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Stability of Multi-Permeable Reactive Barriers for Long Term Removal of Mixed Contaminants

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Abstract The Permeable Reactive Barriers (PRBs) are relatively simple, promising technology for groundwater remediation. A PRBs consisting of two reactive barriers (zero valent iron-barrier and bio-barrier) were designed to evaluate the application and feasibility of the barriers for the removal of wide range of pollutants from synthetic water. After 470 days of Multi-PRBs column operation, the pH level in the water sample is increased from 4 to 7, whereas the oxidation reduction potential (ORP) is decreased to −180 mV. Trichloroethylene (TCE), heavy metals, and nitrate were completely removed in the zero valent iron-barrier. Ammonium produced during nitrate reduction is removed in the biologically reactive zone of the column. The results of the present study suggest that Multi-PRBs system is an effective alternate method to confine wide range of pollutants from contaminated groundwater.

Keywords Bio-barrier · Groundwater · Multi-PRBs · Zero-valent iron

The leachate released from landfills contains various pollutants such as organic matters, nitrogen compounds, chlorinate organic compounds, heavy metals and trace compounds (Lee et al. 2007). Presence of these pollutants in leachate causes serious environmental problems such as soil and groundwater contaminations, which in turn directly or indirectly affect the human beings (Clement et al. 1996). Several conventional methods like pump and treat, slurry wall, grout curtains, sheet piling, liners and surface capping have been applied to remove the pollutants from leachate. However, these methods have moderate removal efficiency with several limitations (Nyer 1993). Recently, many researchers have introduced the permeable reactive barriers (PRBs) system as an alternative method to remove pollutants from the leachate contaminated groundwater (USEPA 2002).

Permeable Reactive Barriers has received a great deal of attention as an innovative, cost effective, and conventional method for in situ remediation of contaminated groundwater. A wide variety of reactive materials has been developed and successfully used in PRBs for the removal of contaminants. Among the reactive materials, Zero Valent Iron (ZVI) is the most promising reactive material for the removal of several pollutants from contaminated groundwater (Henderson and Demond, 2007; Cundy et al. 2008). Even though ZVI exhibits degradation activity on wide range of pollutants, their effect on leachate contaminated groundwater is limited due to the presence of both organic and inorganic pollutants. Therefore, PRBs that contain more than one reactive material is necessary for the complete removal of both

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organic and inorganic pollutants from leachate contaminated groundwater (Lee et al. 2007). Preliminary batch experiment studies have confirmed that the ZVI and bacteria-based biologically active tire materials effectively remove several pollutants from the synthetic water (Lee et al. 2007). Hence, in the present study, we have assessed the application and stability of the newly designed PRBs (Fig. 1a) for the long term removal of pollutants from contaminated water.

Materials and Methods

Waste steel scraps (2–11 mm) and tire rubbers (2.0–7.0 mm) were prepared according to Lee et al. (2007). The municipal anaerobic sludge from the wastewater treatment plant was the source for anaerobic microorganisms and the sludge concentration of 9.81 g l^{-1} of volatile suspended solids (VSS) was used for the experiments. The column experiments were conducted using cylindrical glass columns (V

