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Using Permeable Reactive Barriers to Remediate Heavy Metal-Contaminated Groundwater through a Laboratory Column Experiment

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Abstract: Recently, groundwater sources are being polluted by various activities such as agriculture, livestock, decentralized wastewater treatment systems and acid rain. Groundwater can also be polluted by landfill leachate, sewage, mine tailings, non-engineered deep well disposal of liquid waste and seepage from industrial waste lagoons. There are many studies reported contaminated groundwater remediation using Permeable Reactive Barrier systems (PRBs) and many countries happen to use this system to eliminate groundwater contaminants. This study reports the outcomes of the batch and the column test experiments conducted to evaluate the removal efficiency of four heavy metals: Cd(II), Cu(II), Fe(II) and Pb(II) using five locally available reactive materials (in Sri Lanka) with grain sizes less than or equal to 2.0 mm: Red Soil (RS), Laterite Soil (LS), Bangadeniya Soil (BS), Burnt Clay Tile (BCT) and Coconut Shell Biochar (CSB) as PRB materials. Seven columns (A-G) were filled with the reactive material of CSB (column E) and reactive material mixtures; RS + CSB (column A), LS + CSB (column B), BCT+CSB (column C), BS + CSB (column F), RS + LS (column G), with a weight ratio of 50:50 and RS + BCT + CSB (column D) with a weight ratio of 100/3:100/3:100/3. The results showed that the reactive materials filled in column A, B, D, F and G removed the metal concentrations, with a removal efficiency of over 90%, except Cd in the column with BCT + CSB mixture. Considering both the removal efficiency and the hydraulic conductivity of the columns, materials in column A, B, D and F are more effective than the others as PRB adsorbents for heavy metal remediation, while columns C and E have lower removal efficiency.

Keywords: Groundwater Pollution, Heavy Metal, Reactive Material, Permeable Reactive Barrier, Column Experiment

Introduction

There are many heavy metal elements present in the earth's crust as well as metal elements released from industrial effluents such as microelectronics, electroplating, battery manufacture, metallurgical and fertilizer industries, or acid rain breaking down soils releasing heavy metals into streams, lakes, rivers and groundwater (Munagapati *et al.*, 2009). These metals can dissolve in groundwater by natural processes or degradation of soil pH. Additionally, heavy metals also are released from inappropriate landfill and sewage management, leaching from mine tailings, non-engineered deep well injections and seepage from industrial waste lagoons (Evanko and Dzombak, 1997). Through untreated landfill leachate, depending on the type of landfill, metal contaminants such as Cd, Hg, Ni, Mn, Cu, Zn, Pb, As and Fe are often released

to the environment. Heavy metals have an atomic density greater than 4,000 kg/m^3 or equal to 5 times more than that of water (Garbarino *et al.*, 1995).

Many researchers have found that though some of the metals play as essential micronutrients for living beings, most heavy metals at higher concentrations give extremely harmful effects to humans, animals and plants because of their high toxicity and biological accumulation in the body (Soylak *et al.*, 1999; Arain *et al.*, 2008; Kazi *et al.*, 2009; Afridi *et al.*, 2009; Bermudez *et al.*, 2011). Moreover, heavy metals may cause diseases to humans such as lung damage, renal damage, Wilson's disease (neurological or psychiatric symptoms of liver disease, compounded with heavy metal deposits), insomnia, dermatitis, nausea, chronic asthma, headache, dizziness, rapid respiration, coughing and cancer, etc. (Meena *et al.*, 2005; Guzel *et al.*, 2008).

In recent years, there are many technologies and methods used to remove heavy metals from groundwater or wastewater such as adsorption, chemical precipitation, ion exchange and membrane. These technologies have their own different advantages and disadvantages to remediate heavy metals contaminated groundwater or surface water. However, when heavy metal ions co-exist in the form of cations and anions, Han *et al.* (2015) reported many difficulties in treating them.

For the conventional pump-and-treat technology being utilized for remediating polluted groundwater, its cleanup goals hardly show achieving targets. Moreover, the pump-and-treat technology is a passive treatment operation where it needs much more independence of external labor and energy inputs.

The Permeable Reactive Barrier (PRB) on the other hand is a novel technology used worldwide for remediation of contaminated groundwater. This technology uses adsorption, chemical precipitation and degradation processes in combination to generate physical, chemical or biochemical reaction between contaminants and reactive materials contained in barriers to facilitate waste removal (Thiruvenkatachari *et al.*, 2008). Further, due to its promising removal efficiencies, easier maintenance, longer lifespan (10-20 years), environmentally friendly behaviors and low cost make this system more attractive (Woinarski *et al.*, 2006; Dong *et al.*, 2009). Therefore, PRB is one of the technologies used as in-situ remediation method for heavy metals contaminated groundwater, chlorinated organic, phosphorus, etc. This method was firstly applied in a field study at the Canadian Forces Base, Borden (O'Hannesin and Gillham, 1998).

Bone (2012) has shown that the total 624 publications on PRBs were made between 1999 and 2009. PRB method is worldwide used to carry out the treatment of contaminated groundwater and surface water (Blowes *et al.*, 1998; Conca *et al.*, 2002; Kober *et al.*, 2002). The concept of PRBs is to act as a permeable barrier packed with reactive materials that intercept the path of the contaminated groundwater flow path to treat the contaminant plume. There are many advantages and limitations of PRB which were identified by Carey *et al.* (2002) and Henderson and Demond (2007) (Table 1).

Moreover, the PRBs can be an attractive option for developing countries like Cambodia, India and Sri Lanka to treat contaminated groundwater where risk of contamination is high due to widespread solid waste open dumps. For instance, PRBs was used to remove arsenic from groundwater along river banks of the Mekong River in Cambodia (Marie *et al.*, 2009). However, the high costs of reactive materials make the system unaffordable to developing countries.

