Final Report

Development of a New, Effective and Low-cost Media for Sustainable Management of Polluted Road Stormwater in Highly Urbanized Areas: Wood Mulch Coated with Aluminum-and Iron-Based Water Treatment Residuals

Performing Organization: Manhattan College

March 2018
The Region 2 University Transportation Research Center (UTRC) is one of ten original University Transportation Centers established in 1987 by the U.S. Congress. These Centers were established with the recognition that transportation plays a key role in the nation’s economy and the quality of life of its citizens. University faculty members provide a critical link in resolving our national and regional transportation problems while training the professionals who address our transportation systems and their customers on a daily basis.

The UTRC was established in order to support research, education and the transfer of technology in the field of transportation. The theme of the Center is “Planning and Managing Regional Transportation Systems in a Changing World.” Presently, under the direction of Dr. Camille Kamga, the UTRC represents USDOT Region II, including New York, New Jersey, Puerto Rico and the U.S. Virgin Islands. Functioning as a consortium of twelve major Universities throughout the region, UTRC is located at the CUNY Institute for Transportation Systems at The City College of New York, the lead institution of the consortium. The Center, through its consortium, an Agency-Industry Council and its Director and Staff, supports research, education, and technology transfer under its theme. UTRC’s three main goals are:

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The research program objectives are (1) to develop a theme based transportation research program that is responsive to the needs of regional transportation organizations and stakeholders; and (2) to conduct that program in cooperation with the partners. The program includes both studies that are identified with research partners of projects targeted to the theme, and targeted, short-term projects. The program develops competitive proposals, which are evaluated to insure the mostresponsive UTRC team conducts the work. The research program is responsive to the UTRC theme: “Planning and Managing Regional Transportation Systems in a Changing World.” The complex transportation system of transit and infrastructure, and the rapidly changing environment impacts the nation’s largest city and metropolitan area. The New York/New Jersey Metropolitan has over 19 million people, 600,000 businesses and 9 million workers. The Region’s intermodal and multimodal systems must serve all customers and stakeholders within the region and globally. Under the current grant, the new research projects and the ongoing research projects concentrate the program efforts on the categories of Transportation Systems Performance, Information Infrastructure to provide needed services to the New Jersey Department of Transportation, New York City Department of Transportation, New York Metropolitan Transportation Council, New York State Department of Transportation, and the New York State Energy and Research Development Authority and others, all while enhancing the center’s theme.

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**University Transportation Research Center - Region 2**

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**Project Date:** March 2018

**Project Title:** Development of a New, Effective and Low-cost Media for Sustainable Management of Polluted Road Stormwater in Highly Urbanized Areas

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Abstract
The goal of this project was to develop a new, effective and low-cost media for sustainable management of polluted road stormwater in highly urbanized areas. The overarching objective of this study was to provide the scientific basis for the development and utilization of a novel media consisting of wood mulch coated with a recycled solid waste -- water treatment residuals (WTR) -- for the removal of multiple pollutants (namely, Cu, Pb, Zn and P) from urban road runoff. The specific objectives included to i) collect and characterize iron-and aluminum-based WTR from local water treatment plants, ii) conduct Synthetic Precipitation Leaching Procedure (SPLP) and Toxicity Characteristic Leaching Procedure (TCLP) tests to examine whether the WTR passed the leaching tests and were non-hazardous wastes during rainfall events and disposal, respectively, iii) prepare and characterize WTR-coated mulch, and iv) perform batch and flow-through tests to evaluate the performance of WTR-coated wood mulch media in removing Cu, Pb, Zn and Pb contaminants from simulated urban road runoff under different solution chemistry conditions.

Key Words
Stormwater, sustainable management

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Development of a New, Effective and Low-cost Media for Sustainable Management of Polluted Road Stormwater in Highlly Urbanized Areas: Wood Mulch Coated with Aluminum- and Iron-Based Water Treatment Residuals

Submitted to Region 2 University Transportation Research Center (UTRC)

Authored by

Drs. Kirk Barrett, Dibyendu Sarkar, Yang Deng, and Virinder Sidhu

Submitted by Manhattan College, NY on behalf of all project investigators

March 2018

UTRC Project number 49198-23-27
EXECUTIVE SUMMARY

The goal of this project was to develop a new, effective and low-cost media for sustainable management of polluted road stormwater in highly urbanized areas. The overarching objective of this study was to provide the scientific basis for the development and utilization of a novel media consisting of wood mulch coated with a recycled solid waste -- water treatment residuals (WTR) -- for the removal of multiple pollutants (namely, Cu, Pb, Zn and P) from urban road runoff. The specific objectives included to i) collect and characterize iron-and aluminum-based WTR from local water treatment plants, ii) conduct Synthetic Precipitation Leaching Procedure (SPLP) and Toxicity Characteristic Leaching Procedure (TCLP) tests to examine whether the WTR passed the leaching tests and were non-hazardous wastes during rainfall events and disposal, respectively, iii) prepare and characterize WTR-coated mulch, and iv) perform batch and flow-through tests to evaluate the performance of WTR-coated wood mulch media in removing Cu, Pb, Zn and Pb contaminants from simulated urban road runoff under different solution chemistry conditions.

TCLP and SPLP leaching results for both Fe- and Al-WTR were well below the limit set by the USEPA, validating that Fe- and Al-WTR are non-hazardous and can be safely used as an effective sorbent to remove pollutants from stormwater runoff. SEM analysis showed that the Fe- and Al-WTR had an amorphous nature, while wood mulch had a porous structure. SEM-EDS analysis confirmed a high-intensity peak of Al and Fe in Al- and Fe-WTR, respectively. Similar results were seen after mulch was coated with WTR, rinsed, and air dried, indicating proper preparation of the sorbent for further studies.

Flow-through column studies showed that Fe-WTR-coated mulch of 4-inch thickness was very effective in removing Cu and Pb, consistently removing >90% throughout 120 bed volumes, which was better than the Al-WTR-coated and uncoated mulches. The uncoated mulch was
initially effective, removing ~80% of Cu and Pb, but removal decreased and/or became erratic. Fe-WTR-coated mulch achieved high removal (>90%) for Zn for within 10 bed volumes, but the removal declined. The other mulches, as well as the 2-inch-depth Fe-WTR-coated mulch, were not very effective in removing Zn, with the removal efficiencies of mostly ~50% for Al-WTR-coated-mulch and mostly <20% for uncoated mulch. The 4-inch-depth Al-WTR-coated-mulch was the most effective for the removal of P, with a consistent removal efficiency of ~50%, while the other mulches removed only ~20%. The results for Al-WTR-coated mulch were highly variable for Cu and Pb, with concentrations spiking to ~220% and 170%, respectively, above the inlet concentration; at other times, up to 80% removal of Cu and Pb was achieved. A pronounced improved performance of the 4-inch thickness vs. the 2-inch thickness was seen only in Fe-WTR-coated mulch for Cu, Pb and, to a lesser extent, Cu. Negative removal of P (i. e., effluent concentration > influent) was not observed for any mulch, contrary to what has been sometimes observed in other studies.
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1. INTRODUCTION

According to the U.S. Census Bureau, about 81 percent of the U.S. population lived in urban areas as of the 2010 Census, a boost from the 79 percent counted in 2000 (US Census Bureau, 2012). As more and more people are concentrated in cities in the United States, various environmental pollution problems are occurring such as polluted urban road runoff. Road runoff is typically polluted by various contaminants originating from vehicular activities and is recognized as a major non-point source of urban pollution (McLellan et al., 2007). Among the various stormwater pollutants in urban areas, heavy metals, especially lead (Pb), copper (Cu), and zinc (Zn), are of particular concern because of their non-biodegradability, tendency to accumulate in environment, and toxicity. These toxic metals accumulate in river sediments and soils or enter groundwater. Nutrients in urban runoff such as phosphorous also cause eutrophication in receiving water bodies and contamination of groundwater. These issues have become a great challenge in watershed management across this nation, particularly in highly urbanized areas. Newer urban stormwater management techniques encourage best management practices (BMPs) to deal with the issues of urban road runoff (Lynch & Corbett, 1990). Particularly, decentralized low impact development (LID) techniques allow runoff to infiltrate into soil in a simulated natural environment (New York City Environmental Protection, 2012). Currently, the most common LID technique is bioretention (Hsieh & Davis, 2005). However, bioretention can cause persistent toxicants to accumulate in the topsoil over time. Phosphorus (P) was reported to be ineffectively removed by bioretention and even be released from them (Weiss, LeFevre, & Gulliver, 2008). Therefore, technical viable and low-cost techniques are needed for reduction of the urban road runoff pollutants.
To address these issues, a green sorption filter media has been developed by coating wood mulch with Al and Fe-based drinking water treatment residuals (Al/Fe-WTR). WTR are industrial waste byproducts generated in drinking water treatment plants, which typically use Al or Fe salts as coagulating agents. WTR from drinking water treatment facilities have been studied as an adsorbent material to remove heavy metals (Makris, Sarkar, & Datta, 2006; Nagar, Sarkar, Makris, Datta, & Sylvia, 2009; Soleimanifar, Deng, Wu, & Sarkar, 2016). WTR are mostly composed of amorphous oxides and hydroxides, sediments, organic matter, and/or polymers (Elliott & Dempsey, 1991). WTR have a high potential to immobilize a variety of water pollutants, but suffer from a low permeability (Nagar, Sarkar, Makris, & Datta, 2010). In contrast, wood mulch has excellent hydraulic properties (Kannepalli et al., 2016). Thus, the development of a composite filter media consisting of wood mulch and WTR may provide a promising solution to reduce pollutants in urban runoff.

