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Water treatment residual-coated wood mulch for addressing urban stormwater pollution

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• Abstract

Innovative treatment materials and technologies are demanded to address urban stormwater pollutants that challenge traditional infrastructure. This study aimed to investigate adsorption behaviors of aluminum-based water treatment residual (WTR)-coated mulch for capturing representative runoff pollutants (i.e., P, Cu, Zn, and Pb) and evaluate its treatment performance in a filtration bed. Data from batch studies were fit using the nonlinear least square optimization technique. Adsorption kinetic data followed the pseudo-2nd-order reaction patterns, while the adsorption isotherm data obeyed the Freundlich models. Model fitting passed the chi-square tests, as a statistical goodness-of-fit criterion, at a 90% confidence level. Column studies indicate that the WTR-coated mulch with a bed depth of 5.1 or 10.2 cm could effectively alleviate flow-weighted mean concentrations of these pollutants, with a minimal aluminum release, during treatment of the equivalent annual runoff in a typical U.S. Northeastern catchment. This study demonstrates that WTR-coated mulch is an effective and safe adsorbent media to tackle urban stormwater pollution. © 2019 Water Environment Federation

• Practitioner points

- Aluminum-based WTR-coated wood mulch can simultaneously and effectively capture representative metals and phosphate in urban runoff.
- The pollutant adsorption follows the pseudo-2nd-order kinetic reaction patterns and the Freundlich isotherm model.
- WTR-coated mulch (5.1–10.2 cm bed depth) sufficiently treats the runoff generated annually in a typical U.S. Northeastern catchment.
- Higher and more reliable pollutant removals can be achieved with a greater bed depth of the coated mulch in a filtration bed.
- Aluminium release is minimal during application of the WTR-coated wood mulch.

• Key words

adsorption; nonpoint pollution; phosphate; toxic heavy metals; urban stormwater runoff; water treatment residual; wood mulch

INTRODUCTION

MORE than half of the global population resides in urbanized areas (CIA, 2015). Despite many benefits, a high urbanization leads to many environmental issues such as urban environment pollution due to stormwater runoff. Typically, an urban setting has 50%–100% imperviousness as a result of large impermeable surfaces (e.g., roofs, roads, and garages), which significantly accumulate constituents from atmospheric deposition, vehicular traffic, and other sources; reduce stormwater infiltration; and interrupt a natural water cycle. Besides more frequent flooding (Kong, Ban, Yin, James, & Dronova, 2017), an increased runoff has a higher potential to wash off chemical and microbial pollutants on surfaces and carry them into urban waterways. Therefore, polluted urban runoff represents a principal nonpoint pollution source to threaten urban human and ecological health (Bell, McMillan, Clinton, & Jefferson, 2017).

Urban runoff pollutants include suspended solids, toxic heavy metals, nutrients, pathogens, salts, and hydrocarbons (e.g., gasoline) (Blocken, Derome, & Carmeliet,

2013; Davis, Shokouhian, & Ni, 2001; Pitt, Field, Lalor, & Brown, 1995; Wilson, 2018). Among them, toxic metals and nutrients are of particular concern (Hobbie et al., 2017; Huber, Welker, & Helmreich, 2016). The former pollutant type, such as copper (Cu), zinc (Zn), and lead (Pb), is toxic, chemically and biochemically persistent, and bio-accumulated (Hobbie et al., 2017), while the latter ones can lead to algal blooms in water bodies to degrade water quality (e.g., oxygen depletion, increased turbidity, the production of taste and odor compounds, and the release of toxic algal toxins) (Galloway et al., 2003; Huber et al., 2016).

Conventional urban stormwater management infrastructure like pipes and channels focuses merely upon conveyance of peak flows but cannot effectively alleviate runoff pollutants. Stormwater “Best Management Practices (BMPs)” like detention ponds address both quantity and quality issues of urban stormwater (Brown, Schueler, & Consortium, 1997; USEPA, 2006; Wossink & Hunt, 2003), but are highly effective only at removing particulates, while relatively ineffective for dissolved pollutants. Low Impact Development (LID) techniques are a subset of BMPs, which emphasize small-scale, decentralized treatment systems to preserve or closely mimic the site’s pre-developed hydrologic response and to enable runoff infiltration (Rosa, Clausen, & Dietz, 2015). However, the application of LID techniques is limited by different technical and/or economical restrictions. For example, in bioretention basins (a leading LID technique), persistent pollutants (e.g., toxic metals) can be accumulated in the topsoil so that frequent replacement of soil is required. Moreover, the phosphorus (P) removal efficiencies of bioretention basins are highly unstable. Occasionally, P may even be released from soil into treated stormwater (Dietz & Clausen, 2005, 2006; Hatt, Fletcher, & Deletic, 2009; Roy-Poirier, Champagne, & Filion, 2010; Wu, Holman, & Dorney, 1996). Therefore, there is an urgent demand to develop new, robust, and affordable urban stormwater treatment materials and technologies.

Water treatment residual (WTR) has recently been investigated to capture toxic metals and phosphate in urban runoff (Deng, Sarkar, Rakshit, & Morris, 2011; O’Neill & Davis, 2011a,b; Soleimanifar, Deng, Wu, & Sarkar, 2016). WTR is aluminum (Al) or iron (Fe)-based solid wastes produced from coagulation during drinking water treatment. The United States produces approximately two million tons of WTR every year (Prakash & SenGupta, 2003), most of which is expensively disposed in landfills. WTR is a mixture of different components, including Al or Fe-(hydr)oxides produced from coagulant addition and these substances originally present in water sources and captured by the coagulants (e.g., sands, silts, clay, and natural organic matter) (Edzwald, 2011). With abundant surface functional groups and large specific surface areas, WTR can effectively adsorb various aqueous inorganic and organic pollutants (Elliott, O’Connor, Lu, & Brinton, 2002; Ippolito, 2001; Ippolito, Scheckel, & Barbarick, 2009; Makris, Harris, O’Conno, & Obreza, 2004; Makris, Sarkar, Parsons, Datta, & Gardea-Torresdey, 2007; Punamiya, Sarkar, Rakshit, & Datta, 2013; Sarkar, Makris, Vandanapu, & Datta, 2007).

Direct application of WTR as an adsorbent media is not feasible. Once wetted, WTR powders readily aggregate to

prevent water infiltration. Another possible application mode is the addition of WTR powders into the soil matrix in a stormwater infiltration system (O’Neill & Davis, 2011a,b). However, after WTR is oversaturated with pollutants of concern, pollutant breakthrough will occur. Repeated addition of WTR into soil will lead to a consistently increasing Al or Fe content in soil. This option may be problematic due to the toxicity of these metals, particularly Al. Recently, we proposed synthesis and application of WTR-coated wood mulch chips for stormwater treatment (Soleimanifar et al., 2016).

Mulching is a simple and beneficial practice for landscaping and agriculture (USDA, 2018). Mulch is a protective layer of a material spread on the top of soil. In the mulch market, the most popular product is ground, shredded, or chipped wood due to its low cost and easy availability. Benefits of mulching include protection from soil erosion, moisture conservation, and weed control (USDA, 2018). However, the adsorption capability of wood mulch for typical runoff pollutants is poor in comparison with that of WTR (Jang, Seo, & Bishop, 2005; Saeed, Akhter, & Iqbal, 2005). Our recent studies demonstrated the capability of wood mulch chips coated with WTR for the effective alleviation of toxic metals and phosphate from urban runoff (Soleimanifar et al., 2016). Coating mulch with WTR potentially brings six unique benefits, including: (a) technical effectiveness: The new adsorbent media can remove multiple runoff pollutants without any significantly increased physical footprint, thus making it especially suitable for urban areas where land availability is limited; (b) low cost: WTR is free of charge; (c) versatility: The coated mulch can be employed in combination with existing green infrastructure (e.g., bioretention basins) or alone; (d) easy maintenance and operation: Only annual replacement of the coated mulch, similar to common wood mulch, is required during practices, enabling a long-term pollutant removal capability; and (e) municipal waste reuse: The reuse of WTR gives the waste a new life, saves the limited landfill space, and reduces its disposal costs.

However, the information regarding reactor design and adsorption patterns of the WTR-coated mulch at a continuous flow condition related to a realistic runoff treatment remains limited. The objective of this study was to investigate adsorption behaviors of WTR-coated wood mulch chips for representative urban runoff pollutants and evaluate their long-term treatment performance in a treatment bed. Selected pollutants included three metals (i.e., Cu, Zn, and Pb) and phosphate due to their abundance in urban runoff. Batch studies were firstly performed to determine key adsorption kinetic and isotherm patterns. Subsequently, column studies were carried out to evaluate the coated wood mulch for treatment of the equivalent of the annual runoff from a catchment area 20 times larger than the treatment area at a continuous flow condition.

MATERIAL AND METHOD

Al-WTR-coated mulch and chemical reagents

Al-WTR was collected from the Bridgewater Water Treatment Plant (Bridgewater, New Jersey, USA) in the October of 2014. The WTR was completely mixed, dried by air, and then

sieved through a 2-mm sieve. Timberline cedar wood mulch (Oldcastle Lawn and Garden Inc.) was purchased from a local HomeDepot store and then manually sorted. Mulch chips (ca. 1×2 cm) were selected, rinsed with deionized water three times to remove dusts on the surface, and air-dried. A landscaping mulch glue (Technisoil Global Inc.) was used to coat Al-WTR on the mulch at a mass ratio of WTR to mulch at 1:3, which ensured that the WTR powder could completely cover the mulch surface (Soleimanifar et al., 2016). Appearances of the WTR, mulch, and WTR-coated mulch chips are shown in Figure 1. Scanning electron microscope (SEM) images of the Al-WTR powders are presented in Figure 2a,b, revealing the unique morphologic characteristics of Al-WTR, including: (a) that they had approximately spherical shapes; (b) that the grain sizes broadly varied from a few hundred to a few tens of micrometers; and (c) that the surface was highly rough, which provided a large specific surface area for capturing water pollutants. The SEM images of Al-WTR were very similar to those reported in other studies (Babatunde, Zhao, Burke, Morris, & Hanrahan, 2009; Ippolito, Barbarick, Heil, Chandler, & Redente, 2003; Yang et al., 2006). We also compared the SEM images between Al-WTR and pure aluminum hydroxides (not shown here). Results show that Al-WTR was nearly amorphous, whereas pure aluminum hydroxide had a very regular crystalline structure. The difference could be caused by the poor crystallinity of aluminum hydroxide in Al-WTR and the presence of impurities.

