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CONTROL OF TRICHLOROETHYLENE EMISSIONS FROM SPARGING SYSTEMS BY HORIZONTAL BIO- AND CHEMO- BARRIERS

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ABSTRACT

The scope of this study was to develop a continuous system to clean-up a trichloroethylene (TCE) contaminated gas stream, where biotic and abiotic removal mechanisms are undertaken sequentially simulating the horizontal bio- and chemo-barriers proposed for the in-situ remediation of the contaminated sites. The bio- and chemo-barriers were simulated by using glass columns packed with granular anaerobic mixed culture and Fe(0) filings, respectively. The effect of gas residence time, which is adjusted by the gas flowrate, on the TCE removal efficiency of the reactor system was investigated. TCE removal efficiency of over 90% was achieved at gas residence times above 1hr. Furthermore, the effluent of reactor system contained only ethane and ethylene, which are non-toxic by-products of TCE reduction reactions, along with trace amounts of TCE.

Keywords: Biofilter, Fe(0) packed column, reductive dechlorination, Trichloroethylene

INTRODUCTION

Pollution of groundwater and soil with hazardous substances due to the inadequate handling and disposal from industrial, domestic and agricultural applications became an important issue in a large number of locations throughout the world. Chlorinated ethylenes are placed among the most common contaminants of groundwater [1]. TCE has an important place among those compounds due to its widespread use in many industries, persistent behavior in the environment and toxic effects to both public health and the environment. Because of its physical and chemical properties, TCE spills tend to form dense nonaqueous-phase liquids (NAPL) in the subsurface, creating a source zone, which greatly contribute to long-term contamination of groundwater, posing significant challenges for remediation technologies [2].

Current remediation technologies focusing on the elimination of this source zone are air sparging/solid vapor extraction, soil flushing, chemical and thermal oxidation and biologically enhanced dissolution. The air sparging, which is used to eliminate NAPL source zone by volatilizing the contaminant, is one of the most convenient and economical remediation techniques. Chlorinated ethylenes have a great tendency for volatilization since their vapor pressures are comparatively high.

The Clean Air Act (CAA) Amendments (1990) of the U.S EPA have raised serious concerns about gaseous emissions of hazardous air pollutants (HAPs) and their control [3]. Not only are hundreds of chemical process industries and commercial sources directly impacted by these new regulations but also, several existing and proposed hazardous waste site remediation operations will need to be modified or amended to control capture or treat their off-gas emissions polluted with contaminants. The legal restrictions directly impacted the application of air sparging systems, thus the treatment of off-gas stream released from the sites, where air sparging is applied as a remediation technology, is inevitable. Many off-site treatment options such as activated carbon adsorption were coupled with sparging systems in order to clean-up the gaseous pollutants in the off-gas stream. However, the practical applicability of these technologies is limited by capital and operating cost considerations, residual and side stream formation and trace concentrations etc. [4].

Biotic and abiotic transformations of chlorinated ethylenes to non-hazardous end products such as ethylene and ethane were demonstrated in many studies. Reductive transformations of these compounds such as anaerobic reductive dechlorination as biotic [5-8] and reduction with zero-valent iron (Fe(0)) as abiotic mechanisms [9,10] have gained particular interest among other transformation mechanisms.

The application of these mechanisms in the transformation of TCE and other chloroethylenes in gas phase is not well reported in the literature. The vapor phase treatment of perchloroethylene (PCE) in a soil column by lab-scale anaerobic bioventing was studied and it was concluded that PCE reduction rate in the column was very high at 5 hrs

of residence time [8]. However, the complete reduction of PCE to ethylene has not been achieved and vinyl chloride, which is a toxic gas, was accumulated in the system. In most applications, TCE reduction does not proceed up to ethylene since VC to ethylene reduction is slow. A polishing step is necessary for the complete reduction of TCE to non-toxic ethylene. Zero valent iron is a promising alternative that can be used coupled with biotic processes. The adsorption/reduction reactions of gaseous TCE by Fe(0) were investigated in batch reactors and it was concluded that the removal of TCE from the gas phase was strictly by adsorption up to a critical relative humidity, i.e., 72% for acid washed and 92% for the partially oxidized surfaces, above which dechlorination occurred and the hydrogenolysis by-products appeared [10].

