LANDFILL LEACHATE MANAGEMENT WITH ADSORBENT-ENHANCED CONSTRUCTED WETLANDS

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Final Report

PROJECT TITLE: LANDFILL LEACHATE MANAGEMENT WITH ADSORBENT-ENHANCED CONSTRUCTED WETLANDS

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ABSTRACT:

The dominant landfill leachate management method in Florida is discharge to publicly owned treatment works (POTWs). However, high concentrations of ammonia, recalcitrant organic compounds, metals and salinity in leachate interfere with POTW treatment processes. Results from our Phase I Hinkley Center funded project showed that subsurface-flow constructed wetlands (CWs) enhanced with low-cost adsorbent materials (zeolite and biochar), significantly improved ammonia, COD and color removal than a CW without adsorbent materials by coupling adsorption and biological treatment. *The overall goal* of this project was to optimize the design and operation of low-cost, low-complexity adsorbent-enhanced CWs for landfill leachate management. High-strength leachate collected from an Orange County landfill was treated in a bench-scale adsorbent-amended sequencing batch bioreactor (SBBR). The SBBR achieved higher nitrogen removal rates than during Phase I studies with low strength leachate. Color and sCOD removal in the SBBR declined over time, possibly due to saturation of the biochar. Side-by-side pilot CW studies with and without adsorbents at Hillsborough County's SE landfill showed that adsorbent addition significantly improved ammonia, color and COD removal, and wetland plant growth. Addition of a second stage horizontal flow (HF) CW containing wood chips effectively removed nitrate from the nitrified leachate, resulting in high TN removal efficiencies. A process-based computer model was programmed using open access software to evaluate the effects of uncertainty on leachate quality/quantity and adsorbent composition on CW performance. Results showed that the model successfully computed treatment efficiencies and long-term effluent concentration trends, and the effects of the soil amendments on removing COD and ammonia were evident. Leachate characterization combined with ultrafiltration reverse osmosis (UF-RO) simulation studies and economic analysis were used to evaluate the feasibility of leachate reclamation for industry or agricultural irrigation. Results showed that post-treatment of leachate for reuse by UF-RO is feasible and that the most economical configuration is pre-treatment by zeolite and biochar amended hybrid flow CWs. This project funded 4 students (1 PhD, 2 MS, and 1 undergraduate), has engaged 13 experts in the Technical Awareness Group, has been the subject of two master's theses, one PhD dissertation, two peer reviewed journal articles and several conference papers, posters and presentations. This research will help reduce the volume of leachate needing treatment in POTWs and will allow Florida municipal solid waste managers to reliably meet discharge and/or reuse standards.

Keywords:

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

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Metrics:

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

Lam, T., Yang, X. Ergas, S.J., Arias, M.E. (2023) Feasibility of Landfill Leachate Reuse through Adsorbent-Enhanced Constructed Wetlands and Ultrafiltration-Reverse Osmosis *Desalination,* 545(2023), 116163, DOI: https://doi.org/10.1016/j.desal.2022.116163

Gao, B., Yang, X., Dasi, E., Lam, T., Arias, M. E., Ergas, S. (2021) Enhanced Landfill Leachate Treatment in Sequencing Batch Biofilm Reactors (SBBRs) Amended with Zeolite and Biochar. *Journal of Chemical Technology & Biotechnology* 97 (3) 759-770. DOI: https://doi.org/10.1002/jctb.6964

Lam, T. (2021) *Use of Biochar and Zeolite for Landfill Leachate Treatment: Experimental Studies and Reuse Potential Assessment*, MS Thesis, Department of Civil & Environmental Engineering, University of South Florida, October 2021.

Mulligan, L. (2021) *Development of a Numerical Process Model for Adsorbent-amended Constructed Wetlands*, MS Thesis, Department of Civil & Environmental Engineering, University of South Florida, June 2021.

Yang, X. (2022) *Biochar Amended Biological Systems for Enhanced Landfill Leachate and Lignocellulosic Banana Waste Treatment*, PhD Dissertation, Department of Civil & Environmental Engineering, University of South Florida, November 2022.

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

Ergas, S.J. (2022) Landfill Leachate Treatment & Reuse Using Zeolite and Biochar Amended Hybrid Constructed Wetlands, Invited Seminar, Prague University of Chemistry and Technology, Prague, CZ, October 24, 2022.

Ergas, S.J., Yang, X., Lam, T., Moore, M., Mulligan, L., Arias, M. (2022) Adsorbent enhanced constructed wetlands for landfill leachate treatment, *Association of Environmental Engineering and Science Professors (AEESP) Bi-Annual Meeting*, June 28-30, 2022, St. Louis, MO.

Yang, X., Ergas, S.J., Arias, M.E. (2022) Hybrid Constructed Wetlands Amended with Zeolite/Biochar for Enhanced Landfill Leachate Treatment, *American Ecological Engineering Society (AEES) Annual Meeting*, June 20-23, 2022, Baltimore, MD.

Lam, T., Yang, X., Arias, M., Ergas, S.J. (2022) Feasibility of Landfill Leachate Reuse through Adsorbent-Enhanced Constructed Wetlands and UF-RO, Florida Water Resources Conference, April 24-26, Daytona Beach FL.

Ergas, S.J. (2021) Management of Nutrients and Pathogens Using Hybrid Adsorption Biological Treatment Systems (HABiTS), *American Chemical Society Fall Meeting*, Atlanta GA, August 23, 2021.

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

Lam, Thanh Thieu. *Use of Biochar and Zeolite for Landfill Leachate Treatment: Experimental Studies and Reuse Potential Assessment*. Diss. University of South Florida, 2021.

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, Nisa Ishfaqun and Xia Yang.
- ✓ PhD student Erica Dasi was supported through a McKnight Doctoral Fellowship and an NSF Research Traineeship.
- ✓ Undergraduate students Magdalena Shafee and Irene Castillo were supported by NSF REU supplements.
- ✓ USF Strategic Investment Pool grant was obtained ($10,000) to acquire equipment to produce and test biochar from waste materials.

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

Orange County Utilities Department, Solid Waste Division

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

Hillsborough County is very impressed with our results but is waiting to hear more about upcoming PFAS regulations before moving forward on changes to their leachate management strategy.

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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:

- Nisa Ishfaqun (ishfaqun@usf.edu): Ishfaqun is a graduate student of the MSEV program in the Department of Civil & Environmental Engineering and has a B.S. in Civil Engineering with a major in Environmental Engineering from Bangladesh University of Engineering and Technology. Nisa will complete her masters in the Spring of 2023, focusing on the treatment wetland uncertainty modeling component of this report.
- Thanh “Misty” Lam (ttlam@usf.edu): Ms. Lam is graduate of the MSEV program in the Department of Civil & Environmental Engineering and has a BS in Environmental Engineering from the University of Central Florida. Her thesis focused on upgrading constructed wetlands treated landfill leachate for agricultural irrigation using UF-RO treatment. She is currently working as an engineer at Jacobs Engineering in Tampa.
- 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 successfully defended her dissertation in October 2022 and will start a postdoc at the University of Houston in 2023.

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

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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

AS	Activated Sludge
BNR	Biological Nutrient Removal
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
C-SBBR	Control Sequencing Batch Biofilm Reactor
CSTR	Constantly Stirred Tank Reactor
CW	Constructed Wetland
CZB-SBBR	Sequencing Batch Biofilm Reactor with Zeolite and Biochar
CZ-SBBR	Sequencing Batch Biofilm Reactor with Zeolite
DO	Dissolved Oxygen
EBCT	Empty Bed Contact Time
ET	Evaporation and Transpiration
FA	Free Ammonia
Control-CW	Control Constructed Wetland with Gravel media
Adsorbent-CW	Constructed Wetland with Grave, Zeolite, and Biochar media
HF	Horizontal Flow
HLR	Hydraulic Loading Rate
HRT	Hydraulic Retention Time
HSDM	Homogenous Surface Diffusion Model
IX	Ion Exchange
LECA	Light Expanded Clay Aggregate
MSW	Municipal Solid Waste
NRMSE	Normalized Root Mean Square Error
NTU	Nephelometric Turbidity Units
NRR	Nitrogen Removal Rates
POTWs	Publicly Owned Treatment Works
rbCOD	Readily Biodegradable COD
RO	Reverse Osmosis
SBR	Sequencing Batch Reactors
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
TP	Total phosphorus
TIS	Tank in Series
TSS	Total Suspended Solids
UF	Ultrafiltration

USD	U.S. dollars
USF	University of South Florida
UV	Ultraviolet
VF	Vertical Flow
VSS	Volatile Suspended Solids

EXECUTIVE SUMMARY

In Florida, landfill leachate is typically discharge to publicly owned treatment works (POTWs). However, high concentrations of ammonia, recalcitrant organic matter, color and salinity interfere with POTW treatment processes. Prior studies have shown that constructed wetlands (CWs) can be used to treat landfill leachate; however, additional research is needed to improve their performance. Our prior research showed that addition of low-cost adsorbent materials, zeolite and biochar, can enhance CW treatment landfill leachate by decoupling pollutant and hydraulic residence times (HRTs), reducing concentrations of inhibitory compounds, such as ammonia, and enhancing plant growth and rhizosphere microbial activity.

Objective 1 investigated treatment of high-strength landfill leachate in a bench-scale zeolite and biochar-amended sequencing batch bioreactor (SBBR). The SBBR was operated in a three-stage sequence: 1) fill, 2) low aerobic react, 3) rapid drain, at varying hydraulic residence times (HRTs). High total inorganic nitrogen (TIN) removal rates of 82.9, 109, and 122 mg/L-day were observed at HRTs of 18.9, 14, and 10.5 days, respectively, most likely due to simultaneous nitrification-denitrification and partial nitritation/anammox. High soluble chemical oxygen demand (sCOD) removal rates of 168, 217, and 223 mg/L-day were observed at HRTs of 18.9, 14, and 10.5 days, respectively. High color removals were initially observed, but declined over time. The results indicate that zeolite can be completely bio-regenerated over many SBBR cycles; however, biochar loses its adsorptive capacity for recalcitrant organic matter over time. The SBBR achieved higher TIN and sCOD removal rates than in our Phase I study, indicating adsorbent amended SBBRs can be used for very high strength leachate.

Objective 2 investigated the effects of low-cost adsorbents (zeolite and biochar) addition on the treatment performance of hybrid constructed wetlands (CWs) for landfill leachate treatment. Two pilot-scale hybrid CWs, consisting of a Vertical Flow (VF) tank followed by a Horizontal Flow (HF) tank, were constructed at the Southeast Hillsborough County landfill. The Control-CW was filled with conventional gravel medium, while the Adsorbent-CW was amended with 10% (v/v) zeolite in the VF tank and 13% (v/v) biochar in the HF tank. Both systems were planted with

cattail (*Typha spp*) and cordgrass (*Spartina*) and operated at varying HRTs (11d, 7d, and 4.5d) for ~2 years. To further enhance denitrification, wood chips (Woodchip-CW) were used as a carbon source in a second HF tank after Day 540. Results showed that biochar addition improved sCOD and color removals from 22-33% to 29-43% and from 0-20% to 6-49%, respectively. Zeolite addition remarkably increased nitrification rates in the Adsorbent-VF by 35-96%, especially under higher ammonia loading conditions. Zeolite addition also reduced free ammonia (FA) inhibition to nitrifiers and wetland plants. Implementation of the Woodchip-CW significantly reduced nitrate accumulation by releasing organic matter and enhancing denitrification. After addition of the Woodchip-CW, total nitrogen removals of up to 78-80% were achieved.

Objective 3 investigated the effects of uncertainty on leachate quality/quantity and adsorbent composition on CW performance. A numerical process model was developed to predict the adsorbent-amended CW performance under varying wastewater loads and concentrations. This process model considers changes in water storage, nitrogen transformations, dissolved oxygen (DO) cycle, COD removal, effects of temperature, enhancement effects for zeolite and biochar. The model was developed in Python 3.7 using the data collected from the pilot-scale system described above. The model was able to predict the general effluent concentration trends for all of the modules and was able to predict the adsorption effects of both zeolite and biochar. The model was particularly good at predicting removal efficiencies for both COD and ammonia. The source code of the model will be made available online for further research and to help in the design and operations of adsorbent-amended treatment wetlands.

Objective 4 investigated the potential for highly treated landfill leachate to be reclaimed for irrigation or industrial applications. Chemical characterization of raw and treated leachate, ultrafiltration-reverse osmosis (UF-RO) simulations and a net present value analysis were used in this analysis. Four UF-RO pre-treatment scenarios were compared: 1) no pretreatment, 2) activated sludge, 3) CWs, and 4) adsorbent-enhanced CWs. Samples were collected of untreated leachate, and effluent from pilot-scale CWs (Objective 2) and an onsite activated sludge system. The landfill leachate treatment train consisting of adsorbent-enhanced CW followed by UF-RO attained the highest water recovery rate and greatest cost savings compared with untreated landfill leachate disposal. The results show that addition of low-cost adsorbents to CWs is a promising approach for enhanced pre-treatment prior to UF-RO for landfill leachate reclamation.

1 INTRODUCTION

There are more than 1,900 active landfills in the US, accepting over 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), a toxic substance 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 total ammonia nitrogen (TAN), chemical oxygen demand (COD), recalcitrant organic matter, metals and salinity interfere with physical, chemical and biological processes at POTWs. 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 & 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.

1.1 Hypotheses and Objectives

The overall goal of this project is to develop low-cost, low-complexity adsorbent-enhanced CWs for landfill leachate management that could reduce leachate volume and allow MSW managers to meet Florida discharge and/or reuse standards. The research is grounded in our Phase I Hinkley Center funded project of low-cost adsorbents in CWs (http://constructed-wetlands.eng.usf.edu/). This proposal directly addresses the general issue of landfill leachate management, which has been a consistent item in the Hinkley Center research agenda since 2004.

Specific objectives of the proposed project include:

(1) Investigate treatment of high-strength leachate collected from Florida landfills in bench-scale adsorbent-enhanced bioreactors;

(2) Investigate long-term leachate quality and quantity performance of pilot-scale CWs operated at Hillsborough County's SE landfill under varying conditions;

(3) Evaluate the effects of uncertainty on leachate quality/quantity and adsorbent composition on CW performance using process modeling;

(4) Use simulation software and economic analysis to evaluate the post-treatment feasibility of CW-treated leachate by ultrafiltration reverse osmosis (UF-RO) to meet reuse or disposal requirements.

1.2 Background

1.2.1 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 TAN, refractory organic matter, metals and salinity concentrations (Zhao et al. 2012). Impacts of landfill leachate on POTWs include: 1) nitrification inhibition by high FA concentrations and toxic metals, 2) increased aeration demands (and thus energy requirements), 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). Landfill leachate can be treated to meet industrial and/or agricultural reuse standards. For instance, reclaimed leachate has been previously used for landfill cover irrigation (Justin and Zupancic, 2009).

1.2.2 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 (Bulc, 2006; Silvestrini et al, 2019; Saeed et al, 2020; Saeed et al, 2021). Landfill leachate treated by CWs; however, can have high concentrations of dissolved solids and heavy metals, making it unsuitable for irrigation or industrial reuse. CWs are, however, an excellent pretreatment alternative for UF-RO (Huang et al., 2011).

1.2.3 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 biological nitrogen removal (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 & 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.

1.2.4 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 agricultural and urban 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; 2021).

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 total phosphorus (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.

1.2.5 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 & 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 studies up to date, however, have used process models to predict the effect of adsorption material on CW performance.

1.2.6 Landfill Leachate Reclamation

Landfill leachate has the potential to be treated to meet industrial or agricultural reuse standards (Justin and Zupancic, 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, 1997; Peters, 1998).

1.2.7 Phase 1 Results

Our Phase I Hinkley Center project demonstrated a great improvement in leachate treatment using bioreactors amended with low-cost adsorbents (zeolite and biochar). In our initial studies, three bench-scale Sequencing Batch Biofilm Reactors (SBBRs) were operated with different media materials: 1) light weight expanded clay aggregate (LECA) as a control without adsorbents (C-SBBR), 2) LECA + zeolite (CZ-SBBR), and 3) LECA + zeolite + biochar (CZB-SBBR). The three SBBRs were operated with alternating anoxic and aerobic stages with leachate from

Hillsborough County's Southeast Landfill. 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%). Although high effluent NO_3^- concentrations were initially observed in the biochar amended reactor, after > 1 year of operation NO_3^- accumulation declined and TN removals were > 70% due to combined nitrification/denitrification and anammox activity (see Gao et al., 2022).

Based on the successful bench scale study, two pilot-scale hybrid VF-HF CWs were designed for a side-by-side comparison of leachate treatment performance with and without adsorbent addition (Figure 1). Control-CW contained a conventional gravel medium, while Adsorbent-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 at Hillsborough County's SE landfill in August 2020. 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.

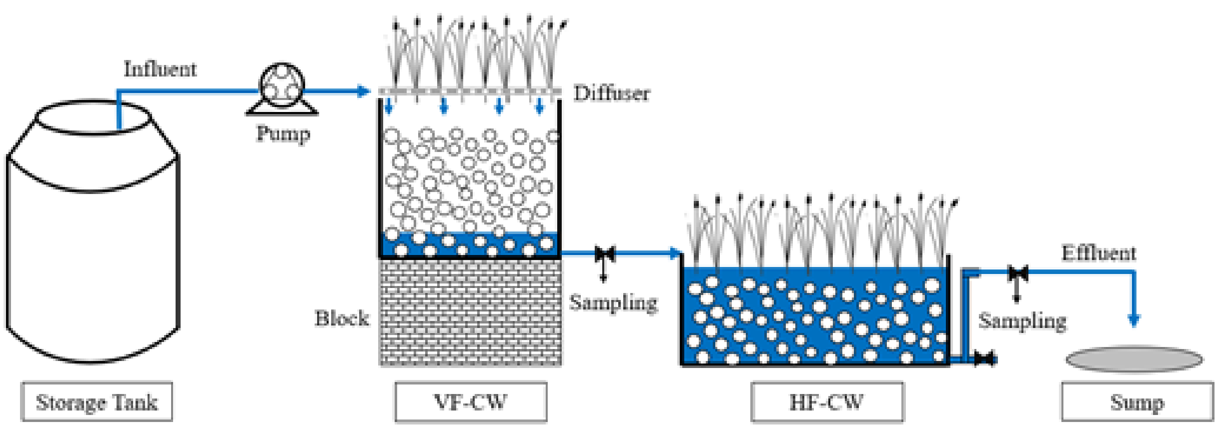


Figure 1. Pilot VF-HW CW schematic.

In Phase I, sCOD removal efficiency was significantly higher in the adsorbent-enhanced VF-HF CW (55%) than in the unamended control (28%). Biochar addition also effectively enhanced color removal from 33% to 67%. sCOD and color trends were similar to those in the bench-scale study, confirming that adsorption of recalcitrant organic matter initially enhanced biodegradation. Moreover, zeolite addition increased TAN removal from 63% to 91% (Fig. 2(b)). In the intermittently loaded VF-CW, NH_4^+ adsorbs to zeolite during the wetting period and is subsequently nitrified as oxygen fills the media pores during the drainage period. NO_3^- accumulation was observed in the effluent from both CWs due to limited organic carbon availability for denitrification due to the low BOD_5/COD ratio (~ 0.1) of the leachate. As shown in Figure 2, biochar addition improved the growth of cordgrass and cattails. Overall, the excellent results documented in Phase I with the adsorbent-enhanced pilot CW justified additional long-term performance monitoring under varying conditions during Phase II.

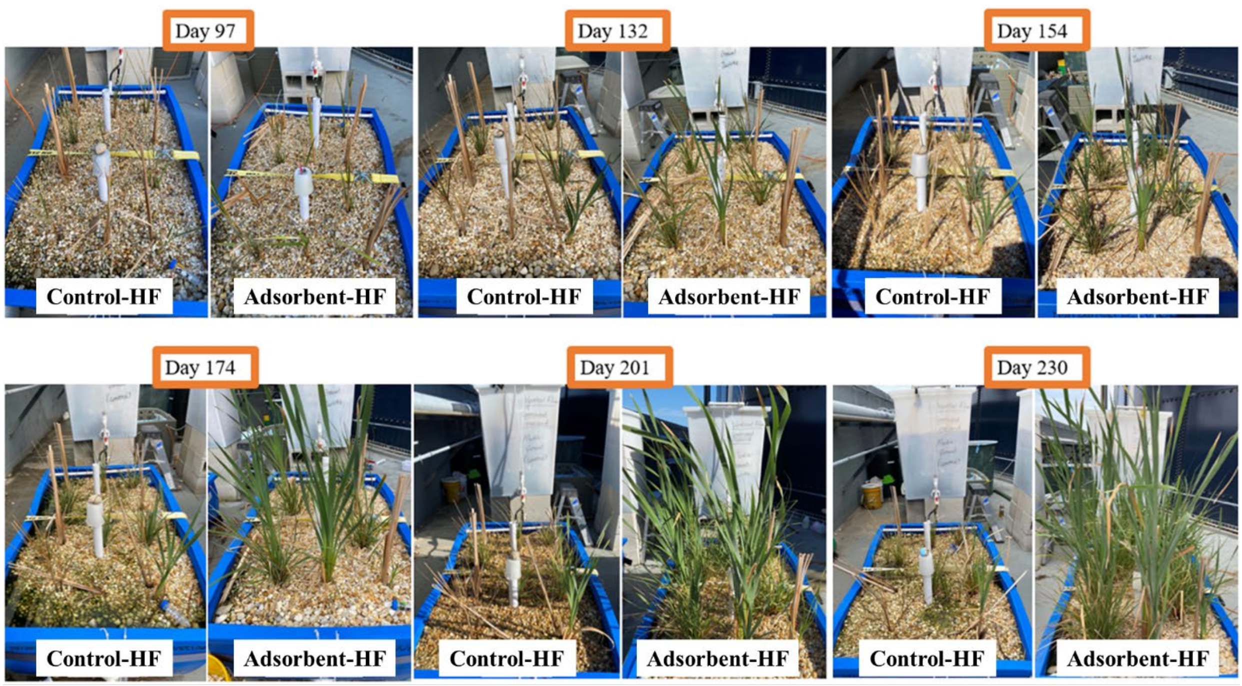


Figure 2. Plant growth in CW-HFs in the Southeast Hillsborough County landfill.

