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Removal of Dichloromethane in Up-Flow Anaerobic Sludge Bed Reactors and Methane Production

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Chlorine has been successfully removed from chlorinated aliphatic compounds under anaerobic conditions. In this research, biological treatment of volatile organic compound (VOC) in high-flow anaerobic reactors was carried out. The resistance of micro-organisms was investigated in an upflow anaerobic sludge blanket reactor with an automated control system, using co-substrate additions, different ratios of organic matter, different hydraulic retention times, stable concentrations of chemical oxygen demand and volatile fatty acids and a range of factors such as pH, alkalinity and temperature (35 ºC) during the anaerobic treatment. Glucose, sodium sulphate, COD, calcium chloride, ammonium bicarbonate, potassium phosphate and methanol were used as co-substrates. The resulting removal rates for dichloromethane and chemical oxygen demand was 60 and 70 %, respectively. The dichloromethane decomposition ratio was 0.136 mg g VSS^{-1} d^{-1}. The highest methane ratio in the biogas was 64 %. Inhibition concentrations after 24 h were determined as IC_{50} = 42.6 and IC_{25} = 16.8.

Key Words: Wastewater treatment, Anaerobic treatment, Methane, Dichloromethane.

INTRODUCTION

Trihalomethanes are formed when cleaning solutions such as sodium hypochlorite enter the sewer system[1] and may react with organic matter and volatile organic compounds to produce compounds such as dichloromethane (DCM). All known volatile organic compounds (VOCs) are carcinogenic or teratogenic[2]. There is no known natural source for dichloromethane and since World War II, they have entered the environment as a result of anthropogenic processes[3].

The first dichloromethane dehalogenation was performed using *Hyphomicrobium* sp.[4]. This type of dehalogenation is specific to dihalomethanes, but other aerobic dichloromethane decomposer organisms were isolated and their dehalogenation

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efficiency is similar to that of dichloromethane[5]. The decomposition of dichloromethane under methanogenic conditions was reported in the literature[6,7]. Decomposition of dichloromethanes was also observed under denitrification conditions[8].

The up-flow anaerobic sludge blanket (UASB) process and its derivatives have provided excellent performance and stability in numerous full-scale operations worldwide[9]. However, there is still a need for simpler and more economical technologies for wastewater treatment by small and medium-sized industries[10]. Moreover, the loss of microbial biomass in the effluent due to excessive bed expansion or poor granulation (*e.g.*, during shock-load conditions) needs to be addressed for single-vessel reactors such as those used in the UASB process[11].

Dichloromethane can be used as a growth substrate in a methanogenic culture, but there is not enough information about dechlorination. Dichloromethane is reduced to CO_2, CH_4 and acetic acid after decomposition[6]. Blake[12] studied the transformation of three chlorinated aliphatic compounds (dichloromethane, chloroform and 1,1,1-trichloroethane) by microbial cultures in the presence of acetate. Vogel *et al.*[13] concluded that the greater the numbers of chlorine atoms were present, the more different compounds were produced.

The evaluation of interactions between primary and secondary substrates in anaerobic reactors fed with glucose and acetate has been studied by Zablon[14]. Dichloromethane, chloroform and 1,1,1-trichloroethane were used as secondary substrates by the microorganisms. Freedman and Gossett[6] have reported that dichloromethane was used as a growth substrate under methanogenic conditions. Some microorganisms that use dichloromethane as their carbon and energy source have been found in sewer wastes[15], in soils exposed to dichloromethane[16,17] and in pure cultures[4-18].

The calculated dichloromethane values are assumed to represent a pure decomposition rate and do not include any products. The decomposition rate for dichloromethane was approximately 0.305 mg g^{-1} VSS d^{-1}. Perchloroethylene (PCE) and dichloromethane decomposition rates were higher than those reported by Long *et al.*[19]. These authors explained differences in dichloromethane decomposition rates due to the biodegradation of carbon tetrachloride into dichloromethane. In addition, these authors used a higher dichloromethane concentration (120 µg L^{-1}) than we used in the present study (5 mg L^{-1}) and this may also explain the unexpectedly high concentration of dichloromethane found at the end of the experimental period.

Long *et al.*[19] reported a PCE decomposition rate of 30 µg DCM g^{-1} VSS d^{-1} and a dichloromethane decomposition rate of 20 µg DCM g^{-1} VSS d^{-1}. The calculated dichloromethane rates were assumed to represent a pure decomposition rate, excluding any products. In another study, 97 % of chloroform was removed and was decomposed to acetate and acetone[20].

Degradation of dichloromethane was studied by Hughes and Parkin[21], but the results differed from those in the present study.

