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ANAEROBIC TREATABILITY AND METHANE PRODUCTION POTENTIAL OF INDUSTRIAL WASTEWATERS IN ESKİŞEHİR

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ABSTRACT: *The wastewaters of three agro-industries in Eskişehir, namely cake production, cheese-making and beet molasses alcohol distillery industries, were studied for their potential for anaerobic treatment and methane generation. biochemical methane potential experiments were conducted for different initial chemical oxygen demand concentrations both with and without a basal medium. the results revealed that nutrient and trace metal suplementation is vital for the anaerobic treatment of the wastewaters studied. anaerobic methane generation was found to be 1062 ml ch_4/g cod (12.7 l ch_4/l wastewater) for the cake production wastewater, 366 ml ch_4/g cod (10.98 l ch_4/l wastewater) for the cheese whey, and 222 ml ch_4/g cod (6 l ch_4/l wastewater) for the alcohol distillery wastewater. the results indicated that anaerobic treatment was possible for all of the wastewaters studied and the produced biogas had a high methane content.*
KEYWORDS: *Anaerobic treatment, biochemical methane potential, cake production wastewater, alcohol distillery wastewater, cheese-whey.*

ESKİŞEHİR'DEKİ ENDÜSTRİYEL ATIKSULARIN ANAEROBİK ARITILABİLİRLİĞİ VE METAN ÜRETİM POTANSİYELLERİ

ÖZET: *Eskişehir'de bulunan kek üretimi, peynir yapımı ve şeker pancarı melası alkol damıtımı olmak üzere tarıma dayalı üç endüstri atıksuyunun anaerobik arıtılabilirliği ve metan üretimi araştırıldı. Biyokimyasal metan potansiyel denemeleri farklı başlangıç kimyasal oksijen ihtiyacına sahip atıksularla bazal ortamlı ve bazal ortamsız olarak yapıldı. Sonuçlar besin ve iz metal ilavesinin çalışılan atıksuların anaerobik arıtımı için önemli olduğunu ortaya çıkardı. Anaerobik metan üretimi kek üretim atıksuyu için 1062 mL CH_4/g KOİ (12,7 L CH_4/ L atıksu), peyniraltı suyu için 366 mL CH_4/g KOİ (10.98 L CH_4/ L atıksu), alkol damıtım atıksuyu için 222 mL CH_4/g KOİ (6 L CH_4/L atık su) olarak bulundu. Sonuçlar çalışılan bütün atıksular için anaerobik arıtımın mümkün olduğunu ve üretilen biyogazın yüksek metan içeriğine sahip olduğunu gösterdi.*
ANAHTAR KELIMELER: *Anaerobik arıtım, biyokimyasal metan potansiyeli, kek üretim atıksuyu, şilempe, peyniraltı suyu.*

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I.INTRODUCTION

The treatment and discharge of high organic loaded wastewaters from agro-industries is an important challenge for city areas having any development of these types of industries nearby. In order to make the treatment of these kinds of wastewaters attractive to the establishment, basic solutions to the problem must be presented. Anaerobic digestion is undoubtedly the most suitable option for the treatment of high strength effluents. The presence of biodegradable components in the effluents, coupled with the advantages of anaerobic processes over other treatment methods, makes it an attractive option. The advantages of anaerobic treatment are widely reported by many workers [1-4]. Anaerobic digestion has a number of advantages: it demands less energy input, anaerobic bacteria are capable of transforming most of the organic substances present into biogas, sludge formation is minimal and nutrient demands are very low. The production of biogas enables the process to generate some energy in addition to reduced consumption; this can reduce operational costs by a large margin compared with high-energy consumptive aerobic processes [5]. Anaerobic digestion has become the most commonly used method for the treatment of medium and high-strength effluents, due to the economy of the process and the low generation of surplus sludge. The biochemical oxygen demand (BOD) and chemical oxygen demand (COD) contents of many high strength effluents from food, fermentation, beverage, and pulp and paper industries can successfully be reduced by anaerobic digestion [6,7].