1.2.8 Research Gaps

Based on the literature review and results of the Phase I study, the following key knowledge gaps were identified, which guided the Phase II study:

- What are the effects of leachate strength and hydraulic loading on CW performance?

- What is the cumulative effect of zeolite and biochar addition on TAN and recalcitrant organic matter removal in VF-HF CWs?
- What are the effects of uncertainty in leachate quality, loading rates, and adsorbent addition on CW performance?
- Does the addition of biochar promote wetland plant growth and leachate transpiration?
- Can adsorbent-amended VF-HF CWs provide a good pre-treatment method for UF-RO to produce reclaim water?

2 METHODS

2.1 High strength leachate treatment with bench-scale SBBR

A bench-scale recirculating SBBR column with zeolite and biochar media amendments was operated in the Environmental Engineering Laboratory at the University of South Florida (USF) (Tampa, FL, USA). Each cycle was operated with slow recirculation to enhance mass transfer or substrate to the biofilm and provide aeration. This section presents information on how this SBBR was designed, operated, and monitored. The schedule of this study is shown in Table 1 with empty bed contact times (EBCTs) and total ammonia nitrogen (TAN) mass loading rates.

Table 1. Schedule of Start-up and Study Periods

<table>
<tr><th>Study Period</th><th>Date</th><th>HRT (days)</th><th>EBCT (days)</th><th>Fill volume per cycle (mL)</th><th>Volume Exchanged per cycle (%)</th><th>TAN fed per cycle (mg)</th></tr>
<tr><td rowspan="2">Start-up</td><td>5/24/2021 – 5/31/2021</td><td rowspan="2">26</td><td rowspan="2">71.9</td><td>50</td><td>9.26</td><td>78</td></tr>
<tr><td>5/31/2021 – 6/21/2021</td><td>100</td><td>18.5</td><td>157</td></tr>
<tr><td>1</td><td>6/21/2021 – 8/2/2021</td><td>18.9</td><td>58.3</td><td>100</td><td>18.5</td><td>157</td></tr>
<tr><td>2</td><td>8/2/2021 – 8/30/2021</td><td>14</td><td>38.9</td><td>135</td><td>25</td><td>212</td></tr>
<tr><td>3</td><td>8/30/2021 – 9/20/2021</td><td>10.5</td><td>29.2</td><td>180</td><td>33.3</td><td>282</td></tr>
</table>

The HRT of the SBBR was calculated by Equation 1:

$$HRT = \frac{V_{leachate,column} \times T_{cycle}}{V_{fill}} \qquad (1)$$

where $V_{leachate,\ column}$ is the leachate volume in the column (540 mL), V_{fill} is the cycle fill volume, and T_{cycle} is one cycle's time (3.5 days).

The EBCT of the SBBR was calculated by Equation 2:

$$EBCT = \frac{V_{total,column} \times T_{cycle}}{V_{fill}} \qquad (12)$$

where $V_{total,column}$ is the total empty volume of the bioreactor column (1,500 mL), V_{fill} is the cycle fill volume, and T_{cycle} is one cycle's time (3.5 days).

2.1.1 2.3.1 SBBR Design

Three media materials were used in this study. LECA was purchased from Trinity Lightweight Aggregate (Livingston, AL). Clinoptilolite, was obtained from St. Cloud Mining Company's Ash Meadows Plant (Inyo County; Nye County, NV). Biochar was obtained from Biochar Supreme Inc. (Everson, WA). Media properties are shown in Table 2.

Table 2. Physical Properties of Media (Adapted from Gao, 2020)

Material	Manufacturer	Bulk Density (g/cm^3)	Particle Size Range (mm)
Large LECA	Trinity Lightweight Aggregate	0.785	0.6 – 2
Small LECA		0.785	2 – 5
Clinoptilolite	St. Cloud Mining Company	0.877	< 0.6
Biochar	Biochar Supreme Inc.	0.090	2 – 4

The bench-scale SBBR (Figure 3) was initially set up in September 2019 for the Phase I study (Gao et al., 2022). The SBBR dimensions are listed in Table 3 and components are detailed in Table 4. The SBBR was filled with 47% by volume of LECA, 8% by volume of zeolite, and 45% by volume of biochar. Adsorbent volumes were selected to meet target adsorbate concentrations (ammonia and COD) in the solution based on preliminary adsorption experiments (Gao et al., 2022). Large LECA particles were placed as a cover layer to prevent adsorbent materials from floating.

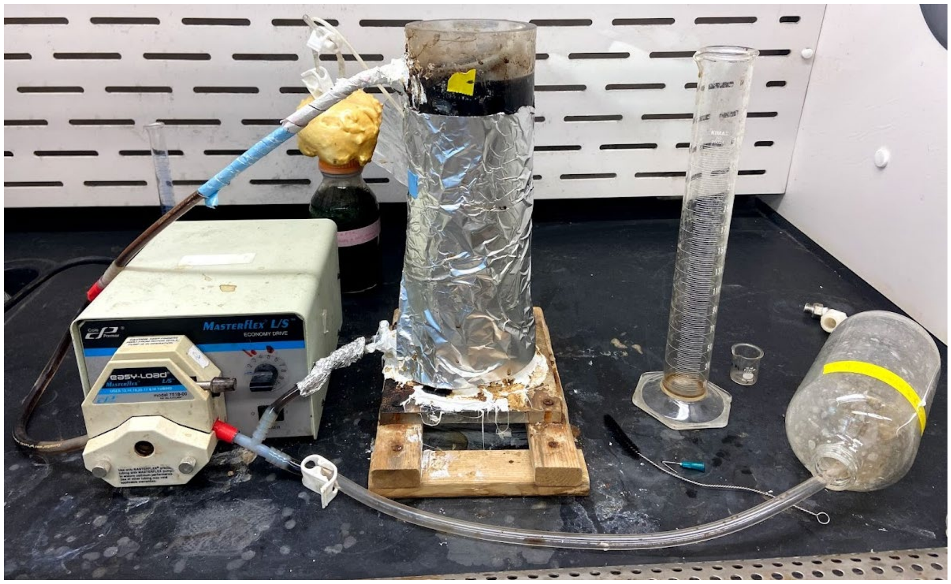


Figure 3. Bench-scale SBBR Column Set-up with Pump

Table 3. SBBR Dimensions (Adapted from Gao, 2020)

Dimension	Value
Outside Diameter	12 cm
Inside Diameter	10 cm
Height	20 cm
Overall Column Volume	1,500 mL
Pore Volume	450 mL
Leachate Volume	540 mL

Table 4. SBBR Components (Adapted from Gao, 2020)

Component	Manufacturer	Material	Quantity
Column	Constructed in-house	Acrylic	1
Recirculation Tubing	Cole Parmer Instrument Company	Lab E 3603 Tubing # L/S 17	50 cm
Discharge Tubing			20 cm
Perforated Tubing			15 cm
¼-inch MPTX × ¼-inch Barb Fitting	McMASTER-CARR	Nylon Hose	2
¼-inch Barb × ¼-inch Barb Fitting			1
3/8-inch MNDR × 3/8-inch BR Fitting			2

2.1.2 Orange County Landfill Leachate Sample Collection

Landfill leachate was collected from the Orange County Landfill in Orlando, Florida at the pump station for Cells 7B and 8. The landfill currently accepts Class I wastes, yard waste, asbestos, tires, as well as construction and demolition debris. Landfill Cells 7B and 8 are designated as a Class I landfill cells and are > 10 years in age. Landfill leachate and wastewater from the site is collected into a master pump station and is pumped to the nearby Eastern Regional Water Reclamation Facility for co-treatment with conventional wastewaters. In May 2021, approximately 10 L of landfill leachate was collected. The sample was stored at 6°C at the USF's Environmental Engineering Laboratory and used throughout the study.

2.1.3 SBBR Operation

The SBBR was set up in a fume hood at room temperature (~25 °C) and was covered with aluminum foil to inhibit algae growth. A backwash was performed on May 10, 2021 to remove excess biofilm before the start of the Phase II study with high-strength landfill leachate. The SBBR was operated on a 3.5-day cycle consisting of the following stages (Figure 4): 1) rapid fill, 2) 3.5-day low aerobic react, and 3) rapid drain. During the react stage, leachate was recirculated at a flow rate of 15 mL/min from the bottom of the reactor to the perforated pipe above the liquid surface. This was done to provide aerobic conditions at the top of the SBBR and anoxic conditions below the surface. To offset water loss by evaporation, the SBBR was replenished with collected effluent every cycle to an indicated line on the column. The SBBR was also cleaned every week to remove any potential algae and dead bacteria on the top of the reactor.

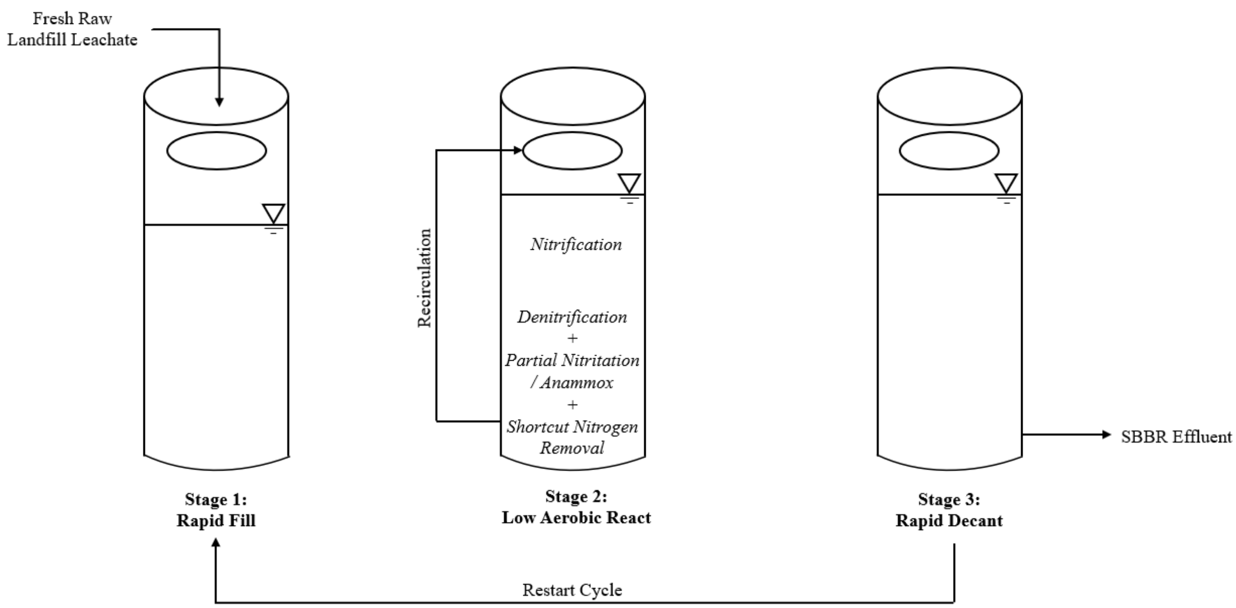


Figure 4. Schematic of Operational Stages of a SBBR Cycle

2.2 Pilot-scale hybrid CW studies

2.2.1 Hybrid CW design and operation

Two pilot scale hybrid CW systems without (Control-CW) and with adsorbent amendment (Adsorbent-CW) were set up at the Southeast Hillsborough County landfill for side-by-side operation (Figure 5). Each system initially consisted of a VF-CW followed by a HF-CW. On day 540, an additional woodchip amended HF-CW stage (Woodchip-CW) was added to the Adsorbent-CW to promote denitrification and enhance total nitrogen removal (Phase 4, Table 5). Each VF-CW had a hydraulic volume of 250 L with a surface area of 0.4 m^2 (0.65 m×0.65 m) and depth of 0.6 m. The HF-CWs covered 1.1 m^2 (1.40 m×0.78 m) with depth of 0.4 m for a total hydraulic volume of 430 L.

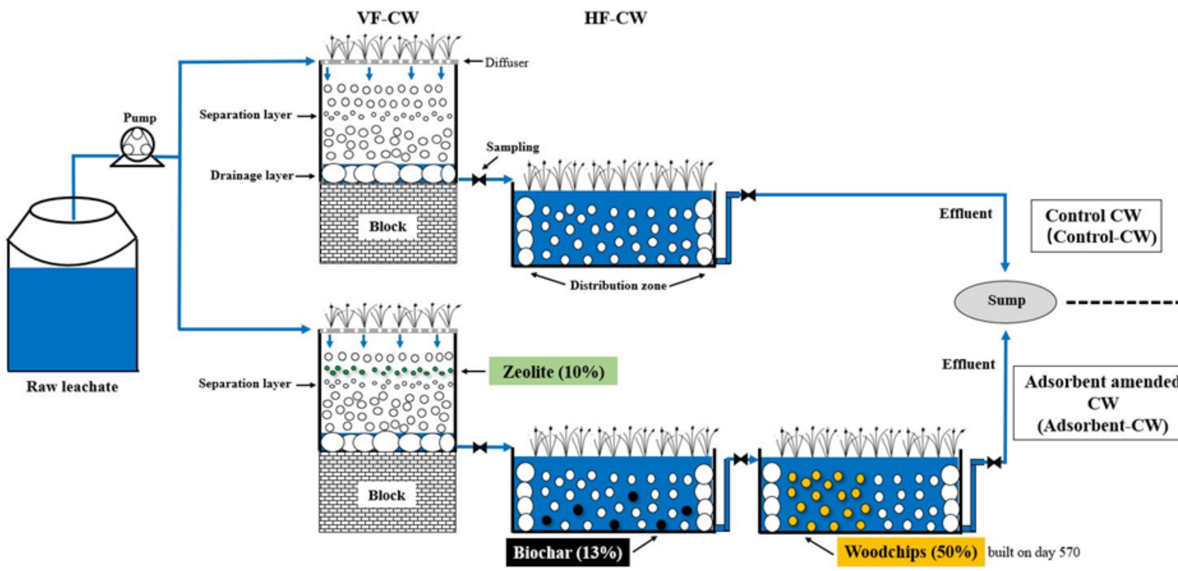


Figure 5. Pilot-scale hybrid CWs (not to scale).

Control-CWs were filled with gravel in both VF and HF tanks (Figure 5). In the adsorbent-CWs, a zeolite layer (10% by volume) was added to the upper level of VF cell to obtain good oxygen availability for nitrification and 13% (by volume) of biochar was mixed with gravel and added to the HF cell to improve contaminant removal and plant growth. The volume of adsorbent added was based on batch adsorption isotherm studies. Based on the adsorption capacity, the dosage of zeolite to VF-CW and biochar to HF-CW were calculated as:

$$P_{adsorbent} = \frac{Q \times C \times t \times SF}{Q_m \times D \times V \times 1000} \times 100$$

where $P_{adsorbent}$ is the adsorbent addition to CWs (zeolite added to VF-CW and biochar added to HF-CW) (%, by volume); Q is the target leachate daily inflow (80 L/d in this study); C is the adsorbate concentration in leachate (NH_4^+-N for zeolite dosage calculation, sCOD for biochar dosage calculation); t is the nitrification time in VF-CW or denitrification time in HF-CW (2 days used in this study); D is adsorbent bulk density (0.97 g/mL for zeolite and 0.088 g/mL for biochar); V is the media volume (250 L for VF-CW and 430 L for HF-CW); SF is a safety factor (2 in this study).

A separation layer consisting of small gravel was added to support zeolite from falling through the gravel due to its much smaller particle size than gravel. Coarse gravel was added as either distribution or drainage zone. Woodchip-CW was filled with woodchips (as carbon source) and gravel (as polishing unit) by zones (1:1 by volume). Wood chip volume addition was based on the NO_3^- loading rate and prior work by our group showing the mass of bioavailable organic matter in wood chips (Lopez-Ponnada et al., 2017) and an assumption that wood chips would be replaced approximately every three to five years. Woodchips consisted of residential yard waste, obtained from the composting unit at the Southeast Hillsborough County Landfill. Based on the personal communication with the President (Gilbert Sharell) at Aquatic Plants of Florida (Sarasota, Florida, USA) and previous studies (Klomjek and Nitisoravut, 2005), two native plants: cattails (*Typha spp*) and cordgrass (*Spartina*) were planted interlaced at a density of 10 plants/m^2 on day 70 for Control-CW and Adsorbent-CW and on day 574 for Woodchip-CW. A digital timer was connected to the peristaltic pump (Cole-Parmer Instrument Company, LLC, IL) to control the switch of the pump for the intermittent feeding of leachate.

The CWs were operated in five phases (Table 5). Phase 1 was an acclimation period to promote biofilm growth on the media. Two hybrid CWs were inoculated with the sludge from the activated sludge treatment system at landfill diluted with a mixture of 25% of raw landfill leachate and 75% of groundwater (by volume) resulting a total solids concentration of 1 g/L. A recirculation flow rate of 160 mL/min between the VF-CW and HF-CW was applied once per week for 4 hours 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 to 5 are experimental phases with different CW operating conditions to investigate the effects of HRT and hydraulic loading rate (HLR) (Phase 2 and 5), leachate feeding frequency (Phase 3 to Phase 4), and woodchip supplement (Phase 4) on contaminant removal.

Table 5. Experimental phases for CWs.

Phase	Inflow (L/d)	HLR (cm/d)	HRT (d)	Feeding frequency	Electron donor supplement	# days operation
1	NA	NA	NA	Regular recirc.	NA	50
2	24	1.6	11	15 min/2h	NA	250
3	40	2.7	7	15min/2h	NA	100
4	40	2.7	7	7min/h	NA	140
					Woodchips	70
5	60	4.0	4.5	6min/30min	Woodchips	100

Note: Feeding frequency x/y means pump on for time x every time y; NA: not applicable.

2.2.2 Pilot-scale Studies Data Analysis

Statistical significance was determined by t-tests using Microsoft Excel. Comparisons with p-values less than 0.05 were considered as significantly different.

2.3 Analytical methods for SBBR and pilot-scale studies

Dissolved Oxygen (DO), pH, and conductivity were measured using an Orion 5 Star Multifunction Meter (Thermo Scientific, USA). NH_4^+-N and NOx-N (sum of NO_2^--N and NO_3^--N) concentrations were measured using a Timberline TL-2800 Ammonia Analyzer (Timberline Instrument, USA). NO_2^--N concentration was measured using Standard Methods (4500) (APHA et al., 2012). NO_3^--N was calculated by subtracting NO_2^--N from NOx-N concentrations. Total Nitrogen (TN) was measured using HACH TNT plus HR test kits (5-40 mg/L) (Hach Company, USA). Organic nitrogen (Org-N) was calculated by subtracting total inorganic nitrogen (TIN = NH_4^+-N, NO_2^--N and NO_3^--N) from TN concentration. sCOD concentration was measured using Lovibond LR test kits (0-150 mg/L) (Tintometer Inc, USA). Standard Methods (APHA et al., 2012) were used to measure UV456 (2030C), sulfate (4500E), alkalinity (2320B), TSS (2540D), VSS (2540E), turbidity (2130B), and BOD_5 (5210B). Cationic metals were measured by Inductively Coupled Plasma Optical Emission Spectroscopy at the USF Geochemistry Core facility. Additional anions and cations were measured using a Metrohm 881 Compact IC Pro Systems (Metrohm, USA). SDI_{15} was measured by ASTM Method D4189.

2.4 CW performance uncertainty modeling

To evaluate the effects of uncertainty on leachate quality/quantity and adsorbent composition on CW performance, a numerical process model has been developed to predict the adsorbent-amended CW performance under varying wastewater loads and concentrations. This process model takes into account changes in water storage, nitrogen transformations, DO cycle, COD removal, effects of temperature, enhancement effects for zeolite and biochar. The model has been developed in Python 3.7 using the data collected from the pilot-scale system elaborated in previous sections. The following tasks have been accomplished under this section-

1. Numerical process model development for hybrid CWs with and without adsorption enhancement.
2. Uncertainty analysis to understand the model's sensitivity to the uncertainty in model parameters.

2.4.1 Model Overview

The steps for developing the numerical process model for constructed wetlands are described in Figure 6. The simulation was performed over a time step of one hour using 6 months' data collected from the pilot-scale system during 25th November 2021- 14th May, 2021, which is the 'Calibration Period' of the model. The hourly rainfall and temperature data collected from 'Lithia, FL Weather History, 2021' were used for precipitation and evapotranspiration. Major nitrogen transformation pathways considered are shown in Figure 7. The pH was assumed to be neutral throughout the whole experiment. The mass balance modules are elaborated in detail in the following sections.

