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Laboratory Experiments on Remediation of Landfill Leachate Contamination with Permeable Reactive Barriers (PRBs) of Reactive Media Derived from Waste

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Abstract: Groundwater at landfills is often contaminated with heavy metals. Permeable reactive barrier (PRB), a potential in-situ treatment system, was investigated in this study, using 'composite reactive media' (COM), primarily composed of waste materials, to remediate heavy metals in groundwater. The COM consisted of 40% Brick and Mortar Waste (BMW), 40% Biochar (BC), 10% Granular Activated Carbon (GAC), and 10% Zeolite, based on volume. In an up-flow column, the average removal efficiencies of Fe, Pb, Cu, As, Mn, Zn, and Cd were 70.9±2.7, 80.9±3.2, 72.2±1.6, 76.3±2.5, 81.6±6.3, 88.0±2.0, and 67.3±4.6%, respectively. In a bench-scale COM-filled PRB (0.85 x 0.25 x 0.3 m), the average removal efficiencies of the same species were 71.4±1.3, 75.4±4.9, 67.4±4.3, 72.9±1.3, 83.6±7.6, 89.8±7.4, and 80.9±7.1%, respectively. Adsorption associated with fixation, and ion exchange could be the main treatment mechanisms. COM also has potential as a filtration medium in other treatment unit processes and to treat some other types of wastewater than landfill-leachate. Further, this use of COM could alleviate the burden of disposing of BMW waste, thereby addressing a significant issue in waste management. As the identification of potential failure points in reactive media is crucial, field-scale experiments are suggested to be conducted for further investigation.

Keywords: Composite, Heavy Metals, Landfill-Leachate, Permeable Reactive Barrier (PRB), Reactive Media, Waste

1. Introduction

Landfill leachate is generated in waste dump sites commonly referred to as "landfills." Groundwater in these landfill sites frequently becomes contaminated with a variety of substances, such as dissolved organic matter, inorganic macro components, nutrients, and heavy metals. There is a potential for landfill leachate to mix with both ground and surface water, making groundwater pollution a significant concern at the forefront of environmental issues. Permeable reactive barriers (PRBs) are used widely to treat contaminated groundwater. In passage through the PRB, the reactive materials interact with contaminants [1]. According to Mohamed and Antia [2], in-situ reactive media offer the potential to significantly reduce costs associated with plume control and eliminate the need for pumping contaminated groundwater for ex situ treatment. One of the key advantages of PRBs is their versatility, as they can be applied to both existing landfills and future landfill construction. Zhou et al. [3] noted that retrofitting the failed bottom layers of operational landfills with new lining systems can be challenging. According to Liu et al. [4], PRBs are efficient technologies for in situ remediation of contaminated groundwater, but their effectiveness greatly depends on the choice of reactive media used. A good reactive material should possess the following features: reactivity, stability, availability, cost, hydraulic performance, and environmental compatibility [2]. Previous studies have used various reactive media in PRBs, including Zero-Valent Iron (ZVI), activated carbons, zeolites, lime, alkaline materials, apatite, transformed red mud,

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oxides, sodium dithionite, and combinations of reactive materials [5]. However, many of these techniques face practical challenges due to their high cost and the generation of toxic sludge. Reactive materials such as ZVI, halogenated aliphatic hydrocarbons, activated carbon, zeolite, and apatite are examples of high-cost materials that produce toxic sludge [5]. Therefore, it is crucial to explore low-cost and readily available reactive materials that have the potential to simultaneously address multiple contaminants commonly found in groundwater at landfill sites.

The use of the same reactive materials as those used in other applications may not be applicable to groundwater treatment at landfill sites. However, there are numerous natural and waste materials that can serve as effective reactive materials. Utilizing waste materials as reactive materials may address the disposal issues associated with them effectively. Obri-Nyarko et al. [5] also noted that extensive efforts have been made to understand the mechanisms of contaminant removal by various reactive media and the factors that control these mechanisms. However, more research is still required, as the understanding of these mechanisms, particularly for newly discovered materials, remains limited.

To evaluate the suitability of different reactive materials for PRBs, a sequential approach involving batch sorption, laboratory-scale column, bench-scale, pilot-scale, and field-scale experiments is necessary. Dayanthi et al. [6] conducted batch sorption experiments to investigate the total iron removal using a composite adsorbent comprising 40% (w/w%) Brick and Mortar Waste (BMW) and 40% (w/w%) Biochar (BC), 10% (w/w%) Zeolite (ZE), and 10% (w/w%) Granular Activated Carbon (GAC). The above study revealed that the removal efficiency of the composite adsorbent was 95.0%, whereas that of the higher-cost ZE and GAC were 89.7% and 93.0%, respectively. Under the optimum conditions, the composite adsorbent achieved a total iron removal efficiency of 99.2%. Zhang et al. [7] utilized a construction waste brick based facility to treat heavy metals in runoff and observed significant removal effects for Cu, Zn, Cd, Pb, and Mn. While batch sorption experiments provide valuable insights into the treatment potential of these materials, conducting laboratory-scale column and bench-scale experiments is essential to confirm their applicability in real-world applications.

