Visakhapatnam Chapter

Proceedings of Indian Geotechnical Conference 2020
December 17-19, 2020, Andhra University, Visakhapatnam

Study on Retention Characteristics of Amended Clay Liner

Anju S[1] and Ajitha A. R[2]

College of Engineering Trivandrum, 695016, Kerala, India
[1]anjus7992@gmail.com
[2] ajithavinod@rediffmail.com

Abstract. Clay amended with activated carbon was developed for possible use as a barrier material as an alternative to bentonite-kaolinite mix. General requirements of a compacted clay liner are coefficient of permeability should be less than 1 x 10^{-9} m/s and unconfined compressive strength greater than 200kPa. The clay liner performance is usually measured in terms of hydraulic conductivity and strength. A series of batch adsorption, and hydraulic conductivity tests were conducted to evaluate the heavy metal sorption capacity and chemical compatibility. Hydraulic conductivity of bentonite- kaolinite mix, with and without activated carbon was experimentally investigated using lead and nickel as permeant fluid at concentrations 10, 20, 30, and 40ppm. The results indicate that hydraulic conductivity increases with increase in concentration of permeant fluid, and this increase was within the limits for the carbon amended clay liner. The batch test results indicated that activated carbon is a potential material for use as adsorptive amendments for trapping heavy metal ions in liners. The Langmuir, Freundlich, and Redlich-Peterson isotherm models were applied to the equilibrium data. According to the R^2 value of both the Langmuir, Freundlich, and Redlich-Peterson isotherms, it was concluded that the three models were reasonably suitable for describing adsorption. However, the Redlich-Peterson equation provided a better fit than the Langmuir and Freundlich equation. In general the properties of the carbon amended clay indicate that it has significant advantages over the clay as landfill liner material.

Keywords: Amended clay liner, Hydraulic conductivity, Adsorption isotherm.

1 Introduction

Improper disposal of Municipal Solid Waste (MSW) in open areas and landfills will cause serious environmental problems. It results in the spread of diseases among human beings and animals, thus affecting the welfare, livelihood, and economic productivity. In addition, it causes contamination of surface water, groundwater, soil, and generation of toxic and greenhouse gases.

Disposal of waste in a properly designed landfill is one of the convenient methods of handling this sort of environmental problem. To safeguard the groundwater and environment from pollutants originating from landfill, an efficient liner system is required. The liner system is used to isolate the landfill contents from the environment and protect the soil and groundwater from pollutants originating from the landfill. The greatest threat to groundwater posed by landfills is leachate. Leachate from landfill is a liquid that has percolated through the waste containing soluble and suspended materials that originate from the products of degradation. Leachate may migrate from the landfill and contaminate soil and groundwater and cause risk to human and environmental health.

Landfill liners are designed and constructed to limit the moisture infiltration into the waste and release of leachate and gasses from the waste. Increased interest in the environment protection issues leads to innovation of new practices in liner construction such as the addition of engineered clays, geomembranes, synthetic lining materials and introduction of advanced leachate collection systems, etc. The most important component of soil liners is clay, which ensures the low hydraulic conductivity of liner. EPA requires that soil liners be built so that the hydraulic conductivity should be less than or equal to 1 x 10^{-9} m/s, unconfined compressive strength greater than 200kPa. To meet this requirement, the soil should have at least 30 percent fines; plasticity index (PI) between 10 and 30%, and coarse fragments less than 10 percent.

Because of low hydraulic conductivity and high adsorption capacity compacted clay soil is traditionally used as liners to prevent subsurface contamination. Generally, bentonite clays are preferred. Due to a lack of high-quality bentonite, it is sometimes necessary to blend imported clay minerals with onsite soils to achieve a suitable blended material. The most common blend is a bentonite kaolinite mix. Freeze-thaw cycles, drying out, and the presence of some chemicals can reduce the effectiveness of clay liners. Blended bentonite with coarser particles is used to reduce the problem of the development of shrink-swell cracks.