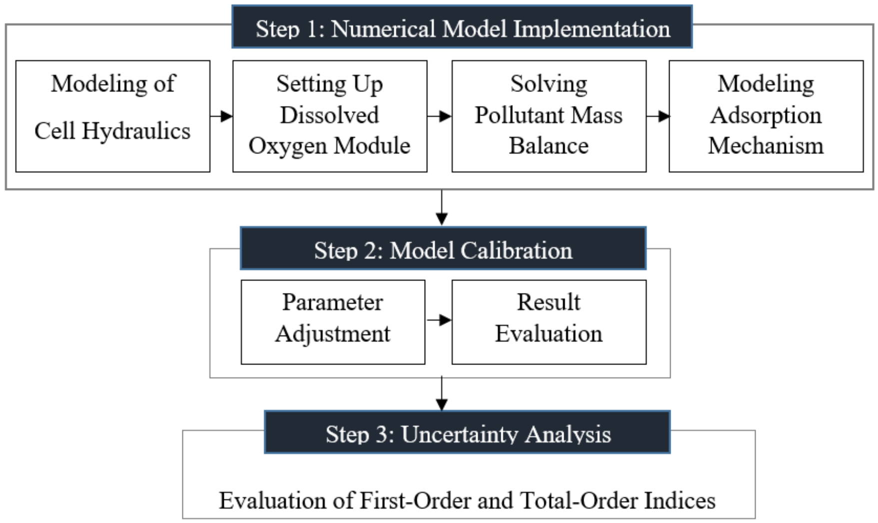


Figure 6. Steps of Leachate CW Modeling Method

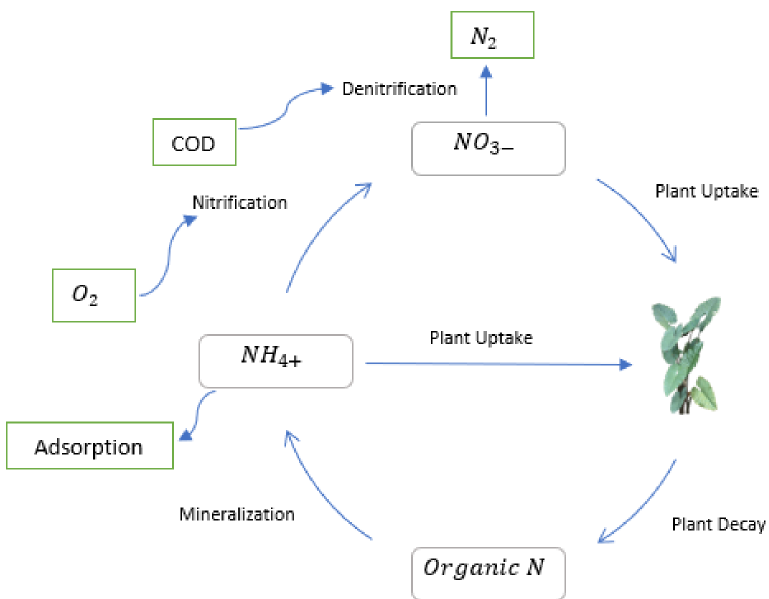


Figure 7. Major Nitrogen Transformation Route

2.4.2 Water Balance Module

To solve for hourly water volume of both VF and HF CWs, the following mass balance equation has been used:

$$\frac{\Delta V}{\Delta t} = Q_i - Q_0 + (PA_s) - (ETA_s) \qquad (3)$$

where V is the volume (m^3), t is time (hour), Q_i is the inflow rate (m^3/hour), Q_0 is the outflow rate (m^3/hour), P is precipitation (m/hour), A_s is the wetland surface area (m^2), and ET is evapotranspiration (m/hour). As for the hydraulic loading rate associated with Q_i, 24L of water has been fed to the system intermittently (for 15min every 2 hours).

2.4.3 VF-CW Hydraulics Simulation

To understand the hydraulics in the VF CW, we performed preliminary computer simulation using Hydrus-1D. This is a public domain Microsoft Windows-based modeling environment that simulates water flow and solute transport of variably saturated porous media in one dimension. It offers an interactive graphic-based interface for data analysis, discretization of the control volume and graphical presentation of results. It has been widely applied for many years for efficiently simulating the movement of water and solute transport (Šimůnek et al., 2016).

For simulating this flow, it is assumed that leachate flux runs through the system from the top to bottom of the bed and the horizontal flow is neglected (Giraldi et al., 2010). A qualitative diagram for the system can be found in Figure 8. We implemented a numerical solution for one dimensional flow systems in our model based on Richard's equation for one-dimensional water flow through porous media in saturated-unsaturated condition (Raats, 2001).

$$\frac{d\theta}{dt} = \frac{d}{dz}\left[K\left(\frac{dh}{dz} - 1\right)\right] \qquad (4)$$

Where θ = Volumetric Water Content [L^3/L^3]; t = Time, [T]; z = Spatial coordinate (positive downwards), [L]; K = Unsaturated hydraulic conductivity, [L/T]; h = Matrix potential, [L]

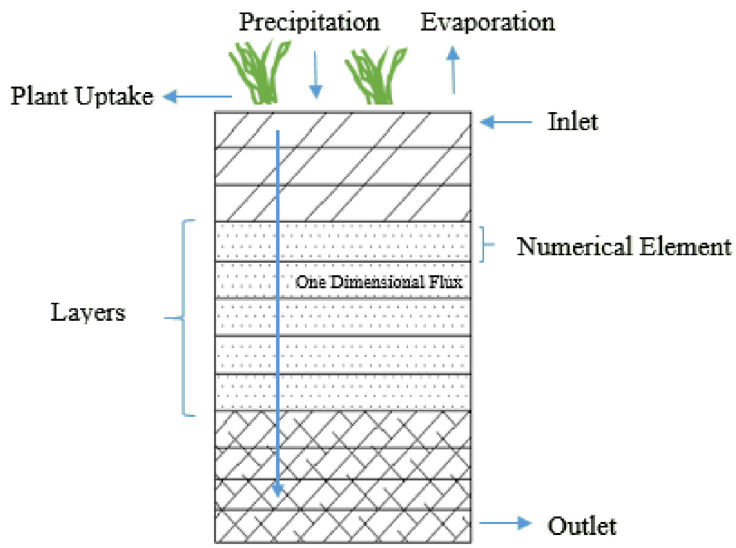


Figure 8. Qualitative Diagram of VF-CW System

For modeling water flow, we used the van Genuchten-Mualem module in Hydrus-1D. In order to use this module, a series of soil hydraulic parameters were defined, including the residual water content θr, saturated water content θs, parameter α and n in the soil water retention function, saturated hydraulic conductivity *Ks* and tortuosity parameter in the conductivity function *I*. The values for these parameters (Mallants et al., 2003) are tabulated in Table 6.

Table 6. Van Genuchten Parameters for Soil Layers

Soil Layer	θr	θs	*a* (1/cm)	n	Ks (cm/day)	I
Main /Coarse Gravel	0.005	0.42	0.493	2.19	302400	0.5
Fine Gravel	0.03	0.33	0.007	2.96	28512	0.5

<u>Calculating Outflow Rate</u>

During the calibration period, 24 L of landfill leachate was pumped into the CW intermittently (15min/2hour) controlled by a timer each day. The outflow of the VF-CW was simulated for the system's HLR (0.033 cm/min) and the result is shown in Figure 9.

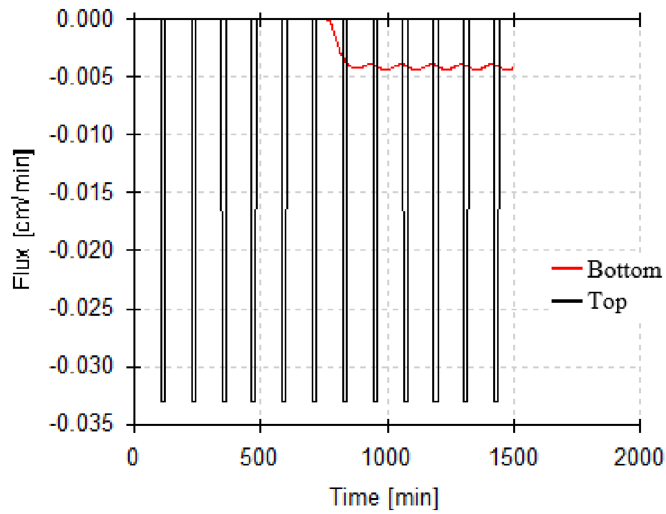


Figure 9. Outflow Rate Simulation in VF-CW

As the model has been set up using a time step of one-hour, the inflow rate was determined to be 0.001 m^3/hour. As can be seen from the result, the bottom flux becomes stable at 0.0048cm/min. As the area of the tank is 0.4 m^2, the outflow rate is 0.0011 m^3/hour. Therefore, the outflow rate can be assumed to be equal to the inflow rate.

2.4.4 HF-CW Hydraulics

For modeling the HF-CW, the saturated water content, θs for coarse gravel was considered for measuring the initial water volume, where θs = 0.42. This is because horizontal subsurface flow mostly occurs in a saturated porous media favoring anoxic condition. So, after each cycle of hydraulic loading, the porous media is mostly saturated with water. The inflow rate of this tank is equal to the outflow rate of the vertical tank and the outflow rate is equal to the tank's inflow rate.

2.4.5 Evapotranspiration

Evapotranspiration was calculated using the adjusted Thornthwaite method, where hourly temperature has been used. The equation is as follows (Wynn & Liehr, 2001):

$$\boldsymbol{ET = 16\left(\frac{dl}{12}\right)\left(\frac{10*t}{I}\right)^{a}} \qquad (5)$$

Where t is the hourly air temperature (°C), I is the annual heat index, and dl is time-length.

2.4.6 Effect of Temperature on Water Quality

Temperature heavily affects the biochemical processes regulating the removal efficiency of treatment wetlands (Kadlec & Reddy, 2001). These effects are mostly significant in nitrogen cycle reactions (mineralization, nitrification and denitrification). However, they have been incorporated in evaluating the parameters for all the modules. The removal rate constants almost always follow a seasonal pattern. For the current model, a modified Arrhenius temperature dependence of rate constants has been used:

$$k = \boldsymbol{k_{20}\theta^{(T-20)}} \qquad (6)$$

Where, k_{20} = removal rate constant at 20 °C, θ = Temperature coefficient

If θ = 1.072, then only a 10 °C temperature increase will double the value of the rate constant. The θ values for organic nitrogen mineralization values have been assumed to be 1.08. Value of θ for nitrification is close to be 1.10 (Kadlec & Reddy, 2001). The value has been set to 1.3 for denitrification. The values for all the rest of the rate constants were assumed to be 1.25.

2.4.7 Dissolved Oxygen

The DO mass balance was solved to determine when each system was aerobic or anoxic. A DO concentration above 1 mg/L was considered aerobic while a DO concentration less than 1 mg/L was considered anoxic. Aerobic and anoxic rates of nitrification, denitrification, and mineralization were used to account for the availability of DO.

The following mass balance equation was used:

$$\boldsymbol{\frac{d(DO)}{dt} = k_R(DO_s - DO) - k_R L} \qquad (7)$$

Where, DO = Dissolved Oxygen concentration (mg/L), DO_S is the DO concentration when saturation is reached (mg/L), L= ultimate COD of organics remaining in the water at any time t, k_R is the temperature-dependent mass transfer coefficient (hr^{-1}), k_d =first-order degradation rate constant.

2.4.8 Pollutant Mass Balance

The mass balances for N species are modeled after a steady-state (Constantly Stirred Tank Reactor) CSTR -in-series model (or TIS model), which is recognized as the best approach to represent internal mixing in CWs (Kadlec & Wallace, 2008). The TIS model has been used assuming the number of tanks in series to be 3. A steady-state CSTR implies there is a continuous flow in and out, there is instantaneous and uniform mixing, temperature is uniform in the reactor, and there are no velocity gradients or dead zones. The general mass balance for a CSTR is as follows:

$$\boldsymbol{V\frac{dC}{dt} = Q_iC_i - Q_oC + (rV)} \qquad (9)$$

where Qi is the inflow rate, Ci is the influent concentration, Qo is the outflow rate, C is the effluent concentration, r is the reaction rate, and V is the water volume on a given hour solved with the water balance. The mass balances for Nitrogen species are solved in a similar manner. The following mass balance equation was used for Organic Nitrogen:

$$\boldsymbol{V\frac{d(Org_N)}{dt} = Q_i(Org_N)_i - Q_o(Org_N) + (k_{pd}Org_NV) - (k_mOrg_NV)} \quad (10)$$

where $(Org_N)_i$ is the influent concentration of organic N (mg/L), Org_N is the concentration of organic N in the system (mg/L), k_{pd} is the rate constant for plant decomposition (hr^{-1}), and k_m is the rate constant for mineralization (ammonification) (hr^{-1}).

The following equation for calculating effluent ammonia concentration was used:

$$\boldsymbol{(NH_4^+)_n = \frac{Q(NH_4^+)_{n-1} + km(OrgN)(\frac{V}{n}) - kn(\frac{V}{n})}{Q + k_{pu,NH4}(\frac{V}{n})}} \quad (11)$$

where $(NH_4^+)_{n-1}$ is the effluent concentration of NH_4^+ (mg/L) in $(n-1)^{th}$ tank in TIS model, $(NH_4^+)_n$ is the concentration of NH_4^+ (mg/L) in n^{th} tank in TIS model, k_n is first-order rate constant for nitrification (mg L^{-1}hr^{-1}) which is dependent on availability of DO and temperature, and $k_{pu,NH4}$ is the zero-order rate constant for plant uptake of NH_4^+ (mg L^{-1} hr^{-1}).

The following equation for calculating effluent nitrate concentration was used:

$$(NO_3^-)_n = \frac{Q(NO_3^-)_{n-1}}{Q + k_{dn}(\frac{V}{n}) + k_{pu,NO3}(\frac{V}{n})} \quad (12)$$

where $(NO_3^-)_n$ is the effluent concentration of nitrate (mg/L) in n^{th} tank in TIS model, $(NO_3^-)_{n-1}$ is the concentration of NO_3^- (mg/L) in $(n-1)^{th}$ tank in the TIS model, k_{dn} is the rate constant for denitrification (hr^{-1}) which is dependent on temperature and availability of carbon, and $k_{pu,NO3}$ is the rate constant for plant uptake of NO_3^- (hr^{-1}).

Models of microbially facilitated denitrification reactions often follow modified Stover-Kincannon model (Abyar et al., 2017). The following mass balance equation was used to estimate the effluent COD concentration:

$$(COD)_n = (COD)_{n-1} - u_{max} \frac{COD_{n-1}(\frac{V}{nQ})}{K_b + COD_{n-1}(\frac{V}{nQ})} \quad (13)$$

where $(COD)_n$ the effluent concentration of COD (mg/L) in n^{th} tank in TIS model, $(COD)_{n-1}$ is the concentration of COD (mg/L) in $(n-1)^{th}$ tank in the TIS model, u_{max} is the specific maximum substrate utilization rate (mg/L/hr), Kb is the saturation constant (mg/L/hr), V is the tank volume (m^3) and Q is the flow rate (m^3/hr).

2.4.9 Amended Adsorption Module

Adsorbent media are added to the CWs to increase the pollutant removal efficiency. Two of such adsorbents are zeolite and biochar. In our pilot-scale system, zeolite was added to the VF-CW while biochar has been added to the HF-CW. Zeolite is a highly porous aluminosilicate mineral with a high IX capacity and high affinity for ammonia. It can adsorb ammonia through Na^+ IX and improve nitrification rates by suppressing FA (Aponte-Morales et al., 2018). On the other hand, biochar has been shown to be an effective alternative to activated granular carbon and high efficiency for COD and nitrogen removal (Gupta et al., 2016). Biochar also has significant contribution to the plant growth.

Both adsorption models for zeolite and biochar have been carried out using the Homogenous Surface Diffusion Model (HSDM), an approach that has shown to be very effective in simulating adsorption kinetics (Payne and Karl, 2018). HSDM assumes the adsorption media to be homogenous and the particles to be spherical. This model is quite appropriate as the adsorption process by zeolite and biochar is mostly dominated by surface diffusion. The properties of zeolite and biochar used in this study are provided in Table 7.

Table 7. Properties of Adsorbent Media

Adsorbent	Density (g/cm^3)	Density (g/m^3)	Diameter (mm)	Radius (m)	Mass in the CW (g)
Zeolite	0.877	877,000	>0.6	~2.5*10^{-4}	23,000
Biochar	0.090	90,000	2-4	~1.5*10^{-3}	2,6000

Following the HSDM approach, the ammonia mass balance equation was modified to incorporate adsorption:

$$\boldsymbol{V\frac{d(NH_4^+)}{dt} = Q_i(NH_4^+)_i - Q_o(NH_4^+) + (k_m Org_N V) - (k_n V) - (k_{pu,NH4}V) + J_{NH_4^+}\, A_{adsorbent} V} \quad (14)$$

where $J_{NH_4^+}$ is the flux of NH_4^+ from the bulk liquid to the solid phase (mg m^{-2} hr^{-1}) and $A_{biochar}$ is interfacial area of the adsorbent sites (m^2/m^3). The adsorption flux J is calculated as follows:

$$\boldsymbol{J_{NH_4^+} = -\rho D_s \frac{\partial q_{NH_4^+}}{\partial r}} \quad (15)$$

where ρ is the particle density (g/m^3), D_s is the surface diffusivity (m^2/hr), $q_{NH_4^+}$ is the maximum adsorption capacity (mg/g), and r is the radial coordinate. Here, r was always assumed to be equal to R, the radius of a zeolite particle (m). Also, since the HSDM assumes the particles are spherical, $A_{adsorbent}$ is calculated as follows:

$$\boldsymbol{A_{adsorbent} = \frac{4\,\pi\, R^2}{{}^4/_3 \pi\, R^3} * \frac{{}^M/_\rho}{V}} \quad (16)$$

where M is the mass of zeolite in the system (g), and V is the volume (m^3).

The COD model was modified to consider COD adsorption into:

$$\frac{d(COD)}{dt} = u_{max} \frac{QCOD_i/V}{K_b + QCOD_{i/V}} + J_{cod} * A_{adsorbent} * V \quad (17)$$

Where COD_i is the initial concentration of COD (mg/L), u_{max} is the specific maximum substrate utilization rate(mg/L/hr), Kb is the saturation constant (mg/L/hr), V is the tank volume (m^3), Q is the flow rate (m^3/hr), J_{cod} is the adsorption flux (mg m^{-2} hr^{-1}) and $A_{adsorbent}$ is the surface area of adsorbent (m^2/m^3). Here J_{cod} and $A_{adsorbent}$ are calculated using the similar equations to Eq. 14 and 15.

2.4.10 Model Calibration

The data collected between November 25, 2020, to May 14, 2021 from the pilot-scale system were used for model calibration for all the kinetic parameters. The input concentrations were assumed to be constant between the experimental data points. Model fitness was evaluated using the normalized root mean square error ($NRMSE$) values:

$$\text{NRMSE} = \frac{\sum_{i=1}^{N} (y_{\text{simulated}} - y_{\text{experimental}})^{2}}{N\,(\max_{\text{experimental}} - \min_{\text{experimental}})} \quad (18)$$

where $y_{simulated}$ is the values simulated by the model, $y_{experimental}$ is the concentration values observed by the experimental data, and N is the number of of the experimental data points. This is a standard metrics to assess the accuracy of a prediction tool as the values are not unit dependent. NRMSE value of 0 indicates the model to be a perfect fit.

2.4.11 Uncertainty Analysis

An uncertainty analysis was performed to understand the model's sensitivity of key outputs (Ammonia and COD) to different model parameters. The analysis was done using Sobol method (Saltelli, 2002) in Python on 12 and 11 different parameters for Ammonia and COD adsorption modules, respectively. The Sobol method determines a first order and a total-order indices to evaluate the parameter's individual contribution and overall contribution respectively. If the total-order indices are significantly higher than the first-order indices, that means there are higher order interactions going on among the parameters. Both the adsorption models were analyzed using

106496 samples each generated by the Sobol method to evaluate the global variability of the parameters.

2.5 Post-treatment of CW Effluent for Reuse

2.5.1 Feed stream samples and analysis

Four different samples were collected from the Hillsborough County Southeast Landfill: 1) Raw (untreated) landfill leachate, 2) landfill leachate treated using an onsite activated sludge (AS) system, 3) control-CW effluent, and 4) adsorbent-CW effluent. Wastewater characterization was guided by the feed stream requirements for the software used to model the UF-RO process. Analytical methods are described in Section 2.3.

2.5.2 Model development

All four feed streams were modeled and evaluated with post-treatment consisting of UF and RO (Figure 10). A water balance, based on 2020 rainfall precipitation and evapotranspiration data from the on-site weather station, was developed for a full-scaled CW system of approximately 47,300 m^2. The results showed that water gains/losses due to precipitation or evapotranspiration were expected to be negligible. Therefore, all four feed streams were modeled based on Hillsborough County's feed flow estimate of 757 m^3 per day (m^3/d) into the post-treatment systems.

