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Original Research

Base-Treated Juniper Fiber Media for Removing Heavy Metals in Stormwater Runoff

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Abstract

The viability of base-treated juniper fiber (BTJF) media for removing toxic heavy metals (Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}) in stormwater runoff was investigated. The sorption ability of the BTJF for all metals was much higher than that of untreated juniper. The affinity sequence of both materials, BTJF and untreated juniper, was Pb > Cu > Zn ≥ Cd. This order is explained by the hydrolysis constants for each metal. A metal desorption and column regeneration test using 0.1 M nitric acid showed that the metal sorption capacity declined slightly from 136.3 to 119.2 µmole/g in the first two cycles and then more significantly at the third and fourth regeneration, 72.3 and 83.1 µmole/g, respectively. Based on the hydraulic conductivity test of BTJF of different size classes, it can be deduced that there is no major headloss-related disadvantage in using BTJF instead of sand as stormwater filter media if the particle size of the BTJF is similar to that for sand.

Keywords: filter, heavy metal, hydraulic conductivity, juniper, stormwater

Introduction

Toxic heavy metals, which primarily originate from automobile-related activities and the exposure of building materials to rain, are among the most important pollutants associated with urban stormwater runoff [1]. Copper, lead, cadmium, and zinc are by far the most common priority pollutant elements. Some of the metals are present often enough, and in high enough concentrations, to be potential threats to the beneficial use of most water resources [2]. Stormwater filters can be used as the effective heavy metal removal method in cases where metal ions, and small particles containing heavy metals, are not trapped by conventional stormwater treatment systems.

Stormwater filters remove pollutants using a variety of mechanisms. These consist mainly of separating larger particles and the sorption and ion exchange of "dissolved" pollutants such as heavy metal ions. Various materials such as sand [3, 4], ion oxide coated sand [5], peat [6, 7], and zeolite [8, 9] have been used as possible filter media to remove heavy metals from stormwater. One advantage of such filter systems is that they require less space than other stormwater treatment systems. Another advantage is that they can be installed below ground.

Lignocellulosic fiber is an unconventional low-cost sorbent that has been examined for its potential use in removing heavy metals. However, the ion exchange or adsorption capacity of lignocellulosic fiber is lower than that of other standard sorbents. A previous study overcame this

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*Corresponding author; e-mail: soohong.min@samsung.com disadvantage by pretreating juniper fiber with a saponification reaction to generate an improved sorbent, base-treated juniper fiber (BTJF). This pretreatment increased the Cd^{2+} removal capacity from 9.18 to 29.54 mg/g, based on batch equilibrium sorption data [10].

In the current study, specific aspects related to the viability of the BTJF media for removing toxic heavy metals in stormwater runoff were investigated. Competitive metal adsorption as well as metal recovery and column regeneration tests were performed. Next, the hydraulic conductivity of BTJF at different sizes, which is one of the most important properties for running a filtration system, was compared with conventional sand and sand+peat filter media. Finally, the heavy metal removal performance of BTJF was studied with solutions containing several heavy metals at very low concentrations, which is more typical of urban stormwater runoff.

Experimental Procedures

BTJF: Juniper (*Juniperous monosperma* (Engelm.) Sarg.) wood chips from New Mexico were air-dried for three months and then ground in a Wiley mill equipped with a 10-mm mesh screen. A NaOH solution (0.5 M, 20 L) was added to a plastic container (40 L) containing juniper particles (5 kg). The mixture was stored for 24 hrs. The alkaline solution was decanted and the media washed continuously with distilled water until the pH of the wash water was less than 8. The BTJF samples were oven-dried at 105°C for 1 day. The dried particles were sieved with different mesh sizes of screens to collect selected sizes of BTJF particles.

Sand: Light weight sand (Aquatic Eco-Systems, Inc. Apopka, FL), which is commonly used for water filter media, was examined for comparison of hydraulic conductivity with BTJF. The density of the light weight sand was 0.4 g/cm^3 (typical sand is about 1.60 g/cm^3).

