Chapter

Evaluation of Physical and Chemical Pretreatment Methods to Improve Efficiency of Anaerobic Digestion of Waste Streams from Grain Processing

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Abstract

Globally, Anaerobic Digestion (AD) industry is booming and biogas, the most sustainable biofuel, produced via AD is in an exponential market growth curve. According to a November 2020 report from US Energy Information Administration (EIA), "25 large dairies and livestock operations in the United States produced a total of about 224 million kWh (or 0.2 billion kWh) of electricity from biogas". However, the growth of AD and the cost-effective use of the generated biogas are hindered by the inconsistencies (composition, suspended solids, flow rate, etc.) of the incoming waste stream and the associated biogas quality (due to the presence of hydrogen sulfide gas). A pretreatment step prior to an AD unit can promote consistency in the incoming stream, minimize the suspended solids; and thereby insures the efficiency of AD. In this study, we evaluated the method of pretreatment of waste streams from three grain processing industries, where 1) we adjusted the pH of a stream corresponding to its isoelectric point (zero zeta-potential), 2) removed solids (and their corresponding COD) that precipitated, and 3) produced a consistent composition stream to feed the AD process. For grain processing industry, the precipitated solids can be returned to their process – thus integrating the pretreatment with the rest of the process. The pH pre-treatment should not add any additional cost to the plant since the pH of the waste streams from grain processing plant needs to be raised per plant permits prior to disposal. Our lab and pilot AD studies showed a positive effect of such pretreatment on these waste streams in terms of increased biogas production (11–60%) and COD removal (12–60%), and in some instances reduction in H_2S content in biogas (8%). This study clearly demonstrated that such a pretreatment method is economical and is effective to improve AD performance on waste waters from grain processing industries.

Keywords: anaerobic digestion, biogas, wastewater treatment, pH adjustment, grain processing

1. Introduction

Handling and treatment of industrial waste water has become one of the biggest problems of the last century due to constantly increasing industrial activity [1]. The amount of the industrial waste water is rapidly exceeding the biological treatment capabilities of the natural ecosystems. Hence, the treatment of industrial effluents became an important topic.

Anaerobic digestion (AD) is potentially an efficient and economically beneficial method of neutralization of industrial waste [2, 3]. Although anaerobic treatment was known for a long time, the process has not been successfully implemented owing to disadvantages, such as low sludge activity, low reactor capacity, unsuitability of the process and inhibitory effects [4]. The introduction of modern reactor designs where hydraulic retention time is uncoupled from the solids retention time led to a world-wide acceptance of the anaerobic technology as a cost-effective alternative to conventional waste water treatment methods. A number of reactor configurations have been developed leading to high biomass concentrations, such as upflow anaerobic sludge blanket (UASB) reactor, anaerobic contact filter, down flow stationary fixed film and anaerobic fluidized bed reactor (AFBR) systems [5]. In AFBR reactors, the sludge granules are fluidized by high up-flow fluid velocities generated by a combination of the influent and recirculated effluents. The fluidized bed process claims various potential advantages over other high rate anaerobic reactors [6]. These are: high sludge activity, high treatment efficiency, no clogging of reactors, no problems of sludge retention, least chance for organic shock loads and gas hold up as well as small area requirements. Currently, this anaerobic technology removes 70–90% of organic pollutants (expressed as chemical oxygen demand, COD).

In order to ensure high efficiency and high throughput of wastewater treatment using AFBR reactors, certain parameters, such as suspended solids, fat-oil-and-grease, complex organics (fiber, proteins), toxic compounds, should be minimized [7]. Pretreatment of industrial wastewater using physical and chemical methods can significantly improve efficiency of wastewater treatment using anaerobic technology [8]. One immediate impact of these pretreatments on the operation of an anaerobic digester is that its hydraulic retention time (HRT) can be lowered. HRT directly impacts the tank volume of the AD (capital cost) as well as the throughput from the digester. Hence the pretreatment methods can not only lower the capital cost of the anaerobic digestion, but also impact its operating cost.

Various physico-chemical pretreatment methods have been used to improve the anaerobic digestibility of the industrial waste streams. Filtration is used to decrease COD content, remove suspended solids, and toxic compounds [9, 10]. Enzymatic pretreatment is often used to improve digestibility of waste streams with high lipids content, such as dairy wastewater [11, 12]. Oxidative treatment with ozone is used to remove toxic organic compounds from the waste stream and improve anaerobic digestion [13]. Electrochemical treatment is often used for the destruction of recalcitrant organics and increase BOD_5/COD ratio [14–16]. pH adjustment has also been successfully implemented for various purposes as a pretreatment method. pH adjustment using $Ca(OH)_2$ was used to force ammonia stripping [17]. pH adjustment was also done to improve sludge dewatering after AD [18]. Alqaralleh [19] demonstrated the use of alkaline pretreatment to enhance the solubility of organics in the waste prior to AD. pH adjustment as a pretreatment method was also employed to precipitate proteins from wastewater [20, 21]. In another work, Cui and Jahng [22] removed proteins from disintegrated waste sludge prior to anaerobic digestion using pH adjustment to the corresponding isoelectric point (IEP) of the proteins.

Control of pH is a key operating parameter during anaerobic digestion process. However, industrial effluents very often have a pH that is not suitable for discharge or further processing. Hence pH adjustment of the waste stream to the discharge permit levels is done as an operating procedure prior to discharging the stream to further treatment. If, on the other hand, pH adjustment to bring the pH close to IEP can also serve as a pretreatment method, then we can reduce solids and other organics loading in the stream. This reduction will benefit a waste treatment process such as AD. Further, as discussed above, this pretreatment will not add any extra cost to the plant.

Solubility of many compounds depends on the IEP of the solution. Depending on the type of material being precipitated by adjusting to IEP, several advantages can be gained, such as decrease in COD, toxic compounds, complex organics, sulfates etc. This can lead to improved digestibility of the wastewater, as well as increased quality of the biogas [22, 23]. Delgenès et al. studied changes in anaerobic digestibility of industrial microbial biomass after thermochemical pretreatment. It was determined that the observed poor biodegradability and biotoxicity of the solubilized microbial biomass is due to high molecular compounds (>100 Da). Removal of these compounds using absorbent resins and precipitation by pH adjustment improved the biogas production. An increase in biogas production and biogas quality was observed as a result of the deproteination using pH adjustment to IEP [22]. In our study, we used pH adjustment to bring zeta-potential of waste streams from grain processing industries, such as distillery, soy protein processing, and oat fibers processing to near IEP as a pretreatment method. The objective is to reduce organic and solutes loading in the stream and thereby improve COD reduction, biogas yield and quality during anaerobic digestion of the waste streams.