Leachate from an untreated landfill or landfill with damaged liners will cause the pollution of soil and groundwater. The unscientific solid waste disposal will cause soil contamination. Generally, municipal solid waste landfill leachate may contain heavy metals like lead, nickel, copper, iron, zinc, etc. These pollutants can modify the soil properties and alter the behavior of soil. The leachate that escapes from the landfill becomes a great threat to the surrounding soil, groundwater, and surface water. Conventional liners are designed for minimizing permeation of leachate through the liner. A method of enhancing pollutants adsorption and thus minimizing the flux of leachate pollutants through liners is to amend the liners with materials capable of strongly adsorbing pollutants.

A new landfill liner system composed of 80% kaolinite, 18% bentonite and 2%activated carbon (KCB2) was proposed. The main objective of this study is determining effect of concentration of heavy metal on hydraulic conductivity and adsorption capacity of liner material.

2 Methodology

2.1 Materials

Bentonite

Bentonite is naturally occurring clay having 70 to 90 percentage of the clay mineral as montmorillonite. It has high affinity for water and swells up to about 15 times its dry bulk volume. Calcium bentonite was used for the study and its properties are listed in Table 1

Table 1. Table captions should be placed above the tables.

Property	Value
Specific gravity	2.79
Liquid limit (%)	355
Plastic limit (%)	40
Plasticity Index (%)	315
Specific gravity	2.79

Kaolinite

The Kaolinite (K) used in this investigation was collected from English Indian clay Limited, Thiruvananthapuram. Various laboratory tests were done to find soil properties such as specific gravity, atterberg limits, optimum moisture content, maximum dry density, and unconfined compressive strength. The soil is classified as highly compressible clay (CH) as per Indian standards. The properties of soil collected are summarized in Table 2.

Table 2. Geotechnical properties of Kaolinite

Property	Value
Colour	White
Specific gravity	2.53
Liquid limit (%)	72
Plastic limit (%)	25
Plasticity Index (%)	47
Shrinkage limit (%)	17.30
Clay (%)	64.20
Silt (%)	28.40
Sand (%)	7.4
Maximum dry density(g/cc)	1.4

Activated Carbon

Activated carbon (C) includes a wide range of amorphous carbonaceous materials obtained by combustion, partial combustion or thermal decomposition of a variety of carbonaceous substances. Specific gravity activated Carbon used for this study was obtained as 2.1.

Chemicals

Chemicals used in hydraulic conductivity and sorption studies were lead nitrate ($Pb(NO_3)_2$) and nickel sulfate ($NiSO_4$). A stock solution of (100mg/L) of Pb^{2+} and Ni^{2+} was prepared by dissolving 0.1598 g of ($Pb(NO_3)_2$) and 0.155g of ($NiSO_4$) in 1L distilled water respectively. Different concentrations of test solutions were then prepared by diluting the stock solution.

2.2 Methodology

The hydraulic conductivity test was conducted on kaolinite bentonite clay mixes with and without activated carbon (AC). The kaolinite percentage on bentonite was fixed as 80% and AC varied as 0% and 2%. The clay - carbon mixture was subjected to hydraulic conductivity test by varying concentration of permeant fluid as 10, 20, 30 and 40 ppm. Batch adsorption test was conducted on Designed clay liner containing 80% kaolinite, 18% bentonite and 2% activated carbon at 10, 20, 30, 40 50, and 60ppm of Pb^{2+}.

Batch Adsorption Test

Batch adsorption studies were conducted according to the ASTM D4646 to assess the heavy metal adsorption capacity of the carbon amended clay with the lead nitrate as heavy metal solution. The soil samples were dried, ground, and passed through a 75 μ sieve, and only the portion passing through the sieve was used. The single species heavy metal solutions were prepared separately and applied to different soil samples at increasing concentration levels. The solutions were applied to the prepared soils in the ratio of 10 g of dry soil to 200 ml of heavy metal solution for varying contact time (10–180 min) in different stoppered conical flasks (250 mL) in a thermostatic water bath shaker at room temperature and optimum pH 4. Initial pH of the solution was adjusted using 0.1mol/L NaOH or HCl by using a pH meter. The soil-suspension samples were equilibrated by shaking at a speed of 200 rpm. The samples were then centrifuged and the supernatant collected. Final concentration of lead ion in the solution was determined using Atomic absorption spectrometer (AAS).