All the reagents used were at least analytical grade, except as noted. For the batch tests, two synthetic urban runoff solutions were prepared, that is, the single-pollutant solution (SPS) and multiple-pollutant solution (MPS). For the column studies, only MPS was used. SPS contained a single pollutant ($100 \mu\text{g/L Cu}^{2+}$, $600 \mu\text{g/L Zn}^{2+}$, $100 \mu\text{g/L Pb}^{2+}$ or 3.10 mg/L P), 0.01 M potassium chloride (KCl), and 5 mM piperazine- $\text{N,N}'$ -bis (2-ethanesulfonic acid) (PIPES). PIPES was used to buffer solution pH during the adsorption. Pb, Zn, Cu, and P were provided from lead nitrate ($\text{Pb}(\text{NO}_3)_2$) (Fisher Scientific, Fair Lawn, NJ), zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Fisher Scientific, Fair Lawn, NJ), copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$) (Acros organic, 98+%), and disodium phosphate (Na_2HPO_4) (Fisher Scientific, Fair Lawn, NJ), respectively. It should be noted that concentrations of the selected urban runoff pollutants were reported to vary within broad ranges in the literature, such

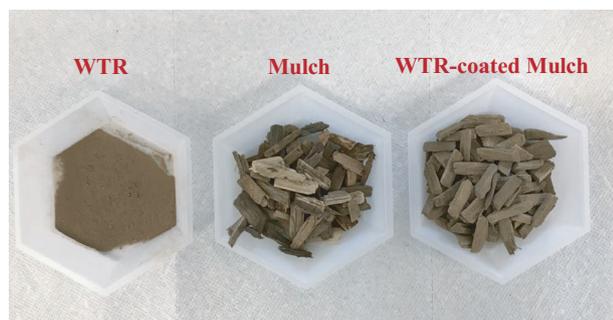
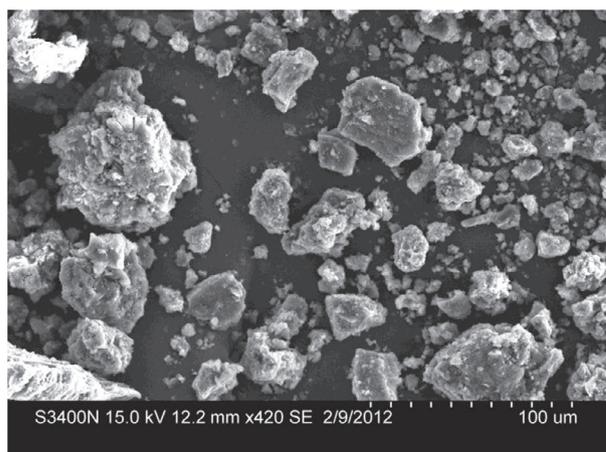


Figure 1. Water treatment residual (WTR), mulch, and WTR-coated mulch.

(A)



(B)

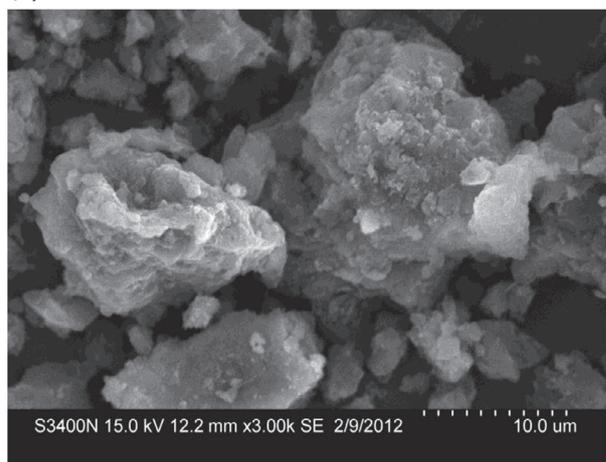


Figure 2. Scanning electron microscope images of Al-WTR powders.

as Cu, $27\text{--}274 \mu\text{g/L}$ (Huber et al., 2016; USEPA, 2006); Zn, $114\text{--}2,234 \mu\text{g/L}$ (Chin, 2006; Huber et al., 2016; USEPA, 1983, 2006); Pb, $15\text{--}160 \mu\text{g/L}$ (Huber et al., 2016; USEPA, 1983); and $\text{PO}_4^{3-}\text{-P}$, $0.1\text{--}21.1 \text{ mg/L}$ (Göbel, Dierkes, & Coldewey, 2007; Lee & Bang, 2000). In this study, levels of the selected pollutants in the synthetic runoff fell within their respective occurrence ranges reported in the literature. Chemical composition of MPS was as follows: $100 \mu\text{g/L Cu}^{2+}$, $600 \mu\text{g/L Zn}^{2+}$, $100 \mu\text{g/L Pb}^{2+}$, $3.10 \text{ mg/L PO}_4^{3-}\text{-P}$, $2 \text{ mg/L NO}_3^- \text{-N}$, $2 \text{ mg/L NH}_4^+ \text{-N}$, 40 mg/L CaCO_3 for alkalinity, 0.01 M KCl for ionic strength, 5 mM PIPES, and 20 mg/L used motor oil. If needed, pH was adjusted to a designated level using 0.1 N NaOH and HNO_3 .

Batch sorption experiments

Bench-scale sorption tests were carried out in a batch mode using 1 L SPS or MPS on a shaker (Thermo Scientific™ Precision™ Shaking Water Baths) at room temperature (22°C). Once an appropriate weight of adsorbents was added, the sorption tests were initiated. During the sorption, pH was not controlled. Throughout the sorption tests, the pH variation was

insignificant ($< \pm 0.1$). In the kinetics tests, five sorbent concentrations (i.e., 5, 10, 25, 35, and 50 g/L) were used. At designated time intervals, 5 ml of samples was withdrawn. In the sorption isotherm tests, samples were collected after 24 hr. Once an aliquot of sample was withdrawn, it was filtered through 0.45 μm cellulose nitrate membrane (Whatman Puradisc syringe filters) before analyses. To understand the effect of pH (6–8), sorption kinetic tests were also performed in MPS at 10 g/L WTR-coated mulch. In the experiments to study the effect of ionic strength, ionic strength was varied within 0.005–0.5 M KCl in SPS with 10 mg/L P and 1 g/L Al-WTR powders.

Models and error analysis

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

$$q = \frac{(C_i - C_f)V}{m} \tag{1}$$

where C_i and C_f represent the initial and final pollutant concentrations in water, respectively; V is the volume of solution (L); and m is the mass of an adsorbent (g). Experimentally measured kinetic data were fit to two kinetic models, that is, the pseudo-1st- and 2nd-order reactions, as follows (Qiu et al., 2009).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{Pseudo-1}^{\text{st}} \text{ order} \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Pseudo-2}^{\text{nd}} \text{ order} \tag{3}$$

where q_t and q_e are the adsorption capacities at any time t and chemical equilibrium, respectively; and, k_1 and k_2 are rate constants of the pseudo-1st- and 2nd-order reactions, respectively.

Two adsorption isotherm models were used to fit the experimental data at chemical equilibrium, including the Langmuir and Freundlich models (Vadi & Rahimi, 2014).

$$q_e = \frac{b C_e q_{\text{max}}}{1 + b C_e} \quad \text{Langmuir} \tag{4}$$

$$q_e = K_f C_e^{1/n} \quad \text{Freundlich} \tag{5}$$

where C_e is the adsorbate concentration in water at chemical equilibrium; q_{max} is the maximum adsorption capacity; and b , K_f , and n are constants.

The nonlinear least square optimization technique was used to evaluate the fit of the aforementioned kinetic and adsorption isotherm models using the Solver Add-In in Microsoft Excel (version 2016). Chi-square tests were used as a statistical “goodness-of-fit” criterion. The chi-square goodness-of-fit test is based on the following equation.

$$\chi^2 = \sum_{i=1}^n \frac{(\text{observed value}_i - \text{expected value}_i)^2}{\text{expected value}_i} \tag{6}$$

where χ^2 is the chi-square value; the observed and expected values are experimentally measured and modeled data,

respectively; and i is the number of experimental measurements. The criterion for acceptable fit is:

$$P(\chi^2 \leq \chi_0^2) = 1 - \alpha \tag{7}$$

where α is the confidence level and $\leq \chi_0^2$ is the chi-square distribution value for $n - 1$ degrees of freedom.

Column treatment experiments

Columns treatment tests were carried out in 30.5-cm high PVC pipes (i.d. 7.6 cm; Figure 3). PVC caps were installed at the bottom of these columns, connected with silicone tubings (0.64-cm i.d.) serving as the outlets. A tubing clamp was installed on each outlet tubing to adjust the infiltration rate to a designated level. Column tests were performed in duplicate under four different conditions, including 5.1-cm-deep raw wood mulch (control 1), 10.2-cm-deep raw wood mulch (control 2), 5.1-cm-deep Al-WTR-coated wood mulch (treatment 1), and 10.2-cm-deep Al-WTR-coated wood mulch (treatment 2). A peristaltic pump (Masterflex L/S model 77202-60, USA) was used to continuously feed synthetic runoff to the top of these columns at a flow rate of 9.5 ml/min. And the outlet flow rate was controlled at the same rate. The flow rate was selected to achieve an infiltration rate (12.60 cm/hr), meeting with the minimum infiltration

