Project title: Prevention of harmful algal blooms through nutrient zero wastewater treatment using a vertical membrane bioreactor with food waste
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1. Problem and Research Objectives

Eutrophication is a key driver causing a number of pressing environmental problems including reductions in light penetration and increases in harmful algal blooms (HABs) [1].The major factors affecting eutrophication are mineral nutrients such as nitrogen and phosphorus in municipal and industrial wastewater [2].

In Ohio's lakes and rivers, the key symptom of eutrophication is cyanobacterial blooms [3]. The increasing occurrence of HABs in fresh water due to eutrophication of surface water has become an emerging concern threatening human and environmental health because cyanobacteria, more commonly known as blue-green algae, can produce and release potent toxic compounds, known as cyanotoxins, in sources of drinking water supply [4-7].

In 1931, the first observations of adverse health effects from exposure to cyanotoxins were reported in Ohio, affecting thousands of people [8]. After that, HABs have been a major issue in Ohio. More recently (August 2014), Lake Erie encountered again a huge formation of blue-green algae producing harmful cyanotoxins. A stream of this algal bloom, which included high level of microcystins (MCs), has found its way to the Toledo's water treatment plant pipes. This required the city of Toledo to issue a "Do Not Use the Water" warning to about half million citizens [9].

In nutrient-sensitive estuaries, municipal and industrial water resource recovery facilities (WRRFs) are required to implement more advanced treatment methods in order to meet increasingly stringent effluent guidelines for nutrients. According to literature, biological nutrient removal (BNR) processes that incorporate coupled nitrification/denitrification have the potential to remove total nitrogen (TN) down to about 5 ~ 12 mg/L, in selected cases, down to 3 mg/L. The TN concentration in effluent is known as less than 10 mg/L at most inland municipal WRRFs.

In BNR processes, phosphorus removal efficiencies are very sensitive to both quantity and characteristics (especially biodegradability) of organic source as poly-P accumulating organisms (PAOs) and denitrifying microorganisms require organic matter for phosphorus release and denitrification [10]. According to the literature, approximately 5 ~ 10 mg and 8 mg of biochemical oxygen demand (BOD) are required to remove 1 mg of each nitrate nitrogen (NO_3-N) and phosphorus, respectively [11, 12].

However, most municipal wastewater (MWW) in the U.S. has insufficient BOD content for effective nutrient removal [13]. For example, in a preliminary analysis, it was found that concentration of biodegradable organic matter in MWW entering the Mill Creek WRRF in Cincinnati (Ohio) is limited at 95.1 mg/L as BOD, but theoretically minimum 150.6 mg/L of BOD is required for complete removal of 25 mg/L TN and 3.2 mg/L TP (*data not shown*). To enhance BNR efficiency, it is necessary to provide external carbon sources such as methanol, ethanol, and acetic acid but it increases overall treatment costs of WRRFs.

On the other hand, over 250 million tons of wastes (35.2% paper, 12.1% yard trimmings, 11.7% food scraps, 11.3% plastics, 8.0% metals, etc.) generated each year in the United States. The top two portions (*i.e.*, paper and yard waste) of the U.S. waste stream have been successfully diverted from landfills through recycling and composting efforts, with recovery rates of 50 percent and 62 percent, respectively. Paling in comparison, the food scrap recovery rate is less than 3% [14].

According to the Ohio Department of Natural Resources (ODNR), food waste (FW) comprises 15% of Ohio's valuable landfill space, but FWs negatively affect the domestic landfills because of their high leachate [15]. FW could be burned with other combustible domestic wastes for energy production. Production of dioxins is one of the main hazards associated with this process [16]. FW also can easily be reused as organic resources in the form of animal feed or compost. However, one problem associated with composting of organic-rich wastes is the production of odor (mainly ammonia) and large quantities of leachate [17]. Therefore, there is a *critical need* in developing engineering solutions for prevention of HABs and sustainable recycling of FW.

Due to the continuously increasing occurrence of HABs in Ohio's lakes and rivers and the inefficient or impractical technologies for the elimination of nutrients such as nitrogen and phosphorus, there is a critical need to develop an effective solution for a satisfactory removal of nutrients (especially phosphorus) from wastewater sources in order to achieve clean and safe drinking water supplies and protect human health.

