TREATMENT OF GASEOUS TRICHLOROETHYLENE BY SEQUENTIAL BIOTIC AND ABIOTIC REMOVAL MECHANISMS

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ABSTRACT

TREATMENT OF GASEOUS TRICHLOROETHYLENE BY SEQUENTIAL BIOTIC AND ABIOTIC REMOVAL MECHANISMS

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Widespread use in industry and its toxic effects make trichloroethylene (TCE) one of the hazardous air pollutants (HAP's). Halogenated organic compounds like TCE in gaseous phase are known to be controlled by conventional treatment systems like activated carbon adsorption etc. However, treatment of these compounds by biotic removal mechanisms such as, anaerobic reductive dechlorination, biosorption etc.,

and abiotic removal mechanisms such as, reductive dechlorination via hydrogenolysis, dihaloelimination, etc. using elementary have gained popularity since they constitute effective and economical treatment alternative.

In this study, treatment of gaseous TCE by biotic and abiotic removal mechanisms in a sequential (biological/chemical) reactor system was investigated. The reactor system consisted of granular anaerobic mixed culture packed biofilter followed by elemental iron metal (Fe(0)) packed column in series. Continuous reactor experiments are performed in two parts.

In the first part of the experiments, the effect of empty bed contact time (EBCT) on the TCE removal efficiency of the reactor system was investigated. The system was fed with 170.6±28.5 ppmv average influent TCE concentration, 5000 ppmv H_2, 2000 ppmv CO_2 and 6000 ppmv N_2 and 0.25, 0.5, 1 and 2.5 hours of EBCTs were applied for biofilter and Fe(0) packed column separately.

An excellent treatment performance was observed by the proposed system during 3 months of continuous operation period. The performances of the system components and overall system in the removal of TCE were determined as 53.4±12.0%, 31.0±2.8%, 13.9±1.8% and 1.1±0.4% in biofilter, 84.6±4.1%, 80.9±6.9%, 62.1±5.2% and 4.6±1.8% in Fe(0) packed column, 93.0±2.3%, 86.7±5.2%, 67.4±4.5% and 5.6±1.8% in overall system for EBCTs of 2.5, 1, 0.5, and 0.25 hours, respectively. Only ethylene and ethane which are the non-toxic by-products of TCE reduction were detected in the effluent of the system.

In addition, a model simulating the effect of EBCT on the sequential system was developed on the basis of the plugflow reactor model. The model curves were then, fitted to the actual data obtained in the first experiment with Berkeley Madonna 8.0.1 Software in order to determine the system parameters, such as, observed TCE removal rate constant, critical TCE removal efficiency, etc. The outcomes of first experiment and the developed model helped to determine the optimum EBCT as 1 hr for the system.

In the second part of the experiments, the effect of initial TCE concentration or TCE loading rate at optimum EBCT on the system was investigated. The system was fed with different initial TCE concentrations in the range of 150 to 650 ppmv (or 150 to 650 ppmv/hr TCE loading rate). The results indicated that the overall system performance in TCE removal did not change compared with the performance obtained in the operation of the system with 1 hr EBCT in the first part. As a conclusion, system has a stable removal efficiency while the TCE loading rate has changed up to 650 ppmv/hr, which is a higher loading rate than the rate applied in the previous applications (Bohn, 1992).

In conclusion, the proposed innovative sequential reactor system is not only unique but also constitutes a promising technology in the control of chlorinated hazardous air pollutants.

Keywords: Trichloroethylene, biofilter, Fe(0) packed column, biotic and abiotic removal mechanisms

ÖZ

GAZ FAZINDAKİ TRİKLOROETİLENİN ARDIŞIK BİYOTİK VE ABİYOTİK GİDERİM MEKANİZMALARIYLA ARITIMI

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İnsan sağlığına ve çevreye yönelik olumsuz etkileri nedeniyle trikloroetilen (TKE), önemli kirleticiler arasında yer almaktadır. Birçok endüstriyel sektörde yoğun olarak kullanılan TKE uçucu özellikleri nedeniyle tehlikeli hava kirleticileri (THK) arasında yer almaktadır. TKE benzeri halojenli bileşiklerin, anaerobik indirgen halojensizleştirme ve biyoadsorpsiyon gibi biyolojik ve çeşitli metallerle indirgenme

reaksiyonlarına girerek de kimyasal olarak, geleneksel TKE arıtım yöntemlerine (aktif karbon adsorpsiyonu vb. gibi) göre daha verimli ve ekonomik bir biçimde arıtımı son dönemde yaygınlaşmaktadır.

Bu çalışmada, gaz fazındaki TKE'nin biyotik ve abiyotik giderim mekanizmalarının gerçekleştiği ardışık (biyolojik/kimyasal) bir reaktör sisteminde arıtılması incelenmiştir. Söz konusu sistem, granüler anaerobik karışık kültür ile paketlenmiş bir biyofiltreyi izleyen elementel demir (Fe(0)) ile paketlenmiş ardışık bir reaktör sisteminden oluşmaktadır. Sürekli reaktör deneyleri iki bölümde gerçekleştirilmiştir.

İlk bölümde, boş yatak bekletme süresinin sistemdeki TKE giderim verimine etkisi araştırılmıştır. Ortalama 170.6±28.5 ppmv TKE, 5000 ppmv H_2, 2000 ppmv CO_2 ve 6000 ppmv N_2 ile beslenen sistemdeki TKE giderimi, her iki kolona ayrı ayrı uygulanan 0,25, 0,5, 1,0 ve 2.5 saatlik BYBSler için belirlenmiştir.

Üç ay aralıksız çalıştırılan sistemde yüksek TKE giderim verimleri sağlanmıştır. TKE giderim performansı, uygulanan 2,5, 1,0, 0,5 ve 0,25 saatlik BYBS'ler için sırasıyla; biyofiltre için ortalama %53.4±12.0, %31.0±2.8, %13.9±1.8 ve %1.1±0.4, Fe(0) paketli kolon için %84.6±4.1, %80.9±6.9, %62.1±5.2 ve %4.6±1.8, tüm sistem için ise %93.0±2.3, %86.7±5.2, %67.4±4.5 ve %5.6±1.8 olarak bulunmuştur. Sistem çıkışında eser miktarda TKE'nin yanında, indirgen klorsuzlaştırma ürünleri olarak sadece zararsız etilen ve etan gazları belirlenmiştir.

Bu çalışma kapsamında, ayrıca, BYBS'nin ardışık reaktör sisteminin TKE giderim verimine etkisini simule eden ve piston akışlı reaktör rejimine dayanan bir model oluşturulmuştur. Oluşturulan model denklemi sonucunda elde edilen eğriler,

Berkeley Madonna 8.0.1 Simulasyon programı yardımıyla ilk deney sonuçlarıyla çakıştırılmış ve sistemi betimleyen denklem parametreleri (görünür TKE giderim sabiti, kritik TKE giderim verimi, vd.) bulunmuştur. Deney sonuçları ve model verilerinden yararlanılarak, sistemin optimum BYBS'si belirlenmiştir. Bu sonuçlar yardımıyla, optimum BYBS 1 saat olarak bulunmuştur.

Deneylerin ikinci bölümünde, ilk bölümde belirlenen 1 saatlik optimum BYBS'de giriş TKE konsantrasyonunun ya da TKE yükleme hızının sistem verimine etkisi araştırılmıştır. Bu doğrultuda sisteme, 150-650 ppmv giriş konsantrasyonları (ya da 150-650 ppmv/saat TKE yükleme hızları) uygulanmıştır. Bu deney sonucunda, 1 saatlik optimum BYBS'de uygulanan farklı yükleme hızlarında, sistemin TKE giderim veriminde önemli bir değişikliğin olmadığı belirlenmiştir.

Sonuç olarak, literatürde bir benzeri bulunmayan bu yeni ardışık reaktör sistemi, TKE gibi ülkemizde de çok sayıda kullanım alanı bulan klorlu bileşiklerin gaz fazındaki gideriminde önemli ve umut vadeden bir teknolojik gelişme olarak görülmektedir.

Anahtar Sözcükler: Trikloroetilen, biyofiltre, Fe(0) paketli kolon, biyotik ve abiyotik giderim mekanizmaları

"The one who loves the cliffs must have wings"

F. W. Nietzsche

To my wings,

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ABBREVIATIONS

TCE	: Trichloroethylene
cDCE	: cis-Dichloroethylene
tDCE	: trans-Dichloroethylene
1,1DCE	: 1,1-Dichloroethylene
VC	: Vinyl chloride
PCE	: Perchloroethylene
EBCT	: Empty bed contact time
VSS	: Volatile suspended solids
GAC	: Granular active carbon
RE	: Removal efficiency
CAA	: Clean Air Act
GC	: Gas Chromatography
HAP	: Hazardous air pollutant

CHAPTER 1

INTRODUCTION

1.1. Statement of the problem

Hazardous air pollutants (HAPs) posses a threat both to the environment and public health. Nowadays, the gaseous emissions of HAPs and their control have gained importance in the world. Many industrialized and industrializing countries including Turkey have regulations to control the emissions of HAPs.

Chlorinated aliphatic hydrocarbons (CAHs), polychlorinated biphenyl compounds, etc. are classified as HAPs due to their physical and chemical properties. 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 adsorbed on a solid media. Main route of release of these compounds to the environment is air emissions.

The VOCs have not been considered as typical air pollutants until recently (Bohn, 1992). Therefore, the regulations and control strategies developed for VOCs targeted their presence mainly in groundwater and drinking water. This is evident from the technologies developed for the control of these pollutants such as remediation of

groundwaters and soil polluted with these compounds (National Research Council, 1997, 1994).

"The Clean Air Act 1990" of USEPA is one of the leading regulations in controlling the HAPs. The Clean Air Act (CAA) Amendments (1990) have arisen 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, air-sparging etc.) will need to be modified or amended to control, capture or treat their off-gas emissions (Khandan, 1994).

Many of the industrial and governmental facilities (such as military services, industries that produce halogenated compounds, automotive industries etc.) around the world are known to have soils and groundwaters contaminated with hazardous organic contaminants, where the above ground technologies have been identified as feasible restoration alternatives (DOE-ER-0547T, 1992). Such kind of facilities will be seriously affected due to potential HAP emissions in countries that have an act for HAPs.

There are 188 air pollutants that have been classified as HAPs in the 1990 Clean Air Act Amendments of US EPA, 90% of these accounting for VOCs. Under Title III of the CAA, these VOCs are to be regulated and requiring their sources to install

Maximum Achievable Control Technologies (MACTs). The USEPA has been charged with the responsibility of issuing and imposing MACT Standards for these sources. As an incentive, a key section of Title III allows sources a 6 year extension from meeting MACT Standards, if they voluntarily reduce emissions to 90% below 1987 levels, before EPA issues the MACT Standard. Thus, industries and other major sources are very much in need of appropriate technologies for controlling the air emissions.

Current MACTs for VOCs under condensation include incineration, carbon adsorption, absorption and catalytic conversions. The practical applicability of these technologies are limited by capital and operating cost considerations, residual and side stream formation and trace concentrations of the VOCs (Khandan, 1994).

In Turkey, the organic vapors and gases has been classified and their emissions are regulated in the Annex-4 of "Control of Air Quality Regulation" in "Türk Çevre Mevzuatı (April 1999)". Among the VOCs that are included in HAPs in 1990 CAA Section 112 of USEPA and Türk Çevre Mevzuatı, trichloroethylene (TCE), a halogenated organic compound, is accounted as one of the most important HAPs. TCE finds widespread use in industry particularly as a degreaser for metal parts in industries fabricating or assembling metal parts including aircraft, appliance, automotive, electronics, and railroad manufacturers. TCE is not only a threat to environment but also it is determined as "probably carcinogenic to humans" by some international research agencies. Previously, TCE was stated as one of the most common groundwater and soil pollutants, and an important air pollutant due to its high volatility (IARC, 1995).

The annual production rate of TCE in USA has been reported as 145,000 tons and 90% of TCE used as degreasing solvent is released to the environment as air emissions (IPCS, 1984; Howard, 1990). Moreover, accidental release of TCE to the environment from the industries and military services accounts more than the controlled releases. There are an estimated 7,300 sites contaminated with chlorinated solvents, TCE being the most commonly detected one, at 1,800 locations owned by Department of Defense of the U.S.A. (National Research Council, 1994). It is also stated that most of the groundwaters in these sites are contaminated by these pollutants. The numerous remedial actions have been performed for the rehabilitation of the land and groundwater contaminated by halogenated compounds in these sites since 1970s, however, there have been no control over the organic vapor emissions at these sites until Superfund Amendments and Reauthorization Act (SARA, 1986). The emissions from the contaminated sites must be abated to avoid atmospheric pollution above ground, since it is considered as a part of the remedial action at the Superfund sites after SARA of 1986.

In summary, the need for development of appropriate technologies for the control of HAPs emissions is inevitable. Moreover, TCE is one of the most important HAPs that its control must be taken as a priority. An economical and effective control technology that is developed to treat the emissions containing TCE would be an outstanding achievement that is beneficial for environment, industry and public.

1.2. Aim of the study

This study aims to develop a technology to control the TCE emissions from the industries and sites that are contaminated with this pollutant. Many control technologies have been developed in order to treat TCE emissions such as condensation, incineration, carbon adsorption, absorption and catalytic conversions. The practical applicability of these technologies are limited by capital and operating cost considerations, residual and side stream formation, trace concentrations etc. Furthermore, these treatment technologies, except incineration, can not serve as an ultimate treatment option for the pollutant but they only transfer the pollutant from one phase to another.

Previous studies have proved that both biotic and abiotic transformation mechanisms such as, reductive dechlorination, can successfully handle the ultimate treatment of chlorinated compounds by transforming them into non-hazardous products like ethylene, acetylene, and ethane (Freedman and Gossett, 1989; deBruin *et al.*, 1992; Tandoi *et al.*, 1994; Arnold and Roberts, 2000). Moreover, biosorption is also considered as an effective removal mechanism that can eliminate these compounds by means of phase transfer rather than transforming them into non-hazardous products (Dobbs *et al.*, 1989; Kennedy *et al.*, 1992; Wang *et al.* 1993; Jacobsen *et al.*, 1996; O'Niell *et al.*, 1999; Ergüder, 2000). Most of these studies are performed to treat the chlorinated compounds in aqueous phase except Mihopoulos *et al.* (2000) and Uludağ-Demirer and Bowers (2000).

On the basis of the previous studies and their results, this study further aims to develop an optimum continuous system to clean-up a TCE contaminated gas stream

simulating several real life conditions as mentioned above, where biotic and abiotic removal mechanisms are undertaken sequentially. The operational conditions of the reactor system have been optimized in a way to develop an economic and effective system. The reactor system has further been modeled to understand the behavior of the system and to illustrate the effects of the operational conditions and proposed reactor design on its performance.

CHAPTER 2

LITERATURE REVIEW

In this chapter, information about TCE as a pollutant, biotic and abiotic removal mechanisms for chlorinated compounds, and biofiltration as an innovative technology for the air contaminant clean-up are reviewed.

2.1. TCE as a pollutant

TCE, classified as chlorinated aliphatic hydrocarbon, is one of the most common groundwater, soil and air contaminants (Oldenhuis *et al.*, 1991). Its physical and chemical properties make TCE a hard to deal with type pollutant that is also carcinogenic, bioaccumulative, and naturally attenuative (Table A.1).

TCE is not known to occur as a natural product. It is commercially produced by chlorination and dehydrochlorination of 1,2-dichloroethane and belongs to the chemical family of chlorinated alkenes. Major use of TCE is in vapor degreasing of fabricated metal parts. It is also used as a carrier solvent in textile cleaning and solvent extraction processes, as a lubricant and adhesive and as a low-temperature heat transfer fluid. TCE is also used in the production of polyvinyl chloride (PVC), paints, coatings and some miscellaneous chemical synthesis. It is estimated that 60-

90% of the world TCE production is released in to the environment and volatilization appears to be its primary transport process (IPCS, 1984).

The fate of TCE in the environment is important in order to determine its adverse effects. TCE released to the atmosphere will exist primarily in the vapor phase based on its relatively high vapor pressure. Atmospheric residence time of 5 days has been reported with formation of phosgene, dichloroacethyl chloride and formyl chloride. It is not subjected to direct photolysis. If TCE is released to water, the primary removal process will be evaporation with a half-life of minutes to hours, depending on turbulence. Biodegradation, hydrolysis and photooxidation are extremely slow by comparison. Adsorption to sediment and bioconcentration in aquatic organisms are not important fate processes for TCE. Release to soil will be partially evaporated and partially leached into ground water, where it may remain for a long time. However, there is some monitoring data that suggests degradation to other chlorinated alkenes in soil (Howard *et al.*, 1990). The reactivity of TCE and its interactions with the components of the environment are summarized in Table A.1.

Widespread use in common and important industries, persistent behavior in the environment and toxic effects to both public health and environment make TCE a priority pollutant among the other chlorinated compounds. Detailed research studies have been conducted to control this pollutant and several technologies have been developed to remediate TCE mostly from groundwater and soil starting in 1970s. These control options targeted mostly the removal of the chlorinated compounds from liquid phase or solid phase, i.e., adsorbed on soil media (National Research Council, 1994).

In the late 1970's, a number of groundwater plumes contaminated with chlorinated solvents were discovered under Air Forces bases of USA. It was soon discovered that this problem was found throughout the Air Force and the Department of Defense (DOD) sites in the USA. There are an estimated 7,300 sites contaminated with chlorinated solvents at 1,800 locations, owned by DOD (National Research Council, 1994). Chlorinated solvents are among the most common contaminants of groundwater. Nine of the 20 most common chemicals found in groundwater at Superfund sites of USA are chlorinated solvents.

Remediation technologies have been divided into three general categories: 1) technologies for solidification, stabilization, and containment; 2) technologies which separate the contaminant from the contaminated media, immobilize the contaminant and extract it from the subsurface, 3) technologies using biological and/or chemical reactions to destroy or transform the contaminant (National Research Council, 1997).

Solidification and stabilization processes are generally appropriate for shallow contamination and soil treatment. These processes focus on decreasing the mobility and/or toxicity of the contaminant by reducing the solubility, volatility, or media permeability. Examples of this technology are asphalt batching, biostabilization, passivereactive barriers, enhanced sorption (using granular active carbon), in-situ soil mixing, and lime addition (National Research Council, 1997). Containment technologies incorporate physical or hydraulic barriers to prevent contaminant movement away from the zone of contamination. Technologies include pump and treat systems, and low permeability barriers utilizing slurry walls, sheet pile walls, and grout walls.

Separation, immobilization, and extraction technologies detach the contaminant from the soil particles, immobilize it into the aqueous phase or airspace in the soil voids, and extract the contaminant to the surface. These technologies can use heat, chemicals, vacuums or electrical current to separate the contaminant from the soil and move it to the extraction zone (National Research Council, 1997).

