

# Water Treatment Residuals and Scrap Tire Rubber as Green Sorbents for Removal of Stormwater Metals

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**ABSTRACT:** Bench scale tests were performed to evaluate two recycled wastes, water treatment residuals (WTR) and scrap tire rubber (STR), for adsorption of selected metals from urban stormwater, and assess their release from used sorbents. Aluminum-WTR alone could rapidly and effectively remove Cu, Pb, and Zn, while STR alone continuously released Zn accompanied with Cu and Pb adsorption. Zn leaching from STR was significantly reduced in the presence of WTR. Very little metals released from used combined adsorbents in NaNO<sub>3</sub> solution, and only part of them were extracted with EDTA (a strong chelating agent), suggesting that metal release is not a concern in a typical stormwater condition. A combination of WTR and STR is a new, effective method for mitigation of urban stormwater metals—WTR can inhibit the STR leaching, and STR improves the hydraulic permeability of WTR powders, a limiting factor for stormwater flow when WTR is used alone. *Water Environ. Res.*, **88**, 500 (2016).

**KEYWORDS:** water treatment residuals, scrap tire rubbers, urban stormwater runoff, heavy metals, adsorption, copper, lead, zinc.

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## Introduction

The United States is an extremely urbanized country where 82% of the people reside in about 500 urban areas (>390 persons/km<sup>2</sup>) (CIA, 2010). Despite many benefits of urbanization, there are also adverse environmental issues, such as polluted stormwater runoff. High densities of impervious surfaces (e.g., buildings, parking facilities, streets, highways) in urban areas significantly increase the quantity and flow rate of runoff that can carry away accumulated constituents from atmospheric deposition, vehicular traffic, and other sources. Increased pollutant loads can foul drinking water supplies, harm fish and wildlife populations, kill native vegetation, and make recreational areas unsafe. Therefore, urban runoff is recognized

among the major nonpoint surface water and groundwater pollution sources (USEPA, 2009).

Toxic metals, nutrients, sediments, pathogens, and organic pollutants have been identified as common urban stormwater pollutants (Chiew et al., 1997). Among them, heavy metals, especially copper (Cu), lead (Pb), and zinc (Zn), are of particular concern due to their non-biodegradability, accumulation in environment, and toxicity. Copper present in stormwater derives from brake pad abrasion (Göbel et al., 2007), fertilizers, paint and pigment industries (Ahmad et al., 2009), and atmospheric deposition (Davis et al., 2001; Sabin et al., 2005). Sources of Pb in urban stormwater runoff include atmospheric deposition, vehicular traffic, and roofing/building materials (Gnecco et al., 2005). Anthropogenic sources of Zn in runoff include tire wear particles, roofing materials, mining activities, fertilizers, and wood preservatives (ATSDR, 2013; Göbel et al., 2007). Among the three metals, Pb is the most toxic, and has consistently ranked #2 in the Agency for Toxic Substances and Disease Registry's (ATSDR) most hazardous chemicals list. The toxic metals either enter surface- or groundwater, or accumulate in top soil and river sediment (Walker et al., 1999). Their concentrations in urban stormwaters vary within broad ranges, as shown in Table 1.

Early urban stormwater management focused merely upon rapid reduction of peak flows (Blick and FredSkupien, 2004). In contrast, new strategies, such as bioretention systems, encourage best management practices (BMPs) to address both quantity and quality issues of urban runoff. However, several limitations have been demonstrated during practice, and may restrict their widespread application without further modification. Besides highly variable phosphorous (P) removal, stormwater loading into bioretention systems result in toxic metal accumulation in top soil (Davis et al., 2003). As a result, periodic replacement of top soil infiltration systems is suggested, thereby making operation and maintenance more complex, and increasing cost (Weiss et al., 2008). Therefore, innovative, technically viable, cost effective technologies are in high demand to address heavy metals in urban stormwater.

Recently, research interests have been directed to new and low-cost sorbents, such as water treatment residuals (WTRs), for urban stormwater treatment (O'Neill and Davis, 2011a, b). WTRs are a byproduct of Al- or Fe salt induced coagulation during drinking water treatment, and typically contain amorphous or poorly crystalline Fe- and Al-oxides. Every day, over 2 million tons of WTRs are generated in the United States

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**Table 1—Ranges of Major Roadway Stormwater Pollutants in Urban Areas.<sup>a</sup>**

Constituent (unit)	Range
Pb ( $\mu\text{g/L}$ )	73 – 1,780
Cu ( $\mu\text{g/L}$ )	22 – 7,033
Zn ( $\mu\text{g/L}$ )	56 – 929

<sup>a</sup> Barrett et al., 1995; Chin, 2006; Geosyntec Consultants and Wright Water Engineers, 2009; USEPA, 1983.

