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Fate of Methanol in an Anaerobic Digester

Jin-Hwa Park† and Jae-Kwang Park

Department of Civil and Environmental Engineering, University of Wisconsin-Madison,
1415 Engineering Drive, Madison, WI 53706, U.S.A.
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Abstract−This paper mill was concerned with the anaerobic biodegradability of methanol, its by-products and the potential for gas stripping the system. A series of laboratory-scale experiments were conducted to evaluate the fate of methanol during anaerobic treatment. According to our research result, more than 99% of methanol contained in the condensate was biodegraded during anaerobic digestion. From an anaerobic digester batch test, the second order biodegradation rate constant, k_{b2}, was estimated to range from 3.97×10^{-3} $m^3/g\cdot day$ (when only condensate was fed) to 4.06×10^{-2} $m^3/g\cdot day$ (when condensate was fed at a proposed rate). The by-products from methanol degradation such as acetaldehyde, and methyl ethyl ketone, were degraded completely in 32 hours. Since the anaerobic treatment process has a retention time of 5 days, condensate by-products are believed to be completely biodegraded. The introduction of condensate into the existing anaerobic pretreatment process appears to improve the treatment efficiency, leading to a more stable anaerobic treatment as well as a reduced sludge generation in the aerobic wastewater treatment process due to the reduced organic loading.

Key words: Biochemical Methane Potential (BMP), Anaerobic Digester, Condensate, Methanol, Paper Mill

INTRODUCTION

Packing Corporation of America (PCA) operates a mill in Tomahawk, Wisconsin in the U.S. that presently uses a large anaerobic lagoon system to process its wastewater. Specifically at the anaerobic treatment system, there has been concern, primarily on the part of the Environmental Protection Agency (EPA), about the introduction of methanol-containing condensate into the treatment system. Condensate contains a high percentage of methanols in an anaerobic system. There has been concern regarding the introduction of methanol-containing condensate into the existing biological treatment system, specifically at anaerobic pretreatment basins. The concern focuses on the anaerobic biodegradability of methanol, its by-products and the potential stripping of organic components in the condensate from a (non-Kraft process) pulp and paper mill, mainly methanol, in the system resulting in the release into the atmosphere. Thirteen companies in the United States (U.S.) produce methanol in large amounts (approximately 1.3 billion gallons in 1992). The U.S. demand for methanol is likely to increase over the next several years. Methanol enters the body when it is breathed in with contaminated air or when it is consumed with contaminated food or water. It can also be absorbed through skin contact. However, it does not remain in the body due to its breakdown and removal through expired air or urine. Although methanol by itself is not likely to cause environmental harm at levels normally found in the environment, methanol can contribute to the formation of photochemical smog when it reacts with other volatile organic carbon substances in the air [U.S. EPA, 1994]. This is the source of the problem in an aerobic system.

Anaerobic processes have been used for the treatment of concentrated municipal and industrial wastewaters for well over a century [Hughes et al., 1981]. These processes convert organic materials into methane, a fuel that can yield a net energy gain from the process operations. Because of recent advances in treatment technology and knowledge of process microbiology, there are now extensive applications for treatment of dilute industrial wastewaters as well [McCarty and Smith, 1986]. To investigate the potential use of an anaerobic digester for treating pentachlorophenol (PCP) wastewater treatment plants (WWTPs), the fate of PCP in a digester was examined. In their study, two laboratory-scale anaerobic digesters were operated in parallel [Chen et al., 2000]. David and Roland [1999] reported to know the nature and origin of the refractory carbon compounds from these effluents and to optimize the biological treatment. The first objective of this study was to investigate microbial analysis of the activated sludge of the pulp and paper mill treatment. Woods et al. [1989] demonstrated that chlorophenols, chloroguaiacols, chloroveratroles, and chlorocatechols were continuously treated in an upflow anaerobic sludge blanket reactor in the presence of high concentrations of readily biodegradable organic compounds. In this study, meta chlorines are removed through acclimation. Previous studies [Chen et al., 2000; David and Roland, 1999; Woods et al., 1989] indicate that the methanol should be readily degraded in such a system. Furthermore, Zafar et al. [1996] investigated the feasibility of methanolic waste treatment in the UASB reactor and demonstrated that methanol can be converted to methane via at least three routes. The pathway of degradation is shown to be governed by the operating pH. At a pH close to 7.0, methanol will either be directly converted to methane (by methanosarcina type species) or through formation of acetate (by acetoclastic methanogens) or through a combination of both. At pH 5.0-6.0, hydrogenotrophic methanogens will be responsible for this conversion (by utilizing H_2 and CO_2). Speece [1988] reported that samples of each sludge were assayed to determine the residual gas production

†To whom correspondence should be addressed.
E-mail: einsteinpark@hanmail.net

rate, the maximum potential acetate and propionate utilization rates, the 5 and 30 day biochemical methane potential (BMP_5)(BMP_{30}).

Many scientific papers and academic books indicate that methanol would be readily degraded in such a system. It was proposed that a modified biochemical methane potential (BMP) test be used to determine/model the fate of methanol from the condensate in an anaerobic system operated in a similar manner to the full-scale treatment process.

