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Evaluation of co-metabolic removal of trichloroethylene in a biotrickling filter under acidic conditions

Dhawal Chheda, George A. Sorial*

Department of Biomedical, Chemical, and Environmental Engineering, College of Engineering and Applied Science, University of Cincinnati, 701 Engineering Research Center, 2901 Woodside Drive, Cincinnati, OH 45221-0012, USA

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ABSTRACT

This study investigated the removal of hydrophobic trichloroethylene (TCE) in the presence of methanol (co-metabolite) in a biotrickling filter, which was seeded with fungi at pH 4. Starvation was chosen as the biomass control strategy. Two systems, Biofilter I (methanol:TCE 70:30) and Biofilter II (methanol:TCE 80:20) were run in parallel, each with varying composition ratios. The TCE loading rates for both biofilters ranged from 3.22 to 12.88 g/m³/hr. Depending on the ratio, methanol concentrations varied from 4.08 to 27.95 g/m³/hr. The performance of the systems was evaluated and compared by calculating removal kinetics, carbon mass balance, efficiencies and elimination capacities. Methanol was observed to enhance TCE removal during the initial loading rate. However, methanol later inhibited TCE degradation above 6.44 g TCE/m³/hr (Biofilter I) and 3.22 g TCE/m³/hr (Biofilter II). Conversely, TCE did not impede methanol removal because over 95% methanol elimination was consistently achieved. Overall, Biofilter I was able to outperform Biofilter II due to its greater resistance towards methanol competition.

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Introduction

Trichloroethylene (TCE) is a three chlorine volatile organic compound (VOC). It is ranked at the 16th position in the 2005 Superfund priority list of hazardous substances by the US EPA (Marco-Urrea et al., 2008a). It has been extensively used as a solvent in the cleaning, refrigerant and electronics industries (US EPA, 2014a; Den et al., 2006; Das et al., 2011). It is estimated that approximately 97% of rural areas in the USA survive on groundwater as their principal water source (Lackey et al., 2003). A majority of these sources are contaminated with TCE due to its usage in the dry cleaning industries (Pant and Pant, 2010). Also, TCE concentrations of up to 170 µg/m³ in the gas phase has been detected in Ohio, USA with the degreasing industry being a major source of vapor release (US EPA, 2015a; Huang et al., 2014).

TCE can affect human nervous, immune and reproductive systems by causing ailments, such as scleroderma and postponed motor response syndrome. It is also a potential carcinogenic compound (Chiu et al., 2013). Thus, US EPA has set a maximum contaminant level (MCL) of TCE in drinking water at 5 µg/L (US EPA, 2014b), thereby making the efficient removal of TCE highly essential. However, to assess remediation technology, it is important to have an understanding of the fundamental properties of TCE and its fate when released into the environment.

First, TCE is sparingly soluble in water with a Henry's Law constant of 0.00892 atm-m³/mol at 20°C (Russell et al., 1992). When released into surface water, it volatilizes and converts to gaseous phase, where its half-life is over 13.2 days. In addition, its natural photo-degradation in the gas phase is not a significant process because it is unable to absorb radiation over 290 nm (US

* Corresponding author. E-mail: george.sorial@uc.edu (George A. Sorial).

EPA, 2014a). Another significant property of TCE is its density of 1.46 g/cm^3 (Bekele et al., 2016). Because of its low water-solubility and high density, TCE forms a dense non-aqueous phase liquid, which is a separate mobile plume. When discharged into the groundwater, it sinks to the bottom impervious layer (Russell et al., 1992; Ramsey Conservation District, 2009). This layer can undergo air sparging or vapor extraction, after which, the air can be subjected to further treatment.

Currently, there are several TCE removal technologies, such as thermal incineration, membrane separation, dechlorination and ozonation. These methods, while efficient, demand high capital investments and operational costs, are energy intensive and can lead to the release of toxic by-products such as dioxins and furans (Huang et al., 2014). Biological degradation is an efficient technology to degrade hydrocarbons. Also, biotrickling filters have proven to result in removal efficacies of as high as 82% and 90.5% for hydrophobic compounds like *n*-hexane and benzene (Aly Hassan, 2010). It should be noted that anaerobic degradation of TCE can result in lethal by-products such as vinyl chloride. In contrast, aerobic degradation can reduce TCE to carbon dioxide and biomass (Mattes et al., 2010). Therefore, this study investigates the bioremediation of TCE, which is regarded as the best available control technology (BACT) to treat the impure gas phase (Aly Hassan and Sorial, 2010a).

