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Anaerobic removal of volatile organic compounds (VOC) from wastewater using methanol and ethylene glycol as co-substrate

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Abstract: Low concentration of chlorinated aliphatic compounds may be found in the wastewater, and has been accepted as toxic compounds for biological life. These volatile organic compounds (VOC) could be removed by different methods, but in this study, anaerobic decomposition was studied removal of VOC from the contaminated water. Aim of this work was treatment of VOC's by up-flow anaerobic blanket reactor (UASB) and to determine effects of different co-substrates (methanol and ethylene glycol) on VOC's removal at the anaerobic conditions. Furthermore, theoretical and practical investigation on the degradation of chlorinated hydrocarbons has importance in the water pollution. According to our results methanol was better co-substrate for VOC removal at anaerobic condition than ethylene glycol. Removal rates of DCM, CF, PCE and TCE in this investigation were approximately 65, 95, 100 and 90 % respectively with using co-substrate methanol.
Key words: Volatile Organic Compounds (VOC), anaerobic treatment, methanol, ethylene glycol.

Introduction

Chlorine has been used for water disinfection and domestic disinfection which has very strong oxidation effect on many chemicals. Furthermore, this usage gives chlorine and chloramines with a number of substation reactions. Disinfectant formed from substation reaction produces too much chlorine aliphatic components (Johnson & Jensen, 1986).Volatile organic compounds as like dichloromethane (DCM), chloroform (CF) and trichloroethylene (TCE) were the important compounds used widespread in the many industry (Davidson *et al*., 1982).Toxic effects of VOC's were found with the most of micro-organisms cultures tested. High concentrations of VOC's have also toxic effect to kidneys, acute toxicity to respiration systems of human and animals. On the other hand, some scientific findings showed that low concentrations of VOC's have genetic effect for human which, all known VOC's have mutagenic, carcinogenic or teratogenic effects (Kokoszka & Flood, 1989; Graham *et al*., 1998).

VOC's have high ability of chemical oxidation, but have not at the aerobic treatment systems. For this reason anaerobic removal processes of these compounds were mostly preferred. In the present, hybrid processes produced from package column were used, which are rapid anaerobic systems, suitable for the fluctuation regimes. Low level of VOC's could be removed by adsorption, incineration and bio-filtration methods, but these methods have some disadvantages with low removal efficiency or high operation cost.

Freedman and Gossett (1989) and Distefano *et al*. (1991) produced the biomass at laboratory conditions in the anaerobic incubator. De Bruin *et al*. (1992) used mixed river sediments and granulated sludge for anaerobic incubation. Freedman and Gossett (1989) used methanol for electron donor and De Bruin *et al*. (1992) lactate. On the other hand, Hollinger et al., (1993) isolated a specific species from anaerobic mixed culture and showed that this species was electron receiver for PCE and TCE.

Removal of PCE efficiency was about 99% in the mixed continuous flow reactor at the study of Vogel and McCarty (1985) but totally removal of vinyl chloride (VC) could never found. Fennell and

Gossett (1997) investigated effects of different electron donors on dechlorination of the PCE. The PCE was turned to the VC and ethylene using as co-substrates butyric aside, ethanol, lactic aside and propyonic aside. In addition, there were many studies on VOC removal using different bacterial cultures, but the removal of carbon tetrachloride (CT) was only possible with anaerobic specific microorganisms in the mixed VOC experiment at many studies (Egli *et al*., 1987; Criddle *et al*., 1990; Petrovskis *et al*., 1994). Egli *et al*. (1987) found chloroform and dichloromethane as last products in their laboratory experiments. Dichloromethane levels were lover than chloroform levels in the last product. The main objective of this study was to compare four different VOC removal efficiencies in the anaerobic incubation used two different co-substrate of methanol and ethylene glycol.

Materials and Method

One hundred and sixty ml capacity serum bottles were used for the incubation pot. Bottles were containing 0.1% Co-substrate as methanol or ethylene glycol (v/v) in liquid content, 10 ml activated mixed sludge, 50 ml supernatant (Table 1) and different VOC's (CF, TCE, DCM and PCE; 98% purity (Merck Company, Germany) and at different concentrations. Experimental sets of the incubation bottles are given in the Table 2. Total liquid content was 150 ml and 10 ml empty volume. Twelve 160 ml capacity bottles were prepared for each VOC test, and incubated in a rotary shaker at 35 ^{o}C constant temperature for about 60 days. Methane concentration was measured in the incubation bottles with using Dragger Tube Method (DRAGER Pac-Ex., Germany).

