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Removal of Lead in Landfill Leachate using Permeable Reactive Barriers with Natural Red Earth and Peat

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Abstract: Most of the municipal solid waste generated in Sri Lanka is disposed in open dumps. This poses a huge threat to the environment. In municipal solid waste, leachate is generated from the waste decomposition process of solid wastes. Since waste contains various materials, the leachate formed also contains extracts of various waste substances. This leachate can easily seep through the ground or mix with the runoff and pollute the adjacent ground and surface water sources. Heavy metals are a major contaminant existing in leachate. In open dumps, leachate cannot be collected. Thus, traditional pump and treat methods are not possible. Permeable Reactive Barrier is a good alternative in these situations. This study focuses on the removal of lead in Landfill Leachate using a Permeable Reactive Barrier which will have as Reactive Materials two natural soils found in Sri Lanka, i.e Natural Red Earth and Peat.

Keywords: Lead, Peat, Natural Red Earth, Leachate

1. Introduction

Though Sri Lanka undergoes development in various sectors, the country's solid waste is not yet properly managed. Most of the municipal solid waste generated is dumped at open dumps with no proper covers or bottom linings. Therefore, these waste dumps create a huge threat to the surrounding air, soil, water and also to the environment.

In municipal solid waste, leachate is generated from the waste decomposition process of solid waste. Since this solid waste contains various materials, the leachate also contains extracts of various waste substances.[Kurniati *et* al, 2014] This leachate can easily seep through the ground or mix with the runoff and pollute the adjacent ground and surface water sources.

The most common pollutants involved are heavy metals like copper, lead, cadmium, mercury etc. High risk groups include the population living close to a waste dump and those whose water supply has become contaminated either due to waste dumping or leakage from landfill sites. [Raman & Narayanan, 2008]

Unlike organic pollutants, heavy metals are non-biodegradable and can accumulate in living tissues particularly in human bodies causing significant physiological disorders such as damage of central nervous system , change in blood composition and the irreversible damage of vital organs of the body. Hence the presence of heavy metals in natural or industrial wastewaters is a subject of great interest in environmental science and is one of the most serious worldwide environmental problems.

Lead (Pb), chromium (Cr), cadmium (Cd), copper (Cu), mercury (Hg) and zinc (Zn) are the most common heavy metal contaminants which in general is a group of elements with density higher than 6 g/cm^3. Because of their material density, heavy metals like lead have the ability to disperse across environmental multimedia, so they are noted as primary contaminants. [Kurniati *et* al, 2014]

Among the different heavy metals, lead is one of the common and most toxic pollutants of the natural waters resulting from various industrial activities such as metal plating, oil refining and battery manufacturing. Lead ions are taken into the body via inhalation, ingestion or skin adsorption. As a result when the body is exposed to lead, it can act as a cumulative poison. [Yarkandi et al, 2014]

Lead accumulates mainly in bones, brain, kidney and muscles and may cause many serious disorders like anemia, kidney disease, nervous disorder, sickness and even death. [Yarkandi et al, 2014]

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Lead can replace calcium, which is an essential mineral required for strong bones and teeth, while playing an important role for the normal functioning of the nervous system. A high level of lead damages cognitive development especially in children. It also acts as an enzyme inhibitor in body, e.g. replaces essential element zinc from the enzymes. [Yarkandi et al, 2014]

A maximum allowable limit of total Pb of 50 gL^1 in drinking water is considered as safe by the World Health Organization, whereas a value less than 15 gL^{-1} is adopted by the United States Environmental Protection Agency. [Yarkandi et al, 2014] Due to toxic effects of lead and other toxic metal ions, the removal of them from water and wastewater is important in terms of protection of public health and environment. [Yarkandi et al, 2014]

Therefore, immediate attention is required to find solutions to treat the contaminated ground water sources adjacent to open waste dumps.

The traditional methods, for the treatment of lead and other toxic heavy metal contaminated wastewater, include complexation, chemical oxidation or reduction, solvent extraction, chemical precipitation, reverse osmosis, ion exchange, filtration, membrane processes, evaporation and coagulation. Besides the classical wastewater treatment techniques, adsorption of heavy metals is the most promising separation and purification method as it has significant advantages including high efficiency in removing very low levels of heavy metals from dilute solutions, easy handling, high selectivity, lower operating cost, minimum production of chemical or biological sludge and regeneration of adsorbent. [Yarkandi et al, 2014]

Where open dumping is done, pump and treat method for leachate contaminated groundwater treatment is not possible.