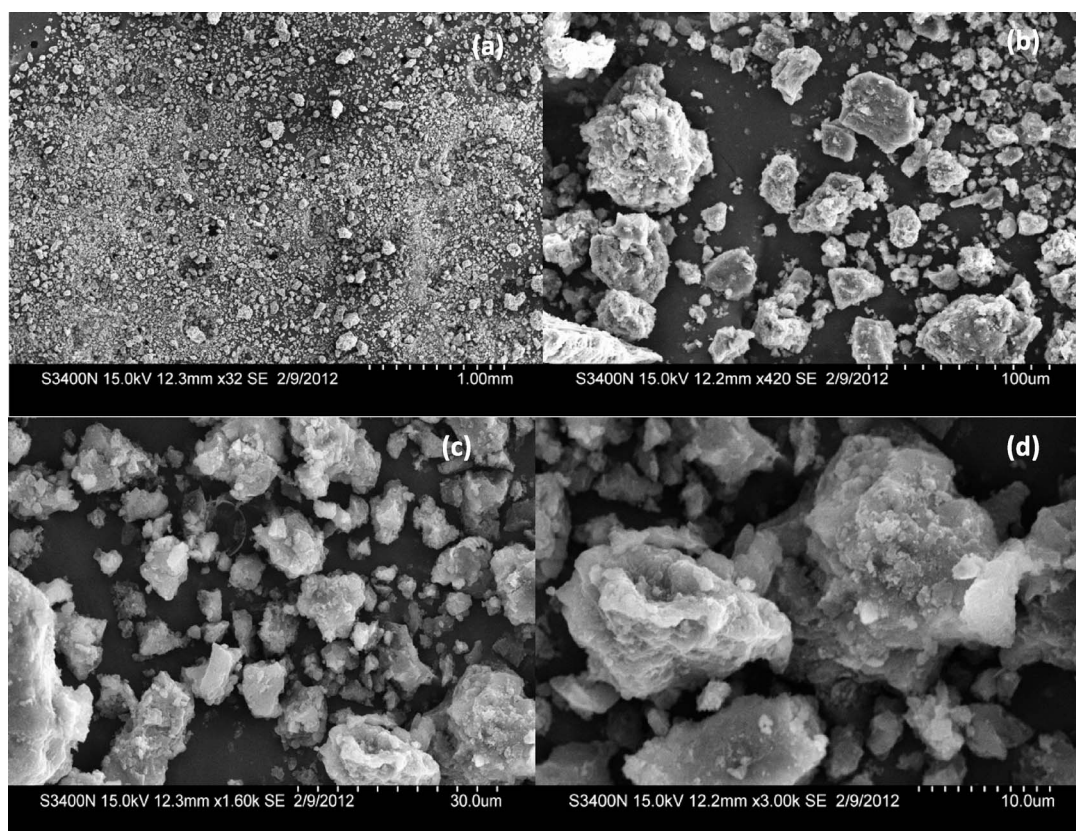
(Prakash and Sengupta, 2003). Over the past one and a half decades, the potential of WTRs has been consistently demonstrated for adsorption of metals, metalloids, emerging organic pollutants, as well as P - due to their high specific surface and abundant active sorption sites (Makris et al., 2006, 2007; Sarkar et al., 2007). O'Neill and Davis (2011a,b) conducted batch and column tests to evaluate WTRs as a bioretention amendment for mitigation of phosphorus in stormwater. They found that 5% WTR-amended bioretention soil media by mass (air dried) adsorbed 88.5% of the applied P mass (68–476  $\mu\text{g/L}$  P), and consistently produced total phosphorus effluent event mean concentrations < 25  $\mu\text{g/L}$ . However, these studies did not test WTRs for removal of heavy metals or any other pollutants in urban stormwater.

In 2003, the U.S. generated approximately 290 million scrap tires. Now, markets for both recycling and beneficial use exist for 80% of these scrap tires. Over the past decades, scrap tire rubbers (STRs) have been intensively studied as an adsorbent for

environmental remediation. These studies are proposed based on two unique properties of STR: a high potential to adsorb different pollutants, and low cost (Alamo-Nole et al., 2011; Calisir et al., 2009). Although numerous studies have well demonstrated the ability of STRs to sorb metals such as Pb, Cu, and Hg (Rowley et al., 1984; Calisir et al., 2009) STRs, when used alone, may leach Zn and certain organic compounds (e.g. benzothiazole) (Smolders and Degryse, 2002; Wik, 2007). The objective of this study was to evaluate the performance of two recycled industrial wastes, WTRs and STRs, for the adsorption of major heavy metals from stormwater, as well as to assess potential leaching of adsorbed metals from used sorbents. During application, these media can be easily employed in different loading modes, such as addition of WTR coated chips on a bioretention basin or direct addition of mixed WTR and STR into soil in a bioretention basin.

### Materials and Method

**Materials.** All the chemicals used are of analytical grade or above. Al-WTR materials were collected from the Manatee County Water Treatment Plant in Bradenton, FL. Once collected, the WTR was thoroughly mixed, air-dried, sieved through a 2-mm sieve, and finally ground into powder prior to use. STR samples were provided from RubbeRecycle Inc., Lakewood, New Jersey. Prior to use, the STR chips were rinsed with Milli-Q water (> 18.2 M $\Omega$ -cm) twice and then air-dried. Simulated metal-contaminated urban runoff solution was prepared using their respective nitrate salts (i.e., Cu (NO<sub>3</sub>)<sub>2</sub> · 2.5H<sub>2</sub>O (Acros organic, 98+%), Pb(NO<sub>3</sub>)<sub>2</sub> (Fisher Scientific, Fair Lawn, NJ), and Zn



**Figure 1—(a)-(d) SEM images of Al-WTR.**

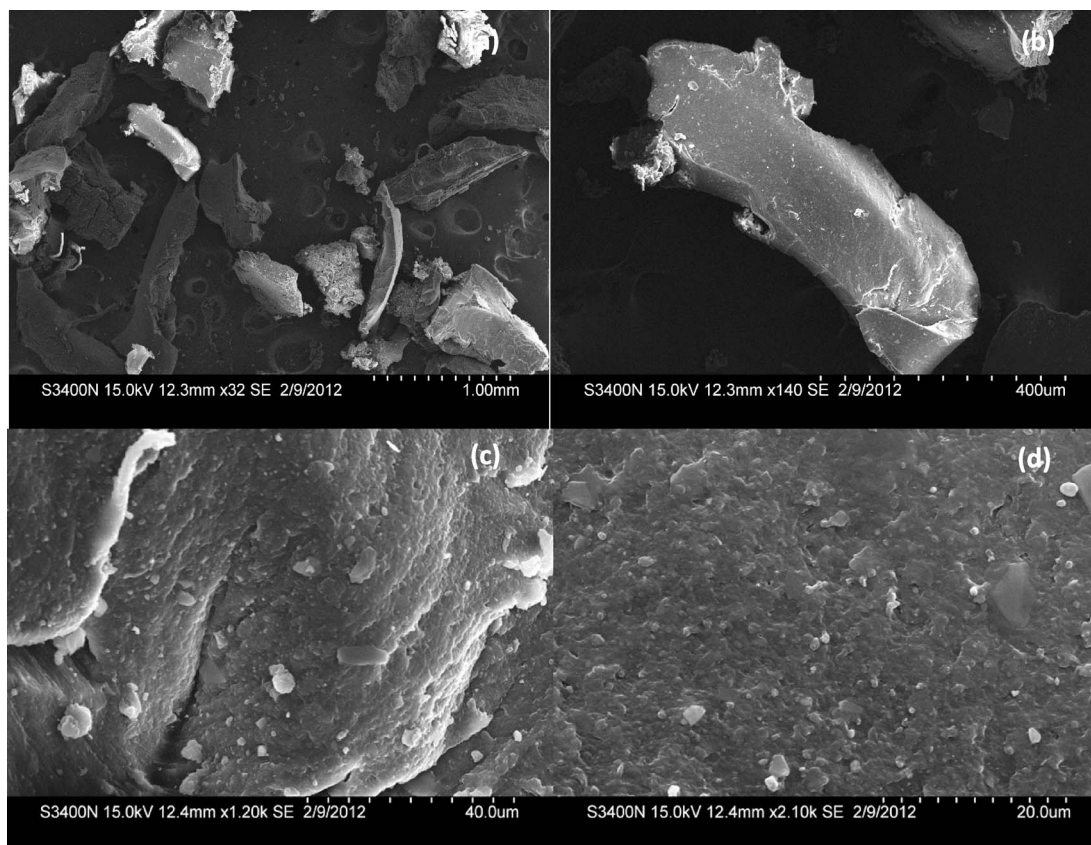


Figure 2—(a)-(d) SEM images of STR.

