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Leaching Characteristics of Heavy Metals (Pb, Cr and Cd)

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Abstract-Column flow through leaching experiments reacting heavy metal solution with sand, slit and clay soil samples were performed to study heavy metal attenuation by three soils with different physical, chemical and mineralogical properties. Saturated solute transport experiments were conducted using one small and one large column packed with three different types of soil. This study examined the leaching experiments of three soils in polyvinyl chloride (PVC) column. A column experiment is very useful apparatus that can be used to study the migration and attenuation of heavy metals through a compacted soil column. Prior to testing all three soils were thoroughly characterized for their physical, chemical and mineralogical properties. All soil columns were permeated using laboratory made solution with concentration of heavy metals 500mg/l at pH 5.0. The experiments results were analysed in terms of breakthrough curves. The breakthrough curves shows that the clay sample has better adsorption capacity on heavy metals as compared to sand and silt soils. Less retention means high concentration of heavy metals was detected in the pore fluid. The order of mobility of heavy metals through leaching column experiment in case of sand and silt was Cr>Cd>Pb and in case of clay the order of mobility was Pb>Cd>Cr. The test results also reflect the influence of soil origin in adsorption of heavy metals, where soil characteristics and surface properties contribute very significantly to the adsorption of heavy metals.

Key Words: Column, Leaching, Heavy Metals, Pb, Cr, Cd, Breakthrough Curves

I. INTRODUCTION

Decrease of nutrients and increase of pollutants in soil has become a serious environmental issue owing to rapid industrial development that has taken place in many parts of the world in recent years [1]. Raised concentration of heavy metals in soils are of potential long term environmental and health concerns because of their tenacity and growing tendency in the environment and their associated toxicity to biological organisms [1,2].Soil is one of the key elements for all terrestric ecosystems. It provides the nutrient bearing environment for plant life and is of essential importance for degradation and transfer of biomass. Soil is a very complex heterogeneous medium, which consists of solid phases containing minerals and organic matter and fluid phases, which interact with each other and ions entering the system. The ability of soils to adsorb metal ions from aqueous solution is of special interest and has consequences for agricultural issues such as soil fertility. Heavy metals are usually defined in terms of characteristics such as malleability or potential of being withdrawn, conductivity, strength and stability of kind of ligand and an atomic number bigger than 20. Some of the most important heavy metals that are toxic and pollutants of environment include Cadmium, lead and chromium [3]. These substances are found naturally inside ores and also to some extent in most soils. The main sources of soil and environmental pollution by heavy metals are industrial and human activities such as mines, metal melting, electroplating, power plants, gas-online preservation and supply stations, production and consumption of chemical fertilizers and pesticides, utilization of effluent and sewage sludge in agriculture and industrial waste landfills [3].
Adsorption is the most common processes regulating the concentration of contaminants between soil particles and soil solution. These processes are related to the type of soil, particularly the content of inorganic colloidal and organic fractions. The transport mechanism of heavy metals through soils and other environmental matrices has long presented great interest to both environmental and soil scientist because of the possibility of ground water contamination through metal leaching [4].To predict the fate and transport of contaminants in the environment, scientists and engineers commonly rely on distribution coefficients and maximum adsorption levels that are obtained from experiments in which it is assumed that the reaction is at equilibrium, but instead are in a state of continuous change because of the dynamic processes occurring [5]. The discharge of heavy metals cations to the water phase and so the tendency for transport processes depends on their solution speciation and their affinity to bind reactive surfaces in the soil matrix and pore water (such as dissolve organic matter or metal (hydroxide) surfaces).
Batch equilibrium tests usually used to determine adsorptive isotherms, utilize small portions of soil and representative contaminants [6].The problem with this method is that the small quantities of soil may not adequately simulate the actual soil conditions. Also, the batch method may not reflect the actual leachate-soil interaction. The ratio of solution to soil and time required to reach equilibrium does not always give a good estimate of the migration and adsorption of heavy metals through a clay barrier. Sorption characteristics obtained from leaching tests provide a better means of estimation

of soil sorption performance and also account for the effects of partial soil saturation [7]. For these reasons leaching tests are more valuable than batch tests of soil [8].