Anaerobic digestion can be considered as a three-step process, even though it is really a coupled sequence of microbiological interactions. In the initial stage, complex organic materials are depolymerized and converted to CO_2, H_2, and volatile fatty acids, mainly acetic, propionic, and butyric acids. In the next stage, all the higher acids are converted to acetic acid. In the final stage, a biogas containing mainly methane and CO_2 is produced along two different pathways: from acetic acid (acetoclastic methanogens) and from CO_2 and H_2 (H_2-utilizer methanogens) [6].

The aim of this study was to determine the anaerobic treatability and methane generation potential of industrial wastewaters in batch reactors, examine the nutrient and trace metal supplementation on the batch anaerobic treatment of three wastewater, and suggest attractive ways of treating agro-industrial wastewaters in view of the data gathered.

MATERIALS AND METHODS

II.I.Characterization of wastewaters

For this purposes of study, wastewaters from cake production (CPW) and beet molasses alcohol distillery (ADW), in addition to cheese-whey (CW), were obtained from the respective factories, all located near the city of Eskişehir, Turkey. Collected samples were stored at 4^0C during the study. The typical characteristic parameters of wastewaters samples were measured using Standard Methods [8], as tabulated in Table 1.

Table 1. Characterization of the industrial wastewaters studied.

Parameters	CPW	CW	ADW
pH	12.25	6.04	4.98
Chemical oxygen demand (mg/L)	12000	30000	107000
Total solids (mg/L)	16809	32480	99666
Suspended solids (mg/L)	8870	3200	3294
Volatile suspended solids (mg/L)	4817	2190	2440

II.II Basal Medium

The composition of the basal medium (BM) used in the experiments is as follows (concentrations of the constituents are given in parantheses as mg/L): NH_4Cl (1200), $MgSO_4.7H_2O$ (400), KCl (400), $Na_2S.9H_2O$ (300), $CaCl_2.2H_2O$ (50), $(NH_4)_2HPO_4$ (80), $FeCl_2.4H_2O$ (40), $CoCl_2.6H_2O$ (10), KI (10), $MnCl_2.4H_2O$ (0.5), $CuCl_2.2H_2O$ (0.5), $ZnCl_2$ (0.5), $AlCl_3.6H_2O$ (0.5), $NaMoO_4.2H_2O$ (0.5), H_3BO_3 (0.5), $NiCl_2.6H_2O$ (0.5), $NaWO_4$ $.2H_2O$ (0.5), Na_2SeO_3 (0.5), cysteine (10), $NaHCO_3$ (6000). This basal medium contains all of the micro and macro nutrients required for an optimum anaerobic microbial growth [9,10].

II.III Biochemical Methane Potential (BMP) Experiments

In order to determine the anaerobic biodegradability and biogas production of the wastewaters studied, the BMP experiments were performed according to Owen et al., 1979 [10]. Hundred *mL*-serum bottles with 40 *mL* working volume including 10 *mL* of anaerobic sludge were used as anaerobic batch reactors. The serum bottles were inoculated with mixed anaerobic sludge obtained from the Greater Municipality of Ankara Domestic Wastewater Treatment Plant, Turkey. The sludge was thoroughly mixed and filtered through a 1 mm pore size screen before use. In addition, resazurin was added to the media (1 *mL*/*L* of media from a 0.2% w/v stock solution) as a redox indicator [11,12].

In order to compare the supplementation of nutrient and trace metals in gas production, one out of two sets of serum bottles received BM for each wastewater. Both the diluted and original CPW, CW ADW, samples were added to serum bottles yielding initial COD concentrations of 3000, 6000, 9000, and 12000 mg/L; 7500, 15000 and 30000 mg/L ; 9000, 11000, 27000 and 54000 mg/L, respectively. The serum bottles were purged with a N_2 gas for 3-4 minute to maintain the proper anaerobic conditions. The bottles were maintained at 35±2^{o}C in an incubator and the gas produced in each serum bottle was measured daily during a period of 60 days.

The control serum bottles were also run in all experiments to determine the background gas production. The serum bottles for one out of four COD concentrations were run as dublicates.

