EVALUATION OF LOCALLY AVAILABLE CLAYEY SOILS FOR THEIR SUITABILITY AS LANDFILL LINERS

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Dedicated to

My
Beloved Parents
&
Brother

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ABSTRACT

Indiscriminate and improper disposal of industrial as well as municipal solid/liquid wastes are highly responsible for the contamination of the soil and surrounding environment. In-order to minimise the contamination, researchers have developed various disposal methodologies such as solidification & immobilization, incineration, and land filling. Among these methods, landfilling is considered to be safe and cost effective method when compared to the rest. The efficiency of the engineered landfills highly depends on the hydraulic conductivity, sorption capacity and cracking intensity of the liner material. In general, the hydraulic conductivity of the liner material is considered as the main criterion for selecting the material and for designing the engineered landfill liner system. However, in addition to the hydraulic conductivity, sorption and cracking characteristics of the soils play a major role in preventing the transport of contaminants through the landfill liner system.

The presence of organic chemicals in the leachate influences the migration of heavy metals through the liner material. Among the various liner materials, compacted clay liner (CCL) is predominantly used in the landfills because of their low hydraulic conductivity and high sorption capacity. Formation of CCL requires large quantity of suitable soil as liner material. At present, in Warangal the biggest city of Telangana, the entire waste is disposed in an open dump yard in the out skirts of the city as there is no engineered landfill system, which is leading to lot of pollution in the surrounding areas. The general soil profile of this city consist of Black cotton soil and Red Earth of considerable thickness followed by murrum to very great depths.

In view of the above criteria, the two abundantly available local soils (Black cotton soil - CH, Red Earth - CI) were selected to evaluate their suitability as liner material based on the physical, sorption, breakthrough and cracking characteristics under the influence of organic chemicals. In the present study an organic chemical Ethylene Diamine Tetra Acetic Acid (EDTA) is used to understand the influence on the behaviour of clay liner.

The sorption characteristics of these materials were established by conducting batch sorption and column flow experiments and the cracking characteristics were evaluated using image analysis criteria. Batch sorption studies have shown that, the adsorption of metal ions by both the soils increase with increase in pH of the heavy metal solution. In the presence of organic chemical (EDTA), the adsorption decreases with the increase in the pH for both the soils. The column flow studies have revealed that due to the multi metal (Pb, Ni, Cd and Cr) interaction, the diffusion of heavy metals increased when compared to the single metal interaction for both the soils. Due to the presence of organic chemical (EDTA) in the heavy metal solution, the diffusion characteristics of soils got further increased. The image analysis on cracked CH and CI soils indicate that, the crack intensity factor (CIF) is increasing with increase in water content and with the presence of heavy metal solution. The migration of heavy metals is observed to be more through both the soils due to the formation of cracks. However, the time to achieve breakthrough of heavy metals (Pb, Ni, Cd and Cr which are considered in the present study) through CH soil is more when compared to the CI soil. Among the four metals considered, chromium exhibited a different sorption behaviour when compared to other heavy metals due to its anionic form. In the presence of organic chemical EDTA, due to the formation of metal EDTA complex, there is an increase in the mobility of heavy metals through the soils.

The crack intensity factor is found to increase with the increase in compaction water content and number of wetting – drying cycles due to contaminants. Similarly, the value of permeability ratio (Kr) is observed to increase with the compaction water content.

The range of increase in the permeability ratio is around 25% to 55% when the water content is increased from dry of optimum to wet of optimum. The diffusion of heavy metals through desiccated soils are in the range of 2.01×10^{-6} to 5.90×10^{-6} m^2/sec for CH soil and 3.06×10^{-6} to 9.9×10^{-6} m^2/sec for CI soil. From these studies, it is observed that the migration of heavy metals through CH soil is less when compared to CI soil. This is due to the fact that, CH soil is having good adsorption and more self-healing capacity when compared to CI soil. Based on the above observations, it can be concluded that, the locally available CH soil can be used more effectively as a compacted clay liner when compared to CI soil.

Key Words: Solid waste land fill, compacted clay liner, sorption studies, diffusion coefficient, crack intensity factor (CIF), permeability ratio (Kr)

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NOMENCLATURE

English Symbols

A	cross sectional area
B	Skempton's pore pressure parameter
B1	fitting parameter used in Eq. 4.11
C	concentration of contaminant
C0	initial concentration of solution
C_e	Equilibrium Concentration (mg/L)
C_1	Concentration of metal in stock solution (1000 mg/L)
C_2	Concentration required (10, 15, 20, 25 and 30 mg/L)
C/C_0	Relative Concentration
D_o	the "free-solution diffusion" co-efficient.
D	Diffusion co-efficient,
D*	effective diffusion co-efficient
G	specific gravity
h	hydraulic head causing flow
J	mass flux of contaminant
k	hydraulic conductivity
k_f	sorption parameter corresponding to Freundlich isotherm
k_1	binding energy related to Langmuir isotherm
k_d	Distribution coefficient
k_r	Permeability Ratio
l	macroscopic characteristic length of sample
L	length of Landfill
L/S	liquid to solid ratio
M	mass of adsorbent
n	constant corresponding to Freundlich isotherm
n	porosity
q	Amount of permeant
q_e	amount of contaminant adsorbed per specific amount of soil (mg/g)
q_m	maximum amount of metal ions required to form a monolayer (mg/g).
R	retardation factor
R^2	coefficient of linear regression
R %	removal efficiency or Percentage adsorption
S	mass of the adsorbed contaminant/unit volume
S_r	degree of saturation (expressed as percentage)
t	time
x	thickness of the sample
V	volume
V_1	Volume of stock solution required (unknown)
V_2	Volume of solution required for M_2 concentration of metal.
va	Darcy velocity
vs	seepage flow velocity