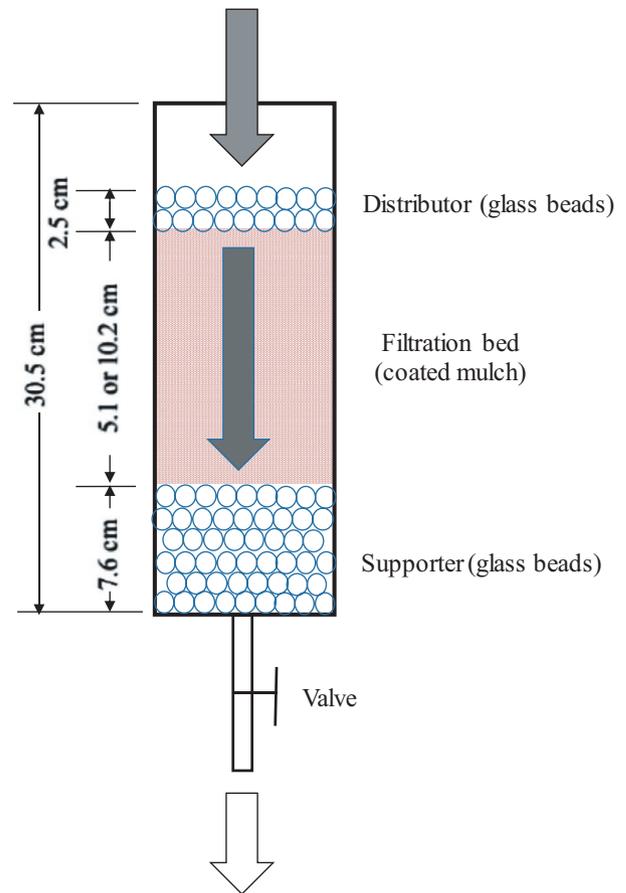


Figure 3. Setup of the filtration beds loaded with Al-WTR coated wood mulch for column studies (arrow lines represent the direction of stormwater flow).

rate (0.50 cm/hr) occurring in an infiltration basin (MPCA, 2017). Each column was loaded with 7.6-cm-deep glass beads as a supporter at the bottom, raw or coated mulch chips in the middle, and 2.5-cm-deep glass beads on the top. The top glass beads uniformly distributed influent into the underlying mulch layer. An aliquot of 600 ml of simulated stormwater was directly added into each column every day prior to the initiation of the experiments. Water table was maintained throughout the experiments. After passing through the treatment bed, all the water was drained out through the outlets. The column studies were carried out for 7 hr every day with 4 L simulated stormwater. In total, 56 L simulated stormwater passed through each column over 14 days, equivalent to the annual runoff from a service catchment 20× larger than the treatment area, assuming 130 cm of precipitation with 50% converted to runoff, which is typical of the northeast United States. Effluents were collected three times every day for analysis.

Analytical methods and data analysis

Solution pH was measured with a Thermo Fisher Scientific ORION 5-Star multiparameter meter. Metals were analyzed using an inductively coupled plasma-mass spectroscopy (ICP-MS Thermo X-Series II, XO 472) in reference to the U.S. Standard Method 200.8. The instrument detection limits are as follows: Cu, 0.002 µg/L; Zn, 0.02 µg/L; and Pb, 0.0004 µg/L. Phosphorus was spectrophotometrically measured using HACH reactive phosphorous test kits (HACH company, detection limit: 0.02 mg/L P). Because metal and phosphorus were measured after 0.45 µm membrane filtration, the measurements represent dissolved metal and P concentrations, respectively. All the treatment tests were conducted, at least, in duplicates. The analytical results reported represent the mean of the replicate samples. Error bars are one standard deviation of these measurements. To compare the pollutant removals using raw and coated wood mulch in the column studies, flow-weighted mean concentrations (FWMC) of these pollutants are calculated as follows.

$$\text{FWMC} = \frac{\sum_1^n (C_i t_i q_i)}{\sum_1^n (t_i q_i)} \quad (8)$$

where n is the number of total sample collection and measurement within a specific time period; c_i is the pollutant concentration in the i^{th} sample; t_i is the time duration for the i^{th} sample; and q_i is the average flowrate in the i^{th} sample. FWMC represents the total pollutant load divided by the total discharge within a specific duration.

RESULTS AND DISCUSSION

Batch treatment studies

For any selected pollutant, its residual concentration in water decreased with contact time due to immobilization of the pollutant to the WTR-coated wood mulch. For example, Supporting Information Figure S1a,b present the kinetic information of residual P concentrations with contact time in SPS and MPS, respectively. As the time increased from 0 to 1,440 min, the

residual P in water gradually dropped from 3.10 mg/L to 0.21–0.05 mg/L and to 0.19–0.01 mg/L in SPS and MPS at the coated mulch concentration of 5–50 g/L, respectively. At any specific contact time, the residual P concentration was decreased with an increasing coated mulch concentration. For example, at 20 min and in SPS, the residual P was 2.71, 2.25, 1.29, 0.72, and 0.29 mg/L at 5, 10, 25, 35, and 50 g/L Al-WTR-coated mulch, respectively, corresponding to the removal efficiencies of 14%, 30%, 61%, 80%, and 91%. This finding is because more filter media with a higher adsorbent concentration provided more active sites for phosphate adsorption. Very similar patterns were also observed for the other three selected pollutants (data not shown here).

Experimentally measured kinetic data for all the four selected pollutants were fit to the two kinetics models. Results showed that, at a 90% confidence level, only the pseudo-2nd-order kinetic models consistently satisfied $\chi^2 \leq \chi_0^2$ at any specific sorbent concentration, regardless of the pollutant species in SPS or MPS, indicating fitting at a 0.10 significance level. In contrast, the pseudo-1st-order kinetic model did not pass the chi-square tests at the same confidence level. Parameters of the pseudo-2nd-order kinetic models are summarized in Table 1. Experimentally measured and modeled data of adsorption of the four selected pollutants on the Al-WTR-coated wood mulch in SPS and MPS are shown in Figure 4a–d and e–h, respectively. As seen, the modeled data well fit the measured data for any specific pollutant. Results from the kinetic tests are in agreement with several previous studies using various aluminum hydroxide products for the adsorption of phosphate or metals (Namasivayam & Prathap, 2005; Yan et al., 2010). The pseudo-2nd-order kinetic reactions were demonstrated to well describe metal hydroxides and other adsorbents for capturing various water pollutants. A literature review comparing the pseudo-1st- and 2nd-order kinetic models (Ho & McKay, 1999) show that, in the most cases, the pseudo-2nd-order chemical reaction kinetics provided the best correlation with experimental data when chemical reaction appeared significant in the rate-controlling step, while the pseudo-1st-order model fit the measured data well only at the onset of adsorption.

Two different adsorption isotherm models were fit with experimental equilibrium data at five sorbent concentrations (i.e., 5, 10, 25, 35, and 50 g/L). At a 90% confidence level, the Freundlich model passed the goodness-of-fit tests at all the studied experimental conditions, while the Langmuir model could not. Because the Langmuir isotherm model builds on the assumption that adsorbates accumulate, at the maximum, at one single layer on the sorbent surface, the finding implies that the adsorption did not occur in a monolayer. Model parameters by nonlinear regression analysis with the Freundlich model are summarized in Table 2. Experimentally measured and modeled data of the four selected pollutants for the adsorption isotherm tests in SPS and MPS are shown in Figure 5. As seen, at any specific aqueous pollutant concentration, the higher adsorption capacity of a selected pollutant was observed in SPS than in MPS, because other pollutants might more compete with the pollutant of concern for available sorption sites on the WTR coating in MPS.

Table 1. Model parameters by nonlinear regression analysis with the pseudo-2nd-order kinetic model for adsorption of different urban runoff pollutants

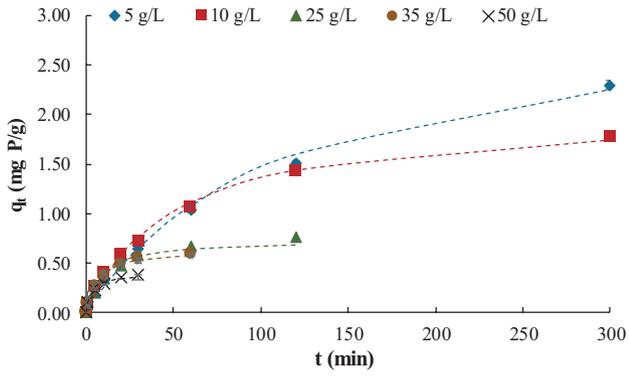
POLLUTANT	SOLUTION	SORBENT CONC. (G/L WTR-COATED MULCH)	Q_E	K	χ^2	DF	χ_0^2
P	SPS	5	3.09	2.85×10^{-3}	0.45	8	3.49
		10	2.04	9.81×10^{-3}	0.10	8	3.49
		25	0.74	1.58×10^{-1}	0.03	7	2.83
		35	0.64	2.46×10^{-1}	<0.01	6	2.20
		50	0.40	9.55×10^{-1}	<0.01	5	1.61
	MPS	5	2.92	5.56×10^{-3}	0.92	8	3.49
		10	1.85	1.50×10^{-2}	0.47	8	3.49
		25	0.77	1.33×10^{-1}	0.06	6	2.20
		35	0.60	2.72×10^{-1}	<0.01	5	1.61
		50	0.36	1.26	<0.01	5	1.61
Cu	SPS	5	73	1.98×10^{-3}	2.11	6	2.20
		10	47	1.19×10^{-2}	1.40	6	2.20
		25	26	5.13×10^{-3}	2.05	6	2.20
		35	17	1.80×10^{-2}	0.48	6	2.20
		50	13	2.04×10^{-2}	1.31	5	1.61
	MPS	5	105	2.07×10^{-3}	2.19	7	2.83
		10	54	3.75×10^{-2}	1.53	7	2.83
		25	23	9.53×10^{-2}	0.12	6	2.20
		35	19	1.39×10^{-2}	0.31	5	1.61
		50	12	1.79×10^{-1}	0.27	5	1.61
Zn	SPS	5	571	3.84×10^{-5}	2.20	7	2.83
		10	285	2.08×10^{-4}	2.09	7	2.83
		25	112	5.42×10^{-4}	1.85	7	2.83
		35	91	1.70×10^{-3}	1.51	7	2.83
		50	62	7.00×10^{-3}	0.81	7	2.83
	MPS	5	560	9.32×10^{-5}	2.29	7	2.83
		10	282	4.62×10^{-4}	0.57	7	2.83
		25	130	1.79×10^{-3}	0.70	7	2.83
		35	89	2.21×10^{-3}	0.48	6	2.20
		50	58	2.88×10^{-2}	0.84	6	2.20
Pb	SPS	5	84	1.68×10^{-2}	0.33	5	1.61
		10	54	6.24×10^{-2}	0.05	4	1.06
		25	15	6.43×10^{-1}	0.01	3	0.58
		35	7	4.69×10^{-1}	<0.01	3	0.58
		50	6	2.36	<0.01	3	0.58
	MPS	5	62	1.61×10^{-2}	1.07	5	1.61
		10	37	1.67×10^{-1}	0.48	4	1.06
		25	13	1.62	0.07	3	0.58
		35	11	2.57×10^{-1}	0.02	3	0.58
		50	8	1.61	0.01	3	0.58

Notes. *df*: degree of freedom; *k*: the rate constant for the pseudo-2nd-order kinetic models: g/mg.min for P, g/μg.min for metals; MPS: multiple-pollutant solution; q_e : the mass ratio of the adsorbate to the adsorbent at chemical equilibrium (mg/g for P; μg/L for metals); SPS: single-pollutant solution; χ^2 : chi-square; χ_0^2 : χ^2 at a specific degree of freedom at a 90% confidence level.

