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Low-Cost Sequential Permeable Reactive Barrier (PRB) to Treat Groundwater Contaminated by Landfill-Leachate

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Abstract: Permeable Reactive Barrier (PRB) is an on-site treatment technique, which can be effectively used for remediating the groundwater contaminated by landfill - leachate. The objective of this study was to investigate the applicability of several low – cost/waste materials as the reactive media in a bench-scale sequential PRB model to treat the contaminated groundwater by landfill – leachate. There were two bench-scale sequential PRB models as experimental and control. Dewatered alum sludge (DAS), washed quarry dust (WQD), fire-wood charcoal (FWC), sea sand (SS) and saw dust (SD) were placed in the experimental model whereas the control model was filled with red laterite soil (RLS), and commonly used zero valent ion (ZVI) and granular activated carbon (GAC) as vertical equal layers. The target wastewater parameters were organic matter (COD and BOD_5), nitrogenous compounds (NH_3-N, NO_3^--N and TN) and heavy metals (Cd, Cu, and Fe). The overall removal efficiency of BOD_5 and Cd were greater than 90% and almost 100%, respectively. Further, the masses of BOD_5 and TN removed during the entire run of the experimental model were almost the same as those of the control model. Hence, it can be concluded that the low – cost/waste materials used in the experimental model have a potential to be used as reactive media in PRBs aiming at treating the landfill – leachate. Further, this would be a sustainable reuse application for waste materials to be dumped.

Keywords: Bench - scale model, Groundwater, Landfill – leachate, Low – cost/waste materials, Permeable reactive barrier

1. Introduction

Landfill- leachate is the longest lasting negative effect of landfills, which is produced when rain flows through the waste [1]. It consists of a wide range of pollutants, including organic compounds, nutrients, and heavy metals that can easily percolate through soil and deteriorate the quality of groundwater and surrounding soil [2]. Therefore, treating landfill-leachate is of utmost importance to attain acceptable standards prior to be released to the environment in order to minimize potential risks to the human health and aquatic flora and fauna [3].

Permeable reactive barriers (PRBs) have been identified as a sustainable and innovative on-site treatment technique to treat contaminated groundwater [4]. An emplacement of reactive materials in a subsurface designed to intercept a contaminant plume, which provides a flow path through the reactive media, is known as a PRB, and it transforms contaminant(s) into environmentally acceptable forms to attain remediation concentration goals down gradient of the barrier [5]. As gravity is used, there is no need of additional energy. In addition, a variety of contaminants, which cannot be removed by conventional methods, can be treated by PRBs, with limited cross contamination under low-cost and maintenance. Furthermore, PRBs are much more economical than the traditional pump – and - treat technologies, even with conventional and expensive reactive materials

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such as granular activated carbon (GAC), zero valent iron (ZVI) and zeolites [6]. PRB technology is usually applied with a single reactive material to treat only one type of contaminant. They are also aimed at treating groundwater contaminated by other means than landfill-leachate. The cost of PRBs can be reduced further by applying low-cost/waste materials as reactive media. A single reactive material is good at treating one contaminant, owing to limited properties. The treatment mainly depends on chemical and physical properties of the reactive materials. The longevity of the reactive barrier depends on the mechanical properties of the reactive media and hydraulic parameters. Liu et al. [7] stated that the effectiveness of PRBs greatly depends on the reactive media. Mohammed et al. [8] stated that a good reactive material should possess reactivity, stability, availability, cost, hydraulic performance and environmental compatibility. According to the same author, the lack of these properties would lead to partial treatment and production of less desirable by-products. Obri-Nyarko et al. [9] stated that conventional high-cost reactive materials such as ZVI, halogenated aliphatic hydrocarbons, activated carbon, zeolite, appetite etc. produce toxic sludge. Unlike groundwater contaminated with one contaminant, landfill-leachate consists of several contaminants. Hence, a reactive media bed treating landfill-leachate should address several contaminants together. Therefore, the conventional single reactive media bed would not be suitable for landfill-leachate. A combination of several materials will possess diverse properties, and thereby would be able to treat several contaminants simultaneously. According to Obri-Nyarko et al. [9], more research is still required to understand treatment mechanisms of diverse reactive media despite that lots of efforts have been made to elucidate the mechanisms of contaminants removal by them.

