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Abstract

This article addresses the effect of ultrasonication as a pretreatment to anaerobic digestion of four types of animal manure, including swine slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent. The effect of ultrasonication on soluble chemical oxygen demand (SCOD) and biochemical methane potential (BMP) were determined, and the energy efficiency of ultrasonic pretreatment was evaluated. Ultrasonic pretreatment was applied at two amplitudes (80 and 160 μ mp) and at two time settings (15 and 30 s) to each of the four manure types. The SCOD of each manure sample was determined before and after ultrasonic pretreatment. In addition, BMP trials were run on each waste with and without ultrasonic pretreatment. As part of the BMP, biogas production was measured and analyzed for methane content and cumulative methane production. Ultrasonic pretreatment of swine slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent increased the average SCOD up to 23%, 92%, 59%, and 33%, respectively, and the average methane yield up to 56%, 43%, 62%, and 20%, respectively. Increasing the ultrasonic amplitude and treatment time resulted in an increase in manure SCOD and methane production; the greatest methane production was obtained using the ultrasonic pretreatment at the highest power and longest treatment time. The observed greatest methane production from swine slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent were 394, 230, 226, and 340 mL CH₄ g⁻¹ VS, respectively. In contrast, the greatest energy efficiency was obtained with the lowest ultrasonic amplitude combined with the shortest treatment time.

Keywords

Animal manure, Biochemical methane potential assay (BMP), Methane yield, Soluble chemical oxygen demand (SCOD), Ultrasonic

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EVALUATION OF ULTRASONIC PRETREATMENT ON ANAEROBIC DIGESTION OF DIFFERENT ANIMAL MANURES

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ABSTRACT. *This article addresses the effect of ultrasonication as a pretreatment to anaerobic digestion of four types of animal manure, including swine slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent. The effect of ultrasonication on soluble chemical oxygen demand (SCOD) and biochemical methane potential (BMP) were determined, and the energy efficiency of ultrasonic pretreatment was evaluated. Ultrasonic pretreatment was applied at two amplitudes (80 and 160 μm_{pp}) and at two time settings (15 and 30 s) to each of the four manure types. The SCOD of each manure sample was determined before and after ultrasonic pretreatment. In addition, BMP trials were run on each waste with and without ultrasonic pretreatment. As part of the BMP, biogas production was measured and analyzed for methane content and cumulative methane production. Ultrasonic pretreatment of swine slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent increased the average SCOD up to 23%, 92%, 59%, and 33%, respectively, and the average methane yield up to 56%, 43%, 62%, and 20%, respectively. Increasing the ultrasonic amplitude and treatment time resulted in an increase in manure SCOD and methane production; the greatest methane production was obtained using the ultrasonic pretreatment at the highest power and longest treatment time. The observed greatest methane production from swine slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent were 394, 230, 226, and 340 mL $\text{CH}_4 \text{ g}^{-1} \text{ VS}$, respectively. In contrast, the greatest energy efficiency was obtained with the lowest ultrasonic amplitude combined with the shortest treatment time.*

Keywords. *Animal manure, Biochemical methane potential assay (BMP), Methane yield, Soluble chemical oxygen demand (SCOD), Ultrasonic.*

Anaerobic digestion is a natural process that has been utilized for decades to produce biogas from animal wastes for energy production. In addition, anaerobic digestion of manure reduces organic matter content, provides substantial odor reduction, reduces greenhouse gas emissions from covered systems, and potentially reduces manure pathogens. In order to enhance the digestion process, this article examines the use of high-power ultrasonics to reduce the particle size of the substrate. By reducing the particle size, the ratio of the surface area to volume is increased, which increases the reactive sites for digestion. High-powered, ultrasonic sound waves at a frequency above 18 to 20 kHz that result in physical or chemical changes in a treated medium are the effect of two fundamental mechanisms in liquids: cavitation and acoustic streaming. Ultrasonic cavitation is the result of the cyclic pressure waves that expand and compress nucleated bubbles that grow as a function of time due to rectified diffusion. Once the bubbles grow

to an unstable size, they implode violently, resulting in high temperatures (+5000 K) and shock waves that break up neighboring particles and surfaces. Acoustic streaming helps mix the fluids and synergistically promotes mass transfer within the fluid (Suslick, 1990). The power dissipated during ultrasonic treatment of a liquid is dependent on the amplitude (peak-to-peak displacement of the vibrating tool) and stiffness of the load. Generally, power is proportional to amplitude and load stiffness. For example, the stiffness of a fluid load can be effectively increased by increasing the pressure (head pressure in a closed reaction chamber).