Table 1. Advantages and limitations of permeable reactive barrier

No.	Advantages	Limitations
1	Relatively cheap passive technology, i.e., inexpensive but effective reactive. Low energy cost; little or no disposal costs for treated wastes; relatively low maintenance and monitoring costs with the exception of initial installation cost	Only contaminants flowing in the direction of the barrier can be treated
2	Allows for treatment of multiple contamination plumes since more than one barrier can be used	Requires proper characterization of the site, aquifer, hydrogeological conditions and accurate delineation of the contaminant plume prior to barrier installation
3	Ability to treat a wide range of contaminants	Restricted to plumes not deeper than 20 m beneath the ground surface
4	The aboveground of the contaminated site can be put to profitable use while treatment is ongoing	A limited field data concerning longevity of barriers
5	No cross-media contamination since contaminants is not brought to the surface	Below-ground structures (e.g., services, foundations) may present problems in construction and performance
6	Requires occasional monitoring to ensure that barriers are functioning properly	Reactive media may have to be removed or be replaced during operation
7	Obviates the handling and loss of large volumes of groundwater	May require long-term monitoring, particularly in the case of persistent contaminants or very slow groundwater flow

The reactive material is the main adsorbent used in Permeable Reactive Barrier system to remove contaminants from groundwater. Many researchers have found various possible reactive materials for organic and inorganic remediation. The commonly used reactive materials, relying on their different high removal ability for contaminated water, are Zero-Valent Iron (ZVI) (Liu *et al.*, 2013; Obiri-Nyarko *et al.*, 2014), zeolite (Kovalick and Kngscott, 1995; Vignola *et al.*, 2011), activated carbon (Natale *et al.*, 2007), Peat (Kao and Yang, 2000). Among these materials, ZVI is widely used in PRBs to clean contaminated groundwater and surface water (Obiri-Nyarko *et al.*, 2014). The review of Guerin *et al.* (2002) and Gibert *et al.* (2011) showed that there are more than 200 PRBs built worldwide in different scenarios of contamination mostly used ZVI.

The main objective of this research is to evaluate the reactive materials which is locally available in Sri Lanka as candidate materials to be used in Permeable Reactive Barrier system (PRBs) for the heavy metals contaminated groundwater remediation. The specific objectives are (1) to examine the hydraulic conductivity of single and mixed reactive materials, (2) to define the removal efficiency of the heavy metals on the single and mixed reactive materials conducted with laboratory column experiment and (3) to analyze the heavy metals (Cd, Cu, Fe and Pb) leaching from raw reactive materials.

Materials and Methods

Physical Properties of the Reactive Material Mixes

Reactive material is the main adsorbent used in Permeable Reactive Barrier system (PRBs) to facilitate the removal of contaminants from groundwater. Main criteria for the selection of material for this study are local availability, reactivity efficiency, mechanical stability, cost effective, hydraulic conductivity performance, environmental compatibility and safety. Red Soil (RS), Laterite Soil (LS), Bangadeniya Soil (BS), Burnt Clay Tile (BCT) and Coconut Shell Biochar (CSB) were used as the reactive materials in the PRBs. These materials are abundant in Sri Lanka and their cost is very low comparing to other commercial reactive materials.

Physical properties of the material fills are important for designing the column experiment and installing PRB. There are three tests to determine the physical properties of the material fill. These are a gradation test for determining the particle size distribution, the standard compaction test for determining the density and moisture content of the fill and the falling head test for determining the hydraulic conductivity. These testes are essential for estimating the quantity (kg) of PRB

material packed into the column pipe as well as PRB system. Particularly, the dry density and moisture content were applied to calculate hydraulic conductivity (K), so that one can select the appropriate passed flow cross packed material in each column. The moisture content in this experiment refers to how much water is added and mixed with PRB material for packing into the column experiment.

A sieve analysis (gradation test) is a commonly used method in civil engineering to determine the particle size distribution of granular materials. Five samples of CSB, RS, LS, BCT and BS were dried in an oven at 105°C for 24 h. Each sample was shaken so that the sample particles passed through many mesh sieve layers starting from 2.000, 1.700, 1.180, 0.850, 0.600, 0.425, 0.250, 0.150 mm, until 0.075 mm. The total mass of each sample is 1,000 g. After being sieved for four minutes, the samples retaining on each sieve mesh size were weighed. The percentages of the sample retaining and passing were calculated as:

$$R = \frac{M_C}{M_t} \times 100 \tag{1}$$

$$P = 100 - R \tag{2}$$

Where:
R = The percentage of material retained on the sieve (%)
M_C = The mass accumulation of material retained on the sieve (g)
M_t = The total mass of materials (g)
P = The percentage of material passing through the sieve (%)

The standard compaction test (Moisture-Density Relation) is the most common practice in soil mechanic field. The objective of this test is to determine the relationship between the optimum moisture content (W) and dry density (ρ_d). The single and mixture samples passing through a sieve of 2.0 mm were selected. The samples were dried in the air for 24 h. Moreover, the required weight of the sample is approximately 2.5 kg.

Water was added into the sample and mixed thoroughly until the sample appeared a uniform color. The Proctor Mold was filled with three equal layers of the mixed sample and each layer was compacted by using 2.5 kg hammer falling at a distance of 30 cm from the surface of each layer. Each layer also received 27 uniformly distributed blows. The compacted sample within the mold is weighed and recorded the mass. The mass of the wet sample was determined by subtracting the weight of the mold. The two samples were withdrawn from the top and bottom of the specimen

and put into small bowls and then dry in the oven at 105°C for 24 h. The small bowls, wet samples and dried samples were weighed and recorded in gram (g). The test was repeated with lesser compacted sample masses until a peak value was reached. The moisture content W (%) and dry density (ρ_d) were calculated as:

$$W = \frac{m_w}{m_{ws}} \times 100 \tag{3}$$

$$\rho_d = \frac{\rho_b \times 100}{100 + W} \tag{4}$$

Where:
W = The soil moisture content (%)
m_w = The mass of water (g)
m_{ws} = The mass of wet sample (g)
ρ_d = The dry density (Mg/m^3)
ρ_b = The bulk density (Mg/m^3)

The falling head test method is commonly used for fine-grained soils whose hydraulic conductivity (K) ranging from 10^{-2} to 10^{-6} cm/s. Furthermore, this method is suitable to determine hydraulic conductivity of the reactive materials mix, both single and mixed samples in this study. The hydraulic conductivity was measured by using the fixed permeable wall under a falling head condition.

The sample mold was connected to a standpipe which provides the head of water and the means of measuring the quantity of water flows through the sample. A reactive material sample was compacted into the mold (11.85 cm in height and 9.95 cm in diameter). The hydraulic conductivity test was conducted with three different values of the moisture content (minimum, optimum and maximum values). Then the mold with compacted sample was soaked in a water basket and kept for a minimum period of 1-2 days in order to allow the sample become fully saturated. The air bubbles were completely released from the standpipe connected with mold specimen.

