

Pilot-Scale Low-Cost Mixed-Media Permeable Reactive Barrier (PRB) System to Treat Heavy Metals in Groundwater Contaminated by Landfill-Leachate

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Abstract: Heavy metal (HM) is one of the notable contaminants that may contribute to groundwater pollution. Landfill-leachate is a source, discharging HMs to groundwater. It is essential to trap HMs in groundwater to avoid consequential adverse ramifications. Permeable Reactive Barrier (PRB) is an in-situ technique that can be adopted to remove HMs in groundwater contaminated by landfill-leachate. The objective of this study was to investigate removal efficiencies of HMs in groundwater contaminated by landfill-leachate using a pilot-scale PRB system. Dewatered Alum Sludge (DAS), Washed Sea Sand (WSS), Washed Quarry Dust (WQD), Red Soil (RS), Saw Dust (SD) and Bio Char (BC) were used as mixed reactive media in sequentially connected two PRB models. Average removal efficiencies of Pb, Mn, Cu, Cd and Fe were 94 %, 81 %, 71 %, 68 % and 68 %, respectively for 140 days of an experimental run. Treatment efficiencies could be stimulated by the presence of Fe, Al and Si oxides in materials. It is revealed that mixed-media PRB system showed a remarkable treatment efficiency without a significant change of material properties even after the increase of HM loading at the latter stage. This would also be an economically and environmentally sound re-use application for abundant waste materials.

Keywords: Groundwater, Heavy metal (HM), Landfill-leachate, Mixed-media, Permeable Reactive Barrier (PRB), Reactive material

1. Introduction

1.1 Background

Heavy metal pollution is frequent and critical in environmental deterioration, particularly in groundwater and surface water. It occurs naturally or artificially and increases over time [1]. One of the man-made sources of heavy metal pollution is uncontrolled landfills [2], [3]. Heavy metals can enter groundwater and soil through landfill-leachate, which is generated as a consequence of water percolation through waste [4]. The most common examples for heavy metals in the landfill-leachate and water bodies are lead (Pb), copper (Cu), zinc (Zn), cadmium (Cd), ferrous (Fe), manganese (Mn), arsenic (As) and chromium (Cr) [1], [5]. They are the most threatening constituents found in the landfill-leachate, attributing to their persistence in the environment. Mobility of heavy metals in different media is notable. Moreover, they are more bioavailable and are absorbed by living organisms [6]. Because of non-biodegradability, they tend to accumulate in living tissues. For example, heavy metals accumulated in human bodies cause acute and chronic health issues [7]. Acute heavy metal intoxications may damage the central nervous function, cardiovascular and gastrointestinal systems, lungs, kidneys, liver, endocrine

glands, and bones. Several degenerative diseases in the same systems occur as chronic heavy metal exposure and may increase the risk of some cancers [8].

The other risk is the long-term accumulation of these substances in the soil that threatens the

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enzymes responsible for mineralization of organic compounds on earth [9]. Thereby, heavy metals become toxic for both plants and microorganisms, once required threshold limits exceed. Similarly, accumulated toxic metals in food structures become greater than those in water and air, and be poisonous to both humans and animals [6]. It is revealed that heavy metals cause continuous adverse ramifications in the environment.

If it is possible to trap the heavy metals in groundwater prior to flowing outside the landfill area, it will contribute to saving the groundwater and environment. Therefore, it is very much essential to remove heavy metals in the groundwater contaminated by landfill-leachate up to acceptable standards before being released to the environment.

Common practice of purifying polluted groundwater had been pump-and-treat methods [10], [11]. Moreover, various types of treatment techniques including physical, chemical and biological processes are available to remove heavy metals in the wastewater [12]. Economical and practical feasibility of those methods play an important role in their application [2]. Permeable Reactive Barrier (PRB) is a promising technique, which can trap a wide range of contaminants, including heavy metals, with notable benefits over the other techniques [13]. Since PRB is an emplacement of reactive materials in the subsurface to intercept a contaminant plume [14], waste and low-cost materials can be applied as alternative reactive materials instead of conventional expensive materials like zeolite and zero valent iron (ZVI). It makes PRBs economically more effective and provides a sustainable solution for waste disposal. Such kind of waste and low-cost materials have been intensively scrutinized as reactive media with different packing configurations in PRBs to remove organic and inorganic compounds, and heavy metals in the laboratory scale experiments [15]. Prior to a real installation, evaluation of long-term performance of PRBs is of utmost importance to prevent any failures that may occur. For that, pilot-scale experiments are inevitable. PRB is phenomenal as an in-situ treatment method. In past research, waste/low-cost materials have received vast attention as alternative reactive media for PRBs to make it more economical. Most of such research is limited to the laboratory scale. Though pilot-scale experiments are important for evaluating the long-term performance of alternative