Therefore, the objective of this study was, using a BMP test, to provide a reasonable (technically valid, quick, and appropriate) evaluation of samples from the PCA site and to determine the fate of methanol from the condensate in an anaerobic system. Utilizing this method, another purpose of the study was to determine the biodegradation rate of methanol in paper mill condensate during anaerobic pretreatment and to estimate the amount of methanol released into the atmosphere through a Styrofoam® cover used to control the temperature in an anaerobic pretreatment process.

METHODOLOGY

1. Properties of Methanol

Methanol (also known as methyl alcohol and wood alcohol) is a colorless liquid that may explode when exposed to an open flame. It occurs naturally in wood and in volcanic gases. Methanol is also a product of decaying organic material. The half-life of methanol under the unacclimated anaerobic condition ranges from 1 to 5 days [Scheunert et al., 1987]. Methanol degradation was measured by Rintala [1991] and Nishio et al. [1993] using an upflow anaerobic sludge blanket (UASB) reactor. In mixed substrates of methanol (8 g/L) and acetate (1.5 g/L), a methanol consumption rate was as high as 75 g/L reactor·day with a methane production rate of 30 L/L reactor·day. Parker et al. [1993] also found that high-rate anaerobic reactors treating segregated kraft mill bleach plant effluent and operating under methanogenic conditions were able to successfully degrade a number of chlorophenolic compounds. High-rate anaerobic treatment substantially reduced the acute toxicity contribution of chlorophenolics as determined by toxicity equivalency factors. The reactor operated with cosubstrate supplementation reduced this factor by 92.7% while the reactor operated without cosubstrate supplementation reduced the toxicity by 64.5%. Kripa et al. [2000] carried out experiments on the feasibility of using a high-rate anaerobic sludge blanket (UASB) system for the treatment of low-strength municipal wastewater at 6 to 32 °C for temperate climate applications. Supplementation of the reactor influent with a synthetic evaporator condensate containing methanol and ethanol improved the removal of a number of the compounds by greater than 80%. Therefore, it is anticipated that methanol will be rapidly biodegraded in an anaerobic treatment process once seeds are acclimated.

2. BMP Tests

BMP tests have been utilized to determine the degree of degradability for industrial wastes and individual compounds. The approach utilizes a series of inoculated serum bottles. The tests are performed in a batch, closed manner so that both liquid and gas samples can be analyzed. In the general BMP analysis, the relative amount and quality of gas produced from the serum bottles is utilized to predict the degradability of the test material. In this test, chemical oxygen demand and methanol were also analyzed to perform a mass/fate balance for the system. A series of BMP tests was performed for 5 to 15 days to assess the degree of anaerobic degradation of condensate. The analysis utilized samples of current influent, condensate, and anaerobic mixed liquor from the mill anaerobic basin. The anaerobic sludge used consisted of equal amounts taken from each of the four anaerobic basins (head end) out of a sludge recirculation line. The sample was believed to be representative of the anaerobic sludge that would be in contact with the condensate stream. The samples were stored in a 4 °C cold room until used. Unacclimated seed to the methanol-containing condensate was obtained from an anaerobic digester at the Nine Springs Wastewater Treatment Plant located in Madison, Wisconsin. The anaerobic digesters receive primary sludge, waste activated sludge and whey, and

Table 1. Experimental conditions of the first series BMP tests

Run no	No. of replicates	Volume, mL					Mixing
		Seed	Influent	Condensate	RAMM[1]	Water	
1-1	5	41.7	8.3	0	0	0	Yes
1-2	3	41.7	8.3	0	0	0	No
1-3	5	41.5	8.3	0.2	0	0	Yes
1-4	3	41.5	8.3	0.2	0	0	No
1-5	5	41.3	8.3	0.4	0	0	Yes
1-6	3	41.3	8.3	0.4	0	0	No
1-7	5	47.8	0	3.2	0	0	Yes
1-8	3	38.3	7.7	0	4	0	Yes
1-9	3	38.3	7.7	0	0	4	Yes
1-10	3	38.3	7.7	0.4	4	0	Yes
1-11	3	38.3	7.7	0.4	0	4	Yes
1-12	3	38.0	7.6	0.4	4	0	Yes
1-13[2]	3	41.7	8.3	0.2	0	0	Yes
1-14[2]	2	47.8	0	3.2	0	0	Yes

[1]Revised anaerobic mineral medium (RAMM) [Shelton and Tiedje, 1984].
[2]Styrofoam® was added.

have 30 days of solids retention time. The experimental conditions of the first series BMP tests are summarized in Table 1.

