Geosciences Journal
Vol. 11, No. 2, p. 131 − 136, June 2007

Feasibility study of the bio-barrier with biologically-active tire rubbers for treating chlorinated hydrocarbons

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ABSTRACT: The leachate from landfill released into the subsurface environment can result in serious environmental problems such as soil and groundwater contaminations because there is no landfill liner system in the unsanitary landfill. The authors developed the multi-permeable reactive barriers (M-PRBs) to treat mixed contaminants in leachate and to get over the limitation of a single reactive barrier. The M-PRBs consist of two reactive barriers using the abandoned materials such as waste steel scrap mixed with converter slag acting as an iron-based barrier and biologically active tire acting as a bio-barrier. In this study, the efficiency of tire rubbers as a sorption media and a biologically active media were evaluated. Tire rubbers extensively adsorbed amounts of chlorinated compounds and the biologically active tire media removed chlorinated organic compounds (93% of TCE and 77% of PCE) as well as organic matters (80%) for 10 days. Overall, this work suggests that biologically active tire media followed by an iron-based barrier in the M-PRBs can effectively treat mixed contaminants in landfill leachates through bioaugmentation.

Key words: unsanitary landfill, bio-barrier, tire rubbers, PRB, leachate, M-PRBs

1. INTRODUCTION

The leachats from municipal solid waste landfill may contain various contaminants such as organic matters (measured by biochemical oxygen demand or chemical oxygen demand), nitrogen compounds (ammonium ion, nitrate, and nitrite), heavy metals, chlorinated organic compounds (trichloroethylene (TCE) and tetrachloroethylene (PCE)), and trace compounds. The best approach to prevent the migration of leachate from landfill is landfill liner system (e.g., compacted clay liners, geomembranes, and geosynthetic clay liners). However, there is no such liner system in unsanitary landfills and the leachate can be released into in the resident space and the subsurface environment. There are several methods used to commonly confine leachate from unsanitary landfills such as cutoff walls. Recently, many researchers have introduced the permeable reactive barrier (PRB) system as an alternative technology to control leachates (Day et al., 1999; Eykholt et al., 1999; Gupta and Fox, 1999; USEPA, 1999; USEPA, 2002; Kalin, 2004).

The PRB with zero-valent iron as a reactive material could be one of the most promising technologies to remediate the groundwater contaminated by chlorinated hydrocarbons (CLHs), nitrate, phosphate, heavy metals, and explosive compounds (Scherer et al., 2000; Oh et al., 2001; Oh and Alvarez, 2002). The treatment of leachate with various contaminants may not be successful by using a single PRB (Bayer and Finkel, 2005). Therefore, a combination or sequence of treatments may be needed for higher removal efficiency of leachate from an unsanitary landfill. The iron and bacteria-based barriers could be applied to treat aromatic hydrocarbons and organic matters. The granular activated carbon can be used as a sorption material as well as biological media (e.g., biologically active carbon) generally being used in the wastewater or water treatment (O'Brien and Keyes, 1997).

In this study, we developed a bio-barrier of the multi-PRBs, called M-PRBs, to treat groundwater contaminated by leachate released from unsanitary landfills. M-PRBs consist of two reactive barriers (Fig. 1), one is an iron-based barrier with waste steel scrap plus converter slags, and the other is a bio-barrier with biologically active tire media. This research used abandoned materials such as waste steel scraps, converter slags, and waste tire rubbers in the M-PRBs. The information about iron-based barriers in the M-PRBs system is discussed in Oh et al. (2006). In this paper, the research focuses on the performance of the biologically active tire media. We evaluates the sorption capacity of tire rubbers and the activity of biologically active tire media.

2. CONCEPT OF M-PRB SYSTEM

The physical and chemical properties of zero-valent iron (ZVI) have been widely studied by many researchers (Robert et al., 1996; Benner et al., 1997; USEPA, 1997; O'Hannesin and Gillham, 1998; Ruiz et al., 2000; Gandhi et al., 2002; Wilkin and McNeil, 2003; Fernandez-Sanchez et al., 2004). ZVI has been used as a reactive material for reme-

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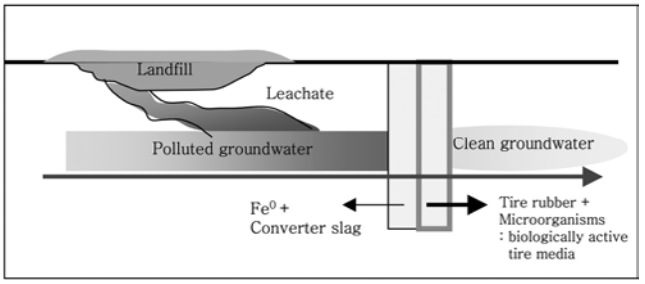

Fig. 1. Schematic diagram of multi-PRBs (M-PRBs).