In this study, the objective was to develop a continuous system to clean-up a trichloroethylene (TCE) contaminated gas stream, where biotic and abiotic removal mechanisms are undertaken sequentially simulating the horizontal bio- and chemo-barriers coupled with modified sparging system proposed for the in-situ remediation of the contaminated sites. The proposed system is predicted as a promising in-situ system that can enhance sparging systems with respect to off-gas quality.

MATERIALS AND METHODS

Bioreactor Packing Media

Granular anaerobic mixed culture that was used as a packing media for the bioreactor was obtained from the anaerobic digester of Ankara Efes Pilsen Brewery having a volatile suspended solids content of 41.447±0.749 g VSS l^{-1}. The culture was stored with nutrient media consisting of (the values in parentheses are in mgl^{-1} units): NH_4Cl (400), K_2HPO_4 (500), KH_2PO_4 (400), $(NH_4)HCO_3$ (4000), $NaHCO_3$ (6000), $CaCl_2.2H_2O$ (50), $CoCl_2.6H_20$ (10), NH_4VO_3 (0.5), $CuCl_2.2H_20$ (0.5), $ZnCl_2$ (0.5), $AlCl_3.6H_20$ (0.5), $NaMoO_4.2H_2O$ (0.5), H_3BO_3 (0.5), $NiCl_2.6H_20$ (0.5), $NaWO_4.2H_2O$ (0.5), Na_2SeO_3 (0.5), Yeast Extract (50) in 500 ml glass bottles prior to experiments. The glass bio-reactor column was filled with 100 ml of this culture. No nutrient was supplied to the biofilter during the operation period. So the only nutrient supply that the granular anaerobic mixed culture received was the initially added basal media as described above.

Fe (0) Column Packing Media

The Fe(0) filings used to pack the Fe(0) column were obtained from Merck Chemical Co., Germany. The filings have 150 μm of effective diameter and were given 17.7% of moisture content by treating with distilled water. The weight of filings in the 100 ml of effective reactor volume was 241.16 g. The Brunauer-Emmett-Teller (BET) surface area of the filings in the reactor was determined as 1.4515 m^2g^{-1} with ASAP 2003 V3.03 (Micrometrics Instrument Corporation).

Experimental Set-up

The continuous reactor system consisted of granular anaerobic mixed culture packed bioreactor followed by elemental iron metal (Fe(0)) packed column in series. In order to eliminate the clogging in the entrances of reactors and achieve a homogenous gas distribution, the first 5 cm of the reactors were filled with glass beads having diameters of 2 mm. All the valves and connections used in the system were made of Teflon. In order to sample the gas in the influent of the system and effluents of the bioreactor and Fe(0) column, 3-way sampling valves were located in the entrance of the bioreactor, and entrance and exit of the Fe(0) column (Figure 1).

The influent gas stream was maintained by achieving a constant flow of helium gas (He) from a pressurized gas cylinder with an exit pressure of 2.48 atm. The He main gas stream was then regulated and its flow was adjusted with a needle valve, which had an exit pressure of 1 atm. The constant He flow was fed to the entrance port of a 6-port valve where a H_2, N_2 and CO_2 gas mixture and TCE gas in 50 ml gas-tight syringes were introduced to the main gas stream through two separate ports by using a WPI SP200i syringe pump (WPI Inc, U.S.A.). The contaminated gas stream from the exit port of the valve was then fed to the inlet of the bioreactor (Figure 1). The flow rate of the gas stream was measured from 3 distinct points that were the entrance and exit of the bioreactor and exit of the Fe(0) column with a bubble flow meter that has a gas flow rate measuring limit of 0.1-10 ml min^{-1}. The effluent gas stream of the system was vented to the outdoor environment.

The reactor system was heated in order to obtain a constant temperature of 35±2°C with a water jacket. The water jacket consisted of a hot water reservoir heated by a bench-scale heater, a high rate liquid pump that pumped water from the reservoir through the flexible Tygon tubing rolled around the reactors. The temperature of the reactors was measured with a Fisher thermometer. The columns in the reactor system were gas tight and were pressurized with helium gas for leak detection prior to experimentation.

