

## QUARTERLY PROGRESS REPORT

March 2020-May 2020

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

#### **PRINCIPAL INVESTIGATORS:**

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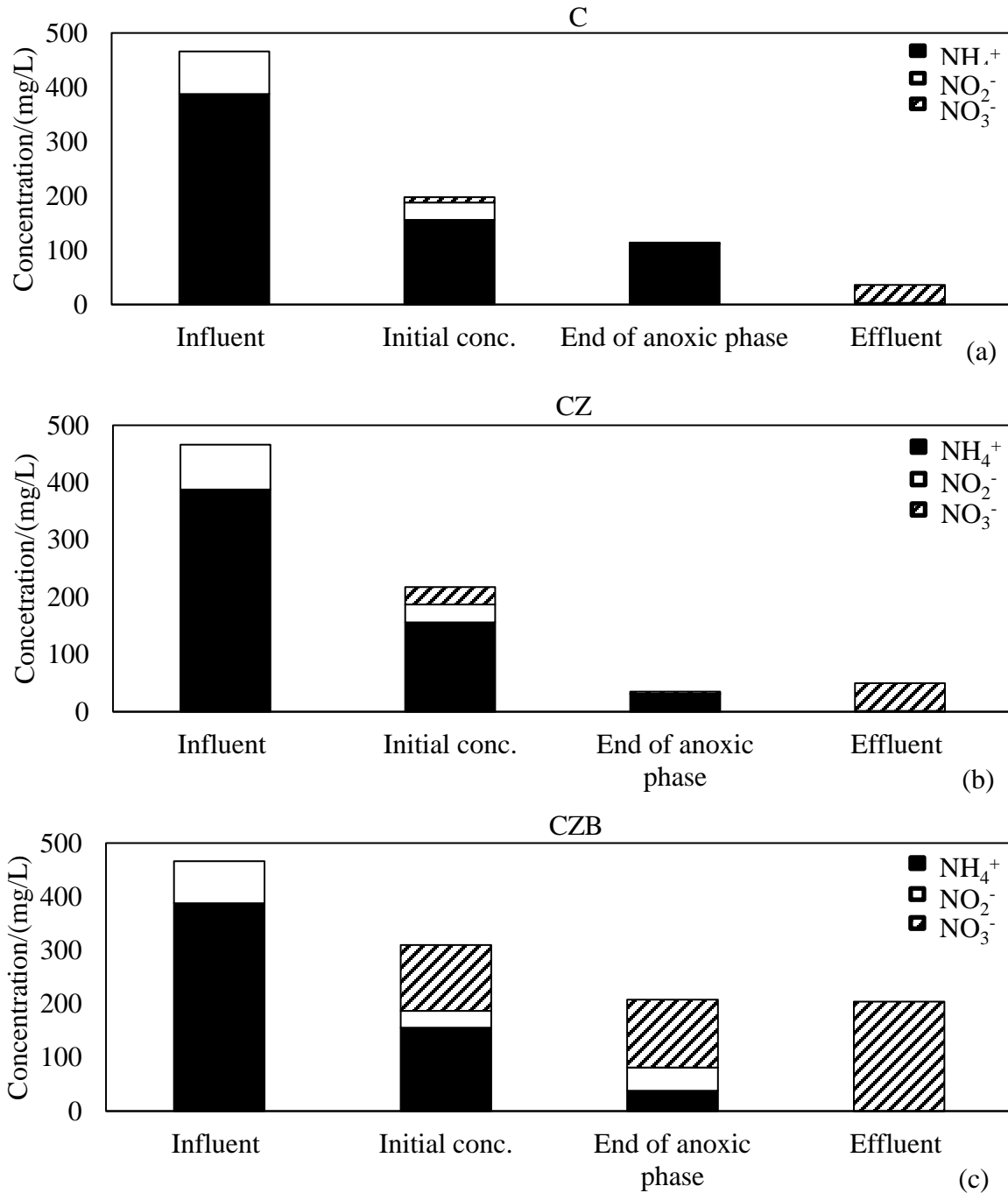
**PROJECT WEBSITE:** <http://constructed-wetlands.eng.usf.edu/>

