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The effects of algae pre-treatment on the biomethane potential of swine wastewater

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Honors Thesis

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Project Summary

Anaerobic digestion is a common method of waste treatment in the agro-industrial and municipal sectors, which utilizes microbial metabolisms that take place in an environment closed to the atmosphere to convert the organic content of wastewater into gas composed of approximately 65% methane and 35% carbon dioxide. This gas can be used as a combustible fuel for the production of heat and/or electricity. Anaerobic digestion is not typically used to treat swine waste because of its low carbon to nitrogen ratio being below the ideal range of 20-30:1. This high nitrogen content of swine waste results in ammonia inhibition of the methanogen microbial consortia, which are responsible for the production of methane.

A periphytic algae cultivator (PAC) is a system in which high nutrient wastewaters; such as swine waste, can be circulated over a bed of algae. In this process, all ammonia nitrogen is taken out of solution through volatilization into the atmosphere and uptake by the algae. Also, the algae facilitate the conversion of carbon dioxide into organic compounds, increasing the carbon to nitrogen ratio of wastewater.

The goal of the project was to test the hypothesis that treating swine wastewaters with a PAC results in a significant increase in biomethane potential of the waste by increasing its carbon to nitrogen ratio and overall organic content, making it a more suitable feedstock for anaerobic digestion. This is significant because, if successful, the research could contribute to the development of a more economically feasible method of utilizing and recycling nutrients in agro-industrial and municipal wastewaters for the cultivation of algae to be used as a renewable energy source.

It was found in the project that algae pre-treatment of swine wastewater results in a lower ammonia concentration and higher VS and COD contents, which leads to a better conversion of the substrate into methane and a larger reductions of VS and COD contents of the wastewater resulting from anaerobic digestion.

Background

Anaerobic digestion is a common method of waste treatment in the agro-industrial and municipal sectors. In this process, bio-solids are fed into a reactor that is closed to the atmosphere in order to be in the absence of oxygen. Within the reactor, the biomass undergoes a series of conversions. The large organic compounds are first converted into simple sugars via hydrolysis. These sugars are then converted into alcohol via acidogenesis. The alcohols are converted into acetic acid by acetogens. Finally, methanogens convert the acetate into methane. Carbon dioxide is also produced during the anaerobic processes. The final products of this process are sludge containing large amounts nitrogen and phosphorous, effluent with 40-65% reduction in volatile solids depending on the biomethane potential of the feedstock, and biogas composed of approximately 65% methane, 34% carbon dioxide, and 1% trace gases. The sludge resulting from this process can be dried and sold as a soil supplement, and the biogas can be used as a combustible fuel. If the biogas is purified to remove all components other than methane, it is essentially the same as natural gas, but it can also be combusted without extensive cleaning as a heat source or to power a generator for the production of electricity. This makes anaerobic digestion a desirable method of waste treatment due to a reduction in energy costs for whoever is treating the waste. It is this quality of anaerobic digestion that is causing a growing implementation of the process in the private agricultural and agro-industrial sectors by those who have suitable waste streams for the process.

There is an increasing demand for sustainable energy sources due to increasing prices of fossil fuels and their controversial environmental impacts. Algae have been gaining popularity in recent years amongst researches as an alternative to field based energy crops for the production of ethanol and biodiesel (Chisti, 2007). One of the leading methods of converting algae into fuel is biodiesel production via lipid extraction from algal cells. However, this method of energy production has not been vastly implemented in society due to the high cost of extraction, water, nutrient, and spatial demands for the cultivation of algae. Thus, recent research has been performed on increasing the efficiency of the process related to water and energy demands. Anaerobic digestion has been suggested to play a crucial part in improving energy efficiency. One study conducted by Sialve et al. (2009) reported that anaerobic digestion of the entirety of the algal biomass is preferred over lipid extraction followed by conversion to biodiesel on an energy balance basis when algal cells have a dry matter lipid content less than 40%. The majority of algal cultures display a lipid content less than 40%. Griffiths and Harrison (2009) reported that only 14 out of 42 species tested in the laboratory could reach a lipid content of 40% or greater when grown in ideal conditions. From a practical standpoint, anaerobic digestion is also a much simpler conversion process than lipid extraction. Markou and Georgakakis (2011) reported algae can be grown from agricultural wastewaters before and after anaerobic digestion. This serves the dual purpose of waste treatment and algae cultivation that could be used for energy conversion. In light of this information, it is reasonable to develop the concept of growing algae from the multitudes of biological wastes being produced, converting the algae into biomethane via anaerobic digestion, and using the remaining nutrients in the digester effluent to grow more algae to also be converted into biomethane.