The main objective of this project is to develop and optimize an engineering process for the efficient removal of nutrients from municipal wastewater (MWW). A bench-scale vertical membrane bioreactor (VMBR) was optimized for simultaneous removal of nitrogen and phosphorus with soluble organic compounds, which will be produced from FW using an ultrasound-assisted anaerobic fermenter for enhanced phosphorus removal. Through this project, we expect to have developed and optimized engineering solutions for the treatment of MWW and FW to prevent HABs.

2. Methodology

2.1 Anaerobic fermentation of food waste with ultrasound

The main component of FW is cellulosic organic compounds such as cellulose, lignin, hemicelluloses, and starch, while the remaining small parts are lipids, proteins, and inorganic [18]. In a preliminary test, FW (chemical oxygen demand, COD = 121.7 g/L) from campus dining halls at the University of Cincinnati (UC) was converted to CFW in an anaerobic fermenter operated at 35 ^{o}C and 12 hr hydraulic retention time (HRT) at pH 5~5.5. **Figure 1** shows a process flow diagram of the anaerobic fermentation system for production of condensate of FW (CFW).

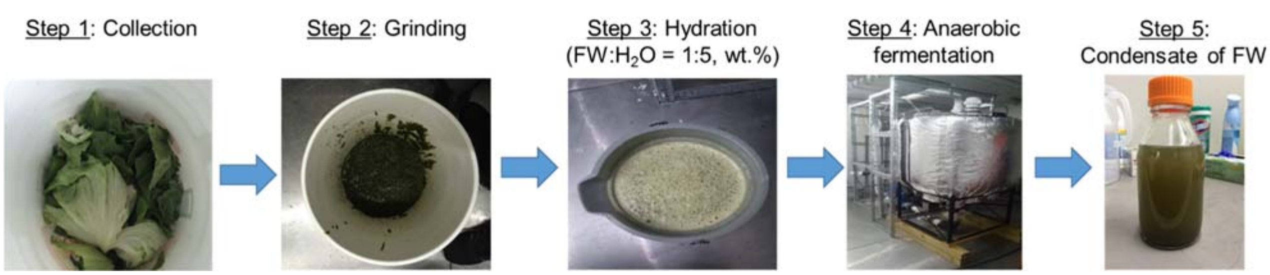

Figure 1. Schematic diagram of an anaerobic fermentation process for production of CFW.

Table 1 summarizes some of the key parameters associated with the CFW, which contains high concentration of VFAs (> 9,000 mg/L as COD) that is composed of 1.5% lactic acid, 80% acetic acid, 10% propionic acid, and 8.5% butyric acid, which could be effectively used as carbon sources for nutrient removal in BNR processes. However, the conversion rate of the COD of FW to soluble COD in the CFW is very limited by 17.5% (= 21.3/121.7 x 100%) by the anaerobic fermenter, indicating there is great potential for optimization and upgrade of the anaerobic treatment.

Table 1. Characteristics of the CFW produced from an anaerobic fermenter.

Item	Typical concentration	Unit
Soluble COD	21,300	mg/L
Total solids (TS)	< 10	mg/L
Total nitrogen (TN)	103	mg/L
Total phosphorus (TP)	25	mg/L
VFAs as COD	9,100	mg/L

In this study, we applied an ultrasound to improve conversion efficiency of cellulosic organic compounds in FW into easily biodegradable organic substances (*i.e.*, VFAs or BOD). Ultrasonic irradiation (also known as "Sonication" or "Sonolysis") causes cavitation phenomena leading to the production of free radicals. The phenomenon of cavitation could possibly contribute towards enhancement of the kinetics and yield of the reaction.

Ultrasonic waves produce cavitation bubbles in liquid solution. After several compression cycles, the cavitation bubbles collapse violently and adiabatically with extremely high temperature over 5000 ^{o}C and pressures of 500 atmospheres [19]. As a result, organic compounds present near bubble/water interface can undergo thermal decomposition, and/or secondary reactions take place between solute molecules and the reactive radicals such as $H^{\bullet}$ and $^{\bullet}OH$. The formation of free radicals during ultrasonic irradiation can be explained from the following Eqs. (1) – (3) in the absence of oxygen [20] where ")))" refers to the application of ultrasound:

$$H_2O \xrightarrow{)))} H^{\bullet} + {}^{\bullet}OH \qquad (1)$$

$$H^{\bullet} + {}^{\bullet}OH \rightarrow H_2O \qquad (2)$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \qquad (3)$$

We hypothesize that the combination of ultrasound and anaerobic fermentation will achieve a higher reaction rate and a lower energy input for the destruction of organic compounds in FW than conventional anaerobic fermentation by (i) producing hydroxyl radicals and (ii) promoting decomposition of the reaction intermediate of recalcitrant organic compounds such as cellulose, lignin, and hemicelluloses in FW.

