



Biometanation of Distillery Wastewater in an Anaerobic Baffled Reactor System

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Summary: Anaerobic digestion is an established technology for distillery effluent treatment which seems to be a promising alternative for Bulgarian industry. In this study the methanogenic activity of two different naturally formed microbial consortiums was compared. The better one was used to start continuous anaerobic digestion of high-strength distillery wastewater (COD 85 520 mgO₂.l⁻¹) in laboratory scale anaerobic baffled reactor system. The average applied organic loading rate and hydraulic retention time were 4.28 kg COD m⁻³.d⁻¹ and 20 d respectively. A COD reduction of about 98 % and specific methane production of 0.39 m³.kg⁻¹ COD_{removed} were reached. Effects of different inhibitory factors such as low pH and presence of oxygen were investigated. In spite of unfavorable factors were applied simultaneously after an adaptation period the reactor showed stable response. The results obtained show the feasibility of this anaerobic process for distillery effluent treatment, representing a valid option to up-grade the existing wastewater treatment processes.

Keywords: Biomethanation, Distillery Wastewater, Inhibitory Effects, Multichamber Reactor.

1. INTRODUCTION

Distillery wastewater, also termed as stillage, is the aqueous by-product from the distillation of ethanol following fermentation of carbohydrates. The pollution potential of stillage can exceed of 100 g/l as chemical oxygen demand [1]. Up to 20 liters of stillage may be generated for each liter of ethanol produced [2].

In general, rural distilleries in Bulgaria often have very little or no treatment equipment for wastewater and stillage is usually directly discharged into the aquatic environment and grass fields.

Without any treatment, distillery wastewater can result in depletion of dissolved oxygen in the receiving water streams, and poses serious threat to the aquatic flora and fauna.



Anaerobic digestion of effluents is a well-known energy recovery biotechnology, whose interest comes from the fact that it produces valuable, recurrent and storable amounts of energy in the form of a gas at costs in the range of the price of natural gas. Anaerobic wastewater treatment technologies are used throughout the world for effective treatment of a wide variety of industrial wastewaters, in particular to wastewaters from the food industry.

The anaerobic baffled reactor (ABR) system has found wide application in the treatment of industrial wastewaters. It is simple in design and has been reported to have many advantages over other well established reactor systems. The ABR comprises a series of vertical baffles to force the wastewater to flow under and over them and therefore, the wastewater comes into contact with a large active microbial biomass. The biological advantages of the ABR systems are well documented [3]. These include higher resilience to hydraulic and organic shock loads, longer biomass retention times and lower sludge yields than many other high rate anaerobic treatment systems. Concentration gradients of organic components should result in the development of populations that are microbiologically selected to best suit the conditions in each compartment.

The aim of the present investigation was to evaluate the appropriateness of anaerobic baffled reactor system for on-site treatment of industrial wastewaters under unfavorable for methanogenesis conditions.

2. MATERIALS AND METHODS

2.1. Distillery wastewater

The wastewater used in our experiments came from industrial plant for ethanol production located near to town Ihtiman. The ethanol was produced from grain starch and by-product was collected immediately after distillation, cooled and stored in plastic bottles.

2.2. Isolation and cultivation of methanogenic consortiums

Two different mixed methanogenic cultures used in the experiments were isolated from natural anaerobic habitats. First one, labeled as “lake culture”, was isolated from bottom sediments in the lake near to village Dolni Bogrov and the second one, labeled as “dung culture” was collected from small cow farm near to Sofia. Both



mixed methanogenic consortiums were enriched and maintained in a fresh anaerobic mineral medium according to Shelton et al. [4]. Natural methanogenic cultures were adapted to the distillery wastewater in continuously stirred batch reactors under strict anaerobic conditions at 37°C for 30 days. The methanogenic activities of the adapted cultures were compared.

2.3. A laboratory-scale anaerobic baffled reactor system

A laboratory-scale anaerobic baffled reactor (ABR) system used in the study was fabricated using plexiglass. The ABR consisted of three chambers equal in size and each chamber was separated by a vertical baffle. The working volume of the reactor was 2.0 l and the total volume was 2.8 l. The reactor was filled with adapted methanogenic consortium and distillery wastewater (titrated to pH 7.0) in the ratio 9:1 (v/v) so as to have a resultant COD of 8.55 g/l. The mixed methanogenic culture was acclimatized for about 30 days in batch conditions to have fast startup of the reactor. The ABR was run continuously by feeding the distillery wastewater at constant flow rate using a peristaltic pump PP 2B - 15.