waste/low-cost materials, very limited studies can be found. Therefore, a study of scrutinizing the long-term performance of waste/low-cost materials for heavy metal removal in the groundwater contaminated by landfill-leachate using PRBs, is a timely need. At the same time, this would sustainably address the waste disposal issues as well.

Hence, the aim of the present study was to investigate removal efficiencies of the selected heavy metals using a pilot-scale PRB system packed with mixed media composed of waste materials. The objectives were to obtain the removal efficiencies, and to find out the effect of heavy metal loading rate on the removal efficiencies.

1.2 Scope of the Study

The pilot-scale experimental set-up of PRB system consisted of sequentially connected components: a lysimeter (modeling a sanitary landfill), two receiving tanks, two overhead tanks, and two mixed-media PRB models (PRB 1 and 2) connected in series. The selected reactive materials were DAS, WSS, WQD, RS, SD and BC. The duration of the experimental run was 140 days. The removal efficiencies of heavy metals were investigated in terms of Fe, Cd, Cu, Mn, and Pb. Kankanige et al. (2019) [16] discussed the results of the organic material removal efficiencies by the same experimental set-up and the changes of physical and mechanical properties of its reactive media before and after the experimental run.

2. Literature Review

2.1 Removal Mechanisms for Heavy Metals

Reactive media in PRBs play a dominant role in removing target contaminants and governing treatment mechanisms. Heavy metal removal occurs particularly via sorption processes caused by interactions between metallic ions and mineral surfaces. Materials consisting of Fe, Al and Si oxides that possess surface functional groups or hydroxyl groups, lead to sorption mechanisms [17].

2.2 Low-Cost/Waste Reactive Materials

2.2.1 Dewatered Alum Sludge (DAS)

Alum sludge is an inevitable by-product of portable water treatment when aluminum sulfate is used as a coagulant [18]. Treatment plants usually produce about tons of alum sludge annually worldwide [18], [19]. Therefore, handling and disposal of sludge has

become a significant challenge to water management facilities since alum sludge is not allowed to be directly discharged to water bodies as it affects water quality and aquatic biota of the receiving water body [18], [20]. However, according to Anjithan et al. [20], in Sri Lanka, 61% of the treatment plants directly discharge sludge into inland surface waters with no treatment while 36% of the treatment plants use the sludge as filling material or for land filling.

Chemical composition, morphological structure, and surface characteristics of alum sludge may affect the adsorption mechanisms [21]. The same authors, Yang et al. [21], observed that alum in the sludge is almost amorphous compared to pure aluminum hydroxide. Irregular surfaces and edges facilitate highly reactive large specific surface area for metal sorption [3]. Aluminum oxide is the major component of alum sludge varying from 14.5 - 46.0 %. Besides, Fe and Ca oxides are also available [21]. Chemisorption is the exchange of metal anions/cations and surface ligands, and the formation of a covalent with the surface is the dominant sorption mechanism of metals and metalloids on water treatment residuals [3]. Therefore, amorphous aluminum ions found in DAS are effective in adsorption and chemical precipitation processes [18]. Thereby, DAS is an effective adsorbent for a wide range of heavy metals [19].

2.2.2 Washed Quarry Dust (WQD)

Quarry dust is generated in bulk volumes as residuals during crushing rock aggregates. WQD is porous with a number of chemically active sites. Adsorption rate of WQD is boosted by specific surface area, average pore radius and internal connectivity of pore network. The greatest chemical component of WQD is silicon dioxide and the second most is aluminum oxide [22]. Therefore, WQD has been used to remove heavy metals in wastewater. Mungathia (2009) [22] provided evidence that WQD can absorb 96% of Zn and 94% of Cu from industrial effluent through column experiments.