( $\text{NO}_3$ )<sub>2</sub>·6H<sub>2</sub>O (Fisher Scientific, Fair Lawn, NJ)) in 10 mM PIPES solution (piperazine-N, N'-bis[2-ethanesulfonic acid] (Acros Organics, 98.5+%). Sodium nitrate ( $\text{NaNO}_3$ , Acros) was used as a background electrolyte to form a desirable ionic strength. All the solutions were prepared using Milli-Q water.

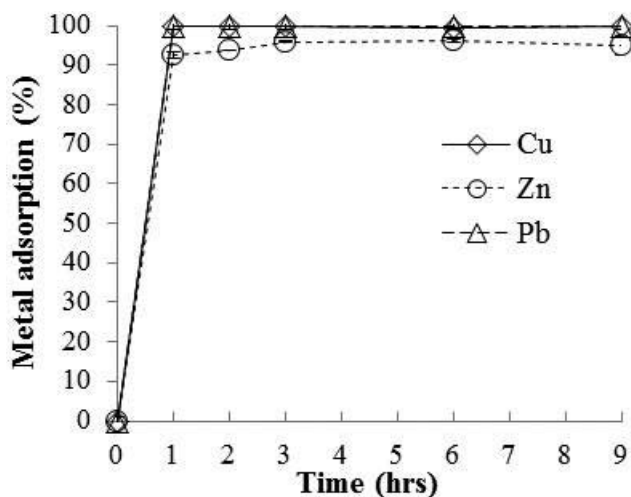


Figure 3—Adsorption of metals by WTR alone with time (10 g/L WTR,  $[\text{Cu}]_0 = 6 \mu\text{M}$ ,  $[\text{Pb}]_0 = 2.45 \mu\text{M}$ ,  $[\text{Zn}]_0 = 6 \mu\text{M}$ , and pH 6.5).

**Adsorption Tests.** 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  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , or  $\text{Zn}^{2+}$  stock solutions to 0.1 M  $\text{NaNO}_3$  PIPES-buffered solution. The initial solution pH was adjusted to 6.5 with 1 M  $\text{NaOH}$  and 1 M  $\text{HNO}_3$ . All the tubes were installed in a shaking bed. A rapid rotation (> 150 rpm) ensured a completely mixing solution state. The adsorption reactions were initiated once appropriate masses of WTR and/or STR were added. In a typical kinetics test, at least, three tubes were sacrificed at each designated sampling time. For adsorption isotherm experiments, shaking proceeded for 24 hours to allow the adsorption to reach a chemical equilibrium. Subsequently, 5 mL sample was collected from each tube, and then filtered through 0.45  $\mu\text{m}$  cellulose nitrate membrane syringe filter. The filtrate was stored in 2%  $\text{HNO}_3$  solution for metal analysis.

**Metal Release Tests.** To assess how strongly the WTR and/or STR retain the metals, the used WTR and STR were collected and added to an EDTA (a well-known strong chelating agent) solution or  $\text{NaNO}_3$  solution to examine how much sorbed metals can be desorbed back to bulk solution. The used sorbents were collected immediately after a group of isotherm tests with 10 g/L WTR and 10 g/L STR in 1,000  $\mu\text{M}$   $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Zn}^{2+}$  mixed solution were completed. The collected sorbents were

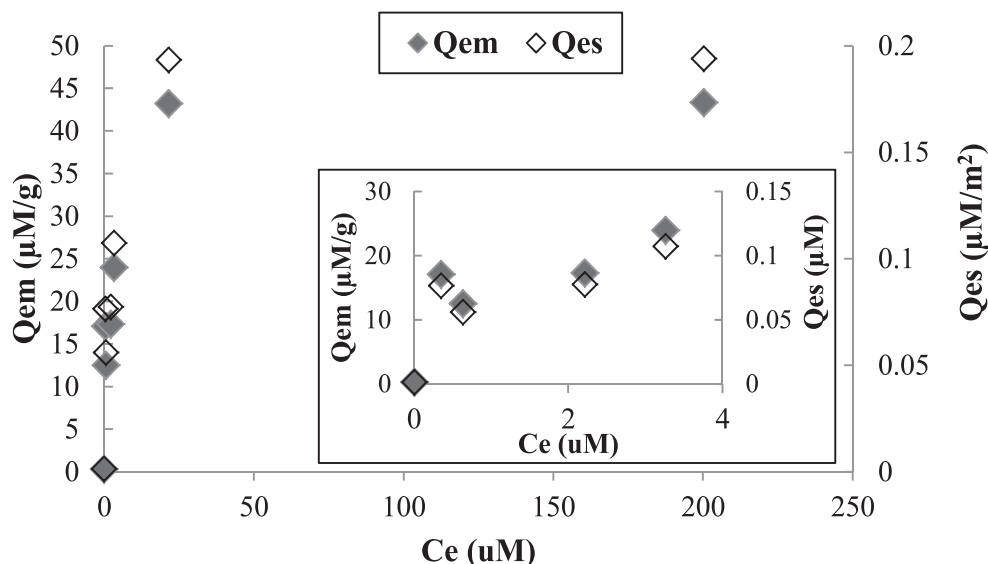


Figure 4—Cu adsorption isotherm on WTR in a mixed metal (Cu+Pb+Zn) solution (20 g/L WTR, pH 6.5, and 0.1 M  $\text{NaNO}_3$ ).

first rinsed twice with Milli-Q water ( $18.2 \text{ M}\Omega\cdot\text{cm}$ ) to remove any residual unadsorbed 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  $\text{NaNO}_3$  solution. The tube was installed in the shaking bed. After 1-hr rotation, 5 mL solution sample was collected from each tube, and then filtered through  $0.45 \mu\text{m}$  membrane syringe filter. The filtrate was stored in 2%  $\text{HNO}_3$  solution for metal analysis.

