

New pretreatment approaches to increase efficiency of anaerobic digesters

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Abstract

Anaerobic Digestion (AD) has been the only technology available for Industrial Food & Beverage (F&B) companies to efficiently treat high-organic process wastewater and recover costs through methane generation. Methane produced from AD installations can be used in the process of cogeneration for heat and electricity or can be injected into an existing natural gas line to offset energy consumption. For these reasons, AD has been beneficial to the economics of managing high-organic wastewater streams that may not be permitted to discharge to sewer or are too costly to haul and land-apply. However, conventional AD requires highly-controlled operational parameters (temperature, pH, mixing, minimal wastewater variation) and nutrient dosing to efficiently treat wastewater and produce meaningful methane. Any change in the production process or ingredients can lead to changes in wastewater that may create toxicity events in the digester. All of these factors may result in many AD systems not achieving the initial design objectives. BioElectrochemical approaches, such as Aquacycl's BioElectrochemical Treatment Technology (BETT™) can act as industrial pretreatment to make AD significantly more efficient and reliable. BioElectrochemical systems (BESs) are anaerobic technologies that use naturally existing bacteria, and their ability to generate electrical currents, to accelerate the hydrolysis of complex carbon sources and enhance fermentation rates to generate the smaller volatile fatty acids that methanogens prefer. As a pretreatment step, BESs normalize the AD feedstock, reducing adverse impacts of production variability, pH, and temperature. By reducing the complexity and variability of the carbon chains and other parameters, the AD will operate more consistently, with less operational input, improved treatment times, fewer toxicity events and higher methane production.

I. Introduction

Anaerobic Digestion (AD) has been the only technology available for Industrial Food & Beverage (F&B) companies to efficiently treat high-organic process wastewater and recover costs through methane generation. Methane produced from AD installations can be used in the process of cogeneration for heat and electricity or can be injected into an existing natural gas line to offset energy consumption. For these reasons, AD has been beneficial to the economics of managing high-organic wastewater streams that may not be permitted to discharge to sewer or are too costly to haul and land-apply. However, despite the continuously increasing popularity, AD still faces social and economic obstacles that prevent its full potential from being leveraged. This is largely due to the sensitivities associated with AD and the requirement for highly-controlled operational parameters, nutrient dosing, and skilled operators to efficiently treat wastewater and produce economic returns through methane recovery.

An efficient AD process requires controlled pH, consistent feedstock, high temperature, narrow redox potential, addition of trace elements and the absence of oxidizing agents []. Any change in the wastewater composition may create toxicity events in the digester. All of these factors may result in AD systems not achieving the initial design objectives. In the case of high inhibition (i.e., toxicity event), the only option to recover AD performance is to discharge the batch reactor and re-initiate the process¹. This is a costly and time-consuming process, many times associated with stopping the production process due to the lack of wastewater treatment alternative.

Many different pre-treatment approaches have been used to enhance AD processes. These range from chemical addition and thermal pre-treatment to the utilization of microbial electrolysis cells to accelerate the hydrolysis and increase methane production efficiency^{2,3}. The BioElectrochemical approach for AD pretreatment offers many benefits including low-cost operation due to electricity offsets and energy efficient operations, low chemical addition, small footprint, and reliability due to fixed-biofilms in the system. However, very few commercial bioelectrochemical systems are available, and until recently none have directly addressed pretreatment for AD.

Aquacycl's BioElectrochemical Treatment Technology (BETT™) system is the first commercial bioelectrochemical system that has been evaluated for industrial pretreatment to make AD significantly more efficient and reliable. BETT is an anaerobic process that uses naturally existing bacteria, and their ability to generate electrical currents, to **accelerate the hydrolysis of complex carbon sources and enhance fermentation rates to generate the smaller volatile fatty acids that methanogens preferentially consume**. The BETT processes also normalizes the AD feedstock, reducing adverse impacts of production variability, pH, and temperature to the AD.

BETT™ reactors operate on the principle of Microbial Fuel Cells (MFCs), which are bioelectrochemical devices for concurrent wastewater treatment and electricity generation⁴⁻⁸. During operation BETT reactors convert the chemical energy stored in the bonds of organic compounds into electrical energy in the form of DC current. The organic compounds present in wastewater are bioelectrochemically transformed into dissolved carbon dioxide and protons at the anode. The protons diffuse from the anode to the cathode. They combine with oxygen passing through the cathode and electrons transferred from the anode to the cathode via an external wire and produce water or hydrogen peroxide. Thus, the final products from BETT reactors are dissolved carbon dioxide and water/hydrogen peroxide. The flow of electrons from the anode to the cathode in BETT reactor generates DC current.