II.IV Analytical Methods

The pH measurements were made with a pH meter (WTW, Inolab Level 2) and a pH probe (BO11207-023, WTW). COD, total solids (TS), suspended solids (SS), and volatile suspended solids (VSS) were measured by following standard methods, 5220B, 2540B, 2540D, 2540E, respectively [8].

A gas displacement device measured gas produced in serum bottles. The headspace gas produced was syringed out for injection into a fully sealed serum bottle containing a concentrated KOH stock solution of 20 g/L at atmospheric pressure. The serum bottles were shaken manually for 3-4 min. The remaining gas in the bottle indicated the approximate CH_4 gas produced as a result of anaerobic degradation of the wastes and CH_4 was syringed out to determine the methane percentage of the biogas produced simply by measuring its volume [3].

III.RESULTS AND DISCUSSION

In BMP experiments, the gas production values of serum bottles with BM and without BM used in the CPW, CW, ADW for 60 days are shown in Figure 1-3, respectively.

For the CPW with BM and initial COD concentration of 3000 *mg/L*, the biomass exerted 94% (109 *mL*) of the total gas production (116 *mL*) in the 38 days, without any indication of inhibition. Biomass for the initial COD concentration 6000 *mg*/*L*, exerted more than 90% of (298 *mL*) total gas production (320 *mL*) in 37 days. Similarly, for the initial COD concentration 9000 *mg/L*, the biomass produced 510 *mL* of gas. In the sample of the highest initial COD concentration of 12000 *mg*/*L*, the biomass with BM exerted more than 90% (604 *mL*) of the total gas production (665 *mL*) in 37 days. Biomass without BM supplementation for the highest COD concentration, the gas production rate was notably lower than those of with BM, and 90% (424 *mL*) of the total gas production (463 *mL*) was produced in 40 days (Fig. 1).

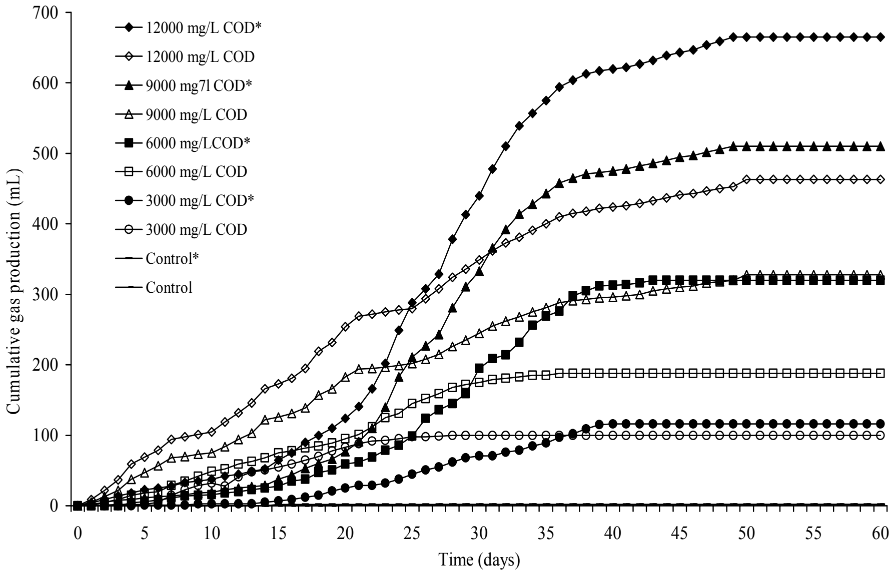

Figure 1. The gas production values of the serum bottles with BM and without BM used in the biochemical methane potential experiments for CPW (*with BM).

CPW with BM addition produced a total 510 *mL* methane gas for the initial COD concentration of 12000 *mg/L* at the end of 60 days. This value indicated that anaerobic methane generation for the CPW studied was 1062 *mL* CH_4/g COD (12.7 *L* CH_4/*L* wastewater). While examining the potential for anaerobic treatment of CPW with 12000 *mg*/*L* COD for batch reactors not containing BM, methane generation at the end of 60 days was observed as 683 *mL* CH_4/g COD (8.2 *L* CH_4/*L* wastewater). The result of a series of determinations indicated that with the presence of BM, the CH_4 content of biogas produced from CPW was 76±1 %; while without BM the CH_4 content was
73±2 %. In addition, COD removal was 95-98% in the effluent with BM, whilst it was 74-78% for the effluent without BM for 60 days (Table 2).