2.4. Analytical methods

The chemical oxygen demand (COD) and biochemical oxygen demand (BOD) contents as well as the total solids (TS) were determined according to APHA (1992) [5]. The protein content was established according to the method of Lowry et al. (1951) [6]. Total reducing sugars were estimated by the dinitrosalicylic acid (DNS) method [7]. Gas production rate measurements were performed using a manual constant pressure liquid displacement system. The biogas composition was estimated by gas chromatography using a Carbovar B Carbo Erba (Milan) gas chromatograph. The pH value of the stillage was measured and adjusted using pH-meter.

3. RESULTS AND DISCUSSION

3.1. Comparison of the activity of adapted methanogenic consortiums

The microbial populations obtained from two different natural habitats were enriched and adapted to distillery wastewater for a month. Their methanogenic activity was tested by mesophilic fermentation at 37°C in a 0.5-litre glass reactor mixed periodically by a magnetic stirrer. Fresh industrial stillage was used as a substrate



in the experiments. The main characteristics of the distillery wastewater are given in Table 1.

Table 1. Characteristics of the distillery wastewater

Characteristics	Value
Chemical oxygen demand, $\text{mgO}_2\cdot\text{l}^{-1}$	85 520
Biochemical oxygen demand, $\text{mgO}_2\cdot\text{l}^{-1}$	53 125
Protein content, $\text{g}\cdot\text{l}^{-1}$	23.05
Total solids, $\text{g}\cdot\text{l}^{-1}$	74.92
Reducing sugars, $\text{g}\cdot\text{l}^{-1}$	4.07
Nitrogen, % (TS)	7.21
Phosphorus, % (TS)	1.32
Sulfur, % (TS)	2.69
pH	3.57

The reactor was filled consecutively with 400 ml of each of the tested cultures. Each of the experiments was started by adding 40 ml deaerated, adjusted to pH 7.0 fresh industrial stillage to the reactor volume. The kinetics of methane productions during both tests is presented in Fig. 1.

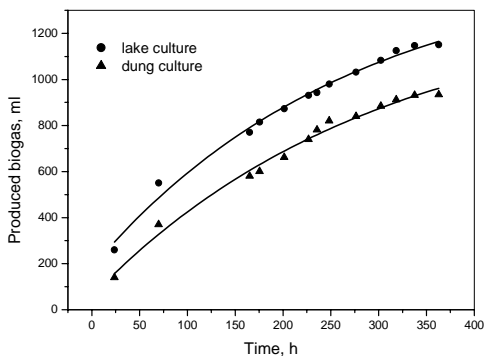


Fig. 1. Comparison of the methanogenic activities of lake and dung cultures

Methanogenic activity of lake culture measured as methane production was higher by 15% than those of dung culture.



As a result of the anaerobic batch tests better acclimatization of the lake culture to the stillage was revealed. Obviously, this type of methanogenic habitat could provide a very useful source of inoculum for seeding anaerobic reactors. In subsequent experiments lake culture was used as inoculum for the laboratory scale anaerobic baffled reactor.

3.2. *A continuous process of biogas production from distillery wastewaters using anaerobic baffled reactor system*

The operation of the ABR was started using an initial COD concentration 4.28 g.l^{-1} at hydraulic retention time (HRT) of 20 days. The reactor system was run continuously and when there were no more fluctuations in different operating parameters such as COD removal, biogas production and methane content the process was assumed to be under steady-state conditions. Measured and calculated parameters of this steady state process are given in table 2.

No disturbances in the process were observed for three month and reached methane yield of $0.39 \text{ l CH}_4 \cdot \text{g}^{-1} \text{ COD}_{\text{removed}}$ was in good agreement with the results reported for such type of wastewaters [8]. During the process flocks formation in the reactor volume was observed. Such process is highly desirable because of its contributions to both increasing the process stability and improving the biomass retention in the reactor volume.

