Modeling of Methanol Release through Anaerobic Pretreatment System Cover

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.

Abstract−A paper mill has recently proposed the treatment of methanol-containing condensate using anaerobic pretreatment system as an alternative control for hazardous air pollutants (HAPs) 40 CFR Part 63 Subpart S - Maximum Achievable Control Technology. To investigate the potential use of an anaerobic digester and to reduce methanol in wastewater treatment plants (WWTPs), the fate of methanol in a digester was examined. A series of laboratory-scale experiments were conducted and a mathematical model was developed to evaluate the fate of methanol during anaerobic treatment. From a mathematical model, the losses of methanol through the Styrofoam® cover system and volatilizations were calculated to be almost zero (<0.01%). Since acetaldehyde and methyl ethyl ketone have one order of Henry's law constants magnitude smaller than methanol, the release of these by-products into the atmosphere is expected to be much smaller than methanol, which was found to have an almost zero loss through volatilization.

Key words: Anaerobic Pretreatment, Condensate, Methanol, Release, Modeling

INTRODUCTION

The Environmental Cooperation Agreement allowed a paper mill to design and install site-specific pollution control devices to limit the releases of HAPs addressed in 40 CFR Part 63, Subpart S (Maximum Achievable Control Technology or MACT I) into the environment [U.S. Wisconsin Department of Natural Resources (DNR), 2000]. In lieu of collecting and incinerating non-condensable gases (NCGs) produced by pulp mill sources as prescribed by MACT I for the semi-chemical subcategory, the paper mill proposed to collect plant anaerobic basins foul condensates blow heat recovery primary and secondary condensers, liquor evaporator non-condensable gas vents, and hot well vents and hard pipe them into the wastewater treatment. The mass balance benefit of the proposed compliance alternative against the MACT I standard is shown in Table 1. The data shown in Table 1 were reduced from low volume high concentration (LVHC) gases and foul condensate tests.

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. The schematic of the wastewater treatment facility at the PCA is explained. Landfill leachate,

Table 1. Mass balance of hazardous air pollutants in a paper mill

Parameter	Collected condensate, lb/yr	LVHC, lb/yr
Methanol	1,197,990	46,413
Acetaldehyde	93,356	59,572
Methyl Ethyl Ketone	43,676	21,491
Formaldehyde	1,471	190
Total	1,338,493	127,666

*Calculation based on actual 1999 pulp production and 11/17/99 emission report.

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

primary sedimentation tank effluent, and mill sanitary wastewater are pretreated in anaerobic basins. Then, the effluent is treated with aerobic treatment. Waste-activated sludge (WAS) from the aerobic basin is discharged either into the anaerobic digester or into the sludge blend tank. The sludge is discarded from the anaerobic digester at 260 m³/day at 3-4% solids concentration. The sludge is thickened with a gravity belt thickener and dewatered with a screw press. Concern has arisen regarding the introduction of a methanol-containing condensate into the anaerobic treatment system. The concern centers on the anaerobic biodegradability and stripping of organic components in the condensate from a (non-Kraft process) pulp and paper mill, mainly methanol, in the system through a Styrofoam® cover.

Castillo et al. [1999] reported that the Monod equation, zero and first order kinetic model, have been used to represent the biodegradation of domestic sewage in a combined treatment system. Another study [Schwarz et al., 1996] dealt with a mathematical model for anaerobic treatment of wastewater from the sugar industry, which has been developed for supporting the scale-up of a fluidized bed reactor. They also suggested that the dynamic model was based on material balance equations for substrates and products in gas and liquid phase. At the same time, the effects taken into account were the biological degradation steps including chemical equilibrium and mass transport between gas and liquid phase as well as convection and dispersion. The purpose of this paper [Gruden et al., 2001] was to study the toxic effects and fate of the two commercially significant benzotriazole isomers used in aircraft deicing fluids during anaerobic digestion. According to results from the studies of Winfrey and Zeikus [1977] and Gunnarsson and Ronnow [1982] there was a significant reduction in the rate of methane production in anaerobic marine sediments in the presence of high sulfate concentrations. Zender [1988] has also tried to explain the reduction of methanogenic activity in the presence of sulfate by comparing the free energies of the various reactions, and through kinetic studies. The main objective of the present study by Ashutosh et al. [1994] was to investigate and compare sulfate reduction and methanogenesis among