Peat+sand Mix: This mixture consisted of 50% sand and 50% peat moss by volume. A similar mixture was recently used as the filter media in an infiltration system for treating stormwater runoff [2]. The peat moss was a commercial brand (Majestic Growth, Agawam, MA) with a density of 0.16 g/cm^3.

Sorption Isotherm Models for Heavy Metal Ions

BTJF (70–80 mesh (212-180 μm)) was used for the isotherm tests. Solutions of various concentrations of Cd^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} (0 to 2.0 mM) were prepared by mixing copper sulfate pentahydrate, cadmium chloride, lead nitrate, and zinc nitrate hexahydrate in distilled water; solutions of NaOH (0.1 M) and HNO_3 (0.1 M) were used to adjust the pH to 4. BTJF (0.1 g) was added to 50 mL of each metal solution and shaken at 150 rpm for 1 day at 25°C. The equilibrium (final) pH after the batch test typically ranged from 6 to 7. Mixtures were removed from the shaker, and the solution filtered through a 0.45-μm (pore size) membrane filter using a syringe. The solution was then measured for dissolved metal concentration by means of inductively coupled plasma (ICP) emission (Jobin Yvon, Inc., Ultima ICP–AES, Edison, NJ). The equation of the Langmuir isotherm is:

$$q_e = \frac{bQ_{\max}C_e}{1+bC_e}$$

where q_e is the amount of metal sorbed at equilibrium (mmole/g), b is Langmuir constant (L/g),and $Q_{\max}$ is maximum adsorbate loading (mmole/g).

Column Test for Mixed Metal Solution and Regeneration

Aliquots of the BTJF (5 g, 20-30 mesh (850- 600 μm)) were packed into glass columns with internal diameters of 15 mm (Bio-Rad Laboratories, Hercules, CA). A solution containing Cd^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} (0.5 mM each) was prepared from stock solutions in 0.01 M of sodium nitrate for ionic strength adjustment; the pH was adjusted to 4 as above. After about 4L of distilled water was passed through the column to eliminate the swelling effect during heavy metal adsorption, the mixed solution was pumped in an up-flow direction through the column by a peristaltic pump (GILSON-FC 204, Milwaukee, WI) at flow rate 4 mL/min. The regeneration step involved circulating 1 L of 0.1 M HNO_3 solution (pH 2) through the column at flow rate 4 mL/min. After this step, 3-4 L of DI water was passed through the column until pH of the effluent reached 6. This cycle was repeated four times in this study.

Column Test for Synthetic Stormwater

BTJF (6 g, 20-30 mesh) was packed into glass columns with internal diameters of 15 mm. A solution containing Cd^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} was prepared by dilution of stock solutions in 0.01 M of sodium nitrate; the pH adjusted to 7 as above. After about 4L of distilled water was passed through the column to eliminate the swelling effect during heavy metal adsorption in the BTJF column, the mixed solution was pumped in an up-flow direction through the column by a peristaltic pump at flow rate 10 mL/min.

Filter Column Design for Hydraulic Test

Fig. 1 shows the column design and experimental setup for the variable flow column experiment. The column unit was built by Affiniti Water Technologies Inc. (Mount Prospect, IL). All column materials, pump tubing, and water holding containers were made of plastic, Teflon tube, and polyvinyl chloride (PVC). The column was 41

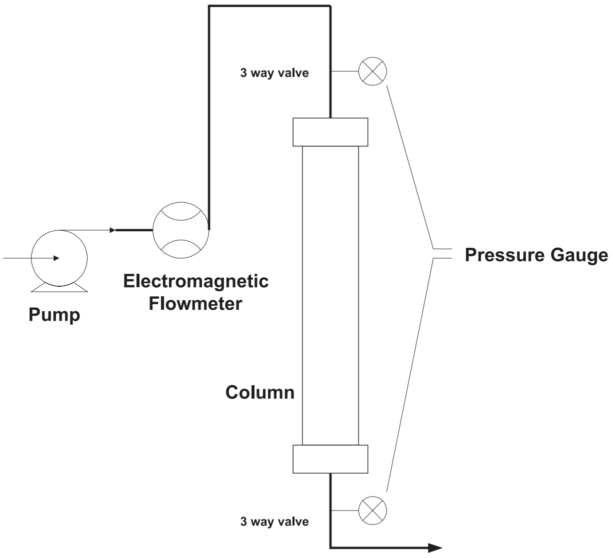

Fig. 1. Experimental column design for hydraulic test.