Previous studies have shown that dichloromethane accumulated in mixed culture, but very low values (20 μg DCM g^{-1} VSS d) of dichloromethane were determined in fixed biofilm bioreactors[19]. Toxicity may result from the low g^{+} charge of carbon in dichloromethane and from low direct and indirect inhibition as in the literature[8].

In the present study, a UASB reactor with automatic controls (using a programmable logic controller PLC) was used to study the removal of dichloromethane from solutions with dichloromethane concentrations ranging between 5 and 50 mg L^{-1}. Methanol was used as the co-substrate at different chemical oxygen demand levels and hydraulic retention times (HRT) for a period of 300 days.

EXPERIMENTAL

The chemical compounds such as CH_2Cl_2, H_2SO_4, NaOH and petroleum ether used in this study were pure analytical-grade stocks (Merck, Darmstadt, Germany). Special spectrophotometric cuvettes were used for the determination of COD the details of which were given below.

A fully automated Brunswick Scientific Edison Bioflo IIc model upflow anaerobic sludge blanket (UASB) reactor was used in present study. The UASB reactor consisted of a circular feed system, gas-solid separators and a gas collection system. The reactor was constructed from a transparent sheet of acrylic glass with an inner diameter of 18 cm, an inner height of 33 cm and a volume of 8 L (Fig. 1). The internal temperature of the reactor was 35 °C. Methane was analyzed by using a Pac-Ex gas analyzer (Drager, Luebeck, Germany) and COD was analyzed by using a UV-visible light spectrophotometer (CADAS-200, Dr. Lange GMBH, Germany). Temperature and dissolved oxygen were measured using an Oxi 330/SET Oximeter (WTW, Weilheim, Germany). pH was analyzed by using a NEL 890 pH meter. Dichloromethane was analyzed by using a gas chromatograph (HP 5890 Series II GC, Hewlett Packard, Palo Alto, Calif.). Activated sludge removed from the reactor and placed in Petri dishes was photographed with an Olympus CX31 microscope.

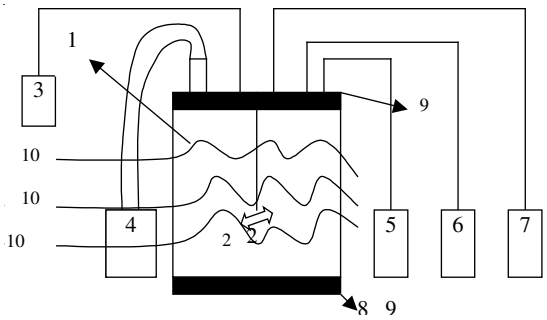


Fig. 1. Schematic appearance of UASB reactor. 1. Reactor; 2. Agitator; 3. Wastewater effluent; 4. Gas effluent; 5. Bas influent; 6. Biomass influent; 7. VOC influent; 8. Heater; 9. Cover plate, 10. Cooling systems

Dichloromethane analysis: Petroleum ether was used as an extraction solution for dichloromethane. Two mL of petroleum ether was added to 1 L of each sample in a round bottom flask and the solution was then shaken for 4 min. The flasks were kept for 1 min at room temperature so that the organic phase could be separated. The process was then repeated with 2 mL of petroleum ether in the water phase. Trichloroethylene was analyzed by using the HP 5890 series II GC with an HP-624 capillary column (i.d., 0.25 mm; length, 30 m; film thickness, 1.4 μm) and an electron capture detector. Extracted samples were injected into the sampling section (column) of the GC through a silicon septum using a hypodermic syringe. The injection volume varied between 0.2 and 0.5 μL. The pressure of the carrier gas (N_2) was 5 kg/cm^2 and the gas flow rate was 1.4 mL min^{-1}. The process temperature was 240 °C for the oven, 250 °C for the injector and 300 °C for detector. Measurement sensitivity is ± 0.001 μg L^{-1}.

Experimental set-up: The general setup of the UASB reactor is shown in Fig. 1. The operating conditions for the reactor were set up for volatile fatty acids[22]. Then the dissolved oxygen, pH, temperature, stirring speed, contact time and nutrient feeding were controlled by four pumps connected to the reactor feeding solutions from four different bottles. The medium inside the reactor was balanced by these pumps depending on the pH value recorded by probes.

A substrate solution equivalent to 3 g L^{-1} COD was prepared with the addition of 1.25 g L^{-1} methanol. The substrate mixture, the properties of which are given in Table-1, was supplied through the inlet port at a rate of 1.3 g L^{-1} and the COD/N/P was 300/5.0/1.0. Anaerobic granules taken from a chips-producing institution were used because our previous research had suggested that they would be a suitable source of microbial biomass.