The packing arrangement of the reactive media bed is also a key factor that can affect the removal efficiency. Laboratory-scale studies have been vastly carried out to identify alternative materials as reactive media. The packing configurations in most of these studies have been scrutinized against either upward or downward flow directions using vertical columns. On the contrary, the contaminant flow inside a PRB wall in a real ground, takes the resultant direction of both horizontal and vertical flow components. Hence, a rectangular model would be closer to reality than a laboratory-scale PRB column. Nonetheless, experiments based on rectangular PRB models aiming at groundwater contaminated with landfill-leachate are limited. On the other hand, if it is possible to alternate PRB walls with low – cost, locally and readily available materials, it will be an obvious, sustainable, and economical solution for reducing groundwater contamination due to landfill – leachate.

According to past research, a number of low-cost/waste materials have been identified as potential packing materials for wastewater treatment in different types of treatment systems. Dewatered alum sludge (DAS) consists of abundant amorphous aluminium ions, which can be reused to remove phosphorus in wastewater since the ions enhance processes of adsorption and chemical precipitation [10]. Fire-wood charcoal (FWC) is a porous carbon material with adsorbent properties. Removal of mercury has been studied by Pulido et al. [11] using FWC. Washed query dust (WQD) is also very porous, which occupies several chemically active sites. Adsorption rate on WQD relies on the specific surface area and the average pore radius [12]. Mungathia [13] found that WQD can adsorb 96% of Zn and 94% of Cu from industrial effluent. Washed SS has been utilized as one of PRB media to adsorb organic compounds by Wagen et al. [14]. Furthermore, Nebagha et al. [15] have used treated SS as an adsorbent to remove Cu^{2+} from aqueous solutions. SS can be used as a siliceous adsorbent to treat wastewater. Saw dust (SD) is an inexpensive, relatively abundant waste material currently being investigated as an adsorbent to remove contaminants from wastewater. By using saw dust chemical substances such as oil, dyes and heavy metals, toxic salts can be removed effectively [16].

Hence, this study was carried out to assess the removal efficiencies of contaminants found in groundwater contaminated by landfill – leachate using a bench – scale sequential PRB model with combined reactive media consisting of low – cost/waste materials. DAS, FWC, WQD, SS and SD were selected as the reactive materials, of which the treatment potential was investigated. The objectives of the study were to obtain the removal efficiencies of different types of contaminants found in landfill – leachate; compare those values with the performances of typical PRB media like ZVI and GAC, and typical soil; and examine the variations of physical and mechanical properties of the reactive media due to the interaction with landfill-leachate.

2. Methodology

2.1 Overall Procedure

There were two rectangular bench – scale models, of which one reactor acted as an experimental - sequential PRB with combined media consisting of low-cost/waste materials, namely DAS, FWC, WQD, SS and SD. The other reactor was the control PRB model, comprising red laterite soil (RLS), zero valent iron (ZVI) and granular activated carbon (GAC). Landfill - leachate was collected from the Galle Municipal Council (GMC) dumpsite. According to a pre-determined schedule, both influent and effluent samples were collected, and then analyzed in terms of several wastewater parameters. The volumes of influent loaded on to reactors and effluent discharged throughout the experimental series were noted down to conduct mass balance analysis to obtain the overall removal efficiencies of each wastewater parameter. Finally, the removal efficiencies of the experimental sequential PRB model and control model were compared.

2.2 Experimental Run

Figure 1 shows the experimental set – up. Two glass tanks (0.550 x 0.295 x 0.500 m) modelled the experimental sequential and control PRB models. Each tank consisted of compartments on either side of the reactive media bed, which were storage tanks for influent and effluent, respectively. A perforated plate was used to separate those compartments from the reactive media. Influent was prepared by diluting the raw landfill - leachate 10 times to make the influent possess approximately similar characteristics to that of the contaminated groundwater with landfill – leachate. The influent was stored in an overhead tank and distributed to the influent compartment of each PRB model under gravitational force. Subsequently, it gradually infiltrated into the reactive media bed. The wastewater plume that percolated through the reactive media bed, could approximately represent a plume of groundwater mixed with contaminated landfill-leachate inside an actual PRB wall underground.