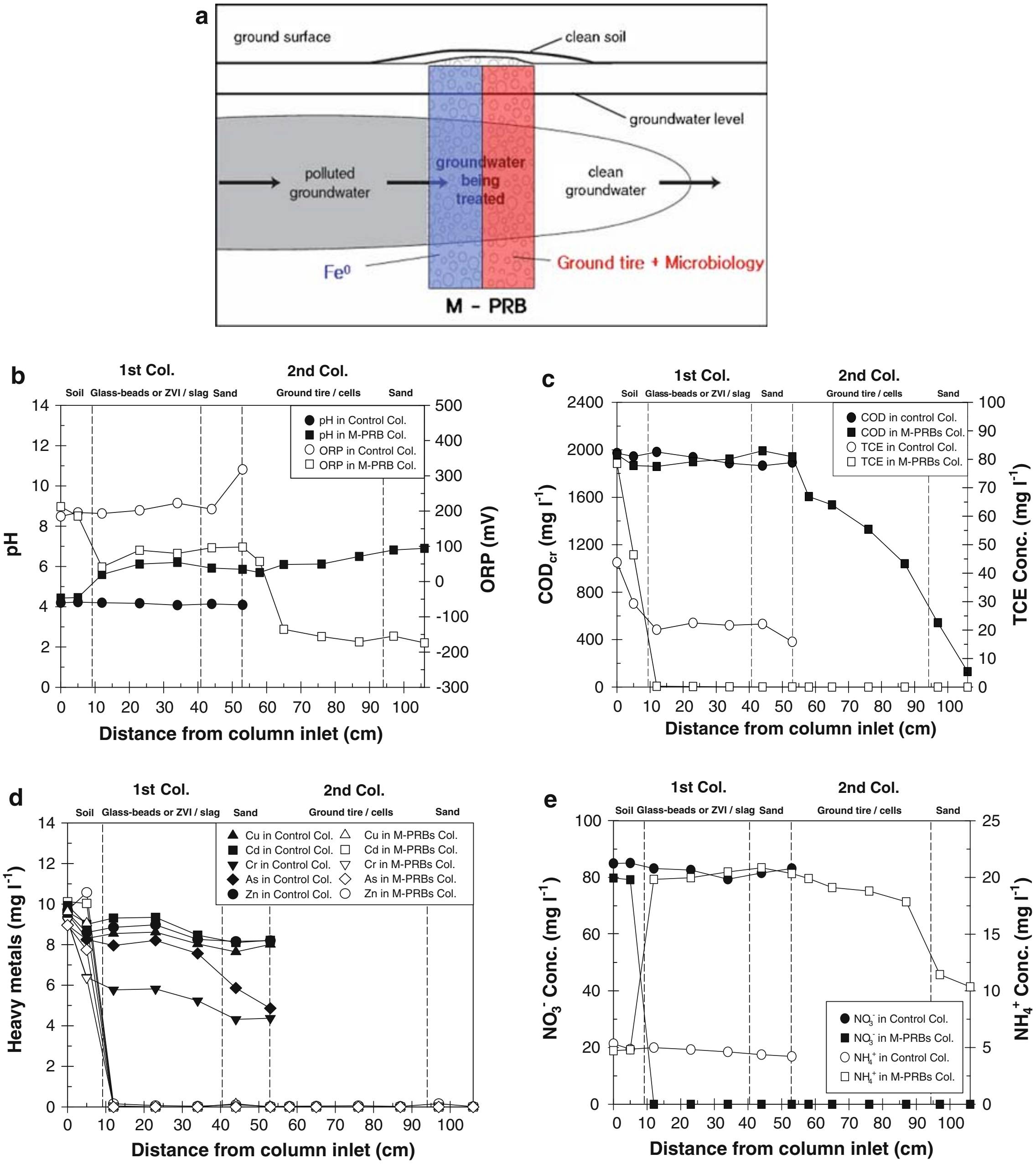

Fig. 1 Schematic diagram of multi-PRBs (M-PRBs) (EPA-542-F-01-005, 2001) (**a**). pH and ORP (Eh) profile (**b**). COD and TCE profile (**c**). Heavy metals (Cu, Cd, Cr, As, and Zn) profile (**d**). NO_3^- and NH_4^+ of M-PRB column after 470 days of operation