Table 1. Modified nutrient solution for evaluation of biologically active tire media.

Compounds	Concentration (g/l)	Remark
$MgSO_4 \cdot 7H_2O$	22.5	
$CaCl_2$	27.5	
$FeCl_3 \cdot 6H_2O$	0.25	Adding 1 ml each nutrient solution per 1 l of contaminants solution
K_2HPO_4	21.75	
KH_2PO_4	8.5	
$Na_2HPO_4 \cdot 7H_2O$	33.4	
NH_4Cl	1.7	

diation of contaminated groundwater by several contaminants. ZVI produces two electrons and hydrogen gas by the corrosion process in the solution. The released electrons and hydrogen contributes to the direct and/or indirect reduction of CLHs. Furthermore, hydrogen gas can also be used as an energy source by hydrogen-consuming microorganisms; more rapid degradation of contaminants are expected with the enhanced biological process (Scherer et al., 2000). This study has imposed synergistic effects occurred by the combining abiotic with biotic processes in the M-PRBs system.

The iron-based barrier can degrade contaminants such as CLHs, heavy metals, and salts ions; on the other hand, the M-PRBs system is much more focused on treating the groundwater contaminated with leachate from unsanitary landfills. CLHs have various pathways to non-toxic ethylene by the ZVI; however, more toxic product compounds (i.e., dichloroethylene and vinyl chloride) can be produced when the sufficient reaction time is not provided. Biologically active tire media followed by iron-based barrier, therefore, can be used to treat intermediate compounds by sorption as well as biodegradation. In addition, organic matters that are rarely degraded by ZVI can also be oxidized on the bio-barrier.

3. MATERIALS AND METHODS

3.1. Materials

Waste tire (in the form of shredded chips) can be used for the wastewater treatment to provide a biologically active media to support the attached microbial growth processes (Reyes et al., 1999), and as a drainage tool or a protective material in landfills (Park et al., 1996; Al-Tabbaa and Aravinthan, 1998). Recently, extractions of valuable oils from waste tire rubbers and shredded tire chips used as sorption media in PRB system have been studied (Kershaw et al., 1997). In this study, tire rubbers were used as sorption and biologically active media.

The tire rubbers obtained from Korea Environment & Resources Co. were sized up as 0.425-0.6 mm and 0.6-1.18 mm. In order to remove the impurities on the surface and pores of tire rubbers, tire rubbers were washed with distilled water and then soaked in a 0.1N nitric acid solution for 24 hrs. Then, they were washed again with distilled water three times and stored under dry conditions until they were used in the experiments.

The source of microorganisms for the biologically active tire media was the municipal anaerobic sludge from a wastewater treatment plant in Seoul, Korea. The sludge concentration was 6 g/l of volatile suspended solids (VSS). Fresh sludge was always used. Biologically active tire media was prepared by adding 10 ml of stock anaerobic sludge to 125 ml-serum bottles containing 70 ml of nutrient solution plus 30 g of tire rubbers (0.6-1.18 mm diameter). The components of the nutrient solution are listed in Table 1. Before adding the anaerobic sludge, the contents were purged for 10 min with nitrogen gas to remove dissolved oxygen. Serum bottles were tightly sealed with Teflon-lined butyl rubbers septa and aluminum crimps, and then purged with nitrogen gas to remove oxygen in the headspace. The microorganisms were incubated quiescently at room temperature in the dark for 30 days.

3.2. Evaluation Methods

Two different evaluations on the biologically active tire media were conducted; 1) sorption capacity of tire rubbers, and 2) the biological activity of the tire media.

3.2.1. Sorption capacity of tire rubbers

Sorption capacity of tire rubbers was examined using batch reactors. Heavy metals (Cr, Mn, Cu, Zn, As, Cd, and Pb) and CLHs (TCE and PCE), which are commonly present in landfill leachates, were used as pollutants. In these experiments, 10 g of pre-treated tire rubbers (no biologically active tire media) were transferred into seven of 200-ml Erlenmeyer flask containing 100 ml of deionized water amended with heavy metals (10 mg/l each), and then Erlenmeyer flasks were shaken on a reciprocating shaker (150 rpm) at 25 for 48 hrs because equilibrium was reached within 24 hrs in preliminary experiments. After 48 hrs of shaking, samples for determining the concentration in the solutions were extracted and analyzed by inductively coupled plasma atomic emission

spectrophotometer (ICP-AES, ICPS-1000IV, Shimadzu, Japan). No treatment controls were prepared without tire rubbers and heavy metals.