During the biodegradation mechanism, the organic source has to be an electron donor. However, because TCE is in a highly oxidized state, it does not act as the necessary beneficial carbon source for the microbes (Tabernacka et al., 2014). Therefore, another growth substrate (co-metabolite) is added along with TCE (or non-growth substrate) to support its biodegradation. This makes TCE more bioavailable. Toluene, methane, phenol, methanol and ammonia have all been proven to be good primary carbon sources when supplied along with TCE to the biofilter (Tabernacka et al., 2014; Shukla et al., 2010). It has been discovered that the co-metabolites help stimulate the release of substrate oxidizing enzymes, such as monooxygenase and dioxygenase. An important property of these enzymes is their non-specificity of the target substrate, which assists in the catalytic degradation of TCE along with the prime substrates (Wilson and Wilson, 1985; Suttinun et al., 2013).

Although there are several advantages of using a fungal consortium, most research works have focused on the utilization of bacteria to degrade TCE (Shukla et al., 2014). Fungal systems are comparatively more resistant to extreme conditions, such as acidification, drying out and declined nutrient and organic feed. In addition, fungal systems form a larger surface area in the gas phase due to the presence of aerial mycelia. This process potentially increases the uptake rate of TCE, which can assist in overtaking the biofiltration rate limiting step. This result is particularly helpful when dealing with a hydrophobic and sparingly soluble compound such as TCE (Estrada et al., 2013). It has been demonstrated that, in a batch process, the white-rot fungi species, *Trametes versicolor*, is able to degrade 65.7% TCE at pH 4.5 with an initial concentration of 10 mg/L TCE in presence of 8 g/L glucose and reoxygenation (Marco-Urrea et al., 2008a). Furthermore, the same group of fungi (white-rot) can release highly non-specific lignin-modifying enzymes, such as peroxidases. These fungi have

been shown to metabolize TCE to less toxic compounds such as CO_2 and 2,2,2-trichloroethanol via the cytochrome P-450 type monooxygenases (Marco-Urrea et al., 2008b).

The enzymes responsible for the organic breakdown are released due to the presence of primary substrates. Accordingly, the co-metabolite and TCE both compete for the same sites on the enzyme. An under supply of the co-metabolite might yield fewer enzymes, and an extra provision of the chief substrate can result in competitive inhibition for TCE (Suttinun et al., 2013). Therefore, this current study investigates the impact of co-metabolite loading rates and the VOC composition ratio on the degradation of TCE in a trickle bed air biofilter. The biofilters were seeded with fungi as the principal microbe source, and methanol was supplied as the co-metabolite. Both methanol and TCE are listed in the 1990 Clean Air Amendment List (US EPA, 1990). It is important to note that the main TCE releasing industries, such as metal, transportation, plastics and rubber, tend to discharge methanol along with TCE (US EPA, 2015b). The methanol to TCE ratios utilized in Biofilters I and II were the average disposal/release ratios for transportation and cement industries, respectively (US EPA, 2015b). Therefore, the aim of this research was to evaluate the performance of the twobiofilters by calculating the TCE removal efficiencies, TCE removal kinetic constants, and carry out a carbon mass balance across each of the biofilters.

1. Experimental

1.1. Chemicals

Trichloroethylene, with 99.5% purity, was obtained from Fisher Scientific (Fair Lawn, NJ, USA). Methanol, with 99.9% purity, was acquired from Tedia (Fairfield, OH, USA).

1.2. Biotrickling filter system

Two identical biotrickling filters were run in parallel. Each had an internal diameter of 0.076 m and height of 1.3 m. The biofilters were filled with diatomaceous earth pellets (Celite® 6 mm R-635 Bio-Catalyst Carrier; Celite Corp., Lompoc, CA), which acted as the media for the biomass to grow on. These pellets were stacked in each system at a depth of 0.6 m (Cai et al., 2007). This research followed a previous project applying the same biofilters to treat different VOCs. A detailed microbial analysis was performed during the previous research and fungal species like *G. moniliformis* (*F. verticillioides*) and *F. solani* were detected (Zehraoui et al., 2014). Two identical biotrickling filters were operated at different methanol to TCE ratios. Both Biofilters I (70% methanol to 30% TCE) and II (80% methanol to 20% TCE) were fed TCE concentrations ranging from 20 to 80 ppmV. The corresponding methanol concentrations ranged from 103 to 711 ppmV. This blend was injected into the air stream flowing at a rate of 1.36 L/min, which corresponded to an empty bed residence time of 2 min. The nutrient solution (buffered at pH 4 using sodium formate) was spiked with the necessary nutrients and micronutrients, such as N, P, Fe, Mg and Mn. The final solution was sprayed on top of the biofilter intermittently via a nozzle at a rate of 2 L/day. The nutrient composition was determined by Sorial et al. (1995) VOC laden air

flow and nutrient liquid flow were flowing co-currently, from the top of the bed to the bottom.

