Environment Protection Engineering

Vol. 36 2010 No. 4

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ANAEROBIC MOVING BED BIOFILM FERMENTER FOR BIOGAS PRODUCTION

On of the most promising technologies in the disposal of agro-industrial organic wastes is biodegradation under anaerobic circumstances. The major, profitable product of anaerobic degradation is biogas, from the environmental aspect a renewable resource. To enhance biogas production and produce a methane-rich final product an integrated anaerobic membrane bioreactor filled with moving biofilm carriers was designed.

In this study, the intensification of anaerobic fermenter was investigated by using polyvinyl-alcohol (PVA) gel beads as biofilm carriers. The solid retention time can be increased by attaching microorganisms to PVA-gel beads and as a result the efficiency of biogas production can be improved.

Two laboratory-scale anaerobic fermenters were run in parallel, one with biofilm carriers and one without. The results showed that, compared to the control system, in the carrier-filled fermenter the efficiency of biogas production was enhanced by 28% as a result of the biofilm formation on the surface of the carriers. In addition, the COD concentration of the effluent was decreased by 80–88%, 10% more than in the control reactor.

1. INTRODUCTION

Nowadays agro-industrial wastes and co-products are formed in higher and higher amounts worldwide and some part of them (e.g. animal manure) may pose a pollution threat to the environment, therefore they should be treated and degraded. Anaerobic digestion of animal manure has several benefits as it improves its fertilizer quality, reduces the quantity of disposable sludge, reduces odours and pathogens and in addition it produces renewable resource, namely biogas [1].

Regardless of its advantages, anaerobic digestion has one main disadvantage, the slow-growing microorganism populations. The generation time of methane-forming bacteria is relatively long compared with that of aerobic bacteria. Typical solids retention times (SRTs) for anaerobic digesters are >12 days. At retention time < 10 days,

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significant washout of methane-forming bacteria occurs. To prevent washout, microorganisms can be attached to various media to be immobilized and to form a biofilm on the surface. The development of the fixed film filter was a significant achievement in anaerobic technology. The material used in fixed-film systems holds the bacteria in the digester for relatively long periods and provides higher microbe density in the fermenter as well as longer SRTs and shorter HRTs (hydraulic retention time). High SRT values maximize removal capacity, reduce required digester volume, provide buffering capacity and may intensify biogas production. Numerous fixed-film systems are available for use in the digestion of municipal and industrial wastewaters and sludges. These systems are capable of treating a variety of wastewaters and sludges, they provide good contact between the wastes and the bacteria, and can treat wastewaters and sludges over a relatively wide range of temperature values (4–55 °C) [2].

Since anaerobic degradation involves the participation of various microorganisms with complex metabolic interaction, the reduction of the transfer distance for intermediate compounds between the microorganisms can enhance the process. The reduction of the transfer distance, and thus enhancing the syntrophic interaction, could be achieved by biofilm formation [3], [4]. The proof is the reduction of the propionate and butyrate degradation rates produced by the destruction of biofilm [5], [3]. If microorganisms, are attached to moving carriers – instead of the fixed media – the transfer distance can be decreased further.

These moving carriers can be solid particles dispersed in the fermenter. In this work, PVA gel beads were used as biofilm carriers, since PVA is nontoxic to microorganisms [6] and provides suitable surface for biofilm formation [7]–[9]. Moreover, PVA-gel beads have a porous microstructure suitable for the retention of bacteria [10] and specific gravity slightly heavier than water.