Ultrasonic pretreatment has been used to treat municipal wastewater activated sludge to improve hydrolysis of anaerobic digestion (Chu et al., 2002; Khanal et al., 2007). The purpose of this treatment is to reduce the size of biosolid particles such that they are more easily converted to biogas in the anaerobic digestion process. Chyi and Dague (1994) concluded that the larger the particle size, the longer the time required for hydrolysis, which can be the rate-limiting step for anaerobic digestion. Nickel and Neis (2007) and Tiehm et al. (2001) demonstrated that ultrasonic pretreatment can disintegrate bacterial cells and increase the quantity of dissolved organic substrate as well as the degradation rate and the digestibility of biosolids during the anaerobic digestion process. Other researchers reported that high energy intensity ultrasonic pretreatment enhances the disintegration of organic solids, reducing particle sizes and increasing the SCOD in the supernatant (Wang et al., 2005; Benabdallah El-Hadj et al., 2006). Numerous studies have been conducted to evaluate the performance of ultrasonic applications for wastewater sludge pretreatment (Khanal et al., 2007). Lafitte-Trouqué and For-

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ster (2002) demonstrated that gas production rates from anaerobic digestion of ultrasonic pretreated sludge were higher than those for untreated sludge. Wang et al. (1999) reported that waste activated sludge with ultrasonic pretreatment produced 64% more methane compared with untreated sludge. Dewil et al. (2006) concluded that particle size reduction caused by ultrasonic pretreatment enhanced biological hydrolysis, resulting in more degradable substrate and increasing methane production. The large enhancement of methane yield that was seen in the study was likely due to particle size reduction caused by the ultrasonic treatment resulting in an enhanced biodegradability. However, the effectiveness of ultrasonic pretreatment applied to anaerobic digestion of animal manure has not been reported.

The objectives of the current study were: (1) to evaluate the effectiveness of ultrasonic pretreatment on biochemical methane potential (BMP) and soluble chemical oxygen demand (SCOD) for four types of animal manure, and (2) to evaluate the energy efficiency (defined in this article as increased energy yield by ultrasonic pretreatment vs. energy used for running the ultrasonic unit) of ultrasonic pretreatment of these manure compounds.

MATERIAL AND METHODS

SAMPLE COLLECTION

Four types of animal manure were analyzed in this study: swine slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent. One individual sample was collected for each manure type used in the experiments. Swine slurry was collected from the collection pit of a hog barn with a shallow pit scrape system at a 2,780-head farrow-to-finish operation (Nevada, Iowa). Beef feedlot manure was collected from the settling basin of a 1,400-head open beef feedlot (Lytton, Iowa) where solid manure was removed from the lot as needed and feedlot runoff was managed with a solid settling basin and a vegetative treatment area. Liquid dairy manure with and without fiber removal was collected from the 400-head Iowa State University Dairy Farm (Ames, Iowa). Manure from the freestall barn was scraped and solid separated with a Vincent KP-10 screw press separator with a 0.038 cm slotted screen. Liquid manure without fiber removal was collected prior to processing in the liquid-solid separation system and is referred to as dairy manure slurry. Liquid manure with fiber removal was collected from a sump after liquid-solid separation and is referred to as separated dairy manure effluent.

SAMPLE CHARACTERIZATION

The collected manure samples were analyzed for total solids, volatile solids, pH, total Kjeldahl nitrogen, ammonia, chemical oxygen demand (COD), soluble chemical oxygen demand (SCOD), and total phosphorus. Total and volatile solids were analyzed using Standard Method 2540 G (APHA, 1980). The pH was determined with a Corning pH combination gel-filled electrode (Corning, Inc., Corning, N.Y.). Total Kjeldahl nitrogen and ammonia were analyzed using a Labconco digester (model 23012) and Labconco Rapidstill II (model 65200, Labconco Corp., Kansas City, Mo.) using Kjeldahl Method 2001.11 (AOAC, 1984). COD and SCOD were measured using a Hach colorimetric digestion method (method 8000, Hach Co., Loveland, Colo.). Supernatant for

SCOD analyses before and after ultrasonic treatment was conducted after filtration through plastic microfiber syringe filters with a pore size of 0.45 μm . Total phosphorus was determined using a Genesys 6 spectrophotometer (Thermo Electron Corp., Waltham, Mass.) with Photometric Method 965.17 (AOAC, 1984).

ULTRASONIC PRETREATMENT AND EXPERIMENTAL DESIGN

In order to facilitate ultrasonic processing and create uniform samples, samples were diluted to 3.9% VS. The ultrasonic equipment utilized in the current study was designed to supply acoustic energy to liquids. Three of the four undiluted manure samples contained relatively high TS. Therefore, the samples were diluted. The dilution factors for swine slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent were 4.1, 6.3, 2.3, and 1, respectively. The resulting total solids content of diluted swine slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent was 4.5%, 4.8%, 4.6%, and 5.3%, respectively. The ultrasonic system used in this study was a 2.2 kW, 20 kHz Branson 2000 series, equipped with a 0 to 20 μm_{pp} converter, a 1:1 gain booster, and a 1:8 gain horn (Branson Ultrasonics Corp., Danbury, Conn.). Ultrasonic pretreatment was applied with two amplitude settings at 80 and 160 μm_{pp} as well as two time settings (15 and 30 s) to each of the four types of animal manure before setting up a benchtop BMP trial. Ultrasonic amplitude and time settings utilized in the study were selected based on previous experiments (Wu-Haan et al., 2010). The manure types were sonicated as batch loads based on the treatment settings previously described; batch loads were performed individually and were not replicated. The experiment had a total of four treatments (2×2 matrix) and a set of untreated controls that were tested for SCOD and biochemical methane potential.