TABLE-1
SUBSTRATE MIXTURE USED FOR THE INCUBATION IN THE UASB REACTOR AFTER[23]

Compound	Concentration (mg L^{-1})	Compound	Concentration (mg L^{-1})
CH_3COONa	1500-1600	$(NH_4)_2SO_4$	27.44
CH_3OH	220-500	NH_4Cl	128.1
CH_3COCH_3	150-335	$NaHCO_3$	1000-2000
K_2HPO_4	11.1	$CaCl_2.2H_2O$	293.5
KH_2PO_4	20.2	CH_2Cl_2	5-50

Reaction kinetics: Two categories of conditions were used throughout the study: high and low organic matter concentrations in the reactor. Table-2 shows that the high organic concentrations (3.5-5.6 g COD L^{-1} d^{-1}) were used for long HRTs (≥ 2 d) and the low organic concentrations (0.4 -2.0 g COD L^{-1} d^{-1}) were used for short HRTs (≥ 2 d).

In both cases, the change in the substrate concentration (S) with respect to time (t) can be defined as eqns. 1 and 2[24]:

TABLE-2
EXPERIMENTAL CONDITIONS FOR DICHLOROMETHANE (DCM)

Experiments runs	Day	OLR, (g COD/m^3d)	F/M rates (kg KOI/kg SS d)	HRT (day)	θ_C (day)	DCM load (mg/L d)
Run 1	0-5	0.62	0.19	3.50	31.0	5
Run 2	5-10	0.63	0.21	1.90	28.0	5
Run 3	10-15	0.91	0.23	1.90	26.0	5
Run 4	15-20	1.26	0.28	1.00	21.0	10
Run 5	20-25	1.04	0.31	0.50	19.0	10
Run 6	25-30	0.62	0.38	0.50	16.0	10
Run 7	30-35	0.70	0.47	0.50	13.0	20
Run 8	35-40	0.56	0.53	0.35	11.0	20
Run 9	40-45	0.55	0.53	0.35	11.0	20
Run 10	45-50	0.48	0.51	0.35	12.0	30
Run 11	50-55	0.63	0.54	0.25	11.0	30
Run 12	55-60	0.57	0.56	0.25	10.0	30
Run 13	0-15	0.63	0.61	0.39	10.7	40
Run 14	15-30	0.59	0.60	0.36	10.0	40
Run 15	30-50	0.59	0.63	0.38	9.5	40
Run 16	0-15	0.74	0.59	0.29	10.0	50
Run 17	15-30	0.81	0.55	0.25	11.0	50
Run 18	30-50	0.78	0.57	0.25	10.5	50

$$\frac{dS}{dt} = R = \frac{R_{max} \times S}{K_S + S} \quad (1)$$

where R = substrate utilization rate (mg L^{-1} h^{-1}); R_{max} = maximum substrate utilization rate (mg L^{-1} h^{-1}) and is equal to $k_{max} \cdot X$, where k_{max} = maximum specific substrate utilization rate (h^{-1}) and X = microbial biomass concentration (mg L^{-1}), S = co-substrate concentration (mg L^{-1}) and K_S is the half saturation concentration (mg L^{-1}). With integration and partial fractionation of eqn. 1 and by assuming that X is constant, S_0 = S at the time t = 0 and t_i = incubation period, then the following equation is obtained:

$$\ln \frac{S_0}{S_i} \times \frac{1}{t_i} = -\frac{1}{K_S} \times \frac{S_0 - S_i}{t_i} + \frac{R_{max}}{K_S} \quad (2)$$

where S_i refers to the elapsed time during the reaction. *Monod kinetics models* have been generally used in studies of dechlorination, biodegradation ratios, co-substrate and VOC removal[25]. The substrate removal ratio is commonly used in studies of batch reactors[26]. The following equation (eqn. 3), which is a general mass balance equation, has been derived by simplifying the Monod equation for lower substrate concentrations (VOC):

$$(Q_{in} \times C_{in}) - (Q_{out} \times C_{out}) - (Q_{outgas} \times C_{outgas}) - (r \times V) = 0 \quad (3)$$

where Q_{in} and Q_{out} represent the input and output flow rates (L d^{-1}), respectively; C_{in} = dichloromethane influent concentration (mg L^{-1}); C_{out} = dichloromethane effluent concentration (mg L^{-1}); Q_{outgas} = gas flow rate (L d^{-1}); C_{outgas} = dichloromethane

concentration in the headspace gas (mg L^{-1}); r = dichloromethane degradation rate (mg dichloromethane L^{-1} d^{-1}) and V = reactor volume (L).

