Water Treatment Residual Coated Wood Mulch for Mitigation of Toxic Metals and Phosphate from Polluted Urban Stormwater Runoff

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WATER TREATMENT RESIDUAL COATED WOOD MULCH FOR MITIGATION OF TOXIC METALS AND PHOSPHATE FROM POLLUTED URBAN STORMWATER RUNOFF

A DISSERTATION

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ABSTRACT

WATER TREATMENT RESIDUAL COATED WOOD MULCH FOR MITIGATION OF TOXIC METALS AND PHOSPHATE FROM POLLUTED URBAN STORMWATER RUNOFF

By Hanieh Soleimanifar

Polluted urban runoff as a primary non-point pollution source poses a serious threat to urban human and ecological health. Various urban runoff pollutants challenge the exiting stormwater treatment systems. To support the development of a sound and sustainable urban stormwater management, this dissertation targets at transforming a common landscaping practice, i.e. mulching, into a new stormwater treatment technology through coating aluminum water treatment residual (Al-WTR) on the surface of wood mulch chips. WTR is an industrial waste produced from drinking water treatment plants and primarily comprises amorphous aluminum (hydr)oxides. The Al-WTR coating on the modified wood mulch enables the adsorption ability for certain urban runoff pollutants.

The primary objective of this dissertation is to evaluate the performance of the Al-WTR-coated wood mulch-based stormwater treatment technologies for alleviation of toxic metals and phosphate in urban stormwater. Three toxic metals (i.e. Cu, Zn, and Pb) and phosphate were selected as representative pollutants due to their abundance in urban runoff and high public and ecological concerns. In order to achieve the primary objective, three tasks were sequentially completed in this dissertation, including: 1) Al-WTR coated wood mulch was synthesized and characterized, followed by treatment trials to examine the treatment ability and leaching potential of the innovative filter media; 2) batch experiments were carried out to determine the adsorption kinetic and isotherm patterns of Al-WTR coated wood mulch for the four selected urban runoff
pollutants, to explore the reaction mechanisms behind the adsorption, and to evaluate the effects of key factors affecting the adsorption behaviors; and 3) two-stage column studies (i.e. small column tests and semi-field experiments) were performed to study the short-term and long-term performance of Al-WTR coated wood mulch for capturing the selected urban runoff pollutants under a continuous flow state, in addition to preliminary cost analysis.

Results show that Al-WTR coated wood mulch is capable of effectively removing toxic metals and phosphate from urban runoff and substantially alleviating the accumulation of these pollutants in the underlying soil. Because the adsorption is kinetically controlled, the depth of a mulch filtration bed plays an essential role in the effluent concentrations. Adsorption of these cationic metals and phosphate is achieved principally via the formation of inner-sphere surface complexes. The irreversible adsorption leads to the minimal leaching of adsorbed pollutants or aluminum from the modified mulch chips. Furthermore, preliminary cost analysis suggests that the cost of Al-WTR coated mulch is moderately increased relative to the price of raw wood mulch. The dissertation demonstrates the potential of the innovative Al-WTR coated wood mulch for revolutionizing urban stormwater treatment and has multiple positive impacts on stormwater management and water treatment industries, environment, and society.

*Keywords*: water treatment residuals, alum sludge, wood mulch, stormwater treatment, urban runoff management, bioretention basins, filter media, heavy metals, phosphate
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DEDICATION

To my parents who have always believed in me

and

My loving husband who has supported me unconditionally.
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LIST OF ABBREVIATION

Aluminum (Al)
Antecedent Dry Period (ADP)
Arsenic (As)
Batch Reactors (BRs)
Bed Volume (BV)
Best Management Practices (BMPs)
Cadmium (Cd)
Carbon (C)
Chemical Oxygen Demand (COD),
Chromated Copper Arsenate (CCA)
Chromium (Cr)
Continuously Stirred Tank Reactor (CSTR)
Copper (Cu)
Dissolved Oxygen (DO)
Energy Dispersive Spectroscopy (EDS)
Energy Dispersive X-ray (EDX)
Extended X-ray Absorption Fine Structure (EXAFS)
Extracellular Polymeric Substances (EPS)
Five-day Biological Oxygen Demand (BOD₅)
Granular Ferric Hydroxide (GFH)
Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS)
Integrated Exposure Uptake Biokinetic (IEUBK)
Iron (Fe)
Lead (Pb)
Life Cycle Assessment (LCA)
Low Impact Development (LID)
Manganese (Mn)
Maximum Contaminant Level (MCL)
Montclair State University (MSU)
Multiple-Pollutants Solution (MPS)
Natural Organic Matter (NOM)
Natural Resources Conservation Service (NRCS)
Nitrogen (N)
Oxytetracycline (OTC)
Phosphorous (P)
Piperazine-N,N′-bis (2-ethanesulfonic acid) (PIPES)
Plug-Flow Reactor (PFR)
Polycyclic Aromatic Hydrocarbons (PAHs)
Practical Quantitation Levels (PQLs)
Precipitation Leaching Procedure (SPLP)
Scanning Electron Microscopy (SEM)
Silicon (Si)
Single-Pollutant Solution (SPS)
Stormwater Control Measure (SCM)
Suspended Solids (SS)
Tetracycline (TTC)
Total Dissolved Solids (TDS)
Total Phosphorus (TP)
Toxicity Characteristic Leaching Procedure (TCLP)
Transmission Electron Microscopy (TEM)
United States Department of Agriculture (USDA)
US Environmental Protection Agency (USEPA)
Water Treatment Residual (WTR)
X-ray Absorption Near Edge Structure (XANES)
X-Ray Diffraction (XRD)
Zinc (Zn)
CHAPTER 1- INTRODUCTION
CHAPTER 1 INTRODUCTION

1.1 Background and Problem Statement

1.1.1 Polluted urban stormwater runoff

In the United States, 82% of residents are living in over 500 urban areas (>390 persons/km²). The urban population fraction is significantly over the world urban rate of 50% (CIA, 2015), indicating that the United States is highly urbanized. In spite of many benefits, a high urbanization degree leads to various environmental issues such as polluted urban runoff, which is the surface stormwater created by urbanization. Urban areas typically have 50-100% imperviousness that significantly increases the flow rate of runoff, and accumulates constituents from atmospheric deposition, vehicular traffic, and other sources. The increasing urbanization has resulted in the significant growth of impervious surfaces (e.g. build roofs, roads, and garages), which can reduce stormwater infiltration and interrupt a natural water cycle in an urban setting. The increased runoff flowrate can trigger more frequent flooding events (Kong et al., 2017). Furthermore, it has a higher potential to wash away diverse anthropogenic pollutants such as heavy metals, fertilizers, pathogens, and petroleum on the ground, and carry them into the urban water environment. The polluted urban runoff represents a primary non-point pollution source that contributes the carried pollutants into receiving water bodies and poses a threat to urban human and ecological health (Bell et al., 2017). For example, urban runoff is recognized among the major nonpoint groundwater pollution sources (USEPA, 2009), as the 2nd most frequent cause of surface water pollution (Warren and Hammer, 2008), and the 3rd largest source of water quality impairments to the US lakes surveyed by US Environmental Protection Agency (USEPA) (USEPA, 2009).
Pollutant sources of urban stormwater runoff are diverse, such as combined and separated sewer overflow systems, road pavement, atmospheric fallout, roofs and motor vehicles (Shaver et al., 2007). Urban runoff pollutants of major concern include suspended solids (SS), toxic heavy metals, nutrients, pathogens, salts, and hydrocarbons (e.g., gasoline). Among them, toxic metals and nutrients are of particular concern. The former pollutant type, such as copper (Cu), zinc (Zn), and lead (Pb), are toxic, chemically and biochemically persistent, bio-accumulated, while the latter one can lead to eutrophication, i.e. algal blooms in water bodies, to degrade water quality (e.g. oxygen depletion, increased turbidity, the production of taste and odor compounds, and the release of toxic algal toxins).

Heavy metals in urban runoff. A variety of heavy metals have been frequently identified in urban stormwater runoff, such as Pb, Zn, and Cu (USEPA, 2006). Pb and Zn, the two common heavy metals present in urban runoff, principally derive from paints and vehicle traffic such as gasoline, exhaust emissions, crankcase, lubricating oils and grease (Brinkmann and Tobin, 2001; Gunawardena et al., 2013). Jacobs et al. (2002) studied Pb-based paint hazards in the U.S. houses. They reported that more than half of 38 million Pb painted houses were potentially hazardous. Many of these units were occupied by low income families with young children. Pb has been demonstrated to negatively impact children’s intelligence and their physical growth. The heavy metal can enter their body by either direct intake of polluted particles and water or inhalation of Pb-polluted dust. The Pb-based paints can pollute water and soil, after Pb is released from the old paints. Children, pregnant women, and poor families are the most vulnerable human groups to Pb poison. Although the Maximum Contaminant Level (MCL) of Pb in the U.S. national primary drinking water standard is 15 µg/L, an exposure to Pb at a lower...
concentration is demonstrated to be poisonous to sensitive groups (Cleveland et al., 2008). Pb poisoning can also reduce avian population (Pattee et al., 1990).

On the other hand, Zn intake at a high concentration (more than 40 mg/day) can also cause problems in human body like nausea, vomiting, and headache. Much worse, Zn entering into the human body can competitively prevent the absorption of necessary Cu and Fe to cause certain blood issues. In the ecological health aspect, though Zn is recognized as a one of micronutrients for plants, its phytotoxicity is of particular concern, when the Zn concentration is too high, in urban areas, especially in regions with an acidic environment (Farfel et al., 2005). Zn is listed in the U.S. national secondary standards for drinking water with a permitted level of up to 5 mg/L (EPA, n. d.).

Cu in urban runoff primarily originates from Cu plumbing, electroplating wastes, pavement wear, vehicle brake pads, Cu pesticides, deposition of Cu air emissions, and soil erosion (Nirel and Pasquini, 2010; TDC-Environmental, 2004). The MCL of Cu in the U.S. national secondary drinking water standards is set at 1.3 mg/L. Eisler (1998) provided a comprehensive list of invertebrates, terrestrial plants, as well as aquatic spices along with their tolerance levels to Cu. He also discussed the effects of Cu on these spices. For certain crops (e.g. sweet orange), once the concentration of Cu is greater than 60 mg/kg of dry soil, the plant growth would be adversely affected. The threshold levels for cucumber and earthworms are 10 and 100 mg/kg, respectively. Besides Cu concentration, the duration of exposure also plays a vital role. For example, bay scallops under a 119-day exposure at 5 µg/L Cu all died. Clams that were exposed for 4 hours at 4 µg/L Cu exhibited abnormal physiological activities, such as greater oxygen consumption and ammonia excretion. For the birds poisoned by Cu, the increases in the weight and liver size were observed. Similarly, Cu can significantly threaten human health. The problems associated with
Cu include liver damage, diarrhea, vomiting, stomach cramps, and even death. These damages can occur from an exposure at 3 mg/kg Cu for infants and with an exposure to 30 mg/kg Cu for adults, separately. When the Cu concentration was increased to 6 - 637 mg/kg, death cases may occur. Particularly, the Wilson disease is an inherited problem due to the Cu accumulation in liver, brain, and other organs, which finally causes the death of children (Uriu-Adams and Keen, 2005). Table 1-1 shows the concentrations and common sources of the aforementioned heavy metals in urban runoff.

**Nutrients in urban runoff.** Nutrients in urban runoff, including phosphorous (P) and nitrogen (N), are also problematic, due to two major reasons. Firstly, they are able to cause eutrophication in receiving natural water bodies such as lakes (Erickson et al., 2013). Secondly, ammonia at a high concentration is toxic to the aquatic life (Galloway et al., 2003). In urban areas, nutrients are primarily derived from fertilizers, animal wastes, detergents, motor oil, road dusts, and the leaking of septic tanks (Kojima et al., 2011a; Pitt et al., 1999). Studies indicate that P and N in urban runoff typically increase logarithmically with increasing impervious surface area (Dietz and Clausen, 2008). In a highly developed area, runoff has up to 0.34 mg/L P, much greater than 25 µg/L P (the eutrophication risk level), and up to 16 mg/L NO$_3^-$-N against 10 mg/L NO$_3^-$- N (the National Primary Drinking Water Regulation level) (Gobel et al., 2007). Elevated levels of P intake can also threaten human health and cause death (Chang et al., 2014).

### 1.1.2 Urban stormwater management

Conventional stormwater management infrastructures (e.g. pipes and channels) focus merely upon the rapid reduction of peak flows of urban runoff. However, it cannot effectively alleviate various pollutants present in the runoff. In contrast, new strategies encourage Best Management
Practices (BMPs) to address quantity and quality issues of stormwater (Brown et al., 1997; USEPA, 2006; Wossink and Hunt, 2003).

BMPs can be structural or non-structural (USEPA, 2006). Structural BMPs treat polluted runoff either at the point of pollution generation (a sewer system) or at the point of discharge to the receiving water bodies, while non-structural BMPs prevent the generation and pollution of runoff. From the perspective of modern urban stormwater, stormwater as a component in the urban water cycle is recognized as a resource that recharges aquifers and surface water, rather than a waste. Different structural BMPs are commercially available in the current stormwater market as follows:

Infiltration systems allows the runoff to pass through a permeable layer (Elliott and Trowsdale, 2007). They reduce the water quantity via storage and infiltration. Runoff pollutants can be removed through different treatment mechanisms such as filtration, adsorption, and biological degradation. The use of vegetation in an infiltration system will enhance the stormwater treatment capacity. Examples of stormwater infiltration systems include infiltration basins, pervious pavement, trenches, and wells. The stormwater infiltration systems are suitable in the areas with abundant permeable soil. However, a drawback is that persistent pollutants may enter into soil and groundwater to cause subsurface pollution.

Detention systems store stormwater and thus reduce the runoff flow (Chin, 2006). They discharge the stored stormwater later to stormwater sewers system or receiving water bodies after the peak flow rate of runoff passes. However, the systems are not specially designed for the capture and/or degradation of stormwater pollutants. Typical examples include detention basins as well as underground vaults and tanks.
Retention systems are designed to store stormwater without discharge. They mimic a natural pond with the dual functions of the stormwater treatment and the water flow control. The associated treatment mechanisms include filtration, biological degradation, sedimentation, and flotation. If the systems are designed without a liner layer, the infiltration may lead to water and soil pollution. Retention systems include retention ponds, surface tanks, as well as underground vaults and tunnels.

Constructed wetlands perform like the detention or retention systems with vegetation (Birch et al., 2004). The presence of vegetation enhances the capacities in nutrient uptake and flow reduction. The treatment mechanisms include volatilization, sedimentation, filtration, adsorption, and desorption. They are particularly suitable for the areas with a high surface water table. They can be designed with an open water or not. If an open water is included in a constructed wetland, the system can behave like a retention basin except that vegetation covers 50% or greater of the surface area (Collins et al., 2010; Mungasavalli and Viraraghavan, 2006).

Vegetated systems are designed with dense vegetation to tackle the stormwater quantity and quality issues through infiltration, filtration, and biological removal. Example vegetated systems include swales and grass filter strips. Swales are shallow vegetated areas with a side slope. They are not suitable for ponding but can be a substitute for conventional street curb and gutters. Grass filters can trap particles in stormwater and serve as pretreatment prior to other BMPs (e.g. bioretention basins).

Filtration systems (biofilters) allow the filtration of captured stormwater through a porous media such as sand, soil, gravel, peat, and compost. They can reduce the flow load and remove certain stormwater pollutants. A filtration system typically comprises a sedimentation basin, a filter media, and a drain.
Bioretention basins are the most widely used filtration system suitable for many different locations (e.g. nearby parking lots) (Davis et al., 2003; Hsieh and Davis, 2005; Yan et al., 2016). Different components in a typical bioretention basin sequentially include: 1) a grass filter for slowing down runoff flow and removing large particles; 2) a ponding area for particle sedimentation; and 3) a porous area for water infiltration, consisting of certain plants, mulch, and soil (Maryland, 2007). After the bioretention, the flow either infiltrates into the underlying soil or enters into a drainage system or water bodies through an underdrain. Plants can reduce the water loading via evapotranspiration and alleviate the nutrient load through root uptake. Soil allows water infiltration to reduce the water loads and remove different pollutants through adsorption, ion exchange, filtration, and biological process. Mulch on the top of soil maintains moisture, controls weed and prevents soil erosion.

Reduction of directly connected impervious surfaces can divert runoff from impervious surface (e.g. rooftops) to flow over a vegetated area, instead of discharging into a sewer system or a receiving water body. As aforementioned, the vegetations can reduce both runoff flow and certain pollutants. To achieve the purpose, traditional curbs and gutters should be replaced with vegetated swales.

1.1.3 Bioretention basins

As a subset of BMPs, Low Impact Development (LID) techniques emphasize small-scale, decentralized treatment systems to preserve or closely mimic the site’s pre-developed hydrologic response to precipitation, and to enable runoff infiltration (Rosa et al., 2015). The marginal maintenance cost of LID systems is typically much lower than conventional stormwater management systems, while improving effluent quality (Houle et al., 2013). As a leading LID technique, bioretention basins utilize soil retention to mitigate stormwater pollutants, and allow
for stormwater infiltration at a small scale in developed areas (Hsieh and Davis, 2005). In practice, bioretention basins are frequently employed in urban stormwater management. A typical bioretention design consists of sands with overlying vegetation and mulch (USEPA, 2006). It can control the flow rate of stormwater runoff and reduce a wide range of pollutants through multiple reaction mechanisms. For example, heavy metals can be adsorbed; nutrients can be taken up by plants; SS can be screened by the soil media; and hydrocarbons can be floated or biodegraded in a bioretention basin. Furthermore, bioretention systems can be flexibly designed at different sizes and coupled with other BMPs. Numerous studies demonstrated that bioretention basins were capable of removing common urban runoff pollutants (Hsieh and Davis, 2005).

Davis et al. (2003) reported that bioretention basins could remove runoff Cu, Zn and Pb by up to > 95%. Their field tests (Davis et al., 2006) demonstrated that the LID technique reduced total phosphorus (TP) mass by up to 80%. Hong et al. (2006) found that a bioretention basin removed oil and grease from stormwater runoff. Diblasi et al. (2009) successfully abated polycyclic aromatic hydrocarbons (PAHs) in a bioretention facility.

Bioretention basins are usually advantageous over many other BMPs. Compared with the infiltration systems, detention basins, retention basins, and reducing directly connected impervious systems, they exhibited a better pollution control capability due to the presence of a variety of vegetation and because they mimic a forest serving as a natural drainage corridor. In contrast, though constructed wetlands have a similar vegetated system, their application is highly limited by the availability of a high water table.

Although a bioretention basin can, to different degrees, remove certain pollutants present in urban runoff, its application is restricted due to the following three aspects. Firstly, stormwater pollutants may enter into underlying soil and groundwater via infiltration and transfer surface
water pollution to subsurface contamination, in case that no underdrain is designed. Secondly, persistent pollutants (e.g. toxic metals) can be accumulated at the topsoil so that frequent replacement of soil is required. If the top soil is not timely dredged, these pollutants in the soil will finally exceed the EPA regulated levels (Weiss et al., 2008). Thirdly, the reported P removal efficiencies of bioretention basins are highly unstable and even P may be released from soil into stormwater (Dietz and Clausen, 2005, 2006; Hatt et al., 2009; Roy-Poirier et al., 2010; Wu et al., 1996). Therefore, there is an urgent demand to develop new, technically viable, and affordable technologies to enhance the performance of bioretention basins for urban stormwater management.

1.1.4 Adsorbents for stormwater treatment

Adsorption represents an important treatment process for mitigation of urban stormwater pollutants. Given that the volume of urban runoff is typically large, the selection of low-cost adsorbents is economically favorable in engineering practices. A variety of low-cost adsorbents have been investigated for the treatment of polluted urban stormwater. Biochar is a substance initially produced for soil amendment by extremely heating (>250˚C) different types of biomass in an oxygen deficient condition (Lehmann and Joseph, 2015). Different biochar feedstocks have been used, such as animal manure, plants, and nut shells. However, the adsorption ability of biochar relies heavily upon pyrolysis conditions and feedstock sources. Besides, the potential leaching of unwanted chemicals (e.g. polycyclic aromatic hydrocarbons (PAHs) that are inherently produced during pyrolysis of the biochar feedstock) from biochar may restrict its applications at agricultural and environmental scenarios (Hilber et al., 2012).

Zeolite, an aluminosilicate mineral, has been long used for the removal of heavy metals and oil from wastewater (Wang and Peng, 2010). The major adsorption mechanisms are cation
exchange and molecular sieving. Chitosan is another economical and natural adsorbent derived from seafood-processing wastes. Typically, its adsorption capacity is relatively low in comparison with zeolite, unless it is appropriately pretreated before use. Presently, very few studies have been performed to test the both aforementioned low-cost adsorbents in stormwater treatment. A mixture of recycled materials such as sawdust and tire crumbs accompanied with different soil types such as sand, silt, and limestone were attempted for the alleviation of nutrients in stormwater (Hossain et al., 2010). However, the effectiveness of these composite materials for heavy metals in stormwater remains unknown. Moreover, it is well known that Zn present in tire has a potential to leach out (Kanematsu et al., 2009; Rhodes et al., 2012). Apatite II™ is another natural sorbent option for the purpose of removing heavy metals from road runoff (Huang, 2012). Unfortunately, phosphate and calcium were observed to leach out from Apatite.

1.1.5 Water treatment residual (WTR) and its application for water treatment

**WTR production from drinking water treatment.** Drinking water is of essence for human being because it is not only used for drinking, but also for food preparation and domestic sanitization (Erickson et al., 2013; FEMA, 2004). In the United States, more than 50% people use surface water (e.g. streams, lakes, reservoirs, and wetlands) as drinking water sources (Erickson et al., 2013). Generally, surface water is more readily contaminated with greater turbidity, color, and microorganisms than groundwater. During algal blooming, taste and odor are also problematic in surface drinking water sources (Davis and Cornwell, 2008).

Traditional drinking water treatment systems are classified into three types, including simple disinfection, softening plants, and filter plants. Simple disinfection is typically applied used for high quality groundwater. After dosing disinfectants, the finished water meets with local drinking water standards. Softening plants are primarily used for the treatment of groundwater
with a purpose of sufficiently removing hardness and inactivating microorganisms. Filter plants are used to treat surface water. A typical treatment train (Figure 1-1) includes screens, coagulation by rapid mixing, flocculation, sedimentation, filtration, and disinfection. The conventional surface water treatment train has proven very effective for the removal of suspended colloids and pathogens in water, as well as for color, natural organic matter, and undesirable taste and odor (Edzwald and Tobiason, 2011).