cm tall and had an inside diameter of 4.8 cm. The water was pumped from a 240 L plastic holding container using Masterflex Model 77601-00 peristaltic pumps to the top of the filter column. The flow rate was simultaneously measured by an electromagnetic flow measuring system (Model: Promag 33. Endress+Hauser Inc. Greenwood, IN). To measure the headloss across the media bed as water passed through, pressure gauges were installed at the top and bottom of the column.

Ten flow rates were selected to give a range of 0.1 to 1.2 min of empty bed contact time (EBCT). Three series were run for each column (a series consisted of running each flow rate once) for a total of 30 runs for each media. The medium was not changed between series.

Results

Adsorption of Cadmium, Copper, Lead and Zinc by Untreated Juniper and BTJF

Isotherm data for Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} ions applied to untreated juniper and BTJF are shown in Fig. 2. The Q_{max} values in Table 1 shows sorption abilities of the BTJF for all metals are much higher than that of untreated juniper. The affinity sequence of both materials, untreated juniper and BTJF, was Pb > Cu > Zn ≥ Cd. The result of a column test (Figure 3 and Table 2) with a solution containing the metals together also indicated that the sorption affinity of BTJF was Pb > Cu > Zn ≥ Cd. These results are in agreement with those observed by others where higher Pb and Cu metal adsorption relative to Cd, Ni and Zn adsorption was explained by hydrolysis constants for the metals [11, 12]. The hydrolysis constants of the heavy metals (log K_1) are as followed: Pb(-7.71) > Cu(-8.00) > Zn(-8.96) > Cd(-10.80).

Table 1. Langmuir isotherm constants for Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} adsorbed onto untreated juniper and BTJF.

BTJF				
Metals	Cd	Cu	Pb	Zn
Q_{max} (mmole/g)	0.169	0.303	0.500	0.196
b (L/g)	4.63	1.10	1.24	2.30
R^2	0.901	0.983	0.988	0.947
Juniper				
Metals	Cd	Cu	Pb	Zn
Q_{max} (mmole/g)	0.153	0.249	0.378	0.095
b (L/g)	1.44	0.919	1.05	4.00
R^2	0.870	0.983	0.984	0.978

A possible explanation of this correlation can be found in the strict analogy between the hydrolysis reaction of metal in solution (1) in both single and mixed environments. The reaction among metals and protonated sites (2) could be another heavy metal removal mechanism of this media given a correlation between quantity of carboxylate ion produced by base treatment and removed cadmium ion in BTJF [10]. In fact, if the ion exchange mechanism on the functional group is supposed (2), a hydrogen ion is extracted and released in solution in both reactions (1) and (2); such a release was observed in BTJF [13].

$$HO\text{–}H + M^{2+} \rightarrow M(OH)^{+} + H^{+} \quad (1)$$

$$A\text{–}H + M^{2+} \rightarrow AM^{+} + H^{+} \quad (2)$$

where M is the heavy metal and A is the active site such as carboxyl group in the protonated form. Consequently, the affinity order analogy with hydrolysis constant supports that the affinity of the surface for the hydrolyzed metal species M(OH) is significantly greater than that for the unhydrolyzed ones also considering that in the usual pH range [M(OH)] >> [M] [14].

