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Scrap Tire and Water Treatment Residual as Novel "Green" Sorbents for Removal of Common Metals from Polluted Storm Water Runoff

Ciapha Nade Morris

MONTCLAIR STATE UNIVERSITY

Scrap Tire and Water Treatment Residual as Novel "Green" Sorbents for Removal of Common Metals from Polluted Storm Water Runoff

By

Ciapha Nade Morris

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Thesis Committee:

[redacted]

Dr. Yang Deng

[redacted]

Dr. Dibyendu Sarkar
Committee Member

[redacted]

Dr. Sudipta Rakshit
Committee Member

ABSTRACT

Although urbanization brings numerous benefits in our history, it has caused many environmental issues such as polluted urban runoff. A variety of pollutants at high concentrations, such as heavy metals, are present in urban runoff. Given that the polluted runoff is finally discharged into receiving waters and leads to non-point pollution in urbanized areas, appropriate management and treatment of the polluted urban stormwater is highly needed. However, current available best management practices (BMPs) are, to different degrees, restricted by their respective limitations. Therefore, there is an urgent demand in development of innovative, effective, and low-cost treatment methods for heavy metals in urban stormwater.

The long term goal of this study is to develop an effective, low-cost BMP to address the pollution issue caused by urban runoff-induced heavy metals. Toward this goal, the overarching objective of this thesis research was to evaluate the performance of two industrial wastes, water treatment residual (WTR) and scrap tire rubber (TR), in the adsorption of Cu, Pb and Zn from water, as well as assess potential leaching of adsorbed metals from spent sorbents. The central hypothesis is that these sorbent materials provide effective adsorption for heavy metals from urban stormwater, without any significant chemical leaching from the spent WTR/TR.

Bench scale tests were conducted in batch mode at pH 6.5 and room temperature to study metal adsorption by WTR alone, TR alone, and combined WTR and TR (WTR/TR), as well as Zn leaching from TR. Results show that WTR alone could rapidly and effectively adsorb the three metals, while TR adsorption was relatively slow but effective for Pb and Cu. However, TR significantly released Zn into bulk solution. The Zn leaching from TR appeared to be, at least partially, due to ion exchange between Zn in

TR and Cu/Pb in bulk solution. Combination of WTR and TR could not only maintain a high adsorption potential for Cu and Pb in water, but also substantially inhibit the Zn release from TR, probably because WTR could immobilize the released Zn. Cu and Pb adsorption onto WTR/TR well followed the Freundlich adsorption isotherm model. High ionic strength enhanced WTR/TR adsorption of Cu and Pb, and 1:2 appeared to be the optimal mass ratio of WTR to TR. Desorption of Pb and Cu from spent WTR/TR was insignificant. However, in the presence of strong chelating agents such as EDTA, the absorbed metals could appreciably desorb into bulk solution.

Column tests were also conducted to investigate the hydraulic behaviors and pollutant removal of the mixed WTR and TR media under continuous flow conditions. Hydraulic conductivities were affected by the mass ratio of WTR and TR and bed height. As the water flowed, the WTR powders might gradually move down to build up a sludge cake layer and clog the flow. Under certain conditions, the metals were effectively removed by the columns under a flow through condition.

This study provides a preliminary investigation to apply WTR and TR for stormwater remediation. The encouraging results demonstrate that TR combined with WTR (WTR/TR) is a potential green sorbent for removal of undesirable heavy metals from urban runoff. Simultaneous of the two solid wastes substantially reduces the stormwater management costs because WTR and TR is almost "free", as well as provides a new recycle pathway to address the two solid wastes that are originally disposed of within landfills.

SCRAP TIRE AND WATER TREATMENT RESIDUAL AS NOVEL “GREEN” SORBENTS FOR REMOVAL OF COMMON METALS FROM POLLUTED STORMWATER RUNOFF

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By:
CIAPHA NADE MORRIS
Montclair State University
Montclair, NJ
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CHAPTER 1. INTRODUCTION

1.1 Problem Statement

United States is a highly urbanized country. In 2000, more than75% of people lived in over 500 urban areas with a population density of >390/km^2 in this nation. Although high urbanization brings numerous benefits, it has led to many environmental issues such as polluted urban runoff. Typically, urban areas are characterized by high densities of impervious surfaces such as buildings, parking facilities, urban streets, highways, or walkways. The imperviousness degree in urban areas is usually > 50% and even reaches 100% in some areas. These impermeable surfaces allow for collection and accumulation of different constituents from atmospheric deposition, vehicular traffic or other sources. Consequently, the impervious surfaces significantly increase the flow rate of urban runoff, as well as efficiently transport numerous constituents into urban runoff. Given that the polluted runoff is finally transported to receiving waters in urbanized areas, appropriate management and treatment of the polluted urban stormwater is urgently demanded.

Among the different pollutants in urban runoff, heavy metals are a major concern due to their non-biodegradability and toxicity to living organisms including humans, microorganisms, plants and animals (Doumett et al., 2008). Copper (Cu), lead (Pb), and zinc (Zn) are the most frequently found metals in urban runoff, among which Pb is the most toxic and has consistently ranked #2 in the Agency for Toxic Substance and Disease Registry (ATSDR) most hazardous chemicals list. If polluted urban runoff directly enters into natural water bodies without any proper treatment, the non-biodegradable metals will accumulate in the environment, thus degrading the quality of water and soil, and threatening public health of local residents. For example, Turer et al. (2001) reported that urban runoff increased the maximum Pb in the top 15-cm soil in an urban area of Cincinnati, OH to 1980 ppm, significantly higher than the local background level.

To address the polluted urban stormwater-induced environmental impacts, best management practices (BMP) shall be employed. However, the most frequently used BMPs are, to different degrees, restricted by their respective limitations. For example, a major disadvantage of bioretention basins is that heavy sediment loading may clog the reactor when they are used where the water table is within 6ft below the ground surface (USEPA, 1999). Grassed swales are not suitable for treatment of a large drainage area. Filters require periodic exchange of spent filter media, probably leading to high operational and maintenance (O&M) costs. Therefore, there is an urgent demand in development of innovative, effective, and low-cost treatment methods for heavy metals in urban stormwater. The new methods are expectedly characterized with the following properties: 1) high capability to remove typical urban runoff heavy metals so that their effluent concentrations are below the levels established by regulatory agencies; 2) rapid cleanup time; 3) low costs in terms of labor, equipment, materials as well as energy consumption; 4) flexibility in reactor scale-up, so that reactors can be readily designed from small to large sizes; and 5) use of “green” treatment materials, if possible.

1.2 Copper (Cu) in Urban Stormwater Runoff

Copper present in stormwater runoff derives from tires and brake pad abrasions (Gobel et al., 2007), fertilizers, paint and pigment industries (Ahmad et al., 2009), and atmospheric deposition (wet and dry) (Davis et al., 2001; Sabin et al., 2005). In particular, brake pad abrasion is regarded as a major source of Cu in runoff (Davis et. al., 2001). Cu is a transition metal, and its oxidation states include zero (Cu^o, solid metal), + 1 (Cu^{1+}, cuprous ion), and + 2 (Cu^{2+}, cupric ion), in addition to + 3 (Cu^{3+}) in very rare situations (Georgopoulos et al., 2001). Cu is itself an essential micronutrient, but may become a concern when its concentration exceeds federal water quality guidelines. In the United States, the maximum contaminant level (MCL) of Cu in National Primary Drinking Water Regulations is 1.3 mg/L (0.02 mM) (USEPA, 2007). Excessive intake may lead to the fatal accumulation of the metal in the liver (Linder, 2000) and cause weakness, dizziness, and anorexia (Mousavi et al., 2010). Cu (II) is the most toxic amongst the different copper valences (Gundersen and Steinnes, 2003; Buck et al., 2007). In addition, the toxicity of Cu is influenced by its speciation (ionic, complex, and precipitated forms), pH, redox potential (Eh), organic matter content, and water hardness (Fleming et al., 1989). Pandey et al. (2000) reported that copper cations can form strong coordinated complexes with organic matters, thereby making them more persistent and bioavailable in the environment (Del Castilho et al., 1993). Beck and Sanudy-Wilhelmy (2007) observed that redox conditions at the sediment- water interface significantly affected the cycling of metals. For example, an oxygen-rich layer is formed on the surface sediments after oxygen penetrates through shallow water. This oxic rich layer can enhance adsorption of dissolved copper and prevent its transport into the overlying water. However, as the oxygen level of the overlying water decreases, the oxic layer is thinned, and more copper is released from sediments into water. It is observed that copper adsorption by particulate organic matter (POM) behaves in a similar manner. After copper is adsorbed to the scavenging POM, it eventually settles out with the POM due to gravity. However, when POM is decomposed through aerobic respiration, the Cu-POM bonds are broken so that Cu is subsequently released into the water column (Skrabal et al., 2000). Typically, copper has a residence time of 2.1 – 10 days in sediment pore water (Widurland, 1996).

Anthropogenic source is the greatest contributor of copper loading into urban storm water runoff (Davis et al., 2001). Source allocations of Cu in a typical urban runoff are listed in **Table 1**. Automobile brake appears to contribute the most Cu to runoff (~ 47%). Total dissolved metal concentration in water can be on a few orders of magnitude greater than the level of the free metal, particularly because of the formation of soluble inorganic metal and organo-metal complexes. Raspor et al. (1980) reported that copper can form stable complexes with certain anthropogenic organic ligands such as EDTA. Natural organic ligands (fulvic acid, humic acid and humin) can also form stable complexes with

Table 1. Copper loadings in urban stormwater runoff[a]

Source	Rate(/ha/yr)	Unit value	Loading(kg/ha/yr)	Percent
Buildings				
Sidings	180,000 m^2	47 ug/m^2	0.0085	22
Roof	450,000L	7.5μg/l	0.0034	9
Total			0.0118	31
Automobile				
Brakes	240,000km	75 μg/km	0.018	47
Tires	48,000g tire	5 μg/g	0.0002	0.6
Oil leakage	48 L-oil	2100 μg/l	0.0001	0.3
Total			0.0183	47.9
Total Building and Automobile			0.0302	78.9

a (Source: Davis et al., 2001)

copper. Natural organic matters (NOM) in natural water systems commonly include the organic ligands as a result of degradation of plant material as well as aquatic organism excreta (Zhou 1997).

1.3 Lead (Pb) in Urban Stormwater Runoff

Lead (Pb), unlike Cu, is not an essential element for plant and animal physiology due to its potential toxicity (Grosell et al, 2006). It can accumulate in living tissues, and eventually damage certain nervous connections, as well as cause blood and brain disorder at a concentration over its threshold level (Selim and Amacher, 1997; Mahatantila et al., 2011). Pb toxicity is involved with oxidative damage in which numerous free radicals are produced to decrease the reservoir of antioxidants and thus result in damage. Adequate data now demonstrate that Pb alters calcium homeostasis, directly interferes with the activation of enzymes, as well as inhibits the adsorption of trace minerals (Patrick, 2006). Ionic lead (Pb^{2+}) is an analogue of Ca^{2+} and tends to exert competition in many body processes such as neurological functions and mitochondrial respiration (Sanmanee, 2002). The MCL (action level) of Pb in National Primary Drinking Water Regulations is 15 μg/L (0.072 μM) (USEPA, 2007).

Sources of Pb in urban storm water runoff include atmospheric (wet and dry) deposition (Mousavi et al., 2010; ATSDR, 2012), vehicular traffic, and roofing/building materials (Gnecco et al., 2005). Davis et al. (2001) found that siding and roofing made the most contributions to Pb in urban runoff with an annual loading of up to 0.055 kg/ha/year. Different Pb loadings in typical urban runoff are summarized in **Table 2**.

Table 2. Lead loadings in urban stormwater runoff[a]

Source	Rate(/ha/yr)	Unit value	Loading(kg/ha/yr)	Percent
Buildings				
Sidings	180,000 m^2	300 ug/m^2	0.054	79
Roof	450,000L	1.5μg/l	0.007	1
Total			0.055	80
Automobile				
Brakes	240,000km		0.0007	1
Tires	48,000g tire		0.0008	1
Oil leakage	48 L-oil		5.0×10^{-5}	<0.1
Total			0.0016	2
Total Building and Automobile			0.0563	82

a (*Source*: Davis et al., 2001)

1.4 Zinc (Zn) in Urban Stormwater Runoff

Zinc (Zn) is also an essential micronutrient for biological growth. However, excessive Zn exhibits toxicity (Fosmire, 1990; Oyaro et al., 2007), and can cause stomach cramps, nausea and anemia, and skin rash (Fu and Wang, 2011). In the United States, the National Secondary Drinking Water Regulation level of Zn is 5 mg/L (0.076 mM) (USEPA, 2003).

Zn present in the environment can be sourced to both natural and anthropogenic activities (ATSDR, 2012). The man-made sources of Zn in runoff include automobile, roof materials, mining, industries, fertilizers, and wood preservatives (Gobel et al., 2007; ATSDR, 2012). Davis et al. (2001) estimated that the Zn loadings in urban stormwater runoff derived from various anthropogenic sources, especially automobile and buildings that may contribute as much as 95% of the total Zn loading (0.646kg/ha/yr). **Table 3** summarizes the Zn loadings in a typical urban runoff.