Thus, as outlined in the study by Dayanthi et al. [6], the aim of this research was to assess the feasibility of utilizing a composite reactive media (COM) consisting of significant proportions of BMW and BC, along with smaller quantities of ZE and GAC, as the reactive media within permeable PRBs. COM possesses multiple properties owned by several single materials which, in turn, enhances the treatment potential of the individual materials. It can also address the simultaneous removal of a number of contaminants. The first objective was to determine the removal efficiencies of heavy metals in groundwater contaminated with landfill leachate. The second objective was to assess the changes in physical and mechanical properties of the composite reactive media resulting from its interaction with the contaminated groundwater. According to Zhou et al. [3], in the early stages of PRB technology, single materials were commonly used as reactive materials. The combination of multiple materials can enhance permeability, reduce costs, increase the number of mechanisms available for single or multi-contaminant removal, enhance and accelerate removal rates, and thus substantially improve the long-term performance of barriers. However, the literature lacks studies on the concurrent conduct of two types of experimental series aimed at investigating PRB reactive materials composed mainly of waste materials. Therefore, the present study is significant in addressing this research gap.

2. Materials and Methods

2.1 Overall Procedure

The research comprised two types of experiments: laboratory-scale column experiments and bench-scale experiments. The columns and PRB reactor were filled with COM consisting of BMW, BC, GAC, and ZE in volume-based proportions. COM consisted of 40% BMW and BC each, and 10% GAC and ZE each. BMW was obtained from a construction site, while BC was sourced from a local bakery. ZE was imported, and GAC was purchased. All materials underwent washing, drying, and grinding to achieve the desired particle size range. Landfill leachate, collected from an inorganic municipal solid waste landfill, was diluted ten times to simulate groundwater conditions.

Wastewater samples analyzed for heavy metals were filtered using 1.2 µm filter paper and then acidified with concentrated nitric acid (HNO_3)

to lower the pH below 2. These samples were subsequently preserved at 4 ˚C in a refrigerator.

The physical and mechanical properties of the reactive media in the columns and bench-scale reactor were analyzed as follows. The COM underwent sieve analysis and standard proctor compaction tests before being filled into the reactors to determine the particle size distribution, optimum initial moisture content, and initial maximum dry unit weight. The specific gravity test was conducted on core samples extracted from the reactive media beds before and after the experimental runs to measure void volume ratio and porosity (physical properties). Similarly, core samples were taken to measure shear strength and hydraulic conductivity (mechanical properties) using the direct shear test and falling head method, respectively. When preparing the COM, the necessary volume of water was determined based on the initial optimum moisture content. All the tests on reactive materials were conducted based on the ASTM standard methods [8]. Before introducing simulated groundwater into the reactors, tap water was applied to flush out easily flushable materials. The flushing operation was concluded once the values of these parameters reached negligible levels, a process that took about one week. Throughout both the column and bench-scale experiments, samples of the influent and effluent were collected every two days. During each sampling, the volume of wastewater collected over the two-day period was measured, and the effluent tank was emptied. The contents of the influent tanks were frequently mixed. To minimize any degradation in the influent quality, the influent concentration for a specific effluent sample was determined as the average concentration of the present and immediately preceding samples. Wastewater parameters were assessed using the guidelines outlined by Clesceri et al. [9]. The wastewater samples were analysed for various heavy metals, including Fe, Mn, Cu, Zn, As, Cd, and Pb. A graphite furnace atomic absorption spectrophotometer was used to analyze the heavy metals. Additionally, parameters such as pH, turbidity, electric conductivity, and Oxidation Reduction Potential (ORP) were measured during both the column and bench-scale experiments.

2.2 Laboratory-Scale Column Experiments

2.2.1 Experimental Set-Up

The experimental setup (Figure 1) consisted of several components, including an overhead influent storage tank, a constant head tank, a downward flow column, an upward flow column, and effluent collecting containers. The reactive media bed had a height of 0.5 m and an internal diameter of 8.9 cm.

2.2.2 Reactive Media Bed Preparation

The particle size selection was based on several factors [10] [11]. Considering all these factors, the particle size selected for the COM was less than 9.5 mm. Both BMW and BC were ground to a particle size smaller than 9.5 mm. As the imported ZE had a particle size range of 3-5 mm, it was not ground. The purchased GAC had a particle size less than or equal to 2 mm. To create the COM, BMW, BC, GAC, and ZE were mixed with water according to the quantities mentioned in Table 1. The reactive media bed was filled in 5 cm thick layers and each layer was compacted with blows. The packing density in each column was 1593.1 kg/m^3.