#### **Work accomplished during this period:**

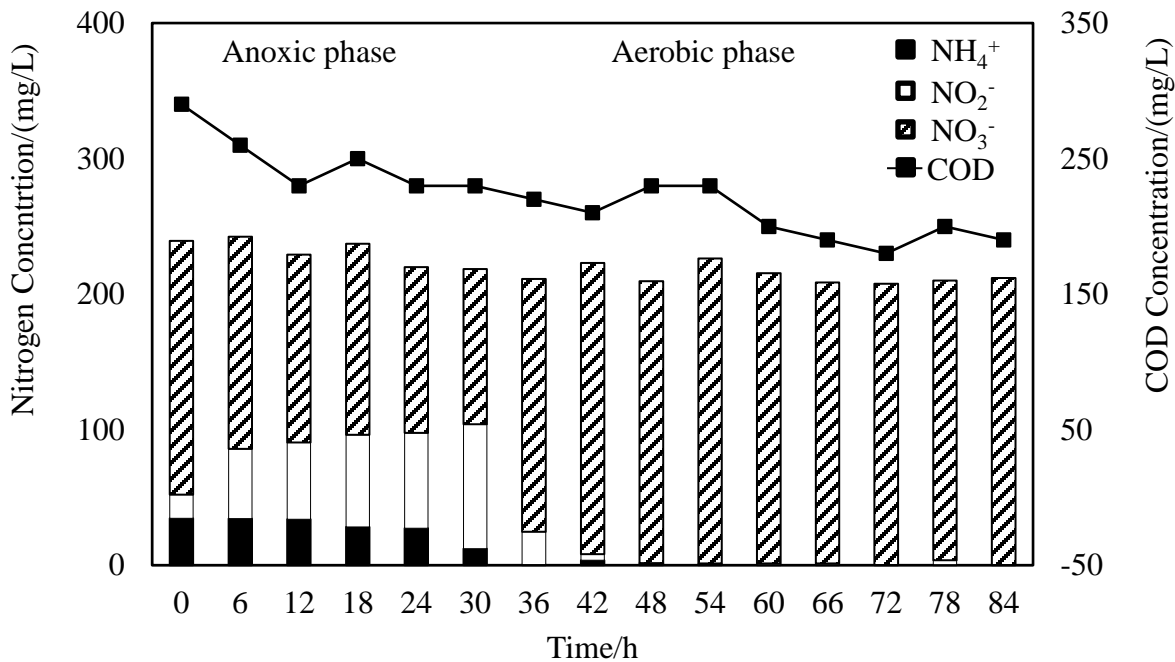
During the third quarter, progress was made on the following objectives: (i) Additional experiments and data analysis with laboratory-scale sequencing batch biofilm reactors (SBBRs) with and without adsorbent addition; (ii) Preliminary microcosm study on post treatment of laboratory-scale SBBR effluent; (iii) Design and construction of pilot-scale hybrid constructed wetland (CW) systems; (iv) Conceptual model for both vertical and horizontal sub-surface flow CWs; (v) Preliminary research on reverse osmosis (RO) post treatment of CW effluent for water reuse; (vi) Preparation of a manuscript for journal submission.