V_T	Cumulative volume of effluent at a specific time of collection from the beginning of the test (ml).
V_V	Volume of voids (cc)

Greek Symbols

γ_d	dry unit weight
γdmax	maximum dry unit weight
ε	strain
η p	porosity
μ	dynamic viscosity of the fluid
ρ	density of the material
Θ	Volumetric water content (= $n*S_r$)
τ	Tortuosity factor

Abbreviation

ICP – OES	Inductively Coupled Plasma Optical Emission Spectrometry
CCL	Compacted clay liner
CEC	Cation-exchange capacity
CH	Clay of high compressibility
CI	Clay of Intermediate compressibility
MMD	Maximum Dry Density (g/cc)
OMC	Optimum moisture content
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
EDTA	Ethylene diamine tetra acetic acid
NTA	Nitrilo-tri-acetic acid
DTPA	diethylene thiamine Penta acetic acid
EDDS	Ethylene diamine-N, N'-disuccinic acid
MHMS	Multi Heavy Metal Solution
CIF	Crack Intensity Factor

CHAPTER – 1
INTRODUCTION

1.1 General

Indiscriminate discarding of industrial as well as municipal solid/liquid wastes are the primary cause for the pollution of surface and subsurface environment due to the pollutants in leachate i.e., the effluent from industrial or municipal solid waste disposal units (Green et al., 1981; Willem, 1981, Chrustensen et al., 1994, Eric et al 2008; Nagarajan et al., 2012; Magada and Gaber 2014; Sabrina, 2014; Alamgir, 2016; Priyanka et al., 2017). Among the contaminants present in the leachate, heavy metals are often problematic environmental pollutants, owing to their toxicity. GWMC (Grater Warangal Municipal Corporation), Warangal is also dumping all the waste in an open dumping yard near Rampur which is alarmingly affecting the surrounding environment. The tests on leachate collected from this location (done at IICT Hyderabad) revels that, some of the heavy metals like lead, nickel, cadmium and chromium are present more than the permissible limits and are considered to be harmful to both human beings and environment (Bolt, 1979; Lawrence, 1981; Yong and Phadungchewit, 1993; Vengris et al 2001; Wong and Selvam, 2006; Chai et al 2006; Karaca et al., 2010). To Control the contamination of surface and subsurface environment, scientists have adopted employed different disposal practices such as solidification, incineration and landfilling. However, the method of landfilling considered as safe and cost-effective method when compared to others (Barrett and Lawlor, 1995). The landfill is hinders the migration of contaminants by placing the barrier. These barrier system usually comprises of compacted clayey soil, or synthetic materials such as geo-membrane liners like high-density polyethylene, chlorinated polyethylene, chloro-sulfonated polyethylene, and ethylene inter polymer alloy, and poly vinyl chloride. Since, these geo-synthetic lining materials are often associated with leakage problems and to avoid such problems, the liners are constructed with naturally available soils that are rich in clay minerals. These soils exhibit low hydraulic conductivity and high sorption capacity which hinders the migration of contaminants from waste disposal sites (Williams 1985; Davis and Kent, 1990; Rowe et al., 1995; Sandhya and Tonni 2003; Met and Akgun 2015).

The efficiency of landfill liner mainly depends on the hydraulic conductivity and adsorption of clay liner material (Du and Hayashi. 2006; Nithya et al 2012; Lei et al 2017) and these properties are generally effected by the pH and type of contaminant present in the leachate (Abollino. et al 2003). While designing the landfill liner system, hydraulic conductivity is considered as a primary criteria (Daniel, 1993; Benson and Trast, 1995; Mollins et al., 1996; Hamdi et al., 2013) and it should have sufficient shear strength to maintain its integrity. However, sorption and diffusion characteristics of the liner material also play a major role in the migration of pollutants through landfill liner system.

Not only the chemicals present in the leachate but also the cracks formed due to the temperature generated within the landfill can affect the performance of clay liner by increasing its hydraulic conductivity (Day and Daniel 1985; Quigley, 1993; Gleason et al, 1997; Rahul and Daniel, 1997; Miller et al 1998; Kaya and Fang 2000; Aldaeef and Rayhani 2014). In view of this problem, some researchers (Green et al., 1981; Gregory and Daniel, 1991; Uday and Singh, 2013; and Uma and Kodikara, 2017) have attempted to study the desiccation effect on the compacted clay liner but very few have attempted to study the influence of chemicals on the cracking and breakthrough characteristics of compacted clay liners.