After the sample was fully saturated, the standpipe was filled with the tap water up to the starting point. Then the test was started by allowing the water to flow up-down through the sample until the water in the standpipe reached a limited lower level. The time reading was recorded every 10 cm of dropping water in the standpipe by using a chronometer. It was repeated until the time reading varied within 5–15%; otherwise, it will not be accepted. Based on the reading results the hydraulic conductivity can be computed as:

$$K = \frac{a}{A} \times \frac{L}{\Delta t} \times \ln\left(\frac{h_1}{h_2}\right) \tag{5}$$

Where:
K = The hydraulic conductivity (cm/s)
a = The cross section area of stand pipe (cm^2)
A = The cross section area of mold specimen (cm^2)
L = The height mold specimen (cm)
Δt = The time of water drop through the specimen (s)
h_1, h_2 = Respectively the water drop level at the beginning and the end of reading time (cm)

Preparation of Synthetic Heavy Metal Solutions

The synthetic heavy metal contaminated water contains the desired concentrations of 20 mg L^{-1} of Cu^{+2}, 20 mg L^{-1} of Fe^{+2}, 5 mg L^{-1} of Pb^{+2} and 5 mg L^{-1} of Cd^{+2} that were prepared from Copper Sulfate Monohydrate (CuSO$_4$.5H$_2$O), Iron Sulfate Monohydrate (FeSO$_4$.7H$_2$O), Lead Nitrate (Pb(NO$_3$)$_2$) and Cadmium Nitrate Monohydrate (Cd(NO$_3$)$_2$.H$_2$O). It should be noted that the stock solution contains all metals together. The quantity of each chemical required to prepare the desired concentration of each heavy metal was calculated as:

$$M = C_C \times \text{Purity of chemical} (\%) \tag{6}$$

$$C_C = \frac{C_m \times M_C}{M_m \times 1000} \tag{7}$$

Where:
M = The mass of chemical (g)
C_C = The concentration of chemical (g/l)
C_m = The concentration of heavy metal (mg/l or ppm)
M_C = The molar mass of chemical (g/mol)
M_m = The molar mass of heavy metal (g/mol)

Analysis of Leaching of Heavy Metals from Reactive Materials

There are four adsorbents of heavy metals (Cu, Fe, Pb and Cd) which were used for the analysis and their sorptivities were checked with CSB, RS, LS, BCT and BS. Five grams of each sample was mixed with 100 ml of distilled water in 250 mL PTFE flasks and then shaken at 240 rpm for 4 h using a shaking incubator. The aqueous phase and suspended solid were then separated by centrifuging with refrigerated ultra at 16,000 rpm for 10 min at a temperature of 20°C. To determine the concentrations of heavy metal, the suspended solids were removed filtering through 0.45 µm-pore-size *Watman* membrane filter paper. Filtered samples were tested for pH. The 10 mL of filtered aqueous samples were preserved at 4°C prior to the metal analysis by using AAS7000, SHIMADZU, Japan.

Column Experiments

The amounts of PRB materials required to fill (CSB, RS + CSB, LS + CSB, BS + CSB, BCT + CSB and RS + BCT + CSB) columns were computed as:

$$M = \gamma_d \times V \times W \qquad (8)$$

Where:

M = The required weight of reactive material (g)
γ_d = The dry buld density of sample (g/m^3)
V = The volume of column packing (989.30 cm^3)
W = The moisture content of maximum hydraulic conductivities (%)

The column experiments were conducted by using the black cylinder PVC pipe which is of 50 cm long with an internal diameter of 7.1 cm (Fig. 1). In this experiment, there were seven columns (A-G); each column consists of three sampling ports (0.4 cm of inner diameter plastic tubes with 2 cm long) inserted along one side of the column located at 5 cm (inlet), 15 cm (port 2) and 25 cm (outlet) from the bottom of each column. The bottom of each column was compacted 5 cm of sand (1-2 mm grain size) to filter out the suspended solid and to provide a uniform flow across each column. A fine screen was placed on the top of the sand layer to prevent the compacted reactive material particles filling in the pore sand layer. The single and mixed reactive materials were filled and manually compacted on the sand layer in each column up to a height of 25.0 cm. A 5 cm of the sand layer (1-2 mm grain size) was then placed on the top of the compacted material for preventing the fine reactive material flow out. The PRB materials were filled and compacted into the column following the procedure: (1) Weigh the reactive materials for the first layer of 10 cm, the second layer of 10 cm and the last layer of 5 cm; (2) Compact manually the reactive material layer by layer in each column until reaching the desired height (25 cm of layer).

A closed container of 50 l was used to fill the synthetic heavy metal solution and placed it at 2.5 m high to get the desired flow rate. A 1.0 cm inner diameter polyethylene tubes was used to deliver the heavy metal solutions to a shearing pipe with seven ports which passing continuously the solutions to each column at the bottom side in the direction bottom-up (Fig. 1). In addition, a white T-valve was used to control the flow from the tank and black small valves were used to control the inflow (influent) and outflow (effluent) of each column.
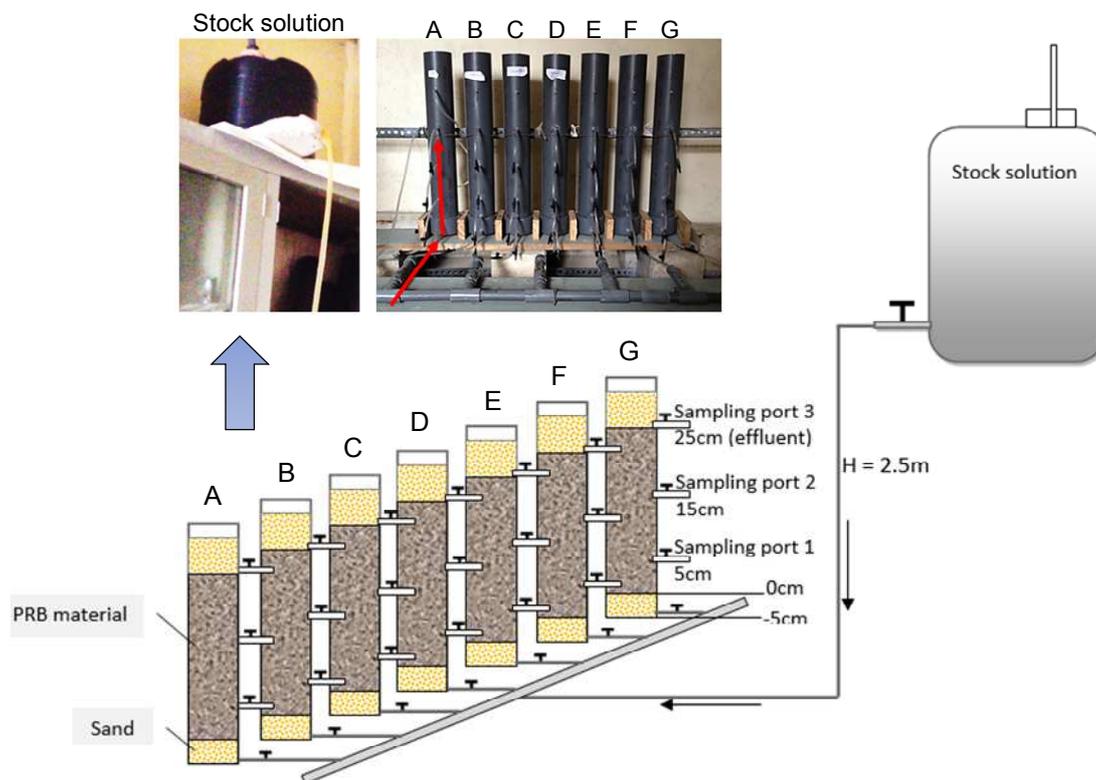