Analytical Methods

Identification, confirmation and quantification of chlorinated ethenes (TCE, cDCE, tDCE, 1,1DCE and VC), ethylene (ETH) and ethane (ETA) were made by ATI Unicam 610 Series gas chromatography equipped with flame ionization detector (FID) and Chrompack CP 7559 Poraplot Q-HT Plot FS column using 100µl gas samples withdrawn directly from the reactor system. Detection limits for TCE, cDCE, tDCE, 1,1DCE, VC, ETH and ETA were 3.84±0.23, 8.66±1.71, 22.27±2.56, 52.24±15.85, 25.54±7.29, 3.16±0.41, 5.26±1.00 ppmv, respectively. TCE and its reduction by-products at the influent and effluents of both bioreactor and Fe (0) column were analyzed during the experimental period. The compounds which were not under the detection limit,

were depicted in the results.

RESULTS AND DISCUSSION

The effect of gas residence time in active transformation zones are related to the gas flow rate and thus directly proportional to remediation efficiency [11]. Therefore, the effect of residence time on TCE removal was investigated in this study by using an innovative experimental set-up (Figure 1) which simulated the proposed horizontal bio- and chemo-barrier system (Figure 2).

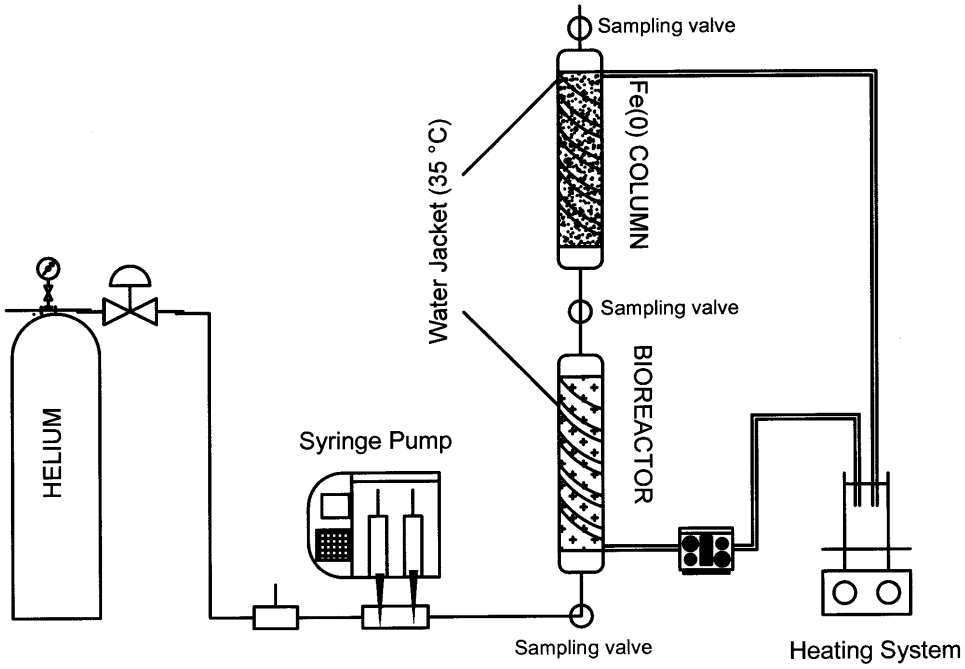

Figure 1. Illustration of continuous reactor system.

