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ADVOCATE bulletin

CL:AIRE's ADVOCATE bulletins describe practical aspects of research which have direct application to the characterisation, monitoring or remediation of contaminated soil or groundwater. This bulletin describes batch and column experiments to select reactive materials to treat contaminated groundwater in a permeable reactive barrier.

Selecting reactive materials for permeable barriers to remediate groundwater contaminated with heavy metals and BTEX: batch and column experiments

1. Introduction

Remediation and protection of groundwater resources has become crucial considering the scarcity and deteriorating quality of freshwater resources in many parts of the world. We face further challenges as at most contaminated sites mixtures of organic and inorganic substances are found. Due to the differences in the physico-chemical properties of these contaminants, their removal from groundwater may require a combination of several traditional remediation methods (Köber *et al*., 2002; Morkin *et al*., 2000).

Permeable Reactive Barriers (PRBs) are an established *in situ* remediation technology that may offer a cost-effective solution to this problem. Within PRBs the contaminant plume flows through a reactive filter (i.e. a barrier containing materials that can react with the contaminants) that is placed across the path of the groundwater flow. The barrier adsorbs, precipitates, and/or breaks the contaminants down into less hazardous forms under *in situ* conditions stimulated by the reactive materials, thereby allowing treated groundwater to emerge. PRBs do not require external energy to move the contaminated water through the barrier; thus the overall cost of using the technology is lower when compared to the pump and treat (P&T) system (Morkin *et al*., 2000; Henderson & Demond, 2007).

Zero valent iron (ZVI) is the commonly used material in PRBs because of its effectiveness in attenuating a wide range of contaminants, such as perchloroethylene (PCE), trichloroethene (TCE), nitroaromatic compounds (NACs), nitrate, heavy metals, dyes, and phenol (O'Carroll *et al*., 2013; Fu *et al*., 2014; Gavaskar *et al*., 2000). However, some issues regarding its cost, longevity and inability to degrade organic contaminants such as BTEX (benzene, toluene, ethylbenzene, and xylene) {Henderson & Demond, 2007; Gavaskar *et al*., 2000) have necessitated the search for alternative materials.

Using mixtures of materials in PRBs may help eliminate or reduce the potential limitations of single/individual materials by improving the permeability, reducing cost of using the single/pure materials, providing multiple mechanisms for contaminants removal, and accelerating the removal rates (Gavaskar *et al*., 2000). This bulletin reports on laboratory batch and column experiments performed to select reactive materials for PRBs to treat groundwater contaminated with heavy metals and BTEX.

2. Laboratory Methods

Both individual materials and their mixtures in different ratios were investigated. The materials were considered because they are locally available, inexpensive and can be obtained in large quantities. Moreover, based on their properties it was presumed that mixtures of some of them may improve the removal efficiency (by providing different removal mechanisms) and hydraulic properties of the barrier. The individual materials investigated included brown coal, zeolite, compost, diatomaceous earth, mulch and ZVI (as control), and the material mixtures were: compost-zeolite, compost-brown coal, compost-mulch and mulch-diatomaceous earth. Brown coal, compost and diatomaceous earth (obtained from the brewery) were included to additionally provide and/or stimulate microorganisms for biodegradation/bioprecipitation of the contaminants. Zeolite was included to additionally improve the permeability. Similarly, mulch was added to additionally improve the permeability and to serve as long-term source of carbon for microorganisms due to its ligniferous nature. Some physical and chemical properties of the materials are presented in Table 1.

Table 1: Physico-chemical properties of materials.

Materials	pH		Moisture content (%)	LOI (%)	CEC (meq/100g)	P_b (g cm^{-3})
	H_20	1M KCl				
ZVI	8.5	n.d.	n.d.	n.d.	n.d.	2.6
Compost	8.1	7.4	44.4	34.9	480.0	0.69
Zeolite	7.1	5.5	5.2	5.2	435.5	0.8
Brown coal	4.9	4.6	16.2	28	1215.0	0.8
Mulch	4.9	4.7	11.3	80.1	n.d.	0.28
Diatomaceous earth	5.2	5.0	62.5	33.9	n.d.	1.2

LOI: Loss on ignition; CEC: Cation exchange capacity; P_b: Bulk density; n.d.: Not determined

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During the laboratory studies, attention was given primarily to Pb and benzene because of their following properties (in combination): ubiquity, mobility in groundwater and toxicity effects on humans and other aquatic life (Vogt *et al.*, 2011; Polish Ministry of Health, 2007; USEPA, 2007).