For the CW with BM and an initial COD concentration of 7500 *mg*/*L*, the biomass exerted 91% (218 *mL*) of the total gas production (239 *mL*) in 41 days without any indication of inhibition. Similarly, biomass with initial COD concentration of 15000 *mg*/*L*, exerted more than 90% of (310 *mL*) total gas production (330 *mL*) in 35 days. For cultures with the highest initial COD concentration of 30000 *mg*/*L*, those with BM exerted more than 90% (479 *mL*) of the total gas production (524 *mL*) in 39 days. In contrast, in those biomass without BM supplementation for the same COD concentration of 30000 *mg*/*L*, the gas production rate was notably lower than those with BM, and 92 % (405 *mL*) of total gas production (440 *mL*) was produced in 40 days (Fig. 2).

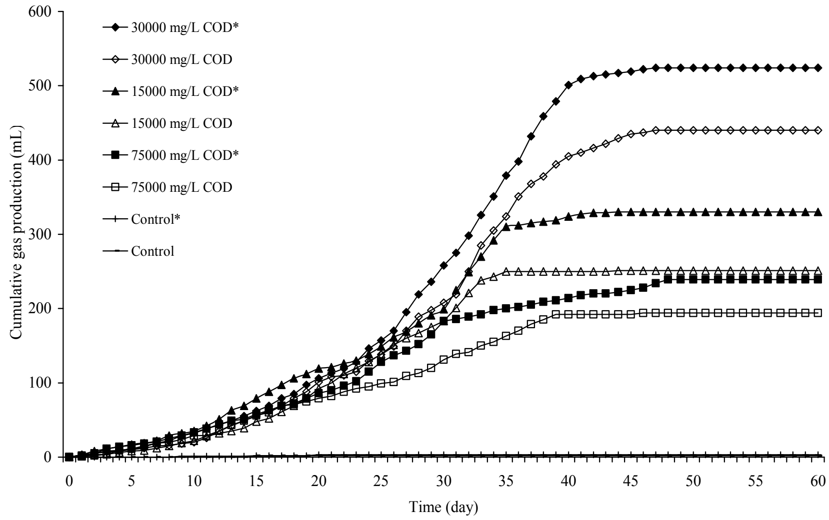

Figure 2. The gas production values of the serum bottles with BM and without BM used in the biochemical methane potential experiments for CW (*with BM).

CW with BM addition, produced a total 440 *mL* methane gas for the initial COD concentration of 30000 mg/L. This value indicated that anaerobic methane generation for the CW studied was 366 *mL* CH_4/g COD (10.98 L CH_4/ *L* wastewater). In the samples being examined for the potential for anaerobic treatment of CW with 30000 mg/L COD for batch reactors containing no nutrients, methane generation at the end of 60 days was observed as 292 mL CH_4/g COD (8.76 L CH_4/L wastewater). The result of a series of determinations indicated that with the presence of BM, the CH_4 content of biogas produced from CW was 82±2 %; whilst without any BM, the CH_4 content was 76±3 %. Furthermore, COD removal in samples with BM was higher than those of without BM for 60 days (Table 2). In a study conducted by Demirer et al. (2000), it was indicated that for the influent COD concentrations of 5525 *mg/L*, 11050 mg/L and 22100 *mg/L*, the CH_4 content of the biogas produced from cheese whey was 77±5 %.

In the samples of ADW with BM, total gas production in serum bottles having COD concentrations of 9000, 11000, 27000 and 54000 *mg*/*L* was observed as 200, 230, 310, 295 *mL*, respectively. ADW samples without any BM produced 130, 145, 212, 250 *mL* of total gas for the same COD concentrations, respectively (Fig. 3). The methane generation of ADW with 27000 *mg*/*L* COD for batch reactors containing no BM was observed as 139 *mL* CH_4/g COD (3.8 *L* CH_4/*L* wastewater) at the end of 60 days. In the reactors with BM, methane generation was 222 *mL* CH_4/g COD (6 *L* CH_4/*L* wastewater). The result of a series of determinations indicated that with the presence of BM, the CH_4 content of biogas produced from ADW was 77±3 %; whilst without BM the CH_4 content was 73 ±3 %. In the sample of effluent with BM, COD removal was higher than that of the sample without BM (Table 2).