Coagulation, flocculation, and sedimentation in the treatment train target at the removal of colloids that remains suspended in water and cannot spontaneously settle. Coagulation destabilizes suspended colloidal particles in source water by the addition of certain chemicals, causing these particles to agglomerate. The chemical agents added are coagulants, which can achieve destabilization through neutralization of colloidal surface charge (charge neutralization), compression of colloidal electrical double layers, adsorption bridging, and/or netting sweeping (Edzwald, 2011). In the ensuing flocculation, a gentle mixing can slowly bring the destabilized colloids into contact, which leads to the formation of larger and denser aggregates, which are called flocs. Following flocculation, the aggregates become settleable. They gradually settle down due to gravity to the bottom (i.e. a sludge zone) of the next treatment reactors – sedimentation basins. The produced sludge at the sludge zone is called water treatment residuals (WTR). As an industrial waste from drinking water treatment facilities, WTR should be appropriately managed (Davis and Cornwell, 2008). Locations of coagulant addition and production of WTR are indicated in Figure 1-1.

Coagulants dosed during coagulation include hydrolyzing metal ions (e.g. aluminum and iron salts) and polymers. Coagulants commonly used in the United States and many other countries such as China are aluminum sulfate (Al₂(SO₄)₃·(14-16)H₂O (commonly referred to as “alum”),
ferric sulfate \( (\text{Fe}_2\text{SO}_4\cdot x\text{H}_2\text{O}) \), and ferric chloride \( (\text{Fe}_3\text{Cl}_3\cdot x\text{H}_2\text{O}) \). Addition of these trivalent cations greatly neutralize negative charges on colloidal surfaces and compress their unique dual electrical layers, promoting the aggregation of these colloids. A general reaction occurring after addition of alum in water is as follows.

\[
\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O} + 3\text{Ca(HCO}_3\text{)}_2 = 2 \text{Al(OH)}_3(s) + 3\text{CaSO}_4 + 6\text{CO}_2(g) + 14\text{H}_2\text{O} \quad \text{Eq.}(1-1)
\]

Where \((g)\) and \((s)\) represent gas and solid products, respectively. The major ingredient in WTR produced from alum addition is solid aluminum hydroxides. Moreover, Al-WTR may also contain other chemical species, such as colloids and NOM originally present in source water and later captured via coagulation. The United States produces approximately two million tons of WTR every day (Prakash and SenGupta, 2003). The most frequently used method for the WTR disposal is landfilling. However, this option is being challenged by the limited landfill space and prohibitive disposal costs.

**Physical and chemical properties of Al-WTR.** Al-WTR is a mixture of different components, including Al (hydr)oxides produced from coagulant addition (e.g. Eq. (1-1)) and these substances originally present in water sources and captured by the coagulants (e.g. sands, silts, clay, and natural organic matter) (Edzwald, 2011). Compositions of Al-WTRs have been comprehensively reviewed in literature (ASCE et al., 1996; Ippolito et al., 2011a). In Al-WTR, the most abundant metal is Al, followed by Fe, Ca, and K. An average mass fraction of Al in Al-WTR reported in literature from 2005-2008 is 11.8%. X-ray diffraction (XRD) analyses were used to analyze Al present in Al-WTR in previous studies. But no crystalline Al hydroxides were observed (Ippolito, 2003; Ippolito et al., 2009), indicating that Al hydroxides are amorphous in nature.
Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to determine the morphology of Al-WTR particles. Results show that shapes and sizes (from several tens of nanometers to a few millimeters) were highly varied (Deng et al., 2012; Makris et al., 2004; Yang et al., 2006). The different morphology observations are caused likely due to different operational conditions among these studies (e.g. pH, coagulant dose, and source water conditions). Another unique morphologic property of Al-WTR is its porous structure. The porous nature was directly noticed via the backscattered SEM technique (Ippolito et al., 2003). Makris et al. (2004) also found the microporosity-specific surface area (104.9 m²/g) was over three-fold of macroporosity-specific surface area (33.0 m²/g ). Due to the porous structure, Al-WTR typically has a large specific surface area, providing a sufficient space for adsorption of other species in water. The reported specific surface area was broadly varied between 28.0 and 120 m²/g (Babatunde et al., 2009; Hovsepyan and Bonzongo, 2009; Makris et al., 2004).

**WTR for adsorption of water pollutants.** WTR has been tested and practiced as an adsorbent for capturing various pollutants from water, including inorganic and organic pollutants (Duranceau and Biscardi, 2015; Lee et al., 2015; Mortula and Gagnon, 2014; Punamiya et al., 2013, 2015a; Trenouth and Gharabaghi, 2015). Inorganic pollutants investigated in previous studies are categorized into two types: 1) anion pollutants such as arsenite, arsenate, and phosphate; and 2) toxic metal cations. On the other hand, Al-WTR has been recently attempted to adsorb traceable emerging organic micro-pollutants such as antibiotics in water (Punamiya et al., 2015b).

Al-WTR immobilization of anions in water have been extensively investigated. Most of the previous endeavors focused on arsenic (As) (Gibbons and Gagnon, 2010, 2011; Makris et al., 2006; Sarkar et al., 2007a; Sarkar et al., 2007b) and phosphorous (Agyin-Birikorang et al.,
Al-WTR has been proven very effective for adsorption of arsenite (As(III)) and arsenate (As(V)). Kinetic tests showed that Al-WTR adsorption of As(III) or As(V) in water is a biphasic process. High adsorption capacities of Al-WTR for As(III) and As(V) were reported at 8 mg/L and 14 mg/g, respectively (Makris et al., 2006). Results from desorption tests with oxalate extraction or in the presence of a high phosphate loading indicate very minimal As desorption, suggesting strong bindings of As(V) and As(III) with Al-WTR (Makris et al., 2007; Makris et al., 2009). Furthermore, X-ray absorption near edge structure (XANES) studies indicates that the adsorption of As(III) or As(V) could not alter the original oxidation state of As. And extended X-ray absorption fine structure (EXAFS) analyses suggested the formation of inner-sphere mononuclear and bidentate complexes between Al-WTR and As, regardless of As(III) and As(V) (Makris et al., 2009).

Al-WTR also provides a low-cost but effective method for mitigation of phosphate from water (Babatunde et al., 2009; Bolan et al., 1985; Gibbons and Gagnon, 2011; Ippolito, 2003; Lee et al., 2015; Makris et al., 2004; Makris et al., 2005; Novak and Watts, 2004; O’Connor et al., 2002; O’Neill and Davis, 2012a, 2012b; Razali et al., 2007). Although variable adsorption capacities of Al-WTR for phosphate were previously reported, including 3.5 mg P/g (Yang et al., 2006), 4.5 mg P/g (Babatunde et al., 2009), 7.7 mg P/g (Makris et al., 2004), 12.5 mg P/g (Ippolito, 2003), and 10.4-37.0 mg P/g (Dayton et al., 2003), the adsorption efficiencies remained fairly high. Phosphate binding to Al-WTR relies heavily upon many factors, such as solution pH, Al-WTR particle size, temperature, and exposure time. For example, an increasing pH from 4.0 to 9.0 led to a decrease of P adsorption capacity from 4.52 mg P/g to 1.74 mg P/g.
(Babatunde et al., 2009). Adsorption of phosphate, similar to As, is kinetically biphasic, i.e. a rapid sorption followed by a long-term slow adsorption (Makris et al., 2005). The fast adsorption occurring at the initial phase reflects the P sorption to the external surface of Al-WTR. In the following phase, a slower phosphate sorption is involved with phosphate diffusion in micropores on the Al-WTR surface (Makris et al., 2005).

WTR adsorption of various heavy metals from water has been also extensively studied (Benjamin and Leckie, 1981; Castaldi et al., 2015; Chiang et al., 2012; Deng et al., 2016; Deng et al., 2012; Lin et al., 2014). Adsorption of various cationic heavy metals were reported, such as Hg, Cu, Pb, Cr, Zn, and Ni. Castaldi et al. (2015) investigated the immobilization of Cu and Pb with Al-WTR and found that the heavy metals were strongly and irreversibly adsorbed to the WTR surface. Results of their FT-IR analysis indicated the formation of inner-sphere surface complexes. Chiang et al. (2012) compared the adsorption capacity of WTR for several metal and metalloid ions with a commercial goethite. They reported that the WTR had a 240% greater removal capacity in a multiple pollutant solution consisting of As, Cd, Pb, and Zn. Lin et al. (2014) studied the metal sorption process with WTR and found different effects of pH on different metal adsorption to WTR. The Cu sorption efficiency was increased with the increasing pH, whereas an opposite pH dependence was observed for WTR adsorption of Cr. They suggested that the adsorption of these metals was ascribed to surface complexation as well as electrostatic interactions.

Recently, WTR has been attempted to adsorb traceable organic micro-pollutants (Punamiya et al., 2013; Punamiya et al., 2015b). One such example is antibiotic compounds. Al-WTR adsorption of tetracycline (TTC) and oxytetracycline (OTC) in water exhibited a pseudo 2nd order kinetic reaction pattern. Al-WTR at 20 g/L could reduce TTC and OTC by 95% within 2
hours. The adsorption efficiency increased with increasing pH up to pH 7 but decreased in the pH range of 8 to 11. The antibiotic adsorption was inhibited in the presence of phosphate, but was not influenced with the presence of sulfate in water (Punamiya et al., 2015a). Based on the surface complexation modeling and Fourier transform infrared spectroscopy analysis, the plausible adsorption mechanism was the formation of a mononuclear monodentate surface complex through strong inner-sphere-type bonds on Al-WTR (Punamiya et al., 2013).

**Challenges of WTR application for stormwater treatment.** Although WTR has been recently used as a soil amendment to enhance heavy metal and phosphorous removal in bioretention basins (Trenouth and Gharabaghi, 2015; Yan et al., 2016), direct application of WTR as filter media for stormwater treatment is not practically feasible, because WTR powders, once wetted, readily aggregate to prevent water infiltration. Recently, some groups have begun to study WTR for mitigation of certain stormwater pollutants. Deng et al. (2016) attempted to combine WTR and scrap tire chips for the removal of metals in stormwater, because tire chips with larger sizes can increase the water permeability when stormwater flows through the mixed adsorbents. In a simulated stormwater solution, WTR alone or WTR combined with scrap tire chips could rapidly remove more than 90% of Cu, Zn, or Pb. More importantly, scrap tire chips, if combined with WTR during application, allow water easily to flow through these filter media. However, toxic Zn originally present in scrap tires could leach-out to increase Zn concentration in stormwater runoff. Another application mode is the direct addition of Al-WTR powders into soil in a stormwater infiltration system. In the studies at the University of Maryland, columns load with a soil matrix with Al-WTR (5% by weight) could consistently reduce influent total P below 70 μg/L (O’Neill and Davis, 2012a, 2012b). Although the P removal was effective, the application mode of Al-WTR is questionable in practices. Once Al-WTR is oversaturated with
phosphate, the phosphate adoption ability is significantly reduced. Continuous addition of Al-WTR into soil will eventually increase the Al content in soil. This option may be problematic due to the toxicity of Al. Therefore, new methods to utilize WTR for stormwater management remained highly needed to allow for a better application of WTR in practice.

1.1.6 Mulching practices and wood mulch

Mulching is a simple and beneficial practice for landscaping and agriculture. Mulch is a protective layer of a material spread on the top of soil. Mulch can be organic such as wood chips, straw, tire rubbers, and grass clipping and inorganic like plastics, brick chips, and stones. When to start the use of mulch replies upon the purposes. In the most cases, mulch is added at the beginning of a growing season. Mulch can assist in maintaining heat during the night to encourage the growth of plants. Later, it can stabilize a moisture content and soil temperature and also prevent the growth of weeds (Bush-Brown and Bush-Brown, 1951; Prosdocimi et al., 2016). Natural Resources Conservation Service (NRCS) of the United States Department of Agriculture (USDA) lists eight benefits from the mulching practices as follows (USDA, 2018).

1) Protects the soil from erosion
2) Reduces compaction from the impact of heavy rains
3) Conserves moisture, reducing the need for frequent watering
4) Maintains a more even soil temperature
5) Prevents weed growth
6) Keeps fruits and vegetables clean
7) Keeps feet clean, allowing access to garden even when damp
8) Provides a "finished" look to the garden
Zion Market Research has recently reported that the global mulch market was valued at USD 3.34 billion in 2017 and is expected to reach USD 4.96 billion in 2024, growing at a CAGR of 6.8% between 2018 and 2024 (Zion-Market-Research, 2018). Rubber and wood mulches are among the most popular mulch available in the U.S. mulch market. Rubber mulch has been widely used as a lining in landfills or a protection surface in playgrounds. They are heavier than natural mulch and thus need a thinner layer than natural mulch to achieve the same effect of weed control. However, the toxicity is an issue for the use of rubber mulch. The most rubber mulch available in the market originates from scrap tires that have been repeatedly reported to leach Zn, a toxic heavy metal, during rainfall (Deng et al., 2012; Kanematsu et al., 2009). Rhodes et al. (2012) observed that the Zn leachability of rubber mulch has a negative correlation with its size but is positively related to an exposure time. Smaller rubber mulch pieces and a longer exposure time caused the more Zn release. The effect of mulch size was because smaller particles had greater specific surface area that offer a larger space for the Zn leaching.

In the mulch market, different types of wood-based mulch are available (ground, shredded and chipped wood mulch). It is popular due to its low cost and easy availability. Although wood mulch does not have an issue of Zn release to the best of our knowledge, some wood mulch may contain toxic As, chromium, and copper if the source wood is chromated copper arsenate (CCA) treated wood. CCA-treated wood was the most popular wood material to build decks and playsets in the United States residential areas before 2003 (EPA, 2002). As, Cr, and Zn were added for extending the wood lifetime. However, the leaching of the three chemicals from CCA-treated wood during its service was repeatedly reported (Jacobi et al., 2007; Shibata et al., 2006; Townsend et al., 2003). In 2003, the treated wood was phased out in 2003, but it is projected that
a large number of CCA-treated wood remains its service until the 2040 (Khan et al., 2006). After its service time, some will be proposed into wood mulch.

Very limited information is available to report the adsorption of runoff pollutants with wood mulch (Jang et al., 2005). Jang et al. (2005) found that three types of wood mulch, i.e. cypress bark, hardwood bark, and pine bark nugget could slightly adsorb heavy metals in runoff, such as Pb and Zn. The adsorption was ascribed to the presence of biomaterials, because the quantity of biomass cells is related to the amount of extracellular polymeric substances (EPS) containing proteins, carbohydrates, nucleic acids, humic-like substances, lipids and heteropolymers (Jorand et al., 1998). The metal cations can be attracted to negatively charged acidic moieties of EPS. However, it should be noted that the adsorption capacity of wood mulch was poor in comparison with the adsorption with WTR. Jang et al. (2005) reported that the adsorption capacity of the wood mulch varied within 0.306 - 0.350 mmol/g for Pb and 0.185 - 0.187 mmol/g for Zn at 25°C. Saeed et al. (2005) found that papaya wood could adsorb 0.02 mmol/g Zn and 0.03 mmol/g Cu. However, the adsorption capacity of wood for heavy metals is much below that of WTR. Ching et al. (2012) reported the sorption capacity of WTR for Cu and Pb at 0.5-0.6 mmol/g.

As an organic matter, wood mulch inevitably decomposes over time on site. Decay rates of wood mulch are highly variable, depending on many factors such as wood species, climate conditions, and the soil environment (Duryea et al., 1999). Duryea et al. (1999) examined the decomposition rates of six different wood mulch, i.e. cypress, eucalyptus, pine bark, pine needle, melaleuca, and a utility trimming mulch (GRU). They found that eucalyptus and GRU mulches exhibited the greatest decomposition after 1 year (21% and 32%), whereas others only had the decay within 3% - 7%. The decomposition rate was negatively correlated with lignin and the
mass ratio of lignin to nitrogen. As the decomposition proceeds, different chemicals, including organic compounds and their decomposition products and different micro-nutrients, are gradually released (Bayala et al., 2005; Kannepalli et al., 2016; Schroth et al., 1992).

Among the leaching chemicals from wood mulch during its on-site use, the release of organic compounds is of interest due to a high mass fraction of organics in wood and because these compounds may play different roles to influence water, carbon and nitrogen dynamics as well as microbial community in the underlying soil (Findeling et al., 2007). For example, insoluble carbon biopolymers in organic mulch can be enzymatically hydrolyzed during decomposition to release aqueous compounds, which can serve as an electron donor for microorganisms to transform electrophilic contaminants in soil and groundwater (Ahmad et al., 2007). The degree of organic leaching from wood mulch is variable. Kannepalli et al. (2016) investigated organic leaching from the large-scale open storage of wood mulch at a wood recycling facility in New Jersey, USA. They concluded that the leachate from the mulch stockpiles could not be directly discharged into surface water because high concentrations of BOD5 (20-3000 mg/L) and TSS (69-401 mg/L) were observed.

Generally, wood cells include a variety of organic compounds such as cellulose, lignin, tannin, and resins. They are subject to decomposition, to different degrees, during the application of wood mulch. Although information on the decomposition of different organic compounds in wood mulch is very limited, mulch decay may refer to the procedure of wood decomposition (Kirk and Cowling, 1984). The procedure is briefly summarized as below. Lignin in wood prevents enzymatic decomposition of cellulose and hemicelluloses. However, the barrier can be destroyed by fungi, insects, and marine borers. Thereafter, cellulose is degraded by endo- and exo-glucanases and b-glucosidases, hemicelluloses by endo-glucanases and glycosidases, and
lignin by nonspecific enzymes. Different degradation products are produced from the
decomposition of different organic compounds. For example, cellulose is an abundant substance
in the cell walls. Fungi can transform cellulose into starch and then various forms of sugar. Cell
walls of wood progressively become tough with the disappearance of protoplasm and the
appearance of lignin (Barceló, 1997). Very little information is available for characterization of
the released organic compounds from wood mulch during application. Rather, aggregate organic
parameters, such as five-day biological oxygen demand (BOD₅) and chemical oxygen demand
(COD), were often used in previous investigations to study the organic leaching from wood
mulch (Ahmad et al., 2007; Saliling et al., 2007).

1.2 Nature and Scope of Research

This dissertation research aims at transformation of a widely used landscaping practice, i.e.
mulching, into an innovative, low-cost, and in-situ urban Stormwater Control Measure (SCM)
for addressing urban stormwater pollution. Wood mulch is commonly applied as a surface layer
in bioretention basins with multiple functions such as erosion prevention, weed control, and
moisture preservation. However, it has a poor adsorption ability for capturing many urban runoff
pollutants (Jang et al., 2005). Coating of wood mulch by WTR is hypothesized to
physiochemically functionalize the common wood mulch chips for pollutant removal. This study
utilized the complementary advantages of the two materials i.e., WTR and wood mulch. The
former has an adsorption potential (Chiang et al., 2012; O’Neill and Davis, 2012a), but a poor
hydraulic conductivity, while the latter allows water to readily flow through, but lacks an
effective adsorption capability. Therefore, the combination of these two materials into a new
composite filter media provides a potential advantage to overcome their respective drawbacks.
The expected benefits of this project are pronged: 1) to reduce pollutants entering the underlying
soil and groundwater; 2) to extend the lifetime of bioretention basins with periodic replacement of the surface modified mulch; and 3) to provide an industrial waste (i.e. Al-WTR) a second life through reuse to save costs.

This dissertation research represents a scientific and engineering effort to develop WTR coated wood mulch as a novel filter media for mitigation of metals and phosphate in urban stormwater. In this dissertation research, bench-scale batch and column tests were performed with both simulated and real urban stormwater. Contaminants tested in this study included three heavy metals (Cu, Zn and Pb) and phosphate. The four pollutants were selected due to their abundance in urban runoff and great public and ecological concerns. Other pollutants of concern are beyond the scope of this study. Furthermore, only Al-WTR was tested, rather than Fe-WTR. Al (hydr)oxides are a potentially better option in the stormwater treatment considering that they are more chemically stable under an anoxic environment, which represents a most likely condition when WTR is used for stormwater treatment. In contrast, Fe(III) in Fe(III) (hydr)oxides tends to be reduced to more soluble Fe(II) at an anoxic condition. For example, Nagar et al. (2010) compared the performance of Al- and Fe-WTR for arsenate adsorption over pH 3–9. They found that As(V) adsorption to Fe-WTR dropped down due to Fe-dioxide dissolution at pH 7–9, while Al-WTR maintained ~100% As(V) adsorption over the entire pH range.

1.3 Objectives and Hypothesis

The long-term goal of this study is to develop effective, low-cost, and sustainable in-situ stormwater treatment technologies to address stormwater pollution in an urbanized environment. The primary objective of this dissertation is to evaluate the performance of a novel filter media, i.e. Al-WTR-coated wood mulch, and develop the new filter media based stormwater treatment
technologies for alleviation of toxic metals and phosphate in urban stormwater. The central hypothesis is that Al-WTR as an active coating on wood mulch is capable of effectively and irreversibly adsorbing heavy metals and phosphate form urban runoff, while wood mulch as a supporter can significantly facilitate water infiltration during the application of the new modified mulch. To achieve the overall objective, the following three specific objectives were pursued:

**Objective I:** to synthesize and characterize Al-WTR coated wood mulch chips, and demonstrate technical feasibility (treatment and chemical leaching) of the new filter media for the treatment of polluted urban runoff;

**Objective II:** to determine key kinetics and isotherm parameters for Al-WTR adsorption of the selected metals and phosphate in batch tests using simulated polluted stormwater and to explore the sorption mechanisms behind the adsorption behaviors;

**Objective III:** to evaluate the short-term and long-term treatment performance of WTR-coated mulches under a continuous flow condition with simulated and real polluted stormwater, along with cost analysis and environmental impact studies.

1.4 Structure

Chapter 1: **Introduction** provides background information on urban stormwater pollution and points out key issues in current stormwater management. Brief literature review was made on existing urban stormwater treatment practices; the production, characteristics, and environmental application of water treatment residual; the mulching practices in the United States; and organic decomposition of wood mulch. Finally, the nature and scope of this dissertation research is proposed.

Chapter 2: **Material Characterization and feasibility Studies** describes a synthesis method to prepare the innovative composite filter media, characterized the Al-WTR coated wood mulch,
and conducted feasibility studies with the filter media to examine two aspects, i.e. treatability and chemical leaching.