#### **Laboratory-scale Sequencing Batch Biofilm Reactors:**

During the third quarter, we continued testing the performance of three bench-scale SBBRs for landfill leachate treatment: a) light expanded clay aggregate (C), b) expanded clay plus zeolite (CZ), and c) expanded clay plus zeolite and biochar (CZB). The fate of inorganic nitrogen species during one cycle (Cycle 10) of the three reactors is shown in Figure 1. Reactors were operated with alternating anoxic and aerobic phases at an HRT=8.75 days, as described in quarterly report #2. Initial inorganic nitrogen species concentrations were calculated based on the influent concentration and dilution from the liquid remaining in SBBRs from the previous cycle. The results show that  $\text{NH}_4^+$  was removed by both adsorption by zeolite and nitrification in CZ and CZB; however, higher effluent  $\text{NO}_3^-$  concentrations were observed in CZB. To understand  $\text{NO}_3^-$  accumulation in CZB, we measured inorganic nitrogen species and soluble COD (sCOD) concentrations every 6 hours over a 3.5 day cycle (Figure 2). The results show that during the anoxic phase, sCOD and  $\text{NO}_3^-$  concentrations decrease during the first 12 hours due to adsorption of organic matter to biochar and denitrification. However, from 12 hours to 24 hours, concentrations of these species were stable, indicating that denitrification was limited by lack of a bioavailable electron donor. SBBRs C and CZ are currently shut down; however, we are continuing to operate CZB to understand its long term performance. Influent and effluent total nitrogen (TN) concentrations are being measured to understand the fate of organic N in the SBBR. We have also sent influent and effluent samples to the USF geochemistry lab for metals analysis (As, Ba, Cu, Cd, Cr, Ni, Pb and Zn). A manuscript on the performance of the bench-scale systems is currently in preparation.



**Figure 1:** Inorganic nitrogen species fate in cycle 10 in SBBRs: (a) C, (b) CZ and (c) CZB. (conc.: concentration).



**Figure 2:** Inorganic nitrogen and sCOD fate during one cycle in SBBR CZB.

### Microcosm Study as a Post-treatment of Laboratory-scale SBBRs:

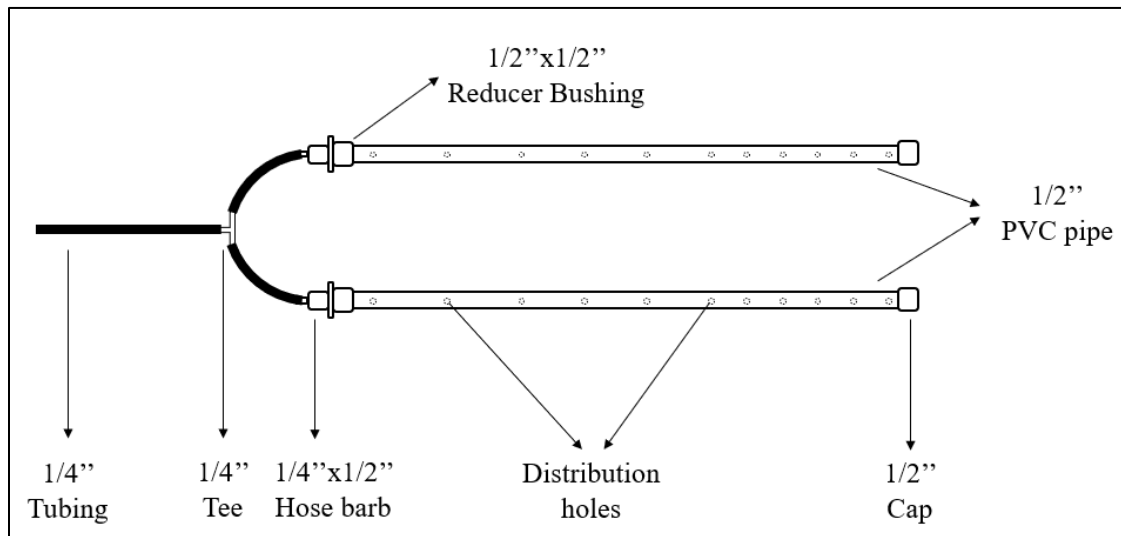
We are currently investigating a post-treatment strategy for reducing the NO<sub>x</sub> concentration after the anoxic stage of the CZB reactor. This strategy applies a sulfur-bearing mineral, sphalerite (Zn, Fe)S, and oyster shells to stimulate mixotrophic denitrification. During this process, denitrifiers employ sphalerite and organic carbon from the oyster shell matrix as electron donors to generate energy for cell synthesis and maintenance. NO<sub>x</sub> is used as a terminal electron acceptor and is reduced to nitrogen gas. Sphalerite is a widespread and abundant mineral found throughout the planet and oyster shells are a waste product of the global seafood industry. These materials have the potential to provide low-cost and sustainable resources for application within constructed wetlands, eliminating the need for complex chemical feed systems for liquid organic substrates, such as glycerol, for heterotrophic denitrification. Furthermore, mixotrophic denitrifiers are slow growing compared to their heterotrophic counterparts, which minimizes sludge production.