1.3. Biomass control strategy

Sustainable growth of biomass is important for an efficient performance of the system. Although an increase in biomass concentration is important for the removal of TCE and methanol, excess biomass can shrink the void space required for the air and liquid to pass through. This can lead to gas channeling and an increase in pressure drop across the bed. Eventually, the operation and the elimination capacities are impacted. Therefore, it is necessary to develop a strategy for biomass control (Aly Hassan, 2010).

Several strategies have been suggested in literature. “Backwashing” is the strategy where the bed is fluidized by passing the liquid nutrients through the system in the reverse direction and at a higher flow rate. The excess biofilms developed on the media shear off and are collected in the effluent. Nutrient limitation, or “Starvation”, is the approach where the nutrients and organic compounds are not supplied to the microbes. The bed is ‘starved’ for a period of time. This can limit biomass growth and can help eliminate excess biomass from the system. Additionally, starvation generally does not have a prolonged effect on the re-acclimation process of the bed (Cox and Deshusses, 2002). “Flow Switching” has been proven to work as a good control strategy by regularly changing the direction of gas flow. This helps in evenly distributing the biomass across the biotrickling filter, rather than possible concentrated growth in a single region (Devinny et al., 1999).

Because TCE is a hydrophobic volatile organic compound, it alone does not support the growth of biomass. This results in a deceleration in the rate of biomass growth. Accordingly, it is necessary to maintain the integrity of the biofilter, which can be damaged during backwashing and flow switching. Therefore, starvation was the biomass control strategy of choice, and the supply of nutrients and gas phase organics (TCE and methanol) was shut down for 48 continuous hours every week.

1.4. Analytical methods

Influent and effluent liquid samples were taken from the biofilters and analyzed twice a week. Volatile suspended solids (VSS) were measured following the procedure stated in the Standard Methods 2540G. Nitrate (NO_3^-) concentrations for the influent and the effluent were analyzed according to the Standard Methods 4500- NO_3^- in a 1240 UV–Vis Spectrophotometer by Shimadzu Corp. (Tokyo, Japan) at a wavelength of 220 nm. Concentrations of total organic carbon (TOC), total carbon (TC) and inorganic carbon (IC) were measured in a Shimadzu TOC-L Total Organic Carbon Analyzer (Shimadzu Corp., Tokyo, Japan) according to the Standard Methods 5310. Chloride (Cl^-) concentrations were determined in an Ion Chromatograph (Dionex Corp., Sunnyvale, California, USA) fitted with an anion exchange column following the Standard Method 4110B (Eaton et al., 2005).

Gas samples were obtained daily from the system influent and effluent ports using gas tight syringes. The samples were analyzed for trichloroethylene and methanol using a Gas

Chromatograph (GC) (Agilent 6890 Series, Foster City, California, USA). The unit was operated in the splitless mode, and the column dimensions were $30\text{ m} \times 320\text{ }\mu\text{m} \times 0.25\text{ }\mu\text{m}$ (HP-5, 5% phenyl methyl siloxane). A flame ionization detector (FID) was employed at a temperature of 250°C while the oven was set to 60°C . Hydrogen (H_2) was supplied as the fuel gas at a flow rate of 40 mL/min. Air was supplied at 450 mL/min. Last, the rate of helium make-up gas was 45 mL/min. With this configuration, the retention times for methanol and trichloroethylene were 1.2 min and 1.6 min, respectively. The effluent carbon dioxide produced was measured in a GC (Agilent 19095P, Foster City, California, USA) fitted with the CarbPLOT capillary column with dimensions of $30\text{ m} \times 530\text{ }\mu\text{m} \times 0.83\text{ }\mu\text{m}$. It was analyzed by a thermal conductivity detector (TCD) according to the method described in detail by Kim et al. (2005).