In order to evaluate the effect of mixing on gas production, several samples were not mixed. The other samples were mixed in a constant temperature water bath equipped with a shaker. The temperature was maintained at 35±1 °C. The first set consisted of the mills anaerobic sludge and current influent (no condensate) with and without mixing (Runs 1-1 and 1-2). The set was charged at a similar loading as the full-scale system. The second set of samples was set up as the first set, but also charged with enough condensate to mimic the anticipated loading increase from the introduction of the condensates into the anaerobic system (Runs 1-3 and 1-4). The third set of samples was set up similar to the first set, but also charged with enough condensate to mimic twice the anticipated loading increase from the introduction of the condensates into the anaerobic system (Runs 1-5 and 1-6). The fourth set of samples was set up with a similar loading as the current full-scale facility, but with the condensate as providing the whole loading (Run 1-7). The fifth set of samples was set up to evaluate the effect of revised anaerobic mineral medium (RAMM) and condensate on gas production (Runs 1-8 to 1-12) with constant mixing. The sixth set of samples was set up to evaluate the effect of Styrofoam® on gas production under the same condition as Runs 1-3 and 1-7. The ratios are based on the last four-month flow/influent BOD, reactor volume/mixed liquor concentration, and the anticipated flow/quality of condensate. These values are summarized in Table 2.

Net methane production from decomposition of wastes was determined by subtracting the quantity produced by the control samples. If the methane production was less than the control, a potential inhibition could be indicated. The most common expression of BMP results is the accumulated volume multiplied by the methane composition and divided by the volume of sludge (vol. methane/vol. of sludge after 5 and 30 days).

During the first series BMP tests, the methanol analysis method did not produce reliable data. Therefore, the second and third series BMP tests were performed to evaluate the degradation of methanol during anaerobic treatment. The experimental conditions are summarized in Tables 3 and 4. The volume of the anaerobic seed was fixed at 50 mL and current influent, condensate, and methanol (HPLC grade) were added. In order to assess the effect of Styrofoam® on gas production, 0.2 g of Styrofoam® was added.

Table 2. Operational conditions of the paper mill's anaerobic pretreatment process

Parameters	Values
Influent flow	23,400 m^3/day
Influent BOD_5	2,046 mg/L
Condensate flow	560 m^3/day
Condensate BOD	6,000 mg/L
Anaerobic basin volume	116,400 m^3
Anaerobic sludge total suspended solids (TSS)	26,000 mg/L
Anaerobic sludge volatile suspended solids (VSS)/TSS	82%
Anaerobic basin hydraulic retention time	5 days
Anaerobic basin mixed liquor estimated BOD_5[1]	18,200 mg/L

[1]Estimated BOD_5=26,000×0.82×1.42 COD/VS×0.6 BOD_5/COD≈ 18,200 mg/L.

Table 3. Experimental conditions of the second series BMP tests

Run no.	Anaerobic seed, mL	Current influent, mL	Condensate, mL	Styrofoam®
2-1	50	10	0	No
2-2	50	10	0.24	No
2-3	50	10	0.24	Yes

Table 4. Experimental conditions of the third series BMP tests

Run no.	Anaerobic seed, mL	Current influent, mL	Condensate, mL	Styrofoam®
3-1	50	0	0	No
3-2	50	10	0	No
3-3	50	10	0.24	No
3-4	50	10	0.24	Yes

3. Analytical Methods

Chemical oxygen demand (COD) and methanol in the liquid phase, gas volume, and CH_4 content in the gas phase were measured to perform a quasi-mass balance to determine the effect of introduction of condensate on the system and to verify removal from the system. Gas volumes were measured frequently. Methanol in the liquid phase was measured on days 0, 1, 5, and 15. Total solids and volatile solids concentrations were obtained from 20-mL samples in accordance with Parts 2540B and 2540E, respectively, of Standard Methods [APHA et al., 1998]. Suspended and volatile suspended solids concentrations were measured by following the procedure outlined in Parts 2540D and 2540G of Standard Methods [APHA et al., 1998] using between 15 and 40 mL samples. Total volatile, suspended, and volatile solids concentration values were computed to the nearest 10 mg/L. COD was determined by diluting all samples and following the method in Parts 5220C of Standard Methods [APHA et al., 1998]. Samples were digested in an autoclave for 2 hours at 150 °C. The digested sludge sample was diluted with 100 parts of deionized water by volume to achieve the most reproducible result. A well-defined standard COD curve was obtained by using the same COD procedure outlined above without any dilution for various concentrations of potassium hydrogen phthalate (KHP). The spectrophotometer used was a Milton Roy Spectronic 301. Each sample's absorbance was measured at a wavelength of 620 nm. Calculated COD values were rounded to the nearest 10 mg/L.

Methanol, methyl ethyl ketone (MEK), and acetaldehyde in the liquid phase were analyzed with a gas chromatograph (GC) equipped with a flame ionization detector (FID). Gas composition was determined with a GC equipped with a thermal conductivity detector (TCD). An aliquot of 10 mL of ASTM Type 1 water and 10 mL of sample were injected. The column temperature was 40 °C. The injection temperature was 50 °C. The detector temperature was 250 °C. Formaldehyde was not reliably detected with the FID. For the vapor phase methanol analysis, a GC equipped with a thermal detector was used.

