Indian Journal of Science and Technology, *Vol 9(33), DOI: 10.17485/ijst/2016/v9i33/99173, September 2016*
ISSN (Print) : 0974-6846
ISSN (Online) : 0974-5645

Study on Suitability of Red Earth as Liner Material based on its Performance with Acidic and Basic Pb (II) Solutions

Jittin Varghese, P. Lakshmi Sruthi*, Mary Harris and P. Hari Prasad Reddy

Department of Civil Engineering, NIT Warangal, Warangal - 506004, Telangana, India;
vjittin@student.nitw.ac.in, plakshmisruthi@nitw.ac.in, hari@nitw.ac.in,

Abstract

Objectives: This paper studies the suitability of Red soil as landfill liners for the retention of Lead. **Method:** The study was carried out for alkaline conditions, acidic conditions and for different initial concentrations of Lead. Both Batch studies and Column studies were conducted. **Findings:** The Freundlich Isotherm is found to be the best fit for the data obtained from Red soils. Breakthrough curves are plotted from column experiment. Red earth under basic condition is found to be suitable as liner material. **Novelty:** The current research proposal is aimed to extract the maximum practical benefits from locally available materials, if necessary by suitable modification.

Keywords: Diffusion, Landfill Liners, Lead Retention, Soils

1. Introduction

Geoenvironment is being highly contaminated by indiscriminate and non-engineered disposal of industrial as well as municipal wastes[1]. Different sources releasing contaminants into the subsurface are 1. Pollutant receptors such as hazardous waste landfills, industrial waste ponds and lagoons. 2. Accidental leakages occurring during transport. 3. Agricultural operations involving arbitrary application of chemicals to the land.

Heavy metals mostly found at contaminant sites are lead (Pb), cadmium (Cd), Copper (Cu), zinc (Zn), nickel (Ni) and chromium (Cr)[2]. Lead is one of the mostly found contaminant. Sources of lead are E-waste, leaded gasoline, lead mining, ceramic glazes, smelting, coal combustion, lead based paint, and batteries and cosmetics which contains lead. The presence of lead in high amount can be toxic to human being[3].

To prevent degradation of the ground water quality and the surrounding geoenvironment, researchers have employed different waste disposal methodologies such as solidification and immobilization, incineration, land filling, etc., for efficient disposal of these wastes[4].

However, landfill disposal is considered to be safe and economic method when compared to the rest. As landfill leachate migrates downward, various contaminants interact with soil components resulting in processes such as physisorption, chemisorptions, precipitation or complexation. Engineered waste landfills with liner systems consisting of low permeable materials (less than 10^{-7} cm/s) need to be used to avoid uncontrolled release and migration of hazardous contaminants into the environment[5]. Among the various available natural liner materials, compacted clay liners are popularly used because of their low cost with reasonable low hydraulic conductivity, high sorption capacity and resistance to damage and puncture. Further, the high specific surface area of the clayey geo-materials permits strong physical and chemical interactions with the chemical contaminants present in the leachate, which result in retention of these contaminants by electrostatic repulsion, sorption or specific cation exchange reactions[6–8].

*Author for correspondence

Contaminant transport through compacted soil liner is controlled by a variety of physical (diffusion, advection and dispersion), chemical (dissolution/precipitation, complexation, hydrolysis/substitution, sorption, and oxidation) and biological (decay) processes[9].

Attenuation of leachate occurs due to adsorption, biological intake, cation and anion exchange and precipitation. The retardation factor for any particular chemical species depends upon factor such as temperature, pH, redox potential, salinity, organic content, and concentrations of other chemical species along with solid surfaces of the porous media.

In[2] in his study observed that heavy metal uptake by clay suspensions involving kaolinite, illite, and montmorillonite increases with pH. There is a tremendous increase in the amount of the metals retained when the soil solution pH rises to value required for precipitation or formation of metal hydroxy species. These increase correspond to the cation exchange capacity values of the clay. Further, it is also noticed that, the range of pH values over which the optimum retention is observed becomes narrow with the increase in heavy metal concentration in the solution[10]. Attenuation of various heavy metals by the geo-materials is quite dependent on pH, since majority of the heavy metals may exhibit the precipitate mechanism by forming compounds such as hydroxides, sulphates, and chlorates species[11]. It has been reported that the buffer capacity of the geomaterial is significantly influenced by the cation exchange capacity, the presence of carbonate content in it and initial concentration of the heavy metal solution, which in turn affects the sorption capacity of the geomaterial[2,3].