A very promising alternative to these situations is the Permeable Reactive Barrier (PRB) which is being used extensively in developed countries. This is a type of barrier across the leachate flume. Typically, contaminated water is carried into the PRBs under natural gradient (creating a passive treatment system) and treated water comes out of the other side. In theory, the field application of PRBs presents a series of advantages in relation to pump-and-treat method, including low operation costs, low maintenance, and low on-going energy requirements. [Park *et* al, 2002]

Thus, it was decided to assess the suitability of a PRB to treat leachate contaminated ground water in Sri Lanka using reactive materials available in Sri Lanka.

2. Material and Methods

2.1 Lead Concentrations in Landfill Leachate

Sewwandi et al (2012) have conducted a thorough study to determine the contaminants found in landfill leachate in Sri Lanka. Several landfills located in the Wet Zone, Dry Zone and Intermediate Zone were selected and the heavy metal concentrations in the leachate therein were determined. Landfills in Matale, Bandargama, Kolonnawa, Gampola, Gohagoda, Wennappuwa, Rathnapura, Negombo and Galle belong to the Wet Zone, Hambanthota and Katharagama Landfills to the Dry Zone and Matara landfill to the Intermediate Zone of Sri Lanka.

The results obtained are shown in the Table 1 below. [Sewwandi et al, 2012]

Table 1 – Lead Concentration of landfill leachate in Sri Lanka

Landfill	**Lead (μgL^{-1})**
Matale	1777
Hambantota	492
Kataragama	123
Bandargama	479
Kolonnawa	421
Gampola	34
Gohagoda	19
Wennappuwa	87
Rathnapura	168
Negombo	333
Matara	60
Galle	169
Max. permissible level	**100**

Sewwandi et al (2012)

According to Table 1, it is evident that the amount of lead found exceeds the maximum tolerance limit in most landfill leachates in Sri Lanka.

2.1 Methodology

It was decided to use materials abundant in Sri Lanka as the reactive materials. The selection of the materials was based on previous research done on heavy metal removal and on the properties of the material. After they were prepared as adsorbents, they were made to react with lead solutions of known concentrations. After allowing the material to react with the metal solution for a pre-determined time, the concentration of the remaining solution was measured using an Atomic Adsorption Spectrophotometer. The comparison of the initial and final lead concentrations confirmed the suitability of the material to remove lead from aqueous solutions.

2.3 Selection of Reactive Materials

The main focus in this study was to select candidate materials suitable for a PRB to be used in Sri Lanka to remove lead.

For low concentrations of metal ions in wastewater, adsorption process is recommended for their removal. The process of adsorption implies the presence of an "adsorbent" solid that binds molecules through physical attractive forces, ion exchange, and chemical binding. It is advisable that the adsorbent is available in large quantities, easily regeneratable, and cheap. [Demirbas, 2008]

Therefore, it was decided to focus on natural Sri Lankan soils. Past research done on heavy metal removal using natural soils and soils with good adsorptive properties was considered for the selection.

Finally, two natural soils, Natural Red Earth and Peat were short listed to be tested as candidate materials for the PRB.

2.4 Natural Red Earth (NRE)

Natural Red Earth (NRE) is a naturally-occurring Fe coated quartz sand abundantly available along the North-Western coastal belt of Sri Lanka. NRE samples used in the study were collected from the Aruwakkaru limestone quarry site in the North Western part of Sri Lanka (latitudes and longitudes of $8^0 14'50''$N and $79^0 45'45''$E respectively).

Figure 1 – A sample of NRE

It is a mixture of different minerals such as Ilmenite, Rutile, Zircon and others. It has been shown that NRE is composed of high Fe^{3+}, up to 6%. [Rajapaksha *et* al, 2011] NRE naturally occurs abundantly in the north-western coastal belt of Sri Lanka underlain by Miocene limestone sequences. [Nikagolla *et* al, 2013]

NRE mainly consists of SiO_2 (54.15 %), Al_2O_3 (20.73 %) and Fe_3O_2 (12.39 %), where SiO_2 is present in crystalline form while Al (as Al_2O_3) and Fe (as Fe_2O_3) exist as an amorphous coating around the silica grains [Vithanage *et* al. 2006]. It occurs as rounded and well-sorted quartz sand in a red clayey matrix with accessory Ilmenite and Magnetite. The brick red colour of NRE indicates the presence of oxidizing conditions for the formation of red hematite. NRE contains 0–1 % Fe^{2+} and typically a higher (>2.0 %) Fe^{3+} content [Nikagolla *et* al, 2013] As NRE consists of two main surface sites (>AlOH and >FeOH), it can be more promising as a good adsorbent species [Mahatantila *et* al, 2011]

Vithanage et al, 2007 have suggested NRE to be a starting material in decontaminating water polluted with As species.