Based on the metal desorption curves by the metal recovery and column regeneration test (Fig. 4), it appears that a recirculating period as short as 40 bed volumes (about 80 min) would release a large portion of the recoverable heavy metals. This means that recovery of metals and regeneration of the BTJF is possible without a significant effect on performance. The data in Table 2 summarize the mass balance for the metal recovery and column regeneration tests. Throughout this experiment, metal recovery rate by 0.1 M nitric acid was 100%. The metal sorption capacity declined slightly from 136.3 to 119.2 µmole/g in the first two cycles but did not significantly affect the column performance. However, the sorption capacity dropped significantly at the third and fourth regeneration, 72.3 and 83.1 µmole/g, respectively. It is

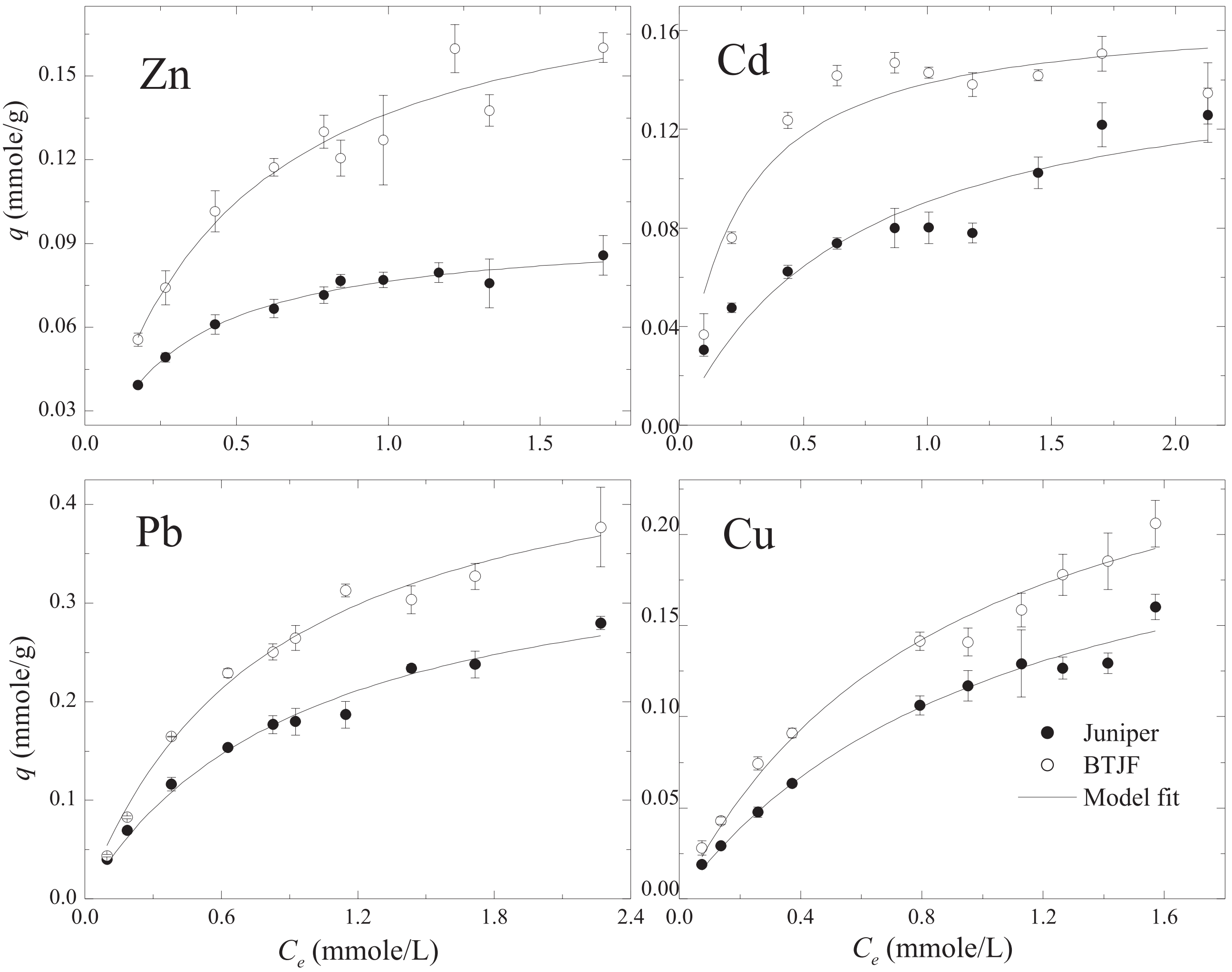

Fig. 2. Langmuir isotherms for Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} adsorption onto BTJF and untreated juniper. ($I = 0.01$ $NaNO_3$, initial pH 4).

