Low-Cost Permeable Reactive Barrier (PRB) System to Treat the Organic Compounds and Nutrients in the Groundwater Contaminated by the Landfill-Leachate

D.M. Kankanige, W.K.C.N. Dayanthi, I.U. Nagasinghe, A.M. Disanayaka and K. Kawamoto

Abstract: When already limited safe groundwater is rapidly contaminated with landfill-leachate, it is a timely need to investigate feasible remediation techniques. In this scenario, Permeable Reactive Barrier (PRB) is a potential groundwater treatment method. If waste materials can be effectively applied as PRB reactive media, the system can be made more economical. This study was focused on a treatment system with two mixed-media PRB models (PRB 1 and PRB 2) connected in series, in which dewatered alum sludge (DAS), washed quarry dust (WQD), washed sea sand (WSS), red soil (RS), bio char (BC) and saw dust (SD) were emplaced in reactive beds, to treat organic compounds and nutrients of leachate-contaminated groundwater. Wastewater parameters were measured in terms of BOD₅, COD, NO₃-N, NH₃-N, TN, PO₄-P and TP. Mean removal efficiencies of BOD₅ (88.2±5.7%), COD (84.2±9.6%) and NH₃-N (95.6±4.2%) were phenomenal with 13.1 days of pore volume hydraulic retention time (HRT) during an experimental period of 140 days. Reactive material properties were not much affected by the interaction with landfill-leachate, thus no considerable change in the removal efficiencies occurred within 140 days. The treatment efficiency of the present system with two reactors connected in series is greater than that of a single PRB reactor filled with the same reactive materials in the same packing configuration.

Keywords: Permeable Reactive Barrier (PRB), Mixed - media, Reactive materials, Landfill-leachate, Groundwater

1. Introduction

Landfill leachate is the aqueous effluent generated as a consequence of rainwater percolation through waste [1]. This leachate consists of a variety of contaminants in the form of organic and inorganic compounds which can be hazardous [2]. Organic compounds such as phenols, esters, ethanes, propanes etc. are abundantly found in it. Among the inorganic compounds, nitrogenous and phosphorous compounds are dominant.

Due to the contamination of these pollutants, the quantity of safe groundwater on earth, which is already limited at the moment, is reducing rapidly [3]. Landfill-leachate has become the leading source of groundwater contamination in developing countries, where there are plenty of unsanitary landfills. Thus, at present, when leachate has become the dominant groundwater pollutant and when safe groundwater is threatened, it is a timely need to investigate remediation techniques to treat contaminated groundwater. It is quite essential that such techniques are economical and practically feasible when their application is considered.

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Permeable Reactive Barrier (PRB) is a novel in-situ technique widely applied to treat the contaminated groundwater [4]. This particular study targets investigation of the treatment of organic compounds and nutrients by a field-scale PRB system that comprises waste materials such as DAS, WSS, WQD, RS, SD and BC in the reactive media beds. The tests were carried out in a field-scale experimental set-up located in Hambantota, Sri Lanka, for a total duration of 140 days. The objective was to determine the removal efficiencies of organic compounds and nutrients in the PRB system, and investigate the changes of the physical and mechanical properties of the reactive materials with the interaction of the landfill-leachate.

2. Literature Review

2.1 Permeable Reactive Barrier (PRB) Concept

As illustrated in Figure 1, PRB is an engineered treatment zone of reactive material(s) that intercepts a contaminant plume and transforms the contaminants into environmentally acceptable forms as they flow through it [5]. Although PRBs are also designed to treat contaminated soil, the common application is still the treatment of groundwater within aquifers [2].

Figure 1 – PRB Concept [2]

2.2 Reactive Materials

The reactive media bed in a PRB performs the physical and chemical processes as well as biological transformations of the pollutants [3]. Physical processes involve sorption through which pollutants are immobilized by adsorption without altering the chemical state [3]. Precipitation, retardation and oxidative/reductive decomposition are instances for chemical treatment mechanisms [3]. Biological transformations occur when organic pollutants are biodegraded into less/non-toxic compounds [3]. Therefore, the selection of the type of reactive media is significant. Reactive media for a field-scale PRB system, which is to be installed below the groundwater table, is decided based on the site

investigation records, site location, PRB design, barrier thickness and barrier length [2]. Prior to such an installation, it is utmost important to consider the results obtained by both laboratory-scale experiments and field-scale models, in which various reactive materials have been utilized by past researchers. Past research reveals that, according to laboratory-scale experiments, waste materials could be utilized in PRB reactive media beds to treat leachate-contaminated groundwater. Waste materials such as quarry dust, dewatered alum sludge, saw dust, coconut coir fibre and firewood charcoal are capable of treating the organic compounds and nutrients [6]. Dewatered alum sludge has the potential of removing phosphorous in wastewater in sewage treatment plants [7]. In developed countries, various other reactive materials are used for PRB reactive beds on a large-scale. Zero-valent iron and Zeolite are such effective, but expensive, adsorbents which are widely used as PRB reactive media in sites of United States [8]. Zero valent iron supports sorption of oxyanions and dehalogenation of chlorinated solvents [9].