BMP ASSAYS

A modified BMP method, based on the procedure outlined by Owen et al. (1979), was used to evaluate anaerobic digestibility and biogas potential. An aliquot of diluted animal manure (4.35 g sample equivalent to 0.17 g VS) was added to a 250 mL serum bottle along with 100 mL of anaerobic inoculum. Inoculum was obtained from a 60 L mesophilic (35°C) continuous stirred-tank reactor (CSTR) with an inoculum concentration of 1.7 g VS L^{-1} . On a daily basis, the inoculum received a slurried mixture of dry dog food and micronutrients as a substrate source. The ratio of manure sample to inoculum VS was 1:1. The head space in the serum bottle was purged with a gas mixture of 70% nitrogen and 30% carbon dioxide at a flow rate of approximately 0.5 L min^{-1} for 5 min. After the air in the head space was removed using a glass syringe, sealed serum bottles were placed on a shaker (150 to 200 rpm) and incubated at 35°C for 30 days. In order to determine endogenous CH_4 production, blank samples that contained only 100 mL inoculum and de-ionized water were also prepared.

Each assay was performed in triplicate. Biogas production was monitored daily via volume displacement with a 50 mL wetted gas graduated syringe with 1 mL gradations. Biogas measurements were conducted under temperature-controlled conditions (35°C). The methane content of the biogas was determined using an NDIR- CH_4 gas analyzer (Sensors Europe GmbH, Erkrath, Germany). Methane volume was calcu-

lated using biogas production as well as methane content and was reported as methane yield at 35 °C. Methane yields were calculated by dividing methane volume (mL) by the mass of the sample VS added to each bottle (g VS added) and reported as mL CH₄ g⁻¹ VS added.

CALCULATION OF ULTRASONIC EFFICIENCY

The ultrasonic energy input (E_{in} , J g⁻¹ VS) into each sample was calculated using equation 1:

$$E_{in} = \frac{P \times t}{V \times VS} \quad (1)$$

where P is the power (W), t is the ultrasonic treatment time (s), V is the volume of sample (mL), and VS is the volatile solids concentration of sample (g VS mL⁻¹). The power was reported by the ultrasonic generator as the power dissipated by the converter.

In addition, the change in methane yield (ΔM , mL CH₄ g⁻¹ VS) due to ultrasonic pretreatment and the energy output (E_{out} , J g⁻¹ VS) as increased methane yield due to ultrasonic pretreatment were calculated using equations 2 and 3:

$$\Delta M = M_t - M_c \quad (2)$$

$$E_{out} = \Delta M \times E' \quad (3)$$

where M_t is the methane yield from a sample with ultrasonic pretreatment (mL CH₄ g⁻¹ VS), M_c is the methane yield from the sample without ultrasonic pretreatment (mL CH₄ g⁻¹ VS), and E' is the energy content of methane (J mL⁻¹). The energy content of methane used for the computation was 38.2 J mL⁻¹ (Walsh et al., 1988).

The overall ultrasonic efficiency (E_{eff}) was calculated using equation 4:

$$E_{eff} = \frac{E_{out} - E_{in}}{E_{in}} \times 100\% \quad (4)$$

STATISTICAL ANALYSES

The SCOD and methane production data were analyzed using the GLM (general linear models) procedure of SAS (SAS, 1990). The model included the fixed effects of ultrasonic pretreatment (untreated and ultrasonic pre-treated), ultrasonic amplitude (80 and 160 μ m_{pp}) and ultrasonic time (15 and 30 s). Differences were deemed significant at $P \leq 0.05$.

RESULTS AND DISCUSSION

MANURE CHARACTERISTICS

To provide information about the consistency of the manures used in this study, the manures were characterized. The laboratory analyses of swine slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent before dilution and ultrasonic treatment are presented in table 1. As noted in the previous section, the total solids content of three of the manures was higher than should be utilized in the sonication equipment, and they were diluted to the volatile solids content of the separated dairy manure effluent.

ENERGY INPUT FOR ULTRASONIC PRETREATMENT

Energy input for ultrasonic pretreatment increased as a function of ultrasonic amplitude and treatment time (fig. 1).

Table 1. Laboratory analysis of pig slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent.

