Removal of tetrachloroethylene (PCE) in up flow anaerobic sludge blanket reactors (UASB)

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Abstract

Low concentration of chlorinated aliphatic compounds may be found in wastewater and contaminated soils from different industrial sources and in the air arisen from these sources. Low levels of Volatile Organic Compounds (VOC)'s could be removed by adsorption, incineration and biofiltration methods. These methods have some disadvantages with low removal efficiency or high operation cost. Chlorine has been removed from the chlorinated aliphatic compounds by anaerobic conditions.

The aim of this research was investigation of biological treatment of VOC's in high flow speed reactors. Resistance capacity of micro-organisms was investigated in an upflow anaerobic sludge blanket reactors (UASB) designed automate control system by feeding with addition co-substrate, by loading different ratio of organic matter, hydraulic retention time (HRT), at stable condition of COD, Volatile Faty Acids (VFA), pH, alkalinity, temperature (35C^{o}) etc. during the anaerobic treatment. Glucose, sodium sulphate, calcium chloride, ammonium bicarbonate, potassium phosphate and methanol were used as the co-substrates. In this studies the removal of PCE was approximately 97,5 % respectively. The decomposition ratios were calculated for PCE as 0,136 mg /gVSS.d respectively. The highest methane ratio in the obtained biogas was 68,3 % for CF. Also inhibition concentrations (IC) in 24 hour were determinated as IC_{50}; 24,9 and IC_{25}; 6,7.

Key Words: Wastewater, CF, UASB, anaerobic treatment, COD, methane,

Introduction

Chlorine used for water disinfection and used domestic disinfection has strong oxidise effect. Furthermore, chlorine and chloramines give a number of substation reactions. (Ozdemir & Dursun, 2004; Ozdemir, 2005). Most important by-product is trihalomethanes (THM) after chlor disinfection (Montgomery, 1985). All of the VOCs are known that carcinogenic and teratogenic (Davidson *et a*l., 1982; Ensley, 1991). PCE/trichloroethylene (TCE) dechlorination has been observed in anaerobic sediments Parsons *et al*., 1984), soil (Kleopfer *et al*., 1985), anaerobic

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attached-film expanded-bed (Narayanan *et al*., 1993; Chu & Jewell, 1994), anaerobic enrichment cultures (DiStefano *et al*., 1991) and in specific cultures (Fathepure *et al*, 1987).

Freedman and Gossett (1989) showed the biological reductive dechlorination of PCE under methanogenic conditions. There are various microbial groups including methanogenes, sulphate bacteria and nitrate removing bacteria that have dechlorination capacity for PCE under anaerobic conditions (Chu & Jewell, 1994). PCE alternately turns into TCE, DCE, VC and CO_2 (Parson et al., 1984). Fathepure and Boyd (1988) examined the role of methanogenes in reductive dechlorination of PCE with anaerobic muds taken from 4 different waste water purification facilities in Central Michigan. Fathepure *et al*. (1987) determined the specific anaerobic bacteria that were successful in dechlorination of PCE. In the collective tests performed by De Bruin *et al*. (1992), the complete transformation of PCE into ethylene was observed and the biomass taken from an anaerobic column was used as graft. Butyric acid, ethanol, lactic acid and propionic acid were considered as electron transmitters related with PCE's reductive dechlorination (Fennal & Gosset, 1997). Vogel and McCarty (1985) investigated the PCE response in anaerobic flow reactors. The utilization of anaerobic consecutive collective biofilm reactors was researched by Hirl and Irvin (1997) to examine the reductive dechlorination of PCE. Hallinger *et al*. (1993) isolated an anaerobic bacterium named as PER-K_{23} and taken from an anaerobic bed column in which PCE experiences reductive dechlorination into TCE, cis-1, 2-DCE, VC and ethylene.

An upstream anaerobic UASB reactor was used by Christiansen *et al*. (1997) in order to investigate the dynamic transformation of PCE. The upflow 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).

In this study a PLC controlled UASB reactor was used and studied for removal of PCE (between 5-50 mg L^{-1}). Methanol was used as the co-substrate, with different COD feedings and HRT was studied for 300 days.

Experimental

Chemicals

The chlorinated organic and other chemical compounds used in this study were from the pure stocks of PCE, H_2SO_4, NaOH, petroleum ether, and spectroscopic kits were used for chemical

oxygen demand (COD) and methanol. All chemicals (from E. Merck, Darmstadt, Germany) were of analytical reagent grade.

