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Evaluation of Biochar as a Potential Filter Media for the Removal of Mixed Contaminants from Urban Stormwater Runoff

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Outline

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1. Introduction

2. Methods and Materials

3. Results and Discussions

4. Conclusions

1.1 Stormwater runoff

Most common non-point source of water pollution to rivers, lakes, estuaries, and beaches.

Beach closings are a growing concern due to the presence of pollutants in stormwater runoff.

Contaminants mainly include nutrients (nitrogen and phosphorus), heavy metals, PAHs, as well as *E. Coli.*

1.2 Stormwater treatment

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Beach water contamination due to stormwater runoff in urban settings:

- aging and poorly designed sewage and stormwater systems
- lack of engineered stormwater systems

Several Best Management Practices (BMPs) have been developed (detention ponds, bioretention, infiltration basins, permeable pavements, etc.)

Problems

- Economically unfavorable
- Technically too complicated
- Not feasible in many urban settings
- Too selective without addressing all contaminants

1.3 Filtration systems

Use of filtration systems have received great attention for their potential to remove particulate matter and other contaminants from urban stormwater runoff.

Filter materials

- Sand, gravel, rocks, zeolite, calcite, iron filings
- Activated carbon, charcoal
- Corn cobs, garden bark, coconut fiber
- Compost, kitty litter

Biochar?

Biochar is expected to have excellent potential as an adsorbent or filter given its large surface area and microporous structure.

1.4 Research Objectives

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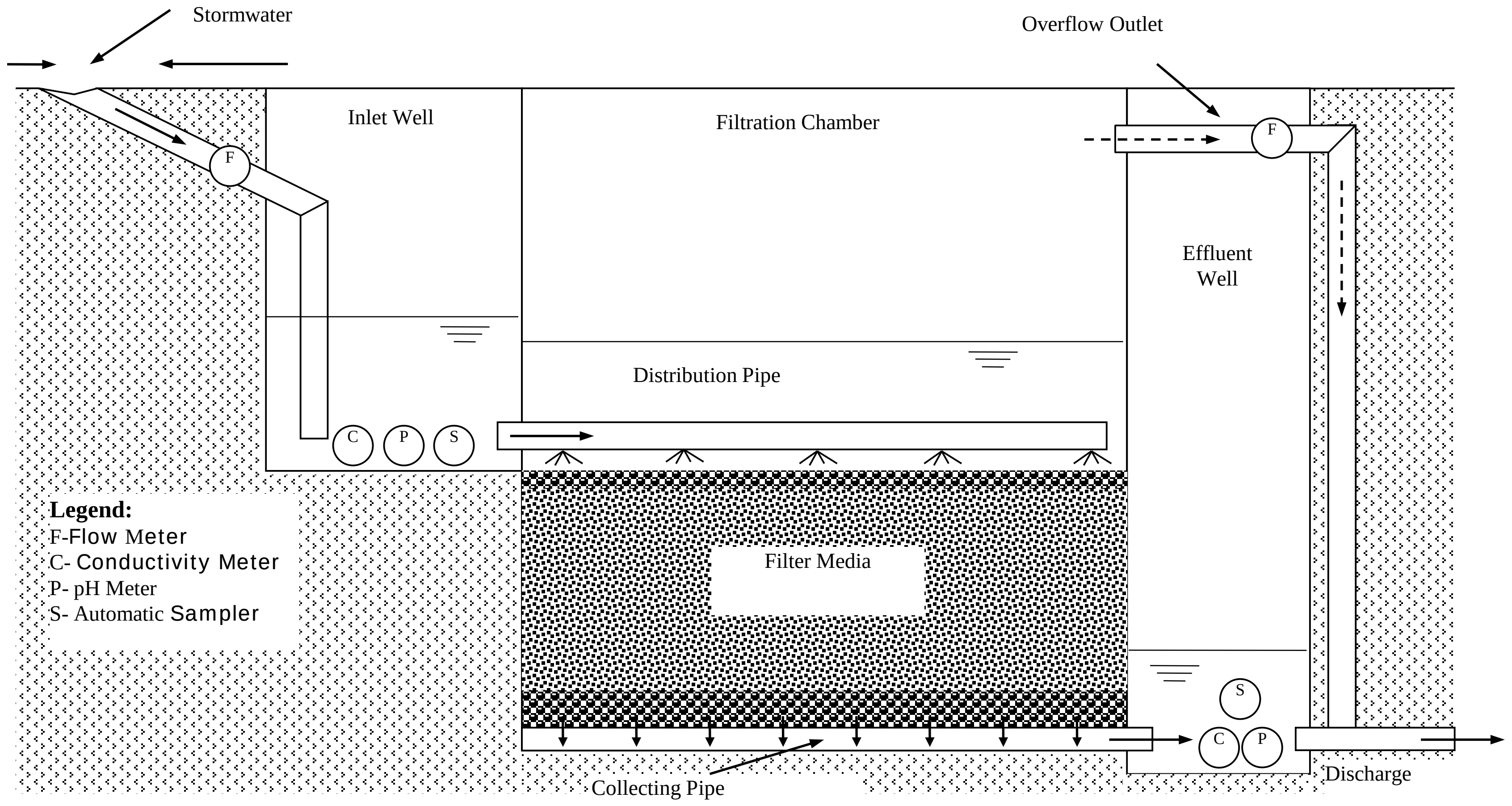
1. Evaluate biochar's potential for contaminants removal in stormwater.

2. Quantify the contaminant attenuation and/or degradation capacity and hydraulic efficiency of biochar under different simulated urban stormwater runoff conditions.

3. Develop an in-ground permeable reactive filter (PRF) system that could remove a wide range of contaminants from stormwater runoff generated from paved and unpaved source areas near urban areas that are dominated by high-traffic loadings.

1.5 Concept of PRF



Source: Reddy (2013)

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2.1 Stormwater quality

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Typical pollutants found in urban stormwater runoff and quality standards

Typical Pollutants	[1]Range (mg/L)	[1]References	[2]National Recommended Water Quality Criteria (mg/L)	[3]Lake Michigan Basin Water Quality Standards (mg/L)
Total suspended solids	43-51	The National Stormwater Quality Database (2005)		
Total dissolved solids	75.9-2792	Lager & Smith (1975)		180
Inorganic Chemicals:				
Aluminum	0.1-16.0	Dannecker et al (1990)	0.75	
Arsenic	0.001-0.21	Cole et al (1984)	0.34	0.05
Barium	0.066-0.087	Dannecker et al (1990)		1
Cadmium	0.00005-13.73	Cole et al (1984)	0.002	
Chloride	0.3-25000	Dannecker et al (1990)	86	12
Chromium	0.001-2.3	Cole et al (1984)	0.000316	
Copper	0.012-0.017	The National Stormwater Quality Database (2005)	0.018	
Cyanides	0.002-0.033	Cole et al (1984)	0.022	
Fluoride	0.1-0.2	Dannecker et al (1990)		1.4
Iron	0.08-440.0	Dannecker et al (1990); Ellis &Revitt (1982); Hall & Anderson (1988)		0.3
Lead	0.005-0.018	The National Stormwater Quality Database (2005)	1.47	0.05
Magnesium	0.02-304.2	Dannecker et al (1990)		0.15
Manganese	0.007-3.80	Dannecker et al (1990); Ellis &Revitt (1982)		1
Mercury	0.00005-0.067	Cole et al (1984)	0.0014	
Nickel	0.001-49.0	Dannecker et al (1990); Cole et al (1984)	0.47	
Nitrogen (all forms)	0.07-16.0	Mance& Harman (1978); Mattraw& Miller (1981); Yousef et al (1985)		10
Total Kjeldahl Nitrogen (TKN)	0.0006-0.0016	The National Stormwater Quality Database (2005)		
Nitrate + Nitrite (N)	0.0006	The National Stormwater Quality Database (2005)		10
Phosphorus (Total)	0.22-0.3	The National Stormwater Quality Database (2005)		0.007
Soluble Phosphorus	0.08-0.17	The National Stormwater Quality Database (2005)		
Potassium	0.01-34	Dannecker et al (1990)		

