Empowering anaerobic digestion of dairy cow manure with pretreatment and post-treatment using vacuum stripping

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Abstract

Although dairy cow manure is an abundant feedstock of anaerobic digestion, pretreatment is needed to increase biogas production. This study introduced the vacuum stripping and absorption (VaSA) process for pretreatment of dairy cow manure, examined the efficacy of VaSA pretreatment on anaerobic digestion, and applied VaSA to digester effluent for ammonia recovery and pathogen reduction. Two 18-L mesophilic digesters were operated semi-continuously with VaSA-treated and raw dairy manure in parallel with two control digesters fed raw manure only. Pretreatment of dairy manure by VaSA for 2 h increased the dissolved fraction of volatile solids by 44.8-45.5%. Consequently, the digesters receiving VaSA-pretreated and raw manure produced 17% more biogas than the control digesters at the volatile solids loading rate of 1.8 $g/L_{reactor}/d$. The pretreatment also improved digestate dewaterability, with time-to-filter and viscosity decreased by 8.5-14.5%. Post-treatment of digestate by VaSA reduced fecal coliform to undetected. Ammonia mass transfer coefficients were similar in VaSA pretreatment of dairy manure and post-treatment of manure digestate (0.21-0.29 1/h). Post-treatment allows more digestate to be applied to nearby land at lower transportation costs and benefits recycling of digestate due to pathogen reduction. Overall, this mini-pilot study proved coupling anaerobic digestion and VaSA to be a profitable strategy to empower anaerobic digestion systems.

Keywords: Alkali treatment; ammonia recovery; anaerobic digestion; dairy manure; thermal treatment; vacuum stripping

1. Introduction

Agricultural waste such as cow manure is an abundant, renewable bioresource for biogas production [1,2]. At the end of 2023, more than 29% of the 21,179 concentrated animal feeding operations in the U.S. had National Pollutant Discharge Elimination System (NPDES) coverage [3]. These animal feeding operations are required to implement a nutrient management plan and meet effluent limitations for both production and land application areas. Besides application of the best available technologies for pollutant control, manure and manure digestate are typically sprayed or injected to cropland at application rates below the agronomic nutrient needs. The land needs for nutrients are field-specific, depending on soil testing for nitrogen and phosphorus, crops to be planted or other land uses, the yield goals of crops or other uses, crop or pasture nutrient requirements, timing, and other factors. Excess manure must be either transported offsite or treated onsite. High transportation costs (more than $1.24/m^3/km), seasonal application, and the potential liability of environmental impacts limit the feasibility of hauling manure for offsite land application [4]. Anaerobic digestion has been adopted by concentrated animal feeding operations to produce bioenergy in the form of biogas while stabilizing manure solids [2,5].

Although dairy cow manure is the second largest feedstock of anaerobic digestion in the U.S., it contains poorly digestible lignocellulosic fibers (lignin, cellulose, and hemicellulose). Lignocellulose accounts for 40-60% by weight of cow manure dry matter [6]. Cows digest the easily-degradable part of the feed with rumen microbes, making the manure fibrous. Spent bedding materials such as straws, sawdust, and composts are removed together with cow manure, further increasing fiber content of liquid cow manure that is a mixture of as-excreted manure, used bedding materials, and washing water. Pretreatment aims at freeing the lignin fraction by breaking the covalent bonds between cellulose and hemicelluloses as well as converting crystalline cellulose into more accessible cellulose [2,7].

Various mechanical, thermal, chemical, and biological methods have been investigated for pretreatment of dairy and beef cow manure [1,2,7]. However, most pretreatment methods were estimated to have costs (up to \$155.4/m^3 feedstock) higher than market values of the increased methane production (\$0.00-3.51/m^3 feedstock) although methane production was increased by 9.6-400% [8-10]. Innovations in pretreatment methods might contribute to the growth and optimization of biogas production from agro-industrial wastes [1,11]. Low-temperature thermal (<100 °C) and mild-alkali (<80 mg NaOH/g-TS; pH 8-12) pretreatments have been found effective for municipal sludge [12-15]. Recently, Tao et al. [16] and Han et al. [17] found that the vacuum stripping and absorption (VaSA) process could not only recover ammonia, but also enhance solubilization of volatile solids in anaerobic digestate due to vacuum-assisted low-temperature thermal treatment and mild-alkali treatment under the VaSA conditions. VaSA raises wastewater pH to 9.0-9.5 and heats it to 65 °C at a vacuum pressure of 25-27 kPa, which increases the fraction of free ammonia to more than 92% of total ammonia (aqueous ammonium NH_4^+ and gaseous free ammonia NH_3). The feed boils at this temperature (65 °C) due to the reduced pressure (25-27 kPa) instead of the normal boiling point (100 °C at 101.3 kPa). At boiling, free ammonia is efficiently stripped out of the feed and solids solubilization is enhanced. Stripped ammonia is absorbed to a sulfuric acid solution, forming ammonium sulfate as a marketable fertilizer. Our hypothesis was that liquid dairy cow manure could be pretreated by VaSA not only to recover ammonia, but also to enhance solids solubilization by the vacuum-assisted low-temperature thermal and mild-alkali treatments of lignocellulosic biomass in dairy manure. When VaSA-treated manure is fed to anaerobic digesters, the heat applied for VaSA is recycled, thus making VaSA a net-zero-energy pretreatment measure. The NaOH added to raise pH for VaSA mitigates digestate acidification. Compared with anaerobic digestion of manure without pretreatment, digestion of manure pretreated by VaSA can yield more biogas or have a shorter hydraulic retention time as solids solubilization is enhanced by VaSA pretreatment.

Digested dairy manure is often spread on agricultural land as a liquid fertilizer or separated into solids for animal bedding and liquid for further treatment or land application [4,18]. However, land application rates of dairy manure digestate are often limited by the high content of total nitrogen (3.4-5.7 g/L), especially the bioavailable ammonia-N at 1.4-4.2 g/L [18-21]. To avoid the high transportation costs for hauling excessive manure digestate to distant crop fields, ammonia needs to be removed or recovered from manure digestate. VaSA has been found to be efficient in recovering ammonia from liquid dairy manure, pig slurry, and dairy manure digestate [19-22]. Upon ammonia recovery, more manure digestate could be applied to a given area of local land while meeting the agronomic application rates.

Land application of manure digestate and recycling of manure solids as cow beddings can lead to the spread of pathogens [23]. The vacuum-assisted alkali/thermal treatment in VaSA is capable of thermal inactivation of pathogens [16]. Pathogen reduction promotes unrestricted land application of manure digestate and utilization of the separated solids as cow bedding materials. Pathogen reduction in animal manure and manure digestate has not been reported for ammonia recovery processes.

This study delved into the capacity and kinetics of ammonia recovery and the synergistic effects of VaSA on biogas production and digestate recycling through pretreatment of dairy cow manure and post-treatment of manure digestate. Both the VaSA system and anaerobic digesters were functional prototypes. The mini-pilot tests were designed to simulate practical application situations. Unlike earlier studies on ammonia recovery from animal manure and manure digestate using VaSA [19-21], the present study investigated the simultaneous effects of vacuum stripping on both ammonia recovery and treatment of manure solids. It was the first effort to comprehensively investigate the efficacy of coupling anaerobic digestion with VaSA pretreatment of digester influent and post-treatment of digester effluent. It demonstrated an integrative approach to empower anaerobic digestion systems for biogas production and digestate recycling.

2. Materials and Methods

2.1. Semi-continuous anaerobic digestion of dairy manure

As shown in Figure 1, two complete-mix anaerobic digesters were operated semi-continuously with VaSA-treated and raw dairy cow manure at 1:1 mass ratio of volatile solids (VS), called digesters with pretreatment hereinafter, in parallel with two control digesters fed raw dairy manure only, called digesters without pretreatment. The digesters were built with 27-L stainless steel cylindrical tanks (inner diameter 30.5 cm; height 36.8 cm) sitting on Guardian 5000 hotplate stirrers (Ohaus, Melrose, MA). The tanks were sealed air-tight by silicone gaskets in the lids. The side walls of the digesters were wrapped with double reflective insulation sheets to minimize heat loss. Based on trial runs for complete mixing and uniform temperature of digestate, the effective volume was set at 18 L. Temperature was targeted at 36 ºC for mesophilic digestion, which is in the predominant temperature range of full-scale heated anaerobic digestion systems. Each digester had a 4-cm octagonal magnetic stir bar for magnetic mixing. The tri-clamp inlets at the center of the lids allowed easy feeding and air-tight closing. There was a ball valve (2.5 cm diameter) at the bottom of each digester for discharge.