Fig. 1. Atomic absorption spectrometer (AAS) test setup

The adsorption capacity Q_e, (mg/g) and percent removal of metal ions were calculated using the following Eqn.1 and Eqn.2.

$$Q_e = [(C_0 - C_e)/W] \times V \qquad (1)$$

$$\% \text{ Removal} = [(C_0 - C_e)/C_0] \times 100 \qquad (2)$$

3 Results and Discussions

3.1 Properties of Designed Liner

Landfill liners are mainly designed based on hydraulic conductivity and strength. To meet this requirement, the soil should possess certain properties. Requirements of Landfill Liner Material recommended by EPA are given in Table 3. According to EPA to achieve hydraulic conductivity within limits soil should have percentage fines greater than 30% and percentage gravel less than 10%. Soil mixes are supposed to sustain a certain amount of static load applied by the overlying waste materials. In this regard, barrier material must have adequate strength for stability.

Table 3. Requirements of Landfill Liner Material as recommended by EPA

Property	Value
Plasticity index (PI)	10 – 30%
Percentage gravel	< 10%
Percentage of fines	> 30%
Coefficient of permeability, k (m/s)	$\leqq 1 \times 10^{-9}$
Unconfined compressive strength (kPa)	>200

The index properties of selected liner material consisting of 80% Kaolinite, 18% Bentonite and 2% Activated Carbon are presented in table 4. For the designed liner clay content is greater than minimum percentage fines of 30%, hydraulic conductivity less than 1x 10^{-9}m/s and unconfined compressive strength greater than 200kPa.

Table 4. Properties of designed liner

Property	Value
Liquid Limit (%)	69
Plastic Limit (%)	42
Plasticity Index (%)	27
Clay content (%)	64
Coefficient of permeability, K (m/s)	1.97×10^{-10}
Max dry density (g/cc)	1.36
Optimum moisture content (%)	36.46
pH	8.58

3.2 Hydraulic Conductivity

Hydraulic conductivity is a measure of the ability to transmit fluids by geologic media. It is a function of the size and arrangement of pores and fractures in the media and of the characteristics of the fluids. The evaluation of the suitability of clay soil for liner material depends mainly on resistibility to increase in hydraulic conductivity and migration of contaminants. The hydraulic conductivity of soil mixes was determined using 1-D consolidation apparatus. The coefficient of permeability (k) of kaolinite and bentonite with distilled water as a permeant fluid was obtained as l.02 x 10^{-8} m/s and 1.96 x 10^{-11} m/s respectively. Kaolinite alone is not suitable for the construction of liner material. The coefficient of permeability (k) changes significantly when 20% of kaolinite was replaced with bentonite. Soil samples 80:20 Kaolinite:Bentonite mix (KB20) and 80:18: 2 Kaolinite:Bentonite:Activated carbon mix (KCB2) both have permeability less than 1 x 10^{-9} m/s. Permeability results of tested soils with water as permeant fluid are illustrated in Table 5.

Table 5. Hydraulic conductivity of soil samples as water as permeant fluid

Soil mix	Hydraulic Conductivity (m/s)
Kaolinite	1.02 x 10^{-8}
Bentonite	1.96×10^{-11}
80% Kaolinite + 20% Bentonite (KB20)	1.76 x10^{-10}
80% Kaolinite + 18% Bentonite + 2% Activated Carbon (KCB2)	1.97 x10^{-10}

Clay liners are subject to change due to interaction with leachate and it becomes difficult to obtain the value less than 10^{-9} m/s. Therefore, transport of contaminants through liners remains the most serious long-term problem. Permeability test was conducted for 80:20 Kaolinite:Bentonite mix (KB20) at different concentrations of lead and nickel as permeant and results are summarised in Table 6.

Table 6. Hydraulic conductivity of 80:20 Kaolinite : Bentonite

Soil mix	Hydraulic Conductivity (m/s) Pb^{2+}	 Ni^{2+}
0	1.76 $\times 10^{-10}$	1.76 $\times 10^{-10}$
10	8.6 $\times 10^{-10}$	1.3 $\times 10^{-9}$
20	2.7 $\times 10^{-9}$	4.7 $\times 10^{-9}$
30	4.3 $\times 10^{-9}$	6.2 $\times 10^{-9}$
40	7.1 $\times 10^{-9}$	8.57 $\times 10^{-9}$