2.3 Packing Configurations of PRB

The packing configuration of reactive media is an equally important factor that affects the PRB treatment efficiency. Research has been focused on both sequential and mixed media arrangements, both of which have showed almost similar treatment potential [10]. However, the former gives construction difficulties while the latter seems more feasible.

2.4 Field-Scale Applications

PRB has become a vastly applied technique in developed countries, where a lot of large-scale PRB walls have been installed to address contaminated groundwater issues. A biological PRB has been selected for the treatment of a BTEX (benzene, toluene, ethyl benzene and xylene) plume occurring in Metropolitan Perth, in Western Australia [11]. Port Kembla in New South Wales suffered from leachate contamination of groundwater, until a PRB wall with coal was installed to control sulphides and alkalinity [3]. A PRB was constructed and operated in a Northern Alberta site in Canada to treat a nitrate plume having a maximum nitrate concentration of 1400 mg/L [12]. This PRB which is designed for 20 years, possesses a maximum treatment efficiency of 80% [12].

2.5 Advantages and Limitations of PRB

PRBs possess several advantages over other conventional groundwater remediation techniques. Since PRBs can degrade contaminants underground, above ground facilities such as facilities for storage, transport and disposal are not required [3]. Groundwater flow through a PRB wall under natural gradient eliminates the need for a continuous energy supply, which will lower the operating costs and ultimately the life cycle cost [3]. PRBs result in fewer environmental impacts when comparing with the Pump-and-Treat system [13]. A fundamental limitation of PRB is being restricted to shallow plumes which make it difficult to create trenches in extremely deep aquifers [2].

3. Methodology

3.1 The Field - Scale PRB Model

The field - scale experimental set-up (Figure 2) consisted of a lysimeter, a receiving tank, two overhead storage tanks, a mixed-media PRB unit with reactive materials having relatively high specific gravities (PRB 1), a mixed-media PRB unit with reactive materials having relatively low specific gravities (PRB 2) and two effluent storage tanks. All these components were connected sequentially. The lysimeter modelled a sanitary landfill while the natural precipitation as well as artificial precipitation provided from a sprinkler system facilitated the leachate production within the lysimeter model. The leachate generated in the landfill model was collected in the receiving tank and pumped into the first overhead storage tank in order to regulate the flow into the PRB 1 unit, where it was partially treated. Its effluent was again pumped into the second overhead storage tank for flow regulation and sent to the PRB 2 unit for further treatment. The effluent of PRB 2 was recirculated to the lysimeter.

Figure 2 - Field Scale Experimental Set-Up

3.2 Reactive Materials

Reactive materials were selected based on the results of the batch and column experiments associated with PRB treatment in the recent

past. The column experiments conducted by Dayanthi et. al. [6] utilized dewatered alum sludge (DAS), quarry dust (QD) and a mixture of organic matter (MOM), each mixed with laterite soil, to treat 5% diluted leachate collected from a dumpsite. Here, the highest efficiencies for COD and nitrogenous compound-removal were achieved in DAS-filter column. In the same study [6], QD showed efficiencies slightly less than those of DAS, having the highest durability in terms of shear strength. Moreover, DAS is recognized as an effective phosphate adsorbent by several researchers (Yang et. al. [14] and Razali et. al. [15]). The study by Ping et. al. [16] reports of carbon-bearing adsorbents made of sewage sludge that showed higher removal rates of COD, Phosphorous and chromaticity colour than active carbon. In another study, Dayanthi et. al. [17] finds red laterite soil (RLS) giving higher average efficiencies for COD ($91.6 \pm 4.1\%$) and BOD₅ ($88.6 \pm 9.53\%$) removal than zero valent iron (ZVI) and granular activated carbon (GAC) that were used as controls. The same experiment [17], where DAS, QD, silica sand (SS), fire-wood charcoal (FWC) and saw dust (SD) were configured in layers (column filter 1) and as a mixture (column filter 2), shows that the latter performed with higher COD removal efficiency than the layered one and both had similar BOD₅ removal efficiencies. Furthermore, Rasheed et. al. [18] suggests that bio char (BC) exhibits better sorbent efficiency for wastewater remediation than char. SS is applied in filters to remove organic materials in laundry liquid waste [19]. Mohajeri et. al. [20] have utilized SD in a bentonite-enriched saw dust-augmented sequencing batch reactor and achieved considerable removal of COD and NH₃-N in landfill leachate samples. Based on these findings, DAS, washed quarry dust (WQD), washed sea sand (SS), red soil (RS), BC and SD were selected for the current study (Figure 3). The mixed media configuration was preferred to layered one, according to findings of Dayanthi et al. [17].