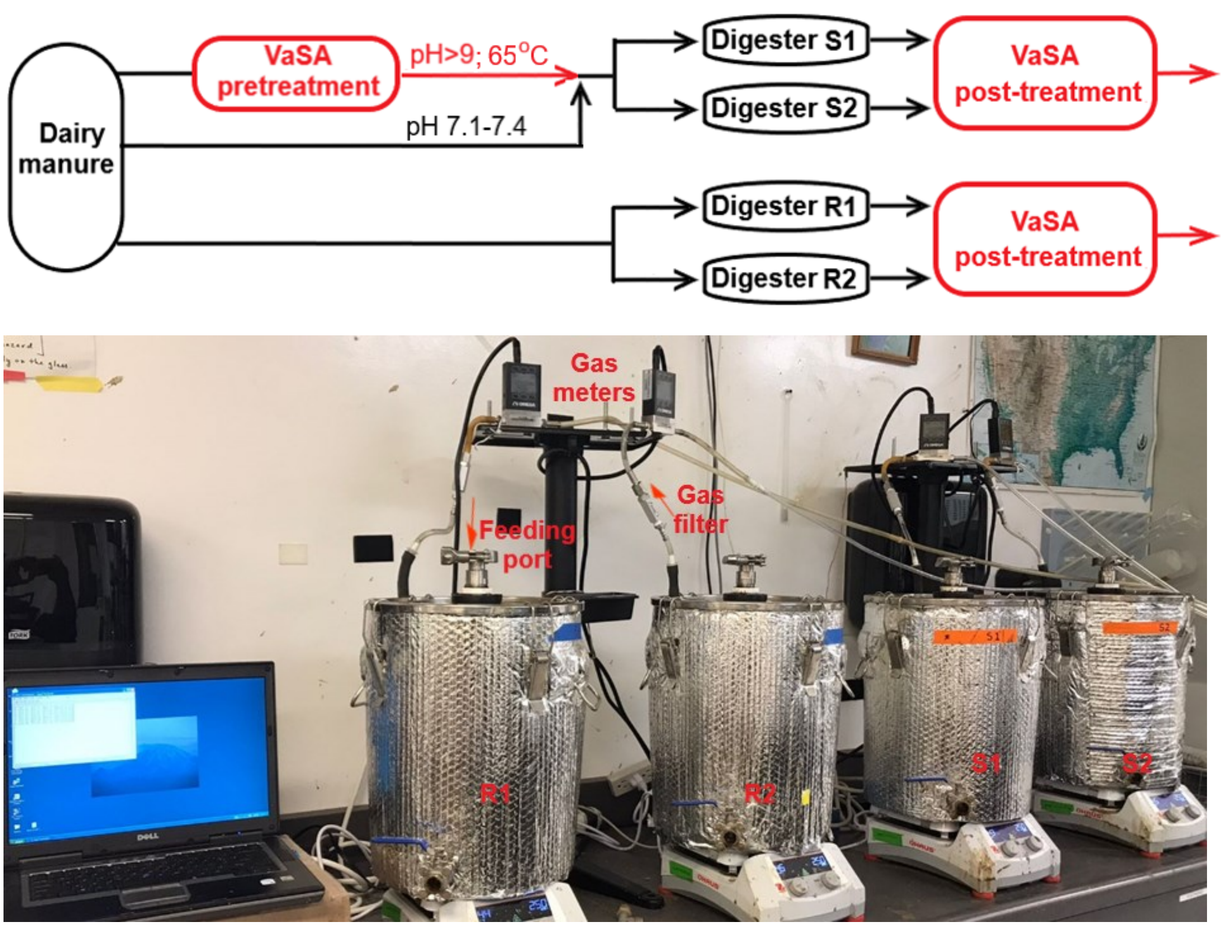

Figure 1. Coupling vacuum stripping and absorption (VaSA) with mesophilic anaerobic digesters fed a mixture of raw manure and VaSA-pretreated manure at 1:1 VS mass ratio (S1 and S2) in parallel with digesters fed with 100% raw manure (R1 and R2).

Cow manure contains fermentative bacteria and methane-producing archaea, making it an inoculum well-suited for the startup of anaerobic digesters [2]. Each digester was inoculated with 18 L of dairy cow manure slurry collected from California Polytechnic State University's manure lagoon at San Luis Obispo, California (Figure A.1). Large objects like wood chips and corn grains were screened out with a #10 mesh (2 mm opening). Heavy particles like sand were removed from the inoculum by 30-min gravity settling. Table 1 presents the characteristics of the inoculum. The inoculum was continuously stirred and heated gradually to approximately 36 ^{o}C in the digesters. The target temperature and mixing intensity were maintained for 4 days to allow for microbial acclimatization.

The digesters were fed daily with dairy cow manure slurry at organic loading rate (OLR) of 1 g-VS/$L_{reactor}$/d in the initial 21 d (startup) and 1.3 g-VS/L/d on Days 22-69 (Period 1) and with liquid dairy manure at 1.8 g-VS/L/d on Days 70-135 (Period 2). Hydraulic retention time was maintained at 26 d by discharging and feeding daily in the same amounts (692.3 g each digester). VS loading rate and hydraulic retention time were kept the same for the digesters with and without pretreatment by adding small amounts of drinking water when feeding. VaSA pretreatment commenced after 21 d of startup. The manure slurry and liquid manure were collected once every 14-28 d from Cal Poly Dairy Farm (Figure A.1). Particles larger than 4.75 mm such as corn and large bedding materials were removed with a screen. A sample was collected from each run of manure collection for characterization as presented in Table 1. Both raw dairy manure and VaSA-pretreated manure were stored in capped buckets at 4 ^{o}C for daily feeding. The combination of VaSA-treated manure and raw manure at 1:1 VS ratio was estimated to have digester influent temperature slightly higher than the mesophilic digestion temperature target of 36 ^{o}C and suitable pH in full-scale applications.

Table 1. Characteristics of inoculum and substrates for anaerobic digestion of dairy cow manure.

Parameter	Inoculum^	Substrate^		
		Manure slurry for Day 0-21 (startup)	Manure slurry for Day 22-69 (Period 1)	Liquid manure for Day 70-135 (Period 2)
pH	8.03	7.43	7.25	7.12 ± 0.15
Conductivity, mS/cm	-	6.10	7.76	8.27 ± 0.90
Alkalinity, g/L as $CaCO_3$	3.17	4.30	5.28	6.98 ± 0.63
Total ammonia-N, mg/L	203	233	435	764 ± 84
Total solids, %	0.91	3.82	4.55	6.76 ± 1.1
Volatile solids, %	0.28	2.77	3.38	5.28 ± 1.1
Ash, % of dry matter (dm)	-	-	25.7	22.4 ± 2.9
Crude protein, % dm	-	-	19.2	13.9
Crude fat, % dm	-	-	4.33	4.20
Lignin, % dm	-	-	8.85	11.5
Cellulose, % dm	-	-	15.1	26.1
Hemicellulose, % dm	-	-	10.6	17.7
Non-fiber carbohydrate, % dm	-	-	16.4	5.2

^: single samples except the averages of 2 samples for physio-chemical parameters on Days 22-69 and average ± standard deviation of 3 samples for physio-chemical parameters on Days 70-135.

The digestate discharged daily from each digester was measured immediately for temperature, pH, and conductivity. Samples were collected weekly for determination of VS, total solids (TS), alkalinity, and total ammonia-nitrogen (TAN = NH_4^+-N + NH_3-N) using the methods described hereinafter in Section 2.4. Kinematic viscosity and time-to-filter (TTF) were measured twice a week from 26 d (one hydraulic retention time) after changing OLR. Biogas flowrate, temperature, and pressure were recorded every 5 min with FMA-1617A mass flow meters (Omega Engineering, Inc., Norwalk, CT). To reduce moisture from the biogas, air filters were interposed in the tubes connecting the gas flow meters and the digesters (Figure 1). The biogas flow rates recorded as mass flow rates at 25 ºC were used to calculate daily biogas production rate at standard temperature (0 ºC) and pressure (101.3 kPa). One-way analysis of variance (ANOVA) was conducted to assess the disparity in biogas production rate, pH, TAN, TTF, and viscosity between the means of the digesters with and without pretreatment. When the P-value was below 0.05, a difference in the means of a parameter was considered significant.

2.2. Pretreatment of dairy manure by vacuum stripping

A functional VaSA prototype (Figure A.2) was used to pretreat dairy manure. VaSA has been optimized to strip ammonia out of dairy manure digestate at the feed depth of 15 cm and pH above 9 [21]. For each batch, 11.67 L of dairy manure were loaded to the vacuum stripper after raising pH to 9.2-9.4 with a 50% NaOH solution. A demister on the stripper refluxes water vapor by surface air cooling. The stripped ammonia gas is sucked by vacuum to an acid solution in the gas absorption column. The absorption solution (300 mL) added to the gas absorption column for the first batch was made of 39 g of concentrated H_2SO_4 and deionized water. The absorption solution was reused upon adding 30-40 g of H_2SO_4 sufficient to react with the NH_3 stripped out of each batch. A 2-L glass flask was installed between the absorption column and vacuum pump to trap remaining water vapor by surface air cooling. Because of the low ammonia concentration (Table 1), the prototype was operated for only 2 h of vacuum stripping in each batch at temperature 65 ºC and pressure 25.1-26.5 kPa.