Petroleum ether was used for extraction of VOC. Two ml of Petroleum ether was added in 1L of each sample in the balloon flask separately and shaken for 4 min, then organic phase was separated. Processes were repeated with a second 2 ml of Petroleum ether on water phase. Volatile organic compounds 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) 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 and flow rate of carrier gas N_2 were 5 kg/cm^2 and 1.4 ml/min respectively. Processes temperature was 240 °C in the oven, 250 °C in the injector and 300 °C at the detector. Measurement sensitivity was 0.001 µg/L.

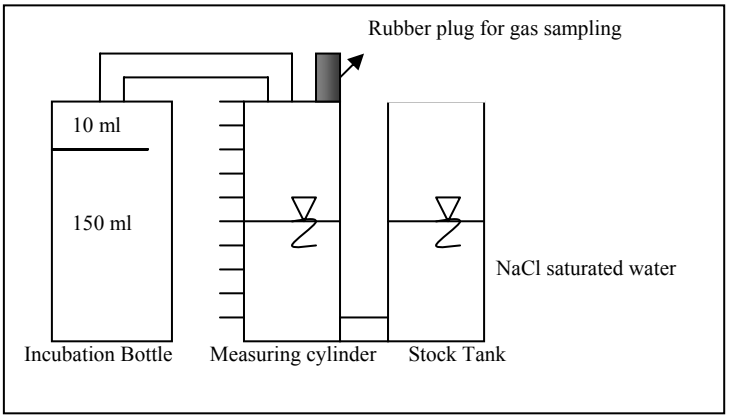

Figure 1. Measurement systems for gas production.

All anaerobic incubation bottles were used to find optimum biological removal conditions for four target chlorinated compounds (CF, TCE, DCM and PCE) in the first stage experiment (Figure 1). All incubation bottles were plugged with Teflon coated rubber stopper and covered with aluminium foil against to air and light intake.

Some preliminary experiments were performed to find the most convenient experimental conditions and for the continuous flow experiment design. Methanol and ethylene glycol pair were used in 12 incubation bottles for carbon source as the co-substrate. Each test was studied at two

different concentrations of VOC and co-substrate. Incubation bottles were treated with the nitrogen gases for 2 minutes to remove dissolved oxygen from the liquid content and immediately closed with rubber plug and covered aluminium foil. CF, TCE, DCM or PCE was added in the each incubation bottle separately to adjust to 1.0 mg L^{-1} concentration of VOC. All incubation bottles were kept in a rotary shaking incubator at constant temperature of 35 ^{o}C for incubation period. In addition, two extra bottles containing mixed VOC with two different co-substrates (Table 1 and 2) and without activated sludge were prepared to test non biological VOC loss.

Table 1. Composition of synthetic wastewater (Prakash & Gupta, 2000)

Compounds	Concentration, mg/l	Compounds	Concentration, mg/l
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		

Table 2. Experimental design of the anaerobic incubation bottles

Incubation period (day)	Co-substrate type	*VOC addition	**Biomass addition
55-60	Methanol	+	+
57-60	Ethylene glycol	+	+
62-63	Methanol	+	-
62-63	Ethylene glycol	+	-

***VOC**: CF, PCE, DCM, TCE; ****Biomass**: Anaerobic reactor sludge of chips industry

Methane and VOC's concentrations in the 10 ml empty volume over the liquid content were analysed by the Dragger tube method and GC respectively. Methane gas from the anaerobic production in the incubation bottles were also measured in the gas volume for incubation periods. Biogas productions were calculated at the standard temperature and pressure (STP).

Results

There were not noteworthy reduction on the VOC compounds in the two control bottles which were not containing substrate and microorganisms. The VOC's reduction records in the test bottles containing microorganisms inoculation and substrate showed that VOC's removal was from the biomass activity.

Chloroform removals during the incubation period are given in Figure 4 and 5. Removal rate was higher than 50% in two days incubation period and reduction productivity was increased more than 95% after 25 days incubation. Similar removals were also found for the other compounds (Figs. 4-11). Cumulative methane production using methanol as a co-substrate was increased logarithmically after 7 days and reduced after 20 days incubation. VOC contents in the control bottles were approximately constant at the end of incubation period (Figs. 2 & 3). This may explain to the VOC contents in the test bottles which expected concentrations.

Methane gas production and total biomass formation were analysed separately in all incubation bottles. VOC residues in the test bottles at the end of incubation period were also measured. Results of measurement are given in the Figures 12 and 13.