Chapter 3: Batch and Mechanistic Studies gives key kinetic and isotherm data for the adsorption. It tries several kinetics and isotherm models to find the best fit to describe the adsorption process of studies elements by the fabricated filter media. It further explores the adsorption mechanisms running several experiments such as evaluating the effect of pH and ionic strength on the adsorption behavior of Al-WTR coated wood mulch.

Chapter 4: Column Studies investigates the short-term performance in continuous flow conditions with small column studies and a one-year semi-field large column tests to examine the long-performance of Al-WTR coated wood mulch with real stormwater runoff. In this chapter, key factors affecting the treatment performance, including mulch types (raw mulch vs. coated mulch) and the presence of plants, were determined. In the semi-field tests, the impacts of Al-WTR coated wood mulch on the quality of both runoff effluent and underlying soil were evaluated. Finally, preliminarily cost analysis was made.

Chapter 5: Conclusion discusses environmental management implications of this dissertation from environmental, economic, and social aspects, summarizes major conclusions from this dissertation research and recommends future research directions.
Table 1-1 Levels and sources of common heavy metals (Cu, Zn and Pb) in urban runoff provided by different references. Levels are varied due to the pollution level change in different urban areas and time difference between references.

<table>
<thead>
<tr>
<th></th>
<th>Concentration (µg/L)</th>
<th>Sources of toxic metals in urban areas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref.</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Pb</td>
<td>154</td>
<td>160</td>
</tr>
<tr>
<td>Cu</td>
<td>27</td>
<td>34</td>
</tr>
<tr>
<td>Zn</td>
<td>114</td>
<td>144</td>
</tr>
</tbody>
</table>

Ref \(^1\) (USEPA, 2006); \(^2\) USEPA (1983); \(^3\) Chin (2006)
Figure 1-1 Flowchart of a traditional filter plant setting for the production of drinking water (locations of coagulant addition and WTR production are indicated)
CHAPTER 2- MATERIAL CHARACTERIZATION AND TECHNICAL FEASIBILITY STUDIES
CHAPTER 2 MATERIAL CHARACTERIZATION AND TECHNICAL FEASIBILITY STUDIES

[Part of the work in this chapter was published in Chemosphere 154 (2016): 289-292]

2.1 Introduction

Urban stormwater runoff represents a major non-point pollution source in urbanized areas (Masters and Ela, 1991). Multiple pollutants have been identified in urban runoff, such as total suspended solids (TSS), toxic heavy metals, nutrients, synthetic organic compounds, salts, and pathogens (Davis et al., 2001; Gobel et al., 2007; Hedberg et al., 2014). Traditional urban stormwater management strategies focused on the reduction of peak flow rates to avoid flooding using gray infrastructures. However, low impact development (LID) techniques have been developed and practiced in many urban areas (Dietz, 2007; Hunt et al., 2010; New York City Environmental Protection, 2012). LID refers to the systems and practices that mimic natural processes for the infiltration, evapotranspiration or use of stormwater to protect water quality and aquatic habitats. Typically, LID techniques are used to simultaneously address both quality and quantity issues of urban stormwater.

A commonly used LID technique is bioretention basins that utilizes soil retention to remove stormwater pollutants and allow for infiltration (Hsieh and Davis, 2005). However, pollutants infiltrating into soil and groundwater may cause subsurface contamination; and toxic metal accumulation requires periodic replacement of top soil, making operation and maintenance more complex and costly (Weiss et al., 2008). Additionally, phosphorus (P) removal in LID systems is highly unstable and occasionally negative (Dietz and Clausen, 2006; Wu et al., 1996). Therefore, there is an urgent research demand for the development of new materials and technologies to address these issues.
WTRs are an industrial waste produced from coagulation in water treatment, primarily composed of amorphous Al or Fe hydroxides capable of adsorbing various pollutants (Makris et al., 2004). Recently, WTRs have been studied for stormwater treatment (Deng et al., 2012; O’Neill and Davis, 2012b). Application of WTRs as a filter media remains challenging because they readily clog to prevent water infiltration. On the other hand, wood mulch is a common surface layer with multiple functions in landscaping practices (e.g., moisture conservation and erosion prevention) (Turgeon et al., 2009). Although wood mulch can adsorb certain metals (Jang et al., 2005), it cannot be comparable with WTRs in terms of adsorption capacity based on the literature data (Chiang et al., 2012). Combination of the two individual materials into a composite filter media appears to be a logic design to keep the adsorption capability of WTR as well as possess an excellent hydraulic conductivity of wood mulch chips. To the best of our knowledge, there has not been any studies to combine the two materials into a composite filter media for the treatment of urban stormwater runoff.

The objectives of the research described in this chapter include: 1) to develop a method to appropriately synthesize Al-WTR coated wood mulch; 2) to characterize the Al-WTR coated wood mulch with different analytical techniques; and 3) to evaluate the technical feasibility of WTR-coated wood mulches for alleviation of heavy metals and phosphate in urban stormwater. The technical feasibility was evaluated in two aspects. Firstly, treatment trials with Al-WTR coated wood mulch were performed to examine the removal of four representative pollutants in a synthetic urban runoff. In this study, the representative runoff pollutants included three heavy metal cations (i.e. Cu\(^{2+}\), Zn\(^{2+}\), and Pb\(^{2+}\)) and one nutrient (i.e. phosphate), which were selected due to their threats to ecological and/or public health as well as their abundance in urban runoff, as discussed in Chapter 1. Secondly, two standardized chemical leaching tests, including the
synthetic precipitation leaching procedure (SPLP) and toxicity characteristic leaching procedure (TCLP), were performed to examine whether unwanted chemicals (e.g. adsorbed pollutants) might largely leach out at rainfall and landfill disposal scenarios, respectively. The study described in Chapter 2 represents the first step toward the development of an innovative modified wood mulch for the alleviation of pollutants present in urban runoff.

2.2 Methodology

Chemical reagents. All the reagents used were at least analytical grade, except as noted. Synthetic runoff was prepared with deionized water (Milli-Q water, 18.2 MΩ) containing 100 µg/L Pb²⁺, 800 µg/L Zn²⁺, 100 µg/L Cu²⁺, 2.30 mg/L P, 120 mg/L CaCl₂, (Fisher Scientific, NJ) and 10 mM piperazine-N,N'·bis (2-ethanesulfonic acid) (PIPES) (Acros Organics, NJ). Selected metals were added using their respective nitrate salts. P was provided from disodium phosphate (Na₂HPO₄). Pb, Zn, Cu, and P were provided from lead nitrate (Pb(NO₃)₂) (Fisher Scientific, Fair Lawn, NJ), zinc nitrate (Zn(NO₃)₂·6H₂O) (Fisher Scientific, Fair Lawn, NJ)), copper nitrate (Cu(NO₃)₂·2.5H₂O) (Acros Organics, NJ), and disodium phosphate (Na₂HPO₄) (Fisher Scientific, Fair Lawn, NJ), respectively. Initial pH was adjusted to 7.0 using 0.1 N NaOH (Acros Organics, NJ) or HNO₃ (Sigma Aldrich, USA). PIPES was used as a buffer chemical to maintain pH during the treatment.

Al-WTR coated mulch fabrication procedure. Al-WTR was collected from the Bridgewater Water Treatment Plant (Bridgewater, New Jersey, USA) in the October of 2014 (Figure 2-1). The WTR was completely mixed, dried by air, and then sieved through a 2-mm sieve (Deng et al., 2016). Timberline cedar wood mulch (Oldcastle lawn and garden Inc.) was purchased from a local HomeDepot store and then manually sorted. The mulch pieces with the size of approximately ~ 1 cm x 2 cm were selected, rinsed with deionized water three times to
remove impurities on the wood surface, and finally air dried. To properly coat the mulch with the Al-WTR powders, a mulch glue (Technisoil Global Inc., an environmentally friendly adhesive commercially available to bind mulch on ground for landscaping) was used. Selected wood mulch pieces were manually dipped in glue and then Al-WTR powders and left to air dry for one day at the room temperature. Figure 2-2 shows the appearance of the Al-WTR powders, raw wood mulch, and Al-WTR coated wood mulch.

**Experiments.** Treatment trials with Al-WTR coated wood mulch were performed in mini columns under a continuous flow condition at the room temperature (22°C). PVC (JM Eagle) columns (D=7.62 cm; H=15 cm) were loaded with 5 cm-depth WTR-coated mulches. A peristaltic pump (Reglo Digital MS-4/8, ISMATEC) was used to continuously feed the columns with the runoff (21 mL/min) through a shower head. After the synthetic runoff passed through designated numbers of bed volume, 5 mL effluent was collected and immediately filtered through 0.45 µm-pore sized cellulose nitrate membranes for water analysis. Filtered samples were stored in the cold room (4°C) until analysis. Before the ICP-MS analysis, 50 µL concentrated nitric acid (70%, Sigma-Aldrich) was added to the filtered sample. Bed volume (BV) is defined as the nominal volume of the filtration bed in the column (Crittenden et al., 2012). The number of BV is the ratio of water passing through the filtration bed to the bed volume. Here, the number of BV is used to indicate the volume of water for the filtration. The treatment trials proceeded until the number of BV reached 50. All the treatment tests were conducted, at least, in duplicates. For chemical leaching tests, two types of Al-WTR coated wood mulch were examined, including unused mulch and spent mulch after the column tests. The SPLP and TCLP tests followed the EPA SW-846 Methods 1312 and 1311, respectively.
**Analytical methods.** Solution pH was measured with a Thermo Fisher Scientific ORION 5-Star multiparameter meter (Thermo Fisher) after the water samples were filtered (0.45 µm) and acidified with the concentrated nitric acid. Metals were analyzed using an inductively coupled plasma-mass spectroscopy (ICP-MS Thermo X-Series II, XO 472). Phosphorus was spectrophotometrically measured using the reactive phosphorous test kits (HACH company). Surface morphology and elemental composition were measured with the scanning electron microscopy - energy dispersive spectroscopy (SEM-EDS) analysis using a Hitachi S-3400N instrument (Hitachi). SEM images of the raw wood mulch and Al-WTR coated wood mulch were captured with different resolutions in order to compare the surface morphology of these two media. The SEM images were also used to visualize the coverage of Al-WTR powders on the wood mulch and determine the optimal mass ratio of Al-WTR to wood mulch, at which, the mulch surface was properly and completely covered with the Al-WTR powders. EDS images provided qualitative information on surface elemental composition of the raw wood mulch, Al-WTR powders, and Al-WTR coated wood mulch. Furthermore, energy dispersive X-ray (EDX) analysis was conducted to further measure the quantitative elemental composition of these media. A CHNS analyzer (Elementar Company, Model: vario EL) was used to measure the mass content of carbon in the Al-WTR powder and raw wood mulch. All the data presented in the figures are the mean values of triplicates and their relative standard deviations were < 6.0%.

### 2.3 Results and Discussion

SEM images of raw wood mulch, Al-WTR powders, and Al-WTR coated wood mulch are presented in Figures 2-3, 2-4, and 2-5, respectively. The SEM images clearly showed a fibrous appearance for raw wood mulch (Figure 2-3). Surface of the fibrous structure was rough, providing the potential space for a coating of fine powders. The SEM images of Al-WTR
powders (Figure 2-4) showed the unique morphologic characteristics of Al-WTR, including: 1) that they had approximately round shapes; 2) that the grain sizes were much smaller than those of wood mulch chips, broadly varying from a few hundred to a few tens of micrometers; and 3) that the surface was highly rough, which provided a large specific surface area for capturing water pollutants. The SEM images of Al-WTR were very similar to those reported in other studies (Babatunde et al., 2009; Ippolito et al., 2003; Yang et al., 2006). We also compared the SEM images between Al-WTR and pure aluminum hydroxides (not shown here). Results show that Al-WTR was nearly amorphous, whereas pure aluminum hydroxide had a very regular crystalline structure. The difference could be caused by the poor crystallinity of aluminum hydroxide in Al-WTR and the presence of impurities.

Different mass ratios of Al-WTR to the sorted wood mulch were used to prepare the coated wood mulch. SEM images showed that the wood surface was completely covered at a mass ratio of 1:3 or greater (Al-WTR to wood mulch). In order to maximize the quantity of Al-WTR on the mulch surface, the optimal mass ratio of Al-WTR to wood mulch (1:3) was used in the following dissertation studies. SEM images of the Al-WTR coated wood mulch are shown in Figure 2-5. The surface morphology was very close to that of Al-WTR powders, suggesting that the wood mulch surface had been modified with Al-WTR.

Because the Al-WTR powders had very small sizes, the coating on the wood mulch was thin. Therefore, after coating, the size of modified mulch was not obviously altered. Based on the comparison in morphology, the new composite filter media possessed similar sizes and shapes with raw wood mulch chips but, had an Al-WTR surface. The surface coating allowed the modified mulch to have similar surface characteristics with Al-WTR powders. We expected that the filter media would overcome drawbacks of the two individual materials. That is, it can
readily allow for water infiltration like wood mulch chips and effectively immobilize various runoff pollutants like Al-WTR powders.

Coating of Al-WTR to wood mulch can alter the surface characteristics in two aspects. Firstly, the specific surface area can be significantly increased, providing more available spaces for capturing pollutants in water. We did not directly measure the BET surface areas of the Al-WTR or wood mulch. But the Al-WTR powders, which were collected in another batch from the same water treatment facility, was reported to have a specific surface area of 223.36 ± 3.14 m²/g (Deng et al., 2012). The high specific surface area is not only due to its small size, but also because of porous structure and even the presence of nanosized particles (Ippolito et al., 2011b). In contrast, the specific surface area of wood mulch chips was reported to range between 0.03-0.49 x 10⁻³ m²/g (Lunguleasa et al., 2009), depending on the wood species and chip sizes. Therefore, the wood mulch modified with Al-WTR has a much greater surface area than common wood mulch. Secondly, more active functional groups were granted to the mulch surface. One of the most important moieties from Al-WTR is the surface hydroxyl group, ≡Al-OH. It is well known that the functional group plays a key role in the adsorption of various cationic metals and anions in water (Stumm, 1992).

EDS graphs of Al-WTR powders, Al-WTR coated mulch, and raw wood mulch are presented in Figure 2-6. Abundant Al was observed in the Al-WTR powder and Al-WTR-coated mulch, but not noticed in the raw wood mulch, due to the successful coating of WTR on the wood surface. Other researchers also characterized Al-WTR as an amorphous material mainly made of Al (Babatunde et al., 2009; Gallimore et al., 1999; Ippolito et al., 2003). Besides Al, other elements were also identified, including Ca, Fe, K, Si, P, S, and Cl. These findings suggest that Al-WTR was a heterogeneous mixture of different chemical species, which allowed it to be
distinct from pure amorphous aluminum hydroxides. Some of the aforementioned elements in our Al-WTR have been identified in other studies (Ippolito et al., 2003; Makris et al., 2004). Ippolito et al. (2003) found Al in their Al-WTR samples. Makris et al. (2004) identified Fe, P, Si, and Ca in Al-WTR. These elements are originally from drinking water sources and the chemicals added for treatment at water treatment plants. For example, Ca is likely from hardness in raw water or lime added for pH adjustment in water treatment; Si is the major element in clays in raw water; S is from sulfate present from aluminum sulfate, which is the coagulant dosed for the removal of water turbidity; and, K, P, and Cl are common elements present in natural water sources.

EDX analysis provided the quantitative mass fractions of several major elements of the three filter media (Table 2-1). Al accounted for 8.3% and 7.5% of the Al-WTR powder and Al-WTR coated mulch, respectively, in terms of mass. The level was slightly below the average Al content (11.8%) of Al-WTR in the literature from 2005-2008 (Ippolito et al., 2011b). In contrast, wood mulch only had 0.5% Al in the overall mass. The finding again validates the predominance of aluminum (hydr)oxide on the Al-WTR coated mulch, in agreement with the aforementioned finding in the EDS analysis. Another abundant element in Al-WTR and Al-WTR coated mulch was Si, which most likely originated from minerals present in water sources and/or captured by Al coagulant in water treatment. A large number of various minerals are present in natural water sources. Some of them exist in the form of colloids and significantly contribute to turbidity in water. The major purpose of coagulation in water treatment is the removal of water turbidity. Addition of coagulant (e.g. alum) can compress the electrical double layers on the colloids to destabilize them from water. Consequently, these colloidal particles gradually aggregate with aluminum hydroxide to form flocs, which later settle in sedimentation basins to become WTR
(Erickson et al., 2013). Many Si-containing minerals have been found in Al-WTR, such as quartz and feldspar (Ippolito et al., 2009). It should be noted that EDX only provides elemental composition at the sample surface. In this study, Al-WTR was the major substance on Al-WTR coated mulch. Therefore, it is not surprising that the EDX results of Al-WTR and Al-WTR coated wood mulch were similar.

Results from the CHNS analysis for Al-WTR and wood mulch show that wood mulch had a much greater C content (23.87 ± 0.05%) than Al-WTR (5.74 ± 0.59%). Carbon in wood mulch originates primarily from abundant organic matter such as lignin and cellulose fibers. In contrast, carbon in Al-WTR might derive from two sources: 1) inorganic carbon in the form of carbonate and/or bicarbonate which originally contributes to water alkalinity; and 2) organic carbon in natural organic matter present in water source and/or captured by alum flocs during water treatment. Carbon content in Al-WTR in this study was lower than the carbon levels reported in other literature (Makris et al., 2004). The difference is caused due to the different source water quality and different water treatment operations between this study and others. The water source from this study was a local river with a relatively low NOM level (typically below 2.0 mg/L DOC). Moreover, the Al-WTR used in several other studies was collected from water treatment facilities that also dosed activated carbon, which could greatly increase the C fraction in the WTR.

Treatment trials with the Al-WTR coated wood mulch were performed under a continuous flow condition. Results are presented in Figure 2-7. As the number of BV increased from 1 to 50, the effluent Pb, Zn, and Cu varied at 0.5 - 8.9%, 33.4 - 46.7%, and 45.8 - 55.8% of their respective initial concentrations. Over the entire filtration period, the total removed Pb, Zn and Cu were estimated at 33.7, 211.8, and 15.9 µg/cm depth coated mulch, respectively, with an
order of Zn > Pb > Cu. In contrast, the effluent P exhibited a different removal pattern. It rapidly increased from 6.4% to 51.9% of the initial P with an increasing BV from 1 to 16. As BV further increased to 36, the effluent P gradually dropped to 34.7%. Thereafter, it almost stabilized until BV reached 50. The overall P removal was estimated at 0.67 mg/cm depth coated mulch.

Of note, the purpose of these trials was to examine whether the Al-WTR coated wood mulch was capable of effectively removing typical runoff pollutants, not for the evaluation of short or long-term performance. The treatment results are encouraging. In practices, mulch is directly added on the top of soil. When runoff is generated and flows over the mulch filtration bed, it flows down through the mulch bed due to a much higher hydraulic conductivity of wood mulch than that of soil and concrete. Depending upon the runoff quantity and hydraulic conductivity of the underlying soil, the runoff may have different contact times with the mulch. At any situation, the runoff treatment with wood mulch is operated under a continuous flow condition, at which the water continuously flows into and out of the mulch filtration bed. Therefore, the treatment trials in this chapter was designed in mini-columns to simulate the realistic runoff flow environment.

In order to examine whether adsorbed pollutants could leach from the filter media at different scenarios, SPLP and TCLP tests were performed, separately. Two types of mulch were used, including unused coated wood mulch and spent one. The spent mulch was collected from the above column tests. SPLP is a standard EPA method to determine the leaching potential of waste under a simulated exposure-to-rainfall environment. And the TCLP test simulates a typical municipal landfill condition to quantify chemical leaching from the waste and determines whether wastes can be disposed of as non-hazardous wastes in municipal landfills. The leaching
results are shown in Table 2-2. Concentrations of the leached contaminants were all below the U.S. SPLP and TCLP criteria.

The leaching results suggest that the release of undesired chemicals under rainfall or landfilling conditions is not a concern during their application in practice. The minimal leaching is caused by the strong binding between the pollutants and Al-WTR coated wood mulch. The two leaching tests reflect two phases of the Al-WTR coated mulch during its lifetime, respectively. In the first phase, Al-WTR coated mulch is used on site. Because the suggested lifetime for common mulching practices in the United States is one year, we would consider one year to be the working duration of the coated mulch during application. SPLP tests highlights that little desorption from Al-WTR coated mulch occurs during use. Once the old Al-WTR coated wood mulch is replaced with the new one, the old one is regarded as a solid waste in the second phase. The common solid waste disposal approach in the United States is landfilling. TCLP provides an estimate of chemical leaching for the Al-WTR coated mulch waste during landfill disposal. TCLP analysis specifically measure 8 hazardous chemicals i.e. Ag, As, Ba, Cd, Cr, Hg, Pb and Se. SPLP measures the same chemicals except for Cr. The results recommend that unused and used Al-WTR coated wood mulches are not a hazardous solid waste. Therefore, it can be safely disposed of in municipal landfills without special cautions.

The innovate filter media for urban stormwater treatment deserves further investigations for its application in a real world. However, three key questions are raised for the following studies:

Firstly, are the adsorption behaviors kinetically or thermodynamically controlled? When an adsorption process gradually occurs, the effluent from the bottom of a mulch filtration bed will heavily rely upon the adsorption kinetics. In this situation, contact time will play an essential role in the effluent concentrations. At a given reaction rate constant, a longer contact time
corresponds to a lower effluent concentration. It should be noted that the contact time for the
treatment of stormwater with the modified mulch ranges varies within a limited range in a real
world. That is, runoff rapidly flow through the mulch layer and down into the underlying soil.
The duration varies between a few minutes to several tens of minutes, depending on the runoff
flow rate, the depth of a mulch filtration bed, and the hydraulic conductivity of underlying soil.
Under the other situation, if the adsorption is instantly completed, the effluent concentration will
only depend on the adsorption isotherm data, as long as the adsorbent is undersaturated.
Therefore, contact time is not a key factor for the engineering design at a thermodynamically
controlled situation. Rather, the adsorption capacity of the adsorbent will be of essence. Design
will be built on the assumption that a sufficient quantity of adsorbent should be employed during
the engineering design lifetime.