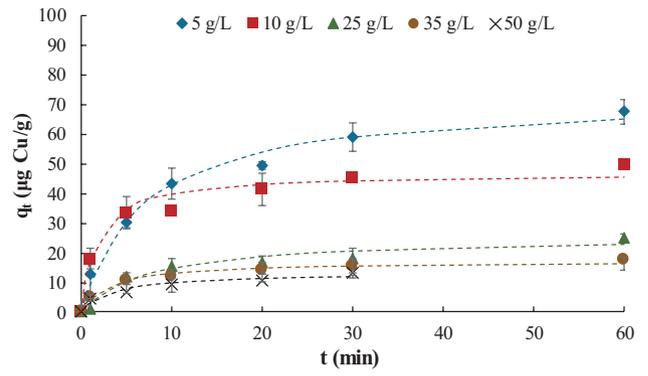
The effect of solution pH (6–8) on Al-WTR adsorption of phosphate with time was evaluated (Supporting Information Figure S2a). As the adsorption proceeded, more P was

immobilized to the solid phase at all the tested pH. Clearly, at any specific contact time, more P was adsorbed at a lower pH. For example, at 120 min, the adsorbed P was 91%, 75%, and

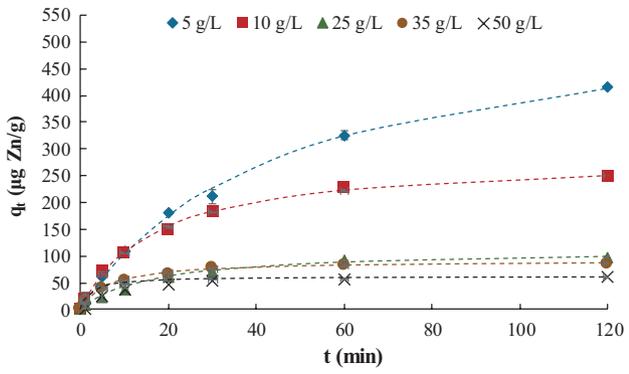
Figure 4. Experimental data and pseudo-2nd-order kinetic model data of Al-WTR coated wood mulch adsorption of the four selected pollutants in (a–d) single-pollutant solution (SPS) and (e–h) multiple-pollutant solution (MPS) (pH = 7.0; mulch dose = 5–50 g/L; SPS: initial P = 3.10 mg/L; MPS: initial P = 3.10 mg/L, initial Cu = 100 μg/L, initial Zn = 600 μg/L, and initial Pb = 100 μg/L in MPS; and scattered symbols and solid lines represent measured and modeled data, respectively).



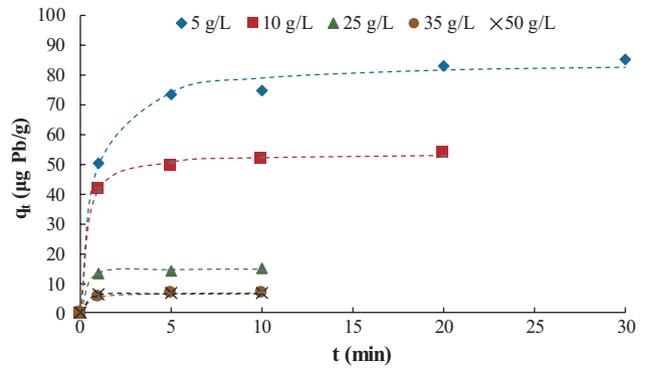
(A) P in SPS



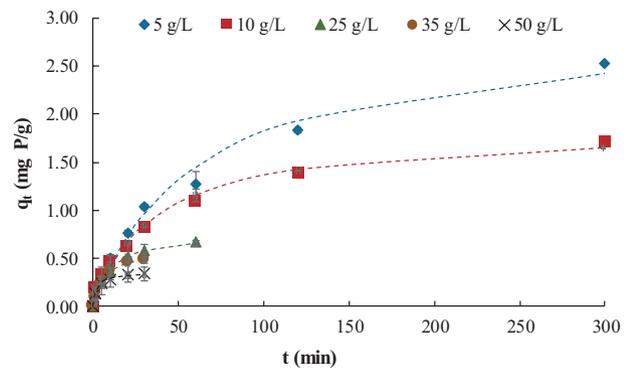
(B) Cu in SPS



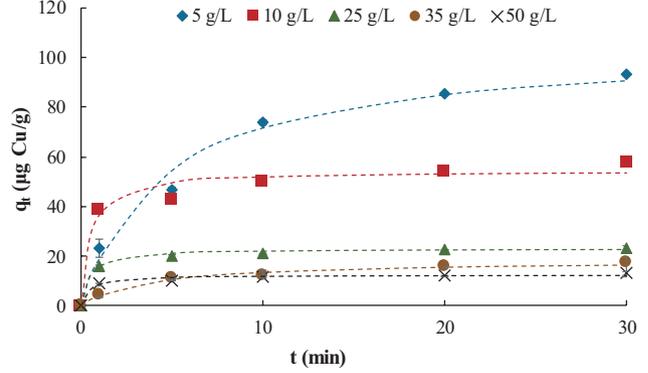
(C) Zn in SPS



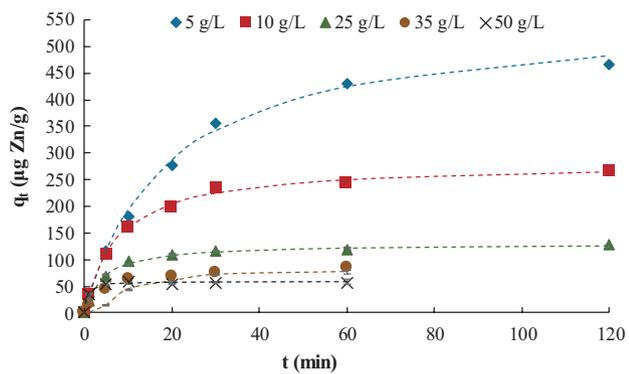
(D) Pb in SPS



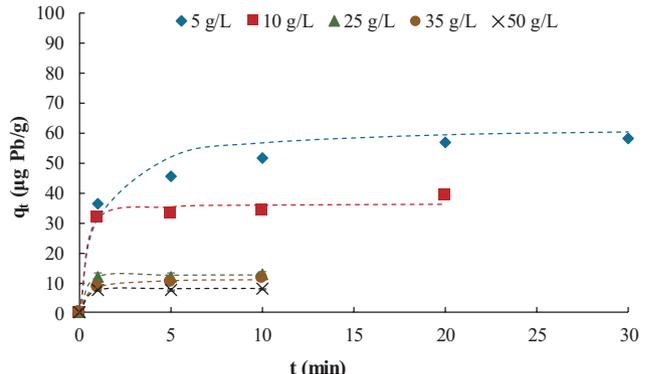
(E) P in MPS



(F) Cu in MPS



(G) Zn in MPS



(H) Pb in MPS

71% of the initial P at pH 6, 7, and 8, respectively. Effects of solution pH (6–8) on the fractions of removed Cu, Zn, and Pb are shown in Supporting Information Figure S2b–d, respectively. Generally, the removed metals were increased with an increasing pH. For Cu and Pb, a marked increase in the metal removal was observed as pH increased from 6 to 7, at which a very high removal fraction was achieved (the removed Cu and Pb accounted for 85% and 99%, respectively, at pH 7 at 60 min). When the solution pH further increased to 8, the adsorption of Cu and Pb was minor. Based on chemical equilibrium calculation with the Visual Minteq 3.1 (a chemical equilibrium

computation software), at pH 8, Cu and Zn were oversaturated while Pb was undersaturated in this study. Therefore, metal precipitation, rather than sorption, played a key role in the removal of Cu and Zn at pH 8 under the studied conditions. Of interest, the calculated removal efficiencies of Cu and Zn were close to 100% at pH 8, greater than their experimentally measured concentrations (i.e., 87% Cu removal and 85% Zn removal at 120 min). The difference between projected and experimentally measured concentrations may be caused due to two reasons. Firstly, the solution system did not reach a true chemical equilibrium state at 120 min. Secondly, the fresh metal hydroxides

Table 2. Model parameters by nonlinear regression analysis with the Freundlich isotherm model for adsorption of different urban runoff pollutants

POLLUTANT	SOLUTION	N	K_F	X^2	DF	χ_0^2
P	SPS	1.71	3.55	0.03	5	1.61
	MPS	1.78	2.52	0.02	5	1.61
Cu	SPS	1.20	2.87	0.41	5	1.61
	MPS	1.13	1.83	1.54	5	1.61
Zn	SPS	1.42	12.76	1.02	5	1.61
	MPS	1.28	5.39	0.93	5	1.61
Pb	SPS	1.14	9.22	1.31	5	1.61
	MPS	1.51	9.32	0.50	5	1.61

Notes. The unit of K_F : $\mu\text{g/g}$ for P; mg/g for metals; MPS: multiple-pollutant solution; SPS: single-pollutant solution; χ_0^2 : the chi-square at the degree of freedom of 5 at a 90% confidence level.