Parameter	Pig Slurry	Beef Feedlot Manure	Dairy Manure Slurry	Separated Dairy Manure Effluent
TS (% ww)	18.4	29.8	10.5	5.3
VS (% ww)	16.1	24.6	9.1	3.9
pH	6.9	7.1	6.9	6.9
COD (g L ⁻¹)	52.1	44.9	29.2	70.3
TKN (mg g ⁻¹ TS)	34.2	29.7	24.3	55.5
NH ₄ -N (mg g ⁻¹ TS)	14.1	6.4	7	25.2
P (mg g ⁻¹ TS)	14.0	12.1	5.1	1.1

Table 2. Soluble chemical oxygen demand (SCOD) of pig slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent treatment without or with ultrasonic pretreatment at varied amplitude (80 and 160 μ m) and time (15 and 30 s).^[a]

	SCOD (g L ⁻¹)			
	Pig Slurry	Beef Feedlot Manure	Dairy Manure Slurry	Separated Dairy Manure Effluent
LSMEAN				
Untreated	8.2	8.4	7.6	22.1
80 μ m _{pp} , 15 s	8.2	8.6	7.7	23.5 a
80 μ m _{pp} , 30 s	10.6 a	9.2 a	9.6 a	25.8 b
160 μ m _{pp} , 15 s	10.6 a	9.8 a	11.8 a	25.2 b
160 μ m _{pp} , 30 s	12.8 b	12.0 b	12.3 b	26.6 c
SEM	0.5	0.2	0.3	3.7
Probabilities (p-value)				
Ultrasound	<0.01	<0.01	<0.01	<0.01
Amplitude	<0.01	<0.01	<0.01	0.01
Time	<0.01	<0.01	<0.01	0.01
Amplitude \times time	0.73	0.01	0.02	0.48

^[a] Within a column, means followed by different letters are significantly different for a given manure type ($p < 0.05$).

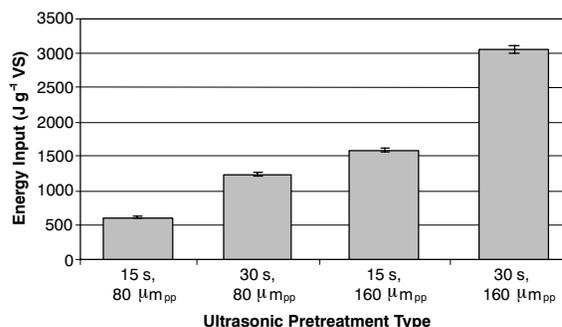


Figure 1. Energy input for various ultrasonic pretreatments.

In the current study, the energy required to ultrasonically treat the animal wastes at an amplitude of 80 μ m for 15 and 30 s were 625 J g⁻¹ VS (531 J g⁻¹ TS) and 1,243 J g⁻¹ VS (1,057 J g⁻¹ TS), respectively. The energy input for treating the animal wastes at an ultrasonic amplitude of 160 μ m for 15 and 30 s were 1,591 J g⁻¹ VS (1,353 J g⁻¹ TS) and 3,053 J g⁻¹ VS (2,596 J g⁻¹ TS), respectively. The energy inputs reported in the literature for ultrasonic application of pretreated waste activated sludge ranged from 660 to 64,000 J g⁻¹ TS in pilot-scale treatment systems (Bougrier et al., 2005; Rai et al., 2004). Limited information is available in the literature on energy inputs for full-scale treatment systems.

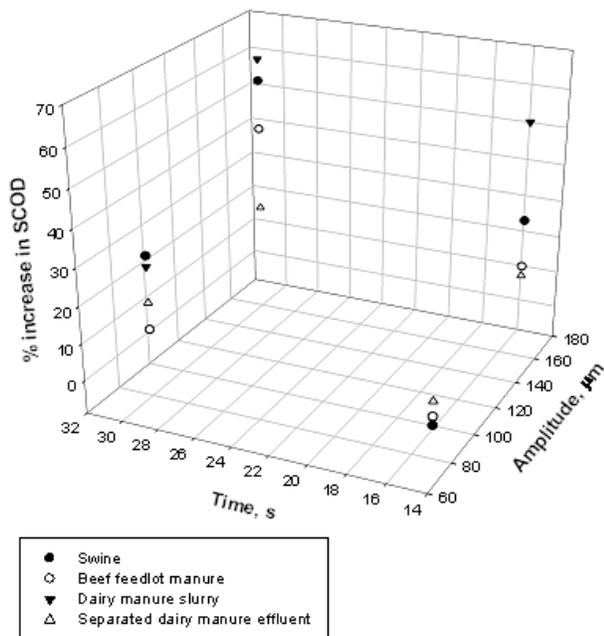


Figure 2. Percentage (%) increase in soluble chemical oxygen demand (SCOD) of pig slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent treatment without or with ultrasonic pretreatment at varied amplitude (80 and 160 μm) and time (15 and 30 s).

