



Short communication

Treatment of high strength acidic wastewater using passive pH control



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ABSTRACT

A passive pH control system to process high strength ($\text{COD} \sim 20,000 \text{ mg l}^{-1}$) acidic wastewater without alkali addition was developed. The low-energy wastewater treatment system consisted of a packed bed up-flow anaerobic reactor followed by an aerobic trickling filter, both of which used biochar as the biofilm support media. The passive pH control process relied on controlled recycle of the effluent leaving the anaerobic stage to adjust the pH of the acidic feedstock. The anaerobic reactor was able to achieve steady state reductions in total chemical oxygen demand (TCOD_{red}) above 91% and the combined system (anaerobic-aerobic) achieved COD reductions above 97% without alkali addition. Methane production was 0.311 m^3 per kg COD reduced. The system was also able to produce an effluent that met EPA regulations in terms of BOD_5 and TSS, possessed a near neutral pH, and was highly nitrified.

1. Introduction

High-strength wastewaters such as effluents from kitchen, food processing establishments, olive oil mill, swine farms, pulp mills, grease traps, and brewery are preferably treated anaerobically, thus providing a potential for energy generation while producing low surplus sludge [1]. Food waste, for example, with high decomposition potential can be successfully digested anaerobically for the production of biogas [2]. For these wastewaters anaerobic digestion is a preferred treatment alternative for several reasons. First, anaerobic digestion is an effective low-energy method to treat high strength wastewater [3]. Anaerobic digestion also produces less sludge per unit pollutant removal (i.e. reduction of chemical oxygen demand (COD) or 5-day biochemical oxygen demand (BOD_5)) and produces a methane-rich biogas [4,5]. Anaerobic digestion can withstand significant disturbances in nutrient overloading or deprivation, temperature and/or pH swings, and toxic shocks. They can also be made low cost [6].

High strength acidic wastewaters can contain constituents (e.g. volatile organic acids) that produce acids when metabolized in the absence of oxygen [7,8]. Low pH negatively impacts the performance of the anaerobic digestion process [9] since a complete anaerobic digestion is executed through the actions of a complex methanogenic microbial community [10]. Each community has a specific role in the degradation of complex organics to methane and carbon dioxide including the methanogens who are responsible for the last series of reactions that reduce acetate to methane and carbon dioxide. While the acido and acetogens can grow optimally in a broad pH range between

5.5 and 7.5, methanogens are pH sensitive and grow best at pH values between 6.8 and 7.5 [9,11]. Acidic wastewaters that directly or indirectly lower process pH can negatively impact these populations and thus the efficiency of methane production.

Treatment of high strength acidic wastewater thus requires operational alternatives to avoid system instability [8]. Although the wastewater could be neutralized through the addition of alkali [12–15], this is problematic at commercial scale because base is acquired in highly concentrated mixtures requiring storage in spill protective enclosures and trained personnel [16]. Alkali addition must also be introduced through pH control loops which require industrial pH probes and efficient mixing. Poor mixing (or faults in the control loop) can result in unwanted excess additions of base that can destroy an entire reactor culture within minutes and force problematic reactor flushing and/or long culture recovery times. For these and other reasons, a process to treat high strength acidic wastewaters without the need of base addition would prove beneficial to small and medium scale businesses that wish to treat their high strength acidic wastewater on-site. More, direct discharge of high strength wastewaters (i.e. discharges with high BOD, total suspended solids (TSS), fat, oil and grease (FOG), and extreme pH) is subject to the National Pretreatment Program, a component of the National Pollutants Discharge Elimination System (NPDES) which requires these discharges to be pretreated (to limit pollutant levels) prior to their discharge to municipal sewers [17] or pay penalties and surcharge fees levied by state governments.

There remains, however, a paucity of literature on methods to treat high strength acid wastewater without base addition. In this work we

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present data on the efficiency of a passive pH control system to treat high strength acidic wastewater (i.e. separated from grease trap waste). Passive pH control was achieved by application of pulsed addition of feed coordinated with timed intervals of effluent recycle from the anaerobic reactor. Applied to a two stage high rate anaerobic – aerobic digester (HRAAD) employing biochar as the biofilm support media, the passive pH control system was able to treat the high strength acidic wastewater without base addition for a period of 5 months. Biochar was used as the support media because it can be produced from waste biomass [18], is considered carbon negative [19], and has shown to host robust methanogenic microbial communities [20]. Results showed the potential of this control system to process both the high strength acidic wastewater without alkali addition and to produce a treated effluent that meets EPA's secondary treatment requirements for BOD₅, total suspended solids (TSS), and pH [21].

2. Materials and methods

2.1. Wastewater feed

The wastewater feed comprised of grease trap waste (GTW) wastewater obtained from a local GTW processing facility (Pacific Biodiesel, Honolulu). The plant collects GTW from food service establishments and separates out the fat, oil, and grease (FOG) as a feedstock for biodiesel production before discharging the high strength acidic wastewater [22]. Analysis of the GTW wastewater determined a COD, TSS, total nitrogen (TN), total phosphorus (TP), total volatile organic acids (TVOAs), hexane extractable materials (HEM), and pH of 19.78 g l⁻¹, 1.16 g l⁻¹, 0.487 g l⁻¹, 0.10 g l⁻¹, 5.42 g l⁻¹, 3.93 g l⁻¹, and 4.0, respectively. The feed was collected in bulk and stored frozen in 10.0 l containers at -20 °C until used. Periodically 10.0 liters of wastewater feed was thawed and transferred to a 16.0 l capacity wastewater feed tank (FT) mixed under magnetic stirring and maintained at 10.0 ± 1 °C using cooling heat exchange tubes connected to a peltier chiller (ThermoTek Ink, USA).