Table 3. Zinc loadings in urban stormwater runoff[a]

Source	Rate(/ha/yr)	Unit value	Loading(kg/ha/yr)	Percent
Buildings				
Sidings	180,000 m^2	2100 ug/m^2	0.378	58
Roof	450,000L	100μg/l	0.045	7
Total			0.423	65
Automobile				
Brakes	240,000km	88 μg/km	0.021	3
Tires	48,000g tire	3,400 μg/g	0.163	25
Oil leakage	48 L-oil	1.25×10^5 mg/l	0.006	1
Total			0.19	29
Total Building and Automobile			0.613	95

a (*Source*: Davis et al., 2001)

The bioavailability, transport and fate of zinc, like many other metals, to aquatic organisms are a function of its speciation (Skrabal et al. 2006; Gardner 1999). Zinc may exist in both suspended and dissolved forms in an aqueous environment. The major zinc form is divalent cation (Zn^{2+}) in a hydrated form (ATSDR, 2012). In the dissolved form, zinc may occur as the free hydrated ion or as dissolved complexes. Solution chemistry such as pH, redox, Eh can influence dissolution and precipitation of Zn in water. Skrabal et al. (2006) reported that zinc forms complexes with both organic and inorganic ligands. At acidic conditions, free zinc (Zn^{2+}) is very soluble and mobile (Stephan et al., 2008) Gundersen and Steinnes (2003) found that <10% of zinc was sorbed onto positive particles or colloids in water at pH 3.1 - 5.1. However, when pH was increased to a neutral condition (pH 6.5 – 7.2), the sorbed Zn was increased to 21% of the total Zn.

1.5 Basic Treatment Processes for Removal of Heavy Metals from Water

Different from organic pollutants in water, heavy metals cannot be removed through chemical or biochemical degradation. A few frequently used water treatment processes for removal of metals in water include chemical precipitation, ion exchange, membrane filtration, and adsorption.

1.5.1 Chemical precipitation

Chemical precipitation is a process in which certain chemical agents are added to water, and transform dissolved metal species into insoluble solid. The solid precipitates can be easily removed by subsequent sedimentation and/or filtration. Removal effectiveness of this process is highly influenced by the target metal species, chemical precipitant species, co-existing ions, solution pH, and reaction temperature. However, to achieve high removal efficiency, a long residence time is typically required to allow for completion of the precipitation reactions. Consequently, the reactor size is significantly increased. Moreover, when chemical precipitation is used for urban runoff treatment, addition of precipitant to a variable and intermittent stormwater flow poses a great challenge. Therefore, chemical precipitation is not suitable for metal removal in stormwater best management practice.

1.5.2 Ion exchange (IX)

When target metal ion-containing solution passes through a column loaded with certain resin, the target metals are sorbed to the resin through ion exchange between the target metal in water and another ion originally existing in the resin, and the latter ion is released into the treated water with the equivalent amount. This process is called ion exchange (IX). After the resin is saturated, it can be regenerated with an acid or alkaline medium to release the sorbed metals through the reversed ion exchange reactions. The commonly applied resins are zeolite and some synthetic materials

Specific functional groups on resins determine the variable selectivity of these resins for different target metals, because the ion exchange process involves the exchange of mobile ions from an external solution for one that electrostatically bound to a functional group contained within a matrix. Generally, positively charged functional groups have an affinity for anions and vice versa.

Ion exchange resins are regenerable, cheap, and energy saving. However, ion exchange may only accomplish very low treatment efficiency for target metals, when it is used for a complex water matrix or the target metals are little relative to many other co-existing chemicals. Bacteria film-induced fouling, organic matter adsorption, and formation of metal scale on resins all limit the application of ion exchange. For example, calcium solid scale may gradually build up on the resin surface during ion exchange if Ca^{2+} is substantially present in water.

1.5.3 Pressure-driven membrane filtration

Pressure-driven membrane process is to remove impurity from water through a permeable organic or inorganic membrane under pressure. The pore sizes on the membrane depend upon the pollutant species to be removed. Common pressure-driven membrane filtration processes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) in terms of the decreasing pore sizes (Fu and Wang, 2011): MF (0.1micron) > UF (0.01micron) > NF (0.001micron) > RO

(0.0001micron). MF can remove most of colloids that contribute to turbidity in water, while RO is able to remove almost all the dissolved or insoluble substances in water, except certain dissolved gases. NF and RO are able to adequately remove Cu, Pb, and Zn from water, and appropriate pre-treatment such as addition of anionic surfactants or polymers is required before UF is used for these metals of concern. However, high costs associated with energy consumption and membrane materials, as well as flux reduction due to fouling and polarity, do not allow the membrane processes appropriate for heavy metal removal in stormwater.

1.5.4 Adsorption

Adsorption is a process to adhere adsorbates (atoms, molecules, or ions) from a gas or liquid to a solid adsorbent. In water treatment, powdered or graduated sorbents are used to adsorb pollutants of concern from water through physisorption and/or chemisorption. Physical adsorption or physisorption occurs when adsorbate molecules are physically attached to the adsorbent molecules via weak Van der Waals force. Therefore, physisorption is easily reversible under heating or pressure drop. Physisorption is multi-layered, with each successive layer forming on the top of the previous layer. The layer number is proportional to the concentration of target contaminant (adsorbate). The strength of the attractive forces determines the reversibility of physisorption. On the other hand, chemisorption involves formation of chemical bonds between adsorbates and adsorbent. Chemisorption process is mono-layered and irreversible. If chemisorption needs to be reversed, adequate energy is required to break the bonds formed between adsorbates and adsorbent.

Adsorption process is characterized as a highly efficient one when compared with other BMPs (Zhu et al., 2012). Besides physisorption and/or chemisorption, biochemical process may also contribute to removal of different pollutants such as metal once appropriate biofilm builds up on sorbents (Xu et al., 2011). Among different adsorbents used, activated carbon is the most widely studied (Fu and Wang, 2011). Abundant micropores and mesopores allow activated carbon to have extremely high specific surface areas (up to 1,000 m^2/g). Numerous studies have demonstrated that activated carbon is very effective for removal of heavy metals. However, high costs associated with activated carbon and its regeneration highly limit its further application in stormwater management. New, technologically effective, and low-cost adsorbent materials are in demand to be alternative for activated carbon.

1.6 Water Treatment Residual (WTR) as a New Adsorbent

Water treatment residuals (WTR) are the chemical by-product from the water treatment process (Dayton et al., 2003; Hovsepyan et al. 2009). To effectively remove turbidity in raw water, appropriate coagulants such as are alums ($Al_2(SO_4)_3.14H_2O$), ferric chloride ($FeCl_3$) or ferric sulfate ($Fe_2(SO_4)_3$) are added to destabilize colloids for formation of flocs during the coagulation in water treatment plants. The flocs become denser and larger in the subsequent flocculation process, and largely settle down from water in the sedimentation reactor (Ippolito et al., 2011). The collected by-products are called water treatment residuals (WTR). WTR are amorphous in nature, highly porous (Ippolito et al., 2011; Babatunde et al., 2008), and are of various sizes and shapes (Makris et al., 2004). They typically contain amorphous or poorly crystalline Fe- and Al-oxides (Ippolito et al., 2011). The highly porous and amorphous characteristics as well as other properties such as particle size, charge, and surface area reflect their ability to absorb a tremendous quantity of charged species. Yang et al. (2006) compared a dewatered Al-WTR sample with pure $Al(OH)_3$, and did not find any significant difference between the two materials in terms of size and shape of particles.

Over 2 million tons of WTRs are daily generated in the U.S. (Prakash and Sengupta, 2003). Most of them are disposed of in landfills. However, limited landfill space and prohibitive disposal costs encourage development of new alternatives for traditional disposal methods. Over the past years, WTRs have been consistently demonstrated to adsorb metals, metalloids, emerging organic pollutants, as well as phosphorus - owning to their high specific surface and abundant active sorption sites. For example, Al-WTR was reported to have a high internal surface area of $120m^2/g$ and a high specific surface area of $48m^2/g$, which allows it to be a very excellent absorbent material (Hovsepyan et al. 2009; Makris et al. 2004). Makris et al (2006) studied Al-WTR adsorption of perchlorate (ClO_4^-) in water. After 2-hr and 24-hr reaction, they removed 65% and 76% of the initial 10 mg/L perchlorate, respectively. Moreover, their desorption studies demonstrate that the perchlorate adsorption to Al-WTR was very stable. WTR has been also well demonstrated to effectively remove a variety of metals such as Hg (Hovsepyan et al., 2009), As(V), As(III), Se (Ippolito et al., 2009), and Cr (Makris et al., 2006, 2007; Sarkar et al., 2007). The metal adsorption was achieved principally via inner sphere surface complexation, and hence, strongly irreversible.

Moreover, particle size of WTR appears to be a critical parameter affecting the adsorption efficiency. Yang et al. (2006) screened Al-WTR into six groups with respect toward their size ranges (< 0.063mm, 0.063mm-0.125mm, 0.125mm-0.25mm, 0.25mm-

0.425mm, 0.425mm-1.0mm, and 1.0mm-2.36mm) and tested their adsorption capacity for phosphorus in water. They found that ~ 0.25 mm WTR (0.25mm) sorbed the most P. This might be related to the amount of available active sites present on the particles with different sizes.

1.7 Tire Rubber (TR) as a New Adsorbent

Tire rubber (TR) as a waste is enormously generated from the transportation industry. In 2003, the U.S. generated approximately 290 million scrap tires (Purakayatsha et al. 2005). Lopez et al. (2011) estimated that 53% of the scrap TR was recovered as rubber or heat source, and the rest was landfilled or disposed of illegally. In solid waste industry, TR represents a major source of municipal solid waste (MSW), accounting for at least 12% of MSW in the United States (Conesa et al., 2004). Therefore, development of new recycling and reuse methods for TR is highly encouraged (Lian et al, 2011). Over the past decades, TR has been intensively studied as an adsorbent for environmental remediation. These studies are proposed based on two unique properties of TR: a high potential to adsorb different pollutants, and low cost (Alamo-Nole et al., 2011; Calisir et al., 2009). Meng et al. (1998) reported the immobilization of mercury (Hg^{2+}) in contaminated soils using tire rubber. Results showed that TR could significantly prevent Hg leaching from a Hg-contaminated clay foam. Gunasekara et al. (2000) attempted to apply TR for adsorption of Hg in water. After a 3-day reaction, ~ 40% of Hg was removed via TR adsorption. The adsorption was involved with the interactions between Hg and different components in TR such as sulfur, carbon black and zinc.

Recently, Gupta et al (2012) developed a new composite material composed of TR and activated carbon (AC) for removal of lead (Pb) and nickel (Ni) in water. They found that the so-called RTAC sorbent material adsorbed as much as 90% of Pb^{2+} and 87% of Ni^{2+}. They ascribed this finding to the numerous mesopores that accelerated diffusion of the metals into micropores on the TR, thereby significantly increasing the adsorption capacity of TR.

The mechanisms behind TR adsorption of inorganic and organic species were discussed by Gupta et al. (2012) and Kim et al. (1997). These mechanisms may be very complex, and depend heavily upon the adsorbate species and solution chemistry. Oladoja et al. (2010) revealed that the high affinity of TR with heavy metals was related to its compositional make-up. Tire rubber is a complex mixture consisting of various organic compounds such as polyisoprene, poly butadiene and styrene-butadiene. Other TR components include zinc oxide (1.9%), stearic acid (1.2%), extended oil (1.9%) and carbon black (39.0%). They noted that sulfur in TR, an anionic monodentate ligand, provided critical adsorption sites for Cu(II) in water. Moreover, they also noticed that carbon black (the second largest constituent of TR) characterized with a large surface area and enhanced surface activity favored Cu(II) adsorption. Alexander-Franco et al. (2011) further pointed out that TR adsorption of Cu, Pb, and Zn from water was primarily controlled by the cross-linked sulfur sites, because the three metals are chacophilic. Chalcophiles are elements that have a high affinity with sulfur through covalent bonds.

Solution chemistry is another key aspect affecting TR adsorption. Rowley et al. (1984) studied TR adsorption of Cd, Hg, and Pb from water, and found that a low pH favored the removal efficiency. Hg and Cd sorption occurred principally through an ion exchange mechanism. However, the mechanistic insight into the sorption of Pb was not reported. Calisir et al. (2009) also investigated Cu sorption onto TR. They concluded that the sorption was highly pH dependent, and the optimal pH for Cu adsorption was 6.0. Mechanistically, the sorption of Cu onto TR was accompanied by a release of Zn into bulk solution, thereby indicating that ion exchange played an essential role.

Although TR exhibits a high potential as an alternative remediation adsorbent, chemical leaching of Zn and some organic compounds is a major concern during its application. Gualtieri et al (2005) reported that pH, particle size and particle aggregation significantly influence the leachability of Zn from TR into bulk solution. More Zn was released at pH 3 than at pH 6 - 7. Large particle size and particle aggregation could lead to a reduced surface area exposed to solution so that the amount of Zn released was reduced. Besides Zn, the toxicity of TR is also caused by certain organic compounds leached from it (Wik and Dave, 2009), such as polycyclic aromatic hydrocarbons (PAHs), benzothiazoles, butylated hydroxyanisole, hexadecane and phenol (Mattina et al, 2007).

To the best of my knowledge, little information is available on WTR, TR, and combined WTR and TR as adsorbents for removal of metals from urban runoff, though WTR and TR have been demonstrated to be excellent adsorbents in many other environmental remediation areas. Application of these industrial wastes as new “green” sorbents for stormwater treatment is contingent on a full understanding of the retention or release characteristics of metals of concern into runoff under different experimental conditions.

CHAPTER 2. HYPOTHESIS AND OBJECTIVE

The long term goal of this study is to develop an effective, low-cost BMP to address the pollution issue caused by urban runoff-induced heavy metals. Toward this goal, the overarching objective of this thesis research was to evaluate the performance of two industrial wastes, water treatment residual (WTR) and scrap tire rubber (TR), in the adsorption of Cu, Pb and Zn from water, as well as assess potential leaching of adsorbed metals from spent sorbents. The central hypothesis is that these sorbent materials provide effective adsorption for heavy metals from urban stormwater, without any significant chemical leaching from the spent WTR/TR. To achieve this goal, the following five specific objectives were pursued:

1. Characterization of the used TR and Al-WTR materials.
2. Kinetics tests for WTR and TR adsorption of metals in water.
3. Adsorption isotherm tests for combined WTR/TR adsorption of metals under different experimental conditions.
4. Evaluate Zn leaching from TR under different experimental conditions.
5. Column studies to test hydraulic and treatment performance using combined WTR and TR adsorbents.