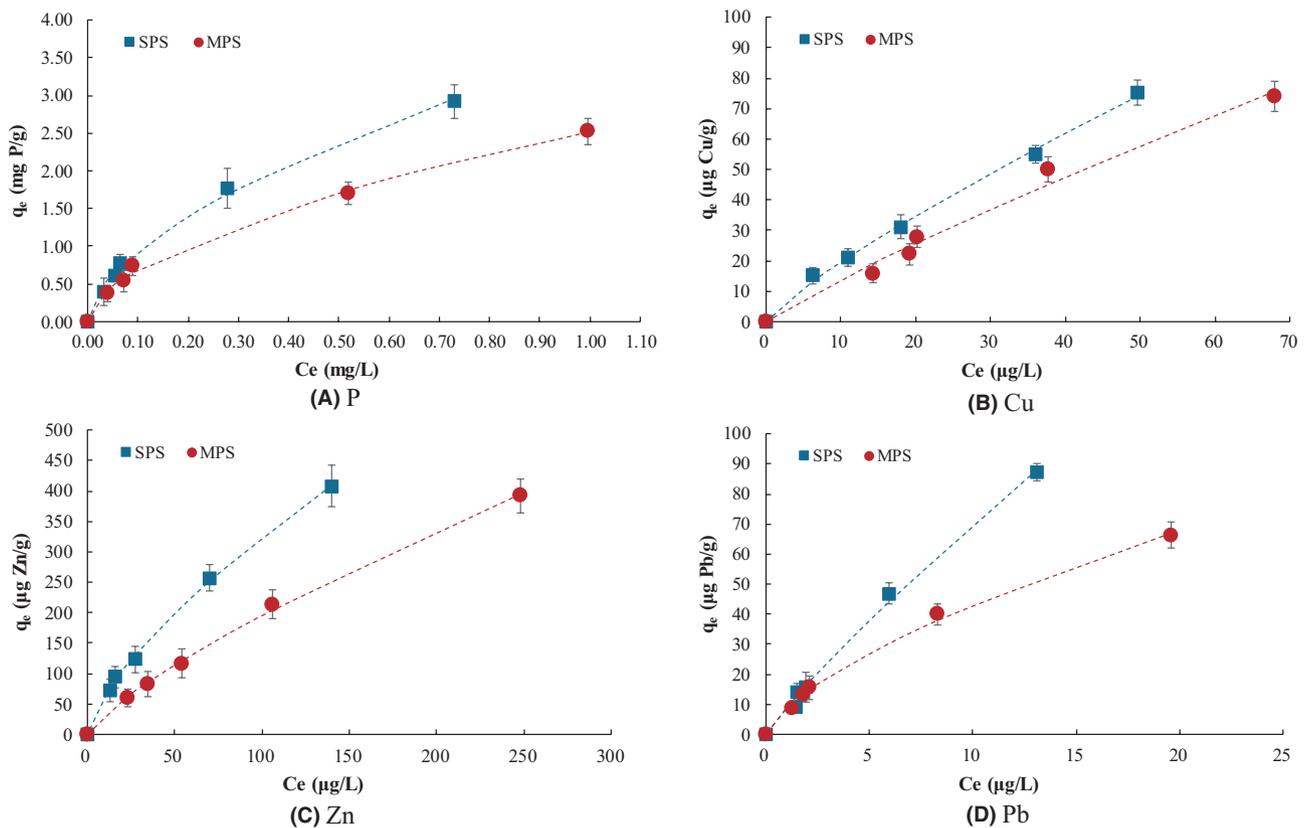


Figure 5. Measured and modeled adsorption isotherm data in the Freundlich model (pH = 7; mulch dose = 5–50 g/L; scattered symbols and solid lines represent measured and modeled data, respectively).

produced from precipitation were very fine particles. In this study, samples were filtered by 0.45 μm membrane before analysis of dissolved metals. However, the filtration could not differentiate truly soluble and nanosized metals in water. Previous studies reported that the sizes of copper hydroxide particles produced from precipitation during a short aging period were extremely small ($<0.05 \mu\text{m}$; Candal, Regazzoni, & Blesa, 1992).

Previous efforts explored the mechanisms in the binding of phosphate or cationic metals to Al-WTR using spectroscopic techniques and revealed that the adsorption of phosphate or cationic metals is primarily ascribed to the formation of surface complexes with aluminum hydroxides (Butkus, Grasso, Schulthess, & Wijnja, 1998; Castaldi, Silvetti, Garau, Demurtas, & Deiana, 2015; Ippolito, 2001). In this study, we assessed the effect of ionic strength on the phosphate surface complex formation equilibria at pH 7 (Figure 6). The fraction of adsorbed P on Al-WTR was increased from 67% to 90% as the KCl concentration increased from 0.005 to 0.5 M, indicating that the phosphate adsorption was positively related to ionic strength. Typically, ions forming inner-sphere surface complexes show little ionic strength dependence or show increasing adsorption with the increasing solution ionic strength (Goldberg & Johnston, 2001). The stronger ion adsorption occurring at a higher ionic strength is due to the higher activity of the counterions in solution available to compensate the surface charge generated by specific ion adsorption. Therefore, this finding implies the principle role of inner-sphere surface complexation in the Al-WTR adsorption of phosphate from water. For the cationic metals, after the complexes between cationic metals and surface hydroxyl groups on Al-WTR are formed, protons are released to water (Stumm, 1992). Therefore, more dissolved metal ions become adsorbed with an increasing pH, which is in agreement with our findings on the pH dependence of cationic metal adsorption on Al-WTR, as shown in Supporting Information Figure S2b–d. Of note, though it was not within the scope of this study to compare adsorption selectivity of the WTR-coated mulch for the three metals, the affinity of the metals was most likely different due to their different structural properties (e.g., ionic radius).

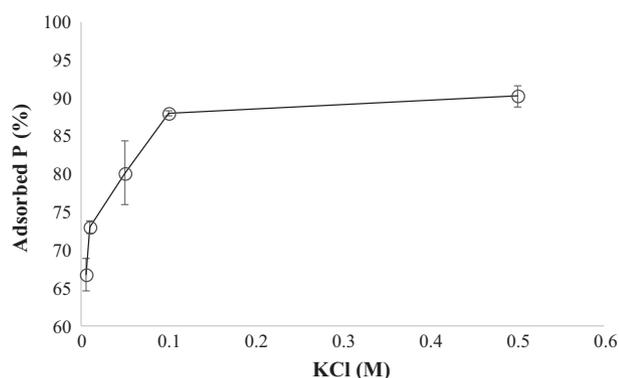


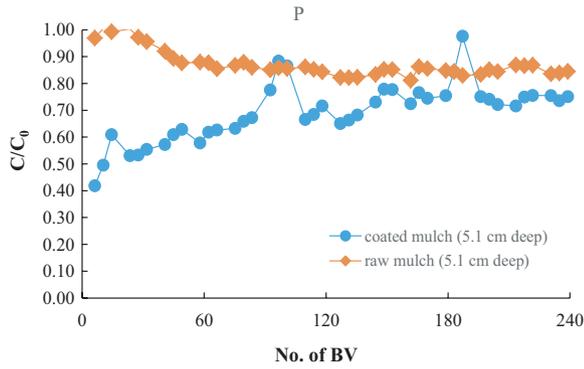
Figure 6. Effect of ionic strength on Al-WTR adsorption of P in water (pH = 7.0; initial $\text{PO}_4^{3-}\text{-P}$ = 10.0 mg/L; and initial Al-WTR = 1.0 g/L).

Column studies

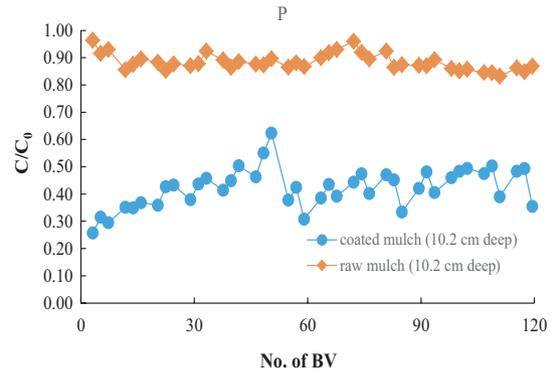
Treatment performance. The ratios of effluent concentration to initial concentration (C/C_0) for each pollutant are plotted against the number of bed volume (BV) in the column studies (Figure 7a–h). BV is defined as the bulk volume of a filter bed (Crittenden, Trussell, Hand, Howe, & Tchobanoglous, 2012). Average values, standard deviations, and coefficients of variation (CVs) of C/C_0 at different column setups are summarized in Table 3. For the adsorption of P, C/C_0 versus the number of BV in the mulch bed depths of 5.1 and 10.2 cm are presented in Figure 7a,b, respectively. Regardless of the bed depth, C/C_0 in the raw mulch beds almost stabilized between 0.87 and 0.88, indicating a limited affinity of phosphate toward the raw wood mulch. In contrast, the decrease in C/C_0 was obviously observed when Al-WTR-coated wood mulch was applied. High CVs (16% and 17% for 5.1 and 10.2 cm depths, respectively) indicate the great variations of C/C_0 with the number of BV. At the 5.1-cm-depth Al-coated mulch bed, C/C_0 gradually increased from 0.42 to 0.75, indicating that the P adsorption was approaching the breakthrough. Moreover, C/C_0 occasionally exceeded the levels of the control columns with raw mulch. In contrast, C/C_0 in the columns loaded with 10.2-cm-depth coated mulch slightly increased from 0.26 to 0.35 with the increasing number of BV to 120, suggesting that the adsorption remained undersaturated throughout the treatment tests. At any specific number of BV, a much lower C/C_0 was observed in the 10.2-cm-depth coated mulch bed than in its control columns with 10.2-cm-depth raw mulch or in the 5.1-cm-depth coated mulch bed.

For the adsorption of Cu, C/C_0 versus the number of BV in the columns with 5.1- and 10.2-cm-deep mulch bed depths is presented in Figure 7c,d, respectively. Regardless of the mulch depths and types, all the columns exhibited effective removals for Cu. For either depth, the average C/C_0 with Al-WTR-coated wood mulch was slightly below that in its control columns with raw mulch (0.32 for coated mulch vs. 0.35 raw mulch at 5.1-cm bed depth; 0.26 for coated mulch vs. 0.28 raw mulch at 10.2 cm bed depth). However, based on the CVs, the Cu adsorption by raw mulch was stable through the tests (11% for 5.1- and 10.2-cm mulch depths). In contrast, great CVs (38% and 31% for 5.1- and 10.2-cm mulch depths, respectively) occurred when Al-WTR-coated wood mulch was used. As seen, C/C_0 noticeably fluctuated over the number of BV for the columns with coated mulch. The fluctuation degree was more noticeable at the 5.1-cm-depth mulch bed. Occasionally, the effluent Cu concentrations in 5.1-cm-depth coated mulch were greater than those in its control columns with raw mulch. The situation rarely occurred for the columns loaded with 10.2-cm-depth wood mulch.