Among the remediation technologies, biological and chemical processes have gained an outstanding attention since they are the only processes that can completely destroy an organic contaminant. Biological and chemical processes transform chlorinated contaminants into their daughter products. Biological processes (bioremediation) rely on microorganisms to transform the contaminant through varying reactions resulting in degraded compounds. Reactions may be aerobic or anaerobic and can be direct or cometabolic. Environmental conditions like temperature, pH, etc., impact microbial metabolism. Some biological treatment technologies are biopiles, bioventing and biosparging, composting, engineered in situ bioremediation, and natural attenuation (intrinsic bioremediation). Chemical processes transform the contaminant through chemical reactions. Chemical processes are used less than biological treatments. Chemical treatment technologies include oxidation, incineration, substitution, and zero-valent ion barriers (Hoefar, 2000). Engineered in situ biotransformation of chlorinated compounds via aerobic cometabolism and anaerobic reductive dechlorination and chemical transformation processes via reductive dechlorination with zero-valent ions have attracted the researchers since they are economical and ultimate treatment options for these contaminants among the others.

Extended research (Freedman and Gossett, 1989; deBruin *et al.*, 1992; Tandoi *et al.*,

1994; Arnold and Roberts, 2000) have been conducted to understand the mechanisms and application of biological and chemical treatment processes to control the chlorinated organic compounds especially chloroethylenes.

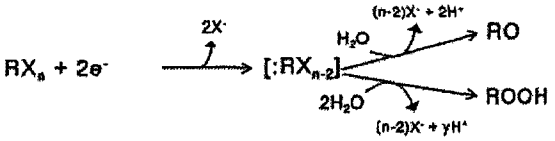
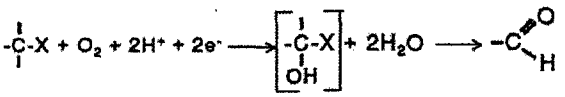
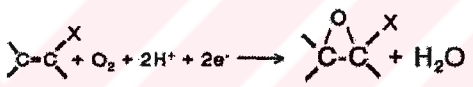
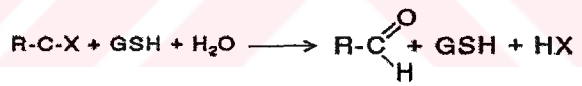
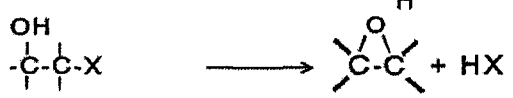
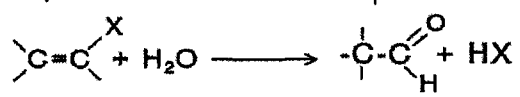
2.2. Biotic and abiotic removal mechanisms for chlorinated compounds

In this section, the biotic and abiotic transformation mechanisms, biosorption as a biotic removal mechanism and their applications are presented with the examples in the literature.

2.2.1. Biotic and abiotic transformation of chlorinated compounds

Several different mechanisms have been described for the biotic and abiotic transformation of halogenated compounds including reduction, oxidation, substitution, hydration and dehydrohalogenation (Vogel et al. 1987, Fetzner and Lingens 1994) (Table 2.1). The main difference between these reaction mechanisms is in the transfer of electrons. Both reduction and oxidation are electron dependent reactions (redox-reactions) and need either the input of an external electron acceptor or electron donor. This is in contrast with substitution, dehydrohalogenation and hydration reactions. During the course of these reactions, the oxidation state of the reacting molecule does not change and therefore no input of an external electron donor or electron acceptor is needed (non-redox reactions) (De Best, 1999).

Table 2.1: Abiotic and biotic reactions of chlorinated aliphatic hydrocarbons (Vogel *et al.*, 1987; Holliger, 1992; Fetzner and Lingens, 1994).

Reactions	Mechanisms
Electron transfer dependent reactions	
1. Reduction	
a. hydrogenolysis	
b. dihaloelimination	
c. coupling	
d. hydrolytic reduction	
2. Oxidation	
a. α-hydroxylation	
b. epoxidation	
Electron transfer independent reactions	
3. Substitution	
a. hydrolysis	
b. conjugation	
c. thiolytic dehalogenation	
d. intramolecular substitution	
4. Dehydrohalogenation	
5. Hydration	

2.2.1.1. Biotic transformation of chlorinated compounds

Biotic transformation of chlorinated compounds can be achieved both in anaerobic and aerobic conditions. Electron transfer mechanisms determine the path of the biotransformation in both conditions. In anaerobic and aerobic conditions both metabolic and cometabolic transformation mechanisms can be achieved. In metabolic transformation, microorganisms can couple these transformation to their metabolism and benefit from the energy released during the transformation of chlorinated compounds. In cometabolic transformation mechanisms, dechlorination is not coupled to growth and is a form of gratuitous metabolism carried out by enzymes or cofactors which normally catalyze other reactions. Biotransformation in aerobic and anaerobic conditions is mainly maintained by oxidation and reduction reactions, respectively (De Best, 1999).

On the other hand biotic biotransformation is limited by certain chlorinated compounds, that is, not all chlorinated compounds can go under either metabolic or cometabolic biotransformation under both aerobic and anaerobic conditions (Table 2.2).

2.2.1.1.1. Biotic transformation of chlorinated compounds under aerobic conditions

Biotransformation of chlorinated compounds under aerobic conditions can be achieved both via metabolism or cometabolism and depends on oxidation reactions (Table 2.2).

Table 2.2: Major chlorinated aliphatic hydrocarbon (CAH)contaminants found in groundwater and biotransformation pathways known to exist (indicated with an X) (Rittmann and McCarty, 2001)

CAH	Formula	Acronym	Primary Substrate			Cometabolism	
			Aerobic Donor	Anaerobic Donor	Anaerobic Acceptor	Aerobic	Anaerobic
Methanes							
Carbon Tetrachloride	CCl_4	CT					X
Cloroform	$CHCl_3$	CF				X	X
Dichloromethane	CH_2Cl_2	DCM	X	X		X	X
Chloromethane	CH_3Cl	CM	X			X	X
Ethanes							
1,1,1-Trichloroethane	CH_3CCl_3	TCA				X	X
1,1,2-Trichloroethane	$CH_2ClCHCl_2$	1,1,2-TCA				X	X
1,1-Dichloroethane	CH_3CHCl_2	1,1-DCA				X	X
1,2-Dichloroethane	CH_2ClCH_2Cl	1,2-DCA	X	X		X	X
Chloroethane	CH_3CH_2Cl	CA	X			X	X
Ethenes							
Tetrachloroethene	$CCl_2=CCl_2$	PCE			X		X
Trichloroethene	$CHCl=CCl_2$	TCE			X	X	X
cis-1,2-Dichloroethene	$CHCl=CHCl$	c-DCE		X	X	X	X
trans-1,2-Dichloroethene	$CHCl=CHCl$	t-DCE		X		X	X
1,1-Dichloroethene	$CH_2=CCl_2$	1,1-DCE				X	X
Vinyl Chloride	$CH_2=CHCl$	VC	X	X	X	X	X

The most common way of biotransformation of chlorinated compounds under aerobic conditions is cometabolic biotransformation via epoxidation. This process is mainly called as co-metabolic oxidation. Methanothrophic bacteria containing monoxygenase and dioxygenase enzymes are widespread in nature, including aquifer environments. The utility of these organisms for oxidative, cometabolic destruction of chloroethenes via formation of chloroethene epoxides has been investigated widely and applied to aquifer environments (Lee *et al.*, 1998). The inducible

oxygenases oxidatively degrade partially chlorinated solvents such as TCE, cDCE, or VC during normal oxidation of hydrocarbons such as toluene, phenol, methane, or propane (Ensley, 1991; Vogel *et al.*, 1987). However, the fully chlorinated ethylene PCE is resistant to degradation via this mechanism

The study of Oldenhuis *et al.* (1989) illustrated the wide spectrum of chlorinated compounds that can be transformed by cometabolic oxidation. *Methyl-osinus trichosporium* OB3b grown in a medium without cupper and contained 20mM, 0.2mM of formate and halogenated compound, respectively, were used for biotransformation process. It was concluded that appreciable transformation of 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1-dichloroethylene, tDCE and cDCE, chloroform was achieved while carbon tetrachloride and tetrachloroethylene were not degraded.

However, many in situ remediation techniques used in the rehabilitation of soil and groundwater contaminated by chlorinated compounds are proceeded under ground level (in vadose zone or below groundwater table) where oxygen accessibility of microorganisms are restricted by low in-through diffusion of oxygen (Lee *et al.*, 1998). This phenomenon led many researchers to investigate the biotransformation of chlorinated compounds under limited-oxygen conditions that is anaerobic conditions.

The results of many researches have shown that anaerobic biotransformation of almost all chlorinated compounds can be achieved successfully (Freedman and Gossett, 1989; deBruin *et al.*, 1992; Tandoi *et al.*, 1994).

2.2.1.1.2. Biotic transformation of chlorinated compounds under anerobic conditions

The biotic transformation of chlorinated compounds under anaerobic conditions occurs both via direct metabolism or cometabolism.

The main biotransformation mechanism of many chlorinated compounds in anaerobic conditions is metabolic that is, anaerobic microorganisms use chlorinated compounds as both electron acceptor and donor in their metabolism and they yield energy from this metabolism. Among these metabolic activities, use of chlorinated compounds as electron acceptors is more common than those as electron donors since the free energy gained by reduction reactions of chlorinated compounds are high in anaerobic conditions. This process is called "anaerobic reductive dechlorination" (De Best, 1999).

Reductive dehalogenation is the removal of one or more chlorine atoms and replacing them with hydrogen which is the electron donor in the process (Table 2.1). In dehalogenation, the chlorinated hydrocarbon is used as an electron acceptor. In effect, microorganisms "breath" the chlorinated compound in the same way aerobic organisms use oxygen (McCarty, 1997) so anaerobic reductive dechlorination is also termed as "dehalorespiration". As an example for reductive dechlorination of chlorinated compounds, PCE conversion to ethylene has been illustrated in Figure 2.1.

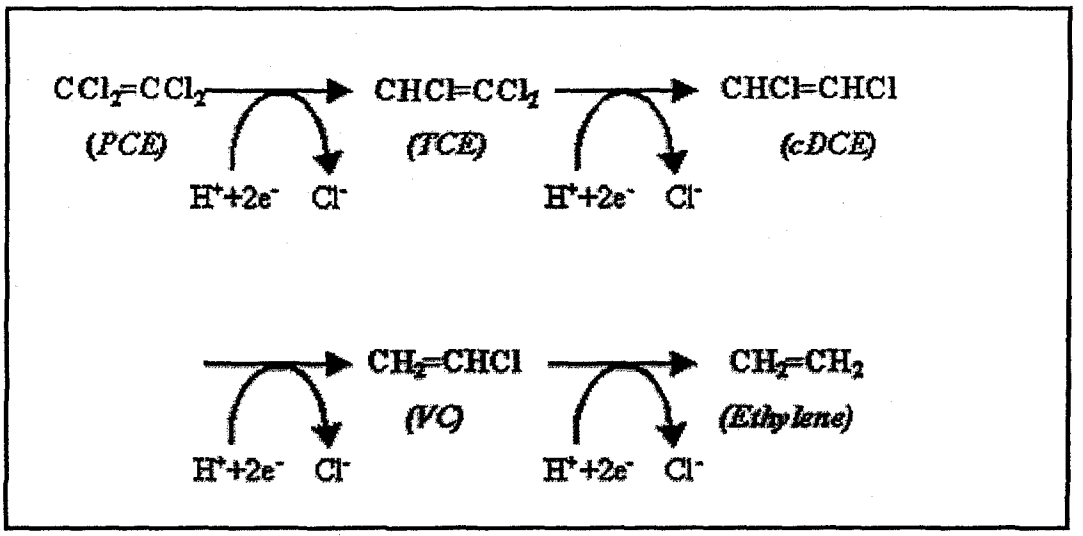


Figure 2.1: Biotransformation of PCE to ethylene via anaerobic reductive dechlorination (Rittmann and McCarty, 2001).

Two electrons and a proton are accepted by PCE, which is converted to TCE, releasing a chloride ion in to the solution. TCE can then be an electron acceptor and is converted in a similar fashion to DCE. Of the three possible isomers of DCE, cDCE, is the product most commonly formed from biotransformation. DCE then can be reduced to VC, which in turn can be reduced to ethylene. Even ethylene can accept electrons and be converted to ethane, although this process is seldom observed (Rittmann and McCarty, 2001).

Many investigators observed the reductive dechlorination of PCE and TCE, and formation of varied products. For instance, Townsend and Suflita (1996) stated that PCE was sequentially dechlorinated to TCE and DCE by cell extracts of *Desulfomonile tiedjei* using hydrogen or formate as the electron donor under anaerobic conditions. Reductive dechlorination PCE to TCE and cDCE was also

achieved by sulfate-reducing enrichment cultures being more substantial in cultures receiving lactated as opposed to acetate, hydrogen, methanol or mixed organic acids (Bagley et al., 1990). De Bruin et al. (1991) observed the complete declorination PCE to ethane in a laboratory-scale fixed bed reactor using lactate as the electron donor. Freedman and Gossett (1989), Fennell *et al.* (1997), and Ballapragada *et al.* (1997) found that PCE and TCE were reductively dechlorinated to ethylene with certain electron donors such as, butyric acid, ethanol, lactic acid, propionic acid and hydrogen.

2.2.2. Biosorption as a removal mechanism for chlorinated compounds

Biotic transformation mechanisms and sorption are two major mechanisms responsible for removal of chlorinated compounds in biological treatment systems (Ning *et al.*, 1999). Biotic transformation mechanisms for chlorinated compounds were described in previous sections. In this section effect of biosorption which is the physical biotic removal mechanism is discussed in this section.

Sorption of some toxic organics onto microbial solids, such as activated sludge, anaerobic granules, digested sewage sludge and mixed-species microbial mats, was studied by several investigators (Woods, 1985; Bell and Tsezos, 1987; Kennedy *et al.*, 1992; Wang *et al.*, 1993; Jacobsen *et al.*, 1996; O'Niell *et al.*, 1999, Ergüder, 2000). In batch tests of sorption dynamics, different results were observed. Dobbs *et al.* (1989) investigated sorption of chlorobenzene and 1,1-dichloroethylene at an initial concentration of about 1 mg/L to primary, mixed-liquor and digested sludge, and reported that approximately 1 hr was needed for the sorption to reach

equilibrium. In studying the sorption of pentachlorophenol at low concentration (12.5-800 μg/L) to laboratory cultivated activated sludge, Jacobsen *et al.* (1996) observed that sorption and desorption equilibria were established in 5 minutes approximately. However, Kennedy *et al.* (1992) indicated that, at an initial chlorophenols (CPs) concentration of 5-60 mg/L, 2 hrs was required for sorption of CPs onto anaerobic granules to reach equilibrium and it was stated that anaerobic granules have relatively high sorption capacity (2.5-9.2 μg CPs/g VSS) compared with other biomasses studied. Similarly, Ergüder (2000) studied the sorption of dieldrin (DLD) with a concentration of 10.4 mg/L onto anaerobic granules. It was stated that the equilibrium was achieved in 24 hrs and partitioning coefficient of DLD on anaerobic granules were determined as 6.51±0.55 mg DLD/g VSS.

Moreover, O'Neill *et al.* (1999) studied the biosorption and transformation of PCE and TCE on mixed-species microbial mats. In this study, the batch reactors including microbial mats, that have aerobic and anaerobic species, were dosed with PCE or TCE at liquid-phase concentrations of 1-10 mg/L. They concluded that biosorption of both PCE and TCE reached the equilibrium in less then 24 hrs and these compounds were biotransformed in minimum 50 days to their by-products. This study indicated that PCE and TCE partitioned rapidly to the microbial mats with a very fast equilibration and a slower transformation and degradation of both compounds followed this rapid partitioning to the mat phase.

These observations suggest that mass transfer limitation between liquid to solid phases in sorption of chlorinated compounds to biomass exists but varies with the characteristics of biomass, sorbate (different chlorinated compounds like TCE, PCP

etc.) and sorbate concentration (Ning *et al.*, 1999).

The biotic removal mechanisms of chlorinated compounds are clearly explained by the researchers conducting many laboratory and site studies. The outcomes of these extended studies on biotic removal of chlorinated compounds formed the basis of biotic part of this study and a proof of the mechanism that may have occurred in the biological reactor during the research period.

2.2.3. Abiotic transformation of chlorinated compounds via zero-valent iron (Fe(0)) reduction

Zero-valent metals such as iron, tin, and zinc are moderately strong reducing agents that are capable of reducing many common environmental contaminants. The first application of zero valent iron metal, Fe(0), as a reductant for chlorinated organic compounds in industrial wastewater treatment was by Sweeny and Fischer (1973). An alternative use of Fe(0) was later proposed for in-situ remediation of ground water systems contaminated by chlorinated organic compounds by Gilham and O'Hannesin (1994). They studied the degradation of 14 chlorinated aliphatic hydrocarbons in aqueous systems, and reported a considerable decline in the concentrations when contacted with Fe(0). Following their study, there has been a great interest in the use of zero valent metals, such as Fe(0), Ni(0) (Appleton, 1996), Zn(0) (Arnold and Roberts, 1998), and Sn(0) (Boronina *et al.*, 1995) to reduce chlorinated organic compounds via in- or ex-situ treatment technologies.

Although there are numerous studies on the transformation reactions of chlorinated organic compounds on the metal surfaces, the exact chemical mechanism of the

reduction reactions is not known. The brief summary of the reduction reactions mechanism(s) for TCE is presented in this section in order to verify and explain the mechanisms occur in the Fe(0) packed column of the proposed sequential system in this study.

The reduction of chlorinated organic compounds by Fe(0) is a redox reaction in which Fe(0) acts as an electron donor (reductant) and chlorinated organic compounds act as electron acceptor (oxidant). The oxidation half reaction of Fe(0) is a corrosion reaction. The corrosion reactions have been under investigation with respect to the protection of Fe(0) since the 1920s (Uhlig and Revie, 1985). In oxygen deficit (anaerobic) water systems, H_2O oxidizes Fe(0) at a rate less than 0.005 mm/year (almost negligible), and the following stoichiometry applies (Uhlig and Revie, 1985):

$$Fe^0(s) + 2\ H_2O \rightarrow Fe(II)\ (aq) + H_2^0\ (g) + 2\ OH^- \qquad \text{(Reaction 2.1)}$$

Oxidation of Fe(0) increases the pH of water and this affects the chemistry of Fe(II) and Fe(III) containing compounds, e.g., Fe(II) and Fe(III) hydroxides form. At high pH, Fe(II) and Fe(III) hydroxides are insoluble, and the surface of Fe(0) becomes covered by the hydroxides and oxides (aged hydroxides) of Fe(II) and Fe(III) (Schwertmann and Taylor, 1977; Stum, 1992).

Similar to the reaction of Fe(0) with H_2O, chlorinated organic compounds oxidize Fe(0) and are themselves reduced. The reduction half reaction of the chlorinated organic compounds may occur by different pathways, such as hydrogenolysis, dihalo-elimination (reductive elimination), and dimerization (radical coupling). Additionally, they may undergo different transformation reactions, such as

hydrolysis (substitution reaction) and dehydrohalogenation, which do not require and external electron donor (Scwarzenbach *et al.*, 1993).

