to 984 with alum modification. The SRP sorption capacity of WTR-BSM without alum (134 mg P/kg at C_e= 0.2 mg P/L), was further increased to 1258 mg P/kg. The sorption capacities of unmodified BSM and montmorillonite-BSM were increased from 4 and 1.6 mg P/kg to 174 and 412 mg P/kg, respectively.

2.3.3 Comparison of the Removal of IHP, AMP and SRP

Results for the removal of IHP, AMP and SRP by A-WTR-BSM are compared in Figure 2-4. The removal of the three P species is in the order: IHP > SRP > AMP. A-WTR-BSM is capable of removing 511 mg P/kg IHP and 131 mg P/kg SRP, however, it only removed 72 mg P/kg AMP (at C_e=0.02 mg P/L, this low concentration was selected to allow for comparison of all media mixtures). The pronounced sorption differences between these three P species is noticeable and possible reasons will be discussed subsequently.

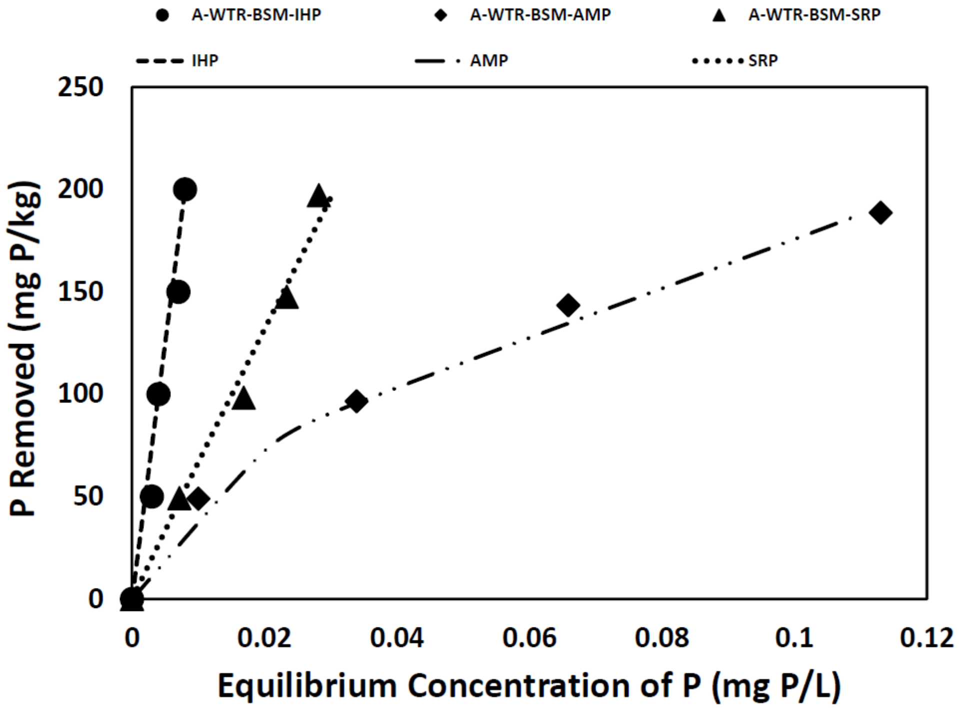


Figure 2-4. Comparison of the sorption of SRP, IHP and AMP by A-WTR-BSM. (Lines are fitted Freundlich isotherms)

2.3.4 Media Characterizations

The results for pH, LOI, and oxalate extraction for the six media mixtures are presented in Table 2-2. BSM, WTR-BSM and montmorillonite-BSM with alum addition (pH=6.17, 6.19 and 6.29, respectively) are slightly more acidic than their native substrates (pH=7.5, 7.38 and 7.37). LOI were measured as 2.3% and 2.6% for BSM and montmorillonite-BSM, respectively. WTR-BSM exhibits higher LOI (4.8 % at 350°C), which can be mainly attributed to the loss of chemical-bound water from hydrous oxides of WTR during the ignition (Elliott et al., 2002).

Table 2-2. Media component characteristics. LOI: loss on ignition; BSM: bioretention soil media; WTR: water treatment residual.

			Oxalate-extractable (g/kg)			Oxalate Ratio
	pH	LOI (%)	Al	Fe	P	
BSM	7.50	2.32	0.49	0.99	0.09	12.3
WTR-BSM	7.38	4.81*	9.37	1.50	0.24	48.3
M-BSM	7.37	2.63	0.79	1.14	0.08	19.2
A-BSM	6.17	1.73	9.32	0.74	0.05	154.3
A-WTR-BSM	6.19	4.23*	11.9	0.40	0.09	201.2
A-M-BSM	6.29	2.91	8.88	0.78	0.07	151.8

Note: BSM: bioretention soil media; WTR-BSM: BSM + 10% WTR; M-BSM: BSM + 10% Montmorillonite;

A-BSM: BSM + Alum; A-WTR-BSM: BSM + 10% WTR + Alum; A-M-BSM: BSM + 10% Montmorillonite + Alum;

* LOI tested at 350°C, indicates some release of bound water.

Data show that BSM contains small amounts of oxalate-extractable Al and Fe, approximately 0.49 and 0.99 g/kg, respectively. However, large increases in media Al_{ox} and Fe_{ox} content were observed with the addition of WTR and montmorillonite to BSM, especially for Al_{ox} content from WTR (Table 2-2). Adding WTR and montmorillonite to BSM improved the OR from 12 to 48 and 19, respectively. SRP retention experiments using WTR-BSM reported OR for BSM and 10% WTR-BSM as 8 and 76 (O’Neill and

Davis, 2012). The improvement in OR indicates that WTR-BSM and montmorillonite-BSM are more effective in removing P than unmodified BSM, which was demonstrated in the sorption isotherm results.

As expected, the alum addition contributed a large amount of Al_{ox} to the mixtures. The Al_{ox} of BSM, WTR-BSM and montmorillonite-BSM were increased from 0.49, 9.37 and 0.79 g/kg to 9.32, 11.91 and 8.88 g/kg, respectively. On the contrary, it was observed that alum addition decreased the amount of Fe_{ox} of the same three mixtures, although this was outweighed by the pronounced increase of Al_{ox}. It should be noted that the large increase of the OR for A-WTR-BSM is mainly due to decrease in P_{ox} (27% increase in Al_{ox} and 63% drop in P_{ox}). This occurs as some P contributed by the WTR was apparently tightly bound by the added alum. Previous works with soil suggested that an OR below 10 can greatly increase the risk for P leaching (Elliot et al. 2002; Agyin-Birikorang and O’Connor, 2007). The OR measured for all six media mixtures were greater than 10, indicating low P leaching potentials.

OR [Eq. (2-1)] was examined as a simple index for the DOP sorption capacity of bioretention media. Positive correlations between Alox and Feox contents of media mixtures and their P sorption capacities have been observed in previous studies (Elliott et al. 2002; Maguire and Sims 2002; Brown et al. 2015). A positive linear relationship between the OR and P removal has been reported (Dayton and Basta 2005; O’Neill and

Davis 2012), which can be a useful tool in estimating media lifetime for P removal. Fig. 2-5 shows the relationship between oxalate ratio and media DOP sorption capacity (at C_e=0.2 mg P/L). Generally, the AMP and IHP sorption capacities of all media mixtures increase with higher OR values (Fig. 2-5). WTR-BSM has the highest OR among the three control mixtures (without alum), which supports its relatively high sorption capacity for both AMP and IHP. Montmorillonite-BSM exhibits higher OR than BSM, and therefore is expected to possess higher DOP removal capacity. However, the amounts of AMP removed using these two media mixtures were not significantly different, and BSM even removed more IHP than montmorillonite-BSM. All alum-modified materials exhibited OR greater than 150, suggesting enhanced DOP sorption capacities. A-WTR-BSM exhibited the highest OR and consistently demonstrated the highest DOP removal.

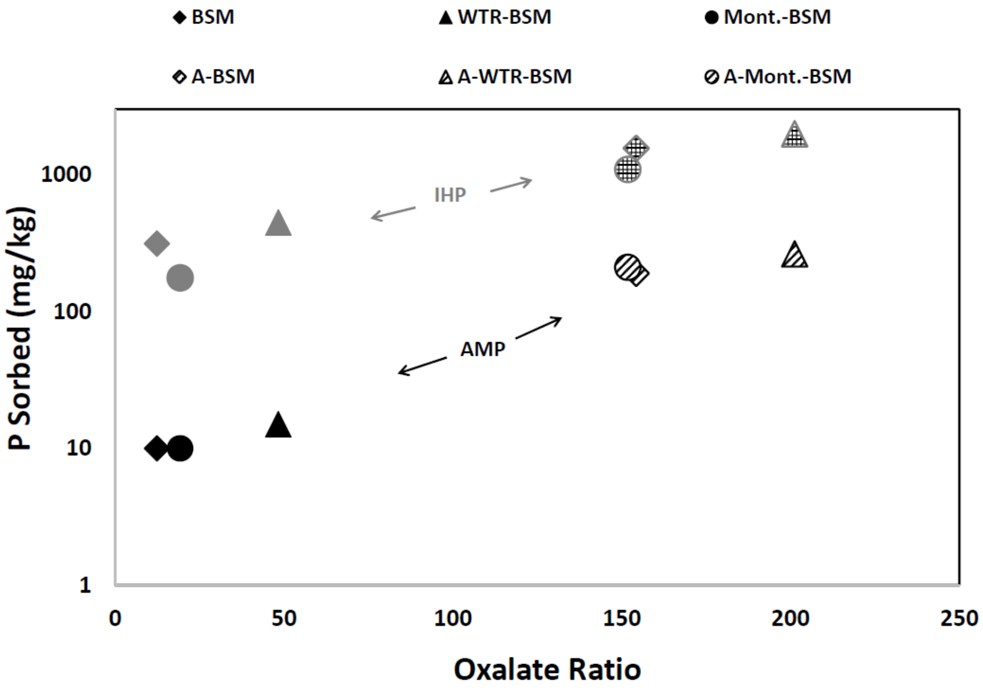
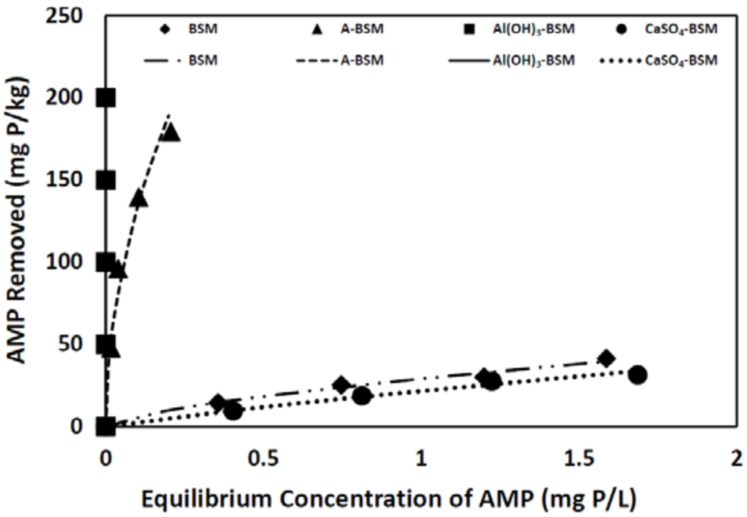


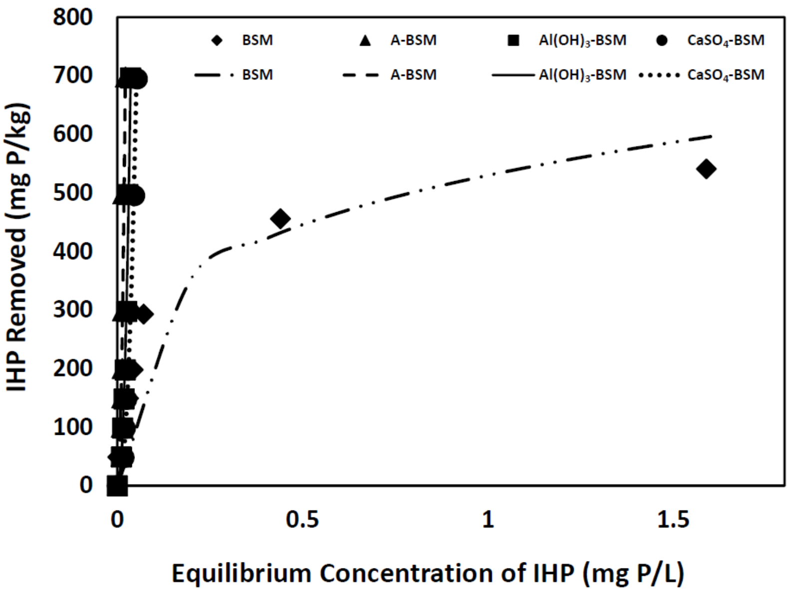
Figure 2-5. Measured oxalate ratio (Eq. 2-1) for mixtures from batch studies and the predicted media equilibrium P sorption capacity. The media equilibrium is for a soluble DOP concentration of 0.2 mg P/L.

The synthesized aluminum hydroxide ($Al(OH)_3$) and calcium sulfate ($CaSO_4$) precipitates were investigated for both DOP and SRP sorption, providing comparison with unmodified and alum-modified BSM. Figure 2-6 clearly shows the sorption of both DOP and SRP by unmodified BSM, A-BSM (both as shown previously), $Al(OH)_3$-BSM and $CaSO_4$-BSM. The highest sorption for all P species is by $Al(OH)_3$-BSM, indicating that $Al(OH)_3$ is an active adsorbent contributing to the enhanced P removal through alum modification. On the contrary, $CaSO_4$ is shown to provide little improvement to AMP sorption compared with $Al(OH)_3$. However, high IHP sorption by $CaSO_4$-BSM is observed in Figure 2-6.

(a)



(b)



(c)

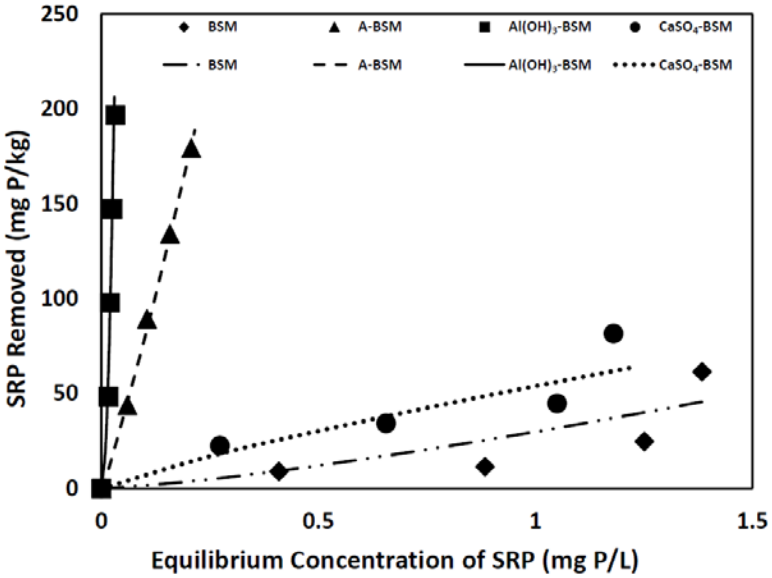


Figure 2-6. P sorption by different precipitates: (a) AMP; (b) IHP; (c) SRP. (Lines are fitted Freundlich isotherms).

The main surface characteristics of BSM, A-BSM, $Al(OH)_3$ and $CaSO_4$ are reported in Table 2-3 and SEM images are shown in Figure 2-7. It is clear from the SEM image that unmodified BSM has a layered and plate-like shape (Figure 2-7(a)). This media has a low specific surface area (SSA) (2.1 m^2/g), as well as pore size (109 Å) and volume (0.01 cm^3/g), which supports its low P sorption capacity.

$Al(OH)_3$ possesses a much higher SSA (62 m^2/g), pore size (162 Å) and volume (0.26 cm^3/g) than BSM. Since diffusion into the pore structure of adsorbents has been suggested as one important mechanism for P retention (Urano and Tachikawa, 1991; McGechan, 2002; Wu and Sansalone, 2013), the large pore volume and width of $Al(OH)_3$ provide additional support for its high P sorption capacity. The SEM image of $Al(OH)_3$ (Figure 2-7(b)) shows that this material exhibits a coarse surface, implying its high SSA and P sorption capacity.

Table 2-3. Specific surface area (SSA) and microporosity of media investigated.

	BET Surface Area (m^2/g)	BJH Pore Width (Å)	Pore Volume (cm^3/g)
BSM	2.1	109	0.01
$Al(OH)_3$	62	162	0.26
$CaSO_4$	14	172	0.06
A-BSM	20	207	0.12

Note: BJH: Barrett-Joyner-Halenda pore analysis.

The large pore size (207 Å) and volume (0.12 cm^3/g) provide support for the excellent P retention performance of A-BSM (labeled as BSM+Alum). Moreover, the fine pore structure of this media is visible in Figure 2-7 (c). This adsorbent has a large surface area and large cavities, which are of particular value for sorption of DOP from urban stormwater.

The poor sorption performance of $CaSO_4$ can be partially explained by its low SSA (14 m^2/g) and limited pore structure (Figure 2-7 (d)).

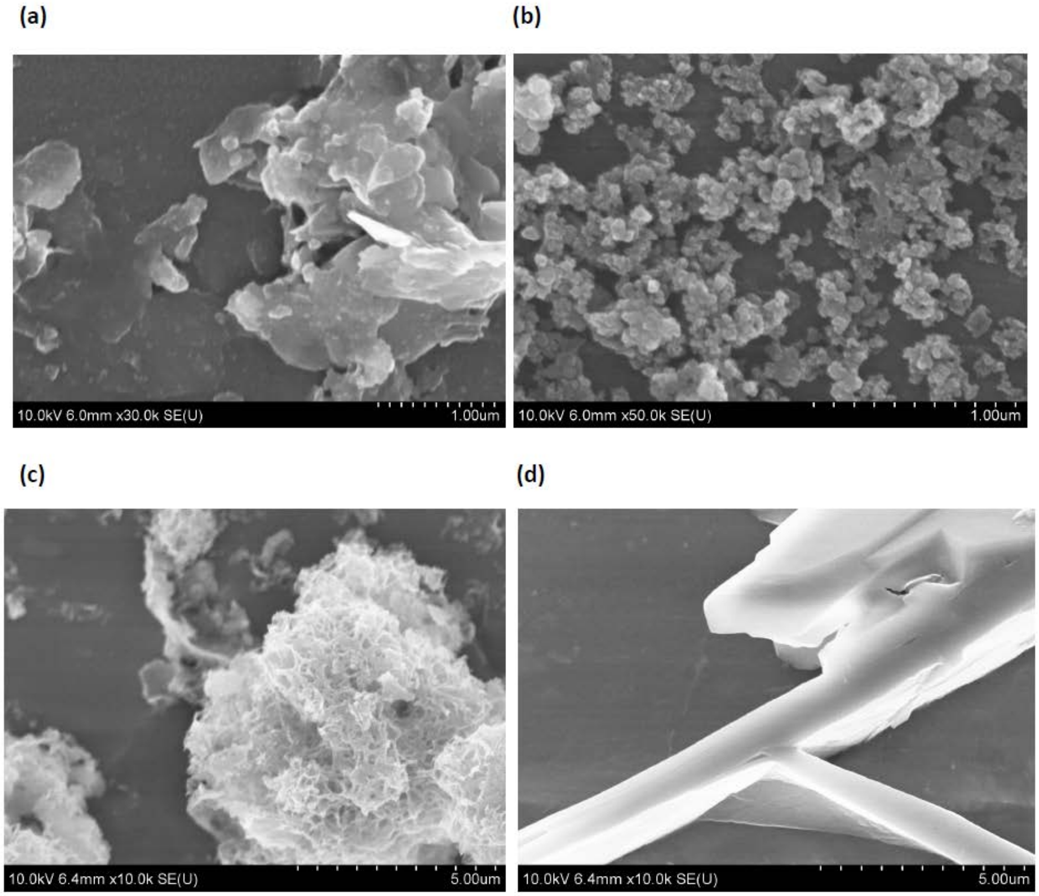


Figure 2-7. Scanning Electron Microscopy images of (a) BSM; (b) $Al(OH)_3$; (c) A-BSM; (d) $CaSO_4$.

2.3.5 Mechanisms for Enhanced Organic P Removal

Two main mechanisms are proposed to explain the enhanced P removal through alum modification: sorption and chemical precipitation. Montmorillonite-BSM removed greater AMP and IHP with alum modification. This can be partly attributed to the modification of the interlayer structure of montmorillonite by Al^{3+} and Ca^{2+}, contributed by alum and limestone. Previous research reported that montmorillonite with divalent cations (such as Ca^{2+} and Mg^{2+}) in the interlayer structures appeared to sorb more than twice as much DOP as that with monovalent cations (Greaves and Wilson, 1969; Bowen et al., 1988; Barba et al., 1991).

The primary proposed removal mechanism for both DOP and SRP is a specific sorption by ligand exchange between the phosphate groups and the surface reactive hydroxyls of the adsorbents (Parfitt et al., 1976; Shang et al., 1990, 1992). Improved DOP and SRP removal with alum addition can be attributed to the formation of high surface area aluminum hydroxide, which is an effective adsorbent for P (Anderson and Arlidge, 1962; Hano et al., 1997):

$$\mathrm{Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3(s) + 6H^+ + 3SO_4{}^{2-}} \qquad (2\text{-}3)$$

DOP capture is enhanced because the aluminum hydroxide surface reacts with DOP according to Eq. (2-4) (For simplicity, R indicates the organic molecular structure of DOP, bold & underlined Al indicates that Al is part of the solid surface). Phosphate groups can replace OH^- groups or H_2O through monodentate or bidentate ligand exchange mechanisms (Bohn et al. 1985) (Figure 2-8 (a)).

$$2\underline{\mathbf{Al}}{-}\mathrm{OH} + \mathrm{R}{-}\mathrm{PO_4}^{2-} \rightarrow \underline{\mathbf{Al_2}}(\mathrm{O_4P}{-}\mathrm{R}) + 2\,\mathrm{OH}^- \qquad (2\text{-}4)$$

The degree of removal of the three P species varied as shown in Figure 2-4, due to differences in the structures of the three P compounds, specifically the number of P groups and molecular size (Celi and Barberis, 2005). IHP was shown to be sorbed by clay minerals to a greater extent than other mono-phosphate compounds (Mackercher and Anderson, 1989; Leytem et al., 2002), which is consistent with the results in this study. The interaction of IHP with the adsorbent surface is believed to be through four of the six phosphate groups, which react with the oxide in the BSM in the same way as the orthophosphate ion via ligand exchange (Goldberg and Sposito, 1985, Celi and Barberis, 2005). The involvement of such a large number of phosphate groups in IHP sorption leads to very stable complexes with the surfaces and limited desorption possibilities (Ognalaga et al., 1994; Martin et al., 2003). However, the sorption of AMP and inorganic phosphate involve fewer phosphate groups, resulting in weaker bonding of P. Inorganic phosphate can be adsorbed to a greater extent than other mono-P organic compounds (Inositol mono-P and glucose-P, McKercher and Anderson, 1989). This is consistent with higher sorption of SRP than AMP in this study.