In this study, an ultrasound horn (20 kHz, 450 Digital Sonifier, Branson Ultrasonics, U.S.A) will be directly applied between the Step 3 and the Step 4 shown in **Figure 1** to increase conversion rate of organic compounds in FW to BOD. We evaluated ultrasound duration (*i.e.*, 0, 1, 2, 4, and 8 hr) on the conversion efficiency of total COD to SCOD and VFAs.

2.2 A bench-scale vertical membrane bioreactor

A bench-scale VMBR (treatment capacity = 10 L/day at HRT = 8 hr) with anoxic and oxic zones in one reactor was operated over 4 months with synthetic wastewater (**Table 2**). To improve nutrient removal efficiency of the bench-scale VMBR, the CFW that was produced from the anaerobic fermenter with 8 hr sonication, was added into influent in Run 2 and Run 3 (**Table 3**).

Table 2. Characteristic of synthetic wastewater.

Item	Chemical formula	Concentration (mg/L)
Glucose	$C_6H_{12}O_6$	150 (as COD)
Ammonium sulfate	$(NH_4)_2SO_4$	30 (as N)
Potassium phosphate	KH_2PO_4	6 (as P)
Sodium bicarbonate	$NaHCO_3$	200 (as $CaCO_3$)
Calcium chloride	$CaCl_2{\cdot}2H_2O$	0.50
Cobalt chloride	$CoCl_2{\cdot}6H_2O$	0.35
Cupric sulfate	$Cu\ SO_4{\cdot}5H_2O$	0.15
Ferric chloride anhydrous	$FeCl_3$	0.80
Magnesium sulfate	$Mg\ SO_4{\cdot}7H_2O$	0.34
Manganese chloride	$MnCl_2{\cdot}4H_2O$	0.50
Sodium molybdate dihydrate	$Na_2MoO_4{\cdot}2H_2O$	0.20
Yeast extract	-	10
Zinc sulfate	$ZnSO_4{\cdot}5H_2O$	0.55

Table 3. Operation conditions of the bench-scale VMBR.

Run	Period	Synthetic wastewater (v/v, %)	CFW with 8 hr sonication (v/v, %)	SCOD concentration in influent (mg/L)
1	1 ~ 60 days	100	0	150.0
2	61 ~ 90 days	99.5	0.5	377.8
3	91 ~ 125 days	99.0	1.0	605.5

2.3 Analysis of membrane fouling

To determine the effects of the CFW on changes in membrane resistance due to membrane fouling, the resistance-in-series model was used to analyze membrane fouling resistances with various CFW mixing ratios (**Table 3**), which describes the permeate flux - transmembrane pressure (TMP) relationship over the entire domain of pressure as described in the previous study [21]. Based on the model, the permeate flux on the applied TMP can be described by Darcy's law as Eq. (4):

$$J_v = \frac{1}{A}\frac{dV}{dt} = \frac{\Delta P}{\mu R_t} \qquad (4)$$

where J_v is the permeate flux ($m^3/m^2/s$), V is the total volume of permeate (m^3), A is the membrane area (m^2), ΔP is the TMP (Pa), μ is the dynamic viscosity of permeate (Pa·s), and R_t is the total membrane resistance (m^{-1}).

2.4 Characterization of food waste and wastewater

Concentrations of various ions such as NO_2-N, NO_3-N, and ortho-P were analyzed using ion chromatography (IC) (Dionex DX-120, U.S.A) after filtering with a 0.45 μm membrane filter (ADVANTEC MFS Inc., Dublin, CA, U.S.A). Temperature and pH were measured using temperature and pH electrodes connected with a pH meter (Orion Model 420A, Orion Research Inc., U.S.A). Concentrations of COD, BOD, total solid (TS), TN, and TP of both FW and CFW were measured according to *Standard Methods* [22]. All experiments of this study were performed at least three times. Analysis of variance (ANOVA) was applied for the statistical analysis and differences from controls was considered significant when $p \leq 0.05$.

3. Principal Findings and Results

3.1 Changes in characteristics of the CFW by ultrasound

Table 4 shows characteristics of CFW that was produced from the anaerobic fermenter. To improve the conversion of organic matter to SCOD, ultrasound has been used between the Step 3 and the Step 4 (**Figure 1**). As sonication time increased from 0 to 8 hr, concentrations of SCOD and VFA in the CFW increased by approximately 115% and 27%, respectively. From these results, it could be concluded that ultrasound was an efficient technology to convert organic matter in FW to soluble organic matter. However, it is required to optimize the anaerobic fermenter to increase production of VFA from the soluble organic matter.