The formation of the radicals has been proposed as the first step in the reduction of the chlorinated organic compounds (Vogel *et al.*, 1987; Matheson and Tratnyek, 1994) and it is usually the rate-controlling step. The nature of an electron transfer from the metal surface to the carbon-halogen bonds has been established as the formation of the carbon centered radical, R^*, and halogen anion, X^-, or (Saveant, 1990; Walborsky and Hamdouchi, 1993):

$$RX + e^- \rightarrow R^* + X^- \qquad \text{(Reaction 2.2)}$$

The radicals are usually very reactive and short-lived compounds (Jacobs, 1997) and they undergo hydrogenolysis, dihalo-elimination, dimerization reactions and dehydrohalogenation under different conditions. The conditions favoring a particular pathway are under careful investigation in the environmental studies because toxic by-products, such as chloroethylenes and cloroacetylenes, may form and accumulate in the system (Roberts *et al.*, 1996; Fennelly and Roberts, 1998).

Two important and common mechanisms of reduction reactions, hydrogenolysis and dihalo-elimination, of chlorinated organic compounds via Fe(0) can be summarized as follows;

Hydrogenolysis: Reduction of the chlorinated organic compounds via the hydrogenolysis pathway consists of sequential replacement of H^+ ions with Cl^- ions that are bonded subsequent carbons. Subsequent chlorine removal from the structure

of the organic compound takes place if the parent organic compound has more than one chlorine atom and the environment is still reducing (March, 1992).

Reduction of the multichlorinated organic compounds, for instance TCE, via hydrogenolysis, has been the center of interest of environmental studies due to the formation of DCE isomers, VC, which are toxic and regulated by drinking water quality standards (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994; Su and Puls, 1999).

Dihalo-Elimination: Reduction of the chlorinated organic compounds via the dihalo-elimination pathway consists of concomitant removal of two chlorine atoms from the neighboring C atoms, and formation of chlorine containing acetylene compounds, which may then be reduced to acetylene by hydrogenolysis (March, 1992; Jacob, 1997).

The overall pathways of reduction of TCE by Fe(0) is determined by Arnold and Roberts (2000) and illustrated in Figure 2.2.

A plausible scheme for the reduction of the chlorinated ethylenes by Fe(0) includes hydrogenolysis (replacement of halogen by hydrogen), reductive elimination (α- or β-dihaloelimination), and hydrogenation (reduction of multiple bonds), as represented in Figure 2.2 (Arnold and Roberts, 2000).

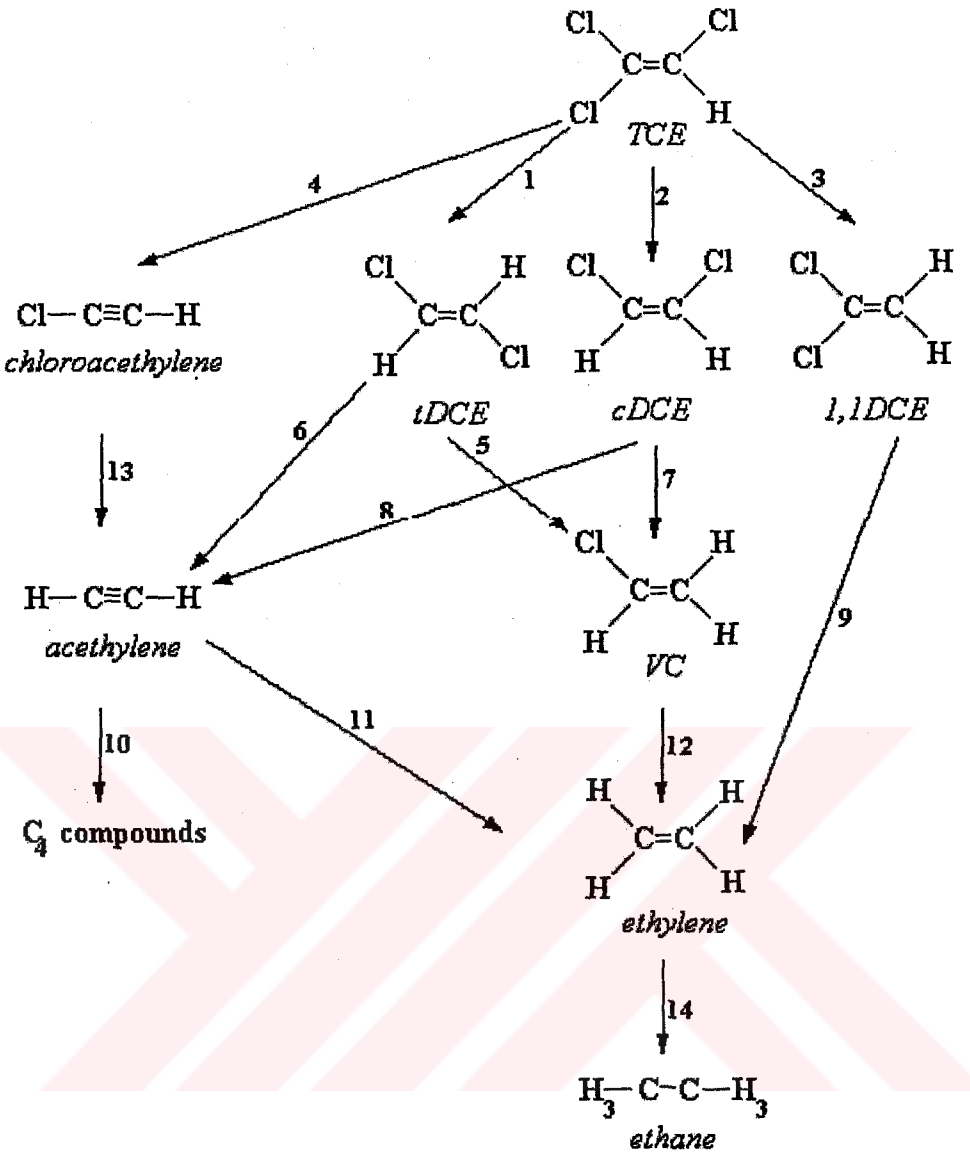


Figure 2.2: Hypothesized reaction pathways for TCE and other intermediates during the reaction by Fe(0) (Arnold and Roberts, 2000).

If the reaction proceeds by hydrogenolysis, with H_2O serving as a proton donor, TCE will undergo to a dechlorination step to form dichloroethylene isomers (cDCE, tDCE and 1,1DCE), or (pathways 1, 2 and 3 in Figure 2.2)

$HClC{=}CCl_2 + H^+ + 2e^- \rightarrow HClC{=}CClH + Cl^-$ *(cDCE and tDCE)* (Reaction 2.3)

$HClC{=}CCl_2 + H^+ + 2e^- \rightarrow H_2C{=}CCl_2 + Cl^-$ *(1,1DCE)* (Reaction 2.4)

The reduction of TCE via dihaloelimination (reductive β-elimination) pathway consists of concomitant removal of two chlorine atoms from the neighboring C atoms or (pathway 4 in Figure 2.2),

$HClC{=}CCl_2 + 2e^- \rightarrow HC{\equiv}CCl + 2Cl^-$ (Reaction 2.5)

The products of pathways 1 and 2 (cDCE and tDCE) then go further dechlorination via hydrogenolysis in the presence of proton donor to form vinyl chloride (VC), or (pathways 5 and 7 in Figure 2.2)

$HClC{=}CClH + H^+ + 2e^- \rightarrow H_2C{=}CClH + Cl^-$ (Reaction 2.6)

Or, the products of pathways 1 and 2 (cDCE and tDCE) can also go further dechlorination via dihaloelimination (reductive β-elimination) form acetylene, or (pathways 6 and 8 in Figure 2.2)

$HClC{=}CClH + 2e^- \rightarrow HC{\equiv}CH + 2Cl^-$ (Reaction 2.7)

The product of pathway 3 in Fig 2.2 (1,1DCE) then go further dechlorination via

dihaloelimination (reductive α-elimination) in the presence of proton donor to form ethylene, or (pathway 9 in Figure 2.2)

$$H_2C{=}CCl_2 + 2H^+ + 3e^- \rightarrow H_2C{=}CH_2 + Cl^- \qquad \text{(Reaction 2.8)}$$

It has been shown that the product of pathway 4 (chloroacetylene) is an intermediate, which may then further be reduced to acetylene through hydrogenolysis in the presence of proton donor, or (pathway 13 in Figure 2.2)

$$HC{\equiv}CCl + H^+ + 2e^- \rightarrow HC{\equiv}CH + Cl^- \qquad \text{(Reaction 2.9)}$$

The product of pathways 6, 8 and 13 in Figure 2.2 (acetylene) can then undergo hydrogenation pathway resulting ethylene in the presence of proton donor, or (pathway 11 in Figure 2.2)

$$HC{\equiv}CH + 2H^+ + 2e^- \rightarrow H_2C{=}CH_2 \qquad \text{(Reaction 2.10)}$$

The product of pathways 5 and 7 in Figure 2.2 (VC) can also go further dechlorination via hydrogenolysis resulting ethylene in the presence of proton donor, or (pathway 12)

$$HClC{=}CH_2 + H^+ + 2e^- \rightarrow H_2C{=}CH_2 + Cl^- \qquad \text{(Reaction 2.11)}$$

In the last step of dechlorination pathways, the product of pathways 9, 11, 12 in Figure 2.2 (ethylene) can then undergo hydrogenation pathway resulting ethane in the presence of proton donor, or (pathway 14)

$H_2C{=}CH_2 + 2H^+ + 2e^- \rightarrow H_3C{-}CH_3$ (Reaction 2.12)

The overall scheme of TCE reduction is important in order to determine the pathway that is dominant in the Fe(0) packed column of sequential system used in this study.

2.3. Applications of biotic and abiotic removal mechanisms for the treatment of chlorinated compounds in gas phase

Over the past few years, considerable research has focused on the biotic and abiotic removal mechanisms of chlorinated organic compounds since the use of these mechanisms can serve as an efficient, economical and ultimate removal of these compounds from contaminated groundwater and soil. On the other hand, chlorinated organic compounds are not only common groundwater and soil contaminants but also they are among the hazardous air pollutants as well. The restrictions under Title III of Clean Air Act Amendments of USEPA (1990) have not only forced the industries to control the HAPs that they release but also limited the use of popular groundwater and soil remediation technologies like air stripping and sparging which cause the release of evaporated hazardous contaminants in to air. In the late 1990s, new technologies have been developed in order to control the air toxics. In order to control the air emissions of chlorinated compounds, researchers focused on the applications of proved biotic and abiotic removal mechanisms on treatment of waste-gases contaminated by chlorinated compounds. Up to now, only a few studies have been performed towards this aim.

Biotic treatment of chlorinated compounds in gas phase has widely been studied using the basis of aerobic co-metabolic biotrasformation mechanisms applied via

biofilters. The first study using bioreactors to remove gas phase compounds degraded by cometabolism was conducted by Wilson *et al.* (1988). In their study, a mixed microbial consortium grown on n-butane was used to cometabolize TCE and 1,1,1-trichloroethane (TCA). Others, using a variety of bioreactor configurations, have utilized bacteria induced by methane (Uchiyama *et al.*, 1992; Speitel and McLay, 1993; Apel *et al.*, 1993; Fayolle *et al.*, 1997), phenol (Ensley, 1992; Kim, 1997; Lee *et al.*, 2000), toluene (Ensley, 1992; Shields *et al.*, 1994; Cox *et al.*, 1998; Dolasa and Ergas, 1999) and propane (Wilcox *et al.*, 1995; Sukesan and Watwood, 1997; Lackey and Boles, 1997) to treat TCE contaminated air. However, biofiltration of chlorinated solvents via aerobic cometabolic mechanism has not been successful. Sustainable removal efficiencies for TCE ranging from 20 to 60% have been reported (Wilson *et al.*, 1988; Speitel and McLay, 1993; Cox *et al.*, 1998). Higher removal efficiencies, up to 90%, have been achieved for short periods of time. The difficulty in sustaining high removal efficiencies for chlorinated solvents is related to the microbiology and biochemistry of the degradation process like competitive inhibition and production of reactive intermediates that inactivate the specific enzyme (Cox *et al.*, 1998). On the other hand, Lackey *et al.* (2001) studied the performance of biofilter inoculated with aerobic bacteria treating TCE with propane as primary substrate. It was shown that the removal of TCE was dependent on the primary substrate feeding rate. They achieved 25% TCE removal in continuous feeding whereas 98% in pulsed or cycled in step-wise fashion . The EBCTs investigated were between 15-60 minutes.

Biofilters treating chlorinated compounds on the basis of cometabolic biotransformation have some disadvantages like supplying a primary substrate, complex microbial activity, low resistance to transformation by-products (inhibition),

competition for primary substrate, low reaction rate thus incomplete transformation of highly chlorinated compounds etc.

There is a study by Mihopoulos et al. (2000) on the treatment of vapour phase perchloroethylene in a soil column by anaerobic bioventing. The soil column inoculated with 1L of anaerobic pentachlorophenol (PCP) degrading culture was fed with certain mixture of anaerobic venting gas including 0.1% CO_2 as carbon source and 0.1-1.0% H_2 as electron donor for PCE reduction, 10 ppmv PCE balanced by N_2 at 5.1 hrs of residence time. The results have shown that, dechlorination of PCE was not observed at H_2 concentrations less than 1000 ppmv. In addition, complete dechlorination was never realized and VC accumulated in the column although H_2 was increased to a concentration of 10000 ppmv. As conclusion, they have stated that high dechlorination rates observed for PCE (k_{PCE}=0.098 min^{-1}) make anaerobic bioventing an attractive method that can potentially be integrated in an in-situ remediation process like air sparging/stripping to treat contaminated soils and groundwaters. However, accumulation of VC, which is extremely toxic compound, in the column possesses a problem and there is a need for additional mechanisms to compensate the complete reduction of chlorinated compounds in an actual anaerobic bioventing system for in-situ applications. Zero valent iron (Fe(0)) is known to be an effective and economical media for the reduction of chlorinated compounds.

Uludağ-Demirer and Bowers (2000) studied the adsorption/reduction reactions of trichloroethylene by Fe(0) in the gas phase. They have concluded that TCE was reduced to form mainly cDCE, VC, and ethylene in gaseous phase and the observed TCE reduction rate constant at 35°C was determined as 0.6 min^{-1} which states that it

was a fast reaction.

In this study, treatment of gaseous TCE by biotic and abiotic reduction reactions in continuous sequential (biological/chemical) reactor system was investigated in order to determine the effectiveness of the sequential biotic and abiotic mechanisms for the complete reduction of the gaseous TCE to non-toxic ethylene and ethane. In addition, this study also aimed to develop an effective technology that can potentially be integrated in an in-situ remediation process like air sparging/stripping to treat contaminated soils and groundwaters by solving the problems occurred in separate applications of biological and chemical systems.

The reactor system proposed in this study consisted of granular anaerobic mixed culture packed biofilter followed by elemental iron metal (Fe(0)) packed column in series. Both reactors are packed-bed filters that aimed to treat the TCE contaminated gas stream. In this manner, the following section not only gives the description of biofiltration which is innovative technology for off-gas treatment but also describes the fundamentals, design and operations principles of packed-bed filters.

2.4. Biofiltration

Engineers are often surprised to learn that biological air treatment is possible. Microorganisms, after all, can only thrive where there is water. But several systems have been devised to provide the water and other environmental conditions in such a way that the air pollutants reach the organisms. "Biofilters", biologically mediated filters, are now one of the most promising air pollutant control technologies used in the treatment of various vapor phase contaminants (Devinny, 1997).

Vapor phase contaminants are found in the off-gases from soil and groundwater remediation operations, from industrial processes, and from wastewater treatment systems. The compounds commonly found in air that are amenable to biological treatment include petroleum hydrocarbons, non-halogenated solvents, sulfides (e.g. H_2S), ammonia and some halogenated solvents. The contaminants must be transferred to the liquid phase to be available for microbial metabolism. Thus vapor phase biological treatment involves three steps; gas-liquid transfer, liquid phase transport to the microorganisms, and microbial transformation of the contaminants. Two general process configurations exist, suspended growth and packed beds. Suspended growth applications have been almost entirely associated with using contaminated air for aeration of activated sludge processes. In such cases the treatment of vapor phase contaminants is a fortuitous artifact rather than an engineered system. Processes designed for biological treatment of vapor phase contaminants have been almost entirely packed beds. The first engineered, packed bed systems were used for controlling the odors at wastewater treatment plants (Pomeroy, 1957, 1982; Carlson and Leiser, 1966). Packing material used in the first systems was soil and volumetric gas fluxes ($m^3/m^2 \cdot s$) were relatively low. The systems were given the name *soil filters* and when alternative packings began to be used the term *biofilter* came into use.

Conceptually, biofilters are very similar to packed bed systems used for wastewater treatment. The principal differences are the presence of vapor phase rather than liquid phase contaminants and the lack of a moving liquid phase. The latter difference has been modified by the introduction of *biotrickling filters*, vapor phase systems to which nutrients are supplied by a continuously recycled liquid stream

added as a spray at the top of the column (Diks and Ottengraf, 1991; Sorial *et al.*, 1995). A modification of the basic biofilter technology is the *bioscrubber*, a process in which a suspended culture is sprayed over the packing, collected at the bottom, and recycled to a suspended growth reactor [Hammervold *et al.*, 1995].

The biofilters currently in use span the range of designs and applications. There are more than 500 operating biofilters in Europe and more around the world. They are used for odor control at coffee roasting plants, meat packing plants, fragrance and flavor manufacturers and chemical process industries.

2.4.1. Advantages of biofiltration

Biofiltration of gases has gained only slow acceptance, even though soil treatment of natural wastes, decomposition of solid and liquid organics in landfills, and biological wastewater treatment have long been accepted. However, biofiltration offers a number of advantages.

Gases are inherently more biodegradable than solids and liquids because they are molecularly dispersed. Biofiltration does not contaminate the soil because the loading rates are very low. In contrast, soil contamination has resulted from adding liquid and solid organics at high loading rates without providing for microbial degradation. Biofiltration of contaminated air is considered new and untested in the world. This is partly because incineration, water and chemical scrubbing, and activated carbon adsorption are entrenched as air pollution control methods (Bohn, 1992).

Actually, biofiltration is not "new". Rather, it is an adaptation of the process by

which the atmosphere is cleaned naturally. VOCs exist in the atmosphere until plants and soil absorb and degrade them. The process has been going on for more than one billion years. However, it is inefficient due to the limited contact of soils and plants with the atmosphere and because the reactions are relatively slow. Biofiltration unit provides maximal contact and allows sufficient time for VOCs to react with biologically active media (Bohn, 1992).

Important advantages of biofiltration systems over other air pollution control alternatives include low capital and operating costs, low energy requirements, and the absence of residuals and by-products requiring further treatment or disposal. Although the intent of conventional systems for VOC removal from gaseous waste streams is gas phase pollution control, each produces a waste stream that must be either treated or disposed. A summary of existing VOC control technologies, process residuals and by-products, energy costs, and process limitations is shown in Table 2.3.