The hydraulic conductivity of the liner material is considered as important parameter while selecting a suitable material for landfill liner system (Mollins et al., 1996). However, the sorption characteristics of liner material also play a major role in preventing the transportation of the contaminants through the liner system (Chotpantarata, et al 2011). The liner system consists of layers of synthetic material (polyethylene, PVC) and natural geo-material (clayey soil) to prevent the escape of toxic and hazardous contaminants from the landfill to the surrounding environment. Among the various liner materials, compacted clay liners are predominantly used because of their low cost and less hydraulic conductivity, high sorption capacity, and resistance to damage (Davis and Kent, 1990; Rowe et al., 1995; Sandhya and Tonni., 2003; Zuhairi, 2003; Tanit et al 2009, Sangiumsak and Pongsakorn, 2014).

If locally available clayey soils are not abundantly available, commercially available materials such as bentonite along with membranes are commonly used to construct compacted clay liner. In some cases, Bentonite is mixed with locally available soils to prepare the compacted clay liner (Bagchi, 1983; USEPA, 1989; Kaya and Durukan, 2004; Lakshmi and Sivapulliah, 2006; Anil et al, 2014). Using membranes as clay liner system is associated with puncture and leakage problems and hence in order to overcome these problems; geo-synthetic clay liners (GCL's) are developed. These GCL's are also facing the problem of Bentonite separation in GCL due to which it is preferred to have reduced thickness of GCL layer. Among the available alternatives, compacted clay liners (CCL's) are more preferable due to their advantages as a landfill liner material. The CCLs can also be made of locally available clayey soils which are having an ability to act as an effective hydraulic barrier and as an effective chemical barrier to prevent the leachate migration.

The properties of leachate changes with the increase in the age of the landfill (Peter et al., 2002). The waste and leachate in the landfill pass through different phases of degradation process throughout the lifetime period of landfill as shown in Fig 1.1. In addition, the complexity of leachate will change with age and phase of the landfill. The leachate in the landfill generally consist of four different types of pollutants such as dissolved organic matter, inorganic macro components, heavy metals, and xenobiotic organic compounds. Among the pollutants present in the leachate, heavy metals are non – biodegradable inorganic compounds and these will appear in the acidic stage which is the second phase and in carbon dioxide phase which is the seventh phase of the landfill. In the landfill, it is observed that along with heavy metals, organic chemicals are also present (Sanjeev and Arun, 2010, Sarvenaz and Mohsen, 2015). The presence of these organic chemicals influences the heavy metal migration through the liner material, which was not attempted by many researchers till now.

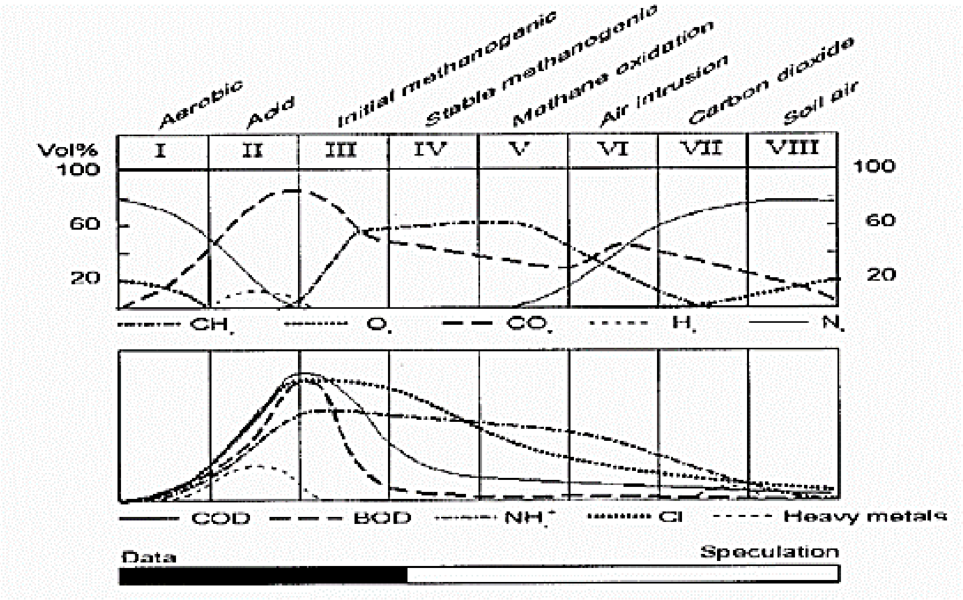


Fig 1. 1 General trends of the gas and leachate quality during the lifetime of the landfill (adopted from Peters et al., 2002)

Based on this research gap observed, an attempt was made to understand the influence of organic chemical on the heavy metal retention capacity by soils. For this purpose, an organic chemical EDTA was selected because, the amount of EDTA present in a landfill leachate is about 30% from the domestic waste (Oviedo and Rodriguez, 2003).