2.2. Reactor system

The system consisted of a mixing tank (MT) followed by an anaerobic packed bed reactor (ANPB) and then an aerobic packed bed trickling filter (TF) all connected in series (see Figure F1, *Supplementary Materials*). The HRT was controlled by precise metering (PULASATron Pulse-a-Feeder™, model 04/14.531243) of the high strength acidic wastewater from the FT into the MT in one minute pulsed increments every hour at the required rate. Thereafter fluid flowed through the system via gravity. The bottom portions of both the ANPB and TF column reactors are tapered inward to form a conical shape to support the accumulation of solids that was periodically pumped back into the MT.

The anaerobic stage comprised an MT reactor (working volume 2.0 l) connected in series to an up-flow biochar packed bed anaerobic column reactor (# 5, Figure F1, working volume 4.0 l). Both reactors were constructed of extruded clear acrylic with inner diameters of 6" and 4", respectively, with combined working volume of 6.14 liters inclusive of transfer plumbing. The temperature of the MT was maintained at 37.5 ± 1.0 °C using a submerged cartridge heater controlled by an external controller (B. Braun Biotech International, Micro DCU Twin). The MT pH was monitored using a submerged pH probe (Mettler Toledo, DPAS-SC K85/225) also connected to the same external controller. Mixing in the MT reactor was achieved through recycle that pumped (Eheim pump, model 1046, Germany) reactor liquid from the bottom of the reactor back to the top. The anaerobic packed bed consisted of 478.0 g of wood derived biochar packed into a plastic mesh basket (5 mm x 5 mm mesh of stretchable molded polyethylene, McMASTER-CARR, USA) of approximately 1.35 l (height: 8", diameter: 3.6", and cross-section area: ~66.58 cm²). Mixing in the ANPB reactor

was achieved by a continuous recycle loop that withdrew fluid through a top port and returned it to the bottom. The temperature of the ANPB reactor was maintained at 37.5 ± 1.0 °C by use of regulated heating tape (BSAT 101002, Brisk Heat, USA) wrapped around the outer wall of the column. To eliminate external contamination of head space gas, the biogas flows leaving each reactor were passed through water traps that provided less than 2.0 mm of head pressure.

The aerobic stage consisted of down-flow TF reactor (working volume ~1.7 × 10⁻³ m³) constructed of extruded clear acrylic (inside diameter: 4") packed with 74.2 g of corn cobb biochar (media) loosely stacked in seven layers (~10.6 g per layer) within a cylindrical basket (same materials as used in the ANPB) of approximately 1.69 l (height 10", diameter 3.6", cross section ~66.58 cm²) to a final density 106.7 g l⁻¹ ± 8.3 g l⁻¹ and void ratio of approximately 50%. The temperature of the TF column was maintained between 30 and 32 °C using heating tape (BSAT 101002, Brisk Heat, USA) wrapped around the outer column wall. Aeration was delivered using an external aquarium air pump (Penn-Plax, Silent air X4) connected to an acrylic tube of 8 mm diameter inserted through the middle of the packed biochar. Effluent accumulated at the bottom of the TF column was recycled back to the top of the column and allowed to trickle down at a recirculation ratio (R) of approximately 30 to ensure aeration and complete media wetting. The lower portion of the TF column was also equipped with an external air lift system to provide additional oxygenation.

Samples from the MT were collected from ports along the side wall and also from its effluent stream. Samples from the ANPB reactor were collected from its effluent stream while samples from the TF were collected from a sampling port at the bottom conical section of the reactor. Samples were either analyzed immediate (total values) or filtered (soluble values) and stored under refrigeration until analyzed.

2.3. Passive pH control

Passive pH control was executed by combining a pulsed feed addition regime with intermittent recycle from the ANPB reactor. Reactor fluid from the ANPB reactor was recycled back to the MT for twenty minutes every hour. This recycle was terminated just prior to addition of a new aliquot of feed and had the effect of raising the pH in the MT above the desired set point through the return of hydroxyl ions that had been "freed up" in ANPB reactor after consumption of organic acids by the methanogenic microbial community. The new aliquot of high strength acidic wastewater pulsed into the MT (added over a 1 min period and at a rate to achieve the desired system HRT) had the effect of returning the pH to the desired set point. After the pulsed addition of new feed both the MT and ANPB reactors were then operated in isolated batch mode (with internal recycle) for 40 min. During this period the pH in the ANPB reactor slowly rose as the volatile organic acids were consumed (and a methane rich biogas produced) and the hydroxyl ions "freed up". After this 40 min batch period was completed, the recycle of ANPB fluid to the MT was repeated for another 20 min cycle until terminated and the next pulse of high strength acidic feed added.

2.4. Analytical

All samples for BOD₅ were analyzed immediately (within 1 h of collection) while all other measurements (COD, TN, TP, TSS, TVOA, and ions) were executed the same day. Soluble measurements (reported for COD, TN, TP, TVOA, and ions) were executed on filtered samples (Whatman 934-AH, UK). Total measurements were made on unfiltered samples. Measurements of TSS reflected the dry weight of solids retained on the pre-weighted 1.5 µm filters (Standard Methods 2540 D) [23]. COD, TN, TP, and TVOAs measurements were executed according to HACH Methods 8000 (HR +), 10072 (HR), 8190, and 8196, respectively, using kit numbers 24159-25, 27141-00, 27426-45, and 22447-00, respectively. Accuracy of all testing was confirmed with standards 22539-29, 24065-49, 2569-49, and 14270-10 for COD, TN,

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