2. Results and discussion

2.1. Performance of the biotrickling filters

As mentioned earlier, two biotrickling filters, Biofilter I and Biofilter II were operated in parallel. Each was tested with different ratios of TCE and methanol. Four phases for both systems were run for 5 weeks/phase under the operating conditions summarized in Table 1. The performances for all of the phases in Biofilters I and II are illustrated in Fig. 1. The removal efficiencies (REs) are statistically presented using box plots, where the upper and lower boundaries of the box represent the 75th and 25th percentiles, the whiskers below and above the box represent the 10th and 90th percentiles, and the line within the box indicates the median. Only the TCE data have been indicated in the figures because the REs for methanol exceeded 95% for all of the phases studied. Also, the chlorides released in this TCE oxidation reaction tend to the release of hydrogen chloride in the effluent liquid. Yet the effluent pH was above neutral since the formate buffer was degraded during the microbial oxidation and the effluent concentration of hydrogen chloride was not high enough to influence the pH. The biomass control strategy, which was starvation once per week for a period of two days, was administered after an acclimation period of 30 days. Consequently, all of the data also accounts for any effect starvation might have had on the performance. Biofilter II did not undergo an acclimation period because it was seeded with the fungal consortium obtained from the acclimated Biofilter I.

For Biofilter I, phase I was carried out after the acclimation period. TCE and methanol were loaded at concentrations of 20 and 103.7 ppmV, respectively. Phase II was next and the microbial bed was fed with 40 ppmV TCE and 207.4 ppmV methanol. Fig. 1a shows that the obtained REs for TCE showed an increase from $79.4\% \pm 4.1\%$ in phase I to $89.1\% \pm 5.9\%$ in phase II. Therefore, methanol was beneficial for TCE removal because a higher concentration of the co-metabolite helped TCE become more accessible to the microbes. However, the REs displayed a downward trend in the latter phases. In phase III, $70.3\% \pm 2.9\%$ of TCE was eliminated when the influent gas phase concentrations entering the biofilter were 60 ppmV TCE and 311.1 ppmV methanol. In phase IV, as the inlet TCE concentration increased to 80 ppmV, the TCE REs dipped further to $65.1\% \pm 7\%$.

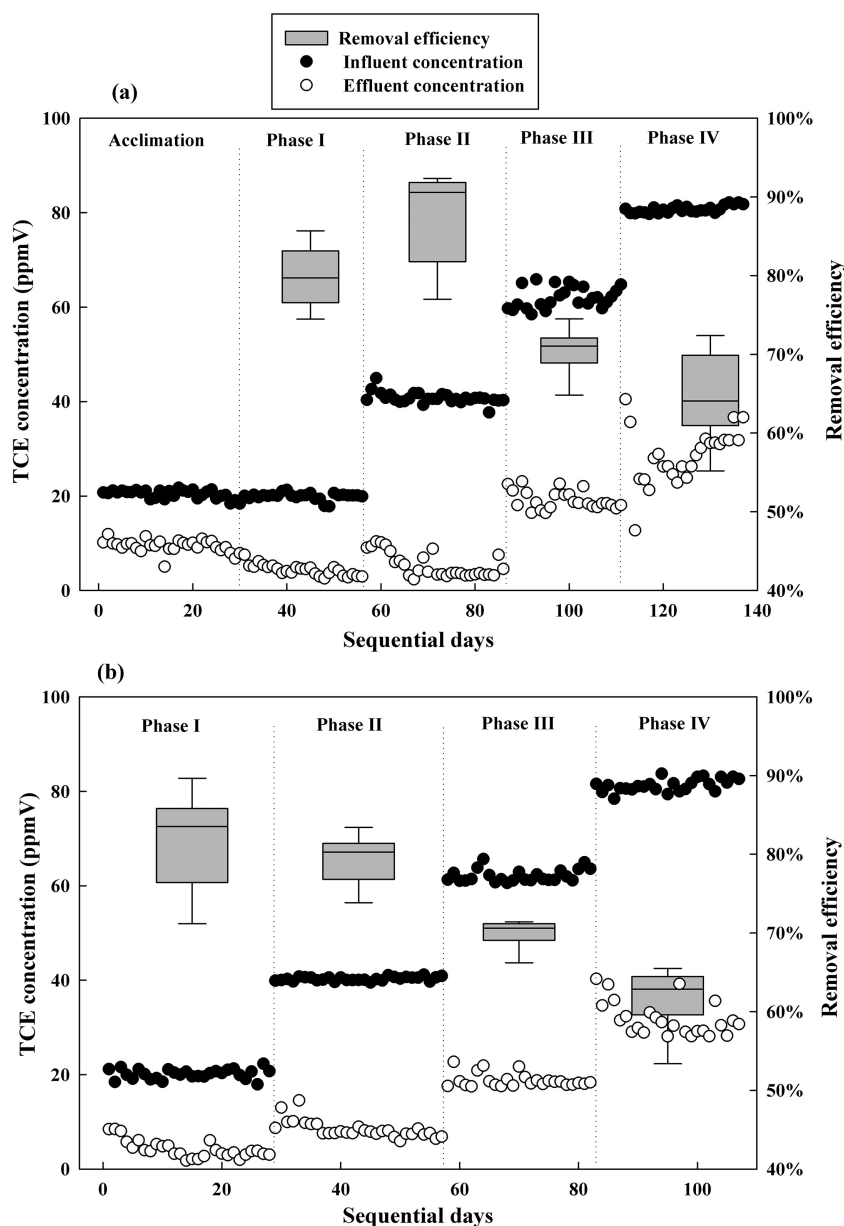
Table 1 – Experimental conditions for Biofilters I and II.

