ENGINEER - Vol. LVI, No. 01, pp. [123-130], 2023
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DOI: http://doi.org/10.4038/engineer.v56i1.7566

Soil Based Adsorption Media for Permeable Reactive Barriers to Adsorb Lead (Pb^{2+}) & Cadmium (Cd^{2+})

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Abstract: Groundwater contamination is one of the predominant environmental problems in Sri Lanka and it is suspected as one of the unseen factors of the country's widespread kidney disease. Heavy metals Cadmium (Cd^{2+}) and Lead (Pb^{2+}) are two potentially harmful contaminants found in polluted groundwater samples in Sri Lanka. Permeable reactive barrier (PRB) is an on-site, cost-effective and efficient groundwater heavy metal remediation technique. However, the effectiveness of the PRB system is highly dependent on the characteristics of the reactive materials being used. Accordingly, Rendzina soil (Hunugala series), Reddish Brown earth soil (Nonagama series), Reddish brown latosolic soil (Melsiripura series), and Bog Soil (Wagura series) were selected based on the basic soil properties which were found by previous researchers. Sieve analysis, Atterberg limits, and Procter compaction tests were carried out to determine the physical properties of the selected soils. The batch tests were carried out to determine the absorption rate of heavy metals, namely, Lead (Pb^{2+}) and Cadmium (Cd^{2+}), and to assess the effects of pH, contact time, and initial concentration on the adsorption characteristics of the selected reactive materials. The results reveal that the Rendzima soil is the most suitable reactive material out of all the reactive materials tested.

Keywords: Adsorption, Adsorbent, Batch experiment, Heavy metal, Local soil series, Permeable reactive barrier (PRB)

1. Introduction

Environmental pollution has brought uncountable hazards to the modern world including health hazards to humankind. In this context, heavy metal contamination in the groundwater is a major concern in Sri Lanka. Lead (Pb^{2+}) and Cadmium (Cd^{2+}) are two such heavy metals mainly found in the groundwater samples at various locations of Sri Lanka, and is believed to be the unseen factor for the kidney disease spreading widely in the country [1]. Derivatives of Lead can act as a cumulative poison in the human body and Cadmium can severely damage the lungs and even lead to death [1]. Therefore, immediate attention is required to find solutions to treat the contaminated groundwater sources adjacent to open waste dumps.

The traditional methods, for the treatment of Lead, Cadmium, 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 [2]. Besides these 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 [2].

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The most common pollutants found 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 leakages from landfill sites [1].

One of the effective methods to rectify above described environmental impacts is the construction of Permeable Reactive Barriers (PRB) which is used extensively in developed countries. A PRB is defined as "an emplacement of reactive media in the subsurface designed to intercept a contaminated plume, provide a flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals down-gradient of the barrier" [3].

In theory, the field application of PRBs presents a series of advantages over pump-and-treat method, owing to low operational costs, low maintenance, and low ongoing energy requirements. [4]. Thus, it was decided to assess the suitability of a PRB to treat leachate-contaminated groundwater using locally available reactive materials. The main focus of this study was to select a highly efficient and effective soil type, most suitable soil to be used as the main adsorption medium in PRBs. There are extensive studies on soil properties of Sri Lanka. Consequently, there were few studies about the adsorption character of heavy metal onto Sri Lankan soils [3]. But there are no investigations about the adsorbing character of heavy metals onto scientifically selected soil samples considering all the series of soils in Sri Lanka. Out of all the soil types available, four soil types representing three major climatic zones were selected based on their properties which affect the adsorption characteristics [5]. Pb^{2+} and Cd^{2+}, which are typical contaminants in landfill leachate, were considered as target waste parameters. The following objectives were achieved: (1) Characterization of adsorption properties of $Pb^{2+}$and Cd^{2+} on selected soil types, and (2) Examination of the effectiveness of tested materials as PRB adsorbents based on quantified adsorption capacities.