2.2.3 Washed Sea Sand (WSS)

Sea sand is an abundant material naturally originated by weathering process [23]. Silicon dioxide is the most common chemical composition in sea sand that is greater than river sand [24]. WSS has been tested as PRB media to adsorb organic compounds by Wang et al. (2001) [11], while Nebagha et al. [25] have

removed Cu (II) from aqueous solution using treated SS.

2.2.4 Red Soil (RS)

According to Moorman and Panabokke [26], RS is common in the largest part of the lowland dry zone in the Northern, North Central, Eastern and Southern provinces in Sri Lanka. The mineral of hematite (Ferrous oxide, Fe_2O_3) causes red color [27]. Moreover, Si and Al oxides are common and cation exchange capacity is high in RS. Abhayawardana [28] used natural red soil and peat collected from Sri Lanka for adsorbing Pb from landfill-leachate. Natural red soil showed 73% of Pb removal efficiency whereas 64% by peat. Dayanthi et al. [15] confirmed a considerable removal of Fe by RS.

2.2.5 Saw Dust (SD)

SD is a by-product of timber industry. Generated in large quantities, it is frequently used as cooking fuel and packing agent in furniture [29]. As per Yu et al. [30], lignin, tannins and other phenolic compounds are the major components of polymeric materials found in SD. The structure of phenolic compounds causes ion exchange of a divalent heavy metal ion attached itself to two hydroxyl groups and two oxyl groups, which could donate two pairs of electrons to metal ions, forming four coordination number compounds and releasing two hydrogen ions into solution. The same authors proved that Maple SD can remove Cu (II) from aqueous solution. Likewise, Yasemin and Zeki [31] showed that walnut SD adsorbed Pb, Cd and Ni from aqueous solutions.

2.2.6 Bio Char (BC)

Pyrogenic black carbon is produced by pyrolyzing of carbon rich biomass in an oxygen limited environment [32], [33]. It has a significant potential as a low-cost adsorbent, particularly for removal of heavy metals in wastewater due to its intrinsic properties like porous structure, high surface area, large pore volume, availability of abundant functional groups, and being environmentally benign [34]. Though many sources are available to produce BC, like industrial by-products and waste tires, BC produced from agricultural and forest residues shows a strong sorption ability, which may be attributed to its surface properties originating from the feedstock materials [33]. Pb(II) in water was attracted by negatively charged surface sites (COO⁻ and OH⁻) by many oxygen containing groups (C=O, C-O, OH⁻) in

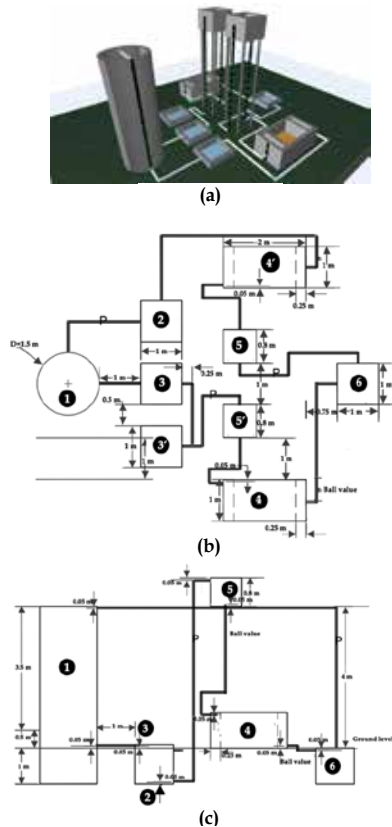


oak bark BC, which are from polyphenolic tannins, flavonoids and suberin contents in the partially aromatized bark materials [35].

3. Methodology

3.1 Pilot-Scale PRB Experimental Set-Up

The pilot-scale experimental set-up located in Hambantota; Sri Lanka is shown in Figure 1.



LEGEND	
1	Lysimeter
2	Collecting Tank
3	Receiving Tank 1 (Leachate)
3'	Receiving Tank 2 (Leachate)
4	Open Treatment Unit (PRB 1)
4'	Open Treatment Unit (PRB 2)
5	Flow Regulating Tank 1 (Overhead)
5'	Flow Regulating Tank 2 (Overhead)
6	Receiving Tank (Treated Water)

Figure 1 - (a) Isometric View; (b) Plan View; (c) Side View of the Pilot-Scale Experimental Set-up

In this set-up, the lysimeter modeled a sanitary landfill and generated leachate to the system. Figure 2 displays the cross-sectional view of the lysimeter. It was constructed using a hume pipe of 1.5 m diameter. The topmost layer of the lysimeter was constructed of loosely packed in-situ red soil as a capping layer. Naturally or artificially made precipitation (via sprinkler) was drained onto the solid waste layer where leachate is formed.

