Cost-Effective Hybrid Constructed Wetlands for Landfill Leachate Reclamation

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Final Report #

PROJECT TITLE: Cost-Effective Hybrid Constructed Wetlands for Landfill Leachate Reclamation

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PROJECT WEBSITE: http://constructed-wetlands.eng.usf.edu/

PROJECT DURATION: August 2019- May 2021

ABSTRACT: Landfill leachate is difficult to treat in conventional biological treatment processes due to high and variable concentrations of ammonia, recalcitrant organic matter, metals and salinity. Hybrid constructed wetlands (CWs) that combine vertical flow (VF) and horizontal flow (HF) stages are potential cost-effective methods for onsite landfill leachate treatment. The *overall goal* of this project was to enhance hybrid CW performance by using low cost adsorbent materials, zeolite and biochar, as CW media. These materials temporarily adsorb ammonium (NH_4^+) and recalcitrant organic matter, allowing more time for their biodegradation. The specific objectives of this research were to: (1) Compare conventional and adsobent amended hybrid CW performance for landfill leachate treatment; (2) Develop a numerical process model that can be used to predict the performance of the of the hybrid CWs under varying operational and leachate characteristics; and (3) Carry out a preliminary evalutation of post-treatment requirements for landfill leachate reuse applications. Side-by-side bench-scale sequencing batch biofilm reactor (SBBR) leachate treatment studies were initially conducted with and without adsorptive media. Although high total nitrogen (TN) removals were observed in all SBBRs, higher color and soluble chemical oxygen demand (sCOD) removals were observed in the biochar amended system. Pilot-scale hybrid CWs, with and without zeolite and biochar, were operated at Hillsborough County's Southeast landfill from August 2020-May 2021. Zeolite significantly improved ammonia removal from 63% in the unamended CW to 91% in the adsorbent amended CW by increasing oxygen availability to nitrifying bacteria under variable flow conditions. Significantly higher sCOD removal was also observed in the adsorbent-enhanced CW (55%) than in the unamended control (28%). Biochar addition also effectively enhanced color removal (33% to 67%) and dramatically improved the growth of wetland plants, cordgrass and cattails. A numerical process model was developed that tracks the mass balance of water, oxygen, and nitrogen species through the CWs. The model can be used to predict the performance of hybrid CWs under varying operational and leachate characteristics. A preliminary investigation showed that adsorbent enhanced CW treated leachate has the potential to be reused for either non-food crop irrigation or industrial cooling water. However, post-treatment using ultrafiltration and reverse osmosis (UF-RO) would be needed to reduce the high salinity and metals concentrations for these reuse applications.

Key words:
Biochar; Bioregeneration ; Clinoptilolite; Constructed wetlands; Hybrid subsurface flow treatment wetlands; Landfill leachate; Sequencing Batch Biofilm Reactor (SBBR); Water reclamation; Wetland system modeling ; Zeolite

METRICS REPORTING

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Metrics:

1. List research publications resulting from this Hinkley Center project.

Gao, B. (2020) Enhanced Nitrogen, Organic Matter and Color Removal from Landfill Leachate by Biological Treatment Processes with Biochar and Zeolite, MS Thesis, Department of Civil & Environmental Engineering, University of South Florida.

Gao, B. Yang, X., Arias, M. Ergas, S.J. Enhanced nitrogen, organic matter and color removal from landfill leachate in a sequencing batch biofilm reactor (SBBR) with biochar and zeolite addition, *J. Chemical Technology & Biotechnology* (To be submitted in May, 2021).

2. List research presentations resulting from this Hinkley Center project.

Gao, B. (2020) Enhanced Nitrogen, Organic Matter and Color Removal from Landfill Leachate by Biological Treatment Processes with Biochar and Zeolite, Thesis Defense, Department of Civil & Environmental Engineering, University of South Florida, 3/11/2020.

Ergas, S.J., Arias, M.A. (2020) Cost-Effective Hybrid Constructed Wetlands for Landfill Leachate Reclamation, SWANA Hinkley Center Symposium (online webinar), 10/14/2020.

Lam, T., Mulligan, L. (2020) Cost-Effective Hybrid Constructed Wetlands for Landfill Leachate Reclamation, S-STEM Scholars Roundtable Meeting, University of South Florida. 11/20/2020.

Yang, X., Lam, T., Mulligan, L., Ergas, S.J., Arias, M. (2021) Enhanced Nitrogen, COD and Color Removal from Landfill Leachate in Treatment Wetlands with Biochar and Zeolite, *Proc. American Ecological Engineering Society Annual Meeting*, May 26, 2021 (virtual).

3. List who has referenced or cited your publications from this project.

Nothing to report at this time.

4. How have the research results from this Hinkley Center project been leveraged to secure additional research funding? What grant applications have you submitted or are planning on submitting?

NSF S-STEM scholarships were secured ($6,400 per student per year) for MS students Lillian Mulligan and Thanh Lam.

USF's Department of Civil & Environmental Engineering provided teaching assistantships for students Thanh Lam, Erica Dasi, and Xia Yang.

PhD student Erica Dasi was supported through a McKnight Doctoral Fellowship and an NSF Research Traineeship.

Undergraduate student Magdalena Shafee, was supported by an NSF REU supplement.

USF Strategic Investment Pool grant was obtained ($10,000) to acquire equipment to produce and test biochar from waste materials.

Co-PI Mauricio Arias received a McKnight Junior Faculty Fellowship from the Florida Education Fund.

Ergas, S.J., Nachabe, M. (to be submitted June 2021) Demonstration of Biochar Enhanced Bioretention for Treatment of Agricultural Runoff, Florida Department of Agriculture and Consumer Services, $120,000.

Ergas, S.J., Nachabe (submitted April 2021, currently in review) BioPod-Hybrid Adsorption Biological Treatment Systems (HABiTS) for stormwater, Oldcastle Industries, $75,000.

5. What new collaborations have been initiated based on THIS Hinkley Center Project?

Name	**Affiliation**	**Email**	**Notes**
Todd Anderson	Geosyntec	TAnderson@Geosyntec.com	Included PIs on team to manage Florida landfill
Viraj deSilva	Environmental Solutions	viraj.desilva@freese.com	New TAG member with expertise in PFAS management, and leachate/wastewater treatment
Scott Knight	Wetland Solutions	sknight@wetlandsolutionsinc.com	New TAG member with expertise in treatment wetlands for pollution control

6. How have the results from this Hinkley Center project been used by the FDEP or other stakeholders?

Nothing to report at this time.

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The PIs thank the Hinkley Center for Solid and Hazardous Waste Management for funding this research and their guidance in carrying out this research.

We especially thank the USF Civil & Environmental Engineering department student researchers who worked on this project:

- Erica Dasi (eadasi@usf.edu): Ms. Dasi is a PhD Candidate in the Department of Civil & Environmental Engineering. She has BS and MS degrees from the University of Maryland Baltimore County. Her research focuses on autotrophic denitrification of water and wastewater, including landfill leachate. Ms. Dasi is expected to defend her dissertation in May 2022.
- Bisheng Gao (gbisheng@163.com): Mr. Gao received his MS in Environmental Engineering from USF in spring 2020. His thesis focused on the use of adsorbent enhanced sequencing batch biofilm reactors (SBBRs) for landfill leachate treatment. He is currently working at the Shanghai Academy of Environmental Sciences (SAES).
- Thanh "Misty" Lam (ttlam@usf.edu): Ms. Lam is a MS student in the Department of Civil & Environmental Engineering and has a BS in Environmental Engineering from the University of Central Florida. Her thesis focuses on upgrading constructed wetlands treated landfill leachate for agricultural irrigation using UF-RO treatment. She is also working as an intern for Jacobs Engineering and expects to graduate in Fall 2021.
- Lillian Mulligan (lillianm@usf.edu): Ms. Mulligan is a MS student in the Department of Civil & Environmental Engineering. She has a BS in Computer Science and Mathematics from Florida Southern College. Her thesis focuses on modeling physical, chemical and biological processes in adsorbent enhanced constructed wetlands and she expects to graduate in Summer 2021.
- Magdalena Shafee (mps1@usf.edu): Ms. Shafee is an undergraduate student in the Department of Civil & Environmental Engineering at USF. She has assisted with research on autotrophic denitrification of landfill leachate. She is currently working as an intern with Turner Construction Co. and expects to graduate in Fall 2021.
- Xufeng Wei (alexwei1@163.com): Mr. Wei received his MS in Environmental Engineering from USF in fall 2019 and continued to work on this project during Spring 2020 as a volunteer. Mr. Wei is currently working as a research assistant in the School of Resources and Environment at the University of Electronic Science and Technology of China (UESTC; Chengdu, China).
- Xia Yang (xiayang@usf.edu): Ms. Yang is a PhD Candidate in the Department of Civil & Environmental Engineering. She has BS and MS degrees from the School of Environmental Science and Engineering in Tianjin University (China). Her research focuses on biochar enhanced processes for anaerobic digestion and constructed wetlands treatment of landfill leachate. Ms. Yang is expected to defend her dissertation in May 2022.

We would also like to thank our Technical Awareness Group for their guidance on this project:

Name	**Position/Affiliation**	**Affiliation**
James S. Bays	Technology Fellow	Jacobs Engineering
Kimberly A. Byer	Solid Waste Management Division Director	Hillsborough County
Stephanie Bolyard	Research and Scholarship Program Manager	Environmental Research & Education Foundation
William J. Cooper	Prof. Emeritus	UC Irvine (Courtesy Prof. UF)
Ashley Danely-Thomson	Assistant Professor	Florida Gulf Coast University
Ashley Evans	Market Area Engineer	Waste Management, Inc., Florida
Melissa Madden-Mawhir	Senior Program Analyst	Florida Department of Environmental Protection
Larry E. Ruiz	Landfill Operations Manager	Hillsborough County

Lastly, we would like to thank the operators at Hillsborough County's Southeast Landfill, the members of the USF Environmental Engineering laboratory and Dr. Zachary Atlas of the USF Center for Geochemical Analysis for their contributions to this project.

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LIST OF ACRONYMS AND ABBREVIATIONS

BNR	Biological Nutrient Removal
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
C-SBBR	Control Sequencing Batch Biofilm Reactor
CW	Constructed Wetland
CZB-SBBR	Sequencing Batch Biofilm Reactor with Zeolite and Biochar
CZ-SBBR	Sequencing Batch Biofilm Reactor with Zeolite
DI	Deionized water
DO	Dissolved Oxygen
EBCT	Empty Bed Contact Time
ET	Evaporation and Transpiration
FA	Free Ammonia
G-CW	Control Constructed Wetland with Gravel media
GZB-CW	Constructed Wetland with Grave, Zeolite, and Biochar media
HF	Horizontal Flow
HRT	Hydraulic Retention Time
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
IX	Ion Exchange
LECA	Light Expanded Clay Aggregate
MLSS	Mixed Liquor Suspended Solids
MSW	Municipal Solid Waste
NOD	Nitrogenous Oxygen Demand
NTU	Nephelometric Turbidity Units
POTWs	Publicly Owned Treatment Works
rbCOD	Readily Biodegradable COD
RO	Reverse Osmosis
S^0	Elemental Sulfur
SBBR	Sequencing Batch Biofilm Reactor
sCOD	Soluble Chemical Oxygen Demand
SDI	Silt Density Index
TAN	Total Ammonia Nitrogen
TIN	Total Inorganic Nitrogen
TN	Total Nitrogen
TON	Total Organic Nitrogen
TP	Total Phosphorus
TSS	Total Suspended Solids
UF	Ultrafiltration
USF	University of South Florida
UV	Ultraviolet
VF	Vertical Flow
VSS	Volatile Suspended Solids

EXECUTIVE SUMMARY

Landfill leachate is difficult to treat in conventional biological treatment processes due to high and variable concentrations of ammonia, recalcitrant organic matter, metals and salinity. Hybrid constructed wetlands (CWs) that combine vertical flow (VF) and horizontal flow (HF) stages are a potential cost-effective onsite landfill leachate treatment method. The *overall goal* of this project was to enhance CW performance using low cost adsorbent materials, zeolite and biochar, as media. These materials temporarily adsorb ammonium (NH_4^+) and recalcitrant organic matter, allowing more time for their biodegradation. The *specific objectives* of this research were to:

(1) Compare conventional and adsobent amended hybrid CW performance for landfill leachate treatment;
(2) Develop a numerical process model that can be used to predict the performance of the of the hybrid CWs under varying operational and leachate characteristics; and
(3) Carry out a preliminary evalutation of post-treatment requirements for landfill leachate reuse applications.

Batch adsorption studies were used to investigate adsorption capacities of zeolite and biochar for ammonia, soluble chemical oxygen demand (sCOD) and color (UV 456) in landfill leachate. Subsequently, three bench-scale Sequencing Batch Biofilm Reactor (SBBRs) were designed with different media: (1) light weight expanded clay aggregate (LECA) as a control (C-SBBR), (2) LECA + zeolite (CZ-SBBR), and (3) LECA + zeolite + biochar (CZB-SBBR). SBBRs were operated with alternating anoxic and aerobic stages with leachate from Hillsborough County's Southeast Landfill. Excellent ammonia removals (> 99%) were achieved in all three SBBRs throughout the study. The combined addition of zeolite and biochar in CZB-SBBR resulted in significantly higher sCOD (61-83%) and color (82-95% as UV456) removal compared with C-SBBR (42-44% and 28-33%) and CZ-SBBR (34-45% and 20-35%). Although high effluent NO_3^- concentrations were initially observed in the biochar amended reactor, after > 1 year of operation NO_3^- accumulation declined and total nitrogen (TN) removals increased to > 70%, most likely due to combined nitrification/denitrification and anammox activity.

Two pilot-scale hybrid VF-HF CWs were designed for comparison of leachate treatment performance with and without adsorbent media (Fig. ES1). G-CW contained a conventional gravel medium as a control, while GZB-CW included zeolite in the VF stage to enhance nitrification and biochar in the HF stage to enhance recalcitrant organic matter removal. The units were set up and operated at Hillsborough County's SE landfill from August 2020-May 2021. An acclimation phase was applied for 50 days, followed by 20 days of flow-through operation without plants. Cattail (*Typha spp*) and cordgrass (*Spartina*) were planted in early November 2020.

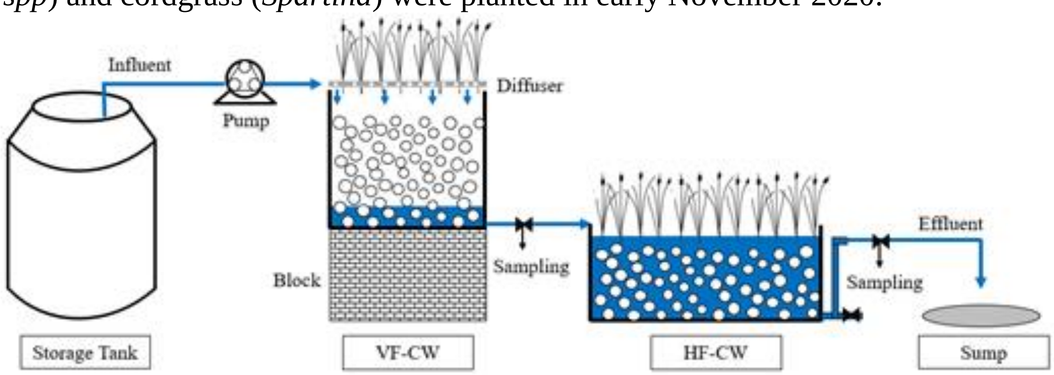

Figure ES1. Pilot VF-HW CW schematic.