2. Literature Review

The process of adsorption implies the presence of an adsorbent solid that binds molecules through physical attractive forces, ion exchange, and chemical bonding. Also, for more reliable operation, the adsorbent should be available in large quantities, inexpensive to regenerate, and cheap. [6]. Therefore, it was decided to focus on natural Sri Lankan soils. Some natural soils are cheaper and more efficient adsorbents for removing $Pb^{2+}$and Cd^{2+} ions from aqueous solutions [3]. Therefore, natural soils with good adsorptive properties have been selected as heavy metal removal mediums in Sri Lanka, and the soil selection was mainly based on the publication of the Soils of Sri Lanka by Mapa [5]. According to Mapa's perspective, all the soils in Sri Lanka are classified according to the major climate zones, namely wet zone, dry zone, and intermediate zone. All the soil types in Sri Lanka were identified with the help of information given in that book.

3. Material and Methods

3.1 Selection of Reactive Materials

The identified soils were tabulated based on the properties that affect adsorption capacity, namely, particle size, permeability, cation exchangeable capacity (CEC), and mineral composition. Out of above listed properties, CEC is considered the most significant property that affects the adsorption mechanism [7]. Considering all the above facts, four soil samples were selected with the highest CEC. The selected soil types were Rendzina soil (Hunugala series), Reddish Brown earth soil (Nonagama series), Reddish brown latosolic soil (Melsiripura series), and Bog Soil (Wagura series).

The soil samples belonging to the Hunugala, Nonagama, the Melsiripura, and the Wagura series were collected from Kivul Linda (Central Province), Hambanthota (Southern Province), Kurunagala (North-Western Province) and Negombo (Western Province), respectively. The respective locations and the related coordinates are shown in Figure 1 and Table 1. The respective soil properties and the categorization based on the FAO (Food and Agriculture Organization) classification system are presented in Table 2.

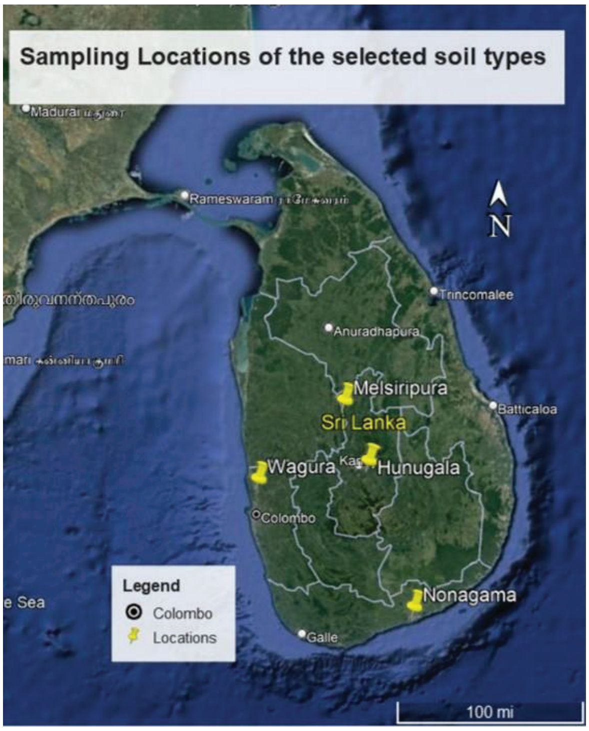


Figure 1 –Locations of the Selected Soil Types

Table 1 - Coordinates of the locations of the Soil Types

Soil Type	Location	Coordinate
Rendzina	Hunugala	Lat: 7° 14′, Lon: 80° 43′; 226.40 km N, 193.90 km E
Reddish brown latosolic soil	Melsiripura	Lat: 7° 41′, Lon: 80° 32′; 276.02 km N, 173.70 km E
Redish Brown earth	Nonagama	Lat: 6° 08′, Lon: 81°05′,105.30km N,233.30km E
Bog soil	Wagura	Lat: 7° 06′ , Lon: 79° 53′, 210 km N,98.35km E

Table 2 - Categorization of the Selected Soils Samples [5]