Previous research in our laboratory has investigated the use of sphalerite and oyster shells for drinking water denitrification. Microcosm containing these materials achieved a nitrate removal efficiency of 90%. Furthermore, 100% phosphate removal was observed within the first 19 days and concentrations were maintained below the detection limit for the remainder of the experimental period (i.e., 48 days). We are currently assessing the feasibility of sphalerite and oyster shells for reducing NO<sub>x</sub> in microcosm studies containing effluent from the CZB reactor. Water quality is being monitored on a weekly basis by measuring the concentration of various nitrogen species (TN, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>), sulfate, and phosphate. Results from this experiment will be presented in the next quarterly report.

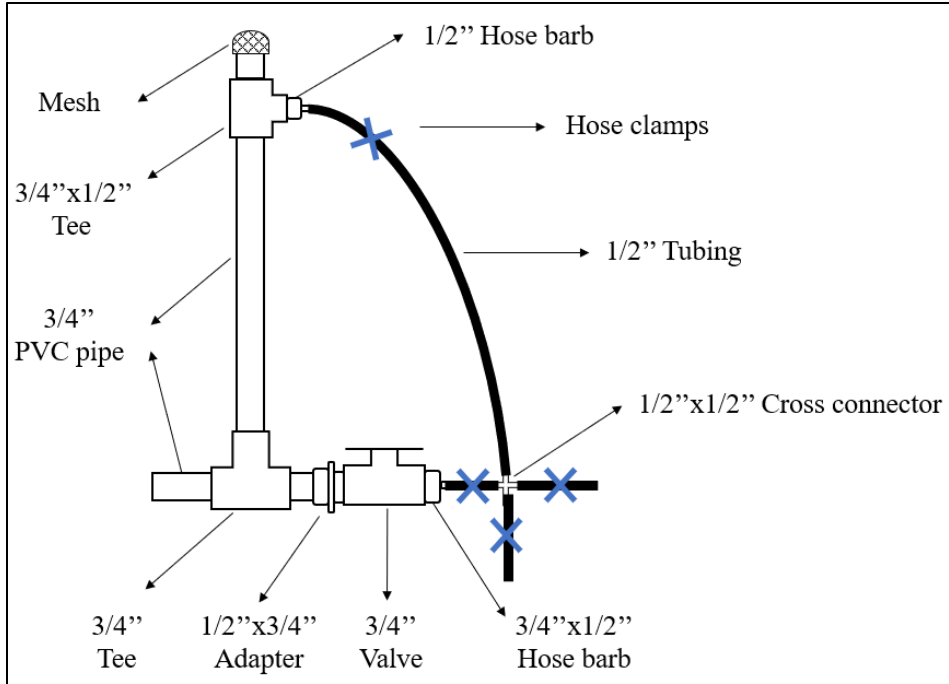
### Pilot-scale Hybrid Constructed Wetland Construction:

Design details for the pilot-scale constructed wetlands (CW) were finalized and the systems are currently under construction. Two systems will be operated in parallel, with and without adsorbent media. For each system, a vertical subsurface flow constructed wetland (VSSF-CW) will be followed by a horizontal subsurface flow constructed wetland (HSSF-CW). Based on our discussion with wetlands experts, plants to be used in the system are cattails and cord grass. We have identified a vendor (Aquatic Plants of Florida) who will have plants ready when they are needed.