Solid waste layer represented municipal solid waste of Hambantota open dump site. Washout of soil particles with water was avoided by a geotextile in between capping layer and the waste layer. Leachate penetrated to the liner along the operational and drainage layer was directed to the receiving tank (1 m x 1 m x 1m) using an under-drainage system. This under drainage system consisted of 0.5-inch PVC pipes connected as branches to 1-inch PVC pipe as the stem. The leachate collected in the receiving tank was pumped to the overhead tank (0.8 m x 0.8 m x 0.8 m) for regulating the leachate flow rate into PRB using a ball valve.

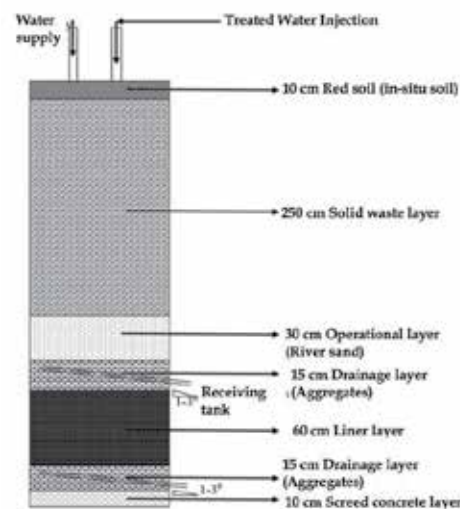


Figure 2 - Cross Sectional View of the Lysimeter

Two identical, PRBs (2 m x 1 m x 1 m) connected in series, provided reactive media beds for leachate to pass through under natural attenuation. A mixture of materials having high specific gravities (DAS, RS, WQD, and WSS) was employed in PRB 1, whereas a mixture of materials having low specific gravities (BC and SD) was employed in PRB 2. All the reactive materials of the PRBs were locally available in Sri Lanka. DAS and SD were collected from the water treatment plant and a local timber mill, respectively, in Hapugala.

BC was taken from a thermal power plant at Embilipitiya and other materials were collected from Hambantota. In each PRB model, two chambers of 0.25 m length facilitated to collect influent and effluent. Kankanige et al. (2019) explained the reactive material preparation and loading procedure into the PRB models.

Leachate from the first overhead tank flowed into the PRB 1, and its effluent was collected in

the first effluent storage tank. Then the effluent was pumped into the second overhead tank. Next, the leachate flowed gravitationally into the influent compartment of the second PRB reactor. Its effluent was collected in the second effluent storage tank.

Additionally, the influent heavy metal concentration of the PRB system was artificially adjusted to the levels found in actual ground water contaminated by landfill-leachate, because lysimeter-produced heavy metal concentration became low during the operation. Heavy metals were added once in two weeks into the overhead tank connected to the influent chamber of PRB 1 from the 98th day. The average influent concentrations and volumetric loading rates of the PRB system before and after the heavy metal adjustment are presented in Table 1.

Table 1 - Average Influent Concentrations and Surface Loading Rates of the PRB System Before and After the Heavy Metal Adjustment

Heavy metal		Pb	Mn	Cu	Cd	Fe
Average influent concentration of PRB system (µg/L)	Before	9.4	2.3	15.3	0.5	73.7
	After	29.4	48.8	165.0	13.9	1559.0
Volumetric loading rate (10 ⁻³) (kg/m ³ . d)	PRB1 - Before	0.88	0.21	1.42	0.05	6.8
	PRB1 - After	2.73	4.53	15.33	1.29	147.8
	PRB2 - Before	0.15	0.09	0.65	0.02	3.1
	PRB2 - After	0.83	1.78	6.94	0.57	45.9
	PRB system Before	0.51	0.15	1.04	0.04	5.0
	PRB system After	1.78	3.16	11.14	0.93	96.8

3.2 Analysis of Heavy Metals

Samples were collected once in two weeks at three points of the PRB system: influent to PRB 1; effluent of PRB 1, which is the same as the influent to PRB 2; and effluent of PRB 2. Graphite furnace of atomic absorption spectrophotometer (TRACE AI1200) was used to analyze Cu, Zn, Cd, and Pb. Determination of Fe was done by the method of complexation of Fe with 1, 10- phenanthroline [36]. For that, UV Visible Spectrophotometer (Serial No.: A10935004596 CD) was utilized.