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 diameter 18 cm, height 33 cm, 6 L in volume (Fig. 1). The reactor was maintained at room temperature. The internal temperature of the reactor was 35^{o}C'dir. For methane analysis a DRAGER Pac-Ex was used, for COD analysis a CADAS 200 (UV Visible spectrophotometer), for thermostat and dissolved oxygen analysis an Oxi 330/SET for pH analysis an NEL pH 890, and for PCE analysis a Hewlett Packard (5890 Series II).

The mud flocks were photographed with a microscope having the brand name of Olympus CX31 and donated with photographing and recording systems. The photographs of the mud samples taken from the reactor were taken by placing them inside Petri containers.

CF analysis

Petroleum ether was used as an extraction solution for the PCE. Two ml of petroleum ether was added in 1 L of each sample in the balloon flask separately and shaken for 4 min, then, the organic phase was separated. The processes were repeated with a second 2 ml of petroleum ether in the water phase. Trichloroethylene was analysed by a HP 5890 Series II gas chromatography supported with a capillary column (HP-624, i.d. 0.25 mm length, 30 m, film thickness 1.4 μm) and using an electron capture detector (ECD. Extracted samples were injected into the sampling section (column) of the GC through the silicone septum using a hypodermic syringe. The amount of injection varied between 0.2-0.5 μL. The pressure of the carrier N_2 was 5 kg $(cm^2)^{-1}$ and the gas flow rate was 1.4 ml min^{-1}. The processes temperature was 240 °C for the oven, 250 °C for the injector and 300 °C for detector. Measurement sensitivity was 0.001 μm L^{-1}.

Experimental set-up

A fully automated Brunswick Scientific Edison Bioflo IIc model upflow anaerobic sludge blanket (UASB) reactor was used in our study. The general appearance of the UASB reactor is shown in Figure 1. For the operating conditions the reactor was set up for VFA (Anderson and Yang, 1992), dissolved oxygen, pH, temperature, stirring speed, contact time and nutrient feeding supported by four pumps connected to the reactor. These pumps balance the medium inside the reactor depending on the pH value recorded by probes.

A substrate solution equivalent to 3 g COD per litre was prepared with the addition of 1.25 g methanol L^{-1}. The substrate mixture in Table 1 was given to inlet port 1.3 g L^{-1} ratios and COD, N and P ratio were 300, 5.0 and 1.0 respectively.

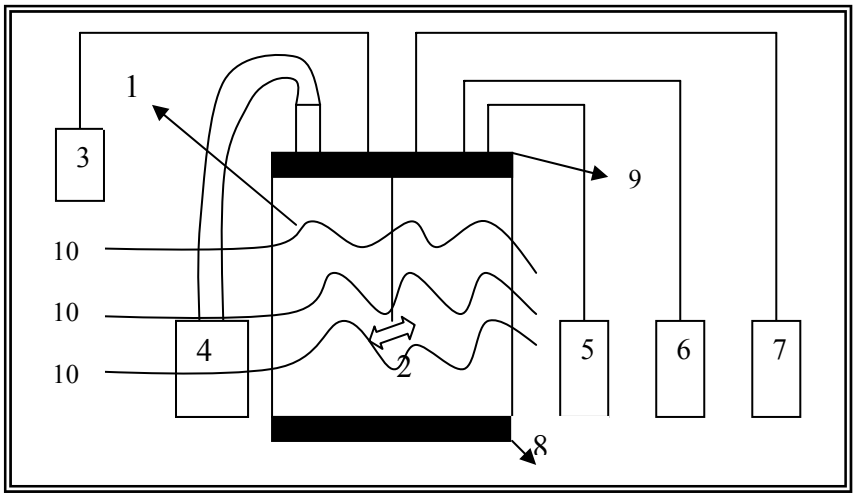

Figure 1. Schematic appearance of UASB reactor. 1. Reactor; 2. Agitator; 3. Wastewater effluent; 4. Gas effluent; 5. Bas influent; 6. Biomass influent; 7. VOC influent; 8. Heater; 9. Cover plate, 10. Cooling systems.

Table 1. The Substrate mixture content of the incubation solution in the UASB rector [Prakash & Gupta, 2000].