This paper describes about the suitability of locally available Red Earth as liner material for minimizing the contaminant migration of lead metal.

2. Methodology

In order to predict the transport and the fate of various pollutant species, the transport parameters involved in the governing set of equations that describe the transport processes need to be accurately defined. The laboratory column experiments and batch studies which can be used to estimate the transport parameters of chemical species migrating through waste containment barrier are discussed. Due to the difficulty in collecting the leachate sample from field, synthetic leachate (model contaminant) is prepared from heavy metal lead (Pb^{2+}) in the nitrate form.

The locally available fine-grained soil studied in this investigation is Red Earth (RE) which is normally available in most parts of India. The soil was collected by open excavation, from a depth of 1 meter from natural ground level in and around Warangal. The soil used in the study is having Maximum density of 1.79 kN/m^3, OMC of 17.1% and with clay content of 29%

Batch sorption experiments were conducted at solid ratio (L/S) of 200 at two different pH conditions namely acidic (pH =5) and alkaline (pH =10). A temperature of about 30^{o}C was maintained constant throughout the experiment. According to[12], it is very difficult to perform batch sorption experiments for *L/S* values less than 4, as the resulting paste hinders separation of the solid particles from the mixture of contaminant solution and geo-materials. Tests are conducted for various initial concentrations such as 50 ppm, 100 ppm, 150 ppm and 200 ppm in 250 mL conical flasks for both pH ranges i.e., acidic and alkaline conditions. The conical flasks were gently shaken by mounting them on a mechanical shaker. The speed of the shaker was adjusted to around 120 rpm and shaking was carried out for a specified interaction time of 8 hours. The samples were then filtered using Whatman filter paper of grade 42. The filtrate i.e., clear solution was analyzed for various heavy metals using ion analyzer (ISE HI4522). To demonstrate the influence of pH (over acidic and alkaline ranges) on sorption characteristics initial concentrations, pH of the lead solution is adjusted to both acidic and alkaline range. The pH of the initial lead solution is almost 5 and in order to make the solution alkaline, 4N NaOH solution was added drop by drop until pH increased to around 10. The results of batch sorption experiments are modeled using the various theoretical sorption isotherms such as Linear, Langmuir and Freundlich isotherms available[13].

Experimental set up for column test consists of the following three major components namely: Influent Reservoir, Column assembly, and Effluent collector. The synthetic solution of lead should be placed in this influent reservoir and is stirred at frequent intervals so as to maintain constant initial concentration. The reservoir was maintained at 1200 cm head. Column test setups are made of Plexiglas cylinder of 15 cm long, 6.3 cm inner diameter and 1.2 cm thick wall. The Plexiglas cylinder will be attached to the base plate. To facilitate the drainage at top and bottom of the specimen, two porous stones along with filter papers were placed at both ends of the sample. The void ratio of the sample was maintained constant throughout the experiment by keeping the height of the sample same with the help of small loading arm and tie rod arrangement. This facility minimizes the change of void ratio of the compacted soil sample due to the swelling during the permeation of the liquids through it.

Soil samples are sieved through 425 μ and dried for 24 h. To reduce the time for the sample to permeate through the soil, samples were compacted to less than their maximum dry density (γd). Studies were carried out at density of 0.9 γd. Measured quantity of RE is taken for 5 cm column height and mixed with sufficient amount of water to achieve required densities. Initially, the soil column is saturated with distilled water to one or two pore volumes under constant hydraulic gradient. Once the steady state flow condition is achieved, distilled water is replaced with model contaminant. The test will be terminated once effluent concentration reaches influent concentration ($C = C_0$). The effluent coming out of the compacted geomaterial is collected at the bottom of the column and withdrawn regularly into a plastic container. The concentration of the effluent samples can be determined using ion analyzer ISE HI4522. The data from column experiment are plotted in the form of breakthrough curves, of relative concentration (C/C_0) versus time.