The following equation[27,28] was used to determine the reaction velocity coefficients:

$$r = k \cdot X \cdot C \quad (4)$$

where k is the rate coefficient (L g volatile suspended $solid^{-1}$ d^{-1}), X = biomass concentration in the UASB reactor (20 g VSS L^{-1}) and C is the effluent TCE concentration (mg L^{-1}).

Statistical analysis: Statistical analysis were performed in Excel for Windows (Microsoft® Office Excel 2003, 11.8105.8107, SP2) at S.U. University computer Centre.

RESULTS AND DISCUSSION

In order to prepare a standard VOC curve, samples from the headspace gas above the solution in every reaction vessel were analyzed with GC. In addition, correlation coefficients (r^2) were determined for each curve to quantify the reliability of the results. The r^2 values for present results were all greater than 0.9.

Samples were taken from the incubation bottles when the biological activity was absent and injected into GC through a silicone septum for each sampling period. The average value of these injections (n = 0.3 μL) was used to determine the gas concentration in the reactor. The final dichloromethane values as a function of the initial dichloromethane load and COD are presented in Table 2. The COD removal rate was between 73 and 77 % in all experimental treatments. However, it was determined that the COD level in the effluent increased with an increasing initial load. This suggests that additional treatment will be necessary to lower the COD to environmentally acceptable levels if the initial load is high. The dichloromethane removal rate (%) increased slightly (by less than 4 % and in most cases, by only 1 or 2 %) when the incubation period was increased from 15-50 days. In addition to this, Table-2 shows that the dichloromethane removal rate for a given incubation period increased slightly as the initial dichloromethane load increased. dichloromethane and COD levels in the effluent and removal efficiency of both parameters as a function of the initial dichloromethane and COD load for up to 50 d experimental incubation period were shown in Table-3.

The mass of each VOC was determined in empty reaction vessels to reveal whether abiotic activity was present. The results are presented in Figs. 2-8. The average values of the reactor output for all levels of initial COD and dichloromethane loads are shown in Table-2.

Dichloromethane addition into the reactor was continued for a total of 50 days. Dichloromethane was determined as an intermediate product in the mixed dichloromethane experiments. Dichloromethane was permanent for longer period when compared with mixed VOCs studied in wastewater. Levels of dichloromethane biodegradation increased with time, despite the addition of new dichloromethane

TABLE-3
DCM AND COD LEVELS IN THE EFFLUENT AND REMOVAL EFFICIENCY OF BOTH PARAMETERS AS A FUNCTION OF THE INITIAL DICHLOROMETHANE AND COD LOAD FOR UP TO 50 DAYS EXPERIMENTAL INCUBATION PERIOD

Exp. runs	Initial DCM load (mg L^{-1})	Incubation period (d)	Mean DCM level in the effluent (mg L^{-1})	Mean DCM removal rate (%)	Initial COD load (mg L^{-1})	COD level in the effluent (mg L^{-1})	COD removal rate (%)
Run 1	5	0-15	2.12	57.6	1700	455	73.3
Run 2	5	15-30	2.10	58.0	2200	580	73.6
Run 3	5	30-50	1.99	61.2	2600	674	74.1
Run 4	10	0-15	3.54	64.6	2900	719	75.2
Run 5	10	15-30	3.46	65.4	3100	775	75.0
Run 6	10	30-50	3.41	65.9	3300	815	75.3
Run 7	20	0-15	6.96	65.2	5400	1306	75.8
Run 8	20	15-30	6.89	65.6	6200	1481	76.1
Run 9	20	30-50	6.82	66.1	7100	1689	76.2
Run 10	30	0-15	11.20	62.7	9000	2241	75.1
Run 11	30	15-30	10.60	64.7	9800	2410	75.4
Run 12	30	30-50	10.40	65.4	9800	2361	75.9
Run 13	40	0-15	13.40	66.5	9800	2224	77.3
Run 14	40	15-30	12.90	67.8	9800	2254	77.0
Run 15	40	30-50	12.70	68.3	9800	2214	77.4
Run 16	50	0-15	17.80	64.4	9800	2361	75.9
Run 17	50	15-30	16.60	66.8	9800	2342	76.1
Run 18	50	30-50	16.10	67.8	9800	2342	76.1

throughout the experiments. It cannot be determined how much dichloromethane was formed as a result of biological activity. dichloromethane was accumulated gradually in spite of dichloromethane removal. The best dichloromethane removal rate (68.3 %, Table-2) occurred with a dichloromethane load of 40 mg L^{-1} with a HRT of 6.9 h. The increases in the removal of dichloromethane and COD with increasing time suggest that increasing HRT from 50 days to 150 or 250 days would further improve the effectiveness of dichloromethane removal. However, such long HRTs are not suitable for operational use to treat wastewater and might be too expensive. Nonetheless, present results clearly show that the dichloromethane concentration decreased in the reactor since it was decomposed anaerobically. The average dichloromethane decomposition rate was calculated as 0.305 mg g^{-1} VSS.