$1{,}456\ cm^3$, D 6 cm, H 52 cm) equipped with 5 lateral sampling ports at 5, 12, 23, 34, and 44 cm from the inlet. Two different columns were used in the study, where the first column was packed with a layer of uncontaminated soil (size 0.15–0.85 mm, H 9 cm), followed by a layer of ZVI scrap (size 2 mm–1.1 cm, H 32 cm) with converter slag filings (95/5 wt%). The highest place of column was packed with a layer of sea sand (size 20–30 meshes, H 11 cm). The outlet of the first column was connected with another column packed with a layer of waste tire rubber scrap (size 2–7 mm, H 41 cm) with municipal sludge (9.8 g VSS l^{-1}) followed by a layer of sea sand. The control column was packed with inert glass beads instead of reactive materials ZVI, converter slag, tire rubbers, and sludge. The columns were continuously fed with anoxic synthetic solution at a flow rate of 5 ml h^{-1} using a peristaltic pump (Gilson Minipuls3, France). The anoxic synthetic solution containing heavy metals (Cu, Cd, Cr, As, and Zn at 10 mg l^{-1} each), salt ions (NO_3^-: 80 mg l^{-1} and NH_4^+: 10 mg l^{-1}) and organic materials (CH_3COONa: 2,000 mg l^{-1}) for chemical oxygen demand (COD) was prepared and adjusted to pH 4.0 with 1 M H_2SO_4. Trichloroethylene (TCE) was supplied separately using a syringe pump fitted with 100 ml gas-tight glass syringes (Hamilton no. 701N, USA). The influent TCE concentration was adjusted to about 70 mg l^{-1} by mixing syringe pump flow with peristaltic pump flow in Teflon three-way switch valves (Hamilton, USA) as described by Gandhi et al. (2002).

Samples were collected from inlet, lateral sampling ports, and outlet of each column after increasing flow rate to 10 ml h^{-1} and analyzed promptly to avoid air exposure. The pH and ORP of the samples was determined using a pH meter (Istek 730P, Korea). TCE was measured using an Agilent Technologies 6,890N gas chromatograph equipped with an electron capture detector and a DB-VRX column (limit of detection = 5 µg l^{-1}). Heavy metals were analyzed using Inductively Coupled Plasma (ICP) (SPECTRO CIROS, Germany) and the instrument was calibrated using standard solutions (ACCU Co., USA). Standard reference materials (MESS-1, National Research Council, Canada) was used to check the accuracy and precision. The recovery rates were: Cu 93.3%, Cd 92.1%, Cr 98%, As 91.8%, and Zn 102%. The results showed good agreement between the certified and analytical values (limit of detection = 0.1 mg l^{-1}). Nitrate and ammonium ions were measured using a nitrogen-phosphorus auto analyzer (FIAstar 5000 Analyzer, FOSS) (limit of detection = 0.5 mg l^{-1}). COD analysis was performed according to reactor digestion method (USEPA approved for reporting wastewater analysis, Method 8000) using potassium dichromate.

On completion of the experiments, tire rubber samples collected from the columns were observed in scanning electron microscope (SEM). The air-dried tire rubber samples were mounted on a sample stub and sputter coated with gold in a JFC-110E (JEOL, Japan) sputter coater. The samples were photographed in a JSM 5,410 V SEM (JEOL, Japan) operated at 20 kV and the digital images were collected using analySIS software (Soft Imaging System GmbH, Germany) (Gandhi et al. 2002).

Result and Discussion

The adsorption capacity of tire rubbers for several organic pollutants such as phenols, cresols, TCE, toluene, methylene chloride, *m*-xylene, and heavy metals have been reported by a number of authors by both batch and column experiments (Kim et al. 1997; Park et al. 1997). Interestingly, biologically active tire rubbers effectively removed 93% of TCE, 77% of tetrachloroethylene and 80% of organic matters from synthetic solution, when compared to wild tire rubbers (Lee et al. 2007). Therefore, we selected ZVI, converter slag, waste tire rubbers and anaerobic municipal sludge (anaerobic organisms) as reactive materials for long term column studies. After 470 days of column operation, samples were collected from the sampling ports and analyzed for contaminants profile. The hydraulic retention time of ZVI barrier was 140 h, whereas the retention time of bio-barrier was 70 h. The pH of the sample is increased to 7 and ORP decreased to −180 mV (Fig. 1b). The increase in pH and decrease in ORP is due to the oxidation (corrosion) of ZVI. As represented in Eq. 1 and 2, the oxidation of Fe^0 by water and oxygen generate Fe^{2+} and OH^- which increases the pH of the sample.