Table 1- The Quantities of Materials Filled in Columns

Material type	Bulk density (kg/m^3)	Mass/ Volume	Mass in 5 cm thick layer (kg)
BMW	2540	6.50 kg	0.32
BC	300	0.77 kg	0.04
ZE	1600	1.03 kg	0.05
GAC	510	0.33 kg	0.02
Water	1000	1570 ml	78.5 ml

2.2.3 Experimental Run

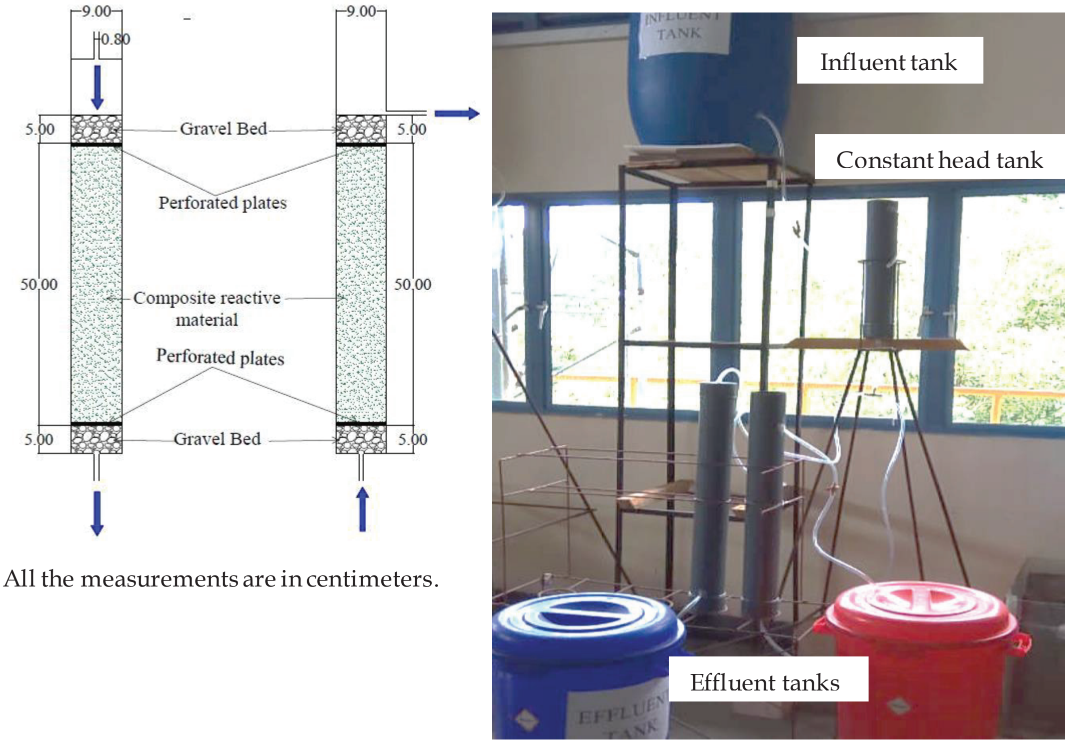
The duration of the experimental run was 30 days. Table 2 and Table 3 depict the hydraulic parameters, while Table 4 presents the average influent concentration and average mass loading rates of each heavy metal.

Table 2 - Hydraulic Parameters -Column Experiments (Upward)

Parameter	Upward Column		
	Avg.	Before	After
Application Flow Rate (L/d)	4.4	4.4	4.4
Hydraulic Loading Rate (L/m^2.d)	31.4	31.4	31.4
Pore Volume HRT (d)	0.17	0.18	0.16
Filtration Rate (L/d)	3.4	3.7	3.2

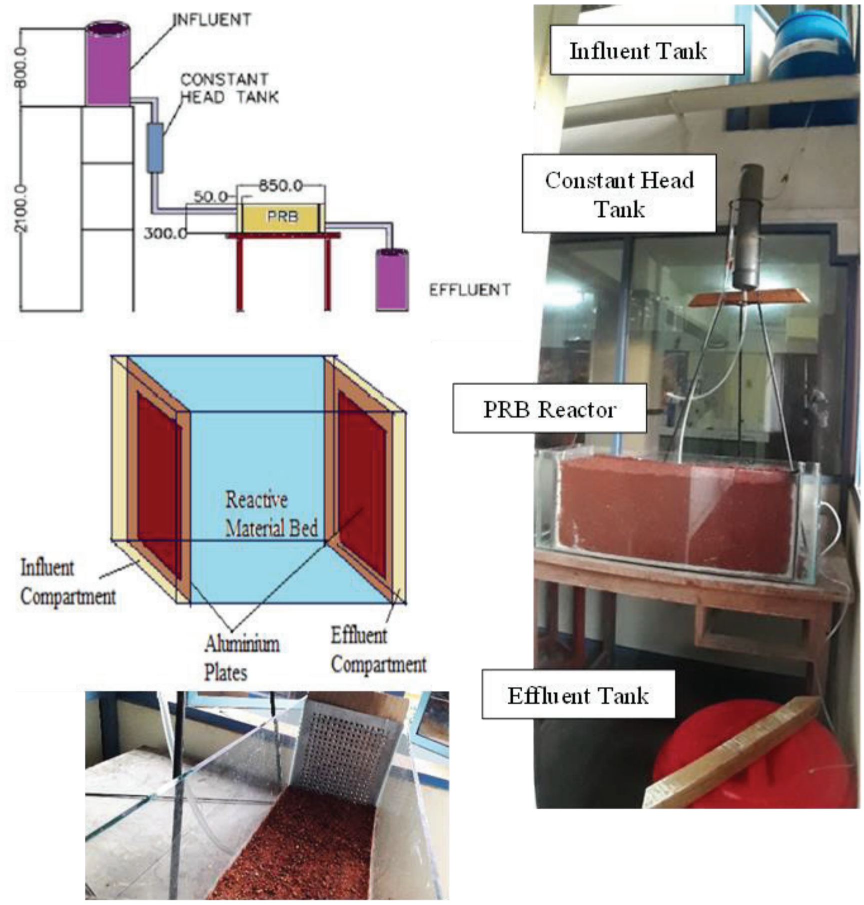
Table 3 - Hydraulic Parameters -Column Experiments (Downward)