2.4.2 Biofiltration performance

2.4.2.1 Chemicals

Following is a nonexhaustive list of specific compounds that have been removed from waste gas streams with biofiltration: ammonia, carbon monoxide, hydrogen sulfide, acetone, benzene, butanol, butyl acetate, diethyl amine, dimethyl disulfide, ethanol, hexane, ethylbenzene, butylaldehide, acetate, scatole, indole, methanol, methyl-ethyl-ketone, styrene, iso-propanol, methane, methyl mercaptant, mono-, di-, tri-chloromethane, nitrogen oxide, nitrogen dioxide, pentane, dimethyl sulfide,

thiophene, toluene, trichloroethylene, terachloroethylene, 2-ethyl hexanol, xylene (Ottengraf and VanDenOever, 1983; Mueller, 1988; Hodge *et al*, 1991; Barshter *et al.*, 1993; Apel *et al.*, 1995; Ergas *et al.*, 1995; Morgenroth *et al.*, 1996; Swanson *et al.*, 1997).

Table 2.3: Comparison of vapor phase pollutant control technologies

Treatment technology	**Residuals/ by-products**	**Energy costs**	**Comments**
Adsorption	spent activated carbon (regenerable systems usually combined with condensation or incineration)	moderate to high	limited to low to moderate concentration emissions and molecular weights between approximately 45 and 130
Absorption	waste water, chemical sludges	moderate	limited to soluble compounds (e.g. H_2S, acetone, methanol)
Thermal oxidation (incineration)	NO_x, CO, HCl, potentially toxic organic compounds	high	stable performance with sufficient time, temperature, and turbulence
Catalytic oxidation (catalytic incineration)	NO_x, CO, HCl, potentially toxic organic compounds	moderate to high	H_2S, HCl, or particulate matter can destroy catalyst
Condensation	compound not destroyed, however, potential for product recovery	high	low range of compounds at high concentrations
Biofiltration	compost media changed every 2-5 years	low	low to moderate concentration biodegradable emissions large foot print
Biotrickling filter	synthetic media, low flow rate cell waste stream	low to moderate	moderate to high concentration biodegradable emissions large foot print

The chemicals treated by biofilters are primarily volatile organics and reduced sulfur and nitrogen compounds, and are typically degraded by either as primary substrates or as cometabolites (Swanson *et al.*, 1997).

Chemicals removed by biofilters must be transported to the aqueous biofilm surrounding media particles. The degree to which a chemical partitions between the waste gas and biofilm phases affects this transport. Theoretically, highly volatile chemicals will be present in relatively low biofilm concentrations, resulting in slower degradation kinetics. However, there is evidence that highly volatile aliphatic compounds such as hexane (Morgenroth *et al.*, 1995) and pentane (Barshter *et al.*, 1993) can be efficiently removed via biofiltration. Thus, partitioning characteristics may not exclude a volatile chemical from being a candidate for biofiltration.

Compounds to be treated must be readily biodegradable and nontoxic; thus, biofilters have treated alcohols, ethers, aldehydes, ketones, monocyclic aromatics, organic amines and sulfides in reasonable concentrations (Leson and Winer, 1991). More complex constituents, such as chlorinated organics, can be handled, but rates are slow. Higher molecular weight organics ($>C_6$) have been removed in a biofilter treating off-gases from a primary screening unit at a municipal wastewater treatment plant. This indicates the possibility of applying biofiltration to a border range of more complex organics (Ergas *et al.*, 1995)

Biofilters can also treat chemical mixtures. However, competitive effects between chemicals can be important in both the mass transfer and biodegradation steps of the biofiltration process.

2.4.2.2. Performance parameters

In this section performance parameters of biofilters are discussed. The parameters indicated here are general parameters for packed filters treating off-gases.

2.4.2.2.1. Empty bed contact time (EBCT)

EBCT is a relative measure of gas residence time within the biofilter medium. EBCT is typically used for comparisons of gas residence times in different biofilters, or under different loading conditions in the same biofilter. The actual gas residence time in the reactor would be calculated as EBCT divided by the air-filled porosity available to gas flow, but such porosity is rarely known (Swanson *et al.*, 1997).

While the chemical residence time is greater than the gas residence time due to partitioning between the gas phase and the liquid and adsorbed phases, it is directly proportional to EBCT. Thus, EBCT is a simplified, relative measure of chemical residence time in a biofilter. Sufficient EBCT is necessary to allow transport and degradation of the pollutant to occur, which makes EBCT a critical design and operating parameter (Swanson *et al.*, 1997).

2.4.2.2.2. Surface loading

Surface loading is a measure of the volumetric gas loading applied to a biofilter. Although often expressed in units of meters per hour (m/hr) and referred as "face velocity", it is really a loading parameter. For a specific biofilter, higher surface loading is characteristic of higher flow, shorter EBCT, and decreased removal

efficiency. Upper limits on surface loading exist due to bed-drying concerns and EBCT requirements (Swanson *et al.*, 1997). Thus, maximum surface loads with efficient moisture control systems are generally less than 200 m/hr (Sabo *et al.*, 1993)

2.4.2.2.3. Mass loading

Biofilter mass loading is defined as the VOC mass applied to biofilter per unit medium volume per unit time. Often an average value for the entire bed volume is reported. However, the plug-flow nature of biofilters causes most of the degradation to occur at the influent end, so deeper reaches of the biofilter receive smaller mass loads. Because mass loading includes the effect of both flow and concentration, a single biofilter can perform differently under identical mass loadings. Higher VOC concentrations create stronger driving forces for diffusion into the biofilm and faster biodegradation kinetics, while low flows (high EBCT) permit longer times to diffusion to occur. Because removal efficiency eventually decreases with higher mass loadings, removal requirements generally determine limits on applied mass loadings. Extremely high loadings can result in biomass clogging of biofilter media and the accumulation and/or emission of toxic and/or acidic intermediates (Devinny and Hodge, 1995; Swanson *et al.*, 1997).

2.4.2.2.4. Elimination capacity (EC)

EC is a normalized measure of VOC removal capacity at a given mass loading. EC is defined as the VOC mass removed per unit medium volume per unit time. Like mass load, this parameter is often reported as a bed-averaged value, but should not be

expected to be uniform over the biofilter depth. EC is a function of mass load and EBCT, medium type, VOC type, and environmental conditions. The EC of a biofilter for any chemical will generally decrease (at a given mass loading) with decreasing EBCT values. For a required level of removal, the average EC will largely determine biofilter size, and thus, process cost (Swanson *et al.*, 1997).

2.4.2.2.5. Removal efficiency (RE)

RE is the operating parameter most often used to judge the success of a biofilter, and likely to be of paramount interest of the regulator. The RE can be expressed as the difference between the concentrations of pollutant in the influent and the effluent of the reactor divided by the concentration in the influent of the reactor.

2.4.3. Design and operation considerations

2.4.3.1.Media selection

Selecting or engineering the proper biofilter medium is an important step toward developing a successful biofiltration operation. Desirable media properties include the following.

- Optimal microbial environment — nutrients, moisture, pH, carbon supply should be non-limiting.
- Large specific surface area — maximizes attachment area, sorption capacity, and number of reaction sites per unit medium volume
- Structural integrity — necessary to resist medium compaction that increases pressure drops and lowers gas retention times.

- High moisture retention — moisture is critical in maintaining active microorganisms.
- High porosity — keeps retention times high and back pressures low.
- Low bulk density — reduces medium compaction potential.

A wide range of biofilter media has been considered. The most widely used medium types are compost, peat, bark mulch, and mixtures of these. These materials possess many of the quantities noted earlier, with the main drawback being mineralization of the organics comprising the bed. This "aging" phenomenon leads to compaction and a limitation on bed life (Medina *et al.*, 1992; Swanson *et al.*, 1997). Although periodically turning media to increase porosity can modestly improve performance, organic filter material eventually will require replacement. Combining organic materials with inert bulking agents has increased the media life to more than five years (Leason and Dharmavaram, 1995; Swanson *et al.*, 1997), although two to four years is more common. Inorganic materials such as GAC and diatomaceous earth also have been used as the sole medium in biofilters (Medina *et al*, 1992). However, use of a solely inorganic medium requires proper seeding with nutrients and organisms (Swanson *et al.*, 1997).

Amendments are commonly added to the primary matrix material. Lightweight bulking agents such as woodchips, perlite, vermiculite, or polystyrene spheres can be added to reduce compaction, improve porosity, homogenize gas flow, prevent cracking, reduce channeling and lower pressure drop (Swanson *et al.*, 1997). Volume fractions of these amendments are typically from 40 to 60% (Corsi and Seed, 1994). Amendments such as GAC can also augment the adsorptive capacity of a biofilter,

thus improving performance under shock VOC loadings (Bishop *et al.*, 1990).

2.4.3.2.Moisture content

Biofilter medium moisture content has been identified as the single most important parameter in biofilter operation (Marsh, 1992). There are many reasons why maintaining an optimal moisture level is critical, and, unfortunately, there are many reasons why achieving that level during operation is difficult. These are addressed as follows.

An overwet biofilter medium causes:

- High backpressures and low gas retention times due to filling of the pore space with water.
- Nutrient washing from the biofilter medium.
- Production of high strength, low pH leachate requiring disposal (Hodge *et al.*, 1991; Marsh,1992).

A dry biofilter medium causes:

- Deactivation of VOC-degrading microorganisms.
- Contraction and consequent medium cracking reducing retention time.
- Frustrated attempts to rewet dry hydrophobic medium materials.

Factors complicating maintenance of optimal medium moisture levels include:

- High-velocity, →100%-relative humidity gas flows that strip moisture from the biofilter medium.
- Exothermic reactions that increase temperatures, which (1) speed up these reactions and further increase temperatures; and (2) lead to increases in water

vapor pressure, further augmenting the moisture-carrying capacity of the gas stream. This mechanism is especially important near the biofilter influent where the highest VOC concentrations exist (Kosky and Neff, 1988)

Optimal biofilter medium moisture contents range from 40 to 60% (wet weight) (Leson and Winer, 1991). Moisture maintenance has been traditionally approached in the following three ways:

1. Influent gas humidification to minimize drying potential, accomplished via:
    - Water and influent gas flowing countercurrently through a packed tower
    - Atomizers or spray nozzles adding water mist to influent stream
    - A combination of both humidification and periodic direct water addition
2. Direct water addition to the surface of the biofilter media with a spray like irrigation system.
3. A combination of both humidification and periodic direct water addition.

2.4.3.3.Temperature

Biofilter operation in the mesophilic range of 25-35°C has been recommended, with 35°C often noted as the optimal temperature for the microorganisms in biofilters (Mueler, 1988; Marsh, 1992). There is a trade-off, in theory, in increasing the reactor temperature. Rates of reaction and diffusion will increase for higher temperatures. However, the water solubility of VOCs and the sorption capacity of filter solids will decrease, thus impeding partitioning out of the gaseous phase at higher temperatures (Leson and Winer, 1991; Bohn, 1993).

CHAPTER 3

MATERIALS AND METHODS

In this chapter, the experimental set-up, inocula, chemicals, sampling and injection equipments and analytical methods used in this study are described.

3.1. Experimental set-up

In this study, treatment of gaseous TCE by biotic and abiotic reduction reactions in a sequential (biological/chemical) reactor system was investigated. The reactor system consisted of granular anaerobic mixed culture packed biofilter followed by elemental iron metal (Fe(0)) packed column in series. The reactors were made up of glass and inoculated with granular anaerobic mixed culture and Fe(0) fillings up to 100 mL of effective volume, respectively. 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 was made of Teflon. In order to sample the gas in the influent of the system and effluents of the biofilter and Fe(0) column, 3-way sampling valves were located in the entrance of biofilter, exit/entrance of biofilter/Fe(0) column and exit of Fe(0) column.

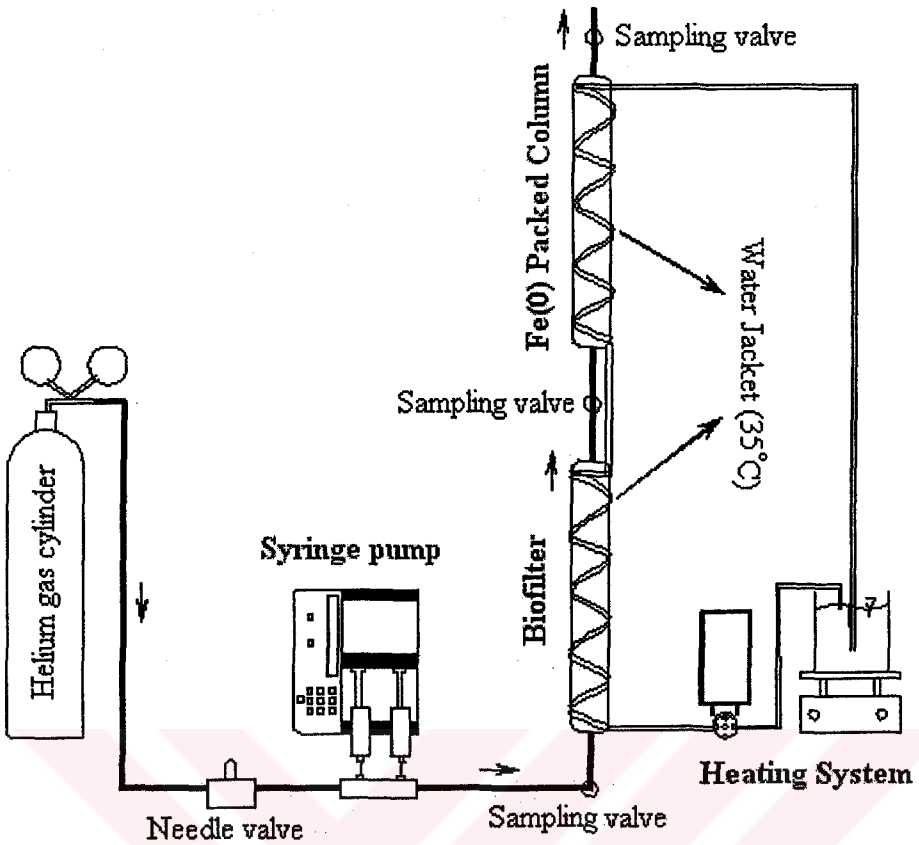


Figure 3.1: Illustration of continuous reactor system

The influent gas stream was maintained by achieving a constant flow of helium (He) gas from a pressurized gas cylinder with an exit pressure of 2.5 bars. 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 exit port of the valve was then fed to the inlet of the biofilter (Fig 3.1). The flowrate

of the gas stream was measured from 3 distinct points that are entrance and exit of biofilter and exit of Fe(0) column with bubble flowmeter that has a gas flowrate measuring limit of 0.1-10 mL/min. The effluent gas stream of the system was vented to 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 pumps water from reservoir through the flexible Taygon tubing rolled around the reactors. The temperature of the reactors is measured with a Fischer thermometer. The reactor configuration is illustrated in Figure 3.1.

The columns in the reactor system were gas tight and were pressurized with helium gas for leak detection prior to experimentation. The presence of leaks were investigated by soap bubbles and no leaks were observed in the system. In order to determine the gas tight property of the system, the air in the empty system were also vacuumed by a glass syringe that have an easily moving slider, when the slider was released, the slider returned its previous position that proves the system was gas tight.

3.2. Inocula

3.2.1. Granular anaerobic mixed culture

Granular anaerobic mixed culture that was packed into the biofilter was obtained from anaerobic treatment system of Ankara Efespilsen Beer Factory having a volatile

suspended solids content of 41.447±0.749 g VSS/L. Anaerobic granules have round shapes like beads with a maximum diameter of 2 mm and consist of anerobic microorganisms including fermentators, acidogens, acetogens, methanogens etc. The VSS concentration of granules represents the concentration of microorganisms in the granules. The moisture content in the biofilter was 100% and this content was maintained in the reactor by adding distilled water on the top of the biofilter media whenever the 3 cm of water level on the media was dropped down throughout the operation period.

3.2.2 Zero-valent iron fillings

The Fe(0) fillings that was inoculated into the Fe(0) packed column was obtained from Merck Chemical Co., Germany. The fillings have 150μm of effective diameter. In order to attain a certain moisture content on the fillings, distilled water was added on the fillings until all the fillings were observed to be wet. The fillings then sieved through a plastic sieve and the excess water was leached from the media. The moisture content of the fillings was determined by weight differences between fillings prior to washing and after washing and it was determined as 17.7%. The weight of fillings in the 100 mL of effective reactor volume was 241.16 g.

3.3. Chemicals

Trichloroethylene (in liquid phase with 99.5% GC purity) that was used in the preparation of calibration standard in gas chromatographic analysis and as a targeted pollutant in continuous reactor system was obtained from Merck Chemical Co., Germany; 1,1-dichloroethylene (in liquid phase with 99.5% GC purity), trans-

dichloroethylene (in liquid phase with 97% GC purity), cis-dichloroethylene (in liquid phase with 97% GC purity), vinyl chloride (in gas phase with 99.5% GC purity), ethylene (in gas phase with 99.95% GC purity) and methane (in gas phase with 99.995% GC purity) that were used in the preparation of calibration standards in gas chromatographic analysis were obtained from FLUKA Chemical Co, Germany. Ethane (in gas phase with 99.95% GC purity) that was used in the preparation of calibration standard in gas chromatographic analysis was obtained from Air Products and Chemicals Inc, USA.

The gases including helium (He), hydrogen (H_2), nitrogen (N_2), carbon dioxide (CO_2) with 99.995%, 99.95%, 99.95%, 99.995% purity respectively, that were used for feeding the continuous reactor system were obtained from Air Products and Chemicals Inc., USA (for He) and OKSAN Kol. Şti., Turkey (for other gases).

3.4. Sampling and injection equipments and procedures

The sampling from inlet of the reactor system and outlets of the system components was performed with using Hamilton 1800 series 100μL gastight syringe. The samples were directly injected into gas chromatography.

The gas mixture of H_2, N_2 and CO_2 that was fed into the system was prepared in TEF gas sampling bags by mixing the certain amounts of gases in the bags. The mixture was then filled into the Hamilton 1000 series 50 mL gastight syringe. TCE in gas phase that was fed into the system was prepared by vaporizing a certain amount of liquid TCE in the Hamilton 1000 series 50 mL gastight syringe. Two syringes were then located on a WPI sp200i syringe pump where the contents in the syringes were

introduced into the He main gas stream and reactor system.