Biochar addition significantly increased sCOD removal efficiency in the adsorbent-amended VF-HF CW (55%) than in the unamended control (28%). Biochar also increased color removal from 33% to 67%. sCOD and color trends were similar to the bench-scale study, confirming that adsorption of recalcitrant organic matter in leachate enhances biodegradation. Biochar also dramatically improved the growth of cordgrass and cattails, most likely because of reduced heavy metal toxicity and enhanced growth of beneficial microorganisms in the rhizosphere. Zeolite addition significantly increased ammonia removal from 63% in the un-amended CW to 91% in the adsorbent amended CW. In the intermittently loaded VF-CW, NH_4^+ adsorbed to zeolite during the wetting period and was subsequently nitrified as oxygen filled the media pores during the drainage period. NO_3^- accumulation was observed in the effluent from both CWs, most likely due to limited organic carbon availability for denitrification due to the low BOD_5/COD ratio (~ 0.1) of the leachate. Batch microcosm experiments carried out with nitrified landfill leachate showed that a low-cost solid electron donor, elemental sulfur pellets (S^0), could be added to the CWs to enhance denitrification. Overall, the study achieved excellent results with the adsorbent-enhanced CW compared with the unamended control.

A numerical process model was developed that tracks the mass balance of water, oxygen, carbon and nitrogen species through the CWs. The model was tested with local weather data, measured influent concentrations, and parameter values from well-cited literature. Preliminary results indicate the model is able to replicate the hybrid CWs' treatment abilities and the conversion of nitrogen species. The model calculates effluent concentrations each day and thus provides a higher temporal resolution than the experimental data. In addition, longer-term performance projections are made using the model. A sensitivity analysis currently under development will give further insight to which parameter(s) are greatly affecting the model and aid in calibrating the model to better fit the experimental data. The model can then be used to predict the performance of hybrid CWs under varying operational and leachate characteristics.

A preliminary comparison of effluent characteristics from the pilot CWs with FDEP reuse standards and reuse guidelines from the literature showed that adsorbent enhanced CW treated leachate has the potential to be reused for either non-food crop irrigation or industrial cooling. However, post-treatment using ultrafiltration and reverse osmosis (UF-RO) would be needed prior to reuse to reduce the high salinity and metals concentrations. An analysis of UF-RO is currently underway using Dupont's Water Application Value Engine (WAVE) software as a design tool.

Despite restrictions due to the COVID-19 pandemic, our Hinkley Center project engaged six graduate (4 MS, 2 PhD) and one undergraduate USF students in MSW management research. The project was incorporated into one MS thesis, and will be incorporated into two additional MS theses and one PhD dissertation. The project was incorporated into classes taught by the PIs, presented at two USF seminars, one regional webinar (FL SWANA) and one national conference (American Ecological Engineering Society). Three peer reviewed journal articles are expected from this research. The PIs received an internal grant from USF's Strategic Investment Pool for equipment for biochar production and have submitted proposals to the Florida Department of Agriculture and Consumer Services and Oldcastle Industries for related research on the topic of agricultural runoff management. Additional student and faculty support was obtained from the NSF S-STEM scholarship program and the Florida Education Fund, as well as TA support from USF's Civil & Environmental Engineering department.

INTRODUCTION

There are > 1,900 active landfills in the US, accepting > 250 million tons of municipal solid waste (MSW; USEPA, 2014). Landfills in the US generate a total of 61.1 million m^3 of leachate (Lang et al., 2017), which must be properly collected and treated to prevent ground and surface water pollution (USEPA, 2000). Most leachate in Florida is discharged to publicly owned treatment works (POTWs); however, high concentrations of ammonia, chemical oxygen demand (COD), recalcitrant organic matter, metals and salinity interfere with physical, chemical and biological processes at POTWs. For this reason, many MSW managers are seeking alternatives for onsite treatment and reuse of landfill leachate. Prior studies have shown that constructed wetlands (CWs) are a cost-effective method for onsite landfill leachate treatment (Vymazal and Kröpfelová, 2009) and volume reduction (Ogata et al., 2015). While detailed design principles exist for wastewater CWs (Kadlec and Wallace, 2008), documentation of leachate management in CWs has been sporadic, with results from case studies suggesting a wide range of performance dictated by design, operation, and leachate characteristics (Mulamoottil et al., 1999). Thus, enhancing CW performance using low-cost media materials and investigating how CWs could be designed and operated for varying leachate characteristics would greatly alleviate key leachate management issues and improve the potential for its safe discharge and reuse.

Hypotheses and Objectives

The *overall goal* of this project was to develop cost-effective hybrid CWs for treatment of landfill leachate for reuse applications. The project was guided by the following hypotheses:

(1) Addition of zeolite, a natural mineral with a high NH_4^+ affinity, to VF-CW media reduces free ammonia toxicity to microorganisms and enhances biological nitrogen removal.
(2) Addition of biochar, a low-cost material produced from organic feedstocks such as wood, to HF-CW media enhances plant growth and retains recalcitrant organic matter, such as humic acids, to enhance its heterotrophic biodegradation.
(3) Adsorbent amended hybrid CWs can provide a cost-effective and low complexity landfill leachate treatment method compared with conventional onsite leachate treatment systems.

The *specific objectives* were to:

(1) Compare conventional and adsorbent amended hybrid CW performance for landfill leachate treatment;
(2) Develop a numerical process model that can be used to predict the performance of the hybrid CWs under varying operational and leachate characteristics; and
(3) Carry out a preliminary assessment of post-treatment requirements for reuse applications.

Background

Landfill Leachate

The flow rates and composition of landfill leachate are highly variable due to differences in waste composition, design and operation, moisture content, oxygen availability, climate, and landfill age. Landfill leachate is difficult to treat in conventional POTWs due to high and variable ammonia, refractory organic matter, metals and salinity concentrations (Zhao et al. 2012). Impacts of landfill leachate on conventional biological nitrogen removal (BNR) processes include: 1) nitrification inhibition by high free ammonia (FA) concentrations and the presence of toxic metals, 2) increased aeration demands (and thus energy requirements) for nitrification and organic carbon oxidation,

3) increased organic carbon requirements for denitrification due to low concentrations of readily biodegradable COD (rbCOD), 4) UV-quenching substances interfere with UV disinfection (Bolyard, 2016), and 5) high salinity interferes with oxygen transfer and sludge settling and the ability of POTWs to meet effluent conductivity standards. Onsite leachate treatment systems include landfill recirculation, evaporation, aerated lagoons and sequencing batch reactors. Physical and chemical processes, such as filtration, flocculation, ion exchange (IX), granular activated carbon adsorption and membrane processes (i.e., UF-RO), are also used for leachate treatment (USEPA, 2000).

Constructed Wetlands

CWs treat leachate through physical, chemical and biological processes (Sun and Austin, 2007; Vymazal and Kröpfelová, 2009). Leachate management with CWs is especially suitable to Florida, where the warm climate is conducive to year-round plant growth, high biological activity, and high rates of evaporation and transpiration (ET). Hybrid subsurface flow CWs that combine vertical flow (VF) and horizontal flow (HF) processes provide both the high oxygen transfer rates needed for nitrification and anoxic conditions needed for denitrification. Prior long-term studies of hybrid VF-HF CW treatment of landfill leachate show that they can provide moderate removal of total suspended solids (TSS), biochemical oxygen demand (BOD), total nitrogen (TN) and metals (Table 1). CW can also reduce the net volume of leachate via ET when compared to evaporation alone (Ogata et al., 2015; Białowiec et al, 2014). Landfill leachate treated by CWs; however, can have high levels of conductivity and high concentrations of dissolved solids and heavy metals, making it unsuitable for irrigation or industrial reuse without additional treatment.

Table 1: Summary of leachate treatment performance with subsurface flow wetlands.

Pollutant type	Inflow concentration (mg/L)	Removal (%)	System type	Source
TN	211	40-84	HF	Sim et al. (2013); Vymazal and Kröpfelová (2009)
	225.7	94	VF-HF	Saeed et al. (2020)
	197.6-411.2	50-93	VF-HF	Saeed et al. (2021)
Ammonia-N	162	40	HF	Vymazal and Kröpfelová (2009)
	122	37-67	VF	Yalcuk and Ugurlu (2009)
	122	30-49	HF	Yalcuk and Ugurlu (2009)
	496	51	VF-HF	Bulc. (2006).
	2484	45-69	VF	Silvestrini et al. (2019)
	478	89	VF-HF	Silvestrini et al. (2019)
	156.1	99	VF-HF	Saeed et al. (2020)
Organic N	18.8	47	HF	Vymazal and Kröpfelová (2009)
TKN	48.8	56	HF	Vymazal and Kröpfelová (2009)
NOx	15.8	19	HF	Vymazal and Kröpfelová (2009)

Table 1: Summary of leachate treatment performance with SSF CWs (cont.).

Pollutant type	Inflow concentration (mg/L)	Removal (%)	System type	Source
NO_2^--N	2497	29-59	VF	Silvestrini et al. (2019)
	5.7	99	VF-HF	Saeed et al. (2020)
NO_3^--N	12.5	12-52	VF	Silvestrini et al. (2019)
	34.5	86	VF-HF	Saeed et al. (2020)
COD	212	13-36	VF	Yalcuk and Ugurlu (2009)
	212	11-61	HF	Yalcuk and Ugurlu (2009)
	485	50	VF-HF	Bulc. (2006).
	3023	44-55	VF	Silvestrini et al. (2019)
	519	66	VF-HF	Silvestrini et al. (2019)
	829	86	VF-HF	Saeed et al. (2020)
	780.4-1275.3	55-76	VF-HF	Saeed et al. (2021)
BOD	-	47	HF	Sim et al. (2013)
	76	59	VF-HF	Bulc. (2006).
	837	60-80	VF	Silvestrini et al. (2019)
	315.8	97	VF-HF	Saeed et al. (2020)
	248.3-294.7	34-89	VF-HF	Saeed et al. (2021)
PO_4^{3-}-P		37-67	HF	Yalcuk and Ugurlu (2009)
	2.3	53	VF-HF	Bulc. (2006).
	30.2	100	VF-HF	Saeed et al. (2020)
	16.4-47.9	69-100	VF-HF	Saeed et al. (2021)
Sulfides	0.05	49	VF-HF	Bulc. (2006).
Chlorides	1369	35	VF-HF	Bulc. (2006).
TSS	345.9	95	VF-HF	Saeed et al. (2020)
	-	57	HF	Sim et al. (2013)
Cd	-	92	VF	Bakhshoodeh et al. (2020)
	-	56	HF	
Cr	-	90	VF	Bakhshoodeh et al. (2020)
	-	32	HF	
Cu	-	14	HF	Bakhshoodeh et al. (2020)
	-	62	VF-HF	
Ni	-	38	HF	Bakhshoodeh et al. (2020)
	-	30	VF-HF	
Pb	-	84	VF	Bakhshoodeh et al. (2020)
	-	43	HF	
Zn	-	89	VF	Bakhshoodeh et al. (2020)
	-	57	HF	
Fe	-	94	VF	Bakhshoodeh et al. (2020)
	-	57	HF	
Mn	-	77	VF	Bakhshoodeh et al. (2020)
	-	49	HF	

Note: data reported with number of significant figures reported by the authors.

Use of Natural Zeolites to Enhance Biological Treatment Processes

The high ammonia concentrations present in landfill leachate (300-2000 mg/L) are problematic for conventional BNR processes. High FA concentrations promote an imbalance in intracellular and extracellular pH of bacteria, affecting the proton motive force and inhibiting many energy-requiring functions of the cell (Martinelle et al., 1996). High ammonia concentrations can also be detrimental to vegetation in CWs (Kadlec and Zmarthie, 2010). To control this issue, two-stage CWs with recirculation of treated effluent have been used to dilute the strength of the leachate being treated (Camaño Silvestrini et al., 2019).

Natural zeolites are porous aluminosilicate minerals with high IX capacities and selectivity for NH_4^+ (Hedström, 2001). They have been used to remove ammonia from swine wastewater (Amini et al., 2017) and landfill leachate (Kargi & Pamukoglu, 2004). Clinoptilolite is the most commonly used zeolite due to its low cost; however, chabazite has a higher NH_4^+ capacity (Amini et al., 2017). In prior studies in our laboratory, natural zeolite materials have been used to enhance nitrogen removal by temporarily adsorbing NH_4^+, which reduces shock loads to sensitive microbial populations. Zeolite amended sequencing batch reactors (SBRs) were used for treatment of centrate produced from anaerobic digestion of swine manure (Aponte-Morales et al. 2016). Zeolite addition consistently reduced FA concentrations below inhibitory levels, resulting in a doubling of the nitrification rate (Aponte-Morales et al., 2018). Importantly, the zeolite materials were *bioregenerated*, eliminating the need for chemical addition or production of waste brines.

Several prior studies investigated zeolite treatment of landfill leachate (Kargi and Pamukoglu, 2004; Luna et al., 2007). ZELIC, which consists of zeolite, GAC, limestone, rice husk ash and Portland cement has been used for co-treatment of landfill leachate and domestic wastewater, with high removal efficiencies of color, ammonia, and COD (Mojiri et al., 2014). Yalcuk and Ugurlu (2009) compared the performance of VF-CWs with and without zeolite addition for treatment of aged leachate from a landfill in Ankara Turkey. Better ammonia removal was observed in the CW system with zeolite than without.

Use of Biochar to Enhance Biological Treatment Processes

Biochar is a low-cost material produced by pyrolysis of organic feedstocks, such as wood chips, at high temperature under oxygen limiting conditions. In agriculture, biochar is used as an amendment to improve the quality of soils (Chan et al., 2007; Lehmann et al., 2011; Xu et al., 2012). Previous studies have shown that biochar addition to soil increases the surface area, surface charge, moisture holding capacity, and soil fertility and attracts beneficial fungi and microbes that enhance plant growth (Mohanty et al., 2014; Lehmann, 2007; Lehmann et al., 2006). Currently our research group is investigating the addition of biochar to bioretention cells for treatment of dairy farm runoff. In side-by-side bench-scale column studies, biochar amended achieved significantly higher TN and fecal indicator bacteria removals than unamended columns (Rahman et al., 2020).

Due to its unique micro-physicochemical properties, such as high surface area, porous structure and various functional groups, biochar has a high adsorption capacity for sCOD, color, nutrients and metals (Lau et al. 2017; Liang et al. 2006; Hale et al. 2012). In addition, biochar addition to CWs has the potential to increase plant growth by reducing the stress of toxic metals and organics on plants (Kasak et al. 2018; Gupta et al, 2016; Zhou et al, 2017). Furthermore, as it contains abundant redox-active functional components (e.g., phenolic moities), biochar has been shown to accelerate denitrification and reduce nitrous oxide emissions (Cayuela et al, 2013; Chen et al, 2018; Sathishkumar et al, 2020). Shehzad et al. (2016) showed that biochar could remove organic and inorganic pollutants from landfill leachate, with the highest adsorptive removal for color

(95.1%), COD (84.94%), and ammonia (95.77%). Paranavithana et al., (2016) showed that biochar addition could increase heavy metal adsorption, with an adsorption capacity of 30.1 mmol/g for Cd^{2+} and 44.8-46.7 mmol/g for Pb^{2+}. Similar results were also obtained when biochar was mixed into the substrate of CWs, showing effective toxic metal immobilization (Zhang et al., 2013; Cao et al., 2009).