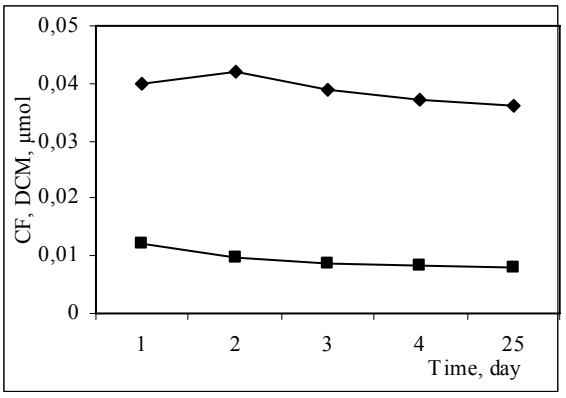

Figure 2. CF and DCM change in the control bottles for 25 days incubation period (♦; DCM, ■; CF)

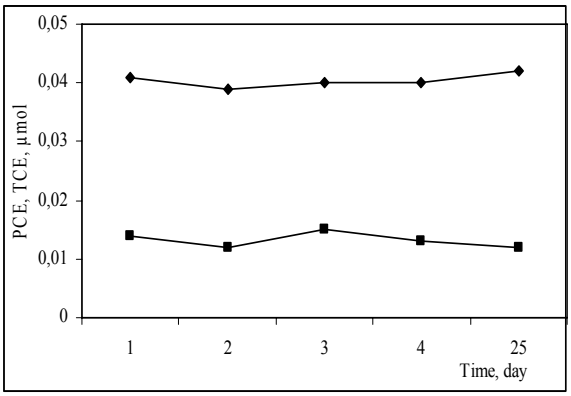

Figure 3. PCE and TCE change in the control bottles for 25 days incubation period (♦; PCE, ■; TCE)

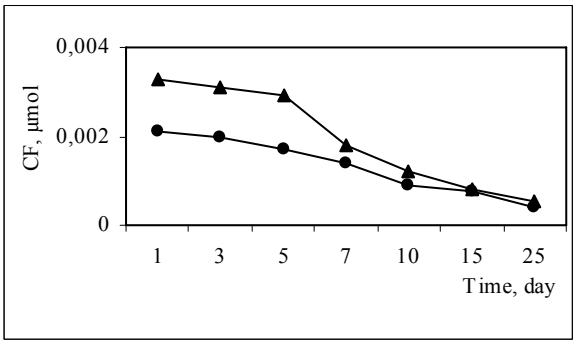

Figure 4. Decomposition of CF with two different initial concentration (♦; 4µmol L^{-1}, ■; 2,5µmol L^{-1}) in anaerobic incubation for 25 days period using methanol as a co-substrate at 35 ^{o}C.

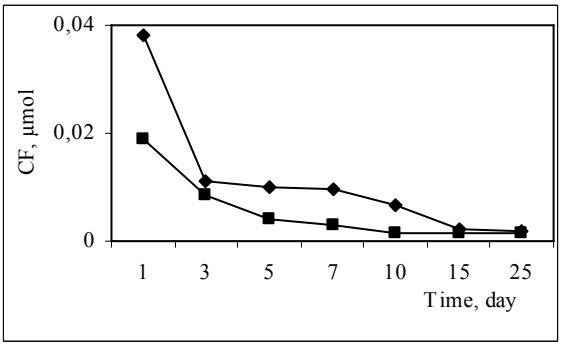

Figure 5. Decomposition of CF with two different initial concentration (♦; 4µmol L^{-1}, ■; 2,5µmol L^{-1}) in anaerobic incubation for 25 days period using ethylene glycol as a co-substrate at 35 ^{o}C.

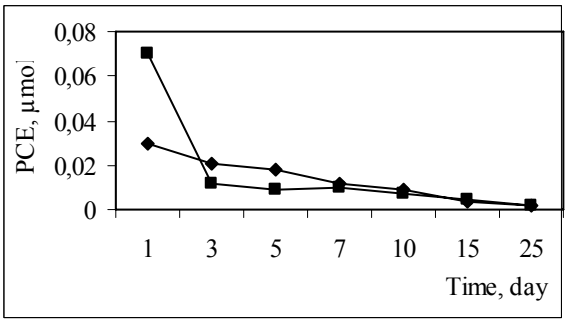

Figure 6. Decomposition of CF with two different initial concentration (♦; 8µmol L^{-1}, ■; 4µmol L^{-1}) in anaerobic incubation for 25 days period with using methanol as a co-substrate at 35 ^{o}C.

