Treatment of Gaseous Trichloroethylene by a Sequential (Biological/Chemical) Reactor System

Ulaş TEZEL
School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA, USA.
e-mail: ulas.tezel@ce.gatech.edu
Göksel N. DEMİRER
Middle East Technical University, Department of Environmental Engineering, Ankara-TURKEY
e-mail: goksel@metu.edu.tr
Sibel ULUDAĞ-DEMİRER
Anadolu University, Department of Environmental Engineering, Eskişehir-TURKEY
e-mail: sudemirer@anadolu.edu.tr

Abstract

The treatment of gaseous trichloroethylene (TCE) by biotic and abiotic removal mechanisms in a sequential (biological/chemical) reactor system was investigated. The reactor system consisted of a granular anaerobic mixed culture packed biofilter followed by an elemental iron metal (Fe(0)) packed column in series. The effect of empty bed contact time (EBCT) and influent TCE concentration on the TCE removal performance of the system were investigated. In order to determine the effect of EBCT on the TCE removal performance of the system and the optimum EBCT for this system, EBCTs from 0.25 to 2.5 h were applied. The system was fed with 170.6 ± 28.5 ppmv of average influent TCE concentration, 5000 ppmv of H_2, 2000 ppmv of CO_2 and 6000 ppmv of N_2. Optimum EBCT for the system was determined as 1 h. The TCE removal performance at this EBCT was $31.0 \pm 2.8\%$ in the biofilter, $80.9 \pm 6.9\%$ in the Fe(0) packed column and $86.7 \pm 5.2\%$ in the overall system. Only ethylene and ethane were detected in the effluent of the system as reduction by-products. In addition, the performance of the system was not altered between the initial TCE concentrations of 150 and 650 ppmv at 1h of EBCT.

Key words: Biofilter, Fe(0) packed column, Reductive dechlorination, Trichloroethylene.

Introduction

Hazardous air pollutants (HAPs) include many pollutants that can potentially be air toxins due to their physical and chemical properties like chlorinated aliphatic hydrocarbons (CAHs), polychlorinated biphenyl compounds etc. Most of these hazardous pollutants can be classified as volatile organic compounds (VOCs) that have high vapor pressures and low boiling points, enabling them to vaporize quickly and not to stay stable in liquid phase or be adsorbed on solid media. The main route of release of these compounds to the environment is by air emissions (Howard *et al.*, 1990).

The 1990 Clean Air Act (CAA) Amendments have aroused serious concerns about gaseous emissions of HAPs and their control. Hundreds of chemical process industries and commercial sources are directly impacted by these new regulations. In addition, numerous conventional waste treatment and storage facilities will also be required to capture and treat their contaminated off-gas emissions. At several hazardous waste sites, remediation operations that are currently in place as well as those proposed (such as air-stripping, soil venting and air-sparging) will need to be modified or amended to control, cap-
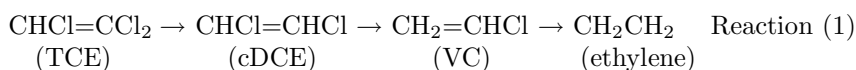
ture or treat their off-gas emissions (Khandan, 1994).

Its widespread use in industry and toxic effects make TCE one of the HAPs. The annual production rate of TCE in the USA was reported as 145,000 t and it is reported that 90% of TCE used as a degreasing solvent was released into the environment as air emissions. On the other hand, TCE is described as "probably carcinogenic to humans" by some international research agencies (Howard *et al.*, 1990).

The cost of technological changes to reduce TCE emissions leads the improvement of the treatment technologies for its removal. The conventional technologies are based on physical/chemical principles for the control of TCE emissions, such as condensation, incineration, carbon adsorption, absorption and catalytic conversions. The practical applicability of these technologies is limited by capital and operating cost considerations, residual and side stream formation, trace concentrations etc. (Khandan, 1994). On the other hand, halogenated com-

pounds are known to be treated biologically, especially with anaerobic reductive dehalogenation and abiotic reductive dehalogenation using elementary metals, such as iron. Biological/chemical dehalogenation systems may lead to very high TCE removal efficiencies by transforming this pollutant into nontoxic end-products like ethylene and ethane at relatively low costs provided that they are efficiently designed and operated.