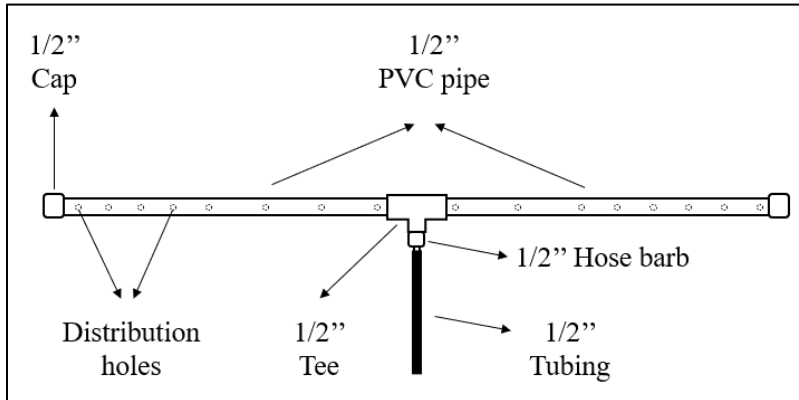
Four polyethylene tanks were purchased from National Tank Outlet (Lake Wales, Florida): two 89 Gallon tanks (25.5" Length x 25.5" Width x 37" Height) with aspect ratio 1.0 as VSSF-CWs, two 110 Gallon tanks (55" Length x 31" Width x 18" Height) with aspect ratio 1.8 as HSSF-CWs. To achieve an even influent distribution to each tank, distribution pipes (PVC pipes with holes of different sizes and intervals) were designed and constructed (Figures 3a and 3c). An elevated outlet pipe equipped with a valve (Figure 3b) was installed in the VSSF-CWs to provide operational flexibility. When the valve is closed, an internal water storage zone is created in the VSSF-CW to create anoxic conditions for denitrification. When the valve is open, effluent will flow directly to the HSSF-CW. The HSSF-CWs are equipped with an elevated outlet pipe (Figure 3d) to achieve saturated conditions throughout the HSSF-CWs. Photographs of the CWs and different media are shown in Figure 4, 5, 6.



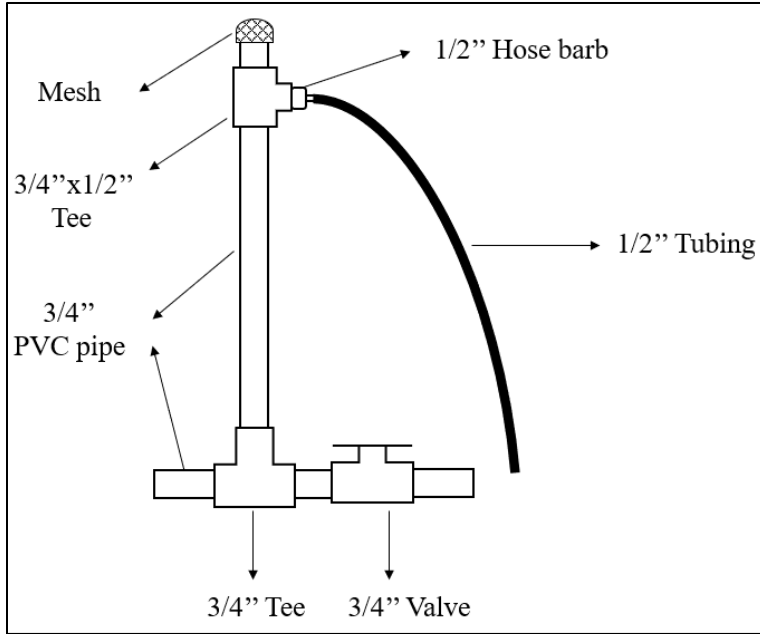
(a)



(b)



(c)



(d)

**Figure 3:** Schematics of CW details: (a) Distribution pipe for VSSF-CW; (b) Outlet pipe (with/without elevated pipe) for VSSF-CW; (c) Distribution pipe for HSSF-CW; (d) Outlet pipe for HSSF-CW.