Although all study conditions resulted in a net decrease in COD (Table-2), some measurements during the 50-d study period revealed that the output COD concentration was higher than the input COD concentration, possibly as a result of endogenous conditions within the reactor. COD decomposition was assumed to be 0 % when a negative COD decomposition was calculated. To determine the toxicity of the dichloromethane and COD loads, the proportional change in methane production as a function of COD load (Fig. 9) was plotted. The decrease of 60 % in

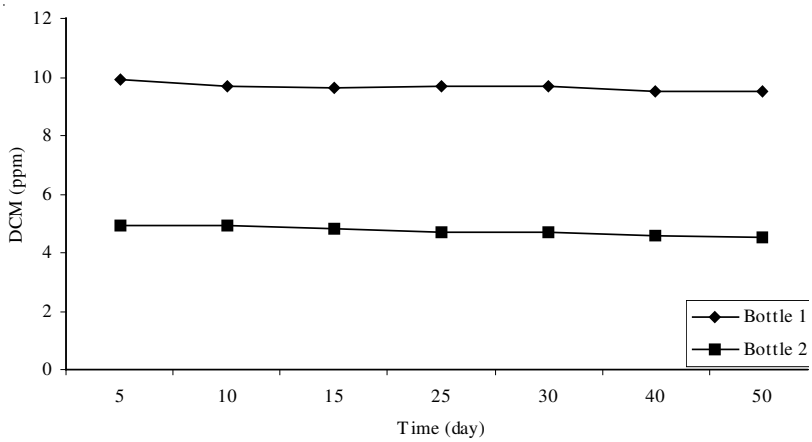


Fig. 2. Change of dichloromethane concentration in serum bottles not including microorganisms against to time

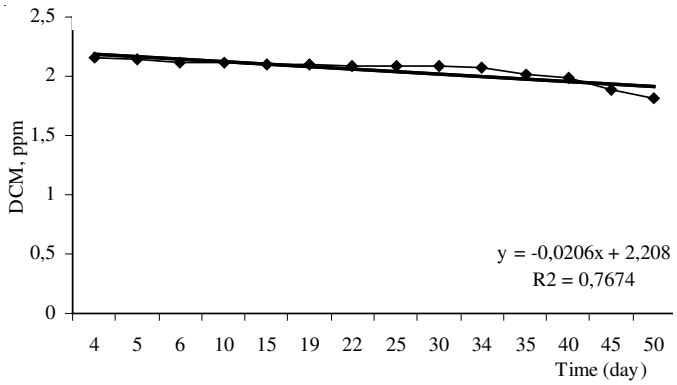


Fig. 3. Results of dichloromethane removal at continue feeding conditions with 5 mg/L DCM in up-flow anaerobic reactor (UASB) for 50 d incubation period

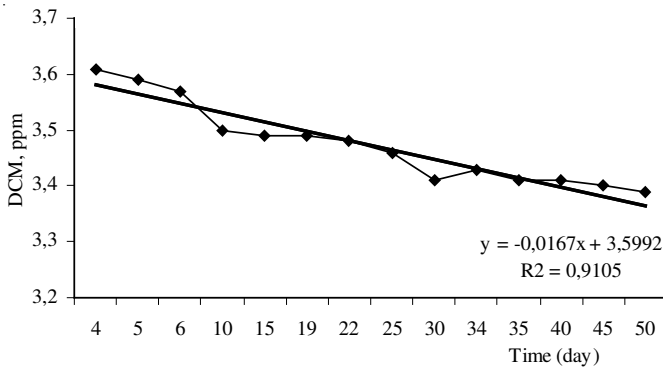


Fig. 4. Results of dichloromethane removal at continue feeding conditions with 10 mg/L DCM in up-flow anaerobic reactor (UASB) for 50 d incubation period

