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Anaerobic Co-Digestion of Oil Sludge with Corn Stover for Efficient Biogas Production

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Abstract: The feasibility of anaerobic co-digestion for the utilization of oil sludge was verified using corn stover, to assess the influence of different raw material ratios and inoculum volumes on the properties of the generated gas. The anaerobic co-digestion method is a novel treatment technology, which may help to solve the problem of pollution by hazardous waste oil sand from the oil exploitation and smelting process. Results showed that single-oil sludge was not suitable for gas production as a digestive substrate due to the lack of organic materials and possible hazardous materials. With the increase in the quality of exogenous organic matter (corn stover), the cumulative gas production volume was proportional to the amount of corn stover material added. It was established that when the mass ratio of corn stover to oil sludge was 4:1, the gas production performance was optimal, with a cumulative gas yield of 1222.5 mL using an inoculum volume of 30 mL. The results of this study provide a fundamental parameter baseline for the treatment of oil sludge and the improvement of gas production efficiency.

Keywords: oil sludge; corn stover; anaerobic co-digestion; biogas

1. Introduction

Oil sludge is a mixture of mud and sand contaminated by crude oil in the process of oil extraction, storage, transportation and processing [1]. Oil sludge contains a large quantity of hydrocarbons and heavy metal components [2–4]. Long-term open stacking not only pollutes the atmospheric environment but also occupies a large amount of land resources [5,6]. In China, the annual output of oil sludge in the petrochemical industry is expected to be 3 million tons [7]. It is estimated that approximately 1 ton of oil sludge is produced for every 500 tons of crude oil processed [8]. Traditional oil sludge disposal methods mainly include incineration, land cultivation, and landfilling, but these methods are costly to carry out and pose environmental risks [9–11]. For example, incineration requires the use of auxiliary fossil fuels to support combustion and also produces harmful gases and harmful ash [12,13]. In addition, landfarming and landfilling will bring leachate, causing water and soil pollution [14]. In order to effectively solve the problem of oil sludge treatment and promote the sustainable development of the oilfield and refinery industry, it is imperative to explore environmentally-friendly, efficient and economical oil sludge treatment technologies.

Anaerobic co-digestion is an effective resource technology for converting solid waste biomass into biogas [15,16]. It has been previously reported that the substrates suitable for anaerobic co-digestion include crop stover, urban sludge, food waste, and livestock waste [17–20]. Many experts have started to study the application of anaerobic co-digestion technologies in the treatment of oil sludge [21], although there remain many gaps in knowledge on combined anaerobic co-digestion technologies and the chemical treatment of oily sludge, in terms of the sustainability of resources, energy, and environmental impact. Therefore, it is of great significance to explore the treatment of oil sludge through systematic design and thorough investigations, in order to overcome the existing environmental problems associated with the commercial application of these systems.

Through previous studies, it was found that the organic matter content of refined oil sludge was commonly very low, with a pungent smell [2,4]. Before and after the pretreatment of single-oil sludge, there was no beneficial effect observed in co-digestion and biogas production, although production was greatly improved by the addition of exogenous nutrients. Considering the fact that industrial applications are often located near cropland, the collection of solid farmland waste such as crop stover biomass is convenient for oil sludge treatment processing. This method can effectively improve the organic matter content of the fermentation substrates, while also reducing the burden of harmful waste substrates that are toxic to microorganisms. When the ultrasound method was combined with anaerobic co-digestion, more advantages were observed, and co-digestion at high temperatures (55 ± 2°C) resulted in better biogas production performance than co-digestion at medium temperatures (35 ± 2°C), with microbial activity more easily activated.

In this study, based on preliminary studies, anaerobic co-digestion technology was adopted to treat oil sludge, to allow synchronous resource utilization of crop stover. Sequential batch experiments were performed to verify the influence of corn stover on the anaerobic co-digestion and the biogas production performance of oil sludge. By adjusting the proportion and inoculation volume of corn stover and oil sludge under high-temperature conditions, this study will provide theoretical support for the subsequent chemical treatment of oil sludge.

2. Materials and methods

2.1. Inoculum and Feedstocks

2.1.1. Oil Sludge

Samples were taken from the first station of the oil production plant of the Shengli oil field, Shandong Province (Tencent Scott, N 37°27′53.18″ E118°30′51.12″), from the sewage outlet of the mixed tank of the three-phase separator. The oil was normal oil, not heavy oil. The oil displacement mode refers to water displacement, and the main components were oil, water and sand, excluding other oil displacement components such as polymers. Moreover, following dosing in the front section of the process, the sludge contained about 100 ppm of demulsifier. The basic physicochemical characteristics are listed in Table 1.

