Landfill Leachate Pretreatment Prior to Discharge to Sewer: Metal Recovery and Nitrogen Removal (Final Report)

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Youneng Tang, Principal Investigator
FAMU-FSU College of Engineering
Department of Civil and Environmental Engineering

Gang Chen, Co-Principal Investigator
FAMU-FSU College of Engineering
Department of Civil and Environmental Engineering

Liang Li, Post-Doctoral Research Associate
FAMU-FSU College of Engineering
Department of Civil and Environmental Engineering

Hinkley Center for Solid and Hazardous Waste Management
University of Florida
P. O. Box 116016
Gainesville, FL 32611
www.hinkleycenter.org

Report #

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PRINCIPAL INVESTIGATOR: Youneng Tang, Ph.D., Assistant Professor
Department of Civil and Environmental Engineering, FAMU-FSU College of Engineering
2525 Pottsdamer Street Suite A130 Tallahassee FL 32310; Tel: 850-4106119; Fax: 850-4106142
ytang@eng.famu.fsu.edu

CO-PRINCIPAL INVESTIGATOR: Gang Chen, Ph.D., P.E., Professor
Department of Civil and Environmental Engineering, FAMU-FSU College of Engineering
2525 Pottsdamer Street Suite A140 Tallahassee FL 32310; Tel: 850-4106303; Fax: 850-4106142
gchen@eng.famu.fsu.edu

PROJECT WEBSITE: https://ww2.eng.famu.fsu.edu/~ytang/project7.html

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ABSTRACT:

Most landfills in Florida discharge leachate to municipal wastewater treatment plants (WWTPs). Only 25% of the landfills pretreat the leachate before discharging it to WWTPs. WWTPs' managers are becoming reluctant to accept non-pretreated landfill leachate since leachate is usually rich in heavy metals, which are toxic to the activated sludge, and nitrogen, which may cause discharge violation according to the Numeric Nutrient Criteria of Florida. The most commonly used leachate pretreatment method (wetland) is not efficient in heavy metal removal. The objective of this study was to evaluate a potentially easy-to-implement, inexpensive, and sustainable onsite leachate pretreatment method for removing and recovering metals and making nitrogen easier to be removed in WWTPs. This method used a submerged anaerobic biological reactor to pretreat the leachate. We sampled and characterized four landfill leachates in Florida and chose one municipal solid waste (MSW) landfill leachate that had the highest concentrations of heavy metals (*i.e.*, 290 mg total Fe/L, 0.299 mg total Ni/L, and 1.98 mg total Pb/L) and total nitrogen (TN) (*i.e.*, 2870 mg N/L). The concentration of the above-mentioned three heavy metals were higher than the discharge to sewer limits set by cities in Florida (*i.e.*, Local limits for City of Tallahassee wastewater facility and wastewater discharge standard of City of Taramac and Miami-Dade County); therefore, they were the focus of the metal research in this project. At a hydraulic retention time (HRT) of 4.5 days, 90% of total iron, 13% of total nickel, and 3% of total lead were removed at steady state (Stage 1). To increase the heavy metal removal, we added sulfate (120 mg S/L) to the leachate and found that the heavy metal removal increased to 95% for total iron, 24% for total nickel, and 10% for total lead at steady state (Stage 2). At Stage 2, the iron and nickel in the reactor effluent met the local discharge to sewer standards, while the lead still violated the standards. The incomplete heavy metal removal was probably caused by metal complexation with bisulfide. While the amorphous iron sulfide was the major metal sulfide precipitated in the reactor, other metal sulfides such as millerite (NiS), galena (PbS), covellite (CuS), and sphalerite (ZnS) might also precipitate at very low percentages. We will separate and recover metal sulfides from the precipitate using magnetic separators at a lab housing two magnetic separators in March 2019. The majority (~98%) of the recalcitrant dissolved organic nitrogen (rDON = ~210 mg N/L) was converted to ammonium or bioavailable dissolved organic nitrogen (bDON) through reactions in the reactor, which should increase the TN removal at WWTPs. The submerged anaerobic biological reactor is an alternative to pretreatment of landfill leachate having high concentrations of metals and rDON.

Key Words: Landfill leachate, Heavy metals, Metal sulfides, Magnetic Separation, Bioavailable dissolved organic nitrogen, Recalcitrant dissolved organic nitrogen

METRICS REPORTING

Student Researchers:

Last name, first name	Email	Anticipated degree	Department
Li, Runwei	rl16h@my.fsu.edu	Ph.D.	Civil and Environmental Engineering
Lambert, Mirdens	mrl16f@my.fsu.edu	B.S.	Environmental Science
Ogden, Amanda	aco15b@my.fsu.edu	B.S.	Chemistry
Grant, Adrian	adriandk615@gmail.com	High school diploma	
Acosta, Jerimiah	jburgess70819@gmail.com	High school diploma	

Metrics:

1. List research publications resulting from THIS Hinkley Center project.
    - Li, R. et al. Fate of heavy metals in anaerobic treatment of landfill leachate, in preparation.

    - Li, L. et al. Carbon and nitrogen speciation in a landfill leachate pre-treated by a submerged anaerobic bioreactor, in preparation.

2. List research presentations resulting from THIS Hinkledy Center project.
    - Tang, Y. Landfill leachate disposal. Chipola Civic Club, Marianna, FL, Sept. 2017.

    - Lambert, M.R.; Ogden, A.; Tang, Y.; Chen, G.; Li, R.; Li, L. Landfill leachate: metal recovery and nitrogen removal. Florida State University Undergraduate Research Symposium, Tallahassee, FL, Mar. 2018.

    - Ogden, A.C.; Tang, Y.; Li, R.; Li, L.; Lambert, M. Landfill leachate pretreatment: metal recovery. Florida State University Undergraduate Research Symposium, Tallahassee, FL, Mar. 2018.

    - Grant, A.; Acosta, J. Removal of organics from landfill leachate using anaerobic filter. Program of Excellence in STEM, Florida A&M University, Tallahassee, FL, Jun. 2018.

    - Tang, Y. Landfill leachate management: state of practice and new challenges. Florida Water Environment Association Big Bend Annual Seminar 2018, Tallahassee, FL, Dec. 2018.

3. List who has referenced or cited your publications from this project.
    None (Papers have not been published).

4. How have the research results from THIS Hinkly Center project been leveraged to secure additional research funding? What grant applications have you submitted or are planning on submitting?
   - The PI and his collaborators have submitted three proposals to the US Environmental Protection Agency and the Environmental Research & Education Foundation to conduct research on landfill leachate treatment. The proposals are being evaluated.

5. What new collaborations were initiated based on THIS Hinkley Center project?
   - The PI collaborated with Geosyntec and submitted their first proposal to the Environmental Research & Education Foundation to investigate emerging contaminants in landfill leachate.

   - The PI initiated collaboration with Professor Bruce Locke in the Department of Chemical and Biomedical Engineering at the FAMU-FSU College of Engineering and submitted a proposal to the US Environmental Protection Agency to study emerging contaminant removal from landfill leachate.

   - The PI initiated collaboration with Dr. Huan Chen and Dr. Amy McKenna, Research Faculty at the National High Magnetic Field Laboratory (*i.e.*, MagLab). They are using Fourier transform ion cyclotron resonance - mass spectrometer at the MagLab to determine the organic nitrogen and carbon speciation in landfill leachate.

6. How have the results from THIS Hinkley Center funded project been used (not will be used) by the FDEP or other stakeholders?
   - Four technical awareness group (TAG) members were FDEP employees. They are spreading the word about a landfill leachate pretreatment alternative – treatment by submerged anaerobic bioreactors.

ACKNOWLEDGEMENTS

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Student assistants:
Runwei Li, graduate assistant
Email: rl16h@my.fsu.edu
University: Florida State University
Department: Civil and Environmental Engineering
Bio: Runwei expects to obtain a Ph.D. degree in Civil Engineering in 2020.

Mirdens Lambert, undergraduate assistant
Email: mrl16f@my.fsu.edu
University: Florida State University
Bio: Mirdens expects to obtain a Bachelor’s degree in Environmental Science.

Amanda Ogden, undergraduate assistant
Email: aco15b@my.fsu.edu
University: Florida State University
Bio: Amanda expects to obtain a Bachelor’s degree in Chemistry.

Adrian Grant, high school student assistant
Email: adriandk615@gmail.com
Program: Program of Excellence in STEM (summer camp) at Florida A&M University
Bio: Adrian expects to obtain a high school diploma and continue to study in Civil Engineering.

Jerimiah Acosta, high school student assistant
Email: jburgess70819@gmail.com
Program: Program of Excellence in STEM (summer camp) at Florida A&M University
Bio: Jerimiah expects to obtain a high school diploma and continue to study science related to musical instruments.

Technical Advisory Group (TAG)

Name & title	Affiliation	Contact information
Edward A. Bettinger, R.S., M.S., Environmental Health Program Consultant	Florida Division of Environmental Public Health	ed_bettinger@doh.state.fl.us
Dean Chaaban, CPM, Supervisor of AP, IP, and CCC Programs	City of Tallahassee (COT)	dean.chaaban@talgov.com
Ashvini Chauhan, Ph.D., Associate Professor	Florida A&M University	ashvini.chauhan@famu.edu
Joseph B. Cheatham, P.E., Wastewater Operations Manager	COT	Joe.Cheatham@talgov.com
Lauren Walker-Coleman, P.E., Project Manager	FDEP	Lauren.Coleman@dep.state.fl.us
Joseph Dertien, P.E., P.E. Professional Engineer II	FDEP	joseph.dertien@dep.state.fl.us
Owete S. Owete, Ph.D., P.E., Professional Engineer III	FDEP	owete.owete@dep.state.fl.us
Shanin Speas-Frost, P.E., MBA, Program Administrator	FDEP	Shanin.SpeasFrost@dep.state.fl.us
Robert J. Wandell, Ph.D., Chief Operating Officer	Advanced Fertilizer Systems	rjw05c@my.fsu.edu
Chao Zhou, P.E., M.S., Senior Staff Engineer	Geosyntec Consultants	CZhou@Geosyntec.com

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS AND ACRONYMS

bDON	bioavailable dissolved organic nitrogen
BOD	Biochemical oxygen demand
$CaCO_3$	Calcium carbonate
CH_4	Methane
CO_3^{2-}	Carbonate
COD	Chemical oxygen demand
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen
DWTP	Drinking water treatment plant
EDX	Energy dispersive X-ray
FA	Fulvic acid
FDEP	Florida department of environmental protection
FeS	Iron sulfide
GC	Gas chromatography
H_2CO_3	Carbonic acid
HA	Humic acid
HS	Humic substances
HCO_3^-	Bicarbonate
HGMS	High gradient magnetic separator
hr	Hour
HRT	Hydraulic retention time
$MgCO_3$	Magnesium carbonate
MGD	Million gallons per day
MS	Metal sulfide
MSW	Municipal solid waste
NPDES	National pollutant discharge elimination system
rDON	recalcitrant dissolved organic nitrogen
SBRs	Sequencing batch reactors
SEM	Scanning electron microscope
SHM	Stockholm humic model
SSA	Specific surface area
SO_4^{2-}	Sulfate
S^{2-}	Sulfide
T	Tesla
TN	Total nitrogen
TOC	Total organic carbon
TSA	Total surface area
VLR	Volumetric loading rate
WWTPs	Wastewater treatment plants

EXECUTIVE SUMMARY

Introduction

In Florida, about 90% of landfills send leachate to wastewater treatment plants (WWTPs), and only 25% of these landfills pre-treat the leachate. Sending leachate to WWTPs without pretreatment has been preferred for its easy maintenance and low operating costs. However, WWTPs' managers are becoming reluctant to accept non-pretreated leachate since it significantly affects the WWTPs' performance partially due to the high concentrations of heavy metals and nitrogen. Thus, the need for leachate pretreatment is increasing.

Among the 25% landfills in Florida that pretreat leachate prior to discharge to WWTPs, 17% use aerated storage tanks or ponds, and 8% use sequencing batch reactors (SBRs). Aerated storage tanks or ponds are not efficient in heavy metal removal and the SBRs require significant operational and management efforts in order to remove heavy metals and nitrogen. Anaerobic pretreatment of landfill leachate has attracted attention due to its potential to remove metals and promote nitrogen removal while reducing chemical oxygen demand (COD) up to 90% and producing biogas. We proposed to use a submerged anaerobic biological reactor for landfill leachate pretreatment and focused on heavy metals and nitrogen removal.

Specific research questions that we investigated include: 1) How much heavy metal can be precipitated in the submerged anaerobic biological reactor? 2) In what forms do metal sulfides exist in the reactor? 3) Is it possible to separate and recover metal sulfides using magnetic separators? 4) How much recalcitrant nitrogen can be converted to bioavailable nitrogen in a submerged anaerobic biological reactor? To answer these questions, the following six tasks were proposed:

- Task 1: Reactor (*i.e.*, submerged anaerobic biological reactor) design;
- Task 2: Leachate characterization;
- Task 3: Reactor (*i.e.*, submerged anaerobic biological reactor) operation and loading optimization;
- Task 4: Dissolved metal speciation modeling;
- Task 5: Nitrogen fate analysis;
- Task 6: Metal sulfides recovery via magnetic separators.

Methods

We sampled and characterized four landfill leachates in Florida. We measured metal species, nitrogen species, and other parameters including pH, conductivity, COD, dissolved organic carbon (DOC), total organic carbon (TOC) in the four leachates and then chose the leachate with the highest heavy metals and nitrogen concentrations for further study. The chosen leachate was injected into the bottom of a submerged anaerobic biological reactor through a syringe infusion pump (Cole-Parmer). The reactor, a plastic column with an inner diameter of 4 cm and a height of 7.2 cm, contained plastic media for biomass attachment, and was operated at a volumetric loading rate (VLR) of 2 kg COD/m^3-day and a HRT of 4.5 days. We characterized both the reactor influent and effluent samples once per week until steady state at which the performance indicators (*i.e.*, COD, TOC, DOC, ammonium, acetate, and CH_4) in the reactor effluent did not change significantly for at least three weeks.

The heavy metals we studied include iron, nickel, and lead; their concentrations in the leachate were above the discharge to sewer standards at some cities in Florida. We measured/calculated total heavy metal, total dissolved heavy metal, particulate heavy metal, and sulfate in the reactor influent and effluent once per week. To further understand the fate of heavy metals in the reactor, we also measured/calculated free metal ions and complexes of the three chosen heavy metals (*i.e.*, Fe^{2+}, Fe^{3+}, Fe complex), sulfide, and redox potential when the reactor reached steady states. There were two stages in the study of heavy metal removal. In Stage 1, we used raw landfill leachate as the reactor influent. In Stage 2, we added sulfate (120 mg S/L) in the reactor influent to promote heavy metal removal. We also evaluated the composition and crystal structures of the precipitates in the reactor at the steady state of Stage 1 using scanning electron microscope - energy-dispersive X-ray (SEM-EDX) and Raman spectroscopy.

We were not able to experimentally measure the heavy metals that complexed with humic acid (HA) versus fulvic acid (FA). Therefore, we simulated the dissolved metal speciation in the influent and effluent using VISUAL MINTEQ, software for equilibrium speciation modelling. The model input included the concentrations of total dissolved metals: Fe, Ni, Pb, Zn, Cu, Ca, Mg, Na, and K, total ammonium (*i.e.*, NH_4^+ and NH_3 (aq)), total acetate (*i.e.*, CH_3COO^- and CH_3COOH (aq)), total DIC (*i.e.* CO_3^{2-}, HCO_3^-, and H_2CO_3 (aq)), and total sulfide (*i.e.* S^{2-}, HS^-, and H_2S (aq)). It also included major anions (*i.e.*, Cl^- and SO_4^{2-}), HA, FA, pH, and redox potential. We simulated the influent and effluent at steady state of Stage 1 and Stage 2.

Similarly, we measured nitrogen species including total nitrogen, total dissolved nitrogen, ammonium nitrogen, nitrate nitrogen, and nitrite nitrogen once per week. To further evaluate the conversion of nitrogen species, we measured recalcitrant dissolved organic nitrogen (rDON) and bioavailable dissolved organic nitrogen (bDON) at weeks that represented significant changes in reactor performance (*i.e.*, Weeks 5, 10, 20, and 24).

To understand the effects of organic matter removal on the heavy metal removal and nitrogen conversion, we conducted the carbon mass balance analysis at the weeks that represented significant changes in the reactor. To determine the composition of the raw leachate, we first measured the TOC and DOC and found that their difference was negligible, meaning that the particulate organic carbon could be ignored. Therefore, we focused on the DOC and measured its fractions including HA, FA, acetate, and non-humic substances other than acetate. To find what the influent DOC was converted to after treatment, we measured or estimated 1) DOC in the effluent, including HA, FA, acetate, non-humic substances other than acetate, 2) total dissolved inorganic carbon (DIC) increase in the effluent compared to the influent, including CO_3^{2-}, HCO_3^-, and H_2CO_3 (aq), 3) Inorganic carbon that precipitated in the reactor including $CaCO_3$ and $MgCO_3$, 4) inorganic carbon that went to the headspace of the syringe collecting the effluent, including CO_2 and CH_4, and 5) carbon that was used for biomass synthesis. We anticipated that the total of the five groups of carbon species would equal to the DOC in the influent based on carbon mass balance.

We used a lab-scale cryo-high gradient magnetic separator (cryo-HGMS) at PhySep Components and Service, Inc. to separate and recover metal sulfides produced in the reactor.

Results and Discussion

Among the four studied landfill leachates, the first municipal solid waste (MSW) landfill leachate (MSW-1) had the highest concentrations of heavy metals (*i.e.*, total Fe = 290 mg Fe/L, total Ni = 0.299 mg Ni/L, and total Pb = 1.98 mg Pb/L) and nitrogen (TN = 2870 mg N/L), and was therefore chosen to be further studied. This leachate also contained a very high concentration of organic matter (COD = 22800 mg/L, TOC = 7980 mg C/L, DOC = 7880 mg C/L). The concentrations of above-mentioned three heavy metals in the leachate exceeded the discharge to sewer limits in some cities in Florida. Iron, nickel, and lead violated the Tamarac wastewater discharge standard. The lead also exceeded the Miami sanitary sewer discharge limitations and local limits for the City of Tallahassee wastewater facility. Therefore, iron, nickel, and lead were the focus of the metal research. The majority of the iron, nickel, and lead existed in the form of metal complexes in this leachate (*i.e.,* Fe complexes = 257 mg Fe/L, Ni complexed = 0.274 mg Ni/L, and Pb complexes = 1.89 mg Pb/L). The TN in the leachate could contribute to 38.7% of the TN in a WWTP assuming a mixing ratio of leachate to municipal wastewater of 1:99 (volume ratio) and a typical TN concentration of 45.95 mg N/L in the wastewater. The dominant nitrogen species in this leachate were ammonium (1978 mg N/L) and dissolved organic nitrogen (DON, 850 mg N/L). bDON and rDON in the MSW-1 leachate were 62% and 38%, respectively. The DOC in the leachate was ~7880 mg C/L, which comprised of acetate-C (23%), HA-C (18%), FA-C (32%) and, the other carbon (27%). The high DOC, acetate, and nitrogen concentrations were expected since the MSW-1 leachate was a very young landfill leachate.