Description	Hunugala series	Melsiripura series	Nonagama series	Wagura series
Location (SriLanka)	Kandy	Kurunegala	Hambanthota	Negombo
Soil description (Local)	Rendzina	Reddish brown latosolic soil	Reddish Brown earth soil	Bog Soil
Local higher category classification (USDA textural classification)	Typiceutrochrepts shallow loamy calcareous isohyperthermic	Rhodudalfs clayey, non-calcareous, non-acid, isohyperthermic	TypicPaleustalfs	TypicSulfihemists
Climate zone	Intermediate zone	Intermediate zone	Dry zone	Wet zone
Texture	Gravelly clay loam	Sandy clay loam to clay loam	Sandy loam to gravelly sandy	Clay loam to sandy
pH	7.5-8.0	5.5-6.0	5.5-7.6	5.2-5.4
Hydraulic conductivity(cmh^{-1})	Not determined	Not determined	Not determined	Surface-7.9,Subsurface-5.2
Cation exchange capacity (cmol/kg)	20-25	15-20	16-27	100-200
Dominant basic cations	Ca,Mg	Ca,Mg	Ca,Mg	Ca,Mg,Na
Available water (mm /m)	82/25	152	56	Saturated with water
Bulk density (gcm^{-3})	1.2	1.6	1.5	0.9-1.1

4. Batch Adsorption Experiment

Batch treatability studies are usually fast, cheaper, and simpler to set up than columns, and allow rapid comparison of various parameters on the experimental results [20]. This makes them the most suitable for screening candidate barrier materials.

Therefore, the standard batch method recommended by the organization of Economic Cooperation and Development (OECD 2000) is used for all batch adsorption experiments to remove the Pb^{2+} and Cd^{2+} from the groundwater. $PbCl_2$ (99%w/w) and $CdCl_2$ (99%w/w) were used to prepare the adsorbate. A water-bath temperaturecontrolled shaker was used for the batch adsorption study and its temperature was set at 298 K (250^{0}C) for Pb^{2+} and Cd^{2+} adsorption while maintaining the constant shaking speed of 100 rpm during the experiment. In each experimental run, clean 15 ml centrifugal tubes were filled with 1 g of each adsorbent, and 10 ml of the adsorbate of known concentrations. Thereafter, the tubes were centrifuged at 4000 rpm for 15min, and supernatants were filtered through a membrane filter of the pore size of 0.11 μm. The concentration ranges of the supernatants were measured by Atomic Adsorption Spectrometer (GBC 932 plus).

4.1 Kinetics Experiment on Pb^{2+} and Cd^{2+}Adsorption

To determine Pb^{2+} and Cd^{2+} adsorption kinetics onto the tested materials, a Pb^{2+} 1.69 mmol/L (~350 ppm) and a Cd^{2+} 2.67 mmol/L (~ 300 ppm) were used. A mass of 1g of soil was used as the adsorbent for each sample. Triplicate samples were sequentially collected from the shaker after 0, 5, 30, 60, 180, and 360 min at natural pH for the adsorbents. Kinetics model's pseudo-first-order kinetics and pseudo-second order kinetics models were used to characterize the adsorption kinetics [3]. The first-order kinetics model can be defined as

$$\frac{dQ_t}{dt} = K_1\,(Q_e - Q_t) \quad \ldots(1)$$

where
Q_e = amount adsorbed per kg of adsorbent at equilibrium (mmol/kg) and
K_1= pseudo first order constant (1/min).

For initial condition at t = 0 and Q_t = 0, Eq. (1) becomes:

$$\ln(Q_e - Q_t) = \ln(Q_e) - K_1 t \quad \ldots(2)$$

The pseudo-second order kinetics model can be defined as

$$\frac{dQ_t}{dt} = K_2\,(Q_e - Q_t)^2 \quad \ldots(3)$$

where K_2 = pseudo-second order constant (kg/mmol/min).

For the initial condition at t = 0 and Q_t= 0, Eq. (3) becomes:

$$\frac{t}{Q_1} = \frac{1}{K_2 {Q_e}^2} + \frac{1}{Q_e} \quad \ldots(4)$$

4.2 Effect of Initial Ion Concentration on Pb^{2+} and Cd^{2+} Adsorption

Batch adsorption experiments were carried out to test the selected soils at natural pH by changing initial Pb^{2+} concentrations from 0.483 to 9.65 mmol/L (100-2000 ppm) and Cd^{2+} concentrations from 0.889 to 17.8 mmol/L (100-2000 ppm). A mass of 1g of soil was used as the adsorbent for each sample. Suspensions of test materials and solutions were shaken for 120 min. The shaking time was decided based on kinetics experiments for Pb^{2+} and Cd^{2+}.The Pb^{2+} and Cd^{2+} adsorption data were fitted to the Freundlich model (Eq.5) and Langmuir model (Eq.6) [5].

