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Short communication

Anaerobic treatability and biogas production potential studies of different agro-industrial wastewaters in Turkey

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Abstract

The anaerobic treatability and methane generation potential of the wastewaters of the three important agro-industries in Turkey, namely, cheese-making, poultry breeding and the olive-oil mill industries were studied. Biochemical methane potential (BMP) experiments were conducted for different initial chemical oxygen demand (COD) concentrations. The results indicate that anaerobic treatment was possible for all the wastewaters studied and the biogas produced had a high methane content.

Introduction

Agro-industries play a significant role and represent a considerable share of the Turkish economy. For example, Turkey is the fifth largest country worldwide involved in the production of olive oil. Furthermore, poultry breeding has spread widely and 3 million tons of wet manure was produced out of 50 million poultry in 1998.

Cheese whey is a protein- and lactose-rich byproduct of the cheese industry. It is highly biodegradable with a very high organic content (up to 70 g COD/L), and low alkalinity (50 meq/L) (Mawson 1994). The high organic content of cheese whey renders the application of conventional aerobic biological treatment costly, mainly due to the high price of oxygen supplementation. Anaerobic treatment requires no oxygen supplementation and generates a significant amount of energy in the form of methane gas. However, Malaspina et al. (1996) stated that raw cheese whey is a quite difficult substrate to treat anaerobically because of the lack of alkalinity, the high chemical oxygen demand (COD) concentration and the tendency to acidify very rapidly.

Poultry breeding wastes are characterized by high total solids and organic content, NH_4-N concentration and pathogens. Because of insufficient or uncontrolled handling and disposal, they present a danger to public health and the environment.

Olive-oil mills are small agro-industrial units located mainly around the Mediterranean, Aegean and Marmara seas and account for approximately 95% of the worldwide olive-oil production. They process olives for the extraction of olive oil either by means of a discontinuous press (classical process), or a solid/liquid centrifuge (centrifugal process). Both processes produce two different forms of waste, namely, olive mill residual solids (OMRS or prina) which contain oil that must be recovered by solvent extraction, and olive mill wastewater (OMWW or black water). The mean waste volumes from classical and centrifugal processes are 1.18 and 1.68 m^3 per ton of olives processed, respectively. The corresponding mean organic loads in terms of COD are 79.2 and 121.7

Table 1. Characterization of the wastewaters studied.

Parameter	Cheese whey	Poultry breeding	Olive-oil mill
pH	3.92	–	4.63
COD	55,250 ± 1344 mg/L*	123,642 mg/L	138,250 ± 7047 mg/L*
Total phosphorus (TP)	124 mg/L	–	55.6 mg/L
Total Kjeldahl nitrogen (TKN)	145.6 mg/L	–	579 mg/L
Suspended solids (SS)	9380 ± 453 mg/L*	103,027 mg/L	42,833 mg/L
Volatile suspended solids (VSS)	8280 ± 396 mg/L*	67,720 mg/L	42,633 mg/L

* These samples were analyzed in duplicate.

kg COD per ton of olives processed, respectively. The maximum biological oxygen demand (BOD) and COD concentrations reach 100 and 200 g/L, respectively (Tsonis & Grigoropoulos 1993; Hamdi 1996; Ubay & Özturk 1997).

Within the olive-growing countries of the Mediterranean area (Greece, Italy, Lebanon, Portugal, Spain, Syria, Tunisia and Turkey), the olive-oil mill effluent production is more than 30 million m^3 per year (Beccari et al. 1996). It is known that olive-oil mill wastes are a significant source of potential or existing environmental pollution in these countries (Bejarano & Madrid 1992; Borja et al. 1992; Angelidaki et al. 1997). The treatment difficulties of olive-oil mill effluents are mainly related with (a) high organic loading; (b) seasonal operation; (c) high territorial scattering; and (d) the presence of organic compounds which are hard to biodegrade such as long-chain fatty acids and phenolic compounds.

Agro-industrial wastes could be a serious environmental concern if they are not properly handled. Therefore, the agro-industrial wastes should be treated with the most economical and efficient technologies before their disposal into the surrounding environments. Anaerobic systems offer such an option for the safe treatment of agro-industrial wastewaters, mainly due to their special advantages such as lower energy requirement, less waste biomass generation, a useful and economically valuable end-product (methane/biogas), suitability for seasonal operations and the elevated organic loading rates achievable. Thus, anaerobic treatment is an attractive option for agro-industrial wastes that are seasonally produced, have a high organic content and the potential toxicity problems.

In this study, the anaerobic treatability and methane generation potential of the wastewater streams of the three important agro-industries in Turkey, namely, cheese-making, poultry breeding and the olive-oil mill industries were studied. Biochemical methane potential (BMP) experiments were conducted and the corresponding methane gas productions were determined. This study constitutes only a part of a broader work on anaerobic industrial wastewater treatment conducted by our research team.