2.1.2. Corn Stover

Samples were taken from farmland near Bincheng District, Binzhou City, Shandong Province (Tencent Scott, N 37°23′51.05″ E118°05′42.29″) in March, 2019. Deionized water was used to wash the corn stover material to remove sand and other impurities, before samples were placed in a 40 °C oven to dry until the moisture content was reduced to less than 5%. Then, the material was crushed to 2-3 cm, the bag was sealed, and it was stored at room temperature for later experiments.

2.1.3. Inoculum

The inoculum was obtained from a high-temperature (55°C) anaerobic fermentation tank of Binzhou Zhongyu Food Co. Ltd., Shandong Province (Tencent Scott, N 37°28′35.84″ E 117°59′34.62″). The fermentation substrate is a byproduct of grain ethanol production after the fermentation of distiller lees.

Table 1. Characteristics of oil sludge, corn stover and the inoculum.

Parameters	Oil sludge	Corn stover	Inoculum
C/% [a]	27.76 ± 0.10	47.44 ± 0.20	30.17 ± 0.60
N/% [a]	3.11 ± 0.20	1.87 ± 0.02	5.01 ± 0.04
Ph	6.5-7.4	ND[b]	7.3-7.7
TS% [a]	64.89	96.75	8.77
VS% [a]	4.94	84.18	5.64

Data expressed as mean values±SD (standard deviation, n≥3); [a] Carbon content and nitrogen content in Volatile Solid (VS) were calculatbased on the sample Total Solid (TS) value; [b] sample not tested.

2.2. Experimental Setup

The anaerobic co-digestion device used in the experiment was made according to the principles of the drainage and gas collection method [22]. A custom-built controllable constant temperature anaerobic co-digestion device was designed, as shown in Figure 1. The device consisted of a 200 mL serum fermentation bottle, a 1000 mL drainage-collecting serum bottle and a 1000 mL measuring cylinder for collection, and the devices were connected via silica gel tubes. Before the experiments, the prepared devices were placed in a constant temperature water bath pot, with the experiments repeated in triplicate for each setting. The temperature fluctuation range was 55 ± 2°C.

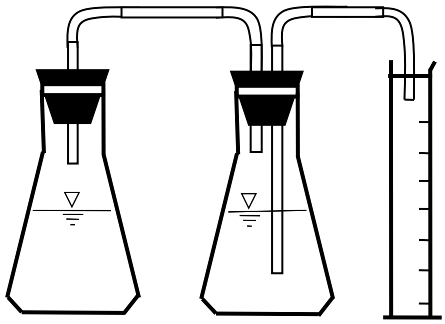

Figure 1. Anaerobic co-digestion system experimental setup.

2.3. Experimental Design

2.3.1. Different Ratios of Corn Stover to Oil Sludge

The 200 mL serum bottle had a 150 mL effective volume. The total solid (TS) value was maintained at 3%, and the inoculum was 40 mL in each bottle. According to preliminary test results, the mass ratios of oil sludge to corn stover were set as 1:0, 1:1, 1:2, 1:3, 1:4 and 0:1 (as shown in Table 2). The fermentation bottle was purged with nitrogen for 5 min to create an anaerobic co-digestion environment and then sealed. The bottles were maintained at 55 ± 2°C, and the gas produced was recorded daily. Three parallel tests were performed for all conditions. Devices containing only the inoculum and water were used as blank groups to correct the biogas production results, and control groups were also prepared to contain pure oil sludge and pure corn stover. Data collection began the day after inoculation. The bottles were shaken twice a day for 10 min. The experiment lasted for 30 days.

Table 2. Substrates qualities under different conditions.

Group	Ratios[a]	Water (mL)	Inoculum (mL)
1	0:1	20.63	40
2	1:1	51.88	40
3	2:1	83.13	40
4	3:1	114.38	40
5	4:1	145.63	40
6	1:0	31.25	40
7	Blank(0:0)	0	40

[a] the ratios refer to the mass ratio of corn stover to oil sludge

2.3.2. Different Inoculum Volumes

The mass ratio of corn stover to oil sludge was maintained at 2:1 to study the effect of inoculation on anaerobic co-digestion and biogas performance. Table 3 shows the added substrate qualities of each fermentation bottle, with each bottle containing 2 g of corn stover, 1 g of oil sludge and 83.13 mL of distilled water.