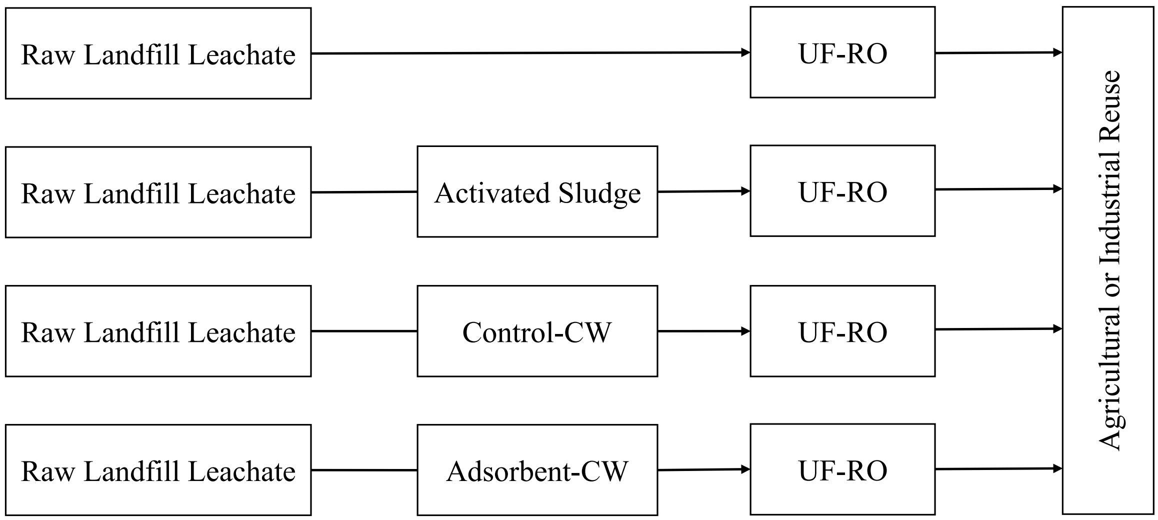


Figure 10. Treatment Strategies for Landfill Leachate.

Post-treatment systems (Figure 11) were modeled using the DuPont™ WAVE design software. This software integrates both UF and RO into a single package, allows input of project-specific parameters with default values and design schematic recommendations, and allows design schematic modifications to be reflected throughout the combined system design. The software can create a comprehensive preliminary assessment of post-treatment design, including design warnings and O&M costs (DuPont, 2021).

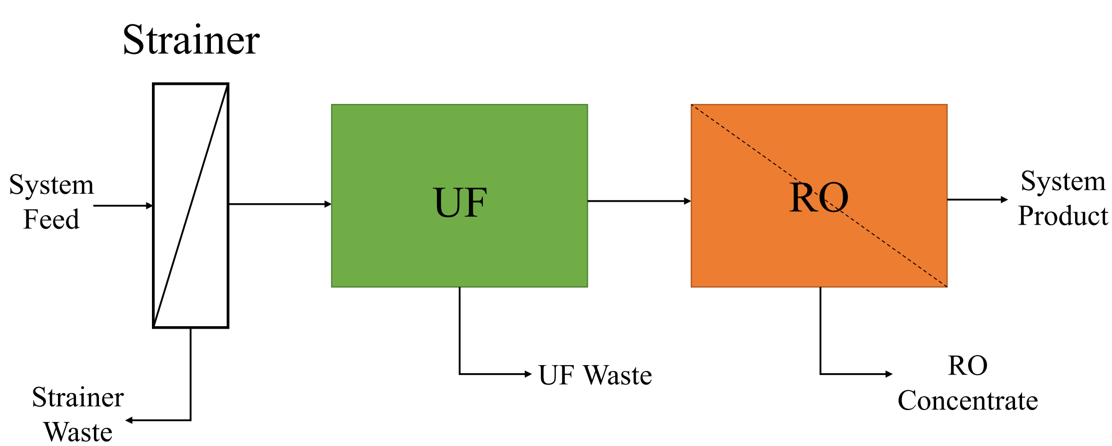


Figure 11. Example of UF-RO system configuration included in the advanced treatment design model.

Initial modeling steps included defining the feed stream composition to accurately simulate the post-treatment design. All four feed streams were classified as wastewater. Water sub-types were suggested through solids content characterized through turbidity, TSS, and Silt Density Index (SDI_{15}). Detailed values of pH and ionic content were also required as inputs for an accurate RO design, with a subsequent charge balance adjustment where all ions were adjusted. Operating temperatures were set at default values at a minimum of 10°C, a design value of 25°C, and a maximum of 40°C.

The initial UF design was set to default values except for module selection and configuration layout. The UF module that was chosen has 35% higher permeability compared to older models, high effective membrane area (77 m^2), flow capacities greater than 50 m^3/hr, and is suitable for treating industrial wastewater. Recommended UF configurations consisted of the number of online trains, standby trains, maximum offline trains that would be backwashed/chemically enhanced backwashed through cleaning-in-place interventions, and number of modules per train. To standardized design, a common configuration across all four systems that contained the fewest online modules and the fewest overall number of modules was initially chosen. This common configuration consisted of 3 online trains, 0 standby trains, and 1 redundant train, with 6 modules per train.

The initial RO design consisted of 2 stages to increase water recovery. The RO element selected has high active area of 41 m^2, feed pressure of 70 bars, permeate flow rate of 34.2 m^3/d, minimum salt rejection rates of 99.25%, and is suitable for handling industrial wastewaters with high electrical conductivity, such as raw landfill leachate. Typical number of elements per pressure vessel range from 6 to 8 for large-scale operations and can be reduced in subsequent stages (DuPont, 2021). The common RO configuration for this study consisted of 2 pressure vessels with 6 elements in the first stage and 2 pressure vessels with 4 elements in the second stage. An increase in the number of RO stages, number of pressure vessels per RO stage, and number of elements per pressure vessel were investigated but were deemed economically infeasible in terms of water recovery and costs compared to the determined common RO configuration. Pre-stage pressure drop and flow factors used were default values in the software, while stage back pressure in stage

1 and boost pressure in stage 2 were recommend values in the DuPont's Introduction to WAVE User Manual (DuPont, 2021). Cleaning-in-place interventions for the RO system were accounted for through literature review and manufacturer dose recommendations.

After initially modeling the four pre-treatment alternatives using a common UF-RO configuration, an optimized UF-RO treatment configuration was modeled for the two CW feed streams. Additional system water recovery was possible due to the higher water quality of the control-CW and adsorbent-CW feed streams. Optimization for both CW feed stream systems included decreasing the number of online UF modules due to the lower solids content compared to raw and AS treated landfill leachate. The RO design was optimized by: 1) Increasing the system recovery and 2) increasing the number of elements per pressure vessel in both stages to accommodate the software design warnings. These alterations of the common UF-RO treatment configuration allowed for an increase in feed flow rate and a slight increase in feed pressure to the RO component for an overall increase in UF-RO system recovery. Adding another pressure vessel to each RO stage and changing the number of elements per pressure vessel were analyzed but did not provide great additional economic and water recovery benefits. All other operating conditions remained the same as the common UF-RO treatment configuration.

2.5.3 Model simulations

Landfill leachate is characterized by a low biodegradability and high salinity (measured as electrical conductivity), COD, NH_4^+-N, and metals. The UF-RO treatment processes create very high quality permeate that are well below the Florida requirements for both non-food agricultural and industrial reuse, which include BOD_5, TSS, nitrate (NO_3^-), NH_4^+-N, TN, and electrical conductivity. Bypassing a portion of the feed water and blending it with the UF-RO treated effluent could meet all reuse requirements while lessening the hydraulic load on the UF-RO system and reducing costs. Therefore, a mass balance based on the most stringent reuse standard of electrical conductivity for industrial reuse of 1,120 μS/cm was developed. Iterations were carried out in Microsoft Excel with the Excel Solver tool.

2.5.4 Alternative design modeling limitations

Although the WAVE software allows for input of project-specific parameters and system customization, it cannot represent every possible scenario. The software allows input of chemical additions to adjust the water stream chemical characterization. For UF, acid, oxidant and coagulants can be added. For RO, pH, CO_2 concentration, solubility of salts, and chlorine concentration can be adjusted. Barium sulfate ($BaSO_4$) scaling was a prominent RO solubility warning across all UF-RO modeling, which indicates a decrease in membrane permeability and an increase in energy requirements to allow for sufficient membrane flux to occur. Barium sulfate scaling is a serious concern that might make RO treatment infeasible. Further work is needed to identify antiscalants that can address this problem. Chemical adjustments were indeed attempted, such as the addition of the antiscalant $Na_6P_6O_{18}$ and hydrochloric acid to avoid scaling; however, the chemical adjustments did not lower the saturation percentage of $BaSO_4$ to an acceptable value (< 100%). There was no flexibility to add another manufacturer's antiscalant into the software to accurately simulate a representative waste profile of the RO concentrate and system product profile of the RO permeate. Therefore, assumptions had to be made that the antiscalant addition from SUEZ did not chemically alter the RO products' profiles and that the RO system operating conditions, including membrane flux, did not change. It is noted that the DuPont software underpredicts solubility of salts, therefore a supersaturation error occurs; however, it can be taken as a conservative value for scaling potential (Boerlage et al., 2002).

2.5.5 Net present value analysis

A levelized cost approach was adopted using a net present value analysis, a landfill leachate flowrate of 757 m^3/day and a 20-year design life (Linares et al., 2016). An assumed discount rate of 5% was based on the requirements of the Hillsborough County Florida Water Enterprise Fund. Six scenarios were evaluated: four reuse alternatives (Figure 10) and two non-reuse alternatives disposal of raw landfill leachate or adsorbent-CW treated effluent. Detailed unit cost estimates based on 2021 U.S. dollars (USD) for system components and materials and their respective references are summarized in Table 8.

For this study, the disposal of waste streams for each alternative, raw landfill leachate or the treated effluent and RO concentrate, was separated into three categories: 1) Spray application on-site, which was approximated at 84.0 m^3/d (Hillsborough County Solid Waste Management Division, 2021), 2) disposal of 83.3 m^3/d via hauling to POTWs at a cost of USD \$55.48 per m^3, and 3) remaining amount of treated effluent and RO concentrate disposal via hauling and solidification at a rate of USD \$224.55 per m^3. Solidification would be performed by the contractor and includes transportation, solidification with absorbent stabilization, and disposal. For the UF-RO alternatives, a cash input was accounted for that includes industrial reuse water resale to a nearby power plant at a rate of USD \$0.10 per m^3. Non-discounted payback periods for the CW alternatives were also calculated based on the initial capital deficit of the CWs and the UF-RO system with cost savings that were inclusive of the annual O&M differential between the raw landfill leachate to direct disposal alternative and the chosen alternative.

2.5.6 Net present value analysis assumptions

The net present value analysis for this study was done as a Class 4 estimate, which is based on limited information and can have wide variability in cost accuracy range. Therefore, the capital costs were accounted for with a 30% contingency (AACE, 2005), as they were given as budgetary estimates (Table 8). The net present value analysis assumed that the construction period for the CWs and UF-RO system was within 1 year, capital costs contained a 30% contingency, UF module replacement occurred every 2 years, RO element replacement occurred every 4 years, RO cleaning chemicals were to be used in a 30-minute cleaning cycle twice per year, and no decommissioning nor salvage costs were considered. Electrical requirements were provided by the WAVE software and RO antiscalant dosages were provided by the manufacturer.

The original research objective was to develop a post-treatment feasibility study of CW effluent; therefore, this analysis does not include the capital and O&M costs for the existing AS treatment system as well as the O&M costs for the CWs. Due to the exclusion of O&M costs for the existing AS treatment system, the alternative is considered to be an underestimate. O&M costs for CWs are also expected to be minimal as O&M is required periodically rather than requiring continuous on-site labor (USEPA, 2000). It was also assumed that the UF-RO design life is 20 years (Linares et al., 2016), but little research has been carried out on long-term RO treatment operation with landfill leachate beyond 10 years of operation (Peters, 1998; Rukapan et al., 2012).

Table 8. Unit cost estimates for net present value analysis

Cost Item	Unit Price (USD)	Unit	Price Reference
Gravel Constructed Wetland[1]	\$65.20	m^2	Kadlec and Wallace (2009)
Zeolite	\$168.46	m^3	Amini et al. (2017)
Biochar[2]	\$301.65	m^3	Green Dream Sustainable Solutions, personal communication, 2020
UF-201K-20 with UF SFP-2860 Module	\$275,000	EA	M. Higazy[3], Pure Aqua, Inc., personal communication, September 17, 2021
UF-262K-26 with UF SFP-2860 Module	\$350,000	EA	M. Higazy[3], Pure Aqua, Inc., personal communication, September 17, 2021
SW-48K-2680 with RO SWC5-LD Element	\$250,000	EA	M. Higazy[3], Pure Aqua, Inc., personal communication, September 17, 2021
SW-24K-2380 with RO SWC5-LD Element	\$150,000	EA	M. Higazy[3], Pure Aqua, Inc., personal communication, September 17, 2021
SW-64K-4480 with RO SWC5-LD Element	\$300,000	EA	M. Higazy[3], Pure Aqua, Inc., personal communication, September 17, 2021
UF SFP-2880 Module[4]	\$2,200	EA	M. Higazy[3], Pure Aqua, Inc., personal communication, September 17, 2021
UF SFP-2860 Module	\$2,000	EA	M. Higazy[3], Pure Aqua, Inc., personal communication, September 17, 2021
RO SWC5-LD Element	\$540	EA	M. Higazy[3], Pure Aqua, Inc., personal communication, September 17, 2021
RO Fortilife XC80 Element[5]	\$945	EA	DWS Advantage
UF System with 20 UF SFP-2880 Module	\$279,000	EA	Replacement of module/element prices and Interpolation Calculations with references to Pure Aqua inquiries
UF System with 26 UF SFP-2880 Module	\$355,200	EA	Replacement of module/element prices and Interpolation Calculations with references to Pure Aqua inquiries
UF System with 24 UF SFP-2880 Module	\$329,800	EA	Replacement of module/element prices and Interpolation Calculations with references to Pure Aqua inquiries
1-stage RO System with 8 RO Fortilife XC80 Element	\$153,240	EA	Replacement of module/element prices and Interpolation Calculations with references to Pure Aqua inquiries
1-stage RO System with 12 RO Fortilife XC80 Element	\$254,860	EA	Replacement of module/element prices and Interpolation Calculations with references to Pure Aqua inquiries
1-stage RO System with 16 RO Fortilife XC80 Element	\$306,480	EA	Replacement of module/element prices and Interpolation Calculations with references to Pure Aqua inquiries
UF Chemical – Citric Acid (100%)	\$1.52	kg	Default values in WAVE Software
UF Chemical – Hydrochloric Acid (32%)	\$0.10	kg	Default values in WAVE Software
UF Chemical – NaOCl (12%)	\$0.33	kg	Default values in WAVE Software
UF Chemical – NaOH (50%)	\$0.258	kg	Default values in WAVE Software
RO Antiscalant – Hypersperse	\$14.93	kg	R. Barbour[6], SUEZ, personal communication, September 10, 2021
RO Cleaning Chemical – Kleen MCT405	\$13.52	kg	R. Barbour[6], SUEZ, personal communication, September 10, 2021
Industrial Energy Costs	\$0.0884	kWh	Electricity Local (2021)

Concentrate Waste Disposal – Solidification	$224.55	m^3	B. Graziano[7], AquaClean, personal communication, September 23, 2021
Wastewater Disposal – Hauling to WWTPs[8]	$55.48	m^3	R. Shuler[9], AquaClean, personal communication, October 5, 2021
Industrial Reuse Resale	$0.10	m^3	G. Blair[10], Orlando Utilities Commission, personal communication, October 6, 2021

Table Notes:

[1]: Gravel CW is assuming that the CW is SSF and the media bed is 60 cm in depth.

[2]: Freight was not included in the estimate for biochar.

[3]: M. Higazy is the Office Manager of Pure Aqua in Santa Ana, CA.

[4]: UF SFP-2880 Module was used for this study. The product data sheet is located at https://www.dupont.com/content/dam/dupont/amer/us/en/water-solutions/public/documents/en/UF-IntegraFlux-SFP-2860XP-SFD-2860XP-SFP-2880XP-SFD-2880XP-PDS-45-D01048-en.pdf.

[5]: RO Fortilife XC80 Element was used for this study. The product data sheet is located at https://www.dupont.com/content/dam/dupont/amer/us/en/water-solutions/public/documents/en/RO-FilmTec-Fortilife-XC80-PDS-45-D01727-en.pdf

[6]: R. Barbour is the Account Manager for Florida of SUEZ.

[7]: B. Graziano is the Vice President of Sales & Marketing for Shamrock Environmental Corporation. AquaClean is a Shamrock Environmental Company.

[8]: Wastewater disposal via hauling to POTWs is capped at 75.7 m^3/d.

[9]: R. Shuler is the Business Unit Manager of AquaClean.

[10]: G. Blair is the Environmental Affairs Director of Orlando Utilities Commission.

3 RESULTS

3.1 High strength leachate treatment with bench-scale SBBR

The goal of this portion of the study was to compare SBBR performance with high strength landfill leachate with our prior Hinkley Center funded project (Phase I) based on input from the TAG and Hinkley Center Board that the system should be challenged with higher strength leachate than we used in Phase I. Experiments were performed with leachate collected from Cells 7B/8 from the Orange County Landfill in Orlando, Florida. Characteristics of the raw landfill leachate from samples collected in May 2021 are shown in Table 9. Note that additional details can be found in the MSEV thesis by Lam (2021).

Table 9. Orange County Landfill Cells 7B/8 Raw Landfill Leachate Characteristics

Parameter	Value	Units
TAN	1,569	mg/L
NO_3^--N	0	mg/L
NO_2^--N	0.633	mg/L
TN[1]	1,821	mg/L
FA[2]	40.9	mg/L
sCOD	6,533	mg/L
BOD_5[3]	870	mg/L
BOD_5/sCOD	0.133	N/A
BOD_5/TN	0.478	N/A
UV254	92.6	A
UV456	5.93	A
pH	7.75	N/A
Alkalinity	7,350	mg/L as $CaCO_3$
Electrical Conductivity	20.76	mS/cm
Turbidity	56	NTU

Notes:

[1]: TN is calculated from the summation of Total Kjeldahl Nitrogen values provided by Orange County Solid Waste Division with NO_3^--N and NO_2^--N values derived from the lab;

[2]: FA concentration was calculated using Equation 13;

[3]: BOD_5 value was provided by Orange County Solid Waste Division;

N/A= Not applicable.

3.1.1 Nitrogen Removal

Influent and effluent TIN concentrations over the course of the study are shown in Figure 12. Profiles of influent and effluent nitrogen species for each HRT condition are shown in Figure 13. As the raw landfill leachate used in this study had a low BOD_5 to TN ratio of 0.48, it is likely that the high TIN removals observed were due to partial nitritation/anammox (Joseph et al., 2020; Gao et al., 2022). The high FA levels present in the landfill leachate (up to 30 mg/L at the beginning of the SBBR cycle) likely provided favorable conditions for ammonia oxidizing bacteria and unfavorable conditions for nitrite oxidizing bacteria (see Lam, 2021). Prior studies have shown that zeolite and biochar addition to biological nitrogen removal systems enhances microbial biofilm attachment (Guerrero et al., 2016; Zhou et al., 2018). Nitrogen removal rates (NRRs) increased with decreasing HRT, as shown in Figure 14. The results indicate that the SBBR could be operated at an HRT of 14 days and achieve high TIN removal performance.

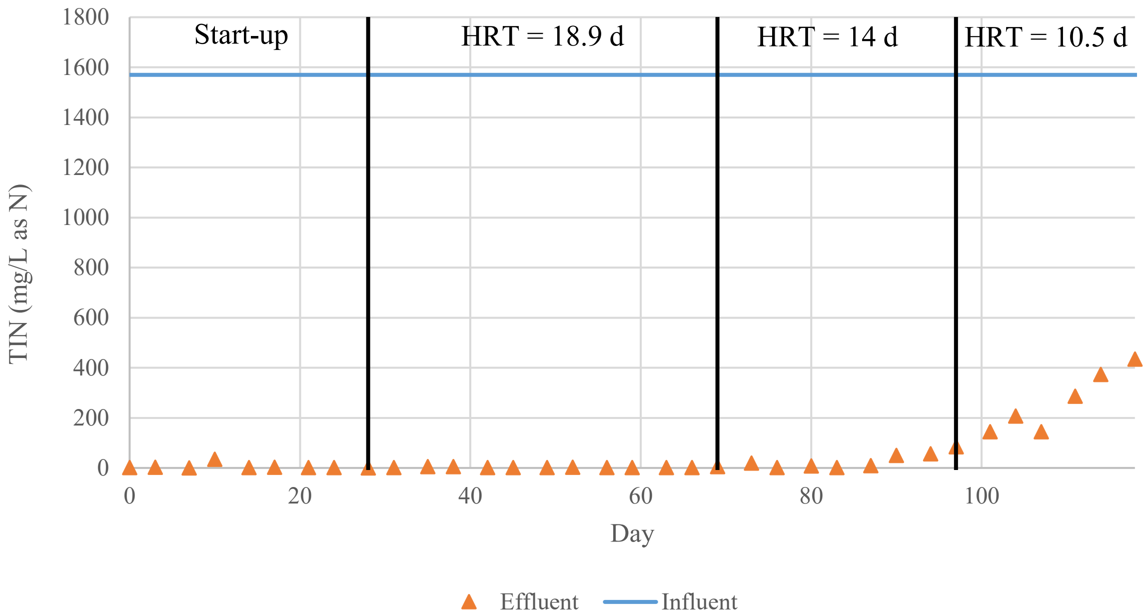


Figure 12. SBBR influent and effluent TIN concentrations over the duration of the project.