One important characteristic of a feedstock to be used for anaerobic digestion is the carbon to nitrogen (C:N) mass ratio of the biomass. The biomethane potential (BMP) of a given organic substrate is the theoretical maximum volume of methane that can be produced per unit mass of digestible material. The C:N ratio of the organic substrate typically has a large effect on its BMP. For optimal conversion of digestible material into methane, the feedstock must have a C:N ratio in the range of 20 – 30 grams of carbon to grams of nitrogen. The closer a feedstock is to this range, the higher the BMP and the faster and more efficiently the process will occur. If the C:N ratio is far below this range, the methanogens in the reactor become inhibited by an excessive ammonia concentration. Bovine manure tends to have a C:N ratio of approximately 17:1 while swine manure tends to have a C:N ratio of approximately 7:1 (USDA, 2014). Thus, it is more common for bovine manure to be treated via anaerobic digestion than swine manure.

A periphytic algae cultivators (PAC) is a system in which wastewater can be circulated over a bed of algae to remove biologically available nitrogen and phosphorus. In this process, algae absorb gaseous carbon dioxide and ammonia to be incorporated into solid organic compounds. These combined effects result in a net increase in the C:N ratio and organic content and a decrease of ammonia concentration in the wastewater. Thus, treating swine waste with an algal turf scrubber would most likely increase its biomethane potential by increasing its C:N ratio, making the ultimate treatment of the waste by anaerobic digestion more feasible with the possibility of a net positive energy production.

The goal of the project was to test the hypothesis that treating swine wastewaters with a PAC would increase the carbon to nitrogen ratio of the wastewater, causing an increase in its biomethane potential and making it a more suitable feedstock for anaerobic digestion. This would in turn help to establish the concept of using wastewater to grow algae as an alternative fuel source with the dual purpose of treating agricultural and municipal wastewater becomes more feasible.

Material and Methods

Lagoon was collected from the University of Arkansas Swine Finishing Unit. Total solids and volatile solids content of the wastewater was determined by first weighing a 30 mL volume of the wastewater in a ceramic crucible and heating the samples in a drying oven at 105 °C for a minimum of 24 hours until only solids remained. The crucible was then weighed after drying in order to determine the mass of solids present in the drying samples. Then the remaining solids were combusted in a muffle furnace at 550 °C for a minimum of 2 hours until only non-combustible ash remained. The crucible was then weighed after combustion in order to determine the mass of ash present in the drying samples. The difference between the solids and ash was taken to be the volatile solids present in the wastewater.

The BMP of the lagoon water was determined by the digestion of three 0.6 L samples in batch mode inside of a temperature controlled water bath maintained at 37 °C. Each batch was inoculated with 0.2 L of active sludge collected from a pilot-scale digester being used in a concurrent project taking place through the Biological Engineering department at the University of Arkansas. The total nitrogen, ammonia nitrogen, and chemical oxygen demand of the wastewater were also determined before digestion. Chemical oxygen demand is a method of quantifying the amount of organic compounds in water and is defined as the mass of oxygen required to oxidize all available organic compound per unit volume of sample water. The determination of total nitrogen, ammonia nitrogen, and chemical oxygen demand were performed using Hach TNT methods and a Hach spectrophotometer. The quantification of nitrogen gave insight to whether the process would show characteristics of ammonia inhibition. The chemical oxygen demand and volatile solids of the wastewater were considered the substrate for anaerobic digestion and were used to determine the specific methane production in terms of volume of gas produced per gram of each substrate. The gas produced during digestion was collected twine in 0.5 L Tedlar bags, analyzed using a gas chromatography machine in order to determine methane content, and quantified using a passive analogue gas flow meter. After 30 days of digestion, it was assumed that all the digestible material had been converted and the ultimate biogas production had been reached. The data collected during digestion can then be used to determine the first-order rate of hydrolysis for the substrate using the equations:

$\frac{dS}{dt} = -k_h S$ (equation 1) and $B(t) = B_\infty(1 - e^{-k_h t})$ (equation 2) ;

Where S is the substrate constant (VS or COD), B is the volume of methane produced at a given time, B_∞ is the ultimate methane production, and k_h is the hydrolysis rate constant (taken to be the rate-limiting step). Specific methane production will also be reported, which is the total amount of methane produced per gram of substrate in terms of VS or COD as described by Angelidaki et al (2009). It is the specific methane production that relates substrate concentration to the volume of gas produced. The first-order rate constant for hydrolysis will be determined by fitting a curve to a plot of the left side of equation 2 with respect to time. The slope of this curve can be taken to be the first-order rate constant.

The same procedures were performed on a mixture of treated swine waste and the algae grown during the treatment process. This feedstock was produced cycling approximately 5 gallons of wastewater over a 7.5 ft^2 PAC for 2 days. According to the hypothesis of the experiment, the results were expected to show that the hydrolysis rate constant (k_h), the specific methane production of the swine wastewater, and the ultimate methane production would increase due to pretreatment with the PAC.

Results

Analysis of the treated and untreated swine wastewater before the digestion process was performed in order to determine the changes in feedstock characteristics that result from treatment of the wastewater with a periphytic algae cultivator (PAC). Table 1 shows the results of this analysis.