We designed a submerged anaerobic biological reactor to pretreat the chosen landfill leachate. After 25 weeks pretreatment at a HRT of 4.5 days, the reactor reached steady state for Stage 1. The COD and DOC removal efficiency reached 54.6% and 52.8%, respectively, at steady state. The CH_4 proportion reached 85% of the produced biogas collected by a syringe, suggesting a very high quality biogas that could be reused. Dividing the CH_4 mass in the biogas by the effluent volume, we obtained an assumed CH_4 concentration of 1606 mg C/L, meaning that 20.4% (= 1606/7880) of the DOC in the influent was converted to methane.

The conversion of organic carbon was investigated in this study. At steady state for Stage 1, the major reactions in the reactor were the conversion of acetate (decreased from 2.20×10^3 mg C/L in the influent to 79 mg C/L in the effluent), non-humic substances other than acetate (decreased from 955 mg C/L in the influent to 227 mg C/L in the effluent), and FA (decreased from 3.10×10^3 mg C/L in the influent to 1.81×10^3 mg C/L in the effluent) to CH_4 (increased from 0 mg C/L in the influent to 1.61×10^3 mg C/L in the effluent), total DIC (increased by 1.37×10^3 mg C/L), CO_2 (increased from 0 mg C/L in the influent to 246 mg C/L in the effluent), and biomass (increased by 186 mg C/L). At steady state, 90% of the non-humic carbon was converted to other forms of carbon.

At steady state of Stage 1, 90% of the total iron, 13% of total nickel, and 3% of total lead was removed. These metals in the effluent did not meet the discharge to sewer standards at cities in Florida. To further improve the removal of heavy metals, particularly nickel and lead, we added sulfate (120 mg S/L) to the reactor influent (Stage 2). When reaching the steady state of Stage 2, the removal of the three heavy metals slightly increased: 95% of total iron, 24% of total nickel, and 10% of total lead. Iron and nickel in the reactor effluent met the local discharge to sewer standards described above, while lead still violated the Tamarac standard. Further analysis based on precipitation kinetics suggested that the incomplete heavy metal removal was potentially caused by the complexation of metals with bisulfide.

The solid analysis by SEM-EDX and Raman suggested that amorphous FeS was the dominant metal sulfides in the reactor. Other metal sulfides such as millerite (NiS), galena (PbS), covellite (CuS), and sphalerite (ZnS) might also exist at very low percentages. Dissolved metal speciation modeling results for Stage 1 suggested that the heavy metal removal was due to 1) the conversion of 41.7% FA to products like acetate and CH_4, which released some Fe (III) from the Fe complexes as free Fe (III), 2) the highly reducing environment in the reactor, which reduced Fe (III) to Fe (II), and 3) the complete reduction of sulfate (119 mg S/L) to sulfide, which precipitated the Fe (II). Precipitate in the reactor was collected and separated by a cryo-high gradient magnetic separator (cryo-HGMS). The composition of the separated metals was then determined by SEM-EDX. The majority of the separated metals were iron; this was consistent with the fact that iron was the major metal removed in the reactor.

Nitrogen fate analysis suggested that after the anaerobic pretreatment, the majority of the rDON (~210 mg N/L) was converted to bDON and ammonium. More than 90% of the rDON was removed since Week 10 and 98% of the rDON in the leachate was removed when reaching the steady state for Stage 1. The ammonium concentration in the reactor effluent was always higher than that in the influent, suggesting the degradation of nitrogen containing compounds (*i.e.*, proteins, urea, and nucleic acid) through processes such as hydrolysis, acidogenesis, and acetogenesis. The bDON decreased from 189 mg N/L in the influent to 132 mg N/L in the effluent, suggesting that some bDON was converted to ammonium too.

Conclusions

The submerged anaerobic biological reactor successfully removed most heavy metals in the leachate. Iron and nickel violated discharge to sewer standards at some cities in Florida, and were removed to meet the standards by the reactor. Amorphous FeS was the major metal sulfide in the precipitate, but other metal sulfides such as millerite (NiS), galena (PbS), covellite (CuS), and sphalerite (ZnS) might also exist at very low percentages. The metals could be separated from the precipitate by a cryo-HGMS for recovery. The reactor also efficiently converted the majority of rDON (~98%) to ammonium and bDON, which would be removed in a tertiary wastewater treatment plant. The submerged anaerobic biological reactor is a promising alternative method for pretreatment of landfill leachate with high concentrations of metals and rDON.

1. INTRODUCTION

In Florida, about 90% of landfills send leachate to WWTPs, and only 25% of these landfills pretreat the leachate (Reinhart, 2016). Sending leachate to WWTPs without pretreatment has been preferred for its easy maintenance and low operating costs (Ahn et al., 2002; Renou et al., 2008; Omar et al., 2015). WWTPs managers are becoming reluctant to accept non-pretreated leachate since it significantly affects the WWTPs' performance partially due to the high concentrations of heavy metals and nitrogen. Typical concentrations of heavy metals in MSW and landfill leachate are summarized in Table 1. Heavy metals are toxic to microbes in the activated sludge in the WWTPs (Welander et al., 1998; Marttinen et al., 2002, 2003; Çeçen and Aktaş, 2004; Renou et al., 2008). Most heavy metals in the wastewater accumulate into the sludge (*i.e.*, biosolids), which are commonly disposed of at landfills. This cycle ends up with an accumulation of heavy metals in the landfill leachate. One way to break this cycle is to remove and recover heavy metals from one link of the cycle. Many discharge to sewer limits set by cities in Florida regulate the metal concentrations. For example, local limit for City of Tallahassee Wastewater Facility regulates the metals accepted by the facility, including silver, arsenic, cadmium, chromium, copper, mercury, molybdenum, nickel, lead, selenium, and zinc.

High concentration of nitrogen in the leachate is also a concern. A typical TN concentration in the landfill leachate is around 1,000 mg N/L, and the highest reported concentration is 13,000 mg N/L (Bodzek et al., 2006; Renou et al., 2008; Reinhart, 2016). In Florida, landfill leachate contributes approximately 1% (by volume) of wastewater and approximately 22% of TN discharged to WWTPs daily (Ábrego-Góngora, 2003; Reinhart, 2016). This may cause a WWTP to violate the discharge standards according to the Numeric Nutrient Criteria of Florida (Chapter 62-650, Florida Administrative Code (F.A.C.); Chapter 62-302, F.A.C.).

Among the 25% landfills in Florida that pretreat leachate prior to discharge to WWTPs, 17% use aerated storage tanks or ponds, and 8% use SBRs (Reinhart, 2016; Tchobanoglous et al., 2003). Aerated storage tanks or ponds are not efficient in heavy metal removal and the SBRs require significant operational and management efforts in order to remove heavy metals and nitrogen. Anaerobic pretreatment of landfill leachate has attracted attention due to its potential to remove metals and promote nitrogen removal while removing COD up to 90% and producing biogas (Abbas et al., 2009; Bracmort, 2010; Gourdon, 1989).

We proposed to use a submerged anaerobic biological reactor for landfill leachate pretreatment and focused on heavy metal and nitrogen removal. Compared to common aerobic pretreatment methods, anaerobic biological reactor takes advantages of high organics removal efficiency, no need of chemical addition and odors control, and low requirement for operation and management effort (Henry et al., 1987; Wang et al., 2007). The effectiveness of anaerobic leachate treatment using submerged anaerobic biological reactors has been demonstrated (Henry et al., 1987; Matarán et al., 2002; Wiszniowski et al., 2006; Abbas et al., 2009; Wang and Banks, 2007; Kelly, 2011; Ghosh and Hasan, 2013). These previous studies focus on the removal of COD and biochemical oxygen demand (BOD), with COD removal reaching up to 90%. However, anaerobic reactors have not been used to pretreat landfill leachate in Florida. Also, the anaerobic reactors have been rarely studied in the context of metal recovery and nitrogen removal from leachate. A metal in a typical landfill could reach thousands of kilograms (Aucott, 2006), suggesting potential of recovery.

Table 1. Metals in municipal solid waste (MSW) and landfill leachate.

Metals	Typical MSW concentration (mg/kg)	Typical landfill leachate concentration (mg/L)
Cadmium	20	0.3
Chromium	350	0.2
Copper	77	0.3
Iron	20,000	500
Lead	400	0.2
Mercury	1.5	0.01
Nickel	57	0.3
Zink	380	4

References: James, 1977; Esakku et al., 2003, 2005; Aucott, 2006; Townsend et al., 2015.

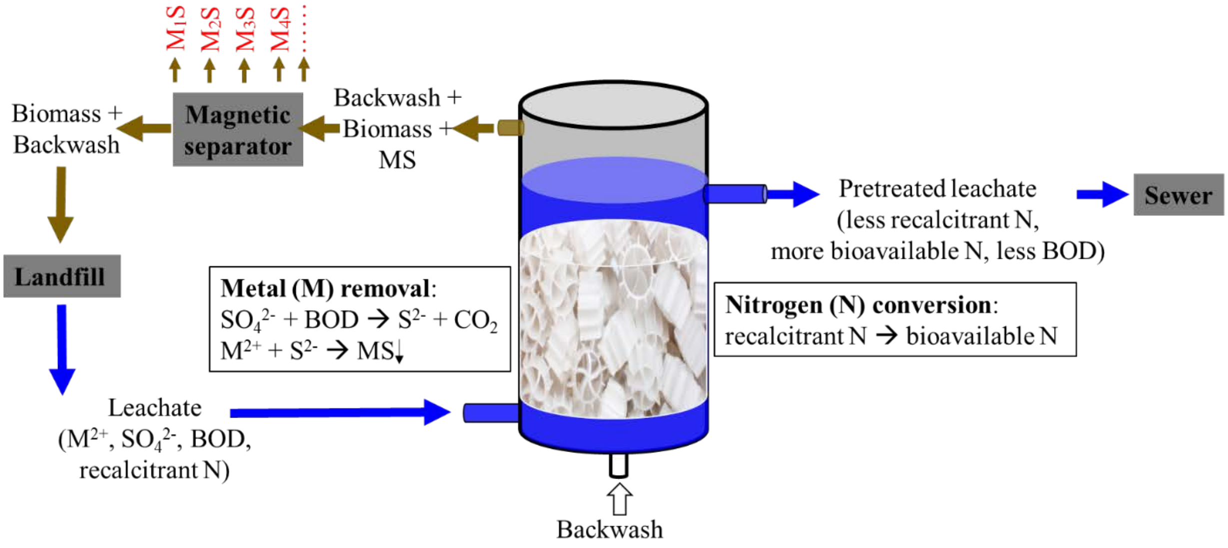


Figure 1. Flowsheet of the proposed approach.
MS: metal sulfide; BOD: biochemical oxygen demand.

The flowsheet for the proposed approach is illustrated in Figure 1. A submerged anaerobic biological reactor is used to pretreat the leachate prior to its discharge to a WWTP. Two processes occur in the anaerobic biological reactor (Rittmann and McCarty, 2001). First, large organic molecules are converted to smaller organic molecules, carbon dioxide (CO_2), and methane (CH_4) through hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Second, sulfate is reduced to hydrogen sulfide (H_2S) through a microbially mediated redox reaction. The first process releases heavy metal ions that bind to large organic molecules (*i.e.*, metal-organic complexes) (Baun and Christensen, 2004). The released free metal ions then precipitate with sulfide produced in the second process. Since metal sulfides differ in magnetic properties (Table 2), they can be potentially separated and recovered using magnetic separators after they are removed from the reactor through backwash. On the other hand, breakdown of the large organic molecules in the reactor makes nitrogen more soluble and bioavailable. Therefore, more nitrogen can be removed when the leachate reaches a WWTP. This pretreatment method requires only one treatment unit that is easy to operate and is not energy intensive. It does not require chemical addition or produce odors since the anaerobic reactor is a closed system.

Table 2. Magnetic properties of some metal sulfides.

Compounds	**Magnetic property**	**Magnetic susceptibility at 25°C ($\times 10^{-6}$ cm^3/mole)**
Fe_7S_8	Ferromagnetic	125,000
FeS	Antiferromagnetic	5,187
CoS_2	Ferromagnetic	4,000
NiS_2	Paramagnetic	700
CuS_2	Pauli paramagnetic	40
$CuFeS_2$	Antiferromagnetic	32
FeS_2	Diamagnetic	10

Reference: Pearce et al. (2006)

Specific research questions that we investigated include:

1) How much heavy metal can be precipitated in the submerged anaerobic biological reactor?
2) In what forms do metal sulfides exist in the reactor?
3) Is it possible to separate and recover metal sulfides using magnetic separators?
4) How much recalcitrant nitrogen can be converted to bioavailable nitrogen in an anaerobic biological reactor?

To answer these questions, the following six tasks were proposed:

- Task 1: Reactor (*i.e.*, submerged anaerobic biological reactor) design;
- Task 2: Leachate characterization;
- Task 3: Reactor (*i.e.*, submerged anaerobic biological reactor) operation and loading optimization;
- Task 4: Dissolved metal speciation modeling;
- Task 5: Nitrogen fate analysis;
- Task 6: Metal sulfides recovery via magnetic separators.

2. METHODS

Methods are organized following the tasks: Methods for leachate characterization and selection are described to complete Task 2, methods for reactor design, operation, and analysis are described to complete Tasks 1, 3, and 5, methods for dissolved metal speciation modeling is described to complete Task 4, and methods for metal sulfides separation and recovery are described to complete Task 6.

2.1 Leachate characterization and selection (Task 2)

We collected four leachate samples from four landfills in Florida, respectively. Three of them were MSW landfills and one was a MSW incineration ash monofill. The leachate sample abbreviations are summarized in Table 3. Metal species, nitrogen species, and other parameters including pH, conductivity, COD, and DOC were evaluated for these four leachates. The measurement methods are described in the sections below. The leachate with the highest heavy metals and nitrogen concentrations was chosen to be further tested in the lab-scale leachate treatment reactor.

Table 3. Leachate source.

Leachate	Type of landfill
MSW-1	Municipal solid waste
MSW-2	Municipal solid waste
MSW-3	Municipal solid waste
Monofill-4	Municipal solid waste incineration ash monofill

2.2 Reactor design, operation, and analysis (Tasks 1, 3, and 5)

2.2.1 Reactor design and operation

The reactor setup is depicted in Figure 2. The reactor volumetric loading rate (VLR = 2 kg COD/m^3-d) and hydraulic retention time (HRT = 4.5 days) were the design criteria of the submerged anaerobic biological reactor in our study. The reactor influent was one landfill leachate, which was chosen after the characterization of the four landfill leachates collected in Florida. We characterized both the influent and effluent samples once per week until steady state at which the reactor performance indicators (*i.e.*, COD, DOC, ammonium, acetate, and CH_4) in the reactor effluent did not change significantly for at least three weeks (*i.e.*, Stage 1). To further remove the heavy metals in the leachate, we externally added sulfate (120 mg SO_4^{2-}-S/L, the same as the sulfate concentration in the leachate) to the leachate (*i.e.*, Stage 2).

2.2.2 Measurement of heavy metals

Metal speciation is depicted in Figure 3. We measured the three representative heavy metals (*i.e.*, iron, nickel, and lead) in both the influent and effluent every week. We also measured the concentration of other heavy metals including copper and zinc at steady state and during the four leachate characterization. The heavy metal measurement methods are summarized in Table 4. Total heavy metal, total dissolved heavy metal, and heavy metal in solids were measured/calculated once per week until steady state. Free heavy metal ions and heavy metal complexes were measured only at the steady state. We also evaluated the composition of the precipitates in the reactor and the crystal structures of the precipitates at the steady state of Stage 1. The precipitate was sampled from the bottom of the reactor and diluted with degassed deionized water in a closed syringe to avoid exposure to air. The diluted sample was filtered by nuclepore track etched membranes (Whatman, USA) (Zhang et al., 2018). Then, the retentate on the membrane was vacuum dried at room temperature (Bazzaoui et al., 2005; Donald and Southam, 1999). The pre-treated sample was characterized by SEM (FEI Nova 400 Nano SEM, FEI) with EDX and Raman spectroscopy (Renishaw).

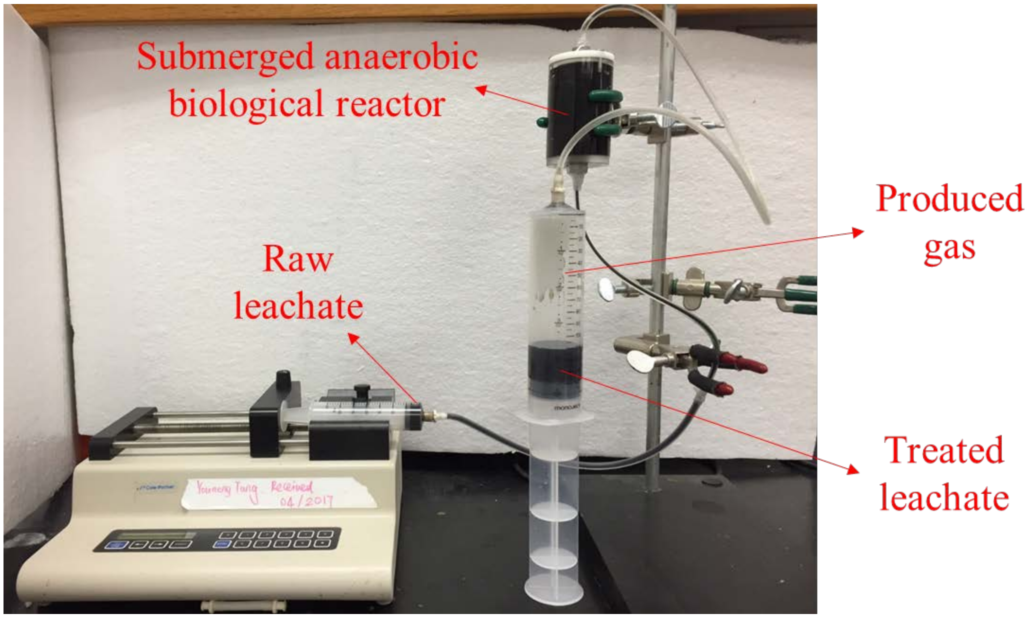


Figure 2. Submerged anaerobic biological reactor.

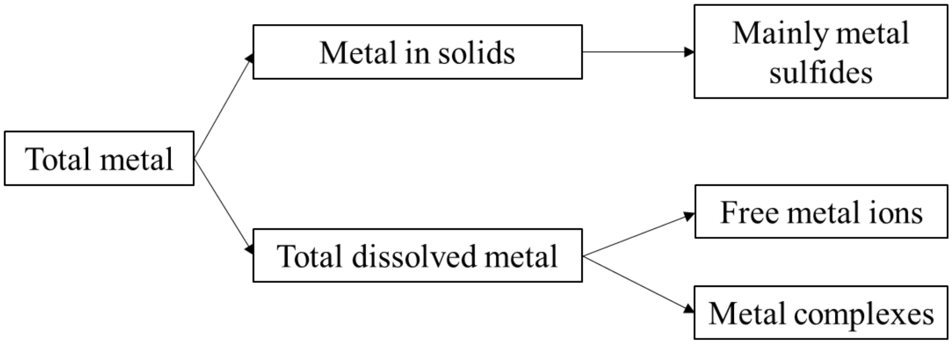


Figure 3. Metal speciation.