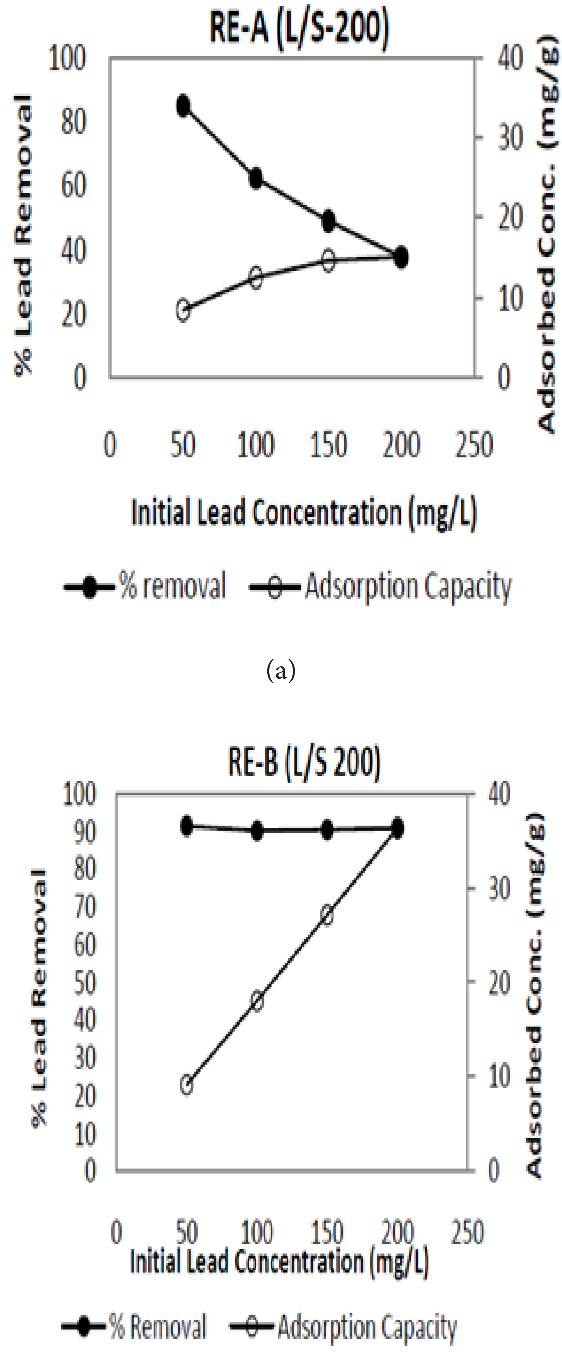
3. Result and Discussions

3.1 Batch experiments

3.1.1 Effect of Initial Concentration

In order to evaluate the effect of initial concentration of lead (Pb^{2+}) present in the solution on sorption characteristics of the red earth, batch sorption experiments were carried out with different initial metal ion concentration. The obtained results are graphically represented in the form of variation of adsorbed concentration of the geomaterial and variation of percentage removal of lead metal with initial concentration for L/S ratio of 200 and depicted in Figure 1.

Red earth being a soil with low specific surface area and low cation exchange capacity has limited number of sorption sites. In acidic condition, there is considerable decrease in percentage removal rate, which indicates



(a)

(b)

Figure 1. The effect of initial concentration on adsorption capacity and percentage removal of lead by L/S-200. (a) For acidic condition. (b) Basic condition.

that there is no improvement in the sorption sites and the available sites become saturated above a certain concentration. However for red earth in basic condition, it is observed that percentage removal rate is almost constant with increase in concentrations compared to acidic condition. This may be due to formation of new minerals in basic condition that results in activation of sorption sites.

In view of the above facts it can be concluded that, geo-materials like red earth can work more effectively under basic condition.

3.1.2 Effect of pH

To demonstrate the influence of pH on sorption behaviour of lead metal, the variation in adsorption capacity of lead sorbed by the red earth with four different initial concentrations (50,100, 150 and 200 ppm) for L/S-200 were obtained for both acidic and basic cycles and presented in Figure 2.