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

$$2Fe^0 + 2H_2O + O_2 \rightarrow 2Fe^{2+} + 4OH^- \qquad (2)$$

The Eq clearly indicate that the pH and ORP of the water is mainly depending upon the oxidation reaction of the ZVI. Moreover, reductive degradation of the pollutants by anaerobic microorganisms present in the M-PRBs column also influences the pH and ORP of the sample (Weathers et al. 1997).

TCE removal along the M-PRBs column is shown in the Fig. 1c. In the control column, more than 40% of TCE has been reduced in the samples collected from the lateral sampling port (12 cm) immediately from the inlet. The reduction was due to the adsorption of TCE by soil materials packed in the column. Similarly, a marked difference in the TCE concentration is observed between the samples collected from the lateral port (44 cm) and the final outlet of the column. The removal is due to adsorption of TCE by sand particles present in the column. On the other hand, a complete reduction (100%) of TCE is observed in the samples collected from the lateral sampling port (12 cm) of

M-PRBs column. The complete removal of TCE is due to the reductive degradation by ZVI, resulting in dechlorination of chlorinated solvent (Roberts et al. 1996).

Removal of heavy metals along the column is shown in Fig. 1d. All the heavy metals were effectively removed (>98%) from the solution after 470 days of operation. The rapid reduction in the heavy metals concentration near the inlet (lateral sampling port 12 cm) is due to the spontaneous adsorption and coprecipitation of heavy metals with Fe(II) and Fe(III) (oxyhydr)oxide phases, which might have formed during ZVI oxidation (Manning et al. 2002). However, a minor decrease in the heavy metals concentration was observed in the control column and the reduction is due to the adsorption of heavy metals by soil materials packed in the column (Markiewicz-Patkowska et al. 2005).

Nitrogen is another harmful pollutant in the leachate contaminated groundwater. Nitrogen usually exists as ammonium and nitrate, and these forms originate from the organic compounds, which are present in the leachate. More than 99% of the nitrate has been removed from the synthetic solution collected after 470 days of operation (Fig. 1e). The rapid decrease in the nitrate concentration in samples collected from lateral sampling port (12 cm) of column is due to the abiotic reduction of nitrate compounds. ZVI acts as a reducing agent and reduce nitrate into nitrogen gas or ammonium. The reaction is described in the following Eq:

$$NO_3^- + 4Fe^0 + 7H_2O \rightarrow 4Fe^{2+} + NH_4^+ + 10OH^- \qquad (3)$$

The results are consistent with the previous work, where Till et al. (1998) reported that the abiotic reduction of nitrate compounds by ZVI. In addition, increased concentration of the ammonium in the water samples collected from the lateral ports of M-PRBs column have further confirmed the ZVI mediated reduction of nitrate compounds. Interestingly, more or less 50% of ammonium concentration has decreased in the samples collected from the final outlet of the M-PRBs column. The decreased concentration might be due to the anaerobic oxidation of ammonium (Anammox process) by microbial cells present in the bio-barrier (Strous et al. 1998).

COD is an important indicator used to assess the biodegradability of the organic compounds. When the water sample is passed through the ZVI barrier of M-PRBs column, a little increase in the COD concentration is observed