(Adapted from Florence and Batley (1980), Christensen and Lun (1989), Holm et al. (1995), and Papini et al., (2001)).

Table 4. Methods for metal speciation.

Parameters to measure	Methods	Equipment	References
Total metal	EPA method 3050B	MP-AES[1]	U.S. EPA, 1996
Total dissolved metal	EPA method 3050B (based on filtered samples)	MP-AES	U.S. EPA, 1996
Metal in solids	Total metal – total dissolved metal		
Free metal ion	Ion exchange resin method (based on filtered samples)		Baun and Christensen, 2004
Metal complexes	Total dissolved metal – free metal ion		
Composition of the precipitates	Energy dispersive X-ray analysis (EDX)	SEM[2]	Baun and Christensen, 2004
Crystal structures of the precipitates	Raman spectrometry	RAMAN[3]	Baun and Christensen, 2004

Notes:

1. MP-AES: Agilent Technologies 4100 Microwave Plasma-Atomic Emission System;
2. SEM: Zeiss 1540 XB Crossbeam Scanning Electron Microscopy;
3. RAMAN: Renishaw Micro-Raman Spectroscopy System.

2.2.3 Measurement of nitrogen species

Nitrogen speciation is depicted in Figure 4 and the detailed measurement methods are summarized in Table 5. All nitrogen species were measured once per week except for bDON and rDON, which were measured in weeks that represented significant changes in the reactor. bDON was measured as the change of DON in the sample before and after a 28-day incubation period (Simsek et al., 2013). Briefly, the bDON test was performed in a 50 mL centrifuge tube under artificial light (with 12 hr light and 12 hr dark). 10 mL of samples was seeded with 2 mL of pure culture algae (S.capricornutum, UTEX) and 2 mL of activated sludge obtained from a local WWTP. The sample was shaken at 80 rpm using an orbital shaker (MAXQ 2000). During the incubation period, the sample tube was open to maintain aerobic conditions. We also conducted a seed control test with de-ionized water replacing the samples to eliminate the effect of seed on the bDON and rDON results. bDON was calculated according to Equation 1:

$$\text{bDON} = [(\text{DON}_i - \text{DON}_f) - (\text{DON}_{bi} - \text{DON}_{bf})] \tag{1}$$

, in which, DON_i is the DON in the leachate sample before incubation and DON_f is the DON in the leachate sample after incubation; DON_{bi} is the DON in the seed control before incubation and DON_{bf} is the DON in the seed control after incubation.

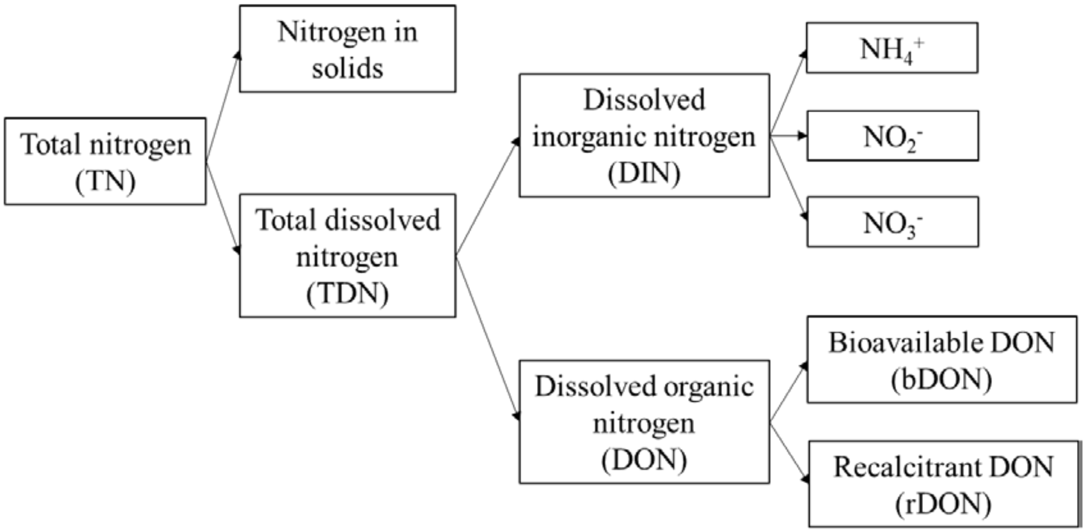


Figure 4. Nitrogen speciation.
(Adapted from McCarthy et al. (1997), Bronk et al. (2000), Petrone et al. (2009), Wadhawan et al. (2014), Watanabe et al. (2014), and Chen et al. (2015)).

Table 5. Methods for nitrogen speciation.

Parameters to measure	Methods	Equipment	References
TN	Persulfate digestion method	Spectrophotometer[1]	Rice et al., 2012
TDN	Persulfate digestion method (based on filtered samples[2])	Spectrophotometer	Hach, 2015a
Nitrogen in solids	TN – TDN		
ammonium	Ion-specific electrode method	Multi-parameter meter[3]	Hach, 2015b
NO_2^-	Ion chromatographic method	IC[4]	Rice et al., 2012
NO_3^-	Ion chromatographic method	IC	Rice et al., 2012
DON	TDN – (NH_4^+ + NO_2^- + NO_3^-)		Knapp et al., 2005
bDON	See the text for details		Simsek et al., 2013
rDON	DON – bDON		Simsek et al., 2013

Notes:

1. Hach DR3900 Benchtop VIS Spectrophotometer
2. Acrodisc Syringe Filter, 0.45 µm
3. Hach Bench-top Multi-parameter Meter HQ440D
4. IC: Dionex Aquion Ion Chromatography System

2.2.4 Measurement of carbon species

We conducted the carbon mass balance analysis at the weeks that represented significant changes in the reactor (*i.e.*, Weeks 5, 10, 15, and 24). Carbon mass balance is depicted in Figure 5 and elaborated in the following sections.

DOC and its composition. DOC in the reactor influent and effluent were measured following the persulfate-ultraviolent method in Rice (2012). Acetate was measured using ion chromatography (IC) (Dionex, Aquion, Thermo Scientific) following Rice (2012). Fractions of DOC, including HA, FA, and non-humic substances other than acetate, were measured following the procedure in van Zomeren and Comans (2007). To precipitate HA from a water sample, hydrochloride acid (6 mol/L) was added to 10 mL of the filtered sample until pH was 1. After 24 hours, the suspension was centrifuged at 3000 rpm for 20 minutes to separate the precipitated HA from the supernatant. After decanting the supernatant to a 15-mL centrifuge tube that was used later for measurement of FA and non-humic substances, the precipitated HA was dissolved by 10 mL potassium hydroxide (1 mol/L) and measured as DOC. FA in the supernatant was separated from the non-humic substances using a column containing 3 mL of prewashed Supelite DAX-8 resin (Supelco, Bellefonte, PA, USA), which adsorbed FA. The supernatant was pumped through the DAX-8 resin column followed by 10 mL hydrochloric acid (0.1 mol/L) at a rate of 6 mL/hr to wash the resin. Then, FA was desorbed from the DAX-8 resin by pumping 20 mL potassium hydroxide (0.1 mol/L) through the column at the same rate. The eluent as the FA fraction was collected and measured as DOC. Non-humic substances were calculated as the difference between the DOC and humic substances (HA and FA). The non-humic substances were further divided into acetate and other non-humic substances.

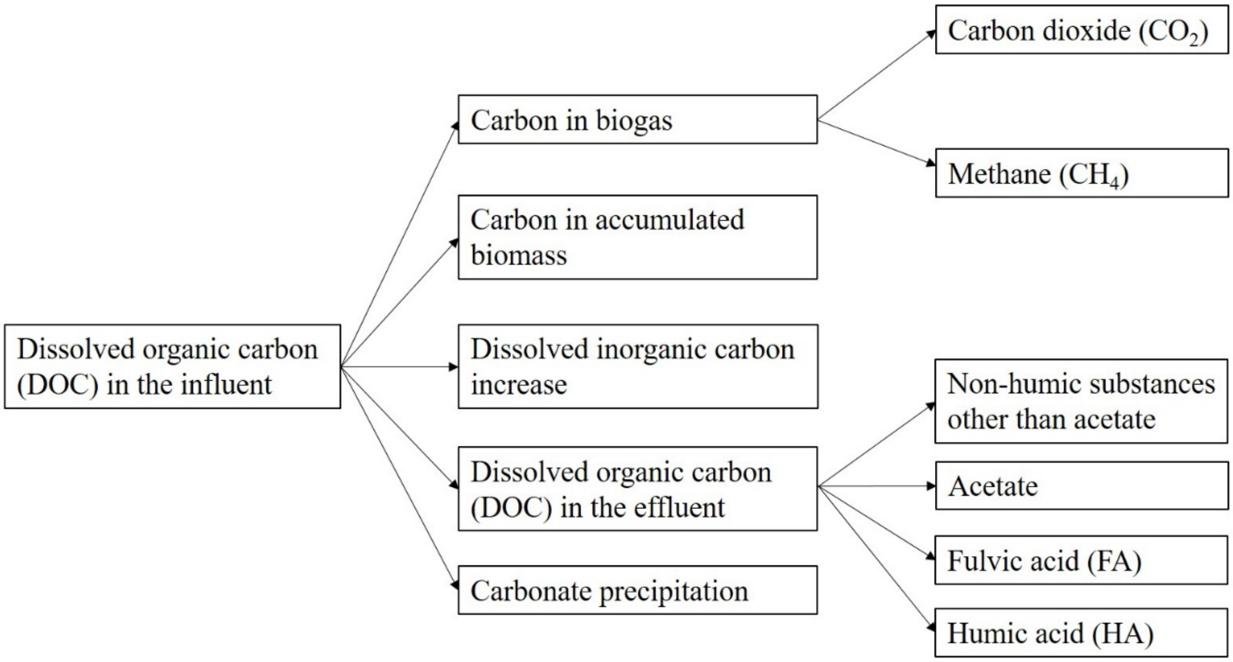


Figure 5. Diagram of carbon mass balance.

Effluent headspace gas and its composition. The treated leachate and produced gas were collected by a closed graduate syringe from which the headspace and leachate volumes were directly read. The headspace mainly contained CH_4 and CO_2. The CH_4 concentration in the headspace was measured using GC (SRI Instruments) (Borges et al., 2011; Özgür and Uysal, 2011). During the measurement, the column temperature was held at 50 ^{o}C for 3 minutes and then increased at a rate of 40 ^{o}C/min until 220 ^{o}C. The headspace gas volume and CH_4 concentration were then used to calculate the total CH_4 mass in the syringe based on Henry's law. The total CH_4 mass was then divided by the effluent liquid volume to calculate the "assumed CH_4 concentration in the effluent", which was later used for the carbon balance analysis in Figure 5. The carbon dioxide concentration in the headspace was estimated by assuming that all the headspace gas except for CH_4 was CO_2. Ideal gas equation was applied to calculate the CO_2 mass, which was further used to calculate the "assumed CO_2 concentration in the effluent" by dividing the effluent leachate volume.

Biomass synthesis. The DOC used for biosynthesis in the submerged anaerobic biological reactor can be estimated as (Ahmed and Lan, 2012; Canziani et al., 2006; Henze et al., 2001; Kennedy and Lentz, 2000; Rittman and McCarty, 2001):

$$Biomass(\frac{mg\ C}{L}) = Y \times (S^0 - S) \tag{2}$$

, in which, *Y* is the yield coefficient 0.024 mg C in cell/mg COD, S^0 is the COD in the influent, and *S* is the COD in the effluent.

Dissolved inorganic carbon. The total DIC including carbonate, bicarbonate, and carbonic acid was estimated for the reactor influent and effluent by Equation 3. The total DIC in the reactor effluent was higher than that in the influent due to the biological conversion of organic carbon to inorganic carbon. The difference between the influent and effluent total DIC (after unit conversion from mol/L to mg C/L) represented the total DIC accumulation used in Figure 5. All the units in Equations 3 to 9 were mol/L.

$$\left[CO_3^{2-}\right]_{total} = \left[CO_3^{2-}\right] + \left[HCO_3^-\right] + \left[H_2CO_3(aq)\right] \tag{3}$$

In the above equation, the three carbonate species on the right side of the equation were further calculated based the following three equations, respectively,

$$\left[HCO_3^-\right] = Alkalinity - 2\left[CO_3^{2-}\right] - \left[OH^-\right] + \left[H^+\right] - \left[NH_3(aq)\right] - \left[CH_3COO^-\right] \tag{4}$$

$$[CO_3^{2-}] = [HCO_3^-] \times 10^{-10.3+pH} \tag{5}$$

$$[H_2CO_3(aq)] = [HCO_3^-] \times 10^{-pH+6.8} \tag{6}$$

In Equation 4, alkalinity was measured using the titration method (Rice et al., 2012), pH was measured using a multi-parameter meter (HQ440D, HACH) through the electrometric method (Rice et al., 2012), and then used to estimate $[H^+]$ and $[OH^-]$, $[NH_3\ (aq)]$ and $[CH_3COO^-]$ were calculated from Equations 7 and 8. Equations 4-6 were solved simultaneously to obtain $[HCO_3^-]$, $[CO_3^{2-}]$, and $[H_2CO_3\ (aq)]$.

$$[NH_3(aq)] = \frac{[NH_4^+]_{total}}{(1+10^{-pH+9.3})} \tag{7}$$

$$\left[CH_3COO^-\right] = \frac{\left[CH_3COO^-\right]_{total}}{(1+10^{-pH+4.7})} \tag{8}$$

In the above equations, $[NH_4^+]_{total}$ and $[CH_3COO^-]_{total}$ were measured using IC (Dionex, Aquion, Thermo Scientific).

For data quality control, two independent methods were used to calculate $[H_2CO_3\,(aq)]$ at steady state and the results were compared. One was based on Equation 6, and the other was based on Equation 9 according to Henry's law, assuming the dissolved CO_2 in the leachate was in equilibrium with the headspace partial pressure of the CO_2.

$$[H_2CO_3(aq)] = [CO_2(g)] \times 0.031 \tag{9}$$

In the above equation, 0.031 is the Henry's law constant for CO_2 in the unit of mol/(L·atm) (Sander, 2015), $[CO_2\,(g)]$ is the gas pressure of CO_2 in the unit of atm (measured before in this section), $[H_2CO_3\,(aq)]$ is in the unit of mol/L.

Precipitated carbon. It is assumed that carbon was precipitated mainly as $MgCO_3$ and $CaCO_3$ following Equation 10 and 11.

$$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3 \downarrow \tag{10}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \downarrow \tag{11}$$

The molar concentration of the precipitated carbon associated with magnesium and calcium were calculated as follows:

$$Carbon_{precipitated} = [Mg^{2+}]_{\inf} - [Mg^{2+}]_{eff} + [Ca^{2+}]_{\inf} - [Ca^{2+}]_{eff} \tag{12}$$

, in which, $[Mg^{2+}]_{inf}$ and $[Mg^{2+}]_{eff}$ were the dissolved molar concentration of magnesium in the reactor influent and effluent, respectively; and $[Ca^{2+}]_{inf}$ and $[Ca^{2+}]_{eff}$ were the dissolved molar concentration of calcium in the reactor influent and effluent, respectively. Dissolved calcium and magnesium concentrations in the influent and effluent were measured using a microwave plasma-atomic emission system (Agilent Technologies 4100) following the EPA method 3050B (EPA, 1996). The molar concentration was then converted to mass concentration of carbon to analyze the conversion of carbon species.

2.2.5 Measurement of other parameters

Parameters evaluated other than metal, nitrogen, and carbon speciation are summarized in Table 6. COD, sulfate, pH, and conductivity were measured once per week, while total sulfide ($[S^{2-}]_{total}$) and redox potential were measured at steady state.

Table 6. Methods other than metal, nitrogen and carbon speciation.

Parameters to measure	Methods	Equipment	References
COD	Colorimetric method	Spectrophotometer[1]	Rice et al., 2012
Sulfate	Ion chromatographic method (based on filtered samples)	IC[2]	Rice et al., 2012
$[S^{2-}]_{total}$	Standard methods 4500-S^{2-} (based on filtered samples)	Spectrophotometer[3]	Rice et al., 2012
pH	Electrometric method	Multi-parameter meter	Rice et al., 2012
Conductivity	Electrometric method	Multi-parameter meter	Rice et al., 2012
Redox potential	Electrometric method	Multi-parameter meter	Rice et al., 2012

Notes:

1. Hach DR2000 Benchtop Spectrophotometer;
2. IC: Dionex Aquion Ion Chromatography System;
3. Shimadzu UV-1650PC Spectrophotometry.

2.3 Dissolved metal speciation modeling (Task 4)

To further understand the fate of the investigated heavy metals in the reactor without sulfate addition (Stage 1) and with sulfate addition (Stage 2), we simulated the dissolved metal speciation in the reactor influent and effluent using VISUAL MINTEQ, a software for equilibrium speciation model development (Cloutier-Hurteau et al., 2007). Stockholm Humic Model (SHM) was used for modeling organic matter complexation with metals. The model input included the total dissolved concentrations of metals: Fe, Ni, Pb, Zn, Cu, Ca, Mg, Na, and K, total ammonium (*i.e.*, NH_4^+ and NH_3 (aq)), total acetate (*i.e.*, CH_3COO^- and CH_3COOH (aq)), total DIC (*i.e.*CO_3^{2-}, HCO_3^- and H_2CO_3 (aq)), and total sulfide (*i.e.* S^{2-}, HS^-, H_2S (aq)). It also included major anions (*i.e.*, chloride and sulfate), HA, FA, pH, and redox potential. The HA and FA concentrations were calculated based on the carbon content in humic substances and typical chemical formula of HA ($C_9H_9NO_6$) and FA ($C_{14}H_{12}O_8$) (National Center for Biotechnology Information, 2018).

2.4 Metal sulfides separation and recovery (Task 6)

We used a lab-scale cryo-high gradient magnetic separator (HGMS) at PhySep Components and Service, Inc. to separate and recover metal sulfides produced in the reactor. A sample was prepared by the following procedure before magnetic separation:

(1). Shaked the reactor so that biofilms and metal sulfides detached from the plastic media and were suspended in the leachate. Removed the plastic media and collected the mixture in a 100 mL glass bottle.

(2). Centrifuged the mixture and removed the supernatant. Added deionized water to re-suspend the precipitate.

3. RESULTS AND DISCUSSION

3.1 Results for Task 1: reactor design

The typical HRT for COD removal (*i.e.*, 4.5 days) by the anaerobic biological reactor was used as the initial guidance to design the submerged anaerobic biological reactor. The reactor was designed and operated using parameters summarized in Table 7. The reactor setup is shown in Figure 2. The reactor was a plastic column with an inner diameter of 4 cm and a height of 7.2 cm and operated at a HRT of 4.5 days and room temperature for about 42 weeks. It contained 45 pieces of plastic media (BioFLO 9, Smoky Mountain Bio Media) for biomass attachment. We used a syringe infusion pump (Cole-Parmer) to inject the MSW-1 landfill leachate into the bottom of the reactor. The surface area of the media was 0.00102 m^2/piece of plastic media. Therefore, the media specific surface area (SSA) was calculated as the total surface area (TSA) of the media divided by the reactor volume, which is around 500 m^2/m^3 (= $0.00102\times45/(\pi\times0.02^2\times0.072)$). Around 20 mL of leachate passed through the column and was collected in another syringe each day. Prior to feeding the leachate into the reactor, the column was inoculated with activated sludge from a local WWTP. The chosen landfill leachates were stored in a refrigerator at 1.6 ^{o}C.