Batch test series lasting 17 days, were performed to screen the reactive materials based on their efficiency in removing ca. 2 mg/L of Pb and benzene from synthetic groundwater. The procedure for sequential chemical extraction of metals (Tessier *et al.*, 1979) was employed to determine the forms of Pb removal by the selected materials (i.e. exchangeable, carbonate, Fe-Mn oxide, organic matter/sulphides). The mechanisms (sorption and biodegradation) of benzene removal were investigated by performing sterile (by addition of 1% sodium azide to the samples to repress microbiological activity) and non-sterile experiments.

The selected materials were evaluated further in column experiments using stainless steel cylinders (Figure 1). The columns were clamped to an upright position and an upward flow (average flow rate = 1.67 cm^3 min^{-1}; residence time = 2.4 hrs) of the contaminated solution through the columns was achieved using a peristaltic pump. Initial concentrations of Pb and benzene in the influent solutions were 1.76 mg/L and 2.4 mg/L, respectively. Prior to the experiments, the columns were saturated with deionized water. Column effluents were sampled at intervals for pH measurement and analysis of Pb and benzene. Breakthrough curves (BTCs) were generated by plotting the normalized concentrations of benzene and Pb against the pore volumes (PVs) eluted to evaluate the performance of the barrier materials.

3. Results and Discussion

From the results of the batch tests zeolite, brown coal, compost: zeolite (1:3), and compost: brown coal (1:3) were selected for Pb based on their removal efficiencies, which were of 98.7%, 99.9%, 97.9% and 99.8%, respectively. These values are comparable to that of ZVI which is 99.9%. The sequential extraction of Pb from these materials showed that less than 20% of the Pb was removed through association with the carbonates and Fe-Mn oxides combined, which may be attributed to the low pH (3.4) or low level of carbonates and Fe-Mn oxides in the materials. The addition of compost to the materials increased the amount of Pb removed by organic matter/sulphides, which ranged between 20 to 40%. The highest removal of Pb (more than 50%) was via ion-exchange, which may be due to the high CEC of the materials. Ion-exchange is a reversible process thus remobilization of Pb may occur, and the presence of other cations may compete with Pb for the exchange sites.

In the case of benzene, zeolite, brown coal, compost: zeolite (1:1) and compost: brown coal (1:5) were selected. Their removal efficiencies were of 99.9%, 93.2%, 99.9% and 93.4%, respectively, which are higher than that of ZVI (55.7%). Experimental results also showed that benzene was removed via sorption and biodegradation, with the latter being observed in experiments with compost and brown coal. Generally, the contribution of biodegradation was low, which may be attributed to the recalcitrance of benzene to biodegradation due to the stability of its π-electron cloud (Weelink *et al.*, 2010), the short duration of the experiment (Vogt *et al.*, 2011) or the effect of sorption on biodegradation (Kim *et al.*, 2003). It is