Typical Pollutants	[1]Range (mg/L)	[1]References	[2]National Recommended Water Quality Criteria (mg/L)	[3]Lake Michigan Basin Water Quality Standards (mg/L)
Selenium	0.0005-0.077	Cole et al (1984)		0.01
Silver	0.0002-0.014	Cole et al (1984)	0.0032	
Sodium	0.18-660	Dannecker et al (1990)		
Sulfate	0.06-1252	Dannecker et al (1990)		24
Zinc	0.039-0.15	The National Stormwater Quality Database (2005)	0.12	
Other Chemical Parameters:				
Dissolved Oxygen	0-14.0	Keefer et al (1979)		≥ 5 mg/L
Alkalinity	8-1273	Keefer et al (1979)	20 mg/L as $CaCO_3$	
BOD	9 to 12	The National Stormwater Quality Database (2005)		
COD	21 to 55	The National Stormwater Quality Database (2005)		
pH	4.5-8.7	Gupta et al (1981)	6.5-9	7.0-9.0
Microbiology:				
Total Coliforms	7-1.8E7 CFU/100 mL	Dutka& Tobin (1987); Dutka&Rybakowski (1987)		
Fecal Coliforms	0.2-1.9E6 CFU/100 mL	Dutka& Tobin (1987); Dutka&Rybakowski (1987)		20/100 mL
Fecal streptococci	3-1.4E6 CFU/100 mL	Dutka& Tobin (1987); Dutka&Rybakowski (1987)		
E.Coli	1.2E1-4.7E3 CFU/100 mL	Gannon &Busse (1989)		126 cfu/100 mL
Organic Compounds:				
Oil/Grease	0.001-110	Stenstrom et al (1984)		0.1
Hydrocarbons	0.64-19.72	Bomboi and Hernandez (1991); Fam et al (1987)		
Aliphatic Hydrocarbons	0.2-24	Bomboi and Hernandez (1991); Fam et al (1987)		
Aromatic Hydrocarbons	0.0004-1.31	Bomboi and Hernandez (1991); Fam et al (1987)		
UCM	1.059-1.4	Bomboi and Hernandez (1991)		
Chlorinated organics	<0.0066	Murphy and Carleo (1978)		
Chlorinated hydrocarbons	<0.000038	Thomlinson et al (1980)		
Alkyl lead compounds	2.5E-6 - 1.2E-4	Harrison et al (1986)		
Organic Chemicals:				
Polychorinated biphenyl	2.7E-5 - 1.1E-3	Cole et al (1984)	1.40E-05	
Total PAH	2.4E-4 - 1.3E-2	Cole et al (1984)		
Benzo(a)pyrene	2.5E-6 - 1E-2	Cole et al (1984)	3.80E-06	
Fluoranthene	3E-5 - 5.6E-2	Cole et al (1984)	3.80E-06	
Benzene	0.0035-0.013	Cole et al (1984)	0.012	0.012

Typical Pollutants	[1]Range (mg/L)	[1]References	[2]National Recommended Water Quality Criteria (mg/L)	[3]Lake Michigan Basin Water Quality Standards (mg/L)
Phenol	0.003-0.01	Cole et al (1984)	0.001	0.001
Pentachorophenol	0.001-0.115	Cole et al (1984)	0.001	
Diethyl Phthalate	0.002-0.010	Cole et al (1984)	17	
Di-n-butyl phthalate	0.0005-0.011	Cole et al (1984)	2	
Bis(2-ethylhexyl) phthalate	0.007-0.039	Cole et al (1984)	1.20E-03	
Butyl benzyl phthalate	<0.010	Cole et al (1984)	1.5	
Aldrin-Dieldrin	5E-6 - 1E-4	Cole et al (1984)	0.00024	
α-BHC	2.7E-6 - 1E-4	Cole et al (1984)	2.60E-06	
β-BHC	<0.0001	Cole et al (1984)	9.10E-06	
δ-BHC	<0.0001	Cole et al (1984)	9.80E-04	
Chlordane	0.0001-0.010	Cole et al (1984)	2.40E-03	
DDD	<8E-6	Carr et al (1982)	3.10E-07	
α-Endosulfan	0.0001-0.0002	Cole et al (1984)	2.20E-04	
Endrin	<0.000005	Carr et al (1982)	8.60E-05	
Heptachlor+ H.epoxide	<0.0002	Cole et al (1984)	5.20E-04	

Source: [1]Makepeace et al (1995); [2]USEPA National Recommended Water Quality Criteria (2009); [3]Water Quailty Standards from Illinois Pollution Control Board: http://www.ipcb.state.il.us/documents/dsweb/Get/Document-33354/

Composition of contaminants in synthetic stormwater

Contaminant		Unit	*Average Range in Stormwater	Synthetic Stormwater Concentration
TSS		mg/L	1 - 36,200	145 - 150
Nutrient	Nitrate	mg/L	0.07 – 16.0	5 – 15
	Phosphorus		0.01 – 7.3	0.5 – 1
Metal	Cadmium	mg/L	0.00005 - 13.73	20 – 30
	Chromium		0.001 - 2.30	1 – 5
	Copper		0.00006 - 1.41	1 – 5
	Lead		0.00057 - 26.0	0.5 – 5
	Nickel		0.001 – 49.0	100 – 120
	Zinc		0.0007 – 22.0	50 – 60
PAHs	Naphthalene	ppb	0.036 – 2.3	10 – 700
	Phenanthrene		0.045 – 10	10 – 100
	BaP		0.1 - 150	10 - 100
E. coli		MPN/100mL	12 – 4700	3500 – 8,200

2.2 Filter materials

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Biochar

Biochar selected for the filter material was produced by Chip Energy (Goodfield, Illinois), created by a gasification process (520°C) using waste wood pellets as feedstock.

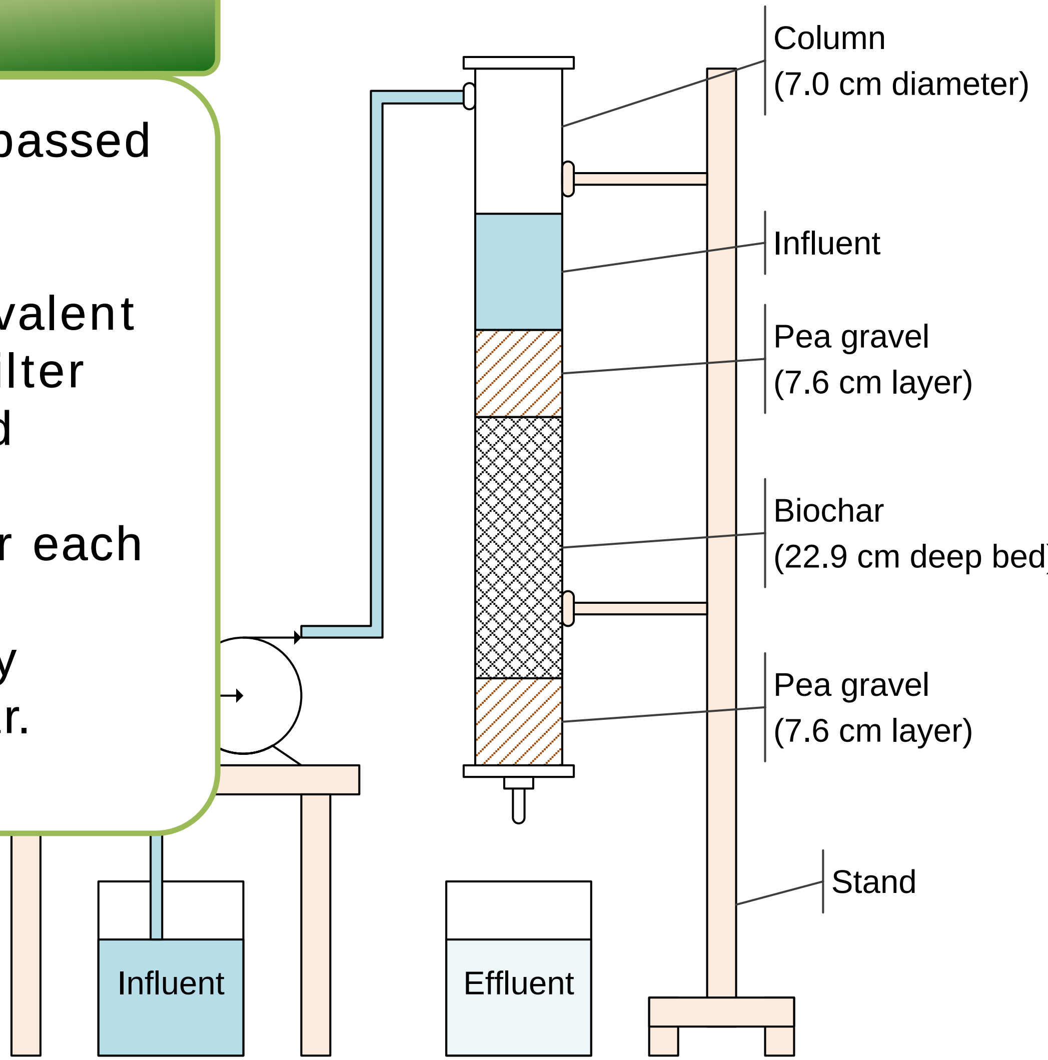
Characterization of Unwashed and Washed Biochars

Media	Unwashed biochar	Washed biochar
Effective Particle Size, D10 (mm)	2.1	2.1
Mean Particle Size, D50 (mm)	3	3.2
As-received Bulk Density (kN/m3)	5	
As-received Water Content (%)	5.7	
Specific Gravity of Solids	1.38	1.38
Dry Density (kN/m3)	4.7	25
Porosity (%)	65	69.4
Organic Content (%)	88.8	91.1
pH	7.6	8
Hydraulic Conductivity K (cm/s)	0.53	0.7
Optimum Moisture Content (%)	40	
Maximum Dry Density (kN/m3)	4.6	

2.3 Column tests

Procedure

- Deionized water was first passed through the biochar.
- Effluent was collected.
- A measured amount (equivalent to three pore volumes of filter media) of SSW was passed through the biochar.
- Effluent was collected after each pore volume.
- Deionized water was finally passed through the biochar.
- Effluent was collected.