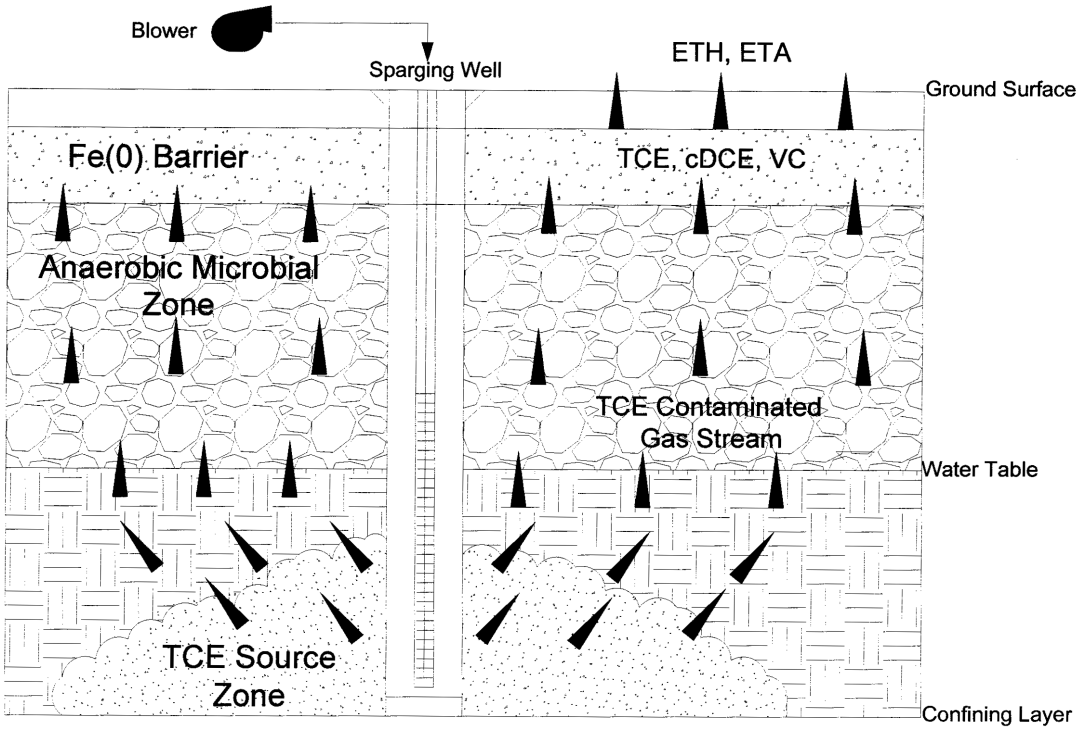

Figure 2. Horizontal bio- and chemo- barrier system.

Effect of Gas Residence Time on Performance of Reactor System

Continuous reactor system was fed with average influent concentrations of 170.6±28.5 ppmv TCE, 5000 ppmv H_2, 2000 ppmv CO_2 and 6000 ppmv N_2 in three months of operation period. In order to determine the effect of gas residence time on the TCE removal performance of the system, the gas residence time was varied as 2.5, 1.0, 0.5 and 0.25 hours for both bioreactor and Fe (0) column separately. The reactor system was operated for 93 days and the steady-state conditions were assumed to be achieved before every gas residence time variation when the coefficient of variation of two subsequent TCE removal efficiencies for both reactors were less than 10%. The effect of gas residence time on effluent characteristics of both bioreactor and Fe (0) column were given in Figures 3 and 4. The TCE removal efficiencies achieved in four different gas residence times were illustrated in Figure 5.

At 2.5 hrs of gas residence time, average TCE removal

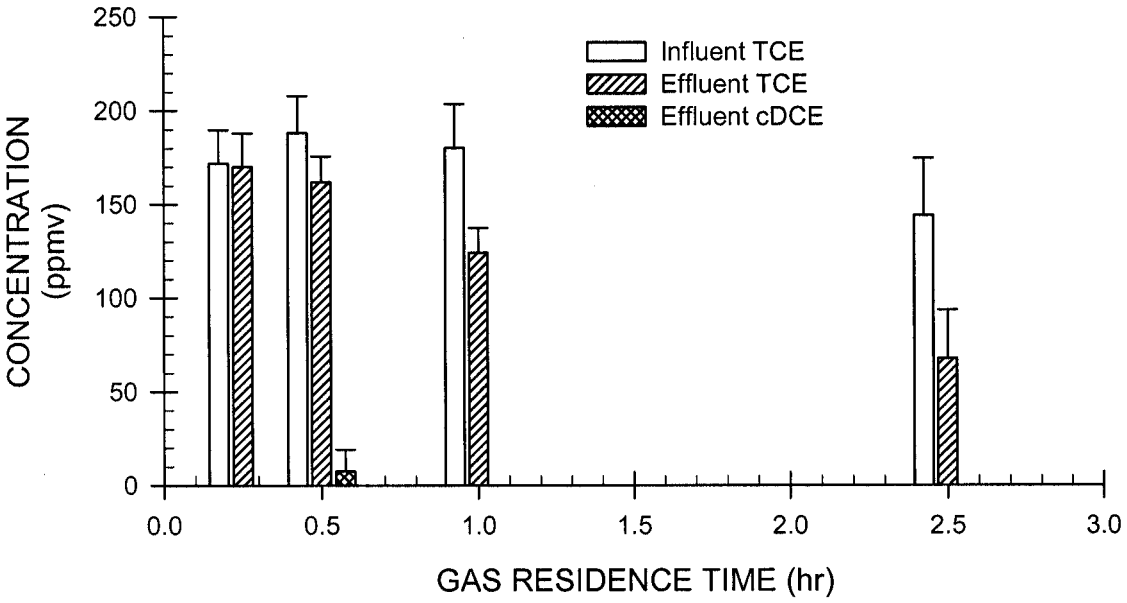

Figure 3. Effect of gas residence time on bioreactor performance.