Fig. 1. Schematic diagram of packed bed columns with reactive materials in the Permeable Reactive Barrier

Prior to each experiment, all columns were soaked and flushed with distilled water until the compacted reactive materials in each column getting fully saturated. After saturation, the valves at the inlet of all columns were opened to release the distilled water. The synthetic solution was then flushed into each column from the bottom (influent) at a flow rate of approximately 1.0 ml/min using the falling head method under gravitational flow. However, the flow rate may vary among the column due to a different porosity/hydraulic conductivity. Bottles were used to collect the effluent water samples from three column ports periodically for the heavy metal concentrations analysis (Cu^{+2}, Fe^{+2}, Pb^{+2} and Cd^{+2}) using Atomic Adsorption Spectrophotometer (AAS7000, SHIMADZU, Japan). The flow rates of each column were measured and recorded weekly. All experiments were carried out in the same room and operated simultaneously.

Atomic Adsorption Spectrophotometer is used to measure the concentration of heavy metals such as Manganese (Mn), Iron (Fe), Nickel (Ni), Copper (Cu), Zinc (Zn), Cadmium (Cd), Lead (Pb), Sodium (Na), Potassium (K), Magnesium (Mg) and Calcium (Ca). The technique of this machine is used by the flame atomic spectrometry to determine the quantity of these elements. The sample solutions were filtered through a 0.45 μm diameter of micro-filter paper, then stored at 4 °C prior to the analysis. The filtered aqueous samples were thoroughly removed the suspended solids to avoid clogging in the nebulizer during the analysis. The pH was also measured by a pH meter after aqueous samples were collected.

Results and Discussion

Physical Properties of the Raw Reactive Materials

The particle size distribution of each reactive material selected were determined. According to the results of the sieving test, the percentage of passing particles was calculated. The particle-size distribution curve was plotted in Fig. 2. It is important to use these curves to pre-identify the hydraulic conductivity of materials. Furthermore, knowing the particle size distribution, it is easy to improve the hydraulic conductivity of a mixture by changing the mixed proportion of CSB with the other reactive materials.

In this research, the compaction test was carried out to determine the optimum moisture contents to achieve the maximum dry density. Having at least a 90% to 92% of maximum dry density at the PRB minimizes settlement issues when in use. The dry density was plotted versus the moisture content, generally called the compaction curve (Fig. 3). The test conducted on CSB was very difficult because it is rich of ash contents. The particles were easily damaged and its particle has a high adsorption capacity of water. However, the experiment was done acceptably. The

results showed that through not a very visible peak, the maximum dry density of CSB is 0.842 Mg/m³, smaller than the other sample mixtures: 1.12 Mg/m³ for BCT + CSB, 1.257 Mg/m³ for RS + CSB, 1.29 Mg/m³ for LS + CSB, 2.119 Mg/m³ for RS + LS, 1.235 Mg/m³ for BS + CSB and 1.354 Mg/m³ for RS + BCT + CSB. In contrast, its Optimum Moisture Content (OMC) is 46.25% greater than that of the other samples (Fig. 3).
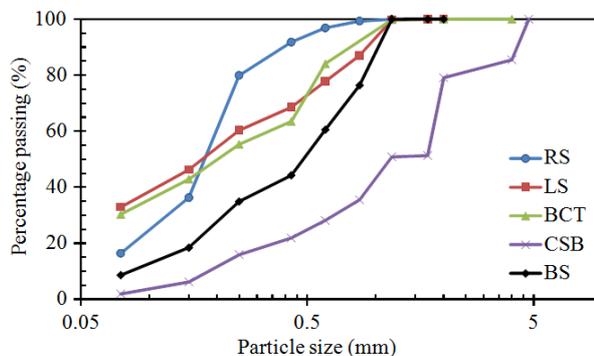
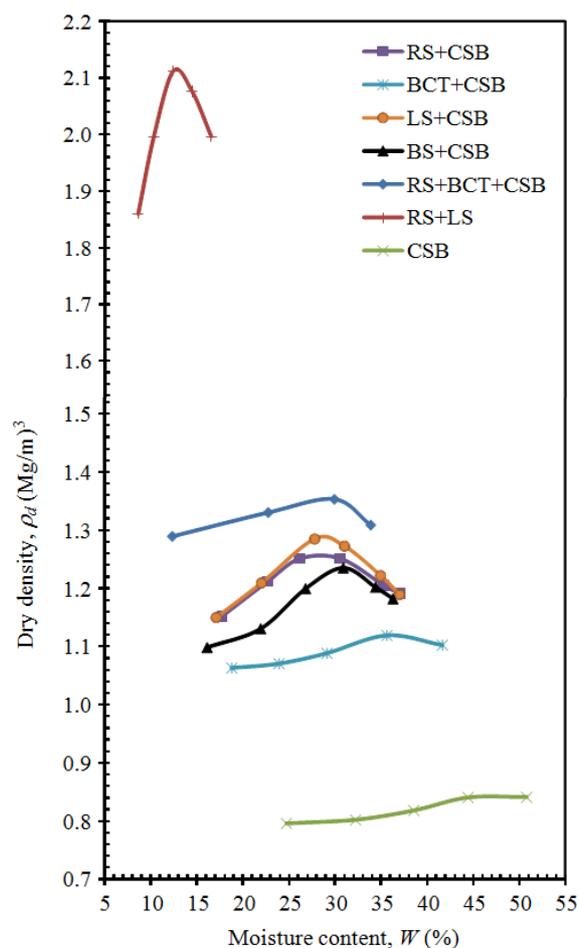Fig. 2. Particle size distribution of raw reactive materials

Fig. 3. Compaction curve of reactive raw materials

The hydraulic conductivity of each material mix at different moisture and density was determined by using the falling head permeability test. The main objective of this test was to find out the appropriate permeable conductivity (K) whose limitation is higher or equal to 10^{-4} cm/s. The K value has a function with the moisture contents (Fig. 4). There are three values of K which were selected for the study: minimum, optimum and maximum value. The results showed that the hydraulic conductivity of each sample increases when moisture content decreases (Fig. 4). However, there were only two samples, CSB and BCT + CSB, which had hydraulic

conductivities (K) larger than the limited value of 10^{-4} cm/s, i.e., CSB has a hydraulic conductivity of about 1.4×10^{-4} cm/s and BCT + CSB has 1.2×10^{-4} cm/s, while the other mixture samples have a K value less than their limit value (10^{-4} cm/s).