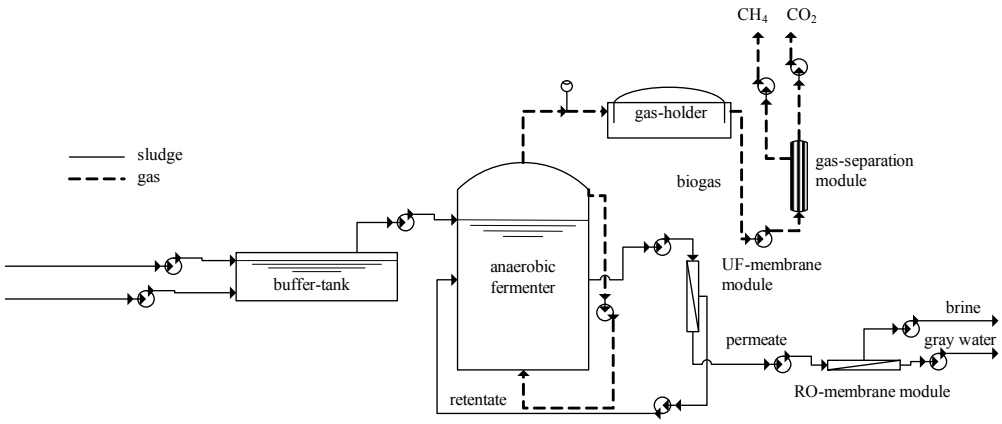

Fig. 1. Scheme of the anaerobic membrane bioreactor system

Our research work is part of a scaled up industrial project where the aim is to produce green (alternative) bioenergy (figure 1). A bioethanol plant is designed and operated while the wastes of the plant (slop) together with other local agro-industrial wastes will be treated in an anaerobic digester to produce biogas and to considerably reduce the effluents of the plant. Moreover, the digestion process will be completed with membrane processes [11] to purify the biogas formed by gas separation technique (to obtain pure methane), to concentrate the sludge by ultrafiltration and gain more biogas, finally to separate the permeate which results in disposable grey water.

In our research work, the purpose is to plan, build and operate a reliable, continuous anaerobic digester adapted to the local conditions and substrates. Anaerobic moving bed biofilm system seems to provide the most effective digester configuration, thus we studied it in batch and semi-continuous operation and – for comparison – a parallel anaerobic fermenter was operated as a control system with similar operational parameters, but without biofilm carriers.

2. MATERIALS AND METHODS

2.1. EXPERIMENTAL SET-UP

A schematic presentation of the studied system is shown in figure 2. The anaerobic fermenter is made of stainless steel with a working volume of 1.8 l (1.5 l bulk liquid and 0.3 l gas volume). The examined reactor was filled with 0.2 l of biofilm carrier (PVA-gel beads), volumetric density of 670 g/l, and 1.3 l of anaerobic sludge, while the control reactor was filled with 1.5 l of anaerobic sludge. The temperatures in the reactors were controlled at 37±1 °C, this means mesophilic temperature range. In the

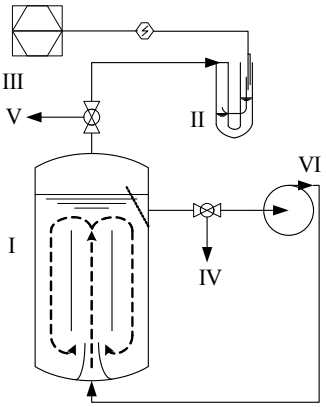

Fig. 2. Schematic representation of the anaerobic bioreactor with sludge mixing:
(I) anaerobic fermenter, (II) gas volume meter, (III) computer for data collection,
(IV) sludge sampling, (V) gas sampling, (VI) peristaltic pump

carrier-filled reactor, in the first set of experiments, the continuous mixing of the anaerobic reactor was achieved by recycling the sludge from the top to the bottom of the reactor. In the second set of experiments, the sludge (and carriers) was mixed by recycling the produced biogas at the bottom of the reactor. In the control reactor, sludge mixing was applied. To follow the change of the sludge properties and the produced biogas, sampling points were created on the reactors.

2.2. MATERIALS

The substrate was taken from a working anaerobic sludge digester (Csenger, Hungary), dealing with biodegradation of liquid manure from cattle and slaughter-house wastes. The properties of sludge were: TSS of 20.32 g/l and COD of 18.00 kg/m^3. The anaerobic systems were fed by synthetic wastewater (COD of 60–66 kg/m^3), the constituents are given in table 1.

Table 1

Composition of synthetic wastewater

Constituent	Source	Concentration
Protein	Meat extract	25 g/l
Carbohydrates	Cellulose	12.5 g/l
Lipids	Sunflower oil	12.5 g/l
Mineral salts	NaCl	25 mg/l
	$MgCl_2 \cdot 6H_2O$	0.72 mg/l
	$CaCl_2 \cdot 2H_2O$	0.44 mg/l

PVA-gel beads were applied as support media for biofilm formation. The beads had an average diameter of 2–3 mm, specific gravity of 1.03, and a porous microstructure suitable for retention of microorganisms.

2.3. ANALYTICAL METHODS

The volumetric biogas production rate was monitored with a special gas meter [12], and its composition was determined by a gas chromatograph (GowMac 550) equipped with GowMac X13 column, using helium as vector gas. The oven, injector and temperature (TCD) detector were set at 120 °C.