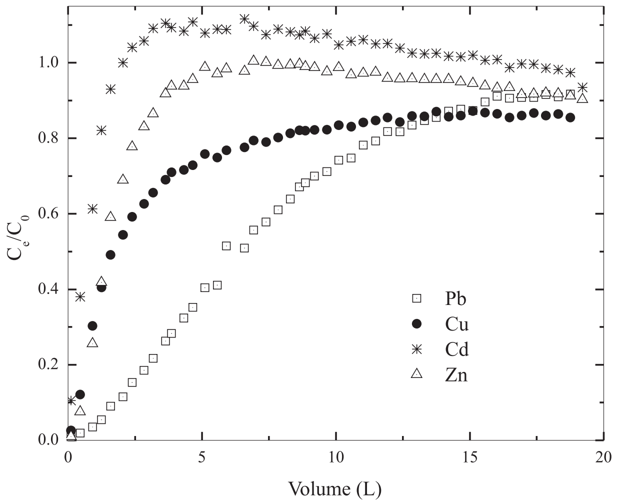

Fig. 3. Breakthrough curves for adsorption onto BTJF from mixed solution of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} ions.

not exactly clear why the metal removal capacity of BTJF changed after the first few times it was used. Perhaps the conditioning step (acid wash followed by neutralization) could gradually deteriorate the lignocellulosics by either decreasing the effective porosity or by changing the cellular structure of the media [15].

Headloss Analysis

The particle size distribution affects headloss through the column, density of the packed media, and other factors influencing column performance and design. Approximately 300 g of sand was placed in the top sieve of a stack on a shaker. The result of the particle size analysis shown in Table 3 shows more than 80% of the sand is in the range of 0.600 to 1.400 mm range. In addition, the d_{10} and uniformity coefficient (d_{60}/d_{10}) for the sand are 0.27 mm and 2.52, respectively.

Headloss curves for different sizes of BTJF are shown in Fig. 5. These data show that headloss constantly increases as the media size decreases as described in the literature [16]. Also shown are headloss profiles for the sand, and sand+peat media. Initially, the headloss of the sand+peat media were much higher than others in every range. Therefore, it can be deduced that