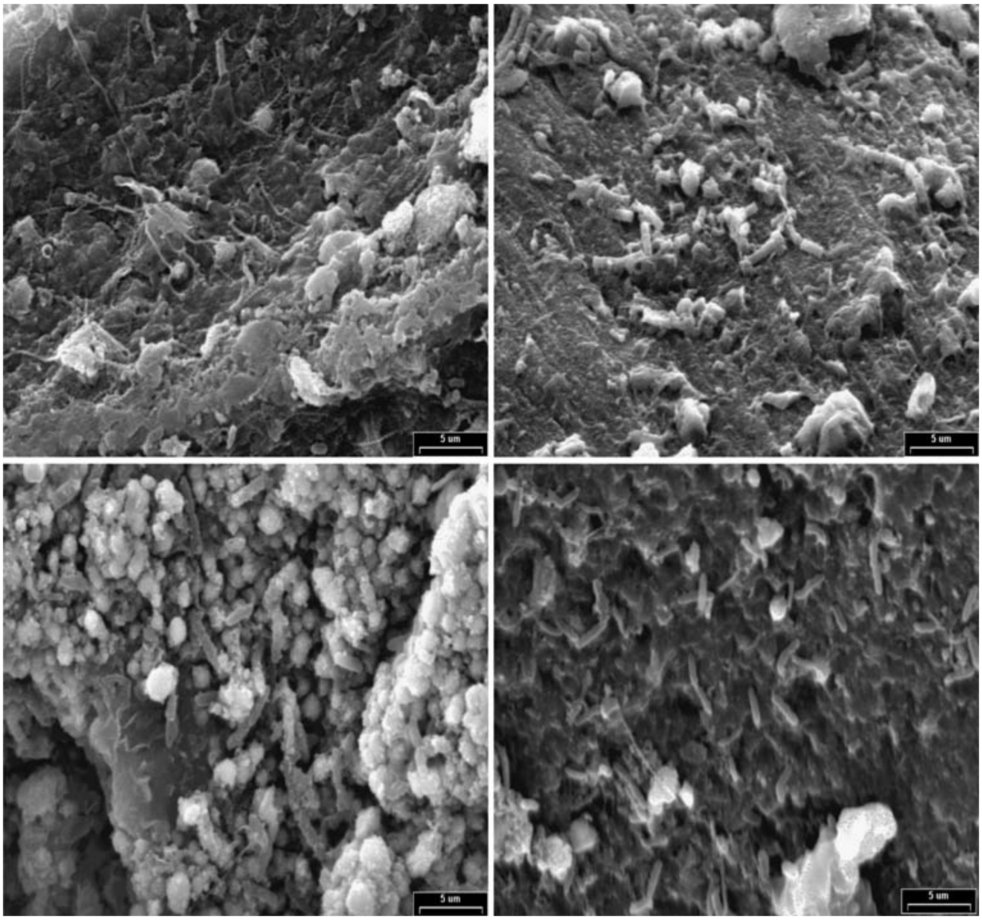

Fig. 2 SEM pictures of tire rubber samples from M-PRBs column after 470 days of operation (×3,500)

(Fig. 1c), which is due to the degradation of complex biodegradable materials into simple compounds. The ZVI might break down the carbon chain of the complex organic matters which leads to the formation of simple biodegradable compounds. The degradation of simple organic materials by anaerobic microorganisms is responsible for the major reduction (93.4%) of COD in the bio-barrier of M-PRBs column. Moreover, increased reduction of COD is due to the increased microbial population in the bio-barrier of the column. Microbiological processes play an important role in the long term performance of PRBs (Scherer et al. 2000). Adaptation and colonization of microorganisms in the reactive materials are required for the enhanced microbial activity. Hence, SEM studies were performed to illustrate the presence of microorganisms on the surface of tire rubbers. Samples from M-PRBs column indicate the presence of three different shaped (rod, cocci, and spiral) microorganisms on the surface of the tire rubbers (Fig. 2).

In the present study, we assessed the feasibility and application of the M-PRBs for the long term removal of pollutants from contaminated groundwater. The presence of two different reactive barriers (ZVI-barrier and bio-barrier) were found to enhance the removal of pollutants in the M-PRBs column by both physico-chemical and biological process. The complete removal of contaminants suggests that M-PRBs system is an effective alternate method for the remediation of contaminated groundwater. Moreover, the recycled waste materials (waste steel scrap, converter slag, anaerobic sludge, and tire rubber) were used as reactive material in M-PRBs system, which is economical and environmentally beneficial to end users.

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