The goal of this project was to develop a new, effective and low-cost media for sustainable management of polluted road stormwater in highly urbanized areas. The overarching objective of this study was to provide the scientific basis for the development and utilization of a novel media consisting of wood mulch coated with a recycled solid waste -- water treatment residuals (WTR) -- for retention of multiple pollutants from urban road runoff. In this study, we conducted batch and flow-through column tests to assess and optimize the composition of Al/Fe-WTR-coated wood mulch by applying synthetic urban road runoff and measuring pollutant removal.
2. METHODS

Tasks that were achieved are summarized below:

1. Collection and preparation of WTR samples
2. Characterization of WTR
3. Leaching tests on virgin WTR
4. Preparation and characterization of WTR-coated mulch
5. Preparation of synthetic urban road-runoff
6. Batch adsorption equilibrium and kinetic tests
7. Leaching tests on spent WTR
8. Flow-through column tests

2.1 Task #1. Collection and preparation of WTR samples

Bulk WTR were collected from local water treatment plants. The samples were collected in five gallons PPE buckets. Upon arrival, the samples were decanted and allowed to air dry for 3 days at room temperature. Except the samples used for the measurement of the moisture and organic matter contents, WTR, after dried, were passed through a 2 mm sieve and then ground into powders.

2.2 Task #2: Characterization of WTR

- **pH, electrical conductivity, moisture content and organic matter content.** The pH was determined at a 1:2 WTR to water ratio. Ten grams of WTR were combined with deionized water, stirred with a glass rod, and equilibrated for 30 minutes. The pH was measured using an Oakton ion 510 series pH/conductivity meter. Electrical conductivity (EC) was determined at the same WTR to water ratio. After the stirring, the solution stood for 4 hours. EC measurements were made in triplicate using an Oakton ion 510 series pH/conductivity meter. Moisture content was determined by placing one gram of WTR into a pre-weighed 10 ml glass beaker and drying at 105°C for 24 hours. The samples were removed and immediately weighed after the 24-hour period. Organic matter content was determined by using the loss-on-ignition method using 0.3 grams of WTR in pre-weighed crucibles. The crucibles were heated for 24 hours at 105°C, weighed, and then placed into a Lindberg muffle furnace for 16 hours at a
temperature of 400°C, cooled, and weighed. All measurements were conducted in triplicates.

- **Carbon-Hydrogen-Nitrogen-Sulfur (CHNS).** CHNS content was determined by combustion at 1010°C using an Elementar CHNS Analyzer. Each sample (15-20 mg) was wrapped in a tin capsule with a spherical shape. The sample was then placed inside the Elementar Vario EL instrument for the determination of carbon, hydrogen, nitrogen, and sulfur contents.

- **Total Al and Fe.** Total Al and Fe were measured for each sample in triplicate using total digestion following USEPA Method 3050B (Test Methods 3050B, 2012). One gram of sample was weighed in a glass beaker, and 10 ml of 1:1 HNO₃ was added under a fume hood. The beakers were then covered with a watch glass and refluxed at 95°C for 15 minutes. The samples were allowed to cool, and then 5 ml of concentrated HNO₃ was added, and covered with a watch glass, and refluxed for 30 minutes at 95°C. This step was repeated until no brown fumes were observed. The samples were then heated to 95°C until they reached 5 ml, and were allowed to cool. A solution of 2 ml deionized water and 3 ml of 30% H₂O₂ was added into the beaker until effervescence was minimal, with no more than 10 ml of 30% H₂O₂ added to the beaker. The samples were then cooled and diluted 50 ml with deionized water, then centrifuged for 15 minutes at 4500 rpm, and filtered. The filtrate was then analyzed using ICP – OES (inductively coupled plasma optical emission spectroscopy).

- **Extractable Al and Fe.** Extractable Al and Fe were measured in triplicate in darkness using acid ammonium oxalate or Tamm’s reagent. The pH was maintained at 3.000 ± 0.005 (Sparks, 1996). One gram of each sample was placed in a 50ml tube; 30 ml of ammonium acetate was added before the reaction proceeded for 1 hour with an intermediate stirring. After the reaction took place the pH was adjusted to 5.5 using acetic acid; the samples were then centrifuged for 15 minutes at 4500 rpm, decanted and washed with deionized water twice; the samples were then allowed to air dry overnight. The samples were then covered with aluminum foil, 30 ml of acid ammonium oxalate was added, and the samples were shaken for two hours, centrifuged for 10
minutes at 4500 rpm, decanted and filtered. The filtrate was then analyzed for Al and Fe concentrations using ICP-OES.

2.3 Task #3 Leaching Tests on Virgin WTR

- **Toxicity Characteristic Leaching Procedure (TCLP).** To simulate leaching in a landfill condition, TCLP tests were performed using EPA method 1311 (Test Methods 1311, 2012) in triplicate for the virgin WTR (i.e., before application of synthetic stormwater). The pH of each sample was tested, indicating pH >5.0. The appropriate extraction fluid by mixing 1988.6 ml of deionized water with 11.4 ml of glacial acetic acid; the pH was adjusted to 2.880 ± 0.005. The extraction fluid was combined with 50 g of WTR and placed in a rotary agitator for 18 ± 2 hours. After the agitation, two aliquots were filtered, collected, and analyzed for RCRA 8 metals, plus nickel, zinc, aluminum, and iron. ICP-OES was used to analyze Al, As, Cd, Cr, Cu, Fe, Ni, Pb, and Zn. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to analyze Ag, Ba, Hg, and Se.

- **Synthetic Precipitation Leaching procedure (SPLP).** To simulate leaching that could occur during slightly acidic rainfall events, the SPLP values were determined using EPA method 1312 (Test Methods 1312, 2012) in triplicates for all WTR samples. The SPLP leaching solution was created by preparing a 60:40 mixture of sulfuric and nitric acid and the pH was adjusted to 4.20 ± 0.05. Fifty grams of WTR were added to 2 liters of the solution before the solution was mixed on a rotary agitator for 18 ± 2 hours. After the agitation, two aliquots were filtered, collected, and analyzed for RCRA 8 metals, plus nickel, zinc, aluminum, and iron. Inductively coupled plasma atomic emission spectroscopy (ICP-OES) was used to analyze Al, As, Cd, Cr, Cu, Fe, Ni, Pb, and Zn. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to analyze Ag, Ba, Hg, and Se.
2.4 Task #4: Preparation and characterization of WTR-coated mulch

Wood mulches were purchased from the Home Depot (cedar mulch, Oldcastle Lawn & Garden, GA). Pieces of mulch approximately 1 cm × 2 cm were selected, rinsed with Milli-Q water (> 18.2 MΩ·cm), and air dried. An environmentally friendly mulch glue (Mulch Lock, St. Louis, MO) was used to bind the WTR onto the mulch. Different mass ratios of WTR to mulch were analyzed via scanning electron microscopy (SEM). Analysis showed that, at a mass ratio ≥ 1 WTR to 3 mulch, was the mulch was completely covered by WTR. Therefore, for subsequent analyses, the WTR-coated mulches were prepared at WTR:mulch = 3.