RESULTS

Table 5. First series BMP test results

Run #	Sample # averaged	Waste composition	Mixing	pH[1]	Gas produced[2], mL	BMP (mL CH_4/mL waste)
1-1	3	Influent	Yes	6.83	57.5	1.15
1-2	3	Influent	No	-	30.9	0.62
1-3	5	Influent+condensate (regular loading)	Yes	7.03	88.1	1.76
1-4	3	Influent+condensate (regular loading)	No	-	27.9	0.56
1-5	5	Influent+condensate (high loading)	Yes	7.18	119.4	2.39
1-6	3	Influent+condensate (high loading)	No	-	36.6	0.73
1-7	5	Condensate only	Yes	7.20	105.6	2.11
1-8	3	Influent+RAMM	Yes	7.19	59.3	1.29
1-9	3	Influent+water	Yes	7.15	55.2	1.20
1-10	3	Influent+condensate+RAMM	Yes	7.15	71.9	1.55
1-11	3	Influent+condensate+water	Yes	7.17	60.8	1.31
1-12	3	Influent+condensate+water	Yes	7.21	62.1	1.35
1-13[3]	3	Influent+condensate+Styrofoam®	Yes	-	88.3	1.76
1-14[3]	2	Condensate+Styrofoam®	Yes	7.21	62.9	1.23

[1]pH of seed, influent, and condensate: 7.06, 6.9, and 6.35.
[2]Average values of samples listed in column 2.
[3]Styrofoam® was added.

1. First Series BMP Tests

The results of the first series BMP tests are summarized in Table 5. Since the objective of this test was to evaluate the effect of methanol addition, mixing, and Styrofoam® on gas production, COD values were not measured.

The BMP value of the current influent condition was 1.15 mL CH_4/mL waste with mixing (Run 1-1) and 0.62 mL CH_4/mL waste without mixing (Run 1-2). These results reflect that the mixing is one of the most important factors in anaerobic digestion of the wastewater. Run 13 had greater BMP values than Run 1. This result indicates that the condensate waste may enhance anaerobic digestion. At the higher condensate waste loading rate, the BMP was significantly greater than the current condition, indicating that the condensate contains a large portion of readily degradable material or some materials that stimulate the activity of anaerobic microorganisms. When RAMM was added (Run 1-8), the BMP value increased slightly compared with Run 1-9. The BMP results of Runs 1-3 and 1-14 were similar; thus, the effect of Styrofoam® was negligible. The BMP value of Run 1-7 was much greater than that of Run 1-14, indicating that when Styrofoam® was added the methane production decreased by over 40%.

Mixing was the most important factor controlling the gas production. When there was no mixing, gas production decreased from 69% to 46%. When condensate was added, gas production increased significantly (Runs 1-3 and 1-5). Condensate appeared to increase the gas production. The behavior of selected chlorinated phenols, guaiacols, catechols, and vanillins during the high-rate anaerobic treatment of segregated Kraft mill bleach plant effluents was investigated by Parker et al. [1993]. Supplementation of the reactor influent with a synthetic evaporator condensate containing methanol and ethanol improved the removal of a number of the compounds by greater than 80%. Therefore, it can be said that the addition of condensate to the existing anaerobic pretreatment process is advantageous.

Samples with RAMM produced more gas than samples with water, indicating that there may be a way to enhance the anaerobic decomposition rate. Samples receiving Styrofoam® produced 28% to 40% less methane than samples without Styrofoam®. Styrofoam® appeared to sorb methanol and other organics significantly.

From the stoichiometric relationship below, the total gas volume can be estimated.

$$CH_3OH \rightarrow 0.75CH_4 + 0.25CO_2 + 0.5H_2O \quad (1)$$

$$V_{CH_4} = \frac{12\text{ g } CH_4}{32\text{ g MeOH}} \times \frac{1\text{ mol}}{16\text{ g}} \times \frac{22.4\text{ L}}{\text{mol}} = 0.525\text{ L } CH_4/\text{g MeOH}$$

$$V_{CO_2} = \frac{11\text{ g } CO_2}{32\text{ g MeOH}} \times \frac{1\text{ mol}}{44\text{ g}} \times \frac{22.4\text{ L}}{\text{mol}} = 0.175\text{ L } CO_2/\text{g MeOH} \quad (2)$$

Therefore, the total gas volume is estimated to be 0.7 L/g methanol (MeOH). The methanol concentration in condensate was measured to be 3,490 mg/L. The gas volumes produced by condensate and current anaerobic basin influent can be estimated as follows:

Total gas produced by methanol in 0.2 mL condensate
$= 0.7\text{ L } CH_4/\text{g MeOH} \times 3{,}490\text{ mg/L} \times 0.2\text{ mL} \times \text{L}/10^3\text{ mL} \times \text{g}/10^3\text{ mg} \times 10^3\text{ mL/L} = 0.5\text{ mL}$

Methane produced by 0.2 mL condensate of 6,000 mg BOD_5/L
$= 0.25\text{ g } CH_4\text{ produced/1 g } BOD_5 \times 1\text{ mol/16 g} \times 22.4\text{ L/mol} \times 6{,}000\text{ mg } BOD_5/\text{L} \times \text{g}/10^3\text{ mg} \times 0.2\text{ mL} = 0.42\text{ mL}$