Materials and methods

The characterization of the cheese-making, poultry breeding and olive-oil mill industry wastewaters used in the experiments were carried out and are tabulated in Table 1.

The COD values were measured using a Hach spectrophotometer (Model: P/N 45600-02) and vials for COD 0–1500 ppm. The pH measurements were taken with a pH meter (Model 2906, Jenway Ltd.), and a pH probe (G-05992-55, Cole Parmer Instrument Co.). The SS and VSS concentrations were measured by following standard methods (2540 E) (Standard Methods 1995). The TP and TKN concentrations were also determined by standard methods (4500-P-E and 4500-N_{org}B, respectively) (Standard Methods 1995).

In order to determine the anaerobic biodegradability and biogas production of the wastewaters studied, the BMP experiments (Owen et al. 1979) were performed in 125-mL serum bottles capped with natural rubber sleeve stoppers. The liquid volume of the serum bottles was 50 mL and they were maintained at 35 ± 2° C in a temperature-controlled room. The serum bottles were seeded with mixed anaerobic cultures obtained from the anaerobic sludge digesters of the Ankara wastewater treatment plant with a solids retention time (SRT) of 14 days. The culture was thoroughly mixed and filtered through a screen with a pore size of 1 mm before use.

The composition of the basal medium (BM) used in the experiments was as follows (concen-

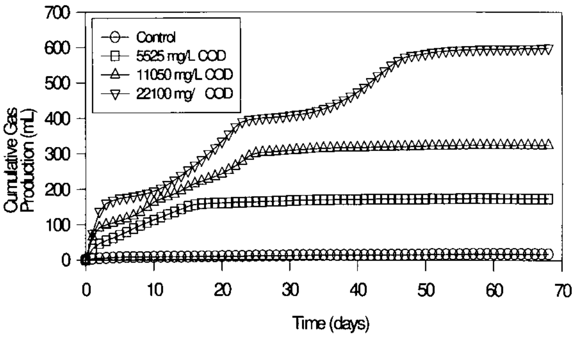

Figure 1. The results of the BMP experiments for cheese whey.

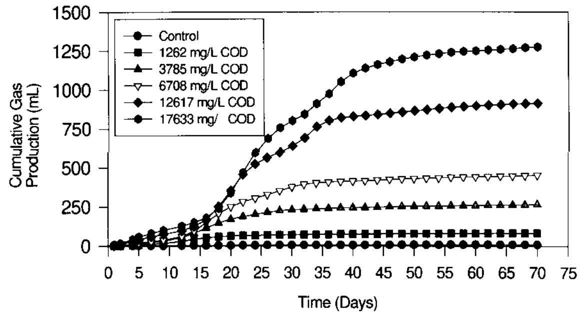

Figure 2. The results of the BMP experiments for the poultry breeding wastewater.

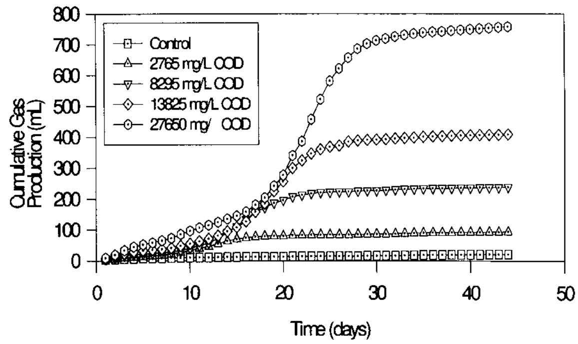

Figure 3. The results of the BMP experiments for the olive-oil mill wastewater.

trations of the constituents are given in parentheses as mg/L): NH_4Cl (1200), $MgSO_4 \cdot 7H_2O$ (400), KCl (400), $Na_2S \cdot 9H_2O$ (300), $CaCl_2 \cdot 2H_2O$ (50), $(NH_4)_2HPO_4$ (80), $FeCl_2 \cdot 4H_2O$ (40), $CoCl_2 \cdot 6H_2O$ (10), KI (10), $MnCl_2 \cdot 4H_2O$ (0.5), $CuCl_2 \cdot 2H_2O$ (0.5), $ZnCl_2$ (0.5), $AlCl_3 \cdot 6H_2O$ (0.5), $NaMoO_4 \cdot 2H_2O$ (0.5), H_3BO_3 (0.5), $NiCl_2 \cdot 6H_2O$ (0.5), $NaWO_4 \cdot 2H_2O$ (0.5), Na_2SeO_3 (0.5), cysteine (10), $NaHCO_3$ (6000). This basal medium contained all the necessary micro- and macro-nutrients required for an optimum anaerobic microbial growth (Demirer and Speece 1998).