The quality parameters of the anaerobic sludge were followed by measuring pH, volatile fatty acids (VFA), total suspended solid (TSS) and chemical oxygen demand (COD), according to standard methods [13], [14]. The VFA concentration was determined by gas chromatograph (5890A GC) equipped with HP-FFAP (Agilent) column, using nitrogen as vector gas. Oven temperature gradient 110–180 °C, injector and detector temperature was set at 250 °C.

Biofilm formation on the PVA-gel bead surface was followed by measuring protein concentration, according to the modified Lowry method [15]. The principle of the

method is that under alkaline conditions the divalent copper ion forms a complex with peptide bonds in which it is reduced to a monovalent ion. A monovalent copper ion and the radical groups of tyrosine, tryptophan, and cysteine react with Folin reagent to produce an unstable product that becomes reduced to molybdenum/tungsten blue. First the carriers were washed with saline solution, then the modified Lowry assay was carried out, and finally the absorbance was measured at 660 nm.

3. RESULTS AND DISCUSSION

3.1. START-UP

At start-up of anaerobic fermenter the continuous mixing of the PVA-gel beads was ensured with continuous fluid recycling. During the first 10 days of reactor operation the organic loading rate (OLR) was 0.21 kg COD/m^{3}d. The biogas production during this period was 1.2 l/day on average, the COD removal efficiency was only about 65%. After 10 days of stable operation and adequate biogas production, the reactor was switched to biogas mixing mode.

3.2. OPERATION

The continuous operation was maintained for 50 days with OLR of 4.4 kg COD/m^{3}d. During the operational time several feeding steps were realized. The time course of the biogas production rate during a feeding step (24 hours) is shown in figure 3 as an example. A sharp increase can be noticed at the feeding time and certain periods can be defined in the curve where the degradation of the different substrate ingredients might occur. Probably, first the cellulose and the oil content of the added synthetic waste water are degraded and finally the protein compounds are decomposed resulting in biogas formation at various rates.

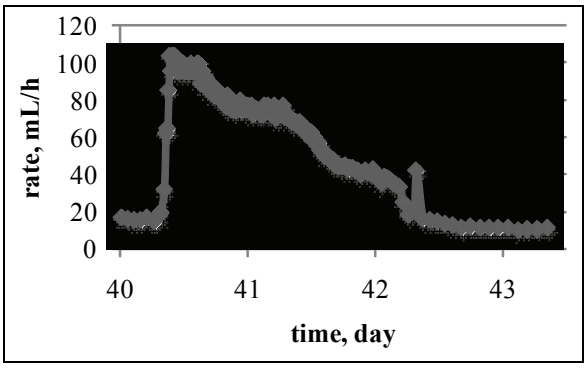

Fig. 3. Rate of biogas production in a feeding step

To follow the organic removal capacity the COD of outlet sludge from both reactors was measured daily. During the start-up – as we mentioned – the removal efficiency was about 60–65%. After 15–18 days of operation, as presented in figure 4, in the control reactor the removal efficiency increased to 70–75%, while in the PVA-gel bead-filled reactor it increased to 80–85%. The difference between the two anaerobic reactors can be attributed to biofilm formation in the carrier-filled reactor. On the 50th day of operation in the examined reactor, the organic removal efficiency reached 88% (figure 4).

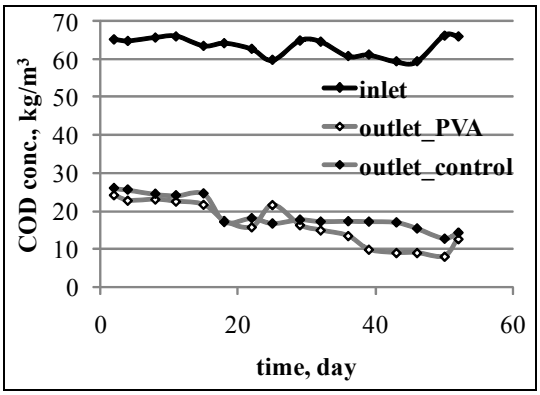

Fig. 4. Organic removal efficiency in fermenters

The concentration of VFA in both control and carrier-filled reactors was about 0.2–0.3 g/l, while the pH was between 7.3 and 7.8. This indicates that biogas formation was not inhibited by over-production of volatile fatty acids [16].

The average biogas production rates of the applied synthetic wastewater for both the PVA (biofilm) and the control reactors were calculated (table 2). The difference between the two reactors was 2.47 l gas /synthetic wastewater, owing – possibly – to the beneficial effect of the biofilm.