Heavy Metal Leaching from Raw Materials

The leaching of heavy metals from the raw reactive materials was also considered as an important factor in selection. The candidate reactive materials shall release excess contaminants when in use.
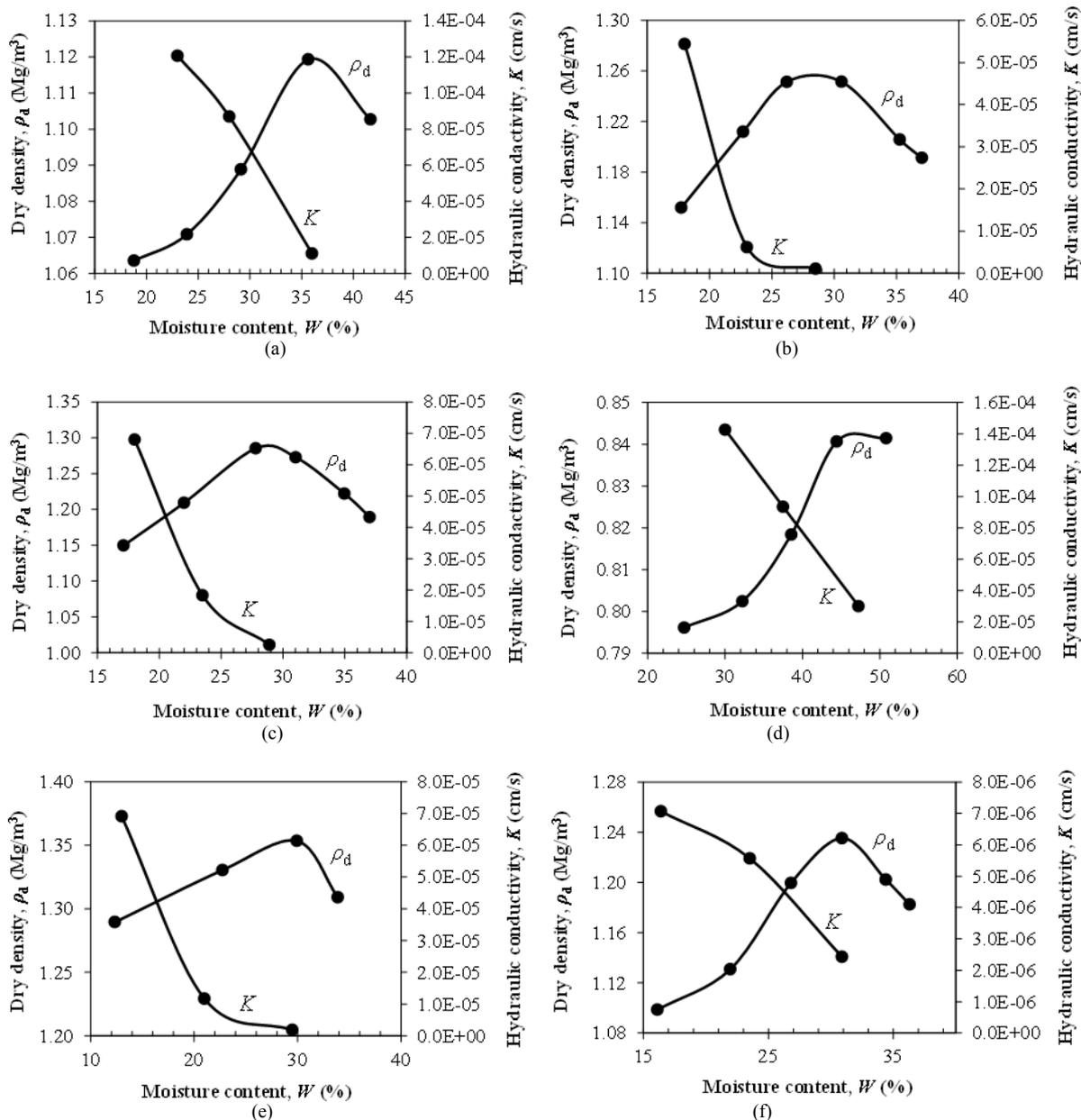

Fig. 4. Relationship between dry density/hydraulic conductivity and moisture content of raw reactive materials (a) BCT + CSB; (b) RS + CSB; (c) LS + CSB; (d) CSB; (e) BCT + CSB + RS; (f) BS + CSB

Leaching tests were carried out for all five selected reactive materials: RS, LS, BS, BCT and CSB at the Environmental Laboratory, Faculty of Civil Engineering, University of Peradeniya, Sri Lanka.

As shown in Fig. 5, RS has the highest concentration of leaching Fe(II), 0.5103 ppm, followed by BS and BCT releasing 0.3297 ppm and 0.2015 ppm, respectively. CSB and LS has a very low Fe(II) leaching, 0.0210 ppm and 0.0093 ppm, respectively. Comparing with past studies, the leaching Fe(II) of RS and LS of the present study are higher (Kaandeepan *et al.*, 2012). However, the Fe(II) levels in all samples are within the 1.0 ppm maximum permissible levels specified in Sri Lankas' Standards for potable water - SLS 614, 1983. Moreover, the testes show RS had the smallest Cd(II) leaching (0.0012 ppm). BCT, BS, CSB and LS leached small amounts of Cd(II), 0.0035, 0.0030, 0.0021 and 0.0018 ppm respectively; values are less than the SLS 614 maximum permissible level of 0.005 mg L^{-1}. On the other hand, leaching Cd(II) in this study was found to be different to that of previous studies which did not find leaching Cd from RS and LS (Kaandeepan *et al.*, 2012). The leaching of Pb was found to be higher than its maximum permissible level of 0.05 ppm, while 0.2191, 0.2068, 0.2001, 0.1882 and 0.1635 ppm leached from BS, RS, BCT, CSB and LS, respectively. Furthermore, Pb(II) leaching from RS and LS is much higher than one recorded in previous studies, 0.0077 ppm and 0.0091 ppm respectively, possibly because of the site of RS collection close to a motorway. The small amount of Cu(II) leaching from RS, BS, CSB, LS and BCT PRB recorded 0.0140 ppm, 0.0123 ppm, 0.0089 ppm, 0.0078 ppm and 0.0078 ppm, respectively (Fig. 5). Compared to 1.5 ppm of Cu(II), the maximum permissible level, there is no toxicity of Cu in the PRB materials. Additionally, the measurement of pH showed the CSB gives the highest value among the materials.
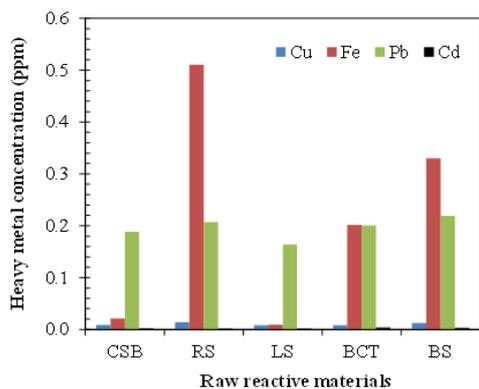