For the tested sample, KB20 permeability increases with an increase in the concentration of pore fluid and it becomes greater than the permissible limit of 1×10^{-9} m/s. The effects of pollutants on soils are complex, and may differ for different types of soils and can be explained by Diffuse Double Layer (DDL) theories. Diffuse Double Layer thickness decreases with decreasing values of the dielectric constant or increasing concentration of cations contained in the fluid. A smaller DDL results in a larger effective pore space, which leads to an increase in hydraulic conductivity.
Hydraulic conductivity test results for 80:18:2 Kaolinite : Bentonite : Activated carbon mix (KCB2) at different concentrations of lead and nickel as permeant are summarised in Table 7. For clay mix with 2% carbon hydraulic conductivity increases with an increase in the concentration of pore fluid, but it is within the permissible limit of 1×10^{-9} m/s.

Table 7. Hydraulic conductivity of 80:18:2 Kaolinite : Bentonite : Activated Carbon

Concentration (ppm)	Hydraulic conductivity (m/s) Pb^{2+}	 Ni^{2+}
0	1.97 $\times 10^{-10}$	1.97 $\times 10^{-10}$
10	2.38 $\times 10^{-10}$	4.21 $\times 10^{-10}$
20	3.41 $\times 10^{-10}$	6.9 $\times 10^{-10}$
30	4.48 $\times 10^{-10}$	8.38 $\times 10^{-10}$
40	6.6 $\times 10^{-10}$	9.03 $\times 10^{-10}$

3.3 Adsorption Mechanism

Adsorption isotherms describe the relationship between the amount of adsorbed ion on the adsorbent and the final ion concentration in the solution. In this study, the Langmuir Freundlich, and Redlich-Peterson Isotherm models were tested to adequately correlate the experimental data to find the best fit model that can be used for design process.

Langmuir Isotherm Model

Langmuir isotherm (Fig 2) is an empirical model that assumes that the thickness of the adsorbed layer is one molecule (monolayer adsorption) in which adsorption process occurs at identical and equivalent definite localized sites. There should be no steric hindrance and lateral interaction, even on adjacent sites, between the adsorbed molecules. The Langmuir Isotherm model assumes that adsorption is homogenous in which sorption activation energy and constant enthalpies are possessed by each molecule. All sites should have equal affinity towards the adsorbate, as well as no adsorbate transmigration in the surface plane. The Langmuir isotherm is expressed as in Eqn.3.

$$(C_e)/Q_e = 1/(bQ_m) + C_e/Q_m \qquad (3)$$

Where Q_m and b are the maximum monolayer adsorption capacity (mg/g) and Langmuir constant (L/mg) calculated from the slope and intercept of C_e/Q_e vs C_e plots. The dimensionless separation parameter (R_L) is a measure of favorable adsorption calculated using the formula

$$R_L = 1/(1+bC_0) \qquad (4)$$

The linear form of the Langmuir isotherm was applied for calculation of the corresponding parameters, given in Table 8. The results indicated that the adsorption capacity corresponding to the monolayer adsorption (Q_m) was 0.54 mg/g, and b, the Langmuir constant related to the free energy of adsorption, was 0.225 (L/mg). When the essential parameter, R_L, is between zero and one, this indicates favorable adsorption, while $R_L = 0$ irreversible and $R_L=1$ indicate linear and unfavorable adsorption isotherms, respectively. Thus, the obtained R_L value of 0.0691 suggested favorable adsorption.