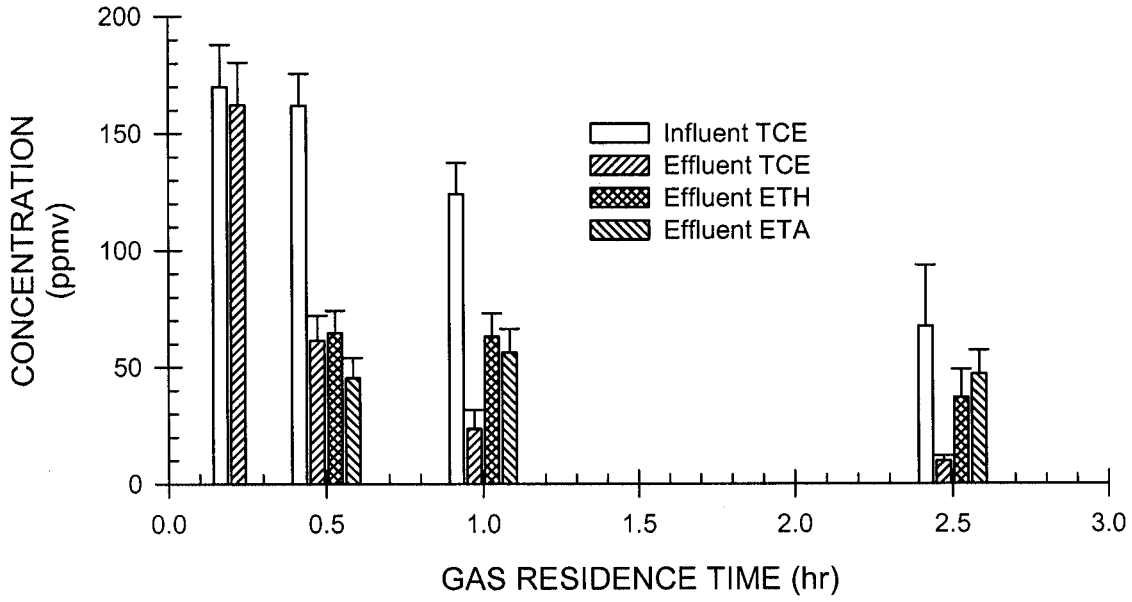

Figure 4. Effect of gas residence time on Fe(0) column performance.