Secondly, what are the mechanisms behind the adsorption behaviors? Adsorption of
phosphate and metal cations by metal hydroxides were previously investigated. Different
mechanisms were proposed to explain the adsorption behaviors (Sposito, 1995; Stumm, 1992).
Ligand exchange and electrostatic attraction were used to explain phosphate adsorption onto
metal oxides. Electrostatic interaction and surface complexation were proposed for the
adsorption of metal cations. Different adsorption mechanisms can greatly influence the
adsorption and desorption behaviors for the application of coated mulch. If inner-surface
complexes are formed between the solid surface and pollutants, the binding is strong, and
desorption of the adsorbed pollutants rarely occurs. In contrast, when an outer-sphere surface
complexation takes place, the adsorption is reversible. This may be risky for the application
because unwanted pollutants can again enter into the urban environment.
Thirdly, what are the long-term on-site treatment performance of Al-WTR coated wood mulch? Many factors may influence its adsorption effects, such as pH, temperature, pollutant strengths, and hydraulic patterns. Treatment performance can be maximized through the optimization of engineering design. When Al-WTR coated wood mulch is applied to a traditional bioretention basin, what are the effluent concentrations from the overall treatment system? What is the pollution extent of underlying soil in bioretention basins?

2.4 Conclusion

Work presented in this chapter serves as the first step toward the development of Al-WTR coated wood mulch for the treatment of polluted urban stormwater. The major contributions from this work are summarized as follows.

1) The method to synthesize coated mulch was developed and the optimal mass ratio of Al-WTR to wood much, at which the wood surface was completely covered by Al-WTR, was determined. The most favorable ratio, 1:3, would be used for the coated mulch in the following dissertation studies.

2) The prepared Al-WTR coated mulch was characterized. Results from the surface characterization show that the mulch surface was modified after the coating. The characteristics of Al-WTR coated wood mulch were close to those of Al-WTR powders, rather than wood mulch. However, the wood mulch serves as a supporter to enable a high hydraulic conductivity. Synthesis of the WTR-coated mulch provides a potentially effective approach to address the issues of WTR and wood mulch in stormwater treatment: 1) WTR capable of adsorbing various pollutants tends to clog for preventing stormwater infiltration; and 2) wood mulch has an excellent capability
to permit water infiltration but, possesses a poor adsorption capacity for water pollutants.

3) Treatment trials showed the removal capability of the new WTR-coated wood mulch for four typical urban runoff pollutants. Meanwhile, TCLP and SPLP results suggest that the pollutant adsorption to the WTR-coated mulch was mostly irreversible. Therefore, the desorption of unwanted chemicals is not a concern during its on-site treatment. And it can be safely disposed in a common municipal landfill after use.

The encouraging results demonstrate that Al-WTR coated wood mulch is a promising filtration media for alleviation of urban stormwater pollution. It deserves further investigations for engineering applications. A few key questions are raised for the in-depth development of stormwater treatment technologies with the innovative filter media, including 1) is the adsorption controlled kinetically or thermodynamically? 2) what are the adsorption mechanisms? And 3) what are the long-term on-site adsorption performance? Answers would be sought in the following studies.
Figure 2-1 Collection of water treatment residuals from a local water treatment plant: (a) American water treatment plant, Bridgewater, NJ, USA; (b) the Al-WTR disposal site within the treatment plant
Figure 2-2 Mulch coating procedure (a) Al-WTR powder; (b) Raw wood mulch; (c) Al-WTR coated wood mulch
Figure 2-3 SEM images of raw wood mulch
Figure 2-4 SEM images of Al-WTR powders
Figure 2-5 SEM images of Al-WTR coated wood (mass ratio of Al-WTR to wood mulch = 1:3)
Figure 2-6 EDS images: (a) Al-WTR powder; (b) Al-WTR coated wood much; (c) raw wood mulch
Table 2-1 EDX analysis- Elemental composition of wood mulch, Al-WTR and Al-WTR coated wood mulch

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<tr>
<th>Element</th>
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<td></td>
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</tr>
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<td>5.1%</td>
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</tr>
<tr>
<td>Fe</td>
<td></td>
<td>1.6%</td>
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</tr>
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<td>K</td>
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</tr>
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<tr>
<td>Rb</td>
<td></td>
<td>-</td>
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Figure 2-7 Effluent pollutant concentrations vs. the BV number during the WTR-coated wood mulch adsorption of Pb, Zn, Cu and P in synthetic polluted water (column tests) (WTR = 10 g/L; pH = 7.0; initial concentrations: Cu = 100 µg/L, Zn = 800 µg/L, Pb = 100 µg/L, and TP = 2.30 mg/L; relative standard deviations were less than 6.0%, not shown in the figure).

(Soleimanifar et al., 2016)
Table 2-2 Results and criteria of SPLP and TCLP tests for the unused and spent WTR-coated mulches (the spent WTR-coated mulch was collected from the column tests)

<table>
<thead>
<tr>
<th></th>
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<th>Ba</th>
<th>Cd</th>
<th>Cr</th>
<th>Hg</th>
<th>Pb</th>
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<td><strong>SPLP Tests</strong></td>
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<tr>
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<td>1.972</td>
<td>10,230</td>
<td>3.295</td>
<td>29.330</td>
<td>2.015</td>
<td>2.043</td>
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<td>1,766</td>
<td>0.803</td>
<td>3.918</td>
<td>1.861</td>
<td>0.593</td>
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<td>3</td>
<td>120,000</td>
<td>80</td>
<td>N/A</td>
<td>40</td>
<td>100</td>
<td>800</td>
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<tr>
<td><strong>TCLP Tests</strong></td>
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<tr>
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<tr>
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<tr>
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<td>100,000.0</td>
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<td>5,000.0</td>
<td>200.0</td>
<td>1,000.0</td>
<td>5,000.0</td>
</tr>
</tbody>
</table>

<sup>1</sup>SPLP criterion: the higher of the health-based leachate criteria or aqueous practical quantitation levels (PQLs) when very little or no site specific information is available (NJDEP, 2013).

<sup>2</sup>TCLP criterion: maximum concentrations of contaminants for the toxic characteristics from 40 CFR 261.24 - Toxicity characteristic. (Soleimanifar et al., 2016)
CHAPTER 3- BATCH STUDIES FOR AI-WTR COATED WOOD MULCH ADSORPTION OF SELECTED RUNOFF POLLUTANTS
CHAPTER 3 BATCH STUDIES FOR Al-WTR COATED WOOD MULCH ADSORPTION OF SELECTED RUNOFF POLLUTANTS

3.1 Introduction

In this chapter, bench-scale batch experiments were performed to find the answers to the first two questions in Chapter 2 (i.e. is the adsorption kinetically or thermodynamically controlled? and what are the adsorption mechanism). Studies from Chapter 2 developed a method for synthesis of a composite Al-WTR coated wood mulch by binding Al-WTR powders on wood mulch. Al-WTR is the byproduct of coagulation step in water treatment plants. It has been demonstrated to serve as an effective adsorbent for heavy metals and phosphate (Chiang et al., 2012; Deng et al., 2016; Ippolito, 2003; Makris et al., 2004; O’Neill and Davis, 2012a). The modified wood mulch is more like Al-WTR powders in terms of surface characteristics, but it has a larger size similar to common wood mulch. Therefore, it overcomes the drawbacks of the two individual materials, i.e. a poor hydraulic conductivity of Al-WTR powders and an inactive surface of wood mulch for adsorbing runoff pollutants. The composite filter media ensures the basic functions of common mulch but, possesses a very active surface capable of capturing different pollutants present in urban runoff. Treatment trials in Chapter 2 provided important information in three aspects: 1) the optimal mass ratio of Al-WTR to wood mulch was determined and would be used in the following dissertation studies; 2) Al-WTR coated mulch is able to effectively adsorb phosphate and heavy metal cations in urban runoff; and 3) the adsorbed pollutants cannot largely leach from the filter media during on-site application or during waste disposal in landfills, suggesting a strong and irreversible binding.

To develop the new filter media for the control of urban stormwater pollution, laboratory-scale batch experiments were performed. During the batch adsorption tests, solution was under a completely mixed state without any inflow or outflow. Under the strictly controlled laboratory
conditions, three tasks were completed, including: 1) to determine the kinetic and isotherm adsorption patterns of Al-WTR coated wood mulch for adsorbing selected runoff pollutants; 2) to explore the mechanisms behind the pollutant adsorption; and 3) to discuss the significance of the experimental data and reaction mechanisms to engineering design with the modified mulch. Meanwhile, effects of key factors likely affecting the adsorption behaviors were evaluated, including solution pH, reaction temperature, and ionic strengths. Data acquired from the batch studies would provide key information to support ensuing column studies.

3.2 Methodology

Chemical Reagents. All the reagents used were at least analytical grade, except as noted. Two pollutant solutions were prepared, i.e. the single-pollutant solution (SPS) and multiple-pollutants solution (MPS), for the batch tests. In the treatment experiments in SPS, solution contained a single pollutant (Cu\(^{2+}\), Zn\(^{2+}\), Pb\(^{2+}\) or P), 0.01 M potassium chloride (KCl) (Sigma Aldrich, NJ), and 5 mM piperazine-N,N′-bis (2-ethanesulfonic acid) (PIPES) (Acros Organics, NJ). PIPES was used to buffer solution pH during the adsorption. MPS was prepared with chemical composition of a synthetic urban runoff reported elsewhere (Davis et al., 2006; Hsieh and Davis, 2005): 0.1 mg/L Cu\(^{2+}\), 0.6 mg/L Zn\(^{2+}\), 0.1 mg/L Pb\(^{2+}\), 3.10 mg/L PO\(_4^{3-}\)-P, 2 mg/L NO\(_3^{-}\)-N, 2 mg/L NH\(_4^{+}\)-N, 120 mg/L CaCl\(_2\) (Fisher Scientific, NJ) for total dissolved solids (TDS), 40 mg/L CaCO\(_3\) (Sigma Aldrich, Japan) for alkalinity, 0.01 M KCl (Sigma Aldrich, USA) for ionic strength, 5 mM PIPES and 20 mg/L used motor oil. Water pH was adjusted to 6.0, 7.0 or 8.0 using 0.1 N NaOH (Acros Organics, NJ) and HNO\(_3\) (Sigma Aldrich, USA). All the heavy metals were externally added from their respective nitrate salts. Pb, Zn, Cu, and P were provided from lead nitrate (Pb(NO\(_3\))\(_2\)) (Fisher Scientific, Fair Lawn, NJ), zinc nitrate (Zn(NO\(_3\))\(_2\)·6H\(_2\)O) (Fisher Scientific, Fair Lawn, NJ), copper nitrate (Cu(NO\(_3\))\(_2\)·2.5H\(_2\)O) (Acros
organic, 98+%), and disodium phosphate (Na₂HPO₄) (Fisher Scientific, Fair Lawn, NJ), respectively. NO₃⁻ N was provided adding NaNO₃ (Acros Organics, NJ). NH₄⁺-N was provided by adding NH₄Cl (Sigma Aldrich, USA).

**Al-WTR coated mulch fabrication procedure.** Al-WTR was collected from the Bridgewater Water Treatment Plant (Bridgewater, New Jersey, USA) (Figure 2-1) once in October 2014. The WTR was completely mixed, dried by air, and then sieved through a 2-mm sieve (Deng et al., 2016). Timberline cedar wood mulch (Oldcastle lawn and garden Inc.) was purchased from a local HomeDepot store and then manually sorted. The mulch pieces with the size of approximately ~ 1 cm x 2 cm were selected, rinsed with deionized water three times to remove impurities like dust on the wood surface, and finally air dried. To properly coat the mulch with the Al-WTR powders, the mulch glue (Technisoil Global Inc.), an environmentally friendly adhesive commercially available to bind mulch on ground for landscaping, was used. Selected wood mulch pieces were manually dipped in glue and then Al-WTR powders and left to air dry for one day at the room temperature. The Al-WTR coated wood mulch (~ 1 cm x 2 cm) was prepared in a mass ratio of WTR to mulch at 1:3.

**Batch adsorption experiments.** Bench-scale batch tests were conducted to obtain key kinetic and adsorption isotherm data. Adsorption tests were carried out using 1 L synthetic urban stormwater (SPS or MPS) on a rotary shaker (Associated Design and MFG. Co., Model: 3740-8-BRE) (200 rpm) at room temperature (22°C). Solution pH was manually adjusted to a designated level. Once an appropriate weight of Al-WTR coated mulch or Al-WTR powders was added, the adsorption tests were initiated. During the adsorption, pH was not controlled. The pH variation throughout the entire adsorption tests was insignificant (< ± 0.1). In the kinetics tests, 5 ml samples were periodically withdrawn at designated time intervals. In the isotherm adsorption
tests, samples were collected after the adsorption proceeded for 24 hours. Once an aliquot of sample was collected, it was filtered through 0.45 µm membrane before analyses.

To understand the effect of stormwater pH, adsorption kinetic tests were also performed in the synthetic runoff with multiple pollutants at a fixed WTR-coated mulch concentration (10 g/L). Three different pH levels, i.e., pH= 6.0, 7.0 and 8.0, were tested at room temperature. To determine the effect of temperature. Another set of tests were carried out at the identical condition with those to study the pH effect, except that pH was fixed at 7.0 and temperature was set at a low (12°C at a water bath (Thermo Fisher Scientific, Model: 2870) with ice packs), medium (22°C, room temperature) or high level (32°C of a water bath). In the experiments to study the effect of ionic strength, ionic strength was varied within 0.005 – 0.5 M KCl in SPS with 10 mg/L P and 1 g/L Al-WTR powders. Results on the ionic strength-dependence of Al-WTR adsorption behaviors provide a simple but valuable method to determine whether surface complex formation between Al-WTR and water pollutants is an inner or outer-sphere complexation reaction. A decreased pollutant adsorption with an increased ionic strength implies the formation of an outer-sphere complexes, while the independence of ionic strength in pollutant adsorption or a positive relationship between ionic strength and pollutant adsorption typically occurs for the inner-sphere complex formation (Goldberg and Johnston, 2001). In other words, if the adsorption decreases with the increasing ionic strength, an outer-sphere surface complex occurs; otherwise, inner-sphere surface complexes are formed.

**Adsorption kinetic and isotherm models.** In this study, the removal efficiency (% removal) is defined as below.

\[
\%\text{Removal} = \frac{c_i - c_f}{c_i} \times 100
\]

Eq. (3-1)
Where, \( C_i \) and \( C_f \) represent the initial and final pollutant concentrations in water, respectively.

Adsorption capacity (q, mg/g), defined as the mass ratio of the pollutant adsorbed (mg) to the adsorbent (g), can be determined as below.

\[
q = \frac{(C_i-C_f)V}{m}
\]

Eq. (3-2)

Where, \( V \) is the volume of solution (L); and \( m \) is the mass of adsorbent (i.e. Al-WTR coated mulch or Al-WTR powders in this study) (g).

Two types of kinetic models were used in this study to fit the experimental data. The first three kinetic models, i.e. the 0th order, 1st-order and 2nd-order kinetic models, focus on the change rate of pollutant concentration in the water phase.

\[
C_i - C_f = k_0 t
\]

Eq. (3-3)

\[
\ln(C_i - C_f) = k_1 t
\]

Eq. (3-4)

\[
\frac{1}{C_i} - \frac{1}{C_f} = k_2 t
\]

Eq. (3-5)

Where, \( t \) is contact time; \( C_i \) and \( C_f \) are the concentrations at time 0 and any time \( t \), respectively; and \( k_0, k_1, \) and \( k_2 \) are the reaction rate constants for the 0th, 1st, and 2nd order reactions, respectively.

The second type of kinetic models are used to describe the change rate of an adsorbate on an adsorbent, including the pseudo 1st and 2nd order reactions, which are also called the Lagergren and Ho models, respectively (Qiu et al., 2009).

\[
\ln(q_e - q_t) = \ln q_e - k t
\]

Pseudo-1st order

Eq. (3-6)
\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]  

Pseudo-2\textsuperscript{nd} order  

Eq. (3-7)

Where, \( q_t \) and \( q_e \) are the mass ratios of the adsorbate to the adsorbent at any time \( t \) and chemical equilibrium, respectively.

Three adsorption isotherm models were used to fit the experimental data at chemical equilibrium, including the Langmuir, Freundlich and Temkin models (Vadi and Rahimi, 2014). Linearized equations of the aforementioned isotherm models are as follows.

\[
\frac{c_e}{q_e} = \frac{1}{b q_{\text{max}}} + \frac{c_e}{q_{\text{max}}}
\]  

Langmuir  

Eq. (3-8)

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]  

Freundlich  

Eq. (3-9)

\[
q_e = B \ln A_t + B \ln C_e
\]  

Temkin  

Eq. (3-10)

Where, \( A_t \), \( B \), \( K_f \), \( n \) and \( b \) are constants. The Langmuir and Freundlich models are the mostly used ones in the adsorption process for water treatment (Crittenden et al., 2012). The former one is built on the assumption that all the adsorption sites on an adsorbent are similar in terms of their energy, while the latter considers the heterogeneity of surface. Furthermore, the Langmuir model is the one for the adsorbate accumulation, at the maximum, at one single layer on the sorbent surface. In contrast, the Freundlich model is the one for a multi-layer adsorption. The Temkin model considers the interaction between adsorbent and adsorbate (Vadi et al., 2010). It is built on the assumption that a linear change in the heat of adsorption, instead of a logarithmic one, occurs.

**Analytical methods.** Solution pH was measured with a Thermo Fisher Scientific ORION 5-Star multiparameter meter. Metals were analyzed using an inductively coupled plasma-mass spectroscopy (ICP-MS Thermo X-Series II, XO 472) after the samples were filtered (0.45 µm).
and acidified. Phosphorus was spectrophotometrically measured using reactive phosphorous test kits (HACH company). All the treatment tests were conducted, at least, in duplicates.

3.3 Results and Discussion

3.3.1 Kinetics studies

Kinetics tests were performed at five different sorbent concentrations (i.e. 5, 10, 25, 35, and 50 g/L Al-WTR coated mulch). For any selected pollutant, its residual concentration in water decreased with contact time. For example, Figure 3-1 (a) and (b) present the kinetic data of residual P concentrations with contact time in SPS and MPS, respectively. As the time increased from 0 to 1440 min, the residual P in water gradually went down from the initial 3.10 mg/L to 0.05-0.21 mg/L in SPS and 0.01-0.19 mg/L in MPS at the coated mulch concentration of 5-50 g/L, separately. Of interest, at any specific contact time, the residual P concentration was decreased with the increasing coated mulch concentration. For example, at 20 min and in SPS, the residual P was 2.71, 2.25, 1.29, 0.72, and 0.29 mg/L at 5, 10, 25, 35, and 50 g/L Al-WTR coated mulch, respectively, corresponding to the removal efficiencies of 14%, 30%, 61%, 80%, and 91%. This finding is primarily because more filter media provided more active sites on the coating for the capture of phosphate in the water phase. Very similar patterns were also observed for the other three selected pollutants.

Experimental kinetic data for all the four selected pollutants were fitted to the five different kinetics models. Parameters of different kinetic models are obtained and summarized in Table 3-1. Results showed that the pseudo 2nd order kinetic models consistently fitted the measured data well at any specific sorbent concentration ($R^2 > 0.96$), regardless of the pollutant species in SPS or MPS. For example, experimental kinetic data and pseudo 2nd order kinetic model data of Al-WTR coated wood mulch adsorption of P in SPS and MPS are shown in Figure 3-2(a) and (b),
respectively. As seen, the modelled data well fitted the measured data. For all the other selected runoff pollutants, Al-WTR coated mulch exhibited the same adsorption kinetic patterns (Table 3-1).

The observed kinetic behaviors of Al-WTR coated mulch for the selected runoff pollutants are in agreement with several previous studies that various aluminum hydroxide products for the adsorption of phosphate or metals obeyed the pseudo 2\textsuperscript{nd} order kinetic reactions (Namasivayam and Prathap, 2005; Yan et al., 2010). The pseudo 2\textsuperscript{nd} order kinetic reactions were demonstrated to well describe metal hydroxides and other adsorbents for capturing various water pollutants. A literature review was conducted to compare the pseudo 1\textsuperscript{st} and 2\textsuperscript{nd} order kinetic models when literature data of different adsorption kinetic studies were fitted to these models (Ho and McKay, 1999). In the literature, different sorbents and biosorbents were used to treat polluted aqueous effluents containing dyes, organics, or metals. Result show that, in the most cases, chemical reaction appeared significant in the rate-controlling step and the pseudo-second order chemical reaction kinetics provided the best correlation with experimental data, while the pseudo-first order model fitted the measured data well only during the beginning phase of adsorption.

Two parameters are important in a pseudo 2\textsuperscript{nd} order kinetic model. Firstly, $q_e$ represents the adsorption capacity at equilibrium (Ho and McKay, 1998). Results from the above kinetic tests provided the estimates of the maximum adsorption capacities for the four selected runoff pollutants. The data is of significance because it can be used to predict the duration of Al-WTR coated wood mulch, during which a runoff pollutant of interest becomes saturated. Therefore, the information can be used to estimate the lifetime of the modified wood mulch during application. On the other hand, $k$ in the pseudo 2\textsuperscript{nd} order model is a rate constant. Generally, a higher $k$ implies a faster adsorption rate of the filter media for a target pollutant.
In order to further investigate variations of the two key parameters with the concentration of Al-WTR coated mulch, \(q_e\) and \(k\) are plotted against mulch concentration for the innovative filter media adsorption of the four selected runoff pollutants in SPS or MPS (Figure 3-3). For each pollutant, the adsorption capacity was decreased with the increasing adsorbent concentration from 5 to 50 g/L in the solution, regardless of SPS or MPS. For example, in SPS, \(q_e\) was deceased from 3.79 to 0.41 mg/g for P, from 0.076 to 0.014 mg/g for Cu, from 0.526 to 0.066 mg/g for Zn, and from 0.095 to 0.007 mg/g for Pb, separately. The finding indicates that the maximum adsorbed pollutant per unit mass of Al-WTR coated mulch declined with the mulch concentration, though a higher mulch concentration could achieve a lower pollutant concentration in water (Figure 3-1). The information is of importance to guide the designs with the innovative filter media. Appropriate quantities of the filter media ought to be considered in terms of the adsorption capacity to ensure a sufficient amount of adsorbent coating for capturing pollutants during the adsorbent lifetime in practices. Pollutant adsorption by Al-WTR coated wood mulch was not proportionally increased with the increased adsorbent concentration, implying that the pollutant adsorption to the Al-WTR coating gradually became difficult as the sorbent concentration increased.

Furthermore, different selected pollutants exhibited different adsorption patterns in SPS and MPS, as shown in Figure 3-3. Any significant difference for P removal was not observed between the two different matrixes, likely because phosphate has an extremely high affinity toward Al-WTR, so that the competition of other adsorbates for active adsorption sites for P was minor. In contrast, the three cationic metal removals were discounted in MPS than in SPS as a result of the adsorption competition among the different pollutants in water, because adsorption
of all the four selected pollutants shared the same active adsorption sites on the surface of Al-WTR coated wood mulch. The adsorption mechanisms would be discussed in detail later.