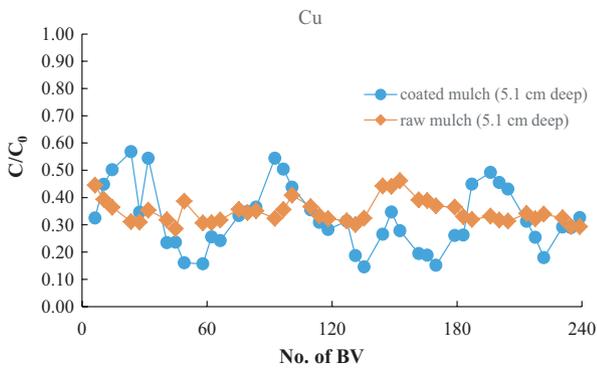
For the adsorption of Zn, C/C_0 versus the number of BV in the columns with 5.1- and 10.2-cm-deep mulch bed depths are presented in Figure 7e,f, respectively. For the control columns with raw mulch, the average C/C_0 was decreased from 0.83 to 0.73 with the increasing mulch depth from 5.1 to 10.2 cm. The small CVs (6%–9%) suggest that the adsorption behavior of raw mulch was stable. On the other hand, at the either mulch depth, lower C/C_0 was observed when Al-WTR-coated mulch was applied. As the mulch depth increased from 5.1 to 10.2 cm, the average C/C_0 went down from 0.66 to 0.59. Similar to the



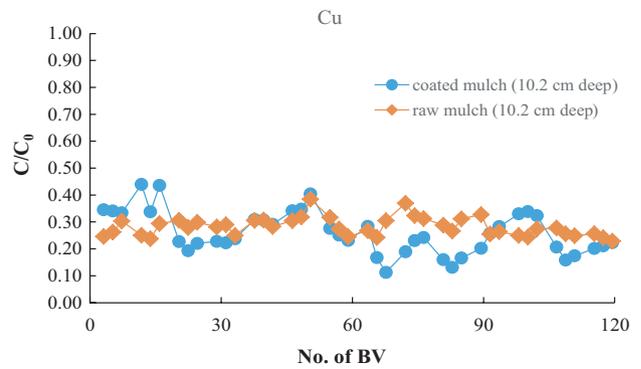
(A) Mulch depth: 5.1 cm



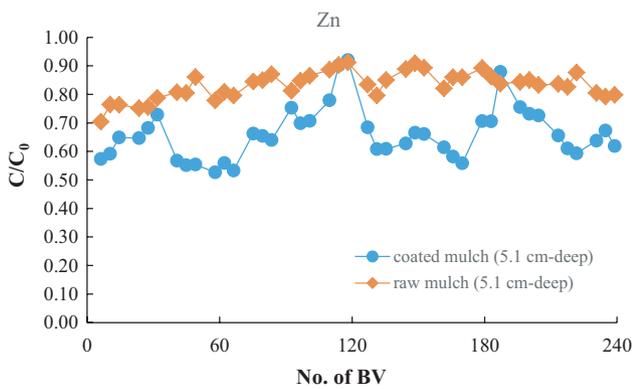
(B) Mulch depth: 10.2 cm



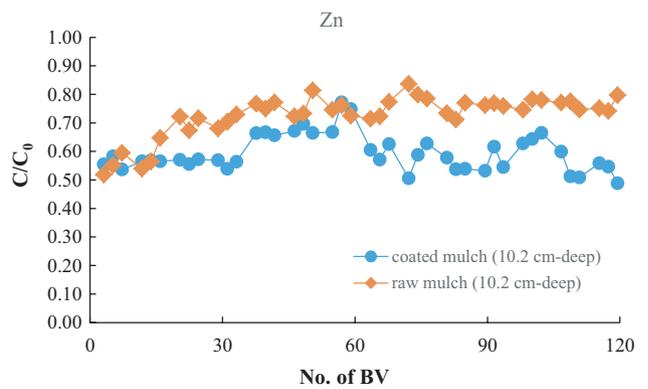
(C) Mulch depth: 5.1 cm



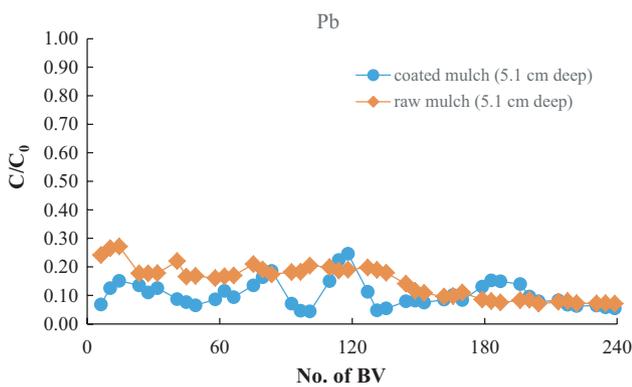
(D) Mulch depth: 10.2 cm



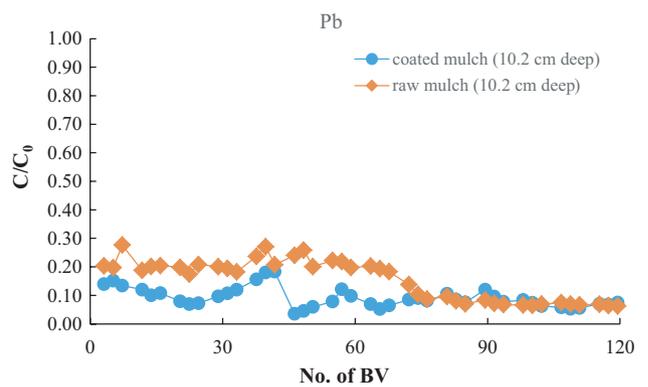
(E) Mulch depth: 5.1 cm



(F) Mulch depth: 10.2 cm



(G) Mulch depth: 5.1 cm



(H) Mulch depth: 10.2 cm

Figure 7. Concentration variation of runoff pollutants versus number of bed volume (BV) in small column studies: (a) P, 5.1-cm-depth mulch; and (b) P, 10.2-cm-depth mulch; (c) Cu, 5.1-cm-depth mulch; and (d) Cu, 10.2-cm-depth mulch; (e) Zn, 5.1-cm-depth mulch; and (f) Zn, 10.2-cm-depth mulch; (g) Pb, 5.1-cm-depth mulch; and (h) Pb, 10.2-cm-depth mulch (filtration rate = 8 ml/min; multiple-pollutant solution [MPS]: 0.1 mg/L Cu^{2+} , 0.6 mg/L Zn^{2+} , 0.1 mg/L Pb^{2+} , 3 mg/L $\text{PO}_4^{3-}\text{-P}$; pH = 7; $T = 22^\circ\text{C}$).

removal of Cu, the greater fluctuation of C/C_0 against the number of BV was observed when the bed depth changed from 5.1 cm to 10.2 cm.

For the adsorption of Pb, C/C_0 versus the number of BV in the columns with 5.1- and 10.2-cm-deep mulch bed depths are presented in Figure 7g,h, respectively. At any specific column setup condition, the lowest C/C_0 was observed for Pb among all the selected pollutants, indicating that Pb was the most readily removed under the studied conditions. Regardless of the bed depth, the average C/C_0 was 0.15 at the control columns with raw mulch. Lower C/C_0 was accomplished when Al-WTR-coated wood mulch was used, because of the stronger affinity of Al-WTR coating with Pb. For the columns with Al-WTR-coated mulch, the average C/C_0 (0.08) at 10.2-cm bed depth was slightly below C/C_0 (0.10) at 5.1-cm bed depth.

Of note, for any selected pollutant, the higher bed depth of coated wood mulch could achieve a more stable and effective pollutant removal in the column studies. The better pollutant removal at a higher bed depth is caused due to a longer contact time, during which more pollutants could be immobilized. As shown in the aforementioned kinetic studies, the selected pollutants were gradually removed with time in the presence of the coated wood mulch. Therefore, the pollutant removal by the Al-WTR-coated mulch is a kinetically controlled process. Generally, longer contact times can ensure lower pollutant concentrations in the effluent from the columns. In this study, for the 5.1-cm bed depth, contact time between the runoff and mulch was approximately 24 min. When the filter bed was increased to 10.2 cm, the contact time was doubled to 48 min. Therefore, it is not surprising to remove more pollutants in the columns loaded with 10.2-cm-deep coated mulch.

Flow-weighted mean concentrations. To assess the overall effects of pollutant removals using the Al-WTR-coated mulch, FWMCs of the selected pollutants under different column setups were compared (Table 4). The FWMCs of P, Cu, Zn, and

Pb in the absence of a mulch filtration bed were 3.10 mg/L, 100 $\mu\text{g/L}$, 600 $\mu\text{g/L}$, and 100 $\mu\text{g/L}$, respectively. For P, FWMCs of the columns with two different depths of raw mulch were very close (2.70 mg/L for 5.1 cm depth and 2.74 mg/L for 10.2 cm depth), with the corresponding FWMC removal efficiencies of 13% and 12%. After the coated mulch was applied, FWMCs of P were further reduced to 2.13 and 1.31 mg/L for 5.1- and 10.2-cm bed depths, respectively. The corresponding FWMC removal efficiencies were dramatically increased to 31% (5.1 cm depth) and 58% (10.2 cm depth). Significant improvement in the FWMC alleviation was similarly observed for Zn and Pb. For Zn, the effluent FWMCs were reduced from 498 and 434 $\mu\text{g/L}$ in the control groups (raw mulch) to 396 and 356 $\mu\text{g/L}$ in the treatment groups (coated mulch) for the bed depths of 5.1 and 10.2 cm, respectively. For Pb, FWMCs in the control groups were 15 $\mu\text{g/L}$, regardless of the bed depths. When the coated mulch was used, FWMCs were further reduced to 10 and 9 $\mu\text{g/L}$ for 5.1- and 10.2-cm bed depths, respectively. In contrast, the abatement of FWMCs in Cu was slightly enhanced when raw mulch was replaced with WTR-coated mulch under the identical experimental conditions. FWMCs of Cu were somewhat decreased from 35 and 28 $\mu\text{g/L}$ in the control to 28 and 26 $\mu\text{g/L}$ in the treatment groups at the bed depths of 5.1 and 10.2 cm, respectively. WTR-coated mulch only decreased the effluent FWMCs of Cu by 2% in comparison with raw mulch. Based on the results of FWMC under the studied conditions, the Al-WTR-coated mulch could greatly improve the abatement of P, Zn, and Pb but only slightly increased the removal of Cu in the continuous flow condition. Moreover, for any selected pollutant, the greater bed depth with a longer contact time generally had a better removal in FWMC.