This mechanism also helps to explain the high IHP sorption capacity of $CaSO_4$ compared with AMP and SRP. Calcium-based materials were found to increase IHP retention (Graf, 1983; House and Denison 2002). Because of the involvement of a large number of phosphate groups in IHP, this molecule can be adsorbed on the surface of a calcium-based adsorbent even at very low concentrations of IHP, and precipitate as calcium phosphate (Celi et al., 2000).

Finally, chemical precipitation must be considered as a mechanism for both enhanced DOP and SRP removal by alum modification. Soil minerals with high iron and calcium contents can precipitate DOP and increase DOP stabilization (Griffin and Jurinak, 1973; Freenman and Rowell, 1981). Formation of insoluble calcium-phosphate or aluminum-phosphate was found to be a significant pathway for SRP removal as well (Wu and Sansalone, 2013). In this study, alum modification introduces Al^{3+} and Ca^{2+}, which can enhance the precipitation processes for both DOP and SRP capture. The proposed precipitation reactions between DOP molecules and Ca^{2+} ions are shown in Figure 2-8 (b) (Yu et al., 2012).

Considering the low DOP concentration in the stormwater runoff, it is possible that DOP is adsorbed initially on the media surface and then precipitated with cations such as Ca^{2+} over long-term treatment. This reduces the possibility of DOP desorption from the media and increases its stability in bioretention systems.

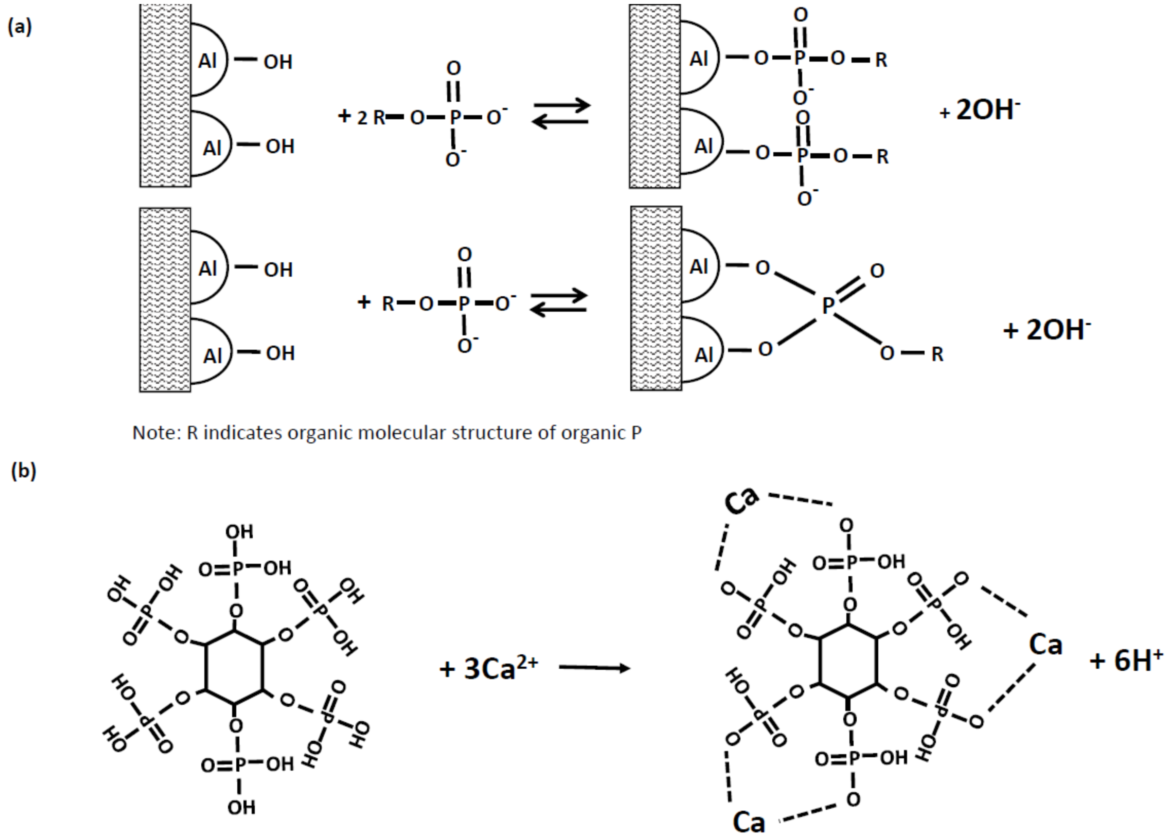


Figure 2-8. Mechanisms for DOP capture (a) sorption (monodentate and bidentate; R indicates organic molecular structure of DOP); (b) precipitation.

2.3.6 Bioretention Application

A-WTR-BSM exhibits extremely high DOP and SRP sorption capacity based on the batch-scale experiments. Therefore, an enhanced DOP capture bioretention practice is proposed. A three-layer bioretention facility can be designed with the top layer for vegetation, the second layer as an alum-modified WTR-BSM media, and the last layer serving as an underdrain layer. Media in the top layer is capable of capturing dissolved metals and suspended solids (Davis et al. 2001) from stormwater. Vegetation in the same layer improves not only the aesthetics of the bioretention system, but also the retention of P by BSM. Henderson et al. (2007) have found that the presence of vegetation substantially improves P retention (85–94% removal), and can prevent P leaching from media. Lucas and Greenway (2008, 2011) reported similar results and they suggested that the rapid microbial immobilization of P (stimulated by the rhizosphere activities of plant roots) contributes to the improved removal performance found in the presence of vegetation. The second layer, constructed of alum-modified WTR-BSM for enhanced DOP capture, is proposed. Considering the sorption capacity, ranging from 263 to 1,988 mg P/kg for AMP and IHP (at C_e=0.2 mg P/L), the lifetime of a bioretention facility sized at 5% of impervious catchment area and a 50-cm DOP-capture media depth is expected to provide approximately 32 and more than 100 years of effective treatment for AMP and IHP, respectively, based on Eq. (2-2).

Concerns about Al toxicity and its effects on plant growth are important when using Al-based media for P removal in bioretention system. Agyin-Birikorang et al. (2009) reported that Al leaching from Al-WTR treated field plots were not significantly different between control and experimental (Al-WTR applied) plots. Furthermore, studies have investigated the impacts of Al-WTR application on crops, and no indications of Al toxicity were reported (Sotero-Santos et al., 2005; Mahdy et al., 2009). Urban stormwater has a neutral pH (6 < pH < 8); within this range $Al(OH)_3$, the dominant Al species in Al-

WTR, is sparingly soluble. Based on this, we assume that significant Al(III) will not be released under normal conditions. Future studies on alum-modified WTR-BSM media will test this assumption.

2.4 Conclusions and Recommendations

Removal performances of alum-modified BSM mixtures were investigated for DOP, specifically IHP and AMP, and SRP at urban stormwater concentrations. Alum-modified media showed greatly improved sorption relative to the unmodified media.

A-WTR-BSM exhibits the highest capacities for DOP sorption; AMP sorption capacity of this mixture was increased by a factor of 17. Enhancements were observed for IHP and SRP capture with alum addition as well. Aluminum hydroxide formed by alum modification has high sorption capacity for DOP, which was supported by the high SSA and large pore structure of this media (confirmed by SEM and BET characterizations). WTR investigated in this study showed lower P sorption capacities compared with other similar studies. WTR is a highly variable material, and its application as a BSM amendment requires further attention.

Generally, a positive relationship was observed between OR and media DOP sorption capacity at 0.2 mg/L. Finally, a bioretention cell with an alum-modified WTR-

BSM layer for enhanced DOP removal may be capable of providing effective treatment for approximately 32 (AMP) to more than 100 (IHP) years of urban runoff P loads.

Chapter 3. Continuous Column Studies

Abstract

Building on previous batch studies, this study further investigated the removal of dissolved organic P (DOP) using small (15 cm) columns with water treatment residual (WTR) and alum as two promising amendments to bioretention soil media (BSM). BSM modified with alum and WTR exhibited higher sorption capacity. Compared with unmodified BSM, significant improvements were observed for adenosine monophosphate (AMP), myo-inositol hexakisphosphate (IHP), and inorganic P (SRP) removal using 10% alum-modified WTR-amended BSM (WTR-BSM), by factors of 26, 7 and 150, respectively. The 10% alum-modified WTR-BSM reduced DOP levels< 0.01 mg/L within 1 min of contact time, demonstrating more rapid DOP sorption processes compared with unamended media. The oxalate ratio (OR), which is based on oxalate-extractable Al, Fe, and P, was employed to provide a criterion for BSM performance with respect to P sorption. Strong correlations (R^2=0.92, 0.96, and 0.65 for AMP, IHP, and SRP, respectively) between the media OR and P sorption capacity of media was observed, which supports the use of the OR to predict P sorption performance of BSM.

Keywords: Bioretention, Water Treatment Residual (WTR), Alum, Dissolved Organic Phosphorus, Column

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3.1 Introduction

Urban runoff discharge is classified as a significant source of water quality impairment in receiving water bodies (U.S. EPA, 1996; U.S. EPA, 1999; U.S. National Research Council, 2008). Water quality degradation occurs when stormwater mobilizes and carries away a variety of pollutants, including nutrients (P and N), from an urbanized area. Phosphorus control in stormwater runoff is important, as it can initiate algal blooms and eutrophic conditions in receiving lakes and rivers (Stumm and Morgan, 1996).

Bioretention, which serves as an effective urban stormwater control measure (SCM), is a proven technology to remove many pollutants, including suspended solids, nutrients, hydrocarbons, and heavy metals (Davis, 2007; Li and Davis 2008; Bratieres et al., 2008; Diblasi, 2009; Li and Davis, 2009; Trowsdale and Simcock, 2011). Phosphorus is present in particulate and dissolved forms in stormwater runoff; in field studies, most of the P mass removal usually results from volume attenuation and particulate P reduction (Li and Davis 2009; Liu and Davis, 2014). Laboratory studies have emphasized the removal of particulate P (PP) and dissolved inorganic P (measured as soluble reactive P, SRP, or orthophosphate) from urban stormwater runoff (Erickson et al., 2007; Hsieh et al., 2007; O'Neill and Davis, 2012a, b), ignoring the importance of dissolved organic phosphorus (DOP).

DOP is a significant component of total dissolved P (TDP) in urban stormwater runoff (mean concentration of 0.03 mg P/L, 10% of the total phosphorus, TP)(Liu and Davis, 2014), and it remains relatively unchanged through the bioretention treatment. Major sources of DOP in stormwater runoff include herbicide application, animal waste disposal, and organic matter decomposition in soils (Celi and Barberis, 2005). For effective P management, research to increase DOP removal from urban stormwater runoff is necessary.

The processes responsible for P removal by SCMs typically include fast P sorption reactions onto charged media surface sites (Fe and Al (hydr)oxides), and the slow precipitation of P with Ca^{2+} , Al(III), and Fe(III) ions (McGechan and Lewis, 2002). Through specific ligand exchange reactions between the phosphate groups and hydroxide groups of the media surface, SRP and DOP can be strongly sorbed onto Al (hydr)oxide adsorbents (Shang et al., 1992; Shang et al., 1996; Agyin-Birikorang and O'Connor, 2007; Wu and Sansalone, 2013).

Based on this concept, an enhanced DOP removal study using batch-scale sorption experiments was conducted by Yan et al. (2016a; Chapter 2). Isotherm experiments in that study investigated the sorption of DOP onto Al-based drinking water treatment residual (WTR)-amended bioretention soil media (WTR-BSM), modified with alum. Inositol hexakisphosphate (IHP, also known as phytic acid) and adenosine monophosphate (AMP) are two important forms of organic P in aquatic environments and were selected as representative DOP substances (Celi and Barberis, 2005). IHP is the most common form of organic P found in the environment (Celi and Barberis, 2007). AMP, which has previously been suggested as a common organic P compound found in animal manures (Leytem et al., 2002), was selected to compare with IHP to investigate how the extent of sorption of organic P changes with the structure and form of the organic P compound, especially in terms of the number of phosphate groups. Improved sorption of IHP and AMP at urban stormwater concentrations by A-WTR-BSM (BSM+10% WTR+10% alum) were quantified (Yan et al., 2016a; Chapter 2). Sorption of AMP and IHP was increased by factors of 17 and 4, respectively, for A-WTR-BSM compared to unmodified BSM.

Building on these earlier batch studies, in this study, BSM with alum and WTR addition was selected as an optimized media mixture and was used in small columns to investigate the removal of DOP and SRP. Batch studies, which allow P sorption to reach a steady state approaching chemical equilibrium, can overestimate the sorption capacities of media in the field (Mateus and Pinho, 2010), plus sorption of P is dependent on solid/water contact time (Ayoub et al., 2001; Riahi et al., 2009; Rout et al., 2014).

Therefore, kinetics experiments of DOP sorption under varied superficial flow velocities were performed to estimate the contact time required for DOP removal. Generally, fast DOP sorption processes are desired, especially in bioretention systems which uses sandy media to promote the infiltration of runoff. Therefore, column studies were undertaken to:

1) Investigate the P removal performances of modified bioretention soil media (BSM) in continuous columns, and provide comparison to batch studies;

2) Determine the contact time required for P sorption, which provides an index for practical bioretention design;

3) Recommend both an optimal media mixture and design information for enhanced P removal, especially for DOP, in bioretention and related stormwater control facilities.

3.2 Materials and Methods

3.2.1 Media and Column Setup

Sorption of dissolved organic P (DOP) and soluble reactive P (SRP) using alum and WTR (both 10% by mass) amended BSM were tested in continuous columns. Four different media mixtures were investigated: BSM, 10% WTR-BSM, 10% alum-modified

BSM, and 10% alum-modified WTR-BSM; they were labeled as: BSM, WTR-BSM, A-BSM, and A-WTR-BSM, respectively. These four media mixtures were loaded into each of four mini columns and were tested for one P compound at a time. All of the media were previously studied in batch systems to determine sorption capacities for both DOP and SRP removal (Yan et al., 2016a; Chapter 2). The BSM comprised 85% sand (Garden Pro All Purpose Sand – Milford, DE), 10% top soil (Garden Pro Top Soil - Milford DE. screened < 2 mm), and 5% clay (PA Red Clay-Resco Products Pittsburgh, PA), with a particle size distribution of a loamy sand, and was obtained from a Maryland local supplier (NutriGrown Co., Columbia, MD).

Aluminum-based WTR was obtained from the Rockville Drinking Water Treatment Plant in Potomac, Maryland. It was stored in watertight containers to retain moisture and maintain its sorption capacity (Yang et al., 2008). All of the media were sieved to 2-mm and air-dried at room temperature (298K) for at least 1 week before use. Alum-modified media were prepared as described in Yan et al. (2016a; Chapter 2). BSM was added to 0.03 M aqueous aluminum sulfate solutions ($Al_2(SO_4)_3 \cdot 14H_2O$, Alfa Aesar, Ward Hill, MA) at a solid/liquid ratio of 1/10, resulting in mass of alum equal to 10% (2% as Al) for each media mixture. Crushed limestone (20% of the media mass, screened < 2mm, Aggtrans™, Harmans, MD) was added to increase the pH above 6 and to assist in the formation of aluminum hydroxide precipitate. The entire mixture was shaken at room temperature (~298K) for 48 h, washed with deionized water (DI water) three times before dried at 378K.

Three experimental groups of four columns each were tested with three P compounds, for a total of twelve column experimental units. Forty g of each medium was added to a 15-cm long x 2.5-cm inner diameter, sealed, upflow column, providing a medium height of 6 cm. Two, 4.5-cm quartz sand filter layers were installed on the top and bottom of each column to prevent medium washout.

3.2.2 Continuous Column Studies

P removal were observed in column studies with synthesized P solutions applied at continuous flow at 0.2 mg P/L. Liu and Davis (2014) reported that the inflow concentration of DOP ranged from less than 0.01 to 0.83 mg P/L, varying over more than an order of magnitude. The mean concentration of DOP was 0.03 mg P/L, which is close to the 0.01 mg P/L P detection limit; a higher concentration level was selected for study in order to better quantify the P measurements. Three P solutions were synthesized and only one P compound was tested at a time. Influent P solutions were made in the laboratory. A peristaltic pump (Model 7553-30, Cole-Parmer Instrument CO., Chicago, IL) transferred solutions from well-mixed influent glass tanks into each column.

Monopotassium myo-inositol hexakisphosphate (IHP, $C_6H_6(H_2PO_4)_6$) (Sigma-

Aldrich, St. Louis, MO) contains 6 phosphate groups bonded to C atoms. It is characterized by a wide range of acidity constants and it is predominantly negatively-charged at pH values > 6.9, principally as IHP^{8-} (pK_8=6.9, Costello et al., 1976; Celi et al., 2001). Adenosine monophosphate (AMP, $C_{10}H_{14}N_5O_7P$)(Acros-Organics, Springfield Township, New Jersey) is also negatively-charged at stormwater runoff pH (pK_1=6.0, pK_2=9.8; Kiss et al., 1991).

IHP, AMP and NaH_2PO_4 (Fisher Scientific, American Chemical Society, Waltham, MA) were used to prepare 0.2 mg P/L (0.64 mM P as TDP) solutions with a 0.01 M KCl background electrolyte concentration (typical background concentration of urban runoff, U.S. EPA, 1983). The pH of each solution was adjusted to 7.0 using 0.1 M NaOH and 0.1 M HCl. The IHP and SRP column studies were performed at 298K. The hydrolysis of AMP in stock solutions was detected by measuring soluble reactive phosphorus (SRP) concentrations before use; therefore, columns treated with AMP were conducted at 277 K to minimize the decomposition of AMP. The SRP concentration in AMP influent solution constantly remained (measured once per week) < 0.01 mg P/L, indicating that hydrolysis reactions were inhibited. Hydrolysis of IHP was not observed during the column studies. Stock solutions of all three P species were measured for TP to verify the influent P concentration (0.2 mg P/L).

The column experiments were started at a superficial flow velocity of 15 cm/h and increased to 20 and 30 cm/h later in an attempt to force column exhaustion. Exhaustion is defined as the time at which the effluent TDP concentration equals the influent TDP concentration. Exhaustion occurred in columns after 9 to 176 d of influent input. Samples were collected and analyzed from each column every other day.

Column breakthrough curves, which show effluent P concentrations as a function of the cumulative number of BV (bed volumes) treated, were used to quantify the maximum possible P removal in each column. BV is calculated by:

$$BV = \frac{Q \times t}{V_{media}} \tag{3-1}$$

where V_{media} is the empty bed volume of the media (33 mL; media bulk density is 1.2 g/mL); Q is the volumetric flowrate (mL/h); t is the P sorption duration of the column (h).

To provide context to the results, the runoff treated by each media mixture was interpreted as rainfall depth in the total catchment area for comparison. Assuming that the bioretention facility is sized at 5% of the impervious catchment area, the rainfall depth treated was calculated by dividing the influent depth by 20.

3.2.3 Kinetics of P Sorption in Column Studies

Kinetics experiments were performed in upflow columns to estimate the contact time required for effective removal of both DOP and SRP. Two columns in a group were treated with AMP (at 277K), IHP, and SRP solutions (0.2 mg P/L, pH 7 and in a background electrolyte of 0.01 KCl), providing a total of 6 columns. Forty g of 10% WTR-BSM or 10% alum-modified WTR-BSM were used in each column, with a medium height of 6 cm and volume of 33 mL. A dynamic environment was simulated by varying the superficial flow velocity and thereby changing the contact time for P sorption. Superficial flow velocities were systematically increased from 0 to 12, 25, 76, 127, 152, 202, and, 253 cm/h. Column experiments were then performed over a decreasing series of flow velocities (from 253 to 202, 152, 127, 76, 25, 12, and 0 cm/h) to exclude possible limitations resulting from limited media sorption capacities. Columns were run at each superficial flow velocity for approximately 120 mL (~4 BVs) before changing to the next velocity. Effluent samples were taken after 3 BV of flow at each velocity.

3.2.4 Analytical Procedures

Oxalate extractions were performed on the media to determine the paracrystalline fractions of Al and Fe(III)(hydr)oxides of all media mixtures. The extractions were performed using 0.275 M acid ammonium oxalate extractant (0.175 M ammonium oxalate + 0.1 M oxalic acid) at a 1:40 medium: solution (mass vs. volume, m/v) ratio with pH controlled at 3.0 (McKeague and Day 1966, 1993). Media mixtures with WTR or the alum amendment used a 1:100(w/v) ratio during the extraction (Dayton and Basta, 2005).

The samples were shaken on an orbital shaker for 2 h in the dark, centrifuged for 13 min at 1610 *g* and filtered through 0.22 μm polyethersulfone membranes (Fisher Scientific, Waltham, MA). Oxalate extractable P was measured using the method of Wolf and Baker (1990). Soluble Fe and Al in all of the extracts were determined using inductively coupled plasma-atomic emission spectroscopy (ICPE-9000, Shimadzu Scientific Instruments, Columbia, MD). Oxalate ratios (OR) were calculated and used to correlate with P sorption capacities observed in this study. The OR is defined as:

$$\mathrm{OR} = \frac{\mathrm{Al_{ox}} + \mathrm{Fe_{ox}}}{\mathrm{P_{ox}}} \qquad (3\text{-}2)$$

where $\mathrm{Al_{ox}}$, $\mathrm{Fe_{ox}}$ and $\mathrm{P_{ox}}$ are oxalate-extractable Al, Fe and P measured in mmol/kg, respectively.

The column effluents were filtered through 0.22 μm polyethersulfone membrane filters (Fisher Scientific, Waltham, MA), and solutions were digested and analyzed for TDP (which was assumed equal to IHP, AMP, or phosphate, as appropriate) using Standard Methods 4500-P B.5 and 4500-P E (described in APHA, 1992). Undigested solutions were measured for SRP as a check for AMP hydrolysis. A 5-cm pathlength cuvette was employed to provide a detection limit of 0.01 mg P/L. Effluent samples were collected from one column (10% alum-modified WTR-BSM) during SRP treatment and were measured for aluminum(III) concentrations once a week using inductively coupled plasma-atomic emission spectroscopy with a detection limit of 1 μg/L (ICPE-9000, Shimadzu Scientific Instruments, Columbia, MD). The pH of selected samples was measured with a glass electrode (Mettler Toledo MA235, Greifensee, Switzerland) with a Ag/AgCl reference.

The P sorption capacity of each column was determined as:

$$q = \frac{\int_{t_0}^{t} (C_{in} - C_{out}) \times Q \, dt}{M} \tag{3-3}$$

where q is the medium P sorption capacity (mg P/kg); M is the mass of media in each column (kg); C_{in} and C_{out} are the P (mg/L) concentrations in the influent and effluent respectively; and Q is the volumetric flow rate (L/h).

3.3 Results and Discussion

Patterns of sorption of AMP (adenosine monophosphate), IHP (Inositol hexakisphosphate) and SRP (soluble reactive phosphorus) of each column are presented by column breakthrough curves, which show effluent P concentrations as a function of the cumulative number of BV (bed volumes) treated over time.