Conductivity, pH, and concentrations of TAN, TS, VS, and dissolved volatile solids (DVS) were determined for the dairy manure samples collected before and after pH elevation as well as upon 0.5, 1, and 2 h of vacuum stripping, using the methods described in Section 2.4. The time series data of DVS/VS ratio were used to evaluate the kinetics of VaSA pretreatment on solids solubilization. Final volumes of the feed and absorption solution in each batch operation were measured with a graduated cylinder. The initial and final TAN concentrations in the absorption solution were determined in each batch. The volume and TAN concentration of the condensate in the flask trap were also measured.

2.3. Post-treatment of manure digestate by vacuum stripping

When more than 12 L of digestate were accumulated from daily discharges, a batch of VaSA was run. There were 5 batches monitored in Period 1 and 2 batches in Period 2. The operating conditions and parameters were the same as for pretreatment described in Section 2.2, except that each batch operation lasted for 4-5 h because of the higher TAN concentrations in the manure digestate. There were fewer batches monitored in Period 2 as TAN and VS concentrations of digestate were stable.

To examine pathogen reduction through VaSA, digestate samples (100 mL) were collected before pH elevation and after 3.5 and 5 h of vacuum stripping during two runs of batch operation in Period 2, one batch with the effluent of the digesters without pretreatment and the other with the effluent from the digesters with pretreatment. The samples were delivered at a temperature below 10 ºC within 1 h to a local certified laboratory for determination of fecal coliform bacteria as described in Section 2.4.

It was suspected that volatile organic compounds (VOCs) would be generated by fragmentation of lignocellulosic and microbial biomass in the vacuum stripping process and co-stripped out of digestate. The U.S. Environmental Protection Agency has classified some VOCs as hazardous air pollutants. To investigate the generation and transport of VOCs, samples (125 mL each) were taken from manure digestate before pH elevation, digestate after 5 h of vacuum stripping, initial absorption solution, and final absorption solution in the same two runs of batch operation as for fecal coliform examination. Upon centrifugation and glass microfiber filtration (pore size 5 and 1.5 μm), 100 mL of filtrate samples were collected for determination of purgeable VOCs. The absorption solution samples were also filtered through glass microfiber filters (pore size 1.5 μm) for VOC determination.

2.4. Methods for sample analysis and testing

Temperature, pH, electrical conductivity, and TAN concentration in the anaerobic digestion samples were measured with a portable multimeter (Model HQ4300, Hach Company, Loveland, Colorado) equipped with a conductivity probe (IntelliCAL CDC401), pH probe (IntelliCAL PHC301), and ammonia selective electrode (IntelliCAL ISENH3181). The ammonia selective electrode detects the change in electric potential due to NH_3 diffusion through a membrane into its electrolyte upon conversion of sample NH_4^+ into NH_3 at pH greater than 11. Alkalinity was determined by titration with 0.2 N H_2SO_4 solutions, following Standard Method 2530B [24]. TS and VS concentrations were determined gravimetrically by drying at 103-105 ºC and ignition at 550 ºC, respectively, according to Standard Methods 2540B and 2540 E [24]. DVS concentration was determined as VS in the filtrate upon centrifugation of digestate samples at 4000×g for 10 min and vacuum filtration through glass microfiber filters (1.5 μm pore size), following Standard Method 2540 [24]. The density of fecal coliform bacteria was determined as the most probable number (MPN) using the 25-tube fermentation technique, following Standard Method 9221 E

[24]. Viscosity of digestate samples was measured with a Fungilab Cannon-Fenske S400 capillary glass viscometer following ASTM D445 and ASTM D446 methods for opaque samples. Digestate TTF was determined using the small-volume Standard Method 2710H [24].

Biochemical composition of manure slurry and liquid manure samples were characterized by Dairy One Forage Laboratory. It followed AOCS Standard Procedure Am 5-04 for determination of crude fat upon diethyl ether extraction at 90 ºC for 60 min using an ANKOM XT15 extractor. Crude protein (including true protein and non-protein nitrogen) was determined by combustion using a CN928 C/N determinator. Lignin, cellulose, and hemi-cellulose were determined by the ANKOM Technology methods based on sequential extraction treatments with neutral detergent fiber solution, acid detergent fiber solution, 72% H_2SO_4, and ashing.

Determination of purgeable VOCs in the samples from post-digestion VaSA treatment followed U.S. EPA Method 524.2 with detailed procedures described by Tao et al. [16]. It used a TRACE 1310 GC/ISQ 7000 single quadrupole MS (Thermo Scientific, Austin, Texas) system equipped with an automated purge-and-trap concentrator (Teledyne Tekmar Atomx XYZ). Calibration standards (500, 80, and 8 ppb) were prepared with U.S. EPA 524.3 VOA MegaMix (Restek) and ultrapure MilliQ water. 5 µL of EPA 524 Internal Standard/Surrogate Mix (Restek) was added to each vial of samples and standards. Ultrapure water was analyzed periodically for quality control.

3. Results and Discussion

3.1. Kinetics and capacity of solids solubilization and ammonia recovery in pretreatment

There were 4 and 3 batches of 2-h VaSA pretreatment of manure slurry in Periods 1 and liquid manure in Period 2, respectively. The average TS and TAN concentrations of liquid manure were nearly two times those of manure slurry (Figure 2a,c). Before loading to the stripper, manure pH was increased to 9.2-9.4 (Figure 2b), which resulted in 94-96% of ammonia in NH_3 that was readily available for vacuum stripping. As alkali thermal pretreatment of volatile solids proceeds, pH decreases due to release of organic acids [13]. Because dairy manure had high alkalinity (Table 1), feed pH stayed around 9 over the 2 h of vacuum stripping (Figure 2b). Both the high fraction of free ammonia and high enough pH ensured efficient stripping of ammonia (Figure 2c). Liquid-phase ammonia mass transfer coefficient (k_La) in the Lewis-Whitman kinetic model [20] decreased from 0.29 1/h with low-TS manure slurry to 0.21 1/h with high-TS liquid manure. The TAN removal efficiencies were 45.6% in 2-h pretreatment of manure slurry and 38.1% in pretreatment of liquid manure, which were similar to 12-72% attained by 4-h steam stripping of chicken manure at similar process pH (9.2-9.9) and temperature (75-85 ºC) [25] and 32% reported by Molinuevo-Salces et al. [26] for pilot-scale ammonia removal from swine manure by 7-d gas permeable membrane separation. The recent review by Yellezuome et al. [25] found that the commercially applied air stripping processes removed 20-92% of ammonia in dairy, swine, and chicken manure, varying with pH, temperature, air-to-water flow ratio, and hydraulic residence time. It is noteworthy that the VaSA operating parameters and demister design for the VaSA prototype had been optimized to minimize water loss from the feed and the loss of latent heat. TS and VS concentrations were hence similar before and after the 2 h of vacuum stripping (Figure 2a).