3.3 Filling Configurations of the PRB Units

PRB 1 unit was loaded with materials having relatively higher particle densities that included DAS, WQD, WSS and RS, mixed in equal volumes, whereas PRB 2 unit was loaded similarly with materials having relatively lower particle densities that included SD and BC. Each PRB reactor (2 m × 1 m × 1 m) comprised influent and effluent compartments and a metal layer (0.1 m) at the effluent side to trap the

impurities that could flow with the effluent. Two geotextiles were also placed at both ends of the reactive bed. The mixed-medium was filled layer by layer (9 layers) where the layer thickness was maintained as 10 cm in each PRB unit. Figure 4 illustrates the reactor-top view and the layer arrangement while the loaded PRBs are shown in Figure 5. In order to achieve the maximum possible contact between the contaminants and reactive media and a high HRT when the plume flows through the filter bed, following steps were undertaken: i) the surface area of reactive materials, especially, that of DAS and RS which had soil lumps, was increased by grinding them, and ii) larger pieces of BC and SD were ground to smaller particles. Figure 6 shows the particle size distribution of each material, followed by Table 1 showing the respective parameters.

Figure 3 - Reactive Materials

Figure 4 - (a) Top View (b) Sectional Front View of PRB Reactor

(a) (b)
Figure 5 - Loaded PRBs [(a) PRB 1 (b) PRB 2]

Figure 6 – Particle Size Distribution of Individual Materials Before Mixing and of Mixed Media Prior to the Experimental Run

A high degree of compaction was provided when loading reactive materials into each PRB unit, in order to reduce the hydraulic conductivity and increase the actual hydraulic retention time as much as possible. Water was added to the mixture to facilitate the compaction process. Bulk density and moisture content of each material were determined prior to mixing (Table 2). The quantity of each material to be filled layer wise was determined theoretically, targeting each mixture to be

packed to the highest bulk density of each group (1704.9 kg/m³ in PRB 1 and 368.95 kg/m³ in PRB 2) (Table 2).

Table 1 – Particle Size Distribution Parameters of Individual Materials before Mixing and of Mixed Media prior to the Experimental Run

Material / media	Effective size (D ₁₀) (mm)	D ₆₀ (mm)	Uniformity coefficient
WQD	0.48	1.70	3.54
WSS	0.50	1.50	3.00
DAS	0.46	1.60	3.48
RS	0.50	1.48	2.96
Mixed media -PRB 1	0.47	1.60	3.40
SD	-	1.60	-
BC	-	1.80	-
Mixed media -PRB 2	-	1.70	-

Table 2 – Bulk Density, Moisture Content and Theoretical Material Quantity per Layer

Reactor	Material	Bulk density (kg/ m ³)	Moisture content (%)	Volume per layer	Material quantity per layer (kg)
PRB 1	DAS	670.57	4.1	0.15 m ³	63.93
	WQD	1704.90	4.0		63.93
	WSS	1279.10	4.2		63.93
	RS	1005.6	4.2		63.93
PRB 2	SD	201.37	3.8		13.84
	BC	368.95	3.9		13.84

However, when loading, the actual quantities varied from theoretical ones owing to practical difficulties incurred during compaction. It was assured that equal quantities were added from each material to a particular layer. Actual material quantities filled in each layer are given in Table 3. Accordingly, the packing density and the moisture content achieved in the final mixed media are indicated in Table 4.

3.4 Hydraulic and Mass Loading Rates

Once the PRB system was operated, as the first step, design parameters such as Pore Volume Hydraulic Retention Time (HRT), Hydraulic Loading Rate (HLR), Organic Loading Rate (OLR) and Nitrogen loading rate of the PRB system were determined in order to identify its hydraulic and loading capacities. Table 5 includes the summary of these data.