Compounds	**Concentration, mg L-1**	**Compounds**	**Concentration, mg L^{-1}**
Sodium acetate	1500-1600	$(NH_4)_2SO_4$	27,44
Methanol	220-500	NH_4Cl	128,1
Acetone	150-335	$NaHCO_3$	1000-2000
K_2HPO_4	11,1	$CaCl_2.2H_2O$	293,5
KH_2PO_4	20,2	CF	5-50

Experimental kinetics

The experimental studies were divided into two categories: high end and low end. High end operations were defined by relatively high organic inner-reactor concentrations (3-5.6 g COD L^{-1} d^{-1}) and long HRTs (≥ 2 d). Low end operations were defined with low organic inner-reactor concentrations (0.4-2.0 g COD $L^{-1}d^{-1}$) and short HRTs (≤ 2 d).

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

with integration and partial fractionation of Eq.(1), and assumptions that X is constant, R_{max} is equal to $k_{max}X$ and $S=S_0$ at $t_0=0$ (Equation 2):

$$In\frac{S_0}{S_i}*\frac{1}{t_i} = -\frac{1}{K_S}*\frac{S_0 - S_i}{t_i}+\frac{R_{max}}{K_S} \qquad (2)$$

where R, substrate utilization rate (mg L^{-1} h^{-1}); $R_{max,}$ (k_{max} .X) maximum substrate removal rate (mg L^{-1} h^{-1}); k_{max}, maximum specific substrate utilization rate (1 h^{-1}); X, biomass concentration (mg L^{-1}); S, co-substrate concentration (mg L^{-1}); $K_{S,}$ half saturation concentration (mg L^{-1}).

Monode kinetic models have been generally used in studies about dechlorination/biodegradation ratios and co-substrate / VOC removal (Chang et al., 2001). Using Monode kinetic models, the substrate removal ratio is commonly used in batch reactors (Grady et al., 1999). The following equation has been derived by simplifying the Monode equation in lower substrate concentrations (VOC). The general mass balance equation in the following was used.

$$Q_{in} * C_{in} - Q_{out} * C_{out} - Q_{outgase} * C_{outgase} - r * V = 0 \qquad (3)$$

where $Q_{in} = Q_{out,}$ flow rate (L d^{-1}); $Q_{outgase}$, gas flow rate (L d^{-1}); $C_{outgase}$, CF gas headspace concentration (mg L^{-1}); $C_{in,}$ CF influent concentration (mg L^{-1}); C_{out} = CF effluent concentration (mg L^{-1}); V, reactor volume (L); r, CF degredation rate (mg CF L^{-1} d^{-1}).

The following equation was used to determine the velocity coefficients.

$$r = k \times C \qquad \text{(Brock, 1991; Hinchee et al., 1991)} \qquad (4)$$

where k, the rate coefficient (L g VSS^{-1} d^{-1}); X, biomass concentration in UASB reactor (20 g VSS L^{-1}); C, effluent CF concentration (mg L^{-1}).

Results and Discussion

For prepare of standard PCE curve, samples were analysis with GC from up blank of every serum bottle. Correlation coefficients (r^2) were determined for each curve and investigated the reliability of results. According to results r^2 values obtained over 0.956 for PCE curves.

Samples were token out when the biological activity was absent and injected to the GC for each sampling period. The average value of these injections was obtained and used to determine of reactor concentration according to serum tests determined before. Each of VOC's mass was determined at the empty serum bottles for determined of abiotic activity was present or not. The

results of empty serum bottles were present in Figure 2. Different PCE mass of 5 and 10 mg/L were added to the empty serum bottles.

Table 2. Mass input-outputs and % efficiencies obtained in PCE dosing

	Time, day	PCE Influent, mg/l	Avr. PCE Effluent, mg/l	Avr. PCE Removal, %	COD Inluent, mg/l	COD Effluent, mg/l	COD Removal, %
Run 1	0-15	5	0.19	96.2	1700	91.6	94.7
Run 2	15-30	5	0.16	96.8	2200	110.3	95.0
Run 3	30-50	5	0.11	97.8	2600	127.1	95.2
Run 4	0-15	10	0.34	96.6	2900	141.8	95.2
Run 5	15-30	10	0.28	97.2	3100	156.7	95.0
Run 6	30-50	10	0.21	97.9	3300	163.8	94.9
Run 7	0-15	20	0.81	96.0	5400	284.4	94.8
Run 8	15-30	20	0.72	96.4	6200	302.3	95.2
Run 9	30-50	20	0.68	96.6	7100	372.9	94.8
Run 10	0-15	30	1.12	96.3	9000	434.2	95.2
Run 11	15-30	30	1.01	96.7	9800	462.1	95.3
Run 12	30-50	30	0.93	96.9	9800	468.9	95.3
Run 13	0-15	40	1.35	96.3	9800	460.7	95.3
Run 14	15-30	40	1.23	97.0	9800	453.3	95.4
Run 15	30-50	40	1.18	97.1	9800	461.8	95.3
Run 16	0-15	50	1.82	96.4	9800	449.1	95.5
Run 17	15-30	50	1.64	96.8	9800	443.8	95.5
Run 18	30-50	50	1.55	96.9	9800	436.3	95.6