Table 7. Summary of reactor design and operation.

Leachate source	Influent COD (mg/L)	HRT (day)	VLR (kg COD/ m^3-day)	No. of media	Media TSA (m^2)	Media SSA (m^2/m^3)	Inflow rate (mL/min)
MSW-1	22600	4.5	2.0	45	0.046	500	0.014

3.2 Results for Task 2: leachate characterization

We characterized four leachates collected in Florida and compared the heavy metals concentrations in the four leachates to their direct discharge standards (Standards 1, 8, 9, and 10) and threshold concentrations (Thresholds 2-7) in Table 8. A threshold concentration of a heavy metal is defined as the concentration in the leachate above which indirectly causes violation of a drinking water, wastewater, or biosolid standard due to its indirect impact. We estimated the threshold concentration based on a standard (Standards 2-7 in Table 8) that regulates the heavy metals concentration in the drinking water, wastewater, or biosolid indirectly impacted by the leachate. The diagram of the threshold estimation is shown in Figure 6. The following seven assumptions are made:

- Volume mixing ratio of leachate to municipal wastewater in a WWTP is 1:99.
- Volume mixing ratio of the discharge municipal wastewater to upstream surface water is 1:9.
- The heavy metal removal efficiency at the WWTP is 50%.
- The heavy metal removal efficiency at the drinking water treatment plant (DWTP) is 50%.
- In the calculation of biosolids threshold, the wastewater treatment capacity at the WWTP is 23 million gallons per day (MGD) (FDEP, 2018) and the biosolids production is 3952 ton/year (FDEP, 2014).

- The typical metal concentrations in the upstream surface water are 10, 1, 25, 15.3, 860.2, 5, and 10 µg/L for copper, cadmium, zinc, nickel, iron, lead, and selenium, respectively (Hand, 2004).
- The typical metal concentrations in the municipal WWTPs are 0.172, 0.035, 0.188, 0.1, 1.98, 0.084, and 0.003 mg/L for copper, cadmium, zinc, nickel, iron, lead, and selenium, respectively (Abdel-Shafy and Hussein, 1996; Linstedt et al., 1971; Ustun, 2009).

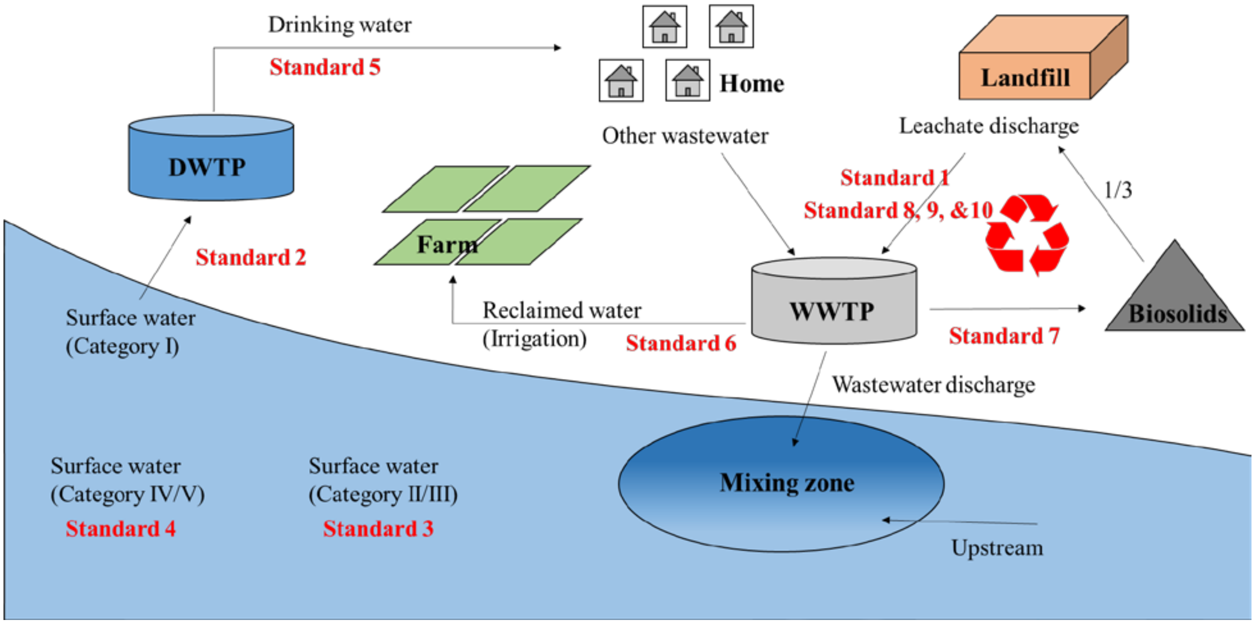


Figure 6. Diagram of thresholds estimation.

Among the four leachates, the MSW-1 leachate had the highest concentrations of heavy metals. Comparing the heavy metals concentrations in the MSW-1 leachate to the thresholds, the iron and lead concentrations exceeded threshold 2, which is the FDEP surface water standard for drinking water supply. The iron concentration also exceeded threshold 4, which is the FDEP surface water standard for irrigation and navigation. The nickel concentration in the biosolid violated threshold 7. The zinc concentration violates the National pollutant discharge elimination system (NPDES) landfill leachate standard (standard 1). Comparing to standards 8, 9, and 10, which are the local discharge to sewer limitations and pretreatment standards in Florida, the iron, lead, nickel, and zinc concentrations were higher than at least one of these standards. The results suggested the need of removing heavy metals such as iron, lead, nickel, and zinc in the leachate prior to discharge to sewer. In this study, we investigated three of the four metals, including iron, nickel, and lead. It should be noted that different assumptions will result in the change of thresholds 2-7 in Table 8.

In summary, the concentrations of four heavy metals in MSW-1 leachate exceeded the discharge to sewer standards. Iron, lead, nickel, and zinc all violated the Tamarac wastewater discharge standard. Additionally, lead exceeded the Miami sanitary sewer discharge limitations and local limits for the City of Tallahassee wastewater facility; zinc also exceeded the NPDES landfill leachate standard. Among these four heavy metals, we chose three of them (*i.e.*, iron, nickel, and lead) as the focus of the metal research.

Table 8. The metal concentrations in the four leachates, their threshold concentrations, and the standards used for estimation of the threshold concentrations.

	Cadmium (mg/L)	Copper (mg/L)	Iron (mg/L)	Lead (mg/L)	Nickel (mg/L)	Zinc (mg/L)
MSW-1	0.064	0.400	290.6	1.98	0.299	2.3
MSW-2	-[1]	0.045	10.59	0.197	0.107	0.006
MSW-3	-	0.043	2.15	0.0973	0.052	0.0002
Monofill-4	-	0.295	2.5	0.0002	0.375	0.065
Threshold 2	NE[3]	NE	59.6	2.2	230.6	557.2
Threshold 3	8.8	NE	NE	NE	NE	89.8
Threshold 4	NR	948	59.6	74.2	152.6	1917.8
Threshold 5	11.26	5148	NE	34.2	352.6	19918
Threshold 6	NE	6	608	983.4	20.2	2.8
Threshold 7	NE	76.2	NR	NE	0.538	51.0
Standard[4] 1	NR	NR	NR	NR	NR	0.200
Standard 2	0.638	25.100	1.000	0.014	0.139	0.320
Standard 3	0.009	0.004	0.300	0.009	0.008	0.086
Standard 4	NR	0.500	1.000	0.050	0.100	1.000
Standard 5	0.005	1.300	0.300	0.015	0.100	5.000
Standard 6	0.010	0.200	5.000	5.000	0.200	0.200
Standard 7	0.008	0.441	NR	0.016	0.245	0.804
Standard 8	0.187	0.500	NR	0.700	0.390	6.800
Standard 9	0.14	1.2	NR	0.39	2.6	5.6
Standard 10	0.10	0.50	10.00	0.2	0.2	1.0

Note:

1. -: Not detected;
2. NR: Not regulated;
3. NE: Negative;
4. Standard 1: National pollutant discharge elimination system (NPDES) landfill leachate standard (EPA, 1992); Standard 2: Florida Department of Environmental Protection (FDEP) surface water, category 1 standard (F.A.C., 2016); Standard 3: FDEP surface water, category 2 and 3 standard (F.A.C., 2016); Standard 4: FDEP surface water, category 4 and 5 standard (F.A.C., 2016); Standard 5: EPA drinking water standard (EPA, 1992); Standard 6: EPA reclaimed water standard for irrigation usage (EPA, 2004); Standard 7: biosolid standard (EPA, 2008); Standard 8: Miami sanitary sewer discharge limitations and pretreatment standards (as one example of city standards, from Code of Ordinances of Miami-Dade County, 2017). Standard 9: Local limits for City of Tallahassee wastewater facility (as another example of city standards, from Code of General Ordinances of the City of Tallahassee, 2017). Standard 10: Wastewater discharge standard of City of Tamarac.

Nitrogen species including TN, TDN, ammonia-nitrogen, nitrate-nitrogen, and nitrite-nitrogen were also measured. Figure 7 shows the distribution of nitrogen species except for nitrite in the four leachates since nitrite was not detected in all sampled leachate.

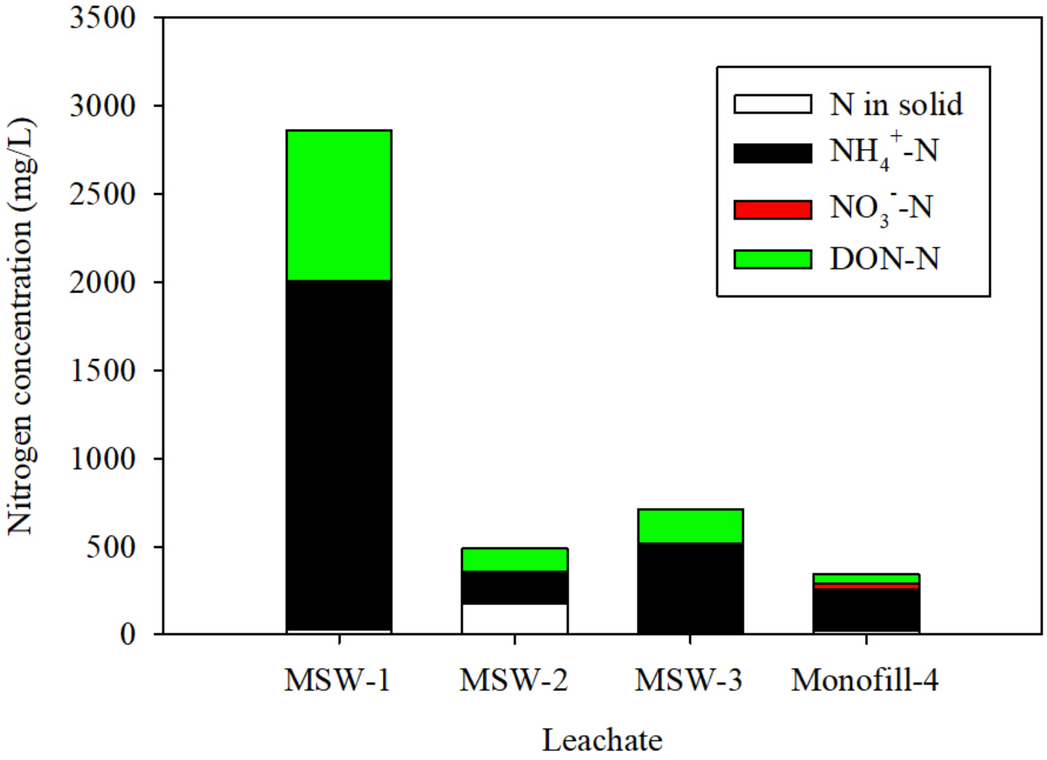


Figure 7. Nitrogen species distribution in the four leachates.

The MSW-1 leachate had the highest TN (2870 mg N/L), which could contribute to 38.7% of the TN in a WWTP assuming a mixing ratio of leachate to municipal wastewater of 1:99 (volume ratio) and a typical TN concentration of 46.0 mg N/L in the wastewater (Reinhart, 2017). The dominant nitrogen species in the MSW-1 leachate and the other leachates were ammonium and DON, the hydrolysis/fermentation products of the nitrogen fraction in the biodegradable MSW (Kulikowska, 2012). This is consistent with the literature. Townsend (2015) reported high ammonium concentrations (6.9-1606.7 mg N/L) in Florida landfill leachate samples. Reinhart (2017) characterized the leachate samples obtained from 16 landfills and found that the majority of the nitrogen was from ammonium followed by DON. DON in leachate is mainly contributed by small molecular weight compounds that may not be removed in WWTPs (Chen et al., 2010) and can potentially be an issue when discharged to WWTPs. Nitrate only represents a small portion of the TN. The Monofill-4 leachate had the lowest TN concentration. This is reasonable since the bottom ash from the MSW incinerator is a mixture of slag, stone, glass, metal, and ceramic debris, which are low in nitrogen (Llyas et al., 2014).

Table 9. Parameters other than metal and nitrogen species in the four leachates.

Leachate	pH	Conductivity (ms/cm)	COD (mg/L)	DOC (mg C/L)	Sulfate (mg S/L)
MSW-1	7.60	28.5	22800	7880	114.0
MSW-2	8.97	7.1	1100	358	7.5
MSW-3	7.49	15.7	2963	1145	325.7
Monofill-4	8.50	18.5	743	125	27.3

Parameters other than the heavy metals and nitrogen species are compared for the four sampled leachates in Table 9. The MSW-1 leachate had the highest COD and DOC concentration. The highest conductivity in MSW-1 suggested the highest ionic strength and the highest total dissolved solids. The Monofill-4 leachate had the lowest COD and DOC concentrations due to the low organic carbon content in the incineration bottom ash. We chose MSW-1 leachate as the feed to the submerged anaerobic biological reactor because of the high concentrations of heavy metals, nitrogen, and carbon. MSW-1 was further characterized. The characterization results are summarized in Table 10.

In the MSW-1 leachate, the majority of the iron, nickel, and lead existed in the form of dissolved metals, particularly metal-organic complexes. Bioavailable and recalcitrant DON in the MSW-1 leachate were 62% and 38%, respectively. The DOC in MSW-1 leachate was 7880 mg C/L, which was comprised of acetate-C (23%), HA-C (18%), FA-C (32%), and the other carbon (27%).

Table 10. Characterization of the MSW-1 leachate.

Parameter (units)	Value (standard deviation)[1]
Total metal	
Cadmium (mg Cd/L)	0.0640 (0.0240)
Copper (mg Cu /L)	0.400 (0.002)
Iron (mg Fe /L)	290 (4)
Lead (mg Pb /L)	1.98 (0.06)
Nickel (mg Ni /L)	0.299 (0.056)
Zinc (mg Zn /L)	2.30 (0.03)
Total dissolved metal	
Cadmium (mg Cd /L)	0.0310 (0.0180)
Copper (mg Cu /L)	0.300 (0.001)
Iron (mg Fe /L)	266 (2)
Lead (mg Pb /L)	1.97 (0.05)
Nickel (mg Ni /L)	0.299 (0.056)
Zinc (mg Zn /L)	1.60 (0.02)

Free metal ions	
Nickel (mg Ni /L)	0.0121 (0.0139)
Lead (mg Pb /L)	0.0298 (0.0870)
Ferric iron (mg Fe /L)	5.76 (1.57)
Ferrous iron (mg Fe /L)	3.18 (0.77)
Nitrogen species	
TN (mg N /L)	2870 (38)
TDN (mg N /L)	2830 (63)
Ammonium (mg N /L)	1980 (153)
Nitrite (mg N /L)	< 0.033
Nitrate (mg N /L)	3.86 (0.29)
DON (mg N /L)	851 (140)
Nitrogen in solids (mg N /L)	40.0 (28.9)
bDON (mg N /L)	526 (39)
rDON (mg N /L)	325 (67)
Parameters other than metal and nitrogen species	
pH	7.60 (0.02)
Conductivity (ms/cm)	28.5 (0.1)
COD (mg/L)	22800 (115)
TOC (mg C/L)	7980 (154)
DOC (mg/L)	7880 (136)
Acetate (mg C/L)	1810 (57)
Sulfate (mg S/L)	114 (4)
Methane (mg C/L)	< 0.075
HS[2] (mg C/L)	3930 (521)
HA (mg C/L)	1410 (85)
FA (mg C/L)	2520 (509)
Non-HS (mg C/L)	3950 (521)

Note:

1. The standard deviations of total metals, total dissolved metals, nitrite, nitrate, ammonium, acetate and sulfate were calculated based on triplicate samples, and the standard deviations of all the other parameters were calculated based on triplicate measurements of the same sample due to the sample volume limitation;
2. HS: Humic substances.

3.3 Results for Task 3: reactor operation and loading optimization

3.3.1 Organic matter removal performance overview

Figure 8 summarizes the organic matter removal in the reactor at Stage 1, which can be divided into four phases. In Phase 1 (Week 1-8), the average acetate concentration increased from 1780 mg C/L (a typical concentration is used unless noted otherwise) in the influent to 2320 mg C/L in the effluent, and ammonium increased from 2250 mg N/L in the influent to 2520 mg N/L in the effluent, suggesting the occurrence of hydrolysis, acidogenesis, and acetogenesis. Representative reactions commonly occurring in the anaerobic bioreactors for leachate treatment are summarized in Table 11. Phase 2 (Week 8-12) was a transition phase since: 1) DOC and COD started to decrease, and 2) acetate started to be converted to CH_4. In Phase 3 (Week 12-22), all the four processes (hydrolysis, acidogenesis, acetogenesis, and methanogenesis) occurred simultaneously. Acetate, COD, and DOC concentration in the leachate effluent kept decreasing steadily while CH_4 concentration kept increasing until week 22. In phase 4 (Week 22-25), the reactor performance parameters as described in Figure 8 were stable. DOC decreased from 7880 mg C/L to 3800 mg C/L, and COD decreased from 22800 mg/L to 11200 mg/L. About 19.9% of DOC was converted to CH_4. The biogas (mainly CH_4 and CO_2) production rate reached 4.0 L biogas/L leachate (Figure 9) which is comparable to the literature (Bohdziewicz, et al., 2008). The CH_4 proportion reached 81% of the biogas (Figure 10), which was higher than the typical value 50-75% (Kim et al., 2003; Tanigawa, 2017; Vergara-Fernandez et al., 2008; Weiland, 2010), suggesting a very high quality biogas that could be reused. The high CH_4 concentration in the biogas could be due to the precipitation of significant inorganic carbon.

