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Volume III

Donald L. Wise

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Biotreatment Systems

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Editor

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PREFACE

Biotreatment Systems is a uniquely valuable reference text consisting of contributed chapters in which are described the most insightful research and development programs around the world. The authors of these contributed chapters are those very conscientious and thoughtful technologists who are investigating pragmatic solutions to environmental problems. This important text has as the major theme the biotreatment of organic residues. This major theme primarily encompasses the field of anaerobic methane fermentation, with an emphasis on treatment of complex wastes. The text is intended to present a comprehensive overview of the most practical research programs that are being carried out in this emerging field of international significance. Due to the fact that both research and development have been carried out at major centers around the world, great care has been taken to include chapters from an international perspective. Further, as a perusal of the chapter titles will indicate, a special emphasis has been made to address both the important research aspects and the practical aspects of the work on biotreatment systems. It is to be noted that each chapter included in this text is the work of a particular individual or group. There are no multiple chapters by more than one author or group. Thus, each of the included chapters most often reflects the dedicated career efforts of these workers. Further, each contributed chapter is presented on a stand-alone basis so that the reader will find it helpful to consider only the theme of each chapter. On the other hand, there is the unifying theme with all chapters of addressing biotreatment systems research and development. A reader of this text, just entering the field, will find this text provides an excellent state-of-the-art presentation of the international import of work on biotreatment systems, with an emphasis on methane fermentation. A reader of this text, who has experience in this field, will find the text to be essential for assessment and referral of this increasingly valuable area of technology.

THE EDITOR

Donald L. Wise, Ph.D., P.E., is Founder and President of Cambridge Scientific, Inc., Belmont, Massachusetts. Dr. Wise also holds the Cabot Chair of Chemical Engineering at Northeastern University, Boston, Massachusetts. Dr. Wise received his B.S. (magna cum laude), M.S., and Ph.D. degrees in chemical engineering at the University of Pittsburgh. Dr. Wise is a specialist in process and biochemical engineering as well as advanced biomaterials development. During his career he has managed a series of programs to develop processes for production of fuel gas, liquid fuels, and organic chemicals from municipal solid waste, an array of agricultural residues, and a wide variety of crop-grown biomass, especially aquatic biomass. Dr. Wise has also been primarily responsible for the initiation of development work on fossil fuels such as peat and lignite to gaseous fuel, liquid fuels, and organic chemicals, and he also originated work on the bioconversion of coal gasifier product gases to these products. Dr. Wise initiated a program to establish the engineering feasibility of converting large-scale combined agricultural residues to fuel gas by the action of microorganisms, a project ultimately involving joint effort with research workers in fifteen countries around the world.

Dr. Wise has worked in the area of biotechnology research and development for 2 decades, has approximately 50 publications in the field, and has edited a number of reference texts. As Associate Editor of *Solar Energy,* the journal of the International Solar Energy Society, he is responsible for the review of manuscripts in the biomass/bioconversion area. Dr. Wise is also on the Editorial Board of *Resources and Conservation,* an international journal published by Elsevier, Amsterdam. He has served as an international consultant in bioconversion for the United Nations and for the U.S. Agency for International Development (AID).

A meaningful portion of these programs that Dr. Wise initiated, and has been carrying out, is his meeting with experts across the U.S. and around the world, to become familiar with both current and practical aspects of bioconversion systems.

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Chapter 1

ANAEROBIC BIOLOGICAL PROCESS FOR THE PREVENTION OF NOXIOUS ODORS IN PULP MANUFACTURING

Ginro Endo and Yasunori Tohya

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I. INTRODUCTION

In the paper mill industry, the recent shortage of energy resources has increased the cost of environmental pollution control methods (such as waste water treatment). This situation is stimulating the introduction of high-performance and energy-saving processes for waste water treatment or air pollution control. One of the most serious nuisances that originate from paper pulping is the problem of malodorous air. This pollution is fundamentally unavoidable because the waste water discharged from the pulping process contains strongly concentrated malodorous pollutants such as dimethyl disulfide (DMDS), dimethyl sulfide (DMS), methyl mercaptan (MM), and hydrogen sulfide (H_2S). The control of this malodorous pollution is the greatest factor in the high cost of environmental protection in pulp manufacturing.

Recently, these process effluents have been deodorized by steam or air stripping before biological waste water processing. Although the steam stripping method can completely remove the above-mentioned malodorous compounds, it consumes a large amount of energy (for the generation of the steam). On the other hand, the air-stripping method is more economical, but does not produce complete deodorization.