Parameter	Downward Column		
	Avg.	Before	After
Application Flow Rate (L/d)	4.4	4.4	4.4
Hydraulic Loading Rate (L/m^2.d)	31.4	31.4	31.4
Pore Volume HRT (d)	0.16	0.18	0.15
Actual HRT (d)	0.22	0.22	0.23
Filtration Rate (L/d)	3.4	3.8	3.3



All the measurements are in centimeters.

Figure 1- Column Experimental Set-Up



All measurements in millimetres

Figure 2 - Bench-Scale Experimental Set-Up

Table 4 - Average Influent Concentration and Average Mass Loading Rates for the Column Experiments

Heavy Metal	Concentration (μg/L)	Mass Loading Rate (g/m². d)
Fe	22050	1.50 x 10
Mn	0.44	3.06 x 10^{-4}
Cu	3.76	2.59 x 10^{-3}
Pb	20.82	1.46 x 10^{-2}
Cd	0.48	3.32 x 10^{-4}
Zn	1.14	7.83 x 10^{-4}
As	33.18	2.24 x 10^{-2}

2.3 Bench-Scale Experiment

2.3.1 Experimental Set-Up

Figure 2 (all the dimensions are in millimetres) depicts a schematic and an image of the experimental set-up. The set-up consisted of a PRB reactor with dimensions of 0.75 m x 0.25 m x 0.3 m for the reactive media bed. It also included an overhead influent storage tank, a constant head tank, and an effluent collection tank. Two compartments, each measuring 0.05 m in length, 0.3 m in height, and 0.05 m in width, were situated on opposite sides of the reactive media bed. One compartment received the influent, while the other collected the effluent. The reactive media bed and each compartment were separated by a perforated metal plate with 5 mm diameter holes spaced at 10 mm intervals. A 5 cm freeboard was maintained, and the reactor was placed on a bench, providing a slight slope of 0.02 in the direction of water flow.

2.3.2 Reactive Media Bed Preparation

An approximate final packing density after compaction was anticipated. To achieve this, the bed was filled in 5 cm thick layers by calculating the mass of reactive media for each layer and subsequently filling and compacting into 5 cm thick layers. The final packing density aimed to minimize hydraulic conductivity while maximizing hydraulic retention time. Water was added to the mixture to aid the compaction process. The bulk density of each material was determined before mixing. Table 5 illustrates the quantities of each material used to fill the bench-scale reactor. The packing density of the reactive media bed was measured to be 1594 kg/m³.

2.3.3 Experimental Run

The duration of the experimental run was 30 days. Table 6 presents the hydraulic parameters, while Table 7 displays the average influent concentration and average mass loading rates of each heavy metal. The hydraulic parameters of the bench-scale reactor were significantly higher than those of the column experiments.

Table 5 - The Quantities of Materials Filled in the Bench-Scale Reactor

Reactive Media	Bulk density (kg/m³)	Volume of 5 cm thick layer (l)	Mass in 5cm thick layer (kg)
BMW	2540	3.75	9.5
BC	300	3.75	1.1
ZE	1600	0.94	1.5
GAC	510	0.94	0.5

Table 6 - Hydraulic Parameters -Bench Scale Reactor

Parameter	Avg.	Before	After
Application Flow Rate (L/d)	13.6	13.6	13.6
Hydraulic Loading Rate (L/m².d)	217.6	217.6	217.6
Pore Volume HRT (d)	0.83	0.89	0.77
Actual HRT (d) (Using Darcy's law)	1.16	1.11	1.21
Filtration Rate (L/d)	12.5	12.7	12.4

Table 7 - Average Influent Concentration and Average Mass Loading Rates for the Bench-Scale Reactor

Heavy Metal	Concentration (μg/L)	Mass Loading Rate (g/m².d)
Fe	22050	4.8 x 10^{0}
Mn	0.44	9.57 x 10^{-5}
Cu	3.76	8.09 x 10^{-4}
Pb	20.82	4.54 x 10^{-3}
Cd	0.48	1.04 x 10^{-4}
Zn	1.14	2.44 x 10^{-4}
As	33.18	6.97 x 10^{-3}