3.3.1 Continuous Column Studies

Sorption of AMP

AMP sorption by the four media is shown in Fig. 3-1. Generally, effluent AMP concentration increased as the volume of influent and loading of P progressed, indicating a reduction in media AMP sorption per unit of influent P over time and BV. Fig. 3-1a shows that the unmodified BSM reached its sorption capacity (exhaustion) first, after receiving 612 BV of influent. This volume was equivalent to 33 m of influent, equivalent to 2 m (Table 3-1) of simulated rainfall over the entire catchment (assuming that a bioretention facility sized at 5% of the impervious catchment area).

The WTR-amended column behaved differently from the unmodified BSM (Fig. 3-1b). Effluent AMP from the WTR-amended column remained < 0.15 mg P/L at 1500 BV. Therefore, the superficial flow velocity in this column was increased to 20 cm/h to force the column to reach its AMP sorption capacity faster (after receiving 157 m of influent (Table 3-1)). The two columns with alum-modified media mixtures exhibited even greater AMP sorption capacities (Fig. 3-1c, d). The AMP concentration in these two columns varied between 0.05 and 0.15 mg P/L over the course of the continuous run. However, increasing AMP concentrations were measured. Superficial flow velocities in these two columns were both increased to 20 cm/h at 1500 BV. Even though they became exhausted nearly simultaneously, the overall effluent AMP concentration in the column (before 2500 BV) with both alum and WTR (which varied between 0 and 0.1 mg P/L) was lower than that in column with only alum (which varied between 0.05 and 0.15 mg P/L). This resulted in a larger mass of AMP removal by A-WTR-BSM (332 mg P/kg) than by A-BSM (268 mg P/kg). The column with both alum and WTR was able to treat approximately 225 m (Table 3-1) of influent before reaching the AMP sorption capacity, demonstrating enhanced P removal performance by this media mixture.

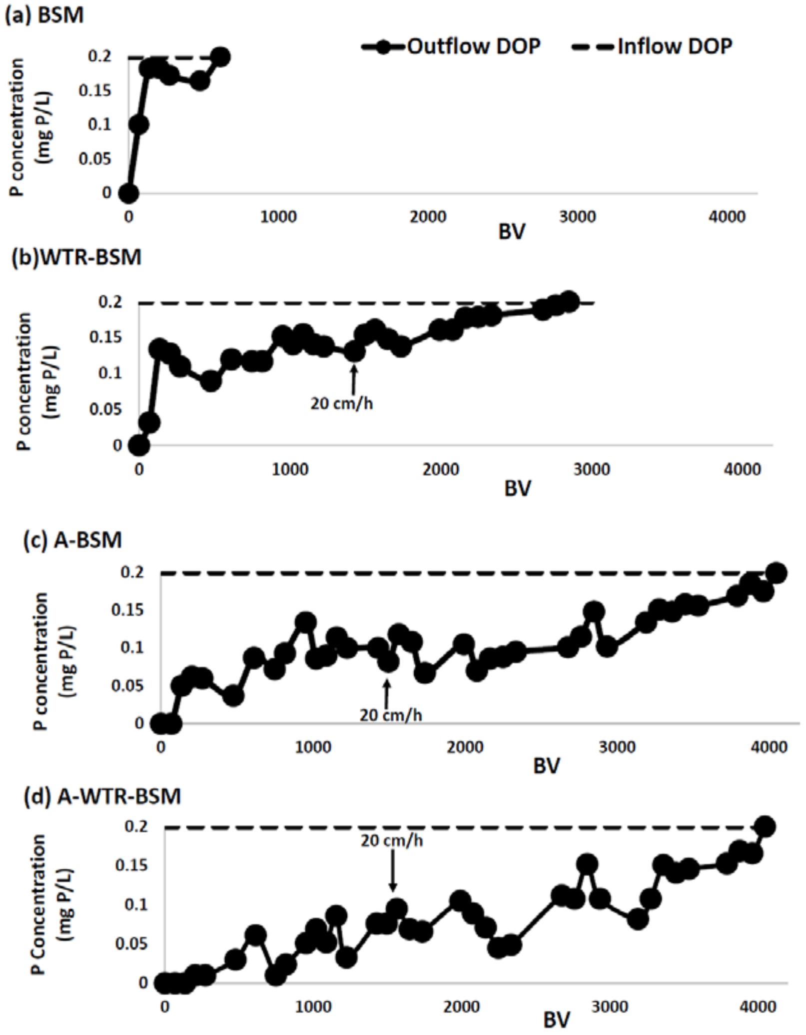
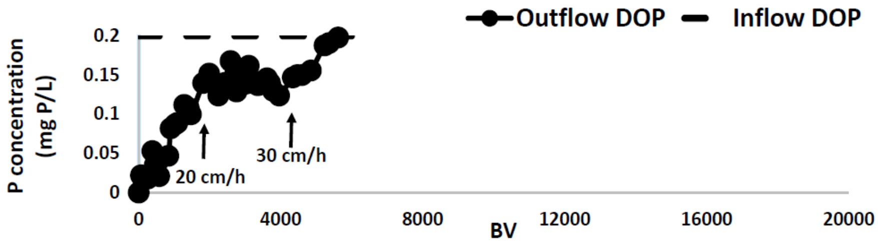


Figure 3-1. Breakthrough curves for AMP sorption: (a) BSM; (b) WTR-BSM; (c) A-BSM; (d) A-WTR-BSM. BV represents empty bed volume.

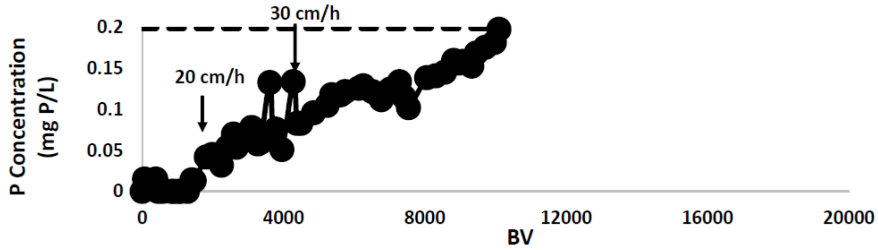
Sorption of IHP

Exhaustion occurred in the four columns for IHP sorption after 65 to 115 d, much longer than the time for AMP (9 to 50 d) (Fig. 3-2). The columns were subjected to superficial flow velocity change from 15 to 20 and then to 30 cm/h at BV of 1500 and 4000, respectively. Similar to the AMP sorption, unmodified BSM reached its sorption capacity first (Fig. 3-2a), after receiving 321 m of IHP influent. Amending BSM with WTR increased the IHP sorption in the second column, which exhibited exhaustion after treating 577 m of IHP influent (Fig. 3-2b; Table 3-1).

(a) BSM



(b) WTR-BSM



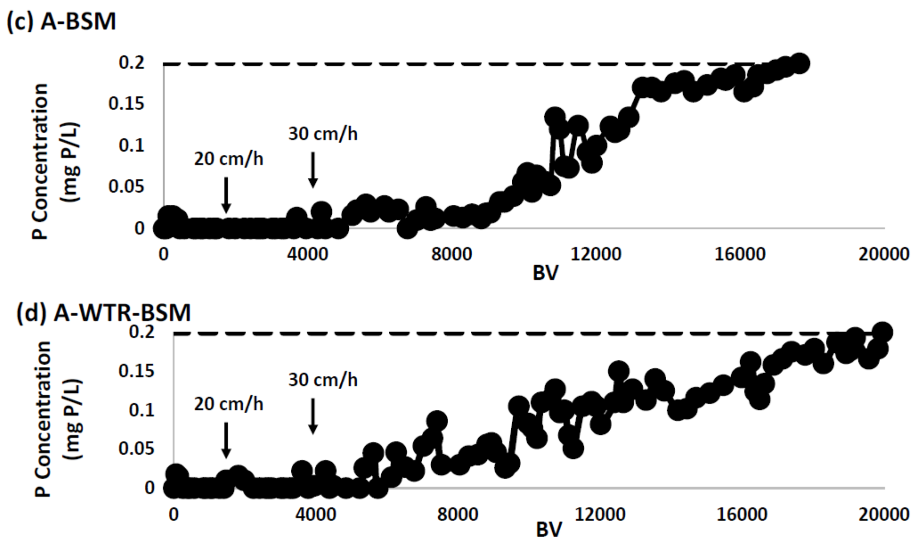


Figure 3-2. Breakthrough curves for IHP sorption: (a) BSM; (b) WTR-BSM; (c) A-BSM; (d) A-WTR-BSM. BV represents empty bed volume.

The data in Fig. 3-2c and 3-2d clearly demonstrate that both A-BSM and A-WTR-BSM have higher IHP sorption capacities than do media without alum. Generally, effluent IHP concentrations in these two columns were less than 0.01 mg P/L when treated BV were less than 4,000. These two columns exhibited reduction in IHP removal only under the highest superficial flow velocity (30 cm/h). A sharp increase in IHP concentration in the A-BSM medium was observed at 11,000 BV, which created a concentration peak and then slightly dropped with continued flow. The tail of the column discharge using A-WTR-BSM fluctuated from approximately 0.05 to 0.15 mg P/L at 6,000-16,000 treated BV. Exhaustion of this column was observed after receiving 20,000

BV of influent (Table 3-1), demonstrating the highest IHP sorption capacity among all media mixtures.

Table 3-1. Bed volumes treated at exhaustion point, runoff influent, and simulated rainfall depth (over the entire catchment assuming a bioretention site sized at 5% of the impervious area) treated by each media mixture for AMP, IHP and SRP, respectively.

	AMP			IHP			SRP		
Media	Bed Volume (BV)	Runoff Influent (m)	Rainfall Depth* (m)	Bed Volume (BV)	Runoff Influent (m)	Rainfall Depth* (m)	Bed Volume (BV)	Runoff Influent (m)	Rainfall Depth* (m)
BSM	612	33	2	5618	321	16	526	30	2
WTR-BSM	2848	157	8	10098	577	29	3282	140	7
A-BSM	4200	220	11	17800	100	50	3829	180	9
A-WTR-BSM	4200	220	11	20000	1080	54	10800	538	27

Note: * Assuming that the treatment facility is 5% of the total catchment area, the rainfall depth treated was calculated by dividing the influent runoff depth by 20.

Sorption of SRP

Data for SRP sorption is presented in Fig. 3-3. Little SRP was removed in the column with unmodified BSM after treating 30 m of SRP influent, showing the lowest removal (Fig. 3-3a; Table 3-1). O'Neill and Davis (2012a) reported SRP retention by columns with unmodified BSM media, and media exhaustion observed after treating only

4.4 m of influent (at an influent concentration of 0.12 mg P/L; superficial flow velocity of 15 cm/h, and a column height 13 cm). This is less than what was observed in this study, which can be explained by the different influent P and BSM characteristics (Nagpal, 1985).

SRP sorption in WTR-BSM was markedly increased compared with unmodified BSM. Exhaustion was not exhibited in this column until 3,282 BV (Fig. 3-3b, Table 3-1). Al-WTR has a high content of paracrystalline $Al(OH)_3$ and has been shown to be effective in sequestering SRP from soils (Elliott et al., 2002) and stormwater runoff (Lucas and Greenway, 2011).

The column with A-BSM reached its sorption capacity at 3,829 BV, which is not greatly different from that of WTR-BSM (Table 3-1). However, the A-BSM column still presented a higher SRP sorption capacity because this column discharged lower SRP than the WTR-BSM column over the course of the experiment, resulting in higher SRP mass removal (293 mg P/kg vis-à-vis 156 mg P/kg).

Media with both alum and WTR addition exhibited the highest SRP removal capacity (treated 538 m of influent). Generally, SRP removal was high at the beginning of the run (SRP< 0.05 mg/L when BV < 2000) and worsened thereafter, especially after superficial flow velocity increased to 20 cm/hr.

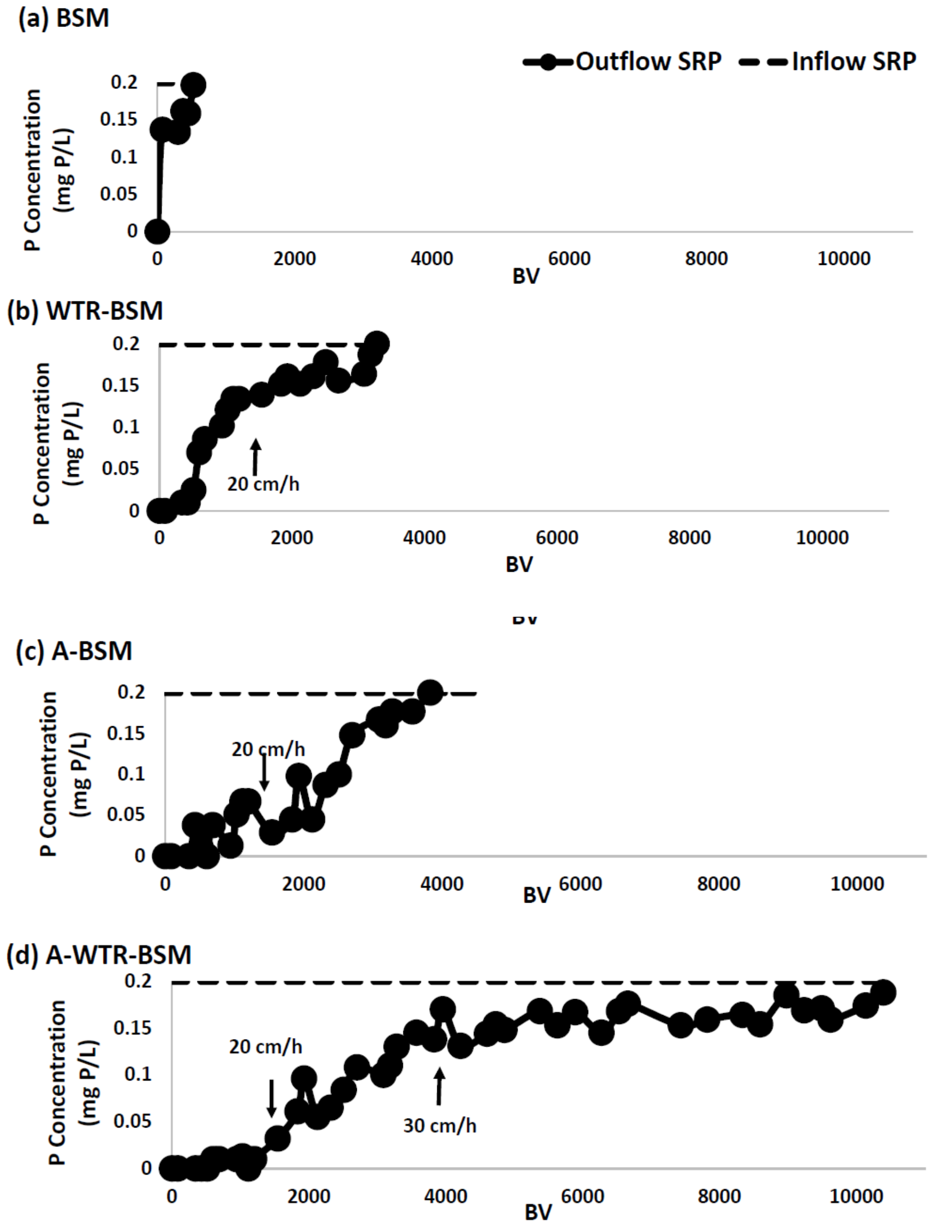


Figure 3-3. Breakthrough curves for SRP sorption: (a) BSM; (b) WTR-BSM; (c) A-BSM; (d) A-WTR-BSM. BV represents empty bed volume.

3.3.2 Comparison of AMP, IHP and SRP Removal

Total P mass removal performances of each column for AMP, IHP, and SRP are compared in Fig. 3-4. As discussed above, unmodified BSM constantly showed the lowest sorption capacities (calculated based on Equation 3-2) for all P species (13, 275, and 5 mg P/kg for AMP, IHP and SRP, respectively) and treated the least amount of influent runoff (equivalent to 2, 16 and 2 m simulated rainfall runoff over the entire catchment for AMP, IHP and SRP, respectively). Amending BSM with 10% WTR improved the corresponding removal for AMP, IHP and SRP to 108, 775, 156 mg P/kg, respectively. The most obvious improvement for the removal of all three P species was observed using media with alum modification, indicated by the significantly higher sorption capacities and greater treated influent. Through alum and WTR modification, AMP, IHP and SRP removals were improved by factors of 26, 7 and 150, respectively (compared with unmodified BSM).

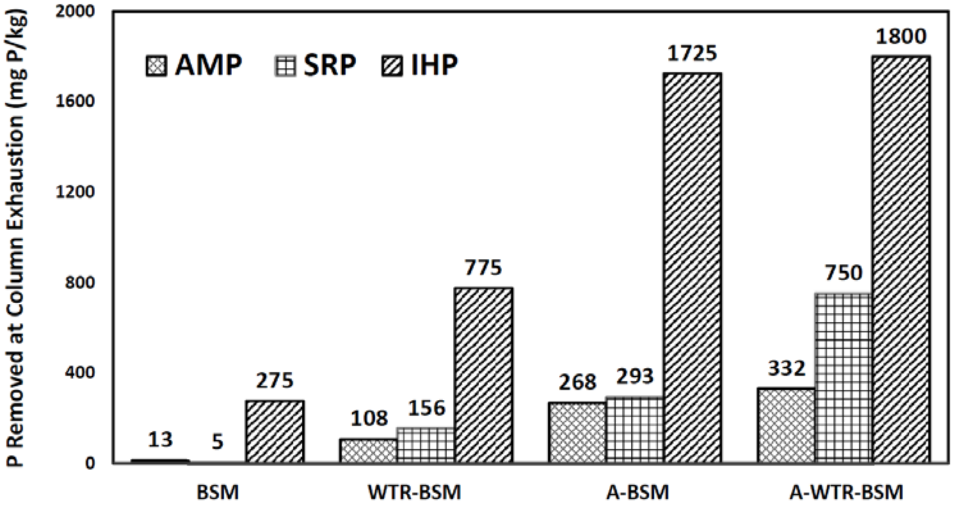


Figure 3-4. Comparison of P sorption capacities of BSM, WTR-BSM, A-BSM, and A-WTR-BSM.

A performance comparison between the batch isotherms (Yan et al., 2016a; Chapter 2) and column results can be made for these four media mixtures. Batch sorption capacities for AMP were determined to be 10, 15, 190, and 263 mg P/kg (at C_e=0.2 mg P/L) for BSM, WTR-BSM, A-BSM, and A-WTR-BSM, respectively. However, all four media mixtures outperformed the batch results in continuous-flow column studies, demonstrated by higher sorption capacities of 13, 108, 268 and 332 mg P/kg.

The overall magnitude of IHP removal was similar in batch and column studies. The predicted IHP sorption capacities for these media mixtures from batch results were 313, 447, 1558 and 1988 mg P/kg, which were observed as 275, 775, 1725, and 1800 mg P/kg in column experiments, respectively. Three of the media mixtures exhibited higher SRP sorption capacities in column studies as compared to batch, the exception being A-WTR-BSM. This medium mixture exhibited a sorption capacity of 1258 mg P/kg from batch isotherms. However, a much lower SRP removal capacity was observed in column (750 mg P/kg), which may be caused by the reduced contact time between dissolved SRP and the media surface in the column studies**.**

Furthermore, Fig. 3-4 clearly indicates that the removal of the three P species is in the order: IHP > SRP > AMP, which is consistent with the batch sorption results reported by Yan et al. (2016a; Chapter 2). The difference in sorption capacity can be partially attributed to the differences in the structures of the three P compounds, specifically the number of P groups (6 P groups for IHP, one P group for AMP and SRP) and molecular size (Celi and Barberis, 2005). Numerous studies have reported that compared with other mono-phosphate species, those with multiple phosphate groups in the compound structures tend to be most easily adsorbed on clay minerals and aluminum (hydr)oxides, through a stronger bonding of P groups (McKercher and Anderson, 1989; Ognalaga et al., 1994; Leytem et al., 2002; Martin et al., 2003).

Both SRP and DOP can be adsorbed onto aluminum hydroxide surfaces via ligand exchange between the phosphate groups and the surface reactive hydroxyl functional groups of the adsorbents (Parfitt et al., 1976; Goldberg and Sposito, 1985; Shang et al., 1990; Celi et al., 1999). These surface complexes can be mono/bi-dentate or binuclear and are generally not readily reversible. From a long-term perspective, P can be chemically precipitated by soil minerals with high aluminum, iron and calcium contents as well (Griffin and Jurinak, 1973; Freeman and Rowell, 1981; Wu and Sansalone, 2013).

Some soil microorganisms can release organic acids to dissolve and utilize precipitated inorganic P (Kucey et al., 1989, Whitelaw, 2000). However, other studies suggest that IHP is of limited availability to maize and wheat in high phosphate-fixing soils (Martin, 1973; Findenegg and Nelemans, 1993). Therefore, the adsorbed P is not likely to be taken up by microorganisms, unless under certain conditions that phosphatase or phytase are produced to react with bound P to release it as the inorganic dissolved form (Richardson et al., 2005).

Temperature can affect sorption of both inorganic and organic P (Beaton and Read, 1963; Barrow, 1979; Sah and Mikkelsen, 1986). According to White and Beckett (1964), the rate of P sorption increases with increasing temperature and results in decreased soluble P concentration in soil. Shang et al. (1990) observed that IHP and SRP sorption by $Al(OH)_3$ at 298 K were 4 and 2 times higher, respectively, than that at 277 K, and compared with SRP, the sorption of IHP was more temperature dependent. Therefore, higher AMP sorption can be expected under more realistic field conditions compared to the 277K laboratory condition. However, the hydrolysis of AMP under field conditions is possible at the same time.

3.3.3 Correlation of Oxalate Ratio with P Sorption

The oxalate ratio, which was calculated using the oxalate extractable Al, Fe and P contents of a medium, has been employed to provide an index for P sorption onto soil media (McLaughlin et al., 1981; Elliott et al., 2002; Maguire and Sims, 2002). The oxalate ratio (Equation 3-2) of each media mixture (BSM, WTR-BSM, A-BSM, and A-WTR-BSM) was correlated with P sorption capacities observed in this study (Fig. 3-5).

In soils, higher P leaching (desorption) can be expected from media with oxalate ratios < 10 (Agyin-Birikorang and O'Connor, 2007; Kovar and Pierzynski, 2009).