All the chloroethylenes have been shown to be biotransformed under anaerobic conditions (Freedman and Gossett, 1989; deBruin *et al.*, 1992; Tandoi *et al.*, 1994). Anaerobic transformation of chloroethylenes may occurr via reductive dechlorination, which involves the sequential replacement of chlorines with hydrogen. Thus chloroethylene serves as an electron acceptor and hydrogen as an electron donor (Ballapragada *et al.*, 1997). Anaerobic reductive dechlorination of TCE is illustrated in Reaction (1).

$$CHCl=CCl_2 \rightarrow CHCl=CHCl \rightarrow CH_2=CHCl \rightarrow CH_2CH_2 \quad \text{Reaction (1)}$$
$$\text{(TCE)} \qquad \text{(cDCE)} \qquad \text{(VC)} \qquad \text{(ethylene)}$$

The hypothesized reaction pathways for TCE and other intermediates during reduction by Fe(0) are illustrated in Figure 1.
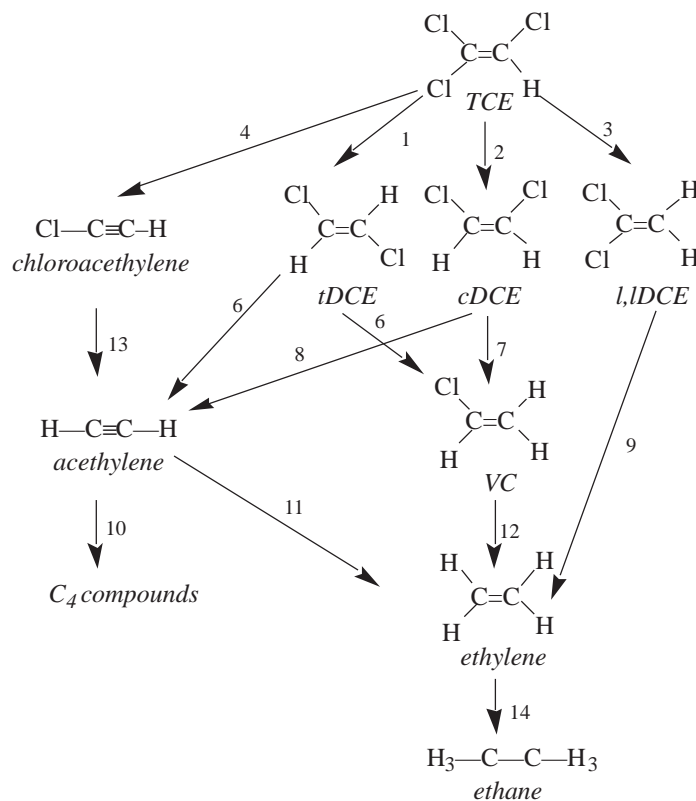

Figure 1. Hypothesized reaction pathways for TCE and other intermediates during reduction by Fe(0) (Arnold and Roberts, 2000).

290

There are a few reports of the application of these mechanisms in the transformation of TCE and other chloroethylenes in gas phase in the literature. Mihopoulos *et al.* (2000) studied the vapor phase treatment of perchloroethylene (PCE) in a soil column by lab-scale anaerobic bioventing and concluded that the PCE reduction rate in the column was very high at 5 h of residence time. However, the complete reduction of PCE to ethylene has not been achieved and vinyl chloride, which is a toxic gas, accumulated in the system. Moreover, Uludag and Bowers (2000) studied the adsorption/reduction reactions of gaseous TCE by Fe(0) in batch reactors and 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 partially oxidized surfaces, above which dechlorination occurred and the hydrogenolysis by-products appeared.

In this study, the application of biotic and abiotic removal mechanisms for the treatment of gaseous TCE was investigated in a sequential biological and chemical reactor system. The effects of important operation parameters like empty bed contact time (EBCT) and influent TCE concentration on the performance of the system were determined and the operational conditions were optimized for an effective and economical TCE removal in the proposed system.