Fig. 5. Heavy metal concentration leaching from raw reactive materials. The concentration of Cu, Fe, Pb and Cd in stock solution is respectively 17.05 ppm, 16.75 ppm, 4.06 ppm and 4.55 ppm

Column Tests: Removal Efficiency of Heavy Metals

The effluent pH of aqueous sample from 5 cm port, 15 cm port and 25 cm port in each column was measured. According to the results, the pH was increased to a range of 6.0-8.9 in the first three days of operations (Fig. 6). Except for CSB and BCT + CSB mix, pH remained stable in all other columns until the end of the experiments. The CSB and BCT + CSB mix's pH gradually decreasing to a 4.0-5.5 range is possibly due to a high flow in these two columns. The increase in pH at effluents could be explained by a reaction of biochar (CSB) which releases the carbonates and hydroxyl ions.
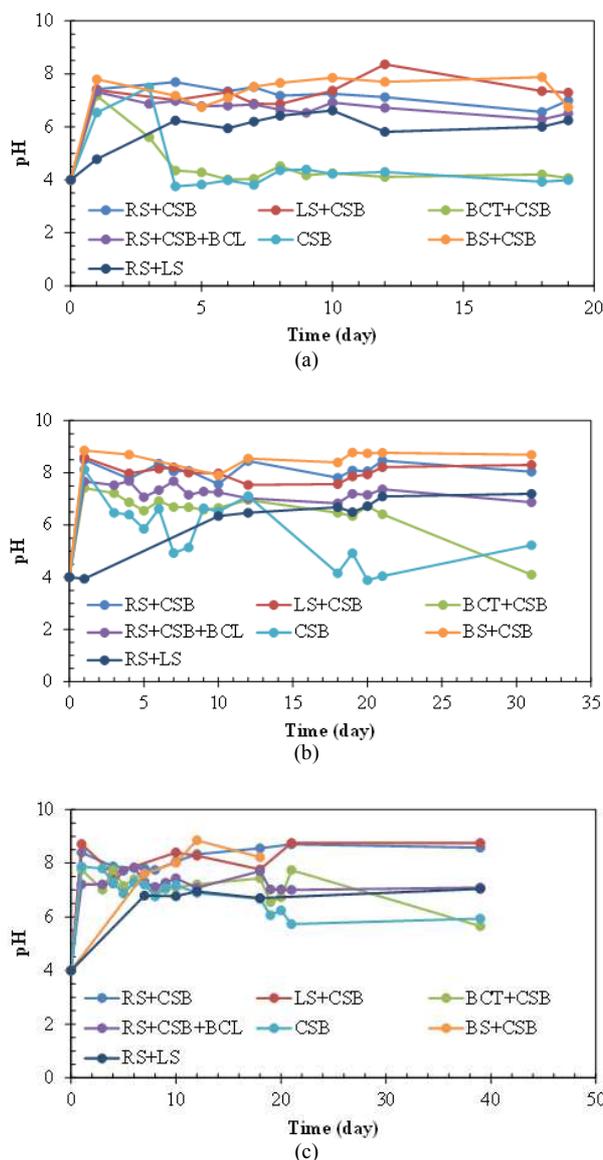

(a)

(b)

(c)

Fig. 6. Time course of pH in effluent (a) Port 5 cm; (b) Port 15 cm; (c) Port 25 cm

In the column experiments, the initially raw value of Cd, Cu, Fe and Pb is respectively 4.55 ppm, 17.05 ppm, 16.75 ppm and 4.06 ppm. The initial pH of the solution is around 4.0. All the results are graphical illustrated in Fig. 7-10. Changes in total effluent concentrations were observed at the three sampling ports as a function of the testing time (Fig. 7-10). The removal efficiencies of metal elements on the column A-G at all ports is increasing similarly over the time of the experiments. It should be noted that the removal efficiency is the difference between heavy metal concentration in stock solution and leaching solution, divided by heavy metal concentration in stock solution.

At the conclusion of experiments, the removal efficiency for Cd from the BCT + CSB mix and the CSB mix at all three ports and the RS + BCT + CSB mix at ports of 5 cm and 25 cm gradually dropped down with a rate of 33.8%, 15.25% and 56.65%, respectively, at the 5 cm port, 15.25% and 2034%, respectively, at the 15 cm port and 29.5%, 30.67% and 77.79%, respectively at the 25 cm port (Fig. 7).
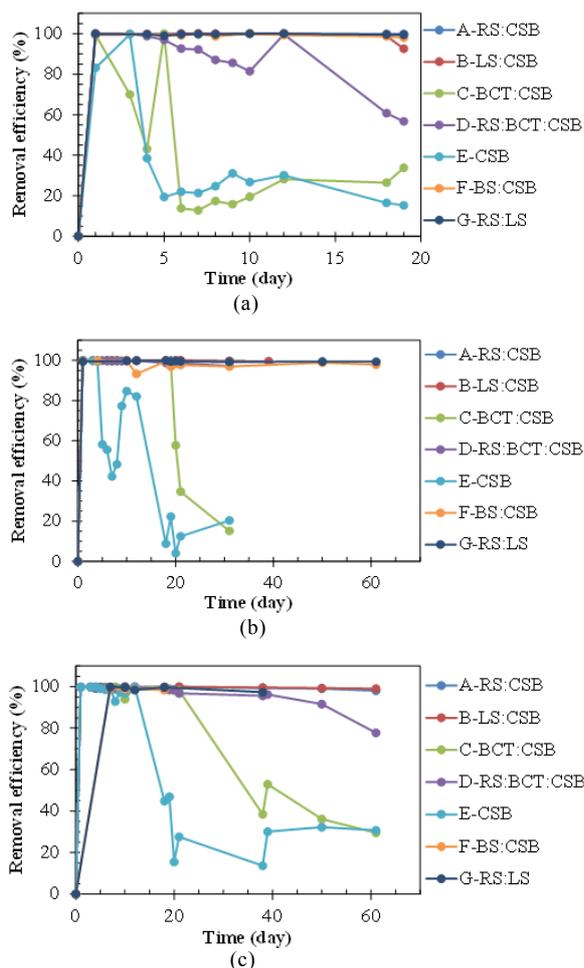
It dropped down because the flow rates in these columns were high (Fig. 11). Besides the columns C, E and D (at ports 5 cm and 25 cm), the removal efficiency of Cd became stable at around 99.0%. Therefore, the reactive materials filled in column A, B, F and G are possible to remove Cd effectively from contaminated water, with a maximum of 99.0%.