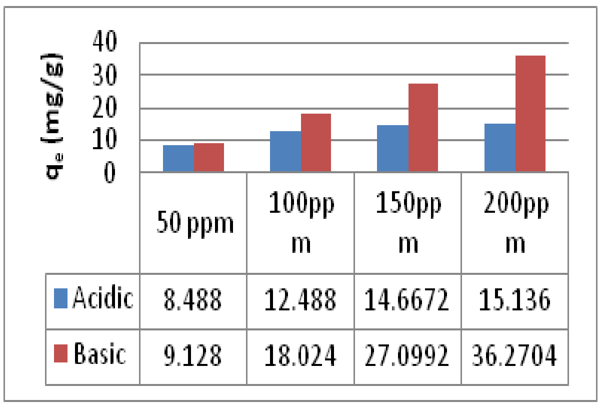
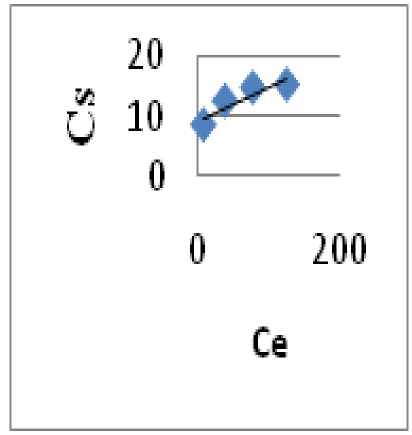


Figure 2. Effect of sorbent on sorption behaviour of lead for acidic and basic condition with L/S 200.

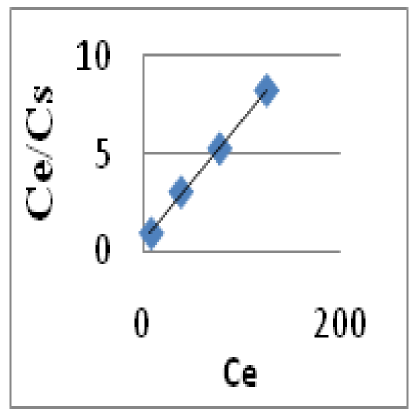
Although RE has lower specific surface area and lesser CEC (~10meq/mg), it can be seen from Figure 2 that RE has significantly good adsorption capacity under basic pH conditions. It is conceivable that at low solution pH values, more number of protons (H^+) are available in the solution and competes with the positively charged heavy metal ions to get sorbed onto the available sorption sites on the geomaterial. Further, as the pH increases, the balance between protons, H^+, and hydroxide ions, OH^-, is significant and only positively charged heavy metal ions get sorbed on the geomaterial[14,15], which results in increase in sorption capacity of the geomaterial.

3.1.3 Isotherms

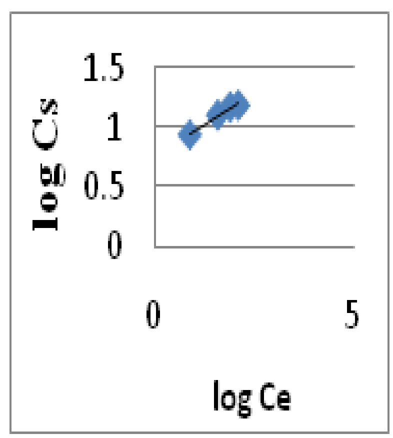
The amount of contaminant sorbed by the geomaterial (q_e) and the equilibrium concentration of the solute (C_e) are used as model parameters to develop the isotherms. The various isotherms obtained for both acidic and basic conditions are depicted in Figure 3 and Figure 4.



(a)



(b)



(c)

Figure 3. Sorption isotherms for Red earth under acidic condition for heavy metal lead. (a) Linear. (b) Langmuir. (c) Freundlich.