1.2 Scope and Objective

Warangal city generates 400 tons of solid waste every day which is disposed at Rampur open dump yard facility leading to lot of pollution in the nearby areas (Shashidar and Ajit 2011). Moreover, Telangana government has proposed to build a textile industry at a nearby place which may also lead to more organic and inorganic contaminants in this area. In order to prevent the geo-environmental pollution, it is necessary to contain the waste and the leachate generated within the landfill itself. As the performance of the landfill depends on the efficiency of the clay liner, it becomes important to use a suitable soil for this purpose. As the construction of a clay liner involves huge quantity of soil, if locally available soil satisfies the requirements of a clay liner, it can be considered as a suitable alternative to construct a landfill. With this scope of investigation, the present study is performed with an aim to evaluate the suitability of the two prominent locally available clayey soils (Black cotton soil and Red Earth) for their applicability as a liner material based on their sorption and diffusion/ breakthrough and cracking characteristics.

The objectives of this study are as follows.

1. Assessment of the sorption characteristics of the soils with varying pH value of contaminant, initial concentration of heavy metal solution and the presence of organic chemical (EDTA).

2. To study the breakthrough characteristics of soils with and without organic chemical.
3. Assessment of crack intensity behavior of soils in the presence of contaminants.

1.3 Research Methodology

In the present study to achieve above mentioned objectives, the whole experimental methodologies are planned as given in Fig 1.2

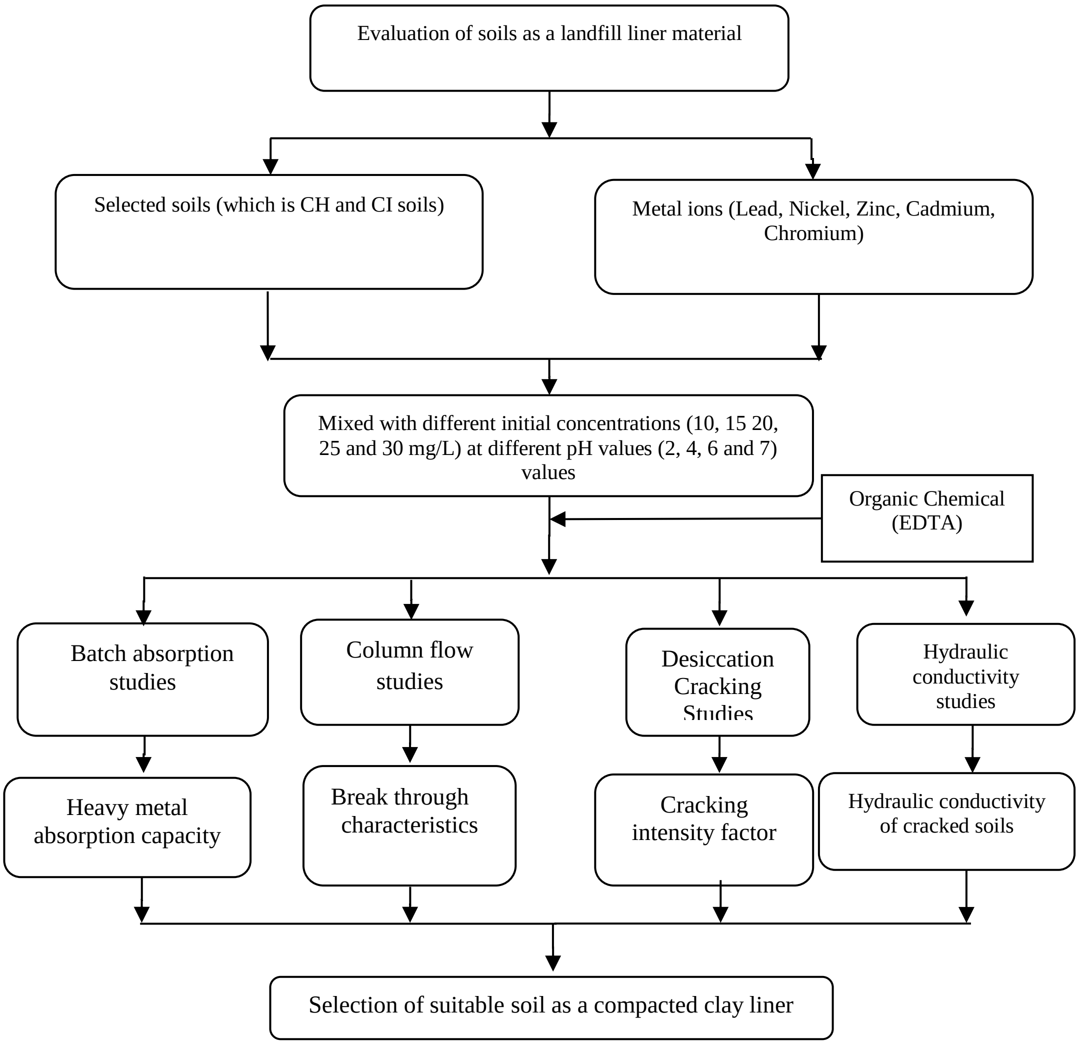


Fig 1.2 Schematic diagram of methodology adopted for the research work

1. 4 Thesis Organization

Chapter 1 describes about introduction, scope and objectives of the research work.

Chapter 2 presents the review of the literature relating to the utilization of various soils as a liner in a landfill. The literature regarding the evaluation of sorption characteristics and transport parameters of the soils, along with the factors influencing sorption characteristics of the various soils are highlighted in this chapter. At the end, based on the reviewed literature, a critical appraisal of the same is also reported.