three different substrates (acetic acid, methanol and formic acid), and they carried out the model development and verification using methanogenesis and sulfate reduction in chemostats. Also the rate-limiting step in anaerobic digestors has been shown to be the methane formation from acetate [Novac and Carlson, 1970; Ghosh and Pohland, 1974]. In order to ascertain the feasibility of anaerobic digestion for the treatment of an alcoholic waste (i.e., fusel oil) consisting of approx. 50% methanol and 50% alcohols, Gatze et al. [1981] performed experiments. Cecilia and Hakan [1999] concluded that the transport of organic compounds with the percolating water through reported that the hydrophobic compounds can be retained in the landfill by sorption to the stationary waste during the transport. Dobbes et al. [1999] reported that the correlations developed provide a basis for predicting the concentration of toxic compounds associated with wastewater solids at a given equilibrium concentration in the aqueous phase. They also said that the sorption on solids is one of the fundamental processes controlling the removal of toxic organic compounds in municipal wastewater treatment plants. The fate of hydrophobic organic pollutants in wastewater systems is highly dependent upon their sorptive behavior. Therefore, it is important to investigate the sorptive properties of wastewater solids in order to better understand the role of this removal mechanism in wastewater treatment processes. Oremland et al. [1982] and Scheunert et al. [1987] carried out the half-life of methanol under the unacclimated anaerobic condition ranges from 1 to 5 days.

The objective of the study was to provide a reasonable evaluation of samples from a paper mill to determine the fate of methanol and other HAPs existing in the condensate in an anaerobic system. A series of the biochemical potential (BMP) tests and batch tests were performed to determine biodegradation rates of HAPs with the seed obtained from the anaerobic pretreatment process. In addition, a sorption test was performed to determine the partition coefficient between Styrofoam® and methanol. Therefore, a mathematical model was developed to assess the fate of methanol in anaerobic digester under various conditions.

EXPERIMENTAL APPROACH

1. Properties of Methanol

The Environmental Protection Agency (EPA) reported that methanol, also called methyl alcohol, is manufactured by 13 producers in the United States (U.S.). Annual production capacity is approximately 1,626 million gallons. In 1992, 1,345 million gallons of methanol were produced in the U.S. 495 million gallons were imported into the U.S. and 50 million gallons were exported [Mannsville, 1993]. Methanol is a colorless liquid and 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 largest users of the methanol in the U.S. are companies that make methyl t-butyl ether, a gasoline additive. They also use methanol to make chemicals such as formaldehyde, acetic acid, chloromethanes, and methyl methacrylate. They add methanol to paint strippers, aerosol spray paints, wall paints, carburetor cleaners, and car windshield washer products. Methanol is also used as a gasoline additive and, in some cases, a gasoline substitute for use in automobiles and other small engines. Although 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 substance in air [U.S. EPA, 1994]. The properties of methanol are summarized in Table 2.

2. Analytical Methods I

The BMP test procedure adopted for this study is as follows:

(1) In an anaerobic chamber, carefully transfer a predetermined aliquot of anaerobic digester sludge into 145-mL serum bottles and spike with wastes.

(2) Mix well and withdraw 10 mL for analysis of Volatile Suspended Solid (VSS) and total and soluble Chemical Oxygen Demand (COD).

(3) Seal serum bottles with butyl rubber stoppers and cap with aluminum cramp seals.

(4) Incubate bottles in the dark at 35 and 55 °C without mixing.

(5) Measure volume and composition of the gas at 1, 3, 5, 15, and 30 days. At the end of the tests, measure the final VSS and total and soluble COD.