Table 4. Effects of sonication on characteristics of the CFW.

Sonication time (hr)	SCOD concentration (mg/L)	VFA concentration (mg/L)	Change in SCOD	Change in VFA
0	21,300	9,100	-	-
1	22,100	9,236	+ 3.8%	+1.5
2	23,400	9,309	+9.9%	+2.3
4	36,600	10,283	+71.8%	+13.0
8	45,700	11,577	+114.5%	+27.2

3.2 Effects of the CFW on removal efficiency of nutrients and membrane fouling in a bench-scale VMBR

In BNR processes, nutrient removal efficiency highly depends on quantity and characteristics of organic source. However, most MWW contains a low carbon-to-nitrogen (C/N) ratio of less than 5 that is insufficient for nutrient removal. For example, 4.2 g COD/g N was required for total-nitrogen removal, including assimilation, when glucose is the carbon source [23]. Since a part of the COD in a combined nitrification–denitrification process was oxidized by oxygen, the COD/N requirement in practice was higher, with typical values lying in the range of 5 ~ 10 g COD/g N [23].

In our previous study, it was found that when the readily biodegradable COD was depleted, both denitrification and phosphorus removal rates significantly reduced [24]. In this situation, acetic acid and methanol are generally recommended as external carbon sources, but these increase operating cost and could decrease pH of the system [25].

In general, FW has relatively high COD content with high C/N ratio over 20, suggesting its potential for nutrient removal when mixed with influent. In this study, we aimed to improve removal efficiencies of nutrients in the VMBR by supplementing the CFW. As shown in **Figure 2**, typical removal efficiencies of nitrogen and phosphorus by the VMBR with synthetic wastewater were 74% and 55%, respectively. As the SCOD concentration increased from 150 to 605.5 mg/L by adding the CFW, removal efficiencies of nitrogen and phosphorus significantly increased up to 96% and 91%, respectively.

The VMBR showed good performance in removing nutrients from low organic-strength wastewater when the CFW was added as an external carbon source. However, the supplemented CFW increased COD concentration in the effluent (**Figure 2**) and also membrane resistance (**Figure 3**). Therefore, there is a critical need in optimizing the ultrasound and anaerobic fermenter for efficient production of VFAs from SCOD to improve BNR performance and to mitigate membrane fouling in MBR.

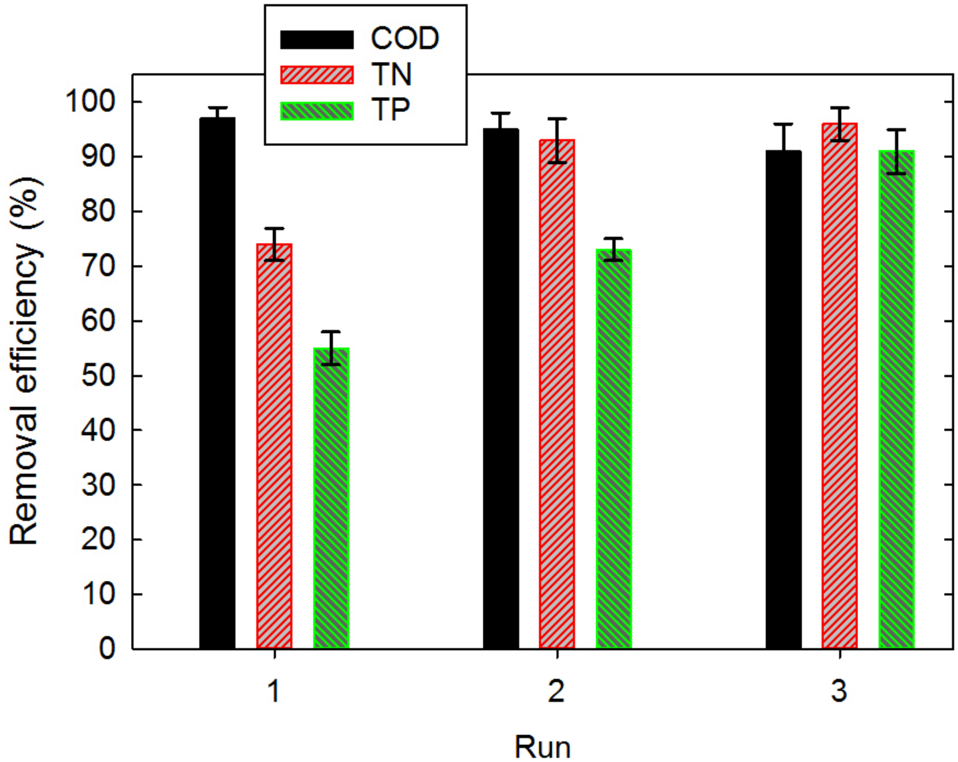

Figure 2. Changes in removal efficiencies of COD, TN and TP during the experimental period.