Phase	TCE conc. (ppmV)	TCE LR (g/m ³ /hr)	Biofilter I			Biofilter II		
			Days of operation	Methanol conc. (ppmV)	Methanol LR (g/m ³ /hr)	Days of operation	Methanol conc. (ppmV)	Methanol LR (g/m ³ /hr)
I	20	3.22	31–56	103.7	4.08	0–25	177.8	6.99
II	40	6.44	57–86	207.4	8.15	26–53	355.6	13.97
III	60	9.66	87–111	311.1	12.23	54–82	533.4	20.96
IV	80	12.88	112–138	414.8	16.31	83–108	711.1	27.95

conc.: concentration, LR: loading rate.

The trends of elimination capacities between Biofilters II and I varied. It should be noted that for each examined phase, the methanol concentration in Biofilter II was higher than in Biofilter I; the former system had 80% methanol versus 70% in

the latter. As detailed in Table 1, phase I to IV had influent TCE concentrations ranging from 20 to 80 ppmV. Meanwhile, the methanol concentrations varied from 177.8 to 711.1 ppmV with equal jumps within the phases. Throughout the runs, the

**Fig. 1 – Performance of Biofilter I (a) and Biofilter II (b).**

increasing influent concentrations had an inverse effect on TCE eliminations for Biofilter II. The RE for TCE achieved in phase I was $81.4\% \pm 6.7\%$. The REs in phases II, III and IV were $78.9\% \pm 4.7\%$, $69.7\% \pm 2\%$ and $61.3\% \pm 4.3\%$, respectively (Fig. 1b). The decrease in removal proficiency is attributed to the increase in both TCE and methanol concentrations. Because TCE is not a beneficial carbon source, it did not degrade at higher concentrations, particularly when a high loading rate of non-toxic methanol was supplied with it. This created an environment of competitive inhibition where methanol ultimately impeded the degradation of TCE. When compared to the literature, fungal biotrickling filters were able to degrade higher concentrations of TCE. A maximum of 60% TCE RE was achieved when biofilters were inoculated with *Pseudomonas putida* and toluene was supplied as a co-metabolite (Cox et al., 1998). Similarly, 70% TCE was removed in a two-stage bioscrubber-biofilter system with phenol and ammonia used as growth substrates (Tabernacka et al., 2014).

When comparing the efficacy of the two systems, the concentration ratio of methanol to TCE is a highly critical parameter. As mentioned earlier, for both systems, the methanol REs were more than 95% across all of the phases. However, the data for TCE removal shows that for an influent loading rate of $3.22 \text{ g/m}^3/\text{hr}$, more TCE was removed within Biofilter II than Biofilter I. However, between phases I and II, as the loading rates doubled, TCE elimination was significantly lower in Biofilter II compared to Biofilter I. An important property governing the biological treatment of VOCs is their hydrophobicity. As reported earlier, during biofiltration, the oxidation of the hydrophilic compounds (like methanol) is preferred over hydrophobic compounds (TCE). This is because the mass transfer from the gas to liquid phase is not limiting for hydrophilic organics. During phase II, the primary substrate hindered the oxidation of TCE because methanol (which is hydrophilic) was more readily available to the fungi compared to TCE. Zehraoui et al. (2012) reported that at a hexane loading rate of $13.2 \text{ g/m}^3/\text{hr}$, the biotrickling filter with a higher methanol loading rate saw a steep decrease in the hexane RE. This was justified by methanol inhibition and backwashing. As the phases progressed, the VOC loading rates increased only by 50% from phase II to III and by 25% from phase III to IV. Therefore, the effect of methanol inhibition was suppressed when comparing the two systems. In addition, the higher loading rates of TCE in the latter phases increased its cytotoxicity. Consequently, there was a 3.8% difference between the TCE REs of Biofilters I and II.