Table 3. Substrate qualities and inoculum volume.

groups	1	2	3	4
Corn stover (g)	2	2	2	2
Oil sludge (g)	1	1	1	1
Water (mL)	83.13	83.13	83.13	83.13
Inoculum (mL)	20	30	40	50

2.4. Analytical Methods

The oil sludge and corn stover selected for co-digestion were analyzed in triplicate for both their physical and chemical properties in all of the experiments. Total solid (TS) and volatile solid (VS) contents were determined according to the American Public Health Association (APHA) standard methods [23]. The elemental contents of C, N and H were determined using an elemental analyzer. The pH value was measured using a pH electrode (PHS-2F, Rex Electric Chemical, China).

The gas yield was determined using the drainage method. The headspace gas produced in the digester bottle was collected and then injected into another bottle. The volume of water collected per day was considered to be the equivalent of daily biogas production. The digested products were analyzed (VS%) for calculation of the mass conversion of feedstock organic materials using APHA standard methods.

Statistics: All analysis was performed using Excel, version 2019. The differences between treatments were determined using one-way analysis of variance (ANOVA, Excel, version 2019).

2.5. Calculation Methods

(1) Volume gas yield (VLR, L/L·d) = daily biogas production (mL)/total bottle volume (mL).

(2) Biogas production per unit vs. (mL/g VS) = daily biogas production (mL)/unit mass substrates.

(3) Organic matter mass conversion (%) = (the vs. value of substrate initial - the vs. value of substrate end)/the vs. value of substrate initial × 100%.

3. Results and Discussions

3.1. Different Ratios between Oil Sludge and Corn Stover

3.1.1. Biogas Performance of Oil Sludge

In order to verify the feasibility of oil sludge as a feedstock for anaerobic co-digestion, pure oil sludge exhibited a low level of biogas production compared to production with co-digestion (Figure 2). Daily biogas production was the highest in the initial stage of co-digestion, and although background organic matter was consumed before the inoculum was added to the fermentation bottle, the organic matter present in the inoculum allowed production to continue throughout the whole process. Moreover, the gas bottle heat bilge cold shrinkage may be caused by gas, not by the oil sludge. Oil sludge has few organic matter contents, as shown in Table 1, and some substances in the oil sludge (e.g., demulsifiers, salts and heavy metal components) may decrease the microbial activity, co-digestion time and biogas production. In order to improve the anaerobic co-digestion performance, the acclimation of microorganisms is an important aspect to develop in the future.

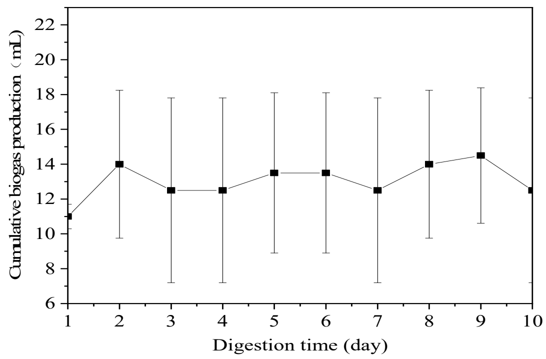

Figure 2. Cumulative biogas production of oil sludge.

3.1.2. Biogas Yield

Biogas production is an indicator that can help monitor co-digestion operational performance and microbial physiological activity [24]. Figure 3 shows the daily biogas production and cumulative biogas production. From these results, daily biogas production was shown to be higher in samples containing ratios of 1:0, 1:1, 2:1, 3:1 and 4:1. During the co-digestion process, the biogas was mainly produced between 1 and 22 days. The results show a positive correlation between corn stover and biogas production. Adding exogenous organic compounds (corn stover) can effectively improve the anaerobic co-digestion performance. This may be due to the fact that the corn stover can provide organic matter for microorganisms to grow and produce metabolites (CH_4, CO_2, H_2 and H_2O). Moreover, peak height and peak emergence time showed significant differences. These results may indicate that the content of organic matter in the fermentation feedstock was increased, and thus, biogas production was increased.