3. Results and Discussion

3.1 Removal Efficiencies of Heavy Metals

Figure 3 illustrates the variation in removal efficiencies of Fe, As, Cd, Mn, Pb, Zn, and Cu in the two columns over the course of the experimental run. Figure 4 presents the same variation for the aforementioned heavy metals in the bench-scale experiment. Table 8 gives the average removal efficiencies obtained from both the column and bench-scale experiments. The overall removal efficiencies of the same heavy metal in the column and bench-scale experiments exhibited slight deviations from each other, with Cd showing the greatest deviation. The fate of contaminants within a reactive media bed is determined by advection, dispersion, retardation, and transformation. These factors can vary not only based on the reactivity of the media but also on the geometry of the reactive media bed and hydraulic parameters. In order to achieve their remediation goals, PRBs must serve two functions: intercepting contaminated groundwater plumes and reducing contaminant concentrations below regulatory limits or remediation goals [12]. To fulfill the first function, the hydraulic conductivity of a PRB must be at least one order of magnitude greater than that of the aquifer [13]. Additionally, the desired chemical, physical, biological, or mixed removal mechanisms can only occur if a sufficient Hydraulic Retention Time (HRT) is guaranteed, based on the relevant kinetic conditions, in order to achieve the second function [14]. Table 3 and Table 7 show that the actual HRT of the bench-scale experiment was one order of magnitude greater than that of the downward column. Although the actual HRT could not be calculated for the upward column, the pore volume HRT was determined. The bench-scale reactor exhibited a pore volume HRT approximately 5 times greater than both the columns. Therefore, if HRT was the only parameter affecting treatment potential, the treatment performance of the bench-scale reactor would have consistently surpassed that of the columns. Two main issues associated with column tests in replicating hydrodynamic conditions of field-scale reactors are possible channelling or wall effects [15]. Hence, the proximity of the column surface could affect the behavior of the reactive media. Reproducing hydrodynamic conditions in practice is somewhat more complex. Additionally, in order to simulate real operating conditions, the column length should be of the same order of magnitude as the filtration path in the full-scale technology [15]. In this research, the column media height was 50 cm while the thickness of the reactive media bed in the bench-scale reactor was 75 cm. Both dimensions were within the same order of magnitude, and therefore, the difference was not quite significant. Consequently, approximately similar hydrodynamic conditions could prevail in both the columns and the bench-scale reactor. The hydraulic loading rate of the bench-scale experiment was three times higher than that of the columns. As a result, the surface mass loading rates of heavy metals on the columns were higher than those of the bench-scale set-up by about threefold. Hence, different treatment efficiencies could be expected from both the columns and the bench-scale reactor, despite using the same reactive media. The removal efficiencies for all heavy metals remained relatively constant or showed a slight decrease by the time the experiment was terminated (refer to Figures 3 and 4). This suggests that breakthrough had not occurred at that point. If breakthrough had indeed occurred, the removal efficiencies would have significantly decreased.

The upward column performed slightly better than the downward column. In the downflow loading system, the media bed can be kept stable, while fines tend to be removed in the upflow loading system [16]. Higher flow rates without fluidizing the bed are possible with the downflow loading system [16]. On the other hand, high flow rates in upflow loading systems may cause the bed to expand slightly. However, a slight expansion of the bed is helpful as it reduces the pressure drop. Compared to upward flow, downward flow results in the highest hydrostatic pressure in the same case. In liquid adsorption, upflow loading can assist in the removal of trapped air and promote bed expansion, which leads to improved mixing. This could be a reason why the upward loading system performed slightly better than the downward loading system.

Table 8 - Average Removal Efficiencies-Column and Bench-Scale Experiments

Heavy Metal	Upward Column	Downward Column	Bench-Scale Reactor
Fe	70.86 ± 2.68	67.26 ± 2.34	71.43 ± 1.29
Cu	72.17 ± 1.61	70.53 ± 1.77	67.38 ± 4.28
Pb	80.87 ± 3.15	68.63 ± 7.37	75.35 ± 4.85
Mn	81.64 ± 6.26	70.57 ± 4.53	83.56 ± 7.64
Zn	88.04 ± 1.99	85.42 ± 2.43	80.94 ± 7.11
Cd	67.33 ± 4.60	66.65 ± 4.18	89.75 ± 7.35
As	76.30 ± 2.54	71.02 ± 4.51	72.87 ± 1.25

The reactive media bed was composed of BMW and BC, which contained limestone, clay, silica, cellulose, lignin, and carbohydrates. Limestone is a commonly found carbonate sedimentary rock. These materials consist of various chemical agents that contribute to the removal of heavy metals from the liquid phase.