Fig. 2 compares the elimination capacities (EC) between the two systems for different loading rates (LR). During phase I, the difference in methanol LR between the two systems is not as substantial. Therefore, Biofilter II was able to metabolize higher concentrations of TCE with an EC of $2.62 \text{ g/m}^3/\text{hr}$, compared to an EC of $2.56 \text{ g/m}^3/\text{hr}$ in Biofilter I. This can be associated with methanol assisting to enhance the bioavailability of TCE. It was observed that for TCE LR of over $3.22 \text{ g/m}^3/\text{hr}$, Biofilter I had higher ECs compared to Biofilter II. For an LR of $6.44 \text{ g/m}^3/\text{hr}$, the EC for Biofilter I was $5.73 \text{ g/m}^3/\text{hr}$ while that of Biofilter II was $5.08 \text{ g/m}^3/\text{hr}$. The ECs obtained during Phase II approached the 45-degree line (100% removal) after which they started to diverge away. The differences in the ECs of TCE between both systems started to widen after phase I. This divergence is due to higher

concentrations of methanol in the feed (i.e., higher methanol LR) of Biofilter II compared to Biofilter I. Overall, the TCE ECs of both Biofilters I and II were comparable to each other with the EC for Biofilter II being always lower than Biofilter I. The maximum difference in the ECs of the two systems occurred in phase II with a difference of 11.4%. At-test was performed to compare the ECs of the two biofilters. The result of the t-test ($p = 0.874$) indicated that there is no significant difference between the two EC groups. It is also worth mentioning that the achieved methanol ECs were consistently near the 45-degree line and were independent on the TCE LRs.

2.2. Carbon mass balance

In both systems, the influent carbon sources consisted of VOCs (TCE and methanol) in the gaseous phase and the influent carbon in the liquid nutrients. These carbon sources were digested to effluent carbon dioxide, effluent VOCs in the gaseous phase, VSS, and total carbon (TC) in the liquid phase. For both biofilters, only TCE and methanol peaks were detected while analyzing the effluent gas samples in the GC-FID. As illustrated in Table 2, the average difference between the effluent and influent chloride concentrations in the liquid phase for Biofilters I and II was 328.01 mg/day and 321.05 mg/day , respectively. Simultaneously, the amount of chloride lost due to TCE oxidation in the gaseous phase i.e. TCE-Cl^- influent minus TCE-Cl^- effluent was 379.47 mg/day for Biofilter I and 387.29 mg/day for Biofilter II. TCE-Cl^- is calculated based on TCE concentrations and the mass percentage of chlorides in TCE (81%). The gaseous TCE chlorides lost were eventually regained in the liquid phase, with recovery rates of 86.4% for Biofilter I and 82.8% for Biofilter II. Therefore, since no additional peaks were detected in the effluent gaseous flow chromatogram, over 86% TOC from the liquid phase was removed (as shown in Table 2) and over 82% chlorides were recovered, it is deduced that no organic byproducts from TCE metabolism were generated in either gas phase or liquid phase during this study.

The amount of the various carbon sources was converted to equivalent carbon in moles. The cumulative carbon in the influent and effluent for both systems I and II are shown in

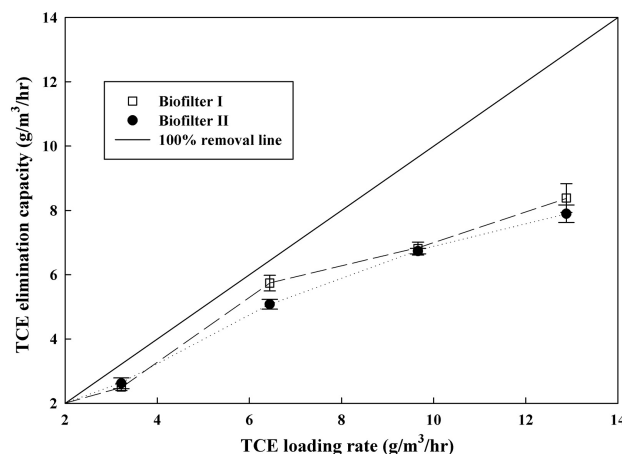


Fig. 2 – Trichloroethylene (TCE) loading rates versus elimination capacities for Biofilters I and II.