MFCs have been widely studied as potential wastewater treatment solutions mainly for domestic and agricultural waste streams^{7,9,10}. The number of scientific studies in the field is overwhelming, unfortunately most of the efforts were not very successful in transferring the knowledge into practical application. Aquacycl BETT system is one of the few that has scaled and applied MFCs to practical wastewater treatment (<https://www.aquacycl.com>).

BETT is suitable for wastewaters with Chemical Oxygen Demand (COD) of 10,000-300,000 mg/L and total suspended solids (TSS) of up to 35,000 mg/L. The extremely high-organic content in these types of wastewaters creates significant challenges for conventional wastewater treatment technologies, including AD. At the same time, BETT cannot replace conventional wastewater treatment for applications that have discharge flows above 570 m³/d (up to 150,000 gpd) or low COD concentrations (below 1,000 mg/L). BETT systems have significantly lower treatment efficiency for wastewaters with COD less than 300 mg/L.

Given the volume and concentration specifications found in many industrial applications, BETT systems are ideal pre-treatment solutions for low volume, high-strength wastewaters such as those generated from confectioneries, sugar refineries, soft-drink and juice producers, etc.

Integrated as a pre-treatment step to AD, BETT system can provide the following benefits:

- 1) Reduce the organic loading rate (OLR) entering AD, which can make the AD more efficient at processing wastewater. BETT systems can treat wastewater with OLR of 10 – 300 kg/m³ day (80 – 2,500 lb/1000-gallon per day), which is up to 30 times higher than conventional AD process^{11,12}. BETT system can reduce the organic load from 10 – 300 kg/m³.day (80 – 2,500 lb/1000-gallon per day) to 2 - 3 kg/ m³.day (20 – 30 lb/1000-gallon per day) and generate waste stream suitable for AD stage. The lower OLR also decreases the amount of sludge being produces by the AD given the lower organic load and reduces the possibility of toxicity events.
- 2) Enrich the wastewater with volatile fatty acids (VFAs), which can be easily transformed to methane in AD. Increasing VFAs (especially acetate) can enhance AD efficiency in methane production and thus reduce the biogas cost.

Figure 1 compares AD pathways of organic compound degradation with the BETT process. BETT can replace and accelerate hydrolysis and acidogenesis steps and thus shorten the overall digestion time.

- 3) Normalizes feedstock concentration and composition, thus reducing adverse impacts of production variability. Complimentary to the normalization process is equalization of pH and temperature to the AD.

The effluents from BETT systems have neutral pH and temperatures in the range of 15 – 30°C (59 - 86°F) depending on the requirements for the influent wastewater. BETT systems work in both, the psychrophilic and mesophilic temperature ranges.

- 4) Removes sulfur species, which eliminates corrosion issues related to the presence of hydrogen sulfide and the effect of sulfate as an oxidizing agent. The resulting effluent increases the efficiency of methanogenesis and reduces the need for chemical addition and/or biogas post-treatment.
- 5) Reduces or completely removes nitrite and nitrate, which eliminates the effect of nitrate and nitrite as oxidizing agents and improves methanogenesis.