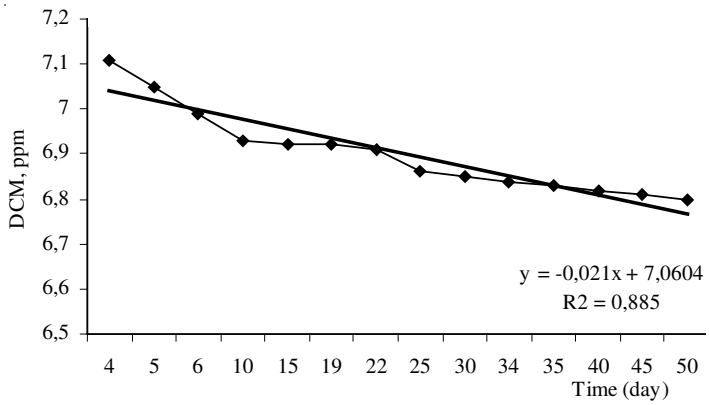


Fig. 5. Results of dichloromethane removal at continue feeding conditions with 20 mg/L DCM in up-flow anaerobic reactor (UASB) for 50 d incubation period

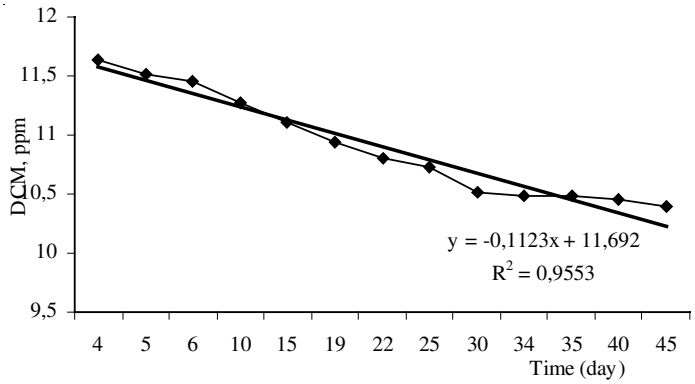


Fig. 6. Results of dichloromethane removal at continue feeding conditions with 30 mg/L DCM in up-flow anaerobic reactor (UASB) for 50 d incubation period

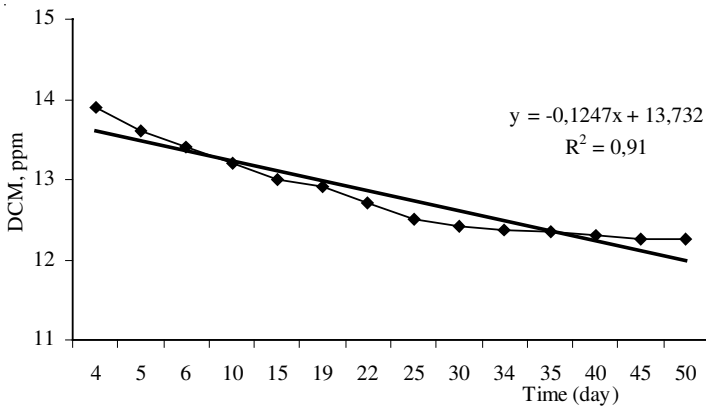


Fig. 7. Results of dichloromethane removal at continue feeding conditions with 40 mg/L DCM in up-flow anaerobic reactor (UASB) for 50 d incubation period

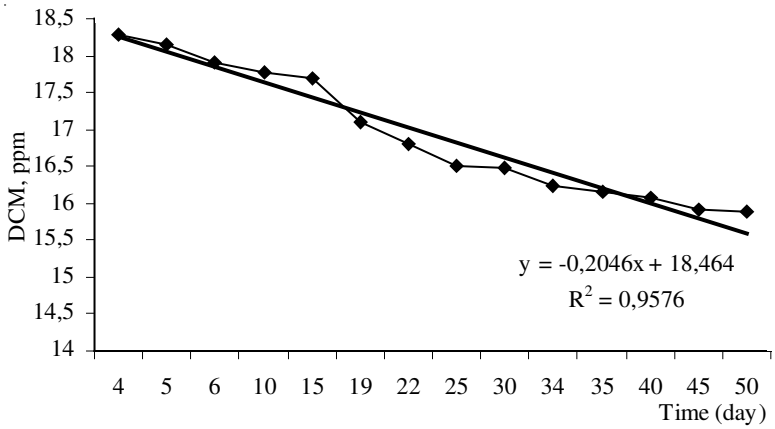


Fig. 8. Results of dichloromethane removal at continue feeding conditions with 50 mg/L DCM in up-flow anaerobic reactor (UASB) for 50 d incubation period

methane production as COD increased from 0-50 ppm indicates significant toxicity of dichloromethane at higher concentrations. Based on the data in Fig. 9, the dichloromethane inhibition concentrations were IC_{25} = 16.8 and IC_{50} = 42.6. This suggests that to maintain the efficiency of this bioremediation process at a level greater than 80 %, it may be necessary to dilute the wastewater until dichloromethane levels decrease less than 10 ppm. However, increasing the concentration of the microorganisms may mitigate this problem. As Fig. 10 shows, increasing the microbial biomass from *ca*. 1.8 unit (at which no methane was produced) to 17.5 unit produced a large increase in methane production. Photographs of the granular structure of the sludge and of the methanogenic stage of the sludge are shown in Fig. 11. The structure of the sludge granules was clearly well developed.