Anaerobic processes are sensitive to inhibition from various substances. In the treatment of alcohol distillery wastewaters, inhibition could arise from high ionic concentrations or high sulfide concentrations caused by biological reduction of sulfate [13]. Moreover, many phenolic compounds are known to be toxic and interfere with the activity of methanogenic bacteria. Since ADW contains these type compounds, anaerobic treatment process slows and decreases the removal of part of its organic content [4]. During the anaerobic treatment of ADW, low COD removal and methane production potential could be due to the aforementioned inhibition effect.

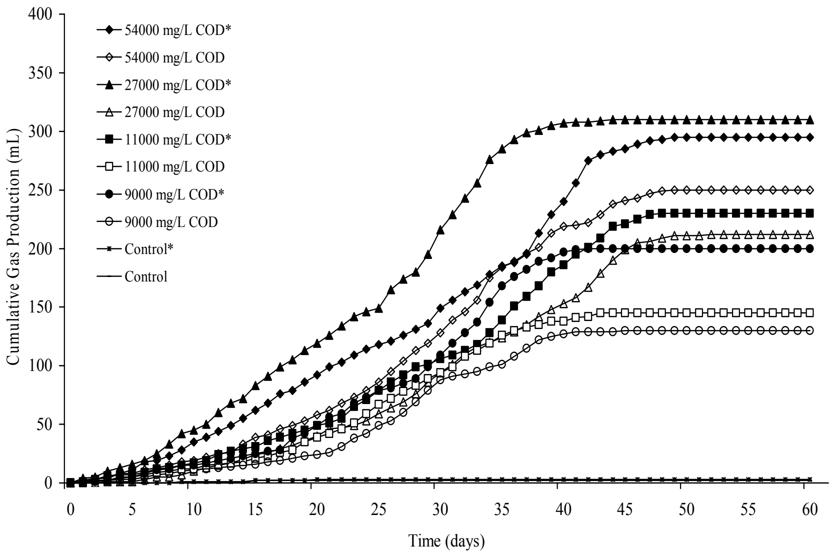

Figure 3. The gas production values of the serum bottles with BM and without BM used in the biochemical methane potential experiments for ADW (*with BM).

Table 2. The experimental results for CPW, CW and ADW studied for 60 days.

Wastewaters	COD concentration range studied (*mg*/*L*)	COD removal (%)	Methane content of the biogas produced (%)	Methane generation (*L* CH_4/*L* wastewater)
CPW*	3000-12000	95-98	77	2.2-12.7
CPW	3000-12000	74-78	70-75	2.0-8.2
CW*	7500-30000	88-92	80-84	4.8-11.0
CW	7500-30000	85-89	74-79	3.6-8.8
ADW*	9000-54000	79-81	75-80	4.0-6.0
ADW	9000-54000	73-78	70-76	2.3-4.8

*with BM

Trace nutrients for example Ni, Fe, Co, Mg and nitrogen and phosphorus significantly influence reactor performance, and most cheese wheys contain these essential elements [14].

Upon investigation of the three wastewaters, the application of BM during the process ensured higher production of COD and gas than trials conducted without BM. In particular, the fact that the results for CW with and without BM were so close needs particular attention. In the results for treatment of CPW, the COD removal for CPW with BM were found to be much lower than that of CPW without BM. Since CPW is a wastewater that doesn’t generally contain toxic metal and chemicals, it doesn’t demonstrate a inhibition effect on the biomass. In the trial conducted without BM, the low result seen for COD and gas production is related to the important fact that there was a lack of trace elements, without which anaerobic microorganisms do not develop [14].