Schematic of the column filter system setup

2.4 Chemical analysis

pH, EC, ORP	ASTM Standard Test Methods D1293, D1125, and D1498, respectively
TSS	USEPA Method 160.2 / Standard Method 2540 D
N/P	A second derivative UV spectroscopy method for the nitrate and the malachite green method for the total phosphorus or orthophosphate
Heavy metals	An atomic absorption spectrophotometer (AAS) in accordance with the USEPA Methods 7130 for cadmium, 7190 for chromium, 7210 for copper, 7420 for lead, 7520 for nickel, and 7950 for zinc
PAHs	External liquid-liquid extraction procedure in accordance with USEPA Method 3520C followed by analysis using Gas Chromatography
E. Coli	IDEXX Colilert-18 testing within 6 hours of sample collection (USEPA Method 600/8-78-017)

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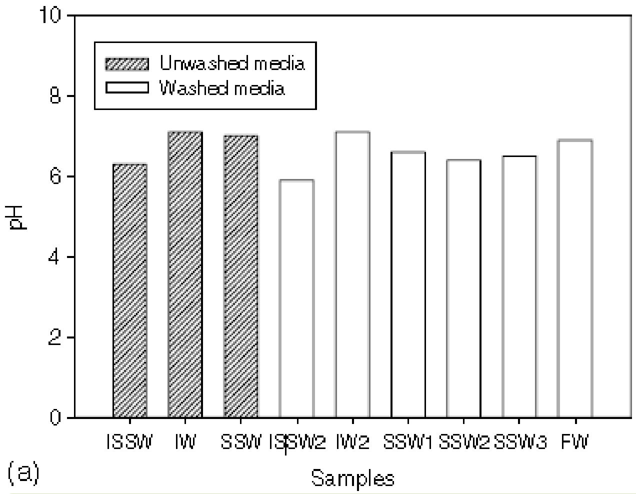
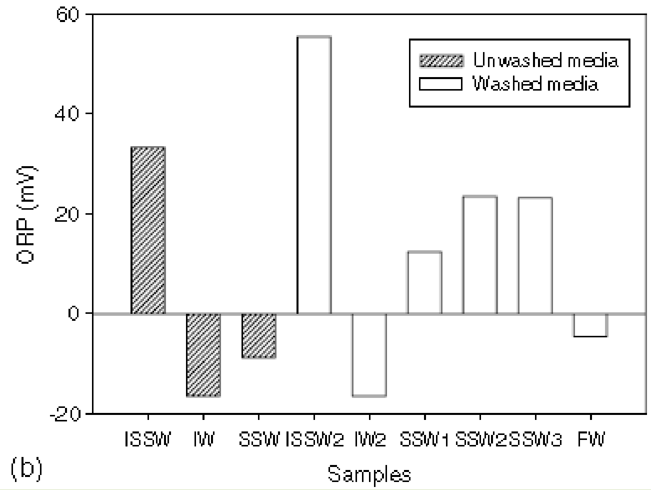
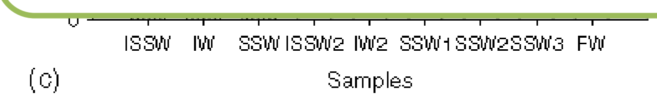
3.1 pH, ORP, EC, and TSS





- ISSW and ISSW2: SSW used for unwashed and washed biochar tests;
- IW and IW2: initial wash for unwashed and washed biochar tests;
- SSW1, SSW2, and SSW3: effluent samples of first, second, and third pore volumes of SSW;
- FW: final wash

- pH variations were small, so the impact of such variation was not considered significant.
- Oxidizing conditions are present in the washed media effluents
- Reducing conditions are present in the unwashed media effluents



Measured pH, ORP, EC, and TSS of SSW samples and the effluent samples collected at different stages of flushing

3.1 pH, ORP, EC, and TSS

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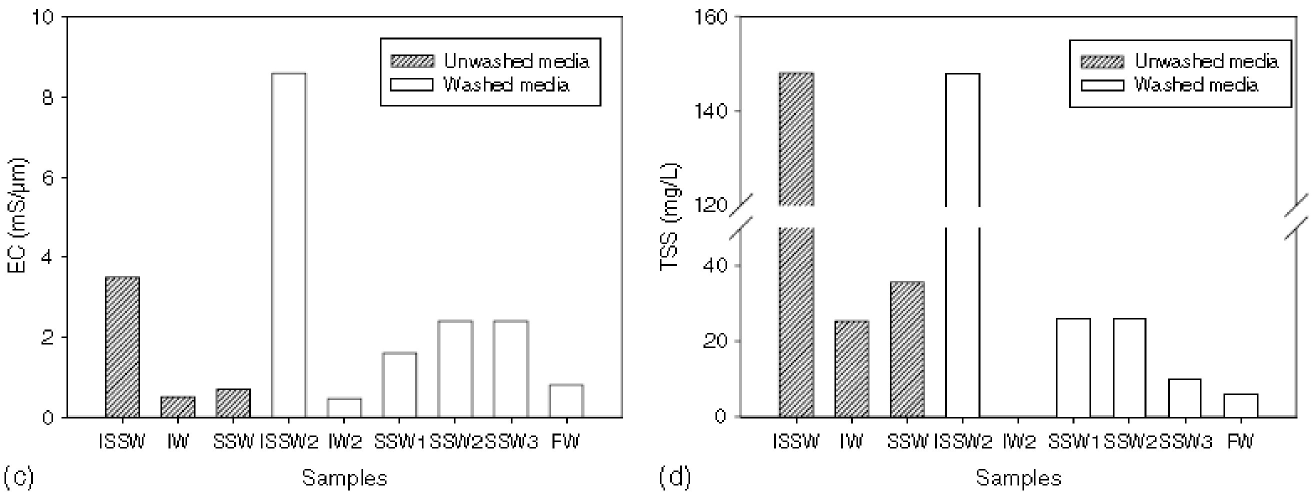
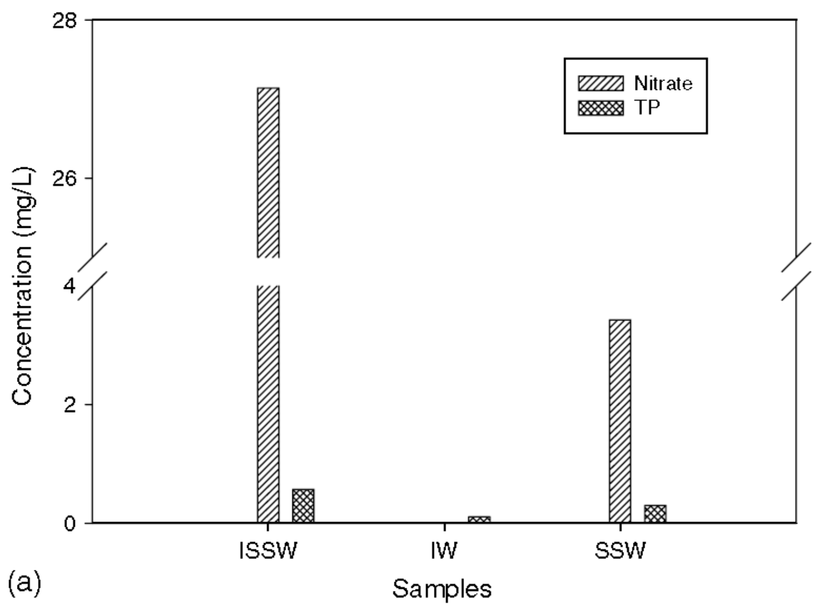
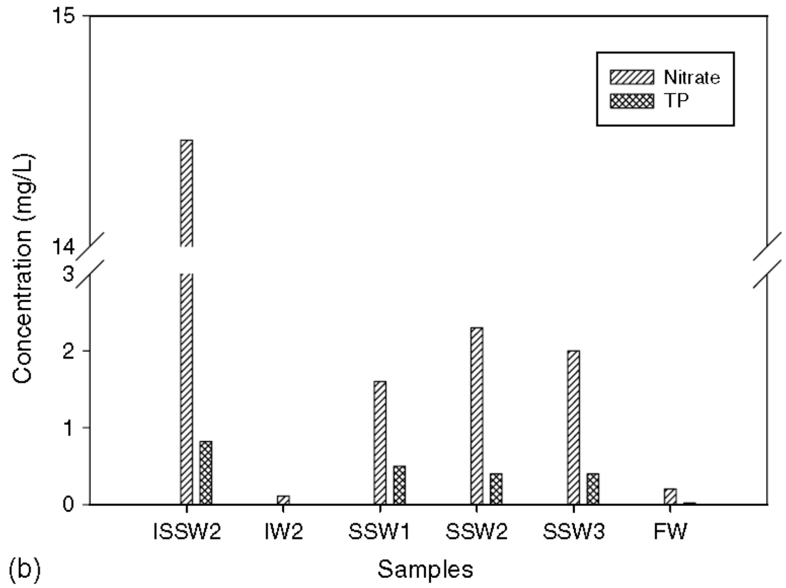
- Some of the ionic constituents in the SSW were most likely eluted, leading to increased EC observed of the effluents.
- SSW contained TSS of 148 mg/L, and it resulted in a very low TSS concentration in the effluent with washed media as compared to that of unwashed media.