Biological waste water treatment is used to remove the biochemical oxygen demand (BOD) components from paper mill waste water. Anaerobic biological treatment is becoming widespread, especially in the treatment of strong waste water, such as the condensate of steam drainage. The waste steam condensates from a vacuum evaporator of pulping liquor and from a wood chip digester can be conveniently treated by a methane fermentation process. This is because such condensates have a high concentration of methanol, acetic acid, and other easily degradable compounds, a low concentration of suspended solids (SS), and a high temperature (45 to 70°C). Almost all malodorous pollutants are contained in these steam condensates.

In this chapter, we will discuss the capability and performance of anaerobic biological decomposition of sulfur-containing malodorous compounds in foul kraft steam condensates, as well as the methane fermentation associated with such decomposition. Through these discussions, an extremely effective and economical process for both BOD removal and odorous air pollution control will be defined.

II. FUNDAMENTAL PHENOMENA IN ANAEROBIC DECOMPOSITION OF MALODOROUS COMPOUNDS

The anaerobic mixed culture that was digesting steam drainage from a vacuum evaporator at a kraft paper mill was investigated to determine the capability for degrading sulfur-containing malodorous compounds. For this purpose, some batchwise experiments were performed. The results of these experiments are shown in Figure 1.

DMDS concentration decreased, MM concentration increased, and DMS concentration remained constant throughout the period of the batchwise experiment. Therefore, we conclude that the S-S linkage of DMDS is reductively split into MM according to the following equation:

$$CH_3S\text{–}SCH_3 + 2H \rightarrow 2(CH_3SH) \qquad (1)$$

The hydrogen donor in this reaction may be a coexisting organic compound such as methanol.

DMS (CH_3SCH_3) does not have an S-S linkage that can easily be split and the sulfur is saturated with methyl groups. In the anaerobic flora of thermophilic seed culture used in this experiment, there was no specific bacteria whose activity could split the S-CH_3 bond.