3.5. Analytical methods

Gas chromatographic analysis was performed in the characterization of the samples. ATI Unicam 610 Series gas chromatography equipped with flame ionization detector (FID) and Chrompack CP 7559 Poraplot Q-HT Plot FS column was used in the analysis. The details of the gas chromatographic analysis method were;

- Detector Temperature: 200°C
- Injector Temperature: 150°C
- Carrier gas Flow: 10 ml/min (H_2)
- Column Temperature: 100°C (for 2 min) ramping to 200°C at 20°C/min, stay (10 min at 200°C)
- Sample Volume: 100μL

The compounds analyzed with this analytical method are: TCE, cDCE, tDCE, 1,1DCE, VC, ethylene and ethane. The peak shapes and retention times of the compounds are given in the Figure 3.4. Calibration curves for these compounds are given in the Figure A.1. The method's minimum detection limits for the mentioned compounds are 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. The MDLs of the compounds are determined by seven consecutive blank injections (only 100μL air) to the GC. The detectable signal for the compounds is assumed to be three times the noise at the residence times of the compounds in the applied GC method, respectively (Ataman, 2002).

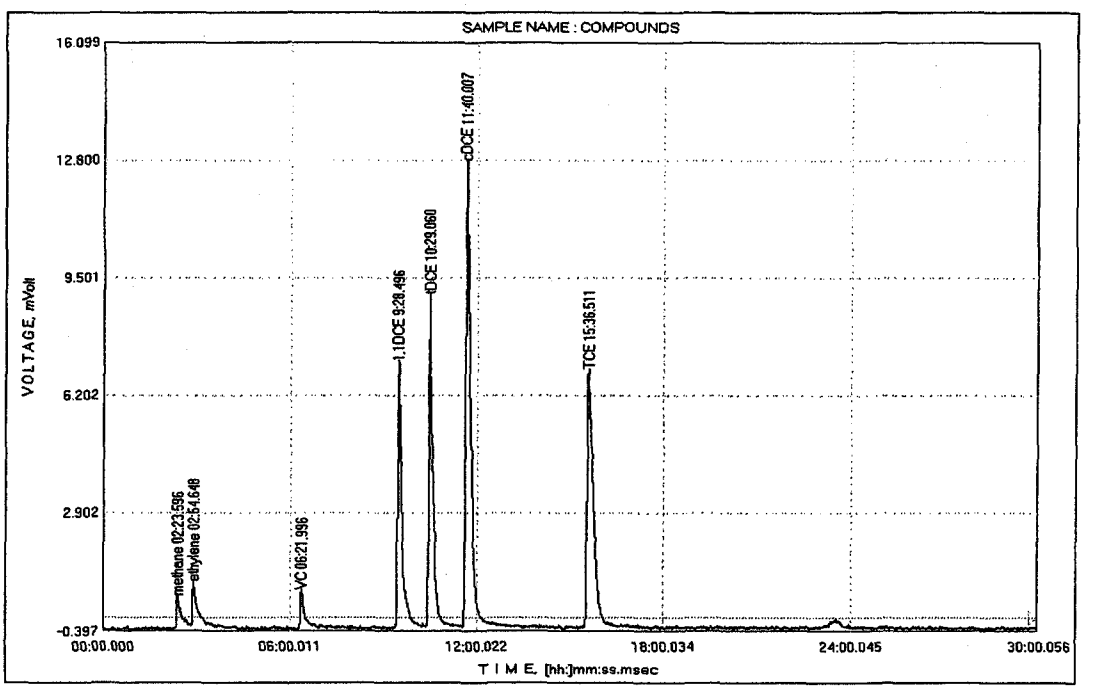


Figure 3.2: Peak shapes and the retention times of the compounds in GC analysis

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the experimental results obtained are presented and the effects of EBCT and the initial concentration of TCE or TCE loading rate on the performance of continuous reactor system designed to treat the gaseous TCE are discussed.

4.1. Effect of EBCT on the performance of continuous 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 EBCT on the TCE removal efficiency of the system, the EBCTs was varied as 2.5, 1.0, 0.5 and 0.25 hours for both biofilter and Fe(0) packed column separately. The results were shown in Figure 4.1 and Figure 4.2.

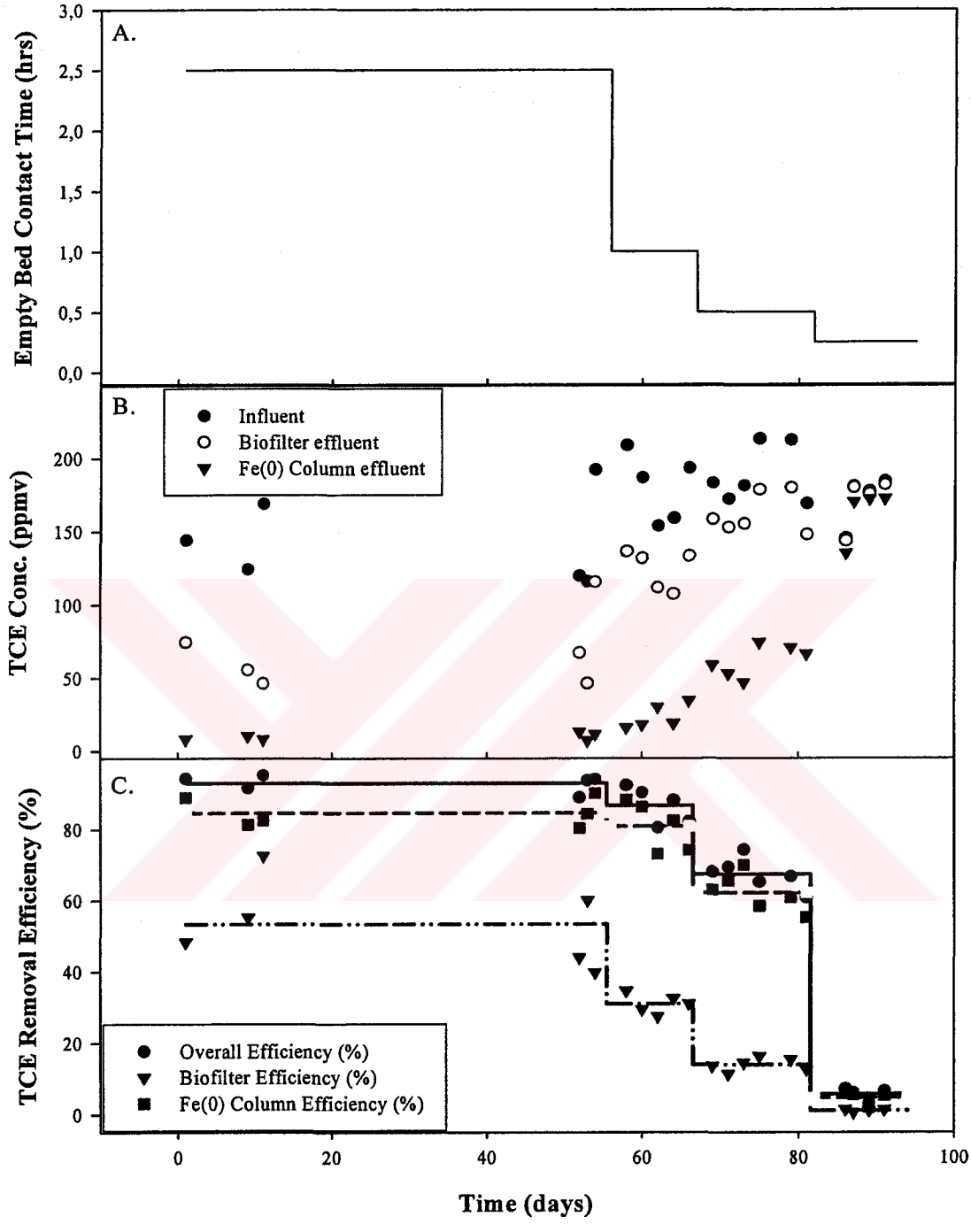


Figure 4.1: Effect of EBCT on the performance of the continuous reactor system; A. Applied EBCT values; B. The range of TCE concentrations tested in this study; C. TCE removal efficiency

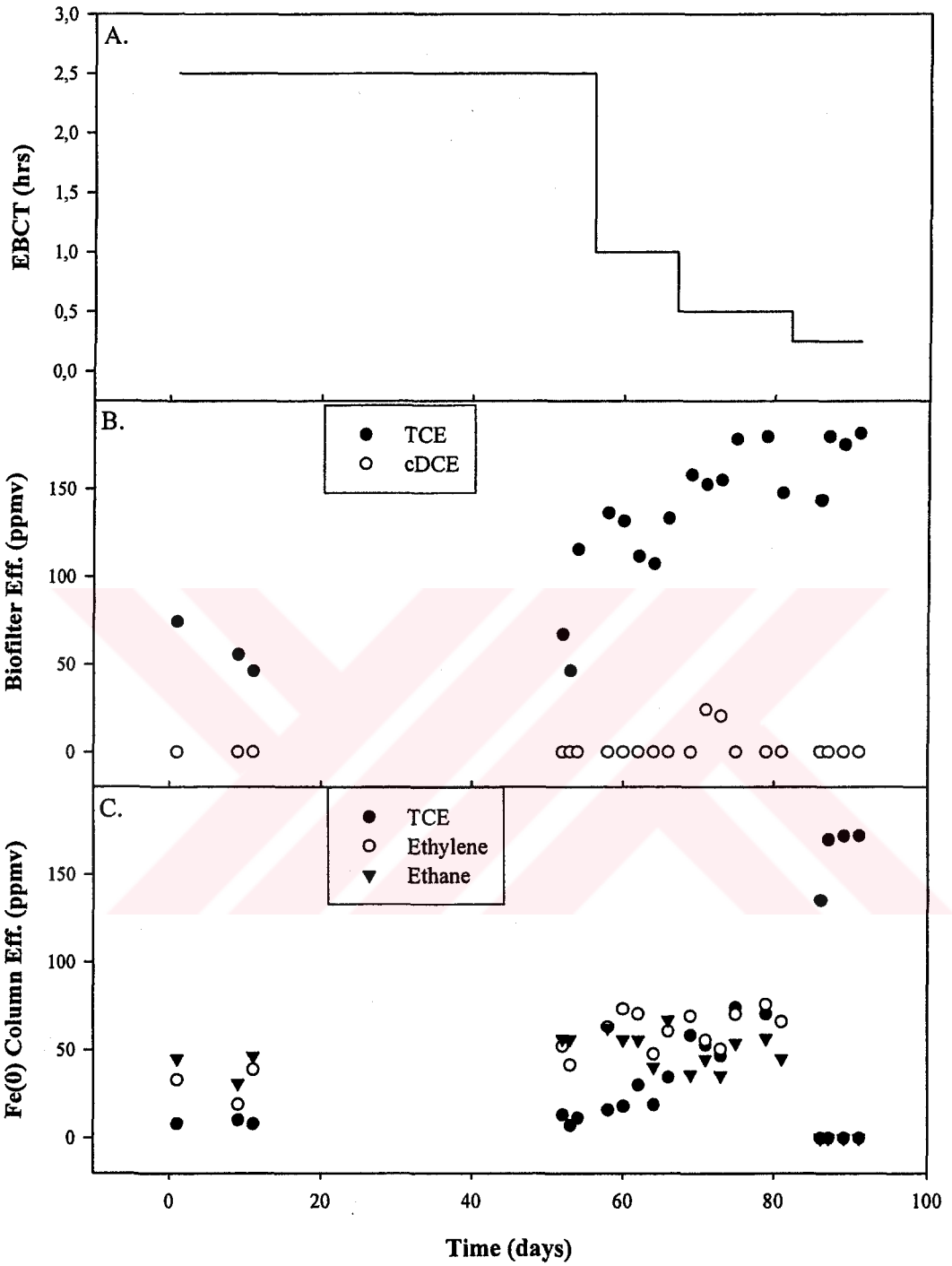


Figure 4.2: Effect of EBCT on the effluent character of the continuous reactor system; A. Applied EBCT values; B. Biofilter effluent; C. Fe(0) packed column effluent

Throughout the continuous reactor system operation period, EBCTs were changed when the coefficient of variation in the removal efficiency of overall system that is, the standard deviation of TCE removal efficiencies obtained at a certain EBCT divided by average of the removal efficiencies at this EBCT, was less than 10% at which steady-state condition was assumed to be reached.

The TCE removal efficiencies for each reactor at applied EBCTs were calculated as the difference between the concentrations of TCE in the influent and the effluent of the reactor divided by the concentration in the influent of the reactor.

At 2.5 hrs of EBCT, average TCE removal efficiencies of biofilter, Fe(0) packed column and overall system were 53.5±12.0%, 84.6±4.1% and 93.0±2.3%, respectively (Figure 4.1.C). In biofilter effluent, only TCE with an average concentration of 67.5±26.1 ppmv was observed while no other reduction by-products of TCE was detected (Figure 4.2.B). Since the granular anaerobic mixed culture has not been enriched for TCE reduction previously, the reductive dechlorination of TCE to its by-products would not been expected in a certain time period in biofilter. For that reason, the TCE removal in the biofilter was due to biosorption on the virgin granular medium at this EBCT (O'Niell et al., 1999). On the other hand, in Fe(0) packed column effluent, TCE and ultimate reduction by-products of ethylene and ethane with average concentrations of 9.7±2.3 ppmv, 36.9±12.1 ppmv and 46.9±10.3 ppmv were detected, respectively (Figure 4.2.C).

At 1.0 hr of EBCT, average TCE removal efficiencies of biofilter, Fe(0) packed column and overall system were 31.0±2.8%, 80.9±6.9% and 86.7±5.2%, respectively

(Figure 4.1.C). The removal efficiencies of Fe(0) packed column and overall system decreased slightly, however decrease in biofilter was higher compared to the Fe(0) packed 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 was detected in the biofilter. The reason of this can be speculated as the removal of TCE in 65 days period in the biofilter was due to biosorption until the equilibrium of TCE between liquid and solid phases has been reached and biosorption was effected by decreasing EBCT in the reactor (Figure 4.2.B). On the other hand, in Fe(0) packed column effluent, TCE and ultimate reduction by-products of ethylene and ethane with average concentrations of 23.5±8.2 ppmv, 63.1±10.1 ppmv and 56.3±10.2 ppmv were detected, respectively (Figure 4.2.C). In Fe(0) packed column at 1 hr EBCT, the effluent ethane concentration (63.1±10.1 ppmv) was less than ethylene concentration (56.3±10.2 ppmv) whereas, it was higher at 2.5 hrs EBCT (36.9±12.1 ppmv for ethylene and 46.9±10.3 ppmv for ethane). As the EBCT was decreased, time that TCE spent in the reactor for reduction reaction was decreased leading to reduced ethylene to ethane conversion.

At 0.5 hrs of EBCT, average TCE removal efficiencies of biofilter, Fe(0) packed column and overall system were 13.9±1.8%, 62.1±5.2% and 67.4±4.5%, respectively (Figure 4.1.C). The decrease in the removal efficiencies of biofilter, Fe(0) packed column and overall system when the EBCT was decreased from 1.0 to 0.5 hrs (31.0±2.8% to 13.9±1.8% in biofilter; 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 EBCT was decreased from 2.5 to 1.0 hrs (53.5±12.0% to 31.0±2.8% in biofilter; 84.6±4.1% to 80.9±6.9% in Fe(0) column; and 93.0±2.3% to

86.7±5.2% in overall system). The reason of this can be expressed as by the decreasing EBCT, time that TCE spent in the reactor for reaction was decreased so the removal of TCE in the reactors was effected by decreasing EBCT. In biofilter 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 EBCT showed that a temporary reduction reaction occurred in biofilter. The existence of cDCE in the effluent of biofilter at 0.5 hrs of EBCT may be due to the fact that TCE was accumulated on the packed media of the biofilter through 70 days and then a certain transformation of TCE to cDCE was occurred possibly due to the endogeneous decay which could supply nutrients for microbial activity for a short time. Similar situation has been observed in the study of O'Niell et al. (1999) where the PCE and TCE adsorbed on the mixed-species microbial mats are biotransformed aerobically and anaerobically in 50 days period. In their study, the adsorption of PCE and TCE on the mixed-species microbial mat is fast as 24 hours but a slower transformation and degradation of both compounds followed this rapid partitioning to the mat phase. On the other hand, in Fe(0) packed column effluent, TCE and ultimate reduction by-products of ethylene and ethane with average concentrations of 61.5±10.7 ppmv, 64.6±9.7 ppmv and 45.3±8.8 ppmv were detected, respectively (Figure 4.2.C). In Fe(0) packed column at 0.5 hrs EBCT, the difference between effluent ethylene and ethane concentrations (64.6±9.7 ppmv for ethylene and 45.3±8.8 ppmv for ethane) was higher than the difference at 1.0 hrs EBCT (63.1±10.1 ppmv for ethylene and 56.3±10.2 ppmv for ethane). As the EBCT was decreased, time that TCE spent in the reactor for reduction reaction was decreased so the reduction of ethylene to ethane was distorted further by reducing

EBCT.

At 0.25 hrs of EBCT, average TCE removal efficiencies of biofilter, Fe(0) packed column and overall system were 1.1±0.4%, 4.6±1.8% and 5.6±1.8%, respectively (Figure 4.1.C). The removal efficiencies of biofilter, Fe(0) packed column and overall system decreased dramatically at this EBCT compared to the other EBCTs. In biofilter, Fe(0) packed column and overall system effluents, only TCE, but no other reduction by-products, with concentrations equal to influent concentration were detected (Figure 4.2.B, Figure 4.2.C).

Moreover, the path of TCE reduction reactions occurred in the Fe(0) column was also investigated by switching the continuous Fe(0) column in to a batch system and injecting a high concentration of TCE into the system after 3 months of operation period. After one day, the effluent of the system was sampled and analyzed with GC. Only VC, ethylene and ethane were detected in the sample. Concentrations of the compounds were not quantified since this experiment was applied only to determine the reduction pathway in the Fe(0) column. As a result, the possible reduction pathway in the Fe(0) column was 2→7→12→14 or 1→5→12→14 as given in the Figure 2.2.

In summary, the main mechanism of TCE removal in the Fe(0) packed column was reduction reactions since ultimate end products of ethylene and ethane were detected in the Fe(0) column from 2.5 to 0.25 hrs of EBCT. On the other hand, a certain and a continuous TCE removal was achieved in biofilter throughout the operation period but the exact removal mechanism in biofilter was not determined in this study.

Biosorption was assumed to be the only mechanism in this reactor. The existence of only biosorption in biofilter may have several reasons like inactivation of microbial activity due to the absence of continuous nutrient supply to the reactor for the cell growth. The ineffective quantification of reduction by-products in biofilter due to the analytical method (high MDL for VC in GC analysis, see Chapter 3) might also lead a problem in the determination of the TCE removal mechanism in this reactor. The extent of biosorption in biofilter was on discussion since a continuous TCE removal in this reactor was observed through the operation period in the absence of equilibrium and the biosorption capacity of anaerobic granules was not determined in this study.

In conclusion, outcomes of this study have illustrated the effect of EBCT on the TCE removal efficiency of the system and reduction reactions occurred in the system. As EBCT decreases, the time that TCE spent in the reactor for the removal also decreases which led an increasing TCE concentration in the effluent of the system also a decreasing TCE removal efficiency. On the other hand, ethylene and ethane which are non-toxic gases were detected from EBCT 2.5 to 0.25 hrs in the effluent of the system but at EBCT of 0.25 hrs no TCE removal was achieved.