The calm situation between 1-18 for COD and PCE was showed in Table 2. Average values of reactor output between 1^{st} -18^{th} experiments were given in Table 2 for COD and PCE. In the experiment each day during 18 day sludge sample and a waste water sample were taken from reactor and analysed with GC. GC analysing of these samples were given in Table 1 as average values. Average values which given in Table 2, current for each study stage. The given average values are valid for each working stage. In the performed study, PCE was kept in a serum bottle for 50-day period in which no physical and biological facts occur. The PCE analyses carried out in intermediate periods indicated that the removal of PCE with this way was not important (Figure 2).

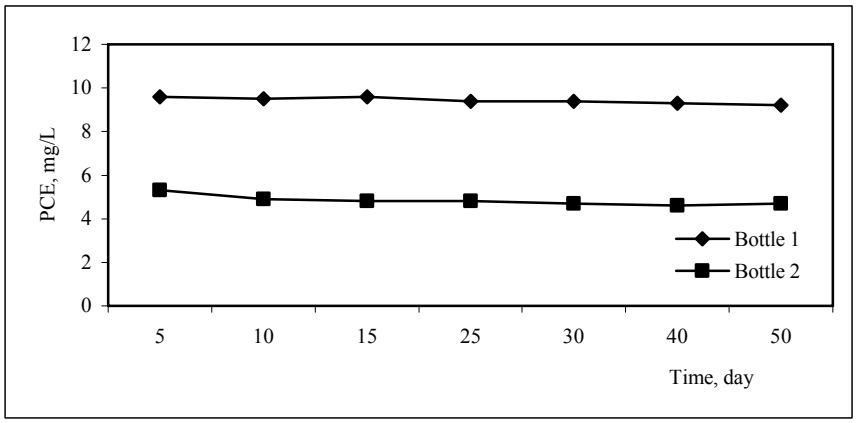

Figure 2. Change of PCE concentration in serum bottles not including microorganisms against to time.

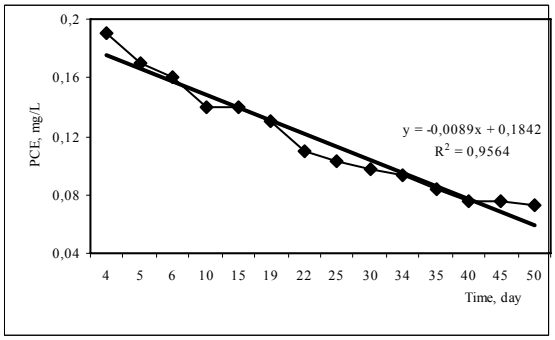

Figure 3. The PCE removal results occurred in 50-day period in an upstream flowing anaerobic reactor (UASB) which was continuously fed by 5 mg/L.

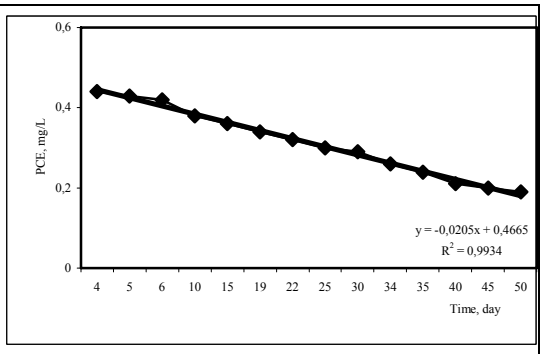

Figure 4. The PCE removal results occurred in 50-day period in an upstream flowing anaerobic reactor (UASB) which was continuously fed by 10 mg/L.