Materials and Methods

Experimental Set-Up

Helium gas, which was the carrier gas was contaminated with TCE and a feed gas mixture of N_2, CO_2 and H_2 prepared in TEF sampling bags was added into the main gas stream with Hamilton 50 ml glass gastight syringes by the help of a WPI sp200i syringe pump. The gas mixture was then fed from the entrance point of a biofilter packed with a granular anaerobic mixed culture. The biologically treated gas stream was then introduced into the Fe(0) packed column following the biofilter. The influent, biofilter effluent and Fe(0) column effluent gas streams were sampled from the 3-way sampling valves located on each point with a Hamilton 100 μl glass gastight syringe and analyzed by gas chromatography (GC) immediately. The flow of the main stream was adjusted with a needle valve installed prior to the syringe pump and the flow of gas stream was measured with a bubble flow meter at the entrance of the system. The temperature of 35 °C in the system was obtained by a water jacket surrounding the reactors (Figure 2).
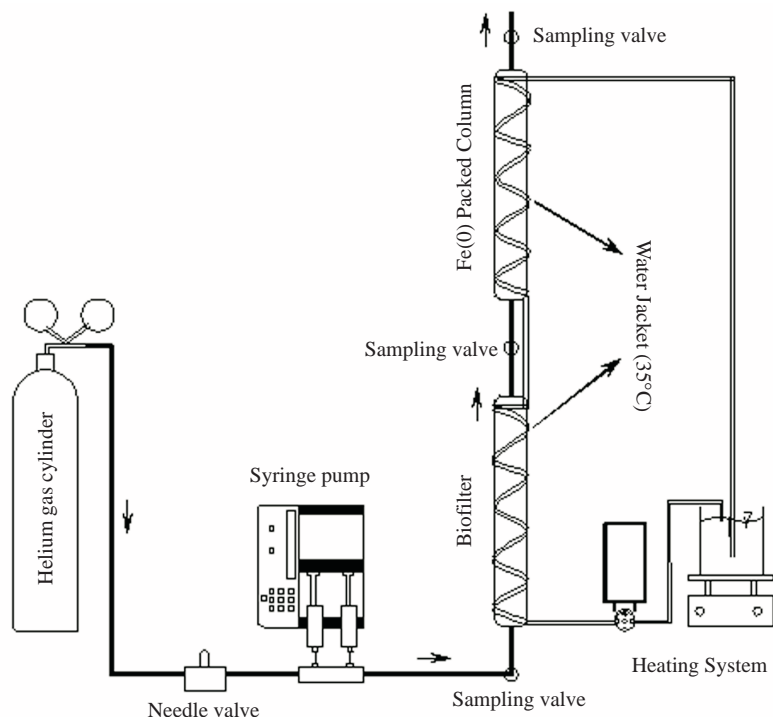

Figure 2. Illustration of the continuous reactor system.

Packing media

Granular anaerobic mixed culture (GAMC). GAMC obtained from the anaerobic treatment system of Ankara Efes Pilsen Beer Factory with a volatile suspended solids content of 41.447 ± 0.749 g of VSS/l was packed into the biofilter up to 100 ml from a 500 ml glass bottle consisting of GAMC and basal media containing following compounds (mg/l): NH_4Cl (400), K_2HPO_4 (500), KH_2PO_4 (400), $(NH_4)HCO_3$ (4000), $NaHCO_3$ (6000), $CaCl_2.2H_2O$ (50), $CoCl_2.6H_2O$ (10), NH_4VO_3 (0.5), $CuCl_2.2H_2O$ (0.5), $ZnCl_2$ (0.5), $AlCl_3.6H_2O$ (0.5), $NaMoO_4.2H_2O$ (0.5), H_3BO_3 (0.5), $NiCl_2.6H_2O$ (0.5), $NaWO_4.2H_2O$ (0.5), Na_2SeO_3 (0.5), and yeast extract (50). The moisture content in the biofilter was 100% and was maintained at 100% by adding distilled water into the biofilter several times. There was no nutrient supply to the biofilter during the operation period other than initially added basal media as described above.

Fe(0) fillings. The Fe(0) fillings that were inoculated into the Fe(0) packed column were obtained from Merck. The fillings had an effective diameter of 150 μm and were given 17.7% moisture content by treating with distilled water. The weight of fillings in the 100 ml of effective reactor volume was 241.16 g.

Chemicals

Trichloroethylene (TCE) (Merck); 1,1-dichloroethylene (1,1DCE), trans-dichloroethylene (tDCE), cis-dichloroethylene (cDCE), vinyl chloride (VC) and ethylene (Fluka Chemical Co., Germany); ethane and helium (Air Products and Chemicals Inc., USA) of GC grade, hydrogen, nitrogen, carbon dioxide (OKSAN Kol. Şti., Turkey) with high purity were used in the GC analysis and in continuous reactor experiments.