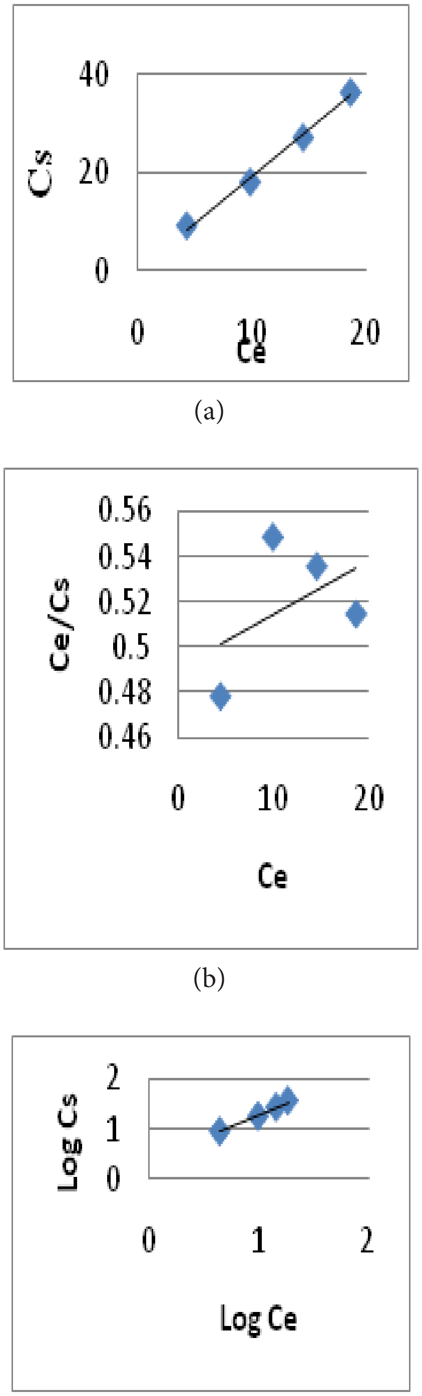


Figure 4. Sorption isotherms for Red earth under basic condition for heavy metal lead. (a) Linear. (b) Langmuir. (c) Freundlich.

The sorption parameters such as K_d, K, n, K_1 and b along with regression coefficient, R^2, for different isotherms are obtained and presented in Table 1.

Table 1. Sorption characteristics of various geo-materials for heavy metal lead

Material		RE (Acidic)	RE (Basic)
Linear	K_d(mg/g)	0.054	1.896
Freundlich	K (mg/g)	5.57	2.22
	N	4.65	4.65
Langmuir	b(l/g)(*100)	4.65	5
	k_1(mg/g)	0.119	0.004
R^2	Freundlich	0.983	0.994
	Langmuir	0.998	0.913
	Linear	0.815	0.994

Based on the isotherm results, it can be concluded that the Freundlich sorption isotherm is considered to be the most suitable sorption isotherm to represent geomaterial contaminant interaction of the selected geo-material. This is in agreement with the literature which says that Freundlich sorption isotherm is considered to be the appropriate isotherm to model the heterogeneous materials which exhibits non-uniform site energy distribution and results in multilayer sorption mechanism[16].

3.2 Column experiment

Breakthrough Curves (BTC) have been plotted to understand the variations in relative concentration (C/C_0) with respect to time. Results obtained from column studies have been given Figure 5.

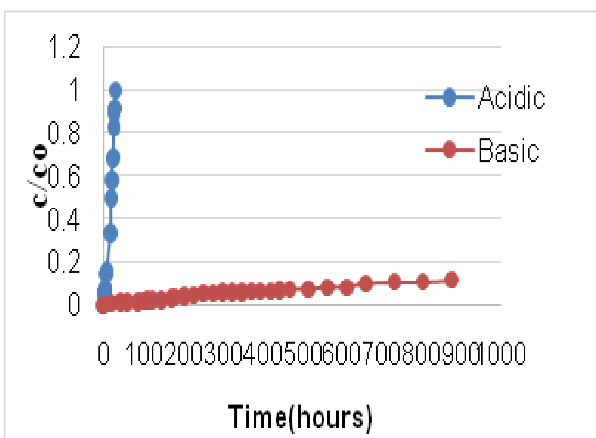


Figure 5. Variation of C/C0 with cumulative time for soils under acidic and basic conditions.