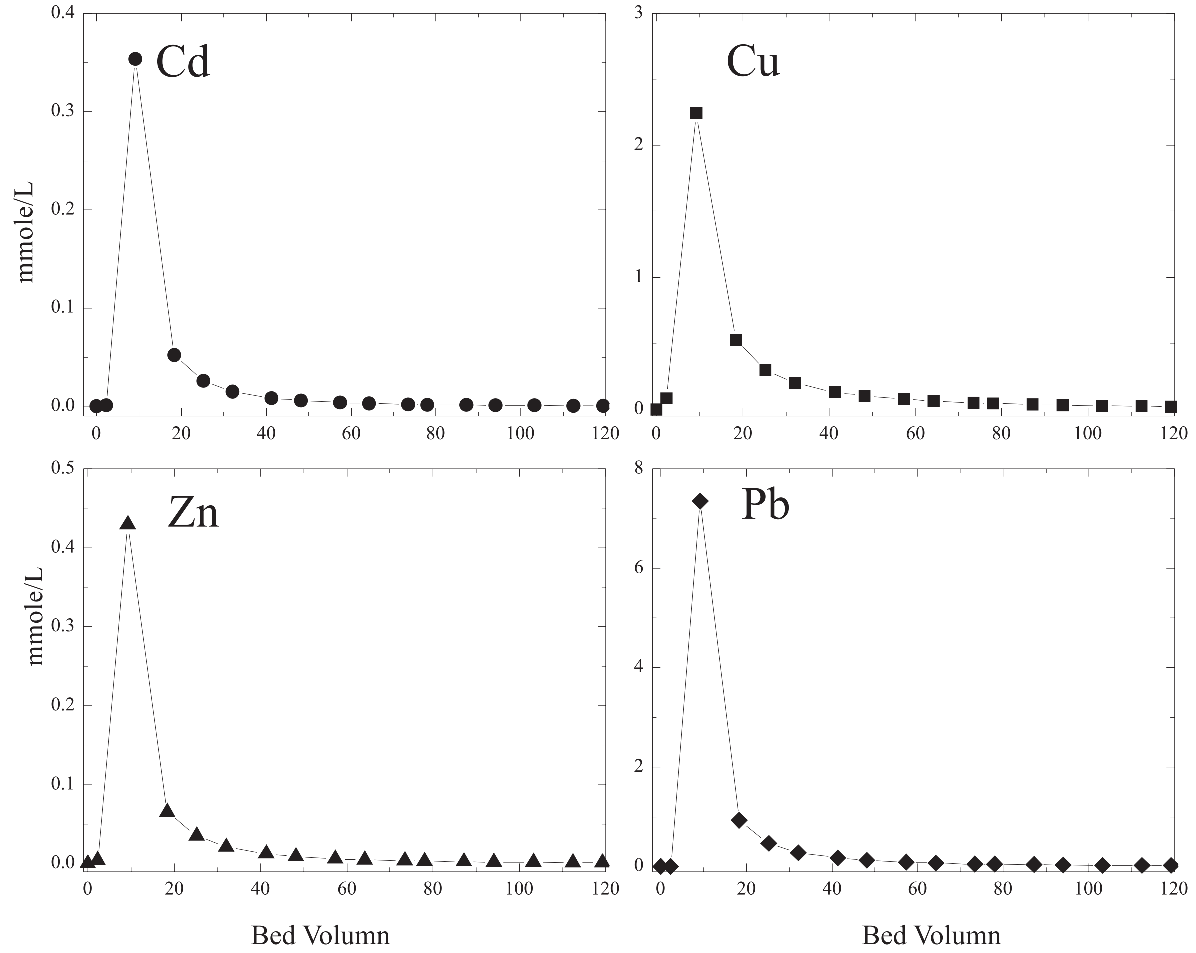

Fig. 4. Effluent metal concentrations during column regeneration by 0.1 M nitric acid (first cycle).

Table 2. Regeneration ability of the BTJF column using 0.1M HNO_3.

Cycle #	Metals	Cumulative metal removed (μmole/g)	Total metal recovery efficiency (%)
0	Cd	5.9	> 100%
	Cu	37.2	
	Pb	69.8	
	Zn	23.9	
	Total	**136.3**	
1	Cd	6.7	> 100%
	Cu	54.8	
	Pb	63.1	
	Zn	10.04	
	Total	**134.6**	
2	Cd	8.7	> 100%
	Cu	49.8	
	Pb	48.1	
	Zn	12.6	
	Total	**119.2**	
3	Cd	3.3	> 100%
	Cu	27.9	
	Pb	34.6	
	Zn	6.5	
	Total	**72.3**	
4	Cd	6.2	> 100%
	Cu	34.6	
	Pb	33.9	
	Zn	8.4	
	Total	**83.1**	

sand+peat media are not ideal media for the stormwater filtration column due to the low hydraulic conductivity compared with other media. Headloss profiles of the BTJF with a size range 14 to 30 mesh were almost identical to the headloss profile of the sand, the most widely used filter media for stormwater runoff treatment. There-

Table 3. Particle size distribution of sand.

