Methane Production from Anaerobic Treatment of Volatile Organic Compounds (VOC)

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ABSTRACT
Worldwide increasing energy problems guided to workers to find new and renewable energy sources. There are many new studies on energy investigation using different materials and technology. These studies were quite important for continuing development, comfortable life and industrial improvement. This investigation is considerable for removal of volatile organic compounds (VOC) frequently found in many wastewaters and methane production behind the wastewater treatment. The study performed in the up flow anaerobic condition sludge blanket (UASB) reactors. Used VOC’s are trichloroethylene, chloroform, dichloromethane and tetrachlorethylene. Removal ratio of these compounds were 87.8% trichloroethylene (TCE), 96.5% chloroform (CF), 67.1% dichloromethane (DCM) and 97.3% tetrachlorethylene (PCE). Methane ratios in the gas production were 67.1% for trichloroethylene (TCE), 72.4% for chloroform (CF), 69.6% dichloromethane (DCM) and 69.8% tetrachlorethylene (PCE).

Keywords: renewable energy, volatile organic compounds, methane production

I. INTRODUCTION
Many important environmental and health problems appeared with the improving technology and using new technological products. Trichloromethane (THM) compound formed with using chlorinated compounds for home cleaning materials and involving to the wastewater systems (Ozdemir and Dursun, 2004). Improving reactions may produce VOC compounds in aquatic system. All of the VOC’s are known that carcinogenic and teratogenic (Davidson et al., 1982). Removal of the VOC’s from the waters is important environmental problems. There are recently many biological VOC removal investigations in laboratory conditions.

Anaerobic granules are dense conglomerates that form in high-rate up-flow anaerobic reactors and well-developed granular sludge is necessary for optimal operation of high-rate anaerobic reactors (Hickey et al., 1991). Benefits include high liquid flows and gas up-flow rates due to high settling rates (Lettinga and Hulshoff Pol, 1991) and decreased fines generation due to higher strength compared to flocks.
The up-flow anaerobic sludge blanket (UASB) process and its derivatives have indicated excellent performance and stability in numerous full-scale operations worldwide (Lettinga, 1995). However, there is still a need for simpler and more economical technologies for wastewater treatment at small- and medium-sized industries (Hulshoff Pol et al., 1997). Moreover, loss of biomass with 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 the UASB process (Guiot et al., 1995). According to Lettinga et al. (1996), average surface speeds to the order of 0.5-0.7 m h\(^{-1}\) are more suitable for UASB reactors, contributing to the increase in the volume of the reactor. The UASB reactor operates with three distinct phases: a liquid phase (the residual water that was treated), a solid phase (the sludge or biomass present in the reactor) and a gas phase (constituted by the gases formed during the anaerobic digestion process, predominantly CO\(_2\) and CH\(_4\)). The gas formed, together with the upward effluent flow, strips with it particles of sludge to the top of the reactor (Claido et al., 2002).

Chlorine substitution causes natural compounds such as methane, ethane, ethylene, propane, benzene, or biphenyl to become recalcitrant to bio-degradation by microorganisms (Janssen et al., 1995).

Data are available include a) mid- to long-term dichloroethane (DCA) bioassays from different investigators (Daniel et al., 1993; Herren-Freund et al., 1987) with water concentrations ranging from 0.05 to 5 mg L\(^{-1}\) (considered as one data set); b) mid- to long-term TCA bioassays from different investigators (Daniel et al., 1993; Herren-Freund et al., 1987; Ferreira-Gonzalez et al., 1995) with water concentrations ranging from 0.05 to 5 mg L\(^{-1}\) (considered as one data set); c) two TCE bioassays with garage doses ranging from 1,000 to 2,400 mg kg\(^{-1}\) d\(^{-1}\) one TCE inhalation bioassay (Chen, 2000) with air concentrations ranging from 100 to 600 ppm; and d) an initiation—promotion (IP) study (Daniel et al., 1993) with ethylnitrouracil (ENU) as initiator and TCE, DCA, and TCA as promoters (considered as three data sets). Oxygen transfer is likely to limit aromatic hydrocarbon degradation rates. The model presents results that cast doubt on the practicality of using methane or propane for the co-metabolic destruction of trichloroethylene in a gas phase bioreactor (Hunt, 1995).

Methanogenic, acetogenic, and sulphate-reducing bacteria can be involved in the dechlorination process (Freedman and Gossett, 1989; Fetzner and Lingens, 1994; Sonier et al., 1994 and Cabirol, 1997). However, acetogens and methanogens are often not responsible for the degradation reactions in anaerobic PCE enrichment culture in batch conditions (Holliger and Schumacher, 1994; Maymo-Gatell et al., 1995).