2.5 Task #5: Preparation of synthetic urban road-runoff

Synthetic urban road-runoff was prepared to simulate actual runoff in tests of the media. The composition of synthetic urban road runoff consisted of toxic metals, nutrients and hydrocarbons with their respective concentrations established by previous reports of actual runoff (Chin, 2013; Makepeace, Smith, & Stanley, 1995; Taylor, Fletcher, Wong, Breen, & Duncan, 2005; U.S. EPA, 1983). As shown in Table 1, synthetic runoff contained 100 µg/L Pb²⁺, 600 µg/L Zn²⁺, 100 µg/L Cu²⁺, 3.0 mg/L P, 120 mg/L CaCl₂, and 10 mM piperazine-N,N’-bis(2-ethanesulfonic acid) (PIPES). Select metals were added using their respective nitrate salts. P was provided from disodium phosphate (Na₂HPO₄). Initial pH was adjusted to 7.0 using 0.1 N NaOH or HNO₃. Along with the mixture of contaminants, single-contaminant solutions were also prepared for Cu, Zn, Pb and P with the same concentration levels as in the mixture.
Table 1: Compositions of synthetic urban road runoff

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>NaOH / HNO$_3$</td>
<td>6, 7 and 8</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu(NO$_3$)$_2$.2.5$H_2$O</td>
<td>100 (µg/L)</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn(NO$_3$)$_2$.6$H_2$O</td>
<td>600 (µg/L)</td>
</tr>
<tr>
<td>Pb</td>
<td>Pb(NO$_3$)$_2$.</td>
<td>100 (µg/L)</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>Na$_2$HPO$_4$.</td>
<td>3 (as P) (mg/L)</td>
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<tr>
<td>Nitrate</td>
<td>NaNO$_3$.</td>
<td>2 (as N) (mg/L)</td>
</tr>
<tr>
<td>Ammonium</td>
<td>NH$_4$Cl.</td>
<td>2 (as N) (mg/L)</td>
</tr>
<tr>
<td>Motor oil</td>
<td>Used oil from local garage</td>
<td>20 (mg/L)</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>CaCl$_2$.</td>
<td>120 (mg/L)</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>CaCO$_3$.</td>
<td>40 (mg/L)</td>
</tr>
<tr>
<td>PIPES</td>
<td>C$<em>8$H$</em>{18}$N$_2$O$_6$S$_2$.</td>
<td>5 (mM)</td>
</tr>
<tr>
<td>Ionic strength</td>
<td>KCl.</td>
<td>0.01 M</td>
</tr>
</tbody>
</table>

2.7 Task #6. Batch Adsorption Equilibrium and Kinetics Tests

To obtain key chemical equilibrium and kinetics data for WTR-coated much adsorption of the synthetic urban road runoff pollutants, we conducted batch tests in beakers. Tests were conducted by adding different amounts of WTR-coated mulch (5, 10, 25 and 50 g) to 1.0 L synthetic urban road runoff, comprised of either a single-pollutant (Cu, Pb, Zn and P at concentrations listed in Table 1) or the mixture of pollutants as per Table 1. The pH was adjusted to 7 with HCl/NaOH, and maintained with PIPES buffer. The beakers were placed rotary agitator at 25°C for 24 hours. Water samples were collected at 1, 5, 10, 20, 30 minutes and 1, 2, 5, 24 hours in 10 ml aliquots. The samples were filtered through 0.45 µm syringe filters and analyzed for Cu, Pb, and Zn by ICP-OES. P was measured using Microplate Reader. Concentrations were compared to the initial concentrations to compute the removal efficiencies at different times and under different treatment conditions.

In addition to the tests at pH 7, additional tests with 10 g/L WTR-coated mulch were conducted at pH 6 and pH 8 to test the performance at different pH levels that bracketed the typical urban road runoff pH range (Göbel, Dierkes, & Coldewey, 2006). Furthermore, since WTR-coated
mulch will be used in all seasons, we analyzed the effect of temperature on adsorption. Thus, we performed the adsorption tests with 10 g/L WTR-coated mulch under 12 °C, 22 °C and 32 °C at pH 7.

2.7 Task #7. Leaching tests on spent WTR-coated mulch

After conducting the batch adsorption tests, we conducted SPLP and TCLP tests with the spent WTR-coated mulch and control (uncoated) mulch to examine whether they passed the leaching tests. The SPLP and TCLP tests were conducted according to EPA SW-846 Method 1312 and EPA SW-846 Method 1311, respectively.

2.8 Task #8. Flow-through column tests

Flow-through column tests were performed in PVC columns (7.62 cm diameter and 40.64 cm length) at 25°C. A peristaltic pump (Ismatec REGLO Digital 4-Ch 8-R Var-Speed Pump) was used to deliver synthetic urban runoff into the top of the columns. Columns were packed with either 2” (5 cm) or 4” (10 cm) thicknesses of mulch, with uncoated mulch used in separate columns serving as control. The column experiments were conducted in duplicate. About 7.5 cm-deep layer of glass marbles layer was below the mulch for support, a 2.5 cm-deep marble layer was placed above to prevent the mulch from floating on top the solution. The columns were filled with 600 ml of synthetic urban runoff and then the peristaltic pump was turned on. The synthetic urban runoff (initial pH =7) flowed into the top of the columns at 8 ml/min for 7 hours per day for 14 days to simulate storm events. Effluent samples were collected at 2, 4 and 7 hours every day in 50 ml aliquots, which were analyzed for Cu, Pb, Zn and P as discussed above.
3. RESULTS AND DISCUSSION

3.1: Characterization of virgin mulch, virgin WTR and WTR-coated mulches

Physico-chemical characteristics of WTR are shown in Table 2. The results show the different characteristics of the Al-WTR and Fe-WTR.

Table 2: Physio-chemical characteristics of Fe- and Al-WTR

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Electrical Conduct. (µS)</th>
<th>Organic Matter %</th>
<th>C %</th>
<th>H %</th>
<th>N %</th>
<th>S %</th>
<th>Total Al (g/kg)</th>
<th>Total Fe (g/kg)</th>
<th>Extractable Al (g/L)</th>
<th>Extractable Fe (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-WTR</td>
<td>7.7</td>
<td>1272</td>
<td>15.76</td>
<td>28</td>
<td>0.91</td>
<td>1.30</td>
<td>4.02</td>
<td>48.3</td>
<td>6.34</td>
<td>26.75</td>
<td>3.55</td>
</tr>
<tr>
<td>Fe-WTR</td>
<td>6.5</td>
<td>984</td>
<td>12.45</td>
<td>9.75</td>
<td>0.75</td>
<td>1.04</td>
<td>3.11</td>
<td>5.44</td>
<td>47.19</td>
<td>2.45</td>
<td>35.45</td>
</tr>
</tbody>
</table>

Tables 3 and 4 compare the characteristics of uncoated mulch, virgin WTR and WTR coated mulch. Both the Al and Fe WTR contained high amount of C, ~28 and ~5%, respectively. Carbon was even higher in wood mulch as well (~44%). Lower nitrogen content in WTR-coated mulch was lower than pure WTR because of mixing of wood and WTR.

Table 3: Physio-chemical characteristics of uncoated mulch, WTR-coated mulch, and virgin WTR

<table>
<thead>
<tr>
<th>Material</th>
<th>Al Concentration (g/kg)</th>
<th>Fe Concentration (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
</tr>
<tr>
<td>Uncoated Mulch</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Fe-WTR 1</td>
<td>5.55</td>
<td>5.54</td>
</tr>
<tr>
<td>Al-WTR 1</td>
<td>48.01</td>
<td>48.05</td>
</tr>
<tr>
<td>Fe-WTR coated 1</td>
<td>0.40</td>
<td>0.42</td>
</tr>
<tr>
<td>Al-WTR coated 1</td>
<td>1.95</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 4: CHNS characteristics of virgin mulch, virgin WTR, and WTR coated mulch (n=3 for all parameters and materials)

<table>
<thead>
<tr>
<th>Material</th>
<th>%C Average</th>
<th>Std Dev</th>
<th>%N Average</th>
<th>Std Dev</th>
<th>C:N Ratio Average</th>
<th>Std Dev</th>
<th>%S Average</th>
<th>Std Dev</th>
<th>%H Average</th>
<th>Std Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated Mulch</td>
<td>44.20</td>
<td>0.10</td>
<td>0.78</td>
<td>0.10</td>
<td>56.7</td>
<td>0.63</td>
<td>0.08</td>
<td>9.15</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>Al-WTR</td>
<td>28.86</td>
<td>0.61</td>
<td>1.20</td>
<td>0.11</td>
<td>24.1</td>
<td>3.20</td>
<td>0.29</td>
<td>4.00</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Fe-WTR</td>
<td>5.02</td>
<td>0.63</td>
<td>0.98</td>
<td>0.07</td>
<td>5.1</td>
<td>0.94</td>
<td>0.14</td>
<td>2.46</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>Al-WTR Coated Mulch</td>
<td>45.02</td>
<td>0.12</td>
<td>0.79</td>
<td>0.04</td>
<td>57.0</td>
<td>1.17</td>
<td>0.22</td>
<td>9.28</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Fe-WTR Coated Mulch</td>
<td>40.22</td>
<td>0.45</td>
<td>0.78</td>
<td>0.04</td>
<td>51.6</td>
<td>0.83</td>
<td>0.07</td>
<td>8.69</td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>
3.2 Leaching Characteristics of virgin WTR

TCLP and SPLP values of the WTR are shown in Table 5 and 6, respectively. The values are well below the limit set by the USEPA. These results reconfirm that Fe- and Al-WTR are non-hazardous and can be safely used as a sorbent to remove pollutants from storm-water runoff.