Chapter 3 summarizes the index, engineering and mineralogical characteristics of the selected locally available soils. The methodologies adopted to assess sorption, diffusion and cracking characteristics of soils are described in detailed in this chapter.

Chapter 4 contains the analysis and discussions along with the inferences on the results pertaining to the sorption, diffusion and cracking characteristics of the selected soils.

Chapter 5 summarizes the conclusions made from present study.

CHAPTER 2
LITERATURE REVIEW

2.1 General

Literature reviewed about the landfills, importance of compacted clay liner (CCL) selection of suitable landfill liner material by considering the influencing parameters and existing code requirements is reported in this chapter. The information regarding the methodologies employed to obtain the sorption characteristics of the liner material and factors influencing the attenuation capacity of soils is also presented in this chapter.

2.2 Landfills

One of the most safe and economical method to dispose the waste effectively is landfilling (Green et al., 1981; Willem, 1981, Chrustensen et al., 1994). These landfills are constructed to contain the waste and leachate well within the landfill system. In modern landfills, the contamination of surface and subsurface environment is prevented by placing the liner between waste and surrounding environment. The schematic diagram of modern engineered landfill is shown in Fig 2.1.

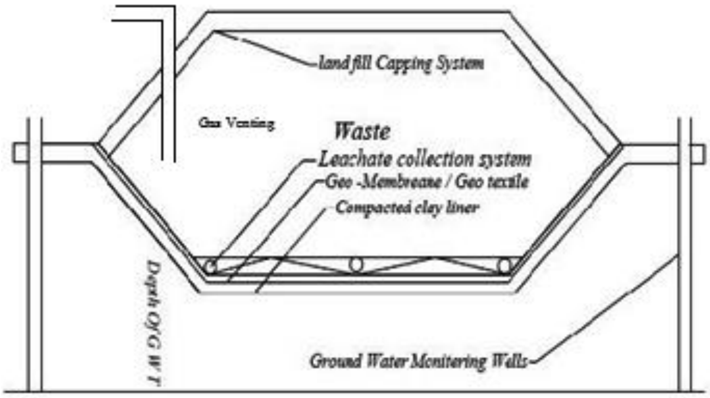


Fig 2.1 Schematic Diagram of an Engineered Landfill

From the figure 2.1, it is observed that, the engineered landfill system mainly consists of bottom liner, leachate collection system, landfill capping and ground water monitoring system. Each and every component has its unique function in terms of retention of contaminant migration from the landfill liner. Among all, the bottom liner of landfill play a significant role in preventing the leachate migration from the landfill. The bottom liners are generally constructed with clayey soils is having less permeability or with synthetic materials (geo-synthetic clay liner and geo-membranes); sometimes, combination of both materials (Benson and Daniel, 1999). The method of construction and material used basically depends on the level of toxic and hazardous nature of the waste. Usage of synthetic materials for construction of bottom liner are associated with the problems like puncturing and tearing. After interaction with strong organic chemicals, these synthetic materials loses their strength and welcomes the leakage associated problems. In order to counter these negative effects, compacted clay liners are inevitable.

2.3 Importance of the Compacted Clay Liner (CCL)

The compacted clay liner is one of the most important component in the landfill system. This liner acts as barrier between the waste and surrounding environment and to prevent contamination of surface and sub-surface water bodies. Generally, the clayey soil used to construct the clay liner should have fines content less than 30% and the permeability less than 10^{-9} m/sec (Benson and Trast., 1995; Burton, 2016). The compacted liners are constructed by using natural clayey soils and Bentonite. In general, the CCL thickness varies from 60 cm to 300 cm based on the type of waste disposed (domestic to highly toxic waste) (Kmet et al., 1981). As the liner thickness is increased, the flow through the liner is significantly decreased.

Compaction water content plays major role in achieving the target permeability of CCL. These CCLs are required to guard against the formation of desiccation cracks formed due to loss of water from CCL and it leads to early migration of leachate by enhancing the permeability. The efficiency of clay liner mainly depends on the sorption and contaminant retention characteristics of the clay liner material.

2.3.1 Performance of Compacted Clay Liner (CCL)

The CCL plays main role in preventing the migration of contaminant front through the engineered landfill system (Aldaeef and Rayhani 2015). Some of the landfill liner systems in Europe and America are shown in the Fig 2.2.