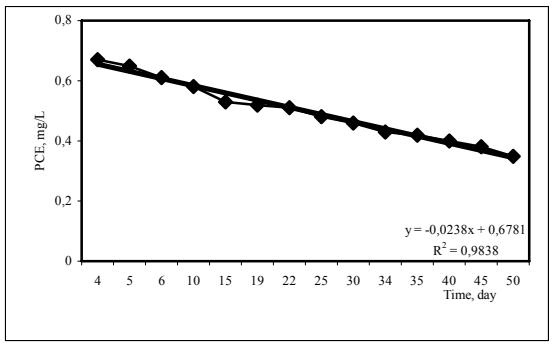

Figure 5. The PCE removal results occurred in 50-day period in an upstream flowing anaerobic reactor (UASB) which was continuously fed by 20 mg/L.

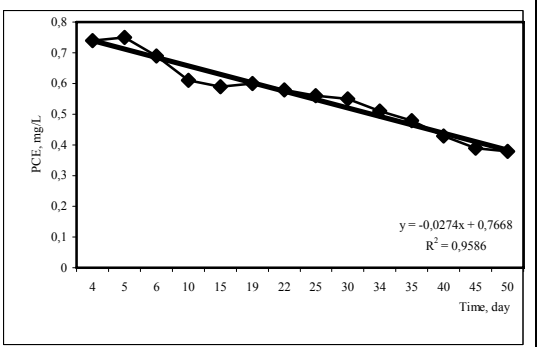

Figure 6. The PCE removal results occurred in 50-day period in an upstream flowing anaerobic reactor (UASB) which was continuously fed by 30 mg/L.

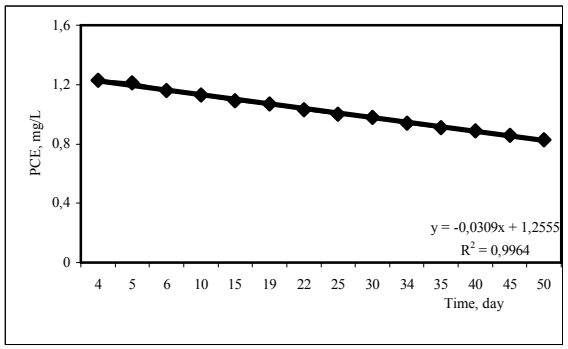

Figure 7. The PCE removal results occurred in 50-day period in an upstream flowing anaerobic reactor (UASB) which was continuously fed by 40 mg/L.

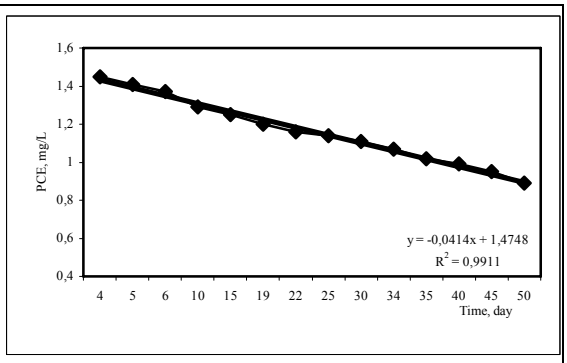

Figure 8. The PCE removal results occurred in 50-day period in an upstream flowing anaerobic reactor (UASB) which was continuously fed by 50 mg/L.

PCE feeding to reactor was continued with increasing value with 50 day interval. Quite low concentrations were determined at the outlet of the PCE reactor and nearly 97.5 % PCE removal efficiency occurred. Meanwhile, with the new PCE additions, the bio-degradation ratio was determined at considerable levels. Considering all the working time, obtaining R^2s between 0.956-0.996 proved the efficiency of the study and the reliability of the results. In the measurements, it is determined that at first PCE turns into DCE then VC. However, the formed DCM concentrations were in lower values.

The best PCE removal occurred at the stage 12 with the hydraulic retention time (HRT) of 13.5 h. According to increases of removal efficiency of PCE and COD with time could more increase with HRT increase (150-250 days). However this HRT values does not suitable for both operation conditions and cost effect. As a result of the PCE concentration decrease concluded that this compound was anaerobically decomposed. PCE decomposition rate was calculated as 0.197 mg/gVSS.

COD decomposition was assumed as %0 for these conditions that negative COD decomposition observed. Methane production plotted against COD loading was shoved in Figure 10. Also the photos of granule structure of sludge and methanogenic stage of sludge were shoved in Figure 11. From Figure 11 it was observed that structure of sludge granules was fairly well. The PCE inhibition concentrations were determined as IC_{25}= 6.7 and IC_{50}= 24.9 (figure 9).