3.3 Determination of Removal Efficiencies

Heavy metal removal efficiency was calculated using Equation (1) [31].

$$\text{Removal Efficiency(\%)} = \frac{[(\text{Influent concentration} - \text{Effluent concentration}) \times 100]}{\text{Influent concentration}} \dots(1)$$

4. Results and Discussion

The greatest removal efficiency was shown for Pb in the PRB system (Figure 3). It was 94% on average throughout the experimental run. The reactive media in PRB 1 (DAS, WSS, WQD RS) composed of Fe, Al and Si oxides, provided large surface areas. The removal efficiency of Pb reached 100 % and remained the same until the completion of 100 days of the experimental run. Just after that, there was a gradual drop and plateauing off at around 60% towards the end. This can be attributed to the decrease of vacant sites, because the proportion of the number of individual active sites favoring the formation of specific complex bonds is characteristic of the different structural forms of Fe and Al oxides, and to a large extent determines their adsorptive properties [37]. A removal efficiency above 60% in PRB 2 may have been achieved by SD and BC through ion exchange and adsorption [31, 35].

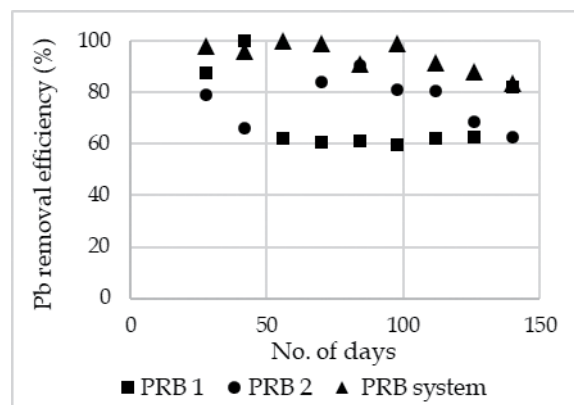


Figure 3 - Variation of Pb Removal Efficiency



Figure 4 displays the removal efficiency of Mn. It was 81% and the second-best efficiency in the PRB system. Both PRB 1 and PRB2 contributed in almost the same degree to remove Mn from groundwater contaminated by landfill-leachate. Li et al. [38] used red mud, a by-product of Al industry, to remove Mn (II) from acid wastewater. The XRD analysis showed the availability of Si, Al and Fe oxides in it. It identified a significant involvement of these oxides in removing Mn (II) through chemisorption. Further, DAS in PRB 1 has been recognized as a potential material for chemisorption [3]. Komnitsas et al. [39] also observed red mud as a potential material to remove Mn (II) via precipitation. Since the reactive media of the PRB system was having somewhat similar characteristics in terms of elements present, chemisorption and precipitation may have contributed to the removal of Mn.

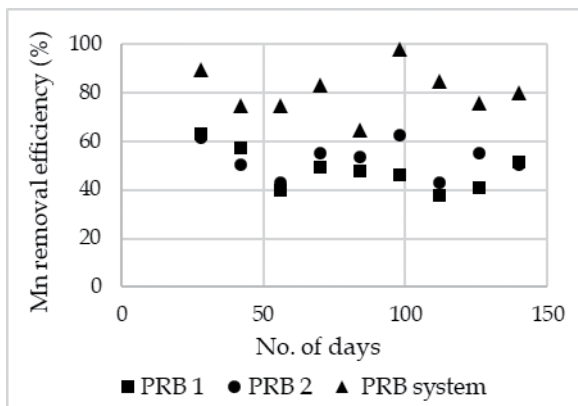


Figure 4 - Variation of Mn Removal Efficiency

Removal efficiencies of Cu and Cd are illustrated in Figure 5 and Figure 6, respectively. The overall removal of Cu was 71 %, whereas Cd was 68 %. Remarkably, both of them displayed a quite similar trend, and the removal efficiency continuously increased from the earlier stage to the latter stage. Komnitsas et al. [39] identified clean up mechanism for Cd and Cu as co-precipitation and sorption. Hence, co-precipitation and adsorption could cause the removal of Cd and Cu.