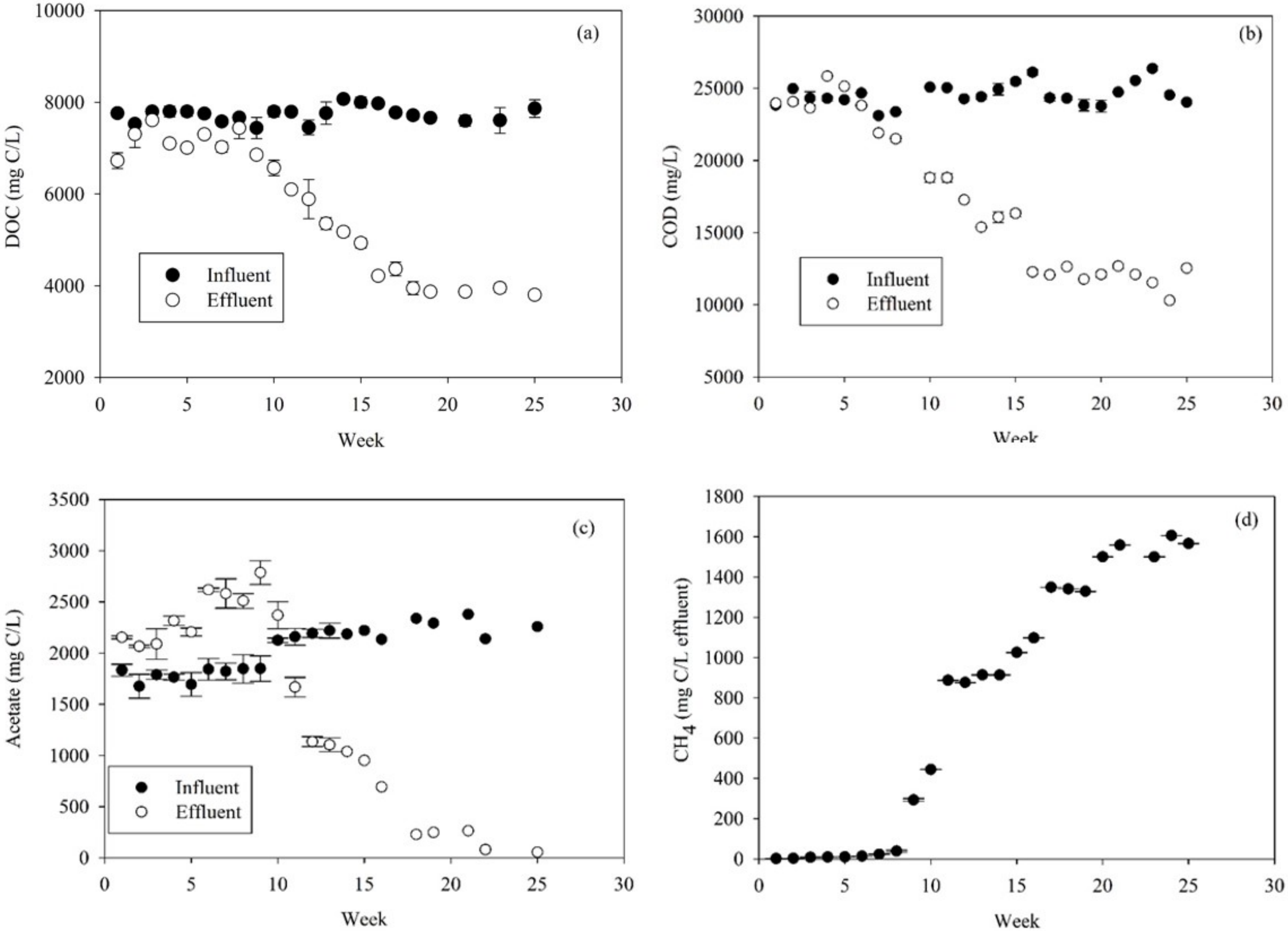


Figure 8. Weekly measured parameters including (a) DOC, (b) COD, (c) acetate, and (d) CH_4.

Note: The CH_4 concentration in panel d) was the "assumed CH_4 concentration in the effluent", which was the total CH_4 mass in the syringe that collected the treated leachate and gas divided by the effluent liquid volume.

Table 11. Representative reactions at four stages during anaerobic digestion.

Process	Representative reactions
Hydrolysis	$C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + H_2$
	$CH_3CH(CH_3)CH(NH_3^+)COO^- + 2H_2O \rightarrow (CH_3)_2CHCOO^- + NH_4^+ + CO_2 + 2H_2$
Acidogenesis	$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O$
	$CH_3CH(OH)CH(NH_3^+)COO^- + H_2 \rightarrow CH_3COO^- + \frac{1}{2}CH_3(CH_2)COO^- + \frac{1}{2}H^+ + NH_4^+$
	$CH_3CH(CH_3)CH(NH_3^+)COO^- + 2H_2O \rightarrow (CH_3)_2CHCOO^- + NH_4^+ + CO_2 + 2H_2$
	$C_6H_{12}O_6 \rightarrow 3CH_3COOH$
Acetogenesis	$CH_3CH_2OH + H_2O \rightarrow CH_3COO^- + H^+ + 2H_2$
	$CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 3H_2$
	$CH_3CH_2CH_2COO^- + 2H_2O \rightarrow 2CH_3COO^- + H^+ + 2H_2$
Methanogenesis	$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$
	$H_2 + \frac{1}{2}CO_2 \rightarrow \frac{1}{4}CH_4 + \frac{1}{2}H_2O$

Reference: Zieminski and Frac (2012); O'Flaherty et al. (2010).

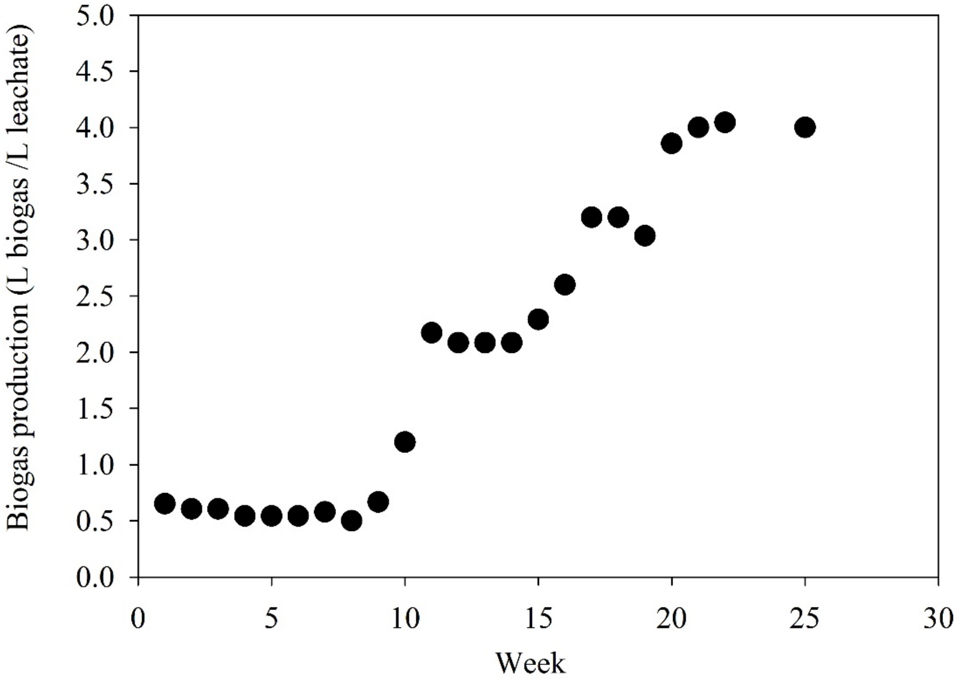


Figure 9. Biogas production rate.

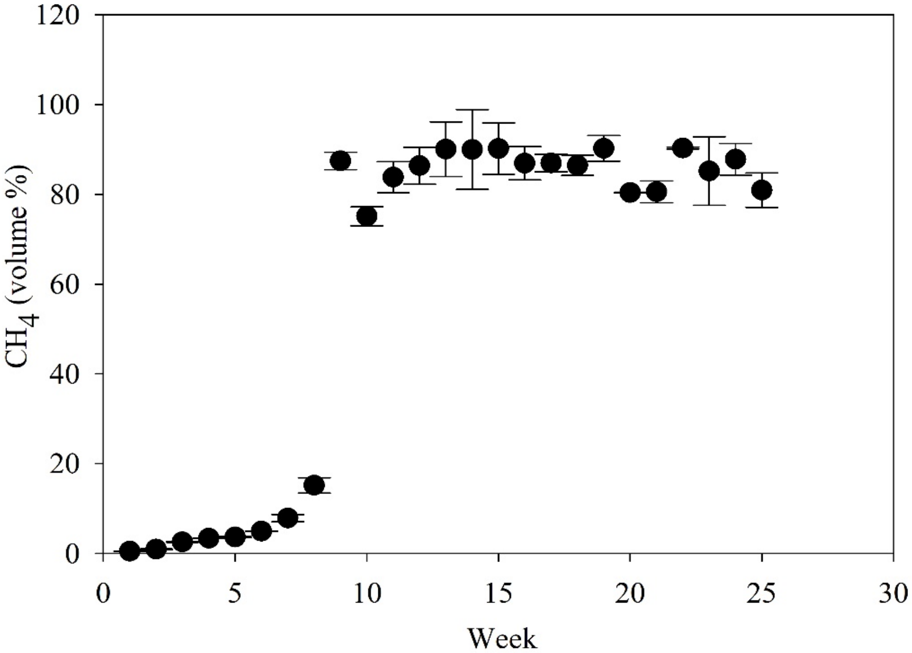


Figure 10. CH_4 volume percentage in the biogas at the syringe headspace.

3.3.2 Insights into the organic matter removal

To gain more insights into the conversion of organic matter in the reactor, carbon balance analysis were conducted at weeks that represented major changes in the reactor. Figure 11 shows the carbon speciation at the four different phases at Stage 1. The influent stored in the refrigerator did not change significantly over Stage 1.

In Week 5 (Phase 1), the major reaction in the reactor was conversion of FA and non-humic substances other than acetate to acetate and CO_2: The FA decreased by 532 mg C/L and the non-humic substances other than acetate decreased by 121 mg C/L, while acetate increased by 513 mg C/L and CO_2 in the gas increased to 300 mg C/L. The CO_2 concentration used here was an assumed value calculated by dividing the CO_2 mass in the headspace by the effluent liquid volume.

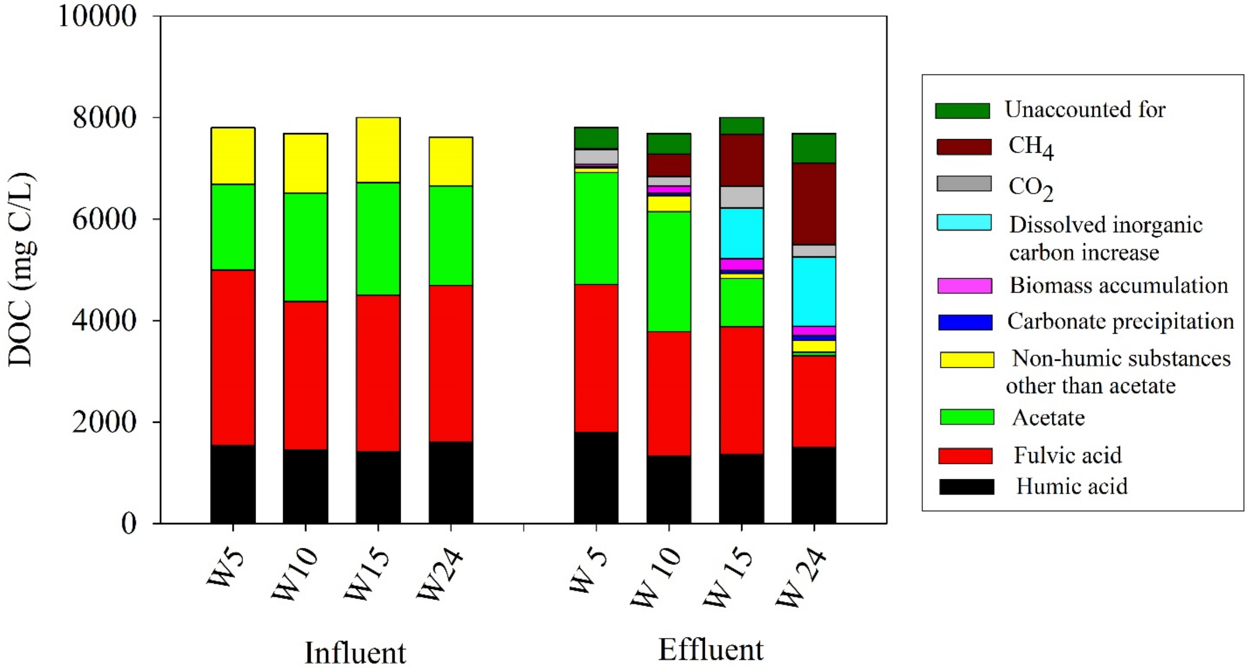


Figure 11. Carbon speciation in the anaerobic reactor. Note: W = Week.

In Week 10 (Phase 2), the major reactions in the reactor were the conversion of non-humic substances other than acetate (decreased from 1.18×10^3 mg C/L in the influent to 315 mg C/L in the effluent) and FA (decreased from 2.93×10^3 to 2.45×10^3 mg C/L) to CH_4 (increased from 0 in the influent to 444 mg C/L in the effluent), acetate (increased from 2.12×10^3 to 2.37×10^3 mg C/L), CO_2 (increased from 0 to 179 mg C/L), and biomass (increased by 150 mg C/L).

In Week 15 (Phase 3), the major reactions in the reactor were the conversion of acetate (decreased from 2.22×10^3 mg C/L in the influent to 950 mg C/L in the effluent), non-humic substances other than acetate (decreased from 1.28×10^3 to 99 mg C/L), and FA (decreased from 3.10×10^3 to 2.53×10^3 mg C/L) to CH_4 (increased from 0 in the influent to 1.03×10^3 mg C/L in the effluent), total DIC (increased by 991 mg C/L), CO_2 (increased from 0 to 428 mg C/L) and biomass (increased by 236 mg C/L). Inorganic carbon precipitation was observed in Phase 3, but not the previous two phases probably due to the increased production of CO_2 (Table 11), which provided CO_3^{2-} in the reactor to precipitate $CaCO_3$ and $MgCO_3$. The pH through the treatment was stable and between 7.5 and 8.0 (Figure 12) probably due to the balance between organic acids production in hydrolysis, acidogenesis, and acetogenesis and acetate consumption in methanogenesis (Table 11).

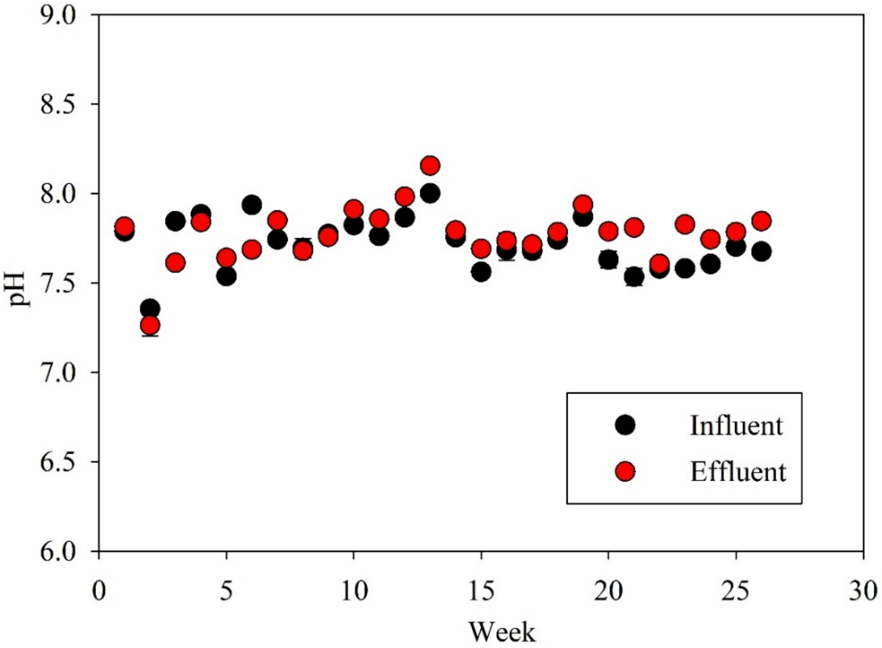


Figure 12. pH in the reactor influent and effluent.

In Week 24 (Phase 4), the reactor was at steady state (Stage 1). The major reactions in the reactor were the conversion of acetate (decreased from 2.20×10^3 mg C/L in the influent to 79 mg C/L in the effluent), non-humic substances other than acetate (decreased from 955 mg C/L in the influent to 227 mg C/L in the effluent), and FA (decreased from 3.10×10^3 mg C/L in the influent to 1.81×10^3 mg C/L in the effluent) to CH_4 (increased from 0 mg C/L in the influent to 1.61×10^3 mg C/L in the effluent), total DIC (increased by 1.37×10^3 mg C/L), CO_2 (increased from 0 mg C/L in the influent to 246 mg C/L in the effluent), and biomass (increased by 186 mg C/L) at steady state (Week 24). At steady state (Stage 1), 90% of the non-humic carbon was converted to other forms of carbon.

For data quality control, the H_2CO_3 (aq) concentration was calculated by two different methods that were based on two independently measured water quality parameters: One was calculated by the Henry's law method in Equation 9 (45.3 mg C/L effluent) and the other by the alkalinity method in Equation 6 (43.7 mg C/L effluent). The result of H_2CO_3 (aq) from these two independent methods were generally consistent. The total concentration of various carbon species in the influent was similar to the total concentration of carbon species in the effluent (Figure 11), which approximately closed the carbon balance, and provided another line of evidence for the data quality control.

3.3.3 Heavy metal removal

The heavy metals investigated in this study included iron, nickel, and lead since their concentrations exceeded at least one of the local discharge to sewer standards in Florida. Two stages, including Stage 1 and Stage 2, were compared. Stage 1 was the pretreatment of the raw landfill leachate. Stage 2 was the pretreatment of landfill leachate with an added sulfate supply at 120 mg S/L. As shown in Figure 13, 90% of total iron, 13% of total nickel, and 3% of total lead were removed at steady state in Stage 1. While 95% of total iron, 24% of total nickel, and 10% of total lead were removed at steady state in Stage 2. Starting in Week 8, some dissolved iron was converted to particulate iron in the influent probably due to the formation of iron crystals during leachate storage, which is further discussed below in the modeling section. In Stage 1, the majority of the total dissolved iron in the reactor influent and effluent was in the form of organic metal complexes (91-96%). All of the iron species decreased in the reactor effluent compared to the influent.