Table 5: TCLP values of RCRA 8 metals, nickel, and zinc measured in virgin Fe- and Al-WTR

<table>
<thead>
<tr>
<th>Analyte (mg /L)</th>
<th>USEPA Limit (mg /L)</th>
<th>Al-WTR</th>
<th>Fe-WTR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>5</td>
<td>1.93</td>
<td>0.025</td>
</tr>
<tr>
<td>Barium</td>
<td>100</td>
<td>1.44</td>
<td>0.79</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1</td>
<td>0.028</td>
<td>0.8</td>
</tr>
<tr>
<td>Chromium</td>
<td>5</td>
<td>0.023</td>
<td>0.001</td>
</tr>
<tr>
<td>Lead</td>
<td>5</td>
<td>0.239</td>
<td>0.001</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.2</td>
<td>&lt; MDL**</td>
<td>&lt; MDL</td>
</tr>
<tr>
<td>Selenium</td>
<td>1</td>
<td>&lt; MDL</td>
<td>&lt; MDL</td>
</tr>
<tr>
<td>Silver</td>
<td>5</td>
<td>0.001</td>
<td>0.45</td>
</tr>
<tr>
<td>Copper</td>
<td>10</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>Nickel</td>
<td>NR*</td>
<td>0.007</td>
<td>0.85</td>
</tr>
<tr>
<td>Zinc</td>
<td>NR</td>
<td>0.244</td>
<td>0.074</td>
</tr>
</tbody>
</table>

** MDL: Method detection limit.

Table 6: SPLP values of RCRA 8 metals, Nickel, and Zinc measured in virgin Fe and Al-WTR

<table>
<thead>
<tr>
<th>Analyte (mg/L)</th>
<th>USEPA Limit (mg/L)</th>
<th>Al-WTR</th>
<th>Fe-WTR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>5</td>
<td>0.002</td>
<td>0.006</td>
</tr>
<tr>
<td>Barium</td>
<td>100</td>
<td>0.049</td>
<td>0.004</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1</td>
<td>0</td>
<td>0.001</td>
</tr>
<tr>
<td>Chromium</td>
<td>5</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Lead</td>
<td>5</td>
<td>0.02</td>
<td>0.001</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.2</td>
<td>0.004</td>
<td>&lt; MDL</td>
</tr>
<tr>
<td>Selenium</td>
<td>1</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Silver</td>
<td>5</td>
<td>&lt; MDL**</td>
<td>0</td>
</tr>
<tr>
<td>Copper</td>
<td>10</td>
<td>0.003</td>
<td>0.004</td>
</tr>
<tr>
<td>Nickel</td>
<td>NR*</td>
<td>0.02</td>
<td>&lt; MDL</td>
</tr>
<tr>
<td>Zinc</td>
<td>NR</td>
<td>0.003</td>
<td>0.052</td>
</tr>
</tbody>
</table>

*NR: Not regulated under the toxicity characteristics. No regulatory value is set by USEPA. ** MDL: Method detection limit.

3.3 SEM imaging of uncoated mulch, virgin WTR and WTR-coated mulch
Figures 1–7 present SEM images of uncoated mulch, virgin WTR and WTR-coated mulch. Fig. 1 shows that virgin mulch had the porous structure of wood. The other figures reveal that Fe- and Al-WTR possessed an amorphous nature.

Figures 8-14 present Energy Dispersive X-ray Spectroscopy (SEM-EDS) analyses. SEM-EDS analysis confirmed high intensity peaks with Al and Fe in Al- and Fe-WTR, respectively. SEM-EDS analysis of mulch showed very low intensity and ratio of Al and Fe (Fig. 14). High intensity peaks with a major ratio for Al or Fe was observed for WTR-coated mulches (Fig. 12 and 13), indicating that the WTR had been properly coated.

![Figure 1: Scanning Electron Microscope image of virgin mulch at 100 µm](image-url)
Figure 2: Scanning Electron Microscope image of virgin Al-WTR at 100 µm

Figure 3: Scanning Electron Microscope image of virgin Fe-WTR at 400 µm
Figure 4: Scanning Electron Microscope image of Al-WTR coated mulch at 50 µm

Figure 5: Scanning Electron Microscope image of Al-WTR coated mulch after rinsing with DI water and air drying at 50 µm
Figure 6: Scanning Electron Microscope image of Fe-WTR coated mulch at 100 µm

Figure 7: Scanning Electron Microscope image of Fe-WTR coated mulch after rinsing with DI water and air drying at 1000 µm
Figure 8: Scanning Electron Microscope - Energy Dispersive X-ray Spectroscopy (SEM-EDS) analysis of Al-WTR.

Figure 9: Scanning Electron Microscope - Energy Dispersive X-ray Spectroscopy (SEM-EDS) analysis of Fe-WTR.
Figure 10: Scanning Electron Microscope - Energy Dispersive X-ray Spectroscopy (SEM-EDS) analysis of Al-WTR coated Mulch

Figure 11: Scanning Electron Microscope - Energy Dispersive X-ray Spectroscopy (SEM-EDS) analysis of Fe-WTR coated Mulch
Figure 12: Scanning Electron Microscope - Energy Dispersive X-ray Spectroscopy (SEM-EDS) analysis of Ae-WTR coated Mulch after rinsing with DI water and air drying.

Figure 13: Scanning Electron Microscope - Energy Dispersive X-ray Spectroscopy (SEM-EDS) analysis of Fe-WTR coated Mulch after rinsing with DI water and air drying.
Figure 14: Scanning Electron Microscope - Energy Dispersive X-ray Spectroscopy (SEM-EDS) analysis of uncoated (virgin) mulch
3.4 Equilibrium Tests with Single Element Solutions

Figures 15 through 22 present the results of the equilibrium adsorption tests at different Fe- and Al-WTR doses in a single-contaminant solution (i.e. Cu, Zn, Pb, or P).

Figure 15-22: Equilibrium percent removal as influenced by dosage rate (5, 10, 25 and 50 g/L) of WTR coated mulch in single element solution (after equilibrating for 24 hours at pH=7).
Data regarding Al-WTR coated mulch are shown in Figs. 15-18 (the left side). At 5 g/L, the media removed 56.9% of Cu (initial concentration = 100 µg/L) after 24 hours of equilibration time (Fig. 15). The percent removal of Cu increased slightly to 57.7% as adsorbent dosage increased to 10 g/L, but decreased subsequently (48.7 and 38.8%) 25 and 50 g/L. Al-WTR coated mulch (5 g/L) removed 93.6% of Pb (initial concentration = 100 µg/L) after 24 hours of equilibration time (Fig. 16). The percent removal of Pb increased slightly with the increase in adsorbent dosage and reached 95.2% with 50 g Al-WTR coated mulch. Al-WTR coated mulch (5 g/L) removed 89.7% of Zn (initial concentration = 600 µg/L) after 24 hours of equilibration time (Fig. 17). The percent removal of Zn increased slightly with increase in adsorbent dosage and reached 96.8% with 50 g Al-WTR coated mulch. Al-WTR coated mulch (5 g/L) removed 93.3% of P (initial concentration = 3000 µg/L) after 24 hours of equilibration time (Fig. 18). The percent removal of P increased slightly with increase in adsorbent dosage and reached 98.4% with 50 g Al-WTR coated mulch.

Data regarding Fe-WTR coated mulch are presented in Figs. 19-22 (the right side above). Coated mulch at 5 g/L removed 91.7% of Cu (initial concentration = 100 µg/L) after 24 hours of equilibration time (Fig. 19). The percent removal of Cu decreased (77.2%) with increase in adsorbent dosage of 10 g/L Fe-WTR coated mulch but increased subsequently (88.3 and 97.0%) with increase in adsorbent dosage (25 and 50 g Fe-WTR coated mulch). Fe-WTR coated mulch (5 g/L) removed 94.6% of Pb (initial concentration = 100 µg/L) after 24 hours of equilibration time (Fig. 20). The percent removal of Pb decreased slightly with increase in adsorbent dosage but then increased to 96.9% with 50 g Fe-WTR coated mulch. Fe-WTR coated mulch (5 g/L) removed almost all (99.8%) of Zn (initial concentration = 600 µg/L) after 24 hours of equilibration time (Fig. 21). The percent removal of Zn did not change with increase in adsorbent dosage of Fe-WTR
coated mulch and stayed almost the same as 5 g Fe-WTR coated mulch/L. Fe-WTR coated mulch (5 g/L) removed 35.8% of P (initial concentration = 3000 µg/L) after 24 hours of equilibration time (Fig. 22). The percent removal of P increased with increasing adsorbent dosage especially for 25 g/L (54.4%) and 50 g/L (87.1%) Fe-WTR coated mulch.

3.5 Equilibrium tests with multiple elements in simulated stormwater:

Figures 23 through 30 present results of the equilibrium adsorption tests for different dosage rates of Fe- and Al-WTR-coated mulch for multiple element solutions with Cu, Zn, Pb and P.