Table 3 - Actual Material Quantities

Layer No.	Material quantity per layer (kg)							
	PRB 1					PRB 2		
	DAS	WQD	WSS	RS	Water	SD	BC	Water
1	29.50	29.50	29.50	29.50	-	13.85	13.85	3.23
2	29.50	29.50	29.50	29.50	-	13.85	13.85	3.23
3	30.00	30.00	30.00	30.00	19.00	13.85	13.85	3.25
4	60.00	60.00	60.00	60.00	19.00	13.85	13.85	3.25
5	60.00	60.00	60.00	60.00	15.00	13.85	13.85	3.25
6	60.00	60.00	60.00	60.00	16.00	13.85	13.85	3.25
7	60.00	60.00	60.00	60.00	18.65	13.85	13.85	4.90
8	27.50	27.50	27.50	27.50	9.50	13.85	13.85	4.90
9	27.50	27.50	27.50	27.50	9.50	27.70	27.70	9.65
% Mixing	23.4%	23.4%	23.4%	23.4%	6.5%	43.8%	43.8%	12.3%

Table 4 - Actual Packing Density and Moisture Content of Mixed Media

Reactive media	Packing density (kg/m ³)	Optimum moisture content (%)
Mixed DAS, WQD, WSS and RS in PRB 1 unit	1216.8	10.9
Mixed BC and SD in PRB 2 unit	234.0	18.0

3.5 Analysis of Organic Compounds and Nutrients

During the experimental run, samples were collected once every two weeks, at the inlet of PRB 1, outlet of PRB 1 and outlet of PRB 2, as the influent to PRB 1, effluent from PRB 1 / influent to PRB 2 and effluent from PRB 2 respectively, and tested in the laboratory. On a particular sampling day, 3 replicates (each 500

mL) were collected from each sampling point (totally, 9 samples per day). The results related to each parameter were averaged across the 3 replicates collected from each sampling point. Parameters were analysed according to standard procedures intended for the examination of wastewater [21]. Removal of organic compounds was tested in terms of BOD₅ and COD. BOD₅ was determined on BOD Track Apparatus (Serial No.: 0600900), while COD was analysed using the open reflux method. Removal of nutrients was analysed in terms of nitrogenous and phosphorous compounds. In these analyses, parameters of concern were Nitrate-Nitrogen (NO₃-N), Total Nitrogen (TN), Ammonia-Nitrogen (NH₃-N), Orthophosphate-Phosphorous (PO₄³⁻-P) and Total Phosphorous (TP) which were analysed by the analysis methods mentioned in Table 6 and tested on UV Visible Spectrophotometer (Serial No.: A10935004596 CD).

Table 5 - Hydraulic and Organic Loading Rates of the PRB System

Design parameter	PRB 1	PRB 2	PRB system
Flow rate (m ³ /d)	0.155	0.137	0.292
HLR (m ³ /m ² .d)	0.172	0.152	0.324
HRT (d)	5.4	7.7	13.1
OLR (kg BOD/m ³ .d)	0.05	0.01	0.06
OLR (kg COD/m ³ .d)	0.088	0.039	0.127
VLR (kg N/m ³ .d)	0.014	0.007	0.021

Table 6 - Methods of Analysis of Nutrients

Nutrient	Method of analysis
NO ₃ ⁻ - N	Screening
TN	Persulphate method
NH ₃ - N	Automated Phenate method
PO ₄ ³⁻ - P	Molybdenum Blue method
TP	Persulphate method

The removal efficiencies of each parameter were determined based on the influent and effluent concentrations. The average influent concentrations of organic compounds and nutrients during the experimental run of 140 days are indicated in Table 7.

3.5.1 Determination of Alkalinity

Total alkalinity which could be used as an indicator of nitrification process, was measured in each influent and effluent by the titration method.

Table 7 – Average Influent Concentrations

Parameter	Average influent concentration (mg/L)
BOD ₅	437.00
COD	765.20
NH ₃ -N	1.98
NO ₃ ⁻ -N	44.10
TN	100.50
PO ₄ ³⁻ -P	0.03
TP	0.48

3.6 Analysis of Reactive Material Properties

Physical and mechanical properties of reactive media were tested prior to and post the experimental run to investigate the variation of those properties with the leachate interaction. The physical properties of concern were effective particle size, uniformity coefficient and porosity, and the mechanical properties were hydraulic conductivity and shear strength.