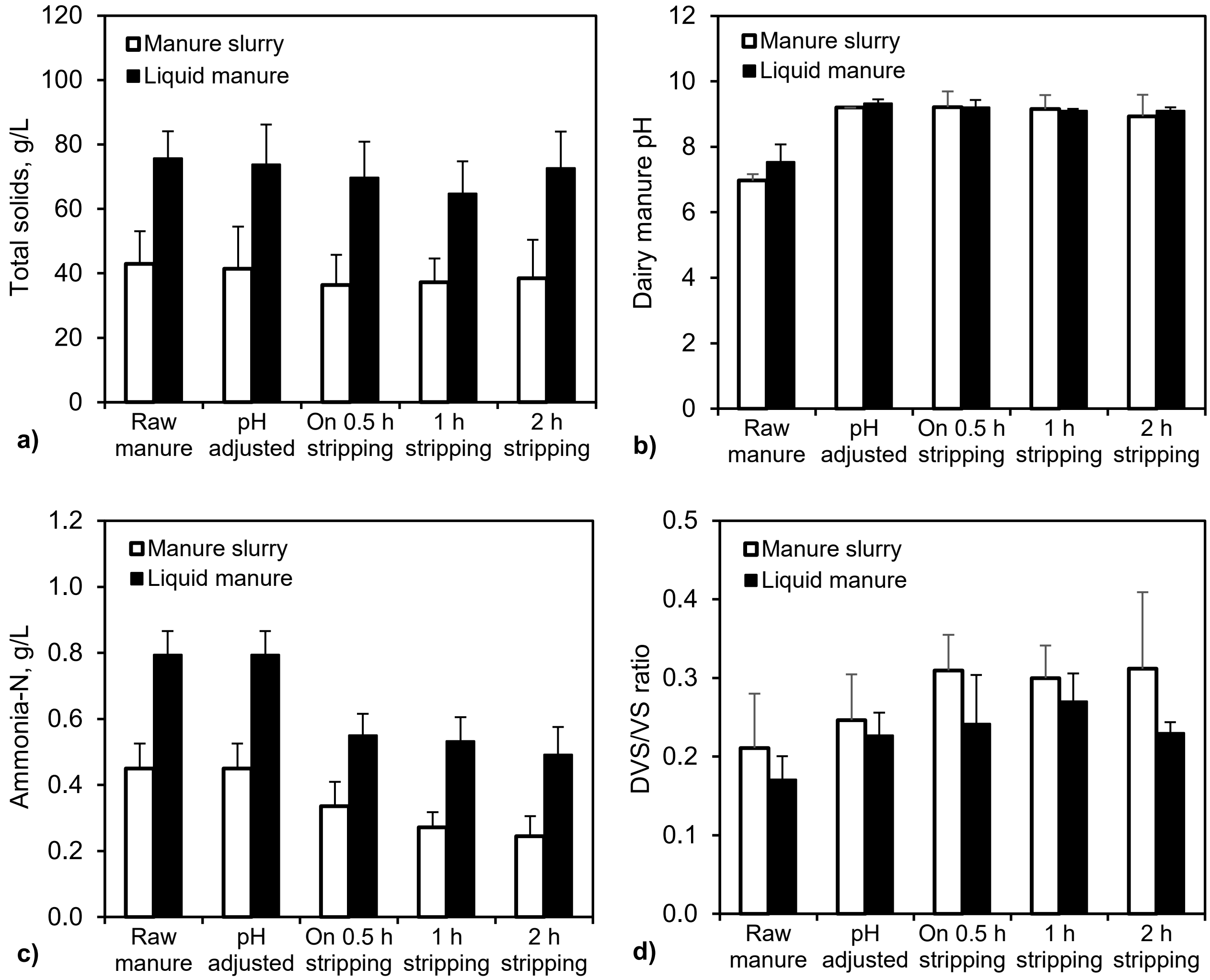

Figure 2. Variations of a) total solids concentration; b) pH value; c) total ammonia-N concentration; and d) concentration ratio of dissolved volatile solids to total volatile solids in dairy manure over 2 h of pretreatment by vacuum stripping. Bar = average of 4 batches for manure slurry and 3 batches for liquid manure; Error bar = standard deviation.

Through pretreatment of dairy manure by VaSA, the fraction of DVS in VS increased by 45.5% in manure slurry and 44.8% in liquid manure (Figure 2d). DVS/VS ratio increased by 16.8-32.9% upon elevation of pH to 9.2-9.4, further increased by 0.07-25.6% in the first 0.5 h of vacuum stripping, and stabilized in 0.5-2 h of stripping, indicating that solids solubilization could be attributed to both alkali treatment and vacuum-assisted thermal/alkali treatment. In contrast, vacuum-assisted thermal/alkali treatment accounted for 70-91% of solids solubilization in sludge digestate and co-digested foodwaste and dairy manure [16,17]. This difference could be attributed to the high fiber content of cow manure, which could be disintegrated and delignified more effectively by alkali treatment than vacuum-assisted thermal treatment.

Thermal treatment accelerates dissolution of lipids and polysaccharides in loosely bound extracellular polymeric substances, disintegration of tightly bound extracellular polymeric substances, and rupture of cell walls [6,27]. It affects solubilization of microbial flocs in dairy manure. Alkali cleaves the intra-lignin linkages as well as ester bonds in lignin-cellulose-hemicellulose complexes [6,28], resulting in disintegration and depolymerization of lignocellulosic biomass in dairy manure. The dosage of NaOH for pH elevation increased from 2.29 g/L for manure slurry to 3.78 g/L for liquid manure as manure alkalinity and VS concentration increased from Period 1 to 2 (Table 1). Alkali treatment selectively removes lignin and increases porosity and interstitial surface area [28]. Vacuum in VaSA poses greater pressure gradient on extracellular polymeric substances, cell walls, and lignocellulosic biomass for deeper penetration of NaOH and subsequently greater disintegration of cells and aggregates [16,17].

3.2. Effect of pretreatment on anaerobic digestion and digestate dewaterability

Because of the high alkalinity of dairy manure (Table 1), digestate pH was stable over time (Figure 3a). Despite the statistically significant differences in pH value between the digesters with and without pretreatment in Period 1 (ANOVA P-value <0.00) and Period 2 (P-value = 0.01), the average differences were very small, 7.45 ± 0.12 in digesters with pretreatment and 7.28 ± 0.14 in digesters without pretreatment in Period 1 as well as 7.50 ± 0.15 in digesters with pretreatment and 7.42 ± 0.17 in digesters without pretreatment in Period 2. The slight effect of VaSA pretreatment on digestate pH suggested that more VaSA-treated manure could be fed to digesters without concern of alkaline pH.

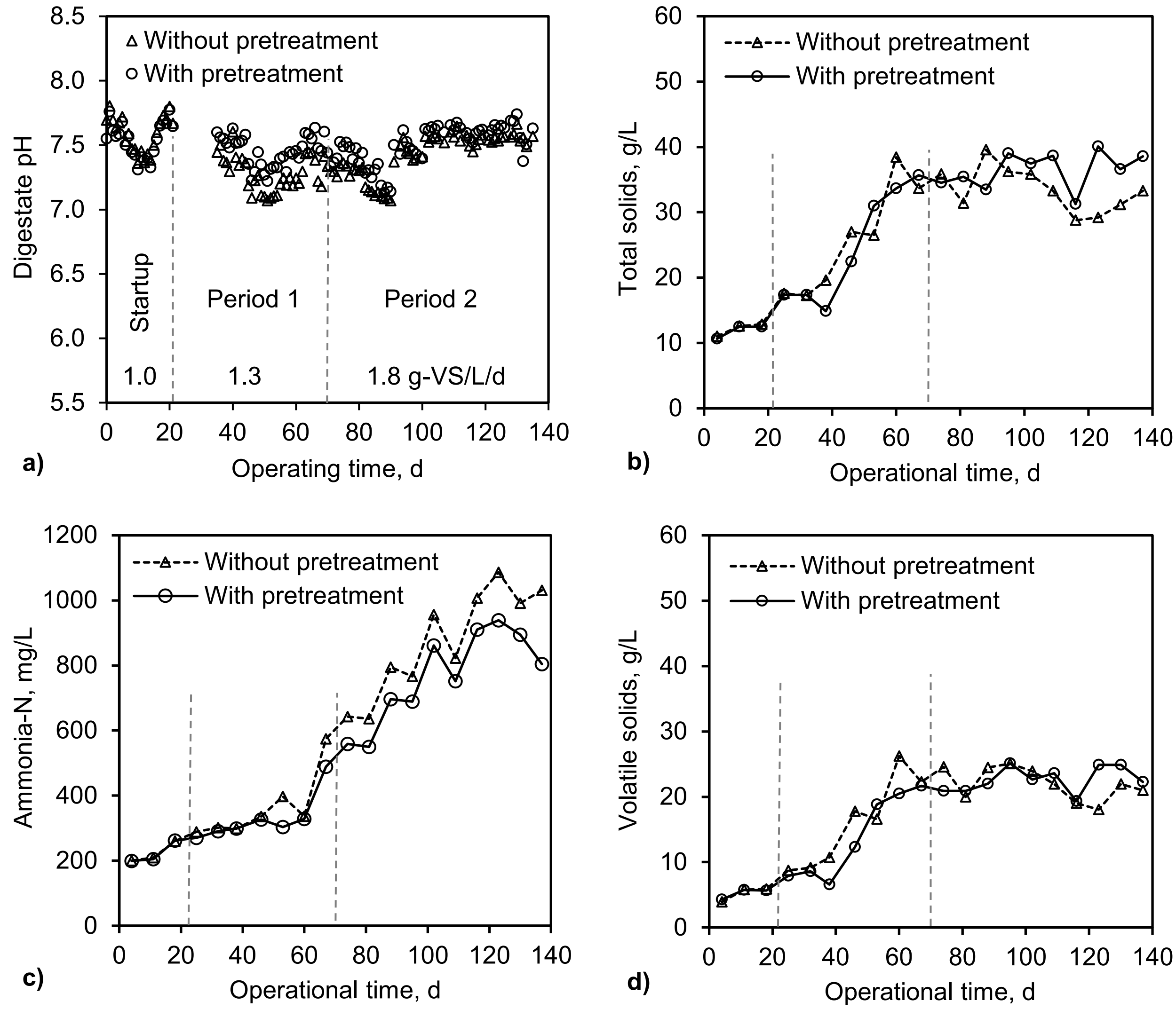

Figure 3. Variations of a) pH value; b) total solids concentration; c) total ammonia-N concentration; and d) volatile solids concentration in anaerobic digesters with and without pretreatment of manure slurry at organic loading rate (OLR) of 1.3 g-VS/$L_{reactor}$/d in Period 1 and liquid manure at 1.8 g-VS/$L_{reactor}$/d in Period 2.