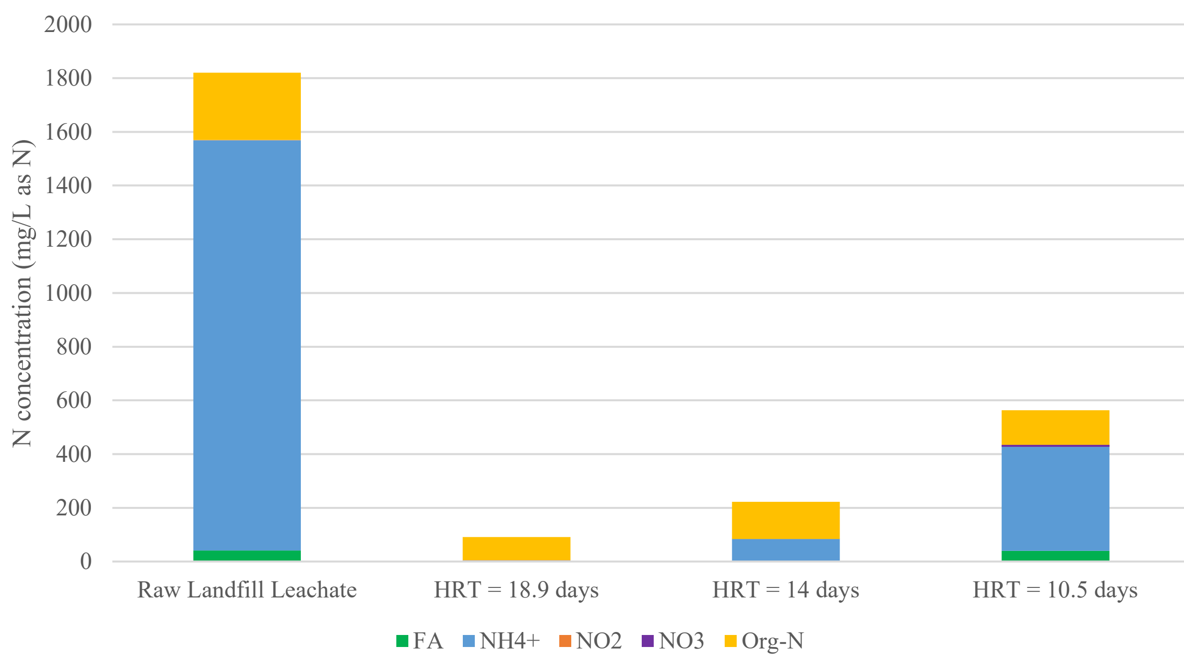


Figure 13. Average SBBR influent and effluent reactive nitrogen species for each HRT condition applied.

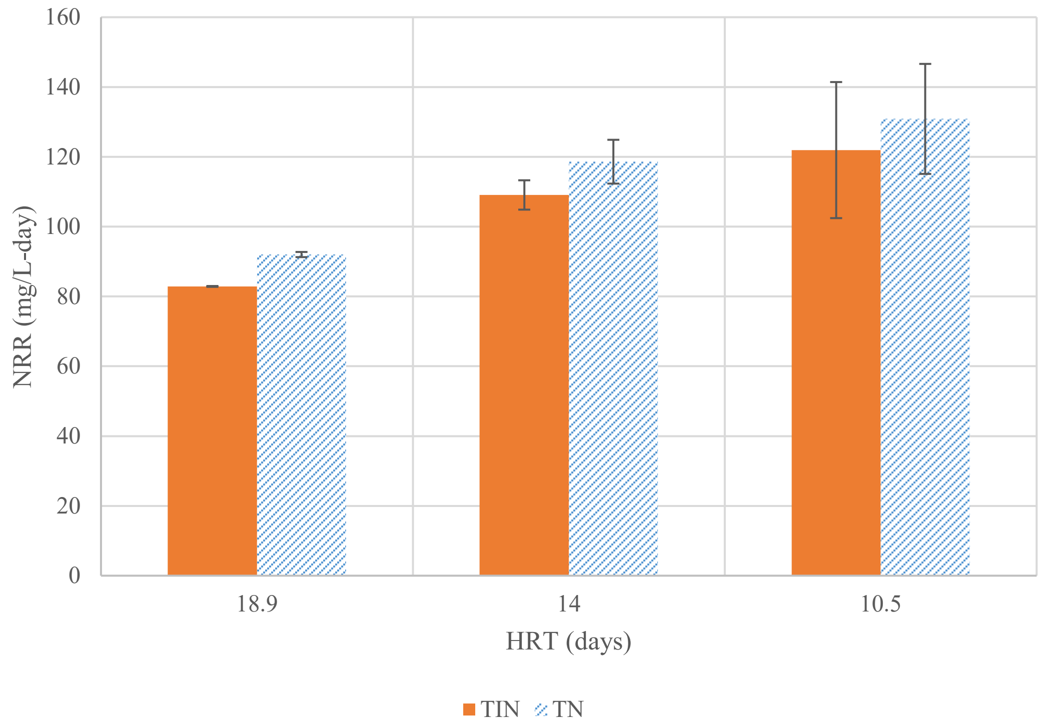


Figure 14. Nitrogen removal rates of TIN and TN for varying HRTs.

3.1.2 Organic Matter Removal

Average sCOD removal efficiencies were 49%, 46% and 36% at HRTs of 18.9, 14, and 10.5 days, respectively. sCOD removal rates at varying HRTs are shown in Figure 15. Similar to the findings in Phase I, the low BOD_5 to COD ratio of landfill leachate hindered biodegradation of organic matter in the SBBR. High COD and low BOD_5 levels in landfill leachate are due to high concentrations of humic acids and other recalcitrant organic compounds (Bolyard et al., 2019). Although biochar has a high initial adsorption capacity for sCOD due to its high adsorptive surface (Gao et al. 2022), adsorption sites were depleted over time.

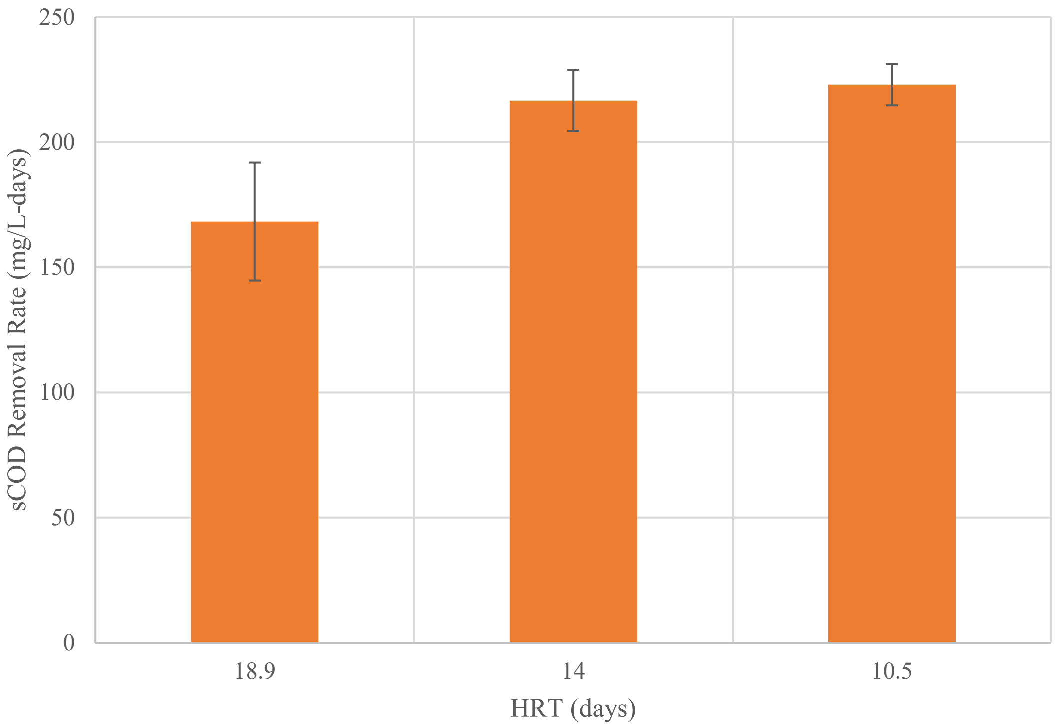


Figure 15. Removal Rates of sCOD for Varying HRT Conditions

3.1.3 Color Removal

The high color index of landfill leachate correlates with a high concentrations of recalcitrant organic matter, which limits its biodegradability. Color also causes disinfection problems at POTWs including UV quenching and formation of disinfection by-products (Bolyard and Reinhart, 2017; Bolyard et al., 2019). Color removal efficiency over the course of the study as both UV254 and UV456 are shown in Figure 16. Color removal can be achieved through adsorption by biochar as well as biodegradation (Joseph et al., 2020; Witthayaphirom et al., 2020). Although color removal was high at the beginning of the study, color removal declined over time and even became negative for UV456 at the end of the study, possibly due to desorption of previously adsorbed organic matter. The results indicate that although biochar initially has a high adsorptive capacity for organic matter in leachate, the material became saturated over time. Therefore, it is recommended that biochar be replaced periodically with fresh material.

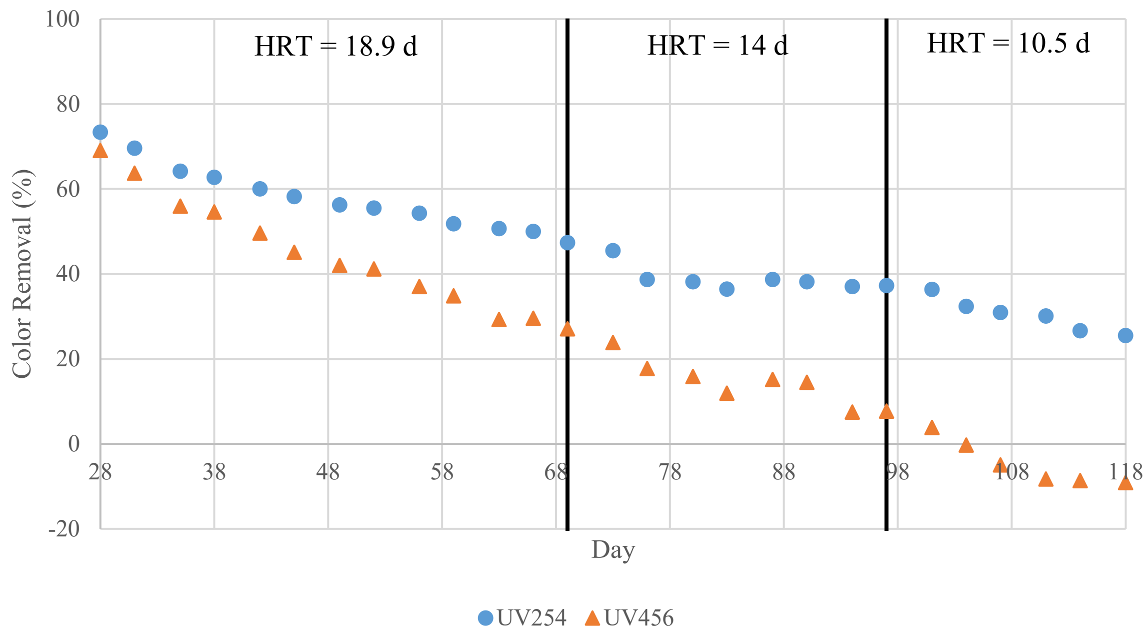


Figure 16. UV254 and UV456 Color Removal Efficiencies for Varying HRTs

3.1.4 Comparison of SBBR Performance with Varying Leachate Strength

A comparison of SBBR performance with Hillsborough County leachate (Phase I) and Orange County leachate (Phase II) at an HRT of 14 days is shown in Table 10. The biochar and zeolite amended SBBR effectively achieved TIN removal efficiencies > 97% in both phases, even at the very high TAN loadings applied in Phase II (> 1,500 mg/L). This is most likely due to adsorption of NH_4^+ onto the zeolite during the loading period followed by desorption and zeolite bioregeneration via partial nitritation/anammox during the react period (see Gao et al., 2022 for additional details). Both sCOD and color removal efficiencies were higher in Phase I than Phase

II, most likely due to the high concentrations of recalcitrant organic matter in the Orange County leachate (sCOD >6,500 mg/L) compared with Hillsborough County's leachate (~400 mg/L). The deep brown color of the Orange County leachate indicated the presence of humic acids and other recalcitrant organic compounds that were not degraded under the conditions applied in the SBBR. In addition, after the long period of operation of the SBBR by the end of Phase II the biochar was reaching saturation. The results indicate that periodic replacement of biochar is required to sustain color removal in landfill leachate applications.

Table 10. Comparison of TIN, sCOD and UV456 removals in Phase I (low strength) and Phase II (high strength) studies at 14 day HRT.

	Removal Efficiency (%)		Removal Rate (mg/L-d)	
Parameter	Phase I	Phase II	Phase I	Phase II
TIN	99	97	33	109
sCOD	83	46	24	217
Color	95	9.8	NA	NA

3.2 Pilot-scale hybrid CW studies

3.2.1 Nitrogen species

Total ammonia nitrogen (TAN) concentrations in raw leachate and VF-CW effluents are shown in Figure 17a. The TAN concentration in raw leachate showed high fluctuations during different seasons, due to dilution of leachate with rainwater during the wet season (summer and fall). Overall, compared with Control-VF, zeolite addition significantly reduced TAN concentrations, especially at the shortest HRT (Phase 5) by adsorption and subsequent biodegradation, which alleviated its toxicity to microbes and CW plants in HF-CWs. As shown in

Figure 17b, zeolite addition remarkably decreased FA concentrations below 10 mg/L, which is the inhibitory level for nitrifiers (Anthonisen et al., 1976).

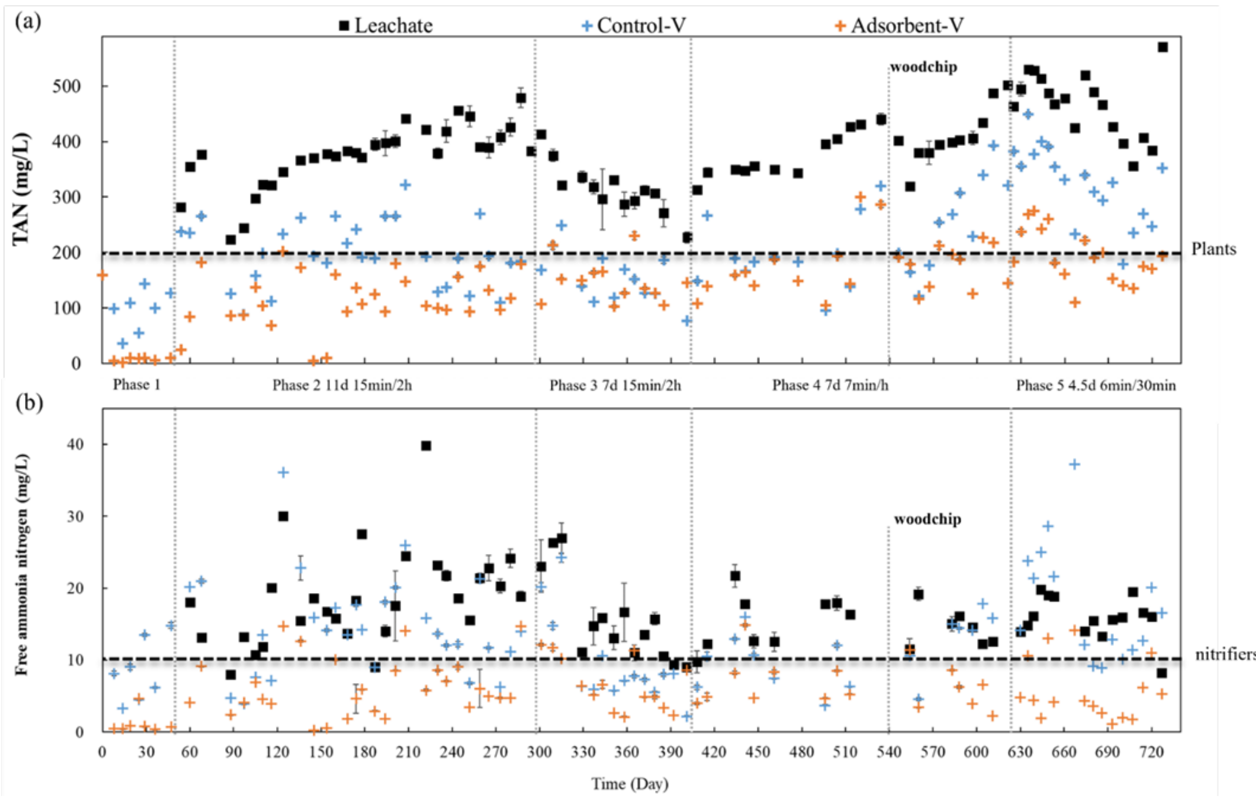


Figure 17. TAN concentration (a) and FA concentration (b).

To evaluate the degradation rate of nitrogen species and microbial activities, nitrification and denitrification rates were calculated and are shown in Figure 18. The average nitrification rates during Phases 2, 3, 4, and 5 were 43, 64, 63, and 83 mg/L/d for the Control-VF and 62, 70, 85, and 163 mg/L/d for the Adsorbent-VF, respectively. Zeolite addition significantly increased nitrification rates by 44% (Phase 2), 35% (Phase 4), and 96% (Phase 5) ($P<0.05$). This was likely due to ammonia capture by zeolite during the rapid loading periods, which extended its residence time for degradation, especially at shorter HRT. The reduced FA concentration (<10 mg/L) in the liquid phase can also contribute to higher nitrification rates in Adsorbent-VF. A previous study by Aponte-Morales et al. (2018) showed that zeolite (chabazite) reduced FA inhibition and increased nitrification rate of centrate from anaerobic digestion of swine waste by 1.25 times compared with controls, from 0.16 to 0.36 mg-N/g-VSS/h. Previous studies also showed that zeolite can provide excellent attachment surface for nitrifiers for enhanced nitrification performance (Miazga-Rodriguez et al., 2012; Smith, 2011). For both VF-CWs, increasing ammonia mass loading rate from 23 g/m^2/d (Phase 2) to 32 g/m^2/d (Phase 3) and from 39 g/m^2/d (Phase 4) to 70 g/m^2/d (Phase 5) resulted in a significant increase in nitrification rate ($P<0.05$). The correlations between nitrification rate and ammonia mass loading rate were +0.624 for the Control-VF and +0.920 for Adsorbent-VF.

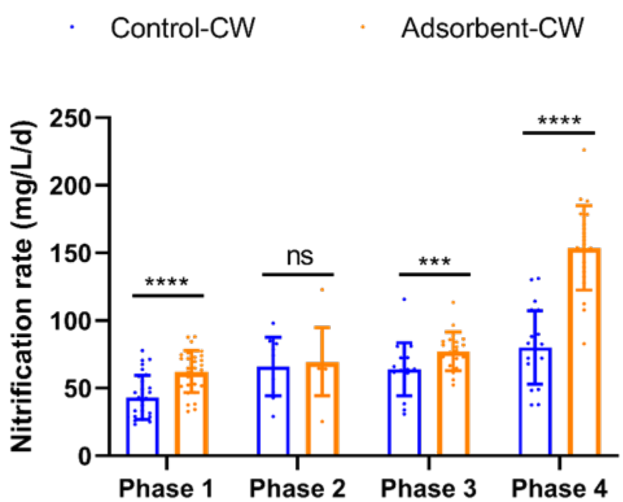


Figure 18. Figure X Nitrification rate within VF-CWs. (Note: * P<0.05, ** P<0.01, *** P<0.001, **** P<0.0001, ns: not significant).

The average concentrations of nitrogen species in the final effluent are shown in Figure 19. Both HF-CWs further removed TAN by nitrification, which might occur on the top layer or around plant root zones where oxygen is available. The final TAN concentrations for Control-CW were 118, 109, 138, and 199 mg/L, with the total removal efficiencies of 67%, 62%, 63%, and 57% for Phase 2, 3, 4, and 5, respectively. Zeolite and biochar addition enhanced total TAN removals to 75-92%, with final TAN concentrations of 29-134 mg/L. However, the TAN concentrations in both CW effluents were much higher than the standards for agricultural (<0.02 mg/L) or industrial reuse (<0.25 mg/L) (Icekson-Tal et al., 2003; Venter et al., 2011).

NOx in the effluent was mainly in the form of NO_3^-, with NO_2^--N concentrations lower than 4 mg/L during all phases (Figure 19). Serious NO_3^- accumulation occurred in both HF-CWs. The final NO_3^--N concentrations of the Control-CW were 54, 28, 81, and 54 mg/L for Phase 2, 3, 4, and 5, respectively. Higher NO_3^--N concentrations were observed in the Adsorbent-CW effluent, with the concentrations of 133, 59, 97, and 95 mg/L for Phase 2, 3, 4, and 5, respectively. This was likely due to the better nitrification performance and limited carbon source availability for denitrification. Due to the NO_3^- accumulation, both CWs had relatively low TN removals of 40-56% at all HRT conditions. To improve TN removal, woodchips were chosen as the carbon source or electron donor for denitrification improvement.