CHAPTER 3. MATERIALS AND METHODS

3.1 Samples preparation and characterization

Aluminum-based water treatment residual (Al-WTR) was collected from a stockpile at the Manatee County Water Treatment Plant in Bradenton, FL. Upon collection, the WTR was thoroughly mixed, air-dried, sieved through a 2-mm sieve, and finally ground into powder prior to use. TR samples were provided from Rubber Recycle Inc., Lakewood, NJ. Before use, the TR was rinsed twice with Milli-Q water (18.2 MΩ·cm) and then air dried.

Material characterization tests include: 1) Scanning electron microscope (SEM)/ electron dispersive spectroscopy (Hitachi S-3400N); and 2) Brunauer-Emmett-Teller (BET) surface area analysis. SEM analysis was conducted at MSU Microscopy & Microanalysis Research Laboratory. And BET specific surface areas were tested in a commercial laboratory - Particle Technology Labs (PTL), Downers Grove, IL.

Bulk density, particle density, porosity and hydraulic conductivity were also determined for combined WTR and TR media. Bulk density (ρ_b) was quantified using the method of Dada et al. (2012). An empty 50 mL beaker was rinsed with DI water, dried, and weighted. The beaker was later filled with the oven-dried Al-WTR and TR samples at a specific mass ratio, tapped lightly on the side, leveled, and weighed. The bulk density can be calculated using the following equation.

$$\text{Bulk density } (\rho_b) = \rho_b = \frac{(W_2 - W_1)}{V} \qquad (1)$$

Where, ρ_b is bulk density (g/ml); W_2 is the weight of the beaker with filter media (g); W_1 is the weight of the empty beaker (g); and V is volume of beaker (mL).

Particle density was determined using methods adopted by Li (2008). A 150ml volumetric flask was washed with DI water, dried, and weighted. Ten grams of the combined media were transferred to the flask together with 40ml of distilled H_2O, and then the flask was stoppered. The flask was heated to boiling for at least 6 minutes, then cooled to room temperature, and finally filled with cooled, pre-boiled distilled water to the 150 ml volume mark. The flask was re-weighted before its outside was cleaned and dried. Finally, the flask was emptied, washed, dried, filled to its graduated capacity with cooled pre-boiled distilled water, and reweighed. Particle density (ρ_s) can be determined as follows.

$$\rho_s = \frac{\rho_w M_s}{M_s - (M_{s+f+w} - M_{f+w})} \qquad (2)$$

Where ρ_s is the particle density (g/ml); ρ_w is the density of water(g/ml); M_s is the mass of the media (g); M_{s+f+w} is the overall mass of the media, flask and the distilled water (g); M_{f+w} is the mass of the flask filled with distilled water to its graduated capacity.

Porosity (n) is calculated using the following equation.

$$n = 1 - [(\frac{\rho_b}{\rho_s})] \times 100\% \qquad (3)$$

Where n is the porosity (unitless); ρ_b is the bulk density in g/cm^3; and ρ_s is the particle density in g/cm^3.

3.2 Chemicals

All the chemicals used were of analytical grade or above, except as noted. Simulated metal-contaminated urban runoff solution was prepared using their respective nitrate salts ($Cu(NO_3)_2 \cdot 2.5H_2O$, Acros organic, 98+%; $Pb(NO_3)_2$, Fisher Scientific, Fair Lawn, NJ; $Zn(NO_3)_2 \cdot 6H_2O$, Fisher Scientific, Fair Lawn, NJ) in 10 mM PIPES solution (piperazine-*N*, *N'*bis[2-ethanesulfonic acid], Acros Organics, 98.5+%). Sodium nitrate ($NaNO_3$, Acros) was used as background electrolyte to form different ionic strengths. All the solution was prepared using Milli-Q water (18.2 MΩ·cm).

3.3 Experimental Analysis

3.3.1 Kinetics and isotherm tests for adsorption

Bench-scale batch experiments were carried out at room temperature (~25°C) with triplicate samples with appropriate analytical controls and standards. All the adsorption kinetics and isotherm tests were conducted in 15 mL centrifuge tubes containing 10 mL simulated metal-contaminated urban runoff. The simulated runoff solution was prepared by addition of appropriate volumes of Cu^{2+}, Pb^{2+}, or Zn^{2+} solutions to 0.01, 0.1 or 0.5 M $NaNO_3$ PIPES-buffered solution. The initial solution pH was adjusted to 6.5 with 1 M NaOH and 1 N HNO_3. All the reactors were installed in a shaking bed. A rapid rotation ensured a completely mixing solution state. The adsorption reactions were initiated once appropriate amounts of WTR and/or TR were added. In a typical kinetics test, at least, three reactors were sacrificed at each designated sampling time. For adsorption isotherm experiments, shaking was stopped at 24 hours that allowed the adsorption to reach a chemical equilibrium. Subsequently, 5 mL sample was collected from each reactor, and then filtered through 0.45 μm syringe membrane filter. The filtrate was stored in 2% HNO_3 solution for metal analysis.

3.3.2. Desorption tests

To qualitatively understand how strongly the WTR and/or TR adsorb the metals, the used WTR and TR from isotherm tests were added to an EDTA (a well-known strong chelating agent) solution or $NaNO_3$ solution to examine how much sorbed metals can be desorbed back to bulk solution. Two groups of isotherm tests with WTR:TR = 1:1 and 1:4 (mass ratios) at a fixed total sorbent dose of 20 g/L were conducted as described in section **3.3.1.** Once the tests were completed, the solid sorbents were collected from each reactor, and then rinsed twice with Milli-Q water (18.2 MΩ•cm) to remove any residual unabsorbed metal on the sorbent surface. Thereafter, all the used sorbents were added back to a 15 mL centrifuge tube with 10 mL 0.02 M EDTA or 0.02 M $NaNO_3$ solution. The reactor was installed in the shaking bed. After 1-hr rotation, 5 mL solution sample was collected from each tube, and then filtered through 0.45 μm syringe membrane filter. The filtrate was stored in 2% HNO_3 solution for metal analysis.

3.3.3. Column tests

Bench scale fixed bed continuous flow tests procedures were conducted to further access the adsorption properties of the filter media. To do this, Al-WTR and TR were packed into individual columns made of polyvinyl chloride.

Column preparation. To avoid the development of air bubbles and preferential flow routes (channel) in the columns, WTR and TR samples should be carefully mixed and pre-saturated before transfer to the columns. The following procedure to pack the media into the columns was judged to be optimal.

1) Place a filter membrane and glass wool at the bottom of the column;
2) Uniformly hand mix pre-saturated WTR and TR samples, and then introduce same into the column from the top while lightly tapping the column. This will improve packing density. Carefully add deionized water and enable the mixed media to be closely packed. But avoid further tapping the column in case that the media settles too much, due to gravity, to cause clogging.

After packing, distilled water is continuously introduced through a pump to flow through the media. Visual inspection was performed to examine whether air bubbles were formed and trapped in the filter bed, and whether there was any preferential flow route. Meanwhile, the flow rate was adjusted until it was stabilized, and the hydraulic conductivity was determined.

Hydraulic Conductivity. The feasibility of using the Al-WTR and TR in a filtration process requires that some basic properties of the material be assessed. The hydraulic conductivity, a property of solid materials to transmit water when a hydraulic gradient is applied, is an important characteristic that complements the process. It represents both the properties of porous media and that of the fluid that flows. The ease with which water flow through a medium such as soil and other materials can be determined using the constant head or falling head permeability test (Fetter, 2001). In this study, the falling head permeability tests were conducted using a down flow transparent polyvinyl chloride pipe (PVC) (length 30 cm, internal diameter (ID) 2.54 cm (1 inch)). Al-WTR and TR were uniformly mixed at different mass ratios of 1:5, 1:8, 1:10, 1:12, and 1:15. Thereafter, the well mixed media was packed into columns. A Reglo digital 4 channel pump was used to deliver DI water into the columns to saturate the media bed and maintain a hydraulic head above. This hydraulic head was allowed to fall from one level to another with the differences in height level and the time taken to fall recorded. For each ratio of AL-WTR/TR, the test was performed in triplicate at constant initial hydraulic head height above the media bed. Darcy's law was used to determine hydraulic conductivity as follows.

$$K_t = \frac{QL}{A\Delta H} \qquad (4)$$

Where K_t is the hydraulic conductivity (coefficient of permeability) at a specific temperature (cm/s); Q is the volume of the discharge in ml (cm^3); A (cm^2) and L(cm) are the cross sectional area and length of media bed, respectively; ΔH is the head difference across the sample.

Column Experiments. Three columns each of 2.54cm (1 inch) internal diameter and 30cm packed with different proportions of Al-WTR and TR were set up (see **Table 8**). At ambient temperature (~25°C), the columns were fed with simulated storm water and it had an initial Pb^{+2} and Cu^{+2} concentration of about $100mgl^{-1}$ (430uM Pb^{+2} and 380 uM Cu^{+2}) each respectively. The simulated stormwater solution was prepared by adding appropriate volumes of the stock solution to 0.1M $NaNO_3$ PIPES buffered solution. The initial solution pH was adjusted to 6.5 with 1 M NaOH and 1 N HNO_3. Inflow was regulated by a peristaltic pump and filtrate samples were collected in a 50ml centrifuge tube every 10 minutes over a period of one hour. Following this, 10 ml aliquots of the filtrate samples were stored in 2% HNO_3 solution for metal analysis.

3.4 Analysis

Cu, Pb and Zn were analyzed using an inductively coupled plasma-mass spectroscopy (ICP-MS Thermo X-Series II, XO 472). Morphology and elemental analysis of WTR and TR were determined with a Hitachi S – 3400N scanning electron microscopy/electron dispersive spectroscopy (SEM-EDS). BET specific surface areas of WTR and TR were measured in a commercial laboratory (Particles Technology Labs, Downers Grove, Illinois). Solution pH was measured with an OAKTON ® 510 Series Benchtop Meter.

CHAPTER 4. RESULTS AND DISCUSSIONS

4.1 Material characterization

Results of BET analysis are summarized in **Table 4**. Al-WTR used in this study exhibited a high specific surface area (SSA) at 223.36 ± 3.14 m^2/g. This data was greater than the finding of Markis et. al. (2004) (104.9m^2/g), but less than 413m^2/g reported by Putra and Tanaka (2011). In contrast, the TR used had a much smaller SSA at 0.064m^2/g.

Table 4. BET characterization of Al-WTR and TR

Material	**B.E.T Specific Surface Area (m^2/g)**
Al-WTR	223.36 +/- 3.14
TR	0.064

SEM images of Al-WTR and TR are shown in **Figure 1(a-d)** and **2(a-d)**, respectively. As seen in **Figure 1(a)-(d)**, the Al-WTR was amorphous and nearly spherical particles with very rough surface. Their particle sizes broadly ranged between a few μm and several-hundred μm. In contrast, TR particles had irregular shapes and smooth surface (**Figure 2(a)-(d)**). Their sizes were on the order of a few mm. The disparity of the both materials in the surface characteristics was the major reason causing their different SSAs. With small size and uneven surface, the SSA of Al-WTR was over 3,000 times as that of TR.