Analytical methods

GC analysis. An ATI Unicam 610 Series gas chromatography device equipped with a flame ionization detector (FID) at 200 °C, a Chrompack CP 7559 Poraplot Q-HT Plot FS column at an initial temperature of 100 °C (for 2 min) ramping to 200 °C at 20 °C/min (10 min at 200 °C), and a splitless injector at 150 °C with a 10 ml/min H_2 carrier gas flow and 100 μl sample volume were used.

The compounds analyzed with this analytical method are TCE, cDCE, tDCE, 1,1DCE, VC, ethylene and ethane with minimum detection limits (MDLs) of 3.84 ± 0.23, 8.66 ± 1.71, 22.27 ± 2.56, 52.24 ± 15.85, 25.54 ± 7.29, 3.16 ± 0.41, and 5.26 ± 1.00 ppmv, respectively. The MDLs of the compounds were determined by 7 consecutive blank injections (only 100 μl of air) to the GC. The detectable signal for the compounds was assumed to be 3 times the noise at the residence times of the compounds in the applied GC method.

Results and Discussion

Effect of EBCT on the performance of the continuous reactor system

The system was fed with 170.6 ± 28.5 ppmv of TCE, 5000 ppmv of H_2, 2000 ppmv of CO_2 and 6000 ppmv of N_2, and 2.5, 1, 0.5 and 0.25 h of EBCTs were applied for both the biofilter and Fe(0) packed column.

A promising treatment performance was achieved by proposed system within 3 months of continuous operation. The average performances in the removal of TCE were determined as $53.4 \pm 12.0\%$, $31.0 \pm 2.8\%$, $13.9 \pm 1.8\%$ and $1.1 \pm 0.4\%$ in the biofilter, $84.6 \pm 4.1\%$, $80.9 \pm 6.9\%$, $62.1 \pm 5.2\%$ and $4.6 \pm 1.8\%$ in the Fe(0) packed column, and $93.0 \pm 2.3\%$, $86.7 \pm 5.2\%$, $67.4 \pm 4.5\%$ and $5.6 \pm 1.8\%$ in the overall system for 2.5, 1, 0.5 and 0.25 h of EBCTs, respectively (Figure 3C).

Moreover, only TCE, ethylene and ethane with concentrations of 9.7 ± 2.3 ppmv, 36.9 ± 12.1 ppmv and 46.9 ± 10.3 ppmv at 2.5 h of EBCT; 23.5 ± 8.2 ppmv, 63.1 ± 10.1 ppmv and 56.3 ± 10.2 ppmv at 1 h of EBCT; and 61.5 ± 10.7 ppmv, 64.6 ± 9.7 ppmv and 45.3 ± 8.8 ppmv at 0.5 h of EBCT were detected in the effluent of the Fe(0) column (or overall system), respectively (Figure 4C). As the residence time of TCE in the system decreased with decreasing EBCT, the TCE removal efficiency and ethylene to ethane conversion also decreased (Figure 3). This observation verifies that the TCE removal and ethylene to ethane conversion rates in the system are dependent on the EBCT.

In the biofilter, by-products of reduction reactions of TCE were not detected at the applied EBCTs except for 22.3 ± 2.6 ppmv of cDCE being detected at 0.5 h of EBCT (Figure 4B). The occurrence of cDCE at 0.5 h of EBCT may be due to the fact that TCE is bioaccumulated on the packed media of the biofilter and then partially transformed into cDCE. A similar situation has been observed in a study by O'Niell *et al.* (1999) in which the PCE

and TCE adsorbed rapidly on the mixed-species microbial mats and a slow aerobic and anaerobic biotransformation of these compounds followed this adsorption within an extended time period of 50 to 628 days.

The TCE removal efficiencies in the system components and overall system at EBCTs greater than 1 h were constant and around 31.1% in the biofilter, 82.8% in the Fe(0) column and 91.9% in the overall system (Figure 5). These removal efficiencies are the maximum removal efficiencies that are obtained in the system. The difference between the maximum removal efficiencies of the biofilter and Fe(0) column could be due to the effectiveness of the packing media in TCE removal.

The optimum EBCT for the system was determined as 1 h, which is the minimum EBCT where the maximum TCE removal efficiency in the overall system is achieved (Figure 5).