MANURE SOLUBLE CHEMICAL OXYGEN DEMAND

The manure soluble chemical oxygen demand (SCOD) is an important parameter for quantifying substrate solubilization, and it is also commonly used for measuring ultrasonic disintegration efficiency. The effect of ultrasonic pretreatment on the SCOD concentration of swine slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent is shown in table 2 and figure 2.

Ultrasonic pretreatment increased the average SCOD of swine slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent up to 56%, 43%, 62%, and 20%, respectively. Ultrasonic pretreatment had a significant effect on the SCOD of all four types of manure ($p < 0.01$). In addition, ultrasonic amplitude and time affected SCOD of all four types of ultrasonically pretreated manure. Increasing the ultrasonic amplitude and time resulted in a greater SCOD, and the greatest SCOD increase was obtained with the highest amplitude and longest treatment time used, which agrees with the studies conducted by others. Grönroos et al. (2005) suggested that ultrasonic power and ultrasonic treatment time have a significant effect on increasing the amount of available SCOD. Tiehm et al. (1997) applied ultrasonic pretreatment to raw sludge and demonstrated that ultrasonic pretreatment increased SCOD in the sludge supernatant and reduced the particle size of sludge solids. In this study, increased SCOD was likely due to a reduction in particle size, offering a larger surface area and increasing the soluble matter fraction (Wu-Haan et al., 2010).

Prior to ultrasonic treatment, the swine slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent contained 15%, 19%, 26%, and 31%, respectively, of their COD in soluble form; after ultrasonic treatment, 20%, 22%, 36%, and 36%, respectively, of the COD was soluble. The change of SCOD (ΔSCOD) of animal manures was used to quantify the ultrasonic disintegration efficiency. The

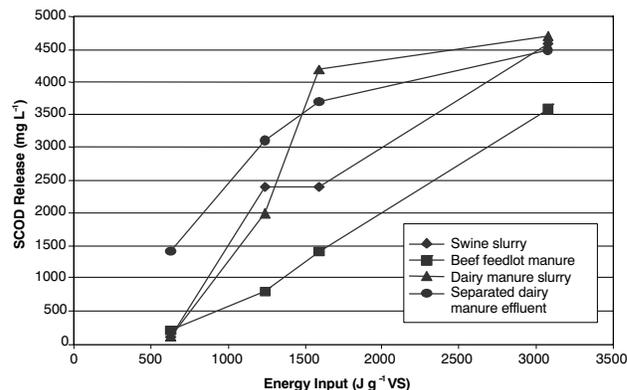


Figure 3. SCOD release (ΔSCOD) due to ultrasonic pretreatment as function of ultrasonic energy input.

ΔSCOD was determined as the difference in the SCOD before and after the ultrasonic treatment. Figure 3 illustrates the ΔSCOD in terms of the ultrasonic energy applied to animal manures.

As shown in figure 3, an increase in energy input results in an overall increase in the SCOD release. This result is in an agreement with Khanal et al. (2006), who studied the release of SCOD concentration of thickened waste activated sludge (3% TS) at different ultrasonic energy inputs and found that the SCOD release clearly increases with increasing energy input. In addition, there is a minimal energy requirement before disintegration starts. For swine manure and dairy manure slurry, the minimum energy input to release 1000 mg SCOD L^{-1} is $\sim 900 \text{ J g}^{-1} \text{ VS}$; for beef feedlot manure, it is $1350 \text{ J g}^{-1} \text{ VS}$.

ULTRASONIC EFFECT ON MANURE METHANE YIELD

The ultrasonic effects on cumulative methane yield from swine slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent are detailed in table 3 and figure 4. For comparison between manure types, reported methane yields were normalized across treatments and are

Table 3. Net BMP methane yields from pig slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent treatment without or with ultrasonic pretreatment at varied amplitude (80 and 160 μm) and time (15 and 30 s). Methane yields are normalized across treatments and are reported as mL CH_4 per g of substrate VS.^[a]

	Methane Yields ($\text{mL CH}_4 \text{ g}^{-1} \text{ VS}$)			
	Pig Slurry	Beef Feedlot Manure	Dairy Manure Slurry	Separated Dairy Manure Effluent
LSMEAN				
Untreated	321	120	142	255
80 μm_{pp} , 15 s	352	151 a	174 a	279 a
80 μm_{pp} , 30 s	365	175 b	185 b	302 b
160 μm_{pp} , 15 s	356	189 b	190 b	317 b
160 μm_{pp} , 30 s	394	230 c	226 c	340 c
SEM	23	9	10	6
Probabilities (p-value)				
Ultrasonic	0.10	<0.01	<0.01	<0.01
Amplitude	0.24	<0.01	<0.01	<0.01
Time	0.10	<0.01	<0.01	<0.01
Amplitude \times time	0.40	0.14	0.06	1.00

^[a] Within a column, means followed by different letters are significantly different for a given manure type ($p < 0.05$).