Batch experiments for sorption of CLHs by tire rubbers were also carried out. Reactors were prepared by adding 6 g of tire rubbers to five 60 ml-serum bottles containing deionized water without headspace. The bottles were tightly sealed with Teflon-lined butyl rubbers septa and aluminum crimps. Then, TCE and PCE (neat liquid) were directly added to each serum bottle to bring the final concentrations to 0.1, 0.5, 1.0, 5.0, and 10.0 mg/l, respectively, using a micro-liter syringe (Hamilton). Reactors were shaken on a reciprocating shaker (200 rpm) at 20. After 24 hrs, the samples for TCE and PCE analysis were taken, extracted by n-hexane, and determined by a gas chromatography mass selective detector (GC MSD, 5973N, Agilent Technologies, U.S.A.). No treatment controls were prepared without tire rubbers and TCE or PCE. The recovery efficiency of samples ranged above 95% in each experiment.

3.2.2. Reactivity of biologically active tire media

TCE and PCE degradation assays were conducted in batch reactors to investigate the ability of microorganisms to degrade TCE and PCE. Municipal anaerobic sludge was used as a mixed culture. Five 60-ml serum bottles for each treatment and control were prepared. All reactors contained 50 ml of nutrient solution and acetate (10 mM) as a carbon source and electron donor. Contents were purged for 10 min with nitrogen gas to remove dissolved oxygen before 10 ml of mixed anaerobic microorganisms were added. The bottles were sealed with Teflon-lined butyl rubbers septa and aluminum crimps. TCE and PCE were spiked to bring the final concentrations to 10 mg/l, respectively, using a micro-liter syringe (Hamilton). Reactors were shaken on a reciprocating shaker (150 rpm) at 25 °C. At preselected times, aqueous samples were collected and analyzed for TCE and PCE degradation, as described previously. The recovery efficiency of samples ranged above 95% in each experiment.

In separate experiments, other batch reactors were used to evaluate the potential for biologically active tire media to degrade the chlorinated organic compounds (TCE and PCE) and organic matters. In this experiment, 6 g of biologically active tire media was transferred to eight 60-ml serum bottles containing 10 ml of biological oxygen demand (BOD) solution plus 50 ml of nutrient solution. The quantity of organic matters in the aqueous sample can be represented as BOD. Sodium acetate as an electron donor was used since it can be easily degraded by microorganisms to produce hydrogen gas during degradation. The BOD concentration of each treatment was theoretically adjusted to 2,000 mg/l with sodium acetate. Contents were purged for 10 min with nitrogen gas to remove dissolved oxygen before adding biologically active tire media. The bottles were sealed with Teflon-lined butyl rubbers septa and aluminum crimps. TCE and PCE were spiked to bring the final concentrations to 10 mg/l, respectively, using a micro-liter syringe. Three sets were prepared: a no-treatment control (without contaminants and biologically active tire media addition), TCE (Reactor 1), and PCE (Reactor 2). Reactors were shaken on a reciprocating shaker (150 rpm) at 25 °C and periodically analyzed for each pollutant. TCE and PCE were quantified as described previously, and BOD concentrations after 10 days were analyzed as described in the Standard Methods for the Examination Water and Wastewater (APHA, 1998).

4. RESULTS AND DISCUSSION

4.1. Sorption of TCE and PCE by Tire Rubbers

Tire rubbers contain 31% of carbon black. Previous studies have reported that tire rubbers can effectively adsorb various organic compounds such as phenol, cresol (Smith et al., 2001), TCE, toluene, methylene chloride, and m-xylene (Park et al., 1996) as well as heavy metals (Netzer et al., 1974; Rowley et al., 1984). Extensive sorption of TCE and PCE by tire rubbers was observed, whereas sorption capacity of heavy metals by tire rubbers was very little (data not shown). Netzer et al. (1974) and Rowley et al. (1984) suggested that sorption of heavy metals by tire rubbers can be nicely fitted to the Freundlich isotherm with a very small distribution coefficient. Therefore, it is hard to conclude that tire rubbers can adsorb heavy metals. Figure 2 shows the adsorption isotherm of TCE and PCE by tire rubbers. The adsorption isotherm can be fitted to the linear isotherm rather than the Freundlich isotherm. The distribution coefficient for TCE and PCE sorption by tire rubbers was determined (see Table 2). According to the results, 1 g of tire rubbers can adsorb approximately 340 ml of TCE solution. The results show that tire rubbers might be used as the sorption material to effectively adsorb chlorinated organic compounds.