Table 2. Physical properties of methanol

Parameters	Values	Reference
CAS registry number	67-56-1	-
Physical state	Colorless liquid	Verschueren, 1983
Molecular weight	32.04 g/mol	Budavari et al., 1989
Melting point	97.8 °C	Budavari et al., 1989
Boiling point	64.7 °C at 760 mm Hg	Budavari et al., 1989
Water solubility	Miscible	Budavari et al., 1989
Density	0.7915 g/mL	Budavari et al., 1989
Vapor density (air=1)	1.11	Budavari et al., 1989
log K_{ow}	−0.77	HSDB, 1994
Vapor pressure	126 mm Hg at 25 °C	CHEMFATE, 1994
Reactivity	Flammable; may explode when exposed to flame	HSDB, 1994
Flash point	12 °C	Budavari et al., 1989
Henry's law constant	4.55×10^{-6} atm m³/mol	CHEMFATE 1994
Fish bioconcentration Factor	<1 (estimated)	HSDB, 1994
Odor threshold	Highly variable, ranges over several orders of magnitude (10 to 20,000 ppm in air)	HSDB, 1994

The amount of gas released from each bottle was measured by water displacement in a burette as follows:

(1) Insert a 23-gauge needle equipped with an on/off valve (closed) into the rubber stopper.

(2) Connect the end of the valve to a rubber hose leading to a water-filled burette held inverted in a tub of water by a clamp on a ring stand.

(3) Record the initial water level in the burette.

(4) Release the pinch clamp on the rubber hose.

(5) Open the valve on the needle 'very slowly' allowing the gas to escape into the burette. These results in the displacement of water were from the burette.

(6) Record the final water level in the burette.

(7) Subtract the two water levels measured in the burette to determine the amount of gas released from the bottle.

After releasing excess pressure from the bottles, collect 2-mL gas samples and analyze them for carbon dioxide, oxygen, nitrogen, and methane using a gas chromatograph (G.C. Varian Model 3300) equipped with a thermal conductivity detector.

(1) Swirl the bottle before taking a gas sample. Be careful to keep the liquid from coming in contact with the rubber stopper.

(2) Collect a 0.4-mL gas sample with a gas-tight syringe equipped with a miniature on/off valve as follows:

a. Insert the needle through the stopper,

b. Flush the syringe three times with at least 1 mL of gas from the bottle,

c. Pull another 1 mL of gas into the syringe,

d. Push the plunger back to the 2-mL mark,

e. Equilibrate the volume at 35 °C for at least 30 seconds,

f. Close the valve on the syringe,

g. Remove the needle from the stopper.

(3) Determine the methane, carbon dioxide, and nitrogen content of the gas by injecting the 2-mL sample into the gas chromatograph.

(4) Calculate net gas production by subtracting the gas produced in unamended bottles (control samples) from that produced in the test bottles.

Methanol, methyl ethyl ketone (MEK), and acetaldehyde in the liquid phase were analyzed with a GC equipped with a flame ion-
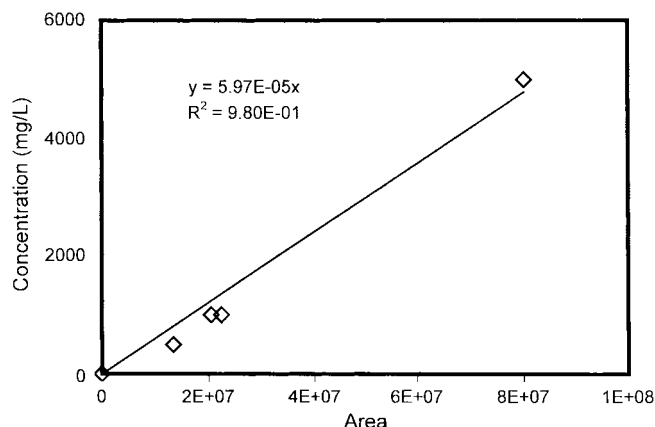

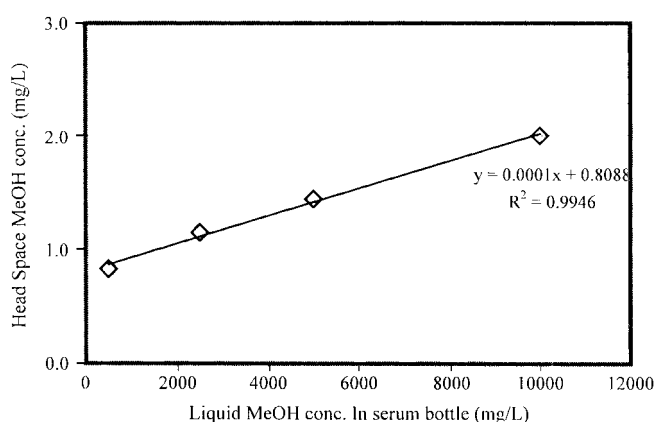
Fig. 1. Methanol calibration curve - liquid phase.