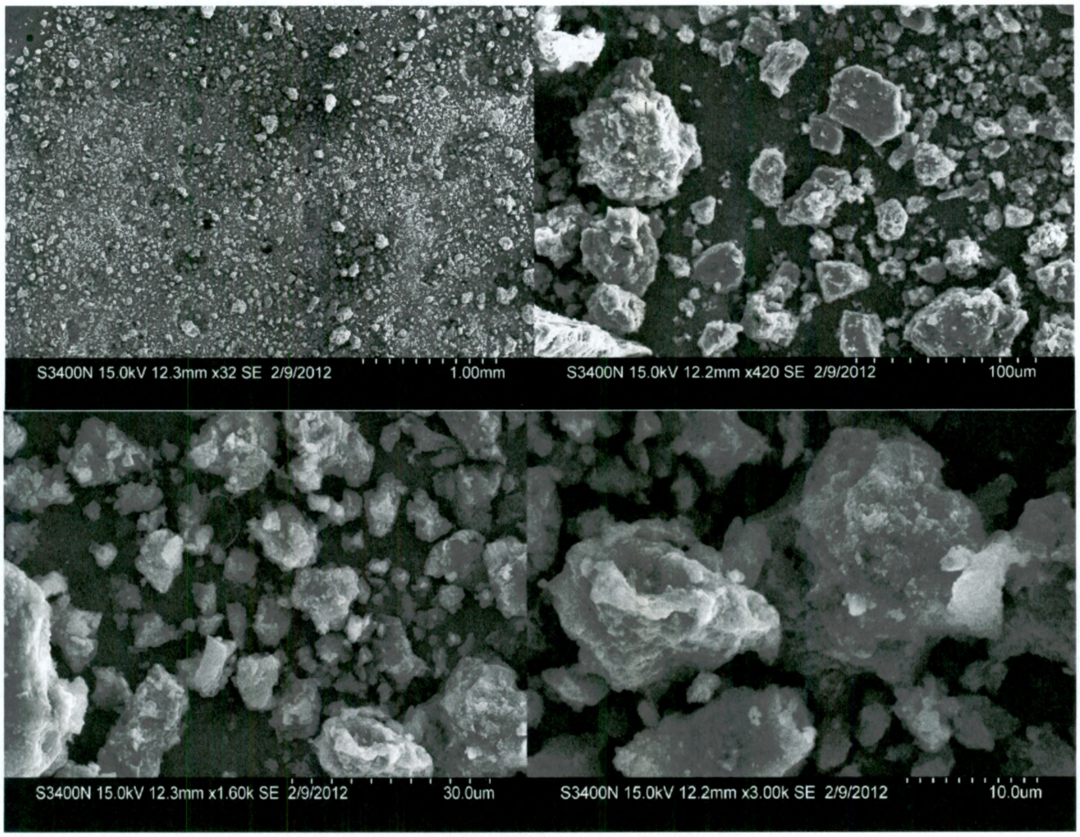

Figure 1. (a) - (d). SEM images of AL-WTR

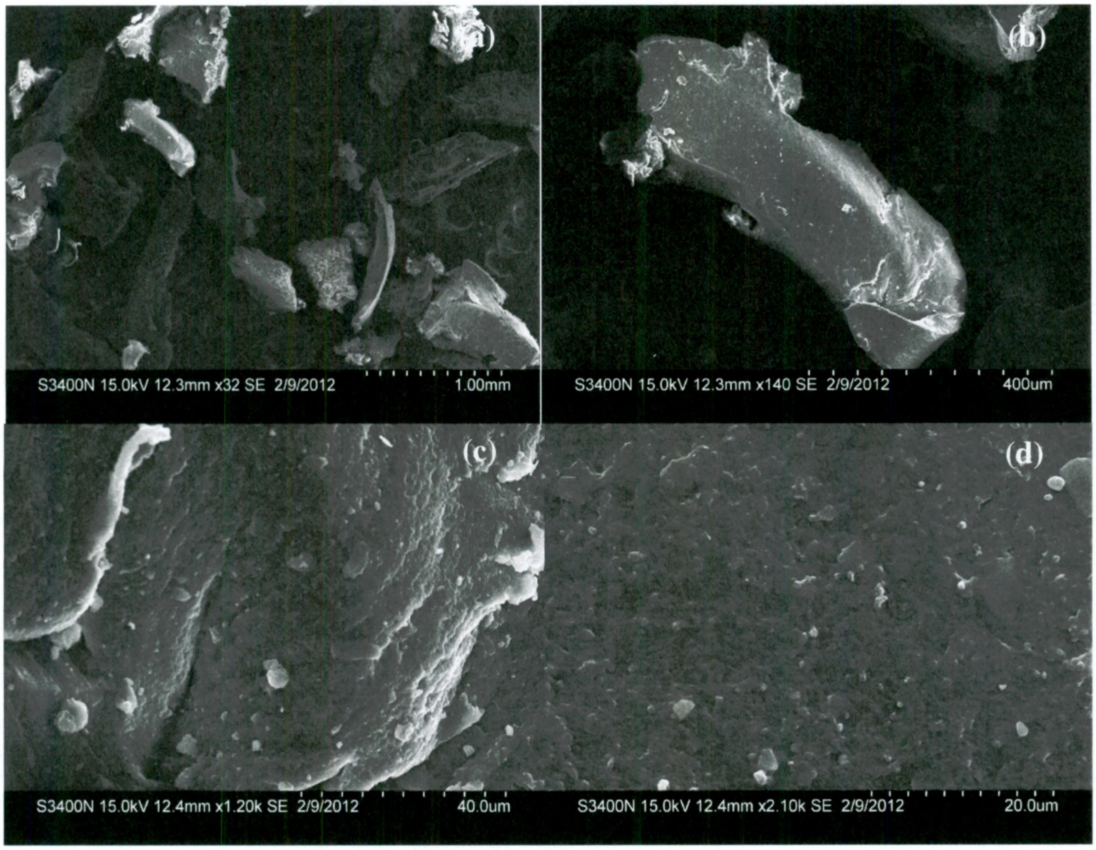

Figure 2. (a) - (d). SEM images of TR

4.2 Leaching characteristics of WTR and TR in Milli-Q water

Maximum contaminant levels (MCL) of Cu and Pb in US National Primary Drinking Water Regulations are 21 μM (1.3 mg/L) and 0.072 μM (0.015 mg/L), respectively. And US National Secondary Drinking Water Regulations sets Zn at ≤ 77 μM (5 mg/L). **Figures 3** and **4** show results of Cu, Pb and Zn leaching from Al-WTR and TR in Milli-Q water, respectively. Regardless of WTR or TR, the concentrations of leached heavy metals followed the order of Zn >> Pb > Cu. For Al-WTR, the leached Zn, Pb, and Cu were 0.010, 0.0032, and 0.0020 μM, respectively. All were significantly below their respective US EPA drinking water regulation levels. For TR, the leached Zn, Pb, and Cu were 0.75, 0.0026, and 0.0020 μM, respectively. Although the leached Zn was significantly greater than that from WTR, the concentration was still below US

National Secondary Drinking Water Regulation level. These findings suggest that both of the materials are safe in Milli-Q water in terms of metal leaching.

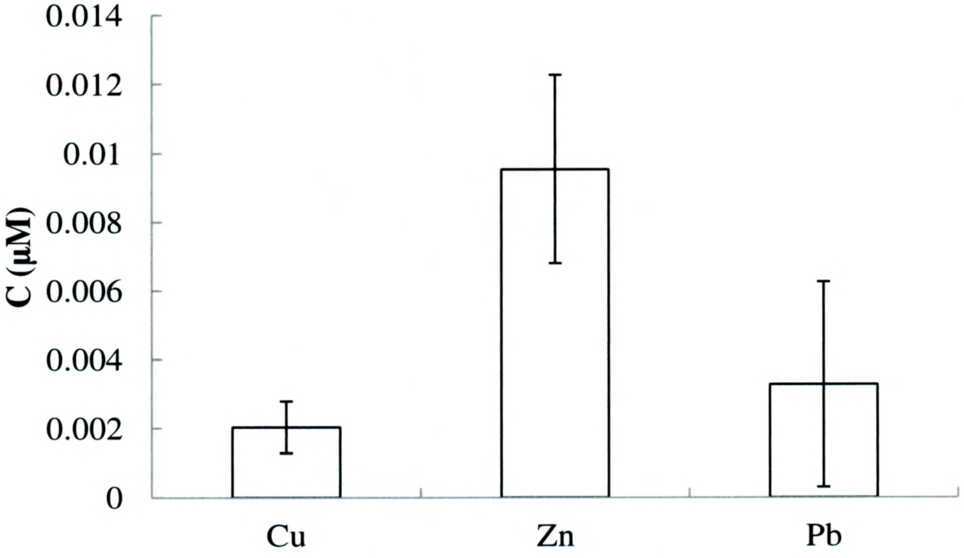

Figure 3. Metal leaching from WTR in Milli-Q water (20g/l WTR, 20 hrs)

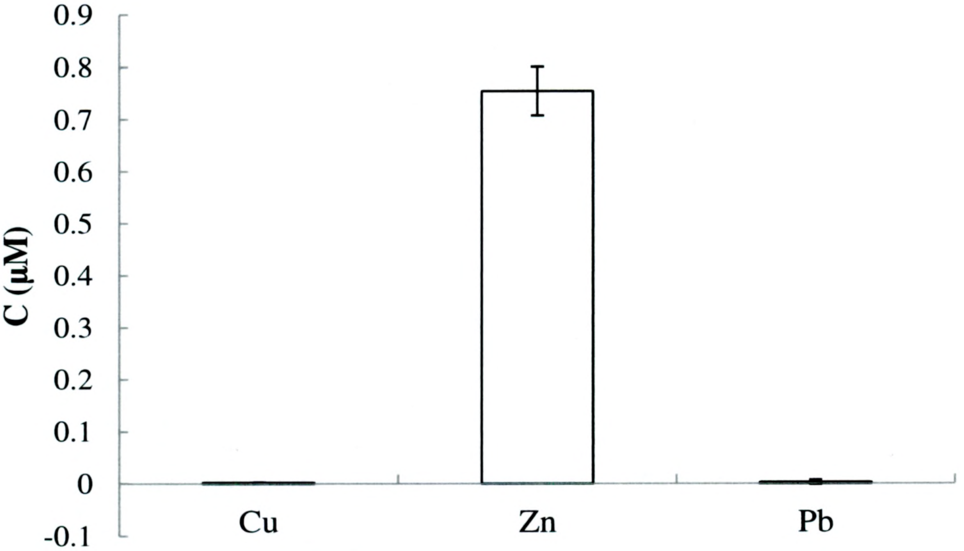

Figure 4. Metal leaching from TR in Milli-Q water (20g/l, 20hrs)

4.3 Kinetics Tests of WTR or TR alone

Results of kinetics tests for metal adsorption by WTR alone in a mixed metal solution are shown in **Figure 5**. The adsorption efficiency is defined as follows.

$$Adsorption\ efficiency = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (5)$$

Where, $C_0$and C_t are the molar concentrations of a specific metal in bulk solution at time zero and any specific time t, respectively. As seen, the removal efficiencies of Cu, Zn, and Pb were 99.7%, 92.6%, and 99.9% within one hour, respectively. Thereafter, the improvement in the adsorption efficiencies was marginal, thereby implying that adsorption equilibrium could be reached within one hour regardless of metal species. This finding is in agreement with early studies that the attainment of equilibrium for sorption of heavy metal onto WTR ranged from a few minutes to 2 hrs (Sarkar et al., 2001).

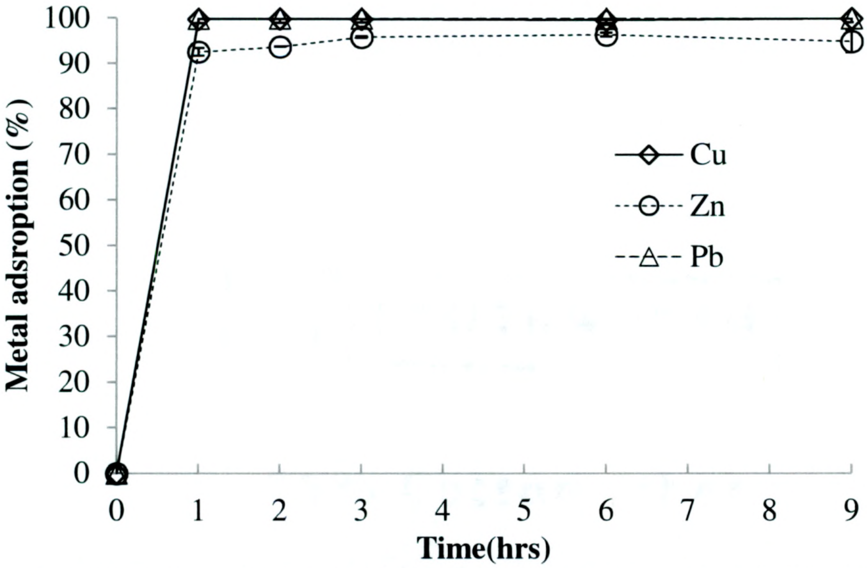

Figure 5. Adsorption of metals by WTR alone with time (10g/l WTR, $[Cu]_o = 6\mu M$, $[Pb]_o = 2.45\mu M$, $[Zn]_o = 6\mu M$, and pH 6.5)

Kinetics results of TR adsorption of Cu and Pb, as well as Zn leaching from TR, are presented in **Figure 6**. Adsorption efficiencies of Cu and Pb were gradually increased from 0% to 97.4% and 97.2% with the increasing time from 0 to 9 hours, respectively. Meanwhile, much Zn leached out from TR into the bulk solution with time. The Zn leaching pattern was unique. Within the first hour, 282 μM Zn entered the solution. However, in the following one hour, Zn in solution dropped to 178 μM. Thereafter, the Zn concentration in water almost stabilized. These findings revealed that WTR alone could adsorb the metals of concern much more rapidly than TR alone. Interestingly, with TR alone, Zn leached out in Milli-Q water was insignificant as demonstrated in section 4.2, but the amount of Zn leaching from TR in a mixed Cu and Pb solution was significant. The result was likely because ion exchange occurred between Zn on TR and Cu/Pb in bulk solution, so that much Zn leached out from TR. Therefore, TR alone cannot be a single sorbent used for stormwater remediation.

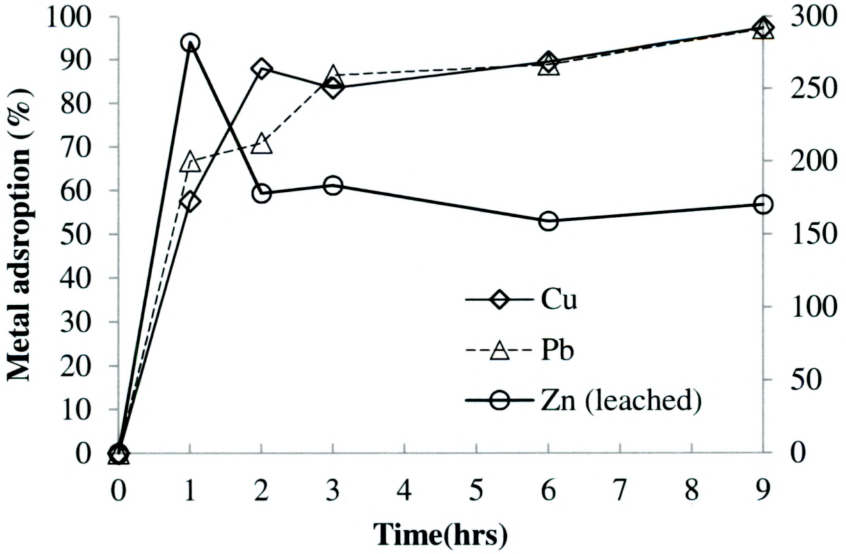

Figure 6. Adsorption of Cu and Pb onto TR and leaching of Zn from TR alone with time (10g/l TR, $[Cu]_o = 6\mu M$, $[Pb]_o = 2.45\mu M$, and pH 6.5)

4.4 Adsorption isotherms with WTR alone

Adsorption isotherms of Cu, Pb, and Zn during WTR adsorption of a simulated Cu, Pb, and Zn mixed runoff are shown in **Figures 7 - 9**, respectively. These figures show relationships between mass and surface area-normalized adsorption capacities of specific metals on WTR (Q_{em} and Q_{es}) and their aqueous concentration (C_e) at chemical equilibrium. The mass-normalized adsorption capacity (Q_{em}) and surface area-normalized adsorption capacity (Q_{es}) of a metal on sorbent are determined as follows.

$$Q_{em} = \frac{(C_0 - C_e)V}{m} \times 100\% \qquad (6)$$

$$Q_{es} = \frac{(C_0 - C_e)V}{SSA} \times 100\% \qquad (7)$$

Where, C_o and C_e are the initial and equilibrium concentrations of an adsorbate in bulk solution, respectively; V is the volume of bulk solution; m is the mass of adsorbent; and SSA is the specific surface area of adsorbent (data for AL-WTR and TR used in this study are shown in **Table 4**).