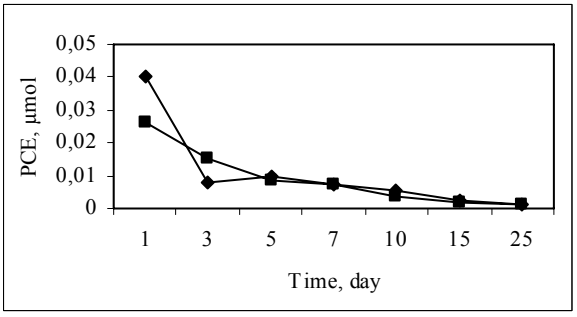

Figure 7. Decomposition of PCE with two different initial concentration (♦; 8 µmol L^{-1}, ■; 4 µmol L^{-1}) in anaerobic incubation for 25 days period with using ethylene glycol as a co-substrate at 35 ^{o}C.

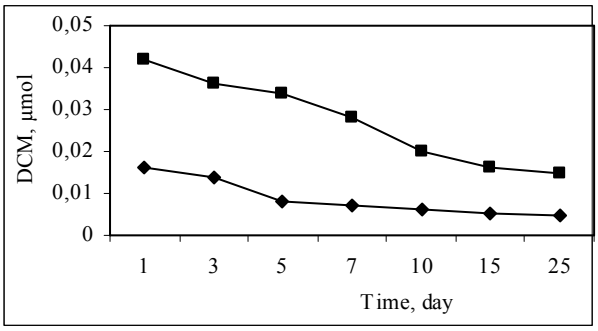

Figure 8. Decomposition of CF with two different initial concentration (♦; 4 µmol L^{-1}, ■; 2,5 µmol L^{-1}) in anaerobic incubation for 25 days period using methanol as a co-substrate at 35 ^{o}C.

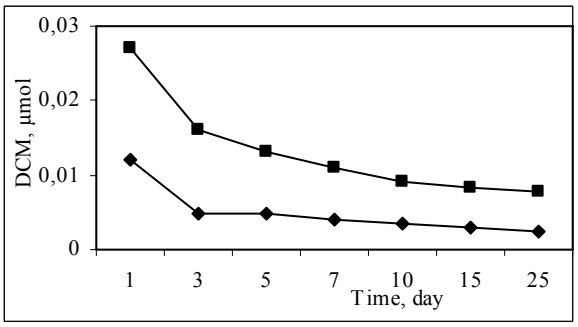

Figure 9. Decomposition of DCM with two different initial concentration (♦; 4 µmol L^{-1}, ■; 2,5 µmol L^{-1}) in anaerobic incubation for 25 days period using ethylene glycol as a co-substrate at 35 ^{o}C.

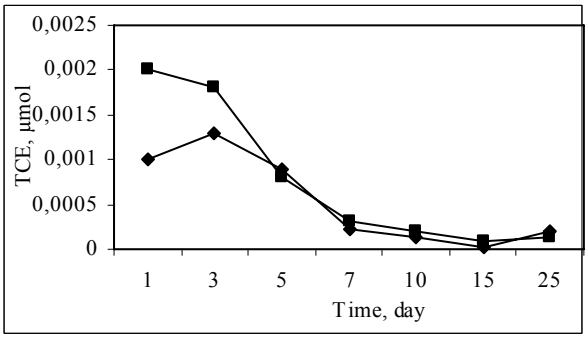

Figure 10. Decomposition of TCE with two different initial concentration (♦; 4 µmol L^{-1}, ■; 2,5 µmol L^{-1}) in anaerobic incubation for 25 days period using methanol as a co-substrate at 35 ^{o}C.

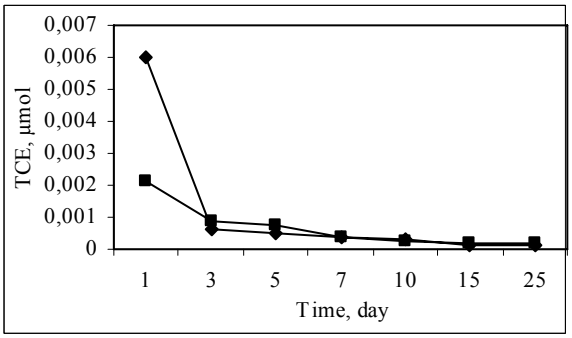

Figure 11. Decomposition of TCE with two different initial concentration (♦; 4 µmol L^{-1}, ■; 2,5 µmol L^{-1}) in anaerobic incubation for 25 days period using ethylene glycol as a co-substrate at 35 ^{o}C.