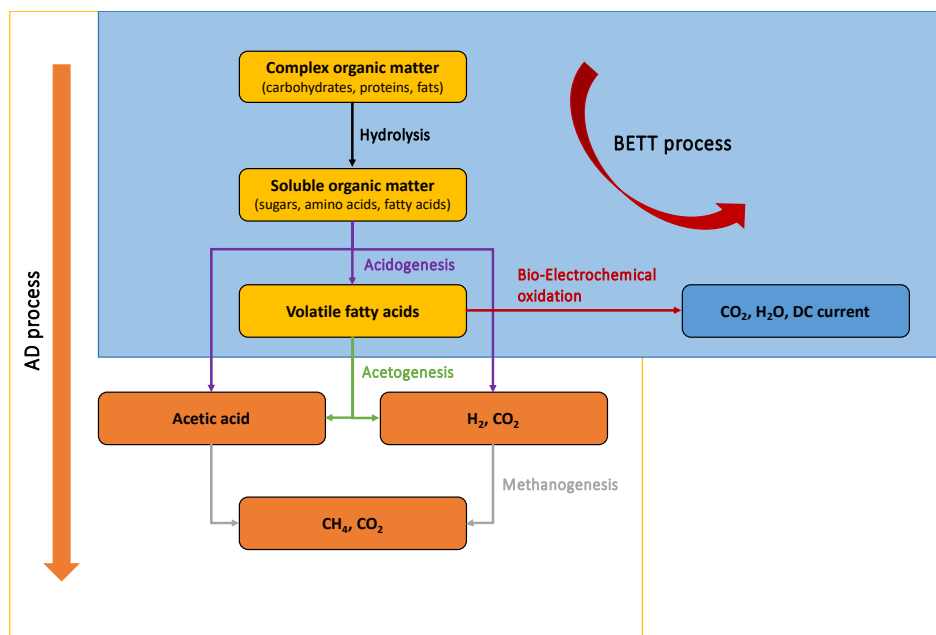


Figure 1: Schematic representation of AD and BETT processes

To-date, bioelectrochemical systems and MFCs have been considered mainly as a post-treatment step for AD¹³⁻¹⁶. The goal of MFCs as a polishing step was to further utilize the organics by converting them into electricity and reduce the organic concentration of the discharged wastewater.

What we propose here is the utilization of BETT technology or MFCs as a pre-treatment technology to AD where MFC processes can normalize and enrich the AD feedstock with easily degradable organics, and low concentrations of sulfur and nitrate/nitrite, suitable for fast and efficient methanogenesis. The following sections describe results from BETT demonstration units running at commercial sites and demonstrating normalized and enriched feedstocks that are ideal for downstream AD processes.

II. Materials and methods

II.1. Demonstration Unit design

BETT Demo Unit system is a standardized, small-scale, bioelectrochemical system for wastewater treatment. The BETT Demo Unit is composed of twelve BETT reactors operating in hydraulic series. Wastewater flows consequently through all BETT reactors where it is partially treated (Fig. 2).

BETT™ Demo Unit is skid-mounted, automated, and designed to operate continuously to demonstrate removal rates according to customer requirements at a volume of 0.6 m³/day (150 gpd). It is equipped with Equalization (EQ) and Collection (CL) tanks, Micro-aeration (MA) unit and a Feeder (FD) tank. The EQ tank (378 L (100 gal)) is used to store and equalize the wastewater before it enters the reactors. The CL tank (378 L (100 gal)) is used to collect the wastewater after it has been treated. The MA unit (276 L (73 gal)) provides a pre-treatment step for the removal of sulfur species such as sulfate and sulfide. The flow through BETT reactors is based on gravity where the elevated FD tank (45 L (12 gal)) was giving the head pressure.

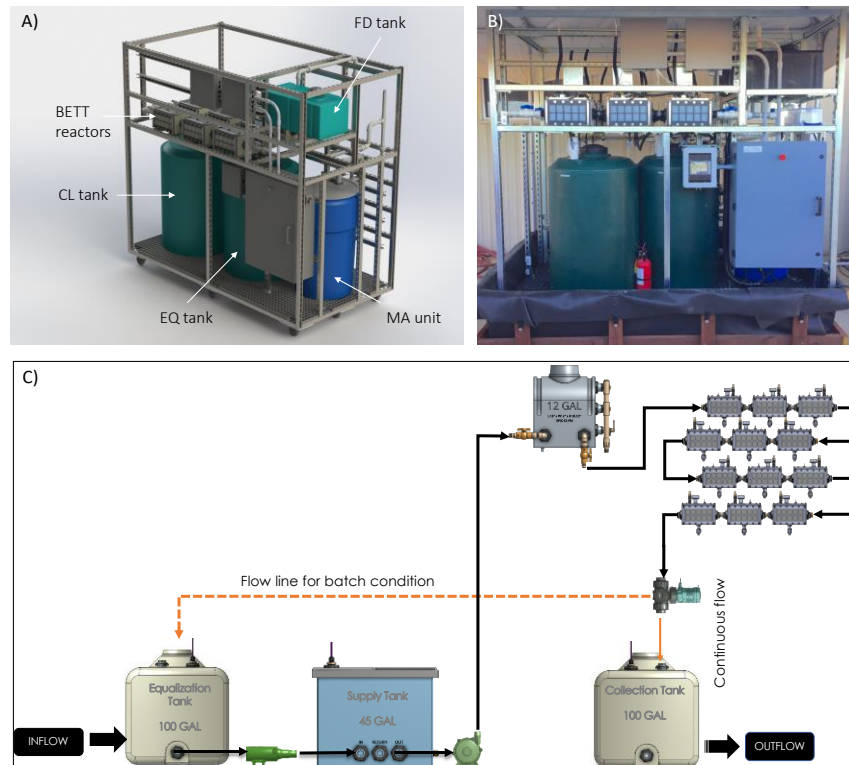


Figure 2: BETT Demo Unit rendering (A), picture (B) and flow diagram (C)

BETT Demo Unit was controlled by a PLC for the operation of valves, sensors and pumps. The Demo Unit was remotely monitored and controlled via specifically designed software and User Interface. The BETT™ reactors (Fig. S1) were remotely controlled by a measurement system with implemented measurement algorithm. The voltage generated from each reactor was recorded every 30min using a specifically designed measurement board.