When reductive chloroform dechlorination compared with other anaerobic condition, methanogenic condition is the most effective situation, because methanogenic conditions give minimum redox potential. Some scientists reported that Free F430 (Krone et al., 1989), and free and bounded vitamin B\(_{12}\) (Wood et al., 1968) may be able to dechlorinate to the chloroform by \textit{in vitro} reduction.

Fathepure and Boyd (1988) found some evidence on methanogens have ability reduction of PCE. These evidence were obtained from reduction of PCE by the pure culture of \textit{Methanosarcina mazei} at the 56 nmol L\(^{-1}\) w\(^{-1}\) average flow rate.
Most of the growth with addition of DCM as the single carbon source was originated by other than methanogenes. This situation shows that some of the DCM change to the CO₂ and others to acetate by non-methanogenes microorganisms. Methanogenes were responsible from the production of CH₄ of later products of DCM. (Wells, 1998). Methane production was higher in the acclimated mixed culture, revealing that there is enrichment in methanogens (Cabirol, 1998).

In this study, a synthetic wastewater was used for production of methane by removal DCM, TCE, CF and PCE in the aquatic environment in UASB reactor.

II. EXPERIMENTAL

a. Chemicals
The chlorinated organic compounds used in the study were PCE (Merck 98%), TCE (Merck 98%), CF (Merck 98%), DCM (Merck 98%), H₂SO₄ (Merck 99%), NaOH (65%) petroleum ether, kit for chemical oxygen demand (COD) and methanol.

b. Experimental apparatus
The UASB reactor consisted of a circular, feed system, gas solid separators and a gas collection system. The reactor was constructed from a transparent acrylic glass sheet with inner dimensions of 18 cm, height 33 cm 6 L in volume (Fig. 1). The reactor was maintained at room temperature. Internal temperature of reactor is 35°C. For methane analysis was used DRAGER Pac-Ex, COD analysis was used CADAS 200 (UV Visible spectrophotometer) and thermostat and DO analysis was used Oxi 330/SET, pH analysis was used NEL pH 890 and VOC analysis was used Hewlett Packard (5890 Series II). Photographs of sludge flocks were taken on the Olympus CX31 Model Microscope equipped with camera and recording system. Sludge samples were put in the Petri dishes and its pictures were taken in the Petri Dishes.

c. Voc analysis
Petroleum ether was used for extraction of THMs. Two ml of Petroleum ether was added on 1 L of each sample in the balloon flask separately and shaken for 4 min, then organic
phase was separated. Processes repeated with a second 2 ml of Petroleum ether on water phase. THM’s were analysed by a HP 5890 Series II gas chromatography with a capillary column (HP-624, i.d. 0.25 mm, 30 m, film thickness 1.4 µm) and using electron capture detector (ECD) and flame ionisation detector (FID). Extracted samples were injected to sampling room (column) of the GC by a silicone septum using a hypodermic syringe. The amount of injection was changing between 0.2-0.5 µL. Pressure of carrier N2 was 5 kg/cm2 and gas flow rate was 1.4 ml/min. Column was 0.25 mm (i.d.), 30 m length and 1.4 µm film thickness. Processes temperature was oven 240°C, injector 250°C and detector 300°C. Measurement sensitivity was 0.001 µm L⁻¹.

### Experimental Set-up
Experiments were run in the full-automated reactor system. An UASB reactor was set up with the modification of in-let and out-let on the reactor system. The reactor is a New Brunswick Scientific Edison production, Bioflo IIc model, a continue system fermentor. Schematic view of the UASB reactor is given in Figure 1. Temperature, pH, dissolved oxygen, flow rate and period settled for operating condition, and acid (H₂SO₄) alkali (NaOH) and nutrient pots connected to the 4 separate peristaltic pumps. These pumps run with the connected control sensors in the reactor until the sets conditions.

Incubation medium was constituted with 3000 mg COD L⁻¹ nutrient solution and methanol 1250 mg COD L⁻¹. Reactor was feed with COD:nitrogen:phosphor ratio 300:5:1 in the solution 1.3 g L⁻¹ in the incubation solution. Nutrient mixture was given in Table 1.