Fig. 2. Methanol calibration curve - vapor phase.

ization detector (FID). Gas composition was determined with a GC equipped with a thermal conductivity detector (TCD). The detailed conditions of two GCs are summarized in Table 3. An aliquot of 10 mL of America Standard Testing Material (ASTM) Type 1 water and 10 mL of sample was injected. The column temperature was 40 °C, injection temperature was 50 °C, and detector temperature was 250 °C. Formaldehyde was not reliably detected with FID. For the vapor phase methanol analysis, a GC equipped with thermal detector was used.

The calibration curve was determined from 0, 500, 1,000, 2,500,

Table 3. Conditions of GCs used for methanol and gas composition

	FID	TCD
Model	Varian 3600	Varian 3300
Column	Capillary column	Stainless steel column
Packing material	Supelcowax-10 mega bore	1) Hayesep N 80/100 2) Molecular sieve 13X 45/100
Diameter	0.75 I.D mm	1) 0.3 cm 2) 0.3 cm
Length	60 m	1) 1.8 m 2) 1.2 m
Temperature programming	15 °C/min	30 °C/min
Column temp.	40 °C→180 °C	30 °C→95 °C
Injection temp	50 °C	85 °C
Detector temp.	250 °C	130 °C
Injection mass	1 μL	200 μL

5,000, and 10,000 ppm of solution. Fig. 1 and Fig. 2 show the calibration curves for methanol in liquid and vapor phases, respectively. Every 10th sample with a known concentration was analyzed for quality assurance. The difference in concentration for two samples from a serum bottle was <5%. Similarly, the calibration curves for other chemicals were prepared. The R^2 values were all >0.98.

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 accumulated volume multiplied by the methane composition and divided by the volume of sludge (vol. methane/vol. of sludge after 5 and 30 days).

3. Analytical Methods II

Total solids and volatile solids concentrations were obtained from 20-mL samples in accordance with Parts 2540B and 2540E, of Standard Methods [APHA et al., 1995]. Suspended and volatile suspended solids concentrations were measured by procedures outlined in Parts 2540D and 2540G of Standard Methods [APHA et al., 1995] 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., 1995].

EXPERIMENTAL RESULTS

1. Fate of Methanol in Anaerobic Digester
Mathematical Model

When methanol in condensate is entered into an anaerobic digester shown in Fig. 3, methanol will disappear through the following pathways: sorption onto biomass, volatilization, biodegradation, and loss through the Styrofoam® cover.

The mass balance within the anaerobic digester can be established as follows:

Acclimation=Input−Output−Loss

$$V\frac{dC_L}{dt}=Q_0C_{L,o}-Q_eC_L-Q_WC_L-R_{sorp}-R_{vol}-R_{bio}-R_{perm} \quad (1)$$

$$Q_0=Q_e+Q_w \quad (2)$$

where V=volume of the anaerobic digester, L^3;
C_L=effluent concentration, M/L^3;
T=time, T;
Q_0=influent flow rate, L^3/T;
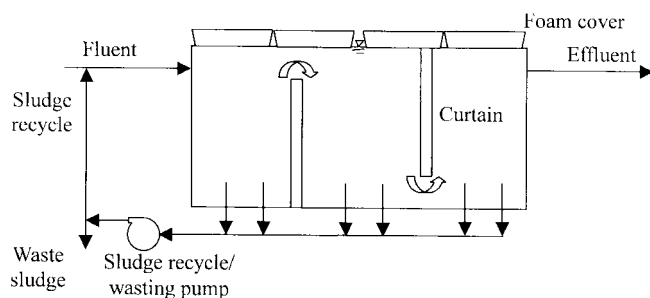$C_{L,0}$=influent methanol concentration, M/L^3;

Fig. 3. Schematic of anaerobic digester.