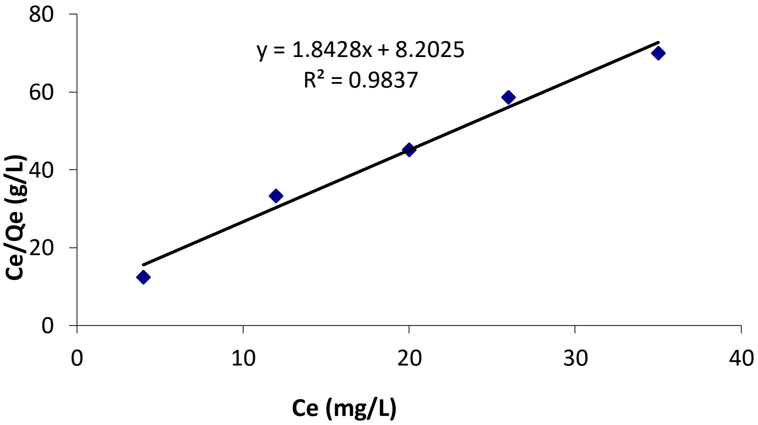

Fig. 2. Langmuir adsorption isotherm plots

Freundlich Isotherm Model

Freundlich adsorption isotherm describes non-ideal and reversible adsorption. Unlike the Langmuir isotherm model, Freundlich model is not restricted to the monolayer formation in which its application to the multilayer adsorption is possible. In this isotherm model, adsorption heat and affinities does not need to be uniformly distributed on the heterogeneous surface. Freundlich isotherm model defines the heterogeneity of the surface as well as the exponential distribution of the active sites and the active sites energies. Freundlich adsorption isotherm assumes adsorption on heterogenous surface. The Freundlich isotherm is expressed as:

$$\text{Log}\,[Q_e] = \text{Log}\,[k_f] + 1/n_f \log\,[C_e] \qquad (5)$$

Where k_f $((mg/g)/(mg/L)^{1/n})$ is the Freundlich adsorption capacity and n_f is adsorption intensity. The values of K_f and n_f were calculated from the slope and intercept of $\log Q_e$ vs $\log C_e$ plot. $1/n_f$ lower than unity suggest favorable adsorption.

The Freundlich isotherm parameters were calculated and summarized in Table 8. Freundlich model is characterized by the heterogeneity factor, $1/n_f$. That is, $0.1 < 1/n_f < 1.0$ indicates good adsorption of metal ions onto the adsorbent. From the isotherm data $1/n_f$ value obtained as 0.2864 which confirm the process to be favorable. Fig.3 gives results on Freundlich isotherm fittings with linear correlation coefficient (R^2) of 0.9413. Freundlich constants i.e., adsorption capacity, K_f and rate of adsorption, n_f are calculated from this plot which are 0.1854 $(mg/g)/(mg/L)^{1/nf}$ and 3.49 respectively.

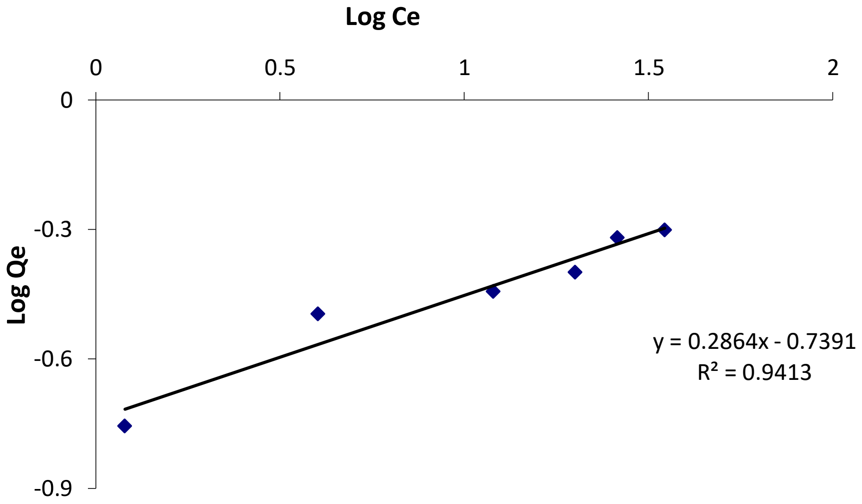

Fig. 3. Freundlich adsorption isotherm plots

Redlich-Peterson Isotherm Model

The Redlich-Peterson isotherm is a mix of the Langmuir and Freundlich isotherms which incorporates three parameters into an empirical equation. It has a linear dependence on concentration in the numerator and an exponential function in the denominator to represent adsorption equilibrium over a wide range of concentrations. It approaches Freundlich isotherm at high concentration and Henry's law at low concentration. The linear form of the Redlich-Peterson isotherm is expressed as follows.

$$\mathrm{Ln}\,[C_e/Q_e] = \beta\,\mathrm{Ln}\,[C_e] - \mathrm{Ln}\,A \tag{6}$$

A plot of Ln (C_e/Q_e) versus Ln C_e enables the determination of Redlich-Peterson constants, where β is slope and A is intercept.