Reactive media in the experimental sequential PRB model was compartmentalized into five portions, each with 0.075 m thickness as shown in Figure 2(a). FWC, SD, WQD, DAS and SS were placed in these compartments from influent storage tank to effluent storage tank according to the descending order of their particle sizes. Pea gravel was placed in the portion immediately before the effluent storage compartment to act as a filtration bed for the treated water coming out of the reactive media bed.

Figure 1 - Experimental Set-Up

Reactive media in the control model was compartmentalized into three portions, and RLS, ZVI and GAC were then placed in these compartments from influent storage compartment to effluent storage compartment as illustrated in Figure 2(b).

Pea gravel was also filled in the compartment immediately before the effluent storage tank to act as a filtration bed. All reactive materials and pea gravel were washed and dried before filling in the PRB models. FWC was cut into about 0.01 m pieces. The packing densities of the reactive materials are shown in Table 1.

Table 1 - Packing Densities of the Reactive Materials

Bench scale model	Reactive material	Total mass (kg)	Packing density (kg/m^3)
Experimental sequential PRB model	FWC	1.84	219.66
	SD	1.46	174.23
	QD	14.29	1704.91
	DAS	8.04	959.91
	SS	10.72	1279.10
Control PRB model	RLS	20.34	1270.45
	ZVI	26.92	2001.11
	GAC	6.35	495.80

After filling reactive materials and pea gravel in both the models, the reactive media bed was flushed out with tap water until there was no readily flushable contaminant in the effluent.

Effluent samples were collected every - five day period, while influent was characterized once every ten day period within a total experimental run of 50 days. Both influent and effluent samples were analyzed in terms of COD, BOD_5, NH_3 – N, NO_3^--N, TN and several heavy metals (Cu, Fe, Cd). All the wastewater analyses were done in accordance with the Standard Methods of the Examination of Water and Wastewater [17].

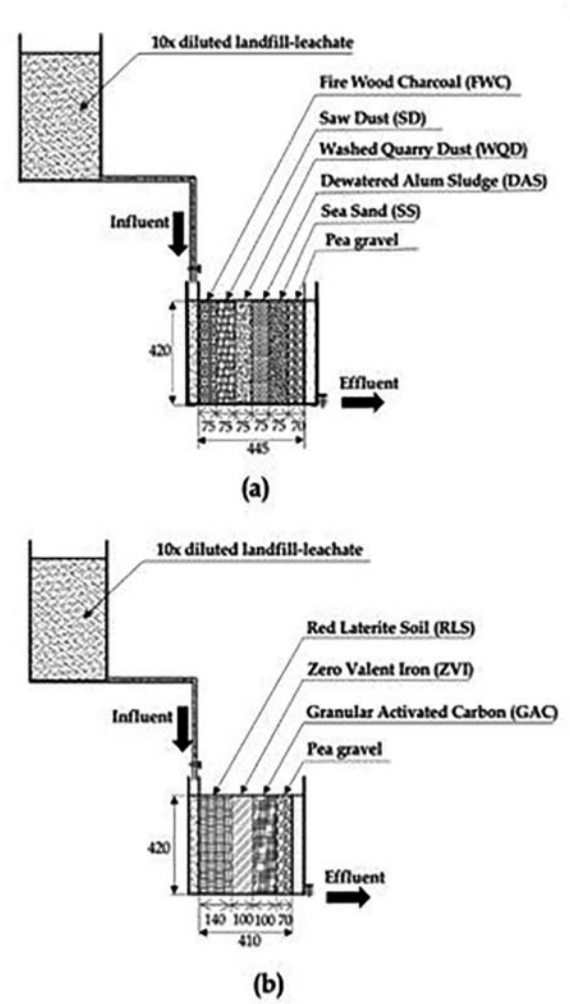

Figure 2 - Schematic Diagram of (a) Experimental Sequential PRB Model (b) Control PRB

2.3 Mass Balance Analysis

Finally, mass balances were performed for the measured wastewater parameters. According to the theory of mass balance, removed mass of the concerned parameter during an entire experimental run was equal to the difference of masses between influent and effluent [18]. In computing the total mass of influent and effluent, the concentration of the concerned parameter was multiplied by the total volume of influent applied and effluent collected during the experimental run, respectively.