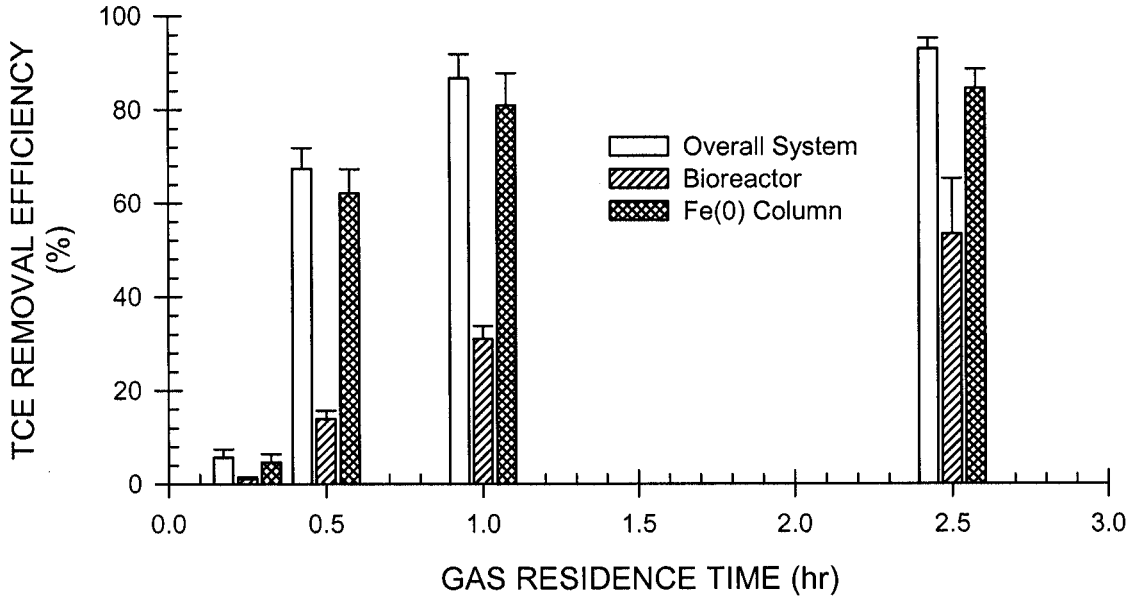

Figure 5. Effect of gas residence time on TCE removal efficiency of the system.

efficiencies of bioreactor, Fe(0) column and overall system were 53.5±12.0%, 84.6±4.1% and 93.0±2.3%, respectively (Figure 5). In bioreactor effluent, only TCE with an average concentration of 67.5±26.1 ppmv was observed while no other reduction by-products of TCE were detected (Figure 3). On the other hand, in the Fe(0) column effluent, TCE and ultimate reduction by-products of ETH and ETA with average concentrations of 9.7±2.3 ppmv, 36.9±12.1 ppmv and 46.9±10.3 ppmv were detected, respectively (Figure 4). Hence, the main TCE removal mechanism at this residence time is reductive transformation (57.3%) occurring in the Fe (0) column. On the other hand, physical elimination of TCE (36.5%) such as gas liquid transfer followed by biomass sorption is apparent (Figure 6a). The partition of dissolved TCE in the liquid phase with granular biomass is a factor of organic carbon partition coefficient of TCE (K_{oc} = 86±0.49 kg water kg organic carbon^{-1}, [12]) and organic carbon content in the reactor (4.15 g). There is a high partitioning between biomass and soluble TCE at steady-state conditions. The extent of mass transfer rate between two phases is important and should be investigated

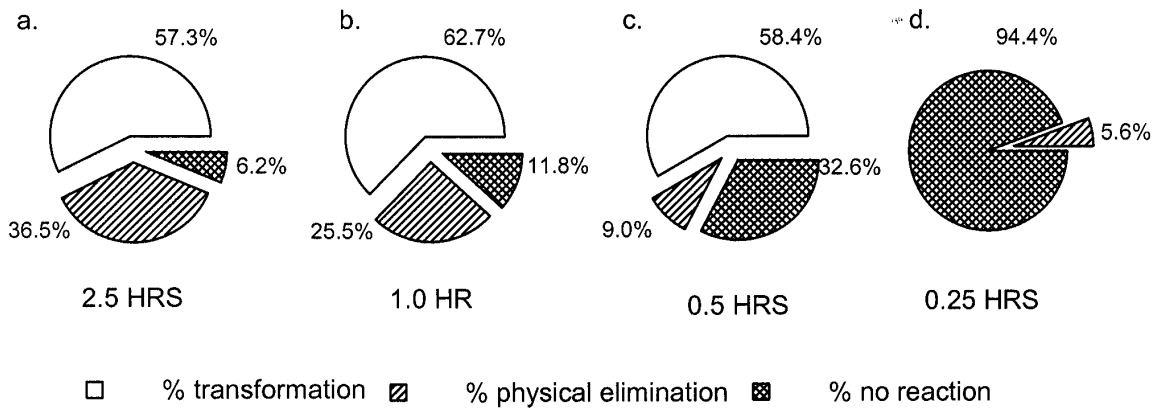

Figure 6. Distribution of TCE removal mechanisms at different gas residence times.

further.

At 1.0 hr of gas residence time, average TCE removal efficiencies of the bioreactor, Fe(0) column and overall system were 31.0±2.8%, 80.9±6.9% and 86.7±5.2%, respectively (Figure 5). The removal efficiencies of Fe(0)column and overall system decreased slightly, however decrease in the bioreactor was higher compared to the Fe(0) column and the overall system. In addition, only TCE with an average concentration of 124.1±13.5 ppmv was observed and no other TCE reduction by-products were detected in the bioreactor effluent. The reason could be the saturation extent of the liquid phase with TCE over 55 days of operation period and mass transfer rate between liquid and solid phases (Figure 3). On the other hand, TCE and ultimate reduction by-products of ETH and ETA with average concentrations of 23.5±8.2 ppmv, 63.1±10.1 ppmv and 56.3±10.2 ppmv were detected, respectively in the Fe(0) column effluent (Figure 4). In the Fe(0) column at 1 hr gas residence time, the effluent ETA concentration (63.1±10.1 ppmv) was less than ETH concentration (56.3±10.2 ppmv) whereas, it was higher at 2.5 hrs gas residence time (36.9±12.1 ppmv for ETH and 46.9±10.3 ppmv for ETA). As the gas residence time was decreased, the time that TCE spent in the reactor for reduction reaction was decreased leading to reduced ETH to ETA conversion. The dominant TCE removal mechanism in the system was reductive transformation occurring mainly in the Fe(0) column.