The Freundlich model can be defined as

$$Q_e = K_f {C_e}^{1/n} \quad \ldots(5)$$

where
K_f = Fruendlich adsorption capacity (mmol/kg),
Ce = equilibrium aqueous metal ion concentration (mmol/L)

The Langmuir model can be defined as

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \quad \ldots(6)$$

Q_e= amount adsorbed per kg of adsorbent at equilibrium (mmol/kg),
b = Langmuir constant related to binding strength (L/mmol), and
Q_m = maximum adsorption capacity

4.3 Effect of Initial pH Ion Solution on Cd^{2+} and Pb^{2+}Adsorption

To determine the effects of initial pH on metal ion solutions of Pb^{2+} and Cd^{2+} adsorption onto testing materials, adsorption experiments were performed. The concentrations of Pb^{2+} and Cd^{2+}solution sutilized were 1.57 mmol/L (325 ppm) and 2.96 mmol/L (333 ppm), respectively. A mass of 1g of soil was used as the adsorbent for each sample and solutions were shaken for 120 min. The tests were conducted for a pH range of 4 to 9. The pH values for metal ion solutions were adjusted by adding either sodium hydroxide (NaOH) or hydrochloric acid (HCl). For every measurement of pH, triplicate samples were used.

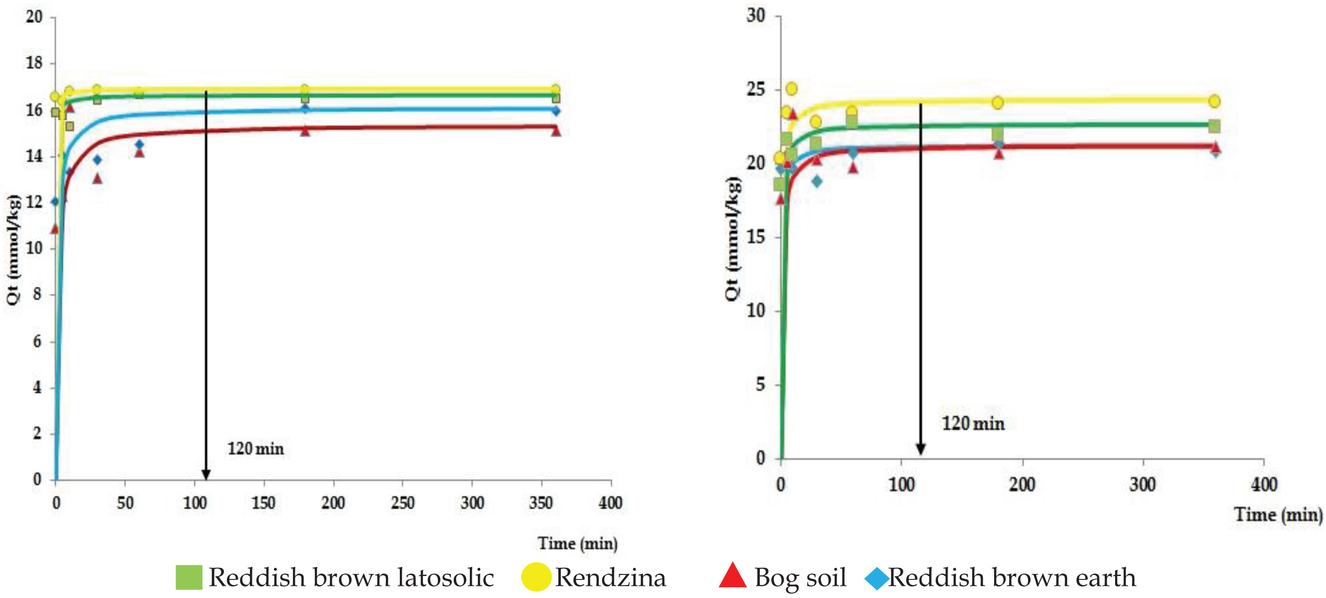
5. Results and Discussion

5.1 Physical Properties of Four Soil Series

Sieve analysis, Atterberg limits, Permeability, and Proctor compaction tests were conducted according to the BS1377-part2:1991 on four soil samples to determine the relevant physical parameters.