In the present study, experimental investigation of the leaching behaviour of Pb, Cd and Cr from three different types of soil i.e. sand, silt and clay at pH 5.0 by using compacted soil in PVC columns (Soil column experiment) was performed against high concentration of heavy metals. Soil column is a very useful physical tool to study the migration of contaminants through a compacted soil [9]. It is used to model the migration of HMs in soil and very useful for experimental studies.

The objective of this study was to evaluate the mobility of heavy metals in three types of soils (sand, silt and clay) having different texture, chemical and mineralogical composition by leaching with spiked distilled water with heavy metals in soil leaching experiments.

II. MATERIAL AND METHODS

Three types of soil namely Sand, Silt and Clay had been selected in order to cover the general spectrum of soil found in field conditions. Collected soil samples were analysed for further physic-chemical properties as shown in Table 2.0.

A. Specimen Imaging and Mineralogical Composition

One of the most important properties affecting the mobility of heavy metals is the microstructure of the soils. The microstructure affects the amount of possible sorption sites in which inorganic contaminants become immobilized. Figure 1 to 3 shows the scanning electron microscope (SEM) images of sand, silt and clay. Figure 4 to 5 shows the mineralogical composition in sand, silt and clay.

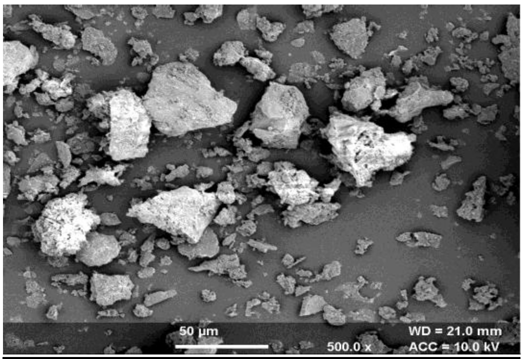

Fig. 1 Scanning Electron Microscope (SEM) images of sand

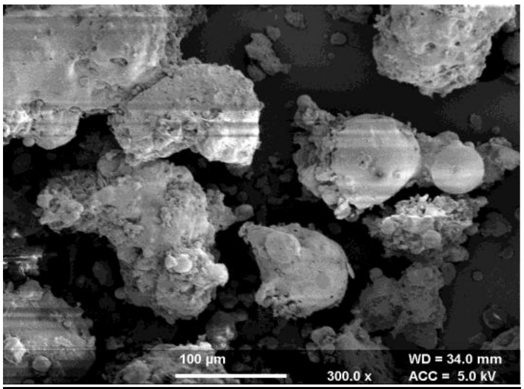

Fig. 2 Scanning Electron Microscope (SEM) images of silt

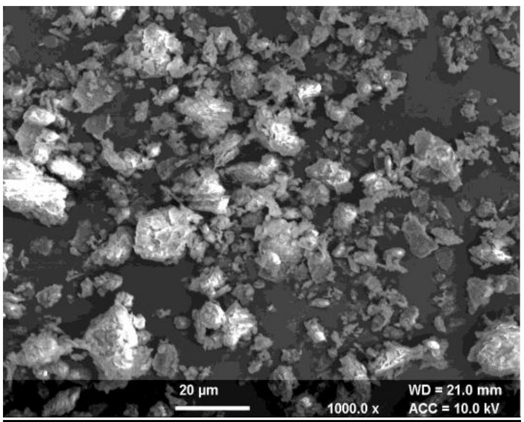

Fig. 3 Scanning Electron Microscope (SEM) images of Clay

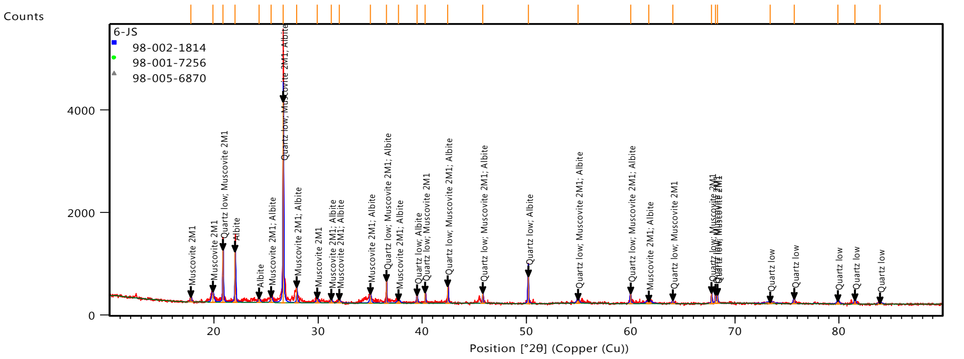

Fig. 4 Mineralogical composition of Sand

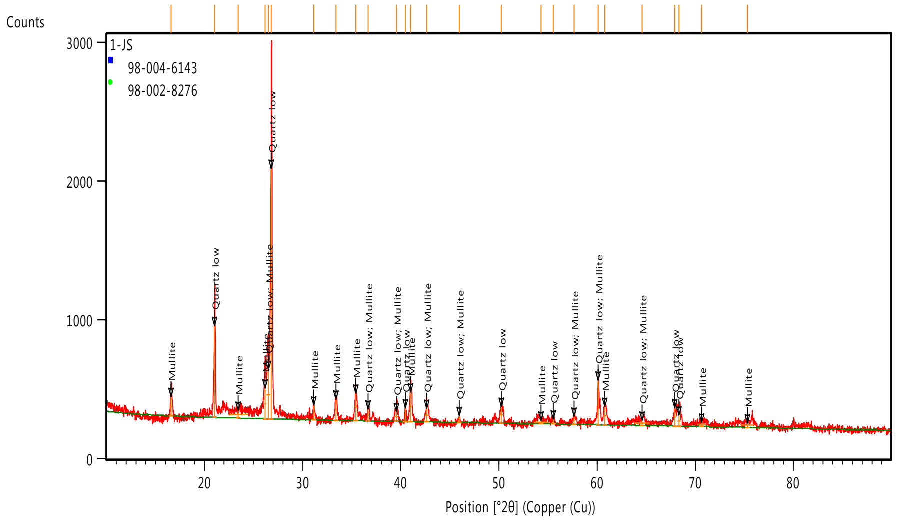

Fig. 5 Mineralogical composition of Silt

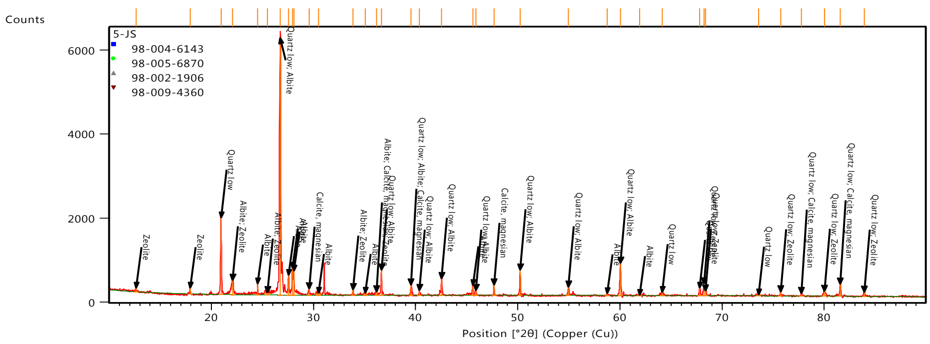

Figure 5.0 Mineralogical composition of Clay

B. Metal Cation Solution

Three metals Cr, Cd and Pb were studied because of their toxicity or their large quantity in soil and waters. The metal solutions were prepared by dissolving 500 mg/l metal nitrate in distilled water. Nitrates were used because these ions have affinity for metals [10]. The pH was adjusted to 5.0. The metals concentrations in solution became unstable during percolation, at a higher pH due to precipitation of metal hydroxides [11].