The steep increases in TS and VS concentrations over time in Period 1 (Figure 3b,d) indicated a process of microbial biomass development in the digesters. The similar trends of VS increase in digesters with and without pretreatment in Period 1 suggested no nutrient limitation to microbial growth. Ammonia at concentrations below 200 mg/L serves as a nutrient for anaerobic biomass growth [29]. Although ammonia accumulated quickly in the digesters when OLR was increased to 1.8 g-VS/L/d in Period 2 (Figure 3c), total ammonia and free ammonia concentrations did not reach the level that may inhibit methanogens [29,30]. TAN concentration in the digesters with pretreatment was lower, but the difference between the digesters with and without pretreatment was statistically insignificant (*P*-value = 0.51 in Period 1 and 0.21 in Period 2) because of the low TAN concentrations and correspondingly short vacuum stripping of dairy manure. This insignificant difference in digestate TAN concentration could partially attributed to the increased conversion of organic nitrogen to ammonia in the digesters with pretreatment where hydrolysis and acidogenesis were accelerated by the VaSA-enhanced solids solubilization. Similarly, Han et al. [17] found a small difference in TAN concentration between the digester with and without ammonia recovery by VaSA.

Since microbial biomass developed in Period 1, biogas production rate increased slightly over time (Figure 4). The difference in biogas production rate between the digesters with and without pretreatment was insignificant in Period 1 (*P*-value = 0.37), possibly due to the developing microbial biomass. Biogas production rate stabilized in Period 2 at 0.83 $L/L_{reactor}/d$ in the digesters with pretreatment and 0.71 $L/L_{reactor}/d$ in the digesters without pretreatment, indicating 17% more biogas production due to pretreatment of one half the dairy manure loading. The differences between the digesters with and without pretreatment were statistically significant in Period 2 (*P*-value <0.001). Considering the non-inhibitory TAN concentrations, the increased biogas production was attributed to the enhancement in solids solubilization by the vacuum-assisted low-temperature thermal and mild-alkali treatments under the vacuum boiling conditions. Besides the increased biogas production rate, pretreatment of dairy manure by VaSA accelerated the overall digestion kinetics as evidenced by the greater jump of biogas production rate soon after feeding each day and the steeper decline before next feeding in the digesters with pretreatment compared to the digesters without pretreatment (Figure 5), further confirming the enhanced solids solubilization that accelerated hydrolysis in the digesters. When digesters are discharged and fed continuously, a greater increase in overall biogas production rate would be achieved.

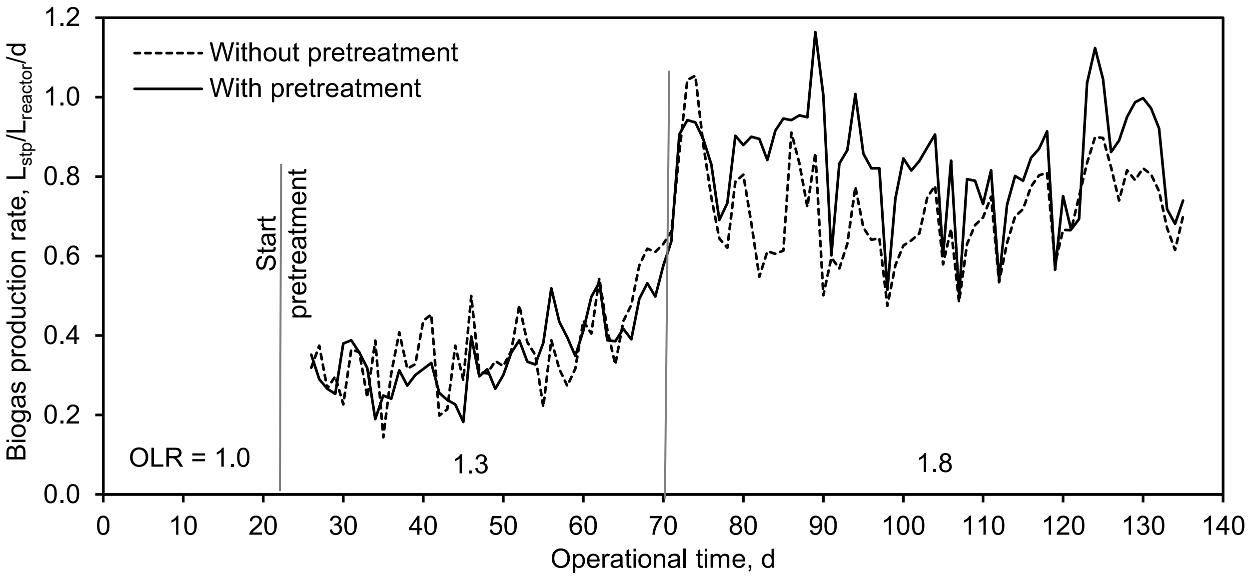

Figure 4. Variations of biogas production in anaerobic digesters with and without pretreatment of manure slurry at organic loading rate (OLR) of 1.3 g-VS/$L_{reactor}$/d and liquid manure at 1.8 g-VS/$L_{reactor}$/d.

To fully utilize the benefits of VaSA pretreatment, it is likely that VaSA-treated alkaline dairy manure can be digested without mixing with untreated manure. The heat in the VaSA-treated substrate could be recycled to dairy manure through heat exchangers. A review by Chen et al. [6] has found that alkaline anaerobic digestion at pH 8.5 and higher is technically feasible and economically favorable for treating livestock manure. As the VaSA-treated dairy manure had a pH near 9, a complete-mix digester would have a pH well below 9 in the digestate although a plug-flow digester may suffer from pH inhibition to methanogenesis near the digester inlet. When all the digester influent is pretreated by VaSA, a 34% increase in biogas production is anticipated. By comparison, a recent review [31] found that low-temperature thermal treatment of dairy, pig, and chicken manure would result in unevidenced to 65% increase in biogas production.

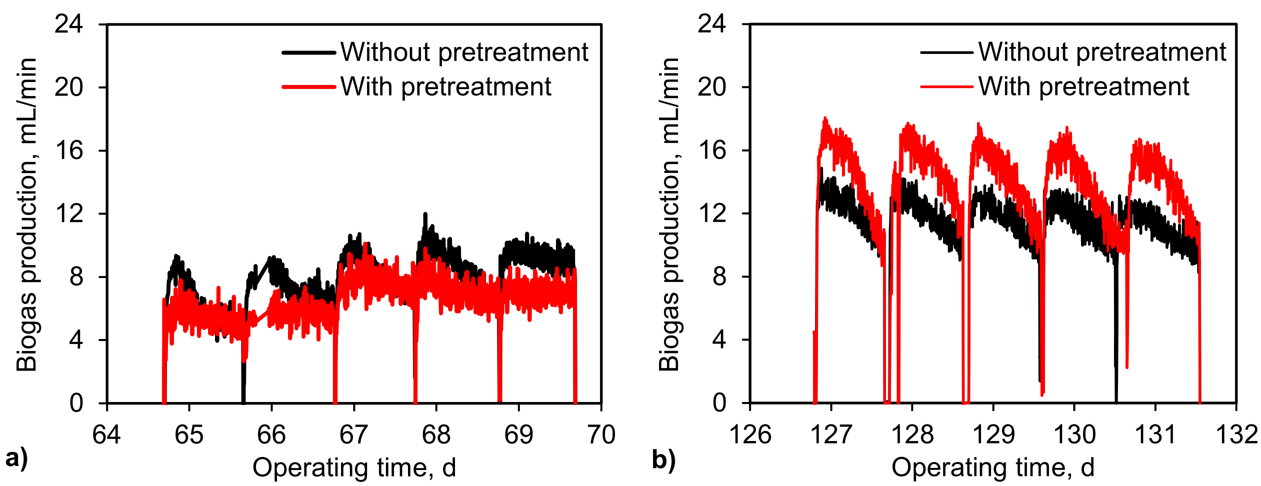

Figure 5. Representative variation of biogas flow measurements after daily feeding of the digesters with and without pretreatment of a) manure slurry at organic loading rate (OLR) of 1.3 g-VS/$L_{reactor}$/d; and b) liquid manure at 1.8 g-VS/$L_{reactor}$/d.

As Figure 6 shows, digestate TTF and viscosity were greater in Period 2 with liquid manure than Period 1 with manure slurry because of the higher OLR and substrate VS concentration in Period 2. Compared with the digesters without pretreatment, the digesters with pretreatment had significantly smaller TTF and viscosity (*P*-value = 0.01-0.03) in Periods 1 and 2 except for the similar TTFs in Period 1 (*P*-value = 0.47). Pretreatment of manure slurry led to an 8.5% decrease in TTF and 14.5% decrease in viscosity in Period 1. The digesters with pretreatment of liquid manure in Period 2 had digestate TTF 11.4% and viscosity 10.6% smaller than those of the digesters without pretreatment. Smaller TTF and viscosity indicate improved dewaterability of digestate [24,32], thus saving costs to separate solids from liquid in digester effluent for further treatment and recycling. Similarly, Han et al. [17] reported that digestate TTF and viscosity were reduced by vacuum stripping and recirculation of co-digested foodwaste and dairy manure. Both thermal treatment and alkali treatment are conditioning technologies to improve sludge dewaterability by disintegration of bioflocs and water releasing from ruptured cells [32]. Low-temperature thermal alkali treatment of sewage sludge and digested sludge improved dewaterability by 0-35% [13].