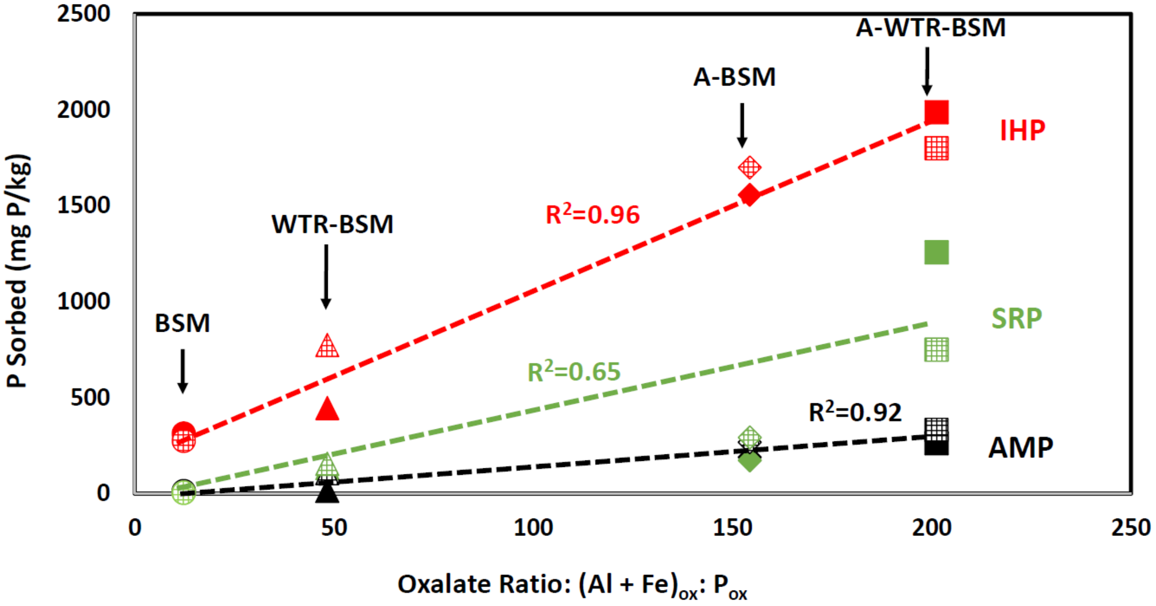


Figure 3-5. Measured oxalate ratio of media mixtures and their P sorption capacities (at Ce=0.2 mg P/L; batch data: solid symbols; column data: hatched symbols). Batch data from Yan et al. (2016; Chapter 2).

Oxalate ratios were 12, 49, 154 and 201 for the four investigated media mixtures. WTR and alum additions significantly improved the oxalate ratio of BSM. Figure 3-5 presents the strong positive correlations between oxalate ratio and media P sorption capacity observed in both the column and batch studies (equilibrium with 0.2 mg P/L influent; batch results from Yan et al., 2016a; Chapter 2). These results clearly show the improving AMP, IHP and SRP sorption with increasing oxalate ratio (based on linear regressions of the results, r^2_{AMP}=0.92, r^2_{IHP}=0.96, r^2_{SRP}=0.65). Recent column studies conducted by Brown et al. (2015) evaluated SRP removal (C_e=1 mg P/L) as affected by using BSM mixtures with varied oxalate ratios. Iron-based WTR was used to increase the oxalate ratio from 1 to 10. A similar positive correlation between oxalate ratio and media P removal capacity was observed, with P in the column effluents decreasing with higher oxalate ratio (>10). This pattern is consistent with the results observed in the present work.

A benchmark value was determined for media P sorption capacity, specifically as 240 mg P/kg, in order to provide 30 years dissolved organic P (DOP) treatment from stormwater runoff (for a bioretention facility sized at 5% of 100% impervious catchment area, approximately 100 cm (40 in.) of rainfall per year, depth of P-capture media selected as 50 cm, and average stormwater DOP concentration of 0.2 mg P/L). Based on the relationships indicated in Fig. 3-5, oxalate ratios of 169, 6 and 80 are needed to meet the targeted sorption requirements for AMP, IHP and SRP, respectively (assuming that each P species is treated independently). Unmodified BSM and WTR-BSM can meet the targeted sorption requirement for IHP. However, they cannot provide effective treatment for AMP and SRP. A-WTR-BSM meet the targeted requirements for all three P species.

3.3.4 Dissolved Al(III)

Excessive amounts of dissolved Al can limit plant growth, mainly through the inhibition of root growth, especially on acid soils (Kochian, 1995; Delhaize and Ryan, 1995). Concerns about Al toxicity and its effects on plant growth are important when using Al-based media for P removal in bioretention systems. Agyin-Birikorang et al. (2009) reported that Al leaching from field plots were not significantly different between control and experimental (Al-WTR applied) plots. Furthermore, studies have investigated the impacts of Al-WTR (as 4% m/m application rate) on crops, and no indications of Al toxicity were reported (Sotero-Santos et al., 2005; Mahdy et al., 2009).

Al(III) will form $Al(OH)_3(s)$ at near-neutral pH values. Hexaquo Al is the major phytotoxic species, therefore, Al toxicity is enhanced by low pH (Delhaize and Ryan, 1995). Outflow samples were collected from one column (A-WTR-BSM) during SRP treatment and were analyzed for Al(III) concentrations. The effluent pH values for all samples ranged from 6.5-7.5, within which Al is expected to be only sparingly soluble. A total of 12 samples were collected with Al(III) concentrations ranging from 0.01 to 0.12 mg/L (mean as 0.06 mg/L). All but two of the Al(III) concentrations were < 0.08 mg/L (0.085 and 0.12 mg/L). In general, Al has a growth inhibition level of 1 mg/L for plant roots (Taylor et al., 1998). Therefore, the Al leaching potential of alum-modified media treated with stormwater runoff (typical pH of 6 to 8) is considered insignificant.

3.3.5 pH effects on P sorption

Reaction pH may affect P sorption by changing the charge of the reacting surfaces of adsorbents (Barrow, 1983; Bolan et al., 1986) and the relative concentration of the anionic forms of adsorbates (Shang et al., 1992). Negative correlations have been found between pH values and sorption of P onto soil minerals, which can be attributed to the formation of repulsive forces between the highly-negative P compounds and the negative surfaces as pH increases (Shang et al., 1992; Celi et al., 2001).

In general, a more pronounced pH effect is reported for IHP sorption than for SRP sorption, due to the higher charge of IHP (IHP^{8-} predominant) in solution. Other organic phosphorus compounds exhibit a weaker pH effect during sorption. However, change of IHP sorption at neutral pH range ($6.5 < pH < 8.5$) is not as pronounced as that at lower pH (< 6.5) (Anderson and Arlidge, 1962). A minimal pH effect on SRP sorption by WTR was observed in the pH range 4.5 to 7.5 by O'Neill and Davis (2012a). The effluent pH values from the columns in the present study ranged from 6.5-7.5; most were between 7.0 and 7.5. Since the pH differences found in this study were relatively small and all values were near neutral (mean pH value: 7.32±3.5), pH was not considered to have a major impact on the dissolved P sorption and minor fluctuations in pH are not considered to significantly affect results.

3.3.6 Kinetics of P Sorption in Column Studies

AMP sorption by WTR-BSM and A-WTR-BSM (at 277K) at different superficial flow velocities (with media contact time indicated) is shown in Fig. 3-6. For WTR-BSM, the reduction in media AMP sorption can clearly be seen by the increasing effluent AMP concentration as the superficial flow velocity increases. This behavior is attributed to the short contact time between the P solution and the media surface, which in turn promotes less sorption and rapid movement of P through the media. Less than 25% AMP is removed by this column when the superficial flow velocity reached 76 cm/hr (contact time of 4 min). These results indicate that approximately 130 min of contact time are required to achieve 95% AMP removal (reduced P concentration in effluent to < 0.01 mg P/L).

However, AMP sorption is minimally affected by the limited contact time in the A-WTR-BSM column. Figure 3-6 clearly shows that little AMP (less than the detection limit of 0.01 mg P/L) was detected in the effluent of this column, even at the highest superficial flow velocity (253 cm/h, contact time less than 1 min), demonstrating very rapid AMP sorption processes.

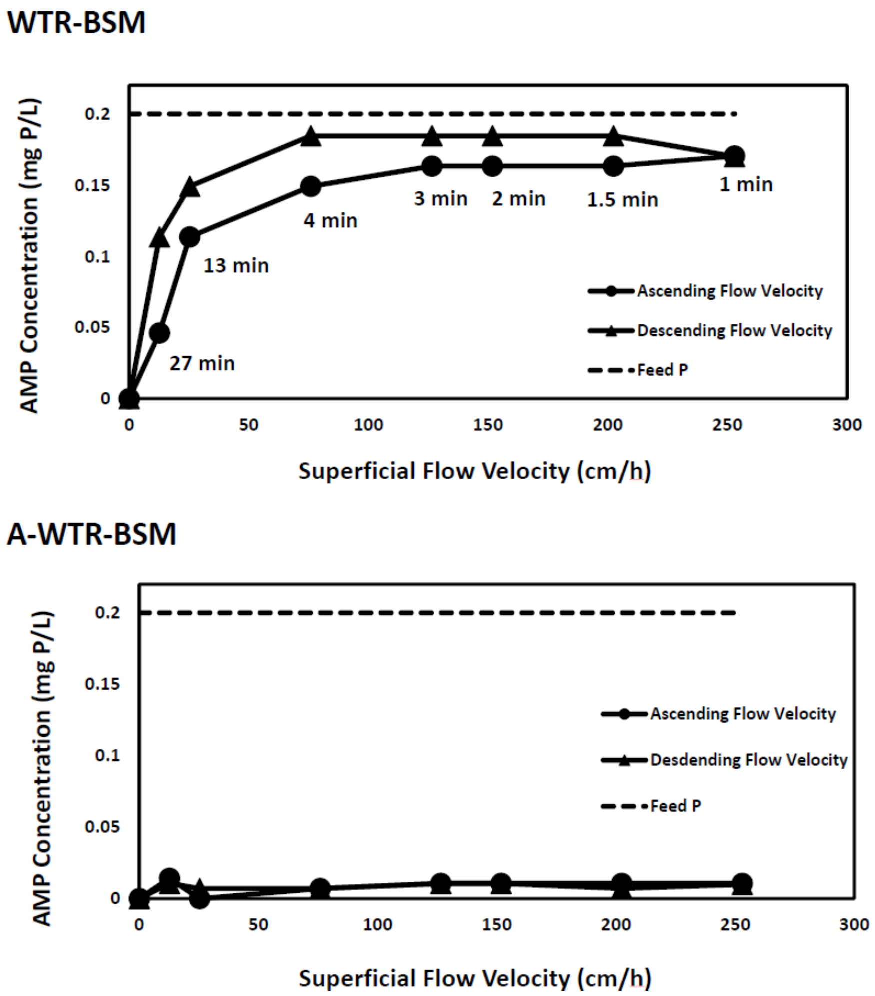


Figure 3-6. Kinetics experiments for AMP sorption in columns.

The WTR-BSM medium was capable of reducing IHP concentrations to < 0.01 mg P/L at lower superficial flow velocities (Fig. 3-7). However, an obvious jump in effluent IHP was observed when the superficial flow velocity increased above 50 cm/h. This column sorbed little IHP with a superficial flow velocity > 127 cm/h (3 min contact time), at which point the effluent IHP concentration equaled the influent value. Based on this, a retention time of at least 7 min is required to achieve 95% concentration reduction (< 0.01 mg P/L) for IHP using WTR-BSM.

The IHP effluent concentrations in the column with alum were below the detection limit (< 0.01 mg P/L) at all superficial flow velocities. Similar to AMP removal, less than 1 min was required for IHP to be sorbed onto A-WTR-BSM.

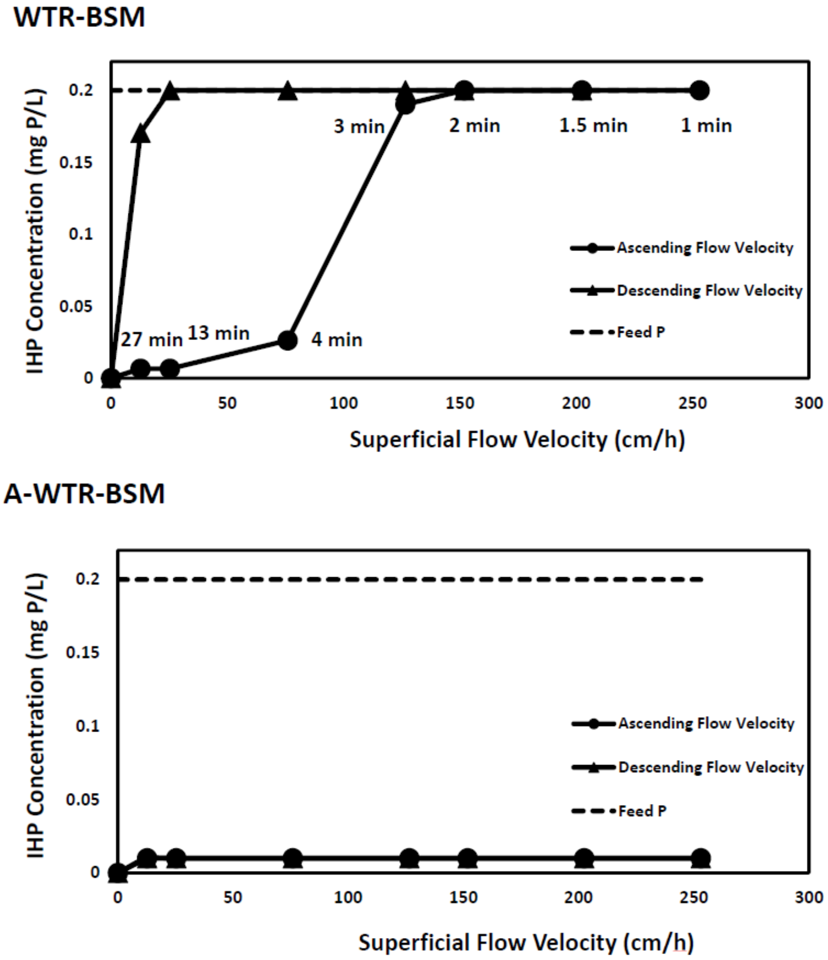


Figure 3-7. Kinetics experiments for IHP sorption in columns.

Figure 3-8 details SRP sorption by WTR-BSM and A-WTR-BSM with varied superficial flow velocities. SRP sorption was not affected by the decreasing contact time initially, as approximately 75% of SRP was captured when superficial flow velocity was 76 cm/hr (effluent SRP~0.05 mg P/L). However, SRP removal was markedly reduced at superficial flow velocity higher than 76 cm/hr (contact time < 4 min). The effluent SRP level was found to equal the influent value at 152 cm/hr. However, in the column with alum-enhanced media, SRP sorption was not limited by the varied contact time, indicated by the low effluent concentration (< 0.01 mg P/L) under all conditions. AMP, IHP and SRP sorption by WTR-BSM at the descending superficial flow velocities indicate a similar trend as that in the ascending velocity, indicating that the sorption was not affected by the media capacity exhaustion.

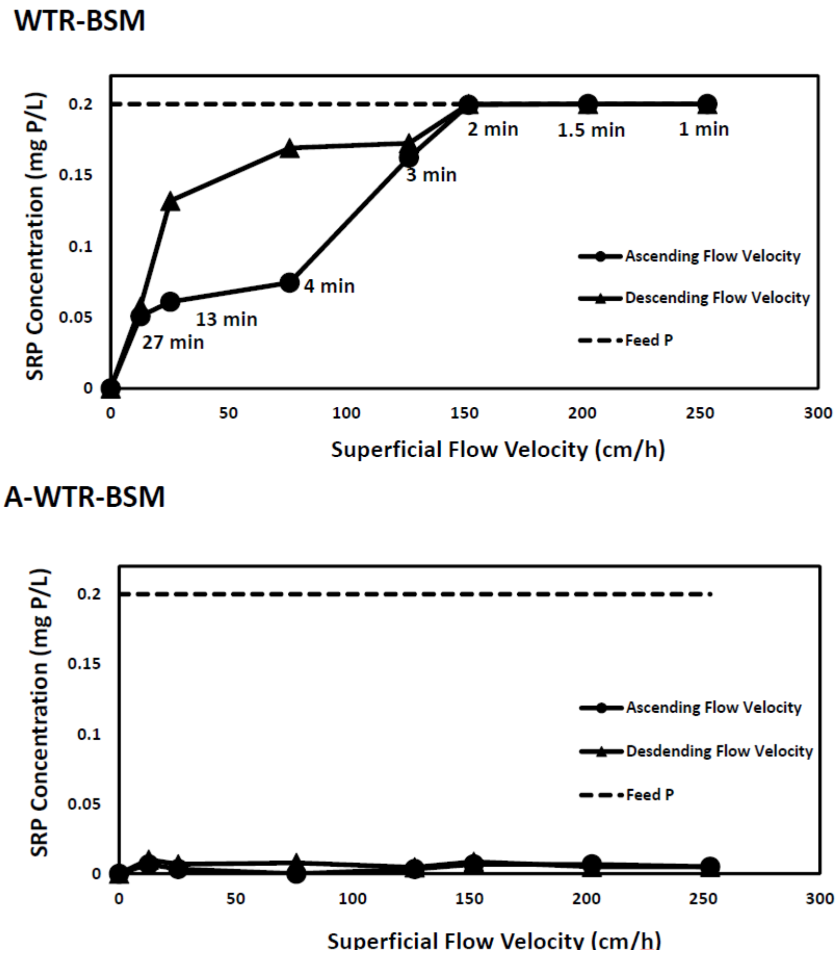


Figure 3-8. Kinetics experiments for SRP sorption in columns.

Based on the kinetics studies, improved P removal was generally observed under lower superficial velocity conditions, which is consistent with results from previous studies (Hsieh et al., 2007; Rentz, 2010; Rout et al., 2014). This can be attributed to the decreased contact time between P solution and media surfaces at higher flow rates (Riahi et al., 2009).

During a rainfall event, stormwater runoff will flow through the bioretention media and the pollutant capture is expected to occur within the infiltration time of the runoff, a period of typically 1 or 2 h (assuming an infiltration rate of 25 cm/h and media depth of 0.5 m). With limited contact time, sorption of DOP under more realistic bioretention conditions may be affected. However, the adverse effects of limited contact time on P sorption can be minimized by using A-WTR-BSM. To reduce concentrations of AMP, IHP and SRP to < 0.01 mg P/L, more than 130, 7 and 130 min, respectively, are required when using media without alum addition. The same goal can be achieved within 1 min using A-WTR-BSM. Enhanced P removal can be attributed to the paracrystalline Al (hydr)oxides in the alum-amended media, as discussed in Yan et al. (2016a; Chapter 2). Furthermore, the strong electrostatic attractions between the highly charged P species and paracrystalline Al (hydr)oxides surfaces can also increase the rate of the removal processes (Shang et al., 1990; Celi, 1999). Kinetic studies showed that the sorption behavior of all three P compounds using A-WTR-BSM was not affected by the limited contact time, even under the highest superficial flow velocity (250 cm/h). Therefore, the breakthrough of IHP and SRP observed in column studies (A-WTR-BSM) when flow velocity increased to 20 cm/hr and 30 cm/hr can be mainly attributed to the exhaustion of sorption capacity, and not the limited contact time.

3.4 Conclusions and Recommendations

Column studies that simulated bioretention flow and P concentrations were conducted in this work. BSM was optimized with respect to the sorption of three P species (AMP, IHP and SRP) by using alum (10% by mass) and WTR (10% by mass) amendments. Comparison of the P sorption performances of unmodified and modified-BSM suggests WTR and alum as promising amendments for BSM.

Columns with A-WTR-BSM discharged lower P concentrations compared with unmodified media and resulted in higher media sorption capacity. Compared with unmodified BSM, significant improvements were observed for AMP, IHP and SRP removal using this media, by factors of 26, 7 and 150, respectively.

Strong agreement between the oxalate ratio, batch, and column P sorption capacity of each media mixture was observed in this study. Based on this relationship, oxalate ratios of 169, 6 and 80 are required to meet the targeted sorption requirements for AMP, IHP and SRP, respectively. Similar to the results from the batch studies, A-WTR-BSM was proven as the most promising media mixture for effective DOP treatment.

Moreover, in order to meet a stringent criterion (<0.01 mg P/L) for P discharge in stormwater runoff, WTR-BSM requires a contact time of at least 130, 7 and 130 minutes for AMP, IHP and SRP removal, respectively. However, media with alum and WTR addition significantly reduced P concentration (< 0.01 mg/L) within 1 min contact time.

Considering the sorption capacity of A-WTR-BSM, ranging from 332 to 1800 mg P/kg for AMP and IHP (at Ce=0.2 mg P/L), a bioretention facility with this media mixture can provide approximately 40 to more than 100 y (based on 240 mg P/kg benchmark for 30 years of DOP removal) of effective treatment for AMP and IHP, respectively, and should not be limited by contact time and flow dynamics. This removal lifetime for A-WTR-BSM media is based on the sorption results observed under column exhaustion conditions. It should be noted that this media mixture may not produce constant DOP removal efficiency over the entire predicted treatment duration in real bioretention systems, especially under wetting and drying cycles and in the presence of other ions.

Furthermore, this study may overestimate the removal capacity of media since three P species are tested separately in this study. Sorption competition is possible when all three P species (or even more complex P species) are simultaneously present in stormwater; it is very likely that IHP is the preferred one for sorption (Anderson et al., 1974; Mackercher and Anderson, 1989; Leytem et al., 2002; Berg and Joern, 2006). Since the P removal capacities predictions are based on high inflow concentrations, 0.2 mg P/L, for lower DOP concentrations sorption rates may be slower. However, for a Freundlich isotherm with $1/n < 1$ (as noted for these P compounds onto modified BSM, Yan, et al. 2016a; Chapter 2), media sorption lifetimes may be greater.

Chapter 4. Permeable Sandy Media for P sorption

Abstract

A high flow medium (HFM), modified with two aluminum-based amendments, alum and partially hydrolyzed aluminum (PHA), was used to achieve enhanced dissolved P removal and promote high infiltration of runoff in urban stormwater control measures (SCMs). Compared with unmodified HFM, the sorption of adenosine monophosphate (AMP), myo-inositol hexakisphosphate (IHP), and inorganic phosphate using PHA-modified HFM were increased by factors of 80, 8, and 163, respectively. Column-scale kinetics studies have shown that the P removal using modified HFM is markedly faster than that using unmodified HFM; PHA-modified HFM can reduce P concentration to <0.01 mg P/L within a contact time < 1 min. Alum- and PHA-modified HFM exhibited different sorption preferences for the three different P species investigated. Scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) surface area analyses supported underlying sorption mechanisms for the enhanced P removal by the amended HFM. Compared with alum, PHA modification is easier to implement because it requires a lower liquid/medium ratio, less consumption of alkalinity, and no required mixing. Therefore, PHA-modified HFM is recommended for use in high flow bioretention systems to provide effective and efficient P removal.