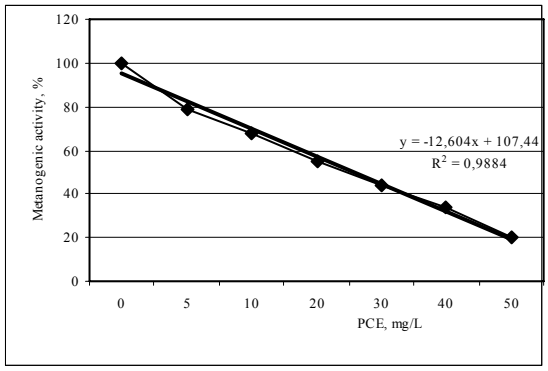

Figure 9. IC_{50} and IC_{25} for PCE (toxicity test results due to 25% (IC_{25}) and 50% (IC_{50}) decrease of methanogenic activity in response to CF dosage)

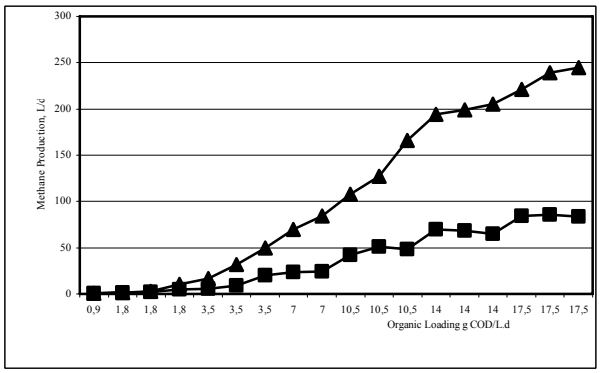

Figure 10. Methane production for PCE in response to various COD loading ratios (test results studied in bottles that became VOC (PCE) (■) and non-VOC (♦) with organic loading)

a **b**

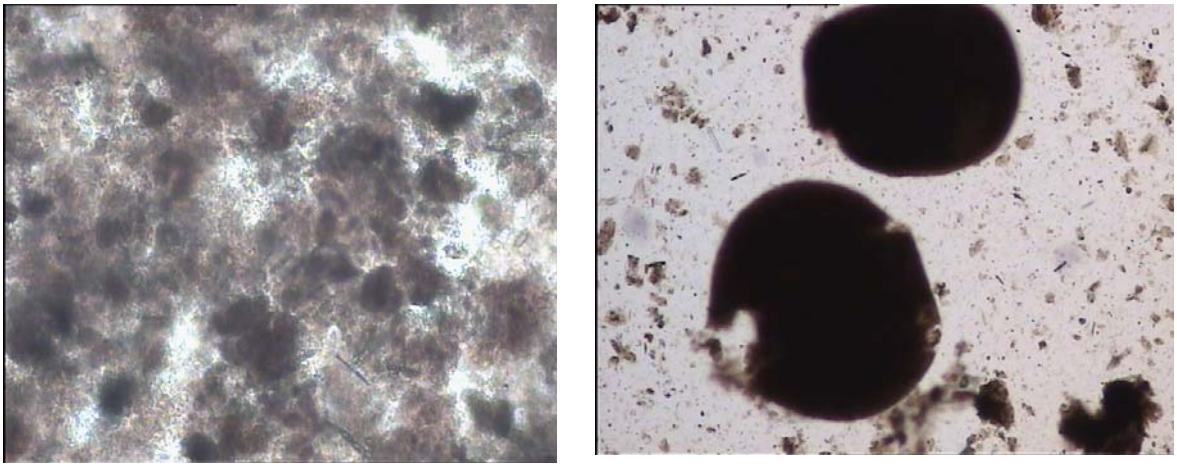

Figure 11. a) Mud granular structure and **b)** mud photographs of methanogene stage *(Methanosargina)* in the specimens taken from the mud in the reactor.

Conclusions

DiStefanoet *et al*. (1991) gave approximately 91 mg/L PCE to the reactor and determined 1 % four days later. De Bruin *et al*. (1992) used lactate as co-substrate then added 0.6 mg/L PCE to the reactor and determined TCE, Cis-DCE, VC as intermediate product. However, 16 days later, only ethylene remained in the reactor. Fennel and Gosset (1997) determined only vinyl chloride and ethylene at the outlet of the reactor as a result of 18 mg/L PCE addition. Long *et al*. (1993) determined 30 µg/gVSS-day as the degradation value of 0.120 mg/L PCE in the mixed culture which was added in the mixed study. Considering the study of Long et al., the PCE decomposition speeds occurred more slowly in this study. The reason could be caused from the differences

between biomass and co-substrates. Methanol was the only common co-substrate used in both of the studies.