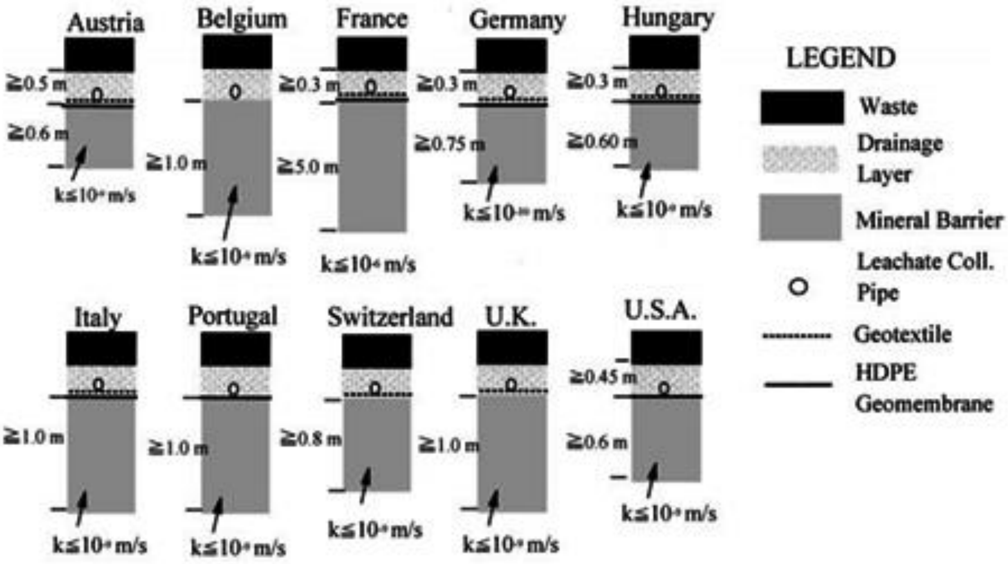


Fig 2.2 European and American bottom liner systems for municipal solid waste (Chai and Miura, 2002)

From the Fig 2.2, it is observed that, CCL are frequently used along with the geo-synthetics materials such as geo – membranes (Benson et al 1999; Chai and Miura, 2002). The primary intention of these bottom liner systems are to prevent the contaminant migration. These contaminant migration is happens through the liner is majorly through the advection and diffusion (Shackelford, 1991; Chai and Miura

2002). The performance liner systems are compared in terms of effectiveness to prevent advective and diffusion migration of contaminants through the CCL, landfill cap and leachate drainage system and this migration was monitored with the help of ground water monitoring stations which is shown in Fig 2.1. These migration primarily depends on the permeability of liner material (Benson and Daniel, 1999) and it is constructed to achieve the permeability $<10^{-7}$ cm/sec. There are several field and laboratory methods are there to measure the permeability of liner material. Along with the permeability of liner material, sorption is most important property in delaying the contaminant migration through the landfill liner. The primary factors like permeability and sorption characteristics of liner material in influenced by the pH, initial concentration and organic chemicals presence. In addition, it is not clear how contaminant sorption and its breakthrough is varies with the presence of organic chemical.

2.4 Sorption Phenomenon

Sorption is the accumulation of a chemicals at an interface between a solid phase and a liquid phase (Heike, 2004; Irena, 1999; ASTM D 4646 – 3). Sorption in soil hinders the migration of contaminants through the soil by its adsorbing on its surface. The contaminant transport influenced by this adsorption phenomena in soil and this factor need to consider while predicting the contaminant fate. The factors which influencing the sorption of heavy metals by the soils are The factors which influencing the sorption of heavy metals by the soil are (1) Effect of Liquid solid ratio (L/S), (2) Effect of Initial Concentration, (3) Effect of adsorbent, (4) Effect of pH, (5) Competition of Heavy metals.

2.4.1 Laboratory Methods for Estimation of Sorption

The sorption characteristics of a sorbent are generally obtained through two types of laboratory tests namely batch sorption test and column flow through experiments. From these tests distribution factor or partition coefficient (k_d) of a sorbent is estimated from which retardation factor is calculated. Fate of heavy metals in contaminated soils is a notion of static nature, dynamic nature and static – dynamic nature. The ratio of these metals in solid phase to those in solution at equilibrium is defined as distribution coefficient (k_d, k_l and k_f). By using these distribution coefficient, it is possible to evaluate the retardation coefficient (Rd). The corresponding equation is show in equation 2.1a

$$Rd = 1 + \left(\frac{\rho}{n}\right) kd \qquad (2.1\ a)$$

2.4.2 Adsorption Isotherm

Adsorption isotherm is a relationship between the concentration of adsorbate in solution (mass/volume) and its adsorbed concentration (mass adsorbate/mass adsorbent) and it is a function of temperature. Therefore, the adsorption equilibrium relationship at a given temperature is typically referred to as adsorption isotherm and it takes the form as shown in equation 2.1b

$$q_e = f(C_e) \qquad (2.1b)$$

Where:

q_e is mass of species adsorbed/mass of adsorbent (mg/g)

C_e defined as equilibrium concentration of absorbable species in solution (mg/L).