Measured pH, ORP, EC, and TSS of SSW samples and the effluent samples collected at different stages of flushing

3.2 Nutrients

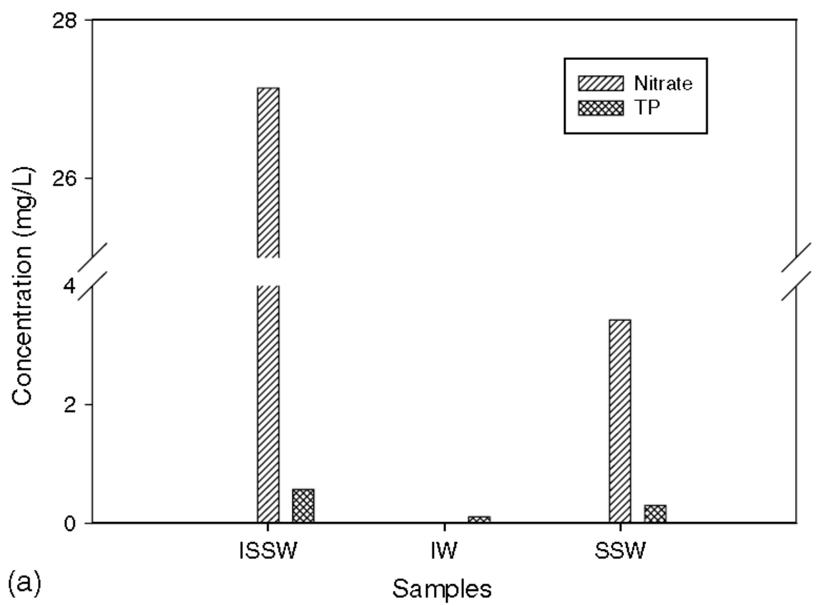


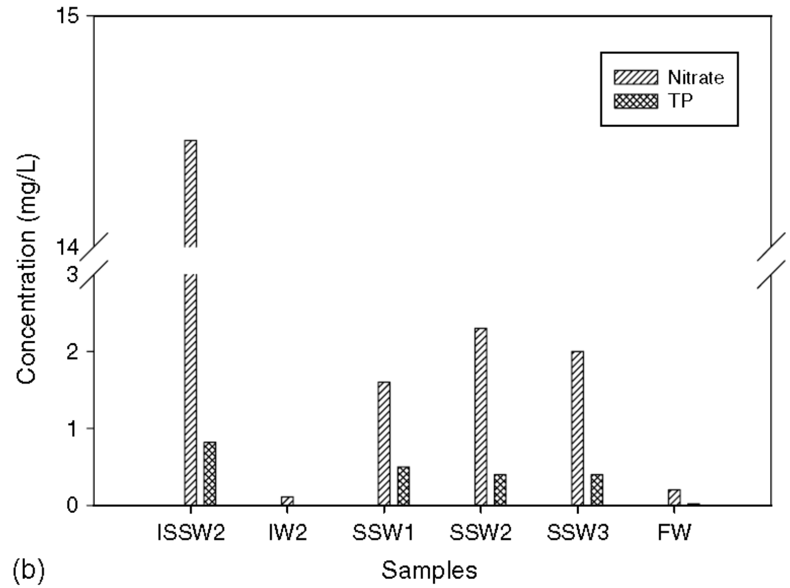


Unwashed biochar

- Nitrate concentration was negligible during the initial flushing with deionized water. Then, SSW that contained nitrate at a concentration of 27 mg/L was flushed through the column. The nitrate concentration in the effluent after SSW flushing was less than 4 mg/L.
- The initial release of phosphate from biochar during initial flushing with deionized water was 0.12 mg/L. After flushing with three pore volumes of SSW that contained 0.57 mg/L of phosphate, the phosphate concentrations in the effluent ranged from 0.3 to 0.4 mg/L.

3.2 Nutrients

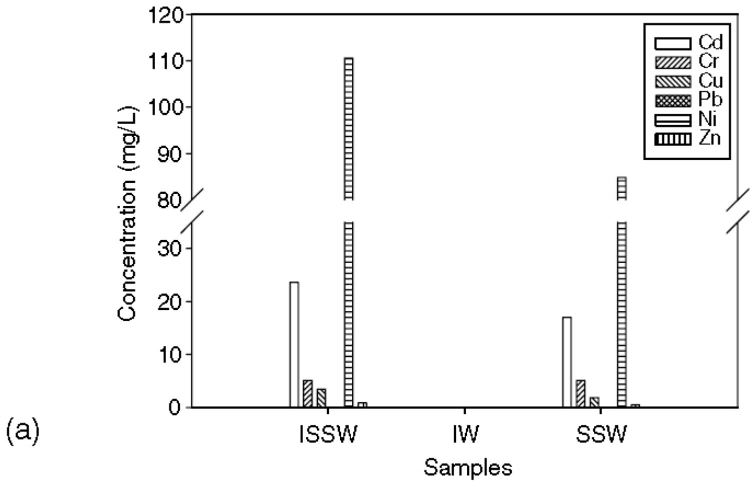


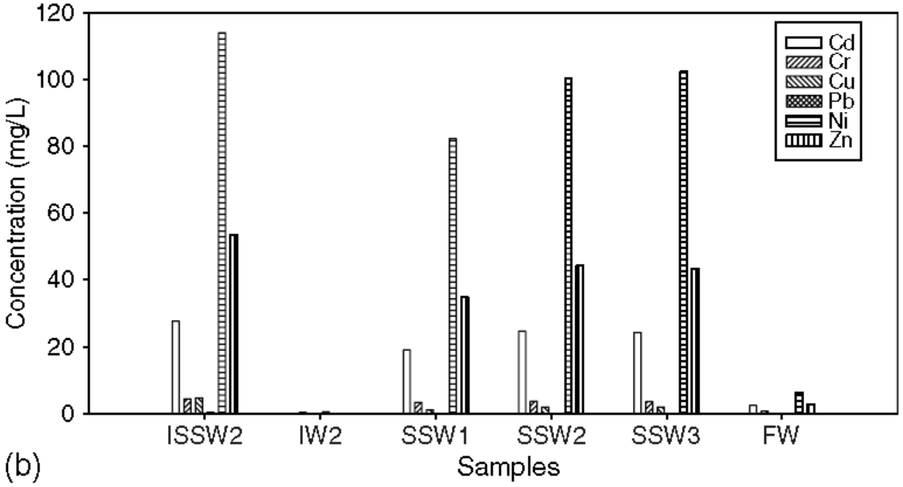


Washed biochar

- During the initial flushing with deionized water (Sample IW), nitrate was released from the biochar at very low concentrations (<0.12 mg/L). Biochar demonstrated high removal efficiencies for nitrate that exceeded 85%.
- No phosphate was released from the washed biochar when it was initially flushed with deionized water. A removal efficiency of 47% for phosphate was achieved.

3.3 Heavy metals

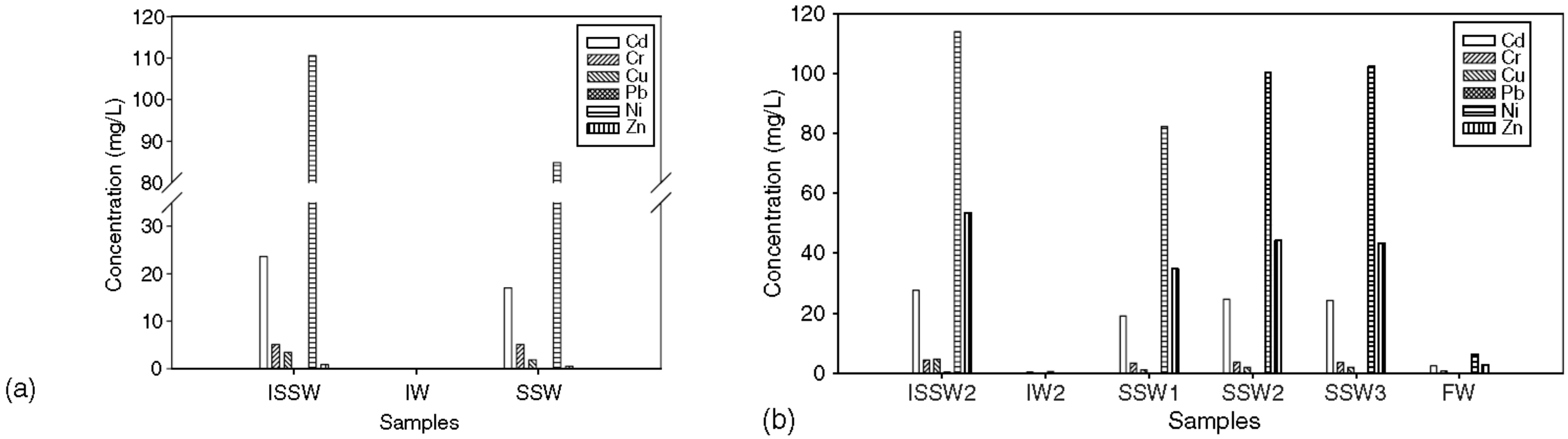




Unwashed biochar

- Initial cadmium used here in the SSW was 23.61 mg/L. The cadmium after flushing with SSW was approximately 17 mg/L.
- Initial chromium in the SSW was 5.13 mg/L, and the chromium in the effluent decreased slightly to 5 mg/L.
- Initial copper of 3.45 mg/L in the SSW > the effluent had a copper of approximately 1.75 mg/L.
- Initial of nickel in the SSW of 110.61 mg/L was reduced to approximately 80 mg/L in the effluent.
- Initial zinc of approximately 0.86 mg/L in the SSW, in the effluents decreased to 0.5 mg/L.
- Lead was undetected in both the initial SSW and the effluent samples.