Table 3 - Physical Properties of the Soil Series

Parameters	Soil Types			
	Rendzina	Reddish brown latosolic	Reddish Brown earth	Bog Soil
Soil classification	well-graded sand with clay (SW-SC)	well-graded sand with clay (SW-SC)	poorly graded sand, gravelly sand with clay and gravel (SP-SC)	Silty, clayey sand (SC-SM).
Moisture content (%)	13.5	15.1	10.8	15.3
Dry unit weight (kN/m^3)	19.0	18.6	19.6	14.4
Hydraulic conductivity (cms^{-1})	9.77x10^{-2}	1.28x10^{-2}	9.61x10^{-3}	9.61x10^{-3}
Plasticity index (%)	14.9	19.8	5.9	10.2



(a) The fitted curve of Pseudo second-order kinetics model for Pb^{2+} adsorption

(b) The fitted curve of Pseudo second-order kinetics model for Cd^{2+} adsorption

Figure 2 - Fitted Curves of Pseudo Second-order Kinetics Model for Pb^{2+}Adsorption and b Cd^{2+}Adsorption

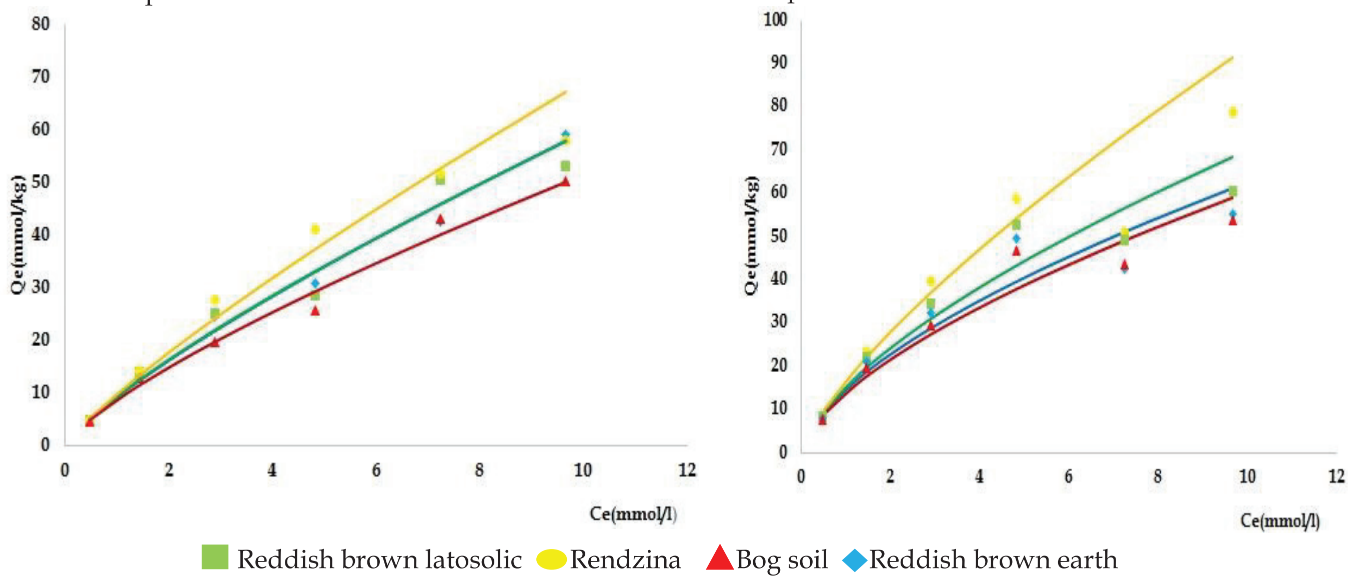
According to Table 3, the Rendzina (Hunugala series) and Reddish brown latosolic (Melsiripura series) are rated as well-graded sand with clay (SW-SC). Redish Brown earth (Nongame series) soil is graded as gravelly poorly graded sand with clay and gravel (SP-SC) and Bog soil (Wagura series) sand is classified as silty, clayey sand (SC-SM). Furthermore, the permeability test results revealed that the Rendzina (Hunugala series) has the highest hydraulic conductivity of 9.77 x 10^{-2}cms^{-1}. Any absorbent for PRBs needs to possess good permeability as well as exceptional adsorbing properties, because PRBs need to assist hydraulic conveyance to draw ground water pollution plumes. Out of selected four soil types, Rendzina (Hunugala series) possesses the highest permeability value which makes it the most promising soil material.