Figure 23-30: Equilibrium percent removal as influenced by dosage rate (5, 10, 25 and 50 g/L) of WTR coated mulch in contact with multi-element solution (after equilibrating for 24 hours at pH=7).
In case of simulated stormwater containing multiple pollutants (Cu, Pb, Zn and P), Al-WTR coated mulch (5 g/L) removed 75.1% of Cu (initial concentration = 100 µg/L) after 24 hours of equilibration time (Fig. 23). The percent removal of Cu increased slightly with increase in adsorbent dosage of 10 g/L (85.4%) and 25 g/L (86.2%) Al-WTR coated mulch but decreased thereafter (75.6%) with increase in adsorbent dosage (50 g/L Al-WTR coated mulch). Al-WTR coated mulch (5 g/L) removed 73.8% of Pb (initial concentration = 100 µg/L) after 24 hours of equilibration time (Fig. 24). The percent removal of Pb increased slightly with increase in adsorbent dosage with 88.9% removal at 10 g/L Al-WTR coated mulch. However, with increasing adsorbent dose (25 and 50 g/L), Pb removal reduced and reached 70.1% at 50 g/L Al-WTR coated mulch. Al-WTR coated mulch (5 g/L) removed 65.3% of Zn (initial concentration = 600 µg/L) after 24 hours of equilibration time (Fig. 25). The percent removal of Zn increased slightly with increase in adsorbent dosage of 10 g/L (69.1%) and 25 g/L (74.7%) Al-WTR coated mulch but decreased thereafter (64.9%) with increase in adsorbent dosage (50 g/L Al-WTR coated mulch). Al-WTR coated mulch (5 g/L) removed 94.0% of P (initial concentration = 3000 µg/L) after 24 hours of equilibration time (Fig. 26). The percent removal of P increased slightly with increase in adsorbent dosage and reached 99.8% with 50 g/L Al-WTR coated mulch.

Fe-WTR coated mulch (5 g/L) removed 99% of Cu (initial concentration = 100 µg/L) after 24 hours of equilibration time (Fig. 27). The percent removal of Cu was same at 10 g/L but decreased slightly with increase in adsorbent dosage and reached 94.5% at 50 g/L Fe-WTR coated mulch. Fe-WTR coated mulch (5 g/L) removed 98.4% of Pb (initial concentration = 100 µg/L) after 24 hours of equilibration time (Fig. 28). The percent removal of Pb increased slightly with increase in adsorbent dosage to reach 99.2% with 50 g/L Fe-WTR coated mulch. Fe-WTR coated mulch (5 g/L) removed 85.2% of Zn (initial concentration = 600 µg/L) after 24 hours of
equilibration time (Fig. 29). The percent removal of Zn increased with increasing adsorbent dosage of Fe-WTR coated mulch. 10 g/L Fe-WTR coated mulch removed 97.6% Zn and adsorption of Zn increased slightly to reach 99.3% removal of Zn at 50 g/L Fe-WTR coated mulch. Fe-WTR coated mulch (5 g/L) removed 28.2% of P (initial concentration = 3000 µg/L) after 24 hours of equilibration time (Fig. 30). The percent removal of P increased with increasing adsorbent dosage, 10 g/L (41.4%), 25 g/L (67.1%) and 50 g/L (90.7%) Fe-WTR coated mulch.

3.6 Kinetics experiments on Al-WTR-coated mulch with single element solutions:

Figures 31-34 present the results for kinetics experiments with Al-WTR-coated mulch and single element solutions of Cu, Pb, Zn and P, respectively.
In the case of Cu solution, the adsorption kinetics demonstrated that adsorption of Cu on Al-WTR coated mulch (5 g/L) removed 55% of Cu (initial concentration = 100 µg/L) within 2 hours of reaction time (Fig. 31A). The percent removal of Cu did not change much after 2 hours and plateaued up to 24 hours for 5 g/L Al-WTR coated mulch. In case of 10 g/L Al-WTR coated mulch, 68.8% Cu was removed from solution, but adsorption reduced slightly to reach 58.7% Cu removal after 24 hours (Fig. 31B). For 25 g/L Al-WTR coated mulch, maximum adsorption reached after 1 hour with 75.5% Cu removal, but Cu removal reduced with time thereafter reaching 33.1% Cu removal at 5 hours and eventually reaching 48.7% Cu removal after 24 hours (Fig. 31C). The same trend (as of 25 g/L) of Cu removal kinetics was observed in 50 g/L Al-WTR coated mulch with maximum Cu removal (83.3%) at 30 minutes (Fig. 31D). Percent Cu removal reduced thereafter with time reaching 38.8% Cu removal after 24 hours.
A.

B.
Fig. 32: Adsorption kinetics of Pb on Al-WTR coated mulch at different concentrations: 5 g/L (A), 10 g/L (B) 25 g/L (C) and 50 g/L Al-WTR coated mulch (D).
Initial Pb concentration = 100 µg/L, pH=7.
For Pb solution, the adsorption kinetics demonstrated that adsorption of Pb on Al-WTR coated mulch (5 g/L) removed 88% of Pb (initial concentration = 100 µg/L) within 2 hours of reaction time (Fig. 32A). Percent removal of Pb increased only slightly thereafter with time and reached 92.9% after 24 hours. In case of 10 g/L Al-WTR coated mulch, 96% Pb was removed from solution at 1 hour and increased to 99.2% within 5 hours and plateaued subsequently with time (Fig. 32B). For 25 g/L Al-WTR coated mulch, maximum adsorption reached after 2 hours with 65.1% Pb removal and it plateaued thereafter with time (Fig. 32C). In case of 50 g/L Al-WTR coated mulch, same trend (as of 25 g/L) was observed with per cent Pb removal reaching 58.1% within 1 hour and Pb removal plateaued subsequently with time (Fig. 32D).
B.

C.
D.

Fig. 33: Adsorption kinetics of Zn on Al-WTR coated mulch at different concentrations: 5 g/L (A), 10 g/L (B) 25 g/L (C) and 50 g/L Al-WTR coated mulch (D). Initial Zn concentration = 600 µg/L, pH=7.

Regarding Zn, the adsorption kinetics demonstrated that adsorption of Zn on Al-WTR coated mulch (5 g/L) removed 82.4% of Zn (initial concentration = 600 µg/L) within 5 hours of reaction time (Fig. 33A). Percent removal of Pb increased slightly thereafter with time and reached 89.7% after 24 hours. The same trend was observed in 10 g/L Al-WTR coated mulch reaching 90.9% Zn removal within 5 hours and eventually increasing to 94.8% after 24 hours (Fig. 33B). For 25 g/L Al-WTR coated mulch, 91.4% Zn was removed within 5 hours and it plateaued thereafter with time (Fig. 33C). In case of 50 g/L Al-WTR coated mulch, same trend (as of 25 g/L) was observed with percent Zn removal reaching 95.2% within 5 hours and Zn removal plateaued subsequently with time (Fig. 33D).
C.

D.

Fig. 34: Adsorption kinetics of P on Al-WTR coated mulch at different concentrations: 5 g/L (A), 10 g/L (B) 25 g/L (C) and 50 g/L Al-WTR coated mulch (D). Initial P concentration = 3000 µg/L, pH=7.
Regarding P, the adsorption kinetics demonstrated that adsorption of P on Al-WTR coated mulch (5 g/L) removed 60.6% of P (initial concentration = 3000 µg/L) within 5 hours of reaction time (Fig. 34A). Percent removal of P kept on increasing with time and reached 93.3% after 24 hours. In case of 10 g/L Al-WTR coated mulch, 91.4% P was removed after 5 hours and it increased to 96.5% after 24 hours (Fig. 34B). For 25 g/L Al-WTR coated mulch, 97.5% P removal was achieved after 2 hours and it plateaud subsequently with time (Fig. 34C). The same trend (as of 25 g/L) was observed in 50 g/L Al-WTR coated mulch with 98.5% removal achieved after just 1 hour and P removal stayed almost the same thereafter with time (Fig. 34D).

3.7 Kinetics experiments on Fe-WTR-coated mulch with single element solutions
Figures 35-38 present the results for kinetics experiments with Fe-WTR-coated mulch and single element solutions of Cu, Pb, Zn and P, respectively.

A.
B.

C.
D.

Fig. 35: Adsorption kinetics of Cu on Fe-WTR coated mulch at different concentrations: 5 g/L (A), 10 g/L (B) 25 g/L (C) and 50 g/L Fe-WTR coated mulch (D). Initial Cu concentration = 100 µg/L, pH=7.

In the case of the solution containing only Cu, the adsorption kinetics showed that adsorption of Cu on Fe-WTR coated mulch (5 g/L) removed 97.8% of Cu (initial concentration = 100 µg/L) within 20 minutes of reaction time (Fig. 35A). The percent removal of Cu reduced slightly to reach 91.7% after 24 hours for 5 g/L Fe-WTR coated mulch. In case of 10 g/L Fe-WTR coated mulch, 87.3% Cu was removed from solution within 20 minutes, but adsorption reduced to reach 77.2% Cu removal after 24 hours (Fig. 35B). For 25 g/L Fe-WTR coated mulch, 97.4% Cu was removed after just 1 minute of reaction time, but Cu removal reduced with time thereafter reaching 88.3% Cu removal after 24 hours (Fig. 35C). In case of 50 g/L Fe-WTR coated mulch, 95.4% Cu was removed after 5 minutes and it almost plateaued thereafter with time reaching 97% Cu removal after 24 hours.
A.