Q_e=effluent flow rate, L^3/T;
Q_w=anaerobic sludge waste, L^3/T;
R_{sorp}=methanol loss by sorption to biomass, M/T;
R_{vol}=methanol loss by volatilization to atmosphere, M/T;
R_{bio}=methanol loss by biodegradation, M/T; and
R_{perm}=methanol loss by permeation through floating Styrofoam® cover, M/T.

Loss by Sorption
The loss by sorption to biomass can be expressed as follows:

$$C_s=K_pC_L \quad (3)$$

where C_s=methanol concentration in biomass, M/M; and
K_p=partition coefficient, L^3/M.

The partition coefficient K_p can be correlated with the Freundlich sorption coefficient as follows:

$$K_p=K_ff_{oc} \quad (4)$$

where f_{oc}=organic carbon fraction=VS/TS ratio in anaerobic digester.
Dobbs et al. [1989] suggested the following equation to determine K_f values from the octanol-water partition coefficient, K_{ow}:

$$Log\,K_f=1.14+0.58\,log\,K_{ow} \quad (5)$$

The loss by sorption can be expressed as follows:

$$R_{sorp}=Q_wK_pX_wC_L\times10^{-6}=\alpha C_L \quad (6)$$

where Q_w=anaerobic sludge waste rate, L^3/T; and
X_w=waste sludge biomass concentration, M/L^3.

Loss by volatilization
The loss by volatilization to atmosphere can be expressed as follows [Namkung and Rittmann, 1987]:

$$R_{vol}=HQ_gC_L=\beta C_L \quad (7)$$

where H=Henry's constant, dimensionless; and
Q_g=gas volume for mixing≈gas generated (L^3/T).

Loss by biodegradation
The methanol biodegradation can be expressed as follows:

$$R_{bio}=k_{b2}X_vVC_L=\gamma C_L \quad (8)$$

Loss through Styrofoam® cover
The loss through Styrofoam® cover can be estimated as follows:

$$R_{perm}=\frac{DK_sC_LA}{l}=\delta C_L \quad (9)$$

where D=diffusion coefficient in Styrofoam®, L^2/T;
K_s=methanol-Styrofoam® partition coefficient, dimensionless;
A=surface area of the floating cover, L^2; and
l=thickness of the cover, L.

Estimation of losses
From Eq. (1), at steady state, Eq. C_L becomes:

$$C_L=\frac{Q_sC_{L,0}}{Q_s+\alpha+\beta+\gamma+\delta} \quad (10)$$

If the anaerobic digester is equivalent to n number of a completely-stirred tank reactor (CSTR) in series, Eq. (10) can be modified by dividing V and Q_g by n and using C_L at the preceding reactor as C_L at the following reactor.

When C_L values determined from Eq. (10) can be inserted into Eqs. (6) through (9), losses by sorption, volatilization, biodegradation, and permeation through Styrofoam® cover can be estimated.

2. Application of the Mathematical Model

PCA has an anaerobic digester followed by an aerobic treatment. The anaerobic digester volume is 25.6 million gallons per day (mgd). The current influent flow rate is 5.15 mgd with Biochemical Oxygen Demand (BOD₅) of 2,050 mg/L. The mixed liquor suspended solids (MLSS) concentration is 26,000 mg/L. The condensate flow rate is 0.12 mgd with BOD of 6,000 mg/L. Thus, the total flow rate is 5.27 mgd with BOD₅ of approximately 2,140 mg/L. The gas generated is directly released into the atmosphere through holes in the cover. The cover has 3-inch thick Styrofoam® and additional 3/8-inch thick concrete layer to add weight. From Eq. (1), the gas produced is estimated to be 27,930 m³/day when the initial COD is 5,000 mg/L and 80% of COD is decomposed in the anaerobic digester. This value was used as the gas flow rate used for stripping methanol from the anaerobic digester.

The parameters used in the model are summarized in Table 4; other values are found in Table 1 or in the main text.