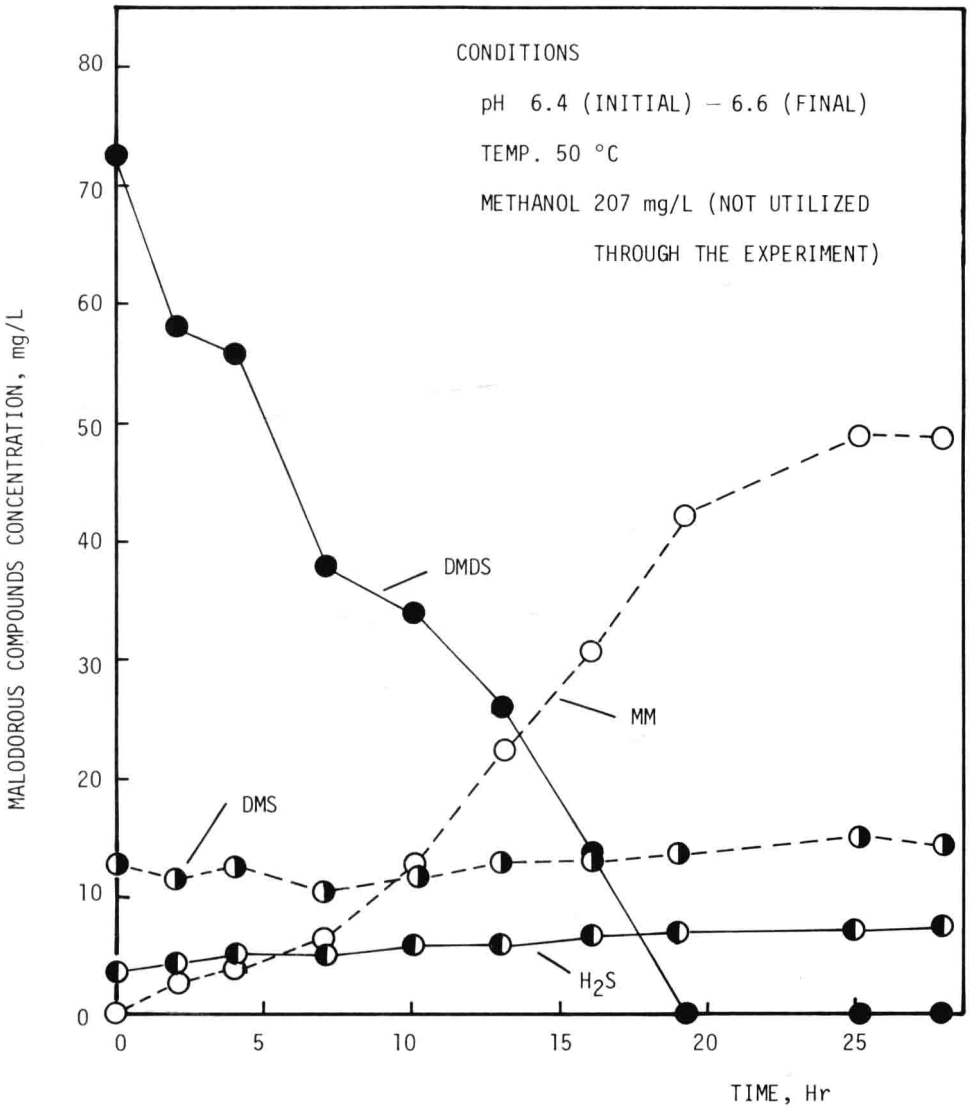

FIGURE 1. Batchwise decomposition of sulfur-containing malodorous compounds by anaerobic thermophilic mixed culture.

Despite the fact that a methane generation did not occur in the batch experiments, DMDS was sufficiently converted to MM. This result shows that the splitting of the S-S linkage is performed by nonmethanogenic bacteria.

III. ANAEROBIC BIOREACTOR FOR THE TREATMENT OF FOUL PULPING CONDENSATES

For the complete treatment of foul pulping condensates, both the removal of BOD and the removal of sulfur-containing malodorous compounds are required. If anaerobic treatment is to be adopted for these purposes, the simultaneous occurrence of methane fermentation is absolutely necessary. Therefore, an anaerobic bioreactor for treating foul pulping condensates must possess favorable conditions for methanogenic bacteria. Because the growth

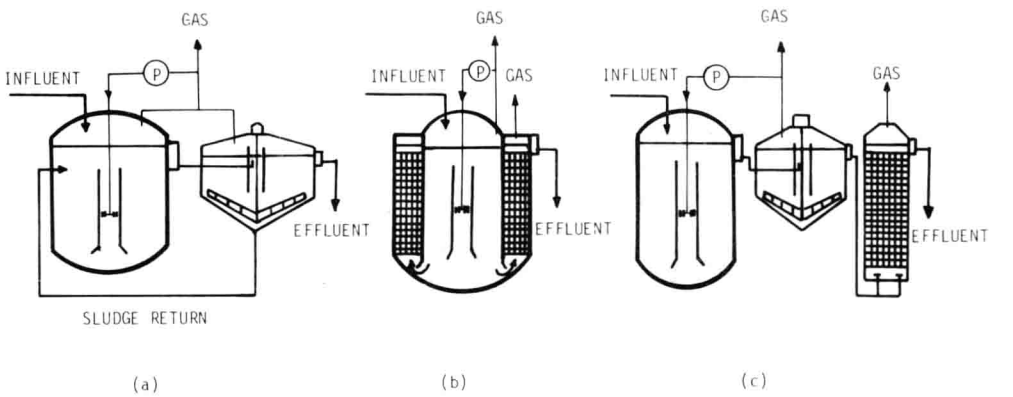

FIGURE 2. The schematic diagrams of anaerobic bioreactors adaptable for anaerobic deodorization and methane fermentation: (a) anaerobic contact process, (b) mixed reactor combined with filter methane fermenter, and (c) anaerobic contact process combined with filter methane fermenter.

rate of methanognic bacteria is so low, special steps must be taken to secure the biological solid retention time for these bacteria.

There are many types of reactors that can be applied to the methane fermentation of waste steam condensates that are discharged from paper mills. Although the plug-flow-type reactors (such as anaerobic filters and anaerobic fluidized bed reactors) perform methane fermentation better than completely mixed reactors, these plug-flow reactors are not as efficient at stripping hydrogen sulfide and other sulfur-containing malodorous compounds during fermentation. The removal of sulfides from the anaerobically fermented liquor of paper mill waste water is very important because such waste water usually contains strongly concentrated sulfur substances. These sulfur compounds are reduced to hydrogen sulfide in an anaerobic fermenter, but the highly concentrated sulfide inhibits the metabolism of methanogenic bacteria. The most effective method for stripping hydrogen sulfide in an anaerobic reactor is by gas sparging in the fermentation liquor (recirculation of produced gas).