Gas produced by 0.2 mL condensate of 6,000 mg BOD_5/L
$= 0.42\text{ mL} \times 4/3\ (75\%\ CH_4\text{ and }25\%\ CO_2) = 0.5\text{ mL}$

Gas produced by 8.3 mL current influent at 2,000 mg BOD_5/L
$= 0.25\text{ g } CH_4\text{ produced/1 g } BOD_5 \times 1\text{ mol/16 g} \times 22.4\text{ L/mol} \times 2{,}000\text{ mg BOD/L} \times \text{g}/10^3\text{ mg} \times 8.3\text{ mL} \times \text{L}/10^3\text{ mL} \times 4/3 = 7.8\text{ mL}$

It is estimated that 0.5 and 7.8 mL of gas are produced when the condensate with BOD_5 of 6,000 mg/L and the current influent with BOD_5 of 2,000 mg/L are added to the anaerobic basin, respectively. Additionally the methanol added could not entirely account for the significant increase in gas production. It appears that condensate enhances anaerobic digestion. The seed contained significant amounts

Table 6. Total and soluble COD values of various wastewater samples

	Total COD, mg/L	Soluble COD, mg/L	BOD_5, mg/L
Influent	4,510	1,990	1,990
Anaerobic basin seed	40,510	1,470	1,840
Condensate	4,410	4,410	2,070

of organic materials capable of producing gas. In the second series BMP tests, the seed was digested without feed for three days before testing.

2. Second Series BMP Tests

The objective of the second series BMP tests was to investigate the fate of methanol under anaerobic conditions and evaluate the effect of Styrofoam® on gas production. Total and soluble COD values of influent, anaerobic seed sludge, and condensate are summarized in Table 6.

Current influent COD was 4,510 mg/L and condensate waste COD was 4,410 mg/L. Most COD of condensate waste is soluble while the current influent has approximately 2,000 mg/L of soluble COD. Theoretically, 0.35 mL CH_4/mg COD is produced. Since the COD values of the two streams were very close, very similar BMP values are expected if both of wastewaters have similar biodegradability. The tests were performed in triplicate under three different waste loading conditions: influent, influent+condensate, and influent+condensate+Styrofoam®. The changes in COD for the three runs are shown in Fig. 1. Soluble COD did not change during the first three days due to production of soluble by-products from other organics in the influent, but decreased thereafter. The run with only the current influent (Run 2-1) had the lowest soluble COD, followed by the run with the mixture of the current influent and condensate with Styrofoam® (Run 2-3) and without Styrofoam® (Run 2-2).

The cumulative gas production rate for 15 days is shown in Fig. 2. After 5 days, most organics appeared to be converted to gas. Because of this, the third BMP test was performed for 5 days. Run 2-3 (with Styrofoam®) had the greatest cumulative gas volume produced, followed by Run 2-2 and Run 2-1.

The theoretical maximum methane production (TMMP) from waste degradation was calculated using the following equation.

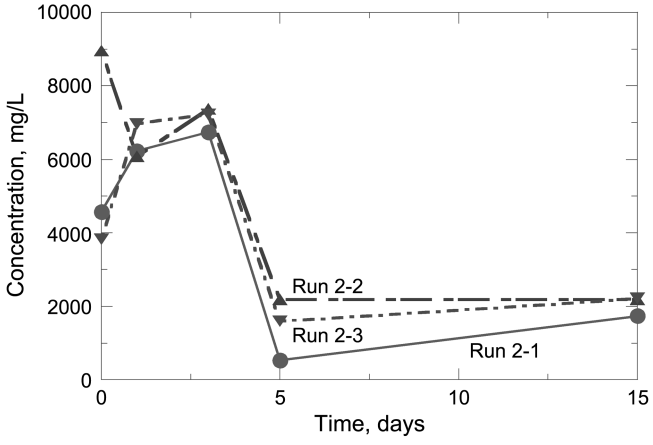

Fig. 1. Soluble COD change over time.

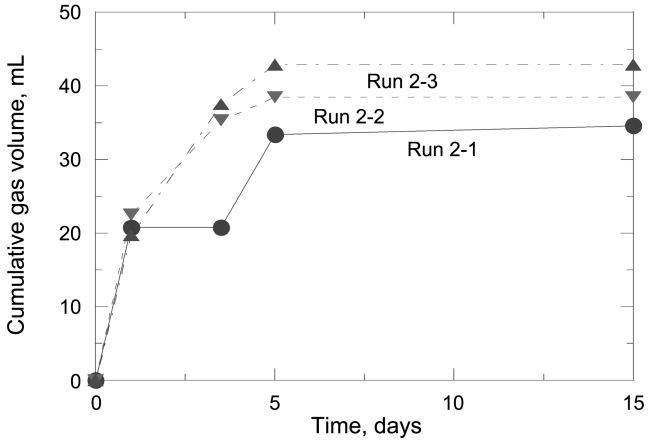

Fig. 2. Cumulative gas volume changes over time.