II.2.1. Inoculation and operation

BETT Demo Unit was located at the property of Joshua Tree Brewery and was treating brewery wastewater generated on site. The brewery did not remove any of the spent grain, hops or other solids prior to discharging wastewater to BETT. The unit was installed outside with only a shade structure and so were exposed to the environmental variables of temperature, humidity, wind, and dust throughout operation (Fig. 2B).

II.2.1.1. Demo Unit Inoculation

The Demo Unit was inoculated with the wastewater composition described in Table 1.

PARAMETER	CONCENTRATION
Chemical Oxygen Demand (T), mg/L	26560
Chemical Oxygen Demand (S), mg/L	26480
pH	5.88
Conductivity, mS/cm	1.46
Sulfide , mg/L	Not detected
Sulfate, mg/L	Not detected
Nitrate, mg/L	11
Nitrite, mg/L	Not detected
Ammonium, mg/L	20.9
Phosphate, mg/L	700
Volatile Fatty Acids (VFA), mg/L	203
Protein, mg/L	232
Total Suspended Solids (TSS), mg/L	2462

Table 1: Chemical composition of raw brewery wastewater at system inoculation.

II.2.1.2. Demo Unit operation

For the first 30 days, the system was operated in a batch mode with recirculation of the inoculum solution through the feeder box and the reactors at a flow rate of 0.38 L/min (0.1 gpm).

Due to the insufficient amounts of brewery wastewater generated by the brewery, the Demo Unit was operated under batch mode for the majority of the study. The batch cycles were usually 7-10 days and when the brewery was not in production, batch cycles could reach 80 days. At the beginning of each batch cycle, new raw brewery wastewater was introduced into the EQ tank (Fig. 2C).

Continuous flow mode studies were periodically performed to evaluate the operation of the system under continuous mode, which is more representative of BETT system operation on a big scale. Ten continuous mode tests were performed at different stages of the Demo Unit operation. The flow rate under continuous mode was 380 mL/min (0.1 gpm) giving a hydraulic retention time (HRT) of 4 hours. The wastewater composition of the inflow and outflow from BETT Demo Unit was evaluated. The inflow was collected from the EQ tank after it has been filled with new raw brewery wastewater. The outflow was collected from a sampling port located after BETT reactors. The outflow samples were taken at the end of the continuous mode tests.

Chemical oxygen demand (COD), sulfide, sulfate, nitrate, nitrite and VFA of inflow and outflow samples were analyzed using Hach DR850 and DR900 instruments and associated methods.

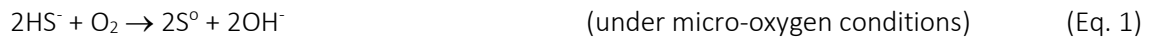
Total suspended solids (TSS) were quantified using EPA method 160.2. pH, conductivity and ammonium were measured by Hach HQ40d meter equipped with pH, conductivity and ammonium (ISENH4181 IntelliCAL) probes. COD removal rate, COD removal efficiency, and COD/VFA conversion efficiency were calculated as indicated in the Supplemental Information.

III. Results and Discussion

III. 1. Removal of sulfur species

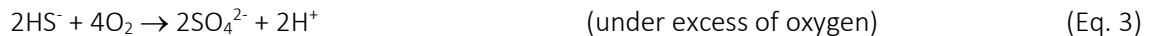
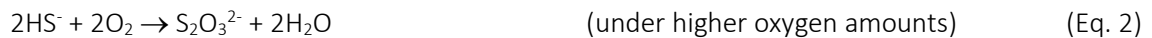
The presence of sulfate in AD feedstock acts as an oxidizing agent and slows AD activity. Caustic is often added to the feedstock to remove sulfate prior to digestion, which adds chemical costs. One of the biggest challenges of AD coupled with a methane cogeneration is the presence of hydrogen sulfide in the produced biogas¹¹. Hydrogen sulfide is extremely corrosive for the cogeneration turbines, causing complete failure of the co-generation (CoGen) installations. Therefore, methane needs to be purified from the sulfides present before it enters the cogen. This purification step is a costly process and requires sophisticated equipment.