The reactions having the function of plug-flow biofilm-type reactors described above are brought about by biomass attached to the surface of the support media. Unfortunately, the gas sparging has negative effects, such as tearing the microorganisms from the support surface. Therefore, for both the mixing of the fermentation liquor and the stripping of hydrogen sulfide by gas sparging, the completely mixed reactors are preferable to the plug-flow reactors. For these purposes, the anaerobic contact process is the most suitable mixed reactor because it has the capability to retain methanogenic bacteria higher than that of any other mixed reactor.

For the anaerobic treatment of foul pulping condensates, a completely closed system is required in order to prevent the escape of odorous pollutants. Therefore, a sealed sedimentation tank for biological sludge returning is preferable to an open tank sedimentor. A sealed sedimentation tank is also favorable for the sedimentation and return of anaerobic biological sludge, because the partial pressure of head space gases in such a sedimentation tank is nearly equal to the pressure in the fermentation tank. For this reason, the release of dissolved gases from the sedimentation tank is decreased and the turbulence that results from the evolution of gas in the sedimentation tank is depressed. A schematic diagram of the anaerobic contact process is shown in Figure 2a.

Other systems that include mixed reactors are also applicable to the treatment of foul pulping condensates. Examples of these combined processes are shown in Figure 2b and c. In these combined anaerobic reactors, the secondary reactor is used as the methane production reactor. The sulfur-containing compounds are decomposed and stripped into the head space

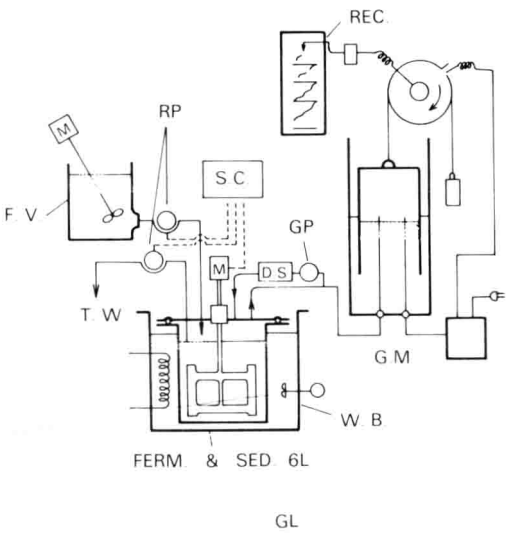

FIGURE 3. Experimental semibatch fermenter. (SC) Sequence controller, (RP) roller pump, (GP) gas pump, (GM) gas meter, (REC) recorder, (FV) feed vessel, (DS) desulfur system, (WB) water bath, and (TW) treated water.

gas of the first mixed reactor by gas recirculation and sparging. Consequently, the sulfide-free effluent flows into the secondary methane fermenter.

There are many types of methane fermenters which can be used in these combined systems. Because methanogenic bacteria have the property of attached growth on the surface of solids, an attached film type reactor (e.g., filter, expanded bed, or fluidized bed) is useful for the secondary methane fermentation.

IV. OPTIMAL CONDITIONS FOR THE ANAEROBIC BIOLOGICAL REMOVAL OF MALODOROUS COMPOUNDS IN KRAFT FOUL CONDENSATE

A. Experimental Apparatus, Materials, and Procedures

Figure 3 shows the bench-scale experimental apparatus used in this study. The anaerobic stirred fermenter was also used as a stationary sedimentation tank for the anaerobic biological sludge in a regular sequence. By the withdrawal of the fermenter supernatant after the settling period, sufficiently long biological solid retention time was maintained for the presence of methanogenic bacteria. The authors call this type of anaerobic fermenter the "semibatch anaerobic contact process".

In these experiments on the effects of residual sulfide, a H_2S scrubbing system with a continuous-feeding pump of the solution of mixture of sodium carbonate and ferrous sulfate or of the solution of sodium hydroxide was equipped in the outer circulation line of fermenter head space gas. In the experiment on the effect of pH, a monitoring and automatic controlling system of the pH of fermenter liquor was equipped.

The fermenter was initially seeded with the thermophilic sludge acclimatized to a synthetic substrate containing methanol as main organic component.