2. Materials and methods

2.1 Materials

Calcium chloride, magnesium chloride, ammonium chloride, potassium phosphate monobasic, sodium sulfate were used as minerals and nutrients for anaerobic digestion tests and were purchased from Sigma-Aldrich. Sodium bicarbonate (Sigma-Aldrich) was used to adjust alkalinity. A proprietary inorganic salt mix (Respirometer Systems & Applications LLC, Fayetteville, AZ, USA) was used as a source of trace elements. Sodium hydroxide and hydrochloric acid (Sigma-Aldrich) were used for pH adjustment. Ethanol was purchased from Sigma-Aldrich and was used as a model source of COD. Granular anaerobic sludge was kindly provided by Anheuser-Busch (St. Louis, MO). The concentration of the bacteria in the sludge was measured as Volatile Suspended Solids (VSS) content and was determined to be 52.0 g/L.

2.2 Anaerobic digestion tests

Experimental set-up for laboratory-scale batch anaerobic digestion tests was acquired from Respirometer Systems & Applications LLC, Fayetteville, AZ, USA, and is shown in **Figure 1A**. It consists of a water bath placed on a 8-position magnetic stir plate, external pump and temperature controller, and a pulse flow respirometer PF-800. 500 ml glass bottles were used as reactors. Up to 8 bottles can be accommodated in the water bath. Trace elements, minerals, nutrients, and $NaHCO_3$ were added to each bottle as described elsewhere [24]. Substrates were added to the bottles in the predetermined amount so that the COD load was the same in each bottle. Bottles were inoculated with granular anaerobic sludge in the quantity so that the ratio between the substrate (expressed as mg/L COD) and the anaerobic bacteria (expressed as mg/L VSS) was 1:2. Bottles with ethanol substrate were used as a control. Ethanol is quickly and easily digested by methanogenic archaea and is

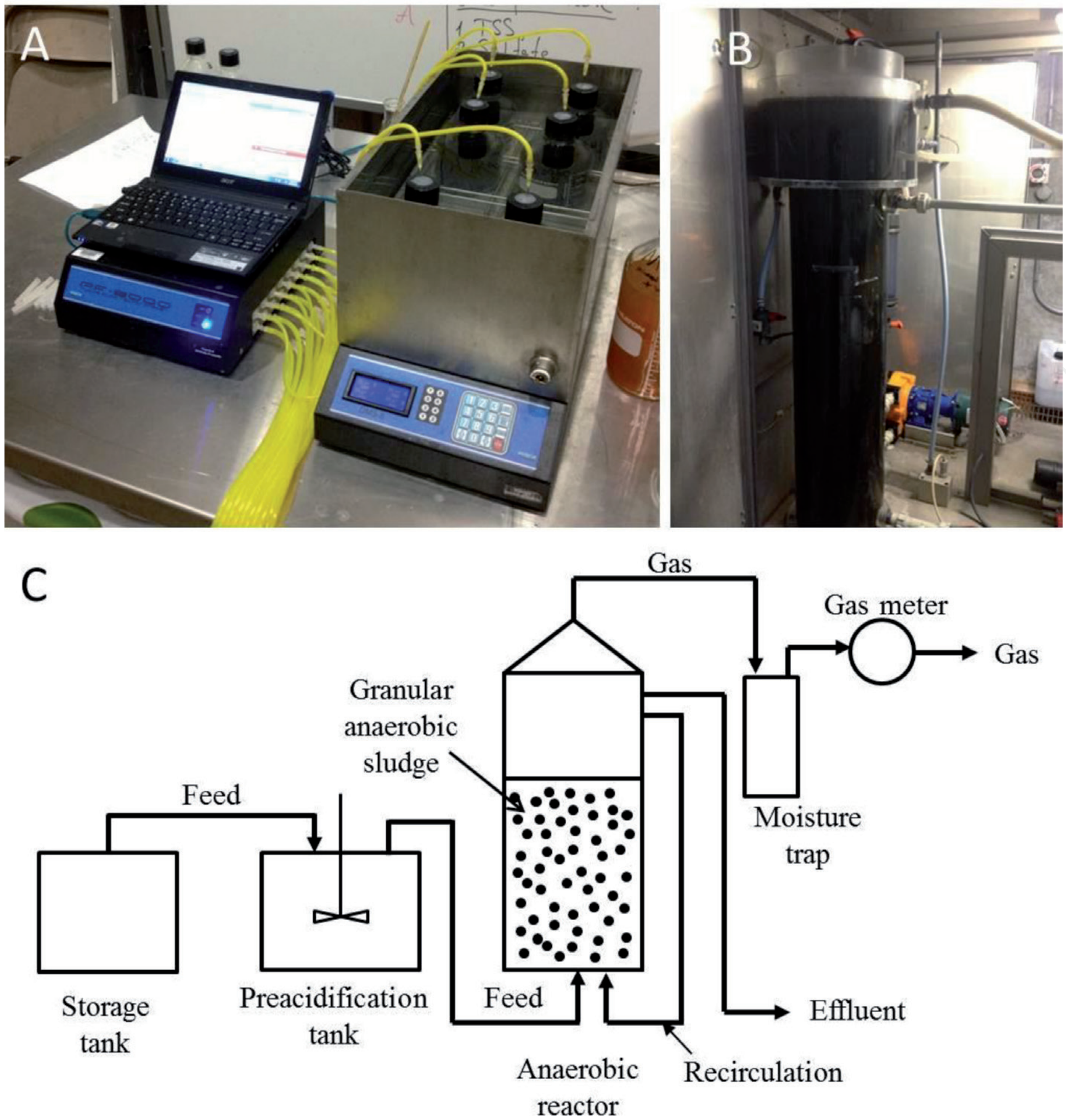


Figure 1.
Experimental set-up used for anaerobic digestion tests: (A) laboratory-scale batch unit; (B) continuous pilot-scale unit (main reactor only), and (C) block-scheme of continuous pilot-scale unit.

therefore used as a benchmark for substrate digestibility [24]. The pH after adding the biomass, substrates, and nutrients was 7. The bottles were degassed with nitrogen for 1 min to ensure anaerobic conditions. The anaerobic digestion tests were conducted under mesophilic conditions (35 °C). The volume of the biogas produced was measured and recorded by the pulse flow respirometer. The test was conducted for two feeding cycles. Each feeding cycle constitutes a reaction time frame during which all nutrients are consumed and gas production stops. After the first feeding cycle ends, the nutrients are replenished and the second feeding cycle starts. For each following feeding cycle, the biomass in the bottle was not removed or added. All the lab tests were performed in duplicate. These lab tests are done prior to pilot tests in order to evaluate the activity of the biomass for each of the streams, digestibility, and biogas quality. The lab tests helped us to better plan and design pilot tests.