3.3 Heavy metals

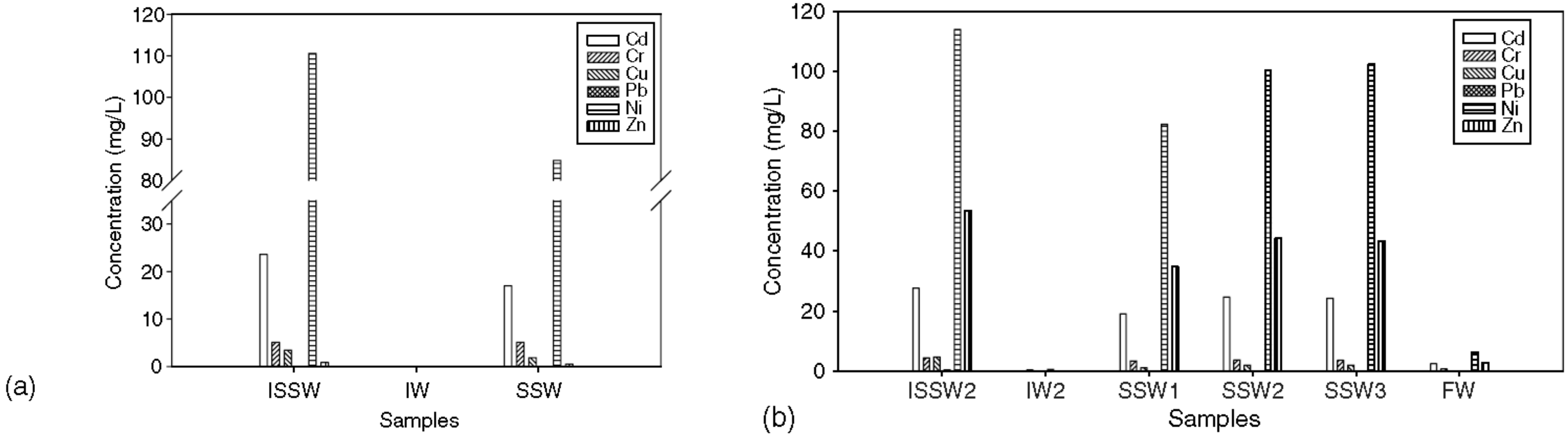


Heavy metal concentrations measured in initial SSW and effluent samples at different stages of flushing: (a) unwashed biochar; (b) washed biochar

Washed biochar-Cd

- When flushed alone with deionized water, the washed biochar media showed approximately a 0.04 mg/L cadmium in the effluent.
- A subsequent flushing of three pore volumes of SSW (Samples SSW1, SSW2, and SSW3) showed a reduction in the cadmium from 27.63 mg/L to approximately 20 mg/L.

3.3 Heavy metals



Heavy metal concentrations measured in initial SSW and effluent samples at different stages of flushing: (a) unwashed biochar; (b) washed biochar

Washed biochar-Cr

- Chromium in the effluent were tested based on an initial concentration in the SSW (ISSW2) of 4.31 mg/L. Following the initial washing with clean deionized water, the chromium in the effluent was 0.29 mg/L. After three pore volumes of ISSW2 flushing, the biochar showed a removal efficiency of approximately 20%.
- Electrostatic attraction of Cr(VI) to the positively charged biochar surface.

3.3 Heavy metals

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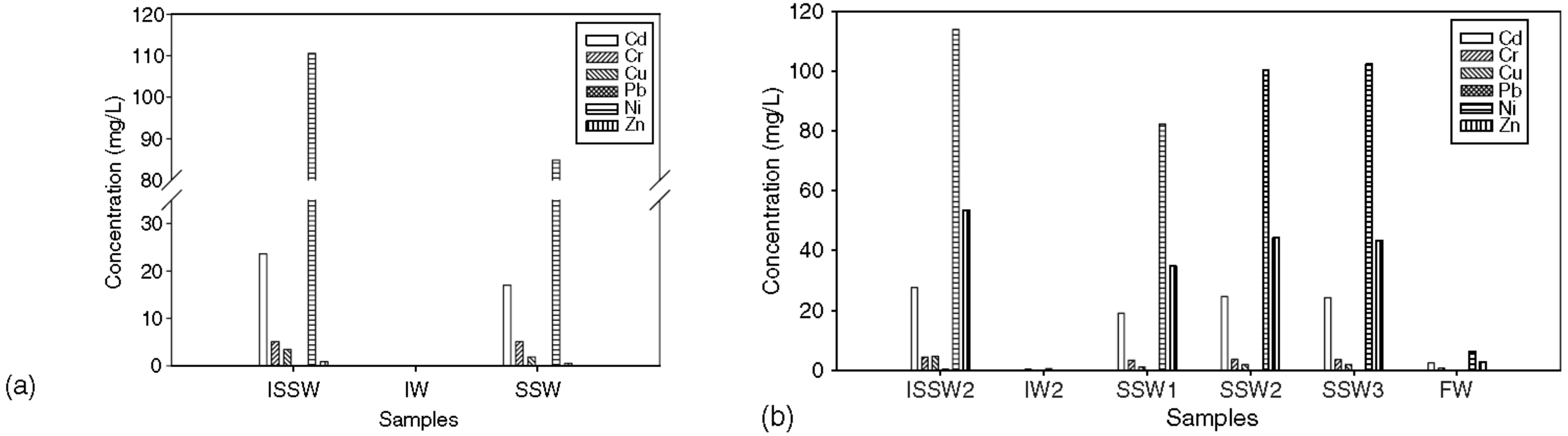

Heavy metal concentrations measured in initial SSW and effluent samples at different stages of flushing: (a) unwashed biochar; (b) washed biochar

Washed biochar-Cu

- An effluent copper of approximately 0.05 mg/L was found with the initial washing with deionized water. Thereafter, three pore volumes of SSW flushing were performed with an initial copper in the SSW of 4.63 mg/L. The results show that the concentrations in effluents were less than 2 mg/L.

3.3 Heavy metals

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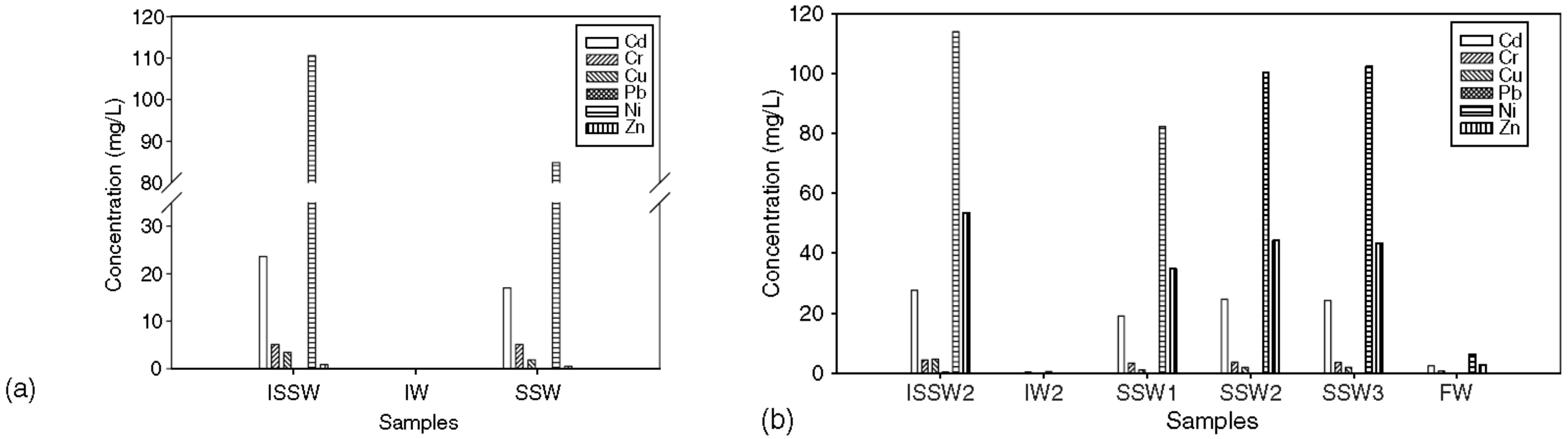
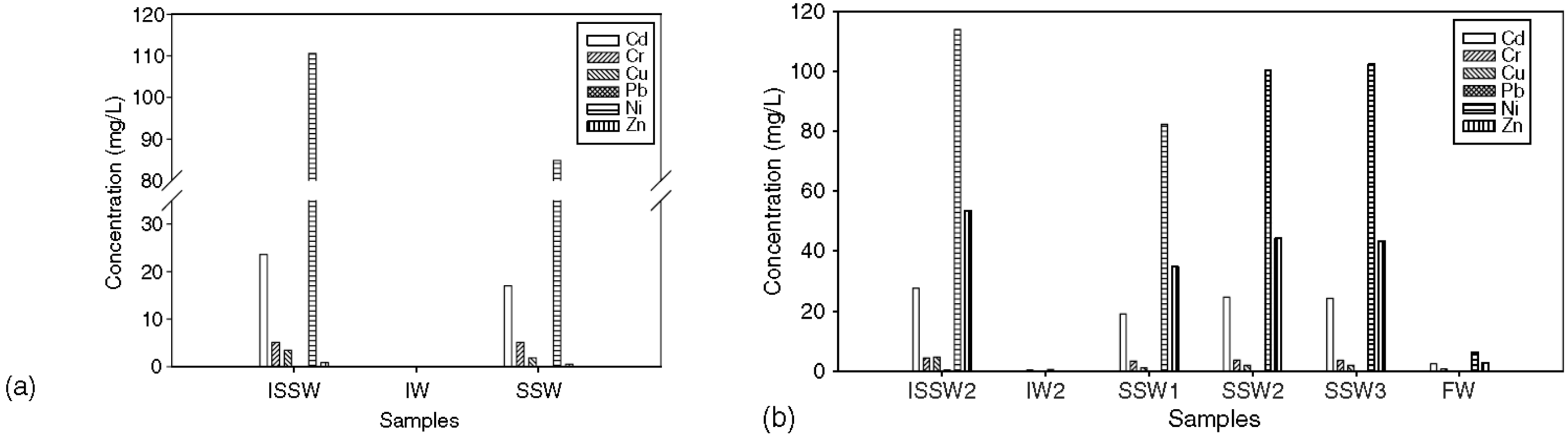