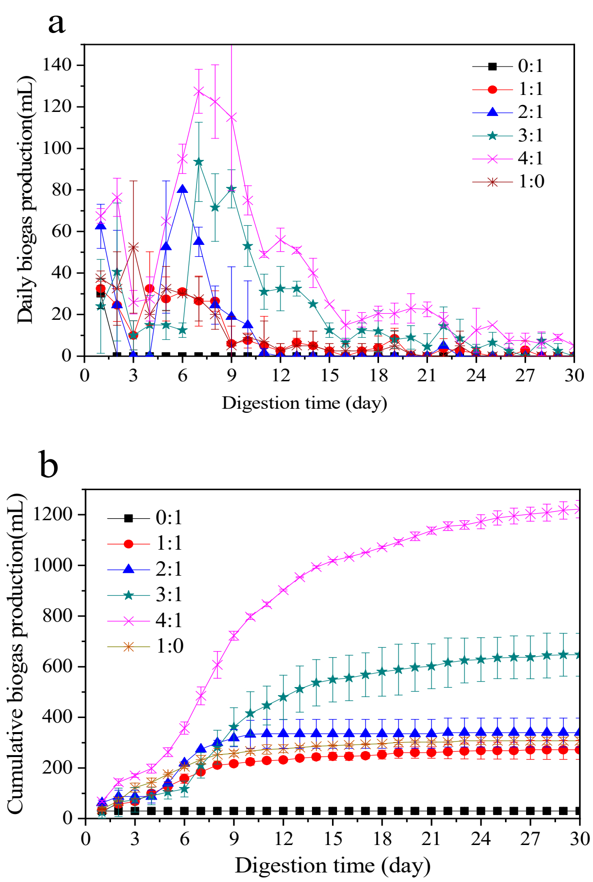

Figure 3. Daily biogas production (a) and cumulative biogas production (b) under different feedstock mass ratios.

Compared with the control sample 0:1, the anaerobic co-digestion of oil sludge with corn stover can obviously increase the cumulative biogas production. During the co-digestion process, the cumulative biogas produced rapidly increased between 1 and 12 days, and the daily biogas production was higher in ratio samples 1:1, 2:1, 3:1 and 4:1 than in 0:1. As the amount of corn stover added increases, the amount of organic matter and the biogas production increase. Besides, corn stover can also dilute and adsorb harmful substances, increasing the number and activity of microorganisms. The results show that the ratio sample 4:1 exhibited the highest gas production yield, at 1222.5 mL.

3.1.3. Organic Matter Mass Conversion

After anaerobic co-digestion, the organic matter in feedstock can be utilized and converted for the production of CH_4, CO_2, H_2 and low molecular organic acids. Table 4 shows the organic matter mass conversion of the feedstock by anaerobic co-digestion technologies, showing that organic matter has a higher conversion rate in the ratio groups 1:0, 1:1, 2:1, 3:1 and 4:1. The mass conversions in ratio groups 1:1 and 2:1 were lower than in ratio groups 1:0, 3:1 and 4:1, indicating that sufficient organic matter can provide nutrition for microorganisms. The high mass conversion in all five groups may not objectively indicate the materials which can be utilized and converted by microorganisms. Soluble organic carbon can be directly used by microorganisms to degrade into CH_4, CO_2, H_2 and H_2O. Mass conversion may depend a lot on soluble organic carbon, and thus, the test indices (e.g., low molecular organic acids, acetic acid, propionic acid, butyric acid) should be analyzed to ensure accurate mass conversion of organic feedstock.

Table 4. Organic matter mass conversion and cumulative biogas production under different feedstock mass ratios.

Groups	Ratios of corn stover to oil sludge	Organic matter mass conversion (%) [a]	Cumulative biogas production (mL)	Average values of daily biogas production per unit of volatile solid (mL/g VS)
1	1:0	97.0625 ± 0.02	307 ± 14.14	12.16
2	1:1	91.7824 ± 0.09	271.5 ± 37.48	10.16
3	2:1	91.6111 ± 0.02	339.5 ± 57.28	6.53
4	3:1	98.629 ± 0.01	647 ± 84.85	8.38
5	4:1	98.4152 ± 0.04	1222.5 ± 34.65	11.93

Data expressed as mean values ± SD (standard deviation, n≥3); [a] The data on organic matter mass conversion were calculated based on the TS value after anaerobic digestion.