The reductive dechlorination of PCE produces low chlorinated organics and sometimes non-chlorinated final-products may be produced. Observing low PCE concentrations at the outlet of the reactor, nearly 97.6 % PCE removal efficiency occurred. Meanwhile, with the new PCE additions, the bio-degradation ratio was determined at considerable levels. There were observed less amount of TCE in the specimens taken from the reactor during the purification process. The existence of TCE in serum bottles showed that the decomposition speed of TCE was slower than the decomposition speed of PCE. In the concluding studies, TCE could not be determined. The transformation of PCE into DCE and VC was determined in the measurements. However, the occurred DCM concentrations were having low values.

Considering the removed KOI, the biomass was observed to be quite active. The high efficiency in VOC removals denoted that biomass used VOCs as the carbon source. However, the highness of the KOI removal efficiency confirmed this judgment. Especially, when methane formation was examined, it was proved that PCE was used by biomass as the carbon source. The PCE inhibition concentrations were determined as $IC_{25}^{=}$ 6.7 and IC_{50}= 24.9. PCE usually didn't inhibit the methanogenes under the concentrations lower than 25 mg/L.

Long et al. (1993), indicated the PCE decomposition speed in the mixture as 30 µg PCE/g VSS.d respectively. PCE, at the firs week of incubation decomposition speed was 250 nmol L^{-1} $gün^{-1}$ and second week 445 nmol L^{-1} $gün^{-1}$ (Fathepure and Boyd, 1988). In our study, decomposition ratios were calculated for PCE as 0,136 mg /gVSS.d respectively.

The production time of 50 ml CH_4 gives some information about the toxicity of PCE upon biomass. This information strongly brings to mind the preventive effect of PCE on biomass and there could be found signs in continuous flow studies. However, the signs can not be common as indicated by continuous flow tests. This parallelism between PCE decomposition and methane production states that methanogenes are responsible for PCE bio-decomposition.

In continuous flow tests, assuming the reactor mixed rather well regularly with the PCE decomposition, the PCE concentration inside the reactor will be less than the initial concentration and this will cause the inhibition effects to become less during the collective tests. The diluting effects of continuous flow reactor will be sufficient to prevent the effects of CF toxicity upon biomass. However, in order to purify VOCs effectively during the continuous flow process, there can be required long HRTs.

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REFERENCES

Brock, T. And Madigan, M. (1991) Gene manipulation and genetic engineering. In: *Biology of Microorganisms* 6th (Ed), Englewood Cliffs, NJ: Prentice Hall. pp. 280-305.

Chang, J.S., Chou, C., Lin, Y.C., Lin, P.J., Ho, J.Y. and Hu, T.L. (2001). Kinetics characteristics of bacterial azo dye decolorization by P*seudomonas luteola*. *Water Research* **35**, 2841-2850.

Christiansen, N., Christensen, S., Arvin, E., and Ahring, B.. (1997). 'Transformation of Tetrachloroethene in an Up-Flow Anaerobic Sludgeblanket reactor. *Applied Microbiology and Biotechnology* **47**, 91-94.

Chu K. H. and Jewell W. J., (1994). Treatment of tetrachloroethylene with anaerobic attached film process, *Journal of Environmental Engineering* **120**, 58-71.

Davidson, W.F., D.D. Sumner and Parker, J.C. (1982). Chloroform : A Review Of Its Metabolism, Teratogenic, Mutagenic and Carcinogenic Potantial. *Drug Chemical Toxicology* **5**, 81-87.

DE Bruin, W., Kotterman, M., Posthumus, M., Schraa, G., and Zehnder, A. (1992). Complete Biological Reductive Transformation of Tetrachloroethene to Ethane. *Applied and Environmental Microbiology* **58**, 1996-2000.

DiStefano T. D., Gossett J. M. and Zinder S. H., (1991). Reductive dechlorination of high concentrations of tetrachloroethene to ethene by an anaerobic enrichment culture in the absence of methanogenesis. *Applied Environmental Microbiology* **57**, 2287-2292.

Ensley, B.D. (1991). Biochemical diversity of trichloroethylene metabolism. *Ann. Rev. Microbiol.* **56**, 283–299.

Fathepure B. Z., Nengu J. P. and Boyd S. A. (1987). Anaerobic bacteria that dechlorinate perchlorethene. *Applied Environmental Microbiology* **53**, 2671-2674.