**Analytical Method.** Cu, Pb and Zn in water were analyzed using an inductively coupled plasma-mass spectroscopy (ICP-MS Thermo X-Series II, XO 472). Morphology and elemental analysis of WTR and STR were determined with a Hitachi S-3400N scanning electron microscopy/electron dispersive spectroscopy (SEM-EDS). Solution pH was measured with a Thermo Fisher Scientific ORION 5-Star multiparameter meter. Specific

surface areas of WTR and STR were determined using a BET surface area analyzer in a commercial laboratory. All the data presented in the figures are the mean values of triplicates with relative standard deviations  $< 5\%$ .

#### Results and Discussion

**Material Characterization.** The Al-WTR used in this study exhibited a high specific surface area (SSA) at  $223.4 \pm 3.1 \text{ m}^2/\text{g}$ . This data was greater than the finding of Makris et. al. (2004) ( $104.9 \text{ m}^2/\text{g}$ ), but less than  $413.0 \text{ m}^2/\text{g}$  reported by Putra and Tanaka (2011). In contrast, the SSA of STR at  $0.064 \text{ m}^2/\text{g}$  was much smaller. SEM images of Al-WTR and STR are shown in Figures 1(a-d) and 2(a-d), respectively. The Al-WTR consisted of nearly spherical particles with very rough surface. Their particle sizes broadly ranged between a few  $\mu\text{m}$  and several-hundred  $\mu\text{m}$ .

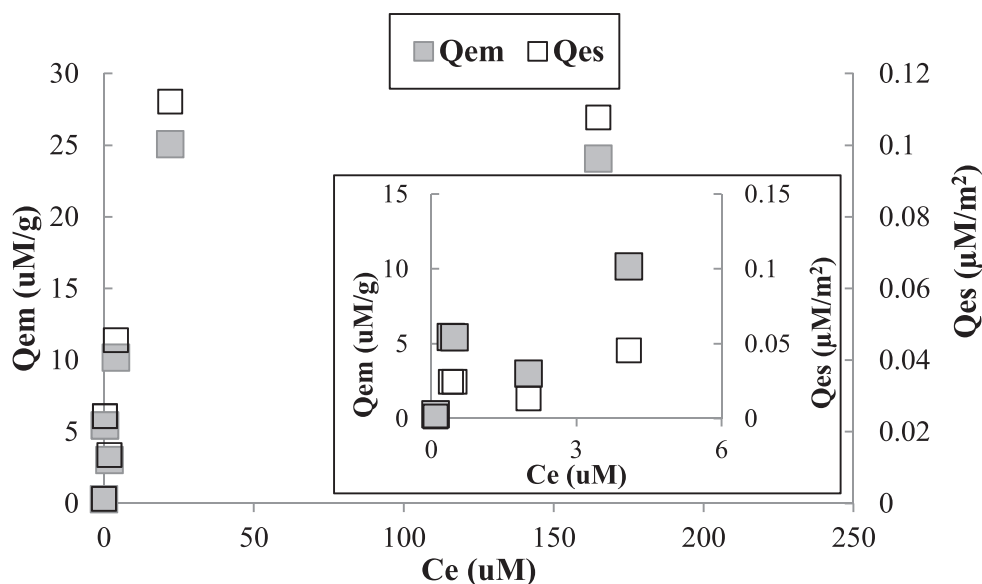


Figure 5—Pb adsorption isotherm on WTR in a mixed metal (Cu+Pb+Zn) solution (20 g/L WTR, pH 6.5, and 0.1M  $\text{NaNO}_3$ ).

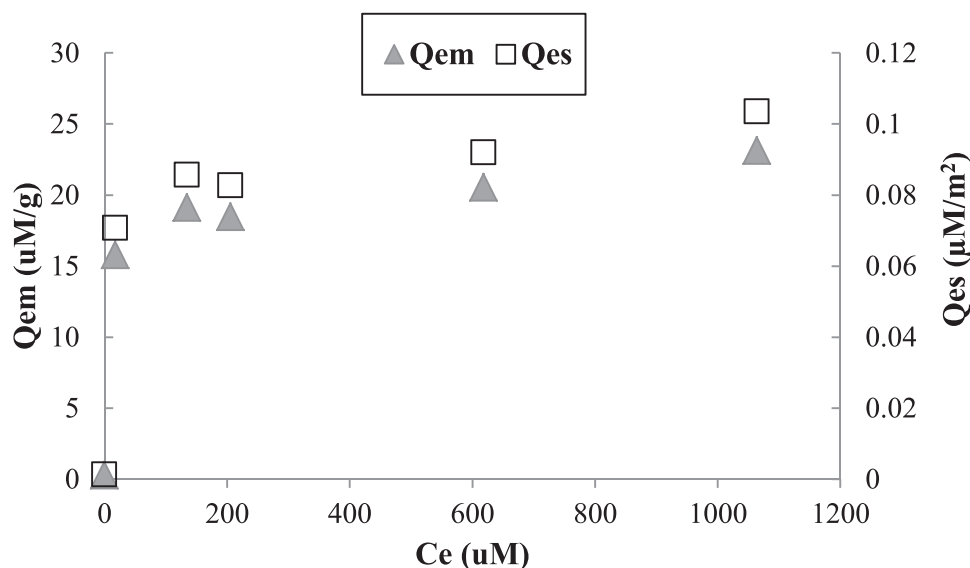


Figure 6—Zn adsorption isotherm on WTR in a mixed metal (Cu+Pb+Zn) solution (20 g/L WTR, pH 6.5, and 0.1M NaNO<sub>3</sub>).

In contrast, STR particles had irregular shapes and smooth surface (Figure 2a-d). Their sizes were in the order of a few mm.

**Adsorption by Al-WTR.** Results of kinetics tests for metal adsorption by WTR alone are shown in Figure 3. In the kinetics tests, the sampling time ranged from 1 to 9 hours, falling within 48 hours that is the typical maximum drawdown time of a bioretention basin after a storm event (Maryland, 2007). 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 suggesting that adsorption equilibrium could be reached within one hour regardless of metal species. This finding is in agreement with our early studies that the attainment of equilibrium for sorption of heavy metal onto WTR ranged from a few minutes to 2 hours (Sarkar et al., 2007).