2.4 Physical and Mechanical Properties of Reactive Materials

To obtain the changes of the reactive media with the interaction of simulated groundwater, several physical and mechanical properties were measured before and after the experimental run. The physical properties included the particle size distribution in terms of effective size and uniformity coefficient, specific gravity, and porosity. The particle size was obtained by conducting a sieve analysis test. Porosity was computed using the specific gravity values measured. The mechanical properties included the shear strength parameters, namely cohesion and friction angle measured using the direct shear test. Table 2 summarises the material properties and corresponding testing methods used.

Table 2 - Material Properties and Corresponding Method

Parameter	Method
Particle size distribution	Sieve analysis
Particle density	Specific gravity test
Permeability	Hydraulic conductivity test
Shear strength	Direct shear test

3. Results and Discussion

3.1 Introduction

Removal efficiencies of organic and nitrogenous compounds and heavy metals along with variations of reactive material properties during the experimental run are discussed in the following sub sections. Figure 3 displays how influent characteristics fluctuated during the experimental run. Treatment mechanism in this system was expected to be greatly similar to natural attenuation mechanisms in soil such as adsorption, biological uptake, cation and anion exchange reactions, dilution, filtration and precipitation, in accordance with Bagchi [19]. Aerobic conditions could prevail in the uppermost parts of PRB models because they were open to the atmosphere. Nonetheless, anoxic zones could also exist.

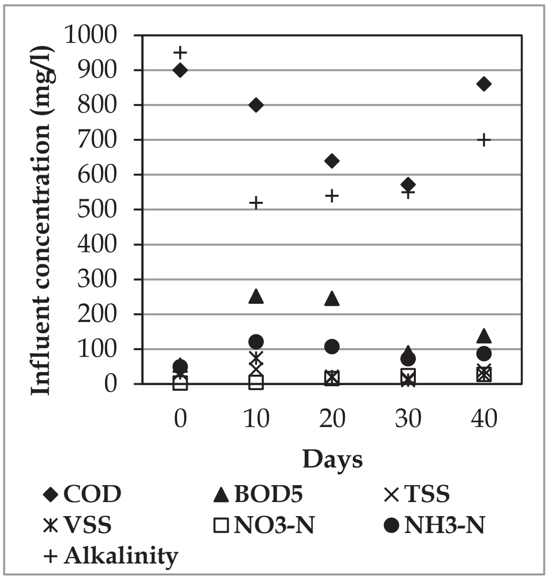

Figure 3 - Variation of Influent Characteristics

3.2 Removal of Organic Compounds

Typical organic compounds found in the groundwater contaminated by landfill-leachate are volatile fatty acids, humic, fulvic compounds, and toxic halogenated hydrocarbons. In this study, organic matter removal was determined in terms of COD and BOD_5. Table 3 depicts the percentage mass removed from each experimental set-up for COD and BOD_5.

Figures 4 and 5 show the temporal variation of COD and BOD_5 removal efficiencies, respectively, for control and experimental PRB models against no. of pore volumes. The control model showed almost 100 % of COD removal efficiency throughout the test run. The experimental model also displayed a considerable potential in COD removal. Though there was rise and fall in the middle, an average removal efficiency around 80% was attained.

Table 3 - Mass Removal of Organic Compounds with Time

Organic compound	Mass removal (%)	
	Experimental model	Control model
COD	77.2	99.8
BOD_5	83.0	83.3

The COD removal efficiencies of both the models were considerably greater than that of a sequential reactor consisting of quartz and ZVI (66.8%), and oxygen releasing compounds (ORC) (75.85%), investigated by Jun et al. [20]. Further, the same authors obtained COD removal efficiencies for a sequential reactor of quartz, ZVI and zeolites (80.5%), and of ORC (51.37%). Most importantly, the current study shows quite steady removal efficiency throughout the run, which implies that PRB models in this study have the capacity to treat COD further.

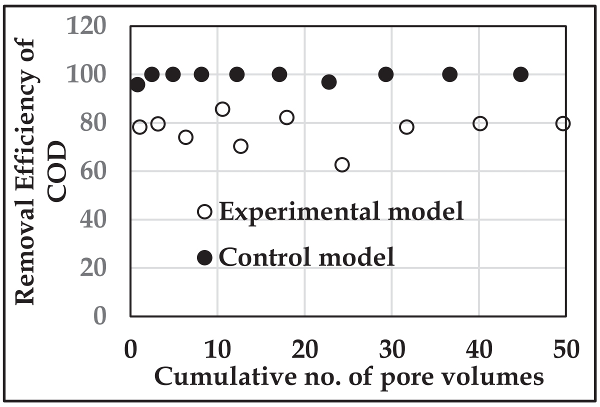

Figure 4 – Variation of COD Removal Efficiency

It is important to note that the overall BOD_5 removal efficiency of the experimental model (83%) was the same as that of the control model. Hence, the BOD_5 treatment potential of the low-cost reactive media was on a par with that of the conventional reactive media and typical soil.