For each selected runoff pollutant, rate constant \( k \) increased with the increasing mulch concentration in SPS or MPS. For example, as the mulch concentration increased from 5 to 50 mg/L, \( k \) for P adsorption in SPS and MPS increased from 0.002 to 1.858 g/mg·min and from 0.004 to 1.223 g/mg·min, respectively (figure 3-3 (a)). The observation indicates that the Al-WTR coated mulch tends to more rapidly adsorb the pollutants at a higher filter media concentration. However, it is inappropriate to consider \( q_e \) or \( k \) alone, when the pollutant concentration in water needs to be estimated at any specific time. Instead, the both parameters need to be considered together.

Half-life of a pollutant in water is defined as the time length during which its concentration in water is reduced to a half of its initial level (Snoeyink et al., 1980). The indicator is commonly used to provide an estimation of the removal rate of a pollutant in water. Based on the definition, at a half-life (\( t_{1/2} \)), we have

\[
C_t = 0.5 C_0, \quad (t = t_{1/2}) \quad \text{Eq. (3-11)}
\]

After Eq. (3-11) is integrated into Eq. (3-7), we can conclude the following equation.

\[
t_{1/2} = \frac{c_0}{k(2c_sq_e^2-q_eC_0)} \quad \text{Eq. (3-12)}
\]

Where, \( C_0 \) is the initial pollutant concentration in water; \( C_s \) is the adsorbent concentration in water; \( q_e \) is the adsorption capacity for a specific pollutant; and \( k \) is the rate constant for the pseudo 2nd order reaction model. Eq. (3-12) reveals a complex relationship of the pollutant removal rate, which is indicated as \( t_{1/2} \), with \( q_e \), \( k \), and \( C_0 \). Generally, half-life of the pollutant
removal from the batch tests is inversely proportional to the rate constant, positively related to the initial concentration, but has a much more complex relationship with $q_e$. As demonstrated in Figure 3-3, as $C_s$ increases, $k$ increases, whereas $q_e$ decreases. Therefore, $t_{1/2}$ does not show a simple correlation with the mulch concentration.

3.3.2 Adsorption isotherm studies

Three different adsorption isotherm models were fitted with experimental equilibrium data at five different sorbent concentrations (i.e. 5, 10, 25, 35, and 50 g/L). The model parameters obtained from the fitting tests are summarized in Table 3-2. Generally, the Langmuir models were not well fitted with all the experimental data in terms of $R^2$ (0.33-0.86). Negative values observed for $Q_{max}$ (marked as “-”) further suggests that the isotherm model is not suitable for the adsorption patterns in this study. However, the Freundlich and Temkin models were both acceptable for the four selected pollutants in SPS or MPS ($R^2 > 0.82$), except that the isotherm data of P removal in MPS was poorly fitted with the Temkin model ($R^2 =0.71$). Figure 3-4 (a) and (b) clearly indicates that the Freundlich and Temkin isotherm models well fit the measured data at chemical equilibrium, respectively. The above observations (the Freundlich model, rather than the Langmuir model, was acceptable for this study) suggest that adsorption of the four pollutants did not occur in a mono layer.

It is of interest to compare the experimentally measured isotherm data with the estimated adsorption capacity for the selected pollutants, which was concluded from the kinetic tests (the pseudo 2nd order model). Results show that the relative deviations between the measured and projected adsorption capacity for the four pollutants varied within ± 9% (data not shown), indirectly validating that the pseudo 2nd order reaction kinetic model and the Freundlich isotherm model appropriately described the kinetic and isotherm behaviors in this study.
For each target pollutant, $q_e$ is of importance to estimate the adsorption capacity. The parameter will provide key information to compute the design quantity of Al-WTR coated mulch for stormwater treatment during a specific design lifetime. In order to compare the utilization efficiency of Al-WTR in the coated mulch for a target pollutant, $q_e$ in this study is compared with the adsorption maxima collected from literature using similar experimental conditions. Because $q_e$ is computed based on the assumption that the overall coated mulch serves as a composite adsorbent, it is impossible to directly compare our adsorption capacity with literature data using Al-WTR as an adsorbent. For example, at 5 g/L coated mulch, the P adsorption capacity of the coated mulch ($q_e$) is 3.54 mg/g Al-WTR which falls within the Al-WTR adsorption capacity range for P previously reported in literature (3.32 mg/g (Razali et al., 2007), 0.3-5.14 mg/g (Dayton et al., 2003), 9.1 mg/L (Makris et al., 2004), and 31.9 mg/g (Babatunde et al., 2009)). The finding implies that the WTR surface loss due to coating did not significantly reduce the P adsorption capacity of Al-WTR, though some surface of Al-WTR was occupied for binding the mulch surface.

### 3.3.3 Adsorption mechanisms

**Al-WTR adsorption of phosphate in water.** Once Al-WTR is dosed to water, the solid surface possesses charges in the most cases. The surface charge is produced due to acid-base equilibrium on the Al-WTR surface (Sposito, 1995).

\[
\equiv \text{AlOH} + H^+ = \equiv \text{AlO}H_2^+ \quad \text{or} \quad \equiv \text{AlOH} + \text{OH}^- = \equiv \text{AlO}^- + \text{H}_2\text{O} \quad \text{Eq. (3-13)}
\]

Where $\equiv \text{AlOH}$, $\equiv \text{AlO}H_2^+$, and $\equiv \text{AlO}^-$ represent different surface groups on Al-WTR. The pH at point of zero charge (i.e. $pH_{PZC}$) of various aluminum hydroxide products ranges between 8.2 and 9.1 (Stumm, 1992). It should be noted that pH used in this study was below the $pH_{PZC}$ range. Therefore, the Al-WTR coated mulch or Al-WTR powders were positively charged in water. The
positive charge decreased with the increasing pH. On the other hand, because phosphate was primarily anions at the pH range (pK_a^1 = 2.12, pK_a^2 = 7.21, and pK_a^3 = 12.67), the pH tested favored the phosphate adsorption on WTR via electrostatic attraction. The electrostatic bonding mechanisms are involved with the formation of outer-sphere complexes (Stumm, 1992).

Another plausible mechanism proposed in previous studies (Farley et al., 1985; Stumm, 1992) is ligand exchange. That is, the surface hydroxyl groups are exchanged with phosphate with the release of OH^- ions, leading to the formation of inner surface complexes (Lü et al., 2013). The dominant phosphate species at the tested pH range are H_2PO_4^- and HPO_4^{2-}:

\[ \equiv\text{AlOH} + \text{H}_2\text{PO}_4^- = \equiv\text{Al-H}_2\text{PO}_4 + \text{OH}^- \quad \text{Surface Complexation- monodentate Eq. (3-14)} \]

\[ 2(\equiv\text{AlOH})+ \text{HPO}_4^{2-} = 2\equiv\text{Al-HPO}_4 + 2\text{OH}^- \quad \text{Surface Complexation- bidentate Eq. (3-15)} \]

As seen above, as solution pH is decreased, more phosphate is adsorbed to the surface of aluminum hydroxide.

The effect of solution pH (6-8) on Al-WTR adsorption of phosphate with time was evaluated, as shown in Figure 3-5(a). As the adsorption proceeded, more P was immobilized to the solid phase at all the tested pH. Clearly, at any specific contact time, more P was adsorbed at a lower pH. For example, at 120 min, the adsorbed P was 91%, 75%, and 71% of the initial P (3.17 mg/L) at pH 6, 7, and 8, respectively. Although the results indicate the relationship between solution pH and the P adsorption efficiency, we cannot determine which of the two aforementioned mechanisms is the dominant one behind our experimental observations, because we can conclude that more phosphate is adsorbed to Al-WTR with the increasing pH based on either of the above plausible mechanisms, i.e. electrostatic attraction and ligand exchange.
It should be noted that the two possible reaction pathways produce different surface complexes. Electrostatic coulombic interactions result in the formation of outer-sphere complexes, which occurs only on the adsorbent surface with opposite surface charges (Strawn and Sparks, 1999). The adsorption involved with the formation of outer-sphere complexation is rapid but reversible. In contrast, inner-sphere complexes are formed when ions bind directly to the surface without the intervention of water molecules. Inner-sphere complexes are typically more stable than outer-sphere complexes, because they involves largely covalent bonding or combinations of covalent and ionic bonding (Stumm, 1992).

To distinguish between inner-sphere and outer-sphere complexes, the effect of ionic strength was assessed on the surface complex formation equilibria in this study. Ionic strength was varied by using different KCl concentrations (0.005 – 0.5 M) in SPS with 10.0 mg/L P and 1.0 g/L WTR powders. The effect of ionic strength on phosphate adsorption to Al-WTR is shown in Figure 3-6. The fraction of adsorbed P on Al-WTR was increased from 67% to 90% as the KCl concentration increased from 0.005 to 0.5 M, indicating that the phosphate adsorption was positively related to ionic strength. Goldberg and Johnston (2001) mentioned that ions that form inner-sphere surface complexes show little ionic strength dependence or show increasing adsorption with the increasing solution ionic strength. The stronger ion adsorption occurring at a higher ionic strength is due to the higher activity of the counter ions in solution available to compensate the surface charge generated by specific ion adsorption. Therefore, the observations in this study highlight the principle role of inner-sphere surface complexation in the Al-WTR adsorption of phosphate from water. The conclusion is in agreement with several previous studies that investigated the mechanisms of various aluminum hydroxide species for the
adsorption of phosphate using different approaches and techniques (e.g. solid-state NMR spectroscopy) (Li et al., 2013; Tanada et al., 2003; Yang et al., 2006; Zheng et al., 2012).

Although the results from the tests to study the ionic strength dependence suggest that the inner-sphere complexation is a dominant mechanism, we cannot rule out the potential role of electrostatic attraction for the phosphate adsorption. It is plausible that electrostatic attraction and inner-surface complexation sequentially occurred to complete the phosphate binding process onto WTR, because adsorption of ions via inner-sphere complexation is usually slower than outer-sphere complexation. The sequential adsorption procedure was reported to aluminum hydroxide adsorption of arsenate, which shares a very similar chemical structure with phosphate, in water (Zhu et al., 2009). Electrostatic attraction is a prerequisite condition enabling the migration of negatively charged phosphate from the bulk solution to the positively charged WTR surface. The ensuing inner-surface complexation achieved a strong binding of phosphate to the active adsorption sites and prevented phosphate accumulation on the outer surface, facilitating more phosphate adsorption.

**Al-WTR adsorption of cationic Cu, Zn, and Pb ions in water.** Effects of solution pH on the fractions of adsorbed Cu, Zn, and Pb cations on Al-WTR are shown in Figure 3-5(b), (c), and (d), respectively. As seen, the adsorbed metal fraction was increased with contact time for any selected pollutant. Clearly, the adsorption of Zn was increased as solution pH was increased from 6 to 8. At 60 min, the adsorbed Zn accounted for 19%, 63%, and 78% of its initial level at pH 6, 7, and 8, respectively. For Cu and Pb, a marked increase in the metal adsorption was observed as pH increased from 6 to 7 at which a very high adsorption fraction was observed (the adsorption fractions of Cu and Pb were 85% and 99%, respectively, at pH 7 at 60 min). When the solution pH further increased to 8, the adsorption of Cu and Pb was slightly increased (the
adsorption fractions of Cu and Pb were 89% and 100%, respectively, at pH 7 at 60 min). Overall, for any selected cationic metal, the adsorption was enhanced with an increasing pH. Different from anionic phosphate in water, these metals exist in the forms of positively charged ions in water. As discussed above, the Al-WTR surface remained positively charged under the tested pH range, though the positive charge became less with an increased pH. Therefore, electrostatic interaction cannot serve as a mechanism responsible for the adsorption of cationic metals in water.

The pH dependence of cationic metal adsorption on Al-WTR provides the evidence of surface complex formation with metal ions. The mechanism has been widely accepted to explain metal oxides for the adsorption of metal cations (Stumm, 1992). The cationic metals could be adsorbed to aluminum hydroxides through the coordination of the metal ions with the oxygen donor atoms and the release of protons from the surface, as follows.

\[
\equiv\text{Al-OH} + M^{2+} \rightarrow \equiv\text{Al-OM}^+ + H^+ \quad \text{Surface complexation} \quad \text{Eq. (3-16)}
\]

Where, M represents the cationic ions of Cu, Zn, and Pb. As seen, as pH is increased, the reaction tends to move from the right side to the left side, so that more dissolved metal ions became adsorbed.

Of note, based on the computation using Visual Minteq, the three metal pollutants remained in a dissolved state over pH 6.0-9.0 in the simulated runoff matrix. That is, precipitation did not occur in water with the pH increase in this study. However, precipitation might take place on the solid surface, where cationic metals were concentrated due to their adsorption onto the WTR. Surface precipitation has been proposed for the adsorption of cations
on metal oxides (CsoBán and Joó, 1999; Farley et al., 1985). The surface precipitation more readily occur at higher pH as follows.

\[ \equiv M^{2+} + 2OH^- = \equiv M(OH)_2 \downarrow \quad \text{Surface Precipitation} \quad \text{Eq. (3-17)} \]

Farley et al. (1985) suggests a surface precipitation model to allow for a continuum between surface complexation and bulk solution precipitation of the adsorbate ions. That is, after the cations are complexed on the surface, a new hydroxide surface is formed. When the cationic ion is present in water at a low concentration, the surface complexation is a dominant adsorption mechanism. As the cationic concentration increases in water, the concentration of surface complexes increases until the saturation of surface sites. Further increase in the cation concentration leads to the precipitation of cations on the solid phase. At this situation, surface precipitation becomes dominant for the adsorption of these cationic pollutants. Overall, surface complexation is a pre-condition for the occurrence of surface precipitation. Therefore, surface complexation plays a principle role in Al-WTR adsorption of these selected metal pollutants from runoff at both low and high concentrations of cationic metals.

**Effect of temperature on the adsorption patterns.** Different from the treatment of drinking water or municipal wastewater, reaction temperature can vary within a broad range during stormwater treatment. Therefore, temperature should be evaluated to examine how it influences the Al-WTR adsorption of the selected runoff pollutants.

Effect of temperature on the WTR adsorption of pollutants is shown in Figure 3-7 (a)-(d). Generally, the adsorption rates of all the selected pollutants increased with the increasing temperature (12-32°C), though the increase extents of the adsorption rates are different. For example, at 120 min, as the reaction temperature increased from 12 to 32°C, the adsorbed P
fractions moderately increased from 56% to 74%, whereas the adsorbed Pb was greatly increased from 41% to 86%. The positive relation of temperature with adsorption efficiency suggests that the adsorption reactions are an endothermic process. Moreover, the results from our studies clearly showed that Al-WTR adsorption of the pollutants in water was a spontaneous process. Therefore, the adsorption occurring in this study is a spontaneous endothermic reaction, suggesting that the changes in enthalpy and entropy yield a negative Gibbs free energy (Snoeyink et al., 1980). The endothermic nature reflects the thermodynamic property of surface complexation reactions between these pollutants and Al-WTR. It has been previously reported that surface complexation occurring on various metal hydroxides is endothermic (Banerjee et al., 2008; Zhao et al., 2011). For example, Banerjee et al. (2008) reported that adsorption rates of As onto granular ferric hydroxide (GFH) increased with reaction temperature. Zhao et al. (2011) also found that the adsorption of Pb(II) on Mg$_2$Al layered double hydroxide was a spontaneous procedure at their study temperatures.

The observations on the temperature dependence provide valuable information for the application of Al-WTR coated wood mulch for urban stormwater treatment. Both adsorption rates and capacities of Al-WTR coated mulch for the four selected pollutants are different at different seasons. Generally, the adsorption behaviors are discounted in a cold weather, e.g. in early spring, late fall, and winter, whereas the best adsorption performs in a warm weather, e.g. in summer. The effect of temperature on the adsorption behaviors should be also considered when the Al-WTR coated wood mulch is applied in different regions. For example, when the filter media is designed in the U.S. Northeast, it is expected that the pollutant removal efficiencies vary throughout the four seasons. In order to maintain a high treatment performance, more filter media may need to be applied for compensating the lower adsorption capability of
Al-WTR in winter. The worst performance of the Al-WTR coated mulch in winter should still meet with the minimum stormwater treatment requirements. However, when the modified mulch is applied in Southern California or South Florida, relatively constant removal efficiencies for urban runoff pollutants will be achieved, considering that the temperature remains high.

**Implication of adsorption mechanisms to Al-WTR engineering design.** Al-WTR adsorption of the four runoff pollutants, of which one is anion and three others are cationic metals, is principally ascribed to inner-sphere complexation reactions. In an inner-sphere complexes, water molecules are not present between the adsorbate and the surface functional group to which it is bound. Because the covalent or ionic binding is strong, the formed inner-sphere complexation-based adsorption is often irreversible. The strong bonds between pollutants and Al-WTR is of significance to engineering application of Al-WTR coated wood mulch for stormwater treatment, because desorption or leaching of the adsorbed pollutants on Al-WTR rarely occurs.

Desorption and leaching from an adsorbent used for stormwater treatment is typically concerned at two scenarios. The first situation is application of an adsorbent during application in field conditions. If desorption occurs for some reason, the captured pollutants would return to runoff and cause water and soil pollution. SPLP tests are recommended by US EPA to evaluate whether undesirable chemicals largely desorb from a solid matter due to rainfall events. The second situation is disposal of the used adsorbents. The most dominant solid waste disposal method in the United State is landfilling, in which more than 50% of U.S. solid wastes are buried in an engineering designed site (i.e. landfills) (Tchobanoglous et al., 1993). At the beginning phase of solid waste disposal within landfills, organic wastes are subject to anaerobic decomposition, which produces a large number of organic acids to create an acidic condition.
The acidic condition facilitates the dissolution of many metal solid phases. In order to estimate whether unwanted chemical leaching significantly occurs during landfill disposal, US EPA recommends the TCLP tests. As demonstrated in Chapter 2, very little leaching was observed in SPLP or TCLP tests. The irreversible binding is ascribed to the inner-sphere complexation reactions occurring between Al-WTR and these selected pollutants.

The irreversible adsorption also enables Al-WTR coated wood much advantageous over many other potential adsorbents for stormwater treatment, which, to different degrees, suffers from undesirable leaching. One such example is scrap tire rubbers. Scrap tires are another major solid waste in the United States. In 2003, the United State generated approximately 290 million scrap tires. Over a few past decades, scrap tire rubbers have been intensively studied as an adsorbent for water and wastewater treatment due to a high potential to adsorb different pollutants and a low cost (Alamo-Nole et al., 2011; Gupta et al., 2014; Kim et al., 1997; Knocke and Hemphill, 1981). Although the potentially new adsorbent shows an excellent ability to capture many runoff pollutants such as Cu, Hg, and Pb, it has been demonstrated to leach out Zn, originally existing in tire rubbers, during stormwater treatment due to ion exchange reactions (Deng et al., 2016; Deng et al., 2012). In contrast, Al-WTR appears to be a better option for stormwater treatment. Once the pollutants are immobilized to the Al-WTR surface, they will little desorb during application on site or during a landfilling disposal phase.

3.4 Conclusion

In this chapter, batch experiments were carried out to determine the adsorption kinetic and isotherm patterns of Al-WTR coated wood mulch for four selected urban runoff pollutants. The mechanisms behind the experimental observations were discussed and validated. Effects of key solution chemistry and operating factors, such as solution pH, ionic strength, and reaction
temperature on the adsorption behaviors, were also evaluated. Major findings in this chapter are summarized as follows.

1) All the four selected urban runoff pollutants can be effectively removed by Al-WTR coated mulch in the batch studies. Al-WTR coated wood mulch adsorption of phosphate, copper, zinc, and lead in synthetics urban runoff well followed the pseudo 2\textsuperscript{nd} order reaction kinetic models.

2) The Freundlich and Temkin models were both acceptable adsorption isotherm models for the immobilization of selected pollutants by Al-WTR coated wood mulch.

3) Inner-sphere complexation reactions play a key role in the Al-WTR adsorption of phosphate and metal cations in synthetic urban runoff. For the phosphate adsorption, though outer-sphere complexation likely occurs via electrostatic attraction before the occurrence of inner-sphere complexation reactions (the former one proceeded more rapidly than the latter one), the ionic strength dependence with the adsorption rates indicate that the most phosphate was finally immobilized on Al-WTR via the formation of inner-sphere complexes. For adsorption of the three metal cations in this study, surface precipitation might also contribute to the metal adsorption, only when the metals are present in water at high concentrations.