Keywords: Bioretention, Water Treatment Residual (WTR), High Flow Media (HFM), Alum, Partially Hydrolyzed Aluminum, Dissolved Organic Phosphorus, Phosphate

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4.1 Introduction

Impervious surfaces (parking lots, roads, buildings, etc.) in urban areas prevent rain from naturally infiltrating into the ground. Instead, surface runoff forms and rapidly enters storm drains, sewer systems, and drainage ditches; many of these systems are directly connected to open discharges, which can pollute surface water bodies and cause flooding. Urban runoff has been classified as a major source of non-point-source pollution (U.S. EPA, 1996). Among the substances conveyed by stormwater, phosphorus (P) is a leading pollutant that can impair water quality, and generate negative aesthetic and eutrophic conditions in receiving lakes and rivers (U.S. EPA, 1998). Bioretention is a Low Impact Development (LID) technology for urban stormwater runoff management, and is commonly used to improve both quantity (promote runoff infiltration and evapotranspiration) and quality (pollutant removal) aspects of urban runoff (Dietz 2007; Davis et al. 2009; Roy-Poirier et al. 2010; Trowsdale and Simcock, 2011).

Characteristics of bioretention soil media (BSM), such as hydraulic conductivity and media reactivity affect both runoff infiltration rate and pollutant removals. Previous studies have investigated the effect of different layered media configurations on runoff infiltration rate, and to determine the effectiveness of P removal. A permeable upper layer can promote rapid runoff infiltration, and a less permeable bottom BSM layer can retain runoff and improve P sorption onto the media, resulting in enhanced removal efficiency of P (Hsieh and Davis, 2005; Hsieh et al., 2007). A bioretention medium containing predominantly sand, which has been termed as a "high flow medium" (HFM), has high hydraulic conductivity and can mitigate peak flow by promoting the infiltration of runoff, especially from infrequent storm events (Hartsig and Szatko, 2012). With large pores, HFM allows rapid infiltration of water (Hillel 1998). This is favored in bioretention systems, since the HFM can treat large volumes of runoff in small-footprint stormwater control measures (SCMs). However, HFM alone may have limited potential to provide effective removal for dissolved P, since fine fractions (such as clay) are chemically active for P sorption, and sustain plant growth (Hunt et al 2012). Furthermore, sorption of P is also dependent on solid/water contact time; clayey media can enhance P retention as it prolongs the contact time (Ayoub et al., 2001; Riahi et al., 2009; Rout et al., 2014). Therefore, there is a trade-off between the permeability of the media and extent of P removal.

Particulate P (PP) accounts for approximately 70-80% of total P (TP) in stormwater runoff, and can be effectively removed through media filtration in bioretention systems. TP in stormwater runoff includes approximately 10% dissolved organic phosphorus (DOP) and 10% soluble reactive phosphorus (SRP) (Li and Davis 2009; Liu and Davis, 2014). Studies on the removal of dissolved P (DP) in bioretention systems have focused on adsorption and/or chemical precipitation of SRP. Davis et al. (2001) reported that approximately 80% of DP was removed by a sandy loam soil in two laboratory-scale pilot bioretention cells. Bratieres et al. (2008) found that 86-88% of SRP can be removed for 8 months at stormwater concentrations.

Poorly crystallized aluminum-rich media mixtures have high P sorption potential (Shang et al., 1992; Shang et al., 1996; Agyin-Birikorang et al., 2009; Lucas and Greenway, 2011; O'Neill and Davis 2012a, b; Hunt et al, 2012). Yan et al. (2016a, b; Chapter 2, 3) have found that alum and Al-based drinking water treatment residual (WTR) are two promising amendments to BSM, and can significantly improve the removal of dissolved phosphorus species (DP). Yet, the modified BSM has shown low permeability (K<1 cm/h), which can limit the use of this media for P removal in SCMs, especially during periods of extreme rain events when large runoff volumes are generated from impervious areas. Also, the alum modification processes, as described in Yan et al. (2016a, b; Chapter 2, 3) requires high consumption of alkalinity, constant mixing conditions, and a high liquid-to-media ratio, which makes large scale implementation difficult.

Based on the enhanced DP removal observed using WTR- and alum-modified BSM, enhanced DP removal using a HFM modified with these two amendments was investigated. Additionally, a partially hydrolyzed Al (PHA, aluminum chlorohydrate) compound is hypothesized to consume less alkalinity during the modification processes compared with alum. Therefore, novel media modification processes were tested in this study, using PHA as an alternative Al amendment. This new amendment is compared with an alum amendment for P removal using HFM. The P-enhancement process can be simplified by dramatically reducing the liquid-to-media ratio, eliminating the requirement for mixing, and lowering the consumption of alkalinity, without sacrificing P removal performance. Therefore, a total of four media mixtures were tested in the column studies: HFM, WTR-amended HFM (labeled as WTR-HFM), alum-amended WTR-HFM (A-WTR-HFM) and PHA-amended WTR-HFM (PHA-WTR-HFM).

This study therefore aims to achieve simultaneously a high infiltration rate and improved DP (organic and inorganic) removal in bioretention systems. The HFM were modified using three aluminum amendments: Al-based drinking water treatment residual (WTR), alum, and PHA. Long-term column studies over months that simulate the DP flux conditions experienced in bioretention systems were performed using unmodified and modified HFM. Kinetics experiments quantified DP sorption under varied flow velocities to ensure that both effective and efficient (reduce P concentration to < 0.01 mg P/L within 1 min of contact time) DP removal can be achieved under high flow conditions. Competitive sorption reactions between different P compounds and/or other anions is possible in real stormwater, therefore, additional column studies were performed using DOP and SRP mixed solutions. The research objectives of this study include:

1) Achieve both high DP removal and high infiltration using HFM modified with three amendments: WTR, alum and PHA;

2) Examine the faster P removal process under high infiltration conditions by using modified HFM;

3) Significantly simplify the P-enhancement processes by using PHA over alum, and propose an optimal media modification recipe, with application to stormwater control facilities.

4.2 Materials and Methods

4.2.1 Preparation of Media Mixtures

Sand was obtained from a local Maryland supplier (Ernest Maier Inc., Bladensburg, MD). HFM was prepared to have a textural profile of 56% very coarse sand, 26% coarse sand, 16% medium sand and 2% fine sand (all measured by volume, porosity as 0.48), Al-based WTR was obtained from the Rockville Drinking Water Treatment Plant in Potomac, MD, and was air-dried for at least 1 wk before use. 10%

WTR (by mass) was added as an amendment to HFM, then this mixture was further modified with alum and PHA, resulting in mass of 3% (as Al) for each media mixture.

Alum-modified WTR-HFM were prepared following the processes reported by Yan et al. (2016a; Chapter 2). WTR-HFM was added to aqueous aluminum sulfate solution (0.03 M $Al_2(SO4)_3 \cdot 14H_2O$, Alfa Aesar, Ward Hill, MA) using a liquid/solid ratio of 10/1, resulting in a total mass of Al equal to 3% for WTR-HFM (1.5% from WTR, 1.5% from alum); limestone (20% of the total media mass) was added to increase the pH above 6, and therefore, provide alkalinity to assist in the formation of aluminum (hydr)oxide precipitate. The medium mixture was shaken at room temperature (~298 K) for 48 h.

For PHA modification, WTR-HFM were added to aqueous aluminum chlorohydrate solutions (DelPAC® XG, USALCO, Baltimore, MD) at a liquid-to-solid ratio of 0.5/1, resulting in total mass of Al equal to 3% for WTR-HFM (1.5% from WTR, 1.5% from PHA). Crushed limestone from a local landscape supply store was sieved through a 2-mm sieve and was added (10% of the media mass) to provide alkalinity to assist in the formation of aluminum (hydr)oxides precipitate. The media mixtures were well-mixed and air-dried at 298K for 48 h.

A total of four media mixtures were prepared for the column studies: HFM, WTR-amended HFM (labeled as WTR-HFM), alum-amended WTR-HFM (A-WTR-HFM) and

PHA-amended WTR-HFM (PHA-WTR-HFM). Each was tested with three P species (two DOP and one SRP) and one mixed P solution, for a total of sixteen column treatments (no duplicate experiments were performed). Forty g of medium were added to each 15-cm long x 2.6-cm inner diameter, sealed, upflow column, providing a media height of 6.2 cm. 4.5-cm quartz sand filter layers were installed on the top and bottom of each column to prevent medium washout.

4.2.2 Media Characterization

Hydraulic Conductivity Tests

The hydraulic conductivities of HFM, A-WTR-HFM and PHA-WTR-HFM were measured using a constant head permeability apparatus. The measurements were also performed on unmodified bioretention soil media (BSM, containing 85% sand, 10% silt, and 5% clay) for comparison. The tests were carried out in a 30-cm high, 10-cm inner diameter cylinder permeability apparatus. Media mixtures were fully mixed with sufficient quantity of water to prevent the segregation of particle sizes during placement into the permeability apparatus. Tap water was allowed to pass through the medium mixture overnight to remove air from the system. Hydraulic conductivities (cm/h) were calculated using Darcy's equation and corrected to 293K:

$$\mathrm{K} = \frac{\mathrm{V} \times \mathrm{L}}{\mathrm{A} \times \mathrm{h} \times \mathrm{T}} \tag{4-1}$$

where V (cm^3) is the volume of water measured, L (cm) is the length of media specimen, A (cm^2) is the cross-sectional area of the permeability apparatus, T (h) is time required for the volume of water V to be collected, and h (cm) is the hydraulic head difference across length L.

Media Extractions

Oxalate extractions, which measure the amorphous fractions of Al- and Fe-minerals, were performed on all mixtures to predict their P sorption and leaching potential. Extractions were performed using a 0.275 M acid ammonium oxalate (0.175 M ammonium oxalate + 0.1 M oxalic acid) extractant. Samples were shaken on an orbital shaker for 2 h in the dark, with a media: solution (weight: volume, w/v) ratio of 1: 40 and pH was controlled at 3.0 (McKeague and Day 1966, 1993); mixtures with high Al content (WTR, alum and PHA) used a 1:100 (w/v) ratio during the extraction as recommended by Dayton and Basta (2005). Samples were centrifuged and filtered through a 0.22 μm polyethersulfone membrane (Fisher Science, Waltham, MA). Oxalate extractable P was measured using the method of Wolf and Baker (1990). The Fe and Al concentrations in all extraction solutions were determined using inductively coupled plasma-atomic emission spectroscopy (ICPE-9000, Shimadzu Scientific Instruments, Columbia, MD).

Scanning Electron Microscope and Brunauer–Emmett–Teller analyses

Scanning Electron Microscope (SEM) and Brunauer–Emmett–Teller (BET) surface area analyses quantified the surface morphology of A-WTR-HFM and PHA-WTR-HFM, following the methods described in Yan et al. (2016a; Chapter 2). A SU-70 field emission scanning electron microscope (SU-70, Hitachi High Technologies America, Gaithersburg, MD) with an accelerating voltage of 10 kV was used to generate morphology information of media surfaces.

The media specific surface area was determined in an accelerated surface area and porosimetry system based on N_2 adsorption and desorption (ASAP 2020, Micromeritics Instrument Corporation, Norcross, GA) (Foo and Hameed, 2010). The microporosity of each medium was determined via the t-plot method (Gregg and Singh, 1982) and the Barrett−Joyner−Halenda (BJH) method (Lowell et al., 2004) based on the N_2 adsorption/desorption data.

4.2.3 P Sorption in Continuous Column Studies

Media sorption experiments were conducted in columns using three P compounds individually and an additional mixed P solution was used to explore competitive sorption when different P species are simultaneously present in stormwater. Two dissolved organic P (DOP) species, monopotassium myo-inositol hexakisphosphate (IHP, $C_6H_6(H_2PO_4)_6$, Sigma-Aldrich, St. Louis, MO) and adenosine monophosphate (AMP, $C_{10}H_{14}N_5O_7P$, Acros-Organics, New Jersey) were tested. IHP, also known as phytic acid, is the most common form of organic P found in the environment; it may account for 30%-50% of soil organic phosphorus (Williams and Anderson, 1968; Anderson and Malcolm, 1974; Turner et al., 2002b). Adenosine monophosphate (AMP) is commonly found in animal manures (Leytem et al. 2002). NaH_2PO_4 (Fisher, Waltham, MA) was used as the SRP solution through all experiments. Both DOP and SRP solutions were prepared at concentrations of 0.2 mg P/L. Based on the components of DP reported by Liu and Davis (2014), mixed solutions were prepared to contain 0.1 mg P/L IHP and 0.1 mg P/L phosphate (SRP), providing a total DP concentration of 0.2 mg P/L. P solutions were prepared with a 0.01 M KCl background electrolyte concentration (typical background concentration of urban runoff, U.S. EPA, 1983). The pH of each solution was adjusted to 7.0 using 0.1 M NaOH and 0.1 M HCl.

P solutions were pumped into each column using a peristaltic pump (Model 7553-30, Cole-Parmer Instrument CO., Chicago, IL) at an initial superficial flow velocity of 15 cm/h and increased to 20 and 30 cm/h later in an attempt to provide the mass loading to force column exhaustion. Exhaustion is defined as the cumulative time or pore volume when the effluent DP concentration equals the inflow DP concentration. Samples were collected and analyzed from each column every other day for 0.5 to 6 months.

The IHP and SRP column studies were performed at 298K; and the AMP column studies were performed at 277 K to minimize the decomposition of AMP. The SRP concentrations of AMP stock solution were monitored (once per week) and found to be < 0.01 mg P/L during column runs, which indicates that the hydrolysis reactions of AMP were retarded.

The cumulative mass output of P from the columns was obtained through integrating concentration with flowrates over time; the cumulative mass of P retained by each medium was calculated by subtracting the total effluent P from the cumulative P loaded for each column as found in Yan et al. (2016b; Chapter 3).

4.2.4 Effects of Contact Time on P Sorption

Effects of contact time on P sorption in each column were investigated by changing the superficial velocity of influent P. Three columns (HFM, A-WTR-HFM and PHA-WTR-HFM) were separately treated with AMP, IHP, and SRP solutions (0.2 mg P/L, pH ~7 and 0.01 KCl), providing a total of 9 columns. The available contact time at each superficial flow velocity is calculated as:

$$\text{Contact time} = \frac{L}{V_a} = \frac{L}{\frac{V_S}{\emptyset}} = \frac{L}{V_S} \times \emptyset \qquad (4\text{-}2)$$

where: L = media length (6.2 cm); $\emptyset = \text{porosity } (48\%)$; Va= advective velocity; and Vs= superficial velocity.

As described in Yan et al. (2016b), superficial flow velocities were gradually increased from 0 to 253 cm/h. Consequently, available contact time for P sorption decreased from 13 to less than 1 min. Effluent samples were collected at each velocity after the column passage of 3 empty bed volumes (BV). BV is defined as the ratio of cumulative volume of P solution (mL) passed through each column to the empty bed volume of the media (33 mL; media bulk density is 1.2 g/mL).

4.2.5 Analytical Procedures

Samples were analyzed for total phosphorus (TP, which was assumed equal to DOP or SRP) using the potassium persulfate method (4500-P B.5) and ascorbic acid molybdenum blue method (4500-P E) at a wavelength of 880 nm (Shimadzu UV-160, Kyoto, Japan) as described in APHA (1992). This method provides a detection limit of 0.01 mg P/L. The Fe and Al concentrations in all extraction solutions were determined using inductively coupled plasma-atomic emission spectroscopy with a detection limit of 1 µg/L (ICPE-9000, Shimadzu Scientific Instruments, Columbia, MD). Oxalate extractable P was measured using the method of Wolf and Baker (1990). The oxalate ratio (Al_{ox} + Fe_{ox}/ P_{ox}) was calculated to provide an index for P binding onto HFM.

Sixteen columns were loaded under continuous flow from 4 to 138 d before reaching exhaustion. Phosphorus removal in columns is shown by breakthrough curves for effluent P concentrations as a function of the cumulative number of BV treated. The runoff depth treated by each media mixture is related to the rainfall depth in the total catchment area for comparison. Assuming that the bioretention facility is sized at 5% of the impervious catchment area, the rainfall depth treated was calculated by dividing the influent depth by 20.

4.3 Results and Discussions

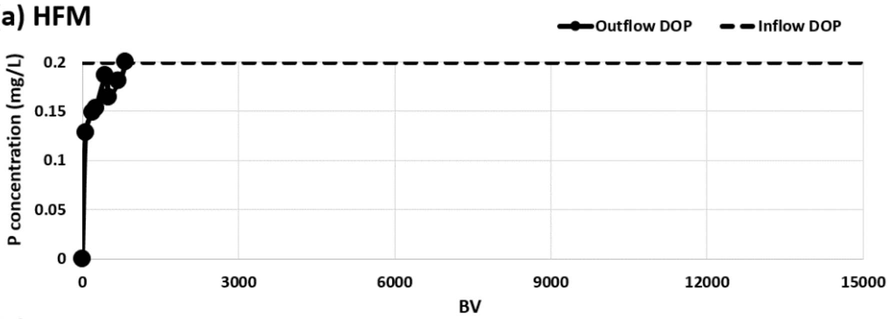
Solution pH may affect P sorption by either affecting the charge of the reacting surfaces of the adsorbents (Barrow et al., 1983; Bolan et al., 1986), or influencing the relative concentration of the anionic forms of adsorbates (Shang et al., 1992). Effluent pH values from each column were determined, and ranged from 6.5-7.5; most were between 6.5 and 7.0. Since the pH values of the effluent from each column are near neutral and their differences were relatively small, so the pH values are not considered to significantly impact the results for P removal.

4.3.1 P Sorption Column Results

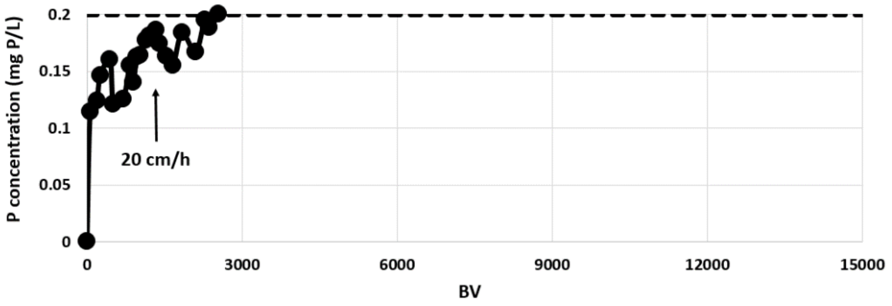
Sorption of AMP

The breakthrough curves for AMP removal by the four media mixtures (HFM, WTR-HFM, A-WTR-HFM and PHA-WTR-HFM) are presented in Fig. 4-1. These four columns started to show breakthrough as the discharged AMP concentration increased, indicating a reduction in AMP sorption by the medium. Unmodified HFM has minimal capacity to remove AMP compared with modified mixtures (Fig. 4-1a). It reached its sorption capacity (exhaustion) after receiving only 832 BV of influent. WTR-HFM provided a longer treatment for AMP compared with unmodified HFM, which increased the AMP removal from 17 to 70 mg P/kg. However, the overall effluent concentration of AMP from WTR-HFM was constantly maintained above 0.1 mg P/L (Fig. 4-1b), still indicating a low removal.

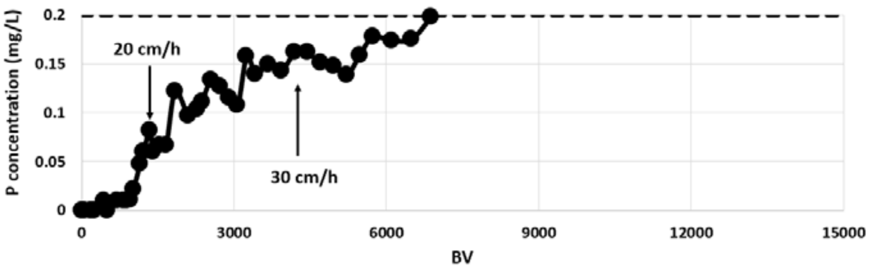
(a) HFM



(b) WTR-HFM



(c) A-WTR-HFM



(d) PHA-WTR-HFM

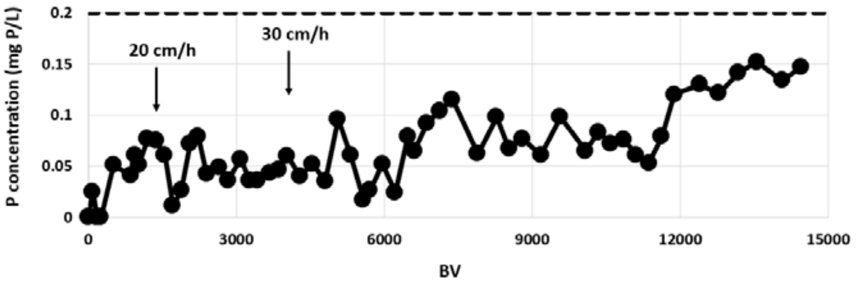


Figure 4-1. Breakthrough curves (effluent P concentration as a function of cumulative column bed volumes of flow) for AMP sorption in four columns. Arrows indicate increases in superficial flow velocity from 15 to 20, and 30 cm/h (influent AMP concentration: 0.2 mg P/L; Column depth: 6 cm; BV: bed volumes; T=277 K). BV represents empty bed volume.

The A-WTR-HFM column demonstrated higher AMP removal compared with the previous two (Fig. 4-1c). The effluent AMP from A-WTR-HFM column remained < 0.01 mg P/L at the beginning of the experiment (< 1000 BV), which is much lower than that observed in HFM and WTR-HFM (both > 0.15 mg P/L at 200 BV). The reduction of AMP sorption can be seen as the effluent concentration slowly increased to > 0.1 mg P/L after 1000 BV, until it reached the exhaustion point at 7000 BV. The initial effluent (<1500 BV) from PHA-WTR-HFM column was higher than that from the A-WTR-HFM column (Fig. 4-1d). However, unlike the continuous increase of effluent AMP in the A-WTR-HFM column, the tail of the AMP discharge using PHA-WTR-HFM fluctuated from approximately 0.02 to 0.1 mg P/L before 12000 treated BV. This produced an overall lower average AMP concentration from PHA-WTR-HFM, resulting in a higher AMP removal capacity of PHA-WTR-HFM than A-WTR-HFM. Due to time limitations, the PHA-WTR-HFM column was terminated at 14000 BV when $C_{effluent}$ = 0.15 mg P/L, without reaching the point of exhaustion.

The superficial flow velocities in A-WTR-HFM and PHA-WTR-HFM were both increased from 15 to 20 and 30 cm/h at 1500 BV and 4000 BV, respectively, to force the column to reach their AMP sorption capacities faster. This resulted in significantly higher AMP removal capacities of these two media mixtures (422 and 1356 mg P/kg, respectively) than that of HFM and WTR-HFM (17 and 70 mg P/kg, respectively, Table 4-1). Table 4-1 also shows that the influent volume treated by each column was equivalent to approximately 2.4, 7.2, 19 and 41 years of rainfall in the District of Columbia. It should be noted that these values represent the complete exhaustion point.

Table 4-1. P removed and estimated rainfall depth (over the entire catchment assuming a bioretention site sized at 5% of the impervious area) treated by each media mixture.