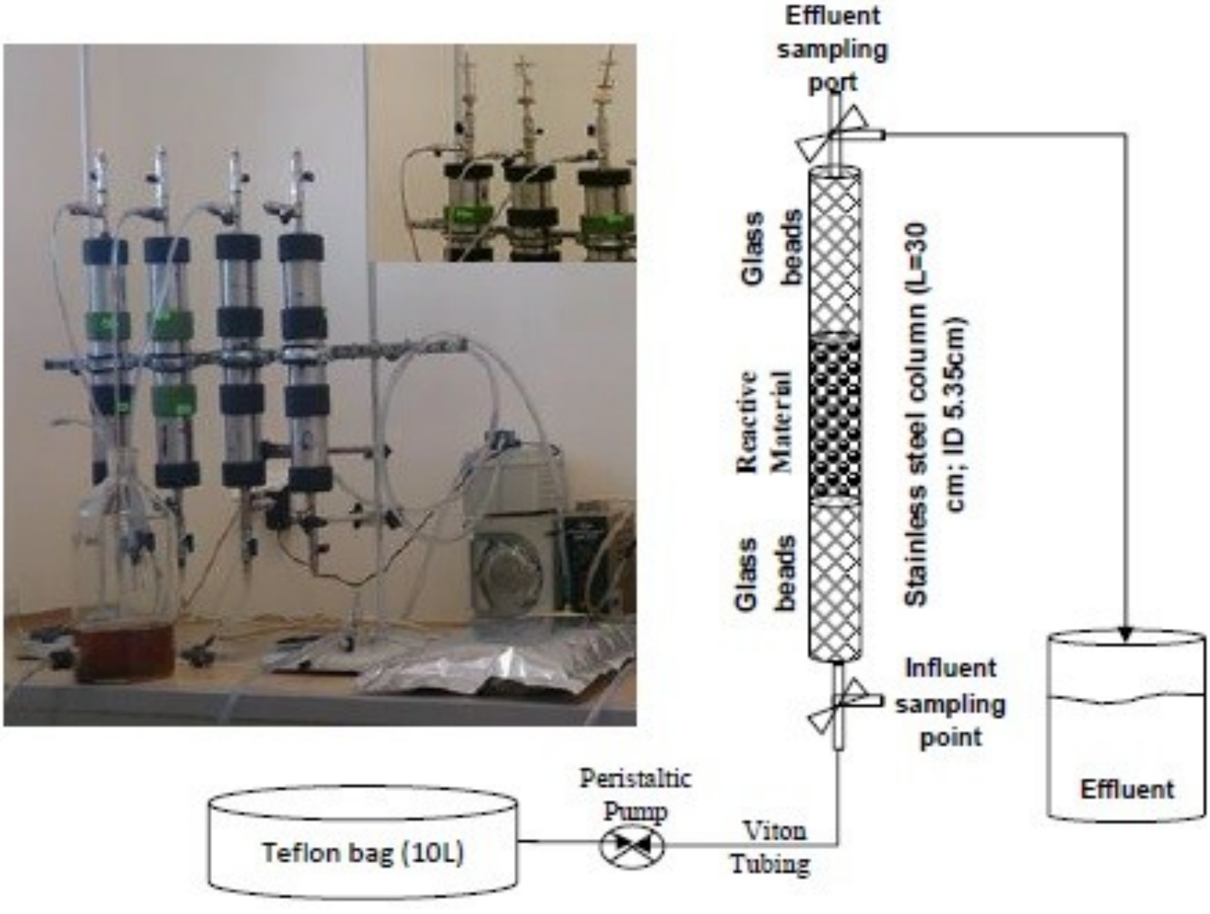

Figure 1: Column experimental set-up.

probable that the sorption of benzene was largely to the organic fraction (represented by the LOI in Table 1) in the materials. However, considering the LOI, the high removal obtained for zeolite may be due to diffusion of benzene into zeolite pores (Jousse & Auerbach, 1997) or the weak interaction of the π-electrons of the benzene with the zeolite terminal silanol (Si–OH) groups (Rungsirisakun, 2006).

The results of the column experiments are shown in Figures 2a and 2b for Pb and 3a and 3b for benzene. In the case of Pb the experiments were run until 80 PV were eluted. The BTCs show that the capacity of the materials to remove Pb was not completely exhausted (C/Co < 1) after 80 PV. A comparison of the BTCs, however, shows that compost: brown coal (1:3) with a removal capacity of >0.19 mg Pb/g at 80 PV may be the most effective in attenuating Pb. Figure 2b shows the effluent pH for the different column materials. The pH values at PV = 0 represent the pH of the columns when they were saturated with de-ionized water. For columns with zeolite and compost: zeolite (1:3), the effluent pH continued to decrease during the column operation, nearing the pH of the influent solution (pH 2.4), whereas that of brown coal and compost: brown coal (1:3) remained in a circumneutral range after the initial decline. These results suggest that brown coal and compost: brown coal (1:3) may be effective in the long-term neutralization of pH. The high pH observed during the initial stages and through the experiments in all the columns may be due to protonation of surface functional groups (particularly for columns with compost and brown coal-based materials), ion-exchange of H^+ with mono- and divalent cations and/or dissolution/release of (bi) carbonate ions.

In the case of benzene, the experiments were performed until 30 PV had been eluted. With the exception of zeolite for which the benzene C/Co =1, the BTCs of the other materials were below 1. A comparison of the BTCs (Figure 3a) shows that compost: brown coal (1:5) is the most effective in benzene removal, as breakthrough occurred after 20 PV. The capacity of the compost: brown coal (1:5) at 20 PV was 0.03mg benzene/g. It is probable that the removal of benzene was largely due to sorption to the organic fraction in the materials as indicated earlier. Columns with C/Co <1 may be due to the effect of biodegradation on the transport of benzene. Figure 3b shows the effluent pH for the different column materials. Similarly, the pH values reported at PV = 0 represent the pH of the columns when they were saturated with de-ionized water. For all the