Table 7. Second series BMP_5 test results

Run no.	Gas produced*, mL	Gas vol. difference, mL	ΔCOD, mg/L	BMP_5, mL CH_4/mL seed	Gas produced/ TMMP
2-1	33.4	0	4,051	0.445	0.393
2-2	38.5	5.1	6,780	0.513	0.270
2-3	42.9	9.5	2,225	0.572	0.915

*Gas produced amount of first day.

$$\text{TMMP (mL)} = W \times \Delta COD \times 0.35\ m^3/(\text{kg COD degraded}) \quad (3)$$

where W=wastewater volume (mL);
ΔCOD=COD reduction during BMP test (mg/L); and
0.35 m^3/kg COD degraded=theoretical value.

The test results are summarized in Table 7. The gas volume difference due to the addition of condensate was 5.1 mL. BMP_5 values ranged from 0.445 to 0.572 mL gas/mL anaerobic seed sludge. When Styrofoam® was added, BMP_5 and gas production increased.

If methanol in a closed vessel is in equilibrium, the concentration in the headspace can be estimated as follows:

$$V_G C_G + V_L C_L = V_S C_{L,0} \quad (4)$$

$$C_G = H C_L \quad (5)$$

where V_G=headspace volume, L;
C_G=methanol concentration in headspace, mg/L;
V_L=liquid volume, L;
C_L=methanol concentration in liquid, mg/L;
V_S=condensate volume; L; and
$C_{L,0}$=methanol concentration in condensate, mg/L.

Thus, C_L can be estimated as follows:

$$C_L = \frac{C_{L,0} V_S}{V_G H + V_L} \quad (6)$$

If V_S=0.24 mL, V_L=60.24 mL, V_G=84.76 mL (in a 145-mL serum bottle used in the second series BMP tests) and H=0.0002, then the mass of methanol in the gas phase is <0.03%. Therefore, it can be said that methanol will not volatilize to the headspace or atmosphere. If biodegradation occurs, the partitioning into the vapor phase

Table 8. Third series BMP_5 test results I

Run #	pH		Gas volume, mL			Cumulative gas volume, mL	Gas/seed, mL/mL	Gas produced/ $TMMP_5$
	Day 0	Day 5	Day 0	Day 3	Day 5			
3-1	7.22	7.22	0	10	14.4	24.4	0.49	1.55
3-2	7.30	7.30	0	20.8	24.8	45.6	0.91	2.74
3-3	7.31	7.31	0	21.4	25.2	46.6	0.93	3.15
3-4	7.48	7.48	0	17.6	24.4	42.0	0.84	2.68

Table 9. Third series BMP_5 test results II

Run #	Influent, mL	Condensate, mL	Gas production difference, mL	Theoretical gas production, mL	% of theoretical gas production
3-1	0	0	0	-	-
3-2	10	0	21.2	22.6	94.0
3-3	10	0.24	22.2	22.9	96.9
3-4	10	0.24	17.6	22.9	76.8

will be further reduced. The methanol concentration in the headspace was estimated by using the above mass balance approach with known methanol concentrations in the liquid phase. Methanol in the headspace for Runs 2-1 to 2-3 was not detected throughout the test. When 0.24 mL of condensate containing 3,490 mg/L of methanol was added to the 145-mL serum bottle along with 50 mL of seed and 10 mL of influent, the estimated methanol concentrations in the liquid and gas phases would be 13.9 and 0.0003 mg/L, respectively.

3. Third Series BMP Tests

The second series BMP tests were repeated due to the problem with methanol analysis by using GC. The third series BMP test results are shown in Tables 8 and 9. Since Run 3-1 did not have either influent or condensate, the methane generated is from the anaerobic seed sludge itself. Through the addition of 10 mL of the influent, 21.2 mL of additional gas was generated. When 0.24 mL of condensate was added in addition to 10 mL of the influent, 1 mL of additional gas was generated. As shown in the first BMP test, the increase in gas production due to condensate addition is anticipated to be negligible. When Styrofoam® was added (Run 3-4), the gas production was slightly lower (42 mL) than Run 3-3 (46.6 mL) while the second series BMP_5 test showed the opposite result. The values of gas produced/$TMMP_5$ were much greater than those for the second series test. The percentages of gas produced compared with theoretical gas production based on COD were 94%, 96.9%, and 76.8% for Runs 3-2, 3-3, and 3-4, respectively. It can be concluded that condensate addition at the ratio tested (influent : condensate=10 : 0.24 by volume) would not affect the performance of the anaerobic basin. Furthermore, the effect of the addition of Styrofoam® to anaerobic basins is anticipated to be negligible.

The changes in total organic carbon (TOC) over time are shown in Fig. 3. With the addition of the influent and condensate, TOC increased. Except for Run 3-4, TOC increased over time.

The concentrations of methanol, acetaldehyde, and MEK in the anaerobic seed sludge, influent, and condensate are summarized in Table 10. The anaerobic seed sludge and influent did not contain methanol. However, the current influent contained low levels of acetaldehyde and MEK. The condensate had high levels of MEK as well as methanol.