One way to remove total sulfur is to allow sulfate to be reduced to sulfide in the equalization tank and then remove sulfide using a surface micro-aeration strategy. Introduction of oxygen to the headspace of soft-capped AD systems has been a long-standing technique for reducing sulfide^{17,18}. Aquacycl has developed a micro-aeration unit that can be adapted to any holding tank and induce the same sulfide removal. The micro-aeration device supplies small amounts of air at the wastewater surface that encourages the growth of sulfur-oxidizing bacteria at the air-liquid interface to convert sulfide into elemental sulfur that is trapped in the biomass, and thus removed sulfide. Typically, micro-aeration allows the supply of small (“micro”) amounts of oxygen (e.g., <0.1 mg/L O₂) to the gas phase, as in the following example reaction.



Under microaerobic conditions, sulfide-oxidizing bacteria convert sulfide to elemental sulfur, which is removed from the gas phase and is no longer an impurity in the biogas or in the liquid.

Under higher oxygen concentrations (e.g., > 0.1 mg/L O₂) sulfide is oxidized back to sulfate or thiosulfate. Therefore, regulating oxygen concentration is critical for sulfide removal and higher oxygen concentrations are undesirable.



Conventional micro-aeration devices have been developed and employed for sulfide removal in a gas phase but have not been previously commercialized for sulfide removal in wastewater^{18,19}.

Micro-aeration (MA) units are integrated into BETT system tanks and storage/equalization tanks that are at a customer site. Figure 3 shows a simplified schematic of the above described process.

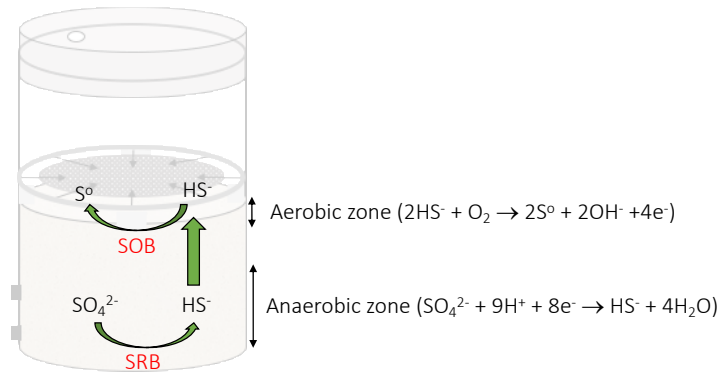


Figure 3: Schematic representation of sulfur cycle in MA unit

III.2. Removal of oxidizing agents

In addition to sulfate, oxygen, nitrate and nitrite can also act as oxidizing agents that prohibit methanogenesis. Methanogenic archaea require a very narrow redox potential between -0.3 and -0.33V vs. standard hydrogen electrode (SHE) for optimal AD performance¹¹. The presence of oxidizing agents will alter the redox potential making it more positive in presence of oxygen, nitrite and nitrate and more negative when sulfate is available in the wastewater.

Aquacycl MA units eliminate the majority of sulfate and sulfide before the wastewater enters the reactors. Figure 4 shows the sulfate profile under continuous mode of operation, demonstrating the lack of sulfate in the wastewater entering BETT reactors. In the cases when the sulfate is not fully removed by the MA unit, the sulfate amount is further reduced in the BETT reactors from 65-100%. Sulfate removal up to 70% was demonstrated in another BETT Demo Unit treating swine wastewater²⁰.

Sulfate was reduced to sulfide, which was confirmed by the increasing sulfide concentration during continuous operation run # 6 (from 0.3 to 1.9 mg/L S²⁻ for inflow and outflow, respectively) and for continuous run # 8 (from 0 to 0.2 mg.L S²⁻ for inflow and outflow, respectively). For the rest of the continuous mode runs the sulfate concentration was zero, therefore not visible in Figure 4.

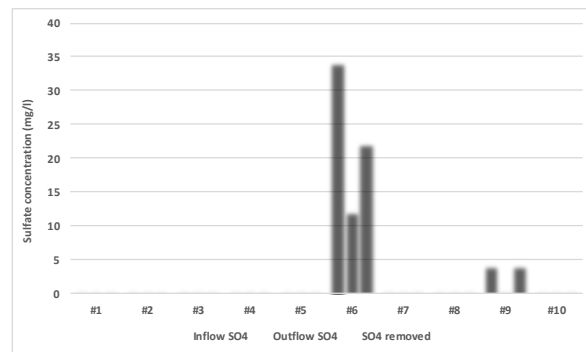
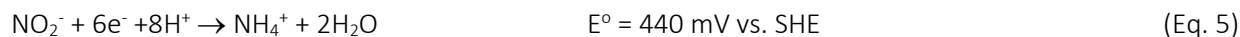
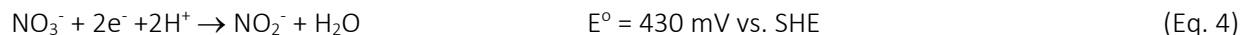


Figure 4: Changes in sulfate concentration under continuous mode of operation.