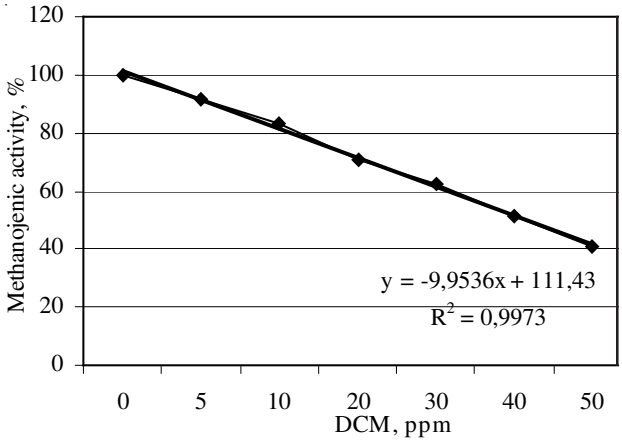


Fig. 9. IC_{50} and IC_{25} for dichloromethane (toxicity test results due to 25 % (IC_{25}) and 50 % (IC_{50}) decrease of methanogenic activity in response to CF dosage)

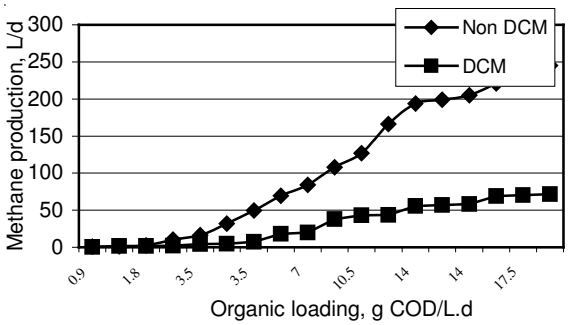
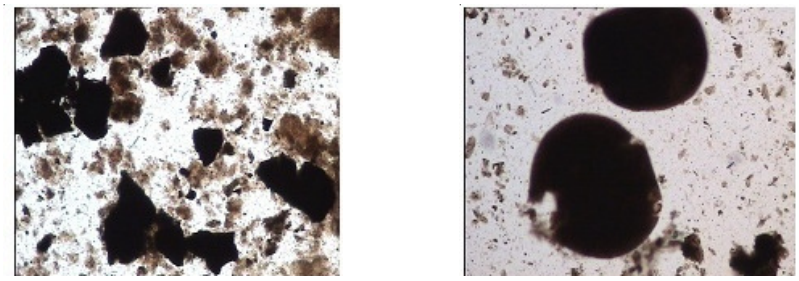


Fig. 10. Methane production for dichloromethane in response to various COD loading ratios (test results studied in bottles that became VOC (DCM) (■) and non-VOC (◆) with organic loading)



(a) (b)

Fig. 11. Photos of activated mud were taken from reactor for dichloromethane. (a) Granulated mud structure, (b) Mud structure at methanogenic stage (*Methanosargina*)

Mass equations were obtained in anaerobic reactors for every VOC and every experimental study. Under steady state conditions, UASB reactor is assumed as a well mixed continuous flow reactor. The following general mass balance equation is used:

$$Q_{input} \times C_{input} - Q_{output} \times C_{output} - Q_{gas\ out} \times C_{gas\ out} - r \times V = 0$$

where $Q_{input} = Q_{output}$ = flow rate (L d^{-1}), $Q_{gas\ out}$ = flow rate of gas (L d^{-1}), $C_{gas\ out}$ = VOC gas upper space concentration (mg L^{-1}), C_{input} = VOC inlet concentration and $C_{out\ put}$ = VOC outlet concentration (mg L^{-1}), V = volume of the reactor (L), r = VOC dedegradation rate (mg VOC L^{-1} d^{-1}).

For biological periods, Monod kinetics is generally used. In spite of this, Monod equation is simplified and the equation given above is formed for low substrate (VOC) concentrations. The reactor kinetics is assumed to follow first-order reaction of the equation. Moreover, this equation is used in order to calculate rate coefficients.

$$r = k \times C^{27}$$

where k = rate coefficient (L/gVSS.d), x = biomass concentration of UASB reactor (20 gVSS/L), c = VOC concentration of waste material (mg/L).