As shown in Figure 19c-d. Woodchip-CW decreased final NO_3^--N concentrations to ~9 mg/L for Phase 4 and ~27 mg/L for Phase 5 with NO_3^- removals of 91% for Phase 4 and 72% for Phase 5. The denitrification rates of the Woodchip-CW were 31 mg/L/d (Phase 4) and 44 mg/L/d (Phase 5), which were 2.0 and 1.5 times of those in the Adsorbent-HF, respectively. Implementation of the Woodchip-CW increased TN removals from 40-56% to 78-80%.

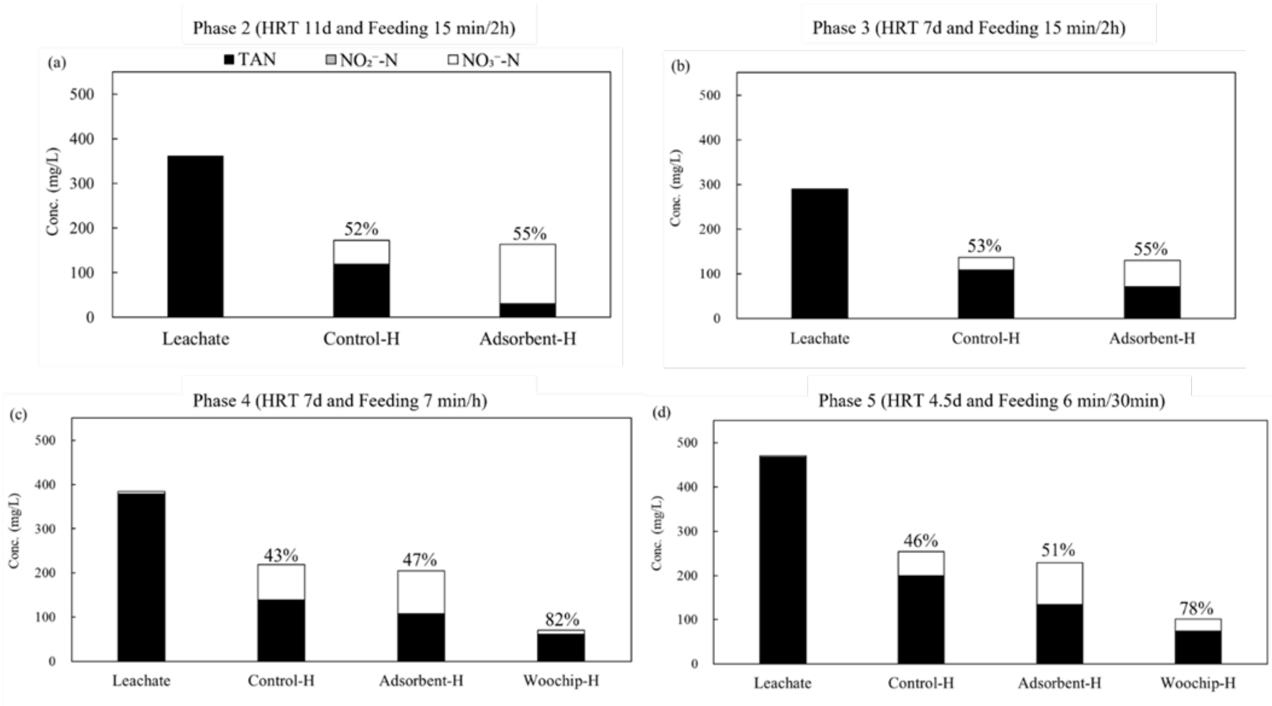


Figure 19. Average concentrations of nitrogen species after HF-CWs.

3.2.2 sCOD and color

The sCOD concentrations in raw leachate and CW effluents are shown in Figure 20. Overall, biochar addition reduced effluent sCOD concentrations at all HRTs by adsorption ($P<0.05$). Woodchips initially increased sCOD concentration up to 245 mg/L due to the release of organic compounds (Phase 4, $P<0.05$). Subsequently, Woodchip-CW achieved similar effluent sCOD concentrations as that in Adsorbent-CW during Phase 5 ($P>0.05$), indicating a good dynamic balance between organic matter release and consumption by denitrifies. The overall sCOD removal efficiencies were 22-33% for Control-CW and 29-43% for Adsorbent-CW.

Landfill leachate has a yellow or brown color caused mainly by recalcitrant organic matter (Aziz et al., 2007), such as humic acid, which can interfere with the Ultraviolet (UV) disinfection process. As shown in Figure 21, the color removal had a similar trend as sCOD removal. Overall, the color removals of Control-CW were 0-20% and biochar addition increased color removals to 6-49%. Woodchip-CW increased effluent color concentrations with decreased color removals of -4% to -59% due to the release of large quantities of organic matter, especially during the initial addition stage (Phase 4). Decreasing HRT with the increased organic matter loading led to the decrease in color removals from Phase 2 to Phase 5.

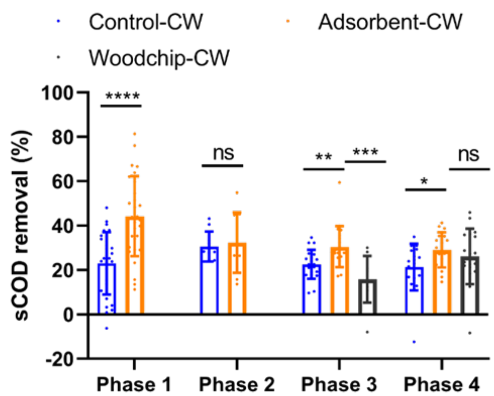


Figure 20. Average concentrations of sCOD after HF-CWs.

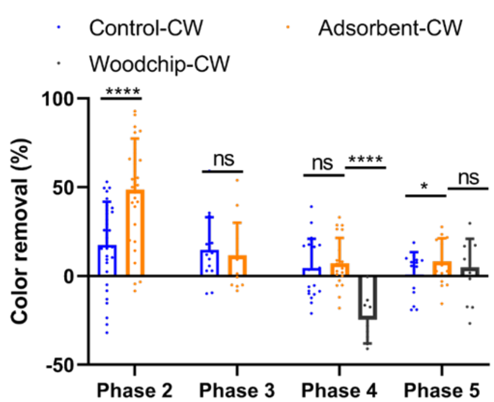


Figure 21. Color after HF-CWs.

3.2.3 Plant growth

As shown in Figure 22, compared with Control-HF, the growth of both plant species was dramatically improved in Adsorbent-HF during the entire operation, which was likely due to biochar addition. Biochar has been shown to shift microbial communities and provide refugia to enhance the population of beneficial root microbes, such as mycorrhizal fungi (Xu et al., 2018; Warnock et al., 2007). Mycorrhizal fungi are important to improve plant survival and growth in all terrestrial vegetation systems. Prior studies showed that biochar addition can increase mycorrhizal fungi's resistance to fungal pathogen infection due to its enhanced root colonization on biochar surface (Atkinson et al., 2010). In addition, biochar has a high cation exchange capacity for nutrient retention, which increases the availability of macro-nutrients (such as phosphorus) for plant growth (Atkinson et al., 2010). Furthermore, prior studies showed that TAN concentrations higher than ~200 mg/L inhibit cattail (Typha spp.) growth (Clarke and Baldwin, 2002; Surrency, 1993). The reduced TAN concentration after Adsorbent-VF might improve plant growth (Rizwan et al, 2016; Elad et al, 2011). pH might be another factor influencing plant growth. The suitable pH ranges for cattails (*Typha spp*) and cordgrass (*Spartina*) growth are 6.5-7.5 and 3.7-7.9, respectively (Amaya-Chávez et al., 2016; Utomo et al., 2018). The lower pH in Adsorbent-HF (~7.8) than Control-HF (~8.1) might favor plant growth.

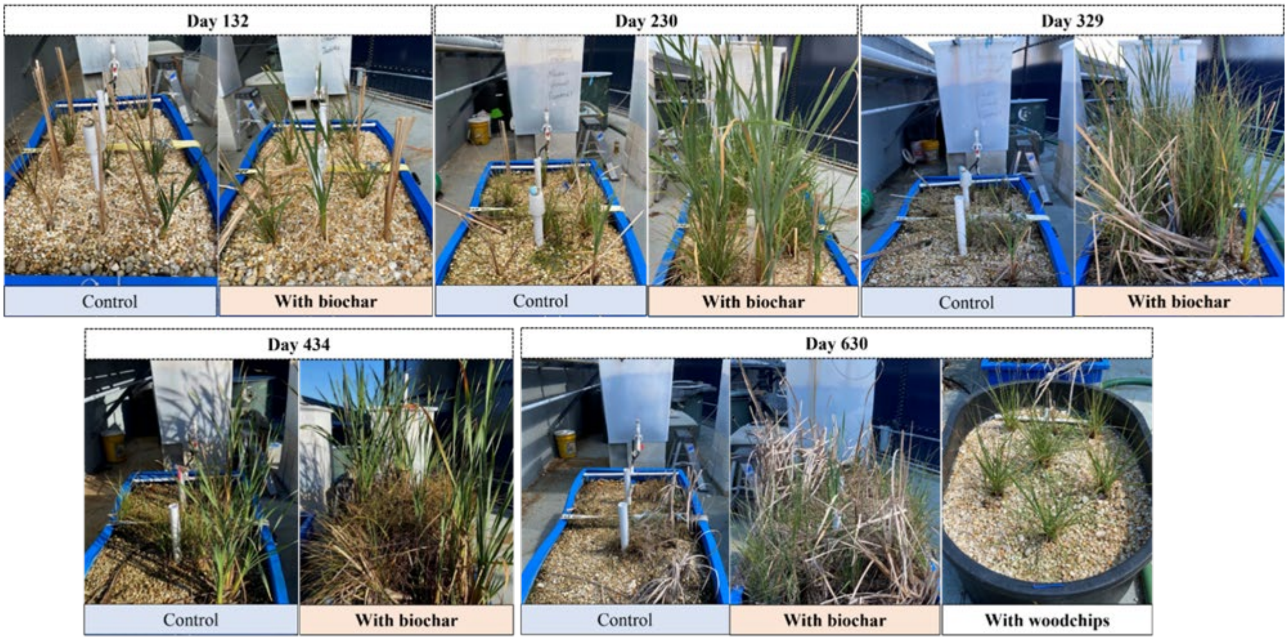


Figure 22. Images highlighting plant growth through the duration experiment.

3.3 CW performance uncertainty modeling

3.3.1 Results for Unamended CWs

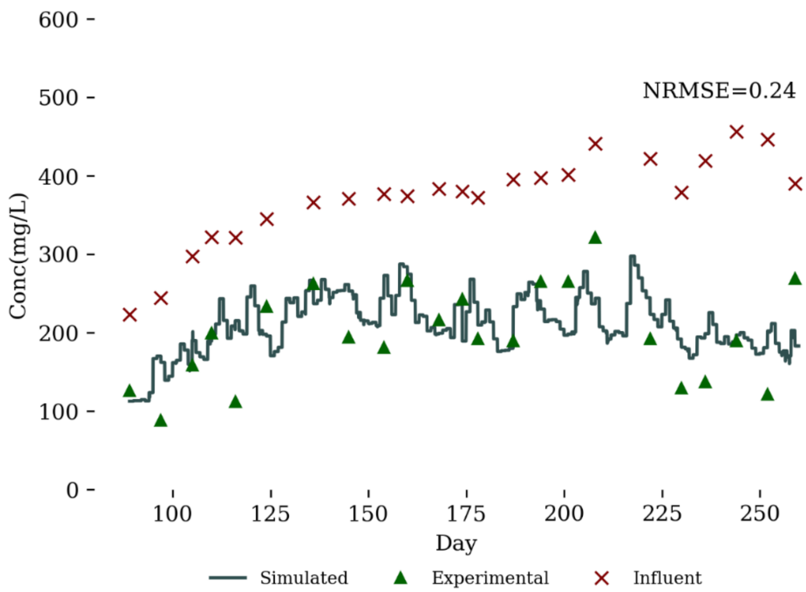
The parameters for the unamended CWs were calibrated first to fit the simulation results with the experimental data. The R^2 values were used as described in the previous section to finalize the calibrated values for each parameter. Parameters were kept within the literature range most of the times. However, some model parameters were not found in previous studies and thus, best fit values were chosen both for VF-CW and HF-CW. The calibrated parameters and literature ranges are presented in Table 11.

Table 11. Calibrated Values for Unamended CW Model Parameters

Parameter	Unit	Calibrated Value for VF	Calibrated Value for HF	Literature Range	Range Source
Saturation Concentration, KB	mg/L/hr	41.25	1177	-	-
Maximum Degradation Rate, mu_max	$hour^{-1}$	990	1609	-	-
Mineralization Rate Constant, $k_{m,aerobic}$	$hour^{-1}$	0.0012	0.0012	0.0004 – 0.002	Martin and Reddy, 1997
Mineralization Rate Constant, $k_{m,anoxic}$	$hour^{-1}$	0.003	0.003	0.0003 – 0.003	Martin and Reddy, 1997
Nitrification Rate Constant, $k_{n,aerobic}$	$mg\ L^{-1}\ hour^{-1}$	0.038	2	6 – 39	Welander et al., 1997
Nitrification Rate Constant, $k_{n,anoxic}$	$mg\ L^{-1}\ hour^{-1}$	1.5	1.5	-	-
Denitrification Rate Constant, $k_{dn,aerobic}$	$hour^{-1}$	0.04	0.04	-	-
Denitrification Rate Constant, $k_{dn,anoxic}$	$hour^{-1}$	0.05	0.05	0.1-0.5	Martin and Reddy, 1997
Plant Uptake Rate of Ammonia, $k_{pu,NH4}$	$mg\ L^{-1}\ hour^{-1}$	0.0025	0.003	-	-

Ammonia: The simulated results for both the VF-CW and HF-CW are presented in Figure 23. Both simulations well capture the NH_4^+ (as N) reduction trend as the NRMSE values are 0.24 and 0.35 respectively, which indicates a good fit. However, ammonia reduction is highly dependent on the input Organic N. As experimental data for organic nitrogen were very limited, that caused some error in the results.

a) VF-CW



b) HF-CW

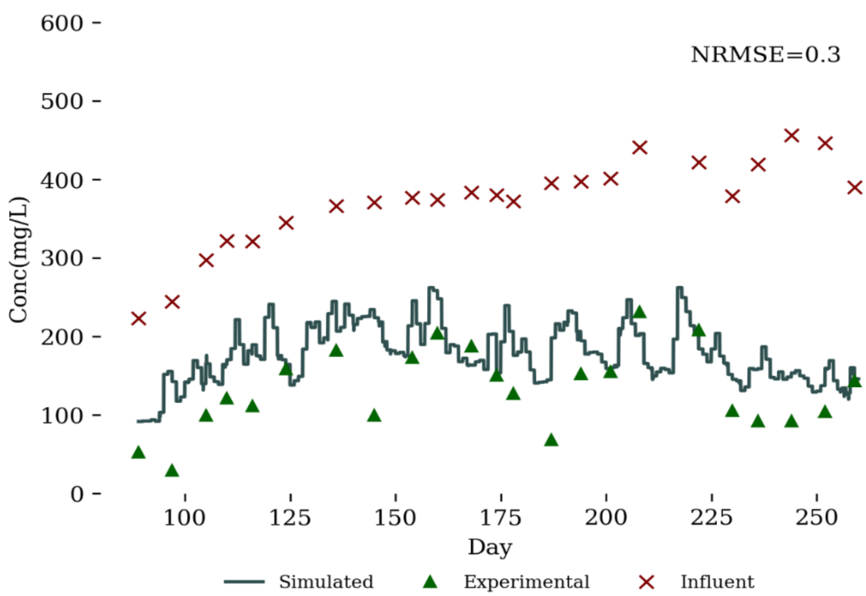
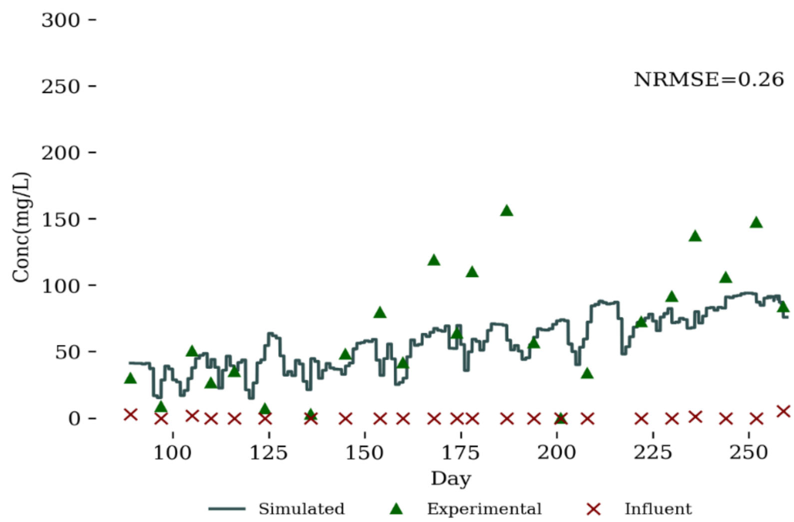


Figure 23. Unamended CW Results for NH_4^+ (as N)

Nitrate

The results for nitrate concentration are in Figure 24, where lower NRME values for both VF-CW (NRME: 0.25) and HF-CW (NRMSE: 24) indicate good model fitness. It is also evident that the model successfully captures the nitrate accumulation in the tanks.

a) VF-CW



b) HF-CW

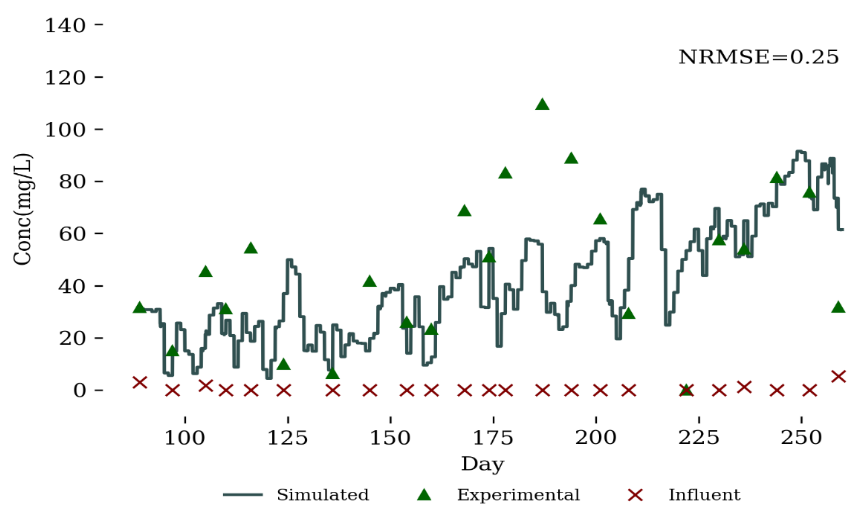
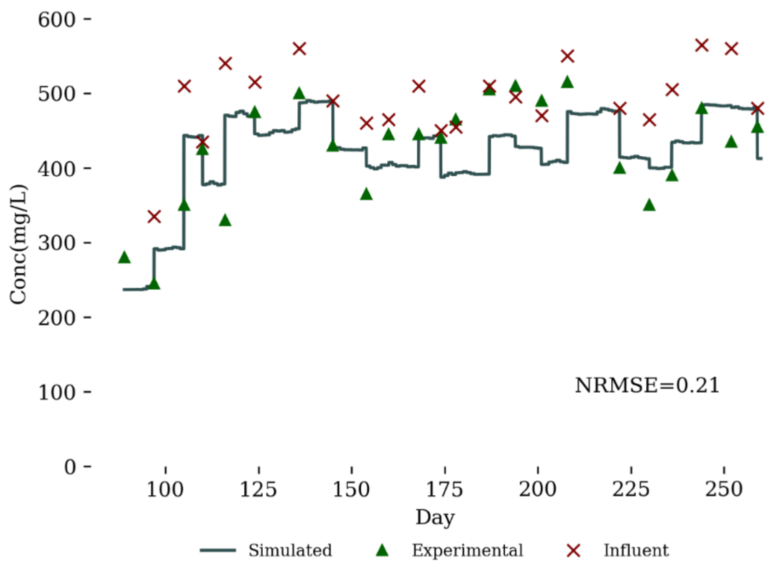


Figure 24. Unamended CW Results for NO3 (as N).