Figure 7 shows the variation of removal efficiency of Fe. The same average removal efficiency of 68% was obtained by Fe as Cd. According to Bagchi [40], attenuation mechanisms of Fe are precipitation, cation exchange, adsorption and biological uptake. Komnitsas et al. [39] also identified that Fe can be removed via precipitation. Hence, the PRB system may have removed Fe via precipitation, cation exchange and adsorption.

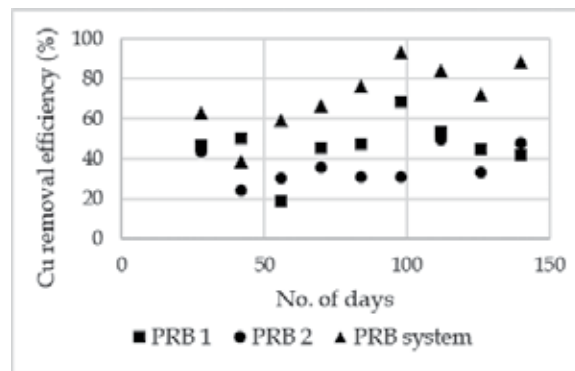


Figure 5 - Variation of Cu Removal Efficiency

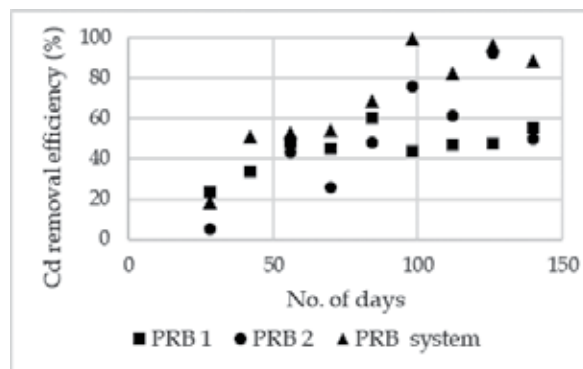


Figure 6 - Variation of Cd Removal Efficiency

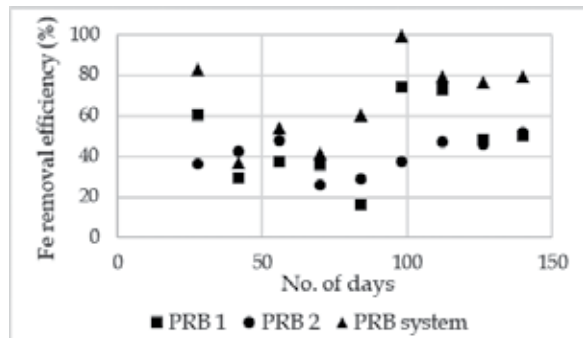
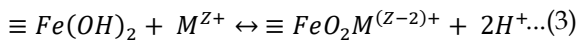
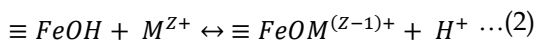


Figure 7 - Variation of Fe Removal Efficiency

Sorption immobilizes the contaminants by partitioning from the dissolved phase to a solid medium [41]. It includes adsorption, absorption, and precipitation reactions [42]. Adsorption has been identified as a feasible mechanism in PRBs. It can take place as three possible mechanisms as abiotic reactions: hydrophobic expulsion; electrostatic attraction; and surface coordination reactions including hydrolysis, metal complexation and ligand exchange. Heavy metal sorption tends to occur particularly by electrostatic attraction and surface complexation reactions. Electrostatic attraction causes indirect attachment and nonspecific adsorption on surface because of intervention of a layer of coordinated water molecule. Thereby, the weaker of two forces attracts a charged compound to an oppositely

charged surface. It can be either outer sphere adsorption or ion exchange. On the other hand, there is no influence of a layer of coordinated water molecule on the complexation reaction. Hence, direct contact with surface is dominant and adsorption becomes specific. Interestingly, the presence of charged oxide surfaces can sorb ions by both electrostatic attraction and surface complexation, which means both nonspecific and specific adsorption [43]. For cations, mono or binuclear surface complexes are formed with a deprotonated hydroxyl group, which is accompanied by the acidification of the environment. Surface complexation between cation (M^{z+}) and Fe hydroxyl groups is presented in the Equations (2) and (3) [44].