4.2. Modeling the sequential reactor system

In this section, a model simulating the effect of EBCT on the sequential system is developed and discussed. The results of the model verified the effect of EBCT on TCE removal and flow pattern of the reactor system. It helped to determine the optimum EBCT for the system and effectiveness of filter media used in the reactors.

The effect of EBCT on the reactor system can be explained by boxes simulating the actual conditions in the system (Figure 4.3).

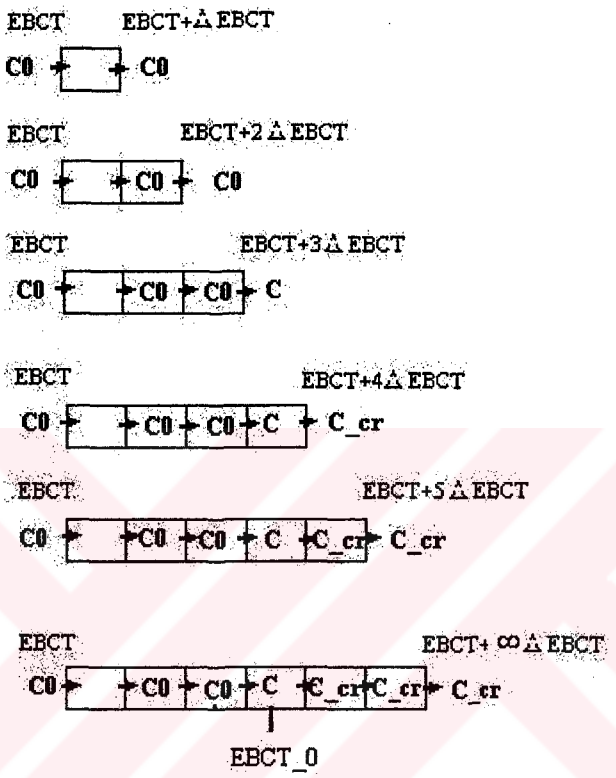


Figure 4.3: Illustration of actual conditions in the reactors of the system

where;

C_0: Influent TCE concentration of the certain reactor, ppmv

C: TCE concentration in the certain reactor, ppmv

C_cr: Critical TCE concentration or the TCE concentration leaving the reactor unreacted although it stays in the reactor for a long time (high EBCTs), ppmv.

EBCT: empty bed contact time applied to the system, hrs.

EBCT_0: empty bed contact time when effluent TCE concentration reaches to an actual TCE concentration, C, hrs.

According to the Figure 4.3, TCE fed into the reactor (C_0) is not removed up to some EBCT applied because TCE does not spend sufficient time in the reactor for the removal to occur. When the time that TCE spent in the reactor increases as EBCT increases, influent TCE concentration in the reactor drops to an actual concentration of, C, at EBCT_0. The effluent TCE concentration decreases further up to C_critical as EBCT getting higher and approaches to infinity. As the EBCT increases, TCE stays in the reactor longer than before and the effluent TCE in the reactor reaches up to a critical concentration. There is no further TCE removal in the reactor after a certain EBCT and TCE concentration in the effluent of the reactor remains constant as C_cr.

The system can mathematically be expressed as follows; the rate of change of TCE concentration converted in the reactor with respect to varying EBCT is dependent on the TCE removal rate in reactor or;

$$\frac{d\Delta C}{dEBCT} = \eta R \qquad \text{(Equation 4.1)}$$

where;

R: TCE removal rate, ppmv/hr

η: effectiveness factor, effectiveness of reaction on the reactor media can also depend on the extend of the non-ideal flow like earliness or lateness in mixing, mass transfer resistances between gas-liquid and liquid-solid phases in the reactor, ($0< \eta <1$), unitless (Levenspiel, 1999).

ΔC: TCE concentration converted in the reactor at any EBCT applied (C_0-C_eff), ppmv.

The TCE removal rate can also be expressed as;

$$R = -k\Delta C \qquad \text{(Equation 4.2)}$$

where;

k: TCE removal rate constant (hr^{-1})

The overall reaction then became;

$$\frac{d\Delta C}{dEBCT} = -\eta k\Delta C \text{ or by substituting} \qquad \text{(Equation 4.3)}$$

$$k\_obs = \eta k \text{ then,} \qquad \text{(Equation 4.4)}$$

$$\frac{d\Delta C}{dEBCT} = -k\_obs\Delta C \qquad \text{(Equation 4.5)}$$

where;

k_obs: observed TCE removal rate constant (hr^{-1})

By setting the following boundary conditions to the Equation 4.5, it yields;

At EBCT goes 0 to EBCT_0, $\Delta C = C_0 - C$

At EBCT goes from EBCT_0 to ∞ $\Delta C = C - C\_critical$

$$\int_{C0-C}^{C-C\_critical} \frac{d\Delta C}{\Delta C} = -k\_obs \int_{EBCT\_0}^{EBCT} dEBCT \qquad \text{(Equation 4.6)}$$

TCE removal efficiency can be written as;

$$RE = \frac{C0-C}{C0} \times 100 \text{ and,} \qquad \text{(Equation 4.7)}$$

or

$$RE\_critical = \frac{C0-C\_critical}{C0} \times 100 \qquad \text{(Equation 4.8)}$$

where;

RE: TCE removal efficiency, %.

RE_critical: Critical TCE removal efficiency that is, maximum TCE removal efficiency achieved in the reactor, %.

By integrating the Equation 4.6 and coupling it with Equation 4.8 and Equation 4.7, the following expression is obtained;

$$RE = \frac{RE\_critical}{1+\exp(-k\_obs \times (EBCT - EBCT\_0))} \qquad \text{(Equation 4.9)}$$

Equation 4.9 is the final expression of the effect of EBCT on the TCE removal performance of the system. Berkeley Madonna 8.0.1 Software, which was developed by Macey and Oster (1997-2001) to numerically solve systems of ordinary differential equations, was used to simulate Equation 4.9 and the sigmoidal (S-shape) curve obtained was fitted with actual TCE removal efficiency data obtained in the study. The S-curve perfectly fitted with the actual data (Figure 4.4) and important parameters in the Equation 4.9, which gave information about the system, for biofilter and Fe(0) column were given in Table 4.1.

Table 4.1: Important model parameters for biofilter, Fe(0) column and overall system

Model Parameters	Biofilter	Fe(0) Column	Overall system
k_obs (hrs^{-1})	12.4467	15.7188	15.192
EBCT_0 (hrs)	0.517376	0.429993	0.427818
RE_critical (%)	31.0743	82.7481	91.8592

As it is seen in Table 4.1, observed TCE removal rate constant (k_obs) of Fe(0) column, that is 15.7 hr^{-1}, is higher than the k_obs of biofilter, that is 12.5 hr^{-1}, which indicates that the TCE removal rate in Fe(0) column is higher than that in biofilter so the TCE removal in Fe(0) column proceeds faster than in biofilter. For that reason, the curve representing the TCE removal in Fe(0) column with respect to EBCT is steeper than the curve representing the biofilter (Figure 4.4).

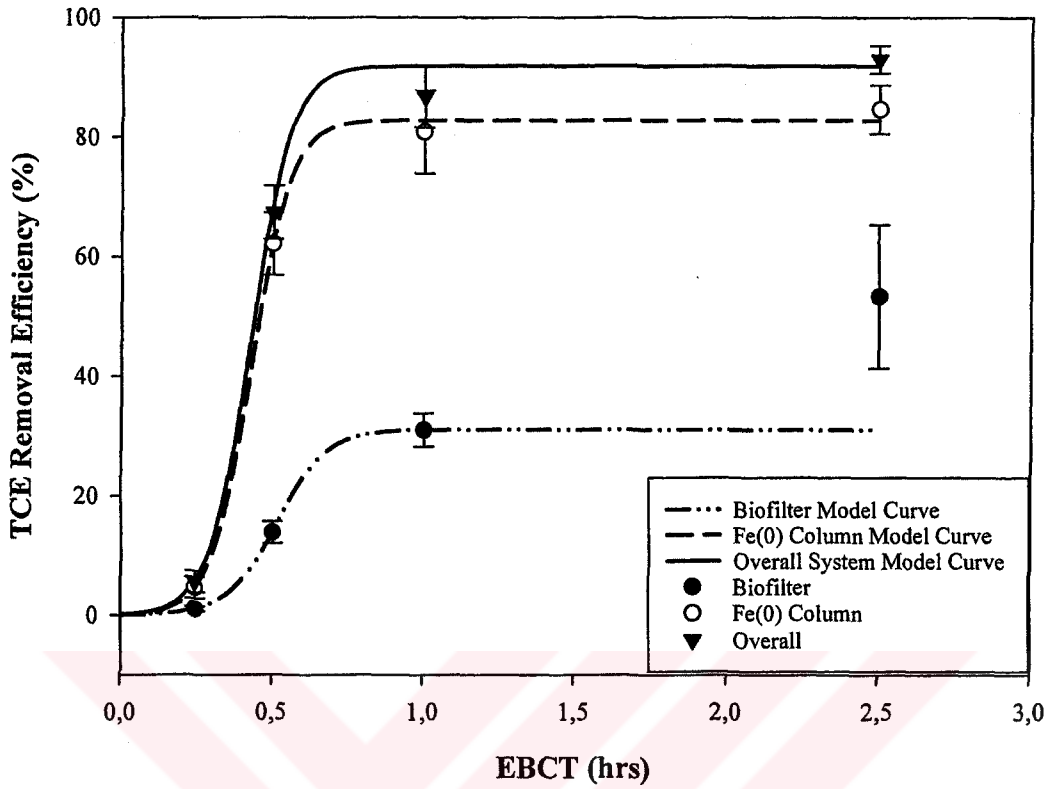


Figure 4.4: Comparison of actual data with model outcomes

Moreover, the EBCT_0 of Fe(0) column, that is 0.43 hrs, is lower than that of biofilter, that is 0.52 hrs, which indicates that the TCE removal in the Fe(0) column starts earlier than in the biofilter (Table 4.1). For that reason, the curve representing the TCE removal in biofilter with respect to EBCT is spreader than the curve representing the Fe(0) column (Figure 4.4).

Critical removal efficiency (RE_critical) is the most important parameter in the model, since it gives information about the effectiveness of media packed in the columns. Critical removal efficiency can be explained as the maximum TCE removal efficiency achieved in the reactors. Ideally, TCE removal efficiency must approach

to 100% as EBCT goes to infinity because TCE stays in the reactor a long time that it can be completely removed by the reaction in the reactor. After approximately 0.75 hrs of EBCT as seen in Figure 4.4, the TCE removal efficiency in both reactors became constant at RE_criticals of 31.1% for biofilter and 82.8% for Fe(0) packed column.

The reactors in this study are multiphase (3-phase) reactors in which gas, liquid and solid phases exist together therefore, the mass transfer of TCE from gas to liquid phase and liquid to solid phase has an important role for the reaction in the reactors since the reaction of TCE occurs on the packing medium. The mass transfer of TCE between these three phases is illustrated in Figure 4.5.

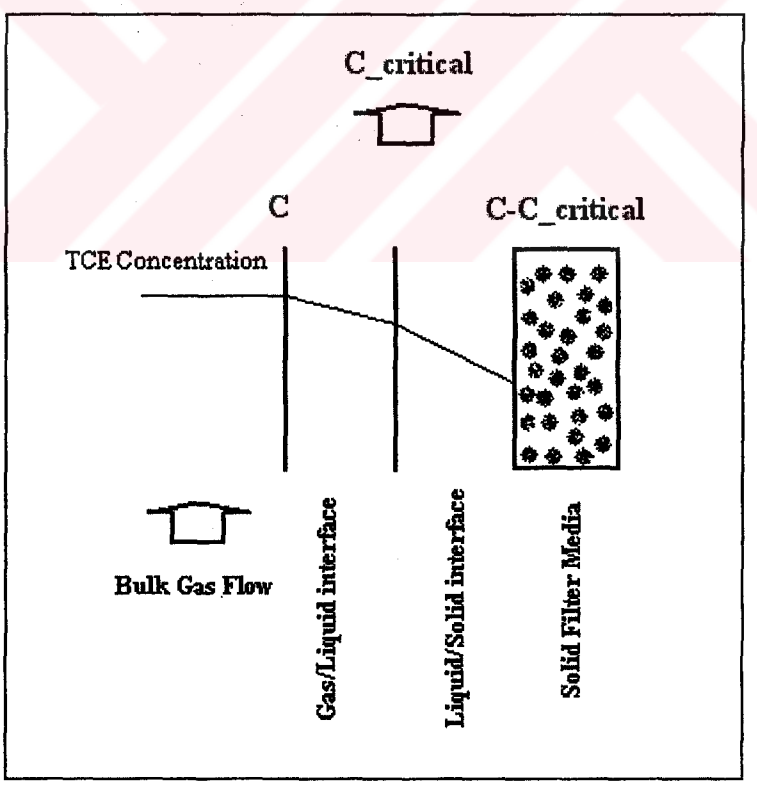


Figure 4.5: Mass transfer of TCE from gas to liquid phase and liquid to solid phase (Levenspiel, 1999)

As it is seen in Figure 4.5, a certain amount of TCE is lost during the mass transfer between the phases which is indicated by critical TCE concentration (C_critical). The amount of TCE reacted on the media is C-C_critical so the TCE removal rate is decreased due to the limitations in the mass transfer from $R = k(C - 0)$ to $R = k(C - C\_critical)$.

The TCE mass transfer from gas to liquid phase is same in both biofilter and Fe(0) column, since the feed gas and liquid in the rectors are the same. However, TCE mass transfer between liquid to gas phase is different in the reactors, since the solid media packed in the reactors are different. For that reason, the critical removal efficiencies in biofilter and Fe(0) column is different. The RE_critical in the Fe(0) column is 82.8% which is higher than the RE_critical in biofilter, that is 31.1%. This significant difference between the RE_criticals verifies that Fe(0) fillings packed in the Fe(0) column is superior media than the granular anaerobic mixed culture packed in the biofilter on the mass transfer basis.

In addition to mass transfer, uncertainties in the flow pattern of the reactors can also effect the TCE removal. Uncertainties in the flow pattern or non-ideal flow in the reactor can be explain as the earliness or lateness of mixing in the reactors at any fluid flowrate. In order to illustrate the effect of mass transfer limitation and non-ideal flow on the reactor system at various EBCTs, the model curves were compared with the ideal curve which represents the ideal flow conditions. The deviations of model curves from ideal ones represent the conditions that limit TCE removal in the reactors separately (Figure 4.6) (Levenspiel, 1999).

Before the discussion of the Figure 4.6, the ideal curve needed to be expressed mathematically.

4.2.1. Mathematical expression of ideal curve

The reactors in the sequential system were operated on the plug-flow mode. However, ideal plug-flow could not been achieved in most of the reactors due to ineffective distribution of fluid throughout the system, channels in the packed media etc. in most cases. For that reason, the flow pattern in the reactor deviates from the ideal case, and the reaction in the reactor is effected (Levenspiel, 1999).

Ideal conditions for our case can be explained as;

1. No mass transfer limitations for TCE between the liquid-solid phases
2. The flow is ideal that is every molecule in the influent gas stream stays equal time in the reactor at any EBCT applied and only the reaction on the reactor media controls the removal mechanism (η=1 at Equation 4.1) (Levenspiel, 1999).

The first condition states that $R\_critical = 100\,\%$ at Equation 4.9, the second condition states that reaction is not effected by any flow conditions so k_obs is so high (k_obs$\rightarrow\infty$). The ideal curve can be expressed with following two limits of Equation 4.9.

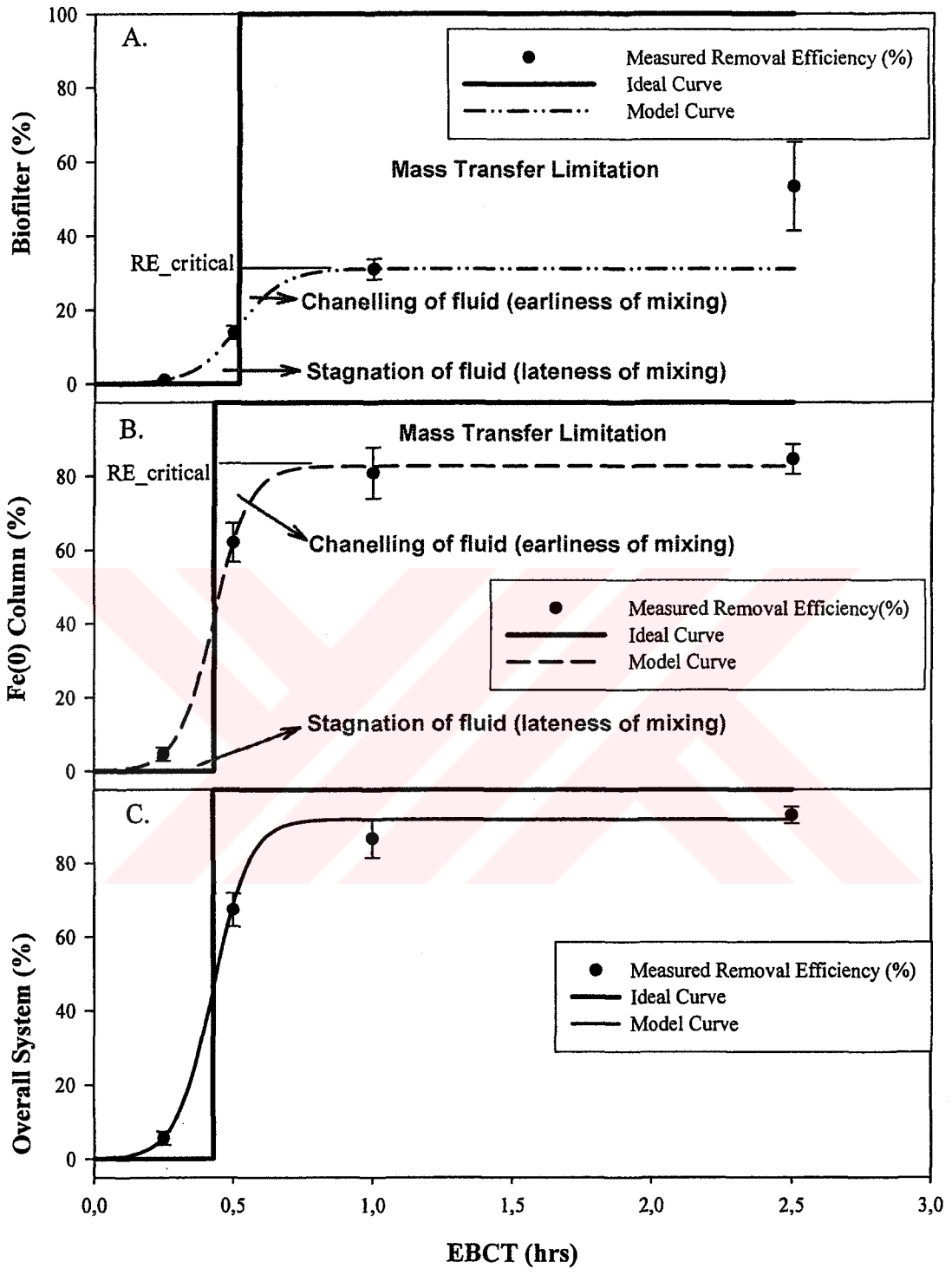


Figure 4.6: The effect of mass transfer limitation and non-ideal flow on the reactor system at various EBCTs; A. Biofilter, B. Fe(0) Column, C. Overall system

$$\lim_{\substack{k\_obs\to\infty \\ 0\le EBCT\to EBCT\_0}} \frac{100}{1+\exp(-k\_obs\times(EBCT-EBCT\_0))}=0 \qquad \text{(Equation 4.10)}$$

For EBCTs from EBCT_0 to infinity, the limit of RE in Equation 4.9 yields 100% which represents the right side of the ideal curves in Figure 4.6.

$$\lim_{\substack{k\_obs\to\infty \\ EBCT\_0\le EBCT\to\infty}} \frac{100}{1+\exp(-k\_obs\times(EBCT-EBCT\_0))}=100 \qquad \text{(Equation 4.11)}$$

For EBCTs from zero to EBCT_0, the limit of RE in Equation 4.9 yields 0% which represents the left side of the ideal curves in Figure 4.6.