Table 2

Efficiency of biogas production

	Biogas production l gas/synthetic wastewater	Standard deviation (+/–)
PVA-gel beads reactor	8.83	0.89
Control reactor	6.36	0.49

As is shown in figure 5, the overall biogas production in the period of 50 days in the studied anaerobic fermenter was 36.2 l, whilst 26.3 l in the control reactor. This means 0.482 m^3/m^3d and 0.352 m^3/m^3d biogas productivity for the PVA-gel beads reactor and the control reactor, respectively. Thus the biogas production efficiency of

the anaerobic reactor filled with biofilm carrier was 28% higher than the efficiency of the control reactor, it is assumed that this was a result of the biofilm formation on the surface of the PVA-gel beads (as a moving bed). However, according to the GC measurements, the content of the produced biogas in both reactors was almost the same (figure 6). It consisted of about 40–50% of CH_4, 40–50% of CO_2 and 2–10% of other gases.

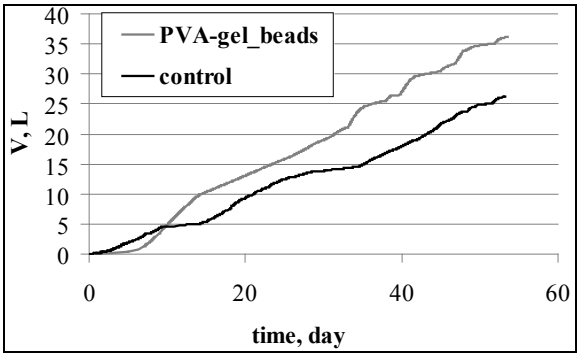

Fig. 5. Cumulative volume of produced biogas in the period of 50 days

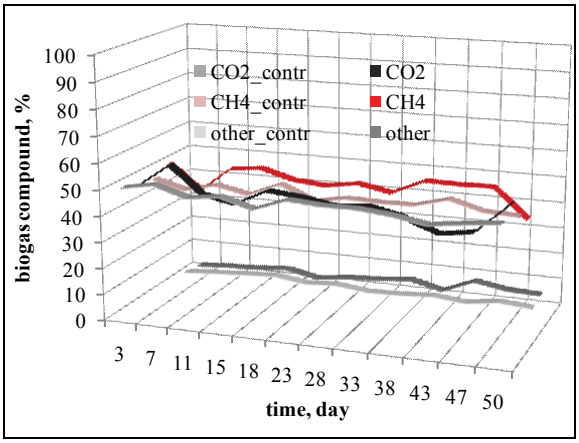

Fig. 6. Change in content of the produced biogas

3.3. BIOFILM FORMATION

Before starting the reactors, PVA-gel beads were white. The biofilm formation was evaluated after 10, 20 and 50 days of operation. The colour of the beads changed from white to brownish (figure 7). The surface of the PVA-gel beads was examined to check whether the microorganisms were attached or not. The test was carried out by measuring protein concentration, according to the modified Lowry method. Firstly the

beads were washed with saline solution, then the protein content was determined. The amount of protein after 10, 20 and 50 days of operation was 0.002, 0.009 and 0.01 g protein/g carrier bead, respectively. Consequently, biofilm formation was achieved.

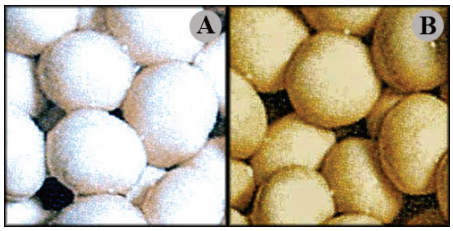

Fig. 7. PVA-gel beads before (A) and after (B) 50 days of usage

4. CONCLUSION

In this work, an anaerobic moving bed biofilm fermenter was studied and compared with a conventional anaerobic fermenter. To attain biofilm formation PVA-gel beads were placed in the anaerobic fermenter. The beads were analyzed after 10, 20 and 50 days of operation, and the measuring results showed 0.002, 0.009 and 0.01 g protein/g beads, respectively, which indicates that the biofilm formation took place. The reactors were stably operated for 50 days, during that time 24.1 m^3/m^3 and 17.4 m^3/m^3 of biogas was produced in the carrier-filled reactor and control reactor, respectively. These results demonstrate that the efficiency of the biogas production in anaerobic fermenters can be increased by at least 28% with biofilm formation. However, further experiments should be carried out with higher organic loading rates and with another type of biofilm carriers.

ACKNOWLEDGEMENT

The research work was supported by the Ányos Jedlik project, entitled *Development of new bioethanol and biogas production technologies* (2007–2010), grant No. BIODDFPE.

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