Based on these findings, important information can be obtained at least in two aspects. Firstly, adsorption of these pollutants by Al-WTR coated wood mulch is mostly kinetically controlled. That is, in the realistic treatment conditions, contact time plays an essential role. A longer contact time will achieve a better removal for the selected pollutant. Secondly, adsorption via the inner-sphere complexation creates a strong binding between the pollutants and Al-WTR. Therefore, the adsorption is irreversible at the most situations. The unique property allows the Al-WTR to be
safely applied on site during stormwater treatment and safely disposed within landfills when its lifetime ends.
Figure 3-1 Kinetic data on residual P concentrations in water during Al-WTR coated wood mulch adsorption of P in (a) SPS and (b) MPS (pH = 7.0; mulch dose = 5 – 50 g/L; SPS: initial P = 3.10 mg/L; MPS: initial P = 3.10 mg/L, initial Cu = 100 µg/L, initial Zn = 600 µg/L; and initial Pb = 100 µg/L in MPS; all the tests were performed in triplicates, and the relative standard deviations are less than 5% (not shown here))
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Figure 3-2 Experimental data and pseudo 2\textsuperscript{nd} order kinetic model data of Al-WTR coated wood mulch adsorption of P in (a) SPS and (b) MPS (pH = 7.0; mulch dose = 5 – 50 g/L; SPS: initial P = 3.10 mg/L; MPS: initial P = 3.1 mg/L, initial Cu = 100 μg/L, initial Zn = 600 μg/L; and initial Pb = 100 μg/L in MPS; scattered symbols and solid lines represent measured and modelled data, respectively; all the tests were performed in triplicates, and the relative standard deviations are less than 5% (not shown here))
Figure 3-3 $q_e$ and $k$ in the pseudo 2nd order kinetic models vs. Al-WTR coated mulch concentrations for the adsorption of different selected runoff pollutants in SPS and MPS: (a) P; (b) Cu; (c) Zn; and (d) Pb (pH = 7.0; mulch dose = 5 – 50 g/L; SPS: initial P = 3,100 mg/L; in SPS or MPS, initial P = 3,000 μg/L, initial Cu = 100 μg/L, initial Zn = 600 μg/L; and initial Pb = 100 μg/L in MPS)
Table 3-2 Parameters of different adsorption isotherm models fitting measured data

<table>
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<tr>
<th>Target Element</th>
<th>Solution Type</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Temkin</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>$Q_{\text{max}}$ (µg/g)</td>
<td>$b$ (L/µg)</td>
<td>$R^2$</td>
</tr>
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<td>P</td>
<td>SPS</td>
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<td>0.81</td>
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<td></td>
<td>MPS</td>
<td>-0.07</td>
<td>0.33</td>
<td>0.61</td>
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Figure 3-4 Measured and modelled adsorption isotherm data in SPS: (a) the Freundlich model; and (b) the Temkin model (pH = 7.0; mulch dose = 5 – 50 g/L; scattered symbols and solid lines represent measured and modelled data, respectively; all the tests were performed in triplicates, and the relative standard deviations are less than 5% (not shown here).
Figure 3-5 Effect of pH on the Al-WTR adsorption of different selected pollutants in SPS (initial P = 3.17 mg/L, initial Cu = 260 μg/L, initial Zn = 730 μg/L, and initial Pb = 350 μg/L; Al-WTR coated wood mulch = 10 g/L)
Figure 3-6 Effect of ionic strength on Al-WTR adsorption of P in water (pH = 7.0; initial PO$_4^{3-}$-P = 10.0 mg/L; and initial Al-WTR = 1.0 g/L)
Figure 3-7 Effect of reaction temperature on the Al-WTR adsorption of different selected pollutants in SPS (initial P = 3.20 mg/L, initial Cu = 260 μg/L, initial Zn = 730 μg/L, and initial Pb = 350 μg/L; Al-WTR coated wood mulch = 10 g/L)
CHAPTER 4 - CONTINUOUS FLOW COLUMN STUDIES FOR Al-WTR COATED WOOD MULCH ADSORPTION OF SELECTED RUNOFF POLLUTANTS
CHAPTER 4 CONTINUOUS FLOW COLUMN STUDIES FOR AI-WTR COATED WOOD MULCH ADSORPTION OF SELECTED RUNOFF POLLUTANTS

4.1 Introduction

Although high urbanization brings many socio-economic benefits, it can also adversely impact the quantity and quality of urban water resources when stormwater management is ineffective (Hering et al., 2013). Urbanized areas typically having up to 50-100% imperviousness may significantly increase peak runoff flow and thus facilitates the transport of various urban pollutants into receiving water bodies, threatening public and ecological health. Therefore, polluted urban stormwater runoff is acknowledged as a major pollution source in urbanized areas (USEPA, 2009).

Typical urban runoff pollutants include heavy metals, nutrients, pathogens, synthetic organic pollutants, and sediments. For examples, heavy metals with highly variable concentrations in urban runoff, such as lead (Pb), zinc (Zn), copper (Cu), chromium (Cr), and nickel (Ni), originate from various sources (Sorme and Lagerkvist, 2002). They are of particular concern due to their non-biodegradability, accumulation in the environment, and toxicity. Another representative urban runoff pollutant type is nutrients, including nitrogen (N) and phosphorous (P) typically originating from fertilizers, motor oil and road dusts (Kojima et al., 2011b; Pitt et al., 1999). They are also problematic, because they can cause eutrophication in receiving water bodies (Galloway et al., 2003).

In this dissertation, a new approach to address urban stormwater pollution with aluminum water treatment residual (Al-WTR) coated wood mulch has been proposed (Soleimanifar et al., 2016). Mulch is a protective layer of certain materials spread on the top of soil for multi-functions, such as moisture retention, weed control, and erosion prevention (Chalker-Scott, 2007;
Mulching is a simple, beneficial, and common practice in the United States landscaping. However, mulch media are mostly ineffective for adsorbing urban runoff pollutants. On the other hand, WTRs are the industrial waste produced from coagulation at drinking water treatment facilities, comprising amorphous Al or Fe hydroxides and colloids originally present in water sources (Crittenden et al., 2012). They have been consistently demonstrated for adsorption of certain metals, metalloids, emerging organic pollutants, and phosphate due to their high specific surface area and abundant active sorption sites (Chiang et al., 2012; Elliott et al., 2002; Makris et al., 2004; Makris et al., 2005; Nagar et al., 2010; Punamiya et al., 2013, 2015a; Zhou and Haynes, 2011). Although WTR has long been applied at agricultural scenarios, the attempts to use it for stormwater treatment have recently emerged (Deng et al., 2016; Deng et al., 2012; O’Neill and Davis, 2012a, 2012b; Soleimanifar et al., 2016).

In Chapter 3, batch tests results were presented. Batch tests were performed to investigate the adsorption kinetic and isotherm patterns of Al-WTR coated wood mulch for four selected urban runoff pollutants, i.e. P, Cu, Zn, and P, to explore the reaction mechanisms for the pollutant removal, and to evaluate the effects of key solution chemistry and operating factors (e.g. solution pH, ionic strength, and reaction temperature) on the adsorption behaviors. The knowledge obtained provides a scientific basis for further development of the innovative filter media in an appropriate large-sized reactor, which simulates the realistic on-site environment during the service of the innovative filter media. Reactors are defined as the tanks in which desirable physical, chemical, and biochemical reactions occur (Tchobanoglous and Schroeder, 1985). They may be large square or rectangular basins, cylindrical tanks, pipes, long channels, columns, and towers (Crittenden, et al., 2011). Selection of a proper reactor type is crucial for treatment because a reactor is where both mixing and reaction occur.
In this study, the reactor selection is primarily based on practical flow patterns during the service of Al-WTR coated wood mulch. In Chapter 3 presented experiments, bench-scale tests were performed in a batch mode (Figure 4-1(a)). Batch reactors (BRs) are used in a fill-and-draw type process with water under a completely mixing state. During the adsorption reactions, no flow enters or leaves, and the reaction rate proceeds at the identical rate everywhere within the reactor (Crittenden et al., 2012). Although the reactor type allows for obtaining basic scientific kinetic and equilibrium data for the adsorption process, the water flow pattern is different from the runoff flow through a mulch layer. For example, the concentrations of a pollutant are not identical over the depth of a mulch filtration bed.

Following the batch tests in Chapter 3, Al-WTR coated mulch would be further tested in a continuous-flow state, which occurs when urban runoff flows down through the mulch and into the soil. In the engineering design and optimization, two major continuous-flow reactors are continuously stirred tank reactor (CSTR) and plug-flow reactor (PFR) (Figure 4-1 (b) and (c)) (Masters and Ela, 1991). In a CSTR, solution is completely uniform without concentration gradients, and any chemical added to the solution is instantly and uniformly distributed throughout the reactor. Of note, the concentrations of any chemical are the same everywhere within the reactor due to the complexing solution state. In contrast, PFRs are ideal reactors in which flow continuously passes through in sequence. Under an ideal state, complete mixing occurs only in the vertical direction, while any mixing does not occur in the lateral direction (Tchobanoglous and Schroeder, 1985). Because of the realistic flow pattern for the runoff flow through a mulch layer, a plug flow reactor type was selected for further tests with Al-WTR coated wood mulch in this chapter. A slight modification was that the tube-type reactor was
installed vertically as a column reactor. Runoff would be fed from the top, flow down by gravity, and leave from the bottom of the column.

This chapter aims at evaluating the short-term and long-term performance of Al-WTR-coated wood mulch at a continuous flow state for the mitigation of urban runoff pollutants. Two stages of column studies were sequentially conducted to develop the innovative filter media for stormwater treatment. In the first stage, a set of short-term column experiments was completed within two weeks to treat the runoff produced over one year in a designed service catchment. Because batch tests described in Chapter 3 confirm that the adsorption of Al-WTR is a kinetically controlled process, the contact time is an important factor affecting the effluent quality. In the short-term small column studies, different bed depths, which resulted in different residential times, would be tested. Moreover, the trials in Chapter 2 showed that the leaching of undesirable chemicals was minimal at the rainfall and landfill disposal conditions using two EPA standard leaching tests (i.e. SPLP and TCLP), respectively. In the short-term small column studies, the desorption and leaching of aluminum, the most abundant metal on Al-WTR, would be monitored to examine the stability of Al-WTR during the application.

In the second stage, a set of long-term semi-field column tests was performed over one year to treat the runoff produced from a designed service catchment. Results from the first stage would be used to determine the favorable bed depth for the second stage. Technical and economic aspects would be studied in the semi-field tests. Technical viability of the innovative filter media was evaluated based on the quality of runoff effluent as well as the pollution of underlying soil. The economic analysis would be made to compare the prices of the modified and raw wood mulch. The major difference between the semi-field tests and the small column studies includes: 1) different influents – real and synthetic urban runoffs were added in the semi-field
tests and small column studies, respectively; 2) different runoff feeding patterns – the runoff feeding in the semi-field tests followed the real precipitation pattern in a United States northeastern town, whereas the runoff in the small column studies was added equally every day at a designated feeding rate; 3) different pollutant strengths – the concentrations of selected runoff pollutants were varied and constant in the semi-field tests and the small column studies, respectively; 4) different designs for the filtration bed – the filtration bed consists of mulch, soil, and plants (if any) in the semi-field tests, whereas mulch only was tested in the small column studies; and 5) different study focuses – pollutants in both effluent and underlying soil were analyzed during the semi-field tests, while the effluent pollutants were only measured in the small column studies.

4.2 Methodology

Chemical reagents. All the reagents used were at least analytical grade, except as noted. For the small column studies, synthetic urban runoff was used with chemical compositions as follows: 0.1 mg/L Cu^{2+}, 0.6 mg/L Zn^{2+}, 0.1 mg/L Pb^{2+}, 3.0 mg/L PO_{4}^{3-}, 2.0 mg/L NO_{3}^{-}, 2.0 mg/L NH_{4}^{+}, 120 mg/L CaCl_{2} (Fisher Scientific, NJ) for total dissolved solids (TDS), 40 mg/L CaCO_{3} (Sigma Aldrich, Japan), 0.01 M KCl (Sigma Aldrich, USA) for ionic strength, 5 mM piperazine-N,N’-bis (2-ethanesulfonic acid) (PIPES) (Acros Organics, NJ) and 20 mg/L used motor oil. Water pH was adjusted to 7.00 using 0.1 N NaOH ((Acros Organics, NJ) and HNO_{3} (Sigma Aldrich, USA). Pb, Zn, Cu, and P were provided from lead nitrate (Pb(NO_{3})_{2}) (Fisher Scientific, Fair Lawn, NJ), zinc nitrate (Zn (NO_{3})_{2}·6H_{2}O) (Fisher Scientific, Fair Lawn, NJ)), copper nitrate (Cu (NO_{3})_{2}·2.5H_{2}O) (Acros organic, 98+%), and disodium phosphate (Na_{2}HPO_{4}) (Fisher Scientific, Fair Lawn, NJ), respectively. NO_{3}^{-}N was provided adding NaNO_{3} (Acros Organics, NJ). NH_{4}^{+}-N was provided by adding NH_{4}Cl (Sigma Aldrich, USA).
For the semi-field large column studies, runoff was collected from a road within the campus of Montclair State University (MSU) (Montclair, New Jersey, USA) in the March of 2016. The road was near a surface parking lot. Once collected, the sample was filtered through 0.45 μm cellulose nitrate membranes to remove particulate matter and then stored in a cold room at 4 °C in MSU’s Water Quality and Treatment Laboratory prior to use. Because the selected pollutants (i.e. P, Cu, Zn, and Pb) concentrations in the runoff were all below expected initial levels, the runoff was spiked with metal salts and Na₂HPO₄ to achieve designated initial concentrations of the selected runoff pollutants. Initial runoff pH was adjusted to 7.0 using 0.1 N NaOH or HNO₃.

**Al-WTR coated mulch fabrication procedure.** Al-WTR was collected from the Bridgewater Water Treatment Plant (Bridgewater, New Jersey, USA) in the October of 2014. The WTR was completely mixed, dried by air, and then sieved through a 2-mm sieve (Deng et al., 2016). Timberline cedar wood mulch (Oldcastle lawn and garden Inc.) was purchased from a local HomeDepot store and then manually sorted. The mulch pieces with the size of approximately ~ 1 cm x 2 cm were selected, rinsed with deionized water three times to remove impurities on the wood surface, and finally air dried. To properly coat the mulch with the Al-WTR powders, the mulch glue (Technisoil Global Inc.), an environmentally friendly adhesive commercially available to bind mulch on ground for landscaping, was used. Selected wood mulch pieces were manually dipped in glue and then Al-WTR powders and left to air dry for one day at the room temperature. The WTR-coated wood mulch (~ 1 cm x 2 cm) was prepared in a mass ratio of WTR to mulch at 1:3, which is the optimal mass ratio demonstrated in chapter 2.

**Small column treatment experiments.** Small columns treatment tests were carried out in 30.5-cm (1-ft) high PVC pipes with an inside diameter of 7.6 cm (3 in). PVC caps were placed at
the bottom of these columns. Silicone tubing (0.64-cm i.d.) was connected to the bottom of each column and served as the reactor outlets. A tubing clamp was installed on each outlet tubing to adjust the infiltration rate to a designated level. A peristaltic pump (Masterflex L/S model 77202-60, USA) was used to continuously feed synthetic runoff from the top of these columns.

Small column tests were performed in duplicate under four different conditions, including 5.1 cm (2 in) deep raw wood mulch (control 1), 10.2 cm (4 in) deep raw wood mulch (control 2), 5.1 cm (2 in) deep Al-WTR coated wood mulch (treatment 1), and 10.2 cm (4 in) deep Al-WTR coated wood mulch (treatment 2) (Figure 4-2). Synthetic runoff was pumped into these columns at a flow rate of 8 mL/min. And the outlet flow rate was controlled at the same rate to ensure that the runoff flew through the columns at a constant flow rate. The flow rate was selected to achieve an infiltration rate occurring in the bioretention soil matrix with a typical soil hydraulic conductivity (MPCA, 2017). Each column was loaded with 7.6 cm (3 in) deep glass beads placed at the bottom, raw or coated mulch chips in the middle, and 2.5 cm (1 in) deep glass beads on the top. The top glass beads were used to uniformly distribute influent into the underlying mulch layer, while the bottom glass beads served as a supporting layer for the above mulch. An aliquot of 600 mL of simulated stormwater was directly added into each column every day prior to the initiation of the experiments. Water table was maintained throughout the filtration experiments. After the filtration, all the water was drained out through the outlets. The column studies were carried out over 7 hours every day for 4 L simulated stormwater to flow through each column. Totally, 56 L simulated stormwater passed through each column over 14 days, equivalent to an annual precipitation in an expected service catchment (the area of a coated mulch filter accounts for 5% of the service catchment and 50% of the precipitation flows on ground as runoff) in the typical U.S. northeast area. Effluents were collected 3 times every day for analysis.
Semi-field treatment tests with large columns. Semi-field tests were performed in larger columns than those used in the small column tests. The columns were built with 61 cm (i.e. 2 ft) high, 10.2 cm (4-inch) i.d. PVC pipes. They consisted of a 5.1 cm (2 in) high freeboard to allow for ponding, a 10.2 cm (i.e. 4 inch) high mulch filtration bed, 38 cm (i.e. 15 inch) deep soil, and 7.6 cm (3 in) deep gravels as a supporter on the base to prevent the escape of soil media. Because the Al-WTR adsorption of the selected runoff pollutants is a kinetically controlled process, as demonstrated in Chapter 3, the depth of a mulch filtration bed was selected at 10.2 cm (i.e. 4 inch), which is the upper level of the suggested mulch depth in the United States landscaping practices, in order to maximize the adsorption efficiency. The soil media included sand (90%), clay (7%) and compost (3%). It was sieved to < 2 mm prior to use. A peristaltic pump (Masterflex L/S, 8-channel, 4-roller cartridge pump head) delivered the runoff stored in a reservoir into the columns. Runoff was uniformly distributed on the top of the mulch, and then passed sequentially through the mulch filtration bed, soil media, and gravel supporter. The filtrate was collected through a 0.64-cm (1/4 in) i.d. tubing. Four column designs were tested with different mulch media with or without plants, including raw mulch (control 1), WTR-coated mulch (treatment 1), raw mulch + plant (control 2), and WTR-coated mulch + plant (treatment 2). The plant used in the columns was lady fern (*Athyrium filix-femina*, a native perennial throughout most of the temperate Northern Hemisphere), which is recommended for use in green infrastructure in the United States’ northeastern area.

Runoff feeding patterns followed the local precipitation profile in Montclair, New Jersey, United States during April 1st, 2016 – March 31st, 2017 (Figure 4-3). The precipitation data was obtained from the Weather Underground website (www.wunderground.com). Within the one-year period, 73 rainfall events that generated runoff occurred with the total precipitation of 85.4
cm. It is assumed that 50% of the rainfall became runoff, and the designed columns were sized at 5% of impervious catchment. Therefore, the volumes of runoff filtered by these columns can be accordingly determined (Figure 4-3). During the one-year period of semi-field experiments, the accumulated volume of runoff passing through the column reactors was 69.2 L, corresponding to 86.2 BV. During each simulated rainfall event, the filtrate from each column was collected and then filtered through 0.45 μm cellulose nitrate membranes before analysis. After the experiments were completed, the overall pollution effect of each pollutant in the soil was estimated as follows. Soil in the columns were separated every 7.6 cm over the depth. Totally, each column of soil was divided into five sections, i.e. 0-7.6 cm, 7.6-15.2 cm, 15.2-22.8 cm, 22.8 – 30.5 cm, and 30.5-38.1 cm. Ten grams of uniform soil samples were collected from each section and then digested following the ISO 14869-1:2001 standard method to determine the soil concentrations of these selected pollutants. For each pollutant, its average soil concentration is estimated as below.

\[ L_{ave} = \frac{\sum_{i=1}^{n} L_i m_i}{\sum_{i=1}^{n} m_i} \]  

Eq. (4-1)

Where, \( L_{ave} \) is the average soil concentration of a pollutant (mg/kg); \( L_i \) and \( m_i \) are the pollutant concentration (mg/kg) and soil mass (kg) in the \( i \)th section of the soil column; and \( n \) is the number of the total soil sections (\( n = 5 \) in this study). For each pollutant, we can determine the average increased pollutant concentration in soil due to the runoff pollution (\( \Delta L \)) based on Eq. (4-2).

\[ \Delta L = L_{ave} - L_{soil} \]  

Eq. (4-2)

Where, \( L_{soil} \) is the background concentration of a pollutant in soil before the treatment. \( L_{soil} \) provides a reference level of the unpolluted soil. Higher \( \Delta L \) indicates a greater pollution on the underlying soil.
Analytical methods. Solution pH was measured with a Thermo Fisher Scientific ORION 5-Star multiparameter meter. Cu, Pb, Zn, and P in water were analyzed using an inductively coupled plasma-mass spectroscopy (ICP-MS Thermo X-Series II, XO 472). All samples (each 5 mL) were immediately filtered through 0.45 µm-pore sized cellulose nitrate membranes for water analysis. Filtered samples were stored in the cold room (4°C) until analysis. Before the ICP-MS analysis, 50 µL concentrated nitric acid (70%, Sigma-Aldrich) was added to the filtered sample. The soil digestion tests followed a standard protocol ISO 14869-1:2001. The soil digestion at MSU laboratory is shown in Figure 4-4 (a) and (b). All the data presented in the figures are the mean values of triplicates. And their relative standard deviations were < 8.0% (not shown in figures).

4.3 Results and Discussion

Small column studies. The ratios of effluent concentration to initial concentration (C/C₀) for each pollutant are plotted against the number of BV in the small column studies (Figures 4-5 to 4-8). Average values, standard deviations, and relative standard deviations of C/C₀ during the small studies for adsorption of different pollutants with raw or Al-WTR coated wood mulch are summarized in Table 4-1. Initial pollutant concentrations were 0.1 mg/L Cu²⁺, 0.6 mg/L Zn²⁺, 0.1 mg/L Pb²⁺, and 3.0 mg/L PO₄³⁻-P. Besides these pollutants of concern, effluent pH was also monitored. The effluent pH was slightly altered (± 0.3) in comparison with the influent pH of 7.0. It should be noted that the same volumes of synthetic urban runoff were fed into the columns with 5.1 and 10.2 cm deep mulches. Because the bed volume of 10.2 cm mulch bed depth was twice as that of 5.1 cm mulch bed depth, the total No. of BV (i.e. 120) for 10.2 cm bed depth was a half of No. of BV (i.e. 240) for 5.1 cm-depth mulch bed in the small column studies, as shown in Figures 4-5 to 4-8. Furthermore, caution should be needed to discuss the data in Table 4-1.
When standard deviations were large relative to their average values (i.e. relative standard deviations are big), the average values could not provide accurate information on the pollutant removal at different BV numbers, because a large relative standard deviation suggests that $C/C_0$ was significantly changed with the No. of BV.

For the adsorption of P, $C/C_0$ versus the number of BV in the columns with 5.1 and 10.2 cm mulch bed depths are presented in Figure 4-6(a) and (b), respectively. Regardless of the bed depth, $C/C_0$ in the raw mulch beds almost stabilized between 0.87 and 0.88 throughout the small column experiments, suggesting a limited affinity of phosphate toward the raw wood mulch. In contrast, the decrease in $C/C_0$ was obviously observed when Al-WTR coated wood mulch was applied. High relative standard deviations (16% and 17% relative standard deviations for 5.1 and 10.2 cm depths) indicates the occurrence of great variations of $C/C_0$ with the number of BV. At the 5.1 cm-depth Al-coated mulch bed, $C/C_0$ gradually increased from the initial 0.42 to 0.75, indicating that the P adsorption on the Al-WTR coated wood mulch was progressively approaching the breakthrough. At the 5.1 cm bed depth, $C/C_0$ occasionally exceeded the levels of the control columns with raw mulch. In contrast, $C/C_0$ in the columns loaded with 10.2 cm-depth coated mulch slightly increased from 0.26 to 0.35 with the increasing number of BV to 120, suggesting that the adsorption level remained below its saturation level for P. At any specific number of BV, a much lower $C/C_0$ was observed in the 10.2 cm-depth coated mulch bed than in its control columns with 10.2 cm-depth raw mulch or in the 5.1 cm-depth coated mulch bed. The observations suggest that a high mulch bed depth can achieve a stable and effective adsorption for phosphate in runoff.