	AMP		IHP		SRP		Mixed P	
Media	Rainfall Depth (year)	P Removed (mg P/kg)	Rainfall Depth (m)	P Removed (mg P/kg)	Rainfall Depth (year)	P Removed (mg P/kg)	Rainfall Depth (year)	P Removed (mg P/kg)
HFM	2.4	17	3.8	138	0.7	13	15	149
WTR-HFM	7.2	70	19	442	8.3	134	26	467
A-WTR-HFM	19	422	43	1526	17	514	49	1103
PHA-WTR-HFM	41	1356	41	1092	64	2119	54	1399

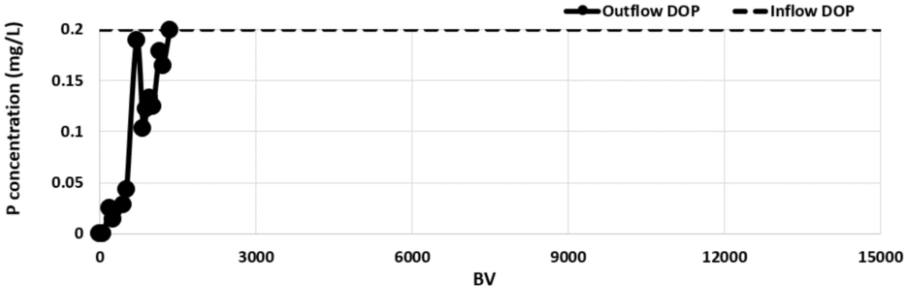
Note: * Assuming that the treatment facility is 5% of the total catchment area, the rainfall depth treated was calculated by dividing the influent runoff depth by 20.

Year of rainfall was estimated based on a typical annual rainfall depth of 1m in the District of Columbia.

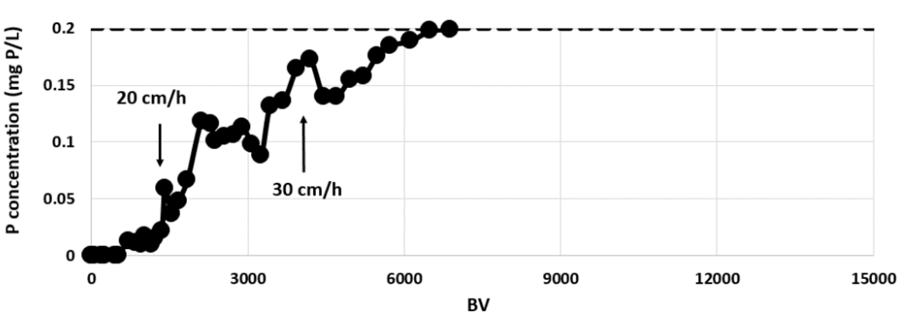
Sorption of IHP

HFM, WTR-HFM, A-WTR-HFM and PHA-WTR-HFM exhibited an overall higher removal for IHP than AMP. Similar to the AMP column studies, the columns that treated 1500 and 4000 BV were subjected to superficial flow velocity increases from 15 to 20 and then to 30 cm/h, respectively. Unmodified HFM demonstrated low removal capacity; this media mixture reached its sorption capacity (exhaustion) first, after only receiving 1344 BV of influent (Fig. 4-2a), corresponding to the lowest IHP removal capacity (138 mg P/kg). WTR-HFM exhibited a higher removal as it discharged low concentrations of IHP (< 0.1 mg P/L, Fig. 4-2b) before 2000 BV. A sharp increase of effluent IHP concentration was observed after 2000 BV, which can be attributed to the increased velocity, as it provides higher P loading into the system; the IHP level continued to increase until the exhaustion point at 7000 BV. Modifying HFM with WTR extended the treatment lifetime and, simultaneously, improved the IHP removal from 138 to 442 mg P/kg.

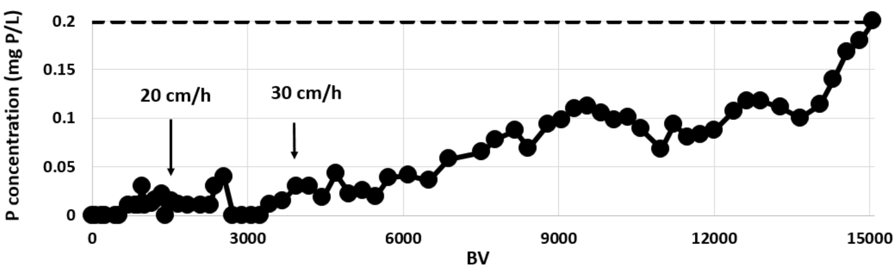
(a) HFM



(b) WTR-HFM



(c) A-WTR-HFM



(d) PHA-WTR-HFM

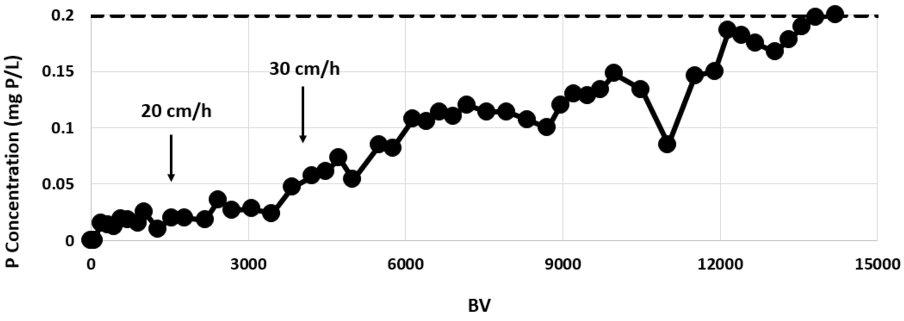
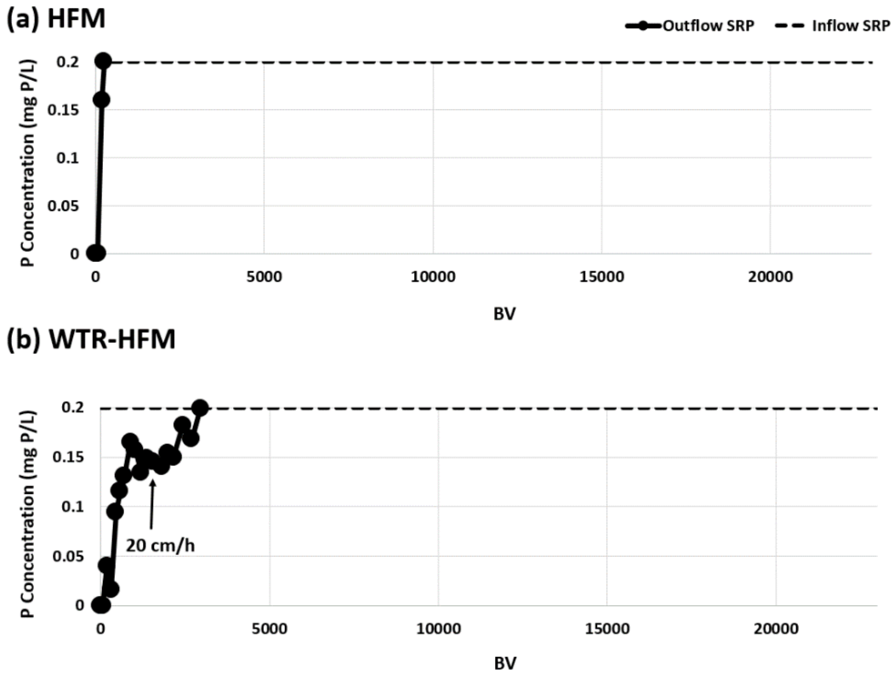


Figure 4-2. Breakthrough curves (effluent P concentration as a function of cumulative column bed volumes of flow) for IHP sorption in four columns (influent IHP concentration: 0.2 mg P/L; Column depth: 6 cm; BV: bed volumes; T=298 K). BV represents empty bed volume.

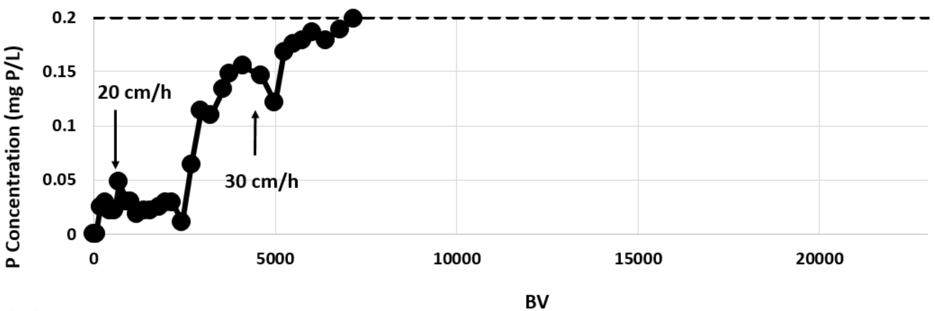
Fig. 4-2c and 4-2d clearly demonstrate that HFM with alum or PHA have higher IHP sorption capacities than do media with only WTR. Generally, IHP removal was high at the beginning of the run and worsened thereafter, especially after the superficial velocity increases. Both A-WTR-HFM and PHA-WTR-HFM discharged IHP < 0.05 mg P/L before 4000 BV, regardless of the increase of the velocities. As experiments progressed, the effluent IHP concentration in the PHA-WTR-HFM column increased to > 0.1 mg P/L at 6000 BV, and this column gradually reached the exhaustion point at 14500 BV. However, the A-WTR-HFM column demonstrated higher removal by constantly discharging low concentration of IHP (< 0.1 mg P/L) until 14000 BV, after which a sharp increase of IHP was observed. Therefore, although these two columns became exhausted nearly simultaneously, the overall effluent average IHP concentration in the A-WTR-HFM column was lower than that in the PHA-WTR-HFM column. This resulted in a larger mass of IHP removal by A-WTR-HFM (1526 mg P/kg) than by PHA-WTR-HFM (1092 mg P/kg). As is shown in Table 4-1, the IHP influent volume treated by each column was equivalent to approximately 3.8, 19, 43 and 41 years of rainfall in the District of Columbia.

Sorption of SRP

Unmodified HFM removed little SRP, and reached exhaustion first, consistently showing the lowest removal capacity (13 mg P/kg, 0.7 year of rainfall depth) among all the media mixtures (Fig. 4-3a). The effluent SRP from WTR-HFM was < 0.1 mg P/L before 500 BV, which continued to increase until the exhaustion point at 3000 BV (Fig. 4-3b). Similar to other studies that show high SRP fixing potential of WTR (O'Neill and Davis, 2012a; Lucas and Greenway, 2011; Yan et al., 2016a, b; Chapter 2, 3), the WTR-HFM column removed significantly higher mass of SRP (134 mg/kg, 8.3 year of rainfall depth) compared with unmodified HFM.



(c) A-WTR-HFM



(d) PHA-WTR-HFM

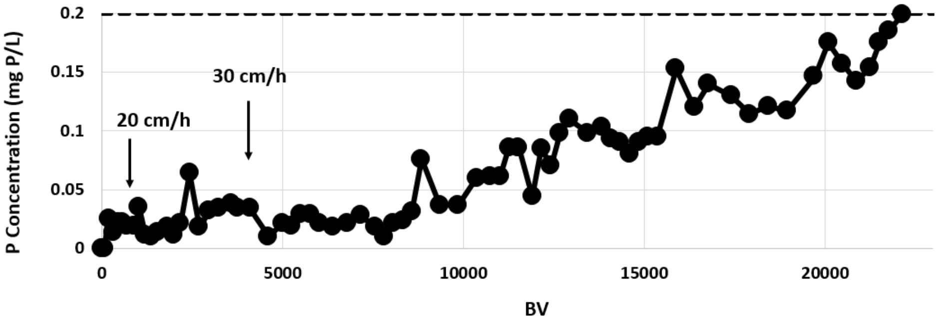


Figure 4-3. Breakthrough curves (effluent P concentration as a function of cumulative column bed volumes of flow) for SRP sorption in four columns (influent SRP concentration: 0.2 mg P/L; Column depth: 6 cm; BV: bed volumes; T=298 K). BV represents empty bed volume.

Amending HFM with alum further improved the SRP sorption capacity to 514 mg P/kg (17 year of rainfall depth). Fig. 4-3c shows that the effluent SRP concentration remained < 0.03 mg P/L until the superficial velocity increased to 20 cm/h at 2000 BV, and then varied between 0.05 and 0.15 mg P/L over 2000 to 4000 BV. SRP concentration continued to increase to > 0.15 mg P/L as velocity increased to 30 cm/h, and this column was exhausted at 7000 BV.

As demonstrated in Fig. 4-3d, HFM with PHA possessed the highest SRP removal capacity (2119 mg P/kg, 64 year of rainfall depth). Despite the increase in velocity, the effluent SRP concentration remained < 0.03 mg P/L even until 10000 BV. The PHA-WTR-HFM column exhausted at 22148 BV, exhibiting a significantly longer lifetime for SRP removal compared with the other three media mixtures.

Sorption of Mixed P

Figure 4-4 details the removal performances of the four media mixtures when IHP and SRP were simultaneously present in the influent. A general trend of higher sorption of IHP compared to SRP was noted in all columns, which was expected based on the higher affinity of IHP to Al (hydr)oxides adsorbents (Celi and Barberis, 2005; Shang et al, 1990, 1992). The HFM column exhibited exhaustion for SRP after treating 3 year of rainfall at 1000 BV, resulted in very low SRP removal (9 mg P/kg). This column removed 140 mg P/kg IHP at 5500 BV, demonstrating longer treatment lifetime compared with SRP (Fig. 4-4a).

As shown in Fig. 4-4b, adding WTR to HFM improved the removal for both P species. The effluent IHP and SRP concentrations from the WTR-HFM column were generally < 0.05 mg P/L before 2000 BV, which increased as higher mass of P was applied into the system. The tails of the IHP and SRP discharge in this column followed a similar pattern until the exhaustion point at 7500 BV (equivalent to 26 year of rainfall depth). As a result, WTR-HFM showed similar sorption capacity for IHP and SRP (214 and 253 mg P/kg, respectively).

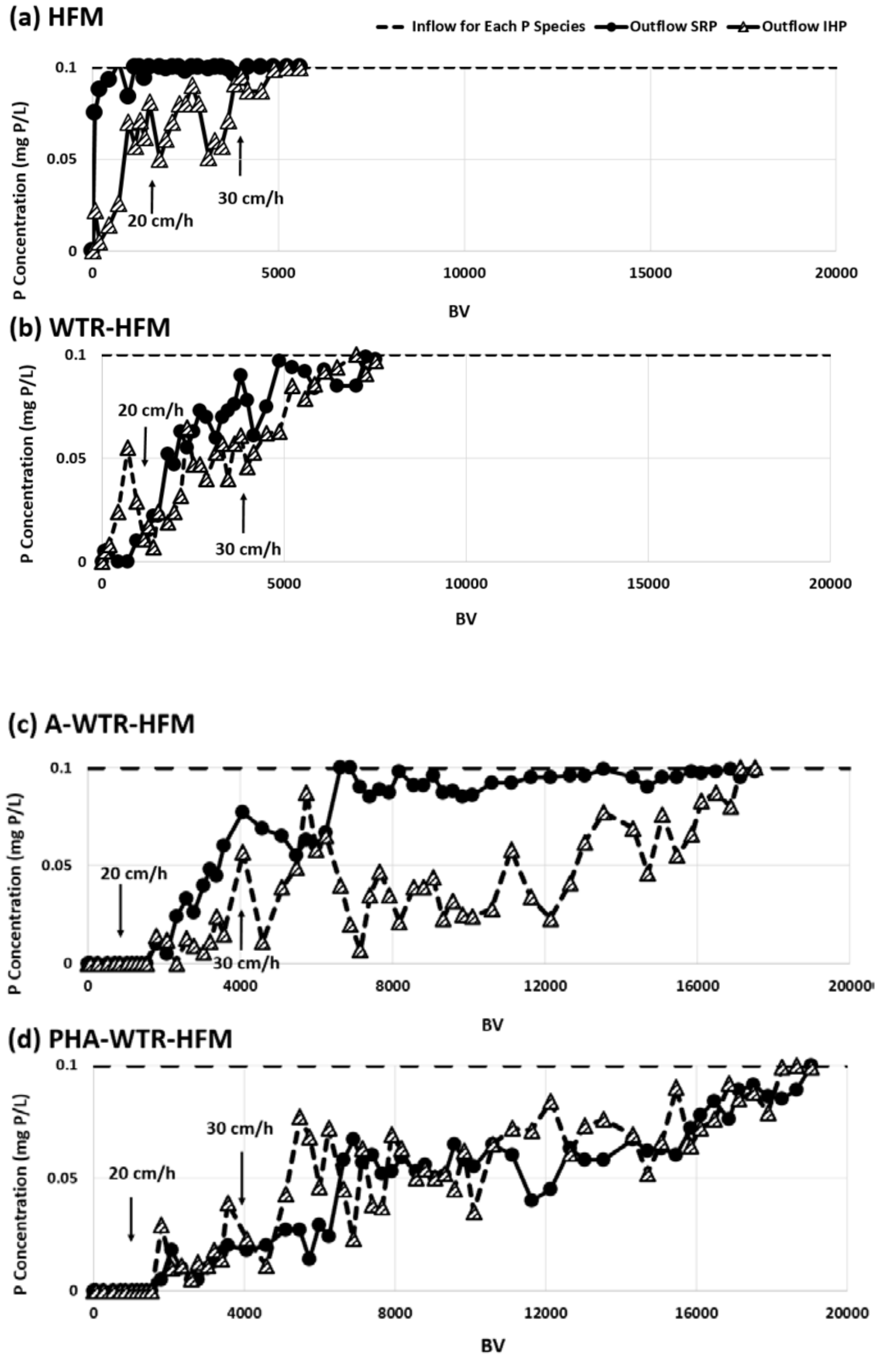


Figure 4-4. Breakthrough curves (effluent P concentration as a function of cumulative column bed volumes of flow) for mixed P sorption in four columns (influent mixed P concentration: 0.2 mg/L; Column depth: 6 cm; BV: bed volumes; T=298 K). BV represents empty bed volume.

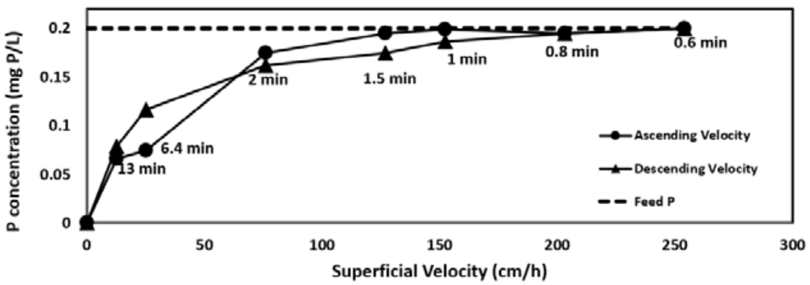
Although A-WTR-HFM and PHA-WTR-HFM columns behaved differently from each other, both of them exhibited longer treatment lifetime compared with HFM and WTR-HFM (Figs. 4-4c and d). IHP and SRP effluent from the A-WTR-HFM columns remained <0.01 mg P/L before 2000 BV, demonstrating very effective removal. Because of the increase of the velocity, concentrations of both P species jumped from 0.01 to 0.05 mg P/L between 2000 and 4000 BV. Exhaustion of SRP removal occurred in this column at approximately 7000 BV. However, unlike the continued increase of SRP concentration in the effluent, the IHP concentration slightly dropped with continued flow after 6000 BV, which stayed at approximately 0.05 mg P/L until 14000 BV (exhausted at 18000 BV). Consequently, this medium removed more IHP (766 mg P/kg) than SRP (337 mg P/kg).

Similarly, removal of both IHP and SRP in PHA-WTR-HFM were high at the beginning of the run (effluent concentrations < 0.01 mg P/L) and decreased thereafter. However, the effluent IHP and SRP increased synchronously, producing two nearly overlapping discharge tails (Fig. 4-4d). This is different than the A-WTR-HFM column, where two divergent discharge tails are observed (Fig. 4-4c). Exhaustion of IHP and SRP sorption capacity both occurred at 19000 BV, with 660 and 739 mg P/kg removed for each.

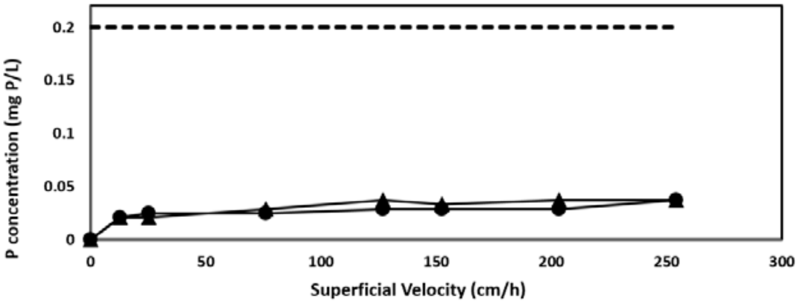
4.3.2 Effects of Contact Time on P Sorption

Fig. 4-5 shows the AMP sorption by HFM, A-WTR-HFM and PHA-WTR-HFM at different superficial flow velocities. The effluent AMP concentration in unmodified HFM increased as flow velocity increased, which can be attributed to the short contact time between the AMP solution and the media surface. Therefore, AMP passed through the media rapidly without being captured, resulting in reduced removal. As indicated by the contact time below each point, little AMP removal was observed when the velocity reached 127 cm/h, at which point the effluent and influent AMP concentrations were equal. A-WTR-HFM and PHA-WTR-HFM were better at AMP sorption at high flows. The effluent AMP levels from these two columns were minimally affected by the varied velocities. A-WTR-HFM discharged AMP concentrations < 0.04 mg P/L, even at the highest velocity (253 cm/h, contact time less than 1 min). PHA-WTR-HFM demonstrated a slightly better performance than A-WTR-HFM by maintaining a lower AMP level (< 0.02 mg P/L) throughout the experiments. Approximately 89, 28 and 5 min of contact time are required to reduce AMP to < 0.01 mg P/L by HFM, A-WTR-HFM and PHA-WTR-HFM, respectively.

(a) HFM



(b) A-WTR-HFM



(c) PHA-WTR-HFM

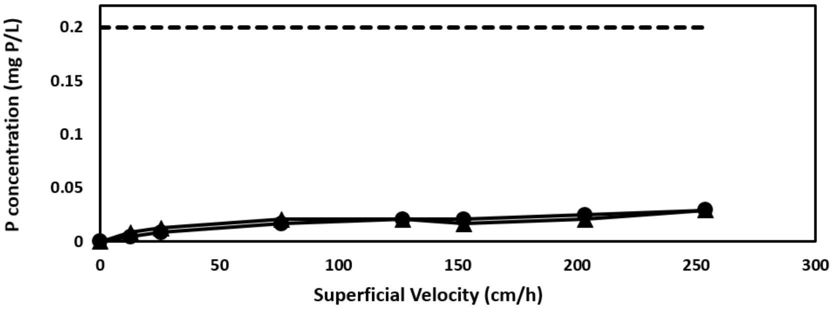
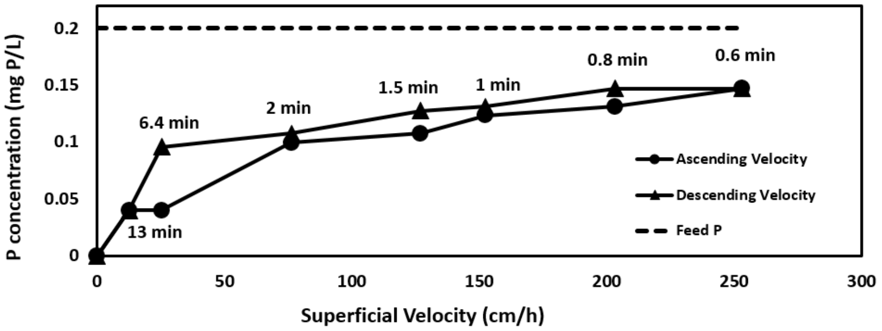


Figure 4-5. Kinetics experiments for AMP sorption in columns.