Heavy metal concentrations measured in initial SSW and effluent samples at different stages of flushing: (a) unwashed biochar; (b) washed biochar

Washed biochar-Pb

- Lead leached from the samples with deionized water flushing were approximately 0.48 mg/L. The concentrations of lead were observed as the three pore volumes of SSW (with an initial concentration of 0.36 mg/L) flushed through the washed media.
- Biochar mainly increased the lead adsorption through the nonelectrostatic mechanism via the formation of surface complexes between lead and functional groups on biochar.
- Biochar has a large amount of oxygen-containing groups on the surface, which is quite effective for lead removal.

3.3 Heavy metals

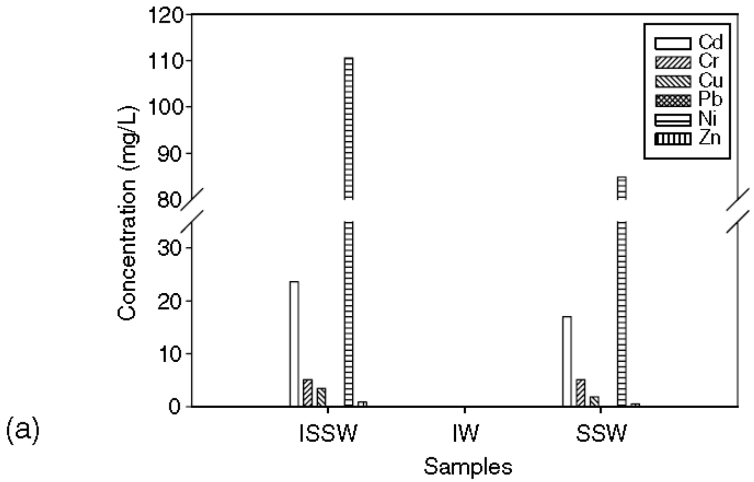


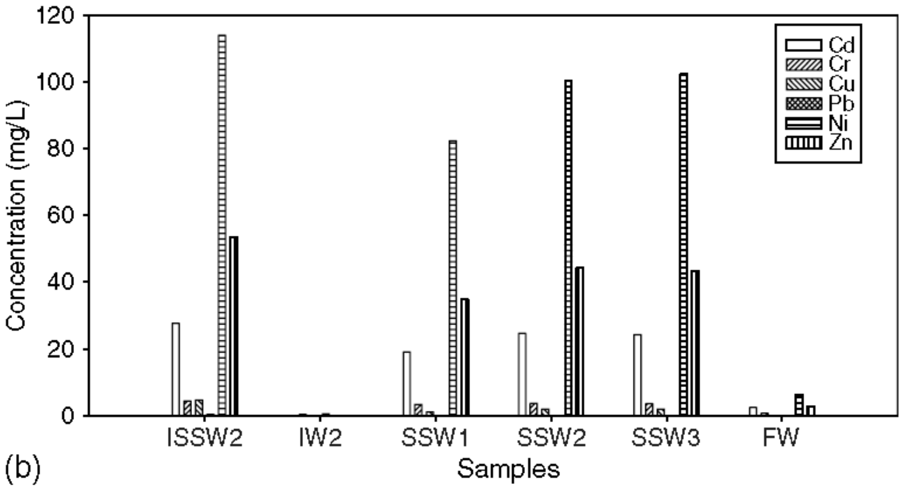
Heavy metal concentrations measured in initial SSW and effluent samples at different stages of flushing: (a) unwashed biochar; (b) washed biochar

Washed biochar-Ni

- Initial nickel leached from the samples with deionized water were negligible (approximately 0 mg/L in the effluent). The initial nickel concentration in the SSW was 113.92 mg/L. The first pore volume of flushing produced the lowest concentration of nickel in the effluent but displayed relatively low removal efficiency (less than 20%).
- Nickel removal occurs through a surface precipitation mechanism.

3.3 Heavy metals



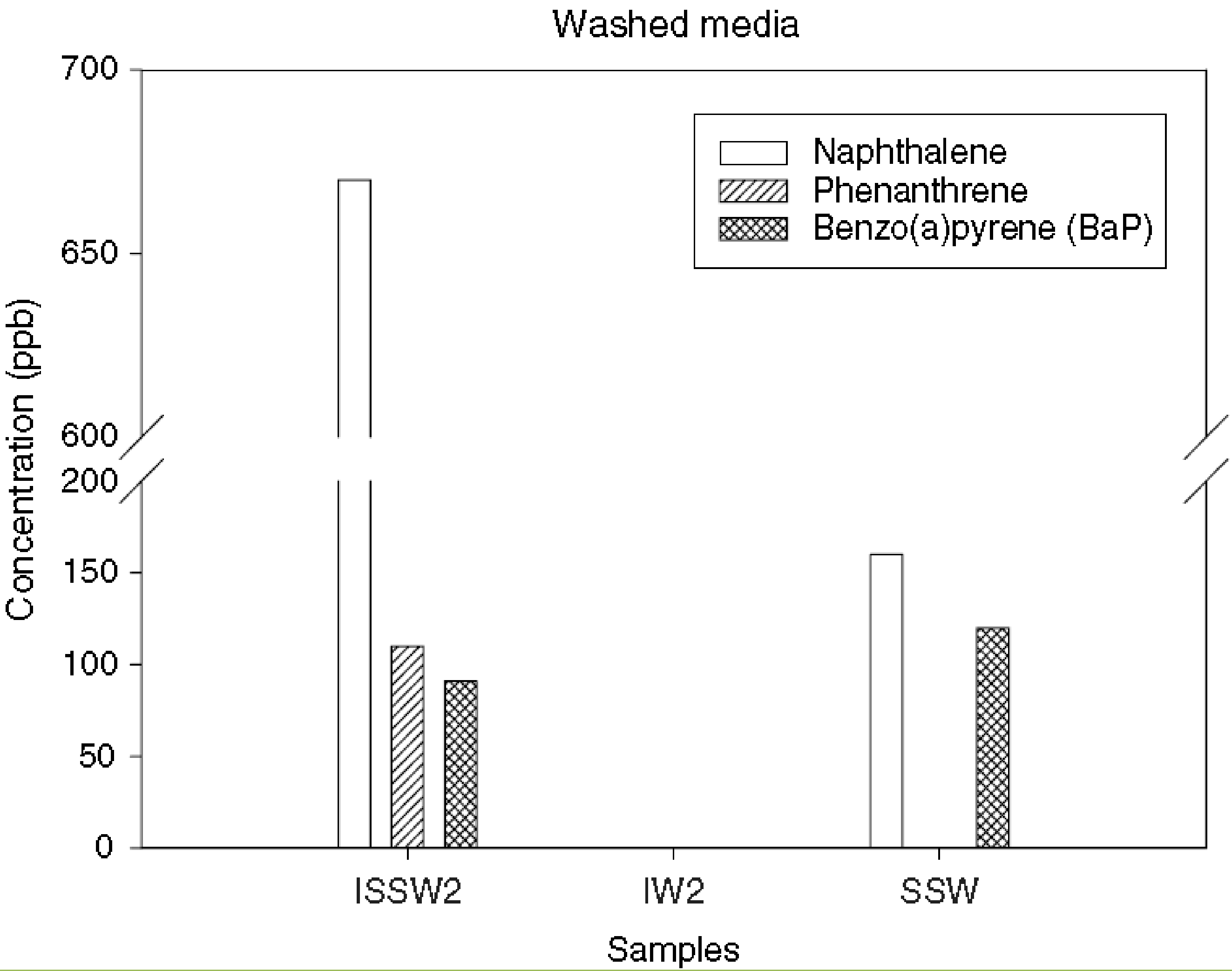


Heavy metal concentrations measured in initial SSW and effluent samples at different stages of flushing: (a) unwashed biochar; (b) washed biochar