The cheese-making, poultry breeding and olive-oil mill wastewater samples were added to the serum bottles yielding initial COD concentrations of 5525, 11050 and 22100 mg/L; 1262, 3785, 6708, 12617 and 17633 mg/L; and 2765, 8295, 13825 and 27650 mg/L, respectively (Figures 1–3). Then the serum bottles were purged with 25% CO_2 and 75% N_2 gas mixture for 3–4 minutes to maintain the proper pH and anaerobic conditions. The gas produced in each serum bottle was measured daily using a gas displacement device. The percentage of CH_4 in biogas was determined as follows. A known volume of the headspace gas (V_1) produced in a serum bottle from Experiment 1 was extracted by a syringe and injected into another serum bottle which contained only a 20-g/L KOH solution. This serum bottle was then shaken manually for 3–4 minutes so that all the CO_2 and H_2S was absorbed in the concentrated KOH solution. The volume of the remaining gas (V_2) which was 99.9% CH_4 in the serum bottle was determined by means of a syringe. The ratio of V_2/V_1 provided the percentage of CH_4 in the headspace gas.

The control serum bottles were also run in all experiments to determine the background gas production. Before the experiments, the serum bottles were operated until the variation in daily gas production was less than 15% for at least 7 consecutive days. The serum bottles for one out of four COD concentrations were run as duplicates.

Results and discussion

Cheese whey wastewater

The gas production values of the serum bottles used in the cheese whey wastewater BMP experiments for 68 days are shown in Figure 1. For the influent COD concentration of 5525 mg/L, the cultures exerted more than 90% (157 mL) of the total gas production (176 mL) in the first 16 days without any indication of inhibition. Similarly, cultures for the influent COD concentration of 11,050 mg/L exerted more than 90% of (292 mL) total gas production (325 mL) in 24 days. For the highest influent COD concentration of 22,100 mg/L, the cultures produced 598 mL of gas. The average anaerobic methane generation for the cheese whey studied was found to be 23.4 L CH_4/L cheese whey. The result of a series of determinations indicated that the CH_4 content of the biogas produced from cheese whey was 77 ± 5%.

Table 2. The experimental results for all the wastewaters studied.

Wastewater	COD concentration range studied (mg/L)	Methane content of the biogas produced (%)	Methane generation (L methane/L wastewater)
Cheese whey	5525–22,100	77 ± 5	23.4
Poultry breeding	1262–17,633	78 ± 3	33.5
Olive-oil mill	2765–27,650	77 ± 6	57.5

Poultry breeding wastewater

The gas production values of the serum bottles used in the poultry breeding wastewater BMP experiments for 70 days are shown in Figure 2. The acclimation time required for the anaerobic cultures to reach the maximum gas production rates were observed as 12, 15, 16, 20 and 20 days for the COD concentrations of 1262, 3785, 6708, 12,617 and 17,633 mg/L, respectively. The increase in acclimation times needed with the increase in initial COD concentrations was expected since none of the cultures used in this study were acclimated to the substrate. Poultry breeding wastewater samples produced 84.1, 266.7, 453.9, 914, and 1274 mL of total gas for the COD concentrations of 1262, 3785, 6708, 12617, and 17633 mg/L, respectively. These values indicated that the average anaerobic methane generation for the poultry breeding wastewater studied is 33.5 L CH_4/L poultry breeding wastewater. The result of a series of determinations indicated that the CH_4 content of the biogas produced from poultry breeding wastewater was $78 \pm 3\%$.

Olive-oil mill wastewater

Daily gas production in serum bottles was monitored for 44 days and the results are given in Figure 3. The total gas production in serum bottles having COD concentrations of 2765, 8295, 13,825 and 27,650 mg/L was observed as 94, 240, 408, and 758 mL, respectively. Before reaching maximum daily gas production levels, the cultures needed acclimation periods of 13, 16, 21 and 23 days for initial COD concentrations of 2765, 8295, 13,825 and 27,650 mg/L, respectively. Depending on the methane gas produced in each reactor, it was found that 1 l of olive-oil mill wastewater produced 57.5 ± 1.5 l of methane gas. The result of a series of determinations indicated that the CH_4 content of the biogas produced from olive-oil mill wastewater was $77 \pm 6\%$.

Conclusions

The following conclusions can be drawn based on the experimental results (Table 2) presented in this paper:

- Anaerobic bioconversion of cheese whey, poultry breeding and olive-oil mill wastewaters yielded biogas with a high methane content of 77 ± 5, 78 ± 3 and $77 \pm 6\%$, respectively.
- The anaerobic methane generation from the bioconversion of cheese whey, poultry breeding and olive-oil mill wastewaters studied was found to be 23.4, 33.5, and 57.5 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.

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