Rajapakse et al, 2011 have observed that NRE is a good adsorbent for As (III) and As (V).

Nikagolla et al, 2012 have also stated that NRE can effectively be used to mitigate Cr(III) from aqueous solutions and this method is found to be simple, effective, economical and environmentally benign.

Mahatantila et al, 2012 have studied the removal of Cd using NRE and the study indicates NRE to be a material suitable for decontaminating environmental water polluted with Cd.

As NRE has been very successful in removing heavy metals in research so far conducted, it was selected as a promising reactive material to remove lead.

2.5 Peat

Peat has been investigated by several researchers as a sorbent for the capture of dissolved metals as well as other pollutants from waste water. Besides being available in many countries and having economic factors, peat possesses important characteristics that make it an effective medium for the removal of dissolved metals and other pollutants. [Bandaranayaka et al., 2013]

Peat samples were collected from the Muthurajawela marsh in the Western Province of Sri Lanka. Peat consists of humic substances, fulvic acids, clay materials, organic compounds and minerals. [Wickramasooriya *et* al, 2014]

Dissanayake, 1984 has stated that the low pH of the peat bog presumably aids the conversion of the metals to 'free' ions which are in turn adsorbed on to clay particles.

Figure 2 - A sample of Peat

Bandaranayake, et al, (2013) have stated that peat from Muthurajawela exhibits significant metal sorption capabilities.

Paliulis *et al*, 2014 have stated that peat can be used for the wastewater treatment of polluted water because of its natural characteristics that ensure high removal efficiencies, little pre-treatment, low cost and availability in large quantities. There is also a need to explore new areas where peat could be used. They have discovered that peat can be used as an effective sorbent for lead adsorption from a solution with a pH value of 6. The maximum sorption capacity of peat is equal to 9.976 mg/g when pH = 4.

The results of the study of Ratoi *et* al, 2014, show that the sphagnum moss peat (from Poiana Stampei, Romania) can be used as a cheaper and efficient sorbent for removing lead ions from aqueous solutions.

Therefore, considering the success of previous studies done using peat to remove heavy metals, peat was selected as a candidate material in this study as well.

2.6 Physical and Chemical Properties of Materials

The following tests were conducted with each of the three types of soils to determine the relevant physical and chemical parameters. Physical properties like particle density, particle size distribution, moisture content and BET surface area were tested and chemical properties like pH and electrical conductivity were also tested. All tests were carried out according to relevant BS or ASTM standards.

Table 2 – Material Properties

Parameter	**Method**
Particle density	BS 1377 Part II-1990
Particle size distribution	BS 1377 Part II-1990
Moisture Content Wet Weight Basis	BS 1377 Part II-1990
BET Surface area	ASTM D3663-03 (2008)
pH value	BS 1377 Part III-1990
Electrical conductivity	BS 1377 Part III-1990

2.7 pH Value of the Experiments

It is known that the pH value of a solution is an important experimental parameter in the removal of metal ions from aqueous solutions, because it affects both the speciation form of metal ion and the ionization degree of functional groups from sorbent surface. [Ratoi *et* al, 2014]

The value of pH for all experiments was maintained at 5.5. This pH value was selected from the previous studies done on adsorption, which indicated it to be the most promising pH value for adsorption. According to the in-situ pH values taken at the bore holes at the Udapalatha dump site in Gampola, Sri Lanka, over a period of one year, it was evident that the pH value of ground water contaminated with leachate is between 5.4-8.7.

2.8 Preparation of Soil Samples

The soil was removed of any alien matter and was dried at room temperature, grounded and sieved to obtain particles less than 75 μm in diameter. They were stored in clean and sealed plastic bottles until their use.

2.9 Preparation of Chemicals

All chemical reagents used in this study were of analytical grade and were used without further purification. The stock solution of lead, containing 1000 μg Pb(II)/mL was prepared by lead nitrate dissolved in distilled water, followed by solution standardization. The working solutions were obtained by diluting the stock solution with double distilled water.

2.10 Batch Testing

To determine the ability of the two soils in removing lead in an aqueous environment, a set of batch experiments under the following conditions were completed.

Sieved soil samples of particle size less than 75 μm were taken for the experiment. Measured amounts of soil (2g/L) were added to distilled water to create the necessary concentration (1 ppm) and the samples were agitated with an Automatic Potentiometric Titrator for 2 hours to homogenize the solution. Then, the pH of the solution was adjusted to 5.5 by the drop wise addition of 1M HCl and 1M NaOH solutions.