A decrease in nitrate concentration was achieved in most continuous mode runs (Fig. 5A). The nitrate removal rate was 4-50% from the initial nitrate concentration. It is believed that nitrate is reduced to ammonium given the increasing ammonium concentration of the outflow water (Fig. 5B). The degradation of proteins and amino acids is another source of ammonium, which also contributes to the increase ammonium concentration in the outflow samples^{1,3}.

Nitrate reduction to ammonium was observed in another BETT system treating swine wastewater ²¹. This effect was attributed to dissimilatory nitrate reduction to ammonium (DNRA), which is a predominant process under anaerobic conditions [DNRA ref]. DNRA is a two-step process where nitrate is first reduced to nitrite followed by nitrite reduction to ammonium (Eqs. 4-5).



In MFC environment, DNRA can occur in the bulk of the reactor or at the cathode competing with oxygen reduction reaction. DNRA usually appears in wastewaters with high C/N ratio²². The C/N ratio, calculated as COD/NO₃-N for the brewery wastewater was determined to be in the range of 0 to 450, highly favorable for DNRA. At the same time, the lower cathodic potential (OCP_{cathode} = 0 to -200mV vs. SHE) observed in BETT system treating brewery wastewater indicates that the DNRA occurs in the bulk of the reactor and not at the cathode surface.

The preferred COD/N ratio for efficient methane production in an AD is from 20-30, where higher COD/N ratio slows microorganisms multiplication and thus lowers substrate degradation^{1,11}. BETT system decreases COD/N ratio as a result of the high COD removal at the anode, which given the fixed film and electrochemical nature of the reaction is independent on bacterial growth and multiplication once the biofilm is established. The COD/NO₃-N for the current system decreased 0.8 to 2 times in 4 hours HRT.

Although high concentrations of ammonia has toxic effects in AD biogas reactors, the ammonium generated in the BETT system was in the range of 2-90 mg/L, which was far below the 1700 mg/L shown to inhibit methanogenesis ²³. Thus, the reduction of nitrate to ammonium in BETT system can be considered as beneficial for AD operation.

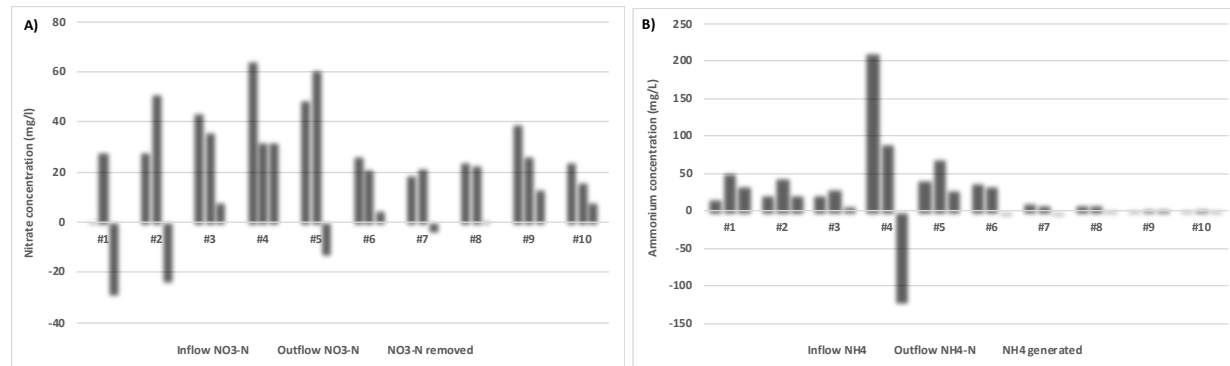


Figure 5: Changes in nitrate and ammonium concentrations under continuous mode of operation

III. 3. COD removal

Using BETT system as pre-treatment for AD can reduce the ORL for the AD, normalize the feedstock and enrich it with easily degradable organics. High ORLs to the AD induce acidification of the bioreactor due to the accumulation of long-chain VFAs and concurrent severe pH drop ^{3,24}.

The main purpose of BETT technology is COD removal and COD conversion. The COD removal rate per system depends on the number of BETT reactors connected in hydraulic series and the HRT. Numerous reactors in hydraulic series comprise a treatment train. More reactors in hydraulic series or longer HRT will lead to higher COD removal. To increase volume, the system is designed to have multiple treatment trains working in parallel. The Demo Unit described in this manuscript has twelve BETT reactors in hydraulic series,

which are able to partially treat the wastewater as a demonstration of technology capabilities. The OLR for BETT Demo Unit was 25 to 76 kg/m³ day (200 to 600 lb/1000-gallon per day).