Organic matter removal could be led by biochemical processes. Both aerobic and anoxic zones that had prevailed inside reactive media could contribute to biochemical decomposition. Anerobic processes could remove suspended solids and reduce organic load for the aerobic degradation, consequently, reduce the oxygen requirement and thereby increase the efficiency of aerobic decomposition [21]. Aerobic microbes could sustain using organic matter as substrate and reactive media as growth media. These processes take some time to execute. Hence, BOD_5 removal attributed to biochemical processes could not happen at the very beginning. Adsorption could contribute to the removal at the very beginning of the experimental run. Besides, hydrophobic expulsion is also a dominant mechanism for removal of the most nonpolar organic compounds [22]. For that, reactive media surfaces consisting of exchangeable molecules are important. The removal attributed to hydrophobic expulsion could decrease at the absence of exchangeable molecules in the latter stage of the experimental run.

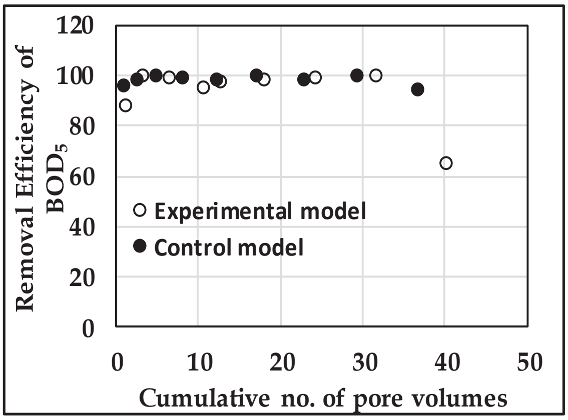

Figure 5 - Variation of BOD_5 Removal Efficiency

Figure 6 depicts the temporal variation of ORP over a period of 50 days. Both models had ORP of around 200 mV during the first few days. It gradually decreased to 50 mV following the same pattern providing evidence that redox status changed to a low oxidizing state from a high oxidizing state [23]. The net change of the ORP indicates the net occurrence of oxidation reactions.

3.3 Removal of Nitrogenous Compounds

Table 4 gives the percentage mass removed from each experimental set-up for nitrogenous compounds. Basically, four forms of nitrogenous compounds can be found in wastewater as organic nitrogen, ammonia nitrogen (NH_3-N), nitrite nitrogen (NO_2^--N) and nitrate nitrogen (NO_3^--N) [20].

Figure 7 shows the variation of removal efficiency of NH_3-N. Adsorption could be the major mechanism. At the same time, nitrification and assimilation could occur [24]. Nitrification might be notable to a considerable extent in the PRB models because of the reactive media being in contact with the atmosphere. NH_3-N removal could be a result of all these mechanisms. The removal efficiency decreased gradually in both the models. The reduction of the vacant sites may have reduced the removal efficiency via adsorption, with time. At the latter part, the removal may have been contributed by the execution of nitrification.

Temporal variation of TN removal is presented in Figure 8. Total kjeldahl nitrogen (organic and reduced nitrogen), NH_3-N, NO_2^--N and NO_3^--N are expressed in TN [13]. Comparatively higher removal efficiency of TN at the early stage could be attributed to the ammonia adsorption. Additionally, as per Gebhard [25], denitrification and immobilization as organic nitrogen could get together with sorption and fixation to yield a net reduction of both ammonium and TN in leachate within 50 days. Therefore, denitrification could occur by the heterotrophic bacteria in anoxic zones within the reactive media. Both models followed approximately similar trend, and the removal efficiency decreased over the time span.