3.2. Different Inoculum Volumes

With the ratio of corn stover to oil sludge at 2:1, the inoculum volumes were set as 20, 30, 40 and 50 mL (Figure 4a). After co-digestion for 30 days, the biogas production was mainly concentrated to within the first 12 days. With the extension of co-digestion time, the biogas production gradually decreased until the end of the experimental period. The biogas production peak height and the time of peak yield were also significantly different in groups with different inoculation volumes. An inoculum volume of 20 mL resulted in no significant biogas production until 4 days of treatment. From 5 to 10 days, the yield was highest, with biogas production reaching a maximum of 44 mL/d on day 7, after which biogas production decreased and remained unchanged until the end of gas production on day 26. It is possible that in this period, with the reduction of organic matter, the proportion of harmful compounds may increase relatively, which may reduce the number of microorganisms and activity. With the increase in inoculation, the number of bacteria increased and when microbes adapted to the environment, the biogas production increased. The results indicate that under the same organic component conditions, the inoculation quantity of the strains had a significant effect on the combined anaerobic co-digestion. The initial reaction was slow, with small inoculation volumes. With the increase in inoculation, the biogas production increased and the initial biogas production yield changed. The factors associated with restriction of anaerobic co-digestion and gas production from oil sands should be studied in the future by high throughput sequencing technology, to confirm the microbial mechanisms. As shown in Figure 4b, the accumulative biogas production response of each group showed a similar trend. The early stages showed the start of biogas production, which then increased rapidly up to about 15 days, at which time the biogas production stopped, or production was significantly reduced. The 30 mL group produced the maximum biogas yield (430 mL), while the 40 mL and 50 mL groups exhibited similar levels of biogas production at 339.5 mL and 343 mL, respectively. The ratio of corn stover to oil sludge was maintained at 2:1, and therefore the groups had the same organic material components. The inoculum volume was changed, resulting in the cumulative biogas production yield presenting significant differences, indicating that the inoculum can affect biogas performance and that an inoculation volume of 30 mL/150 mL is an effective volume.

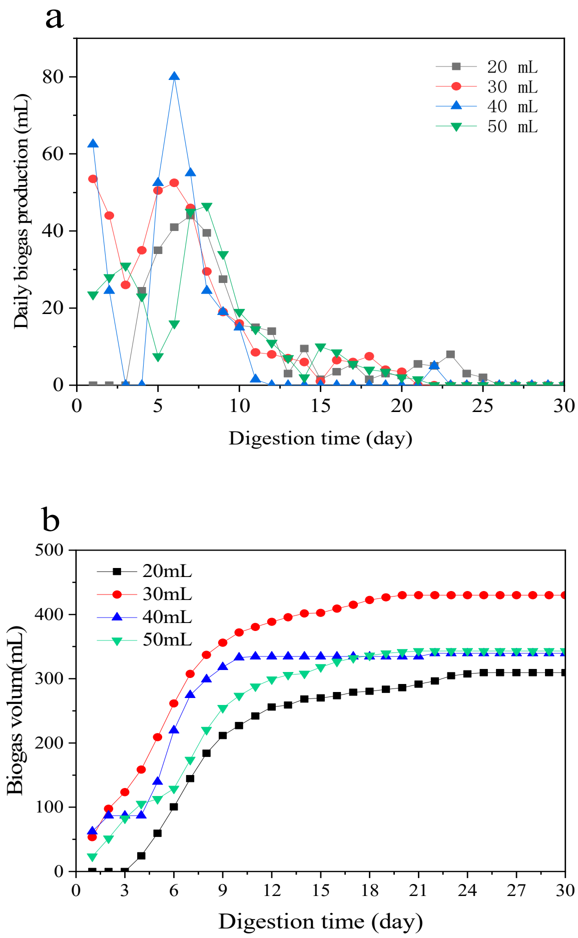

Figure 4. Daily biogas production (a) and cumulative biogas production (b) under different inoculum volumes.

4. Conclusions

Adding corn stover can improve the anaerobic digestibility of oil sludge compared to single-oil sludge. With the increase in quality of exogenous organic matter (corn stover), the cumulative gas production volumes were proportional to the amount of corn stover material added. It was established that when the mass ratio of corn stover to oil sludge was 4:1, the gas production performance was optimal. Moreover, the inoculum volume can also affect the biogas yield performance. With a ratio of corn stover to oil sludge of 2:1 and an inoculum volume of 30 mL/150 mL, the maximum cumulative biogas yield was produced. This research about the anaerobic co-digestion of oil sludge and corn stover determined the optimum mass ratio and inoculation amount of substrates, which can not only solve the problem of sludge-associated pollution, but also allow for energy generation from the reuse of corn stover.

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