Table 2 – Average chlorides, total organic and inorganic concentrations.

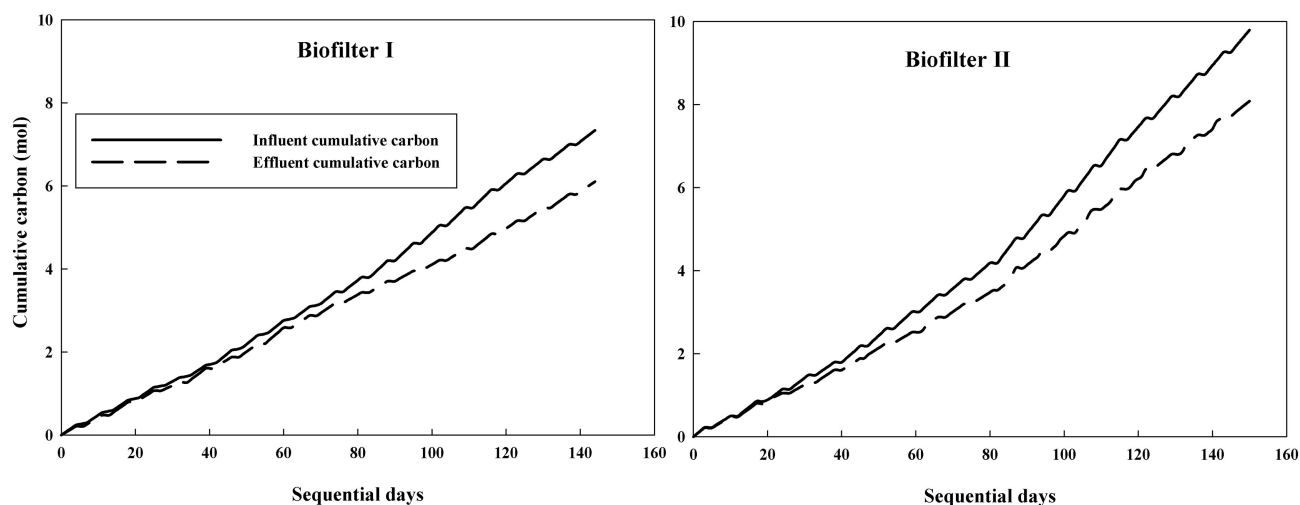
		Influent (mg/day)		Effluent (mg/day)	
		Biofilter I	Biofilter II	Biofilter I	Biofilter II
Liquid phase	Total Organic Carbon	488.52	488.52	66.27	52.08
	Inorganic Carbon	39.19	39.19	353.19	448.21
	Chlorides	470.94	470.94	798.95	791.99
Gaseous phase	TCE - Chlorides	561.77	560.68	182.3	173.39

Fig. 3. The corresponding carbon recovery rates were $88.45\% \pm 4.63\%$ for Biofilter I and $86.5\% \pm 4.35\%$ for Biofilter II. The difference between the influent and effluent carbon can be credited to the loss of carbon in the biotrickling filters while producing biomass (Aly Hassan and Sorial, 2010b). To justify this theory, a t-test was run to compare the loss in carbon from the biofilters to the biomass retention in them. This test was performed assuming that the biodegradation of TCE and methanol are independent of each other and that the biomass is represented by the formula $C_9H_{15}O_5N$ (Zehraoui et al., 2013). The amount of biomass generated is reverse calculated using the daily NO_3^-N consumption data for both systems and all of the phases. The results of the test ($p < 0.05$) suggest that the variance between the loss in the carbon and biomass accumulation in the biotrickling filters is significant.