Under continuous mode with an HRT of 4 hours, the BETT Demo Unit showed COD removal in the range of 350 to 3500 mg/L (2 to 21 kg/m³ day) for COD (T) and 210 – 2800 mg/L (1.3 to 17 kg/m³ day) for COD (S) corresponding to 5% - 42% and 4% - 28% COD removal, respectively (Fig. 6). Figure S3 shows COD removal rates under batch mode.

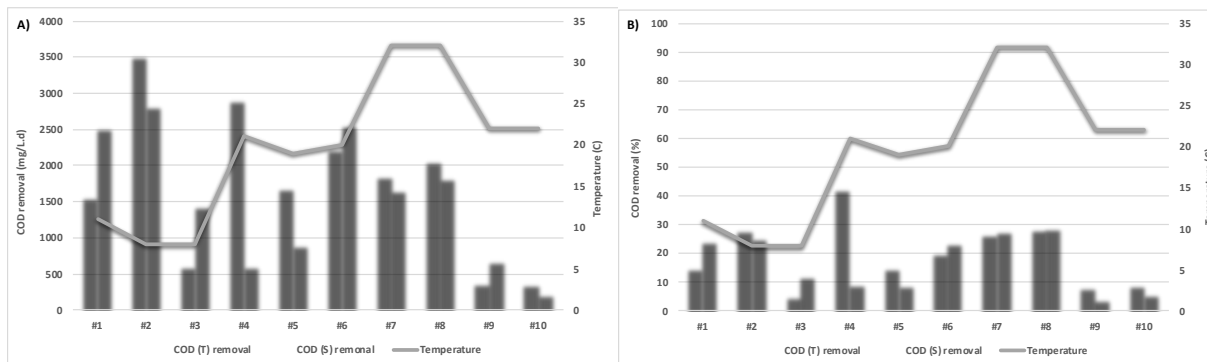


Figure 6: COD removal rates during continuous mode along with the temperature of the wastewater

To achieve higher removal of organics, the number of BETT reactors in hydraulic series should be increased. The COD removal rate increases logarithmically with the number of reactors, whereas the treatment efficiency of the reactors approaches zero when the COD of the wastewater in the reactors reaches 300 mg/L. In general, it was established that the BETT COD removal rate is a function of the inflow COD concentration when all other variables (impedance, operation mode, temperature, flow rate, etc.) are constant. The COD removal rate in terms of mg/L is higher when the COD of the incoming wastewater is higher (Fig. S2). Therefore, the first reactors in the treatment train will have higher removal rate than the reactors at the end.

III.4. COD/VFA conversion efficiency

Under continuous mode with short a HRT of 4-hours, the COD is mainly converted to VFAs with a variable (5-89%) conversion efficiency (Fig. 7). The conversion efficiency of COD to VFA is higher when the initial COD is higher. In general, when the system demonstrates higher COD removal rates, the VFA concentration also decreases given the higher efficiency of the BETT system operation.

As we mentioned earlier, BETT system can accelerate hydrolysis and acidogenesis steps in anaerobic digestion and thus shorten the digestion time. In general, the minimum HRT for VFA production in AD is 1 to 2 days²⁴, which with BETT as a pre-treatment step can be shortened to 4 - 6 hours.

The effluent from BETT system provides normalized feedstock to AD enriched with easily degradable organics. Due to the subsequent oxidations of VFAs at the anode surface of BETT reactor, the VFA concentration in the effluent never exceeded 1200 mg/L under continuous mode, which is far below the VFA threshold causing toxicity events in AD²³. The toxicity induced by high VFA concentrations is a result of sharp pH drops, where VFAs exist in their undissociated form. VFAs in undissociated form can reduce the microbial activity²⁴. The effect is more pronounced for methanogenic archaea than acidogenic and acetogenic bacteria.