Pilot-scale anaerobic digestion tests were performed on 60 L 2-stage Anaerobic Fluidized Bed Pilot Reactor (Voith Meri Environmental Solutions Inc., Appleton WI) shown in **Figure 1(B** and **C)**. In this reactor design, acidogenic and methanogenic stages are spatially separated: acidogenesis occurs mainly in the preacidification tank and the methane formation happens in the main reactor. It is designed to optimize the methane formation. First, the waste water is pumped from a 10 gallon storage tank into the preacidification tank, where it is kept until the acidification degree (ratio between volatile fatty acids content and COD content) reaches approximately 30% (**Figure 1C**). Then, the acidified wastewater is fed into the main reactor from the bottom, where granular anaerobic sludge resides. The stabilized wastewater is recirculated back at the 200 l/h rate. The recirculation is required to fluidize the granular sludge bed. The excess of the stabilized wastewater (effluent) is removed via the overflow channel and discarded. The gas is collected from the top of the reactor and, after passing through the moisture trap and gas meter, is discharged into the exhaust pipe. The reactor was inoculated with 40 L of anaerobic granular sludge. Each test was conducted for a 2-week period. Samples were taken on a daily basis and analyzed. The reactor was maintained at COD load of 3.0 ± 0.2 g-COD/L/day (feed rate 0.75 l/h; HRT 80 hours). The temperature in the preacidification tank and the main reactor was maintained at 36 ± 3 °C. The pH in the preacidification tank was automatically maintained at 5.5 by dosing NaOH. The pH in the main reactor was self-maintained at 6.8.

AD at lab and pilot scale was evaluated on at least two types of streams for each waste water type - a control (no pH adjustment) sample and a pretreated sample. Repeats and additional tests are conducted as needed. The data presented is a compilation of the multiple runs for each stream.

2.3 Analytical methods

Chemical analysis of the waste water was performed spectrophotometrically using commercial test kits and DR 3900 Spectrophotometer (Hach Company, Germany). Gas analysis was performed on SRI 8610C Gas Chromatograph (SRI Instruments Inc., Las Vegas NV) using HayeSep D column (Restek Corporation) and thermal conductivity detector (TCD) for methane and carbon dioxide detection; MXT-1 column (Restek Corporation) and flame photometric detector (FPD) was used for hydrogen sulfide detection. Z-potential measurements were performed on 90 Plus Particle Size Analyzer (Brookhaven Instruments Corporation, Holtsville NY).

3. Results and discussion

3.1 Wastewater characterization

Three types of wastewater streams from local grain processing industries have been used in our experiments: distillery, soy protein processing, and oat fiber processing. These streams have been analyzed for their chemical composition, physico-chemical properties, and solids content (**Table 1**). Samples from each operation were received 3–4 times a week for a three-week period in order to assess variability in the wastewater content. Therefore, some of the data in the table are presented as a range, representing the amplitude of variation of a particular parameter.

The solids in the distillery waste stream were separated by centrifuging at 1000 rpm for 15 min. The resulting liquor had a suitable mineral composition: sufficient nitrogen and phosphorus content and low sulfates. Soy protein processing wastewater had suitable COD content, low suspended solids, sufficient nutrients, but had very high sulfates content, which was in the range of toxicity for methanogenic archaea [25, 26]. Oat fiber processing wastewater had a high COD content, suitable mineral composition, but had a very high initial pH.

		Distillery	Soy proteins	Oat fibers
Electrochemical analysis	pH	3.9–4.6	4.0–4.2	11.3
	Isoelectric point	6.1	5.2	—
	Conductance, mS	6.7–7.1	10.3	22.0
Solids	Total solids, g/L	58.2–62.1	22.4–26.1	72.5
	Total suspended solids, g/L	32.7–34.9	3.2–5.3	11.5
	Total dissolved solids, g/L	25.1–27.1	19.7–21.5	61.0
Oxygen demand	Total COD, mg/L	53,600-57,200	16,500-18,000	85,000
	Soluble COD, mg/L	28,000-33,000	14,500-17,600	72,000
Chemical analysis	Sulfates, mg/L	129–256	4,400-5,500	300
	Phosphates, mg/L	40–226	74–106	300
	Ammonia, mg/L	20–50	44–69	40
	TKN, mg/L	28.9–30.1	37.8–42.3	n/d

Table 1.
Summary of the wastewater characterization.

3.2 Wastewater pretreatment

All three waste streams have initial pH that is not suitable for anaerobic digestion, which should be in the 6.5–7.5 range. Distillery and soy protein processing waste streams come at pH 3.9–4.6, which is too low, whereas oat fiber processing waste stream has pH of 11.3, which is too high. Adjusting pH prior to anaerobic treatment not only ensures the proper conditions for methanogenic archaea, but also makes the stream more consistent, eliminating any possible upsets in the AD reactor. Yet another advantage of pH adjustment is the possibility to precipitate colloidal solids by bringing the system close to its isoelectric point. We studied the pH-induced precipitation in these streams by changing pH in increments from 0.5 to 1.0 and measuring the zeta-potential as a function of pH to determine the IEP of the stream (**Figure 2**). Sodium hydroxide and hydrochloric acid were used for pH adjustment throughout the study. For distillery and soy protein processing streams, the pH-induced precipitation was studied in the range from original pH (~4) until 9. For both streams a precipitation was visually observed upon reaching pH of ~6.0 and ~ 5.4 for distillery and soy protein processing streams respectively. The extent of precipitation as a function of pH was studied by measuring COD at different pH points (**Figure 3**) after the sample has been centrifuged at 4000 rpm for 15 min. The highest decrease in COD content was observed at pH ~7 for distillery sample (6.5% COD decrease) and at pH ~6 for soy protein processing sample (10.3% COD decrease). Both points of highest COD decrease are either close or within the range of optimal pH for anaerobic digestion. It is noteworthy that these pH points are in the vicinity of the corresponding isoelectric points measured for these waste streams (**Figure 2A** and **B**). This suggests that the precipitated material is most likely a fraction of water soluble proteins. Oat fiber processing waste stream also showed pH-induced precipitation. In this case pH was reduced gradually from original pH of 11.3 to 2. After pH was decreased below 5, a significant precipitation was visually observed. The graph in **Figure 1C** shows pH-dependent COD decrease