Sieve No.	Diameter (mm)	Percentage (%) of sand retained on each sieve
10	2.00	0
14	1.40	13.2
20	0.850	41.9
30	0.600	22.0
50	0.300	20.6
60	0.250	0.2
60 >	0.250 >	2.1

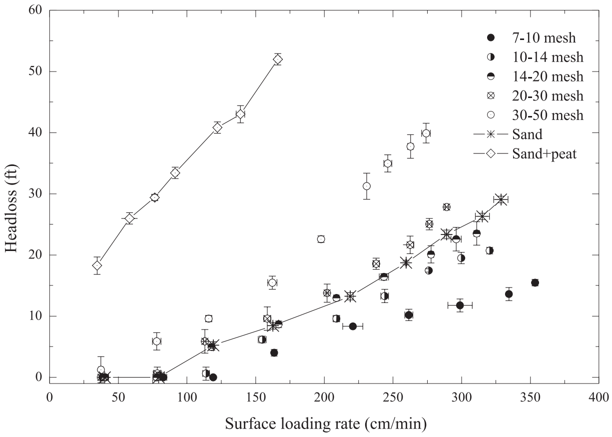

Fig. 5. Headloss curves at various flowrates for different sizes of BTJF, sand, and sand+peat media.

Table 4. Composition of typical stormwater runoff and synthetic stormwater versus discharge criteria.

Metals	[a] Average Heavy metal conc. (μg/L) (Milwaukee I-179)	Synthetic Stormwater (μg/L) (pH 7)	[b] Discharge Criteria (μg/L).	Average effluent conc. (μg/L) through 150 bed volume
Cu	88	200	18	12.2
Cd	32	100	5.6	2.9
Pb	1.457	2.000	82	12.8
Zn	336	500	120	1.30

a: (see ref. [17]); b: Ohio EPA criteria for discharge to modified surface warm water

fore, it appears that BTJF may be used at sites where sand is currently used as the stormwater filter medium as long as the particle size range of the BTJF is within the above-mentioned limits.

Fig. 6 compares the headloss curves between sand and BTJF with similar particle size ranges. Significant headloss differences were observed in Figure 6 (a) and (d) compared to Figure 6 (b) and (c). These data also show that the headloss of BTJF is greater than that of sand as the media size decreases. This result warrants further investigation; however, it can be deduced that different physical properties of the two media such as porosity, morphology, and density could cause such a result [16].

Synthetic Stormwater Column Test

Determining the range of metal concentrations to be treated is crucial to applying BTJF as a stormwater filtration media, since the removal efficiencies of the media, relative to each other, change with varying metal concentrations. Media that were effective at high metals concentrations were outperformed by some media at the low metals concentrations typically found in stormwater [1]. Previous studies showed outstanding heavy metal removal efficiency of BTJF in the high metals concentrations. However, the heavy metal removal performance of BTJF in very low metal concentration had not been tested thoroughly. This column test investigated the treatment of simulated stormwater runoff, whose metal concentration is usually less than 2 mg/L. The composition of the synthetic stormwater solution and discharge criteria is shown in Table 4. In addition, this table shows effluent metal concentrations of synthetic stormwater and their discharge concentration limitation. The effluent concentrations for all metals were lower than their discharge criteria.

Discussion of Results

- Both separate batch isotherm tests, and column testing with a solution containing all of the metal ions confirmed that the affinity sequence of metals was Pb > Cu > Zn ≥ Cd. This affinity sequence agrees with the order of the hydrolysis constants.
- Metal recovery and column regeneration tests showed that 0.1 M of nitric acid, which was effective in removing bound heavy metals, did not significantly affect the performance of the filtration medium. Small decreases in metal sorption capacity may have resulted from a gradual deterioration of the lignocellulosic material.