C. Column Leaching Experiment

Three different types of soil (sand, silt and clay) having different physical, chemical and mineralogical characteristics were chosen for the column leaching experiment.

The samples were air dried. Spiked distilled water, acidified to pH 5 with HNO_3 was used as leachate. The use of spiking is to raise the contaminant dose i.e. a procedure which maximizes the contaminant-soil interaction effects. Before filling of column, the bottom of the column was fitted with perforated disc and whatman filter paper No.42 was placed. The columns were filled with dry soil and then compacted to a dry density of about 1.48 g/cm3, 1.16 g/cm3 and 1.52 g/cm3 for sand, silt and clay.

The soils were compacted in the PVC columns according to a standard proctor compaction test. The columns were carefully packed with soil material. After filling, the top of the column was also sealed with 42 whatman glass fibre membrane filer paper. There were two stages of leaching for column test, first is saturation stage using deionized distilled water and second is leaching stage using a spiked test solution with heavy metals. The chemical composition of spiked test solution is given in Table 1. The samples were collected at different time intervals at the outlet point of soil column and analysed for residual concentration of heavy metals.
Two PVC Columns were used (one column of 8 cm height and 7.5 cm diameter for sand and silt and second of 3.5 cm height and 7.5 diameter for clay). Both columns were closed at both ends by perforated discs. The lower caps hole was connected to a tube for collecting eluates. Glass fibre Whatman filter paper 42 was placed between the cap and the soil to ensure the distribution of the solution [12].
Effluent was percolated from top to bottom varies in between 6 ml/min to 12 ml/min. The effluent was collected and analysed using AAS. All effluents were filtered using Whatman Glass Fibre Filter paper No. 42 prior to analysing to prevent blockage in AAS. The retention capacity was determined by percolating metal solution through soil column.

TABLE 1.0
CHEMICAL COMPOSITION OF SPIKED SOLUTION TEST

Parameter	Value	Unit
Pb	500	mg/l
Cr	500	mg/l
Cd	500	mg/l
Conductivity	2.9	µS/cm
pH	5.0	--

III. RESULTS AND DISCUSSION

TABLE 2.0
PHYSICO-CHEMICAL CHARACTERISTICS OF SAND, SILT AND CLAY

S.No.	Parameters	Unit	Sand	Silt	Clay
1.	pH	--	8.2	7.8	7.4
2.	Organic Matter	%	0.207	0.63	1.02
3.	Bulk Density	gm/cc	1.6	1.47	1.79
4.	Dry Density	gm/cc	1.48	1.16	1.52
5.	Sand	%	89	19	18
6.	Silty	%	6	54	33
7.	Clay	%	5	27	49
8.	CEC	meq/100 gm	12.1	23.2	38.2
9.	Calcium Carbonate	%	8.9	6.2	16.3

A. Breakthrough curves study results from vertical column test and retention assessment

The breakthrough curves were plotted between relative concentrations (Ce/Co) against the discharge volume. Relative concentration (Ce/Co) is a ratio between concentration of heavy metals in the effluent and concentration of heavy metals in the influent [13]. The relative concentration equals to 1 represents the total breakthrough of heavy metals through the compacted soil column.

The leaching test was performed for sand, silt and clay. The dry density was calculated using standard proctor test. The dry density of the material packed in the soil column was 1.48 gm/cc for sand, 1.16 g/cc for silt and 1.52 g/cc for clay. Flow rate varies in between 6 ml/min to 12ml/min during the entire experiment. The leaching experiment was performed continuously to avoid any equilibrium states. The leachates samples were collected in 100ml plastic containers and analysed by Atomic Absorption Spectrophotometer (Elico).