d. Experimental plan
Experimental designs were set in two categories as a high ending and a low ending. The high ending design was relatively high organic concentration (3.5-5.6 gCOD L⁻¹ g⁻¹) and high HRT (≥ 2 g). The low ending design was relatively low organic concentration (0.4-2.0 gCOD L⁻¹ g⁻¹) and high HRT (≤ 2 g). Experimental designs were planned to investigate two extreme points. VOC’s were included in the mixture media before addition into the reactor.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Concentration, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium acetate</td>
<td>1500–1600</td>
</tr>
<tr>
<td>Methanol</td>
<td>220–500</td>
</tr>
<tr>
<td>Acetone</td>
<td>150–335</td>
</tr>
<tr>
<td>K₂HPO₄</td>
<td>11.1</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>20.2</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>27.44</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>128.1</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>1000–2000</td>
</tr>
<tr>
<td>CaCl₂.2H₂O</td>
<td>293.5</td>
</tr>
</tbody>
</table>

**Table 1. Nutrient mixture in the reactor (from Prakash and Gupta, 2000)**
Table 2. Experimental work plans

<table>
<thead>
<tr>
<th>Experimental runs</th>
<th>1</th>
<th>2</th>
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<th>15</th>
<th>16</th>
<th>17</th>
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<tbody>
<tr>
<td>Reactor Volume, L</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
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<td>6</td>
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<tr>
<td>Flow, ml/min</td>
<td>1.7</td>
<td>2.2</td>
<td>2.6</td>
<td>2.9</td>
<td>3.3</td>
<td>3.3</td>
<td>5.4</td>
<td>6.2</td>
<td>7.8</td>
<td>9.0</td>
<td>9.8</td>
<td>9.8</td>
<td>9.8</td>
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<td>9.8</td>
<td>9.8</td>
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<td>9.8</td>
</tr>
<tr>
<td>Biomass, g L⁻¹</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
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<td>18</td>
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<tr>
<td>COD infl., g L⁻¹</td>
<td>0.9</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td>7.0</td>
<td>7.0</td>
<td>10.5</td>
<td>10.5</td>
<td>10.5</td>
<td>14.0</td>
<td>14.0</td>
<td>17.5</td>
<td>17.5</td>
<td>17.5</td>
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</tr>
</tbody>
</table>
Reactor operation conditions, waste flow rates, reactor volume, biomass and influent of COD rates are showed at the Table 2.

III. RESULTS AND DISCUSSION

Determination effect of VOC’s on the biomass, VOC containing incubation bottles were compared incubation bottles without VOC. The results total methane productions were given in the Figures 2-5.

Begging of the experiment, very low gas and methane production were appeared. While methane production increased at ideal conditions and with organic matter.
addition, COD is treated in reactor. Maximum methane production with DCM was found at stage 5 (68.9% and 4.207 L d\(^{-1}\)). However much higher COD removal was not found at this stage, but these working conditions were optimum conditions for the methanogenic bacteria for highest methane production. Figure 2 shows methane production against COD increase.

**Figure 4.** Total Methane production with different COD loading containing CF (■: with CF addition, ●: control)

**Figure 5.** Total methane production with different COD loading containing PCE (■: with PCE addition, ●: control)
The highest methane production with addition TCE was stage 6 (77.8% and 4.689 L d\(^{-1}\)). However much higher COD removal was not found at this stage, but these working conditions were optimum conditions for the methanogenic bacteria for highest methane production. Figure 3 shows methane production against COD increase. The maximum methane release in the fermenter with CF was stage 9 (80.3% and 23.622 L d\(^{-1}\)). However stage 9 was not maximum removal of COD conditions, but it could be were optimum conditions for the methanogenic bacteria growing in the media with CF. Figure 4 shows methane production against COD increase in the media including CF.

Stage 9 was the condition which was the maximum methane released in the fermenter with PCE (82.8% and 24.489 L d\(^{-1}\)). However stage 9 was not maximum removal of COD conditions, but it could be were optimum conditions for the methanogenic bacteria growing in the media with PCE. Figure 5 shows methane production against COD increase in the media including PCE.

C\(_{25}\) and IC\(_{50}\) values 6.7 mg L\(^{-1}\) were much higher than first addition of VOC concentrations. The values given in the Table 3 were calculated slopes produced from methanogenic activity against concentration for data obtained during incubation period. Methane amounts and energy datum were calculated for a study at stable organic loading (Table 4).

### IV. CONCLUSION

Main comment might be obtained from the above data shows that there is an inhibition with addition of VOC’s on methanogenic activity of biomass. There were delays for addition of VOC with comparison with the control. An inhibition was clearly seen with the addition of all VOC comparing with the controls, and the might show toxicity of VOC’s on the methanogenic micro organisms. From the resent results, it is difficult the select the most toxic one in four VOC compounds investigated in this study.

Furthermore, methane conversion and the yield observed in this study were also comparable to the corresponding data, i.e., 94% and 0.055 g VSSyg COD, respectively, reported in a recent study on the UASB treatment of format in wastewater (Chui et al., 1994).