The removal of heavy metal was presumably due to the formation of metal sulfide precipitates, which is further discussed in the modeling section below. Sulfate concentration was reduced from 120 mg S/L to less than 20 µg S/L (the quantification limit) throughout the experiment (Figure 14). To understand how sulfate reduction to sulfide affected the heavy metal removal and precipitation, the hydrogen sulfide species were measured or calculated as follows. The hydrogen sulfide in the headspace, H_2S (g), of the leachate storage bottle and the syringe for collecting the reactor effluent was measured using a portable hydrogen sulfide analyzer (Jerome 631-X): <0.01 mg/L for the storage bottle headspace and 2.78 mg/L for the syringe headspace. Sulfide species in the liquid phase were calculated using Equations 13 to 15 according to Henry's law (Sander, 2015):

$$[H_2S(aq)] = [H_2S(g)] \times 0.11 \tag{13}$$

$$[HS^-] = [H_2S(aq)] \times 10^{-6.96+pH} \tag{14}$$

$$[S^{2-}] = [HS^-] \times 10^{-7.21+pH} \tag{15}$$

in which, $[H_2S\ (aq)]$, $[HS^-]$ and $[S^{2-}]$ were the concentrations of the dissolved sulfide species in the liquid and had units of mol/L. The total liquid sulfide species ($[S^{2-}]_{total}$) in the influent and effluent were calculated in Equation 16:

$$[S^{2-}]_{total} = [H_2S(aq)] + [HS^-] + [S^{2-}] \tag{16}$$

The $[S^{2-}]_{total}$ in the reactor influent and effluent were 0 and 5.99 mg S/L respectively. The results suggested that all of the sulfate was converted to sulfide by sulfate reducing bacteria in the reactor. The produced sulfide was available for metal sulfides precipitation. Assuming the molar ratio of heavy metal and sulfur in possible metal sulfides is 1:1, around 128 mg S/L of sulfate was needed to precipitate all iron, lead, and nickel in the raw leachate.

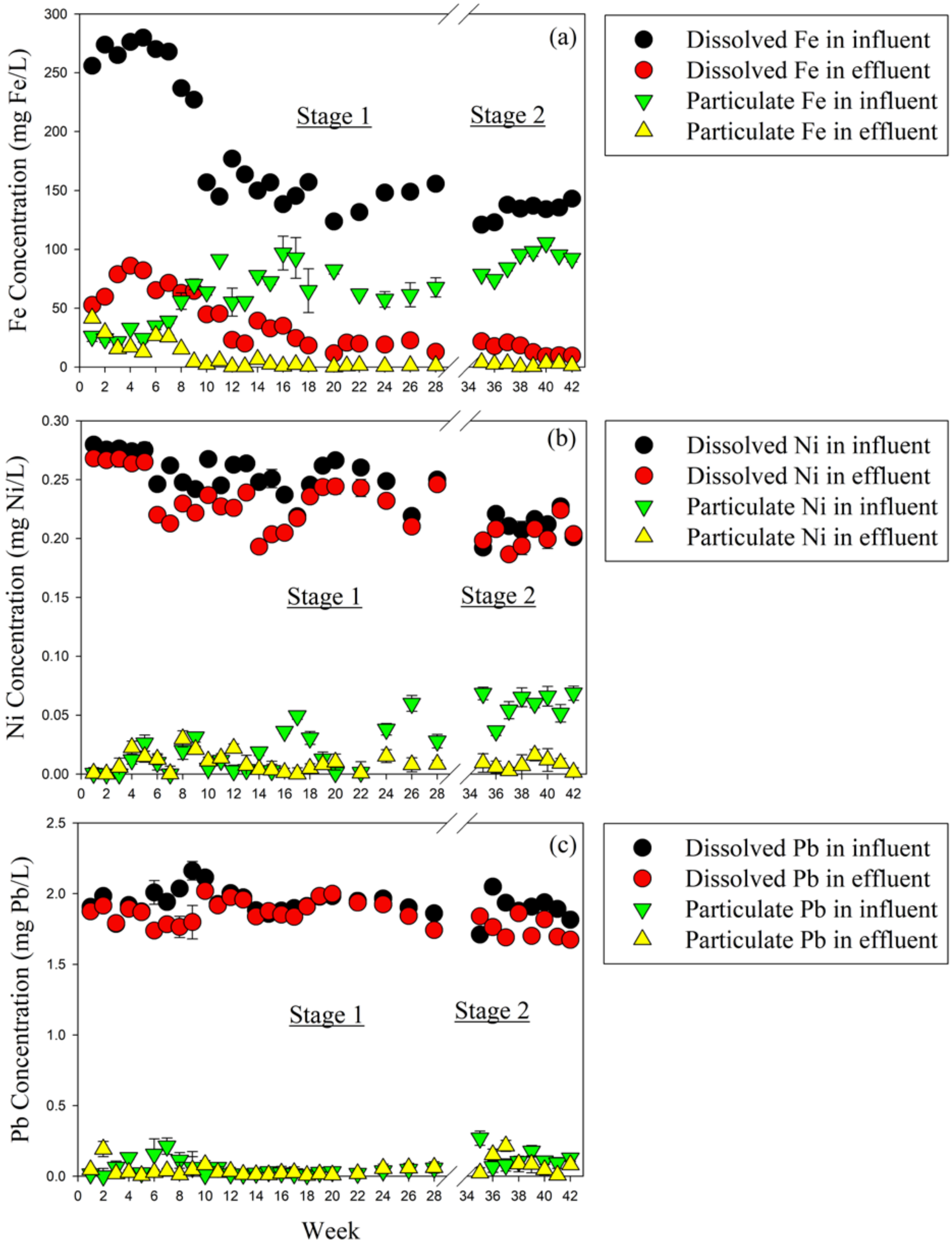


Figure 13. The dissolved and particulate metal concentrations of (a) Iron, (b) Nickel, and (c) Lead in the reactor influent and effluent. Note: The reactor performance from Week 29 to Week 34 was impacted by Hurricane Michael in October, 2018, and not plotted.

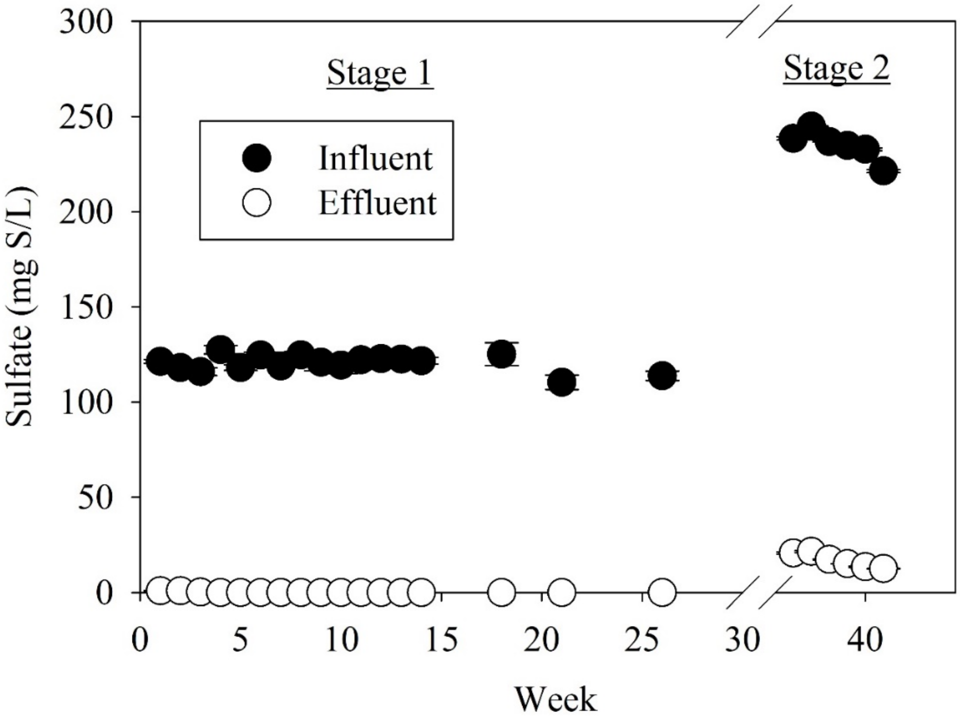


Figure 14. Sulfate concentration in the reactor influent and effluent.

At Stage 2, we added additional sulfate (120 mg S/L) to the reactor influent. Sulfate concentration was reduced from 240 mg S/L to 12 mg S/L in the reactor effluent at steady state. The removal of metals increased: total iron removal increased from 90% to 95%, total nickel removal increased from 10% to 24%, and total lead removal increased from 3% to 10%. However, complete removal of these three heavy metals could not be reached. Both iron and nickel concentration in the effluent met the local leachate discharge to sewer standards (*i.e.*, Tallahassee, Taramac, and Miami standards). Lead concentration in the effluent still did not meet any of the local discharge to sewer standards. The measured total sulfide concentration in the reactor effluent at steady state of Stage 2 was 52.2 mg S/L. For the data quality control, total sulfide concentration in the reactor effluent was also evaluated using the method based on Henry's law through Equation 13-16. The calculated total sulfide concentration in the effluent was 45.3 mg S/L, which was generally consistent with the value obtained from the first method. The incomplete heavy metal removal could be caused by 1) the low concentration of free heavy metal ions or sulfide, 2) the complexation of heavy metals with humic substances, or 3) the complexation of heavy metals with other chemicals. To find out which was the cause, we conducted the following analysis.

The solubility constants of metal sulfides and the corresponding ionic products (Stage 2) are compared in Table 12. Traditional solubility formulation based on $[S^{2-}]$ is not suitable for treating metal sulfides, since HS^- is usually the dominant sulfide species in solution (Licht, 1988). Thus, a different solubility constant for divalent metal sulfide, $K_{sp\text{-}a}$, was calculated using Equation 17 based on the following chemical equation (Licht, 1988). The ionic products of three studied heavy metals were calculated based on Equation 18-20. For all of these three studied heavy metals, the ionic products were higher than the solubility constants, suggesting that the concentration of neither heavy metals nor sulfide was not the reason for the incomplete removal.

$$MS + H^{+} \rightleftharpoons HS^{-} + M^{2+}$$

$$K_{sp-a} = \frac{\left[M^{2+}\right]\left[HS^{-}\right]}{\left[H^{+}\right]} \tag{17}$$

$$Q_{FeS} = \frac{\left[Fe\right]_{free}\left[HS^{-}\right]}{\left[H^{+}\right]} \tag{18}$$

$$Q_{NiS} = \frac{\left[Ni\right]_{free}\left[HS^{-}\right]}{\left[H^{+}\right]} \tag{19}$$

$$Q_{PbS} = \frac{\left[Pb\right]_{free}\left[HS^{-}\right]}{\left[H^{+}\right]} \tag{20}$$

In the above equations, Q_{FeS}, Q_{NiS}, and Q_{PbS} are the ionic products for three metal sulfides. $[Fe]_{free}$, $[Ni]_{free}$, and $[Pb]_{free}$ are the dissolved free metal concentrations of three studied heavy metals. $[H^{+}]$ is the concentration of proton, which was calculated based on pH measurement at steady state (Stage 2).

Table 12. Solubility constants and ionic products of metal sulfides in Stage 2.

Metal sulfide	Solubility constant (Ksp-a) (mol/L)	Dissolved free metal concentration (mol Metal/L)	Dissolved bisulfide concentration (mol S/L)	Ionic product (mol/L)
FeS	1.12 E-3 (Amorphous FeS) 2.51 E-4 (Mackinawite)	3.76E-5	9.03E-6	2.70E-2
NiS	3.02 E-6 (alpha) 6.31 E-12 (beta) 1.90 E-13 (gamma)	3.94E-7	9.03E-6	2.82E-4
PbS	1.20 E-15 (Galena)	1.87E-7	9.03E-6	1.34E-4

Reference: Licht (1988); Gustafsson (2011).

To investigate whether the incomplete removal of iron, nickel, and lead was caused by the complexation of the metals with humic substances and other chemicals, we simulated dissolved metal speciation in the following section since the speciation modeling in VISUAL MINTEQ considers the metal complexation to humic substances and bisulfide. The results of dissolved metal speciation modeling (see the next section) showed that the majority of dissolved heavy metal existed in the form of complexation with bisulfide in the reactor effluent at Stage 2, indicating the incomplete heavy metal removal in the experiment was not caused by the complexation of heavy metals to humic substances. Therefore, metal complexation with bisulfide could be the reason for incomplete removal of iron, lead, and nickel. The optimal sulfide concentration could be investigated in future studies.

Besides iron, nickel, and lead, other heavy metals including copper and zinc were also measured at steady state for Stage 1 and 2. Copper was rarely removed in Stage 1 (4%) and Stage 2 (6%). The removal efficiency of zinc in Stage 2 (85%) was higher than that of Stage 1 (62%). Heavy metal removal efficiencies are summarized in Table 13.

Table 13. Heavy metal removal efficiency at steady state of Stage 1 and Stage 2.

Heavy metal	Stage 1	Stage 2
Copper	4%	6%
Iron	90%	95%
Lead	3%	10%
Nickel	13%	24%
Zinc	62%	85%

To evaluate the metal sulfides separation and recovery potential, the solids in the reactor at steady state of Stage 1 were first assayed using SEM-EDX. Two types of precipitates were identified in the reactor by SEM-EDX (Figure 15). The first type was iron sulfide (Figure 15b and d). The overlap of iron and sulfur in element mapping clearly indicated the formation of iron sulfide precipitates (Figure 16). However, iron sulfides have various forms such as mackinawite, pyrrihotite, pyrite, and amorphous forms, which are different from each other in terms of morphological and chemical characteristics. The results from Raman spectroscopy was used to identify the predominant form of iron sulfide precipitate. The second type of precipitate was calcium carbonate (Figure 15a and c). The precipitation of calcium carbonate in the reactor was probably due to the high concentrations of dissolved calcium and DIC. Most calcium carbonate was clustered with organic matter. One of the most possible reasons was that the landfill leachate used in the experiment was abundant in organic matter, which could provide nucleation sites for crystallization of mineral (Liu et al., 2015). Thus, all identified iron sulfide and calcium carbonate precipitates were mixed with organic matter and the two types of precipitates were sometimes mixed.

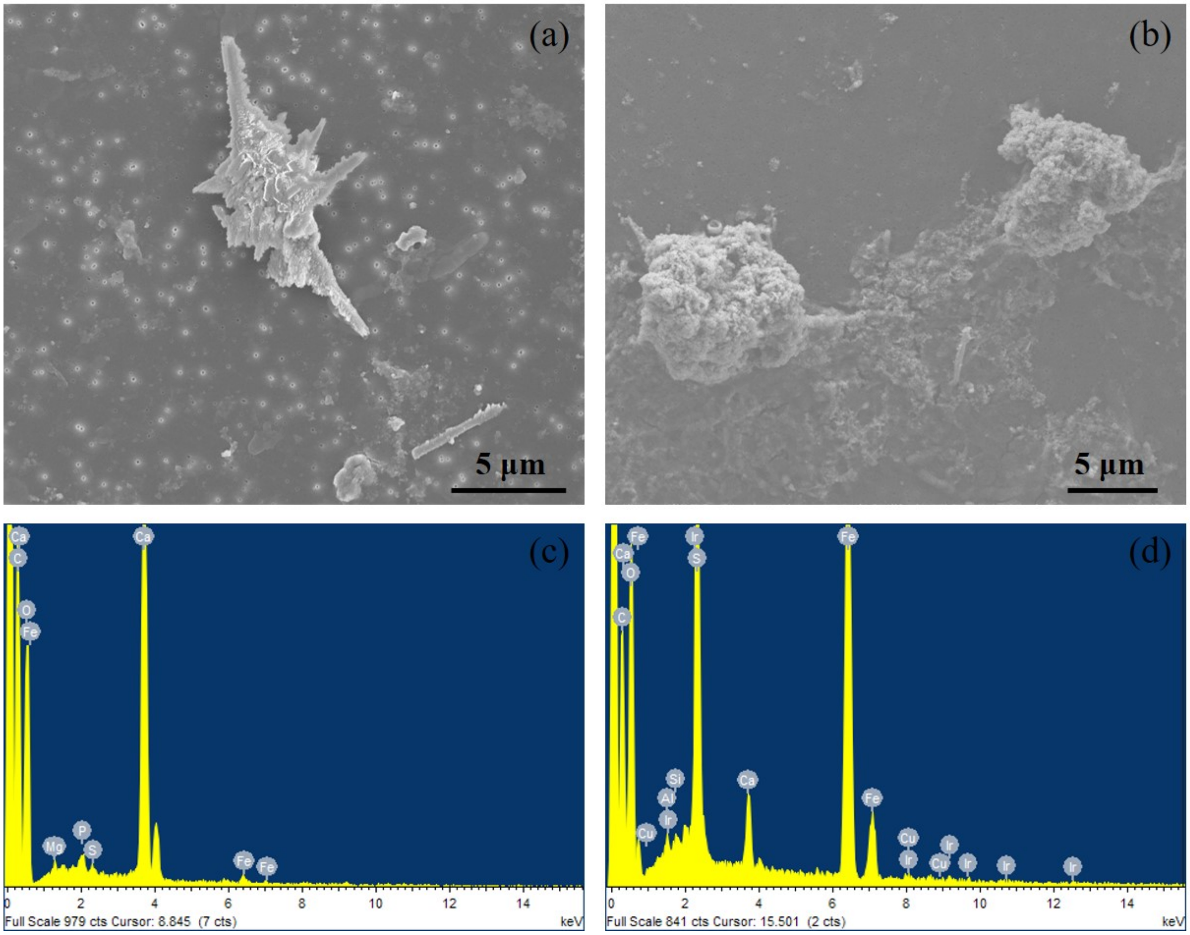


Figure 15. SEM-EDX results of the solids in the reactor: (a) Type 2 precipitate SEM; (b) Type 1 precipitate SEM; (c) Type 2 precipitate EDX; (d) Type 1 precipitate EDX.

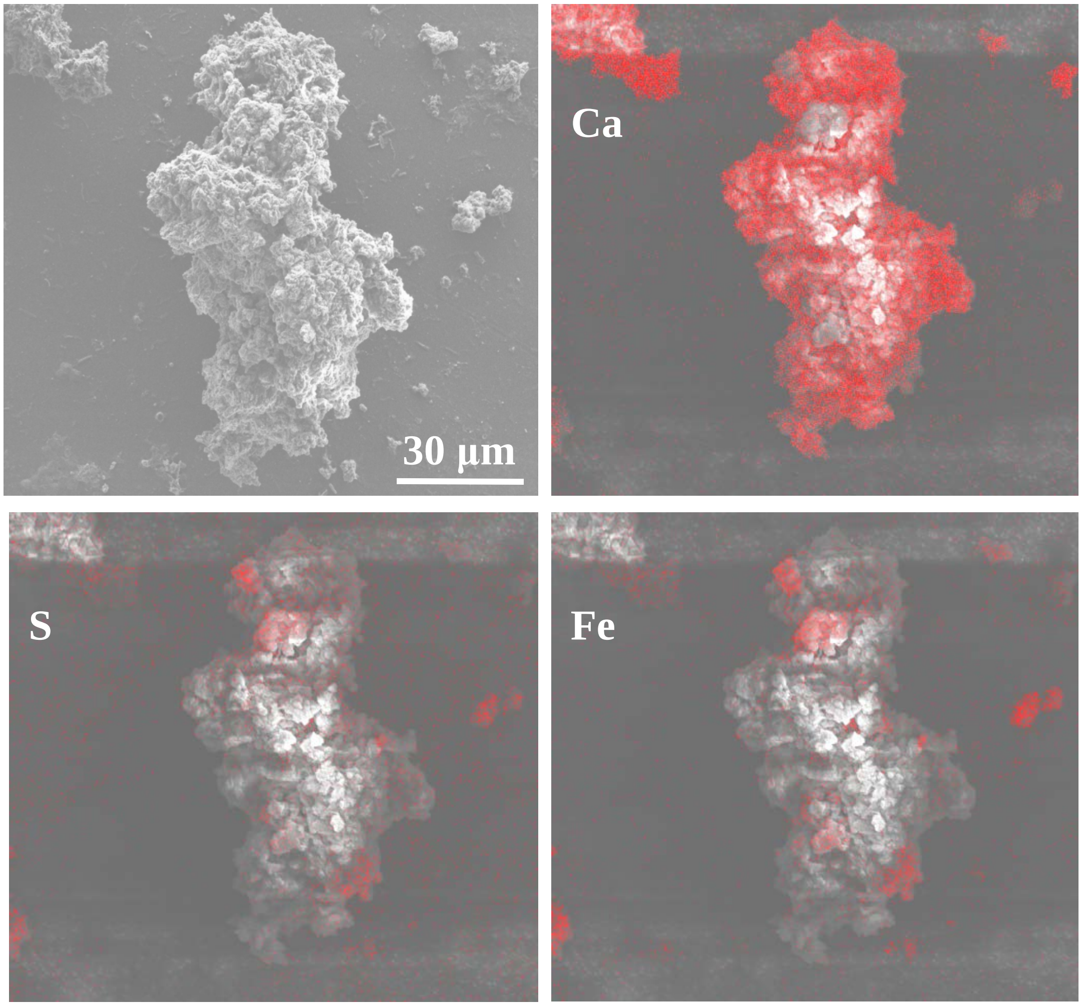


Figure 16. SEM-EDX mapping results of the solids in the reactor.