2.4.2.1 Different types of Adsorption Isotherms

Several soil – contaminant interactions exhibits different types of adsorption relationships (Clair, et al 2002). There are three different types of isotherms are used to fit the data in to the adsorption isotherm model. The generally used isotherms are:

- Linear isotherm
- Freundlich isotherm
- Langmuir isotherm

Linear Isotherm

The linear isotherm is a special case of the Freundlich isotherm. if n = 1, the Freundlich isotherm is become linear isotherm and it indicates that all adsorption sites on the soil are having equal adsorption affinity for contaminant. If the values of n > 1 represents the adsorption empathy decrease with increasing adsorbate density according to henry's law (Ruthven, 1984). Therefore a linear isotherm takes the form as given in equation 2.2.

$$q_e = K_d C_e \qquad (2.2)$$

Freundlich Isotherm

The Freundlich isotherm equation is based on adsorption on heterogeneous surface (Freundlich, 1906) this isotherm can be expressed by the equation 2.3

$$q_e = K_f C_e^{1/n} \qquad (2.3)$$

Here, K_f represents the maximum amount of heavy metal adsorbed by the adsorbent and n represents the affinity of adsorbent for the adsorbate. If n = 1, the Freundlich isotherm becomes a linear isotherm. Evaluation of the coefficients K_f (l/kg) and n can be accomplished by using the linearized form of equation 2.3 as shown in equation 2.4 and the plot is shown in Fig 2.3.

$$\log q_e = (1/n) \log C_e + \log K_f \quad (2.4)$$

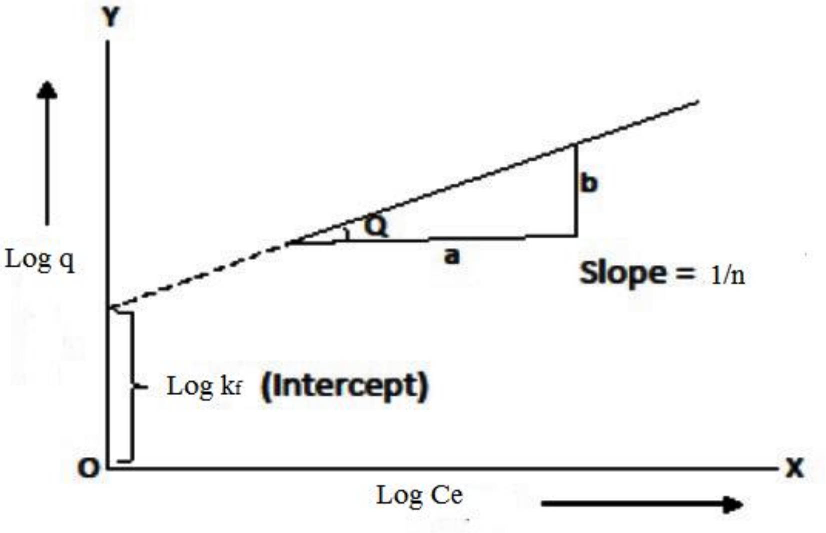


Fig 2.3 Freundlich isotherm plot

Langmuir Isotherm

The Langmuir isotherms model describes the adsorption of adsorbate is happened by forming a monolayer on adsorbent surface containing a finite number of identical sorption sites (Langmuir, 1918). It is used to obtain the maximum adsorption capacity produced from complete monolayer coverage of adsorbent surface. The Langmuir isotherm may be deduced from either kinetic considerations or the thermodynamics of adsorption. Langmuir Isotherm is generally expressing in the form of an equation as given in equation 2.5 and plot is shown in Fig 2.4.

$$q_e = (q_m .K_L.C_e) / (1+K_L C_e) \quad (2.5)$$

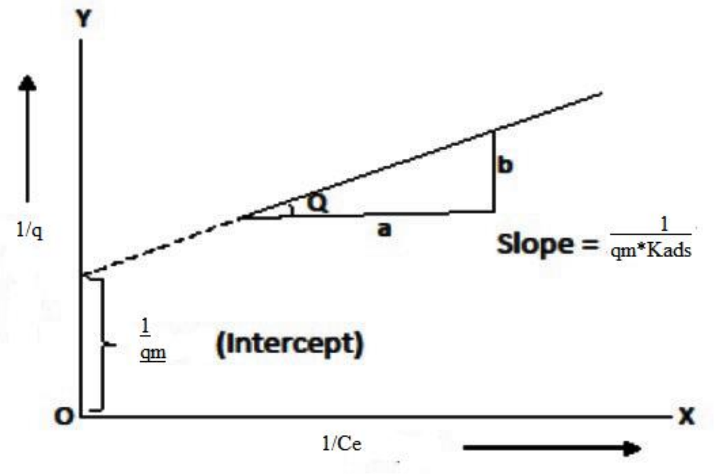


Fig 2.4 Langmuir isotherm plot

The Langmuir equation can be rearranged to linear form for the convenience of plotting and determining the Langmuir constants (K_L l/mg) as given in equation 2.6 and equation 2.7.

$$C_e/q_e = (1/\ q_m)\ C_e + 1/\ (KL.\ q_m) \qquad (2.6)$$

$$1/q_e = (1/K_L.\ q_m)\ (1/\ C_e) + (1/q_m) \qquad (2.7)$$

2.4.3 Previous Studies

The following is a review of contaminant transport processes and models in order to determine the physical and chemical mechanisms that affect the sorption of solutes by soil.

Tessier *et al* (1979) have proposed sequential extraction technique to determine the partition of trace level heavy metals into five different fractions such as exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter and residual in the sediments. The efficiency of the proposed methodology has been validated by comparing, the total concentration of different heavy metals with sum of the partitioned heavy metals in different phases of the sorbent.