**Figure 4:** Photograph of VSSF-CW



**Figure 5:** Photograph of HSSF-CW



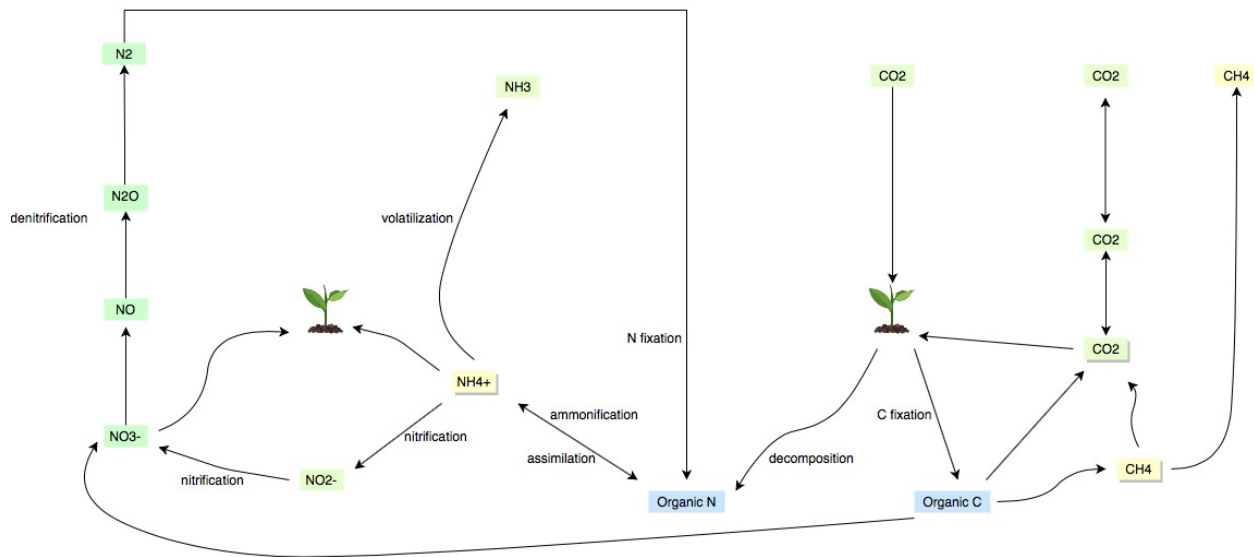
**Figure 6:** Different media used in CWs.

**Pilot Operation Modeling:**

A conceptual model is being developed for the VSSF-CW and HSSF-CW (Figure 7). The model outlines the hydrology, nitrogen and carbon transformations in the systems. This conceptual model will serve as the guide for developing the final mathematical model. The hydrologic

model accounts for sources and sinks of water, via influent flow, precipitation and evapotranspiration. Variables such as bank loss, runoff, and groundwater infiltration are assumed to be negligible due to the controlled nature of the pilot system design. State variables that have been identified include volumetric flow, depth, and hydraulic loading. Inflow of leachate into the vertical flow will be a controlled function. State variables for the nutrient cycling model include concentrations and mass fluxes of ammonia, nitrate, nitrite, nitrogen gas, organic carbon and carbon dioxide. Further review of the literature will be the next step to conceptualize the effects of zeolite and biochar on the system. Additionally, established mathematical equations that describe each process will be added to the conceptual model.

The model is being developed in Python 3.7 and includes mass balances of each nitrogen and carbon species. Python functions are used to incorporate differential equations relating to each constituent. These are solved at each hour over the course of days. Nitrification rates are limited by dissolved oxygen concentrations and denitrification rates are limited by an available organic carbon source as the electron donor. The sequence of functions follows the steps of the processes shown in the figure below. Initially we will use data previously obtained in the bench scale study for input concentrations. Reaction rate  $K$  values will later be calibrated using data that will be gained from the pilot study. Additionally, the hydrology of the system will be incorporated as the model continues to be developed.