As seen, the adsorption isotherm curves exhibited a biphasic pattern. At a low Ce, Q_{em} and Q_{es} were dramatically increased with the increasing C_e. However, when Ce was over a critical level (~ 43 μM/g and 0.19 μM/m^2 for Cu, ~ 25 μM/g and 0.11 μM/m^2 for Pb, and ~ 23 μM/g and 0.10 μM/m^2 for Zn), the improvement of Q_{em} and Q_{es} was almost marginal with the increase of C_e.

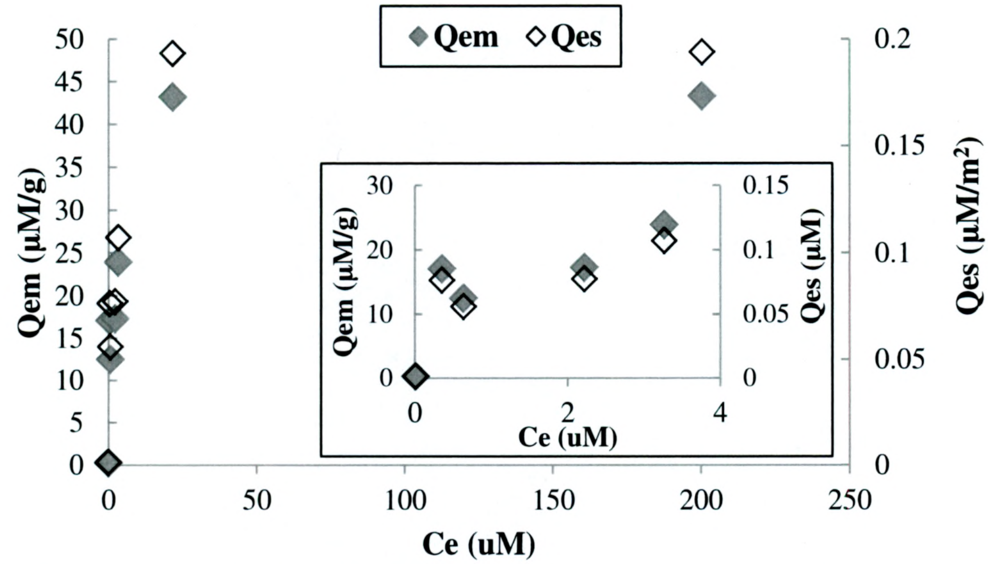

Figure 7. Cu adsorption isotherm on WTR in a mixed metal (Cu+Pb+Zn) solution (20g/l WTR, pH 6.5, and 0.1M NaNO$_3$).

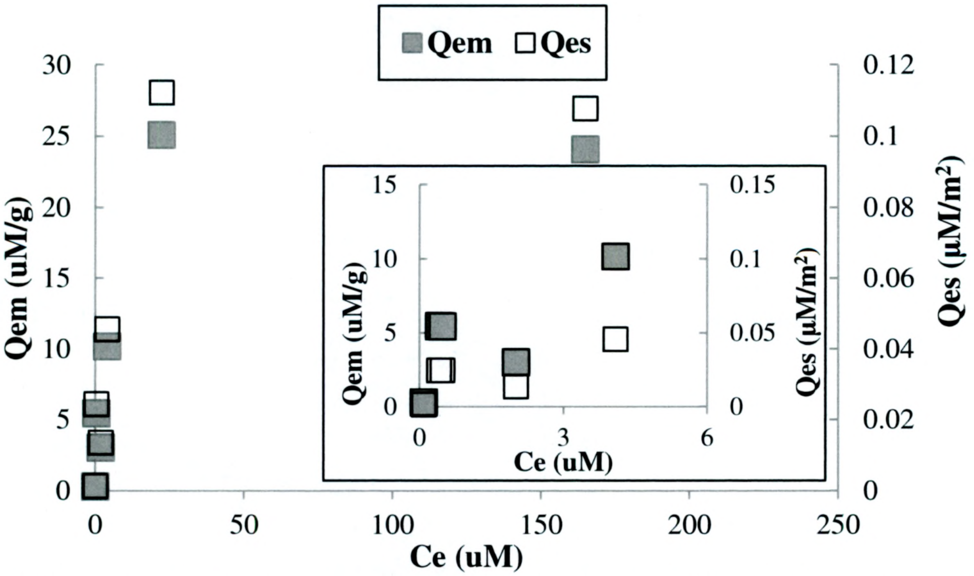

Figure 8. Pb adsorption isotherm on WTR in a mixed metal (Cu+Pb+Zn) solution (20g/l WTR, pH 6.5, and 0.1M NaNO$_3$)

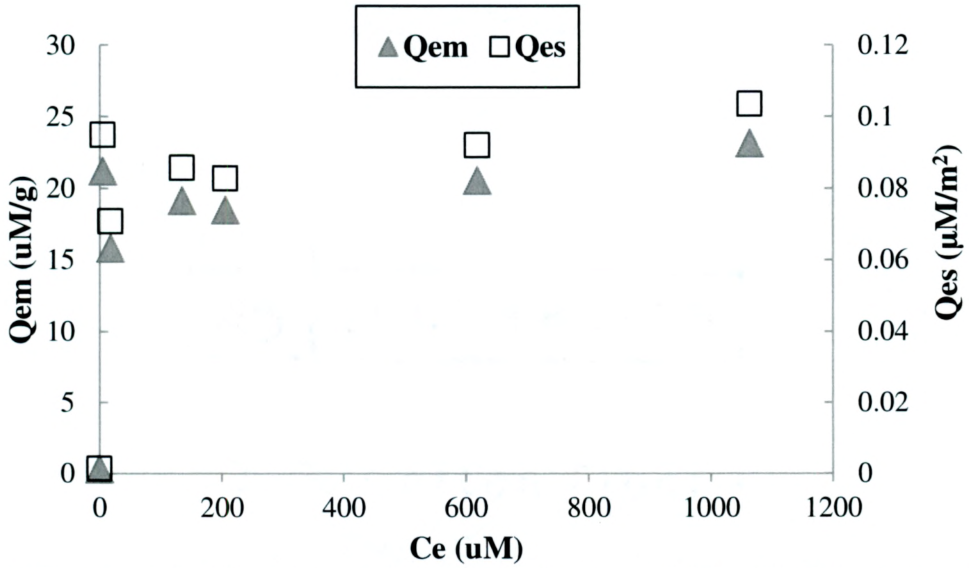

Figure 9. Zn adsorption isotherm on WTR in a mixed metal (Cu+Pb+Zn) solution (20g/l WTR, pH 6.5, and 0.1M $NaNO_3$)

4.5 Adsorption isotherms with TR alone

Adsorption isotherms of Cu and Pb during TR adsorption of a simulated Cu and Pb mixed runoff are shown in **Figures 10-11**, respectively. Similarly, TR adsorption of Cu and Pb also exhibited a biphasic pattern. At a low Ce, Q_{em} and Q_{es} were dramatically increased with the increasing C_e. However, when Ce was over a critical level (~ 6.42 μM/g and 100 μM/m^2 for Cu, and ~ 37.0 μM/g and 579 μM/m^2 for Pb), the improvement of Q_{em} and Q_{es} was almost marginal with the increase of C_e.

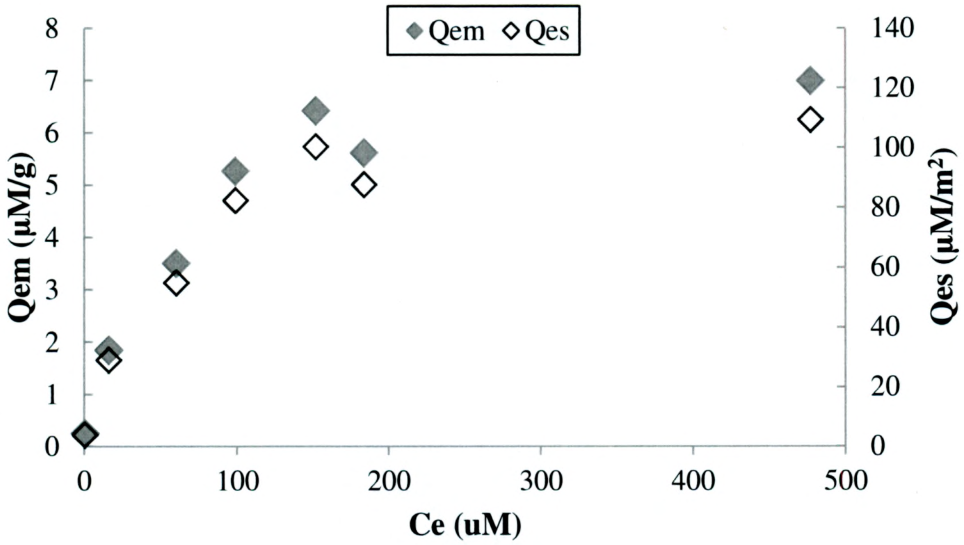

Figure 10. Cu adsorption isotherm on TR in a mixed metal (Cu+Pb) solution (20g/l TR, pH = 6.5 and 0.1M $NaNO_3$)

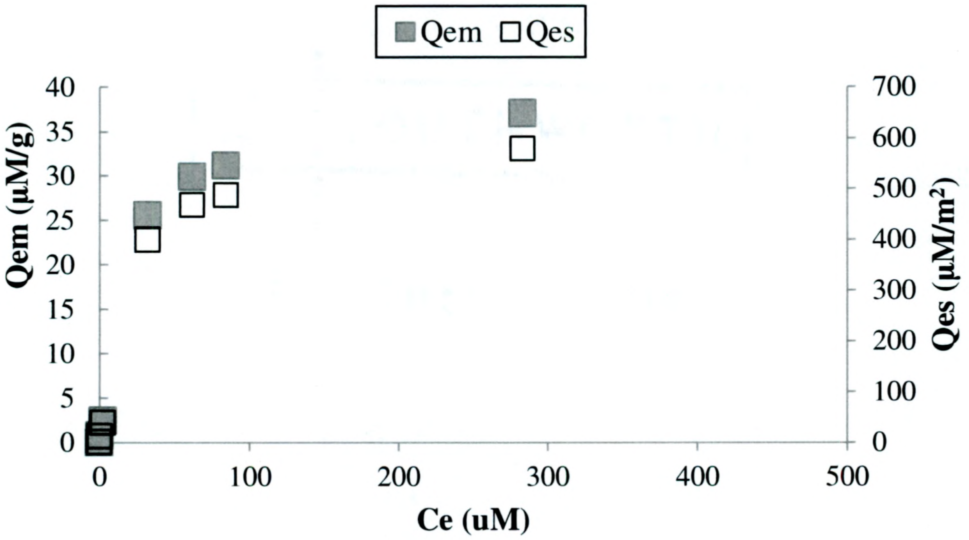

Figure 11. Pb adsorption isotherm on TR in a mixed metal (Cu+Pb) solution (20g/l TR, pH = 6.5, and 0.1M $NaNO_3$)

Zn released from TR versus sum of initial Cu and Pb concentrations is shown in **Figure 12**. As seen, the released Zn was well proportional to $[Cu]_0+[Pb]_0$ ($R^2 > 0.93$). Leached Zn normalized to TR mass and surface area versus sum of TR-mass and surface area-normalized adsorbed Cu and Pb during TR adsorption isotherm tests are shown in **Figure 13** and **14**, respectively. Nearly linear relationships ($R^2 > 0.78$) were observed between the leached Zn and adsorbed Cu/Pb on every unit of mass or surface area TR. These findings implied that ion exchange might be one of the major mechanisms for TR adsorption of Cu and Pb.