Raman spectroscopy was used to further determine the crystal structure of the two types of precipitates in the reactor (Figure 17). Ten major peaks were observed for the solid sample in the reactor. Peaks over 500 cm^{-1} were all assigned for aragonite (a $CaCO_3$ mineral) and organic matter. Peaks around 1435 cm^{-1}, 1335 cm^{-1}, and 1085 cm^{-1} were identified as the typical vibration modes of aragonite (Kontoyannis and Vagenas 2000; Nehrke, et al. 2012), and the other three peaks over 500 cm^{-1} corresponded to organic bonds (Chen and Lord 1976; Ivleva et al. 2009; Wagner, et al. 2009). The peaks around 200 cm^{-1} and 271 cm^{-1} corresponded to asymmetric and symmetric Fe-S vibration modes of amorphous iron sulfide (Matamoros-Veloza et al., 2018) (Figure 17). The other two peaks around 148 cm^{-1} and 329 cm^{-1} could be assigned to different polysulfide species. The peak around 124 cm^{-1} corresponded to minerals containing ferric iron, which might be a result of mineral oxidation during sampling, pretreatment, and measurement. High content of organic matter in the landfill leachate led to expected high background intensity, because of the inherent fluorescence generated by many biological molecules (Lieber and Mahadevan-Jansen, 2003). In summary, the Raman spectroscopy confirmed the presence of aragonite and amorphous iron sulfide, a poorly crystallized precursor for other stable iron sulfides. Other metal sulfides were not detected by either SEM-EDX or Raman spectroscopy, probably because their amount was below the detection limit of the equipment used.

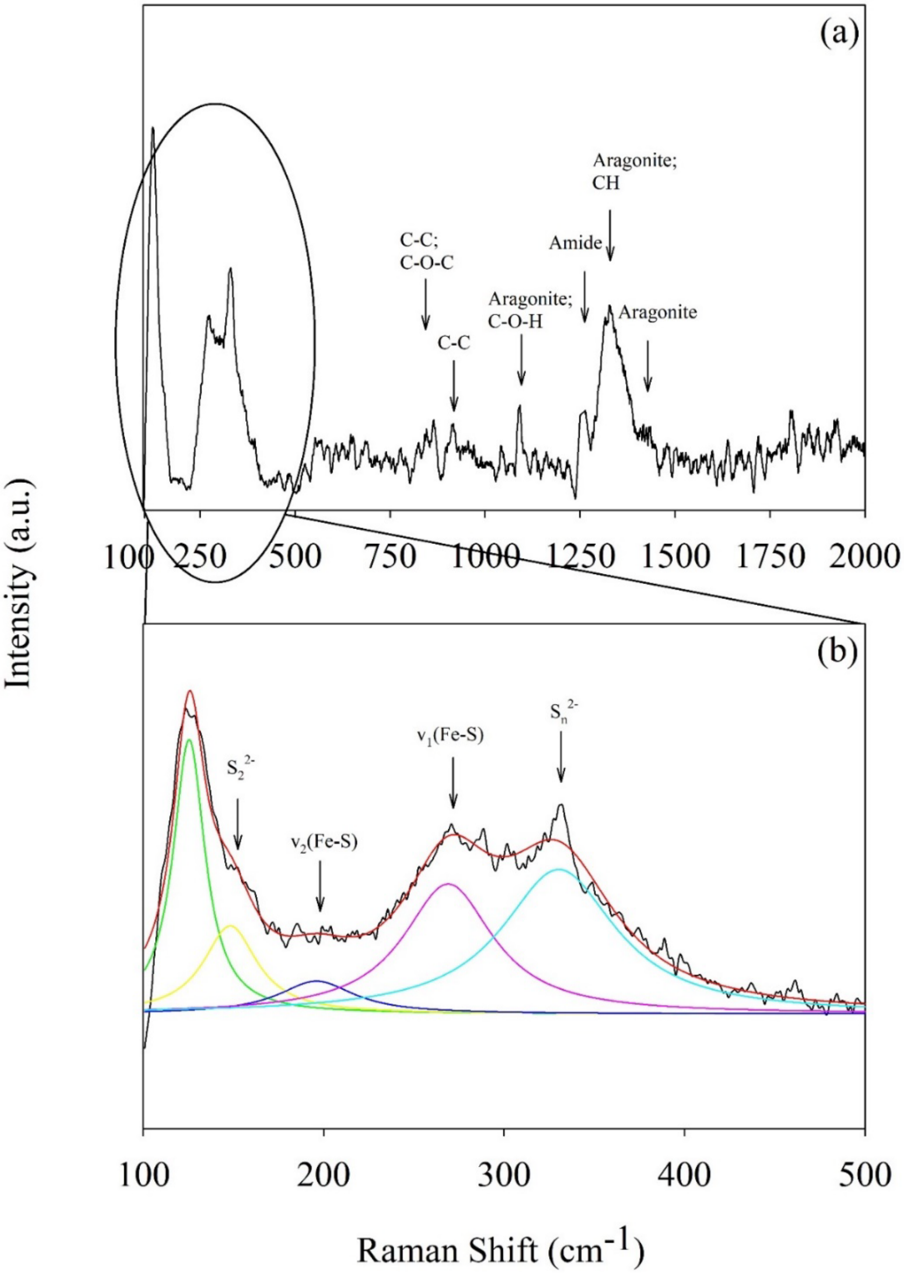


Figure 17. Raman Spectroscopy of the solids in the reactor: (a) Raman spectra over the full range (100 cm^{-1} to 2000 cm^{-1}), (b) Raman spectra in the range of 100 cm^{-1} to 500 cm^{-1}.

3.4 Results for Task 4: dissolved metal speciation modeling

To further understand the fate of the investigated heavy metals in the reactor, the dissolved metal speciation in the reactor influent and effluent at both Stage 1 and Stage 2 were simulated using VISUAL MINTEQ. Both the influent and effluent at steady state were simulated. The model input is summarized in Table 14.

Table 14. Input for the metal speciation models.

Parameter (units)	Stage 1		Stage 2	
	Influent	Effluent	Influent	Effluent
	Total dissolved metal			
Aluminum (mg Al/L)	3.78	3.95	3.10	3.00
Copper (mg Cu/L)	0.524	0.505	0.651	0.620
Iron (mg Fe/L)	148	19.1	135.5	9.9
Lead (mg Pb/L)	1.90	1.84	1.89	1.70
Nickel (mg Ni/L)	0.249	0.229	0.227	0.224
Zinc (mg Zn/L)	1.66	0.63	1.86	0.28
Calcium (mg Ca/L)	500	240	586	110
Magnesium (mg Mg/L)	212	200	197	191
Sodium (mg Na/L)	3300	3060	3280	3290
Potassium (mg K/L)	1090	1010	1130	1160
	Parameters other than metal species			
pH	7.60	7.74	7.78	7.90
Acetate (mg C/L)	2317	54.5	2656	147.7
Sulfate (mg S/L)	115	< 0.02	221	12
Sulfide (mg S/L)	< 0.1	6.0	< 0.1	52.2
HA (mg C/L)	1595	1492	1407	1366
FA (mg C/L)	3098	1806	3228	1765
Redox Potential (mV)	54	-335	57	-390
DIC (mg C/L)	788	2307	1469	1638

At Stage 1, the iron, nickel, and lead speciation modeling results are summarized in Figure 18 and compared to the measured metal species concentrations in Table 15. The model and experiments' results were generally consistent for the free metals and metal complexes.

Table 15. Dissolved metal speciation comparison between the model output and the experimental data in Stage 1.

Species	Influent		Effluent	
	Model	Experiment	Model	Experiment
Complex Fe (mg Fe/L)	139	133	15.9	17.0
Free Fe (mg Fe/L)	3.52	9.50	3.15	2.10
Complex Ni (mg Ni/L)	0.244	0.234	0.226	0.207
Free Ni (mg Ni/L)	4.26 E-3	1.48 E-2	2.16 E-3	2.20 E-2
Complex Pb (mg Pb/L)	1.90	1.90	1.84	1.75
Free Pb (mg Pb/L)	7.00 E-6	0	1.43 E-50	9.60 E-2

The dissolved metal speciation in reactor effluent mainly differed from the influent in two ways (Figure 18). First, Fe (III) existed in the influent (accounting for 10% of the total dissolved Fe) mainly in the form of Fe (III)-FA complex and Fe (III)-HA complex, but almost completely disappeared in the effluent. The main causes were 1) the conversion of FA to products like acetate and CH_4, which released Fe (III) as free Fe (III) and 2) the more reducing environment in the reactor (*i.e.*, lower redox potential in Table 14) reduced Fe (III) to Fe (II). Second, there was a higher concentration of Fe (II) complexed with FA than HA in the influent due to the higher FA concentration and stronger acid sites in FA; however, the concentration of Fe (II) complexed with FA decreased because of the removal of FA.

VISUAL MINTEQ results also included saturation index of 27 Fe-containing minerals, 24 Pb-containing minerals, 9 Ni-containing minerals, and 65 minerals containing other metals for both the influent and the effluent. Out of these minerals, 13 were summarized in Table 16 since their saturation index was positive in the influent, effluent, or both. The 13 minerals included 7 Fe-containing minerals, 1 Zn-containing mineral, 1 Cu-containing mineral, 3 Ni-containing minerals, and 1 Pb-containing mineral.

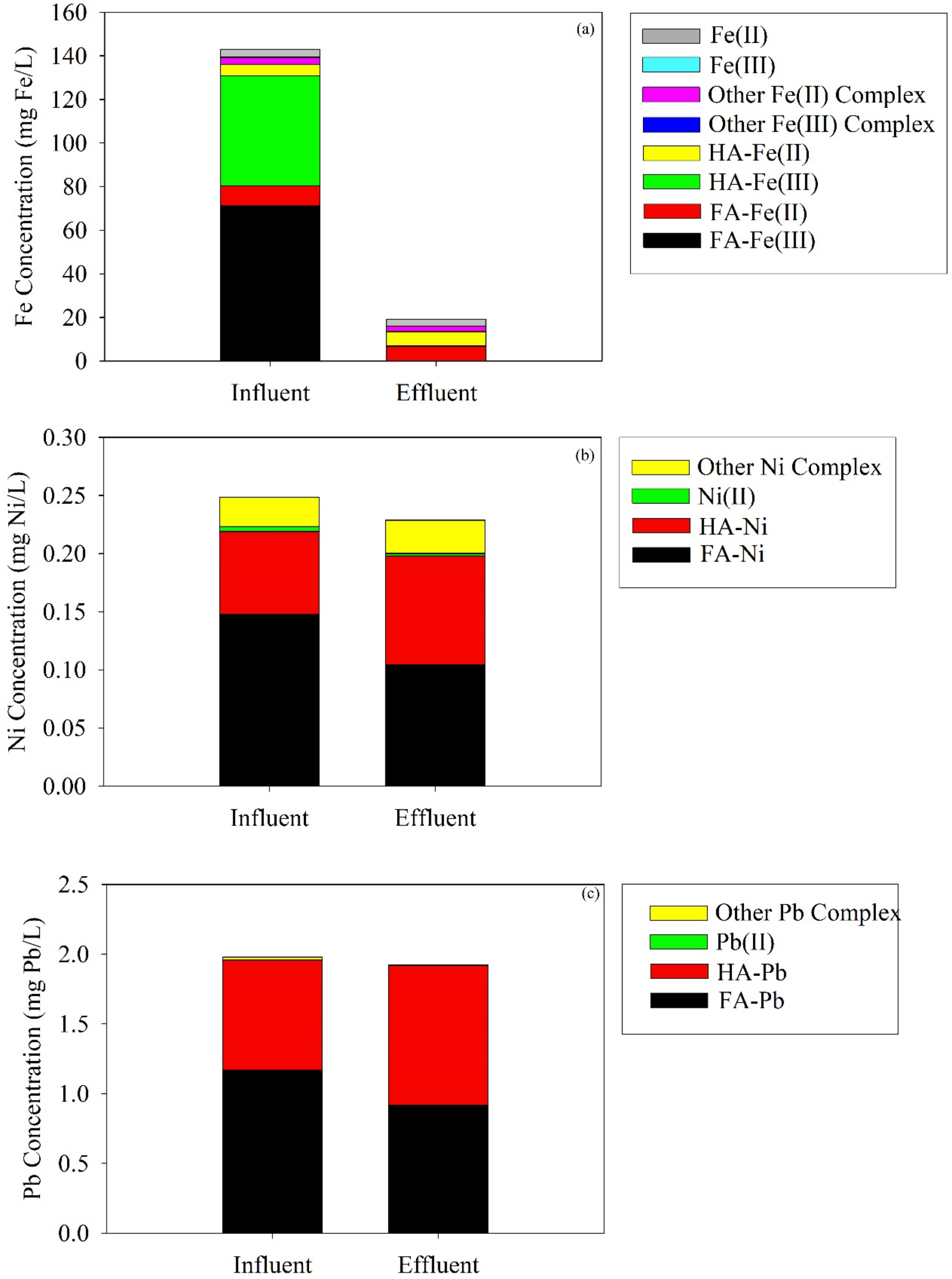


Figure 18. Modeled Fe, Pb and Ni speciation in the reactor influent and effluent at steady state of Stage 1: (a) Iron, (b) Nickel, and (c) Lead.

Note: Other heavy metal complex means the metal that complexes with sulfide, chloride, ammonia, and bicarbonate et al.

Table 16. Minerals that might precipitate in the reactor influent or effluent due to positive saturation index.

Mineral	Chemical formula	Saturation index			
		Stage 1		Stage 2	
		Influent	Effluent	Influent	Effluent
Hematite	Fe_2O_3	13.3	0.8	13.8	-3.4
Magnetite	Fe_3O_4	18.9	6.6	19.5	1.1
Siderite	$FeCO_3$	1.7	2.3	1.9	0.6
Amorphous Iron Sulfide	FeS	-39.4	0.5	-41.3	1.3
Covellite	CuS	-25.8	12.0	-27.5	13.3
Mackinawite	FeS	-38.8	1.1	-40.6	2.0
Greigite	Fe_3S_4	-144	2.6	-151	5.8
Pirrite	FeS_2	-59.7	7.1	-63.1	8.6
Spharelite	ZnS	-33.6	3.9	-35.2	5.0
Galena	PbS	-32.5	6.1	-34.2	5.5
NiS (alpha)	NiS	-39.8	0.5	-41.4	2.0
NiS (beta)	NiS	-34.3	5.4	-35.9	7.5
NiS (gamma)	NiS	-32.6	7.1	-34.2	9.2

In Stage 2, the dissolved speciation of iron, nickel, and lead at steady state were also simulated (Figure 19). The modeling results suggested that the majority of the dissolved iron, nickel, and lead in the influent were in the form of metal complex. While in the effluent, the dissolved iron, nickel, and lead mainly existed as complexes with bisulfide. Compared to Stage 1, more dissolved total sulfides (*i.e.*, H_2S (aq), HS^-, and S^{2-}) were detected in the reactor effluent of Stage 2, while concentrations of other major anions remained unchanged. The simulation results showed that the majority of the metals in the effluent existed as soluble metal complexes, but the major complexing agent changed from HA and FA to bisulfite. Control of the rate of sulfate reduction, hence the ratio between sulfide and heavy metals, should be critical to promote heavy metal precipitation.

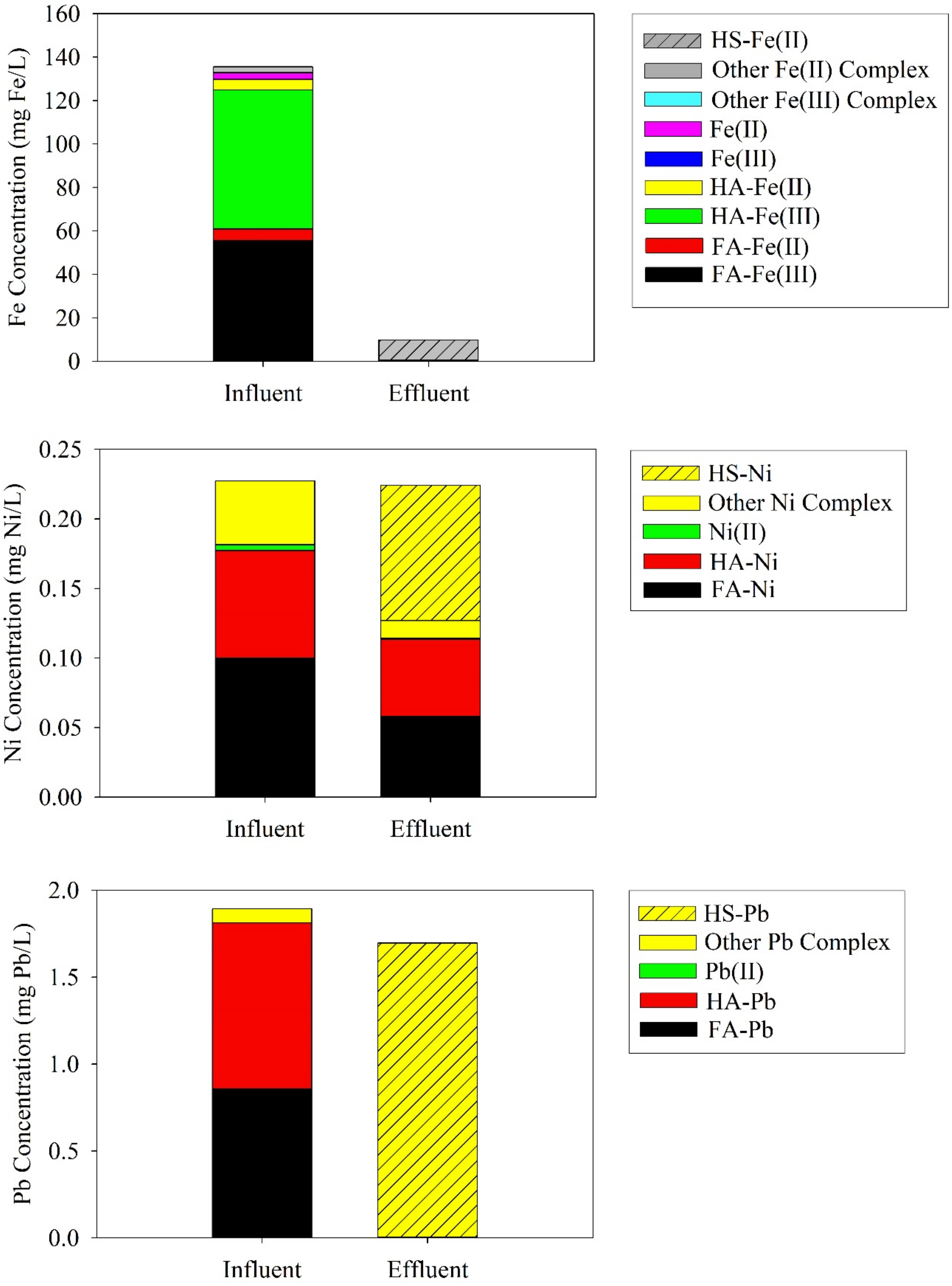


Figure 19. Modeled Fe, Pb and Ni speciation in the reactor influent and effluent at steady state of Stage 2: (a) Iron, (b) Nickel, and (c) Lead.