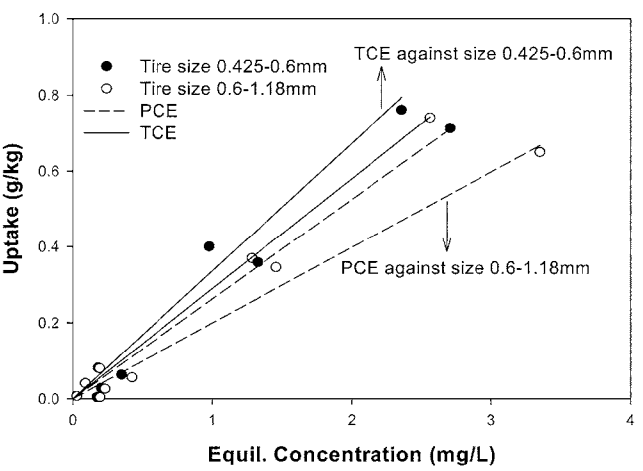

Fig. 2. Linear adsorption isotherm of TCE and PCE by tire rubbers.

Table 2. Distribution coefficient values of two different sizes of tire rubbers for CLHs.

	0.425-0.60(# 30-40)	0.60-1.18(# 16-30)
K_d(l/g) of TCE	0.34	0.29
K_d(l/g) of PCE	0.26	0.20

These results also support the notion that the smaller sizes of tire rubbers give a higher adsorption capacity because the smaller sizes of tire rubbers have larger specific surface area. However, the smaller sizes of tire rubbers may cause several problems in the M-PRBs system. The biological clogging can be one of the problems in the PRB system because the biofilm in the porous media may cause a decrease in permeability. This is also another bio-barrier, which is different from that of M-PRBs, and is used as a landfill liner to prevent the migration of leachate. Another possible problem is that it is not cost-effective to produce smaller sizes of tire rubbers. Smaller size rubbers are also difficult to handle and install in PRB system. Therefore, studies should be performed to determine the proper size of tire rubbers through batch and column experiments.

4.2. Degradation of Contaminants by Biologically Active Tire Media

Two different studies were conducted to investigate the activity of biologically active tire media to CLHs and organic matters. The mixed microorganisms removed about 70% and 50% of the added TCE and PCE in 15 days, respectively (Fig. 3). The extent of the PCE removal, however, was lesser than that of TCE, possibly due to the number of halogen (Cl^-) groups on organic compounds that needs to be dehalogenated. These results are supported by previous studies which indicate that the microorganisms from the digested anaerobic sludge could degrade TCE and PCE in batch studies (Fredrickson and Gorby, 1996; Gandhi et al., 2002). In these experiments, the bacteria utilized CLHs as the terminal electron acceptor during anaerobic respiration; this process is known dehalorespiration. Some microbes that give rise to dehalorespiration require acetate or other organic carbon sources because microbes need hydrogen as an electron donor (Weathers et al., 1997). We infer that organic matters in the anaerobic sludge may have been used as carbon sources in these experiments.

Significant removal of TCE and PCE were observed in reactors amended with sodium acetate (Fig. 4). We also monitored the change of BOD values. For the initial reaction time (3 days), TCE and PCE rapidly decreased, which may be due to complex reactions that were either enhanced biodegradation or sorption process by tire rubbers. It can be inferred that the sorption process is less than the microbial degradation based on the reactive materials although we did not measure the portion of the remaining concentration

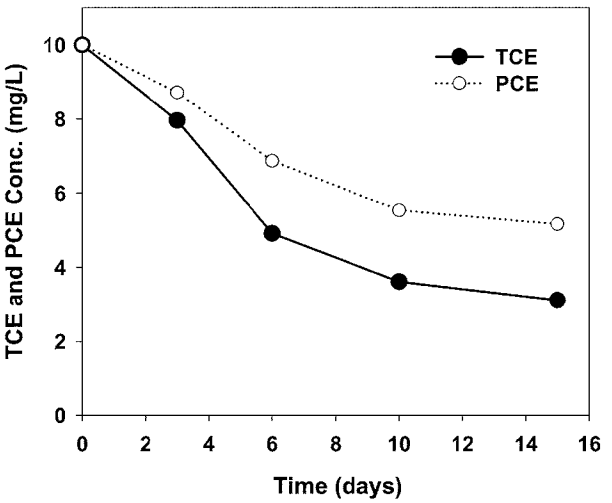

Fig. 3. Changes of TCE and PCE concentrations in reactors amended with anaerobic sludge (20%, v/v).