Adsorption isotherms of Cu, Pb, and Zn during Al-WTR treatment of the simulated Cu, Pb, and Zn mixed runoff are

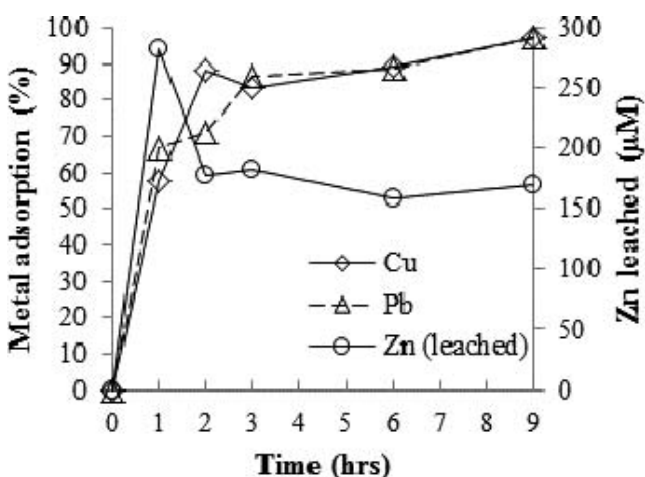


Figure 7—Adsorption of Cu and Pb onto and leaching of Zn from STR alone with time (10 g/L STR, [Cu]<sub>0</sub> = 6  $\mu\text{M}$ , [Pb]<sub>0</sub> = 2.45  $\mu\text{M}$ , and pH 6.5).

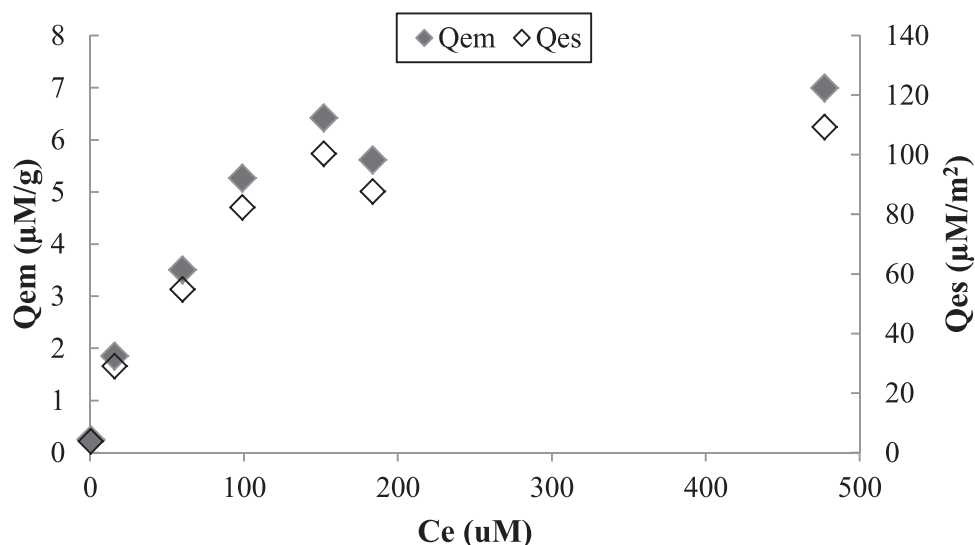
shown in Figures 4 to 6, respectively. These figures show relationships between mass and surface area-normalized adsorption capacities of specific metals on WTR ( $Q_{em}$  and  $Q_{es}$ ) and their aqueous concentration ( $C_e$ ) at chemical equilibrium. The mass-normalized adsorption capacity ( $Q_{em}$ ) and surface area-normalized adsorption capacity ( $Q_{es}$ ) of a metal on sorbent are determined as follows.

$$Q_{em} = \frac{(C_0 - C_e)V}{m} \times 100\% \quad (1)$$

$$Q_{es} = \frac{(C_0 - C_e)V}{SSA} \times 100\% \quad (2)$$

Where,  $C_0$  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. As seen, the adsorption isotherm curves exhibited a biphasic pattern. At a low  $C_e$ ,  $Q_{em}$  and  $Q_{es}$  were dramatically increased with the increasing  $C_e$ . However, when  $C_e$  was above a critical level (21.5  $\mu\text{M}$  for Cu, 22.8  $\mu\text{M}$  for Pb, and 4.8  $\mu\text{M}$  for Zn), the improvement of  $Q_{em}$  and  $Q_{es}$  ( $\sim 43$   $\mu\text{M}/\text{g}$  and  $0.19$   $\mu\text{M}/\text{m}^2$  for Cu,  $\sim 25$   $\mu\text{M}/\text{g}$  and  $0.11$   $\mu\text{M}/\text{m}^2$  for Pb, and  $\sim 23$   $\mu\text{M}/\text{g}$  and  $0.10$   $\mu\text{M}/\text{m}^2$  for Zn) was almost marginal even though  $C_e$  was further increased. All the metal adsorption data well fit the Freundlich adsorption equations ( $R^2 > 0.90$ ).

**Adsorption by STR.** Kinetics results of STR adsorption of Cu and Pb, as well as Zn leaching from STR, are presented in Figure 7. Adsorption efficiencies of Cu and Pb gradually increased from 0% to 97.4% and 97.2% with the increasing time from 0 to 9 hours, respectively. These findings revealed that STR alone could adsorb the metals of concern, although more slowly than WTR alone. Adsorption of metals to STR is a multi-step procedure consisting of metal transfer from water to the STR surface, diffusion within the pores of the STR surface, and sorption itself onto the surface. A previous study (Entezari et al., 2005) found that the internal porous diffusion is the rate-controlling step during STR adsorption of metals from water. As seen in Figure 7,



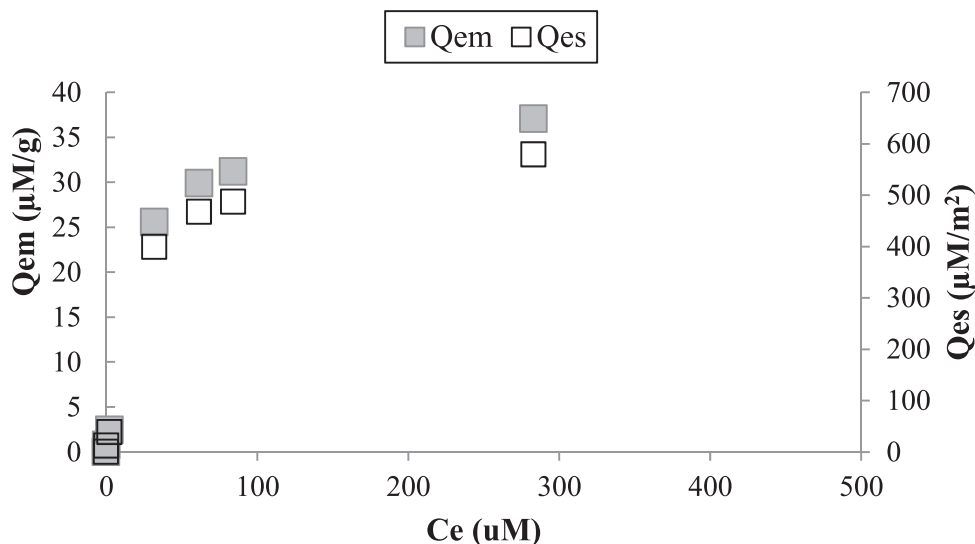
**Figure 8—Cu adsorption isotherm on STR in a mixed metal (Cu+Pb) solution (20 g/L TR, pH = 6.5 and 0.1M NaNO<sub>3</sub>).**