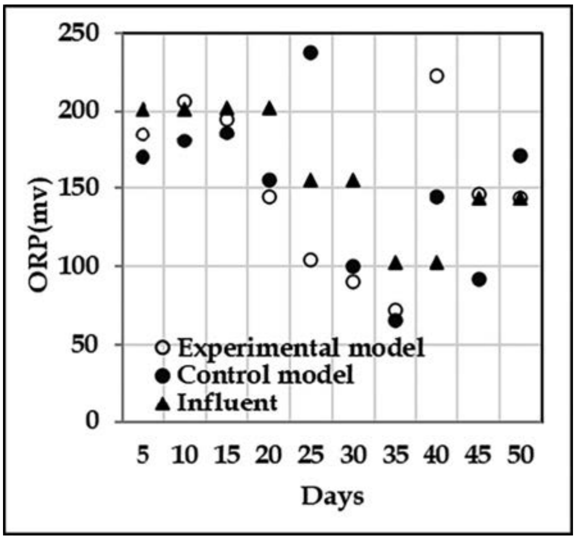

Figure 6 - Variation of Oxidation Reduction Potential (ORP)

Table 4 - Mass Removal of Nitrogenous Compounds with Time

Nitrogenous compound	Mass removal (%)	
	Experimental model	Control model
NH_3 - N	61.2	74.3
NO_3^-N	20.7	86.3
TN	38.7	38.6

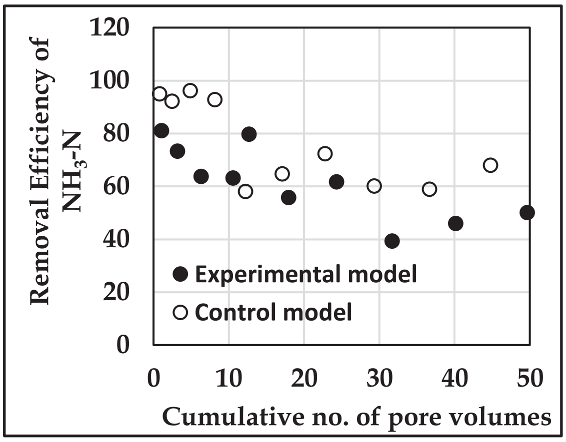

Figure 7 - Variation of NH_3-N Removal Efficiency

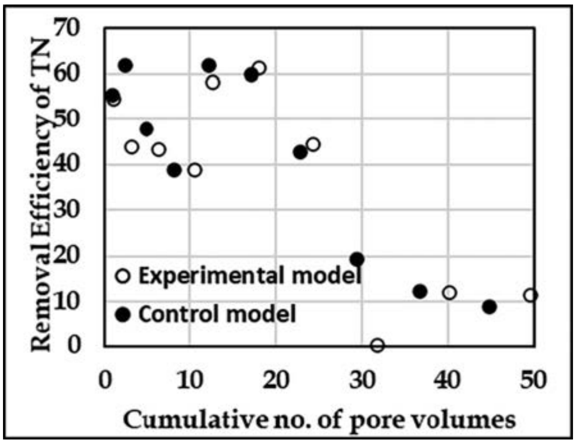

Figure 8 - Variation of TN Removal Efficiency

Figure 9 shows the variation of NO_3^--N concentration with time. This concentration in the influent decreased with time. The concentrations in the effluent were having the same pattern of the variation of influent concentration. The experimental model provided the favourable conditions for the growth of nitrifiers, in terms of optimal pH range (7.0 to 8.0), whereas the control model had pH of lower than 7 (Figure 10). Further, Figure 11 shows lower alkalinity in PRB models than that of the influent. Alkalinity is consumed in oxidizing ammonia into nitrate and generated due to denitrification [25], [26]. Hence, the effluent alkalinity value could be altered by both the processes.