Washed biochar-Zn

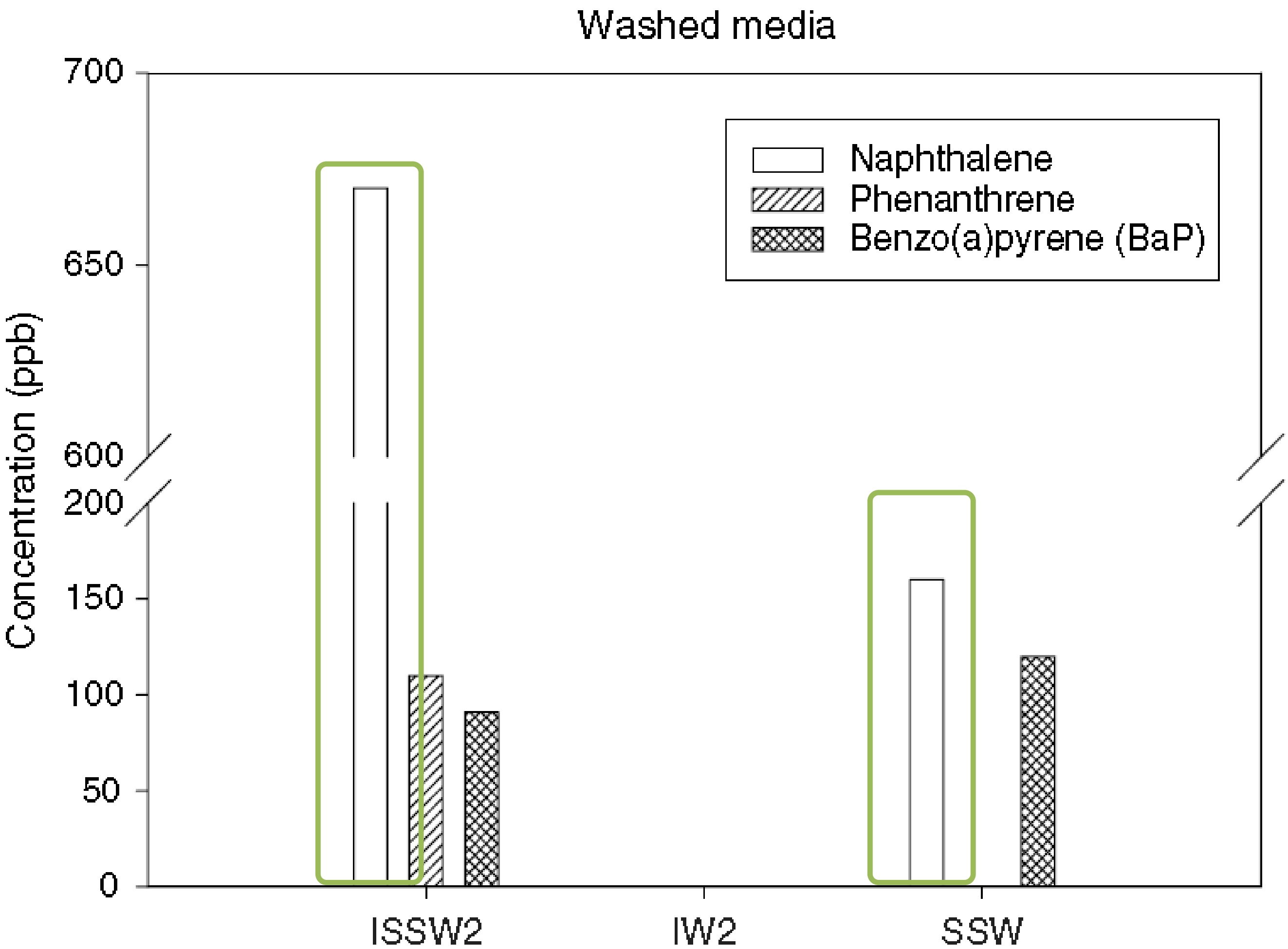
- Initial zinc in the SSW was 53.55 mg/L. The zinc concentrations leached during the initial deionized water flushing were insignificant. The zinc concentrations in the effluent during subsequent three pore volumes of SSW flushing resulted in high zinc concentrations in the effluent, approximately 40 mg/L, resulting in low removal efficiencies (approximately 20% on average).
- Relatively low removal efficiency might be due to the competition among different metals for binding sites on the surface of the biochar, which was confirmed for copper and zinc.

3.4 PAHs



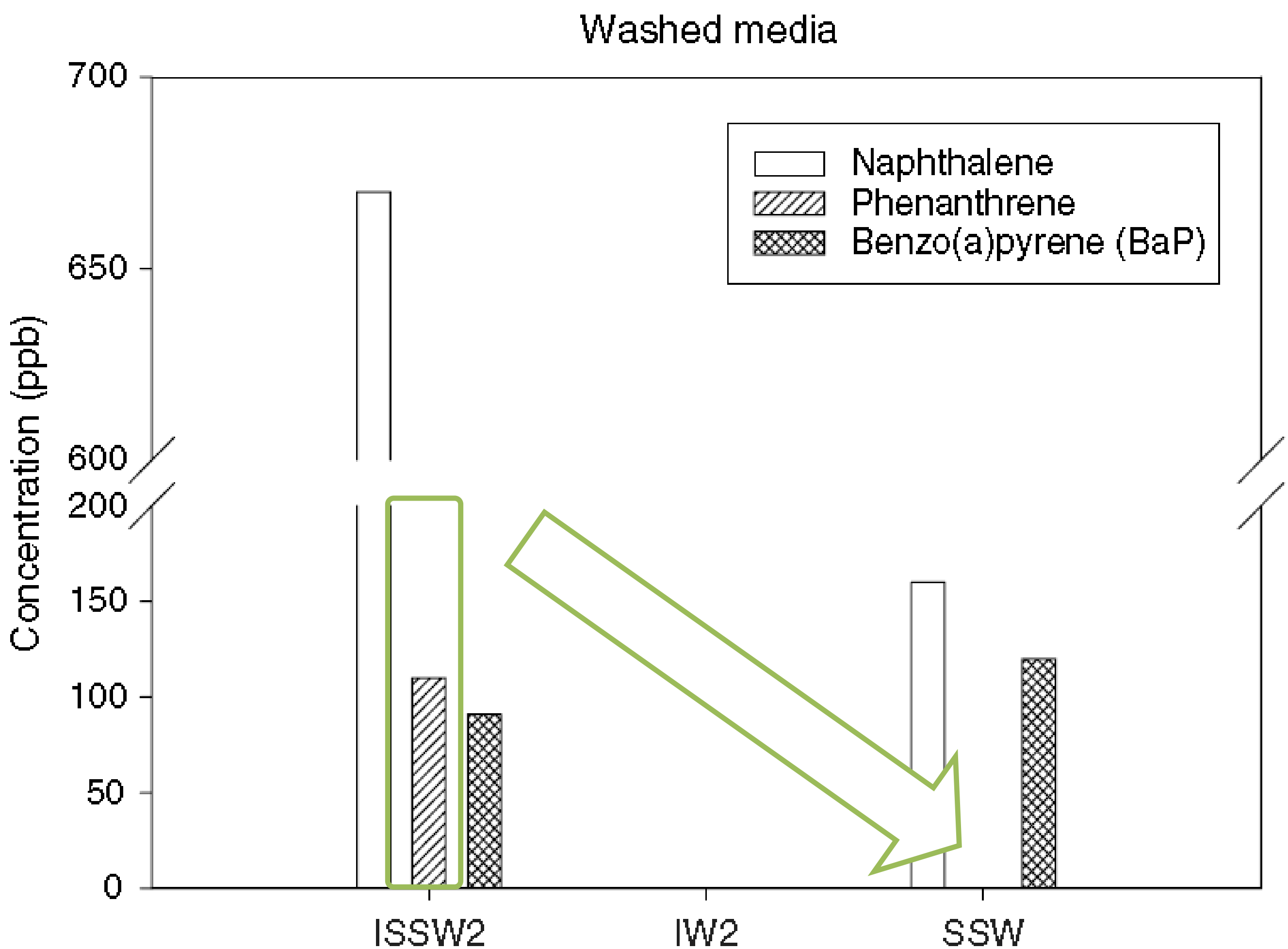
- No PAHs were detected in the effluent during the initial flushing with the deionized water (approximately 0 mg/L in the effluent).