COD

The simulation results for COD are shown in Figure 25. The lower NRMSE values for both VF-CW (NRMSE:0.21) and HF-CW (NRMSE:0.17) model indicate good model fitness.

a) VF-CW



b) HF-CW

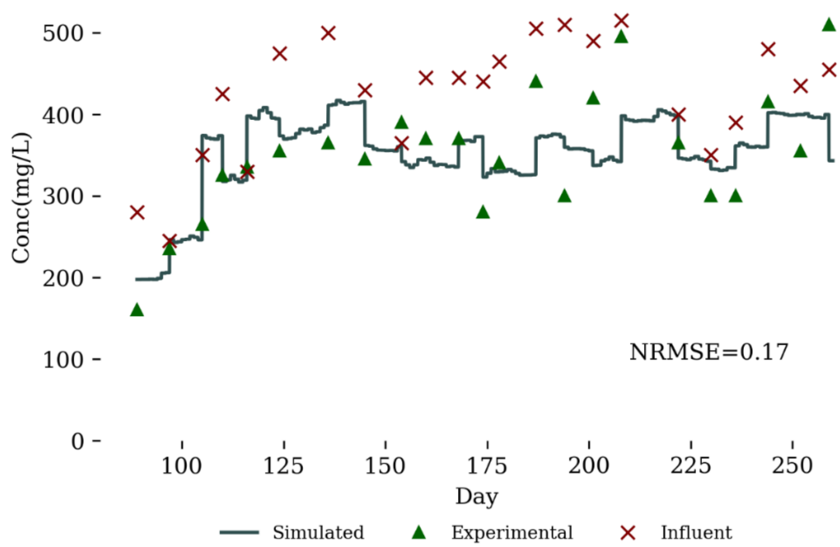


Figure 25. Unamended CW Results for COD

Removal Efficiency

The removal efficiency for each tank has been calculated to compare between the experimental and simulated results. The results show that the model is able to predict the removal efficiency with an average error of %. The results are shown in Table 12.

Table 12: Removal Efficiency Comparison (Unamended System)

Pollutant	Tank	Simulated Removal Efficiency (%)	Observed Removal Efficiency (%)	Error (%)
NH_4^+ (as N)	VF-CW	43.1	46.6	7.4
NH_4^+ (as N)	HF-CW	21.9	20.1	8.9
COD	VF-CW	13.4	11.4	13.3
COD	HF-CW	17.4	16.5	5

3.3.2 Results for Amended CWs

The parameters for the adsorbent-amended CWs were calibrated to fit the simulation results with the experimental data. The $NRMSE$ values were used as described in the previous section to finalize the calibrated values for each parameter. Parameters were kept within the literature range most of the times. However, some model parameters were not found in previous studies and thus, best fit values were chosen both for VF-CW and HF-CW. The calibrated parameters and literature ranges are presented in Table 13.

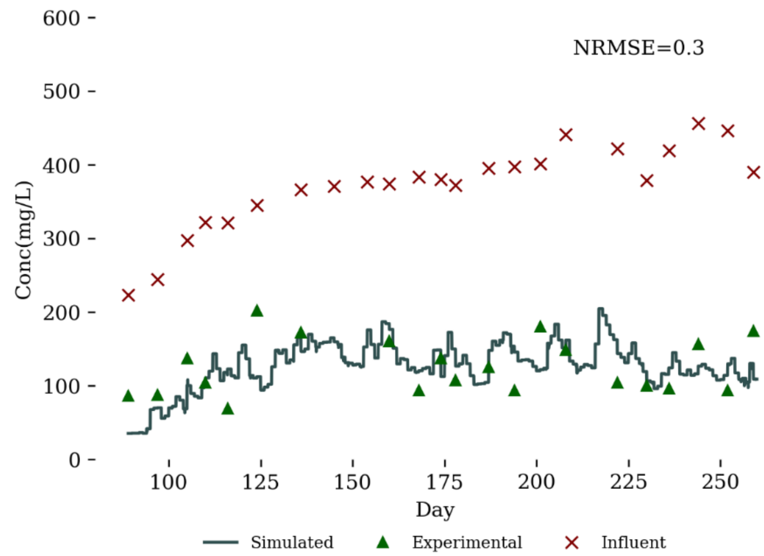
Table 13. Calibrated Values for Adsorbent-amended CW Model Parameters

Parameter	Unit	Calibrated Value for VF	Calibrated Value for HF	Literature Range	Range Source
Saturation Concentration, KB	mg/L/hr	41.25	1177	-	-
Maximum Degradation Rate, mu_max	$hour^{-1}$	990	1609	-	-
Mineralization Rate Constant, $k_{m,aerobic}$	$hour^{-1}$	0.0012	0.0012	0.0004 – 0.002	Martin and Reddy, 1997
Mineralization Rate Constant, $k_{m,anoxic}$	$hour^{-1}$	0.003	0.003	0.0003 – 0.003	Martin and Reddy, 1997
Nitrification Rate Constant, $k_{n,aerobic}$	$mg\ L^{-1}\ hour^{-1}$	0.038	2	6 – 39	Welander et al., 1997
Nitrification Rate Constant, $k_{n,anoxic}$	$mg\ L^{-1}\ hour^{-1}$	1.5	1.5	-	-
Denitrification Rate Constant, $k_{dn,aerobic}$	$hour^{-1}$	0.04	0.04	-	-
Denitrification Rate Constant, $k_{dn,anoxic}$	$hour^{-1}$	0.05	0.05	0.1-0.5	Martin and Reddy, 1997
Plant Uptake Rate of Ammonia, $k_{pu,NH4}$	$mg\ L^{-1}\ hour^{-1}$	0.0025	0.003	-	-
Plant Uptake Rate of Nitrate, $k_{pu,N03}$	$hour^{-1}$	0.0375	0.0625	-	-
Maximum COD Adsorption Capacity, qcod	mg/g	0.29	33.45	-	-
Zeolite Surface Diffusivity, $D_{s,zeolite}$	m^2/hr	$4.77*10^{-12}$	-	$6.82*10^{-12}$ - $4.2*10^{-11}$	Lahav and Green, 2000
Biochar Surface Diffusivity $D_{s,biochar}$	m^2/hr	-	$5.6*10^{-11}$	-	-

Ammonia

The simulated results for both the VF-CW and HF-CW are presented in Figure 26. The NRMSE values are higher compared to the simulation results for the unamended tanks, though both of the values are well within acceptable range. This is expected as the adsorption kinetics involved in these tanks are complex compared to the unamended system as there are more parameter values to be adjusted. The NRMSE for the VF-CW is 0.3 and that for the HF-CW is 0.35.

a) VF-CW



b) HF-CW

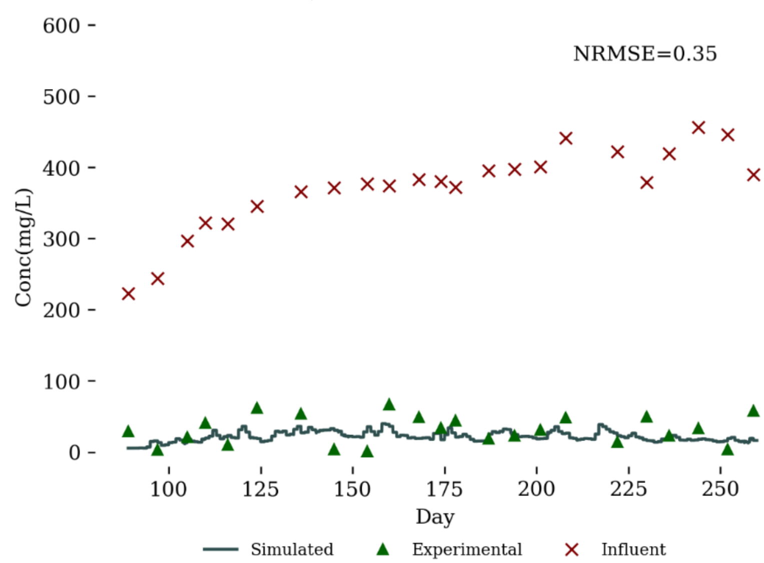


Figure 26. Adsorbent-amended CW Results for NH4+ (as N)

COD

The simulation results for COD illustrate that there is not much significant reduction in COD in the VF-CW, which is expected as COD reduction is favored by anoxic system (Figure 27). Also, zeolite does not have significant adsorption efficiency for COD. The NRMSE values are low for both VF-CW (NRMSE = 0.19) and HF-CW (NRMSE = 0.17), indicating good model fitness.

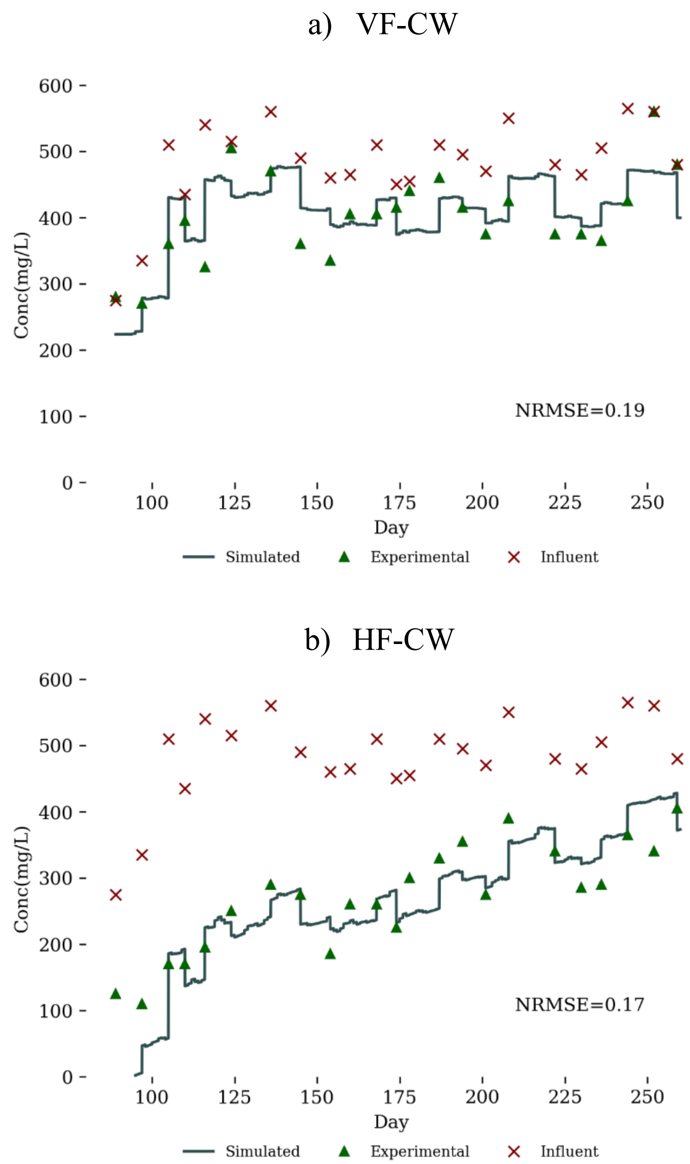


Figure 27. Adsorbent-amended CW Results for COD

Removal Efficiency

The removal efficiency for each tank has been calculated to compare between the experimental and simulated results. The results show that the model is able to predict the removal efficiency with an average error of %. The results are shown in Table 14.

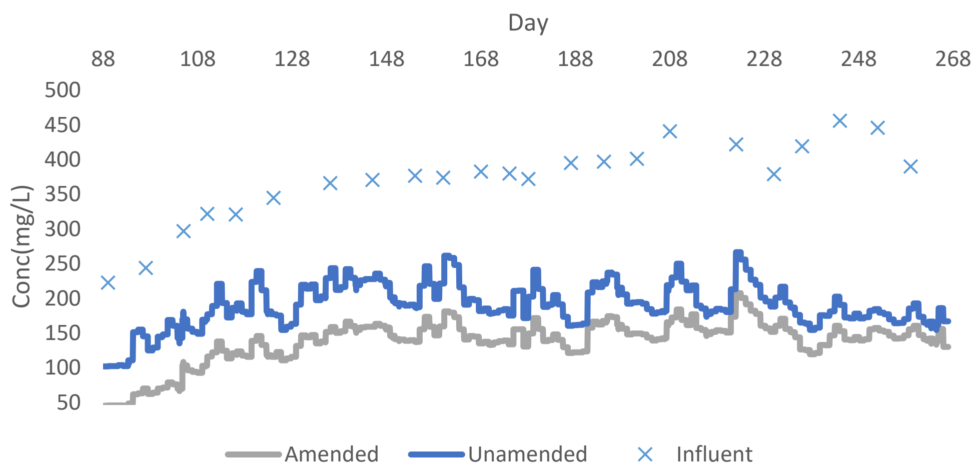
Table 14. Removal Efficiency Comparison (Amended System)

Pollutant	Tank	Simulated Removal Efficiency (%)	Observed Removal Efficiency (%)	Error (%)
NH_4^+ (as N)	VF-CW	67.4	65.7	2
NH_4^+ (as N)	HF-CW	34.5	33.2	3
COD	VF-CW	16.2	16.3	0
COD	HF-CW	38.3	37.6	1.8

3.3.3 Unamended vs Amended Simulation Comparison

The simulated effluent concentration for unamended and amended wetlands was plotted to understand the model's capability to simulate the adsorption mechanism (Figure 28), demonstrating that the simulated results for the amended wetlands are much lower than those of unamended wetlands. This indicates that the model is capable of predicting the adsorption effects for both zeolite and biochar.

a) VF-CW



b) HF-CW

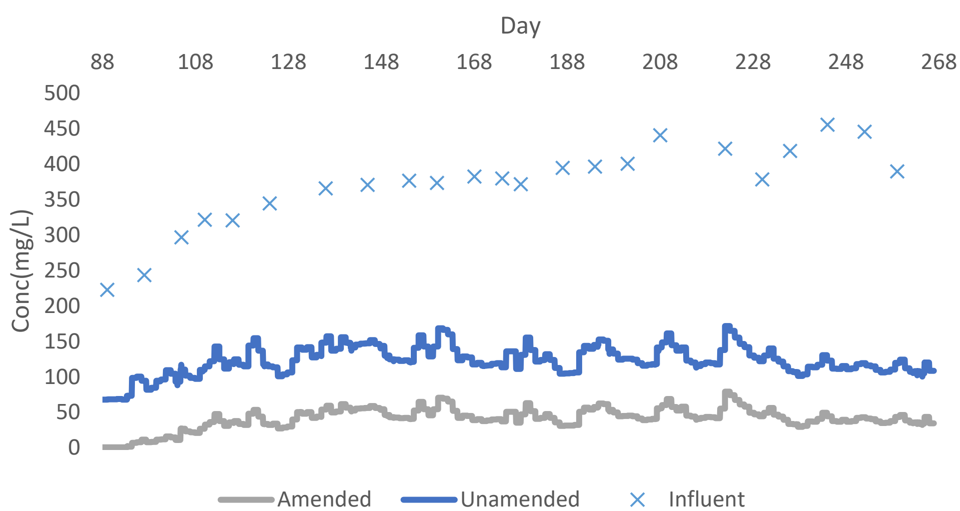
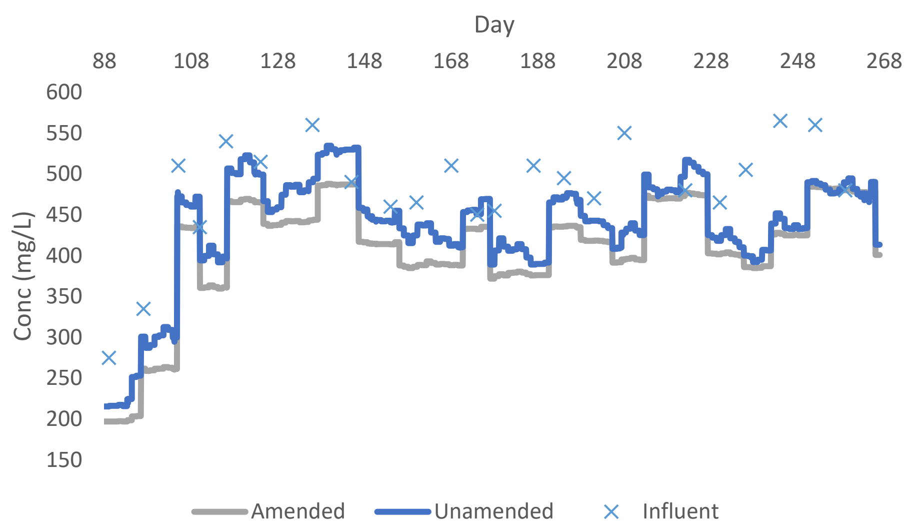


Figure 28. Simulation Results Comparison for NH4+ (as N)

Simulated COD results do not significantly vary between the amended and unamended wetlands (Figure 29). For VF-CW, as zeolite does not have much affinity for COD, the adsorption capacity is very low and this has been reflected in the model. However, for HF-CW, the simulated results for amended are lower than those of unamended as expected until Day 160. After that, the adsorption capacity tends to decrease with time, resulting in higher values for effluent concentration.

a) VF-CW



b) HF-CW

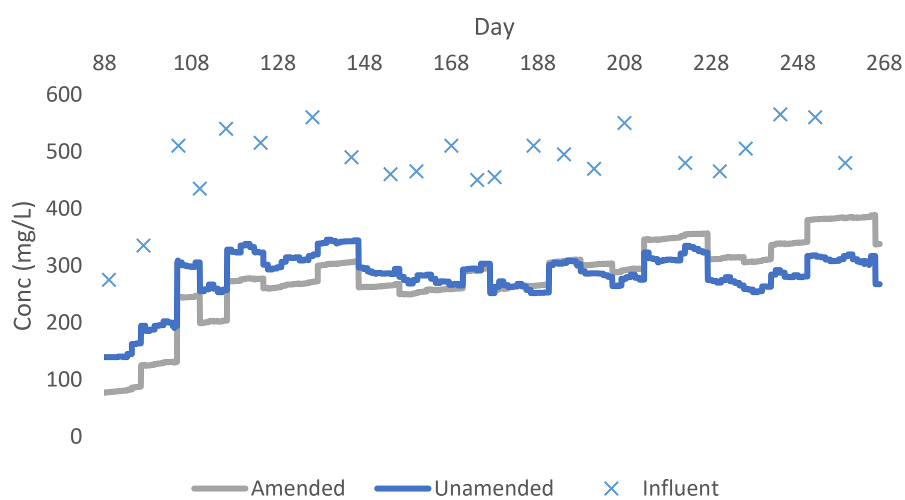


Figure 29. Simulation Results Comparison for COD

3.3.4 Uncertainty Analysis Results

The results from the uncertainty analysis for Ammonia adsorption model are summarized in Table 15. It can be seen the most sensitive parameter is the surface diffusivity of zeolite and the Ammonia adsorption potential. In other words, slight changes in the adsorbent properties can significantly affect the predicted ammonia concentration. We can also see that temperature is the least sensitive parameter in this model which is expected as the seasonal temperature difference in Florida is insignificant.

Table 15. Uncertainty Analysis Results for Ammonia Adsorption Model (Ranked in Descending Order)

Parameter Description	Parameter Notations	Units	Total-Order Indices
Zeolite Surface Diffusivity	Ds_zeolite	m^2/hr	4.14E-01
Zeolite Maximum Ammonia Adsorption	VF_qNH4	mg/g	3.15E-01
Nitrification (Aerobic)	A_kn_a	/hr	1.59E-01
Denitrification (Anoxic)	A_kn_an	/hr	6.73E-02
Plant Uptake (HF-CW)	A_HF_kpu_NH4	/hr	5.23E-02
Biochar Maximum Ammonia Adsorption	HF_qNH4	mg/g	1.40E-02
Biochar Surface Diffusivity	Ds_biochar	m^2/hr	1.37E-02
Mineralization (Anerobic)	km_an	/hr	1.08E-02
Precipitation	precip	m	4.68E-03
Plant Uptake (VF-CW)	A_VF_kpu_NH4	/hr	1.83E-03
Mineralization (Aerobic)	km_a	/hr	3.38E-04
Temperature	temp	℃	1.91E-04

The results from the uncertainty analysis for COD adsorption model are summarized in Table 16. The most sensitive parameters are biomass yield and maximum specific degradation rate, indicating that microbial activities are critical for COD removal from leachate in CWs. We can also see that temperature is the least sensitive parameter in this model which is expected as the seasonal temperature difference in Florida is insignificant.

Table 16. Uncertainty analysis Results for COD Adsorption Model (In Descending Order)

Parameter Description	Parameter Notations	Units	Total-Order Indices
Biochar Max Adsorption	hf_qcod	mg COD/g biochar	7.67E-01
Biochar Surface Diffusivity	ds_biochar	m2/hr	2.51E-01
Max Substrate Utilization Rate (HF-CW)	hf_mu_max	mg/L/hr	4.92E-06
Zeolite Surface Diffusivity	ds_zeolite	m2/hr	2.97E-06
Saturation Constant (HF-CW)	hf_Kb	mg/L/hr	7.39E-07
Precipitation	precip	m	6.54E-09
Max Substrate Utilization Rate (VF-CW)	vf_mu_max	mg/L/hr	2.56E-10
Saturation Constant (VF-CW)	vf_Kb	mg/L/hr	2.67E-20
Zeolite Maximum COD Adsorption	vf_qcod	mg COD/g zeolite	2.28E-20
Temperature	temp	℃	1.83E-20

3.4 Post-treatment of CW Effluent for Reuse

3.4.1 Feed stream and treated effluent characteristics

Characteristics of the raw and treated landfill leachate are summarized in Table 15. As discussed previously, compared with the control-CW, the adsorbent-CW effluent had lower total inorganic nitrogen (NH_4^+-N + NO_x-N), SDI_{15}, TSS, and turbidity values due to the zeolite and biochar addition.

Table 17. Feed Stream and Treated Effluent Characteristics for the Three Treatment Alternatives.