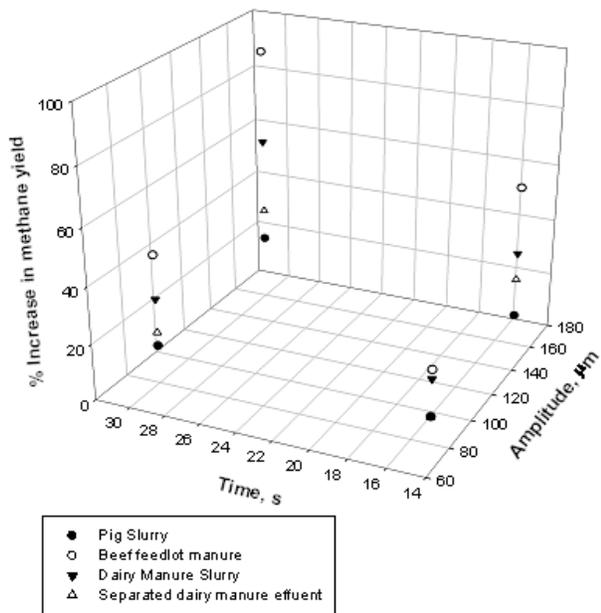


Figure 4. Percentage (%) increase in net BMP methane yields of pig slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent treatment without or with ultrasonic pretreatment at varied amplitude (80 and 160 μm) and time (15 and 30 s).

reported as mL CH_4 per g of substrate VS. The biogas yield resulting from endogenous methane production by the inoculum was determined with blank samples and has been subtracted from the reported yield. The blanks each yielded 25 to 26 mL of biogas during the assay.

Average methane yield from ultrasonically pretreated swine slurry was numerically increased up to 23%. However, this enhanced methane production was not statistically significant. In addition, ultrasonic amplitude and treatment time had no significant effect on cumulative methane yield from ultrasonically pretreated swine slurry. In contrast, ultrasonic pretreatment had a significant effect on average methane yield from ultrasonic pretreated beef feedlot manure, dairy manure slurry, and separated dairy manure effluent ($p < 0.01$). The average methane yield from ultrasonic pretreated

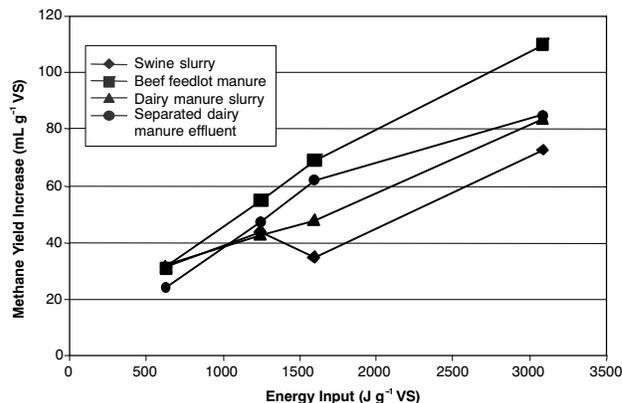


Figure 5. Methane yield increase due to ultrasonic pretreatment as function of ultrasonic energy input.

beef feedlot manure, dairy manure slurry, and separated dairy manure effluent was increased by ultrasonic pretreatment up to 92%, 59%, and 33%, respectively. The beef feedlot manure had the largest increase among the four manure types (fig. 4). In addition, increasing ultrasonic amplitude and treatment time ($p < 0.01$) resulted in higher methane yields from the beef and dairy manures, and the greatest methane yield was obtained with the highest ultrasonic amplitude and longest ultrasonic treatment time. These results are consistent with results found in the SCOD trial, which indicated a significant increase in SCOD (up to 56%, 43%, 62%, and 20%, respectively) for ultrasonically pretreated manure. The large enhancement of methane yield that was seen in the study was likely due to particle size reduction caused by the ultrasonic treatment, resulting in an enhanced biodegradability (Dewil et al., 2006).

Methane yield increase (ΔCH_4) due to ultrasonic pretreatment as function of ultrasonic energy input (E_{in}) is shown in figure 5. An increase in ultrasonic energy input resulted in a larger methane yield, and the largest improvements in methane production were obtained with the highest ultrasonic energy input used. There were larger improvements in methane production for beef manure compared to the other manures observed in this trial.