IV.CONCLUSIONS

The following conclusions can be drawn based on the experimental results (Table 2) presented in this paper: BM is important for the metabolic activity of anaerobic bacteria; BM addition to effluent increases both methane production and COD removal; Anaerobic bioconversion of cake production wastewater, cheese-whey and alcohol distillery wastewater with the highest COD, yielded biogas with a high methane content of 77, 84, 80%, respectively; and lastly

methane generation from the bioconversion of cake production wastewater, cheese-whey and alcohol distillery wastewater had the highest COD 12.7, 11.0, 6.0 *L* CH_4/*L* wastewater. Therefore, it can be stated that anaerobic treatment presents a viable alternative for the treatment of agro-industrial wastewaters in Turkey yielding significant energy recovery in the form of methane gas.
This paper reports that the use of anaerobic treatment, reactor design and detailed optimization research on wastewater may be feasibly applied in industrial scale.

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V.REFERENCES

[1] J. Rodriguez-Martinez, I. Rodriguez-Garza, E. Pedraza-Flores, N. Balagurusamy, G. Sosa-Santillan and Y. Garza-Garcia, "Kinetics of anaerobic treatment of slaughterhouse wastewater in batch and upflow anaerobic sludge blanket reactor", *Bioresource Technology*, Vol. 85, pp. 235-241, 2002.
[2] N. Uzal, C.F. Gökçay, G.N. Demirer "Sequential (anaerobic/aerobic) biological treatment of malt whisky wastewater", *Process Biochemistry*, Vol.39, No.3, pp. 279-286, 2003.
[3] G.N. Demirer, M. Duran, T.H. Ergüder, E. Güven, Ö. Uğurlu and U. Tezel, "Anaerobic treatability and biogas production potential studies of different agro-industrial wastewater in Turkey", *Biodegradation*, Vol.11, pp. 401-405, 2000.
[4] A.M. Jimenez, R. Borja and A. Martin, "Aerobic-anaerobic biodegredation of beet molasses alcoholic fermentation wastewater", *Process Biochemistry*, Vol.38, No.9, pp. 1275-1284, 2003.
[5] D.R. Boone and L. Xun, "Effects of pH, temperature, and nutrients on propionate degradation by a methanogenic enrichment culture", *Applied and Environmental Microbiology*, Vol.53, No.7, pp. 1589-1592, 1987.

[6] R. Solera, L.I. Romero and D. Sales, "The evolution of biomass in a two-phase anaerobic treatment process during start-up", *Chemical & Biochemical Engineering Quarterly.*, Vol.16, No.1, pp. 25-29, 2002.

[7] U. Baumann and M.T. Müller, "Determination of anaerobic biodegradability with a simple continuous fixed-bed reactor", *Water Research*, Vol.31, No.6, pp. 1513-1517, 1997.

[8] American Public Health Association, "*Standard Methods fo the Examination of Water and Wastewater*", 18th Edn., APHA, AWWA,WEF, Washington DC, 1992.

[9] G.N. Demirer, R.E. Speece, "Anaerobic Biotransformation of four 3-Carbon Compounds (Acrolein, Acrylic acid, Allyl Alcohol and N-Propanol in UASB Reactors", *Water Research*, Vol.32, No.3, pp. 747-759, 1998.

[10] T.H. Ergüder, U. Tezel, E. Güven, G.N. Demirer, "Anaerobic biotransformation and methane generation potential of cheese whey in batch and UASB reactors", *Waste Management*, Vol.21, pp. 643-650, 2001.

[11] W.F. Owen, D.C. Stuckey, J.B. Healy, JR., L.Y. Young and P.L. McCarty, "Bioassay for monitoring biochemical methane potential and anaerobic toxicity", *Water Research*, Vol.13, pp. 485-492, 1979.

[12] D.R. Shelton and J.M. Tiedje, "General method for determining anaerobic biodegradation potential", *Applied and Environmental Microbiology*, Vol.47, No.4, pp. 850- 857, 1984.

[13] N. Athanasopoulos, "Anaerobic treatment of beet molasses alcoholic fermentation wastewater in a downflow filter",Resources and Conservation, Vol.15, pp.147-150, 1987.

[14] C.R. Kelly and M.S. Switzenbaum, "Anaerobic treatment: temperature and nutrient effects", Agricultural Wastes, Vol.10, pp.135-135-154, 1984.