Then 20 ml aliquots of solution were taken out and the metal was spiked using micro pipettes in order to prepare the necessary metal solution. Solutions were put in a AT12R Thomas shaking incubator at 25^0C and agitating at 150 rpm for 24 hours to enable the reactions to take place. The final pH was also recorded. All experiments were done in triplicate.

After completion, supernatant from each tested sample was taken into tubes, centrifuged at 16,000rpm for 10 minutes in a Suprema 21 High Speed Refrigerated Centrifuge. Afterwards, they were filtered using 0.45µm filter papers in preparation for the analysis.

All samples were analysed for remaining metal using a Shimadzu AA 7000 Atomic Adsorption Spectrophotometer (AAS).

All tests were done in triplicate.

3. Results and discussion

3.1 Physical and Chemical Properties of the Materials

The results obtained from the laboratory experiments carried out to determine the properties of the three soils are as follows:

3.2 Properties of NRE

Table 3 – Properties of NRE

Parameter	Value
Particle density	1.96 g/cm^3
Particle size distribution	33.20% less than 75µm
Moisture Content Wet Weight Basis	0.73
BET Surface area	15.59 m^2/g
pH value	6.81
Electrical conductivity	283.5 µS/cm

According to the values given above, NRE shows a satisfactory BET surface area value of 15.59 m^2/g making it a good adsorbent. As it has a pH value of 6.81, it does not have the ability to make the treated leachate to be more acidic or basic which is also beneficial. The low electrical conductivity of 283.5 µS/cm shows that it does not dissolve too much ions to the leachate. Thus, the NRE can be selected as a promising candidate material for the PRB.

3.3 Properties of Peat

Table 4 – Properties of Peat

Parameter	Value
Particle density	2.06 g/cm^3
Particle size distribution	52.32% less than 75µm
Moisture Content Wet Weight Basis	0.37
BET Surface area	12.28 m^2/g
pH value	2.95
Electrical conductivity	7470 µS/cm

According to the values given above, peat shows a satisfactory BET surface area value of 12.28 m^2/g making it to be a good adsorbent. The very high electrical conductivity of 7470 µS/cm suggests that it may be prone to dissolving a large amount of ions to the system. The low pH value of 2.95 may cause the leachate to be acidic than in its natural state. However, Dissanayake, 1984 has stated that the low pH of the peat bog presumably aids the conversion of the metals to 'free' ions which are in turn adsorbed on to clay particles. Thus, this low pH can aid lead removal.

3.4 Results of Batch Testing

The removal ability of heavy metals by each soil was assessed from the results obtained from the series of batch tests. The removal percentage of metal by each soil was used to compare the two different types of soils.

The efficiency of lead removal was measured using the common efficiency (E) formula, defined as follows:

$$E = [(Ci-Ce)/Ci]*100\% \qquad (1)$$

where Ci is influent concentration and Ce is effluent concentration. [Kurniati et al, 2014]

3.5 Removal of Lead

The removal of 1 ppm concentrated lead by the two types of materials was as follows.

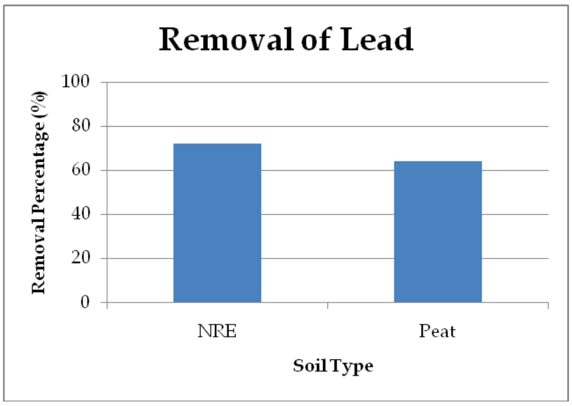

Figure 3 – Removal of Lead by the two soils

According to Figure 3, both soils show satisfactory removal percentages of lead. The removal percentages of NRE are 73% while that of peat is 64%.

The soils were able to remove more than half of the metal present in the solution. Therefore, both soils are suitable as reactive materials to remove lead in the PRB.

5. Conclusions

The water contamination by leachate produced from open waste dumps is very common in Sri Lanka and other developing countries. The heavy metals in the leachate are a hazard to both the humans and the environment alike. Permeable Reactive Barrier (PRB) technology can be very easily used to treat leachate flumes before they reach ground water bodies.

Both NRE and peat show high BET surface areas and remove high percentages of low concentrated lead. Therefore, both materials can be successfully used as PRB materials to treat leachate contaminated with lead.