The effect of biochar addition on organic pollutant removal in CWs treating domestic wastewater has been studied by several researchers. Zhou et al. (2017) showed that adding biochar to VF-CWs could be an effective strategy for low C/N wastewater treatment, resulting in high removal of COD (94.9%), ammonia (99.1%), and TN (52.7%). Rozari et al. (2015) showed that sand amended with varying proportions of biochar in VF-CWs were effective in removing BOD_5, TSS, and volatile suspended solids (VSS). Kasak et al. (2018) also showed that biochar addition increased TN and TP removal (20% for TN and 22.5% for TP) in HF-CWs treating municipal wastewater and also enhanced plant biomass growth. Gupta et al. (2016) and Gao et al. (2018) found that biochar was a valuable SSF CW amendment in HF-CWs, with more efficient removal of COD, TN, and TP. Because the recalcitrant organic matter and metals in leachate, the addition of biochar to HF-CWs treating landfill leachate is a promising strategy. However, no prior literature was found on the use of biochar in CWs treating landfill leachate.

Mathematical Models of Constructed Wetlands for Landfill Leachate

Although there is no comprehensive design manual for leachate treatment CWs, it is known that their design must be site-specific due to highly variable leachate flow rates and composition, as well as local soil and climate conditions (Kadlec and Zmarthie, 2010). Mathematical models are a powerful tool used in design and operations to predict how CW performance would be affected by site-specific conditions. Though CW models are common (e.g., Cancelli et al., 2019; Ophithakorn et al., 2013), the integration of adsorptive media in performance modeling is a novel idea with limited research results up to date. For instance, a recent study simulated the adsorption of biochar in a VF-CW for wastewater reclamation (Nguyen et al., 2021), showing that machine learning algorithms could accurately estimate effluent concentrations. No prior studies, however, have used process models to predict the effect of adsorption material on CW performance.

Landfill Leachate Reclamation

Landfill leachate has the potential to be treated to meet industrial or agricultural reuse standards (Justin et al., 2009; Chen et al, 2014). In prior studies, reclaimed landfill leachate has been used to irrigate non-food crops, such as grass and willow (Justin and Zupancic, 2009). The level of treatment required must be matched to the reuse application. For example, high concentrations of ammonia, salts and metals are toxic to vegetation, agricultural irrigation applications. High salinity can result in scaling and corrosion, limiting industrial reuse applications. The combined processes of ultrafiltration (UF) and reverse osmosis (RO) can be used to reduce the salinity and heavy metal concentrations in landfill leachate to meet reuse standards (Syzdek and Ahlert, 1984; Afonso et al, 2004). However, the high membrane fouling potential of landfill leachate results in low treatment efficiency and high energy and maintenance costs of UF-RO (Huang et al, 2011). CWs have been used successfully for pre-treatment of landfill leachate prior to UF-RO to reduce its fouling potential (Huang et al., 2011). The combined processes of CW-UF-RO can create high quality permeate for agricultural and industrial reuse; however, concentrate disposal also needs to be taken into consideration. The feasibility of concentrate disposal depends on local regulations, and can include disposal to industrial wastewater treatment plants, deep well injection, and solidification with waste amendments (Squire et al, 1996; Peters, 1998).

METHODS

Laboratory Adsorption and Sequencing Batch Biofilm Reactor (SBBR) Studies

Three bench-scale recirculating SBBRs were set up in the Environmental Engineering laboratory at the University of South Florida (Tampa, USA) with varying biofilm support media: 1) lightweight expanded clay (LECA) as a control (C-SBBR), 2) LECA + zeolite (CZ-SBBR) and 3) LECA + zeolite + biochar (CZB-SBBR). Experiments were carried out in different phases (Table 2) over ~ 1 year. Detailed information on all materials and methods is provided in Gao (2020).

Table 2: Experimental phases for SBBR operation.

Phase	# days of operation	Fill volume/cycle (mL)	Exchange volumetric Rate (%)	HRT (d)	EBCT (d)	Influent TAN (mg/L)	Influent sCOD (mg/L)
1	6	NA	NA	100% recirculation	NA	NA	NA
2	84	110	25	14	47	400	410
3	38	180	40	9	29	400	520
4	270	180	40	9	29	370	510

Note: NA = Not Applicable; HRT = Hydraulic Residence Time; EBCT = Empty Bed Contact Time; TAN = total ammonia nitrogen.

Landfill leachate and SBBR media

Landfill leachate was collected from the Southeast Hillsborough County Landfill in Lithia, Florida, USA. The landfill was constructed in 1984 on portions of a phosphate mine. It currently includes a Class 1 landfill, waste tire processing facility, and composting facility for yard waste and biosolids. Leachate was collected from a storage tank in the landfill approximately every two months and was kept at 4^{o}C until use. Raw leachate characteristics are shown in Table 3.

Table 3: Southeast Hillsborough County average raw landfill leachate characteristics.

Parameter	Units	Leachate
pH	NA	7.8 ± 0.07
Conductivity	uS/cm	14,000 ± 490
Alkalinity	mg $CaCO_3$/L	2,000 ± 700
sCOD	mg/L	450 ± 54
BOD_5	mg/L	70 ± 5
TSS	mg/L	42 ± 2
VSS	mg/L	25 ± 1
NH_4^+	mg/L (as N)	400 ± 7
FA	mg/L (as N)	15 ± 1
NO_2^-	mg/L (as N)	70 ± 45
NO_3^-	mg/L (as N)	BDL

Note: NA = Not Available; BDL = Below Detection Limits.

LECA was purchased from Trinity Lightweight Aggregate (Livingston, AL, USA). Zeolite (clinoptilolite) was obtained from St. Cloud Mining Company's Ash Meadows Plant (NV-Na, USA). Biochar was obtained from Biochar Supreme Inc. (Everson, WA, USA). The bulk density and particle size ranges of the media materials used in this study are provided in Table 4. Additional information about biochar properties can be found in Rahman et al. (2020).

Table 4: Bulk density and particle size of LECA, clinoptilolite and biochar.

Material	Bulk Density (g/cm^3)	Particle Size
Large LECA	0.8	2~5 mm
Small LECA	0.8	0.6~2 mm
Zeolite (clinoptilolite)	0.9	<0.6 mm
Biochar	0.1	2~4 mm

Note: Large LECA was added as the cover layer of SBBRs; Small LECA was the main medium in the control SBBR.

Batch adsorption studies

Batch adsorption studies were conducted to investigate the adsorption capacities of zeolite and biochar for ammonia and COD in landfill leachate. These studies were also used to identify appropriate dosages of the zeolite and biochar for the SBBR studies. Zeolite and biochar were washed with deionized water (DI) and dried before use. Varying dosages of zeolite (0, 20, 40, 60, 80, 100, 120, 140, 160, 180, and 200 g/L) and biochar (0, 20, 40, and 60 g/L) were added to duplicate flasks filled with 100mL of raw landfill leachate. Flasks were covered with parafilm and placed on an orbital shaker at 200 rpm and room temperature (25 °C). Raw leachate and supernatant samples collected after 24-hr and were filtered with 0.45 µm glass fiber filter paper. Total ammonia nitrogen (TAN) and COD concentrations were measured as described below.

SBBR design and operation

Bench-scale SBBRs (Figure 1) were constructed from 12-cm diameter by 20 cm height acrylic tubing. The working volume for each reactor (i.e., the volume of media) was ~ 1.5 L and the pore volume (leachate volume) was 450 mL. The SBBRs were filled with the following media materials (percentages given by volume): 1) C-SBBR: 100% LECA; 2) CZ-SBBR: 92% LECA + 8% zeolite; 3) CZB-SBBR: 47% LECA + 8% zeolite + 45% biochar. Large particle size LECA (Table 4) was added to the top of each reactor to prevent adsorbent materials from floating. All SBBRs were placed in a fume hood at room temperature (25 °C). Leachate was recirculated in the SBBRs using Masterflex L/S 17 peristaltic pumps (Cole-Parmer Instrument Company, LLC. IL, USA). To offset water loss by evaporation, bioreactors were replenished with 50 mL of DI every two cycles.

The SBBRs were operated in four phases (see Table 2). Phase 1 was operated as an acclimation phase; SBBRs were seeded with approximately 110 mL (25%, by volume) landfill leachate mixed with 335 mL treated wastewater (75%) and 5 mL mixed liquor suspended solids (MLSS) with total suspended solids (TSS) of 10 g/L from the Valrico Advanced Water Reclamation Facility (Tampa, FL, USA). Slow recirculation at 60 mL/min was applied to promote mass transfer and biofilm attachment. On day 2, 4, and 6, 25% of the total liquid volume was discharged sequentially, and the reactors were replenished with same amount of raw leachate. Phase 1 was concluded on Day 8 after 75% of the pore volume was replaced by raw leachate.

During Phases 2, 3 and 4, SBBRs were operated on a 3.5-d cycle consisting of the following stages: 1) rapid fill, 2) 1-d anoxic react, 3) 2.5-d aerobic react, 4) rapid drain. During the anoxic stage, leachate was recirculated at a flow rate of 30 mL/min from the bottom of the reactor to a diffuser below the liquid surface to reduce surface turbulence and oxygen transfer from the air. At the end of the anoxic stage, 20 mL of effluent was collected for testing. During the aerobic stage, leachate was recirculated at a flow rate of 90 mL/min from the bottom of the reactor to a perforated tube above the liquid surface to provide aeration. At the end of the operating cycle, a specific amount of effluent was discharged to maintain the target HRT and fresh leachate was added to the reactors for the next cycle. HRT was initially set at 14 days and reduced to 9 days on day 90 by increasing the decant/filling volume (Table 2). To understand the fate of nitrogen species and organic matter, samples were collected from CZB reactor every 6 hours during cycle 10 of Phase 3. During Phase 4, the CZB-SBBR was operated to evaluate its long-term performance.

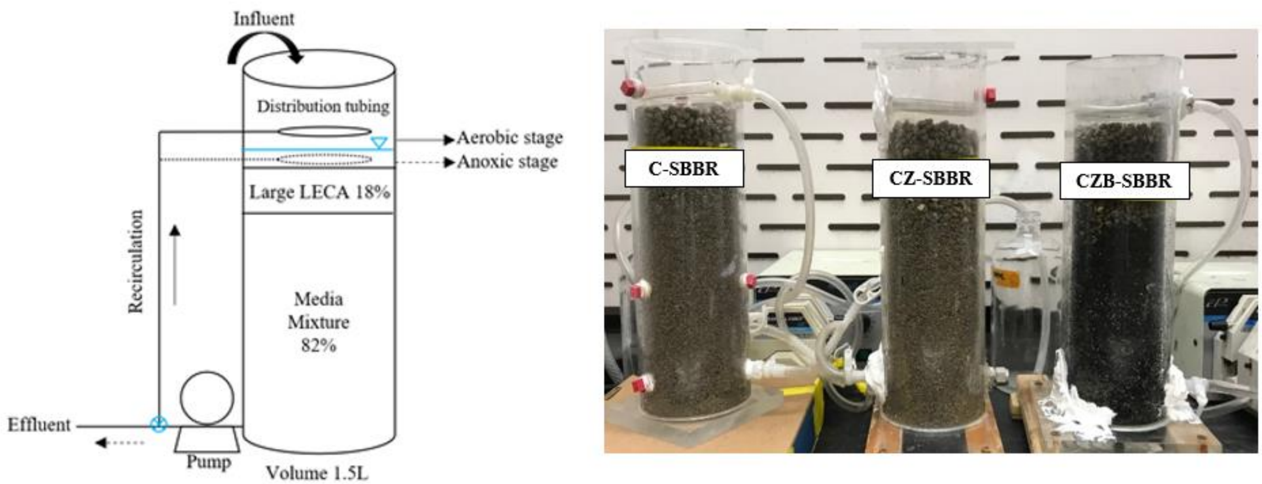

Figure 1: Laboratory-scale SBBR schematic and photograph of reactor.

S^0 Autotrophic Denitrification for Post-Treatment of Nitrified Effluent

A preliminary batch denitrification study was performed to examine the feasibility of elemental sulfur (S^0) autotrophic denitrification for post-treatment of the nitrified effluent from the SBBR. During S^0 autotrophic denitrification, denitrifiers employ S^0 as an electron donor to generate energy for cell synthesis and maintenance. NO_3^- is used as a terminal electron acceptor and is reduced to nitrogen gas. S^0 is a non-toxic by-product of petroleum refining. Therefore, it may be supplied as a low-cost and sustainable resource within CWs, eliminating the need for complex chemical feed systems for liquid organic substrates, such as glycerol, for heterotrophic denitrification. Furthermore, autotrophic denitrifiers are slow growing compared to their heterotrophic counterparts, which minimizes sludge production and therefore operational and management costs.

A single batch reactor was constructed by combining effluent collected after the anoxic stage of the laboratory-scale CZB SBBR with 12g S^0 pellets and 4g crushed oyster shells. As shown in Equation (1), S^0 autotrophic denitrification produces acid (H^+), which decreases the pH and has been shown to decrease denitrification performance (Batchelor and Lawrence, 1978). Therefore, oyster shells (~97% calcium carbonate) were supplied as an alkalinity source to maintain suitable pH conditions for autotrophic denitrifiers (Asaoka et al., 2009). Dosages of S^0 and oyster shells were selected based on previous research in our laboratory (Boles et al., 2012).

$$1.1S^0 + 0.4CO_2 + NO_3^- + 0.76H_2O + 0.08NH_4^+ \rightarrow 0.08C_5H_7O_2N + 0.5N_2 + 1.1SO_4^{2-} + 1.28H^+ \quad \text{(Eq.1)}$$

Pilot-Scale Constructed Wetland Studies

Two pilot scale hybrid CWs (G-CW and GZB-CW) with a total working volume of ~700 L were set up at the Southeast Hillsborough County landfill side by side. Each hybrid CW consists of a VF-CW followed by a HF-CW. G-CW was filled with gravel media (Seffner Rock & Gravel, Tampa, FL) in both the VF and HF cells and served as a control. In GZB-CW, 10% (by volume) of zeolite (St. Cloud Zeolite, Winston, New Mexico) was added to VF-CW, and 13% (by volume) of biochar (Biochar Supreme Inc., Everson, WA) was added to HF-CW. Both hybrid CWs were fed with raw landfill leachate. Effluent from the CWs was drained to a sump for further treatment by Hillsborough County. A process flow diagram of the hybrid CWs is shown in Figure 2. Detailed information about CW characteristics and media distribution are provided in the Appendix.

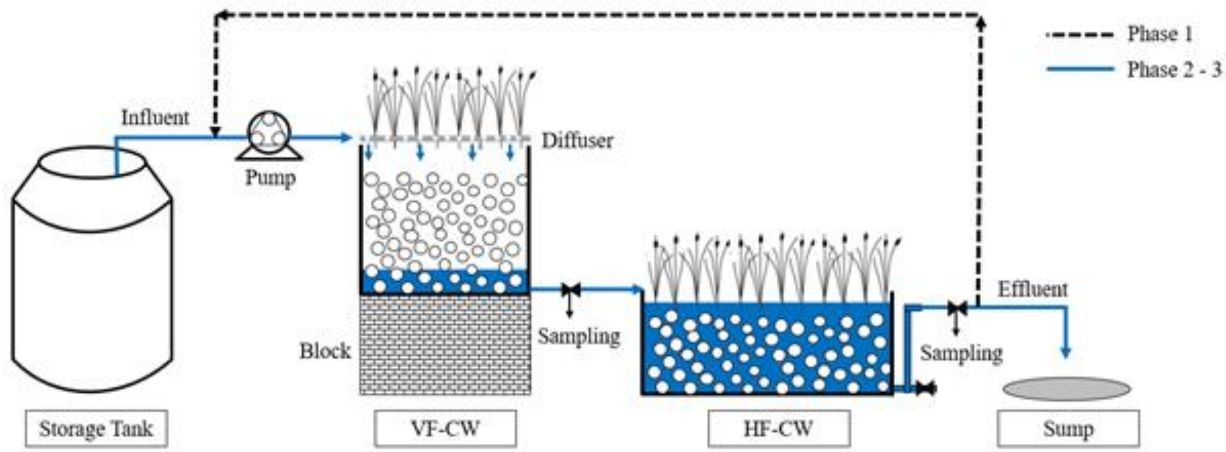

Figure 2: Pilot-scale hybrid CW flow chart (not to scale).