In acidic condition when lead nitrate solution is passed permeability value was measured as 6.38 x 10^{-8}

m/s and has been increased to 11.66 x 10^{-8} m/s. From the graph it can be observed that 50% of the initial concentration ($C/C_0 = 0.5$) of lead is reached at 20.25 hours and 100% of initial concentration ($C/C_0 = 1$) after 30.5 hours. But in basic condition permeability value was 3.5 x 10^{-8} m/s at the beginning and with passage of time it got reduced to 1.4x10^{-9} m/s. Furthermore, it is evident from the graph that 100% of initial concentration of the soil under acidic condition reaches in very short time while under basic condition the relative concentration increases very slowly with time i.e., C/C_0 of 0.1 even after 900 hours. Thus red earth compacted under basic condition showed significant retardation when compared with acidic condition. The reason is OH groups or oxygen atoms are attached to iron and aluminum in the inorganic colloids (e.g.: Al-OH)[17].

4. Conclusion

In this study experiments are performed to assess the suitability of locally available geo-material like red earth as liner material under acidic and basic pH conditions for waste containments systems such as landfills. Red earth in basic condition is showing suitability as liner material when compared to acidic condition. Based on batch sorption experiments on Red Earth, the Freundlich sorption isotherm is found to be most appropriate isotherm to represent the sorption characteristics. Batch study quantifies the influence of various parameters on sorption phenomenon, which will be of great help in establishing the long term behaviour of the liner material. Breakthrough curves plotted from column study establishes that the breakthrough time for Red Earth is significantly more under basic condition. Hence Red Earth under basic condition can be a promising material as liner for landfills.

5. References

1. Li LY, Li F. Heavy metal sorption and hydraulic conductivity-studies using three types of bentonite admixes. Journal of Environmental Engineering. 2001; 127(5):420–9.
2. Adamcova A. Heavy metal retention capacity of natural clay liner of landfills. Geoenvironmental engineering. London: Thomas Telford; 1999. p. 247–54.
3. Yong RN, Phadungchewit R. pH influence on selectivity and retention of heavy metals in some clay soils. Canadian Geotechnical Journal. 1993; 30:821–33.
4. Tackett L. Determination of methanol in gasoline by gas chromatography: A laboratory experiment. Journal of Chemical Education. 1987; 64(12):1059.
5. Barrett A. The economics of waste management in Ireland. Dublin: Economical and Social Research Institute; 1995. p. 129.
6. Benson C, Daniel D. Influence of clods on hydraulic conductivity of compacted clay. Journal of Geotechnical Engineering. 1990; 116:1231–48.
7. Davis JA, Kent DB. Surface complexation modeling in aqueous geochemistry. Reviews in Mineralogy, Mineral-Water Interface Geochemistry and Mineralogical Society of America. 1990; 23:177–260.
8. Rowe RK, Quigely RM, Booker JR. Clayey barrier system for waste disposal facilities. London: E&FN Spon; 1995. p. 390.
9. Michael A, Malusis MA, Shackelford D. Theory for reactive solute transport through clay membrane barriers. Journal of Contaminant Hydrology. 2002; 59:291–316.
10. Freeze RA, Cherry JA. Groundwater. Engle Wood Cliffs: Prentice-Hall, Inc; 1979. p. 1–192.
11. Reed BE, Cline SR. Retention and release of lead by a very fine sandy loam isotherm modeling. Separation Science and Technology. 1994; 29(12):1529–51.
12. Roy WR, Krapac IG, Chou SFG, Griffith RA. Batch type procedures for estimating soil adsorption of chemicals. EPA/530/SW-87/006-F. Washington: USEPA; 1991.
13. Spark DL. Environmental soil chemistry. Amsterdam: Academic Press; 2003.
14. Farrah H, Pickering WF. pH effects in the adsorption of heavy metals ion by clays. Chemical Geology. 1979; 25:317–26.
15. Forbes EA, Posner AM. Quirk JP. The specific adsorption of inorganic Hg (II) species and Co (III) complex ions on geothite. Journal of Colloid and
16. Interface Science. 1974; 49:403–9.
17. Ho YS, Porter JF, McKay G. Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, nickel and lead single component systems. Water, Air, and Soil Pollution. 2002; 141:1–33.
18. Braddy NC, Well RR. Nature and properties of soils. 13th ed. Delhi, India: Pearson Education Pte Ltd; 2002.