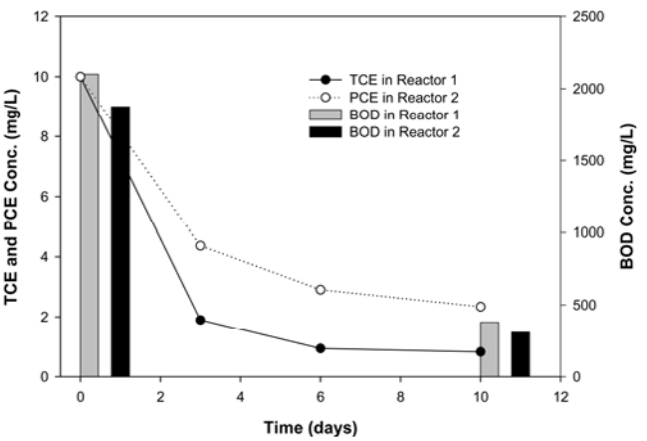

Fig. 4. Changes of TCE, PCE, and BOD concentrations by biologically active tire media in reactors. Reactor 1 contained nutrient solution, acetate, biologically active tire rubbers, and TCE. Reactor 2 contained nutrient solution, acetate, biologically active tire rubbers, and PCE.

through those reactions. Biologically active tire media, which were innoculated with anaerobic sludge for 30 days, were used for evaluating their reactivity to degrade TCE and PCE. The surface of these biologically active tire media may be encompassed with microorganisms and biofilm, which results in little space for sorption. Extensive decrease of BOD concentration supports that the decreases of TCE (93%), PCE (77%), and BOD (80%) for 10 days were due to the microorganisms. The growth of microorganisms in the reactors could be facilitated by the hydrogen gas produced from the degradation of acetate. As discussed in the previous section, the production of water-derived hydrogen by ZVI corrosion increases the availability of an excellent electron donor to support microbial reduction of reducible contaminants and further degradation of some dead-end

products that could accumulate during abiotic reduction by ZVI (Equation 1) (Oh and Alvarez, 2002):

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2 \quad (1)$$

Equation 1 continues under anaerobic conditions that are invariably found in PRBs due to the rapid reduction of dissolved oxygen by iron. Combining ZVI with an active methanogenic consortium significantly enhanced both the rate and extent of the transformation of chlorinated methanes (Weathers et al., 1997). In our experiments, microorganisms were facilitated by utilizing hydrogen gas as an electron donor that results in further degradation of contaminants such as organic matter, residual and/or intermediates of CLHs. In the M-PRBs system, it is inferred that an iron-based barrier can provide an excellent electron donor for the microbial consortium that is present on the surface of biologically active tire media, followed by the iron-based barrier.

5. CONCLUSIONS AND FUTURE STUDY

The authors studied the M-PRBs system composed of two barriers: one being an iron-based barrier, and the other being a biologically active tire media. In order to develop the M-PRBs system, we used abandoned materials such as waste steel scrap as a ZVI and waste tire rubbers as the biological media. This study focused on evaluating the activity of biologically active tire media. The sorption and degradation experiments showed that extensive sorption of TCE and PCE by tire rubbers, and that biologically active tire media could rapidly degrade TCE and PCE, as well as organic matters (BOD), through an enhanced biological process. Laboratory experiments suggest that the M-PRBs system might be a viable alternative to manage groundwater contaminated by landfill leachates. Nevertheless, further studies are needed to determine the applicability and limitations of the *in situ* remediation strategies using the M-PRBs system.

ACKNOWDGEMENT: This work was funded by the Core Environmental Technology Development Project for Next Generation (Eco-Technopia-21), Project No. 042-041-004 and granted from Korea Institute of Environmental Science and Technology.

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Manuscript received May 10, 2006
Manuscript accepted May 21, 2007