The kraft pulping foul condensates which were fed to the experimental fermenter were obtained from a storage tank of the mixture of steam blow condensate from a wood chip digester and of condensated steam drain from a evaporator of pulping black liquor. The nutrients added to this kraft foul condensate and the mean characteristics of the condensate fed to the fermenter are shown in Table 1.

Table 1
NUTRIENTS ADDED TO THE KRAFT PULPING STEAM DRAIN AND CHARACTERISTICS OF THE FEEDING DRAIN

Added nutrients		Average characteristics	
Nutrient	**Conc (mg/ℓ)**	**Item**	**Conc (mg/ℓ)**
Urea	23	SS	73
K_2HPO_4	13	Methanol	1480
$FeSO_4 \cdot 7H_2O$	16.7	BOD	2540
$MgCl_2 \cdot 6H_2O$	6.7	COD	4430
$CaCl_2 \cdot 2H_2O$	6.7	H_2S	3.2
$CoCl_2 \cdot 2H_2O$	0.17	MM	16.7
$MnCl_2 \cdot 4H_2O$	0.17	DMS	214
		DMDS	574

Table 2
TIME SEQUENCE AND OPERATIONAL CONDITIONS OF THE EXPERIMENTAL SEMIBATCH ANAEROBIC CONTACT SYSTEM

Operational time sequence		Digester operational conditions	
Operation	**Time (min)**	**Item**	
Feeding and mixing	5	Digester volume	6 ℓ
Digester mixing	30	HRT	1.0 day
Mixing stop and sludge sediment	20	Mechanical mixing degree	50 rpm
Withdrawal of supernatant	5	pH	6.5, 7.0, and 7.5
		Temp	45 and 50°C

The operational time sequence of the experimental semibatch anaerobic contact process is shown in Table 2. The other operational conditions of the fermentation system are also shown in Table 2.

B. Results

1. Effects of Hydrogen Sulfide Removal

An H_2S gas scrubbing process in the outer circulation line of fermenter head space gas can decrease the H_2S concentration dissolved in fermenter liquor. In this experiment, the conditions of temperature and pH were maintained at 45°C and 6.5, respectively.

The solution of 8% sodium hydroxide was more effective for the desulfurization than the solution of 20% sodium carbonate and 10% ferrous sulfate. The result shows that the desulfurization of anaerobic digesting liquor by 8% sodium hydroxide was effective not only for methane fermentation but also for removal of reduced sulfur (RS = bivalent sulfur) other than DMS. The average steady-state data obtained from this experiment are shown in Table 3.

The most abundant malodorous compound in the kraft pulping steam condensates used in this investigation was DMDS, although immediately after discharging from pulping process MM might be most abundant. From the result in the fundamental batch experiment and from the result in this experiment, DMDS was converted biologically to MM. The removal percentage of DMS was low in both cases of desulfurized fermentation and undesufurized fermentation. The reason for this is probably that DMS cannot be decomposed biologically, and that DMS may be removed physically by stripping into fermenter off-gas.

Table 3
STEADY-STATE DATA OBTAINED FROM EXPERIMENT ON EFFECTS OF DESULFURIZATION

	Not desulfurized		Desulfurized
	Influent	Effluent	Effluent
SS (mg/ℓ)	68	51	222
Methanol (mg/ℓ)	1440	1260	496
BOD (mg/ℓ)	2580	1830	1220
COD (mg/ℓ)	3950	3720	2230
H_2S (mg/ℓ)	2.3	46.2	0.4
MM (mg/ℓ)	12.5	115	Not detected
DMS (mg/ℓ)	101	59.5	42.1
DMDS (mg/ℓ)	418	78.7	3.9

2. Effects of Temperature

In this experiment, the solution of 8% sodium hydroxide was used for the scrubbing of fermenter head space gas. The removal performance of RS was almost the same as that obtained under 45°C, while the removal performance of BOD, COD, and methanol were markedly improved compared with those obtained under 45°C. Because the methane gas production increased to about twice that under 45°C, these improvements were caused by the temperature activation of methanogenic bacteria. The data obtained through experimental time source under temperature of 50°C and pH of 6.5 were shown in Figure 4.

The average data in the steady-state periods are summarized in Table 4. From the results on temperature effects, a temperature higher than 50°C is needed for the anaerobic treatment of kraft foul condensates.