From Figure 4.6, the difference between the RE_criticals of model curves and 100% TCE removal efficiency of the ideal curve represents the effect of mass transfer on the performance of the system. The EBCTs where the ideal curve intersects the model curve represents the EBCT_0s.

On the other hand, the deviations between the model curves and ideal curves represent the effect of non-ideal flow coupled with the mass transfer limitations on the system performance. When EBCT is considerably high, the inefficient mass transfer between gas, liquid and solid phases is the only limitation of further TCE removal. As EBCT decreases, some TCE molecules finds cracks in the packed media and leave the reactor earlier than the rest of them due to the increasing flowrate which creates certain back pressure between the pores of packed media. The earliness of mixing in the reactor causes some molecules leave the system without sufficient time for transfer and reaction than the molecules stay in the reactor at

sufficient time. As the EBCT approaches to EBCT_0, more molecules leave the reactor without sufficient reaction, so the removal efficiency is less than what is expected ideally (Figure 4.6) (Levenspiel, 1999).

On the other hand, at EBCT_0 where ideal curve intersects the model curve, the time that every TCE molecule spent in the reactor is equal but, since the time for transfer and reaction is reduced, the ideal TCE removal efficiency can not be achieved. At EBCTs lower than EBCT_0, the lateness of mixing causes some molecules of TCE stay longer than the rest. As EBCT decreasing from EBCT_0, the flowrate is not sufficient to carry all molecules at the same time through the reactor. Some molecules stay longer and react further in the reactor. However, as flowrate increases further or in lower EBCTs, that are so close to zero, all molecules leave the system at the same time and react at the same extend. This is represented as the intersection of the ideal curve with the model curve at EBCTs that are so close to zero (Figure 4.6). The extend of earliness and lateness of mixing in biofilter and Fe(0) column was presented in the Figure 4.6 (Levenspiel, 1999).

4.2.2. Optimum EBCT for sequential reactor system

The optimum EBCT for the reactor system was determined by using the EBCT versus overall system TCE removal efficiency graph (Figure 4.7). The optimum EBCT was set as the minimum EBCT at maximum TCE removal efficiency (RE_critical) achieved in the overall system. Although, the minimum EBCT at maximum TCE removal efficiency was seen as approximately 0.75 hrs in the Figure 4.7, in order to be on the safe side, the optimum EBCT for the system was set as 1 hr.

At this EBCT, the TCE removal efficiencies of both biofilter and Fe(0) column are also maximum (Figure 4.4).

In conclusion, the model developed in this study not only simulated the effect of EBCT on the system performance but also gave important information about the effects of mass transfer and the flow pattern on the system. It also helped to determine the optimum EBCT for the system. The results showed that, the reactors in the system are not ideal plug-flow reactors, that is, the flow in the reactors was non-ideal which also affected the performance of the system.

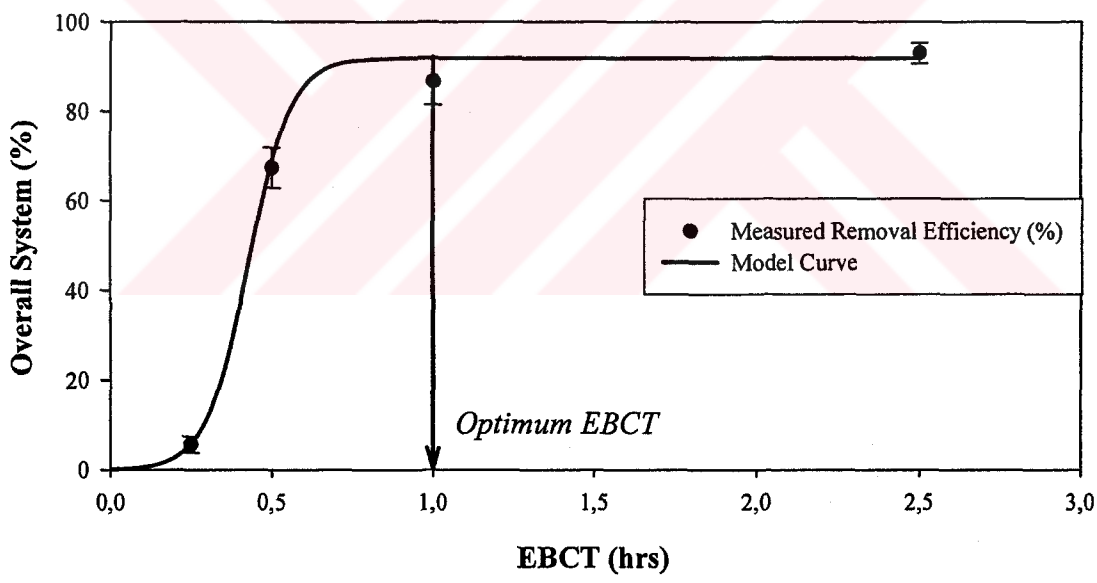


Figure 4.7: The effect of EBCT on the TCE removal efficiency of the overall system

Moreover, the Fe(0) fillings packed in the Fe(0) column are effective media where the granular anaerobic mixed culture packed in the biofilter is not due to its high mass transfer resistance. However, when the TCE removal rate constants of the two reactors are compared, 12.5 hr^{-1} for biofilter and 15.7 hr^{-1} for Fe(0) column, they are so close to each other, that is TCE removal rate in biofilter are comparably as high as that of Fe(0) column.

Furthermore, the main TCE removal mechanism in the Fe(0) is reductive dechlorination whereas, adsorption is the only mechanism in the biofilter. With an effective support media for anaerobic microorganisms, like soil (Mihopoulos, 2000), the mass transfer limitation could be eliminated. In addition, the optimum EBCT of the system was determined as 1 hr at which approximately 90% of TCE removal was achieved. This EBCT is very low when it is compared with the most popular economical and feasible TCE (or other chlorinated aliphatic hydrocarbon, like PCE) control technologies like biofilters operating on the basis of aerobic cometabolism which have 90% TCE removal at 2.5 hrs of EBCT (Bohn, 1992) and their anaerobic counter parts that achieved complete PCE removal with high VC accumulation in the system at 5.1 hrs of EBCT (Mihopoulos, 2000). Application of single biological reactor systems for the treatment of chlorinated compounds have several disadvantages besides their long EBCTs such as the accumulation of more toxic by-products which reduces the efficiency of the system etc (see Chapter 2). On these basis, sequential reactor system in this study has a value in the real world cases like industrial or in-situ applications that aims to control the emissions of volatile chlorinated compounds since it presents an ultimate transformation of these compounds with non-toxic end-products in a comparably short residence times.

4.3. Effect of influent TCE concentration or TCE loading rate on the performance of continuous reactor system

The emissions of HAPs, like TCE, from industries and in-situ remediation technologies like air stripping/sparging are regulated in Turkey and in the world. In Turkey, the organic vapors and gases have been classified and their emissions are regulated in the Annex-4 of "Control of Air Quality Regulation" in "Türk Çevre Mevzuatı (April 1999)" and it set a limit of 30 ppmv for TCE emissions. In USA, TCE is to be regulated, requiring its sources to install Maximum Achievable Control Technologies (MACTs). As an incentive, a key section of Title III in 1990 Clean Air Act Amendments of US EPA allows sources a 6 year extension from meeting MACT Standards, if they voluntarily reduce emissions to 90% below 1987 levels, before EPA issues the MACT Standard. Thus, industries and other major sources are very much in need of appropriate technologies for control of air emissions (USEPA, 1990).

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 to 500 ppmv but not exceeding 2000 ppmv (Bohn, 1992; Lackey, 2001). In this study, 170.6±28.5 ppmv of average influent TCE concentration was applied to the system in three months of operation period and 91.9% of TCE removal was achieved at an optimum EBCT of 1 hr. At this comparably low EBCT, the system performance was stable at the average influent TCE concentration applied. As a result, this system satisfies the regulations for TCE both in Turkey set in Türk Çevre Mevzuatı (<30 ppmv) and in USA set in 1990

Clean Air Act Amendments (90% reduction in current TCE emissions). However, the system performance and stability must be investigated for the TCE concentrations between 0-500 ppmv.

For this purpose, another set of experiment was performed in order to determine the effect of influent TCE concentration or TCE loading rate on the continuous reactor system at 1 hr of optimum EBCT. The influent TCE concentrations between 150 to 650 ppmv were applied and the effects of these influent concentrations on the system performance were investigated (Figure 4.8).

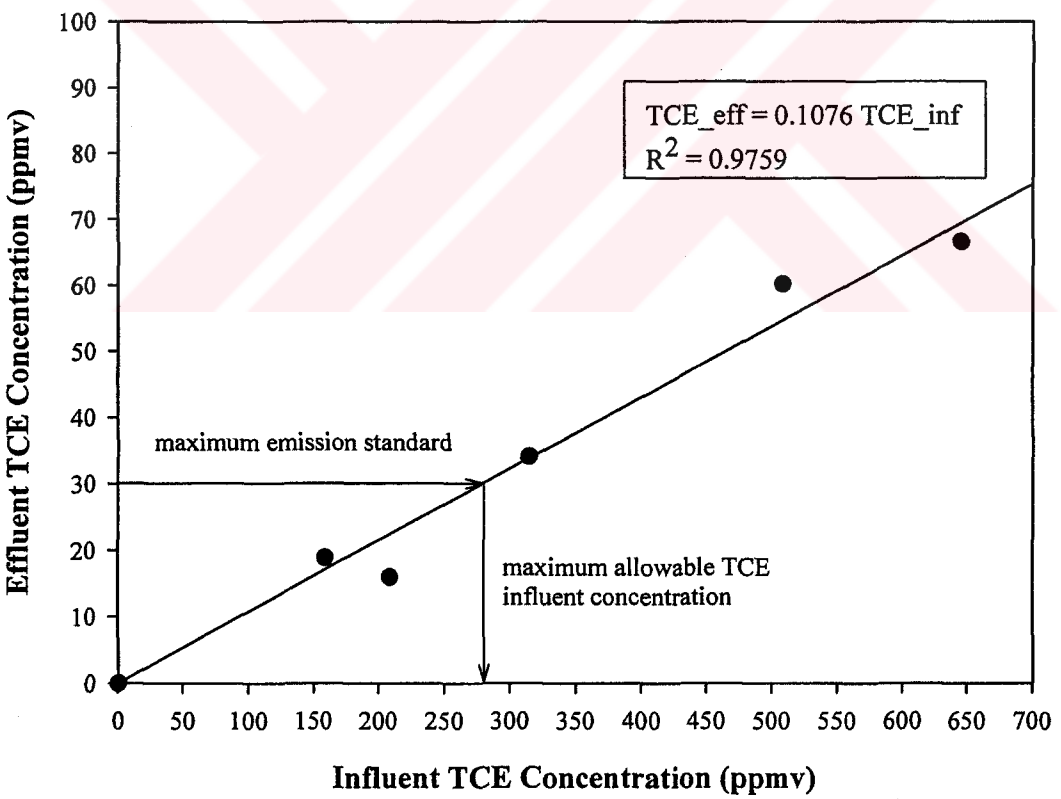


Figure 4.8: The effect of influent TCE concentration on the performance of the continuous reactor system

The results have shown that the influent TCE concentration has no significant effect on the TCE removal efficiency of the system. The system performance is stable between the influent concentrations of 150 to 650 ppmv. The average TCE removal efficiency of the system in different influent TCE concentrations could be represented by;

$$RE = (1 - slope) * 100 \qquad \text{(Equation 4.12)}$$

The average TCE removal efficiency of the system in different influent TCE concentrations at 1 hr of EBCT is 89.2% (by using Equation 4.12) which is almost equal to efficiency (91.9%) obtained in the previous experiment. This result indicates that the system is stable in TCE removal between the influent TCE concentrations of 150 to 650 ppmv.

In conclusion, the sequential reactor system, which operates on the basis of biotic and abiotic reduction reactions, proposed in this study could be applied for the treatment of TCE found in off-gases from soil and groundwater remediation operations, from industrial processes, and from wastewater treatment systems effectively even in varying influent TCE concentrations. This property of the system has several advantages like it eliminates the use of miscellaneous equipments that equalize the influent concentrations in real treatment systems. The system could also be used in soil and groundwater remediation operations like air sparging and stripping as an in-situ horizontal barrier (natural anaerobic zone followed by artificial Fe(0) layer) which also eliminates the off-gas collection and equalization equipments. These advantages of the system also make it an economical system.

In this study, a treatment technology alternative has been proposed for upgrading the efficiency of air sparging systems with integrating the outcomes of this study and the one of Mihopoulos et al. (2000). The system was illustrated in Figure 4.9.

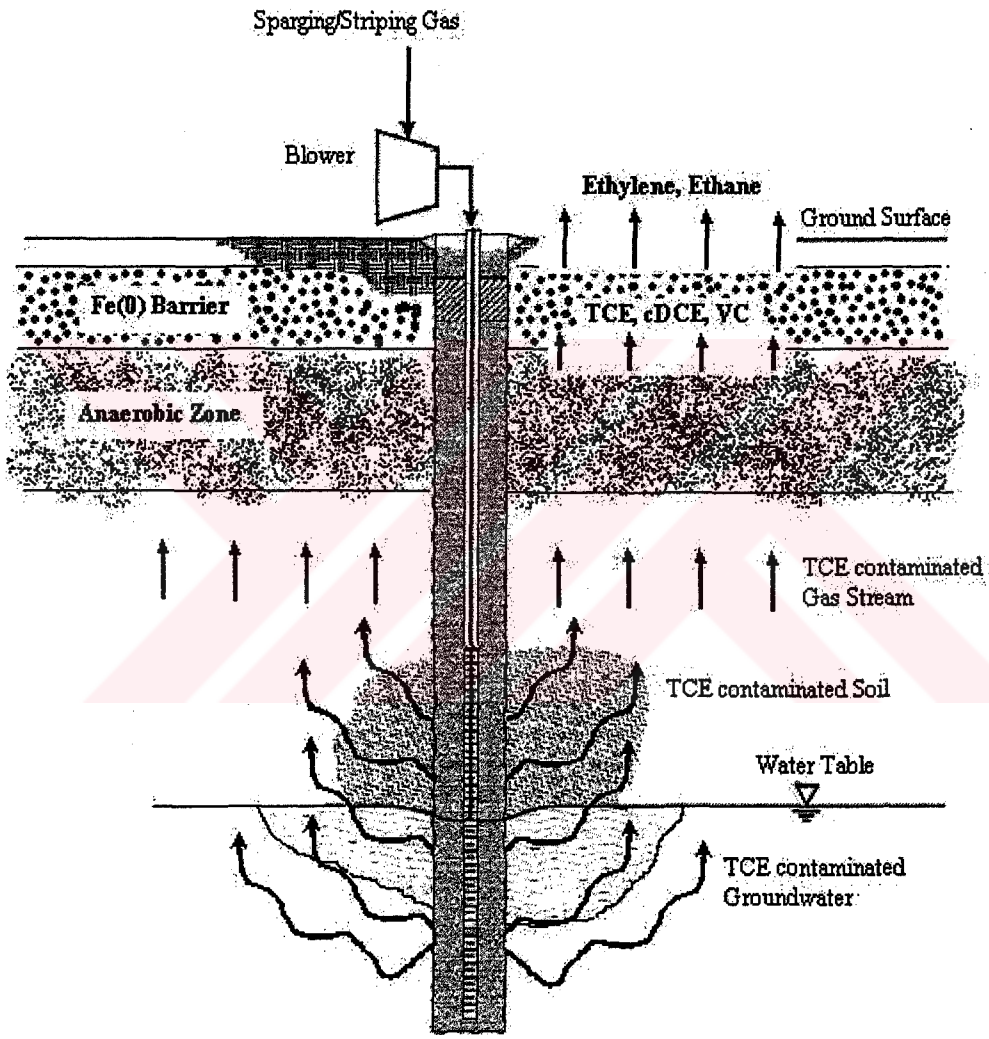


Figure 4.9: Treatment of TCE emissions from air sparging/stripping systems by horizontal bio- and chemo- barriers

In this system, anaerobic bioventing gas composed of H_2, N_2 and CO_2, which supports the natural anaerobic activity at unsaturated zone, is blown through the air sparging well. The gas strips the TCE from soil and groundwater contaminated with this pollutant.

The TCE contaminated gas stream first flows through the natural anaerobic zone (the biofilter in the continuous reactor system which includes anaerobic mixed culture partially simulates the anaerobic zone in the Figure 4.9) where TCE is reduced to its possible by-products like cDCE and VC etc. by the help of an electron donor, H_2. The gas mixture then, passes through the Fe(0) zone (natural soil with certain content of non-oxidized iron, or artificial barrier with Fe(0) fillings/clusters). Finally, TCE in the gas stream is reduced to its ultimate non-toxic end-products of ethylene and ethane.

The advantages of this new technology can be listed as;

1. Elimination of soil vapor extraction systems that collect the stripped gas and expensive off-site treatment systems like GAC columns or chemical oxidizers. Thus reduction of the operation, equipment, and maintenance cost (Batelle, 2001).

2. The contaminant is completely eliminated from the site by bio- and chemo-transformations to non-toxic end products.

3. Natural environment is protected since the system components are natural (anaerobic zone) or semi-natural (soil with a certain Fe(0) content). In most air sparging applications, an aerobic zone which transforms the VOCs in the

gas stream is sustained by blowing oxygen through the sparging well. This aerobic zone is not natural since below the 2 meters of ground surface, there exists a strict anaerobic zone. Thus, the natural biotic characteristics of site is effected (Batelle, 2001).

4. Low residence time of the system (it is determined as 1 hr in this study) enables high volatilization of VOCs that also leads an effective contaminant transport from soil and groundwater. It increases the efficiency of the air sparging system in in-situ soil and groundwater remediation (Miller, 1999; Batelle, 2001).