When output mass is lower than determination limit, waste concentration is assumed to be the determination limit for certain compounds. This corresponds to 0.1 mg L^{-1} liquid concentration for dichloromethane and 0.001 mg L^{-1} liquid concentration for PCE. Since determination limits are used as waste material concentrations, the obtained rate coefficients are minimum predictions. The rate coefficients calculated for this study are given in Table-4.

TABLE-4
RATE COEFFICIENTS FOR VOCS

Empirical stages	k_{TCE}, L/gVSS*d	k_{DCM}, L/gVSS*d	k_{PCE}, L/gVSS*d	k_{CF}, L/gVSS*d
1	1.064	0.202	–	4.537
2	2.152	0.241	13.319	9.075
3	2.571	0.250	18.450	13.336
4	1.843	0.546	7.392	8.523
5	3.836	1.100	18.233	20.187
6	4.117	1.122	16.279	27.194
7	4.667	1.090	20.208	13.819
8	9.798	2.211	–	27.769
9	10.176	2.224	–	33.147
10	12.611	2.922	–	42.110
11	13.172	3.183	–	–
12	13.533	3.280	–	–
13	14.804	4.594	–	–
14	15.166	4.855	–	–
15	15.322	5.015	–	–
16	19.146	5.276	–	–
17	19.436	5.868	–	–
18	19.746	6.141	–	–

Rate coefficients of biodegradation are solved by minimizing the sum of squares of observed and model predicted waste material mass flows. In Table-4, the given rate coefficients are calculated by using determination limit for every target VOC. Since determination limits are used, the coefficients should be evaluated as minimum values and it's difficult to evaluate the effects of HRT or OLR on these coefficients. It can be seen that PCE has a higher value of k than CF and TCE while dichloromethane has the lowest value of k. The reason for the lowest k value of dichloromethane is that high determination limits are used when compared with the ones used for PCE (0.1 mg L^{-1} for dichloromethane, 0.005 for TCE and CF, 0.001 mg L^{-1} for PCE).

It was determined that k values for all compounds increased at the final stages of this study. This is because the input concentrations for these studies were highly significant. Since waste material concentrations were assumed as determination limit concentrations, intra reactor concentration is the single variable in mass balance equation. For this reason, the value of k depends on intra reactor concentrations more and this leads to the formation of higher k values in the following stages. In

spite of this, since the calculated rate coefficients are the protected ones, it's proper to conclude that calculated high k values are the closest ones to the current k values.

IC_{25} and IC_{50} values for 6.7 mg L^{-1} were much higher than first addition of VOC concentrations. The values given in the Fig. 9 were calculated from the slopes of produced methanogenic activity against concentration data obtained during incubation period. Methane amounts and energy datum were calculated for a study at stable organic loading (Table-5).

TABLE-5
POSSIBLE ENERGY PRODUCTION FROM METHANE RELEASE MODELLED FOR 200 m^3 d^{-1} 30 mg L^{-1} VOC CONTAINING WASTEWATER INLET[29]

Organic loading (mg/L.d)	Methane production (m^3/d)	To formed electric energy (kW h)	To formed heat energy (Btu/day)
7	554.0	1606.6	18.7×10^6

Note 1: 1 m^3 methane = 2.9 kW h electricity energy[30], 2: 1 m^3 methane = 33.9×10^3 Btu m^{-3} [31].

With the 40 mg L^{-1} dichloromethane dosage, 68.3 % dichloromethane and 77.4 % COD removal were observed. HRT was 9.1 d^{-1} for dichloromethane treatment. Biogas production was 68.9 % and 4.207 L d^{-1}.

Dichloromethane decomposition is probably slower than the PCE decomposition in some experiments[32]. In the present study, a range of microorganisms was observed. Although methanol and acetate were used as an energy source in the present study, the same results could have been achieved using any suitable electron donor. dichloromethane appears to be less toxic for the microorganisms used in the present study that was the case for dichloromethane in the previous studies.

Conclusion

In this study, the dichloromethane concentration was higher (from 5 mg L^{-1} to a maximum of 50 mg L^{-1}). The reason for degradation of dichloromethane occurred within this wide range of loads is that the microbial culture used in present study was well-adapted to metabolize dichloromethane. Organic compounds with a low degree of chlorination were produced by reductive dechlorination of dichloromethane and sometimes these products contained no chlorine. Methane production was not inhibited even at dichloromethane concentrations were as high as 42.5 mg L^{-1}.

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