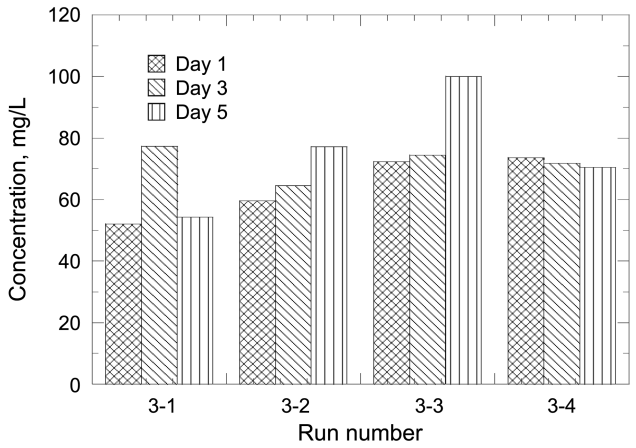

Fig. 3. Changes in total organic carbon over time.

Table 10. Concentrations of methanol, acetaldehyde, and MEK in the anaerobic seed sludge, influent, and condensate

	Methanol, mg/L	Acetaldehyde, mg/L	MEK, mg/L
Anaerobic seed sludge	0	0	0
Influent	0	0.6	22
Condensate	3,490	0.5	658

The changes in the concentrations of methanol, acetaldehyde, and MEK are summarized in Table 11. Since methanol was not detected immediately after mixing with seed and influent, the initial methanol concentration had to be estimated. At Days 3 and 5, methanol was not detected. Acetaldehyde was detected in most runs. It is interesting to note that the run without influent and condensate (Run 3-1) had an acetaldehyde concentration of 1.5 mg/L at Day 3. MEK was detected in the influent and condensate containing runs (Runs 3-2, 3-3, and 3-4) but not detected afterwards.

4. Batch Tests

Batch tests were performed to determine the fate of methanol

Table 11. Changes in the concentrations of methanol, acetaldehyde, and MEK

Run #	Methanol, mg/L			Acetaldehyde, mg/L			MEK, mg/L		
	0 day	3 days	5 days	0 day	3 days	5 days	0 day	3 days	5 days
3-1	0	0	0	0	1.5	0	0	0	0
3-2	0	0	0	0.1	0.6	0	3.7	0	0
3-3	13.9	0	0	0.1	0.3	0	6.3	0	0
3-4	13.9	0	0	0.1	0.5	0.1	6.3	0	0

and the formation of by-products. The first run had the condensate, influent, and seed volumes of 0.24, 10, and 50 mL and the second run had the condensate and seed volumes of 5 and 50 mL, respectively. As shown in Fig. 4 methanol was not detected from the beginning of the test. Methanol in the headspace was also not detected throughout the test. Because of this, the mass balance could not be established.

MEK was detected at low levels and disappeared in 8 hours. Acetaldehyde was formed during anaerobic digestion as shown in the third series BMP test (Table 10), but completely degraded after 32 hours. When condensate was added without influent, methanol did not readily degrade. MEK and acetaldehyde also persisted during 32 hours of the test (Fig. 5). This test was performed since methanol could not be detected under the expected condition at the anaerobic basin. The methanol data was curve-fitted to determine the second order biodegradation rate. It was assumed that the methanol biodegradation rate is a function of biomass concentration and methanol concentration as follows:

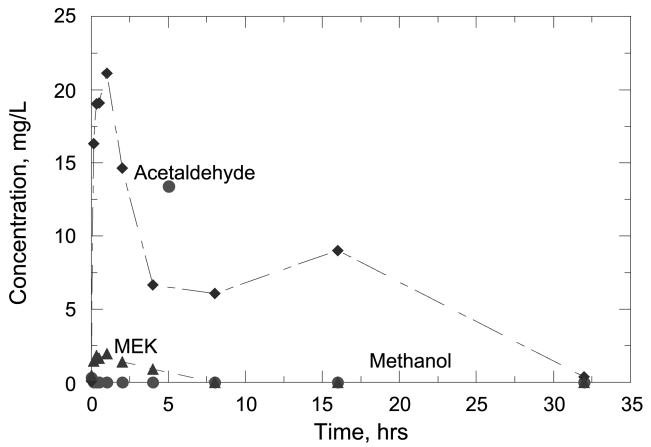

Fig. 4. Changes in methanol, acetaldehyde, and MEK concentrations over time at the condensate, influent, and seed volumes of 0.24, 10, and 50 mL.

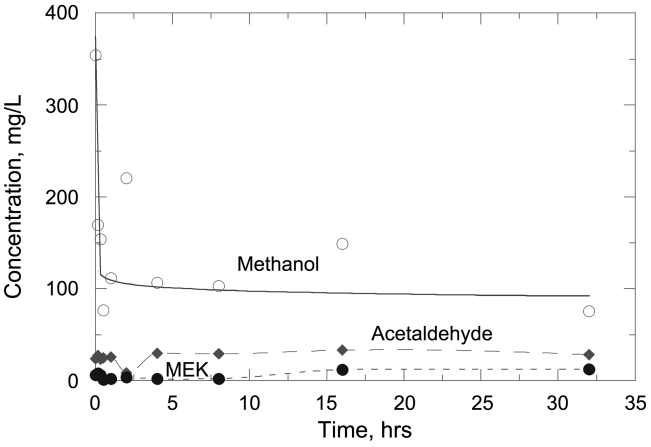

Fig. 5. Changes in methanol, acetaldehyde, and MEK concentrations over time at the condensate and seed volumes of 5 and 50 mL.

$$\frac{dC}{dt} = -k_{b2}X_v C \tag{7}$$

where C=methane concentration, M/L^3;
k_{b2}=second order biodegradation rate, $L^3/M \cdot T$; and
X_v=biomass concentration in anaerobic basin, M/L^3.