The three-parameter model Redlich-Peterson equations is applied to evaluate suitability of isotherm for the adsorption. The calculated isotherm parameters and their corresponding linear correlation coefficient (R^2) values are shown in Table 8. Fig.4 gives results on Redlich-Peterson Isotherm fittings with linear correlation coefficient (R^2) of 0.9901. The higher R^2 values for the Redlich-Peterson isotherms suggest the applicability of this model to represent the equilibrium sorption of lead by the liner material.

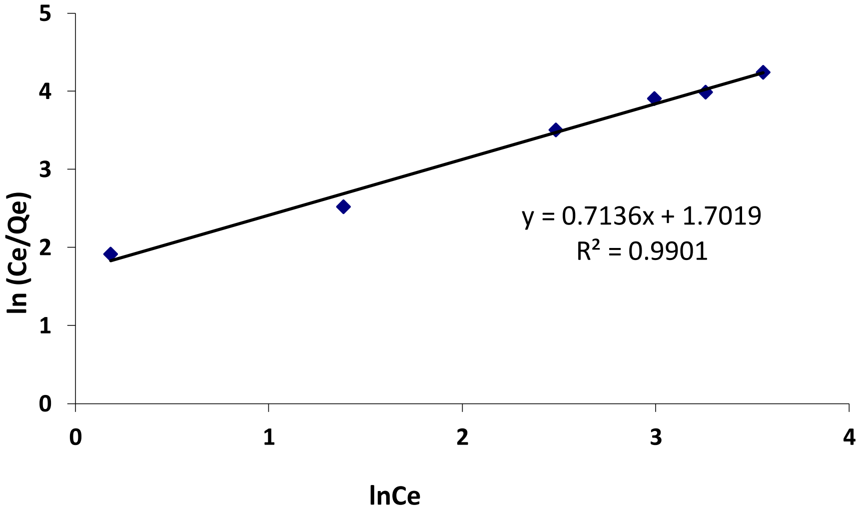

Fig. 4. Redlich-Peterson adsorption isotherm plots

According to the R^2 value of the Langmuir (0.9837), Freundlich (0.9413) and Redlich-Peterson (0.9901) isotherms, it was concluded that the three models were reasonably suitable for describing adsorption. However, the Redlich-Peterson equation provided a better fit than the Langmuir and Freundlich equation.

Table 8. Various isotherm parameters

Isotherm	Isotherm parameters	
Langmuir	Q_m (mg/g)	0.543
	b (L/mg)	0.225
	R_L	0.0691
	R^2	0.9837
Freundlich	K_f (mg/g)/(mg/L)$^{1/nf}$	0.1854
	n_f	3.492
	R^2	0.9413
Redlich-Peterson	A	0.1823
	β	0.7136
	R^2	0.9901

4 Conclusions

The main purpose of the study was to design a new amended liner. Study was conducted to investigate the possible use of activated carbon to replace part of bentonite and kaolinite in environmental containment applications. To study the feasibility of the new landfill liner, its index properties, strength, permeability, and adsorption properties were investigated.

The conclusions drawn from the study include:

1. Threshold ratio of kaolinite - bentonite - activated carbon mix that can be used as liner material is obtained as 80:18:2. The unconfined compression strength of cured samples with 2% carbon is greater than 200kPa and hydraulic conductivity less than $1x10^{-9}$ m/s.
2. Hydraulic conductivity of for 80:20 Kaolinite : Bentonite mix increases with increase in concentration of pore fluid and and it becomes greater than the permissible limit of $1x10^{-9}$ m/s.
3. Hydraulic conductivity of for 80:18:2 Kaolinite : Bentonite : Activated carbon mix increases with increase in concentration of pore fluid and it is within the permissible limit of $1x10^{-9}$ m/s.
4. According to the R^2 value of both the Langmuir, Freundlich, and Redlich-Peterson isotherms, it was concluded that the three models were reasonably suitable for describing adsorption. However, the Redlich-Peterson equation provided a better fit than the Langmuir and Freundlich equation.
5. The results in this paper lead to the conclusion that designed liner (80:18:2 kaolinite-bentonite-activated carbon) could be used as an effective barrier system.

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