4. Results and Discussion

4.1 Removal of BOD₅ and COD

Figure 7 shows the removal efficiencies of BOD₅ and COD in the mixed-media PRB system. The overall BOD₅ and COD removal efficiencies were 88.2±5.7% and 84.2±9.6%, respectively. These results provide the evidence that both biodegradation and adsorption could effectively take place [17]. As mentioned by Bagchi [1], biological uptake and adsorption are the major mechanisms for COD removal, whereas filtration becomes the minor mechanism [17]. In PRB, organic matter acts as a substrate for aerobic microorganisms in aerobic conditions while the reactive media bed supplies an attached growth media for microorganisms [1]. In the process of adsorption, soluble substances in contaminant plume get adsorbed onto the solid-liquid interface present in the PRB treatment zone, where the adsorbent is the reactive media. One factor that affects the adsorption rate is the surface area of particles [17]. When the particle size is small, the surface area is large and it results in a higher adsorption rate [1]. It can be concluded that the particle sizes of two media (D_{10} = 0.47 mm in PRB 1 and D_{60} = 1.70 mm in PRB 2) have contributed to enhance the adsorption process. Moreover, internal pores within the sorption media also affect the adsorption rate [17]. As per Komkiene and Baltreinaite [22], wood bio char possesses a predominant micro-porosity of 10-3000 µm and a specific surface area of 5-600 m²/g, making it a potential adsorbent.

When considering the variation of COD removal efficiency, it has dropped in the middle stage of operation. However, it has increased again towards the end of the run. This particular variation provides evidence that the adsorption process is dominant during the initial stage and drops as a result of the unavailability of empty adsorbent sites within the reactive media [17]. The reason behind the latter increase of the removal efficiency can be stated as the biochemical decomposition of organic matter. Since the microorganisms need some time period for the reproduction of adequate cells and start decomposition, this treatment mechanism may have dominated during the latter stage. This phenomenon is well explained by Bagchi [1] and it is clearly observed in the following results as well.

Figure 7 – Variation of BOD₅ and COD Removal Efficiencies

4.2 Removal of Nutrients

4.2.1 Removal of Nitrogenous Compounds

In wastewater, Nitrogenous compounds exist particularly in four forms: organic nitrogen, ammonia-nitrogen (NH₃-N), nitrite nitrogen (NO₂-N) and nitrate nitrogen (NO₃-N) [23]. Organic nitrogen is converted to ammonia-nitrogen through decomposition by heterotrophic bacteria and it can exist as NH₃ or NH₄⁺ based on the pH of the medium [23]. Nitrite-nitrogen, formed during nitrification, is unstable and easily converted to nitrate nitrogen [23]. Thus, NO₃-N is the most abundant N-compound in wastewater [23]. Based on these facts, the removability of NH₃-N and TN (the sum of ammonia, organic and reduced nitrogen) and variation of NO₃-N concentration were determined throughout the experimental run.

The overall removal efficiencies of NH₃-N and TN (Figure 8) were 95.6±4.2% and 67.1±21.3%, respectively. The mechanism of removing ammonia in PRBs could be adsorption [1]. Additionally, autotrophic nitrification processed by nitrifiers (Nitrosomonas and

Nitrobacter) and assimilation also result in ammonia removal [23]. In case of nitrification, the media should provide adequate oxygen for nitrifiers. Since the reactive bed is open to atmosphere, the topmost region of the reactive media is in contact with adequate O_2 , but when going down the reactive bed, it gradually becomes anoxic/anaerobic. Therefore, it is likely that nitrification does not occur throughout the whole media profile. Another fact is that, during nitrification, assimilative reactions also occur causing NH_4^+ to assimilate onto bacterial cells [23]. Accordingly, apart from adsorption, a portion of ammonium could decrease by overall oxidation and assimilation. However, when looking at the high NH_3 -N removal efficiencies (Figure 8), it is confirmed that not only one, but all of the above mechanisms have contributed to it, as discussed below.

In Figure 8, at the initial stage (up to first 40 days), a high NH_3 -N removal efficiency is observed. However, nitrification cannot be the dominant cause for that, because Nitrosomonas that converts ammonia to nitrite (the first step of nitrification process) has a very slow growth rate [23], hence a high nitrification rate cannot be expected initially. This leaves the conclusion that ammonium adsorption has dominated first. Sudden efficiency drops at the middle stage could be due to adsorbent phases getting limited with time. Thus, during the final stage, adsorption solely cannot be the dominant mechanism.

However, a high NH_3 -N removal efficiency is observed at the latter stage as well. It can be explained with reference to nitrification and by relating NO_3 -N concentration and alkalinity variation shown in Figure 9 and 10, respectively. Among the environmental conditions that favour the growth of nitrifiers, pH maintained above 7 (in alkaline range) is quite important [23]. Theoretically, during nitrification, 7.14 mg of alkalinity as $CaCO_3$ is destroyed per 1 mg of ammonium ions oxidized [23]. Based on this phenomenon, low alkalinity is expected at high NO_3 -N concentrations. As shown in Figure 9, NO_3 -N concentration is higher in the effluent than that in the influent. Figure 10 shows that the alkalinity of the effluent is smaller than that of the influent. Accordingly, it is convinced that within PRB reactors, alkalinity has been consumed to oxidize ammonia into nitrate, resulting in high NO_3 -N concentrations and reduced alkalinity. Furthermore, Figure 9

shows that NO_3 -N in PRB 1 is always higher than that of PRB 2 effluent. These observations imply that while nitrification dominated in PRB 1, denitrification has considerably occurred in anoxic zones of PRB 2. As NO_3 -N does not undergo the process of adsorption due to its high mobility [1], and is not removed by ion exchange due to both nitrates and PRB media are in anion form [1], the only possible way to remove nitrates is denitrification by heterotrophs.