Figure 3-5 shows the Breakthrough curves for Cd, Cr and Pb for sand, silt and clay as observed in leaching soil column. It can be seen that Ce/Co values were increased with the increasing discharge volumes. The plot also showed that Cr was the most mobile heavy metal in case of sand and silt and Pb was the most mobile metal in case of clay. Low Ce/Co values (i.e. Breakthrough curves <1.0) showed that sorption of heavy metals was high [13]. The Breakthrough curves indicated that different heavy metals have different affinity for adsorption, where the affinity of heavy metals adsorption can be ranked as Pb>Cd>Cr in case of sand and silt and the affinity of heavy sorption can be ranked as Cr>Cd>Pb in case of clay. Same adsorption sequence was found in sand and silt but in case of clay sequence was reverse, seems to be related to the fact that Cr was applied in trivalent form and other two heavy metals Pb and Cd was applied in divalent forms. Cadmium and lead ions are adsorbed less on clay soil because they are characterized by larger ionic radii and complexation with surface sited is limited by steric hindrance and lower electrostatic attraction. Cr is the most mobile heavy metal in case of sand and silt and in case of clay Pb is the most mobile heavy metal.

In case of sand the breakthrough time was observed at 104-112 hours, in case of silt the breakthrough time was observed at 128 hours and in case of clay the breakthrough time was observed at 312 hours. The results also indicated high adsorption capacity of soil for Pb in case of sand and silt and Cr case of clay.

The results also indicated that high retention and adsorption breakthrough did not attain, but a trend of immense for getting the same at deferred time lag was noted. However, it was found that both theoretically and experimental results are in agreement to a significant extent.

The concentration of Cd, Cr and Pb in the columns was 500mg/l. For sand, the percent of the total spiked metal leached from sand was in order of Cr (78%)> Cd (76%)> Cd (76%) from silt was in order of Cr (59 %)> Cd (56%)> Pb (49%) and from clay was in order of Pb (44%)> Cd (38%)> Cr (35%).