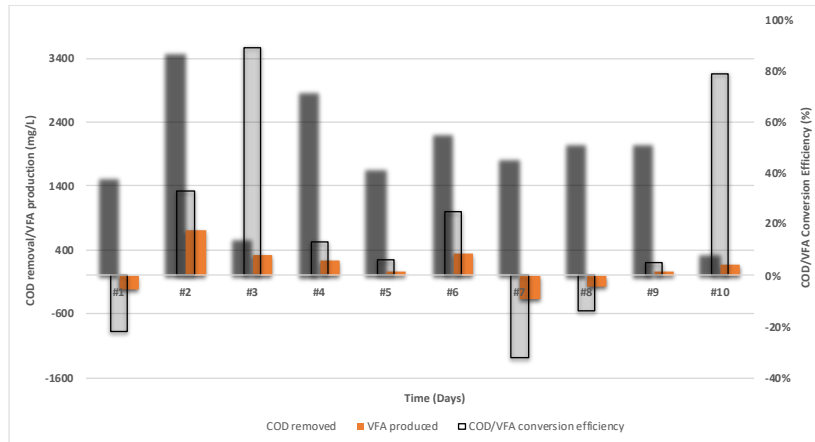


Figure 7: COD removal, VFA production and COD to VFA conversion efficiency profile during continuous mode

The amount of VFAs produced/consumed by BETT system can be controlled by the number of BETT reactor and/or the retention time. Prolonged retention time and/or more BETT reactors in hydraulic series will reduce the VFA concentration in the effluent as evidenced by the COD/VFA profile of BETT system under batch mode. Under batch mode, when the wastewater recirculated through the BETT system for a longer period of time (days as opposed to hours), the organics are first converted to VFAs, which are then consumed at the anode surface. The first day of each batch cycle is characterized with a rapid conversion of the organic COD in the wastewater into VFAs. This step is performed by fermentative bacteria. Once the majority of the COD is converted into VFA, the VFAs are oxidized to carbon dioxide and water by electrogenic bacteria (electrogens) populating the electrode surface²⁵.

Figure 8 shows a batch cycle of 77 days. The system was kept under batch mode due to the lack of raw wastewater. Figure 8A shows the COD and VFA profiles over a batch cycle of 78 days. The VFA concentration increases from day 1 to day 7 after which it gradually decreases from 1394 mg/L at day 7 to 70 mg/L at day 78.

The figure demonstrated the above statement where the conversion efficiency of COD to VFA was 67% for the first day of the cycle and decreased to 5% during the second day. After the first two days, the amount of VFA gradually decreased as a result of their bioelectrochemical oxidation. The same trend was observed in the study of Kim et al. showing MFC treating swine wastewater¹⁵. The authors did not discuss that trend giving that the MFC was used after the AD and higher VFA concentration wasn't the goal of the study.

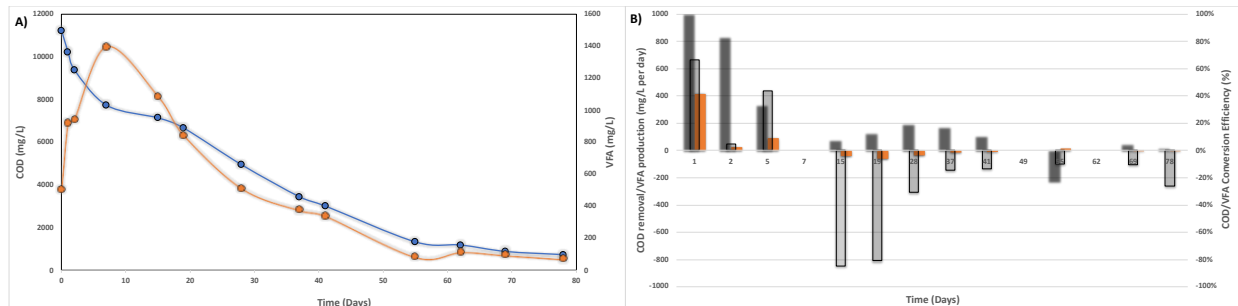


Figure 8: A) COD (T) and VFA concentrations over time and B) COD removal (mg/L.d) and VFA production (mg/L.d) rates, and COD/VFA conversion efficiency under batch mode of operation of BETT system

A golden rule in anaerobic digestion is that pretreatment step/s should not spend more energy that they help to produce. A unique feature of BETT systems is their ability to produce electricity as direct current, which can be used to offset the energy demand of the system. BETT Demo Unit treating brewery wastewater had Net Energy Recovery (NER) of 0.14 kWh/kg-COD treated and Coulombic Efficiency (CE) of 31% at 200Ω. Thus, at OLR of 76 kg/m³.d, the energy generated from BETT unit was 1kWh/d. The NER from this system was comparable to the NER demonstrated from BETT Demo Unit treating swine wastewater²¹ and comparable than other reported in the literature studies^{26,27}.

Conclusions:

Reducing the complexity and variability of carbon chains and other chemical parameters using BETT or other MFC systems will enable AD system to operate more efficiently and with higher reliability, with less operational input, lower cost, improved treatment times, fewer toxicity events and higher methane production.

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