Effect of influent TCE concentration on the performance of the continuous reactor system

The concentration of vapor phase contaminants found in off-gases from soil and groundwater remediation operations from industrial processes and from wastewater treatment systems varies between 0 and 500 ppmv, but does not exceed 2000 ppmv (Bohn, 1992; Lackey, 2002). Therefore, in this study, 170.6 ± 28.5 ppmv of average influent TCE concentration was applied to the system in the 3 months of the operation period and 91.9% of TCE removal was achieved at an optimum EBCT of 1 h. At this EBCT, the system performance was stable at the average influent TCE concentration applied.
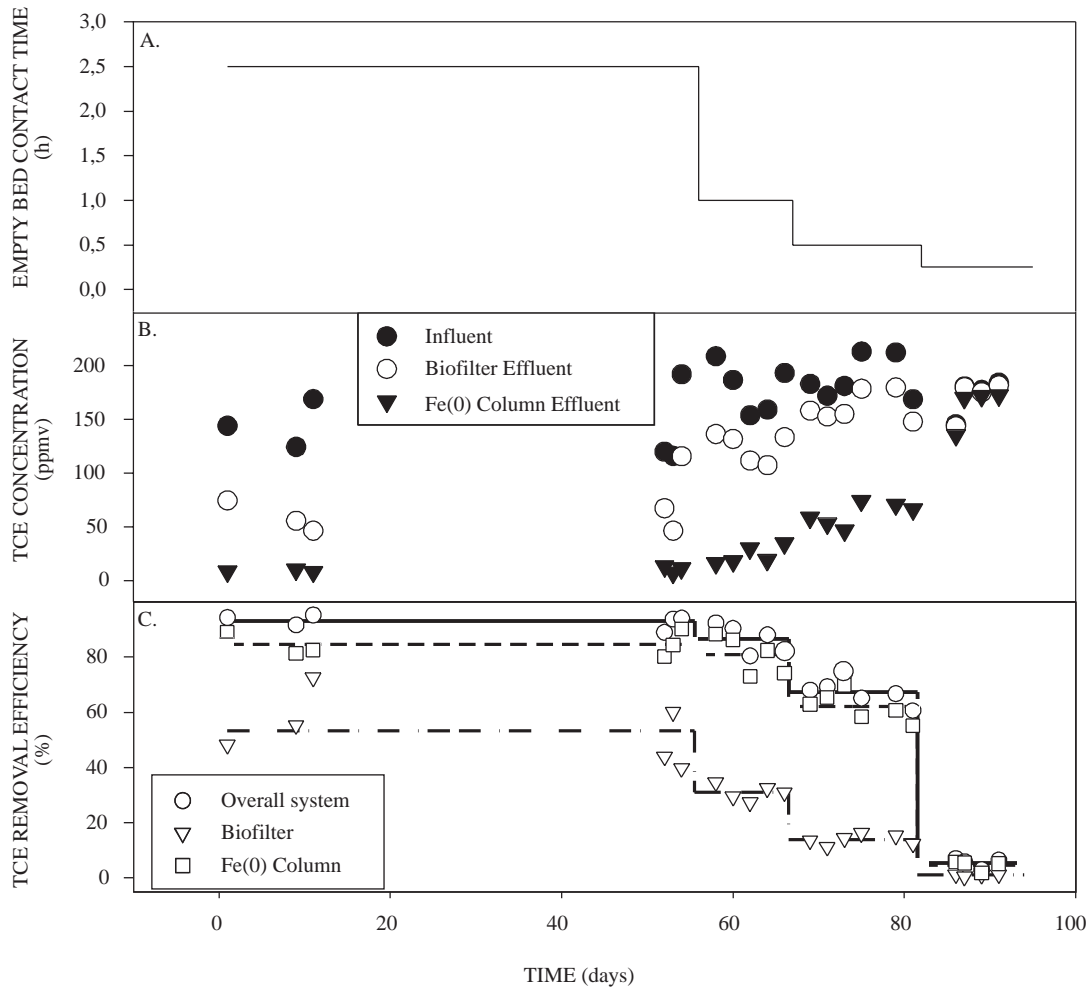