Referring to TN removal (Figure 8), initially a high removal efficiency has occurred because of adsorption of ammonia. The experimental period of 140 days is considerably a sufficient period of time for heterotrophic bacteria to grow largely and anoxic zones to develop within the reactive media. These conditions will result in the removal of nitrate by reducing to nitrogen gas through denitrification process. This could be the main reason for achieving an overall TN removal efficiency of above 60% in the system. TN removal efficiency has dropped in the latter stage, probably due to less availability of adsorbent phases in the reactive media [13].

Figure 8 - Variation of NH_3 -N and TN Removal Efficiencies

Figure 9 - Variation of NO_3 -N Concentration

4.2.2 Removal of Phosphorus Compounds

The overall removal efficiencies of PO_4^{3-} -P and TP were $76.5 \pm 7.6\%$ and $77.8 \pm 22.2\%$, respectively (Figure 11). The responsible factor for this achievement could be the presence of DAS in PRB 1. DAS is an efficient adsorbent for

phosphorous compounds [7] and its adsorption capacity has not significantly reduced over the considered time to make a negative impact on the overall removal efficiency of $\text{PO}_4^{3-}\text{-P}$ and TP.

Figure 10 – Variation of Total Alkalinity

Figure 11 – Variation of $\text{PO}_4^{3-}\text{-P}$ and TP Removal Efficiencies

4.3 Variations of Reactive Material Properties
The physical properties such as effective particle size, uniformity coefficient and porosity, and the mechanical properties such as hydraulic conductivity and shear strength of reactive media (before and after the experimental run) in PRB 1 and PRB 2, are shown in Table 8 and Table 9, respectively. These results are essential to understand the treatment capacity and the durability of the PRB system.

According to Table 8, the effective particle size in reactive media of PRB 1 has increased with the adsorption of contaminants onto material surfaces. However, the observation in reactive media of PRB 2 was opposite due to wearing away of BC (Table 9). As per the case history of the ZVI barrier installed in Kansas City Plant, United States (1998) [24], its design hydraulic conductivity to achieve under 52 lb/ft³ (1836.36 kg/m³) packing density, was 34 ft/d (0.012 cm/s). However, researchers suggest that PRB longevity is affected by permeability loss over time [25, 26], owing to high carbonate, nitrate, DOC (dissolved organic carbon) and TDS (total dissolved solids) concentrations [27].

Accordingly, a hydraulic conductivity of >0.012 cm/s was targeted for two PRBs under packing densities of <1836.36 kg/m³ (Section 3.3). By determining the individual conductivities of the two PRBs, the equivalent hydraulic conductivity of the overall PRB system prior to experimental run, was found to be 0.030 cm/s, which satisfies the above criterion. This equivalent permeability of the system has decreased to 0.027 cm/s after the run, because of reduced porosity due to clogging of particles in voids. The interior molecular attraction due to ion exchange has resulted in increasing the cohesion and the leachate that passes through has caused a reduction in surface friction [1]. As depicted by these values, the resulting variations are not significant enough to affect the efficiency of the system during 140 days.

Table 8 – Physical and Mechanical Properties of Reactive Materials in PRB 1

Parameter	Before the experimental run	After the experimental run
Effective size (D_{10}) (mm)	0.47	0.54
D_{60} (mm)	1.60	2.40
Uniformity coefficient (D_{60}/D_{10})	3.40	4.44
Porosity	0.62	0.60
Hydraulic conductivity (cm/s)	0.023	0.021
Cohesion (kPa)	26.9	34.2
Friction angle (deg.)	42.4	36.8

Table 9 – Physical and Mechanical Properties of Reactive Materials in PRB 2

Parameter	Before exp. run	After exp. run
Effective size (D_{10}) (mm)	–	–
D_{60} (mm)	1.70	1.50
Uniformity coefficient (D_{60}/D_{10})	–	–
Porosity	0.78	0.72
Hydraulic conductivity (cm/s)	0.043	0.039
Cohesion (kPa)	0.3	0.5
Friction angle (deg.)	2.9	2.4

5. Conclusions

DAS, WQD, WSS, RS, BC and SD in mixed-media PRB system have potential to treat organic, nitrogenous and phosphorus compounds of groundwater contaminated by landfill-leachate. Hence, the above reactive materials can be used not only as PRB reactive media, but they can effectively replace the filter media in other leachate treatment units. The properties of these reactive materials have not been subjected to significant variations due to leachate interaction, and removal efficiencies have not been affected by it during 140 days. Hence, the reactive beds seem to have longer effective life time exceeding this 140-day period. Further research on longer experimental runs are recommended to verify the above statement.