2.3. Trichloroethylene removal kinetics in the biotrickling filters

The removal kinetics data for trichloroethylene is shown in Fig. 4. These data were collected weekly by analyzing the concentrations of TCE “through-the-bed” from different ports positioned at depths of 7.6, 23, 38, 53 and 60 cm from the top of the media. The sampling was conducted one day after the starvation period to ensure uniform biomass throughout the bed. An assumption of uniform distribution is made because the average VSS concentration one day after the starvation period (36.7 mg/L for Biofilter I and 49.8 mg/L for Biofilter II) is significantly higher as compared to the same on any other day (20.7 mg/L for Biofilter I and 29.7 mg/L for Biofilter II). The

data were then fit to a linear model to obtain pseudo first order reaction rate constants (k). Also, the removal kinetic trend generally followed the elimination capacity trend. The k values were 0.018 and 0.019 sec^{-1} for phase I in Biofilters I and II, respectively. This corresponded to the removal efficiencies, as Biofilter II was able to oxidize higher concentration of TCE. Comparing all of the phases, TCE degradation was the fastest for an LR of $6.44 \text{ g/m}^3/\text{hr}$ with k values of 0.027 sec^{-1} (Biofilter I) and 0.025 sec^{-1} (Biofilter II). Fig. 4 shows that for phase II and beyond, the reaction rate constants dip gradually from 0.025 sec^{-1} to 0.014 sec^{-1} to 0.012 sec^{-1} in Biofilter II because of increased TCE toxicity. In contrast, in Biofilter I, the reaction rate constants plateaued at approximately 0.018 sec^{-1} for phases III and IV. This data illustrates the ability of Biofilter I to degrade TCE at a faster rate. During the later phases, Biofilter I outpaced Biofilter II similar to the trend observed with TCE REs. Therefore, the 70:30 VOC concentration ratio can be applied in the industry. Lackey et al. (2003) observed a maximum k value of 3.7 hr^{-1} for a TCE LR of $11.3 \text{ g/m}^3/\text{hr}$ and a propane rate of 1069 L/day at 30.4°C . The k value obtained by Jung et al. (2005) was 5.2 day^{-1} when the biofilter influent was spiked with TCE and toluene at concentrations of $970 \mu\text{g/L}$ and $1221 \mu\text{g/L}$, respectively. It is noted that both of these referred biofilters were seeded with bacteria. In this work, the fungal systems achieved higher removal rate constants due to presence of aerial mycelia, which resulted in more rapid oxidation of TCE. In the case of methanol, analyzing the reaction rate constants was not feasible because over 92% was removed at the top port.

**Fig. 3 – Carbon mass balance for Biofilters I and II.**

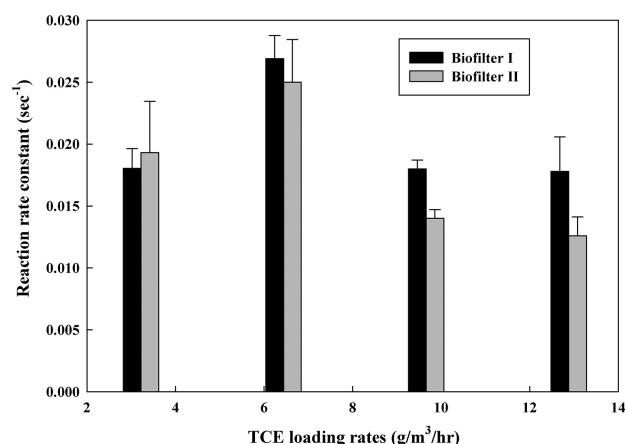


Fig. 4 – Removal reaction rate kinetic constants for Biofilters I and II.

3. Conclusions

This research studied the removal of trichloroethylene in a biotrickling filter with methanol as the primary substrate. Two concentration ratios of methanol to TCE (70:30 and 80:20) were investigated in two identical biotrickling filters labeled Biofilter I and Biofilter II, respectively. The TCE LR for both systems ranged from 3.22 to 12.88 g/m³/hr. In contrast, the methanol LR varied from 103.71 to 414.83 g/m³/hr for Biofilter I and 177.79 to 711.14 g/m³/hr for Biofilter II. A maximum RE of 87.1% for Biofilter I was obtained for a TCE LR of 6.44 g/m³/hr, while a maximum removal of 81.4% for Biofilter II was obtained for a TCE LR of 3.22 g/m³/hr. In the initial phase, Biofilter II was able to degrade more TCE than Biofilter I due to comparatively higher concentrations of methanol, thereby making TCE more bioavailable. However, as the LR increased, higher methanol concentrations began to competitively inhibit the removal of TCE in Biofilter II, which resulted in Biofilter I eliminating more TCE. It is postulated that the microbes preferred to degrade a hydrophilic substrate (methanol) over a hydrophobic type (TCE). The carbon lost during the remediation process was converted to biomass. Based on the effluent TOC, chlorides and GC values, no by-products were generated while oxidizing TCE. Additionally, methanol ECs were not hampered by an increase in the influent concentrations of TCE.

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