The methane content of the biogas was 60–68% throughout the study after reaching steady-state conditions at high COD and CT loadings. About 96% of the total COD removed, was converted to methane, 0.024 g of TSS was yielded for each gram of

<table>
<thead>
<tr>
<th>VOC</th>
<th>IC(_{50})</th>
<th>IC(_{25})</th>
<th>Inhibition period, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCM</td>
<td>42.6</td>
<td>16.8</td>
<td>24</td>
</tr>
<tr>
<td>TCE</td>
<td>31.1</td>
<td>9.9</td>
<td>24</td>
</tr>
<tr>
<td>CF</td>
<td>27.8</td>
<td>7.4</td>
<td>24</td>
</tr>
<tr>
<td>PCE</td>
<td>24.9</td>
<td>6.7</td>
<td>24</td>
</tr>
</tbody>
</table>
COD removed at the end of 230 days of operation period (Sponza, 2002). Of all the COD removed (at the treatment of TCE), an average of 90% was converted to methane, judging from the slope (Sponza, 2003). The trichloroethylene (TCE) was formed on dehalogenation of PCE. Under steady state operation conditions the COD removal of 94.2% and biogas production of $0.559 \pm 0.508 \text{ m}^3/\text{kg COD}$ with methane content of 64.2% was achieved (Prakash and Gupta, 2000). The slope gives an indication of the methane yields, which were 0.23, 0.25, and 0.18 l CH$_4$ g$^{-1}$ COD fed for AMBR, UASB, and ASBR systems, respectively. COD removals were 69.0% for the AMBR, compared with 70.9 and 57.1% for the UASB reactor and ASBR, respectively (Angenent and Sung, 2001). Organic loading rate (OLR): $4.3 \text{ kg COD} \text{m}^{-3} \text{d}^{-1}$, hydraulic retention time: 12 h, superficial velocity: 1 m/h, average biogas productivity: 290L CH$_4$/kg COD fed, biogas composition: 70% ± 75% methane and a COD removal percentage >75% (Araya et al., 1999).

In present study 90.0% TCE and 81.5% COD removal obtained with 20 mg L$^{-1}$ TCE added incubation media. Hydraulic Retention Time (HRT) was found 8.4 h for the TCE treatment. Biogas production was 77.8% and 4.689 L d$^{-1}$. With the 40 mg/L DCM dosage, 68.3% DCM and 77.4% COD removal were appeared. HRT was 9.1 d$^{-1}$ for DCM treatment. Biogas production was 68.9% and 4.207 L d$^{-1}$. Addition of the CF was 10 mg L$^{-1}$ and removal of CF and COD were 97.9% and 94.9%. CF removal HRT was about 12 h. Biogas production was 80.3% and 23.622 L d$^{-1}$. HRT was 13.5 h with 30 mg L PCE dosage, and 98.5% PCE and 97.9 COD removal were obtained. Biogas production was 82.8% and 24.489 L d$^{-1}$.

Electricity and heating requirement of wastewater treatment plant could be provided by the methane production from anaerobic treatment of VOC containing wastewater.

**Acknowledgement**

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**References**


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**Table 4. Possible energy production from methane release modelled for 200 m$^3$ d$^{-1}$ 30 mg L$^{-1}$ VOC containing wastewater inlet**

<table>
<thead>
<tr>
<th></th>
<th>DCM</th>
<th>TCE</th>
<th>CF</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic loading, mg/L.d</td>
<td>554.0</td>
<td>550.6</td>
<td>656.1</td>
<td>680.2</td>
</tr>
<tr>
<td>Methane Production, m$^3$/d</td>
<td>1606.6</td>
<td>1596.7</td>
<td>1902.6</td>
<td>1972.5</td>
</tr>
<tr>
<td>To formed electric energy, kW.h</td>
<td>$18.7 \times 10^4$</td>
<td>$18.6 \times 10^4$</td>
<td>$22.4 \times 10^4$</td>
<td>$23.0 \times 10^4$</td>
</tr>
<tr>
<td>To formed heat energy, Btu/day</td>
<td>$18.7 \times 10^6$</td>
<td>$18.6 \times 10^6$</td>
<td>$22.4 \times 10^6$</td>
<td>$23.0 \times 10^6$</td>
</tr>
</tbody>
</table>

Note 1: 1 m$^3$ methane = 2.9 kW.h electricity energy (Öztürk, 1999).

Note 2: 1 m$^3$ methane = $33.9 \times 10^3$ Btu m$^{-3}$ (Kargı, 1995).