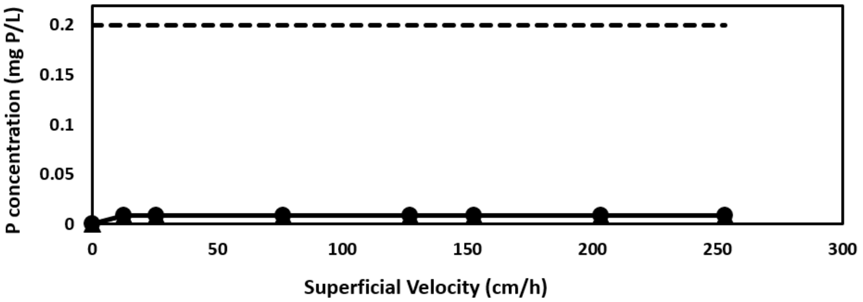
The IHP removal by HFM was also reduced as the velocity increases (Fig. 4-6). The effluent IHP concentrations from the HFM column were < 0.15 mg P/L through the experiments, indicating that the IHP removal is generally higher than that of AMP. Contact times of more than 54 min are required to reduce IHP < 0.01 mg P/L by this medium. However, IHP sorption is minimally affected by the limited contact time in the

A-WTR-HFM and PHA-WTR-HFM columns. Fig. 4-6 shows that the effluent IHP levels from these two columns were constantly below the detection limit of 0.01 mg P/L, even at the highest velocity (253 cm/h, contact time less than 1 min), demonstrating very rapid IHP sorption processes.

(a) HFM



(b) A-WTR-HFM



(c) PHA-WTR-HFM

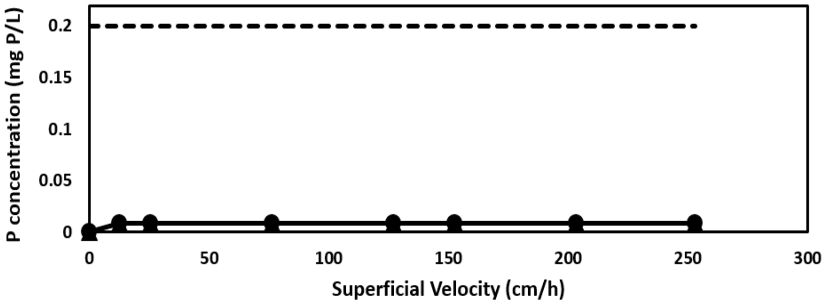
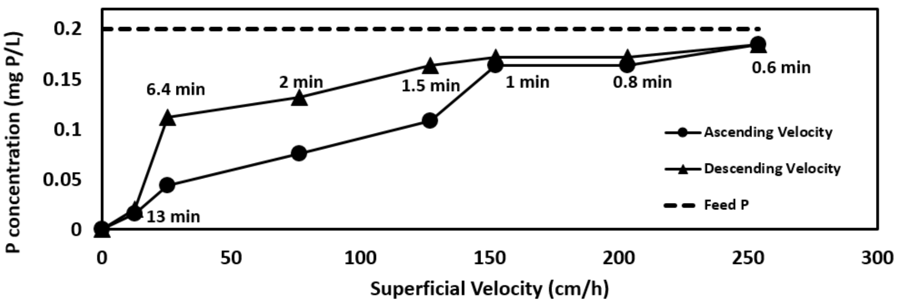


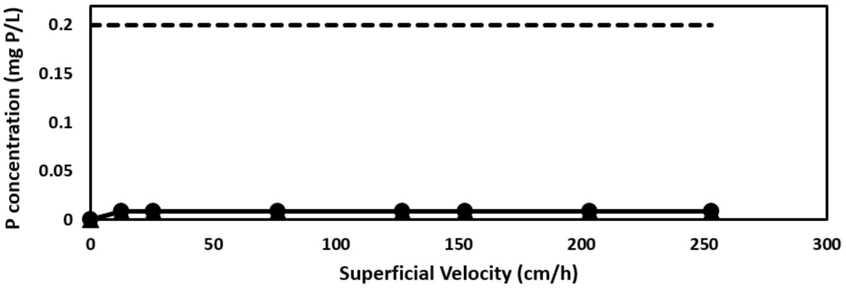
Figure 4-6. Kinetics experiments for IHP sorption in columns.

Similar to AMP and IHP, SRP sorption by HFM was dramatically affected by the short contact time, as only 50% of SRP was captured when the velocity reached 127 cm/h (effluent SRP ~0.1 mg P/L, Fig. 4-7). However, effective SRP sorption was observed in the alum and PHA columns, as low effluent concentrations (<0.01 mg P/L) were observed under all conditions. P removal at the descending superficial flow velocities exhibited similar trends as the ascending ones, ensuring that the P sorption was not affected by the media capacity exhaustion.

(a) HFM



(b) A-WTR-HFM



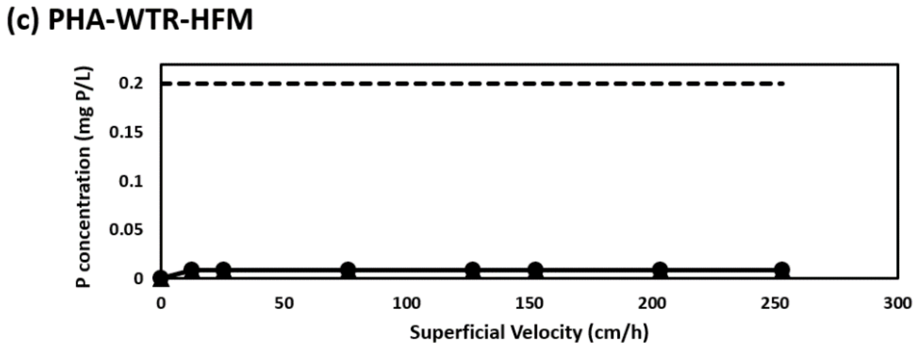


Figure 4-7. Kinetics experiments for SRP sorption in columns.

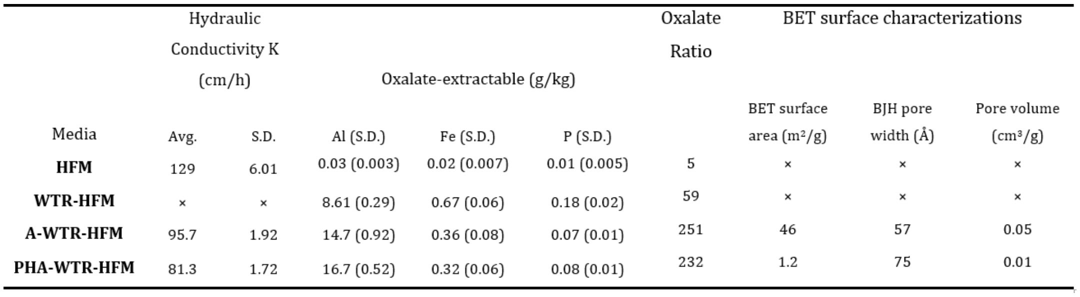
P sorption under high flow rates can be reduced, as the contact time between P and media surfaces is shortened (Riahi et al. 2009; Rentz 2010; Rout et al. 2014). Similar to the results reported by Yan et al. (2016b; Chapter 3), media mixtures modified with aluminum exhibit minimal P-sorption affects in response to limited contact time, providing both efficient and effective P removal (discharge < 0.01 mg P/L) in high flow systems.

Leaching of dissolved Al from Al-rich media at low pH (< 5.5) in bioretention systems is a concern, because excessive Al can limit plant growth (Delhaize and Ryan, 1995). Although previous studies have reported that no Al toxicity was observed with Al-based media (Sotero-Santos et al., 2005; Agyin-Birikorang et al., 2009; Mahdy et al., 2009), and the concentrations of total Al(III) leaching from alum-modified media were found to be lower than 0.08 mg/L (Yan et al., 2016b, Chapter 3), it is important to monitor Al(III) concentrations of column samples in this study. A total of 54 and 42 samples were collected from A-WTR-HFM and PHA-WTR-HFM columns, respectively. The measured total Al(III) concentrations averaged 0.04 (S.D.=0.033) and 0.05 (S.D.=0.048) mg/L for the A-WTR-HFM and PHA-WTR-HFM columns, respectively. Al can inhibit plant growth at approximately 1 mg/L (Taylor et al., 1998). Inorganic monomeric Al ions have been found to be primarily responsible for aluminum aquatic toxicity (Wauer et. al., 2004). Total dissolved Al(III) concentrations measured by ICP measures includes both organic and inorganic species. Therefore, a lower inorganic monomeric Al(III) concentration should be expected based on the low total soluble Al concentration (mostly < 0.05 mg/L). Furthermore, urban stormwater has a neutral pH (6 < pH < 8) in general; within this range Al is expected to be sparingly soluble.

4.3.3 Media Characterization

Hydraulic conductivities of three HFM media mixtures (HFM, A-WTR-HFM and PHA-WTR-HFM) and standard BSM (textural profile of 85% sand, 10% silt, and 5% clay; Yan et al., 2016a) were calculated. The hydraulic conductivities of BSM, HFM, A-WTR-HFM and PHA-WTR-HFM were found to be 9±0.45 (± 1 S.D.), 129±6.0, 95.7±1.9 and 81.3±1.7 cm/h, respectively (Table 4-2, BSM data not shown). Compared with BSM, all of the HFM media mixtures have much higher permeability. Modifying HFM with alum and PHA decreased the hydraulic conductivity by 26% and 36%, respectively, which may be attributed to the formation of aluminum hydroxides precipitates during the modification processes.

Table 4-2. Media Mixture Characterizations



	Hydraulic Conductivity K (cm/h)		Oxalate-extractable (g/kg)			Oxalate Ratio	BET surface characterizations		
Media	Avg.	S.D.	Al (S.D.)	Fe (S.D.)	P (S.D.)		BET surface area (m^2/g)	BJH pore width (Å)	Pore volume (cm^3/g)
HFM	129	6.01	0.03 (0.003)	0.02 (0.007)	0.01 (0.005)	5	×	×	×
WTR-HFM	×	×	8.61 (0.29)	0.67 (0.06)	0.18 (0.02)	59	×	×	×
A-WTR-HFM	95.7	1.92	14.7 (0.92)	0.36 (0.08)	0.07 (0.01)	251	46	57	0.05
PHA-WTR-HFM	81.3	1.72	16.7 (0.52)	0.32 (0.06)	0.08 (0.01)	232	1.2	75	0.01

Note: HFM: high flow media; WTR-HFM: HFM + 10% WTR; A-WTR-HFM: HFM + 10% WTR + Alum; PHA-WTR-HFM: HFM + 10% WTR + PHA;

Hydraulic conductivity tests: triplicate experiments performed for one sample;

Oxalate extractable Al/Fe/P: duplicate experiments performed using two samples;

For bioretention facilities constructed with HFM, A-WTR-HFM and PHA-WTR-HFM at media depth of 50 cm, based on the measured hydraulic conductivities alone, the stormwater contact time would be approximately 23, 31 and 37 min, respectively. Therefore, AMP, IHP and SRP removal by unmodified HFM will be ineffective, as based on the kinetics results, more than 89, 54 and 27 min of contact time are required to reduce P concentration to < 0.01 mg P/L, respectively. However, this can be achieved by incorporating alum and PHA amendments onto the media mixture.

Oxalate extractions (OR) of HFM mixtures are shown in Table 4-2. The small amounts of oxalate-extractable Al and Fe of the unmodified HFM results in a low OR ratio of 5, indicating low P fixing potential by this media mixture. The modified HFM exhibited a range of OR values with the highest OR in A-WTR-HFM at 251, and the lowest OR in WTR-HFM as 59. The WTR, alum and PHA additions contributed a large amount of Al_{ox} and Fe_{ox} to the mixtures. The Al_{ox} of HFM was increased from 0.03 g/kg to 8.6, 14.7 and 16.7 g/kg, respectively, with WTR, alum, and PHA modification. Similar improvements were observed in Fe_{ox}. The P_{ox} values were similar across all media mixtures, with the exception of WTR-HFM. WTR-HFM has a relatively high P_{ox} value; this is consistent with the extraction results reported by Yan et al (2016a). Although the reason is unclear, it is possible for P to be released from WTR during the alum modification process since media mixtures were rinsed with deionized water. However, this cannot be the case with PHA, as no rinse procedures were employed for media mixtures. This suggests that some P contributed by the WTR was more tightly held by the added PHA. Studies have shown that in general, an OR above 10 indicates lower risk for P leaching (Kleinman et al., 2000; Kovar and Pierzynski, 2009). Modifying HFM with WTR, alum, and PHA increase the respective OR values, significantly improving their P fixing potential.

Results from Yan et al. (2016b; Chapter 3) showed that higher AMP, IHP and SRP sorption capacities were observed for media mixtures with higher OR (based on linear regressions, $r^2_{AMP} = 0.92$, $r^2_{IHP} = 0.96$, $r^2_{SRP} = 0.65$), indicating strong positive correlations between OR and media P sorption capacity (equilibrium with 0.2 mg P/L influent). Including the HFM results observed in the present work with the previous data generally reinforced this linear relationship (Fig. 4-8). It is apparent that the PHA-modified media deviate from the media mixes; it is unclear why this is true. Excluding the PHA mixes, linear regressions show $r^2_{AMP} = 0.94$, $r^2_{IHP} = 0.83$, and $r^2_{SRP} = 0.59$. Therefore, media P sorption capacity and OR may be positively correlated, which supports the use of the OR to estimate P sorption performance of a medium mixture.

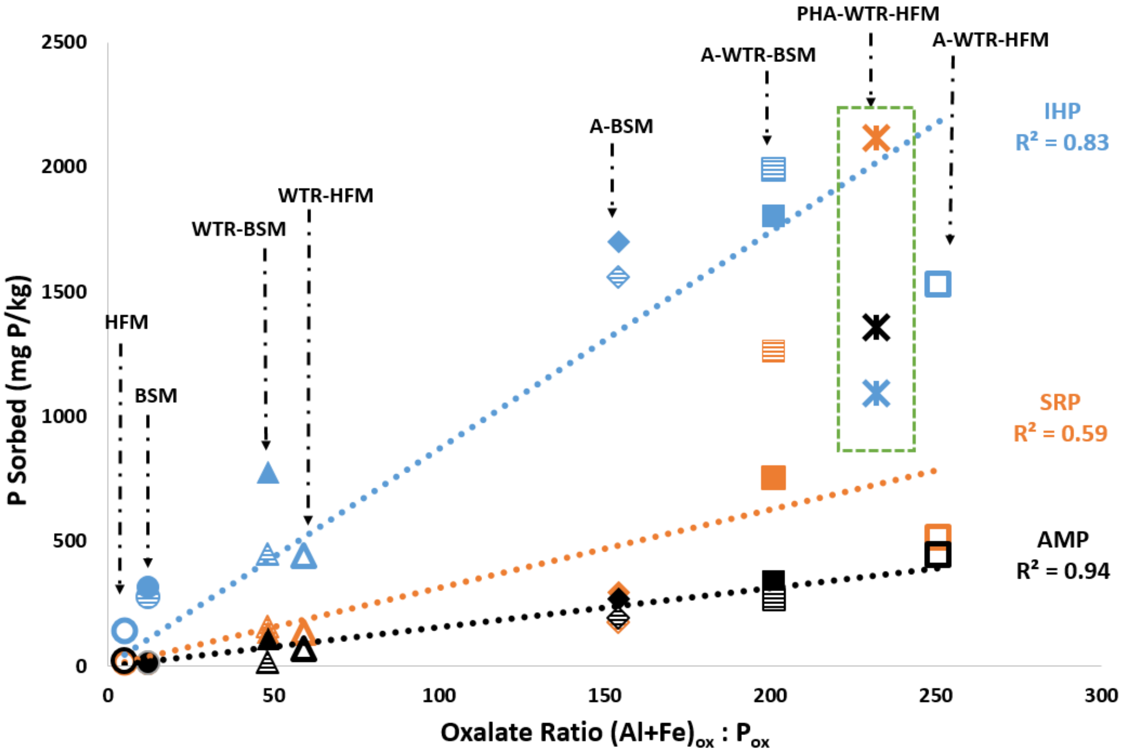
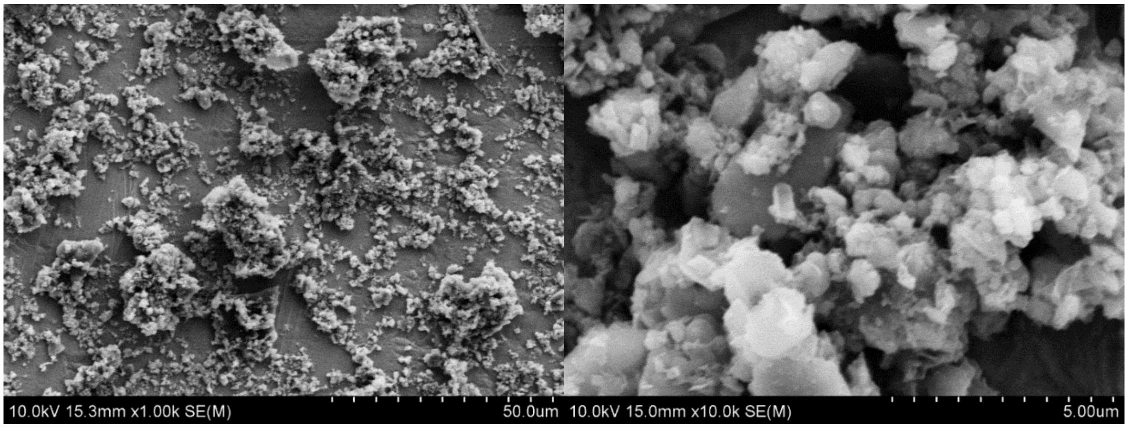


Figure 4-8. Measured oxalate ratio of media mixtures and their P sorption capacities (at Ce =0.2 mg P/L; BSM batch data: hatched symbols; BSM column data: solid symbols; HFM column data: no fill symbols) (BSM data from Yan et al. 2016b). PHA-WTR-HFM data not included in linear regression.

(a) A-WTR-HFM



(b)PHA-WTR-HFM

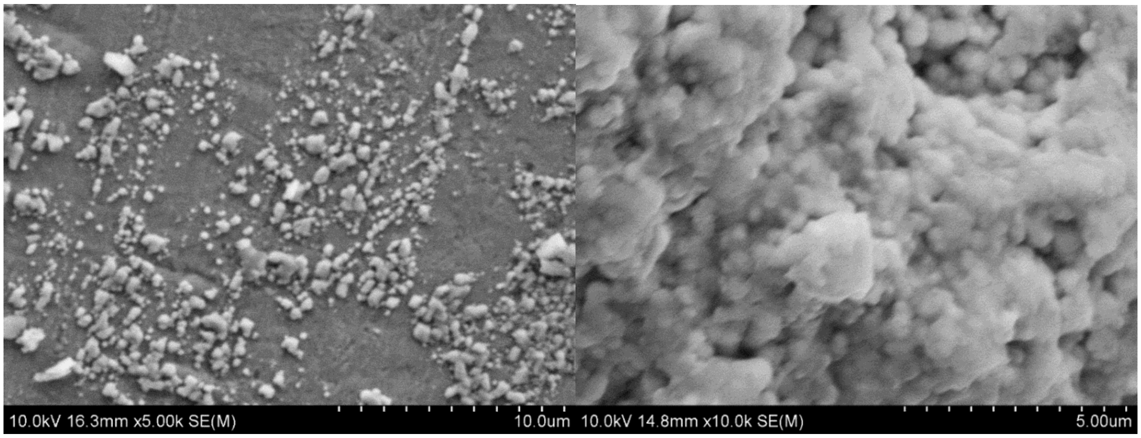


Figure 4-9. Scanning electron microscopy images of (a) A-WTR-HFM; (b) PHA-WTR-HFM.

The BET SSA and pore sizes of A-WTR-HFM and PHA-WTR-HFM are presented in Table 4-2, and SEM images are shown in Fig. 4-9. It is clear that A-WTR-HFM exhibits a rough surface, with a possible porous morphology. The specific surface area (SSA) of A-WTR-HFM was measured as 46 m^2/g, and average pore size was 57 Å. The alum-modified BSM possesses a moderate SSA (20 m^2/g) and large cavities (207 Å) as found by Yan et al. (2016a; Chapter 2). This may be attributed to the formation of aluminum hydr(oxides) precipitates during the alum modification process. However, the surface of PHA-WTR-HFM is smoother than that of A-WTR-HFM, supporting the lower measured SSA (1.2 m^2/g) of PHA-WTR-HFM. This medium also exhibited small pore size (75 Å) and pore volume (0.01 cm^3/g). The BET and SEM results show that alum and PHA modification can result in different media surface morphologies, which may indicate distinct P removal mechanisms when different media mixture are used; these differences may also help to explain the anomalous results of PHA-WTR-HFM observed in Figure 4-8.

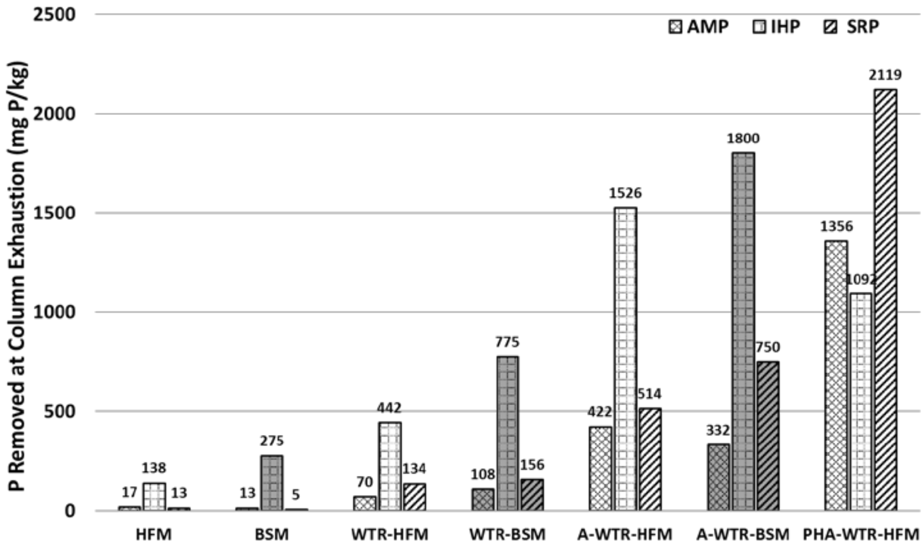
4.3.4 Comparison of P Removal

P sorption performances of four HFM mixtures are compared in Fig. 4-10a. Similar to the results reported by Yan et al. (2016b; Chapter 3), adding Al-rich amendments to HFM can markedly improve P removal, resulting in a general, decreasing removal order of: PHA-WTR-HFM > A-WTR-HFM > WTR-HFM > HFM. Compared with unmodified HFM, the media mixture with alum and WTR additions enhanced AMP, IHP and SRP sorption by factors of 25, 11 and 40, respectively; furthermore, significant improvements were also observed for P sorption by using PHA-WTR-HFM, by factors of 80, 8 and 163, respectively (compared with HFM).