Experimental phases for the CW studies are shown in Table 5. Phase 1 was an acclamation period to promote biofilm growth on the media. Two hybrid CWs were inoculated with the sludge from the activated sludge treatment system in landfill diluted with a mixture of 25% of raw landfill leachate and 75% of groundwater (by volume) resulting a TS of 1 g/L. A recirculation of 160 mL/min between VF-CW and HF-CW was applied once per week for 4 hours using a Masterflex L/S 25 peristaltic pump (Cole-Parmer Instrument Company, LLC, IL) to promote mass transfer and biofilm attachment and growth. On day 14, 25, and 36, 25% of fresh raw landfill leachate was added to the CWs and 25% of treated effluent was discharged. On day 50, Phase 1 was completed.

Phase 2 was a transitional period from batch mode to flow-through feeding mode, which was operated for 20 days to investigate the effects of adsorbent (biochar and zeolite) on CW performance without plants. Raw leachate was pumped into CWs intermittently (30 min/4h) using a pump controlled by a timer each day. The same amount of effluent was discharged to maintain the HRT of 11 days.

Phase 3 investigated the effects of plants and adsorbent (biochar and zeolite) addition on contaminant removals. Cattails (*Typha spp*) and cordgrass (*Spartina*) (provided by Aquatic Plants of Florida, Sarasota, FL) were planted in CWs at a density of 10 plants/m^2. The feeding frequency was increased from 30 min/4 h to 15 min/2 h to enable more uniform influent distribution in the VF-CW. The two systems were normally monitored on a weekly basis.

Table 5: Experimental phases for hybrid constructed wetlands.

Phase	Inflow (L/d)	HRT (d)	EBCT (d)	Operation mode	Feeding frequency	Plants	# days operation
1	NA	Regular recirc.	NA	Batch	NA	NA	50
2	24	11	29	Flow-through	30 min/4h		20
3	24	11	29		15 min/2h	Cattail and cordgrass	150

Note: NA = Not Applicable; HRT = Hydraulic Residence Time; EBCT = Empty Bed Contact Time.

Analytical Chemistry

Dissolved oxygen (DO), pH and salinity were measured using an Orion 5 Star Multifunction Meter (Thermo Scientific, USA). Leachate and effluent samples were filtered through the 0.45 µm glass fiber filters for chemical analysis. TAN (NH_4^+-N + NH_3-N) and NOx-N (NO_2^--N + NO_3^--N) concentrations were measured using a Timberline TL-2800 Ammonia Analyzer (Timberline Instrument, USA). NO_2^--N was measured using a combination of Standard Methods 4500 (APHA, 2018) and Strickland and Parsons (1972). NO_3^--N was calculated by subtracting NO_2^--N concentration from NOx-N concentration. As free ammonia (FA) rapidly equilibrates with NH_4^+ in aqueous solution, high FA concentration can promote an imbalance in intracellular and extracellular pH of bacteria, affecting the proton motive force and inhibiting many energy-requiring functions of the cell (Martinelle et al., 1996). Thus, FA was calculated using the following equation (Hansen et al., 1998):

$$\frac{FA}{TAN} = \left(1 + \frac{10^{-pH}}{10^{-\left([0.09018+\frac{2729.92}{T(k)}]\right)}}\right)^{-1} \quad \text{(Eq.2)}$$

TN was measured using Hach TNTplus® 827 Total Nitrogen test kits. Total organic nitrogen (TON) was calculated by subtracting the total inorganic nitrogen (TIN) from the TN concentration. sCOD was measured using Lovibond LR test kits (0-150 mg/L) (Tintometer Inc, USA). A wavelength of 456 nm was used to measure color, based on Standard Methods 2030C (APHA, 2018). *Standard Methods* (APHA, 2018) were used to measure UV456 (2120C), BOD_5 (5210B), alkalinity (2320B), TSS (2540D), and VSS (2540E). Turbidity was measured using a Hach 2100Q Portable Turbidimeter. Concentrations of metals were measured at USF's core geochemistry facility by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Silt density index (SDI) measurements were performed using ASTM method D19.08.

Wetlands Modeling

A process model was developed in Python that tracks the mass balance of water, oxygen, carbon and nitrogen species through the CWs (Figure 3).

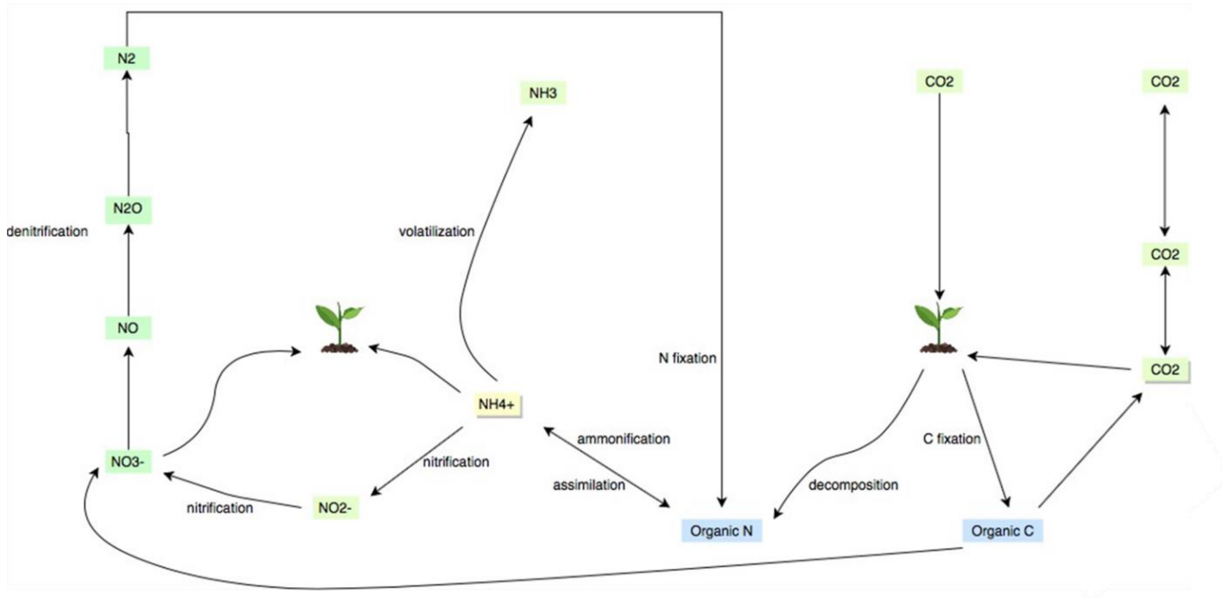

Figure 3: CW model framework.

The overall water balance equation is as follows (Chapra, 1997):

$$\frac{dV}{dt} = Qin - Qout + (P * A_s) - (ET * A_s) \quad \text{(Eq.3)}$$

Where dV is the change in volume, dt is the change in time (days), Qin is the inflow rate (m^3/day), $Qout$ is the outflow rate, P is rainfall precipitation (m), A_s is the wetland surface area (m^2), and ET is evapotranspiration (m). Separate water balance equations are used for the VF and HF tanks, since the size and flow rates of the tanks vary. The outflow rate of the VF tank is assumed to be equal to the inflow rate of the HF tank. Evapotranspiration is calculated using Thornthwaite's Method (Thornthwaite, 1948). The general mass balance equation for DO is as follows (Jorgensen and Bendoricchio, 2001):

$$\frac{d(DO)}{dt} = Reaeration - Consumption + Production \quad \text{(Eq.4)}$$

Where $d(DO)$ is the change in DO concentration (mg/L). Reaeration is accounted for with the following model:

$$\frac{d(DO)}{dt} = k_R * (DO_s - DO) \quad \text{(Eq. 5)}$$

Where k_R is the transfer coefficient and DO_s is the saturation DO concentration (mg/L), and DO is the initial DO concentration (mg/L). The effects of wind are ignored since both wetlands are subsurface flow. The Benson and Krause (1984) model was used to estimate DO_s.

Consumption of oxygen is due to aerobic biodegradation of COD and Nitrogenous Oxygen Demand (NOD). COD can be modeled using first-order kinetics:

$$\frac{d(COD)}{dt} = -k_d * COD \quad \text{(Eq.6)}$$

Where COD is the concentration of organic matter measured as COD (O_2 mg/L) and k_d is the rate coefficient (day^{-1}).

NOD is calculated with the first order kinetic equation for the oxidation of nitrogen:

$$\frac{d(NOD)}{dt} = \delta * k_N * NH_4^+ \quad \text{(Eq.7)}$$

Where δ is the stoichiometric coefficient for the process (g O_2/g NH_4^+), k_N is the rate coefficient (day^{-1}), and NH_4^+ is the concentration of ammonia (mg/L).

Mass balances for organic nitrogen, ammonia, and nitrate are used to keep track of nitrogen in the system. Mass and volume are calculated simultaneously at each time step. Concentration is then simply calculated as $C = {}^{M}/_{V}$. The mass balances for organic nitrogen, ammonia, and nitrate are estimated as follows:

$$V\frac{d(Org_N)}{dt} = Qin * (Org_N)_i - Qout * (Org_N) - (r_m * V) \quad \text{(Eq.8)}$$

$$V\frac{d(NH_4)}{dt} = Qin * (NH_4)_i - Qout * (NH_4) - (r_n * V) + (r_m * V) \quad \text{(Eq.9)}$$

$$V\frac{d(NO_3)}{dt} = Qin * (NO_3)_i - Qout * (NO_3) + (r_n * V) - (r_{dn} * V) \quad \text{(Eq.10)}$$

Where $(Org_N)_i$ is the influent concentration of organic nitrogen (mg/L) and r_m is the rate of mineralization ($mg \cdot L^{-1} \cdot day^{-1}$). $(NH_4)_i$ is the influent concentration of ammonia (mg/L)), r_n is the rate of nitrification ($mg \cdot L^{-1} \cdot day^{-1}$). $(NO_3)_i$ is the influent concentration of nitrate (mg/L), and r_{dn} is the rate of denitrification ($mg \cdot L^{-1} \cdot day^{-1}$). V is the storage on a given day that is solved based on the water balance (L).

Water Reuse Evaluation

Effluent characteristics from the pilot-scale CWs study were compared with reuse water quality standards and previous case studies' recommendations. In consideration of post-treatment, membrane filtration was considered. Monovalent ions, such as sodium and chloride ions, which are responsible for electric conductivity, can be removed through RO. To reduce RO membrane fouling potential, a pre-treatment, such as UF, is needed. The Water Application Value Engine (WAVE) software was selected as a design tool for the UF-RO system. WAVE integrates both UF and RO into a single software and allows modifications to the design schematic be reflected throughout the system design (DuPont, 2021). The software allows input of project-specific parameters with design recommendations and default values to create a comprehensive preliminary assessment and cost of the treatment design. Several chemical parameters needed to be measured to use the WAVE software, including turbidity and silt density index (SDI).

RESULTS

Batch Adsorption Studies

Adsorption capacities of zeolite and biochar for sCOD and TAN are shown in Figure 4. Biochar had a high adsorption capacity for sCOD, with the highest value of 44% at dosage of 40 g/L, however, much lower for TAN (< 3%). In contrast, zeolite had a much higher adsorption capacity for TAN than sCOD. The highest TAN removal was 71% at a dosage of 200 g/L. As FA and NH_4^+ rapidly equilibrate in aqueous solution, adsorption of NH_4^+ by zeolite decreases FA concentrations and reduces its inhibition to nitrifiers (Aponte-Morales et al., 2018).

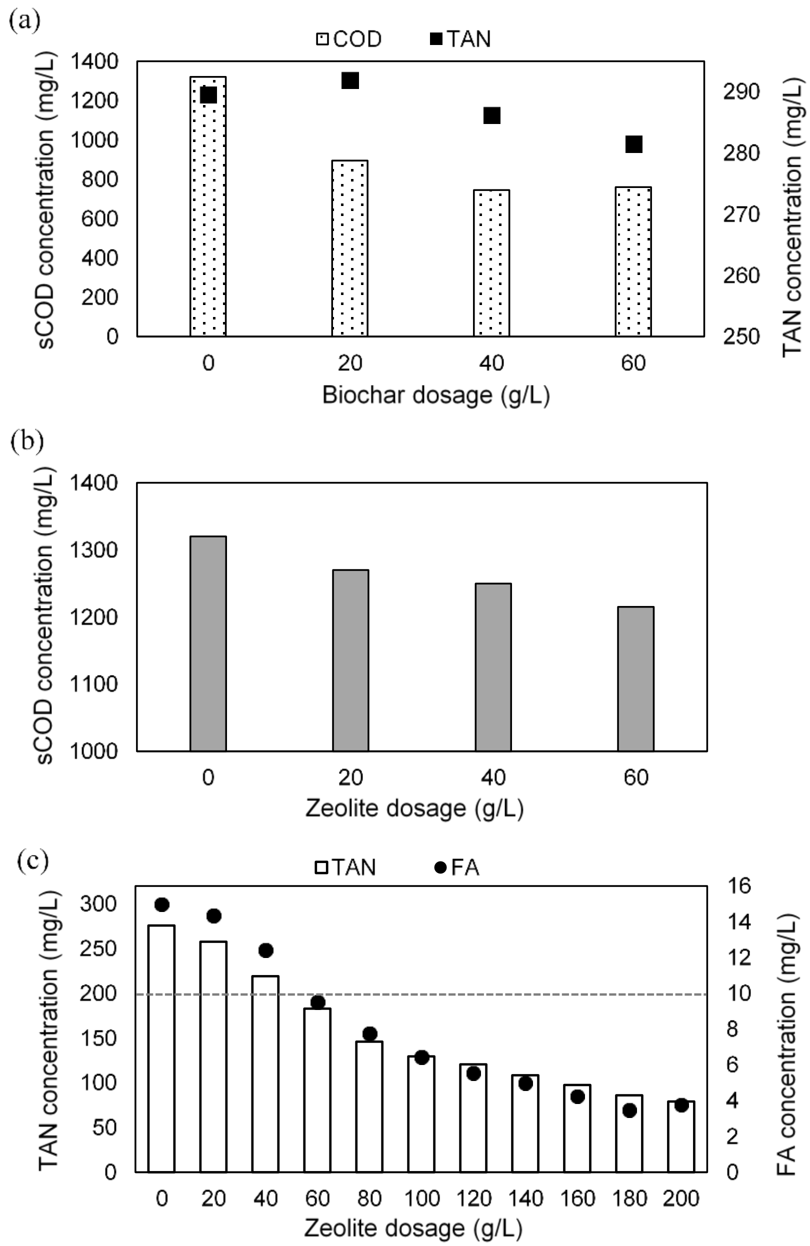

Figure 4: Results from batch adsorption study with biochar and zeolite: (a) sCOD and TAN adsorption by biochar; (b) sCOD adsorption by zeolite; (c) TAN and FA adsorption by zeolite (dashed line shows typical FA toxicity to nitrifying bacteria).