Table 1: Feedstock characteristics of swine wastewater before and after treatment

	TS %	VS (g/l)	COD (g/l)	N_{NH4}(mg/l)	TKN (mg/l)	TN(mg/l)	N_{org}(mg/l)	NO_x(mg/l)
Treated	1.01	3.07	3.52	37.3	223.30	271.25	185.97	47.6
Untreated	0.33	1.45	1.68	271	357.00	367.50	86.33	10.325

It is shown in Table 1 that treatment of the wastewater by the PAC resulted in a 101 % and 111 % increase in volatile solids and COD, respectively, and an 86 % decrease in ammonia. Nitrate and nitrite were increased by 361 %, which suggests that nitrification was taking place in the treatment process. Also, total nitrogen decreased by 26 %, which suggests that denitrification and/or volatilization of ammonia took place as well.

Gas produced by each batch was analyzed and quantified 10 days into the digestion process and again at the end of the 30 day period. The digested samples were then analyzed to determine the volatile solids and chemical oxygen demand. The difference was taken between VS and COD contents before and after digestion in order to determine the percent reduction of each and the amount converted during the digestion process. This was used along with the methane production data to determine the specific methane production (Yps) in terms of methane produced per gram of VS converted and COD converted. The results from this analysis are shown in Table 2.

Table 2: Results for digestion of treated and untreated swine wastewater

	VS_{red} (%)	COD_{red} (%)	CH_4 (%)	B_∞ (L-CH_4)	Y ps (L/g-VS)	Y ps(L/g-COD)
Treated	15.98	32.63	0.67	0.16	0.36	0.120
Untreated	13.45	26.05	0.68	0.06	0.25	0.079

It is shown in Table 2 VS reduction was 16 % and 13.5 % for the treated and untreated wastewater, respectively, and the COD reduction was 32 % and 26 % for the treated and untreated wastewater, respectively. Methane content of the gas produced in each case was nearly identical (67 % for treated and 68 % for untreated), but all other parameters related to the biomethane potential were increased by the PAC treatment of the wastewater. The values for B_∞ and the methane produced 10 days after digestion began were used to estimate the first-order kinetic rate of hydrolysis for each case. Figure 1 illustrates this process.

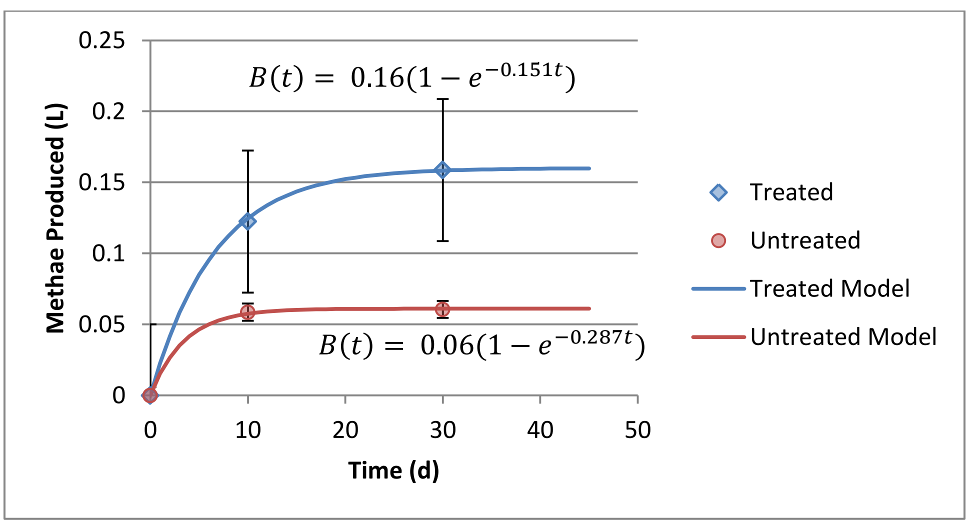

Figure 1: Graph used to determine the first-order kinetic rate constant for each case

Given the relationship in Equation 2, the first-order kinetic rate constant can be estimated using the equations fitted to the data in Figure 1. Thus, the rate constant was taken to be 0.151 d^{-1} for the treated wastewater and 0.287 d^{-1} for the untreated wastewater.

Discussion

It was determined in the study the pre-treatment of swine wastewater with a periphytic algae cultivator system (PAC) results in wastewater characteristics that are more favorable for anaerobic digestion by increasing VS and COD contents and decreasing ammonia concentration. The ultimate methane production of the wastewater was increased by 162 % and the specific methane production, Yps, was increased by 53 %. The kinetic models produced suggest that the rate of hydrolysis, k_h, was decreased by 47 % due to the pre-treatment. This could be due to the aggregation of algal cells in the treated feedstock, which would decrease the contact surface area to volume ratio between the anaerobic bacteria and the biomass.

For future projects, it should be suggested that the anaerobic digestion experiments be set up so that more data points for gas production can be collected, which could produce more robust results. Also, research could be performed to determine the biomethane potential of the algae alone produced from swine wastewater so that the feedstock is less dilute. This would decrease the size of the digester needed and possibly lead to a higher rate of methane production.

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