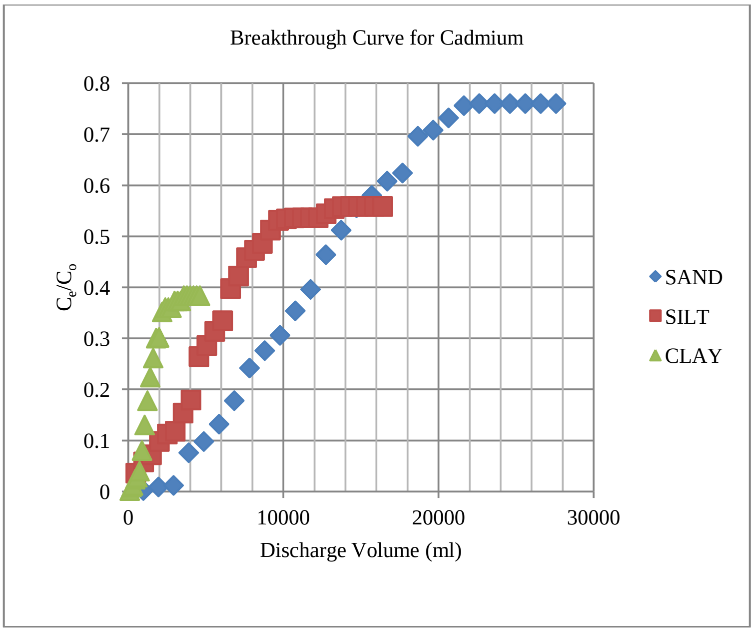

Fig. 10 Breakthrough curve for Cadmium

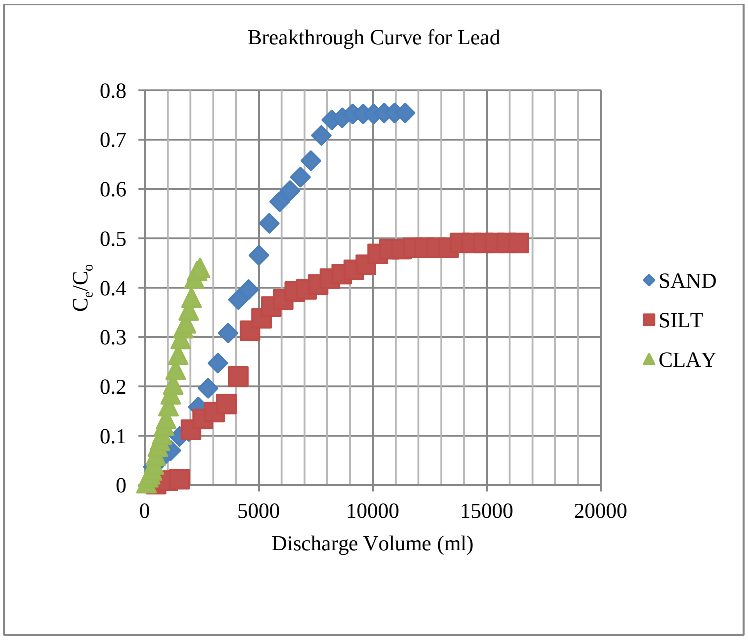

Fig. 11 Breakthrough curve for Lead

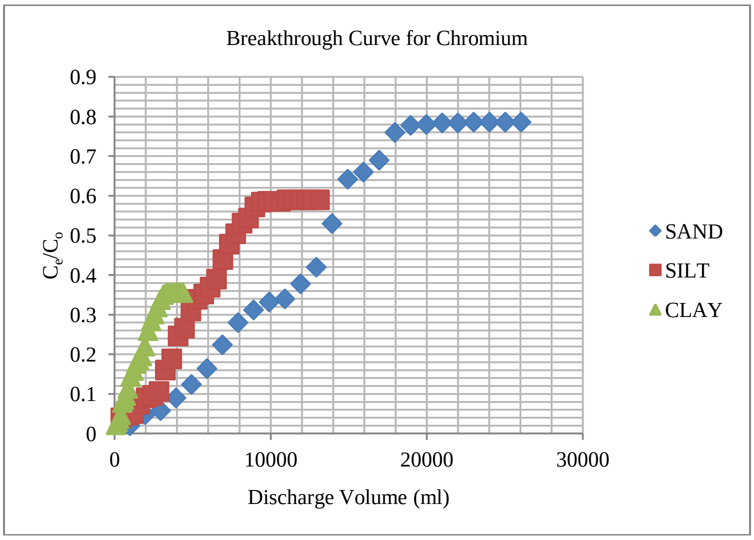

Fig. 12 Breakthrough curve for Chromium

B. Effect of soil structure on breakthrough Curves

Although only a low percentage of its calculated was used to retard heavy-metal migration, the clay soil had the latest breakthrough points and the highest retentions of three soils. The performance of the soil can be explained using the breakthrough results. The shape of a breakthrough curve depends on the manner in which the soil structure affects migration. If the soils had the same structure but different sorption capacities, initial detection would occur at different points and the rate of increase would be similar. As observed in Fig.10.0 to 12.0, the breakthrough curves of the three soils show that initial detection occurred at approximately the same point but the rate of concentration increase differed significantly thereafter. This suggests that the physical structure of the compacted soil had greater influence than the sorption capacity.

IV. CONCLUSION

1. The column leaching experiments provided a useful approach to assess the leachability of the metals for the different soil and also to assess the bio-availability of the spiked metals.
2. Interaction of the three metals with sand, silt and clay soil shows that the soil retention capacity of clay soil was high.
3. The motilities capacities obtained from breakthrough were in the order Cr>Cd>Pb for sand and silt & for clay the order was Cr>Cd>Pb.
4. This experimental study reveals that soil having different capacity to retain heavy metals and very much depending upon their chemical and physical properties.
5. Based on the retention capacity, clay soil has good retention capacity among silt and sand soil and to be selected to function as engineered clay liner.
6. The study also revealed that column test is a good experimental tool to assess the retention capability of the soils on heavy metals, as shown by this study using breakthrough curves.

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