Sequencing Batch Biofilm Reactor Studies

The three SBBRs were operated with alternating anoxic and aerobic stages with leachate from Hillsborough County's Southeast Landfill. Results at the end of Phase 2 (14 day HRT) and Phase 3 (9 day HRT) are shown in Figure 5. Detailed results are shown in the Appendix. Excellent TAN removal (> 99%) was achieved in all three SBBRs throughout the study. The combined addition of zeolite and biochar in CZB-SBBR resulted in significantly higher sCOD (61-83%) and color (82-95% as UV456) removal compared with C-SBBR (42-44% and 28-33%) and CZ-SBBR (34-45% and 20-35%).

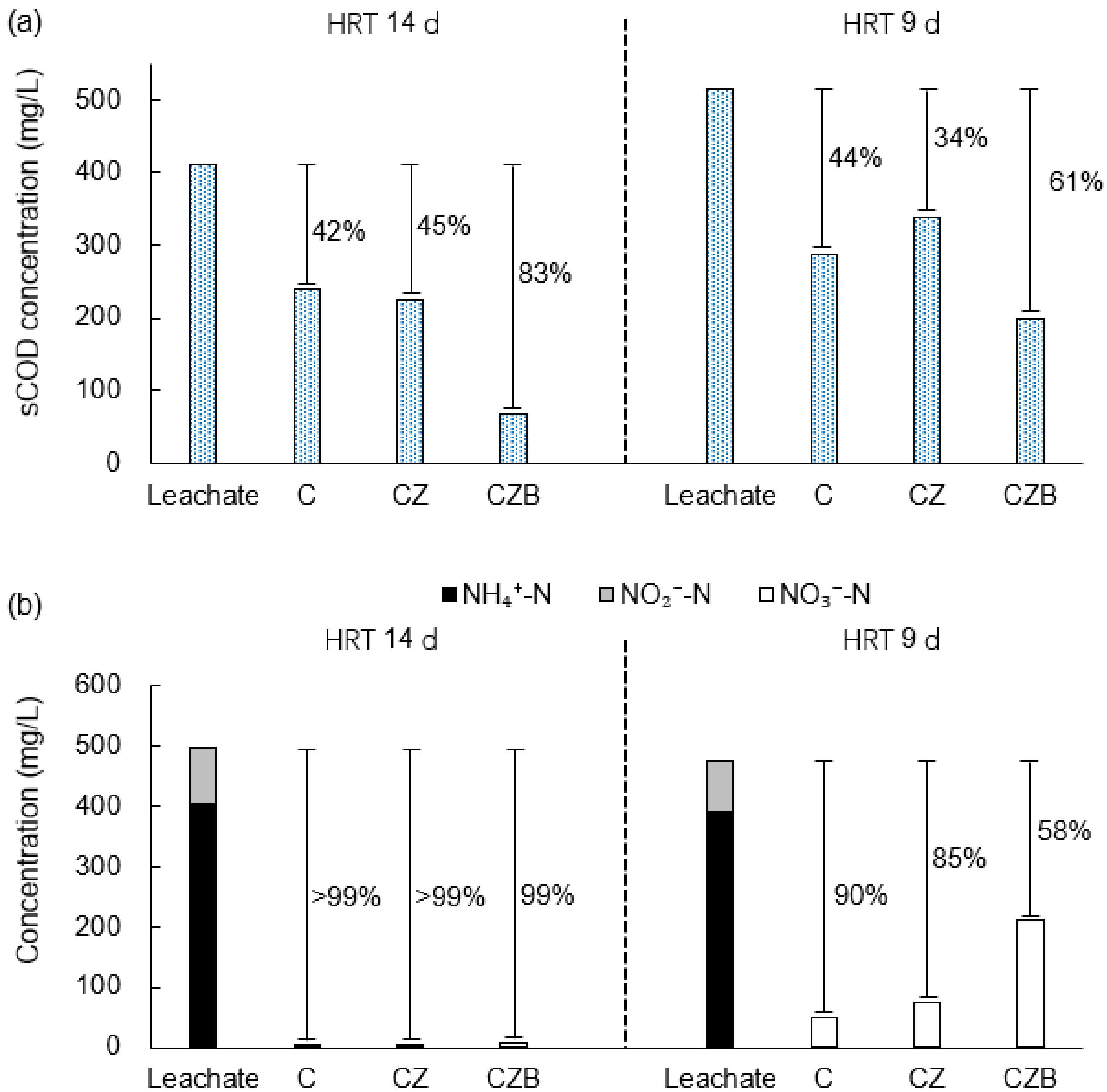

Figure 5: Changes in SBBRs with/without adsorbents: (a) sCOD; (b) N species.

Dynamic changes in sCOD and N species concentrations in the adsorbent amended SBBR (CZB) were investigated over one cycle (3.5 days) at the end of Phase 3. The results are shown in Figure 6. During the anoxic stage, TAN was nitrified to NO_2^- and NO_3^- with a net TAN removal of 23% within 24 hours. Due to limited carbon availability, 65% of NO_3^- remained in the reactor. During the aerobic stage, all of the remaining TAN and NO_2^- were removed within 24 hours. Regarding sCOD, 7% of sCOD was removed within 18 hours and then sCOD concentrations gradually decreased during the remaining time, reaching a maximum removal efficiency of 34%.

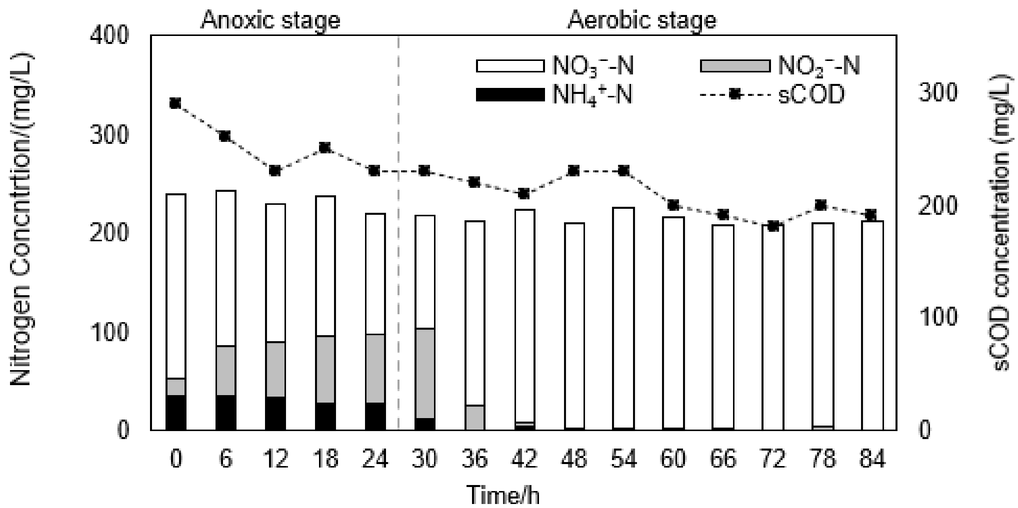

Figure 6: Variations of nitrogen species and sCOD during cycle 10 of Phase 3.

To investigate the long-term performance of adsorbent amended SBBR, the CZB reactor was maintained for an additional 9 months with feeding two times per week to maintain an HRT of 9 days. A comparison of N species removals during short-term (Phase 3) and long-term operation (Phase 4) is shown in Figure 7. Greater than 99% TAN removal was observed in both phases with CZB-SBBR; however, compared with Phase 3, Phase 4 exhibited greater overall TIN removal efficiency (73% vs. 57%) due to lower NO_3^--N accumulation (29 vs. 204 mg/L). The improved TN removal is likely due to the enrichment of slow growing anammox bacteria, such as *Brocadia anammoxidan*, after a long period of operation. Dissolved organic nitrogen removal (DON) was not measured in Phase 3. In Phase 4, DON removal was negligible during the anoxic phase but reached 60% during the aerobic phase.

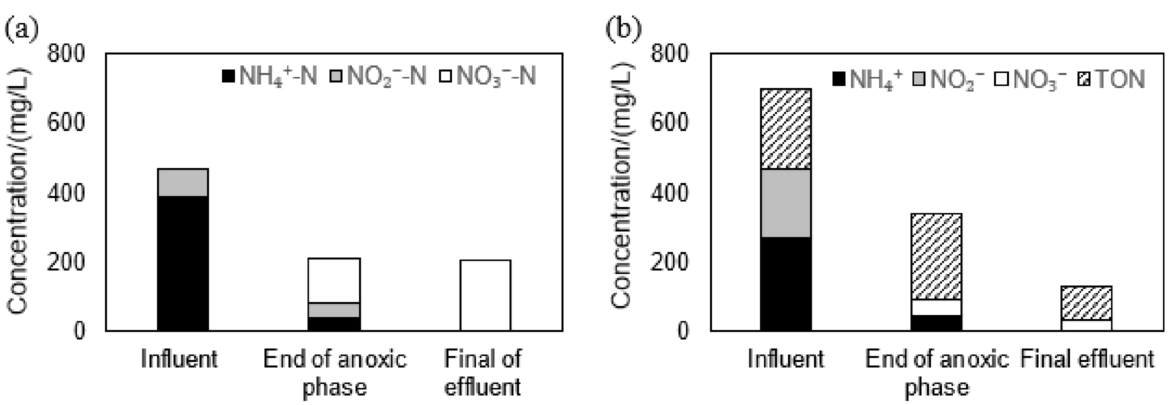

Figure 7: Nitrogen species within CZB: (a) with short-term operation (Phase 3); (b) long-term operation (Phase 4).

S^0 Autotrophic Denitrification for Post-Treatment of Nitrified Effluent

Figure 8 shows NO_3^- and sulfate (SO_4^{2-}) concentration profiles for the S^0 batch denitrification system used to treat nitrified effluent collected from the laboratory-scale CZB-SBBR. Within 17 days, NO_3^--N concentrations declined from an initial concentration of 310 mg/L to 0.96 mg/L (99% removal). After 17 days, fresh nitrified leachate was added to the batch denitrification system to observe its NO_3^- removal performance for another cycle. Within 11-days, the NO_3^--N concentration decreased from 380 mg/L to 52 mg/L. SO_4^{2-} accumulation was observed during both cycles, with maximum concentrations of 1,700 and 3,000 mg/L, respectively. SO_4^{2-} accumulation is an indicator of S^0 autotrophic denitrification. Ge et al. (2019) observed that effluent SO_4^{2-} concentrations between 600 and 800 mg/L did not have a negative effect on plant growth within a HF-CW amended with sulfur-bearing mineral to facilitate autotrophic denitrification of synthetic wastewater. Therefore, S^0 autotrophic denitrification is a promising post-treatment strategy to minimize effluent NO_3^- rather than adding an organic carbon source.

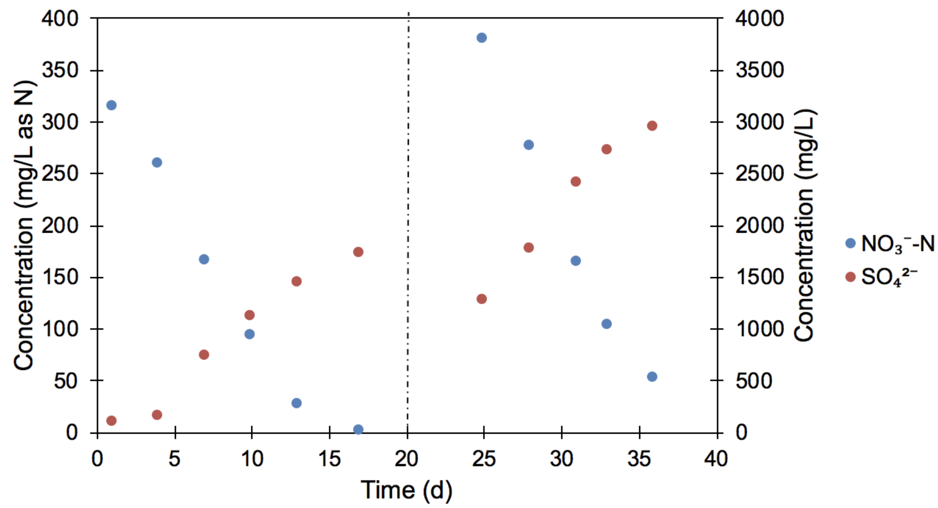

Figure 8: NO_3^- and SO_4^{2-} concentration profiles for batch S^0 autotrophic denitrification studies with nitrified effluent from the CZB SBBR. Cycle 1 and 2 are separated by a dashed line.

Pilot-Scale Constructed Wetland Studies

As shown in Figure 9, sCOD removal efficiency was significantly higher in the adsorbent amended VF-HF CW (55%) than in the unamended control (28%). Biochar addition also effectively enhanced color reduction from 28% to 60%. Similar results were found in previous studies (Shehzad et al., 2016; Abedi and Mojiri., 2019). sCOD and color trends were similar, indicating that the deep color is mainly caused by recalcitrant organic matter, which is consistent with a prior study (Fan et al., 2006). Zeolite addition increased ammonia removal from 63% to 91% (Figure 9(b)). In the intermittently loaded VF-CW, NH_4^+ is adsorbed to the zeolite during the loading period and is subsequently nitrified as oxygen fills the media pores during the drainage period. In addition, zeolite reduced aqueous phase FA concentrations below the inhibitory level of 10 mg/L for ammonia oxidizing bacteria (Anthonisen et al., 1976), resulting in better nitrification performance in HF-CW (Figure 9 (c)). Organic nitrogen was mainly removed in HF-CWs and biochar addition improved its removal from 30% to 64%, possibly due to adsorption and enhanced degradation (Güereña et al., 2013). However, NO_3^- accumulation was observed in the effluent from both CWs, most likely due to limited organic carbon availability for denitrification due to the low BOD_5/COD ratio (0.1-0.8) of the leachate.

Detailed results from the pilot CWs are provided in the Appendix. Influent and effluent pH values for both CWs were between 7.5-8.5, which is suitable for both nitrification and denitrification (Villaverde et al., 1997; Tang et al., 2011). Raw leachate had a high alkalinity of ~ 5,800 mg/L, which is sufficient for nitrification. Raw leachate had a high conductivity, which is about 30% of sea water. Approximately 15% and 18% conductivity removals were achieved in the control and adsorbent amended CWs, respectively.