Zn indeed leached out from STR into the bulk solution with time. The Zn leaching pattern was unique. Within the first hour, 282  $\mu\text{M}$  Zn entered into the solution. However, in the following one hour, Zn in solution dropped to 178  $\mu\text{M}$ , implying that 36.8% of desorbed Zn was re-adsorbed on the STR surface. Thereafter, the Zn concentration in water almost stabilized. It would be noticed that the amount of Zn leaching from STR in a mixed Cu and Pb solution was significant, suggesting that STR, when applied alone, is not a good sorbent for stormwater treatment, and may cause a secondary pollution.

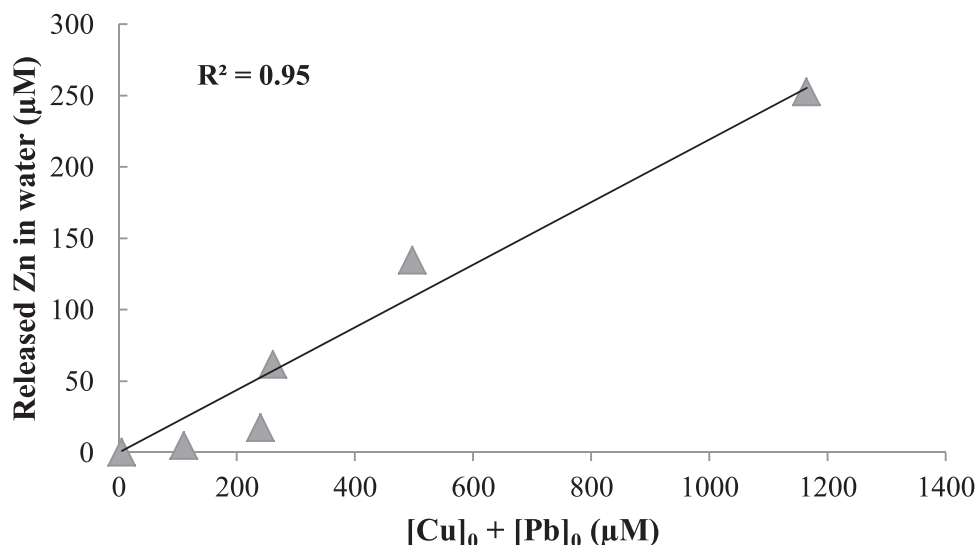
Tires are primarily composed of vulcanized rubber (e.g., styrene-butadiene rubber (SBR)), carbon black that strengthens the rubber and aids abrasion resistance, extender oil, sulfur (a vulcanizing agent to cross-link polymer chains with rubber), accelerators, as well as zinc oxide and stearic acid that control the vulcanization process and enhance the physical properties of rubber (Dodds et al., 1983). Among these different tire rubber

compositions, carbon black accounts for about 31% of the overall STR weight. Carbon black is similar to activated carbon and has the potential to adsorb metals and organic compounds from aqueous solution. This suggests STR to be a good adsorbent for removal of different organic pollutants and heavy metals from water (Gunasekara et al., 2000). On the other hand, STR has a zinc content of about 1% by weight (Councell et al., 2004; Dodds et al., 1983). The zinc is a source that may be released from STR into water under different conditions (Gualtieri et al., 2005), thereby restricting STR application for environmental remediation.

Adsorption isotherms of Cu and Pb during STR adsorption of a simulated Cu and Pb mixed runoff are shown in Figures 8 to 9, respectively. Similarly, STR adsorption of Cu and Pb also exhibited a biphasic pattern. At a low  $C_e$ ,  $Q_{em}$  and  $Q_{es}$  were dramatically increased with the increasing  $C_e$ . However, when  $C_e$  was over a critical level (151.9  $\mu\text{M}$  for Cu and 84.1  $\mu\text{M}$  for



**Figure 9—Pb adsorption isotherm on STR in a mixed metal (Cu+Pb) solution (20 g/L STR, pH = 6.5, and 0.1M NaNO<sub>3</sub>).**



**Figure 10—Released Zn ( $\mu\text{M}$ ) vs. sum of initial Cu and Pb concentrations ( $[\text{Cu}]_0 + [\text{Pb}]_0$ ) during STR adsorption isotherm tests in a mixed metal (Cu+Pb) solution (20 g/L STR, pH = 6.5, and 0.1M  $\text{NaNO}_3$ ).**

Pb), the improvement of  $Q_{em}$  and  $Q_{es}$  ( $\sim 6.42 \mu\text{M/g}$  and  $100 \mu\text{M/m}^2$  for Cu, and  $\sim 37.0 \mu\text{M/g}$  and  $579 \mu\text{M/m}^2$  for Pb) was almost marginal with the increase of  $C_e$ . The Cu and Pb adsorption data well fit the Freundlich adsorption equations ( $R^2 > 0.95$ ).