5.2 Adsorption Kinetics of Pb^{2+} and Cd^{2+}

The amount of Pb^{2+} and Cd^{2+}adsorbed onto tested adsorbent [Q_t = amount adsorbed per kg of adsorbent for shaking time (t)], is shown in Figure 2. For all adsorbents, Q_t values for Pb^{2+} and Cd^{2+}become almost constant after 120min, indicating that adsorption has ceased. The Rendzina (Hunugala series) shows a rapid adsorption process for both Pb^{2+} and Cd^{2+}. Adsorption of both Pb^{2+} and Cd^{2+} reached the maximum after 100min of shaking. Of the two models, the pseudo second order kinetics model performed the best with coefficients of determination (R^2) > 0.996 for both Pb^{2+} and Cd^{2+} adsorption for all adsorbents. By considering the coefficients of determination (R^2) (Table 3) of the two models, the pseudo-second-order kinetics model performed well for both Pb^{2+} and Cd^{2+} adsorption onto all adsorbents. Fitted curves of the pseudo-second-order kinetics model are shown in Figure 2.

5.3 Effect of Initial Metal Ion Concentration on Pb^{2+} and Cd^{2+}

Measured adsorptions of isotherms of Pb^{2+} and Cd^{2+} onto tested adsorbents are shown in Figure 3. In this study, two adsorption isotherm models, namely, Freundlich isotherm model (Eq. 6) and Langmuir isotherm model (Eq. 5), were tested by fitting the two models to the sorption equilibrium data. The regression coefficient (R^2) value for the Freundlich isotherm model performed with R^2>0.956 for both Pb^{2+} and Cd^{2+} better than the Langmuir isotherm model. Fitted curves of the Fruendlich isotherm models are shown in Figure 3. According to Figure 3, the Rendzina (Hunugala series) soil sample has the best adsorption capacity for both Pb^{2+} and Cd^{2+} adsorption.



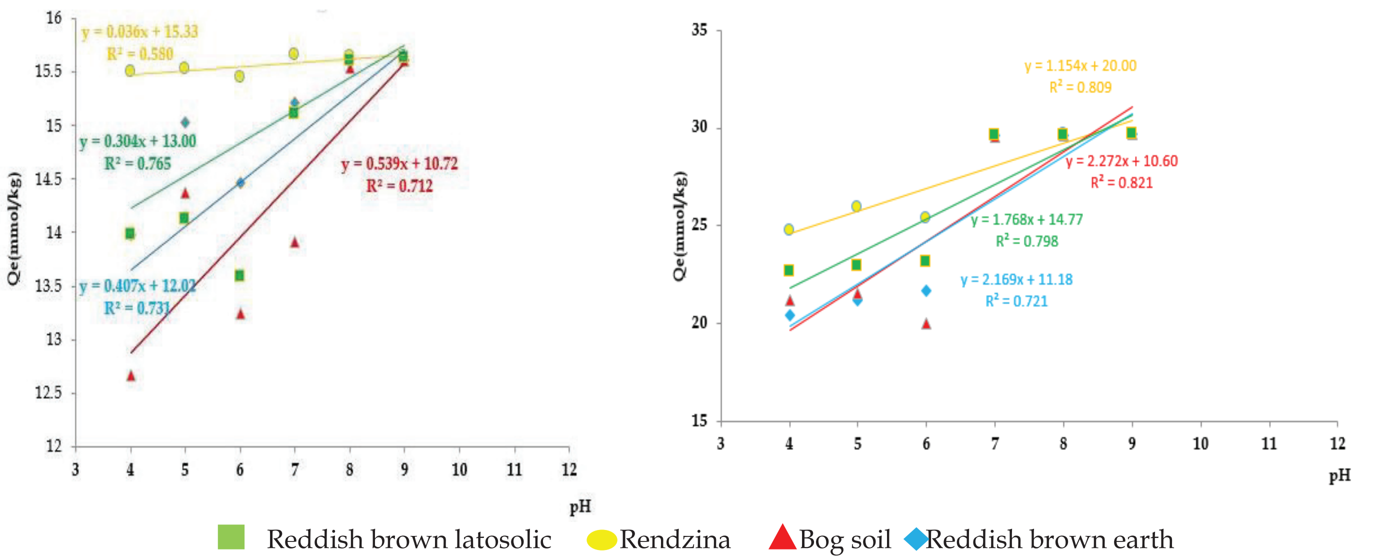
(a) fitted curve of the Freundlich isotherm model for Pb^{2+} adsorption