Figure 3. Effect of EBCT on the performance of the continuous reactor system; A, EBCTs applied; B, TCE concentrations; C, TCE removal efficiencies.
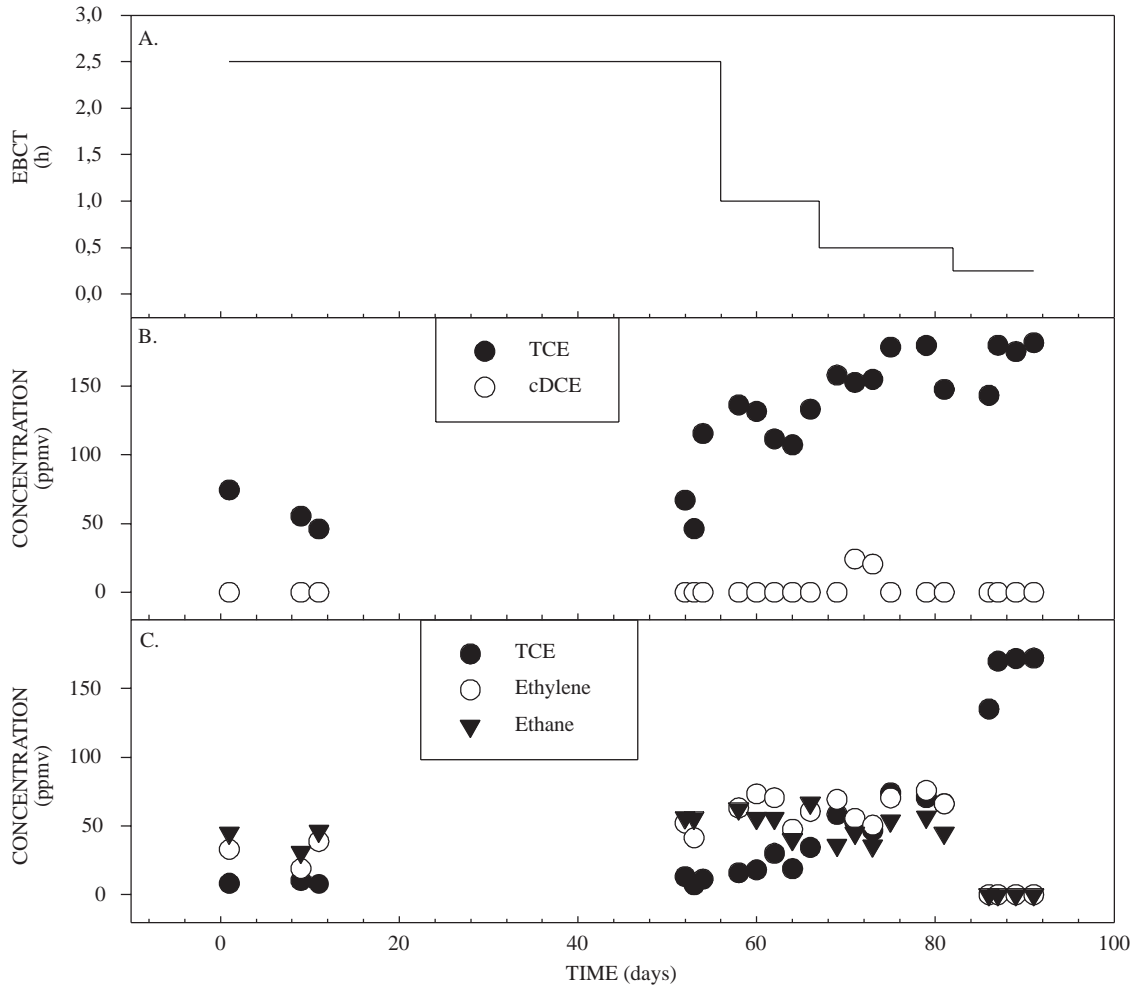
Figure 4. Effect of EBCT on effluent characteristics of B, Biofilter; C, Fe(0) column.
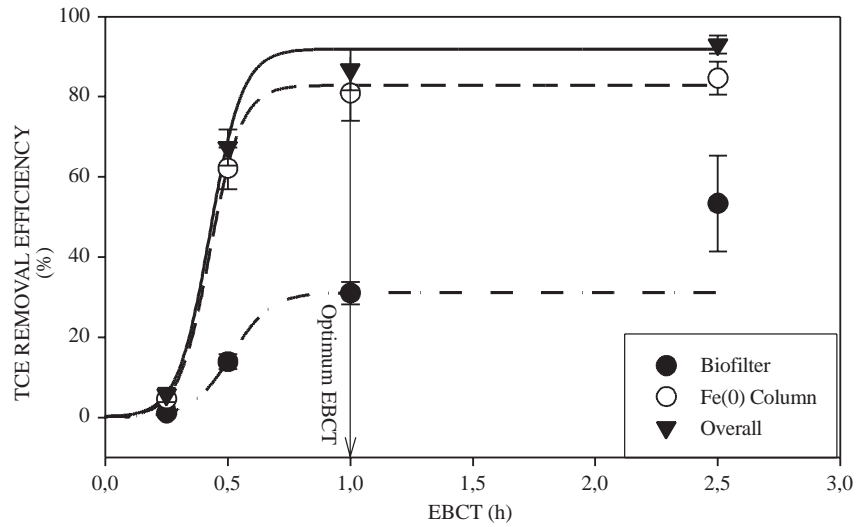