Table 2. Operating parameters of steady-state methanogenic process

Operating parameters	Value
Retention time, d	20
Organic loading rate, $\text{g COD} \cdot \text{l}^{-1} \cdot \text{d}^{-1}$	4.28
$\text{COD}_{\text{influent}}, \text{gO}_2 \cdot \text{l}^{-1}$	85.52
$\text{COD}_{\text{effluent}}, \text{gO}_2 \cdot \text{l}^{-1}$	1.69
Biogas production rate, $\text{l} \cdot \text{l}^{-1} \cdot \text{d}^{-1}$	1.71
COD removal yield, %	98.0
Methane content, %	78
Methane yield, $\text{l CH}_4 \cdot \text{g}^{-1} \text{ COD}_{\text{removed}}$	0.39

3.3. *Anaerobic treatment of distillery wastewater in baffled reactor system under unfavorable conditions*

Generally methanogenic consortiums are sensitive to an unstable environment associated with fluctuations in influent organic load,



wastewater constituents, presence of oxygen or other toxic substances etc. Anaerobic treatment system can completely lose its function (process failure) when the pH drop exceeded certain level. Inhibitory effect of the oxygen on methanogenic bacteria can also cause serious problems in the anaerobic process. The stability of the process against a low pH conditions and oxygen presence in the substrate is of great importance from the viewpoint of practical operation of the process. Distillery wastewater is acidic in nature and could be exposed to air for a long periods before its treatment. Taking such facts into consideration, aerated and titrated to pH 5.5 industrial wastewater was used for evaluation of sustainability of the process. Anaerobic treatment of this aerated, low in pH substrate in the ABR system was carried out for 2 months. Initial organic loading rate was $4.28 \text{ g COD} \cdot \text{l}^{-1} \cdot \text{d}^{-1}$. Some fluctuations in biogas production and content preceded the steady state occurrence, but after an adaptation period that lasts for 25 days new steady state situation was reached. This process is presented in Fig. 2.

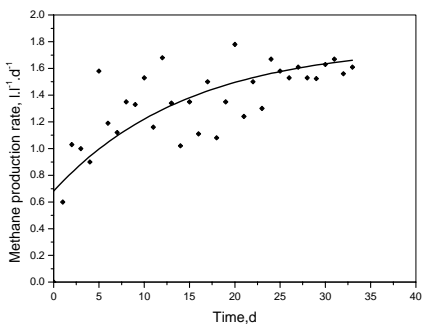


Fig. 2. Continuous process of biogas production under unfavorable conditions

The most considerable operating parameters are resumed in Table 3. The results show that low pH and oxygen presence in the substrate resulted in a decrease in methane content and yield. This can be attributed to increasing activity and grow rate of acidogens in presence of oxygen and non proportional growth of methanogens which consumes CO_2 as a substrate to produce methane.



Table 3. Operating parameters of steady-state methanogenic process under unfavorable conditions

Operating parameters	Value
Retention time, d	20
Organic loading rate, g COD. l ⁻¹ .d ⁻¹	4.28
COD _{influent} , gO ₂ . l ⁻¹	85.52
COD _{effluent} , gO ₂ . l ⁻¹	1.22
Biogas production rate, l. l ⁻¹ .d ⁻¹	1.63
COD removal yield, %	98.6
Methane content, %	72
Methane yield, l CH ₄ . g ⁻¹ COD _{removed}	0.32

However, the reactor showed stable operation under such unfavorable conditions and purification degree retains the same or even become a little bit higher. The last fact may be attributed to the enhanced capacity of the facultative anaerobic acidogens to degrade organic matter in the presence of oxygen.

4. CONCLUSION

In this work simple and reliable method for selection of and adaptation of natural methanogenic consortium for different substrates was demonstrated. It was proven that in absence of industrial source of an active methanogenic consortium different natural anaerobic habitats could provide a very useful source of inoculum for seeding anaerobic reactors.

Biomethanation of distillery wastewater in the laboratory scale anaerobic baffled reactor reveal a number of important advantages over other well established systems such as fast achievement of steady state conditions, relatively high methane yield and purification degree, flock formation etc. Settling in the upflow region of each compartment results in the retention of high concentrations of biomass and higher treatment rates can therefore be obtained, while overall sludge production was characteristically low.

The unique structure of ABR brings about the partial separation of acidogenesis and methanogenesis and prevents most of the biomass being exposed to low pH and oxygen presence during the treatment of the distillery wastewater and enhances reactor stability.



Finally, the present study concludes that anaerobic baffled reactor system has great potential in treating industrial wastewater under unfavorable conditions (such as low pH and oxygen presence) and still enable high removal rates to be achieved.

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