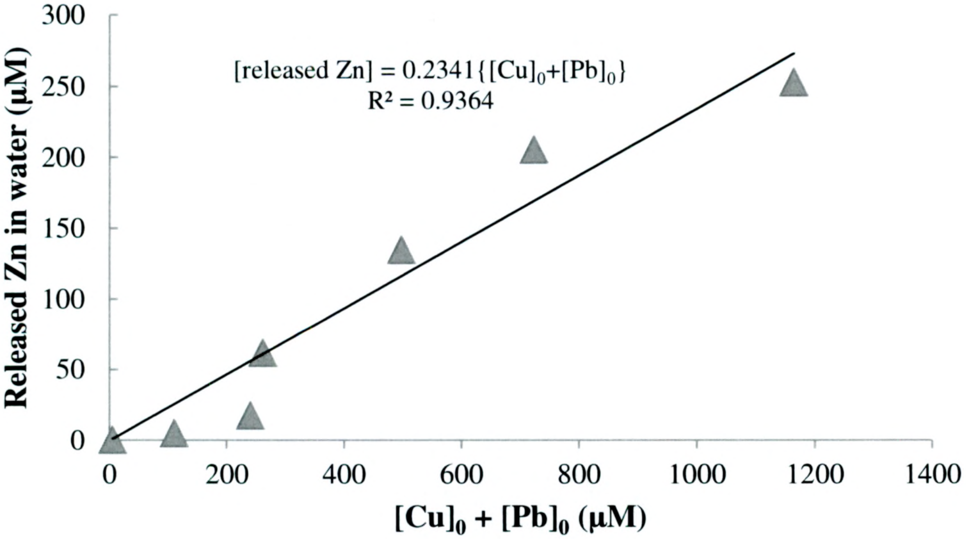

Figure 12. Released Zn (uM) vs. sum of initial Cu and Pb concentrations ($[Cu]_o+[Pb]_o$) during TR adsorption isotherm tests in a mixed metal (Cu+Pb) solution (20g/l TR, pH = 6.5, and 0.1M $NaNO_3$)

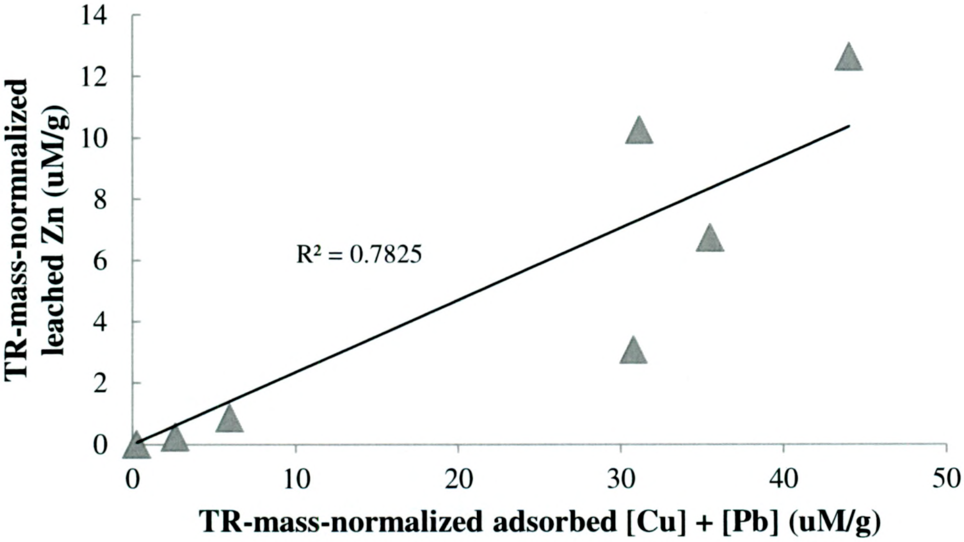

Figure 13. Leached Zn normalized to TR mass (μM/g) vs. sum of adsorbed Cu and Pb normalized to TR mass (μM/g) during TR adsorption tests in a mixed metal (Cu+Pb) solution (20g/l TR, pH = 6.5, and 0.1M $NaNO_3$)

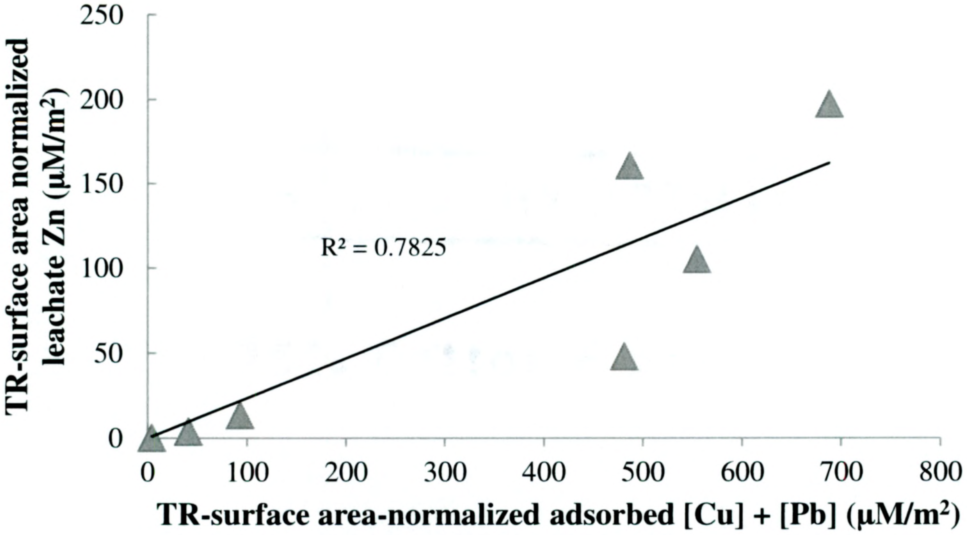

Figure 14. Leached Zn normalized to TR surface area (μM/m^2) vs. sum of adsorbed Cu and Pb normalized to TR surface area (μM/m^2) during TR adsorption tests in a mixed metal (Cu+Pb) solution (20g/l TR, pH = 6.5, and 0.1M $NaNO_3$).

4.6 Adsorption isotherm tests for combined TR and WTR

Results of Cu and Pb adsorption isotherm tests using combined WTR and TR at different ionic strengths are shown in **Figures 15** and **16**, respectively. As seen, Cu and Pb exhibited a similar adsorption isotherm pattern under different ionic strengths. Generally speaking, Cu or Pb adsorption capacity was increased with the increase in its aqueous concentration (Ce); and at any specific aqueous concentration (Ce), higher adsorption capacity was achieved at higher ionic strength. **Figure 17** showed the relationship of the released Zn versus sum of initial Cu and Pb concentrations ($[Cu]_0+[Pb]_0$) during WTR/TR adsorption isotherm tests in a mixed metal (Cu+Pb) solution at different $NaNO_3$ concentrations. Obviously, the released Zn was increased with the initial Cu and Pb concentration. For example, at $[Cu]_0 + [Pb]_0 = 9.8$ and 2,827.9 μM, 2.8 and 30.9 μM Zn was released from 10 g/L TR in the presence of 10 g/L WTR, respectively, at 0.5 M $NaNO_3$. **Figure 18** shows released Zn normalized to TR mass (μM/g) vs. sum of adsorbed Cu and Pb normalized to WTR/TR mass (μM/g) during WTR/TR adsorption isotherm tests in a mixed metal (Cu+Pb) solution at different $NaNO_3$ concentrations. In a similar manner, more adsorbed Cu and Pb on the combined sorbent caused release of more Zn from TR. For example, at 0.1 M $NaNO_3$, when 0.3 μM Cu + Pb was adsorbed to 1 g WTR/TR sorbent, 0.01 μM Zn was released; however, when the adsorbed Cu and Pb was increased to 133.9 μM/g, 1.2 μM Zn would be leached from 1 g mixed sorbent. These findings again suggest that, at least, ion exchange between Zn in TR and Cu and Pb in bulk solution was one of the principal mechanisms for Zn leaching and Cu/Pb sorption.

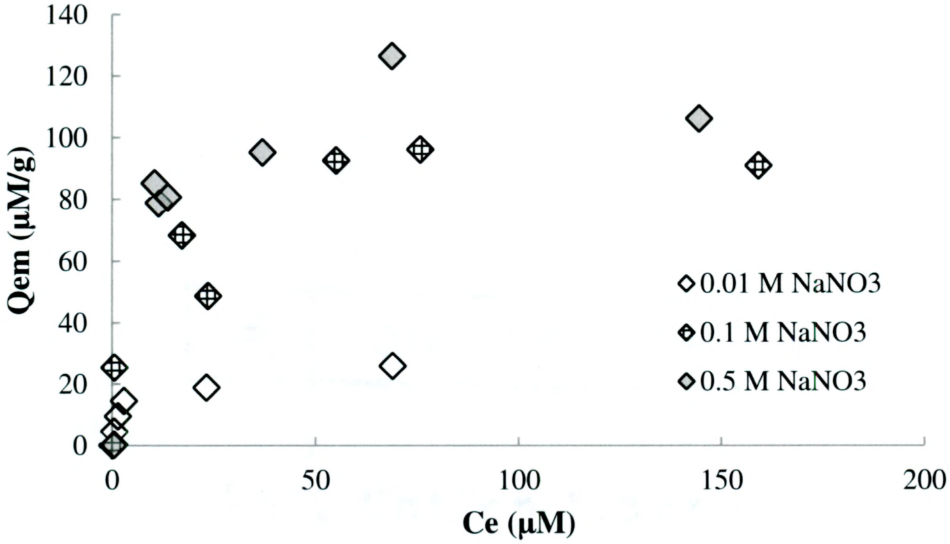

Figure 15. Cu adsorption isotherm of WTR and TR in a mixed metal (Cu+Pb) solution at different ionic strengths (10g/l WTR and 10g/l TR, and pH = 6.5)

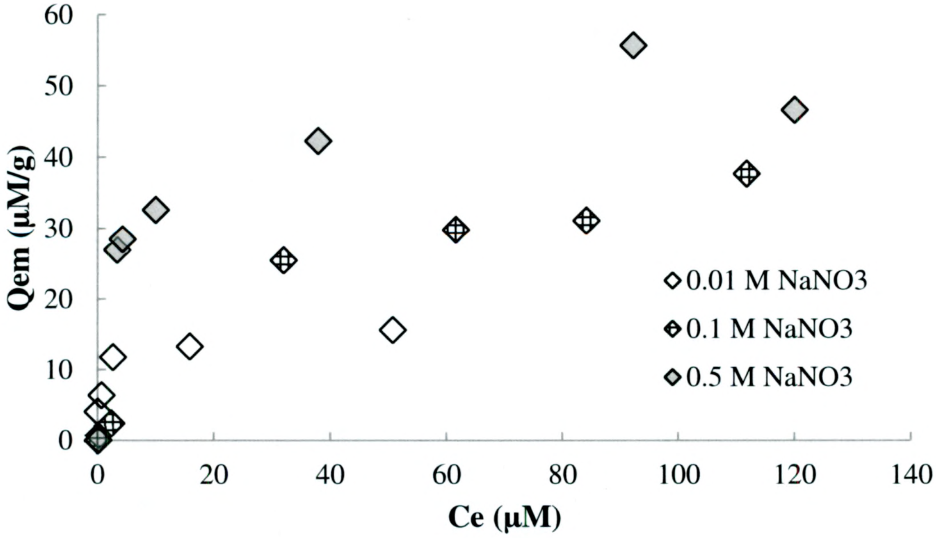

Figure 16. Pb adsorption isotherm of WTR and TR in a mixed metal (Cu+Pb) solution at different ionic strengths (10g/l WTR and 10g/l TR, and pH = 6.5).

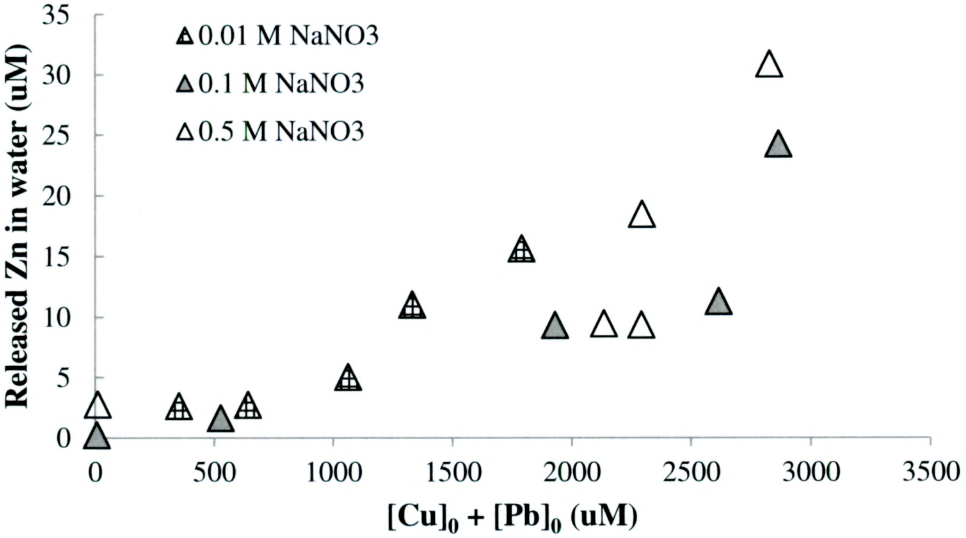

Figure 17. Released Zn (uM) vs. sum of initial Cu and Pb concentrations ($[Cu]_o+[Pb]_o$) during WTR/TR adsorption isotherm tests in a mixed metal (Cu +Pb) solution at different $NaNO_3$ concentrations (10g/l WTR, 10g/l TR, and pH = 6.5)

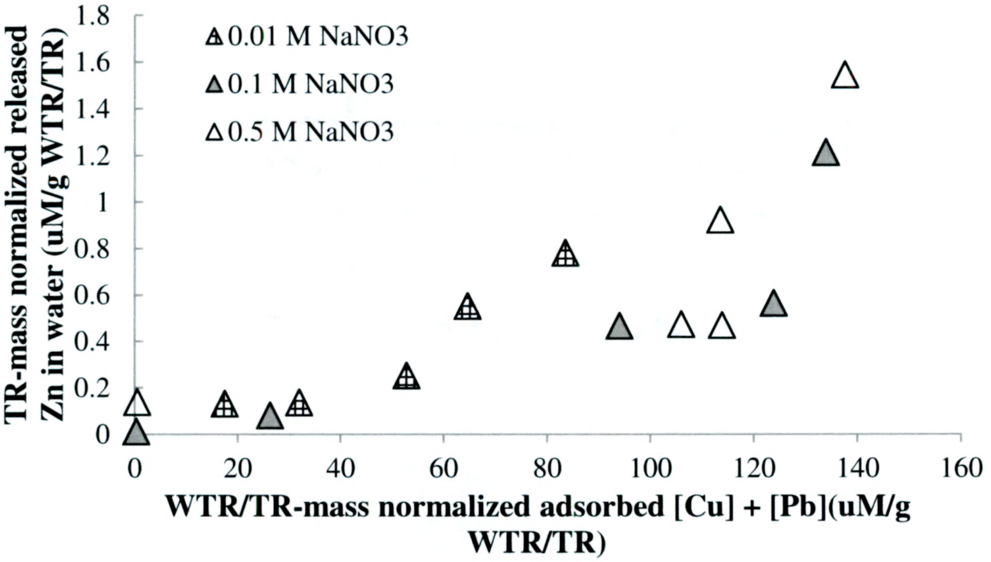

Figure 18. Leached Zn normalized to TR mass (uM/g) vs. sum of adsorbed Cu and Pb normalized to WTR/TR mass (uM/g) during WTR/TR adsorption isotherm tests in a mixed metal (Cu+Pb) solution at different $NaNO_3$ concentrations (10g/l WTR, 10g/l TR, and pH = 6.5)

4.7 Effect of varying mass ratio of WTR to TR

Cu and Pb adsorption isotherm data at different mass ratios of WTR to TR (WTR:TR) are shown in **Figures 19** and **20**, respectively. More Cu and Pb were adsorbed to the mixed adsorbent material at WTR:TR = 1:2 or 1:4 than at WTR:TR = 1:1. A WTR:TR of 1:2 was slightly better than 1:4 in terms of adsorption capacity.