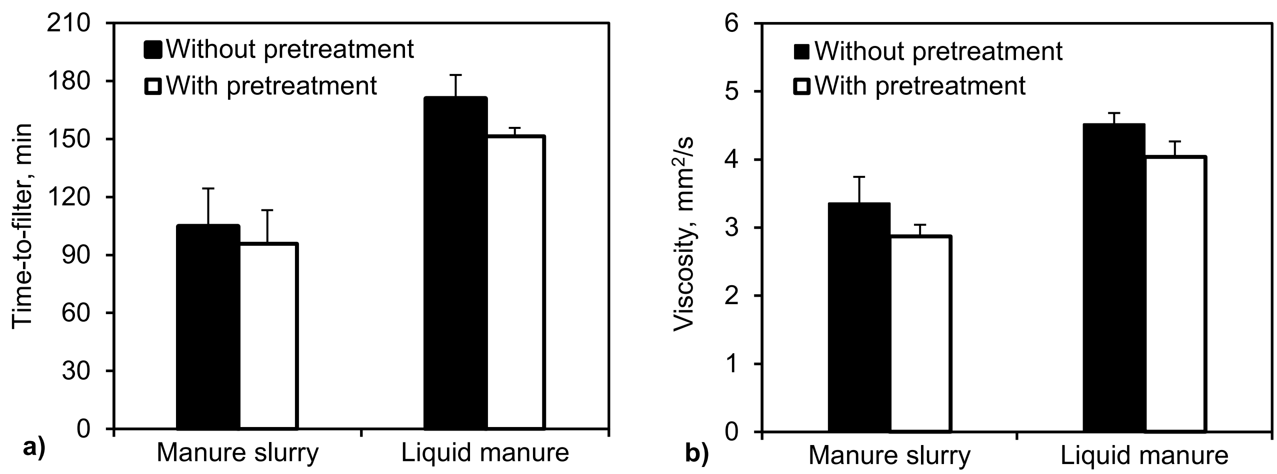

Figure 6. Improvement of digestate dewaterability due to VaSA pretreatment of dairy manure as indicated by a) shorter time-to-filter; and b) lower viscosity. Error bar = standard deviation.

3.3. Kinetics of ammonia recovery in post-treatment of dairy manure digestate

In the post-treatment of dairy manure digestate using the mini-pilot VaSA system, digestate pH was initially raised with NaOH to 8.9-9.2 on average. The NaOH dosages were 1.64 g/L in Period 1 and 2.39 g/L in Period 2, which were lower than those for raw dairy manure because of the higher pH values of manure digestate. After 0.5 h of vacuum stripping, pH increased to 9.4-9.6 due to fast co-stripping of CO_2 (Figure 7a). The digestate collected for VaSA tests had TAN concentrations of 297-520 mg/L in Period 1 and 716-878 mg/L in Period 2 (Figure 7b). The ammonia mass transfer coefficients (k_La) in vacuum stripping of dairy manure digestate, 0.27 1/h in Period 1 and 0.21 1/h in Period 2, were similar to that of dairy manure digestate (0.28 1/h) stripped previously in a similar VaSA system at the same feed depth [21]. The ammonia mass transfer coefficients in vacuum stripping of manure digestate were also similar to those in pretreatment of dairy manure. The ammonia stripping efficiency in 5-h vacuum stripping of dairy manure digestate were 68% in Period 1 and 67% in Period 2, which were higher than 42% reported by Ukwuani and Tao [20] for 4-h vacuum stripping of dairy manure digestate using a similar VaSA system. A recent review by Pandey and Chen [33] found that 25.1-98.9% of ammonia in manure digestate was removed by the commercially applied air stripping process at raised pH (8.0-12.4) and different temperatures (15-80 ºC).

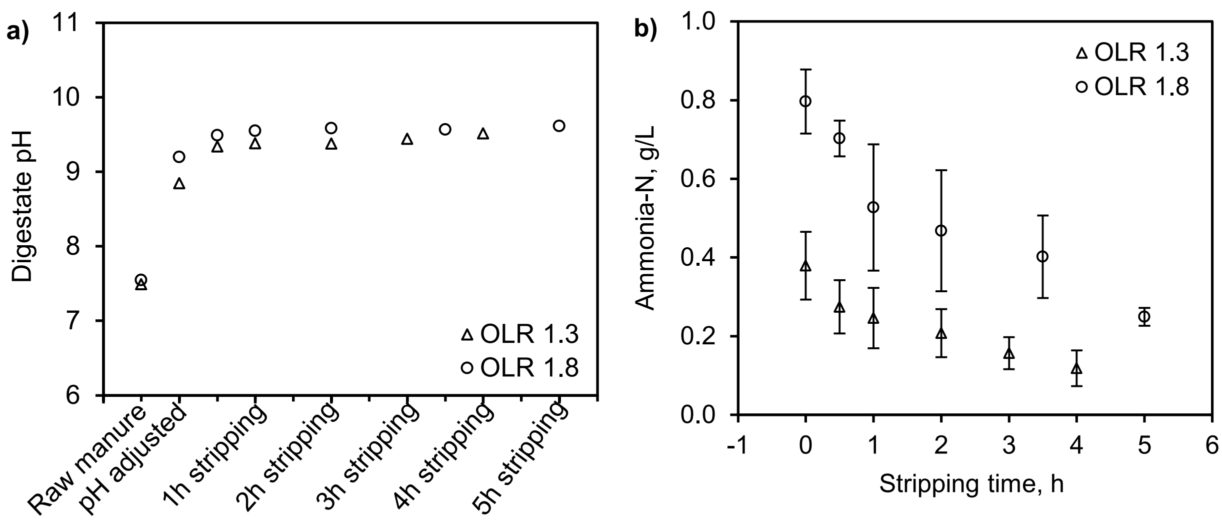

Figure 7. a) Ammonia removal; and b) pH change over 4-5 h of vacuum stripping of manure digestate when digesters were operated at organic loading rate (OLR) of 1.3 g-VS/L/d and 1.8 g-VS/L/d. Error bar = standard deviation of 5 batches at OLR of 1.3 g-VS/L/d and difference of 2 batches at 1.8 g-VS/L/d.

It is noteworthy that more ammonia was absorbed into the acidic solutions (3.63 g/batch in Period 1 and 5.04 g/batch in Period 2) and trapped in condensate (0.52 g/batch in Period 1 and 1.24 g/batch in Period 2) than the ammonia stripped (3.02 g/batch in Period 1 and 6.22 g/batch in Period 2). The greater mass of ammonia recovered than stripped, especially in Period 1 when digestate TAN concentrations were lower, was likely due to the presence of particulate inorganic nitrogen compounds such as fine crystals of struvite ($MgNH_4PO_4 \cdot 6H_2O$) in manure digestate [4,34,35]. The suspended struvite crystals were not dissolved when TAN concentration was determined at pH above 11 using the ammonia selective electrode, whereas the struvite crystals could be dissolved at the high temperature in vacuum stripping [36]. Tao et al. [16] also found a greater ammonia recovery efficiency than ammonia stripping efficiency in pilot VaSA tests with sludge digestate.

The ammonia mass transfer coefficients derived from the post-digestion VaSA tests can be used to estimate the required hydraulic retention time or stripper size in design and operation of full-scale VaSA systems having different ammonia concentrations of dairy manure digestate and different ammonia reduction targets. The TAN concentrations in dairy manure digestate from full-scale animal manure digesters vary in the range of 1.5-6.8 g/L [18,37,38]. In contrast, ammonia inhibition to methanogenesis starts at TAN concentration of 0.9 g/L and reaches 50% inhibition at TAN concentrations of 3.4-10 g/L [29]. Therefore, some anaerobic digesters are operated under ammonia inhibitory conditions. Ammonia needs to be removed or recovered in a return loop or if solids-separated digester effluent is recycled to dilute the high-solids scraped manure before feeding digesters. Reduction of ammonia concentration in digesters also reduces the potential to form the troubling struvite deposits in digestion and downstream treatment facilities. When digester effluent is land applied, removal or recovery of ammonia in digester effluent allows more digestate to be applied to nearby land, saving transportation costs. Furthermore, ammonia recovery from manure digestate reduces downstream emission of ammonia gas, which is a precursor of aerosol and greenhouse gas N_2O [23].