Different methods, including abiotic reduction, biotic reduction, chemical precipitation, and sorption or ion exchange, have been utilized in PRBs to eliminate inorganic contaminants from contaminated groundwater [9]. However, the reactive materials used in this research did not possess strong reducing properties. For biotic reduction, organic reactive materials such as leaf mulch, sawdust, wheat straw, and alfalfa have been employed as electron donors, while municipal waste or compost has served as a nutrient source [17]. As per Jacob et al. [18], bioremediation involves adsorption, reduction or removal of contaminants from the environment through biological resources (both microorganisms and plants). None of the reactive materials used in this study contained biodegradable organic matter. The simulated groundwater was prepared by diluting leachate collected from an inorganic landfill, which provided no nutrients for microbial growth within the columns/reactor. Moreover, no bacterial inoculation was done. Hence, significant biotic reduction was also unlikely to occur.

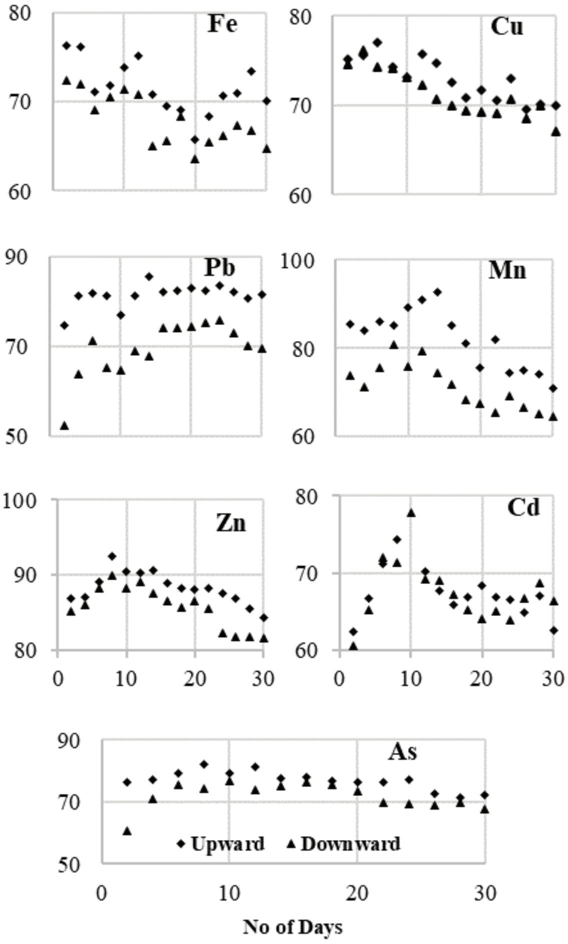


Figure 3 - Removal Efficiencies of Heavy Metals -Column Experiments

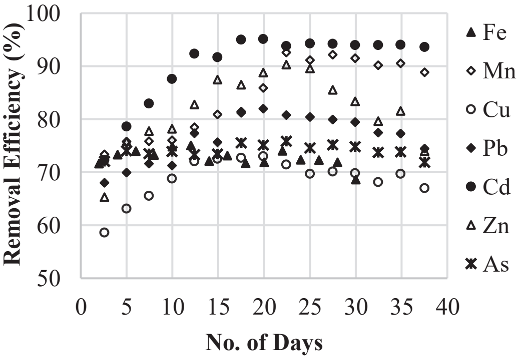


Figure 4 - Removal Efficiencies of Heavy Metals -Bench-Scale Reactor

Contaminants are removed in response to mineral precipitation, which occurs when the pH value increases. Limestone dissolves in the acidic water, increasing alkalinity and raising the pH value. If the pH has increased sufficiently, metal contaminants can precipitate as hydroxides or carbonates [10]. Since BMW contains limestone, the occurrence of precipitation reactions, as mentioned above, is possible.

Generally, heavy metal ions can be adsorbed onto the surface of the adsorbent [19]. GAC and BC are carbon-based adsorbents, while zeolite is a mineral-based adsorbent. BMW contains properties of both cement (limestone) and sand (silica). Zeolites have also been used in PRBs to treat inorganic contaminants. Zeolites are hydrated aluminosilicates with a large internal surface area and high sorption capacity. They treat inorganic contaminants through adsorption and cation exchange, where a contaminant molecule replaces another molecule at the surface of a zeolite particle [10]. Ion exchange and precipitation are integral reactions associated with adsorption. Hence, adsorption could be the major treatment mechanism inside the column/reactor in the present study.

The charged compound is attracted to an oppositely charged surface by the weaker of the two forces. This can involve either outer sphere adsorption or ion exchange [20]. Zeolite, for example, can exchange its cations with heavy metal cations, thereby removing them from the influent [21]. According to Wuana and Okieimen [22], the fate and transport of heavy metals in soil depend significantly on the chemical form and speciation of the metals. Once in the soil, heavy metals are initially adsorbed through fast reactions (minutes to hours), followed by slower adsorption reactions (days to years). Consequently, they are redistributed into different chemical forms with varying bioavailability, mobility, and toxicity [22]. This distribution is believed to be controlled by various reactions of heavy metals in soils, including mineral precipitation and dissolution, ion exchange, adsorption and desorption, aqueous complexation, biological immobilization and mobilization, and plant uptake [22]. The primary role of immobilizing amendments is to transform the original soil metals into more geochemically stable phases through sorption, precipitation, and complexation processes [22]. Since the reactive media bed resembles soil in its porous nature, these mechanisms are applicable to the current columns and bench-scale reactor.