The removal efficiency of Cu in columns C and E at the 5 cm port also gradually decreases with a rate of 59.44% and 36.28%, respectively. At the 25 cm port, the removal efficiency of Cu in columns C and E is 31.44% and 9.94%, respectively. The removal efficiency of Cu in other five columns remains slightly stable as shown clearly in Fig. 8, with the maximum removal efficiency of around 99.8% for Cu.
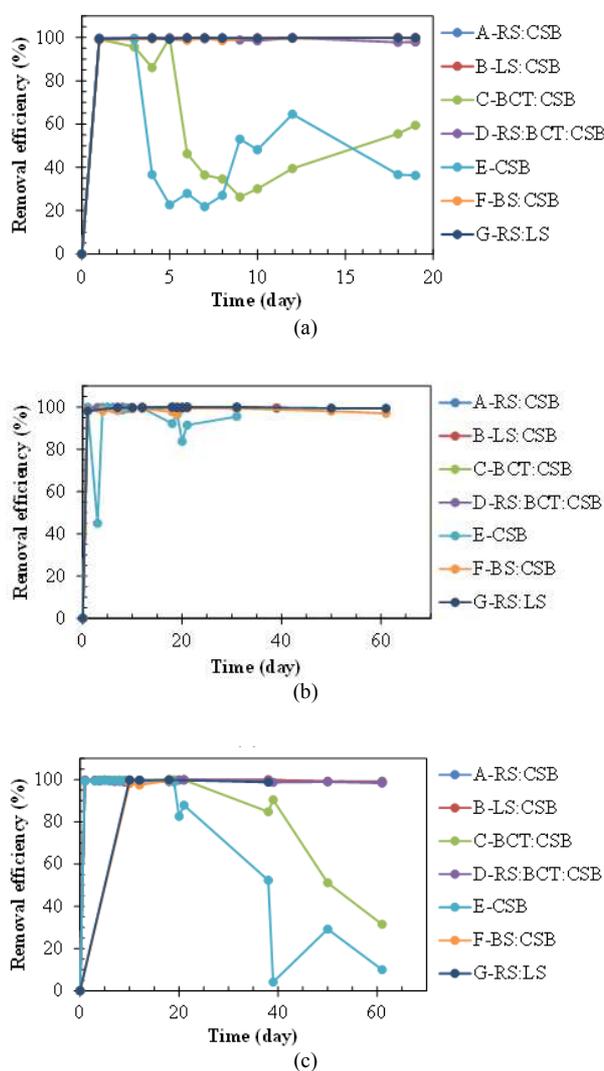

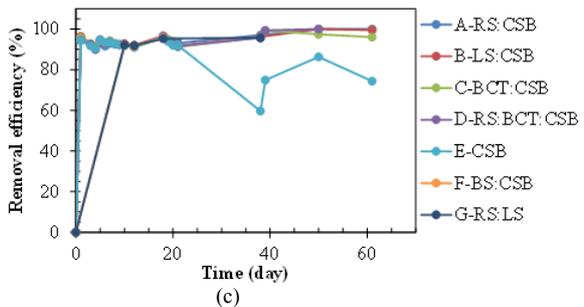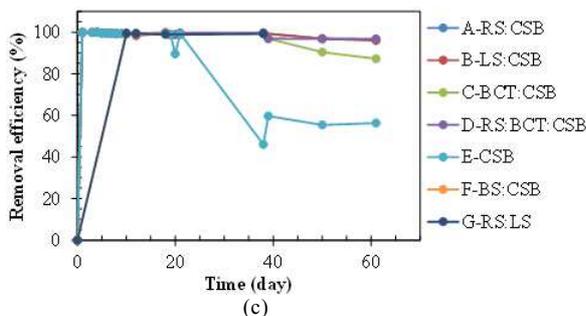Fig. 7. Contaminant removal efficiency of Cd^{+2} (a) Port 5 cm; (b) Port 15 cm; (c) Port 25 cm

Fig. 8. Contaminant removal efficiency of Cu^{+2} (a) Port 5 cm; (b) Port 15 cm; (c) Port 25 cm
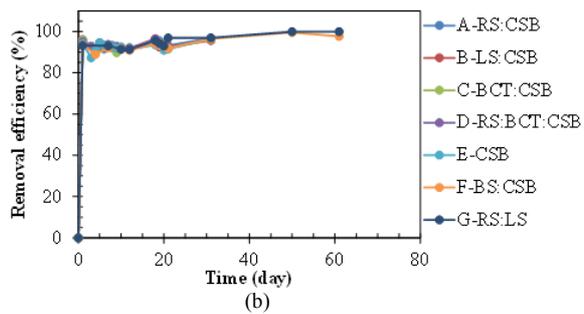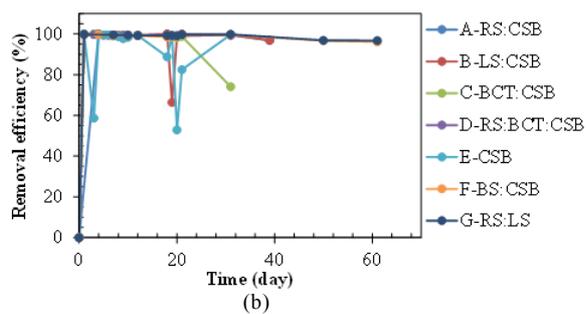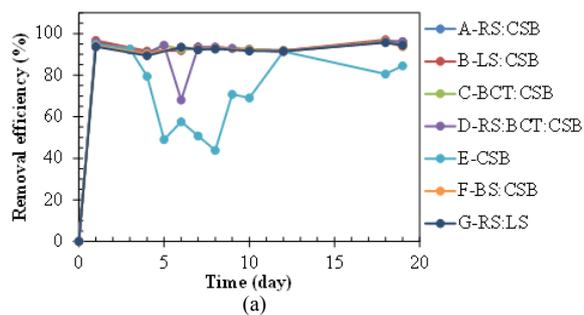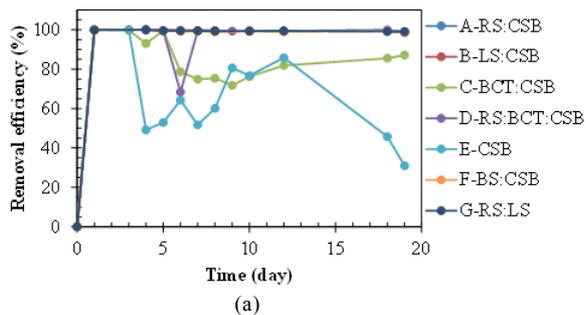
Fig. 9. Contaminant removal efficiency of Fe^{+2} (a) Port 5 cm; (b) Port 15 cm; (c) Port 25 cm