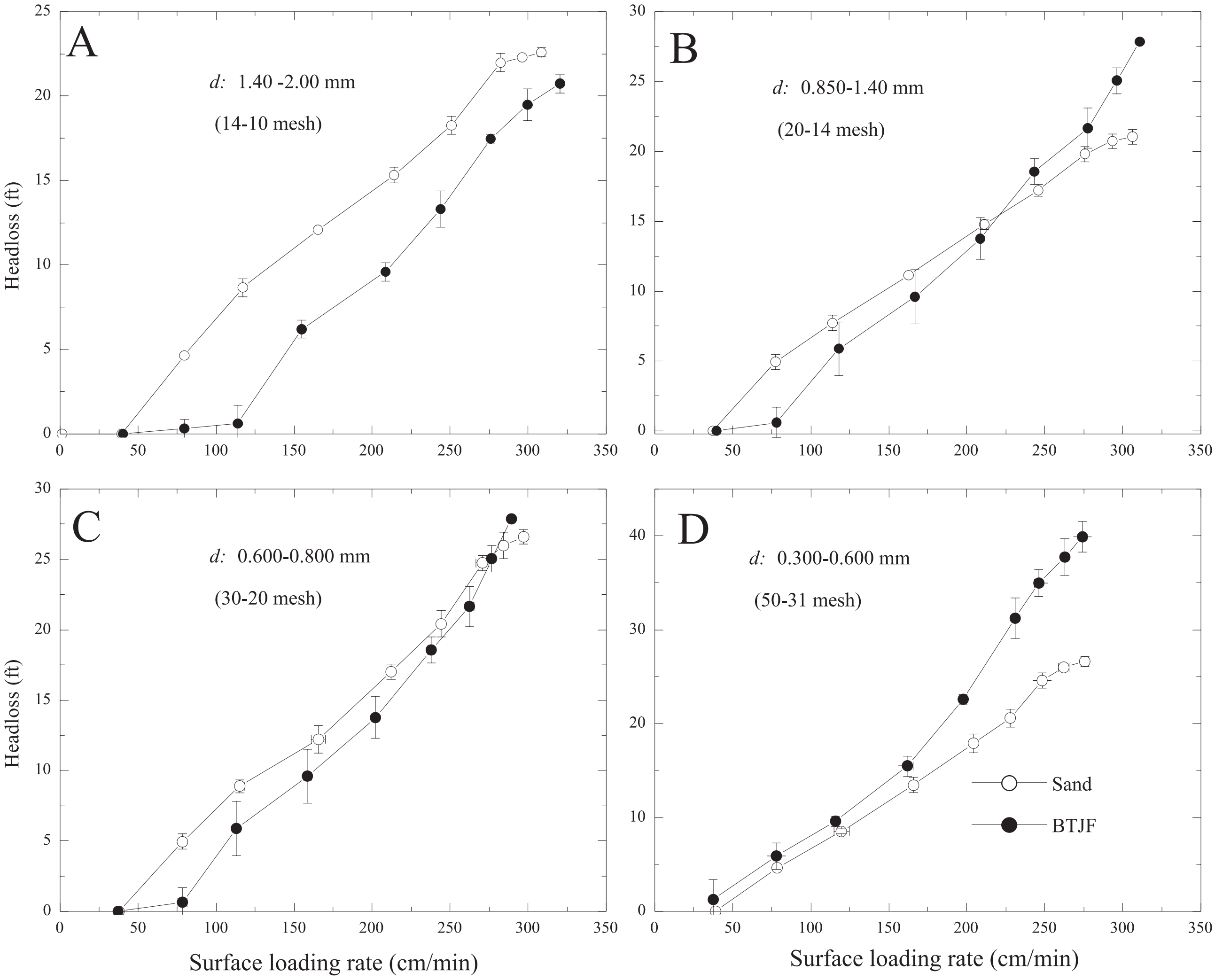

Fig. 6. Comparison of headloss curves between sand and BTJF within the same particle size range.

- A hydraulic conductivity study demonstrated that the headloss constantly increases as the media size decreases. However, there is no major headloss-related disadvantage for using BTJF instead of the sand as the stormwater filter media if the particle size of the BTJF is similar to that for the sand.
- A fixed column study for heavy metal removal performance of BTJF at mixed and very low concentrations of heavy metals in solution, a similar condition to urban stormwater runoff, suggests that BTJF can be used to achieve metal effluent concentrations below their discharge criteria.

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