According to Bagchi [24], the attenuation mechanisms of iron (Fe) include precipitation, cation exchange, adsorption, and biological uptake, while BC causes ion exchange and adsorption of As (Mohan & Pittman, [25]. 'As' and other anionic forms of 'As' behave as chelates and can precipitate in the presence of metal cations. Arsenite can adsorb or co-precipitate with metal sulphides and has a high affinity for other sulphur compounds [22]. The clean-up mechanism for Cd involves precipitation and sorption [26]. In a study by Aziz & Smith [27], limestone was investigated for its ability to remove Mn from water. The results of this research indicated that rough solid media and the presence of carbonate are beneficial in the precipitation of Mn in water. A subsequent laboratory-scale filtration technique was used to confirm that limestone particles could effectively remove Mn from water. The filtration results showed that limestone exhibited a removal efficiency above 90% compared to the gravel media. These findings support the batch results obtained by Aziz et al. [27]. Moreover, various natural zeolites found worldwide have demonstrated good ion-exchange capacities for cations, such as ammonium and heavy metal ions [20]. The inclusion of zeolite in experimental columns may serve as a potential material for removing Cd, Mn, and other heavy metals. The presence of lime can lead to the formation of Pb carbonate, thereby immobilizing it. In the case of zinc (Zn), the removal efficiency in the upward column reached 88% but gradually decreased after reaching a peak initially. Aziz et al. [28] found that the removal of copper (Cu) using activated carbon (without limestone) and limestone (without activated carbon) achieved a similar removal rate of over 95%. The combination of the two also yielded a comparable removal rate. The removal of Cu without any media was approximately 20%. These results indicate that limestone can be used as an alternative medium to replace activated carbon. Batch experiments using limestone and activated carbon demonstrated similar metal removal efficiencies of about 95% [28].

The adsorptive capacity of an individual compound in a solution containing multiple compounds is generally lower than that of a single compound. However, the total adsorptive capacity of the adsorbent may be greater than the adsorptive capacity observed with a single compound [16]. Furthermore, the extent of inhibition caused by competing compounds is associated with the size of the molecules being adsorbed, their adsorptive affinities, and their relative concentrations [16]. As a result, varying removal efficiencies for different heavy metals were observed.

3.2 Variation of the Other Wastewater Parameters

ORP is a crucial variable that governs the potential release of stored pollutants into the aqueous phase during sorption processes [22]. In both the column and bench-scale experiments, the ORP in the effluent was lower compared to the influent, suggesting the occurrence of oxidation-reduction reactions. The decrease in ORP indicates a net prevalence of reductive reactions. The pH of the bench-scale reactor was approximately 8 for the influent and 10 for the effluent. In both the columns, the influent pH remained around 8, while the effluent pH ranged from 9 to 10. This increase in pH indicates an elevation in the alkalinity of the sample. The effluent turbidity was lower than the influent turbidity in both types of experiments.

3.3 Physical Properties of the Reactive Media

The effective size (ES) (D10), D60 and the uniformity coefficient (UC) (D60/D10) before the column experimental run were 0.1, 0.9 and 9, respectively. Table 9 and Table 10 present the changes in these parameters after the column experimental run, and for the bench-scale experiment, respectively. According to Bilardi et al. [15], to avoid channelling or wall effects in column tests, the ratio between the column diameter and the mean particle size should exceed 50. This ratio was 692.3 for the upward column and 600 for the downward column, suggesting that the performance of the reactive media beds was not significantly affected by channelling or wall effects. The particle size of construction wastes has a significant impact on equilibrium time, rate, and adsorption capacity for heavy metals [29]. This applies to the materials used in the present research as well. The interaction between leachate and the reactive media has led to an increase in particle size. This phenomenon provides evidence of adsorption.

Table 9 - Variation of the Effective Size and Uniformity Coefficient - Column Experiments

Upward flow			Downward flow		
ES (mm)		UC	ES (mm)		UC
D10	D60		D10	D60	
0.16	3.2	20	0.2	3.1	15.5

Table 11 and Table 12 illustrate the changes in the physical properties of the reactive media beds. A decrease of 12.5% in porosity and a slight decrease in specific gravity were observed. These variations may be attributed to adsorption, precipitation, coagulation, flocculation, and sedimentation of particles.