HFM exhibited lower P removal capacities than BSM in general (Fig. 4-10a), especially for modified media mixtures, which can be explained by the lower clay fraction in HFM. As a result, both BSM and WTR-BSM outperformed HFM and WTR-HFM in removal of almost all the three P compounds. However, the removal by HFM has been significantly increased through the P-enhancement processes by using alum; A-WTR-HFM even showed higher AMP removal capacities than A-WTR-BSM. This may indicate that alum modification can compensate for the loss of clay fraction in HFM for P removal.

Fig. 4-10b displays the components of mixed P sorption by four HFM mixtures. Compared with the removal performances observed in individual column tests, sorption of both IHP and SRP decreased in all media mixtures, because of the lower input P concentration and/or the competitive sorption. When IHP and SRP are present simultaneously, all media mixtures removed larger mass of IHP than SRP, indicating that IHP is preferentially adsorbed over SRP, agreeing with previous research (Anderson et al., 1974; Celi et al., 1999, Berg and Joern, 2006, Yan et al. 2016b; Chapter 3). This is also consistent with the previous study by Shumaker and Karathanasis (2008) for competitive sorption between IHP and SRP, where they observed the removals by gibbsite were 3000 and 1000 mg/kg (mixed C_e=4 mg P/L IHP and C_e=4 mg P/L SRP), respectively. As discussed below, this can be attributed to the difference in the functionality of P groups in the molecular structure of the P species. The interaction of IHP with the adsorbent surface in soils may involve up to four of the six phosphate groups, which may form multiple covalent bonds on the media surface, indicating very strong bonding strength (Goldberg and Sposito, 1985, Celi and Barberis, 2005). The involvement of such a large number of phosphate groups in IHP sorption also leads to very stable complexes with the surfaces and limited desorption possibilities (Ognalaga et al., 1994; Martin et al., 2003). Furthermore, IHP is a negatively-charged anion at pH values > 6.9 (Celi et al. 2001) and, it has higher charge density than other P species. As a result, it is easier for IHP to approach the positively-charged media surface through a stronger electrostatic attraction (Shang et al. 1990).

(a)



(b)

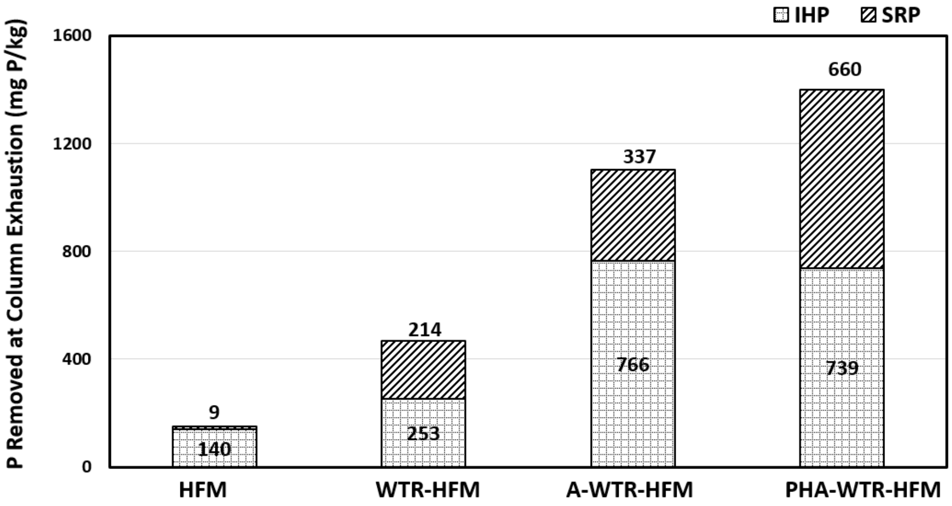


Figure 4-10. Comparisons of (a) AMP, IHP and SRP sorption capacities (grey pattern filled data are BSM results from Yan et al., 2016b); (b) Components of mixed P sorption of HFM, WTR-HFM, A-WTR-HFM, and PAH-WTR-HFM.

Although both A-WTR-HFM and PHA-WTR-HFM exhibited higher removal capacities than HFM, they behaved differently in terms of different P species. Compared with PHA-WTR-HFM, A-WTR-HFM showed a better performance in removing IHP. However, the AMP and SRP removed by PHA-WTR-HFM are 3 and 4 times higher than that removed by A-WTR-HFM, respectively. As distinctly different media surface morphologies were observed in SEM and BET analyses, these differences may be explained by different removal mechanisms for different P species.

In general, three main mechanisms have been proposed for P removal by soil minerals: 1) chemical precipitation; 2) adsorption of phosphate ions onto Al or Fe (hydr)oxides surfaces through specific ligand exchanges processes, forming either bidentate binuclear or monodentate mononuclear surface complexes; 3) chemical complexation reactions between P and metal cations to form insoluble complexes (Ratnaweera et al., 1992; Shang et al, 1992; Celi et al., 1999; McGechan and Lewis 2002; Celi and Barberis; 2005). Aluminum (hydr)oxides maybe the main product of alum modification processes, and it is an effective adsorbent for P (Shang et al. 1990; Tanada et al., 2003; de Vicente et al., 2008). Compared with other organic P species, IHP has the highest affinity to the aluminum (hydr)oxides surface, which can lead to a favorable adsorption process for IHP removal (Celi and Barberis, 2005). Previous studies have attributed this to: 1) involvement of multiple P groups in IHP adsorption onto the aluminum (hydr)oxides surface, which resulted in the formation of very stable complexes on the surfaces with limited desorption possibilities (Shang et al., 1990, 1992; Martin et al. 2003); 2) transformation of IHP-$Al(OH)_3$ surface complexes to surface precipitates, or diffusion of adsorbed IHP into the interior part or micropores of amorphous $Al(OH)_3$ (Yan et al. 2014). This may help to explain the higher IHP removal achieved by using A-WTR-HFM compared to PHA-WTR-HFM.

Previous research has discussed mechanisms of PO_4(-III) removal in coagulation processes, which can be used to explain the higher AMP and SRP removal achieved by PHA-WTR-HFM. PHA is a partially neutralized aluminum salt with a high basicity (~83%), and it can hydrolyze to form highly positively-charged cationic polynuclear Al species (Letterman, 1999), which can be used for coagulation of negatively charged particles through adsorption and particle surface-charge neutralization. Polynuclear hydrolysis products, such as $Al_{13}O_4(OH)_{24}^{7+}$, $Al_8(OH)_{20}^{4+}$, $Al_{14}(OH)_{32}^{10+}$, can form at high total Al concentrations ($>10^{-3}$ M) and at pH values between 4 to 7 (Bertsch, 1986; Bertsch and Parker, 1996; Letterman, 1999). $Al_{13}O_4(OH)_{24}^{7+}$ was believed as the primary hydrolysis product in PHA solutions with basicities greater than about 75% (Bottero et al., 1987).

Chemical precipitation reactions between PO_4(-III) and metal salts has been found to be the most important phosphate removal mechanism in coagulation (Ratnaweera et al., 1992), therefore, fully hydrolyzed species (e.g., $Al(OH)_3$) or prepolymerized coagulant with high OH^-/Al ratios should be less efficient in the precipitation of PO_4(-III) species (Diamadopoulos and Benedek, 1984; Ratnaweera et al., 1992 Chen and Luan, 2010). This is caused by the higher affinity of OH^- ions to interact with Al^{3+}, which results in less interactions between PO_4(-III) and Al^{3+} (Diamadopoulos and Benedek, 1984).

In addition to chemical precipitation, adsorption of PO_4(-III) onto $Al(OH)_{3,}$ and chemical complexation also account for PO_4(-III) removal during coagulations, as suggested by Ratnaweera et al. (1992). Chemical complexation reactions between positive sites on polymeric hydrolysis species and PO_4(-III) ions can produce insoluble complexes (Ratnaweera et al., 1992). It is also suggested that the surface charge density of the Al species determines the interactions between PO_4(-III) and Al during coagulation (Boisvert et al., 1997).

It should be noted that the importance of adsorption and chemical complexation is non-negligible, especially when polymerized Al coagulant is used with possible cationic polymers formed during coagulation, which may result in higher PO_4(-III) removal at a given pH (Lijklema, 1980; Ratnaweera et al., 1992). AMP is found to be negatively charged at neutral pH, and its removal increases with decreased pH, when the media surface is more positively charged (Hashizume, 2015). Therefore, the P removal by PHA-WTR-HFM is likely to be affected by the charge characteristics of the media surface. It is possible that the hydrolyzed Al polymers can attach to media surface, and results in a higher density cationic surface, which could be more efficient in removing AMP and PO_4(-III) through enhanced chemical complexation reactions.

4.4 Conclusions and Recommendations

Alum and WTR have been reported to be effective amendments to BSM for P removal from Yan et al. (2016a, b; Chapter 2, 3). Alum- and WTR-modified BSM exhibited high P sorption capacity from previous column studies, and can effectively capture P within 1 min of contact time. However, a highly permeable media may be preferred in some SCMs as it can rapidly infiltrate stormwater runoff. This study designed and investigated a permeable media to infiltrate stormwater runoff at high flow rates without comprising P removal efficiencies.

With limited clay content and contact time for P sorption, HFM alone has low P removal capacity. Therefore, HFM was modified by WTR, alum and PHA based on the enhanced P removal observed in previous work (Yan et al., 2016a, b). As expected, alum addition improved the removal of AMP, IHP, SRP and mixed P by factors of 25, 11, 40 and 7, respectively, compared with unmodified HFM. Similar to the improvement contributed by alum, PHA also significantly enhanced the removal of these four P compounds by factors of 80, 8, 163 and 9, respectively. Both alum- and PHA-modified HFM showed significantly higher permeability than BSM, demonstrating the potential to promote high infiltration of runoff in SCMs.

In addition to the improvement in P sorption capacity, alum and PHA also enhanced the media performances in dynamic systems with high velocities. A-WTR-HFM and PHA-WTR-HFM both effectively reduced IHP and SRP concentrations to <0.01 mg P/L within 1 min of contact time. This also agrees with the results reported by Yan et al. (2016b; Chapter 3).

Even though both alum and PHA were demonstrated to be promising amendments to improve P removal in bioretention, they responded differently to different P species. Supported by the SEM and BET characterizations, A-WTR-HFM benefits the IHP sorption with its relatively high surface area through an enhanced ligand exchange process; PHA-WTR-HFM outperformed in AMP and SRP sorption by forming highly positively-charged polymers on media surfaces.

Most importantly, the alum modification process is difficult to implement practically in bioretention system construction. The PHA modification provides a practical recipe that can not only achieve rapid runoff infiltration and improved P removal, but also simplify the modification process by reducing the liquid to media ratio (from 10/1 to 0.5/1), lowering alkalinity consumption (20% limestone to 10% limestone), and eliminating the mixing requirement. Therefore, PHA incorporation is recommended as an ideal amendment onto HFM to improve P removal in high flow systems. However, it should be noted that the sorption capacities found in column studies are values observed until the exhaustion point, so a reduced efficiency for DOP removal should be expected over the entire predicted treatment duration in field bioretention systems.

Chapter 5. Conclusion and Recommendations

5.1 Conclusions

Previous research studies showed varied P removal in bioretention systems, and the abiotic removal of P is predominantly depends on media selection. While the removal of PP and SRP have been documented, the capture of DOP has been overlooked. Enhanced P removal was successfully achieved in this work by adding two amendments to BSM: WTR and alum. For the three P species tested (AMP, IHP and SRP), BSM incorporated with 10% WTR and 10% alum (both by dry mass, or 3% as Al totally) constantly exhibited the highest sorption capacity compared with other media mixtures.

Minicolumn experiments investigated the DOP and SRP sorption at concentrations of 0.2 mg P/L under continuous flow conditions. The results further confirmed that BSM was optimized with respect to P sorption by using 10% WTR and 10% alum amendments. The total mass removal of AMP, IHP and SRP using A-WTR-BSM were increased by factors of 26, 7 and 150, respectively, compared with unmodified BSM.

Although A-WTR-BSM achieved effective P sorption, its application in SCMs may be limited because this media has low permeability (K<1 cm/h). A permeable media may be preferred in some SCMs as it can rapidly infiltrate stormwater runoff, and delay the peak discharge, especially during periods of extreme rain events when large runoff volumes are generated from impervious areas. Therefore, a high-permeability engineered media, HFM, was investigated to further promote rapid runoff infiltration to achieve goals of both quantity and quality control of runoff. As expected, HFM with 10% WTR and 10% alum (or 3% as Al totally) amendments showed pronouncedly higher P sorption capacity, compared with unmodified HFM. Generally, HFM exhibited slightly lower P removal capacities than BSM, which can be explained by the lower fines fraction in HFM. A-WTR-HFM has remarkably higher permeability (K~ 96 cm/h) than A-WTR-BSM (K<1 cm/h), demonstrating the potential to promote rapid runoff infiltration without compromising P removal in SCMs.

P sorption can be reduced when the contact time between media surface and P species is inadequate, which was observed with unmodified BSM and HFM. This can be attributed to the short contact time between the P solution and the media surface, which in turn promotes less sorption and rapid movement of P through the media. However, WTR and alum modification has hastened the P sorption process by reducing the contact time of at least 130, 7 and 130 min to less than 1 min for AMP, IHP and SRP removal by BSM, respectively. This is can be important considering that usually there is limited contact time presented for P capture when stormwater runoff flows through the bioretention media during a rainfall event. The same improvement was also observed with HFM using WTR and alum.

While high permeability and improved P sorption was successfully achieved using A-WTR-HFM, the field implementation remains a challenge because the media modification process requires high consumption of alkalinity, constant mixing conditions, and a high liquid-to-media ratio. PHA was studied as an alternative Al amendment to HFM in an effort to develop a practical and effective media preparation recipe for use in bioretention systems. The new prepared HFM mixture has been incorporated with 10% PHA and 10% WTR (by mass, 3% as Al totally). This new recipe is has simplified the P-enhancement process by dramatically reducing the liquid-to-media ratio from 10/1 to 0.5/1, lowering the consumption of alkalinity from 20% to 10%, and eliminating the mixing requirement. Most importantly, media performance of P treatment was not sacrificed using this new recipe; compared with unmodified HFM, mass removal of AMP, IHP and SRP using PHA-WTR-HFM were increased by factors of 80, 8 and 163, respectively; the P removal using this media was not reduced by the shortened contact time, and the high hydraulic conductivity (K~ 81.5 cm/h) was maintained through the modification process.

P sorption competition can complicate the removal process when different P species are simultaneously present in stormwater. Competition for active sorption sites on media surfaces was observed between two P species: IHP and SRP. IHP was observed to be strongly captured over SRP, which is consistent with the previous single-adsorbate studies. This preferred sorption of IHP over SRP can be attributed to the high charge density, and the involvement of multiple P groups in IHP sorption, which resulted in the formation of very stable complexes on the surfaces with limited desorption possibilities. It must be noted that the removal process can be more complex with the presence of different P compounds and other anions in real stormwater, and with diverse media mixtures involved.

Aluminum-mineral adsorbents such as boehmite, gibbsite, and montmorillonite can control the retention of organic P in soils (Anderson Arlidge, 1962; Shang et al., 1990, 1992; Greaves and Wilson 1969; Bowen et al. 1988; Barba et al. 1991). Although P retention is dependent on the type of P compound and the properties of Al-mineral adsorbents, adsorption by ligand exchange between the phosphate groups and the surface hydroxyls groups of the media was hypothesized as the primary mechanism for P removal. SEM and BET surface area analyses demonstrated that alum-modified media mixtures have high SSA, and large pore size and volume, which benefits P adsorption through specific ligand exchange processes. P capture through PHA-WTR-HFM was hypothesized to be somehow dependent on the charge characteristics of the media surface. By hydrolyzing into highly positively-charged cationic polynuclear species (e.g., $Al_{13}O_4(OH)_{24}^{7+}$), PHA showed higher sorption potential for SRP and AMP by providing extra positively charged surface sites, resulting in stronger charge neutralization than fully hydrolyzed species (e.g., $Al(OH)_3$) (Diamadopoulos and Benedek, 1984; Ratnaweera et al., 1992; Boisvert et al., 1997, Chen and Luan, 2010).

Oxalate extractions were used to characterize the media and to develop an index to predict sorption performance. Strong agreement between the oxalate ratio and P sorption capacity of each media mixture was observed in this study. Unmodified media mixtures have lower OR in general, which is consistent with their low P sorption capacities. However, media modified with alum and PHA exhibited higher P fixing potential and lower risk for P leaching. Results indicated that strong positive correlations exists between OR and media P sorption capacity (equilibrium with 0.2 mg P/L influent). Linear regressions are $r^2 = 0.94$, $r^2 = 0.83$ and $r^2 = 0.59$ for AMP, IHP and SRP, respectively. Therefore, media P sorption capacity and OR can be positively correlated, which supports the use of the OR to predict P sorption performance of a medium mixture. It is found that the PHA-WTR-HFM relationship deviates from the media mixes and the reason is unclear.

As discussed above, PHA-WTR-HFM is recommended as a promising media in SCMs for P control, and the use of this media can benefit stormwater management in four ways: (1) Longer media lifetime for P sorption can be achieved compared to unmodified BSM or HFM; PHA-WTR-HFM exhibited sorption capacity of more than 1000 mg P/kg for all P species investigated in this study (at Ce=0.2 mg P/L). Considering a bioretention facility with a media depth of 50 cm and sized at 5% of the impervious catchment area, this media mixture can provide more than 100 years (based on a 240 mg/kg benchmark for 30 years of P removal) of effective P treatment; (2) Permeable PHA-WTR-HFM can promote rapid runoff infiltration to delay peak flows without compromising P removal performance; therefore it can treat large volumes of runoff in small-footprint SCMs, resulting in less materials consumption and labor input, and consequently, lower construction costs; (3) PHA-WTR-HFM discharges low P concentrations (< 0.01 mg P/L) in dynamic systems even under high flow velocities (253 cm/h); (4) Al toxicity for plants can be considered insignificant since Al(III) leaching from this media was found to be low (averaged as 0.05 mg/L); (5) The simplified media preparation process makes the PHA recipe more practical and easy to implement in SCMs. Therefore, PHA-WTR-BSM is recommended to be used in bioretention or related SCMs to obtain both runoff P treatment and flood control.

However, it should be noted that this media mixture may not show constant P removal performance over time for the treatment of real stormwater runoff in bioretention systems, especially in the presence of other ions. Natural organic matter (NOM) present in stormwater may compete with phosphate for adsorption sites, and result in reduced phosphate retention. Numerous studies have investigated the co-adsorption of phosphate and NOM onto iron and aluminum (hydr)oxides in soils (Davis, 1982; Sibanda and

Young, 1986; Guan et al., 2006). NOM is readily adsorbed by alumina and kaolinite in the pH range of natural water; interactions between surface hydroxyls and the acidic functional groups of the organic matter is responsible for the capture of NOM (Davis, 1982). Humic acid and fulvic acid were observed to compete strongly with phosphate for adsorption sites at pH values <4 (Sibanda and Young, 1986). Phosphate adsorption on goethite was reduced by citrate at pH values < 7, with the largest interaction at pH 5; competition for binding sites can determine the competitive adsorption between phosphate and citrate (Geelhoed and Riemsdijk., 1998).

On the other hand, NOM is believed to increase phosphate adsorption indirectly by inhibiting aluminum oxide crystallization (Borggaard et al., 1990). Organic P can be directly adsorbed on organic surfaces, or can be incorporated into the core structure of organic matter (Schulten and Schnitzer, 1993), both of which could result in increased P retention in soils. Therefore, it is hard to predict media performance based on these contradictory results, but varied P removal should be expected. Also, sorption capacities of media mixtures found in column studies are values observed until the exhaustion point, so a reduced efficiency for DOP removal should be expected over the entire predicted treatment duration in real bioretention systems.

Furthermore, in some areas drinking water is treated for naturally occurring radionuclides, which can result in water treatment residuals that are classified as "technologically enhanced naturally occurring radioactive materials" (U.S. EPA, 2005). Therefore, the application or management of WTR in field applications requires special attention, and must be compliant with federal statutes and regulations. Also, although the leaching of dissolved Al (III) from Al-rich media at pH >5 may not be a concern in bioretention systems, more monitoring studies for potential leaching of Al (III) from PHA- and WTR-modified media may be necessary to support the use of this media.

5.2 Recommendations for Further Research

This study has successfully established a media recipe (HFM+10%WTR+10% PHA) to simultaneously achieve both high infiltration rate and enhanced P removal in bioretention systems. This study investigated the competitive sorption reactions between two P species, more information is necessary to understand the P removal performance when different P compounds and/or other anions are presented simultaneously.

Only one mixture of HFM and PHA was analyzed in this study; additional information on other ratios of PHA to HFM would be beneficial in determining a minimum loading amount of PHA to HFM without sacrificing P removal effectiveness.

The effects of wet/dry conditions on media performance should be examined as well. More studies are necessary to understand the P removal under intermitted flow patterns with varied flow rates, and with varied influent P concentrations.

Further investigations may be expanded to field studies to examine how the P removal performance changes through years and the hydrologic performance of the bioretention system should also be monitored. Design guidelines regards to vegetation selection, media depth and facility size can be explored to improve the overall performance of the bioretention system.

Appendix: Quality Assurance and Quality Control (QA/QC) guidance for sampling and analysis of Phosphorus

1) Container and equipment decontamination: all sampling supplies that were used to contact with the sample were cleaned by 0.5 N HCl acid bath overnight, and then triple-rinsed with deionized water;

2) Equipment calibration: pH was measured using pH meters. Meters were calibrated according to the manufacturer’s specifications, using standard buffer solutions;

3) Calibration curves: commercial standard solutions were used to build calibration curve for phosphorus measurement.

4) Method blanks: method blanks were used during each phosphorus analysis to assess potential contamination associated with sampling and laboratory activities.

5) Spiked sample: Spiked sample analysis (or known addition) was used to test the method at varying concentrations of analyte. Known amounts of analyte were added to a sample and the percent recovery was calculated. The accepted recovery was higher than 90%.

6) Data reproducibility: replicate experiments were performed to verify reproducibility and provide QA/QC control. Sample standard deviation is used to show the variability of measured data.

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