B.
Fig. 36: Adsorption kinetics of Pb on Fe-WTR coated mulch at different concentrations: 5 g/L (A), 10 g/L (B) 25 g/L (C) and 50 g/L Fe-WTR coated mulch (D). Initial Cu concentration = 100 µg/L, pH=7.
Regarding Pb, the adsorption kinetics showed that adsorption of Pb on Fe-WTR coated mulch (5 g/L) removed 97.8% of Pb (initial concentration = 100 µg/L) within 1 minute of reaction time (Fig. 36A). Percent removal of Pb plateaued subsequently with time. In case of 10 g/L Fe-WTR coated mulch, 97% Pb was removed from solution at 5 minutes and reduced slightly to 93.3% after 24 hours (Fig. 36B). For 25 g/L Fe-WTR coated mulch, 98.7% Pb was removed after 1 minute and it decreased slightly with time to reach 91.7% after 24 hours (Fig. 36C). In case of 50 g/L Fe-WTR coated mulch, per cent Pb removal reached 95.7% within 1 hour and Pb removal plateaued subsequently with time (Fig. 36D).
B.

C.
D.

Fig. 37: Adsorption kinetics of Zn on Fe-WTR coated mulch at different concentrations: 5 g/L (A), 10 g/L (B) 25 g/L (C) and 50 g/L Fe-WTR coated mulch (D). Initial Zn concentration = 600 μg/L, pH=7.

Regarding Zn, the adsorption kinetics showed that adsorption of Zn on Fe-WTR coated mulch followed the same trend for all dosage rates of Fe-WTR coated mulch. Almost 99% Zn was removed in all Fe-WTR coated mulch rates (5, 10, 25 and 50 g/L) within 60 minutes and Zn removal plateaued thereafter with time across all dosage rates of Fe-WTR coated mulch (Fig. 37A, B, C, D).
A.

B.
C.

D.

Fig. 38: Adsorption kinetics of P on Fe-WTR coated mulch at different concentrations: 5 g/L (A), 10 g/L (B) 25 g/L (C) and 50 g/L Fe-WTR coated mulch (D). Initial P concentration = 3000 µg/L, pH=7.
Regarding P, the adsorption kinetics demonstrated that adsorption of P on Fe-WTR coated mulch (5 g/L) removed 22.5% of P (initial concentration = 3000 µg/L) within 2 hours of reaction time (Fig. 38A). Percent removal of P increased with time to reach 35.8% after 24 hours. In case of 10 g/L Al-WTR coated mulch, 32.3% P was removed after 2 hours and it increased to 36.3% after 24 hours (Fig. 38B). For 25 g/L Al-WTR coated mulch, 53.3% P removal was achieved after 5 hours and it plateaued subsequently with time (Fig. 38C). In case of 50 g/L Al-WTR coated mulch, 83.6% P removal was achieved after 2 hours and P removal increased slightly with time to reach 87.1% after 24 hours (Fig. 38D).

3.8 Kinetics experiments on Al-WTR-coated mulch and multiple elements in simulated stormwater

Figures 39-43 present the results regarding Cu, Pb, Zn and P, respectively, for kinetics experiments with Al-WTR-coated mulch and multiple element solution.

A.
B.

C.
Fig. 39: Adsorption kinetics of Cu on Al-WTR coated mulch at different concentrations: 5 g/L (A), 10 g/L (B) 25 g/L (C) and 50 g/L Al-WTR coated mulch (D). Simulated stormwater had initial Cu (100 µg/L), Pb (100 µg/L), Zn (600 µg/L), P (3000 µg/L) concentrations, pH= 7.

In the case of Cu in simulated stormwater with mixed pollutants (Cu, Pb, Zn and P), the adsorption kinetics demonstrated that adsorption of Cu on Al-WTR coated mulch (5 g/L) removed 74.1% of Cu (initial concentration = 100 µg/L) after 5 hours of reaction time (Fig. 39A). Subsequently, the percent removal of Cu only increased about 1% after 24 hours for 5 g/L Al-WTR coated mulch. In case of 10 g/L Al-WTR coated mulch, 81% Cu was removed from solution and Cu removal increased slightly to reach 85.4% after 24 hours (Fig. 39B). The same trend (as of 10 g/L) was observed in 25 g/L Al-WTR coated mulch with 79.3% Cu removal achieved after 5 hours and then increasing slightly to reach 86.2% Cu removal after 24 hours (Fig. 39C). In case of 50 g/L Al-WTR coated mulch, maximum Cu removal (88.8%) was achieved after 5 hours but Cu removal reduced with time thereafter reaching 75.6% after 24 hours.
A.

B.
Fig. 40: Adsorption kinetics of Pb on Al-WTR coated mulch at different concentrations: 5 g/L (A), 10 g/L (B) 25 g/L (C) and 50 g/L Al-WTR coated mulch (D). Simulated stormwater had initial Cu (100 µg/L), Pb (100 µg/L), Zn (600 µg/L), P (3000 µg/L) concentrations, pH= 7.
Regarding Pb in mixed pollutants, the adsorption kinetics demonstrated that adsorption of Pb on Al-WTR coated mulch (5 g/L) removed 88.4% of Pb (initial concentration = 100 μg/L) within 5 hours of reaction time (Fig. 40A). Percent removal of Pb reduced thereafter with time and reached 73.8% after 24 hours. In case of 10 g/L Al-WTR coated mulch, 94.3% Pb was removed from solution at 2 hours and reduced to 88.9% after 24 hours (Fig. 40B). 25 g/L Al-WTR coated mulch followed the same trend (as of 25 g/L) with 95.6% Pb removal after 2 hours and then reducing to 79.9% Pb removal after 24 hours (Fig. 40C). In case of 50 g/L Al-WTR coated mulch, maximum Pb removal (72.6%) was observed at 20 minutes and per cent Pb removal decreased with time and reached 52.5% Pb removal after 24 hours (Fig. 40D).
B.

C.
D.

Fig. 41: Adsorption kinetics of Zn on Al-WTR coated mulch at different concentrations: 5 g/L (A), 10 g/L (B) 25 g/L (C) and 50 g/L Al-WTR coated mulch (D). Simulated stormwater had initial Cu (100 µg/L), Pb (100 µg/L), Zn (600 µg/L), P (3000 µg/L) concentrations, pH= 7.

Regarding Zn in mixed pollutants, the adsorption kinetics demonstrated that adsorption of Zn on Al-WTR coated mulch (5 g/L) removed 75.7% of Zn (initial concentration = 600 µg/L) within 5 hours of reaction time (Fig. 41A). Percent removal of Zn decreased slightly thereafter with time and reached 65.3% after 24 hours. The same trend was observed in 10 g/L Al-WTR coated mulch reaching 84% Zn removal within 5 hours and eventually decreasing to 69.1% after 24 hours (Fig. 41B). For 25 g/L Al-WTR coated mulch, 88.6% Zn was removed within 5 hours and it reduced thereafter with time to reach 74.7% Zn removal (Fig. 41C). In case of 50 g/L Al-WTR coated mulch, same trend (as of 25 g/L) was observed with per cent Zn removal reaching 91.1% within 2 hours and Zn removal decreased subsequently with time to reach 64.9% after 24 hours (Fig. 41D).
A.

B.
Fig. 42: Adsorption kinetics of P on Al-WTR coated mulch at different concentrations: 5 g/L (A), 10 g/L (B) 25 g/L (C) and 50 g/L Al-WTR coated mulch (D). Simulated stormwater had initial Cu (100 µg/L), Pb (100 µg/L), Zn (600 µg/L), P (3000 µg/L) concentrations, pH= 7.
Regarding P in with mixed pollutants, the adsorption kinetics demonstrated that adsorption of P on Al-WTR coated mulch (5 g/L) removed 67.9% of P (initial concentration = 3000 µg/L) within 5 hours of reaction time (Fig. 42A). Percent removal of P kept on increasing with time and reached 94% after 24 hours. In case of 10 g/L Al-WTR coated mulch, 91.8% P was removed after 5 hours and it increased to 95.5% after 24 hours (Fig. 42B). For 25 g/L Al-WTR coated mulch, 98.3% P removal was achieved after 2 hours and it plateaued subsequently with time (Fig. 42C). The same trend (as of 25 g/L) was observed in 50 g/L Al-WTR coated mulch with 99% removal achieved after 2 hours and P removal stayed almost the same thereafter with time (Fig. 42D).

3.9 Kinetics experiments on Fe-WTR-coated mulch and multiple elements in simulated stormwater:

Figures 43-46 present the results regarding Cu, Pb, Zn and P, respectively, for kinetics experiments with Fe-WTR-coated mulch and multiple element solution.
B.