The results clearly support the possibility of using NRE and peat for the removal of lead and possibly other heavy metals from landfill leachate. In addition to displaying a high adsorption capacity, they do not require any pre-treatment or activation.

Their use as adsorbents for heavy metal ions can be therefore expected to be feasible both economically and technically.

6. Suggestions

The batch tests were done for solutions containing lead only. However, in the natural scenario a mixture of heavy metals in leachate has to be expected. Therefore, the ability of these soils to remove lead in a mixture of metals should be tested.

In leachate, heavy metal mixtures are available. Thus, their removal should be assessed by using metal mixtures for understanding better the PRB application in a real situation.

These tests were done batch wise. Continuous column studies for a considerable period of time are suggested to understand the removal ability of the soils in the long term applications.

Both soil samples tended to increase the turbidity of the solution due to the availability of a large amount of small particles. Thus, the use of a sand filter after the PRB is also suggested.

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References

1. Arneth, J. D., Midle, G., Kerndoff, H. and Schleger, R., Waste in Deposits Influence on Ground Water Quality as a Tool for Waste Type and Site Selection for Final Storage Quality, *Landfill reactions and final storage quality*. Baccini, P. (ed), Springer Verlag Berlin, 1989, pp.339

2. Bandaranayaka, A., Wijeratne, H., Priyantha, N., "Interaction of Ionic Species with Thermally Treated Peat", Annual Research Journal of SLSAJ,Vol. 12, 2012, pp. 27-31

3. Demirbas, A., Heavy Metal Adsorption onto Agro-Based Waste Materials: A Review, *Journal of Hazardous Materials* **157**, 2008, 220–229

4. Dissanayake, C. B., "Geochemistry of the Muthurajawela Peat Deposit of Sri Lanka", Fuel Journal, Volume 63, Issue 11, November 1984, Pages 1494–1503

5. 6.Kurniati, E., Imai, T., Higuchi, T., Sekine, M., "Lead and Chromium Removal from Leachate using Horsetail (*Equisetum hyemale*)", *Journal of Degraded and mining Lands management*, Volume 1, Number 2, January 2014, 93-96

6. Mahatantila, K., Seike, Y. and Okumura, M., Adsorptive Removal of Lead(II) Ion using

Natural Red Earth from its iron and Aluminum Oxide forms, *International Journal of Engi00neering Science and Technology* **3**(2), 2011, 1655-1666.

7. Nikagolla, C., Chandrajith, R., Weerasooriya, R. and Dissanayake, C. B., Adsorption Kinetics of Chromium(III) Removal from Aqueous Solutions using Natural Red Earth, *Environ Earth Sci*, **68**, 2013, 641–645

8. Paliulis, D., Bubėnaitė, J., "Effect of pH for Lead Removal from Polluted Water Applying Peat" The 9th International Conference "ENVIRONMENTAL ENGINEERING", 2014

9. Park, J. B., Lee, S. H., Lee, J. W. and Lee C. Y., Lab Scale Experiments for Permeable Reactive Barriers against Contaminated Groundwater with Ammonium and Heavy Metals using Clinoptilolite, *Journal of Hazardous Materials*, B95, 2002, 65–79

10. Rajapaksha, A. U., Vithanage, M. and Jayarathna, C. L., Natural Red Earth as a Low Cost Material for Arsenic Removal: Kinetics and the Effect of Competing Ions, *Applied Geochemistry*, 26, 2011, 648–654

11. Raman, N., Narayanan, D. S., Impact of Solid Waste effect on Ground Water and Soil Quality nearer to Pallavaram Solid Waste Landfill Site in Chennai, *Rasayan Journal of Chemistry*, Vol. 1, 04, 2008, 828-836

12. Răţoi, M., Bulgariu, L., Macoveanu, M., "Removal of Lead from Aqueous Solutions by Adsorption Using Sphagnum Moss Peat", Chem. Bull. "POLITEHNICA" Univ. (Timişoara), Volume 53(67), 2008, 1-2,

13. Vithanage, M., Chandrajith, R., Bandara, A. and Weerasooriya, R., Mechanistic modeling of arsenic retention on natural red earth in simulated environmental systems, *Journal of Colloid and Interface Science* 294, 2006, 265–272

14. Wickramasooriya, S., Priyantha, N., Lim, L., "Interaction of Aqueous Cu(II) and Pb(II) Species With Fired Muthurajawela Peat", Proceedings Peradeniya University International Research Sessions (iPURSE 2014), Vol. 18, July 4 & 5, 2014, University of Peradeniya, Sri Lanka, 2014, pp. 19