Reductive dechlorination of 1, 2-dichloroethane using anaerobic sequencing batch reactor (ASBR)

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Abstract: The objective of this research was to study the dechlorination of 1,2-dichloroethane (1,2-DCA) in a synthetic wastewater with lab-scale anaerobic sequencing batch (ASBR) reactors. Anaerobic sludge was used as a biocatalyst. Sodium acetate and dextrose served as the main methanogenic substrate. Experimental studies were conducted at wide-range of volumetric (0.25 - 1.25 g COD/L.d) and specific (0.0362 - 0.181 g COD/g VSS.d) loading rates and influent wastewater CODs (500 - 2500 mg/L). During 266 days of reactor operation, the mixed culture degraded 1,2 Dichloroethane at concentrations of up to 50 mg/L, with an HRT of 48 hrs. No chlorinated intermediates or residues were found. 1,2-DCA degradation resulted in ethene and ethane formation. Acetate was the most effective electron donor for dechlorination, although, dextrose was also effective, but to a lesser extent. The mixed culture degraded 1,2 Dichloroethane in the temperature range of 28 ± 4°C, with the pH range of 7.25 to 7.95. The 1,2-DCA removal rates achieved, and the safe nature of the end products, signify the anaerobic sequencing batch (ASBR) reactor technology for practical decontamination of waters containing such types of organochlorines. The COD removal efficiencies were in the range of 95 to 98% depending on volumetric and specific loading rates applied.

Keywords: Anaerobic Treatment; 1,2 Dichloroethane; Reductive Dechlorination; Sequencing Batch Reactors

INTRODUCTION

1,2-Dichloroethane (DCA) is a synthetic chemical which has no known natural sources. DCA is mainly used as an intermediate in the synthesis of vinyl chloride, but it is also used in the production of chlorinated solvents such as trichloroethene, tetrachloroethene, and 1,1,1-trichloroethane. 1,2-DCA has good solubility in water (8.9 g/l), a low sorption coefficient ($\log K_{oc} = 1.28$) and a low Henry coefficient (1.1X10$^{-3}$ atm m$^3$mol$^{-1}$) (Dewulf et al., 1995), it remains in the water phase under average room temperature of 20°C. It is a known carcinogen (Vogel et al., 1987). The combination of its persistence and toxicity makes 1,2-DCA a target molecule to degrade by physico-chemical or biological methods, rather than to replace it from water into another phase (e.g. sorption on sludge, or gas stripping.).

The main objective of this study was to assess the ability of ASBR technology to dehalogenate 1,2-DCA at different volumetric loading rates. The biomass was acclimatized gradually to higher concentrations of 1,2 Dichloroethane and performance with respect to degradation was studied in ASBR. The dechlorination capacity of methanogenic biomass at different concentration of 1,2-DCA mg/l with sodium acetate and dextrose as the main substrate and carbon source was also studied. Anaerobic sequencing batch reactors (ASBR) have been widely studied for wastewater treatment due to certain advantages like good solids retention, elimination of the secondary sedimentation step, efficient operating control, relatively high organic matter removal efficiency and simple operation. Moreover, it could be used to treat some wastewater discharged in an intermittent way (Brito et al., 1997), (Ndon and Dague, 1997a) and (Zaiat et al., 2001) indicate that the anaerobic sequencing batch reactors are a good alternative for low-cost treatment of low-strength industrial and municipal wastewater (Zaiat et al., 2002).
MATERIALS AND METHODS

Chemicals and analytical methods
The 1,2 Dichloroethane was obtained from Merck, India (99%). All other chemicals were of analytical grade and used without further purification. Gases (Ethylene and Ethane) were purchased from Master standards, Vikhroli, Mumbai, India.

Analytical procedures
Alkalinity, pH, COD, SVI, SS, VSS and TSS were analyzed according to the Standard Methods for the Examination of Water and Wastewater (APHA., 1989). 1,2 Dichloroethane was determined by gas chromatograph (Agilent Model: 6890 No. G1530, USA). The liquid sample was filtered through a 0.45 µm membrane filter, and extracted with cyclohexane (1:3) prior to injection into the column and directly analyzed in gas chromatograph equipped with capillary column (Thermo TR-VI 30 mX0.32mmX1.8mm). Nitrogen was used as a carrier gas with electron capture detector (ECD) as a detector. Injector temperature was 250°C. Detector temperature was 280°C. The initial temperature of the column was 70°C followed with a first ramp of 10°C/min to the temperature of 150°C for 1 minute and then final ramp of 25°C/min up to 280°C.