C.
D.

Fig. 43: Adsorption kinetics of Cu on Fe-WTR coated mulch at different concentrations: 5 g/L (A), 10 g/L (B) 25 g/L (C) and 50 g/L Fe-WTR coated mulch (D). Simulated stormwater had initial Cu (100 μg/L), Pb (100 μg/L), Zn (600 μg/L), P (3000 μg/L) concentrations, pH= 7.

In the case of Cu in simulated stormwater with mixed pollutants (Cu, Pb, Zn and P), the adsorption kinetics showed that adsorption of Cu on Fe-WTR coated mulch (5 g/L) removed 94.0% of Cu (initial concentration = 100 μg/L) within 2 hours of reaction time (Fig. 43A). The percent removal of Cu increased slightly to reach 99% after 24 hours for 5 g/L Fe-WTR coated mulch. In case of 10 g/L Fe-WTR coated mulch, 97.3% Cu was removed from solution within 2 hours and Cu removal plateaued thereafter with time (Fig. 43B). For 25 g/L Fe-WTR coated mulch, 98% Cu was removed after 2 hours of reaction time and Cu removal stayed the same with time after that as well (Fig. 43C). In case of 50 g/L Fe-WTR coated mulch, 98.5% Cu was removed after 2 hours and Cu removal reduced slightly with time reaching 94.5% Cu removal after 24 hours (Fig. 43D).
A.

B.
Fig. 44: Adsorption kinetics of Pb on Fe-WTR coated mulch at different concentrations: 5 g/L (A), 10 g/L (B) 25 g/L (C) and 50 g/L Fe-WTR coated mulch (D). Simulated stormwater had initial Cu (100 $\mu$g/L), Pb (100 $\mu$g/L), Zn (600 $\mu$g/L), P (3000 $\mu$g/L) concentrations, pH= 7.
Regarding Pb, in mixed pollutants, the adsorption kinetics showed that adsorption of Pb on Fe-WTR coated mulch (5 g/L) removed 98.9% of Pb (initial concentration = 100 µg/L) after 120 minutes of reaction time (Fig. 44A). Percent removal of Pb plateaued subsequently with time. In case of 10 g/L Fe-WTR coated mulch, 99.4% Pb removal at 60 minutes and it plateaued with time (Fig. 44B). For 25 g/L Fe-WTR coated mulch, 98.5% Pb was removed after 20 minutes and it plateaued with time (Fig. 44C). In case of 50 g/L Fe-WTR coated mulch, per cent Pb removal reached 99.5% within 5 minutes and Pb removal plateaued subsequently with time (Fig. 44D).
B.

C.
D.

Fig. 45: Adsorption kinetics of Zn on Fe-WTR coated mulch at different concentrations: 5 g/L (A), 10 g/L (B) 25 g/L (C) and 50 g/L Fe-WTR coated mulch (D). Simulated stormwater had initial Cu (100 µg/L), Pb (100 µg/L), Zn (600 µg/L), P (3000 µg/L) concentrations, pH= 7.

Regarding Zn in mixed pollutants, the adsorption kinetics showed that adsorption of Zn on Fe-WTR coated mulch (5 g/L) removed 60.2% of Zn (initial concentration = 600 µg/L) after 5 hours of reaction time (Fig. 45A). Percent removal of Zn increased with time and reached 85.2% after 24 hours. In case of 10 g/L Fe-WTR coated mulch, 88.6% Zn was removed after 5 hours and Zn removal increased with time to reach 97.6% after 24 hours (Fig. 45B). For 25 g/L Fe-WTR coated mulch, 99.1% Zn was removed after 5 hours and it plateaued with time (Fig. 45C). In case of 50 g/L Fe-WTR coated mulch, per cent Zn removal reached 99.5% within 60 minutes and Zn removal plateaued subsequently with time (Fig. 45D).
A.

B.
C.

Fig. 46: Adsorption kinetics of P on Fe-WTR coated mulch at different concentrations: 5 g/L (A), 10 g/L (B) 25 g/L (C) and 50 g/L Fe-WTR coated mulch (D). Simulated stormwater had initial Cu (100 µg/L), Pb (100 µg/L), Zn (600 µg/L), P (3000 µg/L) concentrations, pH= 7.
Regarding P in mixed pollutants, the adsorption kinetics demonstrated that adsorption of P on Fe-WTR coated mulch (5 g/L) removed 25.3% of P (initial concentration = 3000 µg/L) within 5 hours of reaction time (Fig. 46A). Percent removal of P increased with time to reach 28.2% after 24 hours. In case of 10 g/L Al-WTR coated mulch, 36% P was removed after 5 hours and it increased to 41.4% after 24 hours (Fig. 46B). For 25 g/L Al-WTR coated mulch, 59.1% P removal was achieved after 5 hours and it increased with time to reach 67.1% after 24 hours (Fig. 46C). In case of 50 g/L Al-WTR coated mulch, 83% P removal was achieved after 5 hours and P removal increased with time to reach 90.7% after 24 hours (Fig. 46D).

3.10 Effect of solution pH

Figures 47-50 present the results regarding Cu, Pb, Zn and P, respectively, for kinetics experiments with Al-WTR-coated mulch and multiple element solution at pH values of 6, 7 and 8. At pH 7, 10 g/L of Al-WTR coated wood mulch in 1L solution containing the mixed pollutants (Table 1) reduced Cu concentration in the solution by about 45% within the first hour (Fig. 47). At pH 6, the adsorption of Cu on Al-WTR coated mulch reduced slightly. At pH 8, adsorption of Cu was affected and the results at pH 6 and 7 could not be imitated. Zn concentration at pH 6 increased slightly by 40% but then decreased subsequently with the passage of time (Fig. 48). At pH 7 and 8, adsorption on Al-WTR coated mulch increased and Zn concentration in the solution reduced by 90% before 400 minutes. The concentration of Pb in the solution also followed the same trend as of Cu. At pH 6, 7 the concentration of Pb in the solution reduced by about 90% within the first 100 minutes (Fig. 49). At pH 8, like Cu, adsorption of Pb on Al-WTR coated mulch was affected and the results at pH 6 and 7 could not be replicated. In case of P adsorption on Al-
WTR coated mulch, the concentration of P in the solution almost reduced by 100% before 400 minutes (Fig. 50). There was not much difference in the P concentration in the solution due to difference in the solution pH (6, 7, 8) (Fig 51).

Figures 51-54 present the results regarding Cu, Pb, Zn and P, respectively, for kinetics experiments with Fe-WTR-coated mulch and multiple element solution at pH values of 6, 7 and 8. There was only a slight effect of solution pH (6, 7 and 8) on percent Cu removal by Fe-WTR coated mulch (10 g/L). Percent Cu removal reduced slightly when the solution pH was 6 and 8 as compared to when the solution pH was 7 (Fig 51). There was not much effect of solution pH on percent removal of Pb and P by Fe-WTR coated mulch (Fig. 52, 54). However, percent removal of Zn increased with increase in solution pH from 7 to 8 and percent removal of Zn reduced with decrease in solution pH from 7 to 6 (Fig. 53).
Fig. 47-50: Effect of solution pH (6, 7, 8) on pollutant removal from solution by Al-WTR coated mulch (10 g/L) with time

Fig 47: Cu (initial concentration = 100 µg/L)

Fig 48: Pb (initial concentration = 100 µg/L)

Fig 49 (initial concentration = 600 µg/L)

Fig 50: P (initial concentration = 3000 µg/L)

Fig. 47-50: Effect of solution pH (6, 7, 8) on pollutant removal from solution by Al-WTR coated mulch (10 g/L) with time
Fig 51: Cu initial concentration = 100μg/L

Fig 52: Pb (initial concentration = 100μg/L)

Fig 53: Zn (Initial concentration = 600 µg/L)

Fig 54: P (Initial concentration 3000 µg/L)

Fig. 51=54: Effect of solution pH (6, 7, 8) on pollutant removal from solution by Fe-WTR coated mulch (10 g/L) with time.
3.11 Effect of temperature