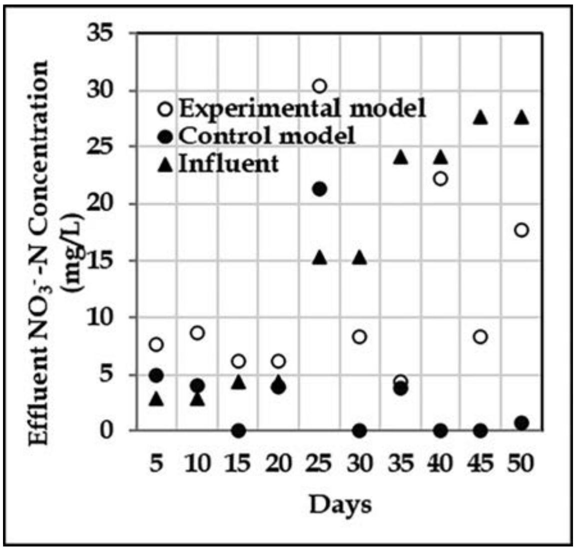

Figure 9 - Variation of NO_3^--N Concentration

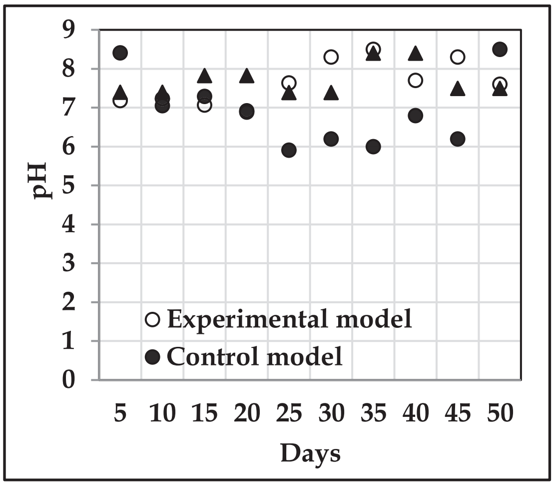

Figure 10 - Variation of pH

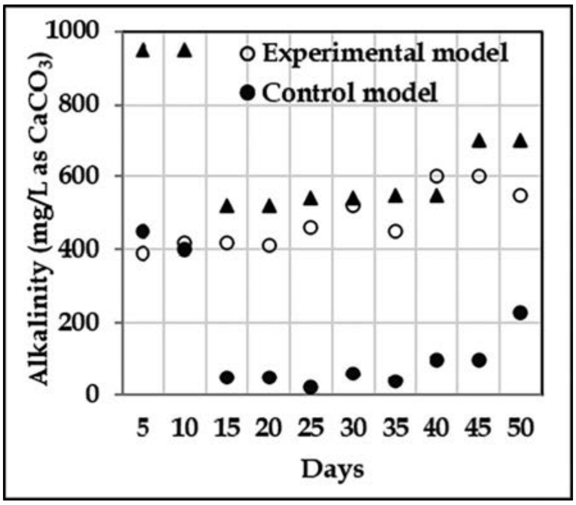

Figure 11 - Variation of Alkalinity

3.4 Removal of Heavy Metals

Heavy metals are the most toxic pollutants that can be found in groundwater contaminated by landfill-leachate. Chaari et al. [26] stated that adsorption has been proved as a promising technique for removing heavy metals, particularly by activated carbon. ZVI has the ability of removing Cr and Pb [25]. Jun et al. [20] stated that the increment of CO_3^{2-} and OH^- results in a precipitation of the heavy metals. In addition to that, some of heavy metals can be precipitated as sulphides. The best treatable heavy metal by experimental PRB model was Cd, which attained complete removal of 100% throughout the experimental run as shown in Figure 12. Jun et al. [20] could achieve Cd removal efficiencies of 88 % and 64.3 % for two reactors filled with quartz and ZVI, and oxygen releasing compounds, respectively. On the other hand, Cu removal was not remarkable by the experimental PRB model (Figure 13). However, control model showed a considerable removal efficiency for Cu. The highest removal efficiency, which was around 90%, was gradually achieved by the 30th day and it dropped below 60 % toward the end of run. The treatment mechanism could be attributed to the limitation of vacant sites for adsorption.

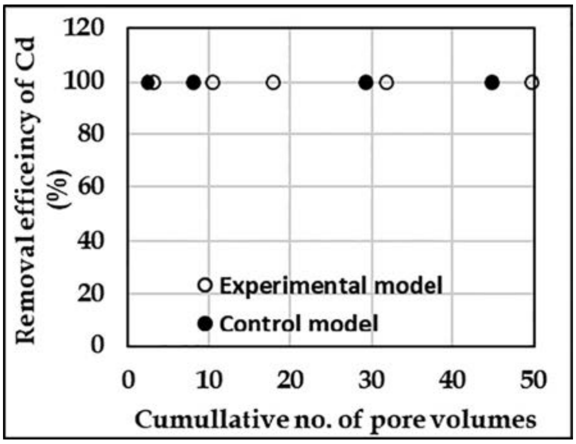

Figure 12 - Variation of Cd Removal Efficiency

Figure 14 indicates the variation of removal efficiency of Fe with time. The control model showed overall removal efficiency around 80% while the experimental model displayed an average removal efficiency above 80%. Precipitation, cation exchange, adsorption and biological uptake are the important attenuation mechanisms of Fe according to Bagchi [19].