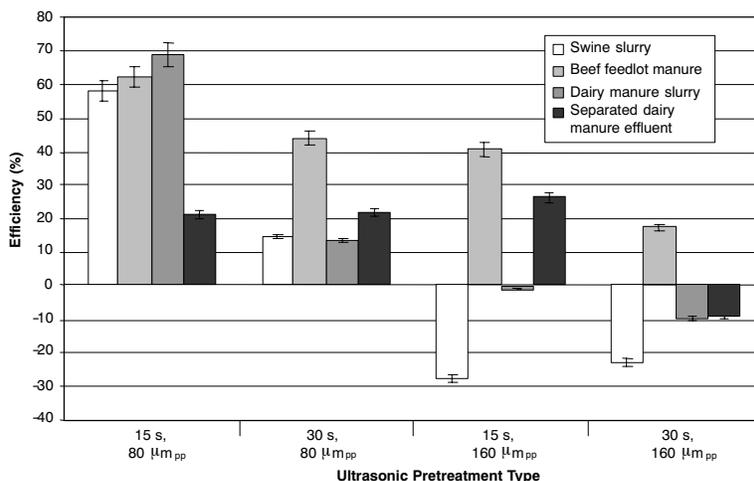


Figure 6. Energy efficiency of ultrasonic pretreatment at various ultrasonic pretreatment conditions. The overall ultrasonic efficiency was calculated using: $Eff = (E_{out} - E_{in}) / E_{in} \times 100\%$.

ENERGY BALANCE ANALYSIS

In order to evaluate the effectiveness of the ultrasonic system in terms of net energy release, an energy balance calculation was conducted using equations 1 through 4. The energy efficiency of ultrasonic pretreatment at various ultrasonic amplitudes and treatment times is detailed in figure 6. A positive value indicates a positive energy return. The overall efficiency of the ultrasonic pretreatments ranged from -28% to 69%, depending on the treatment conditions. A negative efficiency indicates that the energy equivalent of increased methane yields was less than the energy dissipated for the ultrasonic pretreatment.

When ultrasonic pretreatment was applied with 80 μm_{pp} ultrasonic amplitude for 15 s, ultrasonic pretreatment of swine slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent provided more energy (58%, 63%, 69%, and 21%, respectively) than was required to operate the ultrasonic pretreatment process. For manure samples treated with 80 μm_{pp} amplitude for 30 s, swine slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent produced greater energy (15%, 44%, 14%, and 22%, respectively) than the energy required to operate the ultrasonic pretreatment process. Within the 160 μm_{pp} amplitude and treatment time of 15 s, ultrasonic pretreatment of beef feedlot manure and separated dairy manure effluent provided 42% and 26% greater energy than was required for operating the ultrasonic pretreatment process, while swine slurry and dairy manure slurry provided less energy (-28% and -1%, respectively) than was required for operating the ultrasonic pretreatment process. When ultrasonic pretreatment was applied with 160 μm_{pp} amplitude for 30 s, ultrasonic pretreatment of beef feedlot manure provided more energy (17%) than was required to operate the ultrasonic pretreatment process. However, the energy recovered from additional methane production from swine slurry, dairy manure slurry, and separated dairy manure effluent were less (-23%, -10%, and -9%, respectively) than the energy input when ultrasonic pretreatment was applied at 160 μm_{pp} amplitude for 30 s. Overall, the greatest energy efficiency was obtained with the lowest ultrasonic amplitude (80 μm_{pp}) combined with shortest treatment time used (15 s). An increase in ultrasonic amplitude and treatment time resulted in a reduction of energy efficiency. Thus, from an energy efficiency standpoint, the most effective ultrasonic treatment appears to be low-power input with a short treatment time. It is important to note that higher solids contents may require longer treatment time in order to achieve similar results as reported here, and the total solids will be limited by the viscosity.

KINETICS OF ANAEROBIC DIGESTION OF ULTRASONIC PRETREATED ANIMAL MANURES

High-powered ultrasonication reduces substrate particle size (Suslick, 1990). By reducing the particle size, the ratio of the surface area to volume is increased, which increases the reactive sites for digestion process enzymes and microbes. The results have shown that ultrasonication increases methane production. The following discussion addresses the comparable effect of ultrasonication amplitude and time on the rate of methane production. A nonlinear regression model was used to predict the rate of anaerobic reactions under different ultrasonic pretreatment conditions. The nonlinear regression model was defined as:

$$Y = K_{\text{max}}(1 - e^{-KT}) \quad (5)$$

where K_{max} is the estimated maximum methane yield from an exponential decay model ($\text{mL CH}_4 \text{ g}^{-1} \text{ VS added}$) based on model prediction, K is the kinetic rate of anaerobic digestion, and T is the anaerobic digestion time (days). K_{max} and K were obtained using nonlinear regression to minimize the sum of squared errors (SSE) between raw data and predicted values. The values for K_{max} and K are shown in table 4.