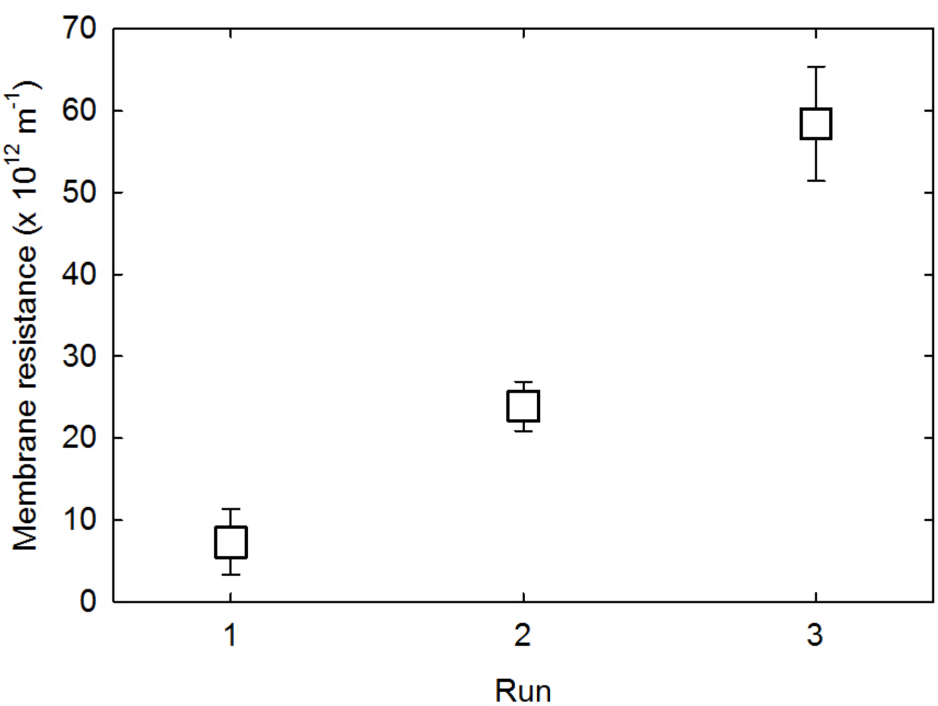

Figure 3. Changes in membrane resistance during the experimental period.

4. Finding Significance

HABs have a significant impact on drinking water quality, fish and animal habitat as well as ecosystem services. The need to reduce anthropogenic nutrient inputs to aquatic ecosystems in order to protect drinking-water supplies and to reduce eutrophication, including the proliferation of HABs and "dead zones" in coastal marine ecosystems has been widely recognized. BNR is one of the most cost-effective treatment technologies for nutrient removal from MWW. However, there is clear a gap in knowledge between the enhanced biological phosphorus removal (EBPR) mechanism and potential applications of renewable carbon sources such as FW for effective nutrient removal. In this study, we report that the VMBR showed good performance in removing nutrients (over 90%) with low organic-strength wastewater when the CFW, which was produced from an anaerobic fermenter with ultrasound, was added as an external carbon source.

The results provide a fundamental understanding of (i) the effects of ultrasound on the fate and conversion of recalcitrant organic compounds in FW, and (ii) the effects of organic matter originated from FW on the EBPR efficiency and membrane fouling in MBR. Such investigations are critical for the development of eco-friendly management of FW and the enhancement of biological phosphorus removal activity in BNR systems to protect watersheds in Ohio from HABs. Also, it will allow for development of novel engineering solutions for the production of easily degradable organic matter that will eventually increase nutrient removal efficiency in BNR systems and also reduce HABs' risks to public health and the environment.