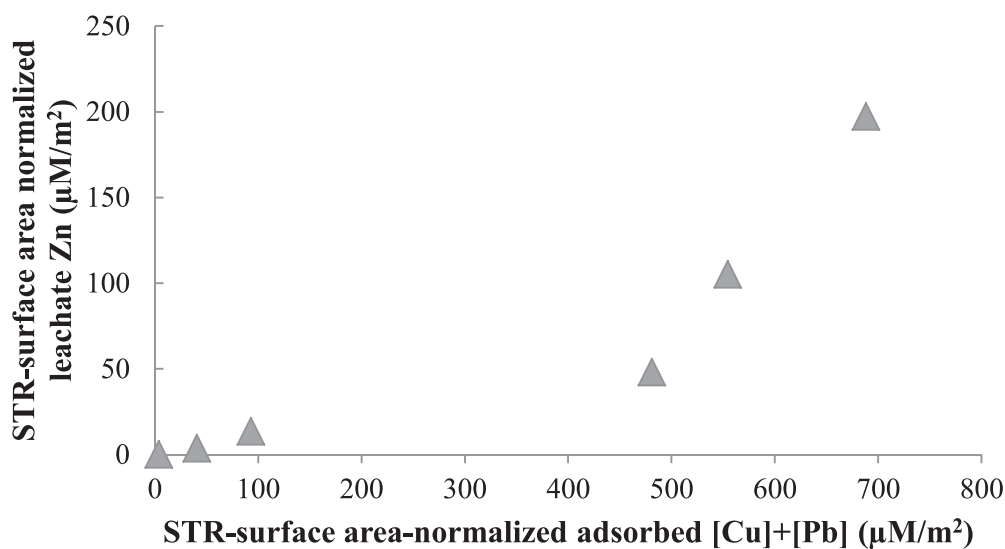
Zn released from STR and the sum of initial Cu and Pb concentrations are shown in Figure 10. A nearly linear relationship between the released Zn ([released Zn]) and the total initial Cu and Pb concentration ( $[\text{Cu}]_0 + [\text{Pb}]_0$ ) was observed as below.

$$[\text{Released Zn}] = 0.2192([\text{Cu}]_0 + [\text{Pb}]_0) \quad (R^2 = 0.95) \quad (3)$$

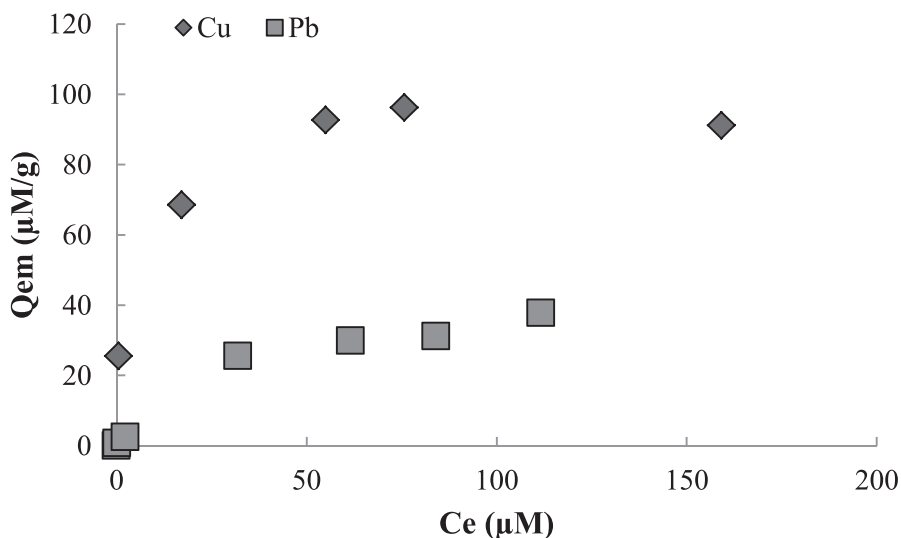
As seen, more Zn was released from STR in the presence of higher concentration of Cu and Pb. The concentration of leached Zn normalized to STR surface area versus the sum of

STR surface area-normalized adsorbed Cu and Pb during STR adsorption isotherm tests is shown in Figure 11. For STR, on a unit surface area basis, as the adsorbed Cu/Pb increased from 4.0 to  $688.1 \mu\text{M/m}^2$ , the leaching Zn from STR into bulk solution increased from 0.1 to  $197.2 \mu\text{M/m}^2$ . These findings implied that ion exchange might occur between the aqueous Cu/Pb and Zn on the STR, and thus lead to the increase of the released Zn in the presence of higher concentrations of Cu and Pb.

**Adsorption with Al-WTR and STR Combination.** Results of Cu and Pb adsorption isotherm tests using combined WTR and STR are shown in Figure 12. As  $C_e$  was increased from 0 to 55.0 and 31.9  $\mu\text{M}$ ,  $Q_{em}$  sharply increased to 92.7 and 25.5  $\mu\text{M/g}$ , respectively. However, the further increase of  $C_e$  did not cause a significant improvement in  $C_e$  for the both metals. Adsorption patterns of Cu and Pb well fit the Freundlich models as below.



**Figure 11—Leached Zn normalized to STR surface area ( $\mu\text{M/m}^2$ ) vs. sum of adsorbed Cu and Pb normalized to STR surface area ( $\mu\text{M/m}^2$ ) during STR adsorption tests in a mixed metal (Cu+Pb) solution (20 g/L STR, pH = 6.5, and 0.1M  $\text{NaNO}_3$ ).**



**Figure 12—Cu and Pb adsorption isotherm of combined WTR and STR in a mixed metal (Cu+Pb) solution at different ionic strengths (10 g/L WTR and 10 g/L STR, pH = 6.5, and 0.1M NaNO<sub>3</sub>).**

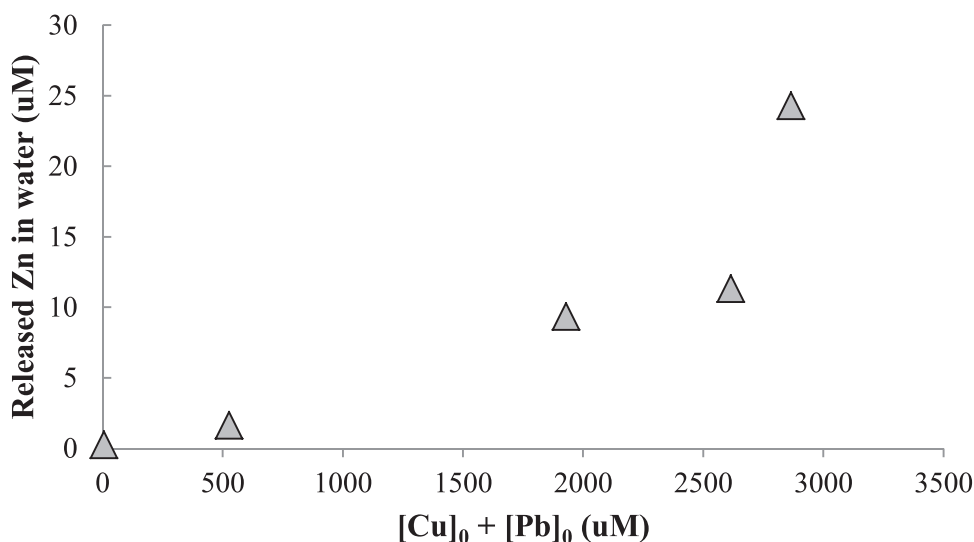
$$\text{Cu adsorption, } Q_e = 31.64 C_e^{0.247} \quad (R^2 = 0.96) \quad (4)$$