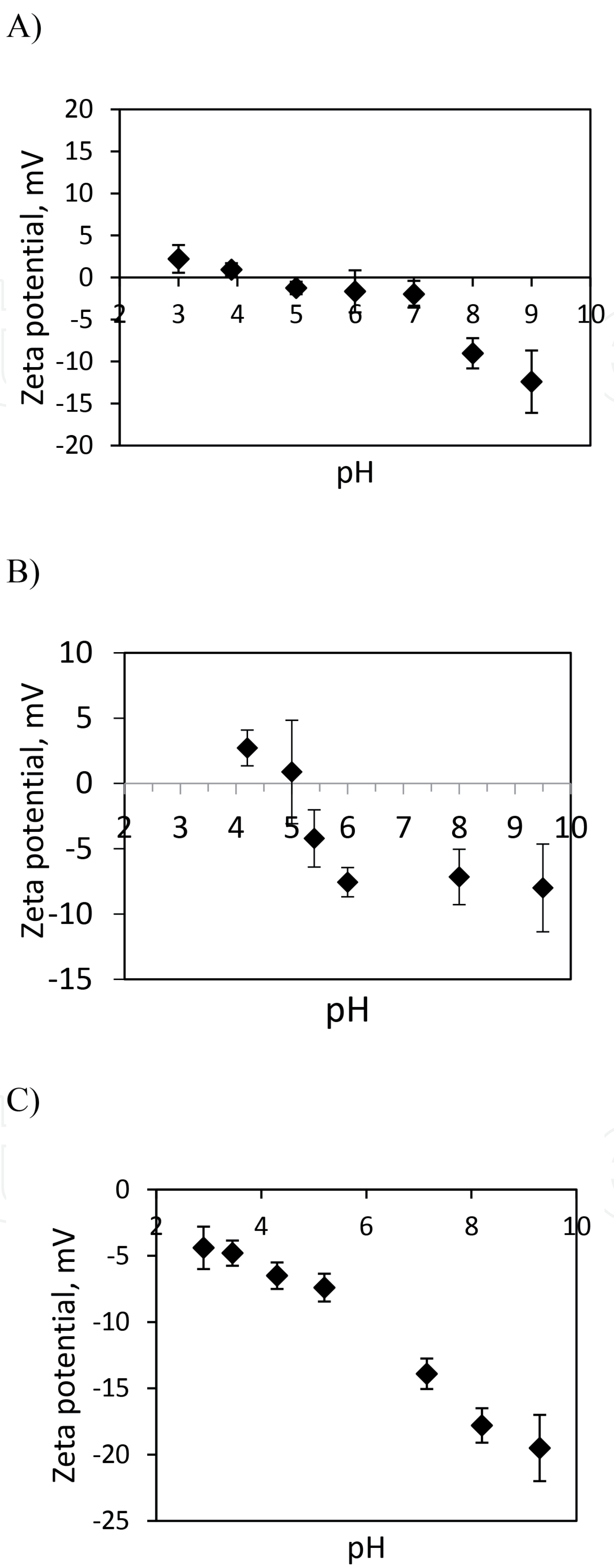


Figure 2.
Z-potential of the waste stream from (A) distillery, (B) soy protein processing, and (C) oat fiber processing as a function of pH.

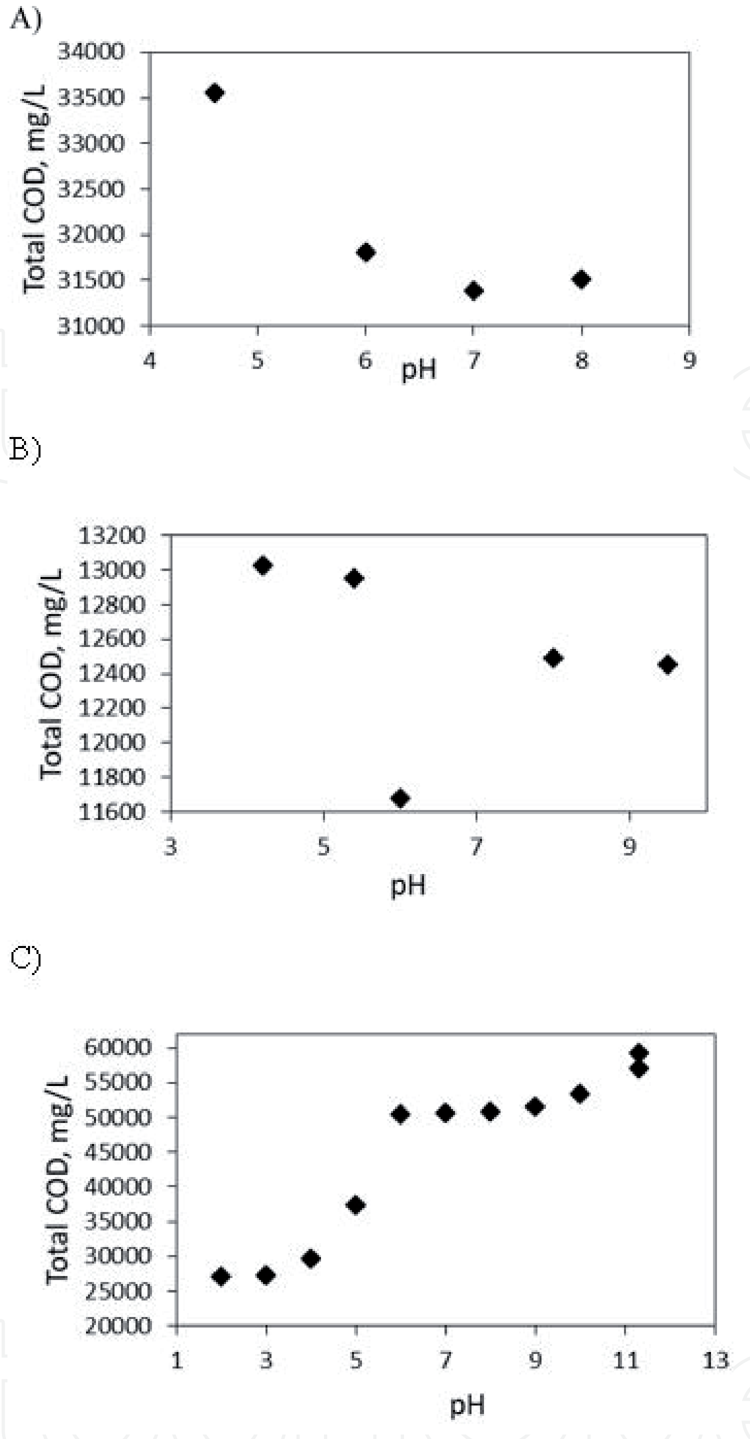


Figure 3.
Total COD as a function of pH of the wastewater from (A) distillery, (B) soy protein processing, and (C) oat fiber processing.

for this waste stream. A slight decrease in COD is observed as pH decreases from 11.3 to 6, followed by a rapid decrease in the pH range from 5 to 3. Overall, adjusting pH from 11.3 to 3 resulted in the removal of nearly 50% COD. Constant increase in precipitation throughout the entire pH range studied, combined with no isoelectric point in this range (**Figure 2C**) suggests that the precipitated material is most likely an alkali-soluble polycarbohydrates.