For the adsorption of Cu, $C/C_0$ versus the number of BV in the columns with 5.1 and 10.2 cm mulch bed depths are presented in Figure 4-7 (a) and (b), respectively. All the columns,
regardless of the mulch depths and types, exhibited effective removals for Cu from the synthetic runoff. For the either mulch depth, the average C/C_0 with Al-WTR coated wood mulch was marginally blew that in its control columns with raw mulch (0.32 for coated mulch vs. 0.35 raw mulch at 5.1 cm-depth mulch beds; 0.26 for coated mulch vs. 0.28 raw mulch at 10.2 cm-depth mulch beds). However, based on the relative standard deviations, the Cu adsorption by raw mulch was stable through the filtration tests (11% for 5.1 and 10.2-cm mulch depths). In contrast, great relative standard deviations (38% and 31% for 5.1 and 10.2-cm mulch depths, respectively) occurred when Al-WTR coated wood mulch was used. As seen in Figure 4-7 (a) and (b), C/C_0 noticeably fluctuated over the number of BV for the columns with coated mulch. The fluctuation degree was more noticeable at the 5.1 cm-depth mulch bed. Occasionally, the effluent Cu concentrations in 5.1 cm-depth coated mulch were over those in its control columns with raw mulch. The situation rarely occurred for the columns loaded with 10.2 cm-depth wood mulch. These findings again validate that the better and more stable removal of Cu from urban runoff can be achieved when a greater mulch depth is selected.

For the adsorption of Zn, C/C_0 versus the number of BV in the columns with 5.1 and 10.2 cm mulch bed depths are presented in Figure 4-7 (a) and (b), respectively. For the control columns with raw mulch, the average C/C_0 was decreased from 0.83 to 0.73 with the increasing mulch depth from 5.1 to 10.2 cm. The small relative standard deviations (6%-9%) suggests that the adsorption behavior of raw mulch was stable. On the other hand, at the either mulch depth, lower C/C_0 was observed when Al-WTR coated mulch was applied. As the mulch depth increased from 5.1 to 10.2 cm, the average C/C_0 went down from 0.66 to 0.59. Once again, the greater fluctuation of C/C_0 against the number of BV was observed at the 5.1 cm-depth wood mulch bed. At the two BV numbers, the effluent Zn concentrations from the treatment columns exceeded
those in their control columns. But the situation did not occur at the 10.2 cm-depth wood mulch bed, highlighting the role of the bed depth on the treatment efficiency and reliable performance of Al-WTR coated wood mulch.

For the adsorption of Pb, C/C₀ versus the number of BV in the columns with 5.1 and 10.2 cm mulch bed depths beds are presented in Figure 4-8 (a) and (b), respectively. At any specific column setup condition, the lowest C/C₀ was observed for Pb among all the selected pollutants, indicating that Pb was the most readily removed under the study conditions. Regardless of the bed depth, the average C/C₀ was 0.15 at the control columns with raw mulch. The lower C/C₀ was accomplished when Al-WTR coated wood mulch was used, as a result of the stronger affinity of Al-WTR coating for capturing Pb. For the columns with Al-WTR coated mulch, the average C/C₀ (0.08) with 10.2 cm bed depth was slightly below C/C₀ (0.10) with 5.1 cm bed depth, indicating that a greater bed depth ensured a better Pb removal for the coated mulch.

Al release from raw mulch and Al-WTR coated mulch versus the number of BV in the small studies was also determined, as shown in Figure 4-9 (a) and (b). Influent Al concentrations in the synthetic runoff were constantly below 4.0 μg/L throughout the experiments. For the raw mulch, the average Al concentrations were slightly increased to 2.8 and 4.5 μg/L at 5.1 and 10.2 cm bed depths, respectively. On the other hand, the average Al concentrations in the effluents from 5.1 and 10.2 cm-depth Al-WTR coated mulch columns were 1.57 and 2.67 μg/L, respectively. Based on the results, we did not observe any significant increase in the effluent Al concentration, as a result of strong and irreversible bindings between the pollutants and Al-WTR, as demonstrated from the batch tests. The only exception is that two spikes in the effluent Al concentrations were found at 19.0 and 13.2 μg/L at the BV numbers of 97 and 218, respectively, from the 5.1 cm-depth coated mulch bed. The sporadic Al release was likely caused because some fine Al-WTR
powders were off from the wood mulch. This phenomenon can be caused under a high shearing force of downflowing water; and/or due to the weathering effect due to the intensive and continuous flushing, because the synthetic runoff produced from a one-year precipitation was continuously added into the coated mulch filtration bed within two weeks in the small column studies. Of note, the United States EPA drinking water standard for Al is set at 200 μg/L, indicating that the occasional Al release is not a concern when Al-WTR coated wood mulch is used on site.

Discussion on results of the small column studies. Results from the small column studies highlighted three important findings for the performance of Al-WTR coated wood mulch under a continuous flow condition. Firstly, for any selected pollutant, Al-WTR coated wood mulch exhibited a better removal than raw mulch due to the stronger affinity of Al-WTR to the pollutant, in agreement with the findings in the batch tests. Secondly, any selected pollutant did not break through the columns throughout the studies. The total volume of synthetic runoff was designed to simulate the quantity of runoff that flows through the mulch bed over one year in a typical United States northeastern urban area. Therefore, the amounts of Al-WTR coated wood mulch, for either 5.1 or 10.2 cm bed depth, was sufficient for capturing the selected pollutants in a one-year operation duration. Thirdly, for any selected pollutant, the better performance was observed when the greater bed depth was used. The better performance was reflected in two aspects: 1) the higher removal efficiency indicated as average C/C₀; and 2) the more reliable adsorption, as demonstrated by the fact that the pollutant concentrations were more frequently higher in the treatment columns than in the control columns when a 5.1 cm deep Al-WTR coated mulch was applied. The more variable removal efficiencies for the lower bed depth was likely caused by the more nonuniform water flow within the coated mulch bed. As demonstrated in the
batch tests, the adsorption behavior of Al-WTR relies heavily upon contact time. When runoff flows down through the mulch filtration bed, the contact times for each small portions of water in the plug flow reactor should be equal only if the filter media is homogenously distributed. However, mulch typically has a high porosity (over 0.4) due to the heterogenicity of the mulch shape and size. Under such a situation, some flows may find shortcuts to go through the filtration bed with a much lower real contact time, behaving like a short circuiting, thereby leading to a lower pollutant removal. Therefore, a high bed depth is recommended to minimize the possibility of shortcutting for the further technology development. Fourthly, Al release from Al-WTR coated wood mulch during its on-site use at a continuous flow condition is minimal. Little Al leaching reflects the strong binding between the pollutants and Al-WTR.

After the column studies simulating the filtration of a one-year runoff in a certain service area, the estimated pollutant removals per unit depth of coated mulch in the 5.1 cm-depth columns with coated mulch were 1.89 mg/cm for P, 128 μg/cm for Cu, 395 μg/cm for Zn, and 170 μg/cm for Pb, respectively. When the bed depth was doubled to 10.2 cm, the corresponding pollutant removals nominalized to the bed depth were all increased to 3.40 mg/cm for P, 140 μg/cm for Cu, 481 μg/cm for Zn, and 172 μg/cm for Pb, respectively. The finding suggests that pollutant removals normalized by bed depth are increased by the bed depth, to different degrees, indicating that the increase in the bed depth can increase the utilization of adsorbent under a continuous flow condition, due to the increased contact time between the adsorbent and pollutants in water. The conclusion can explain why a better and more stable pollutant adsorption was observed for the greater bed depth.

It is also of interest to compare the pollutant adsorption on Al-WTR between the small column treatment tests and the treatment trials in Chapter 2, because very similar chemical
compositions of synthetic runoffs and column setups were used in the two sets of experiments. At the number of BV at 50 for the columns with 5.1 cm-depth coated mulch, the adsorption quantities of P, Cu, Zn, and Pb in the small column studies were 0.64 mg/cm, 26 \( \mu \)g/cm, 185 \( \mu \)g/cm, and 36 \( \mu \)g/cm, respectively, very close to the corresponding pollutant adsorption in the treatment trials (i.e. 0.67 mg/cm for P, 33 \( \mu \)g/cm for Cu, 212 \( \mu \)g/cm for Zn, and 34 \( \mu \)g/cm for Pb), indicating the results of the small column studies and treatment trials were in agreement.

Pollutant adsorption quantities determined from this column studies were also compared with the adsorption capacities obtained from the batch tests. The Al-WTR coated wood mulch had a bulk density of 0.6 g/cm\(^3\) and a porosity of 0.6. Because the Al-WTR coating approximately accounted for 17% of the overall coated mulch consisting of wood mulch, Al-WTR, and landscaping glue, we could determine the weights of Al-WTR in the columns with 5.1 and 10.2 cm bed depths. After the small column tests, the estimated adsorption amounts of P, Cu, Zn, and Pb were 0.70 mg/g, 47 \( \mu \)g/g, 145 \( \mu \)g/g, and 62 \( \mu \)g/g, respectively, for the 5.1 cm bed depth; and 1.2 mg/g, 52 \( \mu \)g/g, 177 \( \mu \)g/g, and 63 \( \mu \)g/g, respectively, for the 10.2 cm bed depth. The measured data were much below the estimated adsorption capacities in the batch tests (up to 3.54 mg/g for P, 920 \( \mu \)g/g, 910 \( \mu \)g/g, and 1066 \( \mu \)g/g for Pb). The gap implies that the 10.2 cm depth of coated mulch is sufficient to treat urban runoff in the planned service catchment under the given conditions.

**Knowledge input from the small column studies to the following semi-field tests.** In the small column studies, we translated the knowledge from batch tests into plug flow reactor experiments that are more relative to the realistic treatment conditions with Al-WTR coated wood mulch. The most essential information acquired from the small column studies is for determination of the bed depth for the ensuing semi-field tests. The small column studies clearly indicate that a
greater depth can enhance the removal efficiency and treatment reliability due to a longer contact time. Moreover, the small column studies at either bed depth demonstrated that the quantities of adsorbed pollutants on Al-WTR coated mulch were below their respective adsorption capacities on the Al-WTR adsorbent. Therefore, 10.2 cm was selected as the only mulch depth for the semi-field tests, because that 10.2 cm is an upper limit of the recommended mulch depth in the United States landscaping practices. On the other hand, Al release during the on-site use of Al-WTR coated wood mulch, in addition to chemical leaching from the coated mulch during landfill disposal as demonstrated in Chapter 2, suggests that desorption and leaching of undesirable chemicals are not an issue for the application of Al-WTR coated mulch. The results inform us the safety of the innovative composite filter media during its use and disposal.

**Semi-field treatment studies.** Runoff concentrations of Pb, Zn, Cu, and P for the columns in the absence of plants during different rainfall events are shown in Figure 4-10 (a), (b), (c), and (d), respectively. Influent concentrations of Pb, Zn, Cu, and P highly varied within 5.7-624.9 μg/L, 276.6-1119.2 μg/L, 30.8-449.0 μg/L, and 1875.0-4840.6 μg/L, respectively. After the treatment with the large columns, for any specific contaminant, effluent concentrations were substantially reduced. Specifically, the effluent concentrations of these columns loaded with raw mulch and coated mulch were 26.1-3291.0 and 8.1-2901.1 μg/L for P; 3.8-46.2 and 3.2-23.3 μg/L for Cu; 0.1-279.1 and 0.1-391.4 μg/L for Zn; and, 0.1 - 24.2 and 0.1-17.9 μg/L for Pb, respectively. The mean values and standard deviations of pollutant log removals among different column conditions are summarized in Table 4-2. Log removal is defined as the following equation (Crittenden et al., 2012).

\[
\text{log removal} = \log_{10} \frac{c_0}{c_f} \quad \text{Eq. (4-1)}
\]
Where, $C_0$ and $C_f$ are the influent and effluent concentrations of a specific pollutant in water, respectively. Relationship of log removal with removal efficiency ($\%\text{removal}$) defined in Eq. (3-1) and $C/C_0$ is as follows.

\[
\text{log removal} = - \log_{10}\left(\frac{\%\text{removal}}{100}\right) = -\log_{10}\left(1 - \frac{C}{C_0}\right) \quad \text{Eq. (4-2)}
\]

For example, 1 log removal = 90% removal efficiency (i.e. $C/C_0 = 0.10$); 2 log removal = 99% removal efficiency (i.e. $C/C_0 = 0.01$); and 3 log removal = 99.9% removal efficiency (i.e. $C/C_0 = 0.001$). Log removals of all the pollutants from the coated mulch columns were significantly greater than those from their control columns with raw mulch ($p < 0.01$), because WTR-coated mulch provides a better adsorption capability for these representative urban runoff pollutants than raw mulch due to the presence of WTR as an active adsorbent. Particularly, for phosphate, WTR-coated mulch achieved a log removal of 1.20, almost twice as that accomplished in the column with raw mulch (0.66), implying that WTR coating was extremely effective for capturing phosphate in urban runoff, in agreement with the finding in the batch tests and small column studies. Furthermore, the breakthrough of any pollutant was not observed throughout this study, validating that the 10.2 cm bed depth of Al-WTR coated wood mulch was sufficient for alleviating the runoff pollution for the service area within a one-year duration.

Pollutant concentrations for the columns in the presence of plants are shown in Figure 4-11 (a), (b), (c), and (d). For any specific contaminant, effluent concentrations from the columns with coated mulch were also considerably decreased. The effluent concentrations of the raw mulch + plant and coated mulch + plant groups ranged within 12.7-3579.2 and 16.3-2345.2 $\mu$g/L for P; 3.3-43.5 and 16.5-18.9 $\mu$g/L for Cu; 2.8-372.2 and 0.1-400.0 $\mu$g/L for Zn; and, 0.1-14.0, and 0.1-15.5 $\mu$g/L for Pb, respectively. As presented in Table 4-2, the mean log removals of all
the pollutants by WTR-coated mulch were significantly greater than those by raw mulch (p < 0.01), indicating that the WTR coating also enhanced the pollutant removal in the presence of plants.

When WTR-coated mulch was used, log removals of the three metals were statistically comparable between the absence and presence of plants (p < 0.46 for Pb; p < 0.46 for Zn; and p < 0.28 for Cu). Because any selected pollutant was captured by the WTR-coated mulch prior to the plant uptake, the aforementioned finding indicates that the contribution of plant uptake in the removal of the three metals was minor in this study. For the P removal, the log removals of coated mulch (1.20) and coated mulch + plant (1.12) were also close.

Average increased soil pollutant concentrations ($\Delta L$) of different large columns after the semi-field experiments are presented in Figure 4-12. $\Delta L$ was caused by the passage of polluted runoff. The greatest $\Delta L$ was observed for P among all the four selected pollutants. For P, the greatest $\Delta L$ (50.8 mg/kg) was observed for the raw mulch column, followed by raw mulch + plants (46.6 mg/kg), coated mulch (40.4 mg/kg), and coated mulch + plant (22.7 mg/kg). Moreover, the $\Delta L$ levels of Zn and Pb were also high. For Zn, the top two $\Delta L$ values were found in the columns loaded with raw mulch (6.1 mg/kg) and raw mulch + plants (5.6 mg/kg). In contrast, when Al-WTR coated wood mulch was applied, $\Delta L$ were reduced to 3.6 mg/kg for Zn and 3.3 mg/kg for Pb in the absence of plants, and 3.0 mg/kg for Zn and 3.0 mg/kg for Pb in the presence of plants. The finding indicates the effective removal of Al-WTR for Zn from water. Among all the selected runoff pollutants, the soil pollution with Cu was minimal, regardless of the column setup conditions. The $\Delta L$ values for the columns from raw mulch, raw mulch + plants, coated mulch, to coated mulch + plants slightly went down from 1.1, 1.0, 0.9, to 0.6 mg/kg. Compared to the Cu background concentration in soil (15.2 mg/kg), the increase varied
between 4% and 7%. The observation suggests that the buildup of Cu in soil was not a great concern. Of interest, except for Pb, the average increased soil concentrations of the other three pollutants followed the same order of raw mulch > raw mulch + plants > coated mulch > coated mulch + plants. For the Pb pollution in soil, the order was slightly modified as follows: raw mulch > coated mulch > raw mulch + plants > coated mulch + plant.

**Discussion on results of the semi-field studies.** Semi-field studies were performed over one year to allow for evaluating the long-term performance of Al-WTR coated wood mulch under different operating conditions. The treatment performance was determined through two aspects in the dissertation studies: 1) the overall removal efficiencies of coated mulch, soil, and plants (if any) in a typical bioretention basin setup; and 2) the accumulation of pollutants in soil. The two aspects were quantitatively evaluated using the effluent pollutant concentrations and the average increased pollutant concentrations in soil, respectively.

Result on the effluent pollutant concentrations again highlights the essential role of Al-WTR in the adsorption of the selected pollutants, in agreement with the observations in the batch tests and small column studies. The observation is due to the greater affinity of Al-WTR toward these pollutants than that of wood mulch. The enhanced effect of Al-WTR in the P removal from runoff was reported previously in another column study at the University of Maryland (O’Neill and Davis, 2012b), which demonstrated that direct addition of Al-WTR powders into the soil matrix could significantly enhance the removal of phosphate in runoff. However, the study was different from this dissertation in two aspects. Firstly, the innovative mulch coated with Al-WTR as a protective layer above soil, instead of mixing Al-WTR powders with soil, was used in this dissertation. Secondly, besides P, three heavy metals were tested in the long-term column studies.
On the average, the large columns exhibited better pollutant removal efficiencies than the small columns, at the identical column setups (i.e. 10.2 cm bed depth and the absence of plants). Pollutant $C/C_0$ in the effluents in small column studies and log removals of pollutants in the large columns are shown in Table 4-1 and 4-2, respectively. The conversion between $C/C_0$ and log removal is shown in Eq. 4-2. After the conversion, for the coated mulch column, $C/C_0$ was 0.42 and 0.06 for P, 0.26 and 0.12 for Cu, 0.59 and 0.05 for Zn, and 0.08 and 0.03 for Pb in the small and large columns, respectively. For the columns with raw mulch, $C/C_0$ was 0.88 and 0.22 for P, 0.28 and 0.18 for Cu, 0.73 and 0.06 for Zn, and 0.15 and 0.03 for Pb in the small and large columns, respectively. Considering that the major different setup between the two column studies is the use of the soil matrix in the large columns, but not in the small ones, the increased pollutant removal in the large columns is ascribed to the additional adsorption from the soil.

Soil sorption of various heavy metal ions have been extensively studied (Bradl, 2004; Brümmer, 1986; Elliott et al., 1986; Fontes and Gomes, 2003; Gomes et al., 2001; Harter, 1983). The loss of metals when water passes through soil is generally associated with three processes, including adsorption, surface precipitation, and fixation (Bradl, 2004). Adsorption is a two-dimensional accumulation of heavy metal ions on the interface of water and soil. It may occur through surface complexation reactions between metal ions and their respective functional groups on clay minerals, soil organic matter, and metal (hydr)oxides in soil, electrostatic interactions, and surfactant adsorption of metal-polyelectrolyte due to the decreased surface tension (Bradl, 2004). Surface precipitation is the growth of a new metal solid phase on the soil in three dimensions (Sposito, 1984). The metal soils precipitate as oxides, carbonates, sulfides, or phosphate. The occurrence of surface precipitation relies heavily upon solution pH. Fixation is a process in which aqueous metal species diffuse into the soil. For example, the metal species
adsorbed on clay minerals may enter into the lattice structures of these minerals (Sposito et al., 1999). On the other hand, the sorption of phosphate to soil has been also repeatedly reported (Barrow, 1973, 1975; Fink et al., 2016; Goldberg and Sposito, 1984; Sakadevan and Bavor, 1998; Sibanda and Young, 1986). The phosphate immobilization on soil is primarily ascribed to its interactions with iron and aluminum (hydr)oxides present in soil (Haynes, 1982; Sanyal et al., 1993). Although the removal of the four selected runoff pollutants by soil is out of scope in this dissertation studies, the role of the soil matrix in the improvement of overall removal efficiencies for target runoff pollutants should be highlighted.

Removals of metal species and phosphate from water with plants were intensively investigated (Albers and Camardese, 1993; Feng et al., 2013; Feng et al., 2016; Krebs et al., 1998; Mattina et al., 2003; Qian et al., 2012; Salt et al., 1995; Sims and Kline, 1991). The utilization of plants for metal uptake is applied as phytoremediation technologies in engineering practices for groundwater and soil cleanup. The pollutant removal may be associated with multiple mechanisms such as phytoextraction, phytostabilization, rhizofiltration, and phytovolatilization (Ali et al., 2013; Tangahu et al., 2011). However, in this dissertation studies, the presence of plants did not show an obvious decrease in the effluent pollutant concentrations during the semi-field studies, as shown in Table 4-1. The observation was likely due to the slow removal process of plant uptake. In this dissertation studies, the measured retention time of added urban runoff in the columns was within ten minutes. Under such a short duration, the uptake of these heavy metals by the plants might be very slight.

As discussed above, the presence of soil in the large columns contributed to the removal of pollutants from runoff. A question is raised. How much is the underlying soil polluted in the absence or presence of Al-WTR coated wood mulch? In reality, the pollution of soil is an issue
for existing green infrastructure in current stormwater management practices (Mungasavalli and Viraraghavan, 2006; Sabin et al., 2005). Accumulation of toxic heavy metals in soil within the stormwater treatment systems (e.g. green roofs, rain gardens, and bioretention basins) may lead to the violation of local soil cleanup criteria. In order to answer this question, the average increased pollutant concentration in soil (ΔL) was used to evaluate the degree of soil pollution (Figure 4-12). Results from the semi-field treatment experiments clearly indicate the buildup of these selected pollutants in the soil of a bioretention system. The data obtained from the one-year study provides valuable information on the rate of soil pollution. In New Jersey, USA, Pb of the three toxic heavy metals has the lowest residential direct contact soil cleanup criteria, i.e. 400 mg/kg (NJDEP, 1999). The Pb standard was established based on the USEPA Integrated Exposure Uptake Biokinetic (IEUBK) model utilizing the default parameters. The 400 mg/kg level is considered to protect 95% of target population (children) at a blood lead level of 10 μg/L. At the worst scenario in the semi-field treatment tests, the greatest soil pollution rate of Pb (6.1 mg/kg) occurred when 10.2 cm-depth raw mulch was applied. Considering that the background Pb level in the original soil was 9.9 mg/kg, the buildup of Pb in the soil can exceed the New Jersey soil cleanup standard at 64 years. The duration is short relative to the ages of the most U.S. cities. However, when Al-WTR coated wood mulch was used, the Pb pollution rates in soil were reduced to 3.6 mg/kg and 3.0 mg/kg in the absence and presence of plants, respectively. The actions can correspondingly extend the violation durations to 108 and 130 years, respectively, dramatically extending the lifetime of clean soil in an urban environment.