The overall HRT of the PRB system (13.1 days) has resulted in better removal of contaminants, especially in COD, when compared with an up-flow anaerobic sludge blanket (UASB) reactor operated for actual sewage treatment and removed total COD by 70% at a fixed HRT of 4.7 hours [28]. The usage of more than one PRB unit connected in series has increased the treatment efficiencies when compared with the results of a single PRB unit (same PRB unit with the same reactive materials) conducted by the authors in the recent past [10].

It can be concluded that this PRB system provides economic benefits as well as encourages waste material reuse, contributing to the environmental sustainability. Therefore, it can become a quite feasible application in all aspects.

As future directions, it is recommended to do more studies on the long-term performance of the PRB system. It has to be achieved by building up a relationship between the removal efficiencies and reactive material properties. Once such a relationship is built up, it can be used to identify the exact treatment failures of the system. This finding will be quite beneficial to the accurate prediction of the duration for which the reactive bed can be used. Based on that, appropriate measures could be taken to enhance the design life.

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References

1. Bagchi, A., *Design of landfills and integrated solid waste management*, 5th ed., 2004.
2. Snow, D. H., *Overview of Permeable Reactive Barriers*, pp. 184, 1999.
3. Thiruvengkatachari, R., Vigneswaran, S. & Naidu, R., "Permeable Reactive Barrier for ground water remediation: a review", *Journal of Industrial and Engineering Chemistry*, Vol.2, No.14, pp. 145-156, 2008.
4. Obiri-Nyarko, F., Grajales-Mesa, S. J., & Malina, G., "An overview of permeable reactive barriers for Insitu sustainable groundwater remediation", *Chemosphere*, Vol. 111, pp. 243-259, 2014.
5. Carey, M. A., Fretwell, B. A., Mosley, N. G. & Smith, J. W. N., *Guidance on the use of permeability reactive barriers for remediating contaminated ground water*, Solihull: Environmental Agency, Rio House, Waterside Drive, Aztec West, Bristol, BS32 4UD, September, pp.102-118, 2002.
6. Dayanthi, W. K. C. N., Arthanayaka, A. M. C., Asiri, K. K. V. L. & Malkanthi, K. A. R., "Applicability of Waste Matter as Reactive Media in Permeable Reactive Barriers (PRBs) to Treat Landfill-Leachate Contaminated Groundwater", *Transactions 2014, Institution of Engineers, Sri Lanka (IESL)*, Vol.1-Part B, pp. 203-210, 2014.
7. Bugabee, G. J. and Frink, C. R., *Alum sludge as a soil amendment: Effects on soil properties and plant growth*, pp. 1-3, November 1985.
8. Scherer, M. M., Richter, S., Valentine, R. L., & Alvarez, P. J. J., "Chemistry and Microbiology of Permeable Reactive Barriers for In Situ Groundwater Clean Up", *Critical Reviews in Environmental Science and Technology*, Vol. 30, No. 3, pp. 363-411, 2000.
9. Naidu, R., "Recent advances in contaminated site remediation", *Proc., Taipei International Conference on Remediation and Management of Soil and Ground Water Contaminated Site*, Taipei: International convention centre, 2012.
10. Chathuranga, W. G. O., Rathnasekara, J. P. A. S., Dayanthi, W. K. C. N., Kawamoto, K., Perera, K. K. D. M., Praneeth, K. G. M., Asela, W. A. P., Inoue, Y. & Sandamali, M. A. N., "Field-Scale Study on Treating the Groundwater Contaminated by Landfill-Leachate with Permeable Reactive Barriers (PRBs)", *ACEPS*