We also studied changes in the mineral composition of the waste streams upon pH adjustment (**Table 2**). Removal of dissolved solids upon pH adjustment in the soy protein processing wastewater resulted in the decrease of sulfates content by 16% and phosphates by 11%. Reduction of sulfates concentration is beneficial because

	Distillery		Soy protein processing		Oat fiber processing	
	Non-pretreated	Pretreated	Non-pretreated	Pretreated	Non-pretreated	Pretreated
pH	4.6	7.0	4.2	6.0	11.3	3.0
Sulfates, mg/L	134.2	131.4	4430.3	3710.7	306.2	304.4
Phosphates, mg/L	63.7	61.9	75.6	67.2	300.0	290.4
Ammonia, mg/L	26.4	25.9	48.4	46.8	40.1	38.8

Table 2.
Changes in the chemical composition of the wastewater upon pH adjustment.

high concentration of sulfate ions cause sulfide toxicity during anaerobic digestion process [25] Ammonia content did not decrease significantly. The above minerals in the other two waste streams did not change noticeably upon pretreatment.

3.3 Batch anaerobic digestion tests

We performed a laboratory-scale batch anaerobic digestion study in order to evaluate the effect of pretreatment on the anaerobic digestion of the wastewater in terms of biogas production, its quality, and possible inhibitory effects on the biomass activity. Pretreatment of the waste streams was performed by adjusting pH to the value that resulted in maximum decrease of COD content (**Figure 3**). Thus, the pH of the distillery and soy protein processing streams was adjusted to 7 and 6 respectively. The pH of the oat fiber processing waste stream was first adjusted to 3 to induce precipitation and, after removal of the precipitate, the pH was increased to 6 to bring it within the range suitable for methanogenic archaea. In all AD tests, separation of the precipitated solids was performed by carefully decanting the liquid after the precipitate was allowed to settle.

3.3.1 Distillery wastewater

Results of batch digestion test for the distillery wastewater before and after pretreatment are summarized in **Figure 4**. The experiment was conducted for two feeding cycles. Cumulative biogas production over each feeding cycle is presented in **Figure 4A** and corresponding specific methane production is shown in **Figure 4B**. For both feeding cycles, a clear increase in gas production is observed from the pre-treated sample. The total biogas production from the pretreated sample after 40 hours of digestion was 18% and 11.5% higher for 1st and 2nd feeding cycle respectively, compared to the non-pretreated sample (**Table 3**). As a result of pretreatment, COD reduction during the second feeding cycle increased from 80.2% to 89.4% (compared to control). Analysis of biogas samples (**Table 3**) indicated a slight decrease (8%) in H_2S concentration after the pretreatment, which may be due to the removal of the fraction of soluble proteins upon pH adjustmet. Protein-rich streams are known to have increased levels of H_2S in biogas [27]. In addition, corn gluten is particularly rich in sulfur-containing aminoacids, compared to other seeds [28]. The biogas composition, presented in **Table 3** and subsequent tables, does not add up to 100%, because biogas contains other minor components (typically hydrogen, nitrogen, oxygen, and moisture). Since, the emphasis of the study was on COD conversion, biogas production, and methane content as a function of pretreatment, elucidation of the complete biogas composition was beyond the scope of this manuscript.