**Preliminary cost analysis.** The above semi-field tests only demonstrated the technical aspect of Al-WTR coated wood mulch for the treatment of urban stormwater runoff. Another important factor for the acceptance of the innovative filter media for application is financial
consideration. In this chapter, costs are preliminarily analyzed based on the data obtained from this dissertation study and relevant information from literature. The cost analysis aimed to compare the material expenses of raw wood mulch chips and WTR-coated mulch chips. The assumptions for the cost estimation are made as follows.

1) Al-WTR is available free of charge because it is a solid waste produced from drinking water treatment facilities.

2) The major expense difference between raw and coated mulch is the cost of mulch glue to bind Al-WTR powders on wood mulch chips.

3) We assume that the selected wood chips have a size of 1 cm × 2 cm × 0.5 cm, which was used in this dissertation study. The surface area/volume is 7 cm² / 1 cm³ (i.e. 213 ft²/ft³).

4) Wood mulch chip (60% porosity) has a market price of $60/yd³ which falls within a typical range of wood mulch chips in the market.

5) Mulch glue concentrate: a 1/2-gal bottle of mulch glue has a market price of $21. Therefore, the unit price of the glue is $42/gal. One gallon of glue concentrate can cover up to 3000 ft². Therefore, the cost of glue used to cover 1 ft² is ($42/gal) / (3000 ft²/gal) = $0.014/ft².

For one cubic yard of wood chips (60% porosity), the real volume of wood chips = 1 yd³ × (1-60%) = 10.8 ft³. The corresponding surface area of wood chips can be calculated as follows.

10.8 ft³ × 213 ft²/ft³ = 2300 ft²

Therefore, the cost of the much glue = 2300 ft² × $0.014/ft² = $32.

Overall, the WTR-coated mulch chips cost ($60+$32)/yd³ (i.e. $92/yd³), corresponding to an increase of 53% in comparison to the price of raw wood mulch chips. To sum up, the price of coated mulch is moderately increased.
4.4 Conclusion

Based on results from the batch tests operated under a batch mode, column studies were further developed to evaluate Al-WTR coated wood mulch for the treatment of polluted urban runoff at a continuous flow condition in this chapter. Two stages of column studies were sequentially performed, i.e. the two-week small column studies and the ensuing one-year semi-field studies.

Major conclusions of the small column studies with raw and Al-WTR coated wood mulch are made as follows.

1) Al-WTR coated wood mulch can effectively reduce concentrations of the four selected pollutants in comparison with raw mulch under a flow through condition. The bed depth plays an essential role in the effluent quality. The two bed depths tested (5.1 cm and 10.2 cm) are both sufficient for the treatment of one-year runoff without the breakthrough of any selected pollutant. The greater bed depth can achieve better removal efficiencies and treatment reliability of Al-coated wood mulch.

2) Aluminum release during the treatment of one-year runoff is much below the U.S. drinking water standard when Al-WTR coated mulch is applied. Therefore, aluminum leaching from the on-site application of the coated mulch is not an issue when the coated mulch is used on site.

Major conclusions of the semi-field column studies including raw/coated mulch and soil in the presence or absence of plants are summarized as below.

1) Any pollutant breakthrough is not observed in all the columns, suggesting that the simulated bioretention columns with raw or coated mulch sufficiently alleviate the
pollution of runoff pollutants to underlying soil/groundwater or receiving urban surface water bodies during one-year service duration.

2) Effluent concentrations of pollutants are dramatically reduced during the semi-field tests, exhibiting the better removal efficiencies than the small column experiments, due to the additional removal ability of the soil matrix.

3) The presence of plants does not greatly reduce the effluent pollutant concentrations when Al-WTR coated wood mulch was used.

4) Polluted runoff can lead to the accumulation of heavy metals and phosphate in soil. Application of Al-WTR coated wood mulch can alleviate the soil pollution and extend the lifetime of clean soil in an urban environment.

5) The price of Al-WTR coated wood mulch is moderately increased in comparison with that of raw mulch.

The column studies show that Al-WTR coated mulch is technically viable and economically affordable filter media for the control of urban stormwater pollution. Technical benefits of the innovative filter media include the reduction of pollutant concentrations in the effluent from the treatment system and the mitigation of pollutant accumulation in the underlying soil. The economic benefit is ascribed to two reasons: 1) the mulch cost is only moderately increased when the traditional mulch is replaced with Al-WTR coated mulch; and 2) the costs associated with mulch only accounts for a very small fraction of the overall expenses to build and operate a biofiltration basin. On the other hand, desorption and chemical leaching are minimal during the on-site use of and the disposal of Al-WTR coated wood mulch. The innovative material can serve as a stormwater treatment filter media as well as traditional mulch for erosion minimization, moisture retention, and weed control. To sum up, this dissertation has
demonstrated that Al-WTR coated wood mulch is a promising material in green urban stormwater management. It deserves a further full-scale field tests to optimize the system design and operation.
Figure 4-1 Flow patterns in three types of reactors: (a) a batch reactor (this reactor type was used in Chapter 3); (b) a continuously stirred tank reactor; and (c) a plug flow reactor (this reactor type was selected for further studies with Al-WTR coated wood mulch)
Figure 4-2 Small column set-up (column inside diameter= 7.6 cm, column height= 30.5 cm, mulch depth= 5.1 or 10.2 cm, filtration rate= 8 mL/min); MPS (0.1 mg/L Cu$^{2+}$, 0.6 mg/L Zn$^{2+}$, 0.1 mg/L Pb$^{2+}$, 3.0 mg/L PO$_4^3-$-P, 2 mg/L NO$_3^-$-N, 2 mg/L NH$_4^+$-N, 120 mg/L CaCl$_2$, 40 mg/L CaCO$_3$, 0.01 M KCl, 5 mM PIPES and 20 mg/L used motor oil, pH=7, T=22˚C)
Figure 4-3 Patterns of local precipitation and runoff feeding (Montclair, NJ, USA) during April 1\textsuperscript{st}, 2016 – March 31\textsuperscript{st}, 2017
Figure 4-4 Soil Digestion Process, ISO 14869-1:2001 standard method; (a) core sample (b) safety covers
Figure 4-5 Concentration variation of P versus No. of BV in small column studies: (a) 5.1 cm-depth mulch; and (b) 10.2 cm-depth mulch (filtration rate= 8 ml/min; MPS: 0.1 mg/L Cu^{2+}, 0.6 mg/L Zn^{2+}, 0.1 mg/L Pb^{2+}, 3 mg/L PO_{4}^{3-}-P; pH=7; T=22˚C)
Figure 4-6 Concentration variation of Cu versus No. of BV in small column studies: (a) 5.1 cm-depth mulch; and (b) 10.2 cm-depth mulch (filtration rate = 8 ml/min; MPS: 0.1 mg/L Cu^{2+}, 0.6 mg/L Zn^{2+}, 0.1 mg/L Pb^{2+}, 3 mg/L PO_4^{3-}; pH = 7; T = 22°C)
Figure 4-7 Concentration variation of Zn versus No. of BV in small column studies: (a) 5.1 cm-depth mulch; and (b) 10.2 cm-depth mulch (filtration rate= 8 ml/min; MPS: 0.1 mg/L Cu$^{2+}$, 0.6 mg/L Zn$^{2+}$, 0.1 mg/L Pb$^{2+}$, 3 mg/L PO$_4^{3-}$; pH=7; T=22°C)
(g) Mulch depth: 5.1 cm

(h) Mulch depth: 10.2 cm

Figure 4-8 Concentration variation of Pb versus No. of BV in small column studies: (a) 5.1 cm-depth mulch; and (b) 10.2 cm-depth mulch (filtration rate= 8 ml/min; MPS: 0.1 mg/L Cu$^{2+}$, 0.6 mg/L Zn$^{2+}$, 0.1 mg/L Pb$^{2+}$, 3 mg/L PO$_4^{3-}$-P; pH=7; T=22°C)
Table 4-1 Average values, standard deviations, and relative standard deviations of C/C₀ during the small studies for adsorption of different pollutants with raw or Al-WTR coated wood mulch (filtration rate= 8 ml/min; MPS: 0.1 mg/L Cu²⁺, 0.6 mg/L Zn²⁺, 0.1 mg/L Pb²⁺, 3 mg/L PO₄³⁻; pH=7; T=22°C)¹

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<th>Raw mulch (5.1 cm depth)</th>
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¹ A large relative standard deviation implies that C/C₀ was greatly changed over the number of BV in the column studies. Further analysis of the C/C₀ profile with the number of BV is needed for the pollutant with a large relative standard deviation.

² Std., standard deviation;

³ Std.% , relative standard deviation.
Figure 4-9 Concentration variation of leached Al versus No. of BV in small column studies: (a) 5.1 cm-depth mulch; and (b) 10.2 cm-depth mulch (filtration rate= 8 ml/min; MPS: 0.1 mg/L Cu$^{2+}$, 0.6 mg/L Zn$^{2+}$, 0.1 mg/L Pb$^{2+}$, 3 mg/L PO$_4^{3-}$-P; pH=7; T=22°C)
(a) Runoff P (µg/L)

(b) Runoff Cu (µg/L)
Figure 4-10 Runoff concentrations for the columns in the absence of plants during different rainfall events: (a) P; (b) Cu; (c) Zn; and (d) Pb
Table 4-2 Mean values and standard deviations of log removals for different urban runoff pollutants among different column conditions in the semi-field tests

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Raw mulch</th>
<th>Coated mulch</th>
<th>Raw mulch + plants</th>
<th>Coated mulch + plants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean log removal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>1.48</td>
<td>1.56</td>
<td>1.48</td>
<td>1.57</td>
</tr>
<tr>
<td></td>
<td>Standard deviation</td>
<td>0.30</td>
<td>0.24</td>
<td>0.24</td>
</tr>
<tr>
<td>Zn</td>
<td>1.21</td>
<td>1.30</td>
<td>1.15</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>Standard deviation</td>
<td>0.44</td>
<td>0.51</td>
<td>0.26</td>
</tr>
<tr>
<td>Cu</td>
<td>0.75</td>
<td>0.91</td>
<td>0.73</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>Standard deviation</td>
<td>0.12</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>P</td>
<td>0.66</td>
<td>1.20</td>
<td>0.77</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>Standard deviation</td>
<td>0.25</td>
<td>0.45</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(a) Runoff P (µg/L)

(b) Runoff Cu (µg/L)
Figure 4-11 Runoff concentrations for the columns in the presence of plants during different rainfall events: (a) P; (b) Cu; (c) Zn; and (d) Pb
Figure 4-12 Average increased pollutant concentrations in soil after the semi-filed studies (the average increased pollutant concentration = average pollutant concentration after the semi-field tests – pollutant concentration before the semi-field tests (i.e. the background soil concentration of the pollutant)); background pollutant concentrations in soil are 190.0 mg/kg for P, 15.2 mg/kg for Cu, 46.2 mg/kg for Zn, and 9.9 mg/kg for Pb)
CHAPTER 5- CONCLUSION
CHAPTER 5 CONCLUSION

5.1 Implications in Environmental Management

Scientific and engineering endeavors of this dissertation research were made to transform a common landscaping practice, i.e. mulching, into a new stormwater treatment technology through coating Al-WTR on the surface of wood mulch. Batch and column studies from this study demonstrate that the innovative Al-WTR coated wood mulch has a potential to revolutionize urban stormwater management and bring about profound impacts on environmental management.

Implication to urban stormwater and solid waste industries. Although WTR has been early demonstrated to remove a variety of pollutants from soil and water, the approach for its utilization in stormwater treatment has been challenged. Direct addition of WTR into the soil media in biofiltration systems cannot provide a long-lasting treatment, because the WTR-derived adsorption becomes ineffective once the adsorbent is oversaturated with certain pollutants. Continuous addition of WTR into soil to maintain the adsorption potential is not practical, because this option can lead to the accumulation of aluminum or iron in soil, depending on the type of WTR. On the other hand, the direct infiltration of polluted runoff through filters loaded with WTR powders is technically infeasible. The fine powders tend to clog to prevent water flow. The issue can be overcome after WTR is appropriately coated on mulch. The new approach proposed in this dissertation research takes advantage of complementary characteristics of the both materials and develops a new stormwater filter media, which simultaneously addresses multiple pollutants in urban stormwater. It should be noted that this dissertation has two essential impacts on the industrial sector. Firstly, the dissertation proposes a new approach, i.e. coating low-cost and active adsorbents on mulch, to address stormwater pollution. In future research,
many affordable and technically effective adsorbents can be attempted in a similar manner for the treatment of polluted urban runoff. Other potential adsorbents include zeolites and biochar. Secondly, though this dissertation targeted at the quality issue of urban stormwater runoff, the innovative filter media and the proposed stormwater treatment technology can be readily transferred to other fields, such as agricultural stormwater management.

Besides traditional functions of wood mulches (e.g. erosion prevention, moisture retention, and weed control), the functionalized mulching practice as a new stormwater treatment technology will bring six unique benefits to stormwater and solid waste industries, including:

1) *Technical effectiveness*: the new filter media has been demonstrated to rapidly adsorb multiple urban runoff contaminants to improve runoff quality without any significantly increased physical footprint, thus making it especially suitable for urban areas where land availability is limited.

2) *Cost effectiveness*: the materials for synthesizing the composite filter media are affordable. Particularly, WTR is almost free of charge. The economic advantage allows the innovative filter media to be more economically competitive in the stormwater treatment market.

3) *Versatility*: the coated mulch can be employed in combination with existing green infrastructures (e.g. bioretention basins, rain gardens, and green roofs) or independently used.

4) *Easy maintenance and operation*: only annual replacement of the coated mulch is required during practices. The periodic replacement is also required in the common
mulching practices. This action enables a long-term pollutant removal capability. Furthermore, no additional operation is needed.

5) Improved capability of water infiltration: as discussed above, the new composite filter media overcomes the poor water permeability of fine WTR powders to prevent local water flooding.

(6) Municipal waste reuse: the reuse of WTR gives the waste a new life, saves the limited landfill space, and reduces their disposal costs.

5.1.1 Environmental benefits

This modified wood mulch will benefit environmental health, at least, in two aspects. Firstly, application of the WTR-coated mulch can directly mitigate urban stormwater pollution in an urban environment and thus safeguard both ecological and human health. As demonstrated in this dissertation study, toxic heavy metals and nutrient phosphate in the urban runoff can be largely alleviated after the treatment with WTR-coated mulch. The reduction of urban runoff-induced toxic substances and nutrients can protect the health of ecological systems and mitigate the impacts of these stressors on vulnerable populations. For example, the decreased loading of nutrient to the urban aquatic environment reduces the risks of eutrophication and thus protects the water bodies from the depletion of dissolved oxygen. Secondly, the irreversible adsorption ensures that no or very little desorption or leaching of unwanted chemicals occurs from the Al-WTR coated wood mulch during rainfall events or landfill disposal, thus avoiding a secondary environmental pollution.
5.1.2 Social benefits

The impacts of this dissertation study are also of significance in the social aspect, including:

1) *Life quality and public health.* The mitigation of urban stormwater pollution with the innovative modified wood mulch will significantly improve the quality of aquatic environment, particularly the watersheds where drinking water sources are located, thereby safeguarding human health and promoting the residents’ quality of life.

2) *Local economic impacts.* The cleaner water creates more opportunities (e.g. transportation, recreation, and real estate) to support the development of more livable and resilient communities. The safe and reliable water can stimulate the economy by providing local business with the assurance of water supplies for agricultural, manufacturing, recreational, or other activities. Therefore, more job opportunities are expected to be created.

3) *Sustainability awareness.* The waste recycle in this technology will help expand public awareness and understanding of sustainability in their normal living.

4) *Aesthetics.* The new filter media can improve the quality of runoff. Once the treated runoff is collected and recycled to irrigate parks, golf courses and other recreational facilities (e.g. fountains and lakes), aesthetic values will be accordingly produced.

5.2 Overall Conclusions

In this dissertation, material preparation and characterization, batch tests (sorption kinetics and isotherm studies, mechanistic discussion, and the evaluation of different factors affecting the adsorption), short-term small column studies, and long-term semi-field tests (technical and economic evaluations) were consecutively performed. The systematic studies provide an
approach to transforming traditional landscape mulching into a technically viable and economically affordable stormwater treatment option with the innovative Al-WTR coated wood mulch as filter media for the alleviation of urban stormwater pollution. The modified filter media can be prepared through coating Al-WTR, an industrial waste from drinking water treatment facilities, on the surface of raw wood mulch chips using a mulch glue. After the coating, surface characteristics of the modified mulch chips are more similar to those of Al-WTR powders, but these coated mulch chips, like uncoated mulch, have a high porosity to allow for easy flow infiltration of water through a mulch filtration bed. Results from this dissertation study demonstrate that the Al-WTR coated mulch can largely reduce the pollutants from runoff and alleviate the pollution of underlying soil matrix, offering an effective protection for the urban aquatic and soil environment. Moreover, the minimal leaching and desorption of unwanted chemicals from the modified mulch demonstrates that the innovative filter media do not cause a secondary pollution during its use or disposal. Furthermore, preliminary cost analysis suggests that the cost of Al-WTR coated mulch is moderately increased relative to the price of raw wood mulch, primarily due to the use of mulch glue. Information collectively presented in this dissertation suggests that Al-WTR coated mulch chips can serve as an innovative filter media in urban stormwater treatment. They can be readily applied independently or combined with the existing green infrastructures (e.g. bioretention basins). Low cost, easy operation, and simple maintenance allows them to be more acceptable for end users and more competitive in the stormwater treatment market. More importantly, the approach, i.e. the application of low-cost adsorbent coated wood mulch chips for stormwater treatment, is innovative. Other potential adsorbents can also be applied in the similar fashion for stormwater treatment. Application of the new modified filter media using a recycled industrial waste can improve the quality of our urban
environment and promote public awareness on urban sustainability, potentially impacting local economics and increasing the aesthetic value.

5.3 Future Research

This dissertation study represents the first step toward the development of WTR-coated wood mulch-based stormwater treatment technologies at an urban environment. Although encouraging data have been obtained, this study has not addressed all the issues or explored all the aspects on the new adsorbent-based stormwater treatment. These aspects that deserve further investigation in the future are discussed below.

1) Reduction of material costs. Although the Al-WTR coated mulch has been demonstrated to be highly technically effective for runoff metals and phosphate, its price is moderately increased (approximately 1.5-fold of the price of common wood mulch). A vast majority of the increased expense is from the landscaping glue for binding the Al-WTR on mulch. In order to further reduce the material cost, new, cost-effective, and environmentally friendly methods need to be developed to coat WTR powders on the surface of wood mulch chips.

2) Roles of temperature and microbes. Semi-field tests were carried over one year in our laboratory to investigate the performance of Al-WTR-coated mulch at the field conditions. However, many field conditions that likely affect the adsorption could not be appropriately simulated in the laboratory-controlled environment. One such example is temperature. All the semi-field tests were completed at room temperature and could not reflect the variation of temperature with seasons throughout one year. As demonstrated in batch tests, the adsorption behaviors for selected pollutants may be highly different at
various temperatures. Besides the adsorption rate, temperature may affect many others such as the solubility products of selected pollutants in water.

Another important factor is microbial community. We did not investigate how microbial activities influenced the fate of runoff pollutants in the coated mulch filtration bed. A primary reason is that our semi-field experimental environment could not create a completely identical field environment (e.g. the difference of temperature and humidity between our laboratory and the field environment). Consequently, the microbial community in our laboratory columns was most likely different from that in the field conditions. Role of microbes in the metal removal and P adsorption has been demonstrated previously. Furthermore, microbes may alleviate other runoff pollutants not to be investigated in this dissertation study. For example, nitrogen from nitrate. It is well known that the inorganic nitrogen can be biochemically transformed into nitrogen gas to achieve the removal of nutrient nitrogen in water. A possible anaerobic environment near the bottom of the mulch layer may facilitate the nitrogen removal.

3) **Effect of organic leaching from wood mulch.** Organic leaching from wood mulch occurs over time. The compounds are the ones originally present in wood and/or their decay products. The degree of organic leaching from wood mulch is variable, heavily depending on wood species, climate conditions, and the soil environment. The potential role of these organic compounds is to discount the pollutant removal efficiencies of Al-WTR coated wood mulch via two mechanisms: 1) increasing the solubility of certain pollutants (e.g. heavy metals) and reducing their affinity toward Al-WTR via complexation of metal cations with organic compounds serving as ligands; and 2) occupying the active sorption sites on Al-WTR for target pollutants to inhibit their
adsorption. The negative effect of organic compounds on the metal adsorption on metal oxides has been reported. For example, Davis (1984) found that the presence of natural organic matter (NOM) significantly lowered the removal of Cu on alumina colloids. However, we did not monitor the organic leaching in column studies and did not evaluate the impacts of these compounds on the treatment performance of Al-WTR coated wood mulch. Moreover, it is of also interest whether the landscaping glue and Al-WTR coating may reduce the organic leaching due to the presence of a coating. This aspect should be further investigated.

4) *Effect of pollutant loadings, ADP/rainfall duration, and rainfall temporal distribution.*

Between different rainfall events, the pollutant loadings, antecedent dry period (ADP)/rainfall duration, and rainfall temporal distribution are different. Even at a single precipitation event, the pollutant loading is different over time. It is well known that the initial runoff typically contains much more pollutants during the beginning phase of a rainfall due to an initial flushing effect. However, the pollutant concentrations were varied within relatively narrow ranges in comparison to their realistic levels. Moreover, in a real rainfall event, the flow rate of runoff is more closely described by a log normal distribution. But a constant feed rate was used to pump runoff into our columns during each rainfall event in this study.

5) *Life-cycle assessment of WTR-coated wood mulch.* In this dissertation, a life cycle assessment (LCA) was not performed. However, LCA is highly recommended in the future research because it will evaluate the trade-offs between improved water quality and the incremental climate, energy, and economic costs of implementing WTR-coated mulch for stormwater treatment in a typical U.S. urban watershed. Based on the results from LCA,
we can identify significant findings and issues of the new stormwater treatment practice and determine whether the coated mulch is environmentally and economically sustainable.
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