Al leaching. Al release from raw and coated mulch versus the number of BV was also determined, as shown in Supporting Information Figure S3a,b, respectively. Influent Al concentrations in the synthetic runoff were constantly below

Table 3. Results of average values, standard deviations, and coefficient of variance of C/C_0 in study of metal adsorption on raw and Al-WTR-coated wood mulch (Experimental condition: filtration rate = 8 ml/min; MPS: 100 $\mu\text{g/L}$ Cu^{2+} , 600 $\mu\text{g/L}$ Zn^{2+} , 100 $\mu\text{g/L}$ Pb^{2+} , 3.10 mg/L $\text{PO}_4^{3-}\text{-P}$; pH = 7; $T = 22^\circ\text{C}$)^a

POLLUTANTS	C/C_0											
	COATED MULCH (5.1 CM DEPTH)			RAW MULCH (5.1 CM DEPTH)			COATED MULCH (10.2 CM DEPTH)			RAW MULCH (10.2 CM DEPTH)		
	MEAN	SD	C.V.%	MEAN	SD	C.V.%	MEAN	SD	C.V.%	MEAN	SD	C.V.%
P	0.69	0.11	16%	0.87	0.05	6%	0.42	0.07	17%	0.88	0.03	3%
Cu	0.32	0.12	38%	0.35	0.04	11%	0.26	0.08	31%	0.28	0.03	11%
Zn	0.66	0.09	14%	0.83	0.05	6%	0.59	0.06	10%	0.73	0.07	9%
Pb	0.10	0.02	20%	0.15	0.06	40%	0.08	0.02	25%	0.15	0.07	47%

Notes. c.v.%: coefficients of variance; SD: standard deviation.

^aA large relative standard deviation implies that C/C_0 was greatly changed over the number of BV in the column studies. Further analysis of the C/C_0 profile with the number of BV is needed for the pollutant with a large relative standard deviation.

Table 4. Comparison of FVMCs of selected pollutants in column studies (Experimental condition: filtration rate = 8 ml/min; MPS: 100 µg/L Cu²⁺, 600 µg/L Zn²⁺, 100 µg/L Pb²⁺, 3.10 mg/L PO₄³⁻-P; pH = 7; T = 22°C)

POLLUTANT	FVMC				
	NO MULCH FILTRATION	RAW MULCH (5.1 CM DEPTH)	COATED MULCH (5.1 CM DEPTH)	RAW MULCH (10.2 CM DEPTH)	COATED MULCH (10.2 CM DEPTH)
P (mg/L)	3.10	2.70	2.13	2.74	1.31
Cu (µg/L)	100	35	33	28	26
Zn (µg/L)	600	498	396	434	356
Pb (µg/L)	100	15	10	15	9

Note. FVMC: flow-weighted mean concentrations.

4.0 µg/L. For the raw mulch, the average Al concentrations were slightly increased to 2.8 and 4.5 µg/L at 5.1 and 10.2 cm bed depths, respectively. On the other hand, the average Al concentrations in the effluents from 5.1- and 10.2-cm-depth Al-WTR-coated mulch columns were 1.6 and 2.7 µg/L, respectively. Any significant increase in the effluent Al concentration was not observed, except that two spikes were found at 19.0 and 13.2 µg/L at the BV numbers of 97 and 218, respectively, in the 5.1-cm-depth coated mulch bed. The sporadic Al release was likely because some fine Al-WTR powders were washed off from the wood mulch. This phenomenon can be caused under a high shearing force of downflowing water; and/or due to the weathering effect of the intensive and continuous flushing. The United States EPA drinking water standard for Al is set at 200 µg/L. Therefore, the occasional Al release is not a concern when Al-WTR-coated wood mulch is used on site.

Implications

Results from the laboratory-scale studies have important implication to the design of urban stormwater treatment with the WTR-coated wood mulch.

Firstly, the adsorption kinetic and isotherm data are essential to the stormwater reactor design with the WTR-coated wood mulch. Al-WTR adsorption of these pollutants is kinetically controlled. Longer reaction times would lead to lower aqueous pollutant concentrations. The importance of contact time is also highlighted in the column studies, in which greater pollutant removals were observed in the columns with a greater bed depth. Therefore, kinetic information is key to determining the effluent concentrations in an engineering application. The data from adsorption isotherm studies allow for the determination of the adsorption capacity of WTR-coated wood mulch for each pollutant. The data will be used to determine the quantity of the media needed in a treatment device to provide an expected service lifetime.

Secondly, the column studies did not show any breakthrough of any pollutant. It should be noted that the total volume of synthetic runoff was designed to simulate the quantity of runoff that flows through the mulch bed over 1 year in a typical United States northeastern urban area. Therefore, the amounts of Al-WTR-coated wood mulch, at either 5.1- or 10.2-cm bed depth, were sufficient for capturing the selected pollutants in a 1-year operation duration. The either depth falls within the mulch depth range of the U.S. mulching practices.

Finally, for any selected pollutant, better performance was observed when the greater bed depth was used. Better performance was reflected in (a) the greater removal efficiency; and (b) less variable adsorption. Variable removals observed for the lower bed depth were likely caused by the more nonuniform water flow within the coated mulch bed. When runoff would flow through the bed, the contact times for small portions of water in the bed would be equal only if the filter media is homogeneously distributed. However, mulch chips typically have a high porosity (over 0.4) due to the heterogeneity of the mulch shape and size. Consequently, some flows may find shortcuts to pass through the filtration bed with a shorter contact time, thereby leading to a lower pollutant removal. Therefore, a high bed depth is recommended to minimize the possibility of shortcutting.

CONCLUSIONS

Laboratory-scale batch and column studies were carried out to test Al-WTR-coated wood mulch as an innovative adsorbent media for treatment of polluted urban runoff. The modified mulch is capable of concurrently and effectively capturing phosphate and cationic heavy metals typically present in urban runoff as a result of the strong affinity of the Al-WTR coating with these pollutants of concern. Meanwhile, aluminum release from the Al-WTR coating is minimal. Therefore, the innovative adsorbent media can serve as an effective and safe barrier for polluted urban runoff. It can be simply applied like common wood mulch in green infrastructure such as an infiltration basin for mitigation of the pollutant loadings to topsoil and/or treated stormwater. It can also be employed alone as an adsorbent media for the abatement of runoff pollutants.

ACKNOWLEDGMENTS

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REFERENCES

- Babatunde, A. O., Zhao, Y. Q., Burke, A. M., Morris, M. A., & Hanrahan, J. P. (2009). Characterization of aluminium-based water treatment residual for potential phosphorus removal in engineered wetlands. *Environmental Pollution*, 157, 2830–2836. <https://doi.org/10.1016/j.envpol.2009.04.016>