The modeling results are summarized in Table 5. Losses through sorption, volatilization, and the cover were almost negligible due to low octanol-water partition coefficient, Henry's law constant, and Styrofoam®-methanol partition coefficient. In general, methanol is more biodegraded when the digester configuration is closer to a plugflow type. Since the PCA anaerobic digester consists of four cells, the fate of methanol predicted from four CSTRs in series appears to be more plausible. Loss through the Styrofoam® cover appears to be negligible. Since a 3/8-inch thick concrete layer is sitting on top of the Styrofoam® cover, the loss through the cover can be ignored entirely.

If the anaerobic seed is acclimated with condensate, it is anticipated that the methanol biodegradation rate increases. The fate of methanol at various biodegradation rates in a completely stirred tank reactor is shown in Fig. 4. It can be seen that if biodegradation rate is low, the majority of methanol comes out in effluent. As the biodegradation rate increases to $>10^{-3}$ m³/g·day, the removal is anticipated to be >99%. The losses through the cover, volatilization, and sorption were negligible.

Due to the uncertainty in the Styrofoam®-methanol partition coefficient, K_s sensitivity analysis was performed when k_{b2} was 3×

Table 4. Parameters used in the model

Partition coefficient, K_s	MLVSS/ MLSS	Diffusion coefficient, cm²/sec	Cover thickness, m
0.016	0.73	1×10^{-6}	0.075

Table 5. Pathway of methanol under different biodegradation rate and reactor configuration

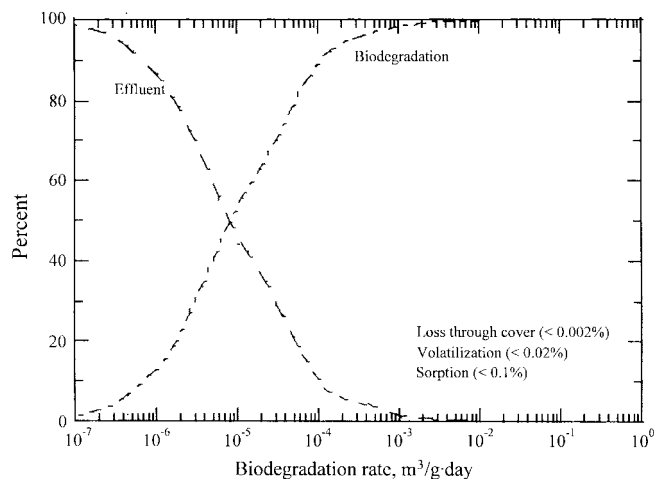| k_{b2}, m³/g·day	4.06×10^{-2}	4.06×10^{-2}	3.97×10^{-3}	3.97×10^{-3}
No. of CSTRs in series	1	4	1	4
% sorption	0.00	0.00	0.00	0.00
% volatilization	0.00	0.00	0.00	0.00
% biodegradation	99.97	100.00	99.73	100.00
% loss through cover	0.00	0.00	0.00	0.00
% in effluent	0.03	0.00	0.27	0.00

Fig. 4. Fate of methanol in a CSTR anaerobic digester under various biodegradation rates.
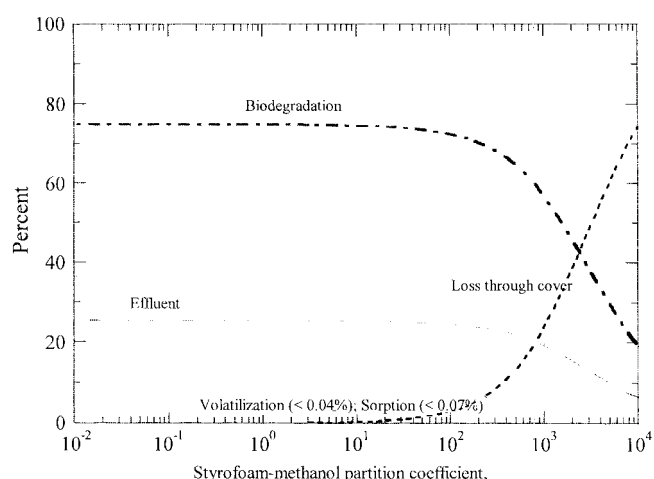

Fig. 5. Fate of methanol in a CSTR anaerobic digester under various Styrofoam®-methanol partition coefficients.