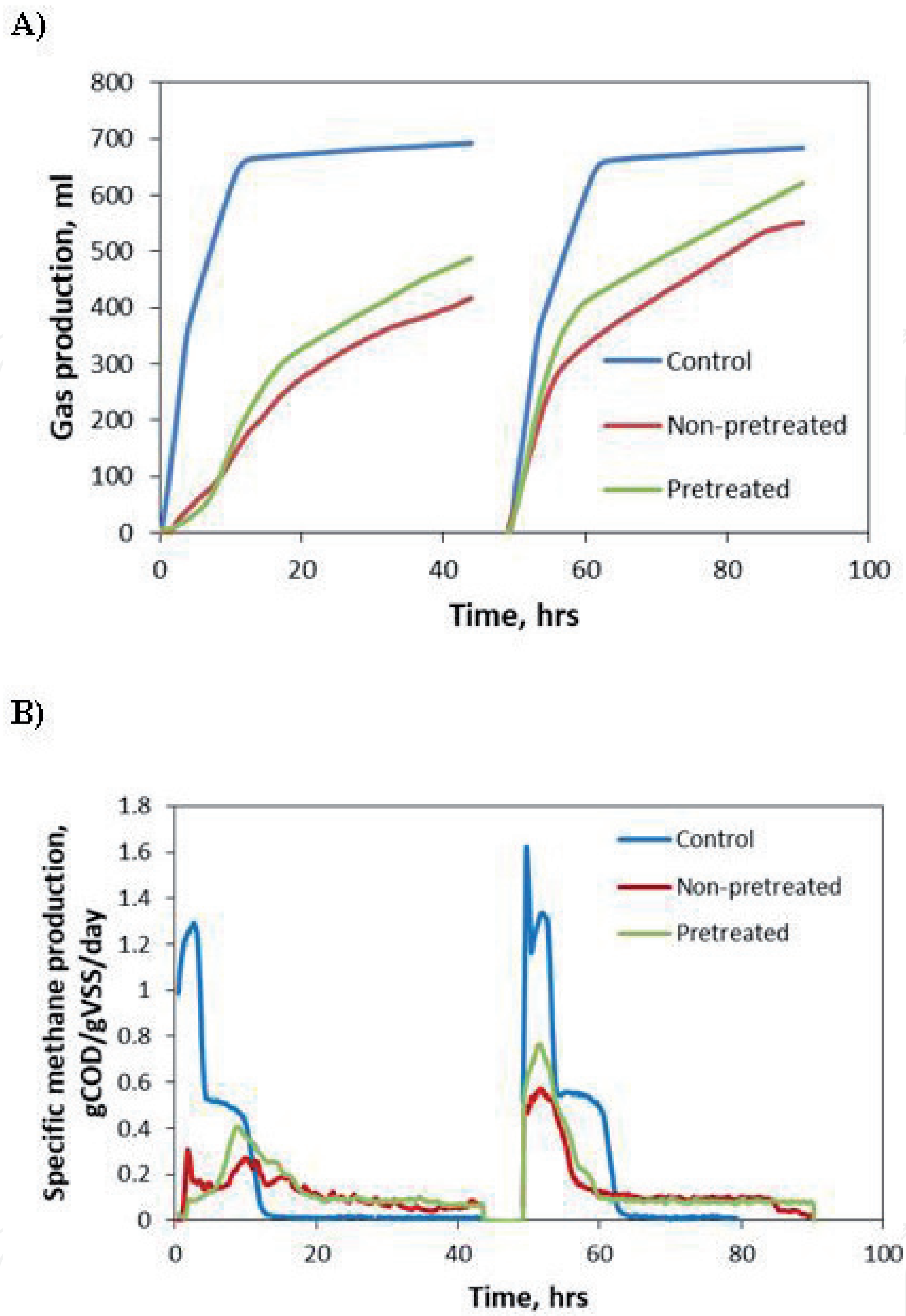


Figure 4.
Total gas production (A) and specific methane production (B) for the distillery wastewater.

3.3.2 Soy protein processing wastewater

Chemical analysis of the soy protein processing wastewater showed that it contains high concentration of sulfates. High sulfate concentration has adverse effect on anaerobic digestion for two reasons: it decreases the content of methane in the biogas, because reduction of sulfur competes with methanogenesis; second, inhibition of methanogenic archaea with hydrogen sulfide can occur [26]. Typically, a safe level of sulfates is considered to be when the ratio of COD to sulfates is at least 10. In our case this ratio is 3–3.5. Thus, the inhibition of anaerobic activity may be expected. Adjustment of pH from original 4 to 6 resulted in the decrease in sulfates concentration by 16.2%. For control, we performed additional removal of sulfates

	Biogas yield, ml		COD reduction, %		Biogas composition, % vol.		
	Cycle 1	Cycle 2	Cycle 1	Cycle 2	CH_4	CO_2	H_2S
Non-pretreated	396 ± 38	548 ± 32	57.5 ± 2.5	80.2 ± 2.7	61.1 ± 1.0	34.8 ± 0.3	1.33 ± 0.02
Pretreated	467 ± 42	611 ± 24	67.8 ± 3.5	89.4 ± 3.2	60.0 ± 2.7	36.5 ± 0.4	1.23 ± 0.03

Table 3.
Biogas yield, % COD reduction, and biogas composition after 40 hours of digestion of the distillery wastewater.

by adding $BaCl_2$. $BaCl_2$ selectively precipitates sulfates by forming insoluble salt $BaSO_4$. As a result of this treatment, 86.4% of sulfates have been removed (sulfates content decreased from 4970 to 600 mg/L).

We performed anaerobic digestion tests of this waste stream using three samples: 1) non-pretreated at initial pH, 2) treated by adjusting pH to 6, and 3) treated with $BaCl_2$ (after pH was adjusted to 6), which is referred to as "w/o sulfates". Results of the test are summarized in **Figure 5** and **Tables 4** and **5**. During the first feeding cycle the biogas production from the non-pretreated (pH 4) and pretreated (pH 6) samples is nearly the same. During the second feeding cycle, a significant decrease in the gas production is observed for the non-pretreated sample. The amount of biogas produced after 24 hours from the non-pretreated sample decreased by 40% during the second cycle. The biogas production from the pretreated sample decreased only by 7%. Such a decrease in biogas production can be attributed to the expected inhibition of methanogenic archaea by high sulfates concentration. This assumption is supported by the fact that the sample treated with $BaCl_2$ had higher biogas production than the pretreated sample, and no decrease in the biogas production was observed during the second feeding cycle.

Nearly 60% decrease in methane content during the second feeding cycle was observed in the non-pretreated sample (pH 4). The pretreated sample (pH 6) had lesser (25%) decrease in the methane content during the second cycle. On the other hand, the methane content in the biogas from the sample treated with $BaCl_2$ did not change. These results again suggest the inhibitory effect of the high sulfates concentration.

3.3.3 Oat fiber processing wastewater

Results from the anaerobic digestion test of the oat fiber processing waste stream are summarized in **Figure 6** and **Table 6**. The results show that the pretreatment significantly improves the digestibility of this stream. The amount of biogas produced after 40 hours during the first feeding cycle is 87% higher for the pretreated sample. An increase in digestibility for both samples is observed during the second feeding cycle (53% and 31% for the non-pretreated and pretreated sample, respectively). Upon the pretreatment, COD reduction during the second feeding cycle increased from 48.3% to 77.6%.

The gas quality, however, decreased upon the pretreatment (**Table 6**). The methane content decreased by 20%, carbon dioxide increased by 50%. The reason for this decrease in quality can be high concentration of NaCl, which accumulated as a result of pH adjustment with HCl and NaOH [25, 29].

All three waste streams, especially soy processing wastewater, contain fairly high amount of hydrogen sulfide, which, although unavoidable, is highly undesirable as it decreases the quality of biogas, causes corrosion of the piping, turbines, and other equipment [30]. It also forms a greenhouse gas SO_2 during combustion of H_2S-containing biogas. There is a number of methods to decrease or remove the H_2S