The model results indicated there were correlations between the ultrasonic energy input and K_{max} . For three of the four manure types, the highest maximum methane yield was obtained with the highest energy input. Specifically, for the dairy manure slurry and the separated dairy manure effluent, K_{max} was strongly correlated to ultrasonic energy input ($R^2 = 0.91$ and 0.75 , respectively), but the kinetic rate (K) was not ($R^2 = 0.09$ and 0.09 , respectively). While a slightly weaker correlation, the K_{max} for swine slurry was also correlated to energy input ($R^2 = 0.55$), although K was not ($R^2 = 0.23$). The beef manure results did not follow similar correlations; model results showed that K ($R^2 = 0.60$) was more correlated to ultrasonic energy input than K_{max} ($R^2 = 0.30$). The results for the dairy and swine manures may seem counterintuitive. Because the manure overall VS content would not increase with ultrasonic treatment, one might think that the maximum methane yield would be the same between energy treatments within each manure type. However, like COD, the overall VS would not change with ultrasonication, but what was available to the microbes (i.e., the soluble fraction) did change. Therefore, K_{max} could increase with ultrasonication because energy input increases the food source accessible to the microbes. Predicted methane yields vs. observed methane yields are shown in figure 7. In general, the predicted methane yields are higher than the observed methane yields.

Table 4. Kinetic of anaerobic digestion of animal manure pretreated with ultrasonic.

Ultrasonic Energy Input ($\text{J g}^{-1} \text{ VS}$)	Swine Slurry			Beef Feedlot Manure			Dairy Manure Slurry			Separated Dairy Manure Effluent		
	$K_{\text{max}}^{[a]}$	K	SSE	$K_{\text{max}}^{[a]}$	K	SSE	$K_{\text{max}}^{[a]}$	K	SSE	$K_{\text{max}}^{[a]}$	K	SSE
0	411	0.20	140	171	0.18	13	161	0.3	106	355	0.23	89
625	427	0.22	78	194	0.18	35	188	0.29	109	346	0.27	93
1243	417	0.25	84	238	0.15	18	193	0.31	101	419	0.22	231
1592	396	0.26	100	257	0.16	51	188	0.34	82	431	0.22	310
3078	491	0.23	76	218	0.35	129	245	0.27	148	445	0.23	460

[a] K_{max} is in units of $\text{mL CH}_4 \text{ g}^{-1} \text{ VS}$.

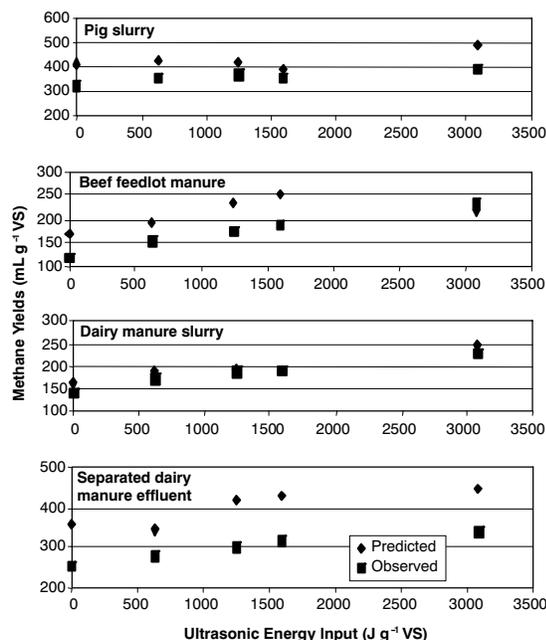


Figure 7. Predicted vs. observed methane yields due to ultrasonic pretreatment as a function of ultrasonic energy input.

CONCLUSION

Average methane yield from ultrasonically pretreated swine slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent was shown to increase up to 23%, 92%, 59%, and 33%, respectively; average soluble chemical oxygen demand (SCOD) of ultrasonic pre-treated manure samples increased up to 56%, 43%, 62%, and 20%, respectively. Results from this study showed that an increase in ultrasonic amplitude and the length of exposure to ultrasonic treatment resulted in an overall increase in SCOD and methane production. The greatest methane yields were obtained with the highest ultrasonic amplitude and longest treatment time. However, the greatest energy efficiency was obtained with the lowest ultrasonic amplitude combined with shortest treatment time. Methane yield increases corresponding to the greatest energy efficiency were 10%, 26%, 23%, and 9% for pig slurry, beef feedlot manure, dairy manure slurry, and separated dairy manure effluent, respectively. An increase in ultrasonic amplitude and treatment time resulted in a reduction in energy efficiency. The most efficient ultrasonic treatment was a low-power input with a short treatment time. With ultrasonic pretreatment, a larger improvement in methane production for beef and dairy manure slurry was observed.

This study demonstrated that application of ultrasonic pretreatment in anaerobic digestion of animal waste has some potential. The optimization of methane yield by ultrasonic pretreatment will likely make recovery of energy from animal manure more economically feasible in the future. However, for the process to be economically feasible, the optimization of energy consumption is essential for the use of ultrasonic as a pretreatment method prior to anaerobic digestion

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