Biogas composition was analyzed by injecting 10 g gas samples to GC equipped with Flame Ionization Detector. The analysis was done at an oven temperature of 40°C, injector temperature of 100°C and detector temperature of 280°C, using SS molecular sieve M16,3X1/8” column. The carrier gas was nitrogen, applied at a flow rate of 30ml/min. Hydrogen and zero air were used as fuel.

Volatile fatty acids (VFA) in the effluent were measured by injecting 2ml of filtered acidified samples through gas chromatograph (Agilent Model : 6890 No. G1530, USA) equipped with Flame Ionization Detector using a 10% free fatty acid phase (FFAP) on (6O/80) Chromosorb WHP/0.1% H3PO4 stainless steel column. FFAP is cross-linked and bonded to resist the damage that can occur when injecting water based samples and can be used at operating temperatures at 60–250°C. The analysis was carried out at an oven temperature of 150°C, injector temperature of 180°C and detector temperature of 250°C. Hydrogen and moisture free zero air were used to fuel the flame, while nitrogen as carrier gas was applied at the rate of 20 ml/minute.

Reactor configuration and operation
Two identical laboratory-scale sequencing batch reactors were used (one served as a control reactor, R1). Each reactor was made of 6 mm-thick glass cylinder with an internal diameter of 18 cm and height of 30 cm. The operating liquid volume was 5.0 l. Feeding, decanting were controlled by manual operations. Mixing was provided by magnetic stirrers. SBRs were operated in five phases. The first phase consisted of filling the reactor for about 2 minutes. The second phase was the main biodegradation phase wherein the effective biological reactions were carried out. This phase was maintained for about 21.50 hrs. The last two phases consisted of drawing the decant from the reactor (5 min) and an idle period of 3 minutes before starting the next cycle. Therefore after decanting 2.5l of the supernatant, the reactor was replenished with fresh feed after a cycle time of one day. Throughout the study, the temperature was kept constant at 28 ± 4°C. There was no attempt to control the pH, which was in the range 7.5 ± 0.5 during the reaction period.

Start up and Acclimation of the Reactors
The start up was carried out by stepping up the organic loading to produce biomass development. Organic loadings were increased by influent COD concentration upon attainment of pseudo-steady state. Pseudo-steady state is defined based on the consistent COD removal efficiency. The reactors were fed with synthetic feed comprised of sodium acetate, dextrone in reactor 1 (R1, control) and with sodium acetate, dextrone and 1,2 Dichloroethane in reactor 2 (R2). The selection of sodium acetate and dextrone (an isomer of glucose) as supplemental substrates was based on the fact that either compound is capable of supporting biological systems, which is reflected in their frequent use as carbon sources in wastewater treatment studies (Hickman and Novak, 1984). Sodium bicarbonate (400 mg/l) was used as buffer to maintain the pH of the solution in the range of 6.8 to 7.8. The COD:N:P:S ratio of 300:5:1:1 was maintained in the feed.
Major nutrients in the feed include 163 mg/L ammonium chloride; 210 mg/L calcium chloride; 48 mg/L dipotassium hydrogen ortho phosphate; 40 mg/L magnesium sulphate; 100 mg/L yeast extract; 600-800 mg/L sodium bicarbonate. Trace metal solution was prepared in distilled water by dissolving per litre 100 mg. zinc sulphate; 5000 mg. manganese chloride; 640 mg. ammonium molybdate; 880 mg. cobaltous chloride and 6000 mg. ferric chloride; 100 mg. boric acid powder; 1000 mg. copper sulphate; 1000 mg. nickel sulphate and 5000 mg. magnesium sulphate. Two milliliter of this solution was added per litre of the feed solution. These compositions are comparable to those used by Prakash et al., (1998) in their study on granulation in UASB reactors.

The experiments were conducted in two laboratory scale identical ASB reactors and were operated on a batch mode for a period of 60 days. During the study period, the ASB reactors were operated continuously in batch mode with a constant hydraulic retention time (HRT) of 48 h. An initial sludge concentration of 7.3 g VSS/l was maintained in the reactor. The VSS/SS ratio was observed to be in the range of 0.45-0.5. The reactors were initiated with a COD of 500 mg/l and further increased stepwise from 1000 to 1500 mg/l and finally to 2500 mg/l. The COD of 2500 mg/l corresponds to sludge loading rate (SLR) of 0.181 kg COD/kg VSS.d and organic loading rate (OLR) of 1.25 kg COD/m³.d. The day on which 5 mg/l of 1,2 Dichloroethane was added is considered as day one. Subsequently the concentration of 1,2 dichloroethane was increased to 10, 20, 30, 40 and 50 mg/l during 266 days of reactor operation. At each loading condition, the reactors were closely monitored until a pseudo steady state was reached. The stability of the system was judged by the consistent depletion of substrate and co-substrate concentration in reactors 1 and 2 respectively. The operating conditions of digester are shown in Table 1.