3.4 PAHs



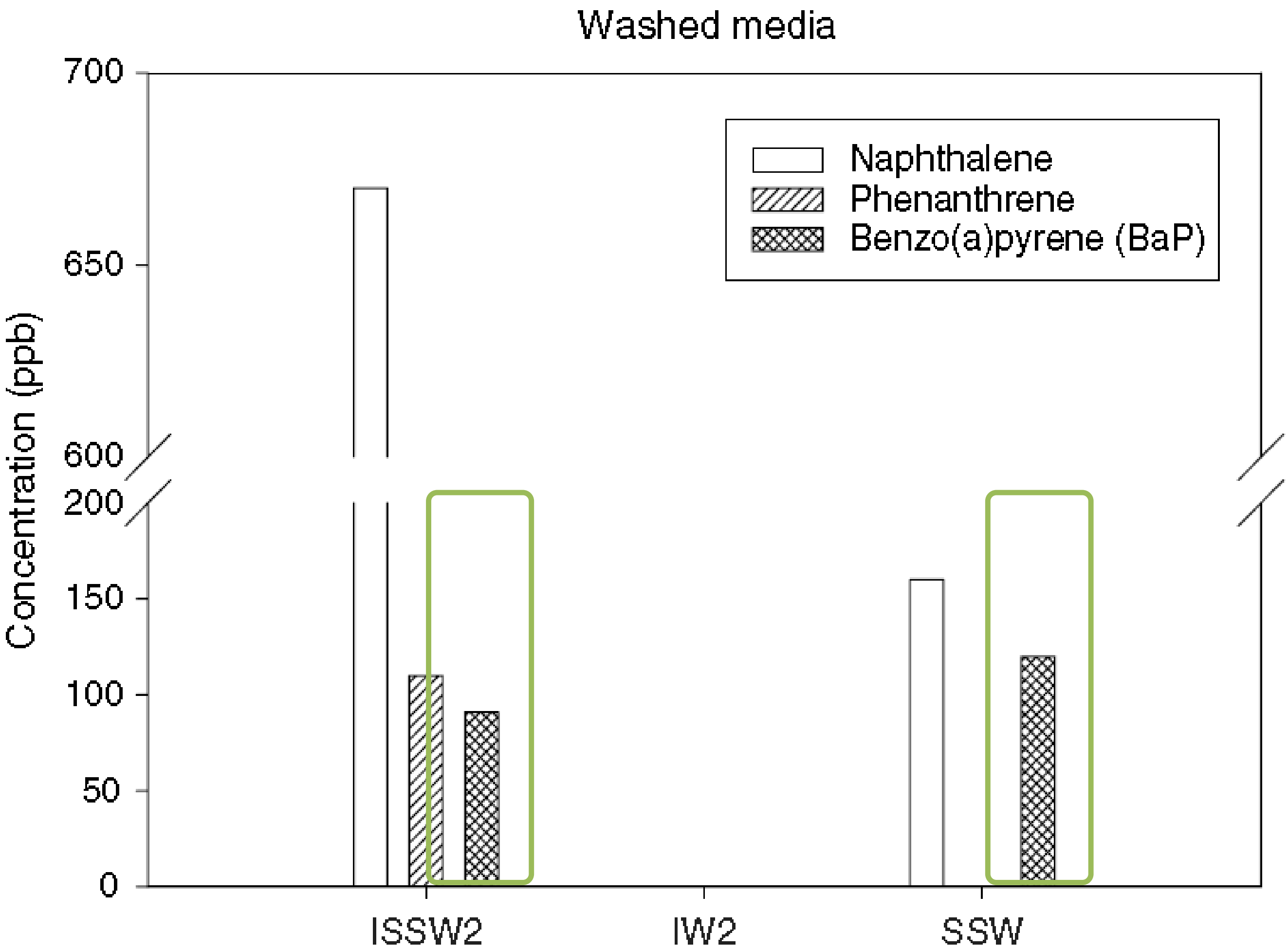
- Naphthalene concentration was reduced significantly. Biochar was able to adsorb naphthalene due to its specific interactions with naphthalene.

3.4 PAHs



- Phenanthrene was completely removed. Hydrothermal biochars consist of a lot of amorphous aliphatic-C, which may possibly be responsible for its high sorption capacity of phenanthrene.

3.4 PAHs



- In terms of BaP removal, biochar was least successful.

3.5 *E. coli*

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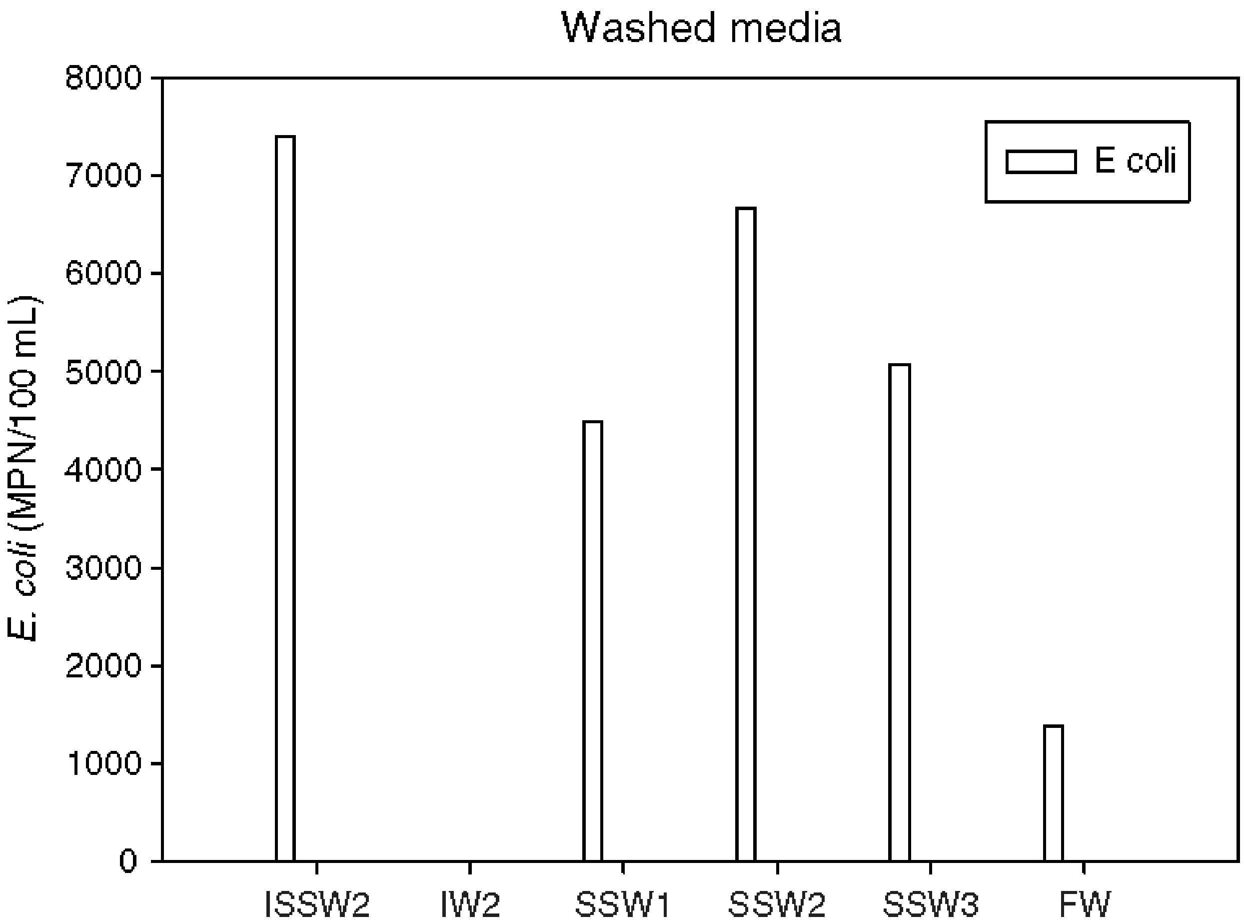

- Overall, biochar showed a low removal rate for E. coli—below 30% on average.
- Microbial removal was usually significantly affected by inflow concentration and antecedent microbial levels.

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1. Biochar reduced the TSS in the stormwater effluent by an average of 86% and, similarly, the concentrations of nitrate and phosphate were reduced by 86 and 47%, respectively.
2. Heavy metals such as cadmium, chromium, copper, lead, nickel, and zinc concentrations were decreased by 18, 19, 65, 75, 17, and 24%, respectively.
3. Overall 68% reduction in the total PAHs was found, but the removal of individual PAHs varied significantly. Phenanthrene was completely removed, 76% of naphthalene was removed; and none of BaP was removed.

4. Conclusions

4 Biochar was not efficient in removing E. coli from stormwater; the concentration of 7,400 MPN/100 mL in the inflow was reduced to 5,000 MPN/100 mL in the outflow, representing a mean removal efficiency of 27%.

5 Removal efficiency of the different contaminants showed that biochar has potential to be an effective medium for the treatment of selected contaminants found in stormwater.

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Evaluation of Biochar as a Potential Filter Media for the Removal of Mixed Contaminants from Urban Storm Water Runoff

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Abstract: Urban storm water runoff can carry a wide range of contaminants, many of which exceed federal maximum contaminant levels, into surface water resources (e.g., rivers and lakes). The use of filtration systems has received greater attention for its potential to remove particulate matter and other contaminants. Biochar is expected to have excellent potential as an adsorbent or filter given its large surface area

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Questions & Answers