3. Effects of pH

The pH value of the kraft foul condensates used in this study was high (9.5 to 10.5). In addition, the scrubbing of the fermenter head space gas removes not only H_2S but also carbon dioxide, so that the pH value of fermenter liquor rises to the unfavorable range if no control of pH is done. In this experiment, the solution of 6% hydrochloric acid was used for the control of fermenter liquor pH, and the temperature was 50°C.

The experimental data obtained from these experiments on pH effects are shown in Table 5 as the averages in the steady-state periods of the experiment. In the experiment under a pH of 7.0, the removal percentages of methanol and BOD decreased somewhat compared with that under pH of 6.5, while the removal of RS other than DMS was stable and perfect under a pH of 7.0. In the experiment under pH of 7.5, the removal percentage of methanol and BOD decreased. These results were probably induced by the increase of H_2S concentration in the fermenter liquor and the influence of pH on the microbial activity.

The removal performance of RS other than DMS was held high even under a pH of 7.5, in spite of the damage of methane fermentation. Therefore, it is considered also from these results in the continuous fermentation experiments that methanogenic bacteria are not involved in the decomposition of sulfur-containing malodorous compounds.

V. MAXIMUM LOADING RATE OF THE ANAEROBIC TREATMENT

A. Experimental Apparatus, Materials, and Procedure

The anaerobic contact process shown in Figure 2a was used to study the maximum loading rate. The anaerobic fermenter and biological sludge sedimentor were installed in a constant-