Figure 5. Average TCE removal efficiencies obtained at different EBCTs applied to the continuous reactor system.
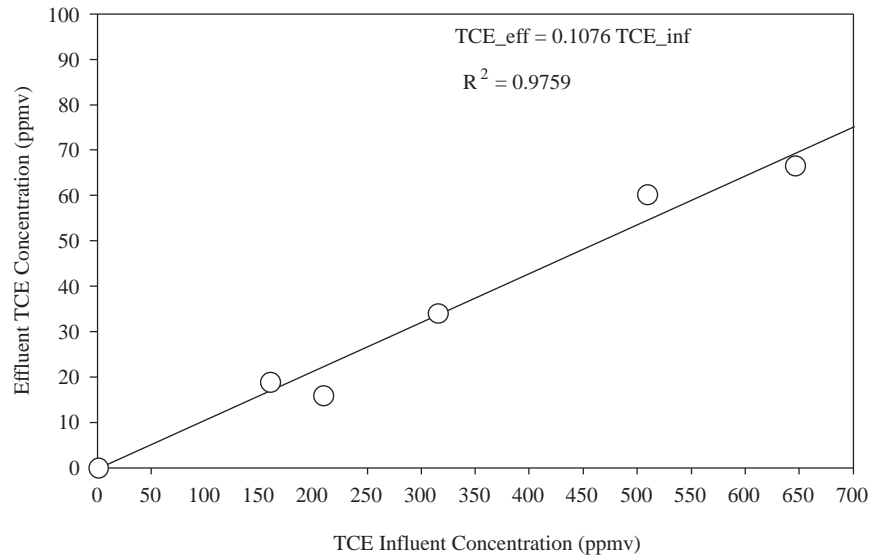
Figure 6. The effect of influent TCE concentration on the performance of the continuous reactor system.

In order to determine the effect of influent TCE concentration on the continuous reactor system at 1 h of optimum EBCT, influent TCE concentrations between 150 and 650 ppmv were applied and the effects of these influent concentrations on the system performance were investigated (Figure 6). The results showed that the influent TCE concentration range studied had significant effect on the system performance in terms of TCE removal efficiency. The average TCE removal efficiency of the system at different influent TCE concentrations at 1 h of EBCT was 89.2%.

Conclusion

The TCE removal efficiency of the continuous reactor system is 91.9% at a very low optimum EBCT of 1 h compared with the other economical treatment options for chlorinated compounds in the gas phase (Bohn, 1992; Mihopoulos et al., 2000). At this EBCT, the effluent gas stream from the system contains only trace amounts of TCE and non-toxic reduction end-products, ethylene and ethane. The effluent composition of the system shows that efficient reductive dechlorination processes have occurred in the system predominantly in the Fe(0) column (Fig-

ure 4).

According to the maximum TCE removal efficiencies obtained in the biofilter and Fe(0) column, the Fe(0) fillings are a more effective medium than granular anaerobic mixed culture in terms of TCE reduction (Figure 5).

The TCE removal performance of the sequential reactor system at different influent TCE concentrations between 150 and 650 ppmv at 1 h of EBCT was stable, at around 90%.

The high TCE removal efficiency at low EBCT, compared to the other economical and feasible treatment options (Bohn, 1992; Mihopoulos et al., 2000), makes the use of sequential biotic and abiotic transformation mechanisms an attractive method that can potentially be integrated to an in-situ remediation process, like air-sparging, to treat contaminated soils and groundwaters with TCE, or applied in industries that need to control their TCE emissions.

Acknowledgment

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