Freundlich model was used to fit the experimental data. The Freundlich equation is an empirical adsorption isotherm model as expressed below.

$$Qe = K_f\, C_e^{1/n} \qquad (8)$$

Equation (8) can be expressed as a linear relationship in Equation (9).

$$\ln Q_e = \ln K_f + 1/n \ln C_e \qquad (9)$$

Where, K_f and n are constants for certain adsorbate and adsorbent at a given temperature.

Measured data and model data for Freundlich modeling of WTR/TR adsorption of Cu and Pb are shown in **Figures 21** and **22**, respectively. Parameters of the Freundlich isotherm models and regression coefficient (R^2) are summarized in **Tables 5**. For any particular WTR:TR, the measured data well follow the Freundlich adsorption isotherm patterns ($R^2 > 0.85$). These findings suggest that WTR/TR could effectively adsorb Cu and Pb, and the optimal mass ratio of WTR to TR was 1:2.

Table 5. Parameters of the Freundlich isotherm models for WTR/TR adsorption of Cu and Pb at various mass ratios of WTR to TR (pH = 6.5, at ambient temperature)

Cu sorption onto various ratios of WTR/TR				**Pb sorption onto various ratios of WTR/TR**			
Ratio	**1/n**	**K_f**	**R^2**	**Ratio**	**1/n**	**K_f**	**R^2**
1 to 1	0.3073	7.731	0.8987	1 to 1	0.184	8.056	0.9449
1 to 2	0.4587	7.228	0.859	1 to 2	0.2464	15.31	0.9762
1 to 4	0.4237	6.16	0.9055	1 to 4	0.2179	13.94	0.9525

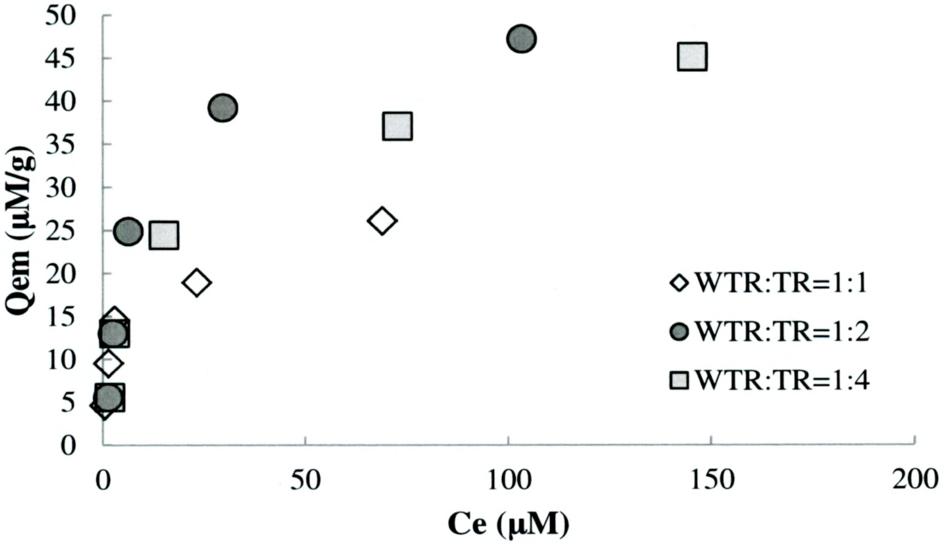

Figure 19. Cu adsorption isotherm at different mass ratios of WTR to TR (pH = 6.5, and 0.01M $NaNO_3$)

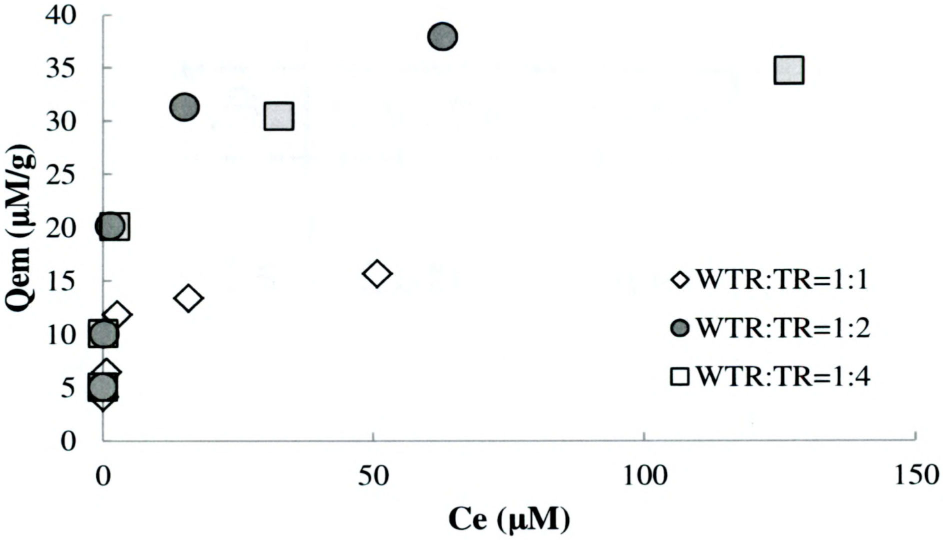

Figure 20. Pb adsorption isotherm at different mass ratios of WTR to TR (pH = 6.5, and 0.01M $NaNO_3$)

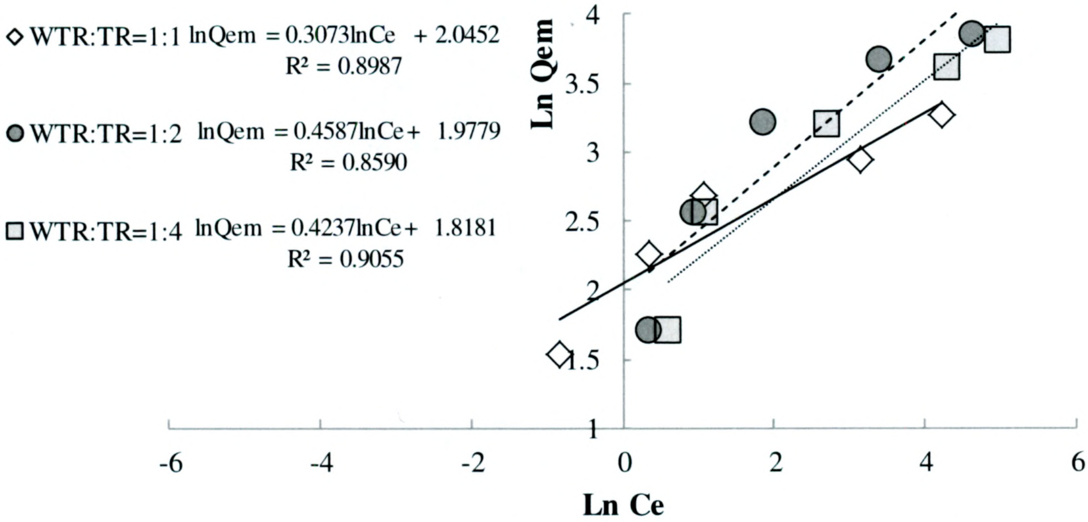

Figure 21. Freundlich model data vs. measured data of Cu adsorption isotherm at different mass ratios of WTR to TR (pH = 6.5, and 0.01M $NaNO_3$)

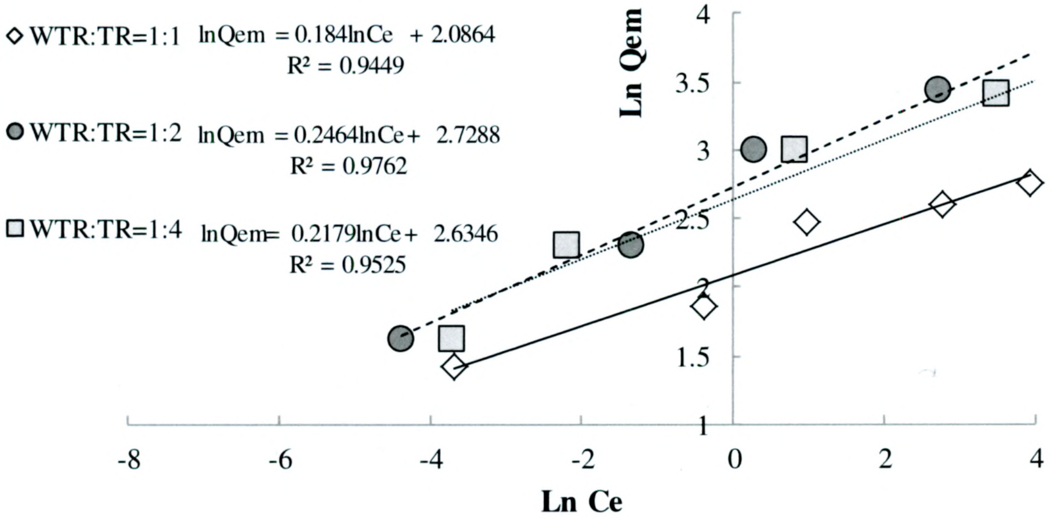

Figure 22. Freundlich model data vs. measured data of Pb adsorption isotherm at different mass ratios of WTR to TR (pH = 6.5, and 0.01M $NaNO_3$)

4.8 Desorption analysis

During development of an adsorption process, desorption of adsorbed metal on sorbents into bulk solution under different conditions is extremely interesting. In this study, it is important to understand how strong the adsorption occurs between our green sorbents and metals of concern. Desorption rate of a metal from the studied sorbents is defined as:

$$\text{Desorption rate} = \frac{\text{Amount of desorbed metal into bulk solution}}{\text{Amount of total adsorbed metal}} \times 100\% \qquad (10)$$

Where, the "amount of total adsorbed metal" is the mass of metal that is adsorbed onto the adsorbent during adsorption isotherm tests; and the "amount of desorbed metal into bulks solution is the mass of the adsorbed metal that is released into bulks solution under certain experimental conditions.

Desorption rates of Cu and Pb from WTR and TR under 0.02 M EDTA or 0.02 M $NaNO_3$ solution at different mass ratios of WTR to TR are shown in **Figure 23**. As seen, adsorption of Cu and Pb was irreversible in $NaNO_3$ solution. Only in presence of a strong ligand (EDTA in this study), part of sorbed Cu and Pb desorbed into bulk solution. In **Figure 23**, 0.02 M EDTA extracted ~ 52% sorbed Cu and ~ 56% sorbed Pb into bulk solution, regardless of WTR:TR ratio. These findings suggest that WTR/TR adsorption of Pb and Cu was somewhat strong and irreversible, and desorption only occurred in the presence of a strong chelating agent.

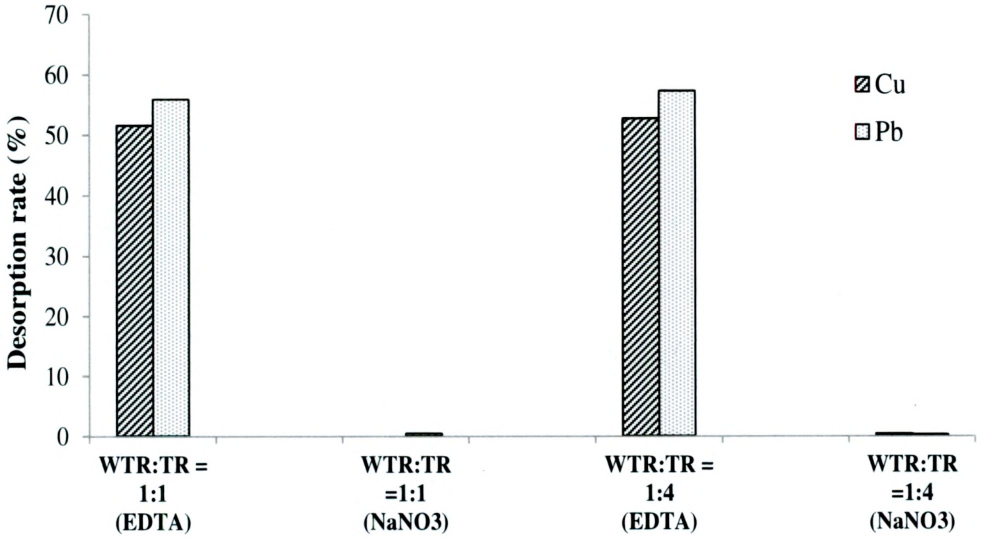

Figure 23. Desorption of Cu and Pb from WTR/TR sorbents in EDTA and $NaNO_3$ solutions at different WTR and TR ratios.

4.9 Column tests

Although WTRs exhibited better adsorption capacities for the three metals than TR and did not significantly release undesirable chemicals, it cannot be directly used as filter media because fine WTR powders tend to block stormwater flow in a down-flow filter bed. On the other hand, STR has a better hydraulic permeability, but releases Zn and causes an unwanted secondary pollution when used alone. A logic approach to apply the two solid wastes is to combine them and take advantage of their complementary properties – STR improves the permeability, while WTR inhibits the STR leaching. To further explore whether combination of WTR and TR is a technically feasible method, column tests were performed.

Physical properties of different media. Bulk densities, particle densities, and porosities of

WTR, TR, and combined media, as well as the hydraulic conductivity of the mixed media, are summarized in **Table 6**.