5. Ethylene and ethane are valuable products. Since the off-gas from the system includes these compounds, they can be separated from the gas stream with an appropriate system and collected for use.

The disadvantages of the system can be listed as;

1. Supplying of anaerobic bioventing gas, transport of soil with certain Fe(0) content or Fe(0) fillings/clusters and excavation to locate the Fe(0) barrier can increase the cost. However increase in the cost is though to be non-comperable with the eliminated operation, equipment and maintenance costs of the conventional system. A detailed cost-benefit analysis is necessary.

2. Fe(0) has a high specific gravity, thus Fe(0) barrier can lead to the compaction in the site soil which reduces the porosity of the soil and causes problems in gas transfer in the site. However, the extend of compaction depends on the height of the Fe(0) barrier. Since the retention time for

complete reduction of TCE and its probable chlorinated by-products through the Fe(0) barrier is low, the height of this barrier predicted to be also low.

In conclusion, the high TCE removal efficiency at very low EBCT of the continuous reactor system in this study make the use of sequential biotic and abiotic transformation mechanisms an attractive method that can potentially be integrated in an in-situ remediation process, like air sparging, to treat contaminated soils and groundwaters with TCE.

CHAPTER 5

CONCLUSIONS

The results of this study can be concluded under the following headings;

- *Performance of the continuous reactor system*

The TCE removal efficiency of the continuous reactor system is 91.9% at very low EBCT of 1 hr compared with the other economical treatment options treating chlorinated compounds in 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 character of the system offers that an efficient reductive dechlorination processes have occurred in the Fe(0) column of the system.

- *Comparison of the TCE removal rates in the reactors*

The main TCE removal mechanism in the Fe(0) is reductive dechlorination whereas, adsorption is the main mechanism in the biofilter, however, extent of adsorption and other possible physical TCE removal mechanism in biofilter were not investigated in this study. When the TCE removal rate constants of the two reactors are compared,

12.5 hr^{-1} for biofilter and 15.7 hr^{-1} for Fe(0) column, they are so close to each other, that is TCE removal rate in biofilter are comparably as high as that of Fe(0) column.

- *Reliability of the model*

The model developed in this study satisfactorily simulated the sequential reactor system. The actual data obtained during the study were fitted the model outcomes precisely (see Figure 4.4) . The model outcomes also helped to identify the effect of EBCT, packing media and flow pattern on the system performance.

- *Effectiveness of the fluid phase*

In this study, the treatment of gaseous TCE is investigated. TCE is a highly volatile compound an naturally it has a high tendency for vaporization. The treatment of this compound in gas-phase is more logical than that in liquid phase. The results of this study also shows that, reductive dechlorination rate of gaseous TCE in Fe(0) column is extremely high and the final end products are ethylene and ethane. The transformation of TCE up to ethane has not been coincide in the literature that has deal with the treatment of aqueous TCE with reductive dechlorination. Uludağ (1999) has also stated that reductive dechlorination rate of gaseous TCE is higher than that of aqueous TCE in her study. The reason of high reaction rate and achieving ultimate reduction end product of ethane in the study dealing with the gaseous form of TCE is that in gaseous form molecules are homogenously dispersed and inherently more reactable than that of solids and liquids.

- *Application of this system*

The high TCE removal efficiency at very low EBCT of the continuous reactor system in this study make the use of sequential biotic and abiotic transformation mechanisms an attractive method that can potentially be integrated in an in-situ remediation process, like air sparging, to treat contaminated soils and groundwaters with TCE, or application in industries that have need for the control of their TCE emissions .

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APPENDIX A

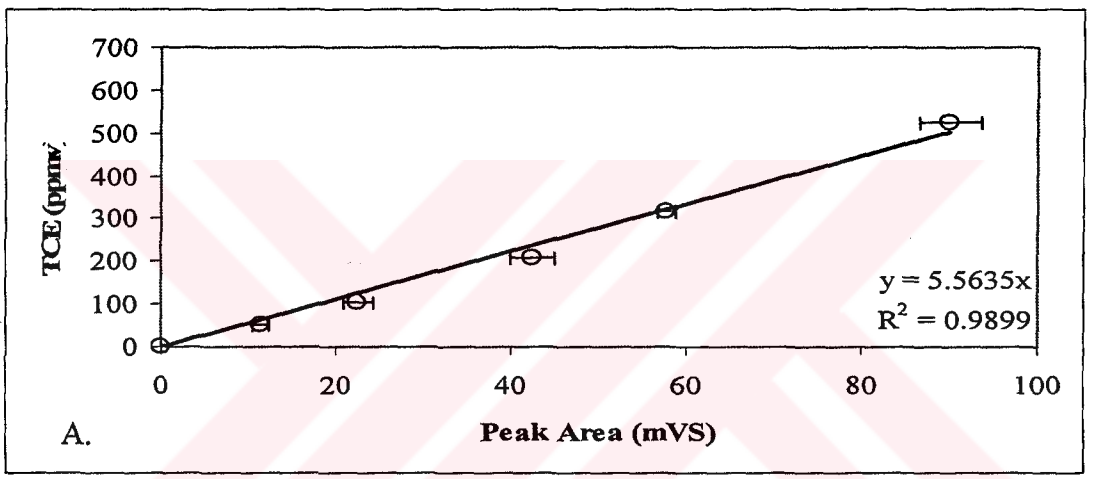
CHEMICAL AND PHYSICAL PROPERTIES OF TCE

Table A.1: Summary of chemical and physical properties of TCE

Description	**Value**
Molecular Weight (g/mol)	131.4±3.9 x 10^{-4}
Octanol-Water Partition Coefficient	320±0.32
Melting Point (K)	189.7±0.026
Vapor Pressure (Pa)	9700±0.021
Solubility (mol/m3)	11.0±0.15
Henry's Law Constant (Pa-m3/mol)	890.0±0.18
Diffusion Coefficient in Pure Air (m2/d)	0.68±0.05
Diffusion Coefficient in Pure Water (m2/d)	9.0x10^{-5}±0.25
Organic Carbon Partition Coefficient	86.0±0.46
Partition Coefficient in Plants Relative to Soil Concentration [ppm(pFM)/ppm(sFM)]	0.25±4.0
Biotransfer Factor in Plants Relative to Air Concentration (m3/kg[pFM])	0.011±14
Bioconcentration Factor in Fish Relative to Contaminant Water Concentration	53.0±1.0
Reaction Half-Life in Air (d)	3.50±0.11
Reaction Half-Life in Ground-Surface Soil (d)	930.0±1.7
Reaction Half-Life in Root-Zone Soil (d)	930.0±1.7
Reaction Half-Life in Vadose-Zone Soil (d)	760.0±1.4
Reaction Half-Life in Ground-Water Zone Soil (d)	800.0±1.5
Reaction Half-Life in Surface Water (d)	120.0±0.9
Reaction Half-Life in the Sediment (d)	220.0±0.7

APPENDIX B

CALIBRATION CURVES



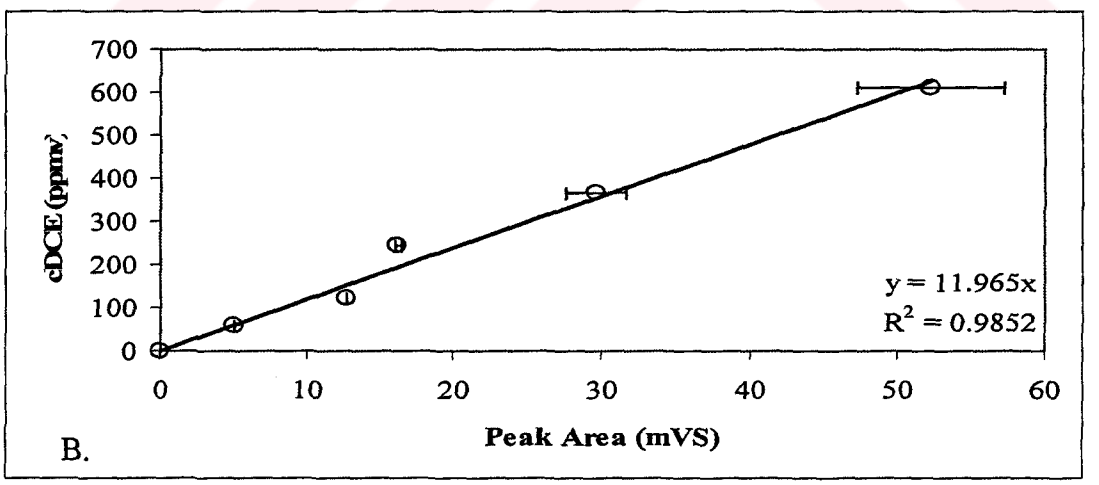
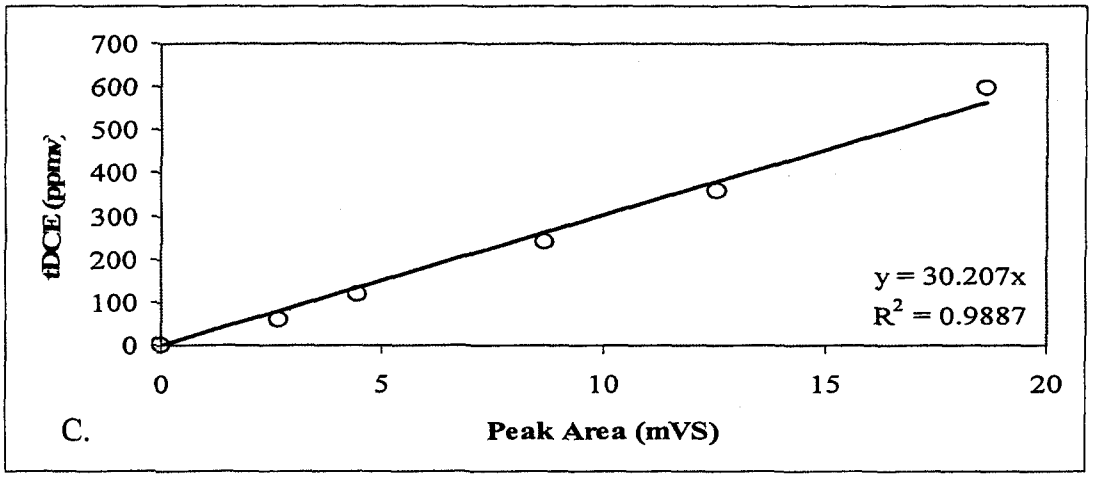
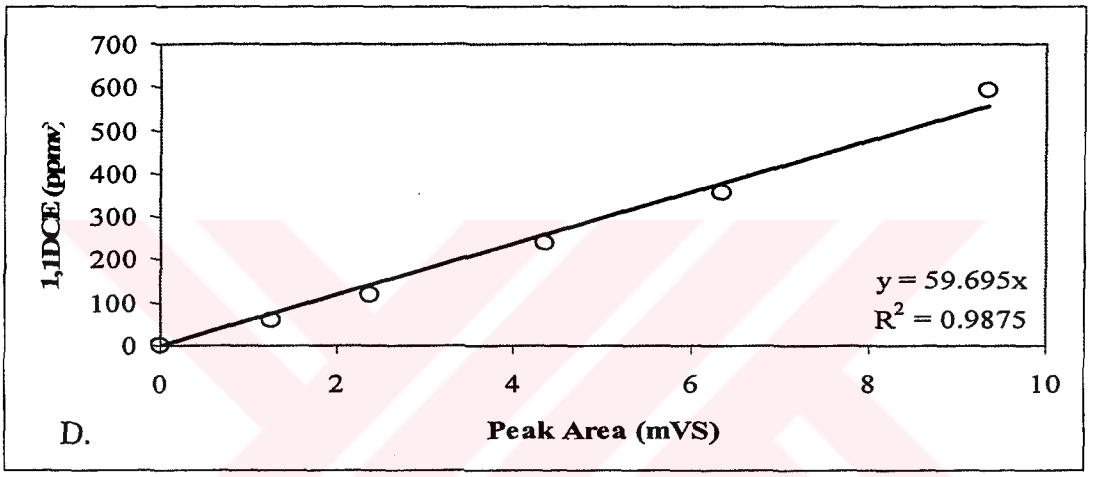


Figure B.1: GC calibration curves for the compounds; A. Trichloroethylene, B. cis-Dichloroethylene, C. trans-Dichloroethylene, D. 1,1-Dichloroethylene, E. Vinyl chloride, F. Ethylene, G. Ethane.





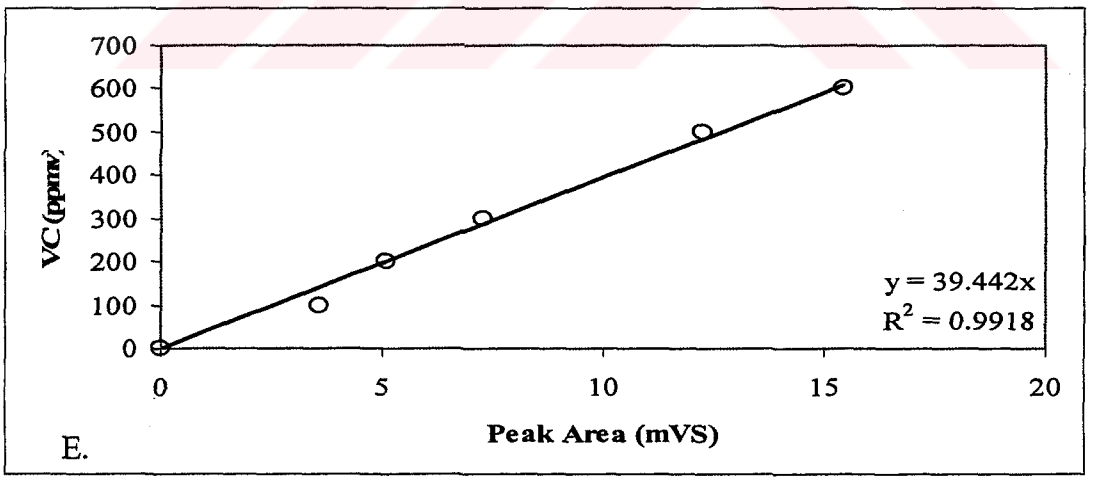
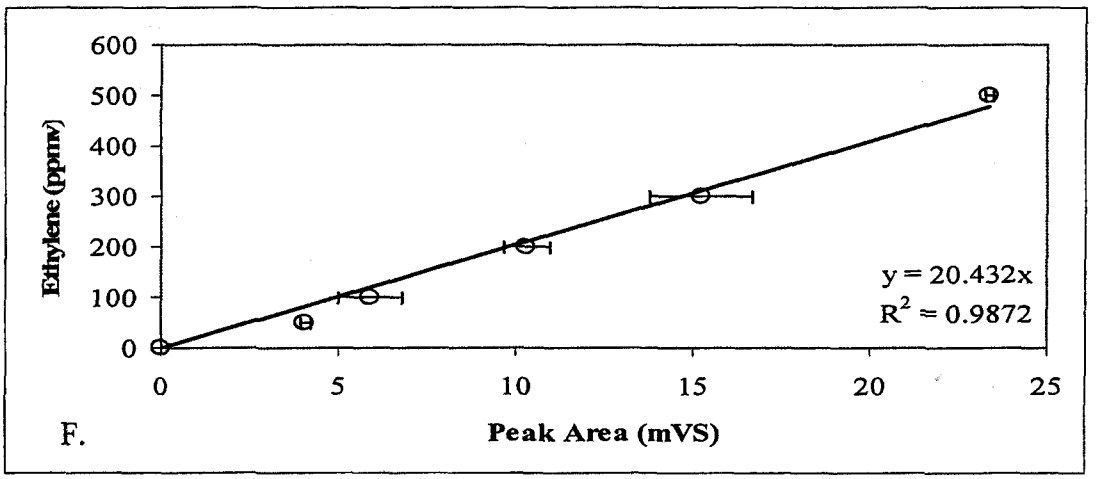
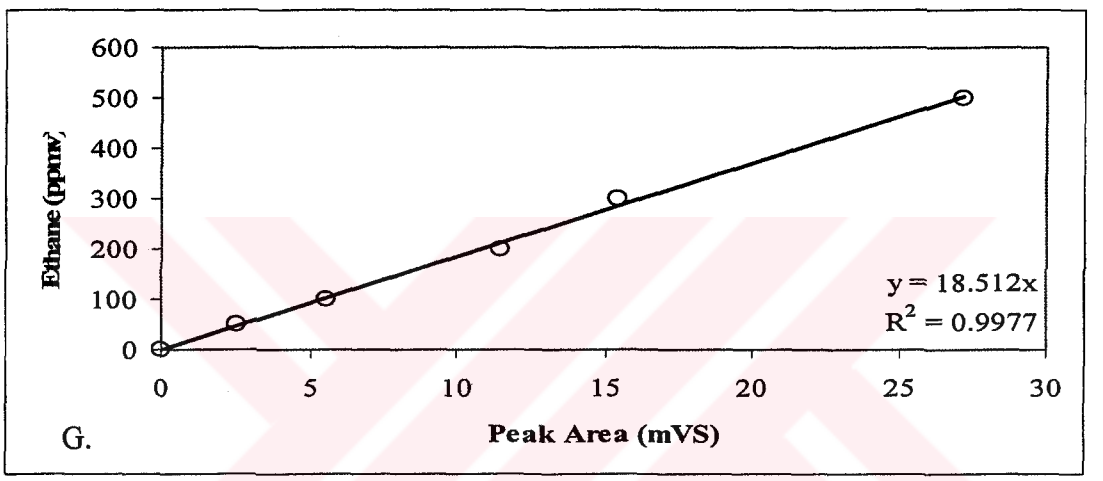


Figure B.1 continued



F.



G.

Figure B.1 continued

APPENDIX C

LIST OF HAZARDOUS AIR POLLUTANTS

Table C.1: List of forty potential section 112(k) HAPs in 1990 Clean Air Act Amendments (U.S EPA, 1999)

1,1,2,2-Tetrachloroethane	Ethyl Acrylate
1,1,2-Trichloroethane	Ethylene Dibromide (1,2-Dibromoethane)
1,2-Dichloropropane (Propylene Dichloride)	Ethylene Dichloride (1,2-Dichloroethane)
1,3-Butadiene	Ethylene Oxide
1,3-Dichloropropene	Formaldehyde
1,4-Dichlorobenzene	Hydrazine
Acetaldehyde	Lead Compounds
Acrolein	Manganese Compounds
Acrylamide	Mercury Compounds
Acrylonitrile	Methyl Chloride (Chloromethane)
Arsenic Compounds	Methylene Chloride (Dichloromethane)
Benzene	Methylene Diphenyl Diisocyanate (MDI)
Beryllium Compounds	Nickel Compounds
bis(2-Ethylhexyl)phthalate	Polycyclic Organic Matter (POM)
Cadmium Compounds	Quinoline
Carbon Tetrachloride	Styrene
Chloroform	Tetrachloroethylene (Perchloroethylene)
Chromium Compounds	Trichloroethylene
Coke Oven Emissions	Vinyl Chloride
Dioxins/Furans	Vinylidene Chloride (1,1-Dichloroethylene)