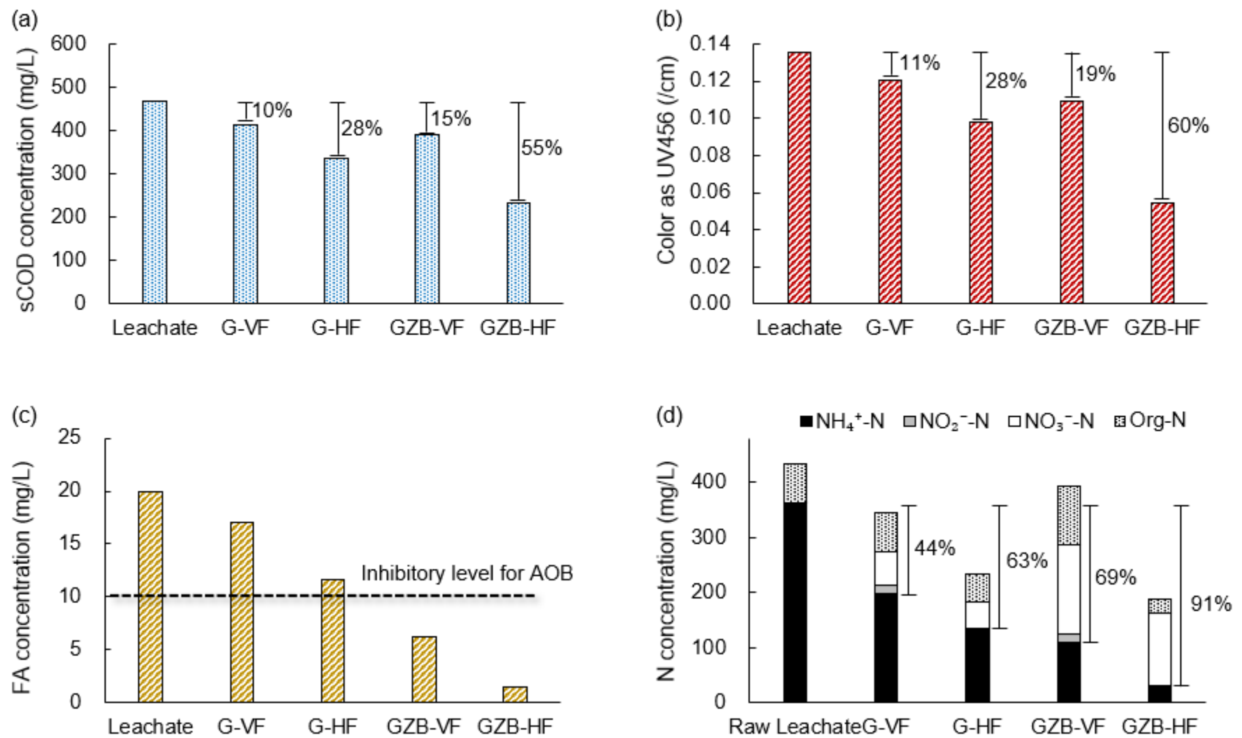

Figure 9: Changes in Vertical and Horizontal stages of pilot CWs without adsorbents (G-VF and G-HF) and with adsorbents (GZB-VF and GZB-HF): (a) sCOD; (b) color as UV456 absorbance; (c) free ammonia (FA); (d) N species. G-VF and G-HF are vertical and horizontal stages of conventional gravel CWs.

As shown in Figure 10, biochar addition also improved the growth of wetland plants, cordgrass and cattails. This is likely due to reduced FA and/or heavy metal toxicity or enhanced growth of beneficial microorganisms in the rhizosphere, which has been shown in other studies (Rizwan et al, 2016; Elad et al, 2011). Raw leachate and effluent from both CWs were collected and sent to a geochemical analysis lab at University of South Florida for metal analysis by ICP-OES. The concentrations of barium (Ba), copper (Cu), and zinc (Zn) were 280 μg/L, 264 μg/L, and 88 μg/L in the control CWs; 550 μg/L,225 μg/L, and 64 μg/L in adsorbent amended CWs, respectively. However, Cu concentrations in both CWs were above the value (20-270 μg/L) that has been shown to be toxic to plants in prior studies (Wong et al., 1982; Craig, 1977).

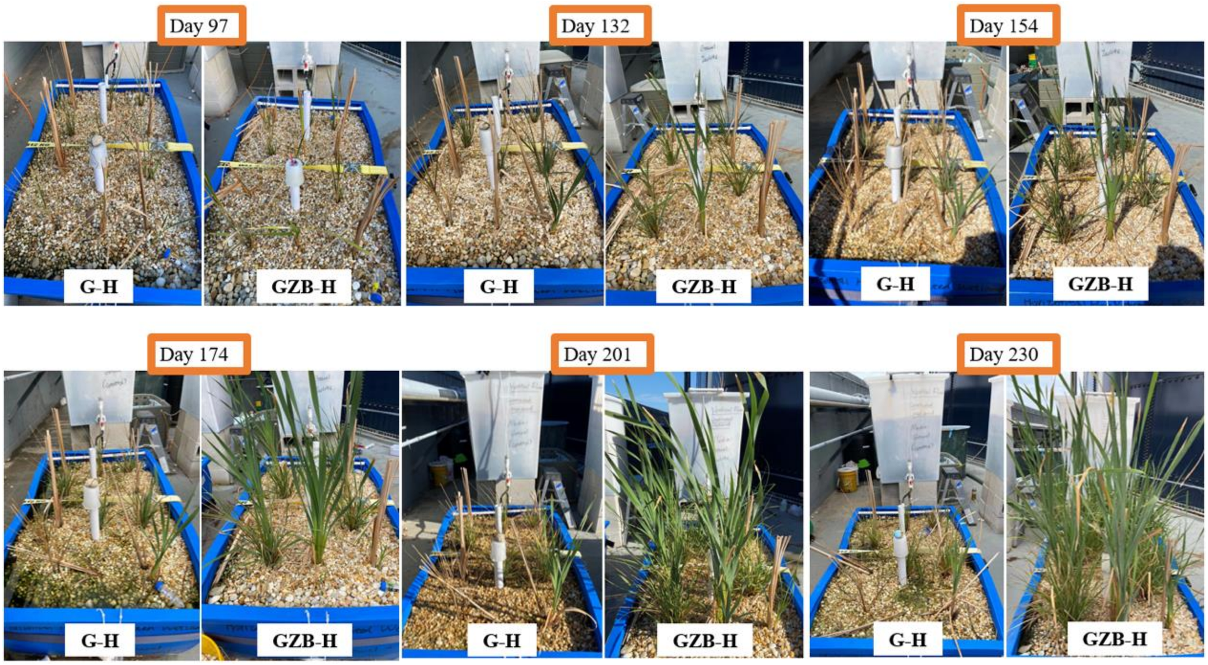

Figure 10: Plant growth in CW-HFs in the Southeast Hillsborough County landfill.

Wetlands Modeling

The model was used to predict the concentration of nitrogen species leaving the unamended pilot scale CWs each day. Model parameters are shown in Table 6. Influent leachate concentrations and weather data were obtained and read into the model via Excel. The influent of the VF-CWs was assumed to be the average of the measured influent concentrations. The influent of the HF-CWs was assumed to be the effluent concentration of the VF-CWs. Model results and experimental effluent concentrations for TAN and NO_3^- are shown in Figure 11 and 12, respectively. The concentration of TAN was initially reduced in the VF-CWs and continued to decrease in the HF-CWs. Figure 12 shows that NO_3^- accumulation occurred in both CWs, but higher NO_3^- concentrations are observed in the HF-CWs. The difference in concentrations could be due to the varying volume of water storage in each tank or the availability of oxygen. Overall, results up to date demonstrate the model is able to replicate the general patterns of treatment and nutrient conversions observed in the pilot CWs, while providing much higher temporal resolution and longer-term performance projections. A sensitivity analysis currently under development will give further insight to which parameter(s) are greatly affecting the model and aid in calibrating the model to better fit the experimental data.

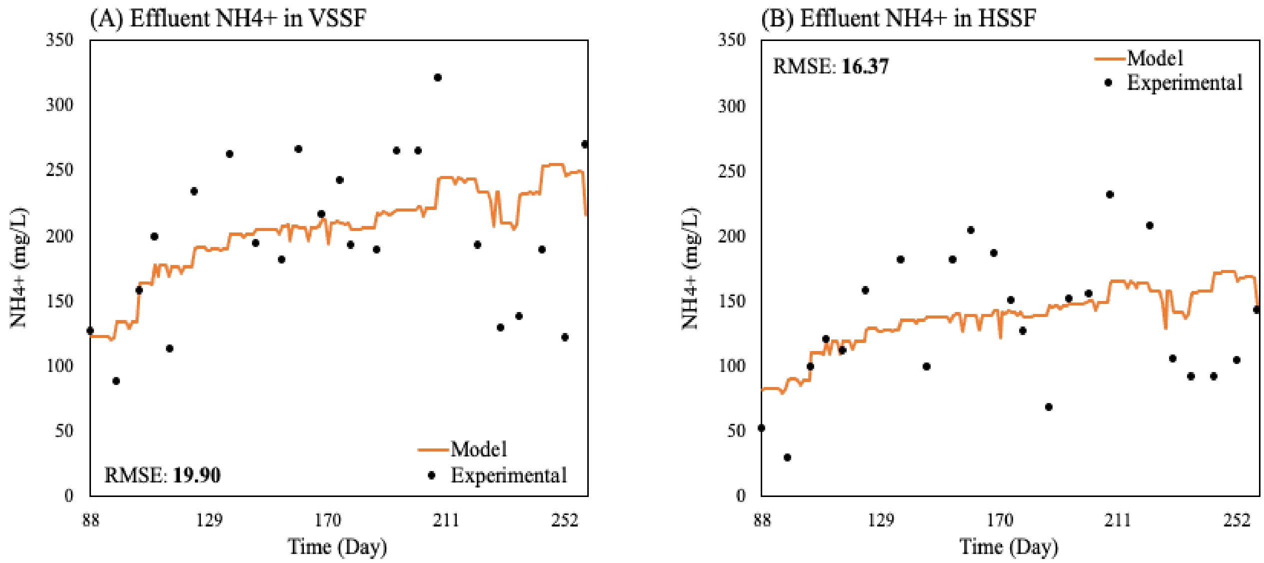

Figure 11: Preliminary model results of NH_4^+ changes in the CWs.

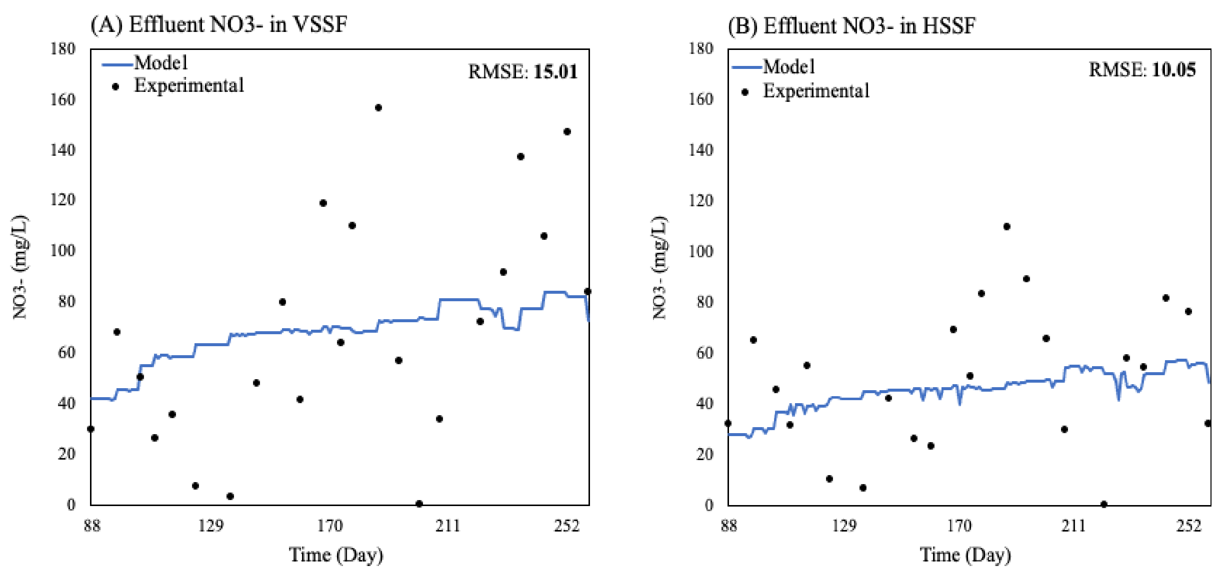

Figure 12: Preliminary model results of NO_3^- changes in the CWs.

Table 6: Literature values for parameters used in model oxygen and nitrogen balances.

Parameter	Value	Unit	Source
α	2.33	NA	Bennet and Rathbun, 1971
β	0.674	NA	Bennet and Rathbun, 1971
γ	1.865	NA	Bennet and Rathbun, 1971
k_d	0.8	day^{-1}	Jorgensen and Bendoricchio, 2001
δ	4.3	g O_2/g NH_4^+	Jorgensen and Bendoricchio, 2001
α_1	0.18	mg O_2/mg $Chl-a$	Jorgensen and Bendoricchio, 2001

Table 6 cont: Literature values for parameters used in model oxygen and nitrogen balances			
α_2	0.018	mg O_2/mg $Chl-a$	Jorgensen and Bendoricchio, 2001
μ	.06	day^{-1}	Jorgensen and Bendoricchio, 2001
ρ	.012	day^{-1}	Jorgensen and Bendoricchio, 2001
k_m	0.015	day^{-1}	Martin and Reddy, 1997
k_n	1.2	day^{-1}	Martin and Reddy, 1997
k_{dn}	2.5	day^{-1}	Martin and Reddy, 1997

Note: data reported with number of significant figures reported by the authors; NA = Not applicable.

Water Reuse Evaluations

As mentioned previously, in water reuse applications the level of treatment required must be matched to the reuse application. High concentrations of TAN, salts and metals are toxic to vegetation, limiting reuse applications for agricultural irrigation. High salinity can result in scaling and corrosion, limiting industrial reuse applications (e.g., as cooling water). In addition, state water reuse standards must be met. A comparison of CW effluent concentrations of BOD_5, TSS, turbidity and TN with FDEP standards for agricultural and industrial reuse are shown in Table 7. Based on the comparison, the adsorbent enhanced CW (GZB) meets the requirements for BOD5, turbidity and TN but requires further treatment for TSS. Additional (non-regulatory) guidelines for agricultural and industrial reuse from the literature are compared with CW effluents in Table 8. Based on this analysis, post treatment, such as UF-RO, is needed to remove salts and further remove N species, particularly NO_3^- from the CW effluent. An analysis of effluent metal concentrations is currently being done and will be included in the final report.

Table 7: FDEP water reuse regulations compared with effluents from pilot systems. Source: EPA, 2012

Water Quality Parameter	Agricultural reuse (Non-food crops)	Industrial reuse	G Pilot	GZB Pilot
BOD_5	20 mg/L (ann avg) 30 mg/L (mon avg) 45 mg/L (wk avg) 60 mg/L (max)	20 mg/L (ann avg) 30 mg/L (mon avg) 45 mg/L (wk avg) 60 mg/L (max)	16 mg/L	16 mg/L
TSS	20 mg/L (ann avg) 30 mg/L (mon avg) 45 mg/L (wk avg) 60 mg/L (max)	5 mg/L (max)	30 mg/L	24 mg/L
Turbidity	NS	2.0~2.5 NTU	2.9 NTU	1.6 NTU
Nitrogen	NS	NS	240 mg/L	190 mg/L

Note: NS= not specified by the Florida state's reuse regulation; avg = average; ann = annual; mon = month; wk = week; yr = year.

Table 8: Recommendations (non-regulatory) for agricultural and industrial water reuse compared with effluents from pilot systems.