Fathepure, B., and Boyd, A. (1988). Reductive Dechlorination of Perchloroethylene and the Role of Methanogenesis. *FEMS Microbiology Letters* **49**, 149-156.

Fennell, D., and Gossett, J. (1997). Comparison of Butyric Acid, Ethanol, Lactic Acid and Propionic Acid as Hydrogen Donors for the Reductive Dechlorination of Tetrachloroethene. *Environmental Science and Technology* **31**, 918-926.

Freedman, D., and Gossett, J. (1989). Biological Reductive Dechlorination of Tetrachloroethylene and Trichloroethylene Under Methanogenic Conditions. *Applied and Environmental Microbiology* **55**, 2144-2151.

Grady, C.P.L, Daigger G.T. and Lim, H.C. (1999) *Biological Wastewater Treatment*, 2nd Ed. Marcelll Dekker, Newyork.

Guiot S. R., Safi B., Frigon J. C., Mercier P., Mulligan C., Tremblay R. and Samson R. (1995). Performances of a full-scale novel multiplate anaerobic reactor treating cheese whey effluent. *Biotechnol. Bioengng*. **45,** 398–405.

Hinchee RE, Downey DC, Dupont RR, Aggarwal PK, Miller RN. (1991). Enhancing biodegradation of petroleum hydrocarbons through soil venting. *J Hazard Mater* **27**, 315-325.

Hirl, P. and Irvine, R. (1997). Reductive Dechlorination of Perchloroethylene using Anaerobic Sequencing Batch Biofilm Reactors (AnSBBR). Water Science and Technology 35, 49-56.

Hollinger, C., Schraa, G., Stams, A. and Zehnder, A. (1993). A Highly Purified Enrichment Culture Couples the Reductive Dechlorination of Tetrachloroethene to Growth. *Applied and Environmental Microbiology* **59**, 2991-2997.

Hulshoff, P.L.W., Dolfong, J., van Straten, W.J., de Zeeuw, W.J. and Lettinga, G. (1984) Pelletization of anaerobic sludge in up flow anaerobic sludge bed reactors on sucrose-containing substrates, in *Current Perspectives in Microbial Ecology*, Ed by Klug MJ and Reddy CA, American Society of Microbiology, Washington, DC. pp 636-642.

Kleopfer R. D., Easley D. M., Haas B. B., Deihl T. G., Jackson D. E. and Wurrey C. J. (1985). Anaerobic degradation of trichloroethylene in soil. *Environ. Sci. Technol*. **19**, 277-280.

Lettinga G. (1995). Anaerobic digestion and wastewater treatment systems. *Antonie van Leeuwenhoek* **67**, 3–28.

Long, L. J., Stensel, H.D., Ferguson, J. F., Strand, S. E. and Ongrth, J. E. 1993. Anaerobic and Aerobic Treatment of Chlorinated Aliphatic Compounds. *J. Environmental Engineering* **119**, 300-320.

Maymo-Gatell, X., Chien, Y-T,Gossett, J.M., Zinder, S.H. (1997). Isolation of a bacterium that reductively dechlorinates tetrachloroethene to ethane. *Science* **276**, 1568–1571.

Montgomery J.M. (1985) *Water Treatment Principles and Design*. John Wiley and Sons Inc., USA.

Narayanan B., Suidan M. T., Gelderloos A. B. and Brenner R. C. (1993). Treatment of VOC's in high strength wastes using an anaerobic expanded-bed GAC reactor. *Water Research* **27**, 181-194.

Ozdemir, C, Dursun, S. (2004). Trihalomethane Determination and Removals from Main Disgharge Channel of Konya (Turkey). *Journal of Environmental Technology* **25**, 1091-1096.

Ozdemir, C. (2005) *Removal of Chlorinated Volatile Organic Compounds (VOC) in the Wastewater with Upflow Anaerobic Sludge Bed Reactors*. Ph.D. Thesis, Selcuk University graduate School of Natural and Applied Sciences Department of Chemistry, Turkey.

Parson, F, Wood, PR, Marco, J. (1984). Transformation of tetrachloroethylene and trichloroethylene in microcosms and groundwater. *J. American Water Works Assoc*. **76**, 56-59.

Vogel, T. and McCarty, T. (1985). Biotransformationof Tetrachloroethylene to Trichloroethylene, Vinyl Chloride and Carbon Dioxide Under Methanogenic Conditions. *Applied and Environmental Microbiology* **49**, 1080-1083.