Parameter	Raw Landfill Leachate	AS Treated Effluent	Control-CW Effluent	Adsorbent-CW Effluent
Turbidity (NTU)	86.3	42.3	2.87	1.58
TSS (mg/L)	118	94.5	30.3	24.2
SDI_{15}[1]	> 6.67	> 6.67	6.44	6.26
TDS[2] (mg/L)	14,000	12,600	12,700	11,900
LSI[3]	-4.03	-4.83	-4.02	-4.71
pH at 25°C	7.61	6.95	7.83	7.30
BOD_5 (mg/L)	29.5	NM[4]	6.2	1.7
COD (mg/L)	482	NM[4]	373	273
Ca^{2+} (mg/L)	1,930	1,120	1,050	669
Ba^{2+} (mg/L)	0.250	0.388	0.363	0.559
NH_4^+-N (mg/L)	367	4.55	144	46.5
K^+ (mg/L)	671	618	673	582
Na^+ (mg/L)	3,290	3,070	3,410	3,330
Mg^{2+} (mg/L)	640	276	466	281
CO_3^{2-} (mg/L)	BDL	BDL	BDL	BDL
HCO_3^- (mg/L)	BDL	BDL	BDL	BDL
NO_3^--N (mg/L)	BDL	251	79.5	176
Cl^- (mg/L)	6,410	6,000	6,040	5,810
F^- (mg/L)	BDL	BDL	BDL	BDL
SO_4^{2-} (mg/L)	137	121	104	128
PO_4^{3-} (mg/L)	3.84	BDL	BDL	BDL
Br^- (mg/L)	BDL	BDL	BDL	BDL

Notes:

[1]: SDI_{15} > 6.67 are a resultant that the total time required for 100 mL of sample to pass through the 0.45 µm filter exceeded 60 seconds, indicating greater than 90% pluggage and it is deemed that it is not necessary to continue the test [45].

[2]: TDS concentrations were obtained from the WAVE software, based on the ionic balance of the feed stream composition.

[3]: LSI was calculated based on pH at 25°C, TDS concentration, Ca^{2+} concentration, HCO_3^- concentration (assumed to be 1 µg/L as its method detection limit) , and temperature of 25°C. LSI<0 are indicative of water being undersaturated with respect to calcium carbonate and has a tendency to corrode.

[4]: BOD_5 and COD for the AS treated effluent were not measured in this study.

[5]: Sr^{2+}, SiO_2, B, and CO_2 are parameters that can be inputted into the WAVE software but were not measured in this study.

[6]: BDL = Below detection limit; NM = Not measured

3.4.2 Modeling different UF-RO design alternatives

Details of the common and optimized UF-RO treatment configurations are presented in Figure 30. Optimization allowed for the creation of two additional alternatives apart from the four standardized alternatives that were based on the common UF-RO treatment configuration. In addition, some feed water was able to bypass the UF-RO system due to the resulting high quality permeate with very low contaminant levels, especially electrical conductivity. The target product water conductivity was based on EPA standards for industrial reuse and was set at 1,120 μS/cm. The feed water inflow to the UF-RO system and bypass quantities of the six different alternatives are summarized in Table 16.

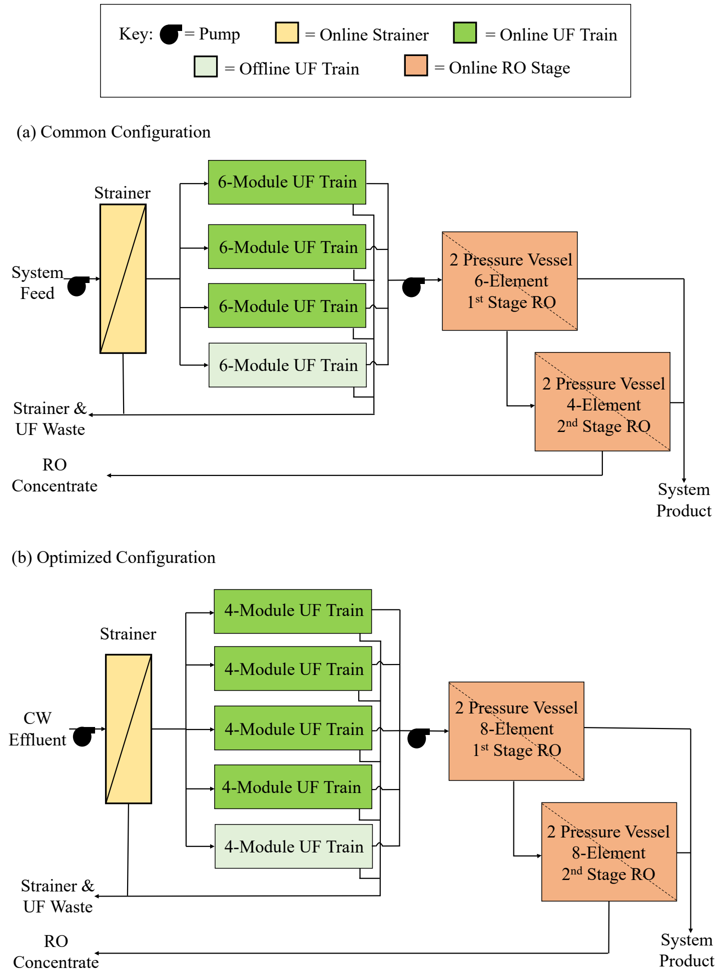


Figure 30. UF-RO Design Configurations.

Table 18. Feed Water Inflow and Bypass Quantities.

Alternative	**Inflow Quantity (m^3/d)**	**Bypass Quantity (m^3/d)**
Raw Landfill Leachate	741	16.2
AS Treated Landfill Leachate	739	18.0
Control-CW	737	20.6
Control-CW Optimized	740	16.9
Adsorbent-CW	733	24.6
Adsorbent-CW Optimized	737	19.8

The control-CW and adsorbent-CW systems both had the potential to generate more system product due to the higher water quality of the feed stream compared to the raw landfill leachate and AS treated landfill leachate feed streams (Figure 31). Optimization for both CW feed stream systems included decreasing the number of online UF modules, increasing RO system recovery, and increasing the number of RO elements per pressure vessel in each stage. A reduction in the total number of UF modules also reduced capital and O&M costs. This optimization process overall generated a 12.9% enhancement in system product for the control-CW system as it increased from 322 m^3/d to 363 m^3/d. For the adsorbent-CW system, the optimization process overall generated an 11.9% enhancement in system product for the adsorbent-CW system as it increased from 354 m^3/d to 396 m^3/d.

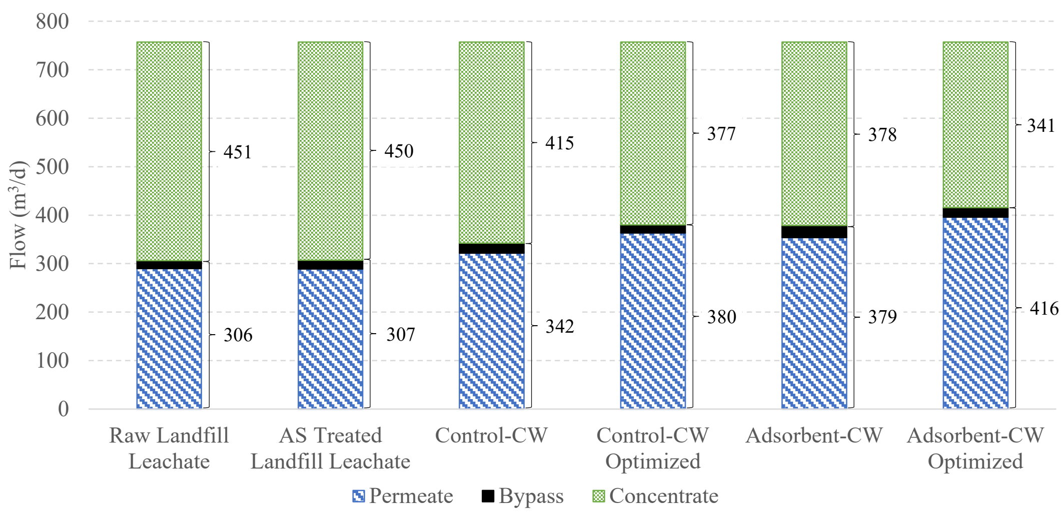


Figure 31. UF-RO Flow Outputs for each alternative. Reclaimed water consists of the permeate and bypass flow streams. Concentrate consists of the strainer, UF, and RO wastes.

3.4.3 Net present value analysis

The net present value analysis results per m^3/d of landfill leachate treated in 2021 USD for the study are presented in Figure 32. The optimization of the control-CW to UF-RO system and of the adsorbent-enhanced system to UF-RO would lead to cost savings of USD $38.6 million and USD $37.9 million, respectively. The non-discounted payback period for the control-CW to optimized UF-RO system is 5.0 years, whereas the non-optimized alternative has a payback period of 5.4 years. The payback period for the adsorbent-CW to optimized UF-RO system is 4.9 years, whereas the non-optimized alternative has a payback period of 5.3 years. The optimization process reduced O&M costs, therefore reducing the payback periods and achieving an effluent that could meet reuse standards.

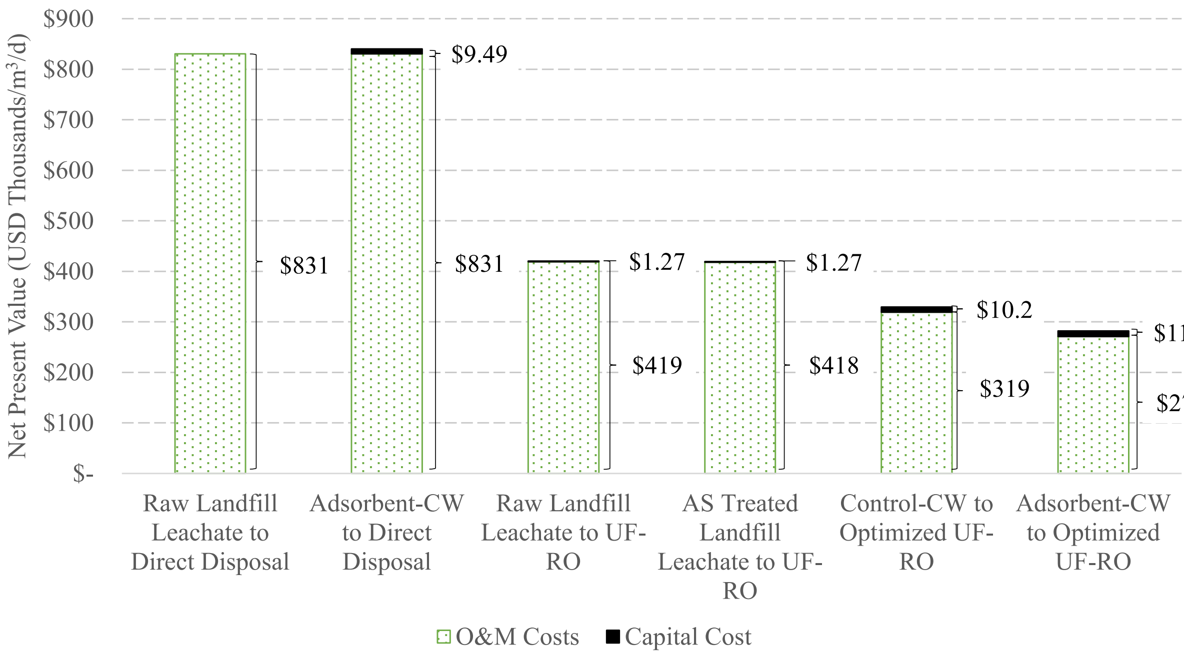


Figure 32. Summary of Net Present Values per m^3/d of Leachate Treated for Various Treatment Alternatives.

Across all alternatives, capital costs for constructing the on-site treatment systems are minimal compared to O&M costs (Figure 33). The main cost drivers for all alternatives are disposal costs, which accounts for 99% of the annual O&M costs. Solidification is the largest contributor due to POTWs limiting the amount of landfill leachate that can be accepted into their facilities. In this case study, the amount of landfill leachate that was accepted by POTWs via the hauling contractor was 75.7 m^3/d, which is approximately 10% of the landfill leachate treated. Therefore, on-site treatment of landfill leachate has the potential to provide great economic benefit while providing water recovery for reuse purposes. In addition to economic benefit, environmental benefits of on-site landfill leachate treatment include: reduction of human contact with untreated leachate, environmental risks caused by spills during transportation of leachate, and negative publicity.

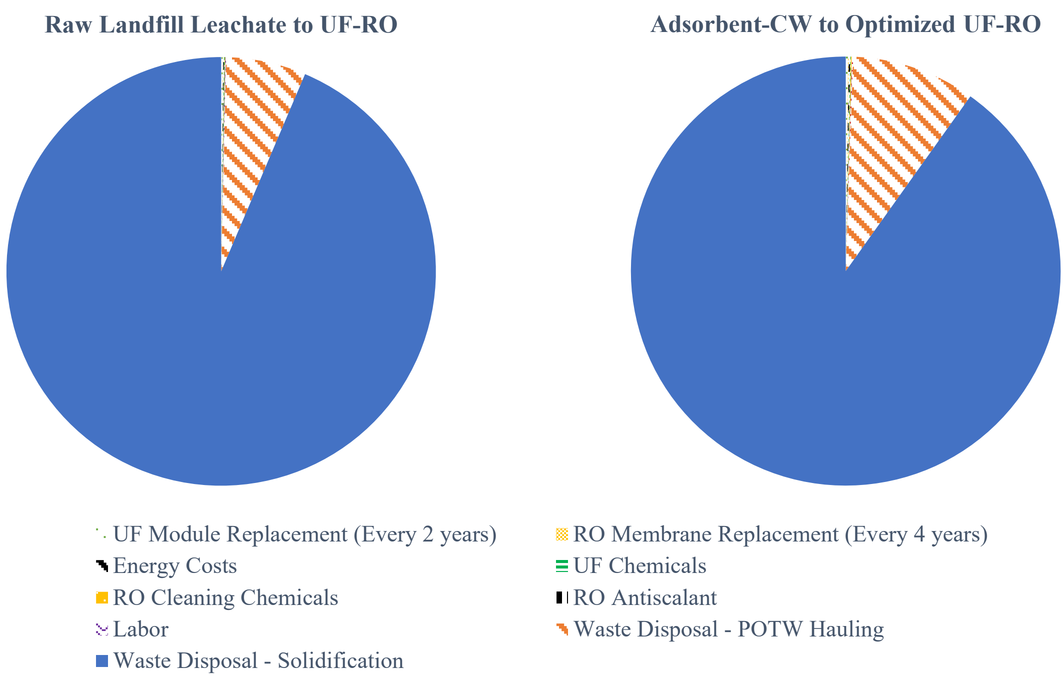


Figure 33. Annual O&M Cost Breakdown for Raw Landfill Leachate to UF-RO and Adsorbent-CWs to Optimized UF-RO Alternatives.

4 CONCLUSIONS

4.1 Objective 1: Investigate treatment of high-strength leachate collected from Florida landfills in bench-scale adsorbent amended SBBR.

During our Phase I project, three bench-scale sequencing batch biofilm reactors (SBBRs) were set up to test the efficacy of using zeolite and biochar to enhance landfill leachate treatment. The results showed that zeolite and biochar addition significantly enhanced removal of ammonia, organic matter (measured as sCOD) and color (measured as UV254 and UV456 absorbance). However, questions were raised by the TAG and Hinkley Center Board as to whether the adsorbent enhanced SBBR process could be used to treat high-strength landfill leachate. Therefore, during Phase II, high-strength landfill leachate (TAN > 1,500 mg/L, sCOD > 6,500 mg/L, deep brown color) was obtained from a mature Florida landfill and used as an influent feed. The SBBR was operated in a three-stage sequence: 1) fill, 2) low aerobic react, 3) rapid drain. Varying hydraulic residence times (HRTs) were applied over a 5 month period. High TIN removal rates of 82.9, 109, and 122 mg/L-day were observed at HRTs of 18.9, 14, and 10.5 days, respectively, most likely due to simultaneous nitrification-denitrification and partial nitritation/anammox. High sCOD removal rates of 168, 217, and 223 mg/L-day were observed at HRTs of 18.9, 14, and 10.5 days, respectively. High color removals were initially observed, but declined over time. The SBBR achieved higher TIN and sCOD removal rates than in our Phase I study, indicating adsorbent amended SBBRs can be used for very high strength leachate. The results also show that zeolite can be completely bio-regenerated over many SBBR cycles; however, biochar loses its adsorptive capacity for recalcitrant organic matter over time.

4.2 Objective 2: Investigate long-term leachate quality and quantity performance of pilot-scale CWs operated at Hillsborough County's SE landfill under varying conditions.

Two mesocosm hybrid CWs, with and without biochar/zeolite amendment, were used to treat landfill leachate at the Southeast Hillsborough County Landfill in Lithia, Florida. The Control-CW was filled with conventional gravel medium, while the Adsorbent-CW was amended with 10% (v/v) of zeolite in the VF tank and 13% (v/v) of biochar in the HF tank. To reduce NOx accumulation, a HF-CW containing wood chips (Woodchip-CW) was set up downstream of the Adsorbent-CW on Day 540. The wood chips served as a carbon source to enhance denitrification. CWs were planted with cattail (*Typha spp*) and cordgrass (*Spartina*) and operated at varying HRTs (11d, 7d, and 4.5d) for ~2 years. Results showed that zeolite added to VF tank improved the nitrification rate, resulting in high ammonia removal. This was due to the combined effects of ion exchange and biodegradation, especially under higher ammonia loading conditions. Biochar addition to the HF tank significantly improved sCOD and color removals through adsorption. In addition, the lower ammonia concentrations exiting the zeolite-amended VF tank reduced free ammonia toxicity to plants and microbes in the biochar enhanced HF-CW. After addition of the Woodchip-CW, total nitrogen removals of up to 78-80% were achieved. Note that the highest HLR applied to the CWs in this study was relatively low (4.0 cm/d), compared with typical CW HLR values (2-20 cm/d). Based on the current HLR (4.0 cm/d) condition, a CW surface area of ~0.9 to 1.9 hectares would be needed to treat the daily leachate volume produced by the Southeast Hillsborough County Landfill (100,000-200,000 gallons/day). In addition to chemical analysis, the microbial community of the Adsorbent-CW and Control-CW is currently being analyzed and compared. These results will be made available upon request.

4.3 Objective 3: To evaluate the effects of uncertainty on leachate quality/quantity and adsorbent composition on the performance of a pilot-scale CW system.

A numerical process model in Python 3.7 was developed using mass balance modules for water, DO, different forms of nitrogen and COD. The model takes into consideration the effects of temperature on reaction rate constants. Data from Task 2 was used to develop and calibrate the model. An uncertainty analysis was also performed under to evaluate the effects of parameter uncertainty on model performance. The model was able to predict the general effluent concentration trends for all of the modules and was able to predict the adsorption effects of both zeolite and biochar. The model was particularly good at predicting removal efficiencies for both COD and ammonia. The source code of the model will be made available online for further research and to help in the design and operations of adsorbent-amended treatment wetlands.

Despite its novelty and promising results, there are still several limitations associated with this model and its implementation, most of which can be resolved in future research. First, the model was developed using data collected over 6 months, but it is likely that a larger span of observations could have resulted in more robust model fitness. Also, limited data for DO and Organic Nitrogen were available, which made it difficult to properly calibrate those modules. The model was also developed for a constant hydraulic loading rate, something which can be modified to simulate results for varying HLRs. Moreover, the model could be easily used to simulate the operations of a larger (full-scale) system, something which could be helpful for better design and operations of leachate treatment wetlands.

4.4 Objective 4: Evaluate the most technically and economically viable landfill leachate treatment and reuse strategy using Hillsborough County as a case study.

The potential for highly treated landfill leachate to be reclaimed for irrigation or industrial applications was investigated using a combination of chemical characterization of raw and treated leachate, ultrafiltration-reverse osmosis (UF-RO) simulations and a net present value analysis. Four UF-RO pre-treatment scenarios were compared: 1) no pretreatment, 2) activated sludge pre-treatment, 3) conventional SSF CWs, and 4) adsorbent-enhanced SSF CWs. Samples were collected of untreated leachate, an onsite activated sludge system at the Hillsborough County SE Landfill and effluent from Control-CW and Adsorbent-CW (Objective 2). These characteristics were used as input parameters to DuPont™ WAVE design simulation software to optimize UF-RO system design for each scenario. The landfill leachate treatment train consisting of Adsorbent-CW followed by UF-RO attained the highest water recovery rate and greatest cost savings compared with untreated landfill leachate disposal.

In an economic analysis for Hillsborough County (Florida, USA), raw landfill leachate to direct disposal resulted in a net present value cost of USD \$831,000 per m^3/d of landfill leachate treated. With treatment using adsorbent-enhanced CWs followed by an optimized UF-RO system, the net present value cost decreased to USD \$282,000 per m^3/d of landfill leachate treated. The Adsorbent-CW to UF-RO alternative is a promising option to reduce the amount of high strength landfill leachate that requires disposal. In addition, this option reduces the risk of potential leachate spills during transport and enhances the opportunity to beneficially reuse the water for industry and non-food irrigation. Implementation of these results with on-site leachate treatment facilities would be of economic and environmental benefit to Hillsborough County and other municipalities as it reduces the toxicity, flow, and risk of the industrial wastewater.

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