At 0.5 hrs of gas residence time, average TCE removal efficiencies of bioreactor, Fe(0) column and overall system were 13.9±1.8%, 62.1±5.2% and 67.4±4.5%, respectively (Figure 5). The decrease in the removal efficiencies of the bioreactor, the Fe(0) column and overall system when the gas residence time was decreased from 1.0 to 0.5 hrs (31.0±2.8% to 13.9±1.8% in bioreactor; 80.9±6.9% to 62.1±5.2% in Fe(0) column; and 86.7±5.2% to 67.4±4.5% in overall system) was higher than the decrease in efficiency when the gas residence time was reduced from 2.5 to 1.0 hrs (53.5±12.0% to 31.0±2.8% in bioreactor; 84.6±4.1% to 80.9±6.9% in the Fe(0) column; and 93.0±2.3% to 86.7±5.2% in overall system). The reason for this can be speculated that the time the TCE spent in the reactor for reaction was decreased by the decreasing gas residence time, so the removal of TCE in the reactors was affected by decreasing gas residence time. In bioreactor effluent, TCE and reduction by-product of cDCE with an average concentration of 161.9±13.7ppmv and 22.3±2.6ppmv were detected, respectively. The evidence of cDCE detection at 0.5 hrs of gas residence time indicated that a temporary reduction reaction occurred in the bioreactor. The existence of cDCE in the effluent of bioreactor at 0.5 hrs of gas residence time may be due to the fact that TCE was accumulated on the packed media of the bioreactor through 70 days and then a certain transformation of TCE to cDCE occurred. A similar situation had been observed in another study [13] where the PCE and TCE adsorbed on the mixed-species microbial mats were biotransformed aerobically and anaerobically in 50 days period after 24 hrs of rapid adsorption on the organic mat. On the other hand, in the Fe(0) column effluent, TCE and ultimate reduction by-products of ETH and ETA with average concentrations of 61.5±10.7 ppmv, 64.6±9.7 ppmv and 45.3±8.8 ppmv were detected, respectively (Figure 4). In the Fe(0) column at 0.5 hrs gas residence time, the difference between effluent ETH and ETA concentrations (64.6±9.7 ppmv for ETH and 45.3±8.8 ppmv for ETA) was higher than the difference at 1.0 hrs gas residence time (63.1±10.1 ppmv for ETH and 56.3±10.2 ppmv for ETA). Residence time dependency of the reaction rate was the key issue. On the other hand, the main TCE removal mechanism in the system was reductive transformations and the contribution of this mechanism was slightly decreased in the case of half residence time reduction (Figure 6).

At 0.25 hrs of gas residence time, average TCE removal efficiencies of the bioreactor, Fe(0)column and overall system were 1.1±0.4%, 4.6±1.8% and 5.6±1.8%, respectively (Figure 5). The removal efficiencies of the bioreactor, Fe(0) column and overall system decreased dramatically at this residence time compared to others. In the bioreactor, Fe(0)column and overall system effluents, only TCE, but no other reduction by-products, with concentrations almost equal to influent concentration were detected (Figure 3, 4, 5).

CONCLUSIONS

The in-situ horizontal bio- and chemo- barriers are a promising alternative for the treatment of TCE contaminated gas streams resulting from sparging systems. In this study, the effect of residence time, which is correlated with the remediation efficiency of the sparging systems, on the performance of the reactor system *i.e.* effluent gas composition and removal efficiency was investigated. The results clearly illustrated that at comparably low residence times, TCE removal efficiency of the system was over 90% and the effluent gas stream contained only non-toxic reduction end-products of TCE, *i.e.* ETH and ETA.

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