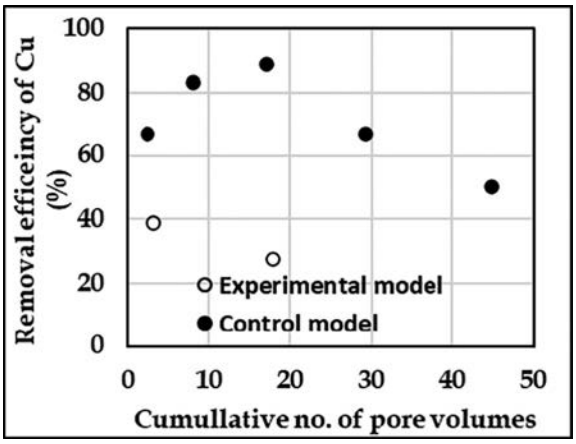

Figure 13 - Variation of Cu Removal Efficiency

3.5 Physical and Mechanical Properties of Reactive Materials

Table 5 shows the values of physical and mechanical properties of the reactive media in the experiemntal and control model before and after the experimental runs. Porosity, which is a measure of voids in SD, QD, FWC, DAS and ZVI, had decreased with the interaction of leachate. Adsorption could be a reason for reduction of porosity while increment of pores could be explained by the wearing process of particles. Furthermore, there could be particle breaking into small pieces during the leachate run.

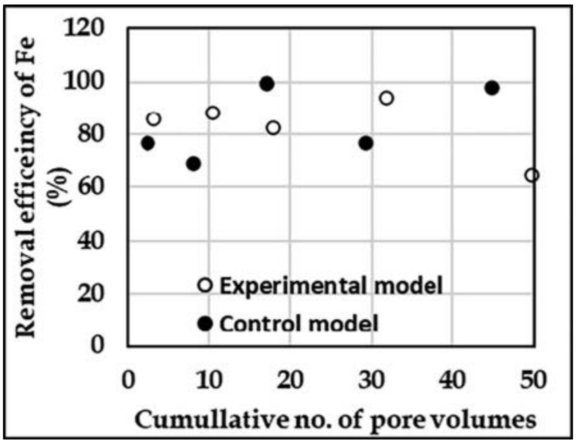

Figure 14 - Variation of Fe Removal Efficiency

In order to evaluate the longevity of materials without a structural failure, initial and final values of cohesion and friction angel were compared. Cohesion of ZVI increased by 2 kN/m^2 whereas other materials displayed a drop in cohesion. SS and DAS showed the same initial and final value of friction angle, which had a reduction though others displayed an increment.

Table 5 – Variation of Properties of Reactive Materials

Material	Porosity		Cohesion (kN/m^2)		Friction Angle (ϕ) (^{0})	
	Initial	Final	Initial	Final	Initial	Final
SS	0.577	0.598	12	6	44	43
SD	0.870	0.868	-	-	-	-
QD	0.369	0.366	10	8	40	45
FWC	0.574	0.521	-	-	-	-
DAS	0.566	0.561	28	22	44	43
ZVI	0.633	0.594	8	10	49	55
GAC	0.713	0.715	12	8	49	50
RLS	0.530	0.429	16	6	47	47

4. Conclusions

Reactive materials used in the experimental model FWC, SD, QD, DAS, SS displayed a considerable potential to remove a range of contaminants in groundwater contaminated by landfill-leachate. Particularly, BOD_5 showed more than 90 % removal efficiency. Similarly, heavy metals like Cd had achieved 100% removal efficiency throughout the experimental run. When comparing the removal efficiencies of both the experimental and control models, the removal efficiencies of the experimental model are quite considerable, given the fact construction and operation of this model in real practice is more cost effective than that of the control model.

In addition, the overall reduction of the shear strength of waste materials due to leachate interaction is quite similar to RLS. It indicates that the tested waste materials can perform as PRB reactive media with the same durability and strength loss as a typical soil.

However, further studies on the changes of the physical and mechanical properties of the reactive media with the application of leachate have to be done to find the strength and failure potential of a PRB barrier.

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