The following first order equation can be obtained.

$$C_t = C_0 e^{-k_{b2} \cdot X_v \cdot t} \tag{8}$$

The initial methanol concentration of 13.9 mg/L estimated from the methanol concentration in the condensate at time 0 and zero concentration after 10 minutes were used to determine the second order biodegradation rate. Since the biomass concentration was approximately 35,000 mg/L, the second order biodegradation rate was estimated to be 4.06×10^{-2} $m^3/g \cdot day$. During the second test when the biomass concentration was 18,000 mg/L, the second order biodegradation rate was estimated to be 3.97×10^{-3} $m^3/g \cdot day$. The line shown in Fig. 5. was calculated by using the second order degradation rate determined through regression analysis.

5. Partition and Diffusion Coefficients of Methanol in Styrofoam®

Due to the limited time given for this study, the diffusion coefficient of 1×10^{-6} cm^2/sec determined by Park et al. [1993] for polyethylene and methylene chloride was used for the study. One batch test was performed after adding 0.2 g of Styrofoam® into the 140-mL serum bottle. The result is shown in Fig. 6. The initial methanol concentration was 10,000 mg/L. Styrofoam® quickly sorbed methanol and reached steady state (3,160 mg/L) after 3 hours.

From the following Freundlich sorption relationship, the partition coefficient between methanol and Styrofoam® can be determined.

$$\frac{X}{M} = K_s' C_{L,e} \tag{9}$$

$$K_s = K_s' \times \rho_s \tag{10}$$

where X=mass of methanol sorbed, g;
M=mass of Styrofoam®, g;
K_s=partition coefficient, dimensionless;
K_s'=partition coefficient, L/g;

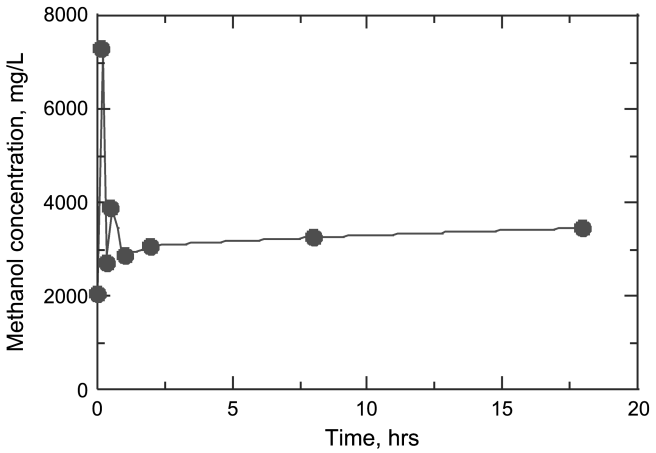

Fig. 6. Changes in methanol concentration over time.

$C_{L,e}$=liquid-phase methanol concentration in equilibrium, mg/L; and
ρ_s=density of Styrofoam® (g/L).

If the density of Styrofoam® is 0.016 g/cm^3, then K_s value is estimated to be 0.016. This indicates that the partition coefficient is very low.

CONCLUSIONS

From the laboratory experiments, the following conclusions can be drawn:

If the condensate is to be added to the anaerobic basin, the gas production and decomposition of persistent organic compounds in the existing influent may increase. Mixing is an important factor in gas production. The second order biodegradation rate constant, k_{b2}, was estimated to range from 3.97×10^{-3} to 4.06×10^{-2} m^3/g·day. It is anticipated that methanol is almost completely biodegraded in the anaerobic basin. From a mass balance computation, the methanol release from the anaerobic basin is negligible (<0.03%).

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NOMENCLATURE

W : wastewater volume [mL]
ΔCOD : COD reduction during BMP test [mg/L]
V_G : headspace volume [L]
C_G : methanol concentration in headspace [mg/L]
V_L : liquid volume [L]
C_L : methanol concentration in liquid [mg/L]
V_S : condensate volume [L]
$C_{L,0}$: methanol concentration in condensate [mg/L]
C : methane concentration [M/L^3]
k_{b2} : second order biodegradation rate [L^3/M·T]
X_v : biomass concentration in anaerobic basin [M/L^3]
X : mass of methanol sorbed [g]
M : mass of Styrofoam® [g]
K_s : partition coefficient, dimensionless
K_s' : partition coefficient [L/g]
$C_{L,e}$: liquid-phase methanol concentration in equilibrium [mg/L]
ρ_s : density of Styrofoam® [g/L]

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