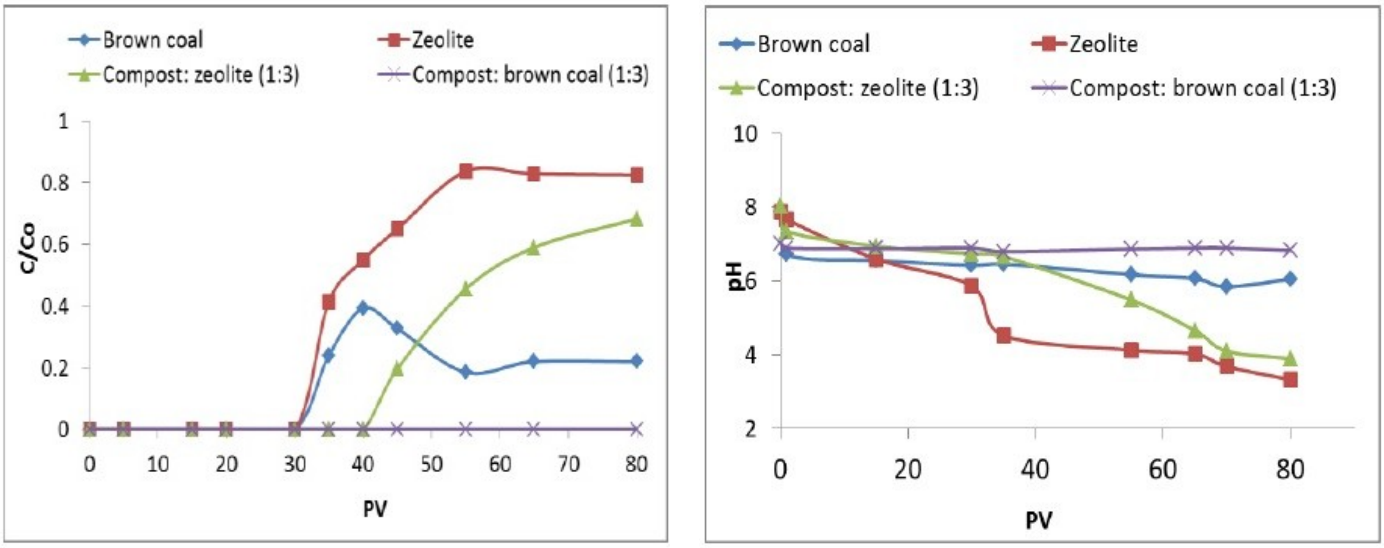

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Figure 2: (a) Pb breakthrough curves and (b) pH profiles.

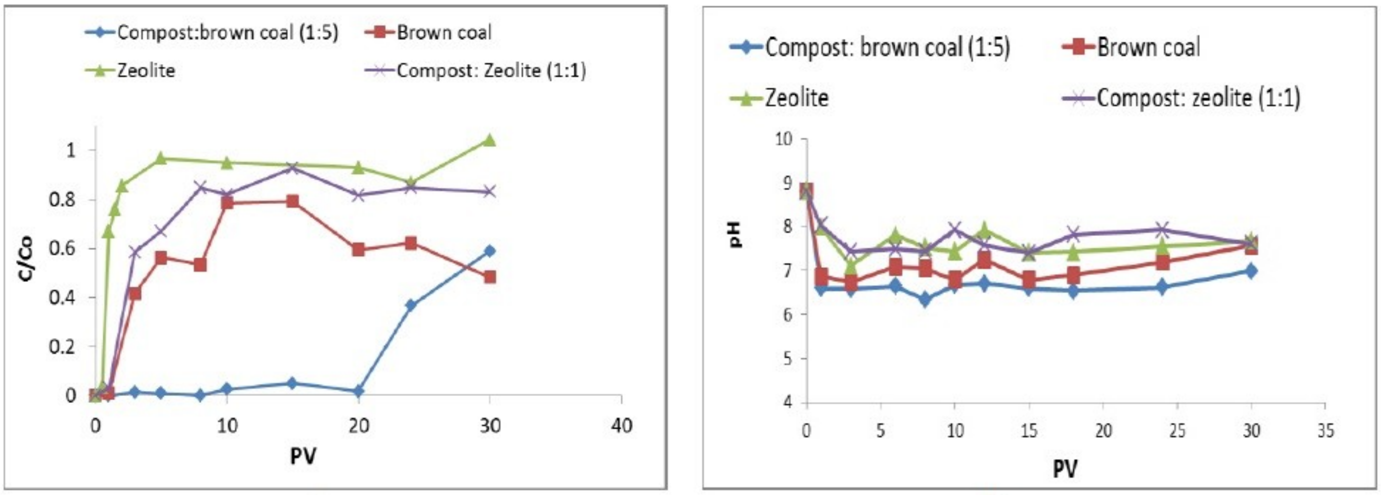

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Figure 3: (a) Benzene breakthrough curves and (b) pH profiles.

materials, the pH decreased initially and was kept in a circumneutral range thereafter. This may be due to deprotonation in the case of compost and brown coal-based materials and interaction of the OH^- with the Brønsted acidic sites of the zeolite (Rivera *et al.*, 2000)].

The selected materials will be evaluated further in a pilot field-scale experiment in which native groundwater containing a mixture of these contaminants will be used. Currently, geochemical modelling is being performed to assist the interpretation of the laboratory results.

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5. References

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