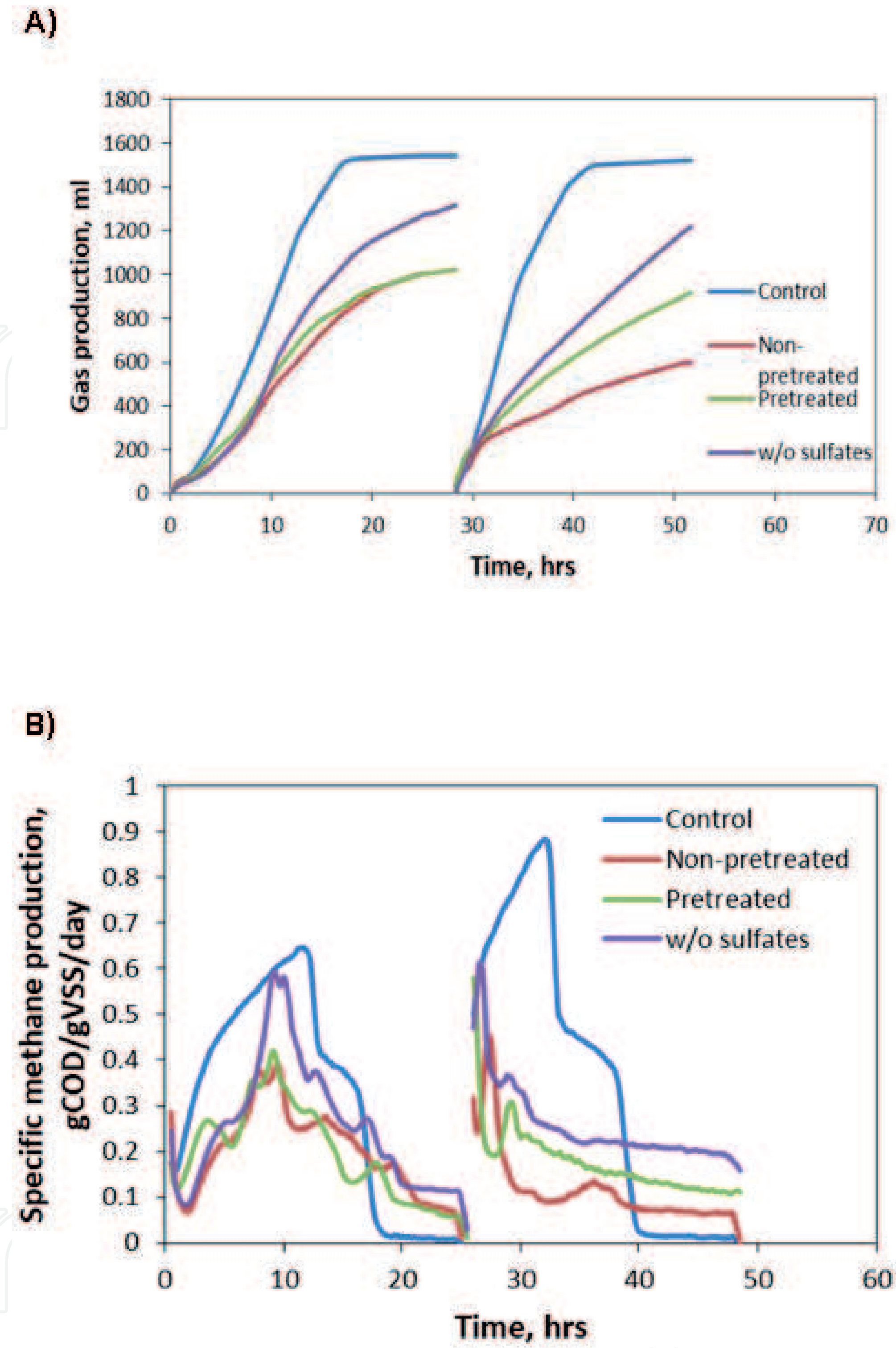


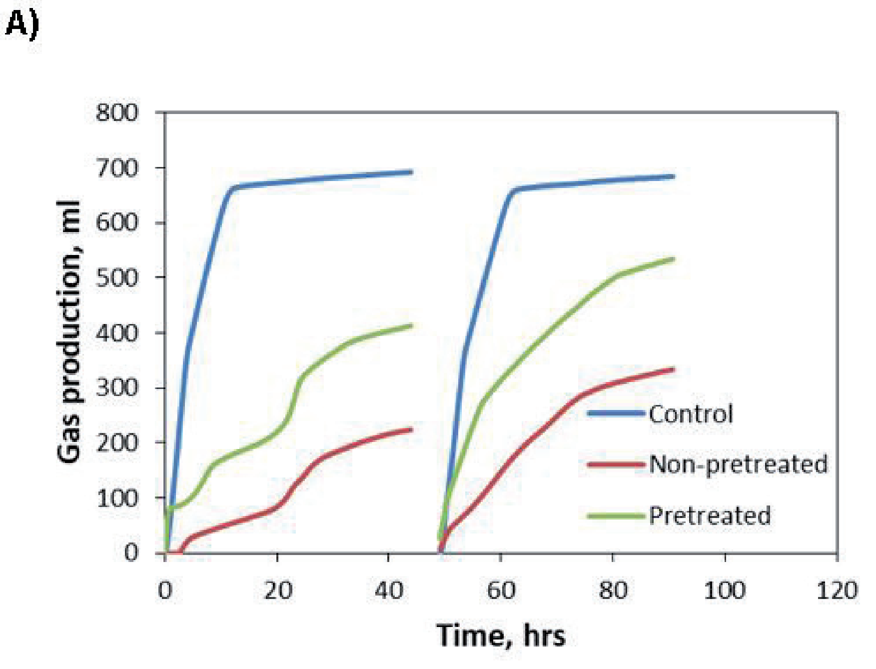
Figure 5.
Total gas production (A) and specific methane production (B) for the soy protein processing wastewater.

	Biogas yield, ml		COD reduction, %	
	Cycle 1	Cycle 2	Cycle 1	Cycle 2
Non-pretreated	992 ± 81	599 ± 62	64.3 ± 4.1	39.3 ± 2.5
Pretreated	990 ± 95	924 ± 85	64.2 ± 4.8	60.7 ± 5.7
W/o sulfates	1247 ± 132	1228 ± 121	80.8 ± 6.4	80.7 ± 7.3

Table 4.
Biogas yield and % COD reduction after 24 hours of digestion for the soy protein processing wastewater.

	Biogas composition, % vol.					
	Cycle 1			Cycle 2		
	CH_4	CO_2	H_2S	CH_4	CO_2	H_2S
Non-pretreated	42.3 ± 0.8	40.1 ± 0.6	3.12 ± 0.08	17.2 ± 0.4	59.3 ± 1.2	3.27 ± 0.05
Pretreated	44.1 ± 0.7	33.8 ± 0.6	2.23 ± 0.07	33.4 ± 0.7	38.4 ± 0.9	3.18 ± 0.07
W/o sulfates	45.3 ± 1.1	34.2 ± 0.8	1.35 ± 0.05	44.1 ± 0.9	45.3 ± 1.7	1.38 ± 0.05

Table 5.
Biogas composition after 24 hours of digestion for the soy protein processing wastewater.