- 2016: *Proceedings of the 5th International Symposium on Advances in Civil and Environmental Engineering Practices for Sustainable Development*, Department of Civil and Environmental Engineering, University of Ruhuna, Sri Lanka, pp. 149-155, 2016.
11. Blowes, D. W., Ptacek, C. J., Benner, S. G., McRae, C. W. T., Bennett, T. A., Puls, R. W., "Treatment of inorganic contaminants using Permeable Reactive Barriers", *Journal of Contaminant Hydrology*, Elsevier Science, Vol. 45, pp.123-137, 2003.
 12. US Environmental Protection Agency, *Permeable Reactive Barrier Technologies for Contaminant Remediation*, pp.168-241, 1998.
 13. Higgins, M., *Environmental assessment of in situ ground water remediation with reduced iron reactive media*, Michigan, pp. 208-2016, 2011.
 14. Zhao, Y. Y., Babatunde, Y. Q., Wang, L., Ren, Y. X., & Han, Y., "Characteristics and Mechanisms of Phosphate Adsorption on Dewatered Alum Sludge", *Separation and Purification Technology*, Vol. 51, N. 02, pp. 193-200, 2006.
 15. Razali, M., Zhao, Y. Q., & Bruen, M., "Effectiveness of a Drinking-Water Treatment Sludge in Removing Different Phosphorous Species from Aqueous Solutions", *Separation and Purification Technology*, Vol. 55, No. 03, pp. 300-306, 2007.
 16. Ping, F., Chaoping, C., Dingsheng, C., & Zhixiong, T., "Carbonaceous Adsorbents Prepared from Sewage Sludge and its Application for GH0 Adsorption in Simulated Flue Gas", *Separation Science and Engineering, Chinese Journal of Chemical Engineering*, Vol. 18, No.02, pp. 231-238, 2010.
 17. Dayanthi W. K. C. N., Shanthapriya, S. J. P., Nayomi, S. D., Kawamoto, K. & Sandamali, M. A. N., "Laboratory-Scale Column Experiments of Waste Matters as Reactive Media in Permeable Reactive Barriers (PRBs) to Treat Groundwater Contaminated by Landfill-Leachate.", *Transactions 2015, Institution of Engineers, Sri Lanka (IESL)*, Vol.1-Part B, pp.315-322, 2015.
 18. Rasheed, A., Sana, S., Kashif, S., Umer, Z. & Khatoon, M., "To Evaluate the Efficiency of Char and Biochar for Waste Water Treatment", *Journal of Waste Recycling*, Vol. 2, No. 2:7, 2017.
 19. Assiddieq, M., Darmayani, S., & Kudonowarso, W., "The use of silica sand, zeolite and activated charcoal to reduce BOD, COD and TSS of laundry waste water as a biology learning resources", *Indonesian Journal of Biology Education*, Vol. 3, No. 3, pp. 202-207, 2017.
 20. Mohajeri, P., Selamat, M. R., Aziz, H., A., & Smith., C., "Removal of COD and Ammonia Nitrogen by a Sawdust/Bentonite-Augmented SBR Process", *Clean Technologies*, Vol. 1, pp. 124-140, 2018.
 21. American Public Health Association, *Standard methods for the examination of water and wastewater*, 18th ed., Washington, DC, 1998.
 22. Komkiene, J., & Baltrenatite, E., "Biochar as adsorbent for removal of heavy metal ions [Cadmium (II), Lead (II), Zinc (II)] from aqueous phase", *International Journal of Environmental Science & Technology*, Vol. 13, pp. 471-482, 2016.
 23. Cheremisinoff, N. P., *Biotechnology for Waste and Wastewater Treatment*, 1st ed., Noyes Publications, Westwood, New Jersey, USA, pp. 151-174, 1997.
 24. Korte, N. E., "Zero-Valent Tron Permeable Reactive Barriers: A Review of Performance, Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 87831, pp. 2-8, April 2001.
 25. Phillips, D. H., Gu, B., Watson, D. B., Roh, Y., Liang, L. Y., & Lee, S. Y., "Performance Evaluation of a Zero Valent Iron Reactive Barrier: Mineralogical Characteristics", *Environmental Science and Technology*, Vol. 34, No. 19, pp. 4169, 2000.
 26. Liang, L. Y., Sullivan, A. B., West, O. R., Moline, G. R., & Kamolpornwijit, W., "Predicting the Precipitation of Mineral Phases in Permeable Reactive Barriers", *Environmental Science and Technology*, Vol.20, No. 06, 635, 2003.
 27. Henderson, A. D., & Demond, A. H., "Long-Term Performance of Zero-Valent Iron Permeable Reactive Barriers: A Critical Review", *Environmental Engineering Science*, Vo. 24, No. 4, pp.402, 2007.
 28. Uemura, S., & Harada, H., "Treatment of sewage by a UASB reactor, under moderate to low temperature conditions", *Bioresource Technology*, Vol. 72, No. 3, pp. 275-282, 2000.