3.4. Effects of alkali/thermal treatment on pathogen reduction and VOCs transport

The density of fecal coliform bacteria was 170,000/100 mL in the dairy manure digestate sample from the digesters without pretreatment and 35,000/100 mL in the sample from the digesters with pretreatment of dairy manure. The difference in fecal coliform density indicated greater pathogen reduction by VaSA pretreatment of liquid dairy manure. All the digestate samples collected after 3.5 and 5 h of vacuum stripping had fecal coliform bacteria undetected (detection limit = 2/100 mL), attaining more than 4.9 and 4.2 log pathogen inactivation in the digestate samples from the digesters without and with pretreatment. As found by Tao et al. [16] in pilot VaSA tests with sludge digestate, the efficient pathogen inactivation by vacuum stripping of manure digestate could be attributed to its unique combination of three actions: low-temperature thermal treatment, mild-alkali treatment, and enhancement of the two treatments by vacuum.

VOCs represent a group of organic compounds characterized by a boiling point below 260 °C under normal atmospheric pressure. Purgeable VOCs were found to be at low concentrations in the dairy manure digestate and after 5 h of vacuum stripping (Table 2). Most of the major VOCs (>0.1 mg/L) were chlorinated and aromatic hydrocarbons. There were 15 VOCs identified in the effluent of the digesters without pretreatment. All the VOCs maintained the same concentrations after 5 h of vacuum stripping, except for one additional aromatic compound detected post-stripping. In contrast, there were only 4 VOCs identified in the effluent of the digesters with pretreatment while 24 VOCs were detected after 5 h of vacuum stripping of this digestate sample. Nevertheless, the total concentration and total mass of all the detected VOCs in the VaSA-treated samples were similar in the treated digestate samples from the digesters with and without pretreatment.

Table 2. Major volatile organic compounds (VOCs) in digestate of liquid dairy manure and absorption solutions before and after vacuum stripping and absorption^.

Parameter	Digesters without pretreatment		Digesters with pretreatment	
	Digestate	Absorption solution	Digestate	Absorption solution
Concentration of major VOCs, mg/L:				
Allyl chloride	1.032(1.032)	0.097(0.094)	0.122(0.134)	0.095(0.099)
1,1,2,3,4,4-hexachloro-1,3-butadiene		0.000(0.419)	(0.548)	0.173(0.422)
2-ethoxy-2-methylbutane			(0.132)	
1-methylethylbenzene			0.118(0.124)	0.117
1,1,1-trichloroethane	0.105(0.105)	0.103	(0.115)	0.107
Propylbenzene	0.114(0.114)	0.110(0.111)	(0.114)	0.113(0.113)
1-chlorobutane			(0.115)	
Chlorobenzene	0.107(0.107)	0.105(0.106)	(0.108)	0.107(0.107)
(E)-1,2-dichloroethylene	0.100(0.100)	0.092(0.094)	(0.105)	0.095(0.095)
(Z)-1,3-dichloro-1-propene	0.071(0.071)		(0.104)	
2,5-Octadecadiynoic acid, methyl ester				1.317(0.216)
Total number of VOCs	15(16)	10(7)	4(24)	14(10)
Total concentration of all VOCs, mg/L	2.104(2.155)	0.692(0.926)	0.329(2.543)	2.451(1.276)
Total mass of VOCs, mg/batch	24.55(22.63)	0.21(0.38)	3.84(28.73)	0.74(0.59)

^: values given as before (after) vacuum stripping; Major VOCs have a concentration >0.1 mg/L.

Because the absorption solutions had been reused for 3-4 batches of VaSA tests, the presence of VOCs in the absorption solutions was not related only to the transport in the monitored batches. There were fewer VOCs in the absorption solutions before vacuum stripping than after vacuum stripping, but the total concentration and mass were similarly low before and after each batch of vacuum stripping. Overall, the minor changes in the total concentration and mass of all VOCs before and after 5-h VaSA tests and the small amounts of VOCs in the absorption solutions suggested little generation and transport of VOCs throughout the VaSA process. Tao et al. [16] concluded similarly on the generation and transport of purgeable VOCs in the VaSA tests with sludge digestate, although sludge digestate had more VOCs (13-27) detected and at greater total concentrations (9.1-17.8 mg/L).

3.5. Economic analysis and feasibility to integrate VaSA for dairy manure treatment

Taking a medium-sized dairy farm with 1000 milking cows as an example, 110 m^3/d of liquid manure is generated based on a unit generation rate of 110 L/head/d [4]. Operating costs, including materials and energy inputs, were estimated in Equations 1-4 for both pretreatment and post-treatment based on the following assumptions and summarized in Figure 8:

- TAN concentration is 800 mg/L in liquid manure and manure digestate;
- Pretreatment by VaSA for 2 h decreases TAN concentration to 526 mg/L in liquid manure and post-treatment for 5 h decreases TAN to 280 mg/L in manure digestate, based on the ammonia mass transfer coefficient of 0.21/h estimated by this study;
- It is assumed that dairy manure has a temperature of 15 ºC and 86% of the heating energy input for VaSA pretreatment is reclaimed by heat exchangers to raise manure temperature to 40 ºC;
- Average price of electricity for industrial customers in the U.S. is \$0.08/kWh [39]; and
- The market price is \$0.24/kg of sulfuric acid and \$0.14/kg of caustic soda [40].

$$E_h = (65-T)\times h_v\times Q\times \rho_m/3600 \quad (1)$$

$$E_e = h_e \times f_e \times A \times \rho_m \times t/3600 \quad (2)$$

$$M_b = D_b \times Q \quad (3)$$

$$M_a = 3.5 \times \Delta TAN \times Q \quad (4)$$

where E_h = energy required to raise the temperature of manure and digestate to vacuum boiling point (65 °C), kWh/d; E_e = loss of latent heat of evaporation due to water efflux, kWh/d; T = temperature of manure out of heat exchangers (40 °C) and digestate temperature (36 °C); h_v = specific heat of manure at measured TS concentration of 75 g/L (3.97 kJ/kg/°C) and digestate at TS concentration of 49 g/L (4.05 kJ/kg/°C) [41]; h_e = latent heat of evaporation (0.310 MJ/kg) at the demister temperature and pressure [16]; f_e = water vapor efflux out of stripper = 1.7 L/m^2/h [16]; A = total surface area of feed in strippers (733 m^2 at the design flow rate) at the optimum feed depth of 15 cm [21]; Q = manure flow rate, m^3/d; ρ_m = density of manure (991 kg/m^3); t = hydraulic retention time of strippers for pretreatment (2 h) and post-treatment (5 h); M_a, M_b = consumption of sulfuric acid and caustic soda, kg/d; D_b = NaOH dosage to increase pH to greater than 9 in liquid manure (3.78 g/L) and manure digestate (2.39 g/L) as measured in this study; ΔTAN = decrease of TAN concentration, g/L; 3.5 = stoichiometric mass ratio of H_2SO_4 to NH_3-N in the acid absorption reaction; and 3600 = conversion factor from second to hour.

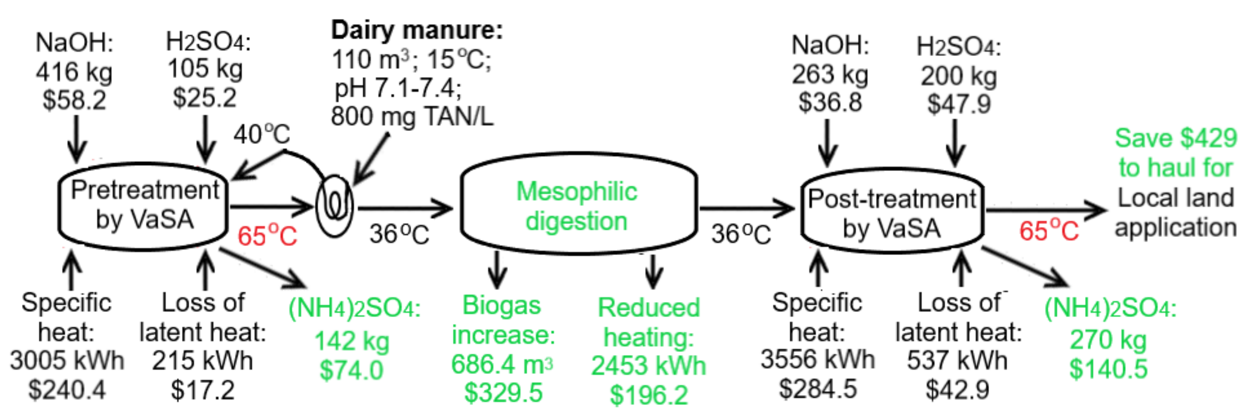

Figure 8. Daily costs and benefits for equipping anaerobic digestion with VaSA for pretreatment of dairy manure at 110 m^3/d and post-treatment of manure digestate.