### Table 1. Operating Conditions and Digester Efficiency During Acclimation Study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reactor One</th>
<th>Reactor Two</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate COD, mg/l</td>
<td>2500</td>
<td>2500</td>
</tr>
<tr>
<td>COD removal, (%)</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>HRT, (h)</td>
<td>48</td>
<td>48</td>
</tr>
<tr>
<td>OLR, (kgCOD/m³.d)</td>
<td>1.25</td>
<td>1.25</td>
</tr>
<tr>
<td>Reactor pH</td>
<td>7.7</td>
<td>7.8</td>
</tr>
<tr>
<td>Alkalinity, (mg/l. CaCO₃)</td>
<td>1800</td>
<td>2000</td>
</tr>
<tr>
<td>Biogas, L/d</td>
<td>1.35</td>
<td>1.3</td>
</tr>
<tr>
<td>1,2 DCA conc.,mg/l</td>
<td>-</td>
<td>50</td>
</tr>
</tbody>
</table>

### RESULTS AND DISCUSSION

#### Degradation of 1,2-DCA in ASB reactors

During start up operation, the synthetic wastewater containing 5mg/l of 1,2 Dichloroethane was fed to the reactor 2 (R2). The biogas production was observed without any lag and the COD removal of more than 95% was also observed. From the first day of dosing, the 1,2-DCA was degraded by the methanogenic sludge, unadapted to 1,2-DCA. The degradation occurred without any lag phase. The production of biogas was linked to the 1,2 Dichloroethane and COD removal efficiencies.

Figure 1 shows the degradation efficiency of reactor 2 in relation to the loading rates of 1,2-DCA. The corresponding COD removal and the biogas production are shown in figure 2 and figure 3 respectively. The biogas production was 1.25 l/d and the COD removal was more than 96%. The volatile fatty acid concentration in the effluent was below 40 mg/l (data not shown). After 30 days of operation, the concentration of 1,2 Dichloroethane in the synthetic wastewater was increased to 10 mg/l. On day one, there was slight lag in production of biogas was observed. This was carried out for 30 days. The same pattern of degradation for higher concentration of 1,2 Dichloroethane was observed throughout reactor operation period. Small amount of sludge was washed out during the decantation period and the granulation was not observed in the reactor.
Figure 1: Removal of 1,2 Dichloroethane during acclimation

![Figure 1](image1)

Figure 2: Removal of COD during acclimation

![Figure 2](image2)

Figure 3: Biogas produced during the acclimation phase in reactor 2

![Figure 3](image3)
**Transformation of 1,2-DCA to ethene and ethane**

The dechlorination of 1,2-DCA was tested by conducting batch experiments. In bio-sludge, the main transformation of 1,2-DCA was carried out by dichloroelimination reactions, resulting in the production of ethene (65-70%). Another type of reductive dechlorination mechanism, reductive hydrogenolysis has produced only small amounts of ethane (less than 1%). A conversion of 1,2-DCA into carbon dioxide cannot be excluded (Bouwer and McCarty, 1983). 1,2-DCA changed very little without the addition of electron donor (Wildeman et al., 2001). These tests confirmed the need for metabolic activity to enhance the reductive dechlorination reactions of 1,2-DCA.

The transformation of 1,2-DCA to ethylene is a dihalo-elimination and transformation to chloroethane via hydrogenolysis (Vogel et al., 1987). Chloroethane is further dechlorinated via hydrogenolysis to ethane. The production of ethane is inhibited by 1,2-DCA, may be due to competition of the two chlorinated compounds for the same electrons (Holliger et al., 1990). The inhibition of dechlorination of a lower chlorinated compound by the higher chlorinated compound, has also been observed in mixed microbial systems like sewage sludge for aromatic compounds (Boyd & Shelton., 1984; Mikesell & Boyd., 1986; Fathepure et al., 1988; Bosma et al., 1988) as aliphatic compounds (Vogel & McCarty., 1985; Barrio-Lage et al., 1986).

**CONCLUSIONS**

The ASB reactor technology used in the present study was able to degrade 1,2-DCA contaminated waters. The study shows using mixed culture, the concentrations of 1,2-DCA up to 50 mg/l were degraded to lower chlorinated compounds. The rate of dechlorination of 1,2-DCA is dependent on metabolic activity of the cells. As the end products of the degradation processes consist of non-toxic molecules, the use of ASB reactors inoculated with methanogenic sludge and operated under defined conditions, could be an attractive tool to treat organochlorine polluted waters.

**REFERENCES**