(b) fitted curve of the Freundlich isotherm model for Cd^{2+} adsorption

Figure 3 - Fitted Curves of Freundlich Isotherm Model for a Pb^{2+} Adsorption and b Cd^{2+} Adsorption

Table 4 - Results Summarization of the Coefficient of Determination (R^2) Values for Pb^{2+} and Cd^{2+} Adsorption for Kinetics Models

Soil Type	R^2 value			
	First Order Kinetic Model		Second-Order Kinetic Model	
	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
Rendzina	0.989	0.991	1.000	1.000
Reddish brown latosolic	0.979	0.981	1.000	1.000
Redish brown earth	0.975	0.977	0.996	0.999
Bog soil	0.968	0.97	0.999	0.999



(a) Relationship between equilibrium Q_e and pHfor Pb^{2+} adsorption

(b) Relationship between equilibrium Q_e and pHfor Cd^{2+} adsorption

Figure 4 –Relationship Between Equilibrium Qe and pH for Pb^{2+}Adsorption and Cd^{2+}Adsorption

5.4 Effect of the Initial pH of Metal Ion Solution on Pb^{2+} and Cd^{2+}

Figure 4 shows the relationship between metals adsorbed onto adsorbents [Q_e = amount adsorbed per kg of adsorbent at equilibrium mmol/kg)] and its pH variation. It can be seen from Figure 4, that there is a good linear relationship between Q_e and pH for both Cd^{2+} and Pb^{2+}adsorption for all the adsorbents. At a pH 4-6, Q_e decreases as pH increases, however the reduction is not significant. The reason for this change is that $Pb^{2+}$and Cd^{2+}ions precipitate in the form of hydroxides, thus reducing the rate of adsorption and consequently the removal capacity of heavy metals [8]. It is evident from Figure 4 that the Q_e values for both Cd^{2+} and Pb^{2+} are between pH values of 7-9 for all soil series. This may be because Q_e increases rapidly with pH at basic pH conditions mainly due tothe negative charges on both organic matter and inorganic solid surfaces of soil [2]. The results indicate that, out of four soil samples tested, the Hunugala series (Rendzina) from Kandy shows higher adsorption capacity over other soils with regards to pH variation.

6. Conclusions

This study was conducted to find the adsorption of Pb^{2+} and Cd^{2+} onto local soils, as potential adsorbents for treating landfill leachate in PRBs. The results of the batch experiments indicated that adsorption kinetics of Pb^{2+} and Cd^{2+} onto all adsorbents were fitted well with the pseudo-second-order kinetics model and adsorption isotherms were well described by the Freundlich isotherm model. Based on the results of the Batch adsorption study, the Rendzina (Hunugala series) was found to be the best adsorption media for Pb^{2+} and Cd^{2+} adsorption in groundwater. Further, Rendzina (Hunugala series) demonstrated the highest hydraulic conductivity compacted at maximum dry density out of all four soil samples selected. Therefore, the Rendzina (Hunugala series) was the most suitable soil-based adsorption media for permeable reactive barriers (PRBs) to adsorb Pb^{2+} and Cd^{2+} in groundwater.

Acknowledgment

The authors wish to extend their gratitude to the Faculty of Science, University of Colombo Sri Lanka, for their kind support given to successfully carry out this research.

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