10^{-5} m³/g·day (Fig. 5). It can be seen that when the K_s value is >1,000, the loss through the cover becomes significant (>20%). If k_{b2} is $>1\times10^{-3}$ m³/g·day, the losses through the cover, volatilization, and sorption are almost zero.

Since K_s is anticipated to be <1 and 3/8-inch thick concrete is sitting on top of the cover, it can be said that the loss through the cover is negligible in a worst case.

By-products of anaerobic digestion of methanol may include acetaldehyde, formaldehyde, and methyl ethyl ketone. These compounds have one order of magnitude smaller Henry's law constant than methanol [Yaws and Yang, 1992]. Therefore, it is anticipated that these compounds will be significantly less released into the atmosphere than methanol, which showed very little volatilization.

CONCLUSIONS

From the laboratory experiments and mathematical modeling, the following conclusions can be drawn. With a mathematical model, methanol is predicted to either biodegrade or come out as effluent. For methanol at various biodegradation rates in a completely

stirred tank reactor, it can be seen that if biodegradation rate is low, the majority of methanol comes out in effluent. As the biodegradation rate increases to $>10^{-3}$ m^3/g·day, the removal efficiency is anticipated to be >99%. The losses through the cover, volatilization, and sorption are negligible. The losses of methanol through the Styrofoam® cover system and volatilizations were estimated to be almost zero (<0.01%). The introduction of condensate into the existing anaerobic digestion process appears to improve the treatment efficiency, leading to a more stable anaerobic treatment process operation as well as reducing sludge generation in the aerobic wastewater treatment process due to the reduced organic loading.

ACKNOWLEDGMENT

NOMENCLATURE

V	: volume of the anaerobic digester [L^3]
C_L	: effluent concentration [M/L^3]
T	: time [T]
Q_0	: influent flow rate [L^3/T]
$C_{L,0}$	: influent methanol concentration [M/L^3]
Q_e	: effluent flow rate [L^3/T]
Q_w	: anaerobic sludge waste [L^3/T]
R_{sorp}	: methanol loss by sorption to biomass [M/T]
R_{vol}	: methanol loss by volatilization to atmosphere [M/T]
R_{bio}	: methanol loss by biodegradation [M/T]
R_{perm}	: methanol loss by permeation through floating Styrofoam® cover [M/T]
C_s	: methanol concentration in biomass [M/M]
K_p	: partition coefficient [L^3/M]
f_{oc}	: organic carbon fraction=VS/TS ratio in anaerobic digester
Q_w	: anaerobic sludge waste rate [L^3/T]
X_w	: waste sludge biomass concentration [M/L^3]
H	: Henrys constant, dimensionless
Q_g	: gas volume for mixing≈gas generated [L^3/T]
D	: diffusion coefficient in Styrofoam® [L^2/T]
K_s	: methanol-Styrofoam® partition coefficient, dimensionless
A	: surface area of the floating cover [L^2]
l	: thickness of the cover [L]

REFERENCES

APHA, AWWA and WEF, "Standard Methods for the Examination of Water and Wastewater," 20th Edition, (1998).

Asutosh, G., Joseph, R. V., Munish, G., Gregory, D. S. and Makram, T. S., "Methanogenesis and Sulfate Reduction in Chemostats-I. Kinetic Studies and Experiments," *Wat. Res.*, **28**(4), 781 (1994).

Asutosh, G., Joseph, R. V., Gregory, D. S. and Makram, T. S., "Methanogenesis and Sulfate Reduction in Chemostats-II. Model Development and Verification," *Wat. Res.*, **28**(4), 795 (1994).

Budavari, S., O'Neil, M. J., Smith, A. and Heckelman, P. E., "The Merck Index," 11th ed. Merck & Co., Inc., Rahway, NJ, 939 (1989).

Castillo, A., Llabres, P. and Mata-Alvarez, J., "A Kinetic Study of a Combined Anaerobic-Aerobic System for Treatment of Domestic Sewage," *Wat.Res.Tech.*, **33**(7), 1742 (1999).