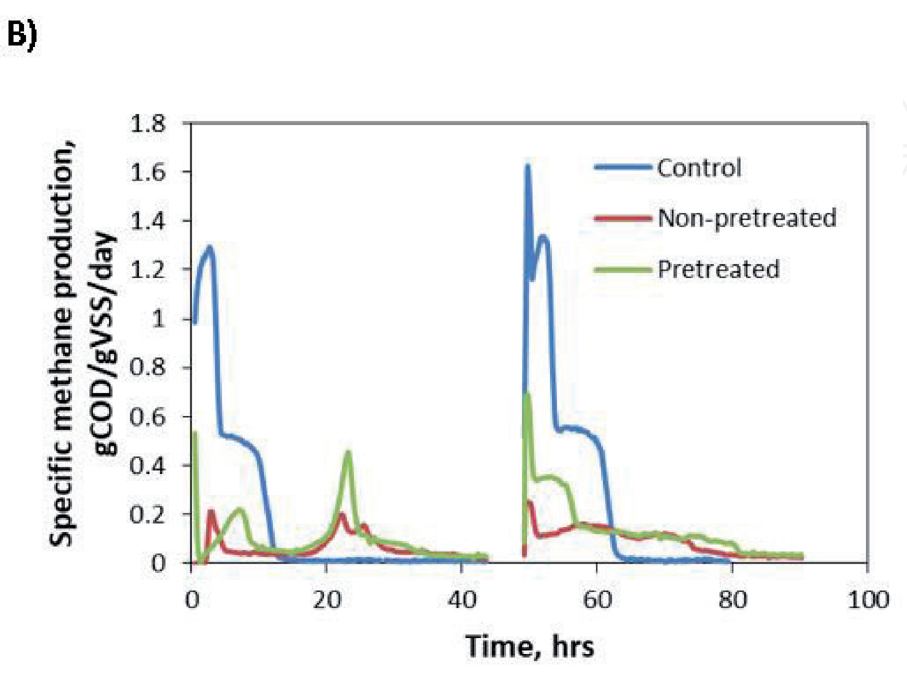


Figure 6.
Total gas production (A) and specific methane production (B) for the oat fiber processing wastewater.

	Biogas yield, ml		COD reduction, %		Biogas composition, % vol		
	Cycle 1	Cycle 2	Cycle 1	Cycle 2	CH_4	CO_2	H_2S
Non-pretreated	216 ± 27	330 ± 43	31.3 ± 4.3	48.3 ± 3.9	65.6 ± 1.7	27.3 ± 0.4	1.24 ± 0.08
Pretreated	404 ± 45	530 ± 61	58.5 ± 5.4	77.6 ± 6.9	52.8 ± 2.1	40.9 ± 0.8	1.45 ± 0.10

Table 6.
Biogas yield, % COD reduction, and biogas composition after 40 hours of digestion for the oat fiber processing wastewater.

content in biogas. They are broadly divided into two categories: 1) post-treatment of biogas and 2) prevention of H_2S formation during the AD process. The first category includes absorption, adsorption, and membrane filtration, and biological filtration techniques [31]. The second category includes in-situ chemical removal and in-situ bioconversion using microaeration [32–34]. Each individual method has its advantages and disadvantages. Therefore, best strategy is integration of several technologies to achieve a balance between efficiency, feasibility, and cost.

3.4 Pilot-scale anaerobic digestion tests

In order to verify that results of batch studies are transferrable on a larger scale, we performed AD tests on a continuous upflow fluidized bed pilot reactor using only one of the tested streams. We selected for this purpose the oat fiber processing wastewater, as it seemed to benefit the most from the pretreatment. Non-pretreated and pretreated wastewater was fed continuously for a 2-week period. The anaerobic sludge in the reactor was preliminary activated by feeding with a standard nutrient solution [24] using ethanol as a source of COD at ~2 g-COD/Lday volumetric loading rate (VLR) for one week. Prior to feeding the wastewater, the biomass in the reactor was starved for 2 days. The COD content of the wastewater was adjusted to 10.0 g/L by dilution with tap water. The wastewater was supplemented with nitrogen in the form of ammonium chloride (10 g per 50 L every second day). COD of influent and effluent, as well as biogas production were measured daily. The results of this test (**Table 7**) indicate that the pretreatment of the wastewater by pH-induced precipitation resulted in the increase of biogas production by 23.1% and increase of the COD removal efficiency by 25.2% compared to the original wastewater. We attribute this improvement to the decrease in the amount of the poorly digestible compounds, such as alkali-soluble polycarbohydrates and lignins, which were precipitated and removed. Methane content, however, was slightly lower in the case of pretreated wastewater, which is consistent with the results of the batch tests. The reason for this is most likely the same as in batch studies – high level of NaCl. Although batch studies did not reveal any adverse effects of this waste stream on the anaerobic biomass, the operation of the pilot reactor was not stable in both non-pretreated and pretreated streams. While the volumetric loading rate (VLR) was kept constant at fairly low level, the volatile fatty acids (VFA) concentration in

	VLR, g-COD/L/day	Gas production, L/day	COD removal efficiency, %	Methane content, % vol.
Non-pretreated	3.0 ± 0.2	65.0 ± 4.0	65.8 ± 3.1	77.8 ± 1.2
Pretreated	3.0 ± 0.2	80.0 ± 3.0	82.4 ± 1.4	74.4 ± 0.9

Table 7.
Summary of anaerobic digestion of the oat fiber processing wastewater using a continuous pilot-scale reactor.

both cases was constantly increasing throughout the entire feeding period, suggesting a possible toxic effect. Elucidation of the long-term effects of the above waste stream on anaerobic biomass was, however, beyond the scope of this study.

4. Conclusions

In this study, pH-induced precipitation has been evaluated as a method of pretreatment of industrial effluents in order to improve anaerobic treatment efficiency. The pH adjustment was done to bring the pH of the solution close to its isoelectric point. Such pretreatment resulted mainly in the removal of suspended and dissolved solids. The effect of the pretreatment was studied on the laboratory and pilot scale using wastewater from local grain processing industries: distillery, soy protein processing, and oat fiber processing plants. The anaerobic digestibility of all three waste streams benefited from the pretreatment. Lab-scale batch AD tests showed the increase in COD reduction from 80.2% to 89.4% for the distillery waste stream, from 39.3% to 60.7% for the wastewater from the soy protein processing, and from 48.3% to 77.6% for the oat fiber processing wastewater. Benefit of the pretreatment was further verified on the pilot scale using an upflow fluidized bed reactor with the oat fiber processing wastewater as a feed. After two weeks of continuous feeding, an increase in the daily biogas production by 23% and COD removal efficiency by 25% has been observed as a result of the pretreatment.

Our lab-scale and pilot-scale AD studies showed a positive effect of the pH-induced precipitation on these waste streams in terms of increased biogas production (11–60%) and COD removal (12–60%), and in some instances reduction in the H_2S content in biogas (8%). This study clearly demonstrated that pH-induced precipitation is an effective pretreatment method to improve AD performance on wastewaters from grain processing industries.

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