Table 10 - Variation of the Effective Size and Uniformity Coefficient- Bench-Scale Reactor

Parameter	Before (mm)	After (mm)
D10	0.10	0.12
D60	0.82	1.1
UC	8.2	9.1

Table 11 - Physical Properties -Column Experiments

Parameter	Before	After	
		Up	Down
Average Specific Gravity	2.3	2.2	2.3
Void Ratio	0.32	0.28	0.27
Porosity	0.24	0.22	0.21
Optimum Moisture Content (%)	18.2	17.7	17.9
Maximum Dry Unit Weight (kN/m^3)	16.9	17.1	17.5
Packing Density (kg/m^3)	1593		
Degree of Compaction (%)	92.5	91.4	89.3

Table 12 - Physical Properties -Bench-Scale Experiment

Parameter	Before	After
Uniformity Coefficient (UC)	8.2	9.2
Optimum Moisture Content (%)	18.2	17.7
Maximum Dry Unit Weight (kN/m^3)	16.9	16.5
Average Specific Gravity	2.27	2.15
Void Ratio	0.32	0.27
Porosity	0.24	0.21
Packing Density (kg/m^3)	1594.2	
Degree of Compaction (%)	92.5	94.8

3.4 Mechanical Properties of the Reactive Media

The longevity of the reactive media bed is influenced by the durability of the treatment mechanisms facilitated by the bed [22]. Additionally, the resistance of the reactive media bed to structural failures caused by external forces affects its lifespan. Evaluating the resistivity of the PRB reactive media bed to lateral forces (shear failures) involves analysing the variation in shear strength throughout the experimental process. Structural failures in the PRB reactive media bed, such as fractures and cracks, can create undesired flow paths, allowing contaminated groundwater to bypass the reactive materials without proper reactions [30]. Table 13 and Table 14 present the changes in cohesion, friction angle, and shear strength of the reactive media beds, in the columns and the bench-scale reactor, respectively. The shear strength measurements were obtained from the middle plane of the reactive media bed, halfway through its height. As shown in Table 14, both cohesion and friction angle have increased in the columns, while the friction angle has slightly decreased in the bench-scale reactor. Overall, the shear strength has increased by 19.2% and 50.7% in the upward and downward columns, respectively. The bench-scale reactor exhibited an 8.5% increase. These findings suggest a positive indication of the longevity of the reactive media bed concerning structural failures. The changes in shear strength may be attributed to particle wear, breakage into smaller pieces, and the coagulation, flocculation, and sedimentation of particles during the experimental process. The geometry of the reactive media beds significantly influences shear strength. The increase in cohesion could be attributed to intermolecular attraction resulting from ion exchange. The decrease in friction angle could be a result of reduced surface friction as leachate passes through the bed and the wearing off of reactive materials due to the reactive processes.

Table 13 - Shear Strength Variation-Column Experiments

	Cohesion (kPa)	Friction Angle (^{0})	Shear Strength (kPa)	% Increase
Before run	7.8	43.3	9.47	-
After run-Upward	8.4	57.2	11.29	19.2
After run – Downward	8.7	70.9	14.27	50.7

Table 14 - Shear Strength Variation of Reactive Media- Bench-Scale Experiment

	Cohesion (kPa)	Friction angle (^{0})	Shear Strength (kPa)	% Increase
Before	7.8	43.3	9.47	-
After	8.9	39.5	10.28	8.5

The hydraulic conductivity is a critical design parameter of PRBs. It is important for the hydraulic conductivity of the reactive media bed to be higher than that of the aquifer material [22]. Consequently, the hydraulic conductivity varies depending on the site conditions where a PRB is installed. The objective is to maintain the hydraulic conductivity within the desired range for the specific site to ensure unimpeded water flow through the PRB. In Table 15, the variations in hydraulic conductivity are presented. The results show a slight increase in hydraulic conductivity, indicating the occurrence of adsorption, precipitation, filtration, and sedimentation. However, the reduction is minimal, as indicated by the comparable order of magnitudes (-3 for columns and -2 for the bench-scale reactor) observed before and after the experiments.

Table 15 - Hydraulic Conductivity(cm/s) Variation

Experiment	Before	After
Downward Column	2.63×10^{-3}	2.52×10^{-3}
Upward Column	2.65×10^{-3}	2.53×10^{-3}
Bench Scale Reactor	3.9×10^{-2}	3.6×10^{-2}

4. Conclusions

The composite reactive media showed high treatment efficiencies for both the column and bench-scale experiments. Adsorption associated with fixation and ion exchange could be the main treatment mechanisms. There was a slight increase in the average particle size in terms of the effective diameter, accompanied by a slight decrease in the void volume ratio and porosity. The shear strength of both the columns and the bench-scale reactor increased. This observation is a positive point in terms of practical applications of the composite reactive media. The reduction in hydraulic conductivity in both the experiments was slight, thus, is favorable for practical applications.

Comparisons of the results with both the discharge and drinking water standards in the country show that only Fe (iron) requires further treatment before discharging, while all other heavy metals comply with the above standards.

The composite reactive media have the potential to be used as packing media for any other treatment unit process/operation to treat landfill leachate, as well as other types of wastewaters. Furthermore, this composite consists of materials with high and low particle densities that can improve permeability, enhance and accelerate removal rates, and may improve the long-term performance of PRBs. Literature lacks studies on the conduct of two types of experimental series, together with the aim of this research. The use of waste materials as reactive media would reduce the burden of proper disposal. Identifying the failure potential of the reactive media is essential. Hence, field-scale experiments are suggested as further recommendations.

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