Cecilia, O. and Hakan, R., "Transport Fate of Organic Compounds with Water Through Landfills," *Wat. Res.*, **33**(10), 2247 (1999).

CHEMFATE. Syracuse Research Corporation's Environmental Fate Data Bases, Retrieved 8/5/94. Syracuse Research Corporation, Syracuse, NY (1994).

Dobbs, R. A., Wang, L. and Govind, R., "Sorption of Toxic Organic Compounds on Wastewater Solids: Correlation with Fundamental Properties," *Env. Sci. & Tech.*, **23**(9), 1092 (1989).

EPA regulation 749-F-94-013 (1994).

Gatze, L., Willem, de Z. and Els, O., "Anaerobic Treatment of Wastes Containing Methanol and Higher Alcohols," *Water Research*, **15**, 171 (1981).

Ghosh, S. and Polhland, F. G., "Kinetic of Substrate Assimilation and Product Formation in Anaerobic Digestion," *J. Wat. Pollut. Control Fed.*, **46**, 748 (1974).

Gruden, C. L., Dow, S. M. and Hernandez, M. T., "Fate and Toxicity of Aircraft Deicing Fluid Additives Through Anaerobic Digestion," *Water Environment Research*, **73**(1), 72 (2001).

Gunnarsson, A. H. and Rannow, P. H., "Interrelationships Between Sulfate-reducing and Methane Producing Bacteria in Coastal Sediments with Intense Sulfide Production," *Mar. Biol.*, **69**, 121 (1982).

HSDB. Hazardous Substances Data Bank. MEDLARS Online Information Retrieval System, National Library of Medicine, Retrieved August (1994).

Namkung, E. and Rittmann, B. E., "Estimating Volatile Organic Compound Emissions from Publicly Owned Treatment Works," *Jour. Water Poll. Cont. Fed.*, **59**(7), 670 (1987).

Nishio, N., Roberto, G. S., Kazuhiko, H. and Shiro, N., "High Rate Methane Production in a USAB Reactor Fed with Methanol and Acetate," *Jour. Fermentation and Bioengineering*, **75**(4), 309 (1993).

Novac, J. T. and Carlson, D. A., "The Kinetic of Anaerobic Long Chain Fatty Acid Degradation," *J. Wat. Pollut. Control Fed.*, **42**, 1932 (1970).

Oremland, R. S., Marsh, L. M. and Polcin, S., "Methane Production and Simultaneous Sulphate Reduction in Anoxic Salt Marsh Sediments," *Nature*, **296**, 43 (1982).

Scheunert, I., Vockel, D., Schmitzer, J. and Korte, F., "Biomineralization Rates of 14C-Labeled Organic Chemicals in Aerobic and Anaerobic Suspended Soil," *Chemosphere*, **16**, 1031 (1987).

Schwarz, A., Yahyavi, B, Mosche, M., Burkhardt, C., Jordening, H.-J., Buchholz, L. and Reuss, M., "Mathematical Modeling for Supporting Scale-Up of an Anaerobic Wastewater Treatment in a Fluidized Bed Reactor," *Wat. Sci. Tech.*, **34**(5-6), 501 (1996).

Verschueren, K., "Handbook of Environmental Data on Organic Chemicals," 2nd Ed., Van Nostrand Reinhold Company, New York, 818 (1983).

Winfrey, M. R. and Zeikus, J. G., "Effect of Sulfate on Carbon and Electron Flow during Microbial Methanogenesis in Freshwater Sediments," *Appl. Enviro. Microbiol.*, **51**, 572 (1977).

Wisconsin Department of Natural Resources (2000). http://www.dnr.state.wi.us/org/caer/cea/ecpp/agreement/pca/pca.htm

Yaws, C. L. and Yang, H. C., Henry's Law Constant for Compound in Water, In "Thermodynamic and Physical Property Data," Edited by Yaws, C. L., Gulf Publishing Company, Houston, TX, **181** (1992).

Zehnder, J. B. A., "Biology of Anaerobic Microorganisms," Wiley-Liss, New York (1988).