Water Quality Parameter		Agricultural reuse [1]	Industrial reuse [2]	G Pilot	GZB Pilot
pH		7.0 ~ 8.0	7.9 ~ 8.7	7.8	7.3
Electric Conductivity		< 1,400 µs/cm	< 1,100 µs/cm	13,000 µS/cm	12,000 µS/cm
Total Alkalinity		< 340 mg/L	< 160 mg/L	< 4,000 mg/L	< 2,000 mg/L
Total N		NS	< 2.3 mg/L	230 mg/L	190 mg/L
NO_3 - N		< 9 mg/L	< 0.1 mg/L	80 mg/L	180 mg/L
NH_4 - N		< 0.02 mg/L	< 0.25 mg/L	140 mg/L	47 mg/L
Metal	Antimony (Sb)	NS	< 4 µg/L	13 µg/L	13 µg/L
	Arsenic (As)	NS	< 6 µg/L	11 µg/L	9 µg/L
	Barium (Ba)	NS	< 22 µg/L	280 µg/L	550 µg/L
	Copper (Cu)	< 3 µg/L	< 3 µg/L	264 µg/L	225 µg/L
	Zinc (Zn)	NS	< 21 µg/L	88 µg/L	64 µg/L
	Lead (Pb)	NS	< 3 µg/L	BDL	BDL

Note: BDL = Below Detection Level.
Remarks:
[1]: Based on the case study (Icekson-Tal et al., 2003) about reclaimed water treated by SAT (Soil Aquifer Treatment) use for irrigation of a variety of crops (both food and non-food crops) in Dan region, Israel;
[2]: Based on the case study (Venter et al., 2012) about reclaimed water use for cooling at Tampa Electric Company's (TECO) Polk Power Station (PPS) in Polk County (City of Lakeland), Florida, US
Notes: NS= not specified by the author(s)

Post-treatment design and analysis is currently being done using the WAVE software (DuPont, 2021). Input chemical parameters for the WAVE software are included in Table 9. Due to the high SDI_{15} above 6.33 in both pilot-scale systems, a pre-treatment to RO, such as UF, is required to reduce membrane fouling potential.

Table 9: Preliminary analysis of input water quality parameters for DuPont's WAVE software.

Water Quality Parameter	G Pilot	GZB Pilot
Turbidity (NTU)	2.9	1.6
TSS (mg/L)	30	24
SDI_{15}	6.4	6.3
pH at 25 C	7.8	7.3
TAN (mg/L)	144	47
NO_3^--N (mg/L)	80	180
NO_2^--N (mg/L)	0.4	0.3

CONCLUSIONS

Results from this project showed that the performance of hybrid constructed wetlands (CWs) that combine vertical flow (VF) and horizontal flow (HF) stages could be enhanced through the addition of biochar and zeolites to the CW media. These materials temporarily adsorb recalcitrant organic matter (biochar) and NH_4^+ (zeolite), allowing more time for their biodegradation by attached microbial biofilms. For zeolite, no additional adsorbent needs to be added and no waste brines are produced. For biochar, additional research is needed to determine whether periodic biochar addition is needed to maintain its adsorptive capacity. The following is a summary of the results of this research by objective.

Objective 1: Compare conventional and adsobent amended hybrid CW performance for landfill leachate treatment.

- Batch adsorption studies with landfill leachate showed that biochar had a high adsorption capacity for sCOD and color and a low adsorption capacity for NH_4^+. Zeolite had a much higher adsorption capacity for NH_4^+ than sCOD. As free ammonia (FA) and NH_4^+ rapidly equilibrate in aqueous solution, adsorption of NH_4^+ by zeolite decreases FA concentrations and reduces its inhibition to nitrifying bacteria.
- Side-by-side bench-scale Sequencing Batch Biofilm Reactor (SBBR) studies achieved excellent ammonia removal throughout the study. Biochar significantly enhanced sCOD and color removal. During initial phases of the bench-scale study, total nitrogen (TN) removal was limited because the low BOD_5/COD ratio of the landfill leachate did not support complete denitrification. However, after a long period of operation, TN removal increased to > 70%, most likely due to the activity of anammox bacteria.
- Batch studies were used to evaluate the potential for post treatment of nitrified landfill leachate via elemental suflur (S^0) autotrophic denitrification. The high rates of denitrification observed in this study indicate that S^0 pellets are an effective solid slow release electron donor source to improve TN removal in CWs. S^0 is a low cost by-product of the petroleum refining and S^0 autotrophic denitrification has low residual sludge production.
- Biochar addition significantly increased sCOD removal efficiency in the adsorbent-amended VF-HF CW than in the unamended control. Biochar also increased color removal, confirming that adsorption of recalcitrant organic matter in leachate enhances biodegradation.
- Biochar dramatically improved the growth of wetland plants, cordgrass and cattails, compared with the unamended control. The high plant growth rates were likely due to reduced heavy metal toxicity and enhanced growth of beneficial microorganisms in the rhizosphere.
- Zeolite addition significantly increased ammonia removal in the adsorbent amended VF-HF CW compared with the un-amended control. These results differed from the bench-scale SBBR studies. In the intermittently loaded VF-CW, NH_4^+ adsorbed to zeolite during the wetting period and was subsequently nitrified as oxygen filled the media pores during the drainage period.
- NO_3^- accumulation was observed in the effluent from both CWs, most likely due to limited organic carbon availability for denitrification due to the low BOD_5/COD ratio (~ 0.1) of the leachate. A low-cost solid electron donor, such as S^0 or wood chips, could be added to the CWs to enhance denitrification.

Objective 2: Develop a numerical process model that can be used to predict the performance of the hybrid CWs under varying operational and leachate characteristics.

- A numerical process model was developed in Python. Effluent concentrations were caculated using a mass balance framework. For ease of use, input data was read in from Excecl files.
- Results up to date demonstrate that the model is able to replicate the general patterns of treatment and nutrient conversions observed in the pilot CWs, while providing much higher temporal resolution and longer-term performance projections.
- The model allows for inputs of varying leachate influent concentrations and weather data (temperature and precipitation). One can use the model to predict how the hybrid CWs perform under different nitrogen loadings and extreme weather events.
- A sensitivity analysis of the model is being developed to show which parameters the model is most sensitive to. The model will then be calibrated to fit the experimental data from this study.

Objective 3: Carry out a preliminary evalutation of post-treatment requirements for landfill leachate reuse applications.

- A comparison of effluent characteristics from the pilot CWs with FDEP reuse standards and reuse guidelines from the literature showed that adsorbent enhanced CW treated leachate has the potential to be reused for either non-food crop irrigation or industrial cooling.
- Post-treatment using ultrafiltration and reverse osmosis (UF-RO) is recommended prior to reuse to reduce the high salinity concentrations in the CW effluent, which would limit its reuse potential due to toxicity to plants or scaling potential.

APPENDIX

Sequencing Batch Biofilm Reactor Studies

Changes in sCOD, color, and N species within three SBBRs at varied HRTs are shown in Figures A1 and A2.

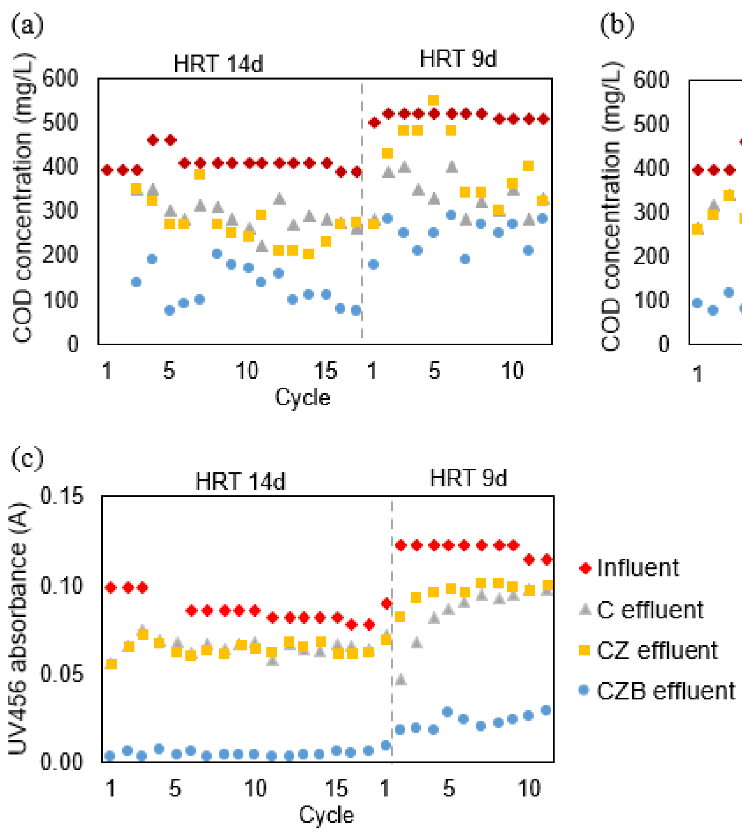

Figure A - 1: sCOD and color variation at various HRTs: (a) sCOD after anoxic phase; (b) sCOD after aerobic phase (final effluent); (c) color (UV456 absorbance) in final effluent. C is the SBBR filled with light weight expanded clay aggregate (LECA) served as the control; CZ reactor was filled with LECA and zeolite; CZB reactor was filled with LECA, zeolite and biochar.

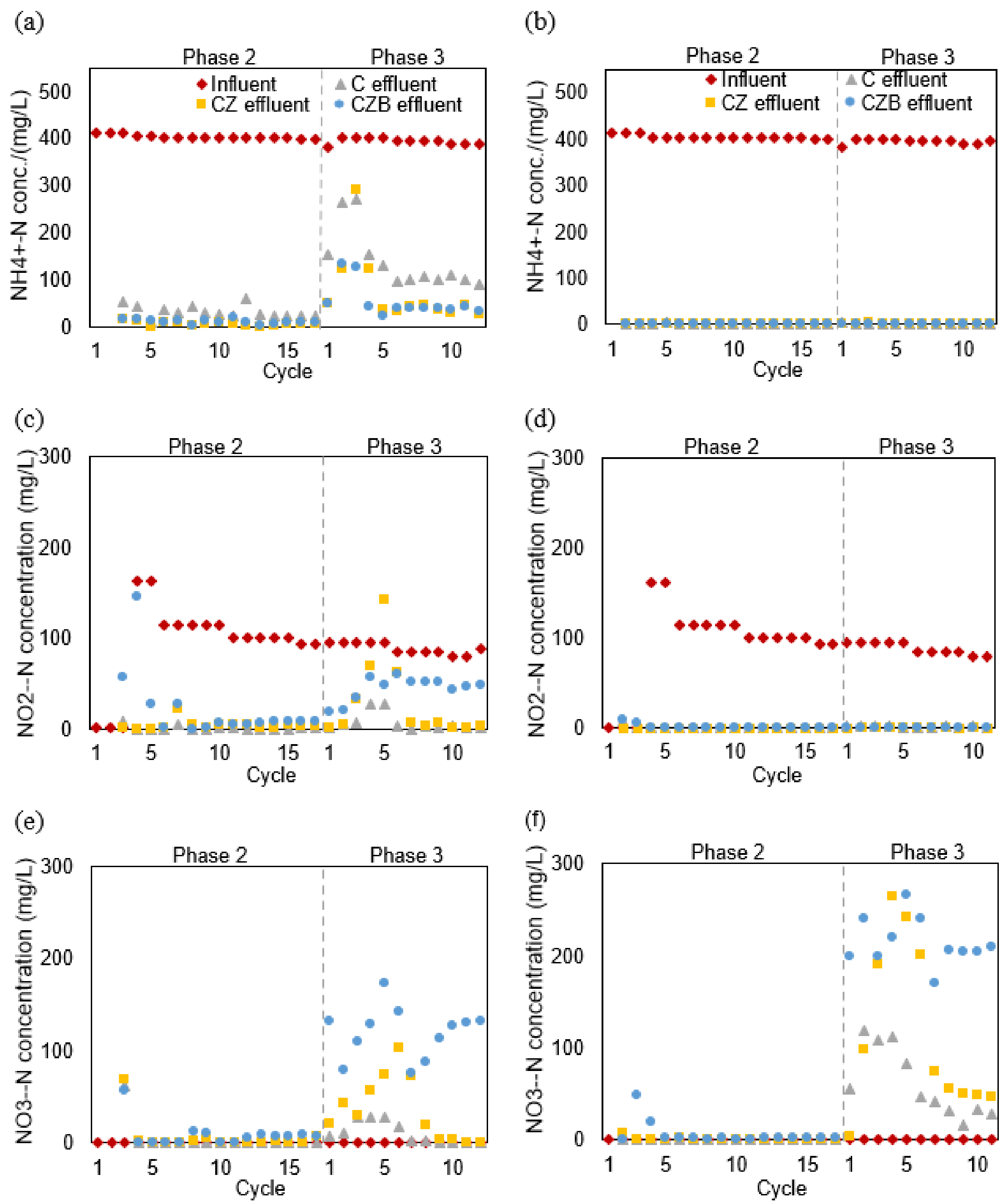

Figure A - 2: Nitrogen species variation: (a) NH_4^+-N after anoxic phase; (b) NH_4^+-N in final effluent; (c) NO_2^--N after anoxic phase; (b) NO_2^--N in final effluent; (c) NO_3^--N after anoxic phase; (b) NO_3^--N in final effluent.

Pilot-Scale Constructed Wetland Studies

Detailed information about CW characteristics and media distribution is shown below.

Table A - 1: Basic characteristics of each CW.

	CF-CW	HF-CW
Working volume	250	440
Aspect ratio (length : width, m)	1.0 (0.7 : 0.7)	1.8 (1.4 : 0.8)
Area (m^2)	0.4	1.1
Water depth (m)	0.6	0.4

Table A - 2: Media characteristics.

	Particle Size (mm)	Bulk Density (g/cm^3)
Coarse gravel (drainage/distribution layer)	19	1.5±0.03
Main Gravel	13	1.4±0.08
Fine gravel (separation layer)	1- 6	1.4±0.02
Zeolite	0.4 - 1.4	0.1±0.0035
Biochar	0.2 - 3	0.1±0.0002

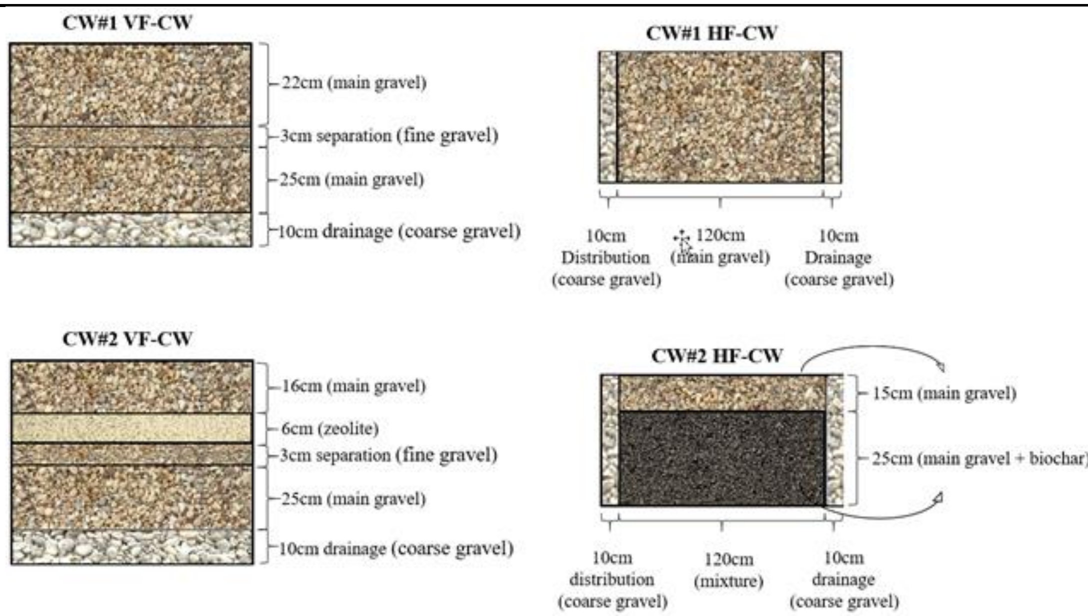

Figure A - 3: Media distribution in hybrid CWs (not to scale).