The PRB system explained in the present study was rich in a mixture of materials comprising Fe, Al and Si oxides together with phenolic structures. Divalent cations are selectively adsorbed by Fe and Al oxides [45]. Phenolic compounds exchange divalent cations [30]. McKenzie et al. [46] confirmed that the presence of Fe would enhance the heavy metal adsorption. Mohammadian et al. [47] also revealed that the iron oxide particles were able to adsorb heavy metals even at pH-values between 4 and 6 where low adsorption would have been expected, via application of iron oxide nanoparticles for installing adsorption barriers for heavy metals in contaminated groundwater under real conditions.

Therefore, filter beds in these PRB models stimulated the removal mechanisms of heavy metals efficiently as a system. At the same time, a number of different types of heavy metals were removed simultaneously. The addition of heavy metals on the 98th day of the experimental run did not affect the treatment efficiency significantly. Though the influent concentration was notably increased at the latter stages, PRB system could withstand an average removal efficiency of 65% for all the heavy metals.

Figure 8 and Figure 9 show the variation of ORP and EC, respectively, throughout the experimental run. Both of them are master variables controlling the potential release of stored pollutants to the aqueous phase. Generally, ORP is a governing factor of heavy metal mobility. Initial ORP of 400 mV decreased to 100 mV indicating the net

occurrence of oxidation reactions. Komnitsas et al. [39] also observed the reduction of ORP from 450 mV to 150 mV during removal of heavy metals. Further, aerobic processes were dominant in the system since ORP was positive over time.

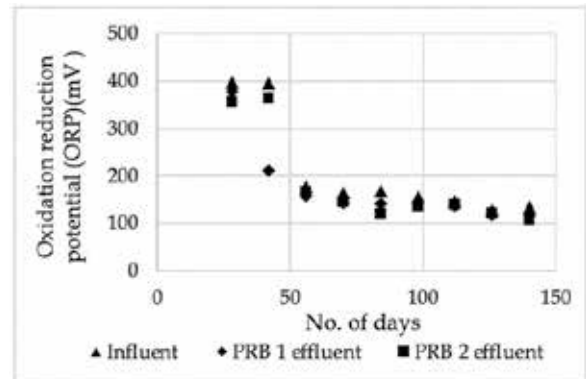


Figure 8 - Variation of ORP

The ability of conducting an electrical current is measured as electrical conductivity (EC). The electrical current is transported by ions in solution, and the conductivity increases with the increase of ion concentrations. In this treatment unit, EC varied around 2 mS/cm.

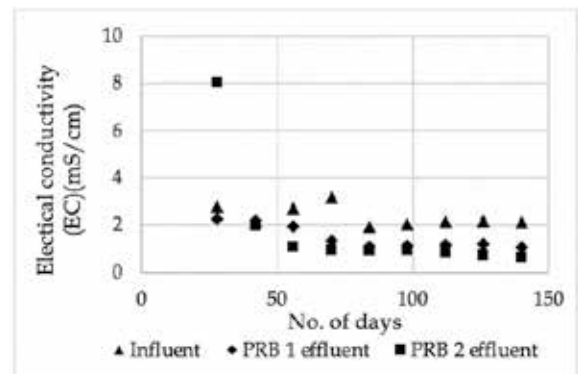


Figure 9 - Variation of Electrical Conductivity

5. Conclusions

It can be concluded that a composite made of DAS, WQD, WSS and RS, and BC and SD has the capacity to remove heavy metals from groundwater contaminated by landfill-leachate. The heavy metal removal is executed by Fe, Al and Si oxides together with phenolic structures present with the above reactive materials. Adsorption, co-precipitation and ion exchange can be considered as the dominant treatment mechanisms. The increase of heavy metal loading rate does not affect the treatment efficiency much. The simultaneous treatment of more than one heavy metal is one of the notable features of the PRB system of the present study. This PRB system can be used to treat even



another type of wastewater contaminated by heavy metals. The materials used in the reactive media have the potential to be used as a filter media or packing media in any other treatment unit process aiming at treating heavy metals.

The results prove that the treatment potential is enhanced by a system of two reactors connected in series, compared to that of a single reactor.

Furthermore, the majority of materials used in the PRB system are abundant by-products, which needs proper disposal. Therefore, the application of waste materials as PRB reactive media is an environmentally friendly and economically feasible solution.

However, long-term experiments have to be conducted in the field to come up with exact design criteria for a reactive media bed composed of the materials tested.

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