5. Publication citations (all journal articles, proceedings and presentations at conferences)

1) Fangang Meng, Shaoqing Zhang, Yoontaek Oh, Zhongbo Zhou, Hang-Sik Shin, So-Ryong Chae. Fouling in membrane bioreactors: An updated review. Water Research, 114, 151-180, 2017 (http://doi.org/10.1016/j.watres.2017.02.006).
2) So-Ryong Chae. Advances and Challenges in Recycling of High Strength Organic Waste and Wastewater for Clean Water and Energy. The 252th ACS National Meeting and Exposition, Philadelphia, PA, August 21 – 25, 2016.

6. Students Supported - Number and name of students supported by the project (MS/PhD/undergraduate/post docs) as well as their majors

1) Murugesan Brindha, M.S. student, the Environmental Engineering and Science Program, Department of Biomedical, Chemical, and Environmental Engineering, University of Cincinnati.
2) Jiong Gao, Ph.D. student, the Environmental Engineering and Science Program, Department of Biomedical, Chemical, and Environmental Engineering, University of Cincinnati.

7. Profession Placement of Graduates including sector (if known and applicable) and Teaching Assistantship

Not applicable

8. Awards or Achievements (patents, copyrights)

Not applicable

9. Any additional funding for this project

Not applicable

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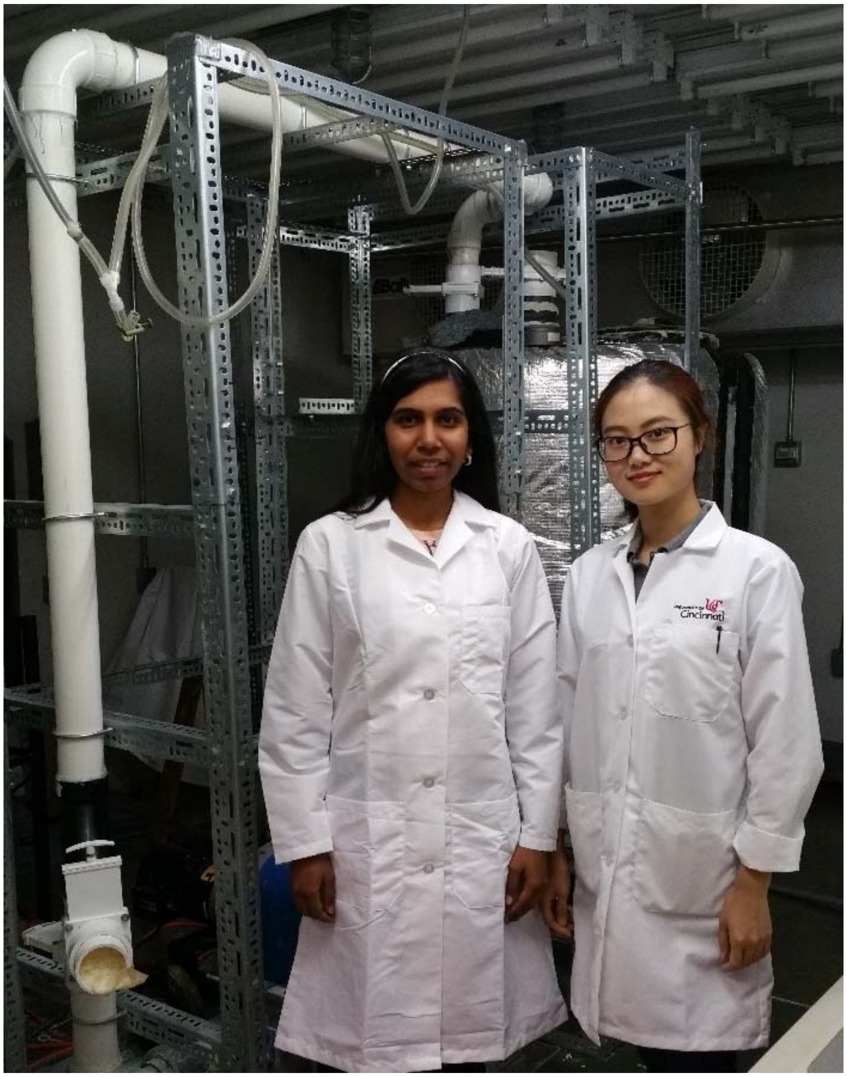

A pilot-scale anaerobic fermenter, which was operated by Ms. Brindha Murugesan, M.S. student (left) and Ms. Jiong Gao, Ph.D. student (right) for production of soluble organic matter from food waste. By supplementing soluble organic matter into wastewater, nutrient removal efficiency of a membrane bioreactor significantly improved.