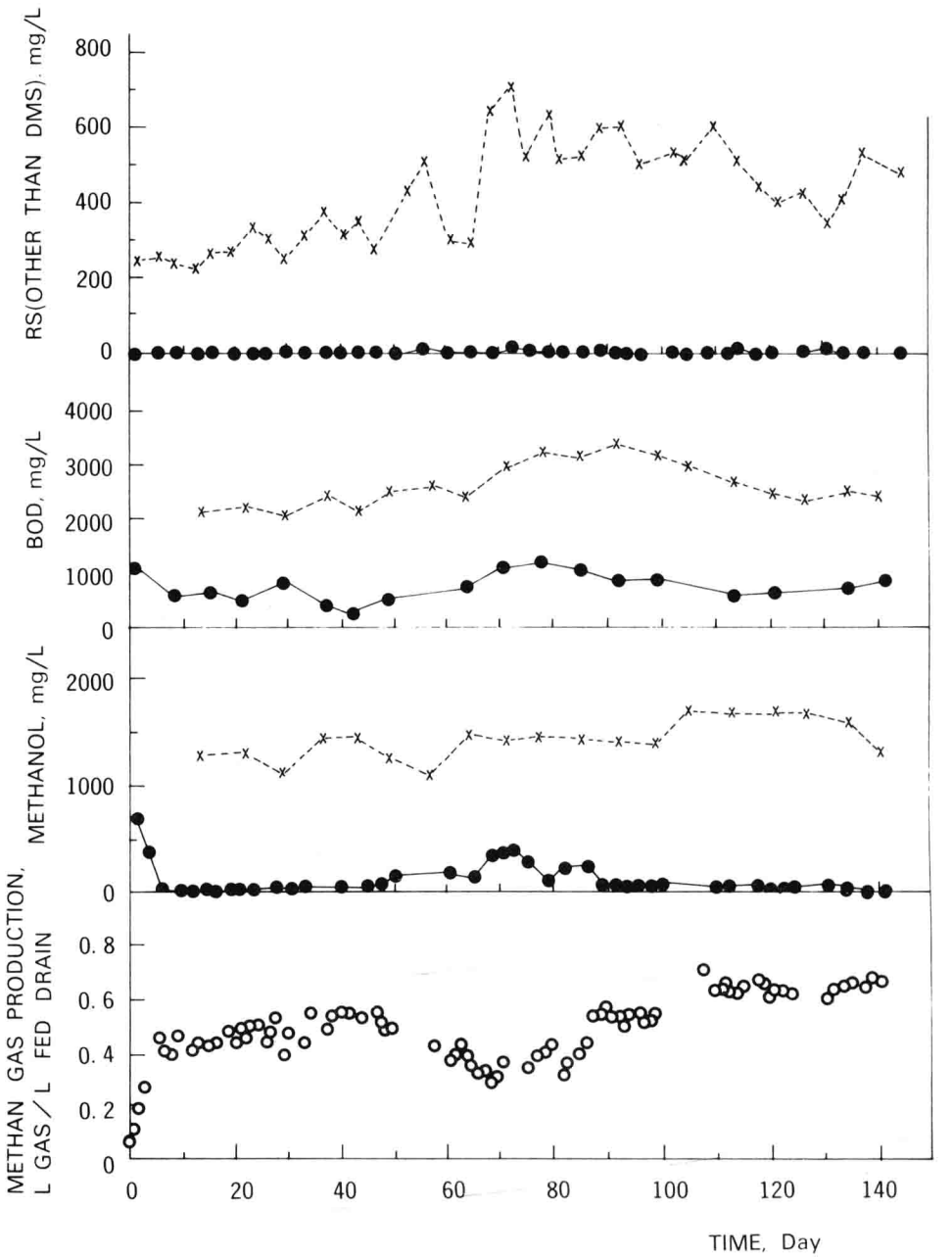

FIGURE 4. Experimental data under the conditions of 50°C and pH 6.5. (●) Effluent, (×) influent, and (○) methane gas production.

temperature bath and heated to 50°C. The fermentation liquor volume was 6 ℓ and the loading rate was controlled by the feeding rate (of raw foul kraft condensate). The liquid volume of sedimentor was set at 3 ℓ. The hydraulic retention time (HRT) was reduced from 24 to 8 hr during the course of the experiment.

The seed sludge was the same mixed fermentation liquor that was used previously in the experiment on optimal reaction conditions. The characteristics of the raw waste water and the added nutrients were nearly the same as those shown in Table 1. The analytical methods were also the same as those used in the previous experiment.[1]

Table 4
STEADY-STATE DATA OBTAINED FROM EXPERIMENTS UNDER 45 AND 50°C

	Temp			
	45°C		50°C	
	Influent	**Effluent**	**Influent**	**Effluent**
SS (mg/ℓ)	68	222	82	287
Methanol (mg/ℓ)	1440	496	1570	50
BOD (mg/ℓ)	2580	1220	2930	779
COD (mg/ℓ)	3950	2230	4970	2360
H_2S (mg/ℓ)	2.3	0.4	4.2	0.4
MM (mg/ℓ)	12.5	Not detected	25.1	0.03
DMS (mg/ℓ)	101	42.1	289	143
DMDS (mg/ℓ)	418	3.9	689	5.5

Table 5
STEADY-STATE DATA OBTAINED FROM EXPERIMENTS UNDER pH OF 6.5, 7.0, AND 7.5

	pH					
	6.5		7.0		7.5	
	Influent	**Effluent**	**Influent**	**Effluent**	**Influent**	**Effluent**
SS (mg/ℓ)	82	287	81	236	71	92
Methanol (mg/ℓ)	1570	50	1430	101	1420	1050
BOD (mg/ℓ)	2930	779	3220	909	2120	1580
COD (mg/ℓ)	4970	2360	5190	2830	4370	3470
H_2S (mg/ℓ)	4.2	0.4	3.0	1.5	3.1	7.6
MM (mg/ℓ)	25.1	0.03	17.7	0.1	12.5	0.1
DMS (mg/ℓ)	289	143	342	188	252	166
DMDS (mg/ℓ)	689	5.5	798	6.8	617	13.0

In this experiment, a solution of 8% sodium hydroxide was used for the H_2S scrubbing from the recirculating fermenter head space gas. The pH of the fermentation liquor was automatically controlled at 6.7 ± 0.2, using a solution of 8% hydrochloric acid automatically titrated by a pH controller.

B. Results

The results obtained during the experimental periods of steady-state are shown in Table 6 as average data. At a loading rate of about 5 kg/m^3/day as COD, the quality of effluent treated by this anaerobic contact process was nearly equal to that in the experiment with a semibatch anaerobic contact process operated under the same conditions (24-hr HRT, 6.5 pH, and 50°C temperature). Under these loading conditions, the removal percentages of COD and BOD were 61 and 74%, respectively. (These removal percentages were very stable throughout the period of the experiment.) H_2S, MM, and DMDS were totally removed by the experimental anaerobic contact process used in combination with the alkaline scrubbing process (recirculating fermenter head space gas).

The experimental data obtained under the COD loading conditions of 7.5 kg/m^3/day (16-hr HRT), 10 kg/m^3/day (12-hr HRT) and 15 kg/m^3/day (8-hr HRT) are shown in Figure 5. From these results, we conclude that the maximum loading rate of COD for the anaerobic treatment of foul kraft condensates is 10 kg/m^3/day. However, the allowable loading rate is