$$\text{Pb adsorption, } Q_e = 1.45 C_e^{0.742} \quad (R^2 = 0.98) \quad (5)$$

Zn release in the presence of Cu and Pb is shown in Figure 13. As the initial concentration of Cu and Pb increased from 6.3 to 2615.9  $\mu\text{M}$ , the released Zn was almost linearly increased from 0.2 to 11.3  $\mu\text{M}$ . The Zn release was considerably reduced in comparison with the Zn leaching without WTR (Figures 10 and 11) for at least two reasons. Firstly, WTR simultaneously adsorbed Cu and Pb, reducing the amounts of Cu and Pb adsorbed to STR and thus lowering STR-released Zn due to ion exchange with Cu and Pb. Secondly, WTR was able to sorb aqueous Zn as demonstrated in Figure 6, even if some Zn was indeed released from STR. Although the Zn release sharply increased to 24.3  $\mu\text{M}$  when the initial Cu and Pb concentration

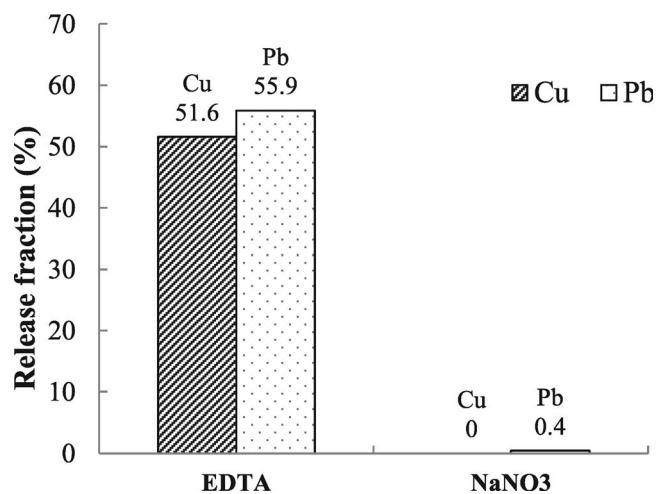
reached 2866.4  $\mu\text{M}$ , the released Zn was still much lower than that without WTR.

To the best of our knowledge, this study represents the first scientific attempt to apply WTR and STR together for stormwater treatment. WTR powders have a high potential to immobilize various water pollutants, but an extremely low permeability. Thus, it is very difficult to use WTR as filter media in a down-flow packed bed, unless it is added directly to soil in bioretention cells. In contrast, the open packing introduced by STR chips leads to excellent hydraulic conditions in a filter. Although STR is also able to adsorb certain water pollutants, it may leach undesirable chemicals (e.g., Zn). This study demonstrates that addition of WTR can significantly inhibit the Zn release from STR. Therefore, the combination of the two recycled solid wastes provides an innovative stormwater treatment technology with the complementary properties of



**Figure 13—Released Zn ( $\mu\text{M}$ ) vs. sum of initial Cu and Pb concentrations ( $[\text{Cu}]_0 + [\text{Pb}]_0$ ) during WTR/STR adsorption isotherm tests in a mixed metal (Cu+Pb) solution (10 g/L WTR,  $[\text{Cu}]_0 : [\text{Pb}]_0 = 1:1$ , 10 g/L STR, pH = 6.5, and 0.1M NaNO<sub>3</sub>).**





**Figure 14—Release of Cu and Pb from WTR/TR sorbents in EDTA and NaNO<sub>3</sub> solutions.**

the two recycled wastes; STR chips improve permeability of the filter media, while WTR inhibits the STR leaching.

**Release Tests.** Release of adsorbed metals from a sorbent into bulk solution is of great interest for an adsorption process. Release fraction of a metal from a sorbent is defined as follows.

$$\text{Release fraction} = \frac{\text{Amount of released metal into bulk solution}}{\text{Amount of total adsorbed metal}} \times 100\% \quad (6)$$

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 released metal into bulk solution” is the mass of the adsorbed metal that is released into bulk solution under certain experimental conditions. Release fractions of Cu and Pb from the used WTR and STR are shown in Figure 14. EDTA (0.02 M) and NaNO<sub>3</sub> (0.02 M) solutions were applied to separately test metal release behavior. As seen, the desorbed Cu and Pb were 0.0% and 0.4% in NaNO<sub>3</sub> solution, and 51.6% and 55.9% in EDTA solution, respectively. Thus, WTR/STR adsorption of Pb and Cu was strong and largely irreversible, and significant release only occurred in the presence of a strong chelating agent. Considering that chelating agents are not abundant in typical urban stormwater, release of the adsorbed metals from used or spent WTR and STR sorbents should not be a concern. Moreover, the leaching of benzothiazole from STR in the presence or absence of WTR was also tested. At pH 6.5, 10 g/L STR leached 6.56 μM benzothiazole without WTR at 7 hours. However, the leaching was dramatically reduced to 2.14 μM with 10 g/L WTR. This finding suggests that WTR is also capable of inhibiting the leaching of compounds, besides Zn, from STR.

## Conclusions

In this study, two recycled industrial solid wastes were evaluated to immobilize common metals in urban stormwater. WTR could rapidly and effectively adsorb Cu, Zn, and Pb from water. In contrast, though STR also sufficiently adsorbed Cu and Pb, it continuously released Zn to cause a secondary pollution, at least partially due to ion exchange between Zn present in STR

and aqueous metals (i.e., Cu and Pb). Consequently, it is not appropriate to apply STR alone for stormwater treatment. However, the combination of WTR and STR was able to inhibit the Zn leaching from STR, besides providing for removal of Cu and Pb in water. These findings suggest that combined application of WTR and STR for removal of stormwater metals should be considered as a new, effective stormwater treatment method that fully takes advantages of their complementary properties: WTR can inhibit the STR leaching of Zn, while STR may improve permeability of WTR powders as filter media. In addition, the mixed adsorbents are expected to reduce certain stormwater nutrient loading, considering that WTR is a good adsorbent for phosphorus as demonstrated in many earlier studies. Meanwhile, this “green” option provides a sustainable approach to recycle wastes originally disposed of in landfills, thereby significantly reducing waste disposal costs and saving landfill spaces.

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