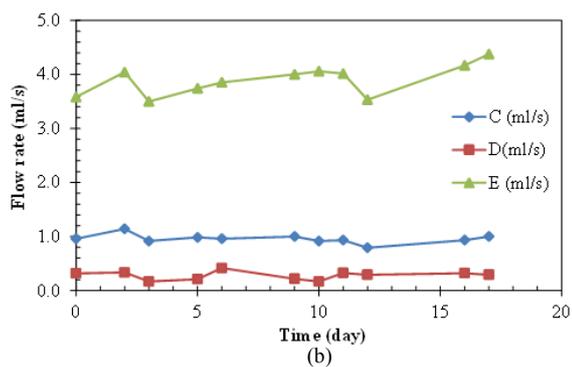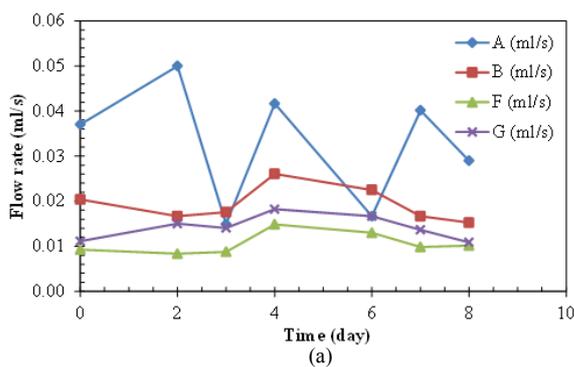Fig. 10. Contaminant removal efficiency of Pb^{+2} (a) Port 5 cm; (b) Port 15 cm; (c) Port 25 cm

Fig. 11. Flow rate from (a) columns A, B, F and G; (b) columns C, D and E

The Fe removal efficiency of reactive materials in column C was decreased with a rate of 31.03%, 74.11% and 87.213% in port 5 cm, 15 cm and 25 cm, respectively. In column E, the Fe removal efficiency was also decreased with a rate of 87.14%, 56.3% at port of 5 cm and 25 cm, respectively; and it was increased with a rate of 99.8% at the port of 15 cm (Fig. 9). For the other columns at the sampling port of 15 cm and 25 cm, the

removal efficiency of Fe decreases approximately to 96.8%, while it is about 99.1% at the port 5 cm.

The removal efficiency of Pb on the columns A, B, C, D, F and G, are more than 93.7% at port 5 cm, more than 95.65% at the port 15 cm and more than 95.66% at the port 25 cm. At the column E at the port 5 cm and 25 cm, the removal efficiency was decreased with a rate of 84.5% and 74.4%, respectively. The effluent flow rate from the seven columns was measured weekly (Fig. 11). The flow from columns C, D and E is higher than that from columns A, B, F and G. This was expected as the hydraulic conductivity of reactive materials in columns C, D and E is higher than that of the other reactive materials in columns A, B, F and G.

Conclusion

In this research, the locally available reactive materials, i.e., Red Soil (RS), Laterite Soil (LS), Bangadeniya Soil (LS), Burnt Clay Tile (BCT) and Coconut Shell Biochar (CSB) show its potential in remediating the heavy metal contaminant in the groundwater. It is expected that the materials are potentially used to replace the high cost reactive materials, for example, Activated Carbon (AC), Zero-Valent iron (ZVR) or Zeolite (Zeo) that are highly efficient to remove the metal elements and commonly used in developed countries.

The single reactive material of CSB and reactive material mixtures such as RS + CSB, LS + CSB, BS + CSB, BCT + CSB (with a weight ratio of 50:50) and RS + BCT + CSB (with a weight ratio of 100/3:100/3: 100/3) used as PRB adsorbents were tested for removing the Cd(II), Cu(II), Fe(II) and Pb(II) from the synthetic water solutions carried out through the laboratory column experiment. The hydraulic conductivity of both single and mixed reactive materials was determined. It is one of important parameters for the PRB design. After the test, the hydraulic conductivity of CSB and BCT + CSB (with a ratio of 50:50) is greater than the suggested value of 10^{-4} cm/s, with 1.4×10^{-4} cm/s and 1.2×10^{-4} cm/s, respectively, while RS + CSB, LS + CSB, BS + CSB, RS + LS and RS + BCT + CSB have a value of 5.44×10^{-5} cm/s, 5.40×10^{-5} cm/s, 7.10×10^{-6} cm/s, 5.60×10^{-5} cm/s and 6.90×10^{-5} cm/s, respectively.

The experimental column studies are very important to estimate the removal efficiency of heavy metal contaminants in the water and provide the useful information to design the PRB system in the field. At the end of the experiment, the removal efficiencies of reactive materials filled in the column A (RS + CSB), column B (LS + CSB), column D (RS + BCT + CSB), column F (BS + CSB) and column G

(RS + LS) are very efficient, with the removal efficiencies of more than 90%, except Cd that only in column C (BCT + CSB), the removal efficiency is less than 90%. Moreover, the removed concentrations of heavy metals from these columns are smaller than that of the maximum permissible level of Sri Lanka Standards for potable water - SLS 614, 1983. On the other hand, the removal efficiencies of reactive materials filled in columns C and E were low in comparing with the other five columns.

Since the flow rate are not the same in different columns, it is recommended that the analysis of column experiments as a function of pore volume should be taken into account. It is defined as tQ/V, where t is the time, Q is the flow rate and V is the pore volume.

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Author's Contributions

Somean Yin: Conducted all experiments, data analysis and preparation of the draft manuscript.

Gemunu Herath: Refined research framework and coordinated the experimental operations.

Sokchhay Heng: Advised research design, organized the manuscript's structures and edited the manuscript.

Senajith Kalpage: Provided idea on setting up research methodology and operation of experiments.

Ethics

This article contains unpublished and original work of the authors. All authors have read and approved the manuscript and no ethical issues involved.

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