Table 6. Physical properties of WTR, TR, and the combined WTR and TR media.

Media Ratio	Bulk Density(g/cm^3)	Particle Density(g/cm^3)	Porosity	Hydraulic Con.(cm/s)*
WTR/TR(1:5)	0.578	1.57	0.629	0.00493
WTR	0.849	1.79	0.523	N/A
TR	0.619	1.16	0.475	N/A

*Hydraulic conductivity

Hydraulic conductivity at different mass rations of WTR to TR. Different hydraulic conductivities at different bed depths and with different Al-WTR:TR are shown in **Table 7.** Obviously, hydraulic conductivity increased with the increasing TR fraction in the mixed media, because TR chips had much larger sizes to allow water more readily to flow through the filter bed. At a specific WTR:TR, the effect of the bed height on the hydraulic conductivity appeared to be complicated. This finding reflects the complex flow patterns within the column, and indicates that the bed height is not the only key factor affecting the hydraulic conductivity. In practice, hydraulic conductivity plays an essential role in the column reactor design. Higher conductivity allows for flow to move smoothly and reduce the size of a reactor, but reduces the retention time so that the contaminants may not be sufficiently treated.

Table 7. Hydraulic conductivities of the mixed media at various ratios of Al-WTR to TR

Ratio (WTR:TR)	Bed Height(cm)	Hydraulic Con.($x10^{-3}$cm/s)
1 to 5	8	4.93
"	10	8.2
"	13.5	4.11
1 to 8	8	3.29
"	10	8.2
"	13.5	9.86
1 to 10	8	18.4
"	10	16.45
"	13.5	10.2
1 to 12	8	19.5
"	10	24.2
"	13.5	23
1 to 15	8	34
"	10	44
"	13.5	21.3

Filtration rate. Filtration rates were tested in three columns at various ratios of Al-WTR to TR and different bed depths (1: 5, 14cm; 1:5, 12cm; and 1:8, 9cm) (ambient room temperature (~25°C), pH 6.5, and ionic strength = 0.1M $NaNO_3$). All the columns were operated in a downward saturated flow mode. The filtration proceeded for 60 min, or until the water flow was clogged (Table 8). Our tests show that all the filtration flow was maintained at a high rate within the first 30 minutes, and then gradually declined as a result of the filter bed clogging. The clogging was because many fine WTR particles moved downward from the top bed layer due to gravity and the flowing water, and then built up a sludge cake layer within the bed. As seen in **Table 8**, all the three trials were completed within 60 min. However, the filtration rate was reduced as a result of flow clogging, and their final filtration rates varied 42-50% of the initial filtration rate.

Table 8. Variation of the initial and final filtration rates in column tests

Column Experiment	Media (Ratio)	Filtration Rate (ml/min)			Duration(min)	Remark
		Initial	Final	Final/initial(%)		
1	*AL-WTR/TR(1:5)*	3	1.25	42	60	Clogged
2	*AL-WTR/TR(1:5)*	3	1.5	50	60	Sluggish
3	*AL-WTR/TR(1:8)*	4.5	2.1	47	60	Clogged

Bed depth vs. flowrate. Different flowrates were tested at different bed depths as a function of the media ratio as shown in **Table 9**. At WTR:TR = 1:5 and 1:8, the flow rates were 3.0 and 4.5 mL/min, regardless of bed depths within the tested ranges in this study (12.0-14.0 cm bed depth for WTR:TR of 1:5, 9.0cm bed depth for WTR:TR of 1:8).

Table 9 Column Parameters

Al-WTR/TR (Ratio)	*Flow Rate (ml/min)*	*Bed Depth(cm)*	*Bed Vol.(cm^3)^a*	*Media mass(g)*	*Column dia.(cm)^b*	*Column length(cm)*
1 to 5	3	12	60.8	24.2	2.54	30
1 to 5	3	14	70.9	30.8	2.54	30
1 to 8	4.5	9	46	18.4	2.54	30

a. Bed volume b. Column diameter

Column tests for metal removal. Columns were designed to treat solutions containing Cu and Pb at different bed heights with conditions of 25°C and pH 6.5 and background electrolyte of 0.1M $NaNO_3$ ionic strength. Three columns were installed, and each one was packed with different ratios of Al-WTR/TR samples as shown in **Table 9.** Simulated urban storm water was added. As shown, the data of the effluent Cu and Pb at 9 cm bed depth are unstable with time. This finding is likely caused by the column wall effect in which part of solution directly and rapidly flows down along the inner wall region without sufficient contact with the media. Anyhow, Cu or Pb was removed from the simulated runoff. Generally, at any specific time, the effluent contained less Pb than Cu, suggesting that the combined media preferentially adsorbed Pb under the experimental conditions (**Figures 24** and **25**). After 20 min filtration, the effluent concentrations became relatively stable. Higher bed depth accomplished lower effluent metal concentrations. Within 60 min, breakthrough did not occur for Cu or Pb, but the media clogging significantly reduced the flow rate so that the filtration had to be stopped. Therefore, the filtration seemed to be controlled principally by hydraulic performance, rather than metal breakthrough.

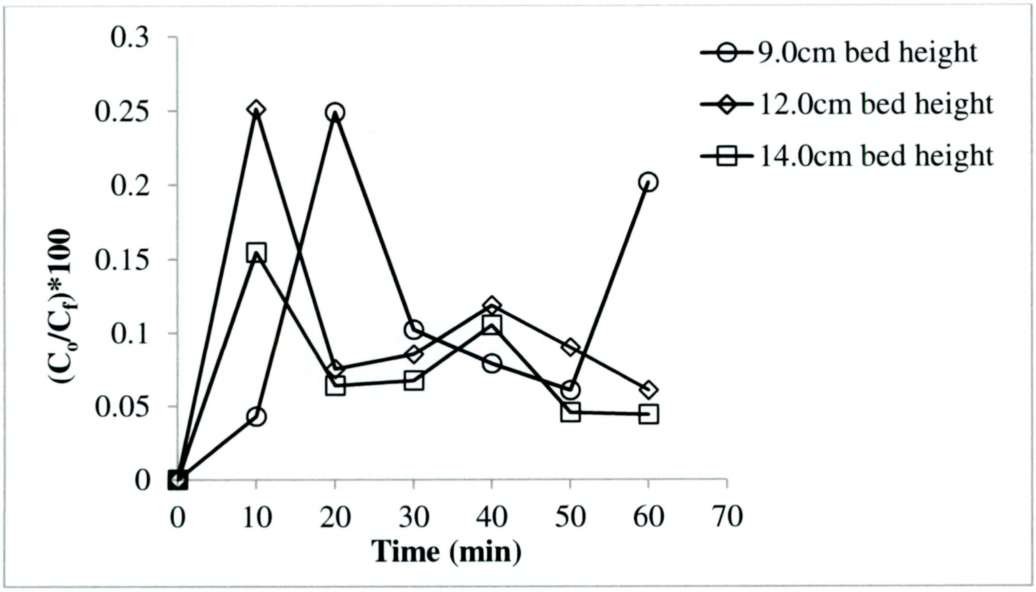

Figure 24. Normalized Cu^{+2} adsorption on different ratios of combined WTR/TR in a mixed metal system ($[Pb]_o$ = 430μM; $[Cu]_o$ = 380uM; pH = 6.5; Temp. 25°C and 0.1M $NaNO_3$)

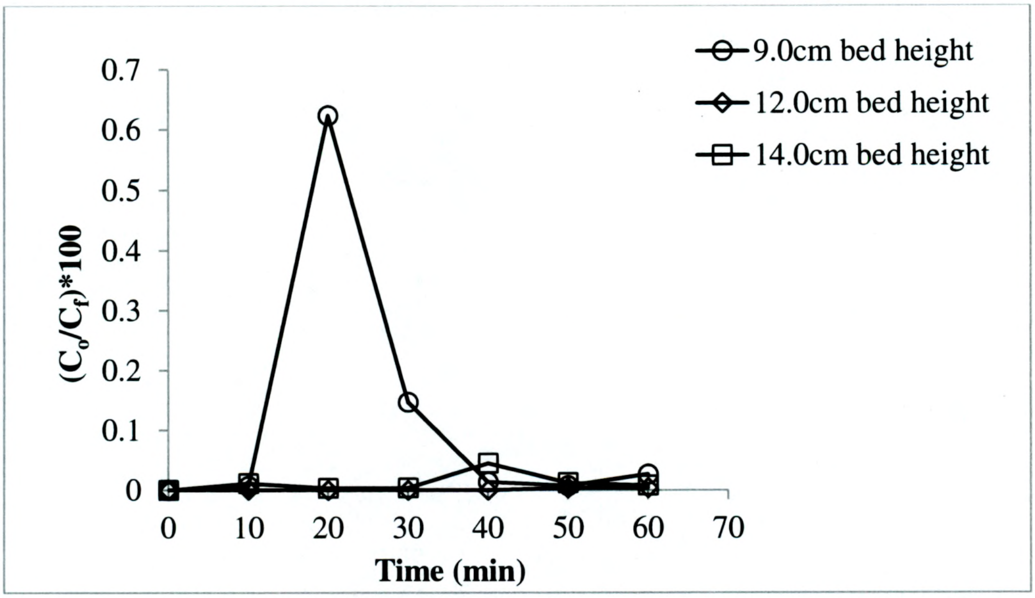

Figure 25. Normalized Pb^{+2} adsorption on different ratios of combined WTR/TR in a mixed metal system ($[Pb]_o = 430\mu M$; $[Cu]_o = 380\mu M$; pH = 6.5; Temp. 25°C and 0.1M $NaNO_3$)

CHAPTER 5. LIMITATIONS OF THE PROPOSED TECHNOLOGY AND THIS THESIS STUDY

Limitations of the proposed technology and this thesis study are summarized as below, separately. WTRs and TR are capable of immobilizing metals from water; however, the ability of these media for adsorption of organic compounds is relatively poor, unless WTRs contain sufficient activated carbon that is widely applied in drinking water treatment plants. Dissolved organic matters (DOMs) in stormwater runoff may be abundant, such as hydrocarbons from leaked gasoline, pesticides, and herbicides. These organic molecules play an important role in water pollution. For example, biodegradable organic compounds entering water bodies can deplete dissolved oxygen and degrade water quality. The DOMs with certain functional groups such as carboxylic (-COOH) and phenolic(-OH) groups are capable of complexing heavy metals, and thus increase the mobility of metals as well as decrease the metal sorption on a solid phase (Zhou and Wong, 2001). Therefore, the proposed adsorption technology alone is not expected to effectively remove organic pollutants in stormwater pollutants. Modification of the technology should be considered, if the removal of DOMs is also a goal in a stormwater management project. Octanol/water partition coefficients may be used to predict the DOM adsorption.

The limitations of this thesis study include:

1) Simulated stormwater used in this study only contained target metals, pH buffer, and inert chemicals controlling ionic strength. Many other substances existing in real stormwater matrix were not included. Consequently, their effects were not evaluated here. The substances of major interest include suspended solids,

nutrients (particularly phosphorus), and hydrocarbons. Suspended solids tend to block water flow and reduce hydraulic conductivity of the mixed media in column reactors. Phosphorus is expected to adsorb on the WTR surface and occupy the active sites for the metal adsorptions, thereby reducing the metal removal efficiency. Hydrocarbons may complex certain metals and lower their adsorption on WTR/TR.

2) The effect of pH was not tested. Varied pH most likely affected the metal adsorption. For example, pH can alter the zeta potential of WTRs, and change the metal adsorption efficiency.

CHAPTER 6. CONCLUSIONS & SUGGESTIONS

Bench-scale batch and column tests were conducted to investigate the removal of major metal contaminants (i.e. Cu, Pb and Zn) from simulated urban storm water with two “free” industrial solid wastes - aluminum water treatment residual (Al-WTR) and scrap tire rubber (TR). Batch tests showed that WTR alone was able to effectively remove Cu, Pb and Zn from the simulated stormwater runoff, and the adsorption could be rapidly achieved within 1 hour. In contrast, TR alone could also effectively adsorb Cu and Pb in water, but certain amounts of Zn was released from TR into bulk solution. Compared with WTR-induced adsorption, the TR adsorption process was relatively slow. The nearly linear relationship ($R^2 > 0.78$) between the leached Zn and adsorbed Cu/Pb on every unit of mass or surface area of TR implies that ion exchange was a principal mechanism for the TR adsorption of Cu and Pb, as well as Zn leaching from TR. Hence, TR alone is not a proper sorbent for stormwater treatment. However, simultaneous application of the two sorbents could significantly reduce the Zn release. Meanwhile, the presence of TR in the mixed WTR and TR media increased the hydraulic conductivity (the fine WTR powders alone has an extremely low permeability). Therefore, the combination of WTR and TR is a reasonable strategy to apply both wastes in stormwater treatment. The ensuing column tests examined hydraulic performance and pollutant removal under a flow through condition. Hydraulic tests with DI water showed that hydraulic conductivity could be affected by the mass ratio of WTR to TR and bed height. As the water flowed through, fine WTR powder moved down to build up a sludge layer thus increasing head loss and reducing the flow rate. Treatment tests using the columns packed with the mixed media demonstrated that Cu and Pb could be effectively removed.

This study provides a preliminary investigation to explore WTR and TR for stormwater remediation. Results demonstrated that the combination of WTR and TR is a reasonable method for removal of undesirable heavy metals from urban runoff. Application of the two solid wastes not only achieves the remediation and substantially reduces the stormwater management costs, but also provides a new recycle pathway to address the two solid wastes that are originally disposed of within landfills.

Future tests should be performed to further the new stormwater remediation technology. Some suggestions are made as follows.

1) The effects of suspended solids and dissolved organic matters, probably existing in stormwater, should be evaluated. Particularly, the particles may reduce hydraulic conductivity of the mixed media in column reactors.
2) The effect of pH on the mixed media adsorption of metals should be investigated.
3) The reduction of nutrient, phosphorus in particular, should be tested.

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