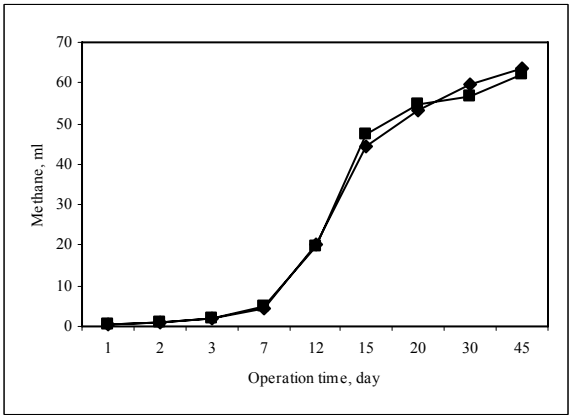

Figure 12. Cumulative methane production in the incubation bottles using methanol as a co-substrate (♦; bottle 1, ■; bottle 2).

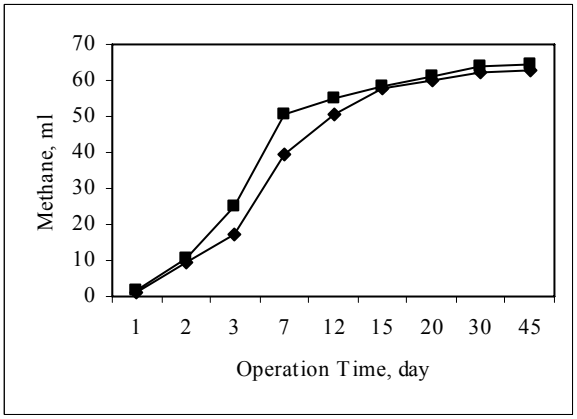

Figure 13. Cumulative methane production in the incubation bottles using ethylene glycol as a co-substrate (♦; bottle 1, ■; bottle 2).

At the beginning of the experiment, CF, TCE, PCE and DCM concentration were in order 0.5, 1.0, 1.0 and 8.0 mg L^{-1} respectively. Granulated sludge value was 5 ml with 95 ml supernatant volume so that VSS was 1.95 mg L^{-1}. For enough carbon sources during the incubation period, 0.4% co-

substrate was added in each incubation bottles. Ethylene glycol and methanol were used as the co-substrate in this study different than former investigation in the literature. Ethanolamine was not preferred as a co-substrate because its reduction was not easy during the experimental period.

Mean methane content of biogas were between 52 -65 %. Methane production was used for indicator of microbial activity.

Discussions

Hollinger *et al*. (1993) were isolated a specific species anaerobic microorganism from the mixed culture and they showed that this species may be used PCE and TCE for electron acceptor. Effect of electron donor compounds on PCE was not clear. PCE might be changed to Dichloroethylene (DCE) with using acetate and lactate as the primer electron acceptor in the SBR reactor (Hirl & Irvine, 1997). On the other hand, DCE was not decomposed totally, and TCE and cis-DCE were found together at end of incubation period. Long *et al*. (1993) were used a mixed carbon source containing glucose, acetate, benzoate, phenol and methanol at dechlorination experiments. PCE, TCE and CF at the same concentration (120 µg/L) were put in the anaerobic reactor at same conditions mentioned above and their concentration were reduced to 3, 2, 21 µg/L respectively at the end of incubation period. Study of De Bruin *et al.* (1992) show that when lactate was not used in the substrate, products without chlorine were found end of incubation period and electron acceptor was not inhibited. They found as sub-product TCE, cis-DCE and vinyl chloride (VC) in few days, but only, ethylene was detected after 16 d incubation period.

Methanol was used as a co-substrate with removal of PCE, TCE, DCE and VC in separate tests by Skeen *et al*. (1995), generally, primer dechlorination products were found. Same DCE isomers were still found until end of the experimental period in a UASB reactor using co-substrate ethanol (Christiansen *et al.* 1997). They measured methane production during comparison of two co-substrate decomposition for total experimental period. Isomer of DCE was found at UASB reactor using co-substrate ethanol (Christiansen *et al.* 1997). Prakash and Gupta (2000) studied the biodegradation of TCE in a UASB reactor containing 5–50 mg TCE/l to develop granular sludge. 90% TCE and 92% COD removal efficiencies were obtained.

Period of 40 ml gas formation was investigated for the measurement of methane production rate, which was about half of the potential methane production for 500 methanol or ethylene glycol mg L^{-1}. Methane production rate (37.9 ml/day) was twice more than Ethylene glycol (41.7 ml/day). The removal of DCM, CF, PCE and TCE in our investigation was approximately 65, 95, 100 and 90 % respectively.

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