Note: HS-Metal means the metal that complexes with bisulfide. Other heavy metal complex means the metal that complexes with chloride, ammonia, and bicarbonate et al.

3.5 Results for Task 5: nitrogen fate analysis

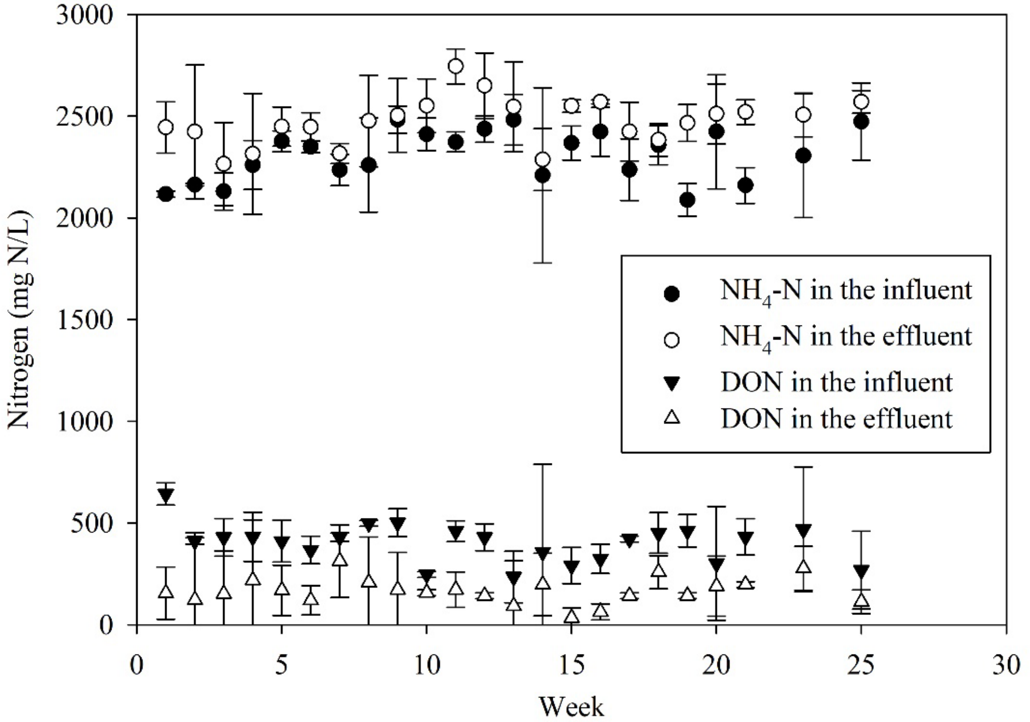


Figure 20. Change of ammonium and DON in the submerged anaerobic biological reactor.

The change of nitrogen in the pretreatment of landfill leachate was investigated at Stage 1. The ammonium concentration in the effluent was always higher than that in the influent, suggesting the degradation of nitrogen containing compounds (*i.e.*, proteins, urea, and nucleic acid) through processes such as hydrolysis, acidogenesis, and acetogenesis (Figure 20). Nitrite was less than 0.033 mg N/L (the quantification limit) in the reactor influent and effluent through the pretreatment. Nitrate was less than 8 mg N/L in the reactor influent in the first three weeks, and it became less than 0.017 mg N/L (the quantification limit) in both the influent and effluent after the first three weeks. Through the pretreatment, DON was reduced from 403 mg N/L in the influent (average of DON in the influent from Week 1 to Week 25) to 165 mg N/L in the effluent (average of DON in the effluent from Week 1 to Week 25), contributing to the production of ammonium, which increased from 2310 mg N/L in the influent to 2475 mg N/L in the effluent. This is consistent with that reported in the literature (Sanchez et al., 2000). Sanchez (2000) has reported the degradation of organic nitrogen to ammonia nitrogen in the anaerobic digestion of cattle manure.

To further understand the conversion of DON in the pretreatment of landfill leachate, bDON and rDON were measured at the weeks that represented significant changes in the reactor at Stage 1. Nitrogen speciation in the representative weeks is shown in Figure 21 and the nitrogen recovery at all studied weeks ranged from 91-103%. Nitrogen recovery is defined as the percentage of total nitrogen in the effluent over the total nitrogen in the influent. After the pretreatment, the majority of the rDON was converted to bDON and ammonium (Figure 21). At Week 5, 53% of the rDON was converted to ammonium, bDON or both. More than 90% of the rDON was removed since Week 10 and 98% of the rDON in the leachate was removed when reaching steady state. DON such as free amino acids can be bioavailable to algal uptake directly or become bioavailable after hydrolysis (Simsek et al., 2013), while the rDON is believed to be mainly comprised of heterocyclic compounds (Almendros et al., 2003). The ammonification of the recalcitrant organic nitrogen during the anaerobic digestion process is also reported in Delée et al. (1998).

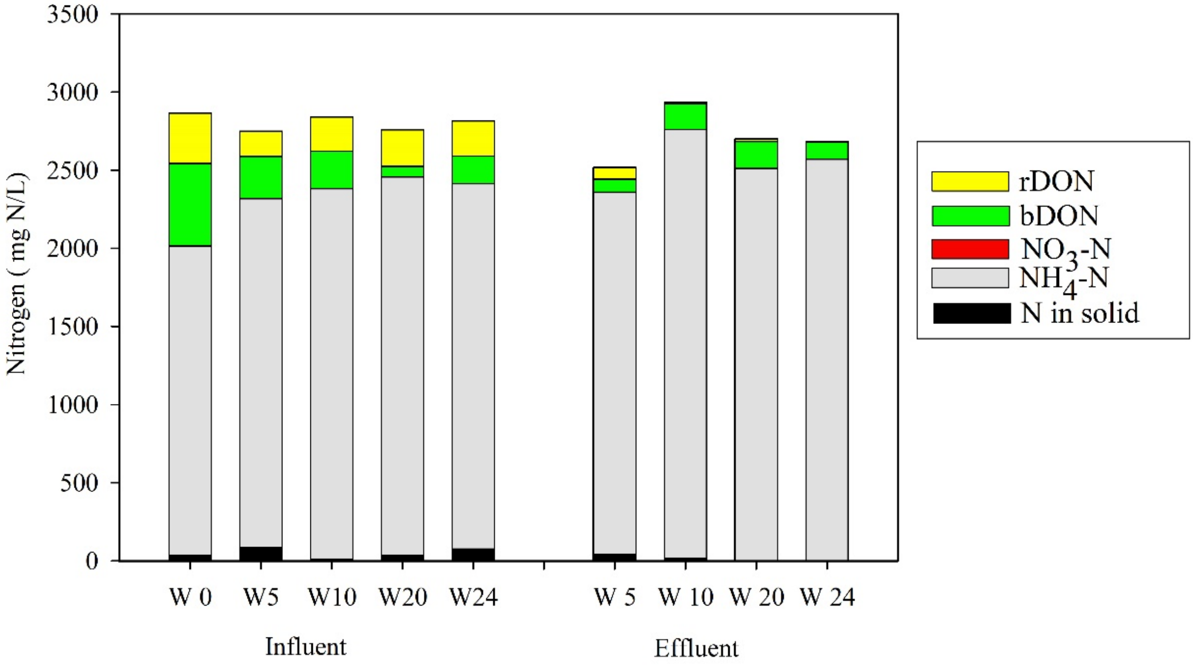


Figure 21. Nitrogen distribution in the submerged anaerobic biological reactor.

Although most rDON was converted to bDON and ammonium, some rDON (5-76 mg N/L based on Figure 21) still existed in the effluent as persistent rDON. To evaluate the rDON concentration from humic substances, we did the following calculation. Assuming the average mass ratio of carbon to nitrogen in HA (24:1) and FA (50:1) (Bronk et al., 2007), the nitrogen in the HA and FA in the influent were around 62 mg N/L (= 1496/24, 1496 is the average carbon concentration in the HA in the influent) and 63 mg N/L (= 3146/50, 3146 is the average carbon concentration in the FA in the influent), respectively. The ratio of bDON to rDON in humic substances has not been investigated, but it was reported that bioavailable nitrogen including amino acids, amino sugars, ammonium, and nucleic acids account for 46-53 % of the nitrogen in HA and 45-59 % of the nitrogen in FA (Bronk et al., 2007). Assuming the rDON contents are 50% and 48% in HA and FA, we estimated that the rDON in the HA and FA of the influent were around 31 mg N/L (= 62 × 50%) and 30 mg N/L (= 63 × 48%), respectively. These recalcitrant nitrogen might become bDON in the effluent when the HA and FA transformed. Swift and Posner (1972) find the decrease of nitrogen content with the decrease of the HA molecular weight. The change of DON and ammonium nitrogen after the treatment (Figure 22) shows that the rDON in the effluent were probably from the FA and HA in the influent.

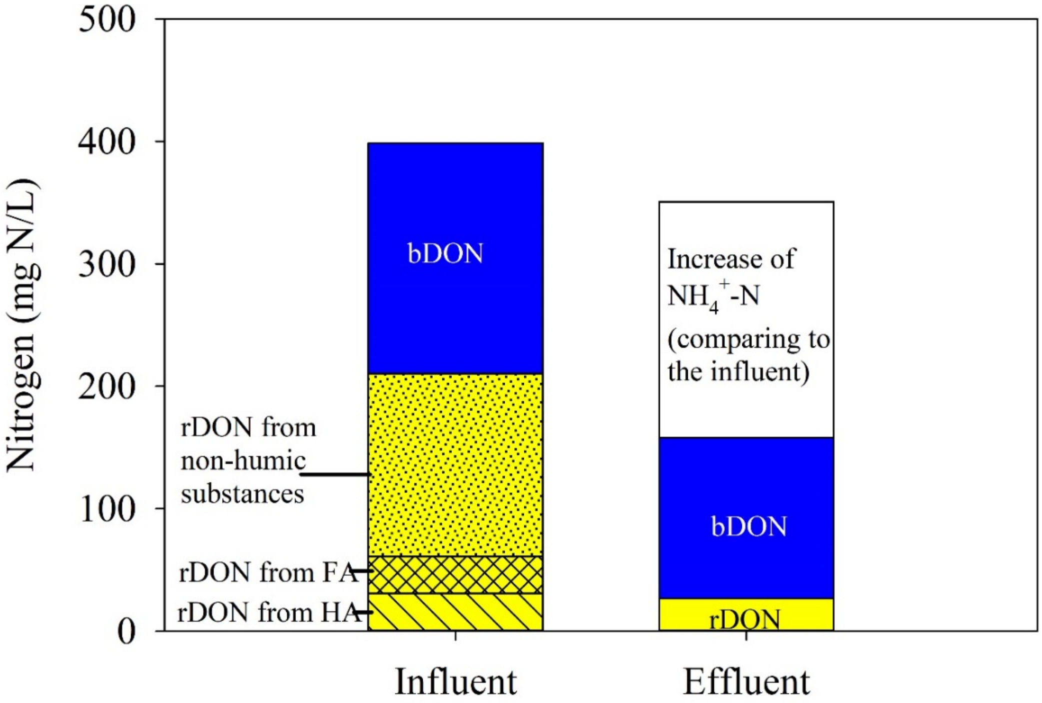


Figure 22. Change of bDON, rDON and NH_4^+-N (average concentrations) from the influent to the effluent.

3.6 Results for Task 6: metal sulfides recovery via magnetic separators

Based on the dissolved metal speciation modeling results and reactor precipitate analysis results, the possible forms of metals in the reactor are summarized in Table 17. We expected that greigite, amorphous iron sulfide, mackinawite, and millerite would be separated from the precipitate when the magnetic flux density increased to 5 T. As expected, iron was the major metal in the separated metals (Figure 23).

Table 17. Magnetic susceptibility and electrostatic resistivity of possible metal sulfides in the reactor.

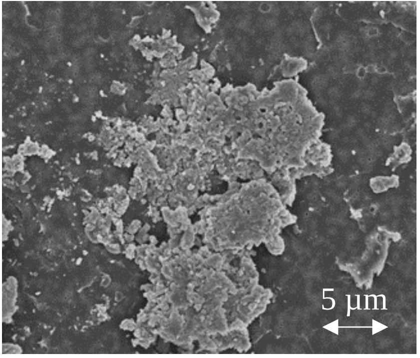
Possible metal sulfides	**Positive saturation index**	**Observed metal sulfides**	**Magnetic response**		**Electrostatic resistivity (ohm)**
			Magnetic property	**Magnetic susceptibility ($\times10^{-6}$cm^3/mole)**	
Covellite (CuS)	×		NM[1]	-2	10^{-7} to 10^{-3}
Amorphous Iron Sulfide (FeS)	×	×	P[2]	NA[4]	NA
Galena (PbS)	×		NM	-84	6.8×10^{-6} to 17.5
Greigite (Fe_3S_4)	×		F[3]	NA	NA
Mackinawite (FeS)	×		P	NA	NA
Millerite (NiS)	×		P	700	3×10^{-7}
Pyrite (FeS_2)	×		NM	NA	10^{-3} to 10^{4}
Spharelite (ZnS)	×		NM	-25	2.7×10^{-3} to 10^{12}

Notes:

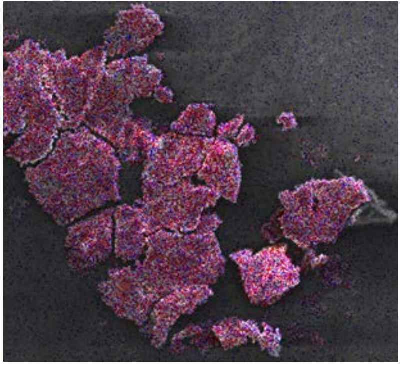
1. NM: Non-magnetic;
2. P: Paramagnetic;
3. F: Ferromagnetic;
4. NA: Not available.

Reference: Pearce et al. (2006).

a) Metals separated from the precipitate in the anaerobic biological reactor



b) An SEM image of the separated metals



c) Composition of the separated metals (The red color represents iron.)

Figure 23. Metals separated from the reactor.

4. CONCLUSIONS

We designed a lab-scale submerged anaerobic biological reactor to pretreat landfill leachate. The reactor was a closed plastic column with an inner diameter of 4 cm and a height of 7.2 cm, and operated at the room temperature and a HRT of 4.5 days. We sampled and characterized four landfill leachates in Florida and pretreated one municipal solid waste (MSW) landfill leachate (MSW-1) that had the highest concentrations of heavy metals (*i.e.*, 290 mg total Fe/L, 0.299 mg total Ni/L, and 1.98 mg total Pb/L) and total nitrogen (*i.e.*, TN = 2870mg N/L). We focused the research on iron, nickel, and lead since they violated local discharge to sewer standards. The TN in the MSW-1 leachate could contribute to 38.7% of the TN in a wastewater treatment plant (WWTP) assuming a mixing ratio of leachate to municipal wastewater of 1:99 (volume ratio) and a typical TN concentration of 46.0 mg N/L in the wastewater. The dominant nitrogen species in the MSW-1 leachate were ammonium and dissolved organic nitrogen (DON). Bioavailable DON (bDON) and recalcitrant DON (rDON) in the MSW-1 leachate were 62% and 38%, respectively. The dissolved organic carbon (DOC) in MSW-1 leachate was 7880 mg C/L, which was comprised of acetate-C (23%), Humic acid-C (18%), Fulvic acid-C (32%), and the other carbon (27%).

After 25 weeks pretreatment, the reactor reached steady state of Stage 1. The chemical oxygen demand (COD) and DOC removal efficiency reached 54.6% and 52.8%, respectively. CH_4 concentration reached 1606 mg C/L effluent (*i.e.*, total produced CH_4 mass divided by the leachate volume) and the CH_4 reached 85% of the biogas (by volume). 90% of total iron, 13% of total nickel, and 3% of total lead were removed at steady state. The solid analysis suggested that the main metal sulfide in the reactor was amorphous FeS. Dissolved metal speciation modeling and the experiments suggested that the majority of metals existed as metal complexes in both the raw and treated leachate. To promote heavy metal removal, we added sulfate (120 mg S/L, the same as the sulfate concentration in the raw leachate) to the reactor influent in Stage 2. When reaching the steady state of Stage 2, the removal of heavy metals increased: total iron from 90% to 95%, total nickel from 10% to 24%, and total lead from 3% to 10%. While iron and nickel in the reactor effluent met the local discharge to sewer standards, lead still violated the standards. Further modeling analysis suggested that the major cause of incomplete heavy metal removal was metal complexation with bisulfide. We separated metal sulfides in the reactor via a lab-scale cryo-high gradient magnetic separator (cryo-HGMS). The major metal separated was iron.

The reactor converted more than 90% rDON (~210 mg N/L) to ammonium and bDON, both of which could be removed when the leachate reached a tertiary WWTP. The ammonium concentration in the reactor effluent increased by ~165 mg N/L compared to the influent, and the bDON decreased from 189 mg N/L in the influent to 132 mg N/L in the effluent, suggesting that some bDON was also converted to ammonium.

The submerged anaerobic biological reactor was able to remove most heavy metals from the landfill leachate and convert most rDON to bDON and ammonium; therefore, it may replace the oxidation pond (wetland) if heavy metals and rDON in the leachate are the major concerns. The metal removal efficiency seems to be low for copper and lead, but high for other metals. The sulfate to metal ratio in the leachate should also be considered when using this treatment method and the optimal sulfide concentration for the heavy metal removal could be determined in future research. Too much sulfate would result in the production of hydrogen sulfide, a major cause of landfill odor.

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