- Bell, C. D., McMillan, S. K., Clinton, S. M., & Jefferson, A. J. (2017). Characterizing the effects of stormwater mitigation on nutrient export and stream concentrations. *Environmental Management*, 59, 604–618. <https://doi.org/10.1007/s00267-016-0801-4>
- Blocken, B., Derome, D., & Carmeliet, J. (2013). Rainwater runoff from building facades: A review. *Building and Environment*, 60, 339–361. <https://doi.org/10.1016/j.buildenv.2012.10.008>
- Brown, W., Schueler, T. R., & Consortium, C. R. (1997). *The economics of stormwater BMPs in the Mid-Atlantic region: an examination of the real cost of providing storm water control*. Center for Watershed Protection.
- Butkus, M. A., Grasso, D., Schulthess, C. P., & Wijnja, H. (1998). Surface complexation modeling of phosphate adsorption by water treatment residual. *Journal of environmental quality*, 27, 1055–1063. <https://doi.org/10.2134/jeq1998.00472425002700050010x>
- Candal, R. J., Regazzoni, A. E., & Blesa, M. A. (1992). Precipitation of copper (II) hydroxide oxides and copper (II) basic salts. *Journal Of Materials Chemistry*, 2, 657–661. <https://doi.org/10.1039/jm9920200657>
- Castaldi, P., Silvetti, M., Garau, G., Demurtas, D., & Deiana, S. (2015). Copper (II) and lead (II) removal from aqueous solution by water treatment residual. *Journal of hazardous materials*, 283, 140–147. <https://doi.org/10.1016/j.jhazmat.2014.09.019>
- Chin, D. A. (2006). *Water-quality engineering in natural systems*. Hoboken, NJ: John Wiley & Sons. <https://doi.org/10.1002/0471784559>
- CIA (2015). *The World Factbook*. New York, NY: Skyhorse.
- Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J., & Tchobanoglous, G. (2012). *MWW's water treatment: Principles and design*. Hoboken, NJ: John Wiley & Sons. <https://doi.org/10.1002/9781118131473>
- Davis, A. P., Shokouhian, M., & Ni, S. B. (2001). Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. *Chemosphere*, 44, 997–1009. [https://doi.org/10.1016/S0045-6535\(00\)00561-0](https://doi.org/10.1016/S0045-6535(00)00561-0)
- Deng, Y., Sarkar, D., Rakshit, S., & Morris, C. (2011). *Scrap tire and water treatment residuals as novel "green" sorbents for removal of common metals from polluted urban stormwater runoff*. Submitted to New Jersey Water Resources Institute, Final Report; Montclair State University.
- Dietz, M. E., & Clausen, J. C. (2005). A field evaluation of rain garden flow and pollutant treatment. *Water, Air, and Soil Pollution*, 167, 123–138. <https://doi.org/10.1007/s11270-005-8266-8>
- Dietz, M. E., & Clausen, J. C. (2006). Saturation to improve pollutant retention in a rain garden. *Environmental Science & Technology*, 40, 1335–1340. <https://doi.org/10.1021/es051644f>
- Edzwald, J. K. (2011). *Water quality & treatment: A handbook on drinking water*. New York, NY: McGraw-Hill.
- Elliott, H., O'Connor, G., Lu, P., & Brinton, S. (2002). Influence of water treatment residuals on phosphorus solubility and leaching. *Journal of Environmental Quality*, 31, 1362–1369. <https://doi.org/10.2134/jeq2002.1362>
- Galloway, J. N., Aber, J. D., Erisman, J. W., Seitzinger, S. P., Howarth, R. W., Cowling, E. B., & Cosby, B. J. (2003). The nitrogen cascade. *BioScience*, 53, 341–356. [https://doi.org/10.1641/0006-3568\(2003\)053\[0341:TNC\]2.0.CO;2](https://doi.org/10.1641/0006-3568(2003)053[0341:TNC]2.0.CO;2)
- Göbel, P., Dierkes, C., & Coldewey, W. (2007). Storm water runoff concentration matrix for urban areas. *Journal of contaminant hydrology*, 91, 26–42. <https://doi.org/10.1016/j.jconhyd.2006.08.008>
- Goldberg, S., & Johnston, C. T. (2001). Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling. *Journal of colloid and Interface Science*, 234, 204–216. <https://doi.org/10.1006/jcis.2000.7295>
- Hatt, B. E., Fletcher, T. D., & Deletic, A. (2009). Pollutant removal performance of field-scale stormwater biofiltration systems. *Water Science and Technology*, 59, 1567–1576. <https://doi.org/10.2166/wst.2009.173>
- Ho, Y.-S., & McKay, G. (1999). Pseudo-second order model for sorption processes. *Process biochemistry*, 34, 451–465. <https://doi.org/10.1042/bj3440451>
- Hobbie, S. E., Finlay, J. C., Janke, B. D., Nidzgorski, D. A., Millet, D. B., & Baker, L. A. (2017). Contrasting nitrogen and phosphorus budgets in urban watersheds and implications for managing urban water pollution. *Proceedings of the National Academy of Sciences of the United States of America*, 114(16), 4177–4182. <https://doi.org/10.1073/pnas.1618536114>
- Huber, M., Welker, A., & Helmreich, B. (2016). Critical review of heavy metal pollution of traffic area runoff: Occurrence, influencing factors, and partitioning. *Science of the Total Environment*, 541, 895–919. <https://doi.org/10.1016/j.scitotenv.2015.09.033>
- Ippolito, J. A. (2001). *Phosphorus adsorption/desorption of water treatment residuals and biosolids co-application effects*, Ph.D. diss., Colorado State Univ. Fort Collins.
- Ippolito, J. A., Barbarick, K. A., Heil, D. M., Chandler, J. P., & Redente, E. F. (2003). Phosphorus retention mechanisms of a water treatment residual. *Journal of Environmental Quality*, 32, 1857–1864. <https://doi.org/10.2134/jeq2003.1857>
- Ippolito, J. A., Scheckel, K. G., & Barbarick, K. A. (2009). Selenium adsorption to aluminum-based water treatment residuals. *Journal of colloid and interface science*, 338, 48–55. <https://doi.org/10.1016/j.jcis.2009.06.023>
- Jang, A., Seo, Y., & Bishop, P. L. (2005). The removal of heavy metals in urban runoff by sorption on mulch. *Environmental pollution*, 133, 117–127. <https://doi.org/10.1016/j.envpol.2004.05.020>
- Kong, F. H., Ban, Y. L., Yin, H. W., James, P., & Dronova, I. (2017). Modeling stormwater management at the city district level in response to changes in land use and low impact development. *Environmental Modelling & Software*, 95, 132–142. <https://doi.org/10.1016/j.envsoft.2017.06.021>
- Lee, J. H., & Bang, K. W. (2000). Characterization of urban stormwater runoff. *Water research*, 34, 1773–1780. [https://doi.org/10.1016/S0043-1354\(99\)00325-5](https://doi.org/10.1016/S0043-1354(99)00325-5)
- Makris, K. C., Harris, W. G., O'Conno, G. A., & Obreza, T. A. (2004). Phosphorus immobilization in micropores of drinking-water treatment residuals: Implications for long-term stability. *Environmental science & technology*, 38, 6590–6596. <https://doi.org/10.1021/es049161j>
- Makris, K. C., Sarkar, D., Parsons, J. G., Datta, R., & Gardea-Torresdey, J. L. (2007). Surface arsenic speciation of a drinking-water treatment residual using X-ray absorption spectroscopy. *Journal of colloid and interface science*, 311, 544–550. <https://doi.org/10.1016/j.jcis.2007.02.078>
- MPCA. (2017). *Minnesota stormwater manual*. https://stormwater.pca.state.mn.us/index.php?title=Main_Page
- Namasivayam, C., & Prathap, K. (2005). Recycling Fe (III)/Cr (III) hydroxide, an industrial solid waste for the removal of phosphate from water. *Journal of hazardous materials*, 123, 127–134. <https://doi.org/10.1016/j.jhazmat.2005.03.037>
- O'Neill, S. W., & Davis, A. P. (2011a). Water treatment residual as a bioretention amendment for phosphorus. I: Evaluation studies. *Journal of Environmental Engineering*, 138, 318–327.
- O'Neill, S. W., & Davis, A. P. (2011b). Water treatment residual as a bioretention amendment for phosphorus. II: Long-term column studies. *Journal of Environmental Engineering*, 138, 328–336.
- Pitt, R., Field, R., Lalor, M., & Brown, M. (1995). Urban stormwater toxic pollutants: Assessment, sources, and treatability. *Water Environment Research*, 67, 260–275. <https://doi.org/10.2175/106143095X131466>
- Prakash, P., & SenGupta, A. K. (2003). Selective coagulant recovery from water treatment plant residuals using donnan membrane process. *Environmental Science & Technology*, 37, 4468–4474. <https://doi.org/10.1021/es030371q>
- Punaniya, P., Sarkar, D., Rakshit, S., & Datta, R. (2013). Effectiveness of aluminum-based drinking water treatment residuals as a novel sorbent to remove tetracyclines from aqueous medium. *Journal of environmental quality*, 42, 1449–1459. <https://doi.org/10.2134/jeq2013.03.0082>
- Qiu, H., Lv, L., Pan, B., Zhang, Q., Zhang, W., & Zhang, Q. (2009). Critical review in adsorption kinetic models. *Journal of Zhejiang University-SCIENCE A*, 10, 716–724. <https://doi.org/10.1631/jzus.A0820524>
- Rosa, D. J., Clausen, J. C., & Dietz, M. E. (2015). Calibration and verification of SWMM for low impact development. *JAWRA Journal of the American Water Resources Association*, 51, 746–757. <https://doi.org/10.1111/jawr.12272>
- Roy-Poirier, A., Champagne, P., & Filion, Y. (2010). Bioretention processes for phosphorus pollution control. *Environmental Reviews*, 18, 159–173. <https://doi.org/10.1139/A10-006>
- Saeed, A., Akhter, M. W., & Iqbal, M. (2005). Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. *Separation and purification technology*, 45, 25–31. <https://doi.org/10.1016/j.seppur.2005.02.004>
- Sarkar, D., Makris, K. C., Vandanapu, V., & Datta, R. (2007). Arsenic immobilization in soils amended with drinking-water treatment residuals. *Environmental pollution*, 146, 414–419. <https://doi.org/10.1016/j.envpol.2006.06.035>
- Soleimanifar, H., Deng, Y., Wu, L., & Sarkar, D. (2016). Water treatment residual (WTR)-coated wood mulch for alleviation of toxic metals and phosphorus from polluted urban stormwater runoff. *Chemosphere*, 154, 289–292. <https://doi.org/10.1016/j.chemosphere.2016.03.101>
- Stumm, W. (1992). *Chemistry of the solid-water interface: Processes at the mineral-water and particle-water interface in natural systems*. New York, NY: John Wiley & Son Inc.
- USDA. (2018). *Mulching*. Retrieved from https://www.nrcs.usda.gov/wps/portal/nrcs/detail/national/home?cid=nrcs143_023585.
- USEPA (1983). *Results of the nationwide urban runoff program*. Washington, DC: Water Planning Division.
- USEPA. (2006). *Urban storm water BMP performance monitoring*. Technical report (EPA-821-B-02-001)
- Vadi, M., & Rahimi, M. (2014). Langmuir, freundlich and temkin adsorption isotherms of propranolol on multi-wall carbon nanotube. *Journal of Modern Drug Discovery and Drug Delivery Research*, 1, 1–3.
- Wilson, D. C. (2018). Potential urban runoff impacts and contaminant distributions in shoreline and reservoir environments of Lake Havasu, southwestern United States. *Science of the Total Environment*, 621, 95–107. <https://doi.org/10.1016/j.scitotenv.2017.11.223>
- Wossink, G., & Hunt, B. (2003). *The economics of structural stormwater BMPs in North Carolina*. Water Resources Research Institute of the University of North Carolina.
- Wu, J. S., Holman, R. E., & Dorney, J. R. (1996). Systematic evaluation of pollutant removal by urban wet detention ponds. *Journal of Environmental Engineering*, 122, 983–988. [https://doi.org/10.1061/\(ASCE\)0733-9372\(1996\)122:1\(983\)](https://doi.org/10.1061/(ASCE)0733-9372(1996)122:1(983))
- Yan, L.-G., Xu, Y.-Y., Yu, H.-Q., Xin, X.-D., Wei, Q., & Du, B. (2010). Adsorption of phosphate from aqueous solution by hydroxy-aluminum, hydroxy-iron and hydroxy-iron-aluminum pillared bentonites. *Journal of hazardous materials*, 179, 244–250. <https://doi.org/10.1016/j.jhazmat.2010.02.086>
- Yang, Y., Zhao, Y., Babatunde, A., Wang, L., Ren, Y., & Han, Y. (2006). Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge. *Separation and Purification Technology*, 51, 193–200. <https://doi.org/10.1016/j.seppur.2006.01.013>