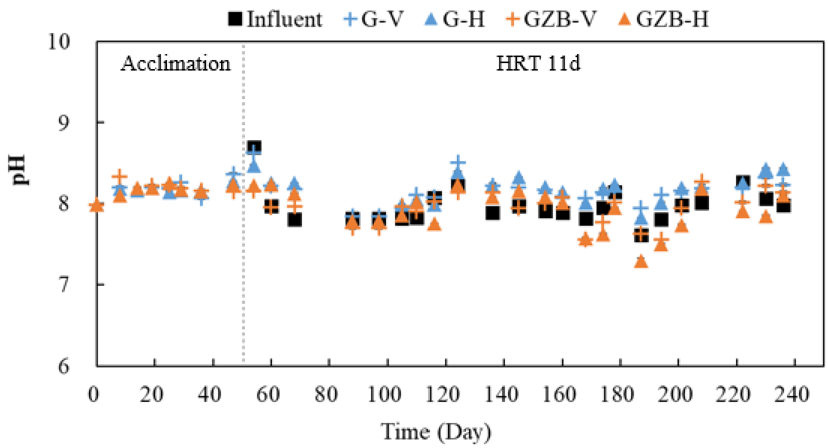

Figure A - 4: pH changes in CWs with/without adsorbents. G-V and G-H are vertical and horizontal stages of conventional gravel CWs. GZB-V and GZB-H are vertical and horizontal stages of adsorbent amended CWs.

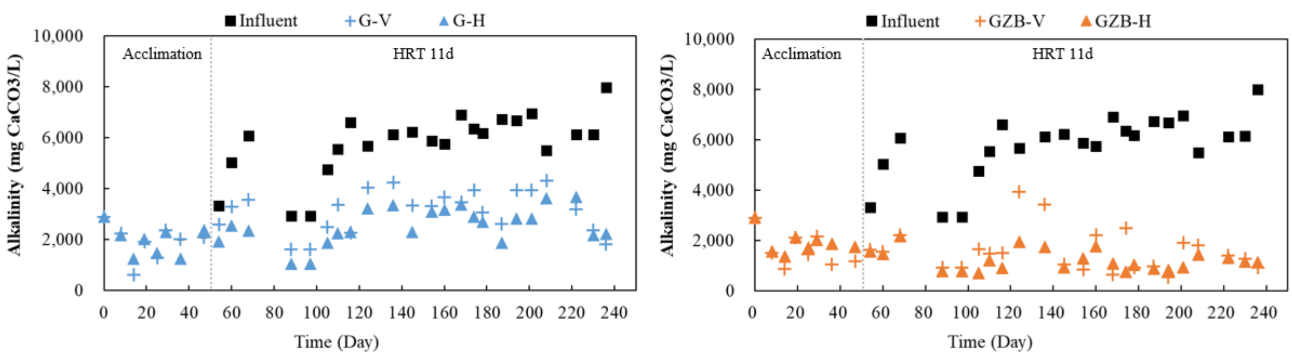

Figure A - 5: Alkalinity changes in CWs with/without adsorbents.

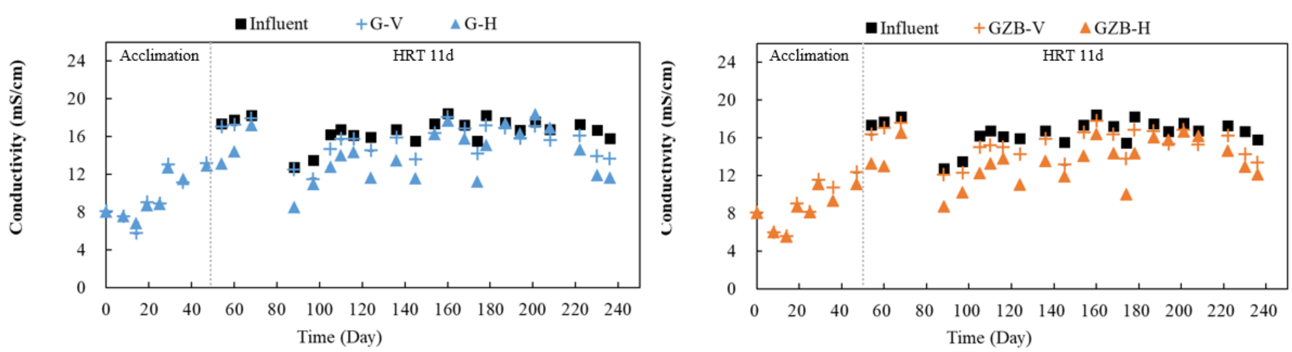

Figure A - 6: Conductivity changes in CWs with/without adsorbents.

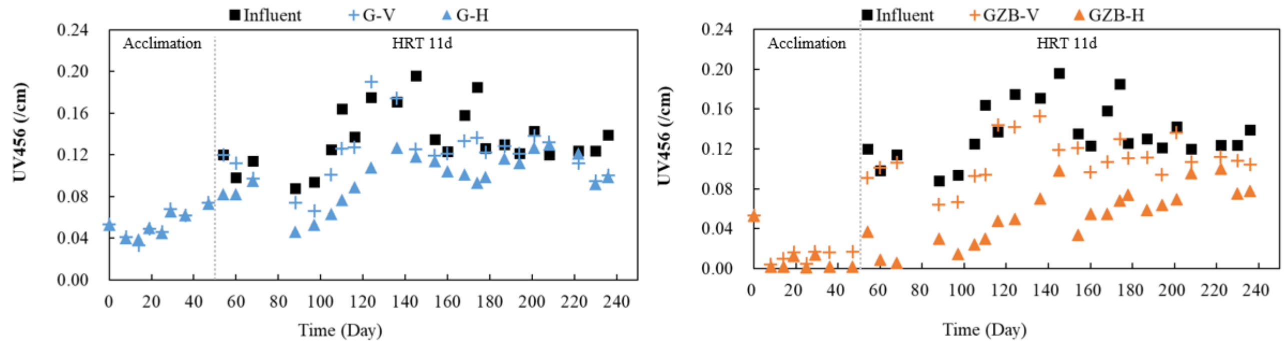

Figure A - 7: Color changes in CWs with/without adsorbents.

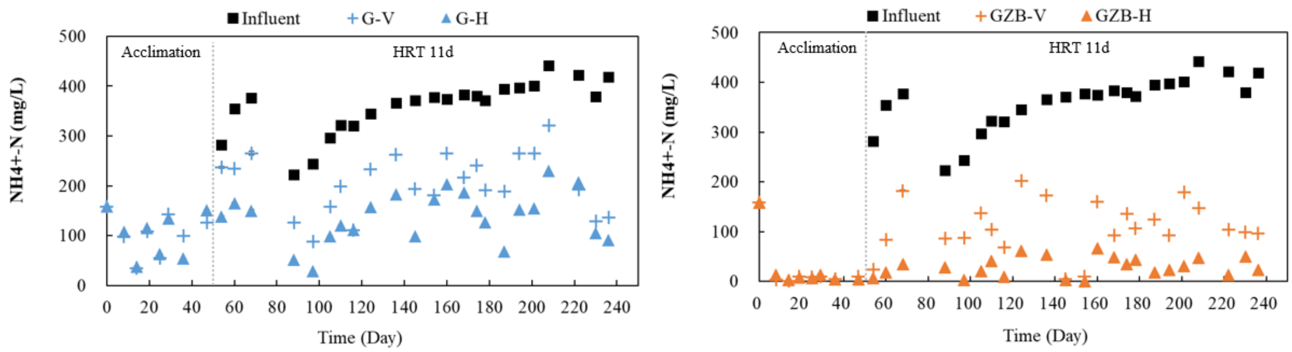

Figure A - 8: Ammonia changes in CWs with/without adsorbents.

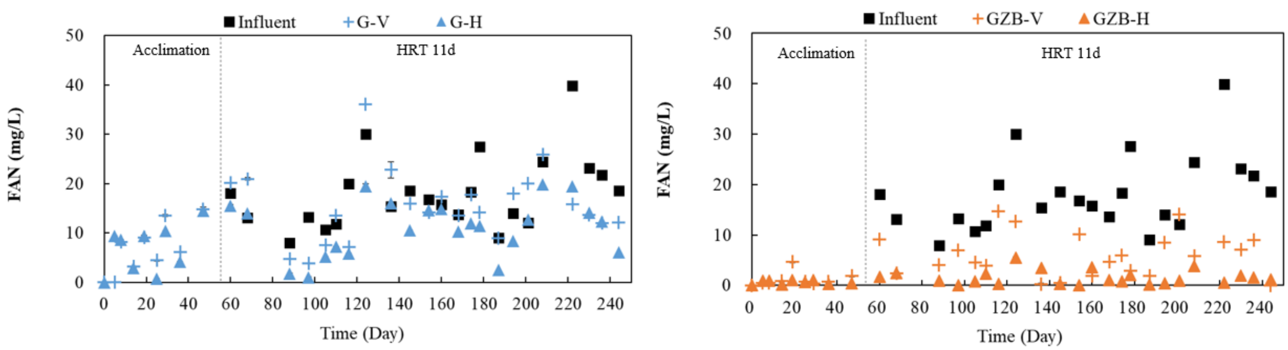

Figure A - 9: Free ammonia changes in CWs with/without adsorbents.

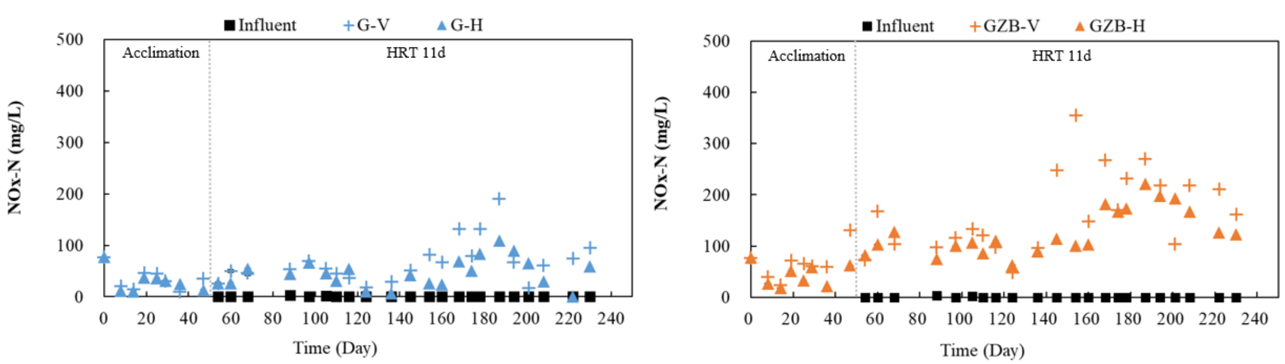

Figure A - 10: NOx changes in CWs with/without adsorbents.

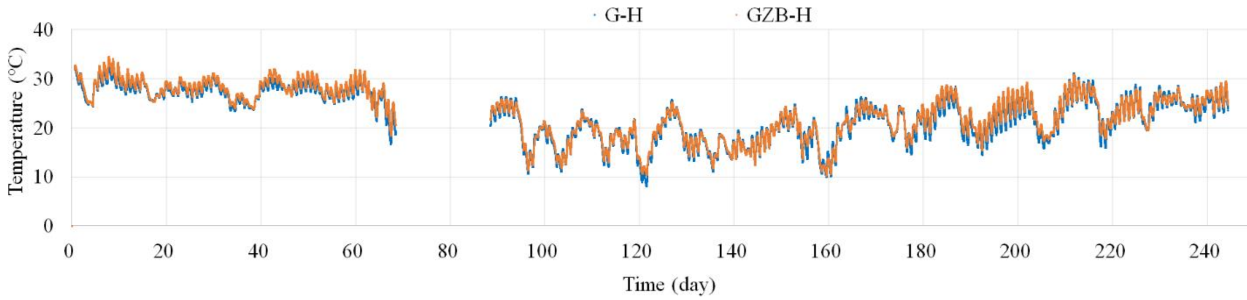

Figure A - 11: Temperature changing in CWs with/without adsorbents.

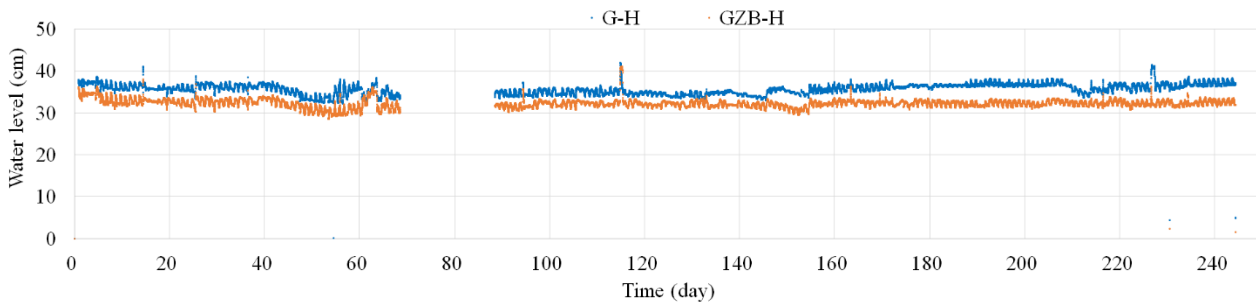

Figure A - 12: Water level changes in CWs with/without adsorbents.

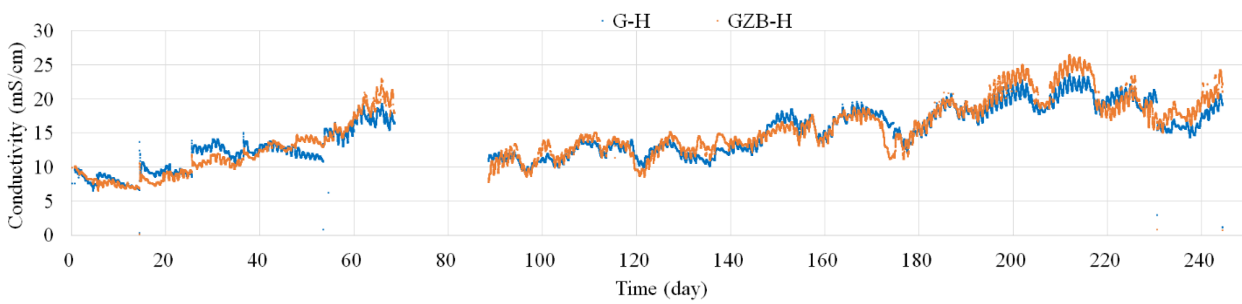

Figure A - 13: Conductivity changes in CWs with/without adsorbents.

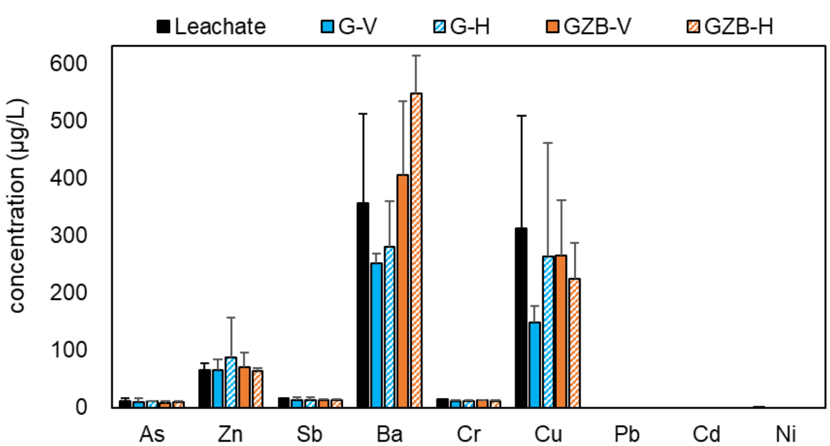

Figure A - 14: Heavy metal concentrations in CWs with/without adsorbents.

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