The revenues from coupling anaerobic digestion with VaSA as presented in Figure 8 include wholesale of recovered ammonium sulfate crystals, increased biogas production, eliminated digester heating due to pretreatment of manure by VaSA, and saved cost to haul manure for land application. The energy saved from eliminated heating of digester influent could be estimated in Equation 1. The revenues from selling ammonium sulfate and increased biogas production were estimated in Equations 5 and 6 with the following assumptions:

- The recovered $(NH_4)_2SO_4$ fertilizer is sold at \$521/ton [16,42];
- Biogas production rate increases by 34% from 0.71 $L/L_{reactor}/d$ to 0.95 $L/L_{reactor}/d$ when linearly extending from 50% pretreatment in this study to 100% pretreatment at solids residence time of 26 d;
- The selling price of biogas is \$0.48/m^3 [6]; and
- The cost to haul manure for land application is reduced from more than \$6.6/m^3 for more than 12 km of hauling to \$2.7/m^3 within 8 km [43].

$$M_c = 4.7\times \Delta \mathrm{TAN}\times Q \quad (5)$$

$$V_g = \Delta Y\times Q\times \theta \quad (6)$$

where M_c = production of $(NH_4)_2SO_4$ fertilizer, kg/d; 4.7 = stoichiometric mass ratio of $(NH_4)_2SO_4$ to TAN in the acid absorption reaction; V_g = increased biogas production, m^3/d; ΔY = increment of biogas production rate, $L/L_{reactor}/d$; θ = solids residence time in digesters, d; and ΔTAN and Q the same as in Equations 1-4.

When VaSA is applied to both pretreatment and post-treatment as shown in Figure 8, the total revenues (\$1,169.2/d or \$10.63/m^3) will be greater than the total operating costs (\$764.6/d or \$6.95/m^3), indicating a benefit/cost ratio of 1.5. By comparison, the review by Li et al. [10] on the input and output costs of different pretreatment methods found a median benefit/cost ratio of 0.21 only and only 4 out of the 15 reviewed methods had benefit/cost ratio greater than 1. Heating energy accounts for 69% of VaSA's operating costs. The daily operational costs for feed pumps, acid dosing pump, and heat pumps were estimated to be $11.5 only. When VaSA is applied to pretreatment only, the total revenues ($5.45/m^3) and total costs ($3.18/m^3) will be smaller, but benefit/cost ratio will be slightly higher (1.7). When VaSA is applied to post-treatment only, the digestate TAN concentration can be 1600 mg/L and hydraulic retention time will be increased to 8.9 h for reducing TAN concentration to 280 mg/L. Subsequently, the revenues ($7.13/m^3) and costs ($4.72/m^3) were estimated with Equations 1-6, resulting in a benefit/cost ratio of 1.5. Based on the above cost and benefit estimates, therefore, VaSA can be applied to pretreatment for increased biogas production, post-treatment for fertilizer production and local land application of manure digestate, or both pretreatment and post-treatment for multiple benefits.

Using NaOH to increase pH for vacuum stripping would increase Na^+ concentration and contribute to conductivity or salinity of the treated manure and digestate, leading to potential risks to soil salinity and plant growth after long-term land application of VaSA-treated manure digestate. As shown in Figure 9a for 2-h pretreatment and 5-h post-treatment, conductivity increased upon pH elevation and decreased as NH_4^+ , HCO_3^- and CO_3^{2-} were converted to NH_3 and CO_2 and stripped over time (Figure 9). Besides ion removal, 2-h VaSA pretreatment and 5-h post-treatment would concentrate manure and digestate by only 2.3% and 5.7%, respectively, at the water vapor efflux rate of 1.7 L/m^2/h. Overall, the digesters with pretreatment of liquid manure in Period 2 had conductivity (11.80 mS/cm) slightly higher than the digesters without pretreatment (11.13 mS/cm); and the post-treatment of digestate even decreased conductivity from 11.10 mS/cm to 9.50 mS/cm. Therefore, both pretreatment and post-treatment by vacuum stripping are unlikely to change the risk of manure land application on soil salinity.

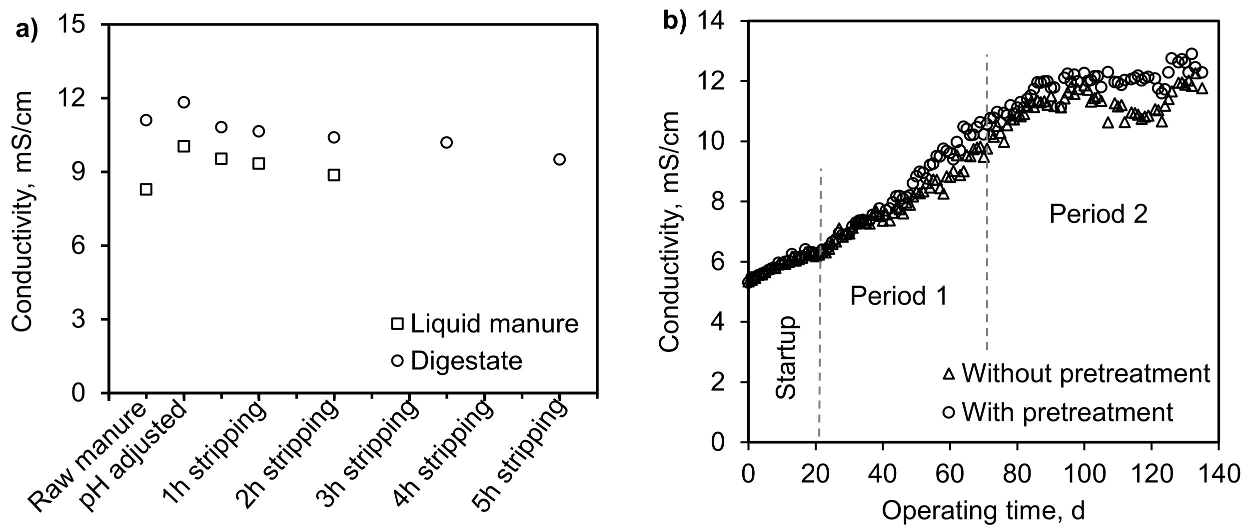

Figure 9. a) Conductivity variation throughout batch post-treatment of manure digestate in Period 2; and b) conductivity difference between digesters with and without pretreatment of cow manure by vacuum stripping.

Unlike the slight changes in conductivity due to NaOH dosing, sodium concentration would increase by 2.17 g/L in liquid manure at the average NaOH dosage of 3.78 g/L and by 1.37 g/L in manure digestate at the dosage of 2.39 g/L. Tao et al. [4] estimated Na content in dairy slurry in the U.S. at 0.90 g/L. Stürmer et al. [44] found the average Na content in anaerobic digestate at 1.74 g/L based on the digestate testing results of 132 Austrian biogas plants (105 agricultural and 27 waste plants) surveyed in 2014-2018. Therefore, VaSA treatment may make a substantial increase in Na content. Nevertheless, the effect of Na on soil conductivity and salinity is contextual and dependent on soil properties [45]. The European legal frameworks on use of digestate as fertilizer do not have requirements for pH and Na content [44]. The alkalinity of manure digestate with VaSA pretreatment (10.3 g/L as $CaCO_3$) and without pretreatment (9.1

g/L) would be high enough to keep soil pH stable despite land application of the alkaline digestate. To mitigate the potential risks of excessive Na from VaSA treated digestate, NaOH may be replaced, partially or fully, by KOH for pH elevation. KOH would not change the performance of vacuum stripping while amending K as a macronutrient.

4. Conclusions

This study proved that coupling anaerobic digestion with the novel vacuum stripping and absorption process is an integrative strategy to empower anaerobic digestion. When liquid dairy manure is pretreated by vacuum stripping, solubilization of the lignocellulosic solids in dairy cow manure is enhanced by the vacuum-assisted low-temperature thermal and mild-alkali treatments under the vacuum stripping conditions. Consequently, anaerobic digestion of VaSA-pretreated dairy manure produces more biogas and discharges digestate with improved dewaterability. When the vacuum stripping and absorption process is further applied to post-digestion treatment of digestate, ammonia is recovered as $(NH_4)_2SO_4$ fertilizer and allows more digestate to be applied to nearby land at lower transportation costs. Post-treatment by vacuum stripping also benefits recycling of manure digestate due to pathogen reduction.

Pretreatment of dairy manure by VaSA for 2 h increased the dissolved fraction of volatile solids by 45%. When one half of the digester influent was pretreated by vacuum stripping for 2 h, anaerobic digestion of liquid dairy manure could produce 17% more biogas and decrease time-to-filter and viscosity of digestate by 9-15%. 100% of the digester influent could be pretreated by VaSA to produce 34% more biogas without concern of alkaline pH and overheating digesters if heat exchangers were added between VaSA and digesters. Post-treatment of manure digestate by vacuum stripping for 3.5 h reduced fecal coliform to undetected. Ammonia was recovered from liquid dairy manure and manure digestate at similar liquid-phase ammonia mass transfer coefficients, 0.21-0.29/h. Post-treatment of manure digestate by VaSA made minor changes in the total concentration and mass of volatile organic compounds. Pretreatment and post-treatment together would bring in a total benefit of $10.63/m^3 versus a total operating cost of $6.95/m^3.

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