Figures 55-58 present results regarding Cu, Pb, Zn and P, respectively, for kinetics experiments with Al-WTR-coated mulch and multiple element solution at temperatures of 12, 22 and 32°C. At 12°C, 10 g of Al-WTR coated mulch removed Cu by 50% within the first hour but Cu concentration in the solution did not decrease subsequently with time (Fig. 55). The concentration of Cu in the solution reduced with increase in temperature (22°C and 32°C) and maximum adsorption onto Al-WTR coated mulch was achieved at 22°C and it was slightly less at 32°C. Zn concentration in the solution reduced by 70% at 12°C and 32°C before 400 minutes (Fig. 56). Zn concentration was reduced further slightly at 22°C achieving the maximum adsorption of Zn onto Al-WTR coated mulch. In case of Pb concentration, it was reduced very rapidly within the first few minutes at 22°C but adsorption on Al-WTR coated mulch reduced slightly at the end of 24 hour period. At 12°C, Pb concentration in the solution was reduced less than 50% of its initial concentration (Fig. 57). At 32°C, Pb concentration in the solution was reduced by 80% before 400 minutes although adsorption on Al-WTR coated mulch started to reduce at the end of 24 hour period. P adsorption on Al-WTR coated mulch at different solution temperatures (12°C, 22°C and 32°C; Fig. 58) followed the same trend as in case of adsorption for different solution pH (6, 7 and 8). The concentration of P in the solution almost reduced by almost 100% before 400 minutes at all the solution temperatures (12°C, 22°C and 32°C; Fig. 58). There was not much difference in the P concentration in the solution due to difference in the solution temperature.
Fig. 55-58: Effect of solution temperature (12°C, 22°C, 32°C) on % removal from solution by Al-WTR coated mulch (10 g/L) with time.
Figures 59-62 present results regarding Cu, Pb, Zn and P, respectively, for kinetics experiments with Fe-WTR-coated mulch and multiple element solution at temperatures of 12, 22 and 32 C. There was not much effect of solution temperature on percent removal of Pb by Fe-WTR coated mulch (10 g/L; Fig. 60). There was a slight drop in Cu removal percent when the temperature was increased from 22 C to 32 C (Fig. 59). However, there was not much difference between Cu removal percent at 12 C and 22 C. In case of Zn removal percent by Fe-WTR coated mulch, the Zn removal percent decreased at 24 hours when the temperature was reduced to 12 C and also when it was increased to 32 C as compared to 22 C (Fig. 61). The same trend (as of Zn removal) was also observed in P removal per cent (Fig. 62).
Fig. 59-62: Effect of solution temperature (12°C, 22°C, 32°C) on %P removal from solution by Fe-WTR coated mulch (10 g/L) with time.

3.12 Column Tests with WTR-coated and uncoated mulch

Figures 63-68 present results regarding Cu, Pb, Zn and P, respectively, for flow-through columns containing Al-WTR-coated mulch, Fe-WTR-coated mulch, and uncoated mulch, for mulch depths of 2” and 4”. None of the tests showed the classic shape of a breakthrough curve – only Zn and P in Fe-WTR-coated mulch (both 2-inch and 4-inch depths) showed pronounced decrease in removal as the bed volumes increased. Fe-WTR-coated-mulch at 4-inch depth was very effective in removing Cu and Pb, consistently removing >90% through 120 bed volumes, which was better than the Al-WTR-coated and uncoated mulches. The uncoated mulch was initially effective at removing of Cu and Pb (~80% removal), but removal subsequently decreased and/or became erratic. Fe-WTR-coated mulch achieved high removal (>90%) for Zn for about 10 bed volumes, but then removal decreased. The other mulches, as well as the 2-inch Fe-WTR-coated mulch, were not very effective regarding Zn removal, with removal of mostly ~50% for Al-WTR-coated-mulch and mostly <20% for uncoated mulch. The 4-inch Al-WTR-coated-mulch was the most effective at removing P, with removal consistently ~50%, while the other mulches removed only ~20%. The results for Al-WTR-coated mulch were highly variable for Cu and Pb, with concentrations spiking to ~220% and 170%, respectively, above the inlet concentration. At other times, up to 80% removal of Cu and Pb was achieved. Concentrations greater than the inlet occurred for both the two-inch and four-inch depths. A pronounced improved performance of the 4-inch depth vs. the 2-inch depth was seen only in Fe-WTR-coated mulch for Cu, Pb and, to a lesser extent, Cu. Negative removal of P (i.e., effluent concentration > influent) was not observed for any mulch, contrary to what has been sometimes observed in other studies (Paus, 2014)
Fig. 63-68: Fractions of remaining of Cu, Pb, Zn and P in effluent vs. bed volume for tests of Al-WTR-coated, Fe-WTR-coated and uncoated wood mulch with 2-inch and 4-inch filter-bed heights (WTR concentration = 10 g/L; initial pollutant concentrations: Cu = 100 µg/L, Pb = 100 µg/L, Zn = 600 µg/L, and P = 3000 µg/L).
3.13 pH of Effluent from Column Tests with WTR-coated and uncoated mulch

Fig. 69 and 70 shows the pH of effluent samples of 2 and 4 inch filter bed height columns. The initial pH of synthetic stormwater solution was 7.0. The samples were taken after 7 hours of the experiment each day. There was not much variation in the effluent pH of the Al-WTR, Fe-WTR and uncoated mulch.

Fig. 69: pH of effluent samples of 2 inch filter bed height columns (3 inch diameter, 16 inch height) packed with Al-WTR coated mulch, Fe-WTR coated mulch and uncoated mulch with bed volume; (relative standard deviations were less than 10%, not shown in the figure).

Fig. 70: pH of effluent samples of 4 inch filter bed height columns (3 inch diameter, 16 inch height) packed with Al-WTR coated mulch, Fe-WTR coated mulch and uncoated mulch with bed volume; (relative standard deviations were less than 10%, not shown in the figure).
### 3.14 Leaching tests on spent WTR-coated mulch

SPLP and TCLP tests were performed separately on spent mulch was collected from the above column tests. SPLP is a standard EPA method to determine the leaching potential of waste under a simulated exposure-to-rainfall environment. The TCLP test simulates a typical municipal landfill condition to quantify chemical leaching from the waste, and determines whether wastes can be disposed of as non-hazardous wastes in municipal landfills. Results are summarized in Table 8. The leached contaminants were all below the required SPLP and TCLP criteria, suggesting that the release of undesired chemicals under rainfall or landfilling conditions is not a concern.

<table>
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<tr>
<th>Contaminants (µg/L)</th>
<th>Ag</th>
<th>As</th>
<th>Ba</th>
<th>Cd</th>
<th>Cr</th>
<th>Hg</th>
<th>Pb</th>
<th>Se</th>
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<td><strong>SPLP Tests</strong></td>
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<td></td>
<td></td>
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<tr>
<td>Unused mulch</td>
<td>0.02</td>
<td>1.97</td>
<td>10230</td>
<td>3.23</td>
<td>29.3</td>
<td>2.02</td>
<td>2.04</td>
<td>0.00</td>
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<tr>
<td>Spent mulch</td>
<td>0.26</td>
<td>0.87</td>
<td>1766</td>
<td>0.80</td>
<td>3.92</td>
<td>1.86</td>
<td>0.59</td>
<td>0.00</td>
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<tr>
<td>SPLP criterion</td>
<td>800</td>
<td>3</td>
<td>120,000</td>
<td>80</td>
<td>N/A</td>
<td>40</td>
<td>100</td>
<td>800</td>
</tr>
<tr>
<td><strong>TCLP Tests</strong></td>
<td></td>
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<td></td>
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<td></td>
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<tr>
<td>Unused mulch</td>
<td>0.03</td>
<td>2.98</td>
<td>3603</td>
<td>2.41</td>
<td>47.3</td>
<td>4.29</td>
<td>7.51</td>
<td>0.00</td>
</tr>
<tr>
<td>Spent mulch</td>
<td>0.07</td>
<td>2.26</td>
<td>8565</td>
<td>3.03</td>
<td>38.6</td>
<td>3.14</td>
<td>4.74</td>
<td>0.00</td>
</tr>
<tr>
<td>TCLP criterion</td>
<td>5000</td>
<td>5000</td>
<td>100,000</td>
<td>1000</td>
<td>5000</td>
<td>200</td>
<td>1000</td>
<td>5000</td>
</tr>
</tbody>
</table>

The unused mulch and spent mulch was used for SPLP and TCLP tests, separately.
4. CONCLUSIONS

Batch and column tests both showed the potential of WTR-coated mulches for removal of metals and P from urban runoff. This media utilizes complementary advantages of two materials, i.e., the adsorption capability of WTR and the good permeability of mulches. It can installed in conventional LID infiltration systems and provides a beneficial reuse of a waste product typically disposed of in landfills, thereby reducing waste disposal costs and saving landfill space.

The results of SPLP and TCLP tests presented the leached contaminants were all below the U.S. SPLP and TCLP criteria that suggest that the release of undesired chemicals in storm water runoff is not a concern.

In batch test for single pollutant, the results showed removal of Cu, Zn, Pb and P by WTR-coated wood mulch.

In flow-through column tests, Fe-WTR-coated-mulch at 4-inch depth was very effective in removing Cu and Pb, consistently removing >90% through 120 bed volumes. The uncoated mulch was initially effective, removing ~80% of Cu and Pb, but removal decreased and/or became erratic. Fe-WTR-coated mulch achieved high removal (>90%) for Zn for about 10 bed volumes. The 4-inch Al-WTR-coated-mulch was the most effective at removing P, with removal consistently ~50%. Negative removal of P (i.e., effluent concentration > influent) was not observed for any mulch, contrary to what has been sometimes observed in other studies (Paus, 2014)

For the future, we recommend a field study of WTR-coated mulch to test performance under real conditions in an existing or new bioretention system.
ACKNOWLEDGEMENTS

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5. REFERENCES