**Figure 7:** Conceptual diagram showing the chemical processes included in the model

### Water Reuse Applications:

Based on our bench-scale results and a review of the literature, the proposed hybrid SSF-CW cannot meet conductivity requirements for urban or agricultural irrigation reuse, industrial reuse (e.g., cooling water) or aquifer storage and recovery applications (Table 1). Post treatment of the CW effluent using either reverse osmosis (RO) or combined ultra-filtration (UF) and RO is required. The proposed hybrid SSF-CW is expected to provide excellent pre-treatment for the UF-RO system (Huang et al., 2011). We have identified software that will be used to design and simulate the operation of UF-RO systems for various feedwater compositions and effluent water quality goals ([www.dupont.com/water/resources/design-software.html](http://www.dupont.com/water/resources/design-software.html)). We are currently recruiting a student who can help design this system and estimate capital and O&M costs.



**Table 1:** CZB effluent conductivity comparison with potential reuse applications.

Water type	Conductivity ( $\mu\text{s}/\text{cm}$ )
CZB effluent	15,700
Irrigation reuse*	<1,360
Industrial reuse*	<1,120
Aquifer recovery**	<1,000

**TAG Meeting:**

No TAG meetings were held during this quarter.

**Metrics:**

1. Students working on the project:

Name	Deg. prog.	Department	Email
Xia Yang	PhD	Civil & Environmental Engineering	xiayang@usf.edu
Bisheng Gao	MS	Civil & Environmental Engineering	bisheng@usf.edu
Lillian Mulligan	MS	Civil & Environmental Engineering	lillianm@usf.edu
Xufeng Wei	MS	Civil & Environmental Engineering	xufengw@usf.edu
Erica Dasi	PhD	Civil & Environmental Engineering	eadasi@usf.edu
Magdalena Shafee	BS	Civil & Environmental Engineering	mps1@usf.edu

2. List research presentations resulting from (or about) this Hinkley Center Project.

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

An abstract was submitted to the American Ecological Engineering Society Annual Meeting in Quarter 2; however, the conference was cancelled due to the COVID-19 pandemic. We plan to submit an abstract for the 2021 conference.

The following Manuscript is in preparation: Gao, B. Yang, X., Arias, M. Ergas, S.J. (in preparation) Enhanced nitrogen, organic matter and color removal from landfill leachate in a sequencing batch biofilm reactor (SBBR) with biochar and zeolite addition, *J. Chemical Technology & Biotechnology*.

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

Nothing to report yet.

4. How have the research results from this Hinkley Center project been leveraged to secure additional research funding? What additional sources of funding are you seeking or have you sought?

USF departments of Integrative Biology, Geoscience, and Civil & Environmental Engineering recently received a funding from the NSF for an S-STEM scholarship grant. The grant will fund MS students who are interested in the broad topic of “managing the nitrogen cycle.” Lillian

Mulligan is partially supported through this scholarship program. We have recruited an additional S-STEM scholar who will be joining this project in Fall 2020, Thanh (Misty) Lam.

Erica Dasi, a doctoral student in the Department of Civil & Environmental Engineering, is the lead student working on post treatment of landfill leachate using spalerite and oyster shells. Ms. Dasi is supported by a Florida Education Fund (FEF), McKnight Doctoral Fellowship.

We have had a preliminary discussion with EREF program director, Stephanie Bolyard, about applying for funding from EREF. The topic of landfill leachate treatment is not part of the current rfp; however, we were encouraged to submit in the fall.

The following grant was funded: Equipment to produce biochar from waste materials for environmental applications, USF Strategic Investment Pool, PIs: S.J. Ergas, M. Arias, J. Cunningham, M. Nachabe, J. Kuhn, K. Ghebremichael, R. Gonzalez, B. Joseph, \$10,000, 4/20-6/21.

Xia Yang applied for a 2020 EREF Scholarship.

5. What new collaborations were initiated based on this Hinkley Center project?

No new collaborations to report.

6. How have the results from this Hinkley Center funded project been used (not will be used) by the FDEP or other stakeholder?

Nothing to report yet.

### **References:**

Huang, X. F., Ling, J., Xu, J. C., Feng, Y., & Li, G. M. (2011). Advanced treatment of wastewater from an iron and steel enterprise by a constructed wetland/ultrafiltration/reverse osmosis process. *Desalination*, 269(1-3), 41-49.