Tyler and McBride (1981) have studied the competitive sorption and desorption of various heavy metals such as Cd, Cu, Ni, and Zn in three geomaterials of different chemical composition. For this purpose the study employed is column experiments to assess the desorption rate of the selected heavy metal from acidic as well as nonacidic geomaterials. It has been noticed that, the mobility of various heavy metals through the geomaterials having high pH and cation exchange capacity is insignificant. It is also observed that, majority of the sorbed heavy metals get extracted from the lime treated geomaterials when it interacts with 0.1 N hydrochloric acid due to the irreversible binding action. On the other hand, non-acidic and geomaterials with significant amount of organic matter, exhibited very low desorption rate. This may be attributed to the fact that, the major portion of the organic matter presents in the acidic geomaterials preferentially complexes with aluminium oxides present in it when compared to the heavy metals present in the permeant.

USEPA (1989) has provided guidelines regarding type of materials used for construction of liner in a landfill, which is used for disposing various municipal and hazardous waste in terms of threshold values for hydraulic, plasticity characteristics and percent of coarse grained fraction present in it. It is recommended that, the hydraulic conductivity of the liner material should not be more than 1×10^{-9} m/s. To achieve this, the liner material should contain a minimum of 15 to 20 percent silt size or lower size particles in it with the plasticity index more than 10 percent. On the contrary, in the view of difficulties associated with the construction and swelling behaviour of the highly plastic geomaterials, the maximum plasticity index is limited to 30 percent. Further, it is also suggested that, the liner material should not contain more than 10 percent coarser fragments of particle size greater than or equal to 50mm.

Yong *et al* (1990) have investigated the influence of buffer capacity (which is defined as the property of soil, having a ability to absorb more acid/base without change in the pH of soil) on sorption characteristics of various geomaterials such as kaolinite, Illite and smectite, for heavy metal lead, using batch sorption experiments over wide range of pH. It has been reported that the buffer capacity of the geomaterials 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 geomaterials

Peters and Shem (1992) have attempted to understand the sorption and desorption characteristics of different geomaterials for heavy metal lead with and without chelating agent (Ethylene Diamine Tetra acetic Acid, EDTA). It has been reported that, the sorption capacity of a geomaterials reduces significantly due to the presence of EDTA, as it alters the sorption phenomena. Further, the geomaterials with high silt and clay content exhibits high sorption capacity and this has been attributed to the increased cation exchange capacity of geomaterials.

Yong *et al* (1993) have studied the distribution of heavy metals in various clayey soils by using selective sequential extraction method. The study also attempted to quantify the role of various solid phases present in the geomaterials such as clay minerals, organics, amorphous materials and carbonates on sorption capacity, over wide range of solution pH. The selective sequential extraction method works based on the fact that different forms of heavy metals get sorbed by various solid phases of geomaterials, which can be extracted selectively by using appropriate reagents. It is observed that, the precipitation mechanism is quite dominant at higher solution pH whereas cation exchange mechanism is significant at low solution pH.

Yong and Phadungchewit (1993) have studied the sorption capacity of four different types of geomaterials and the influence of solution pH on selectivity order. It has been observed that a variation of the solution pH results in change in the retention mechanism for both single and composite heavy metal solutions. It has also been reported that the retention capacity of the geomaterials for single and composite heavy metal solution is significantly high, if its buffer capacity is high. Further, it is concluded that, retention capacity of the geomaterials for composite heavy metal solution is low when compared to that of single heavy metal solution.

Reed and Cline (1994) have evaluated the retention mechanism of fine sandy loam for heavy metal lead over wide range of concentration values, soil to liquid ratio and pH of the solution. It has been observed that, the retention of heavy metal lead by the geomaterials strongly depends on the pH of the solution. Further, the study modelled the retention behaviour of the geomaterials using various theoretical sorption isotherms such as Langmuir, Freundlich and BET.

Weng and Huang (1994) have investigated the efficiency of the fly ash for removal of heavy metals from the industrial wastewater. It has been reported that, the fly ash can be used as effective metal adsorbent for heavy metals such as Zn (II) and Cd (II), as it exhibited high and reasonable sorption affinity towards the zinc and cadmium, respectively. Further, it is noticed that fly ash exhibited reasonable compressive strength hence it can also be used as secondary construction materials.

Rowe *et al* (1995) have reported the clay liner specifications for disposal of municipal solid waste. Authors have suggested that, the cation exchange capacity, CEC, of the liner material should be minimum of 10 meq/100g. In addition to the

USEPA hydraulic conductivity criteria, authors have recommended that, the liner material must be chemically compatible enough so that its hydraulic conductivity does not change upon prolonged interaction with chemically aggressive leachate.

Nhan *et al* (1996) has investigated the efficiency of composite material made up of fly ash, lime dust and bentonite as a barrier material. Authors have assessed the hydraulic characteristics of this composite material with water and synthetic leachate. The retention behaviour of the composite material was evaluated with the synthetic leachate which contains various heavy metals such as lead, zinc and iron. It has been observed that, the precipitated ferrous, zinc and lead ions transformed into their hydroxides and carbonates, respectively. Based on the observed results it is suggested that, composite barriers made up of fly ash, lime dust and bentonite are quite effective to dispose various municipal solid wastes.

Reddy and Devulapalli (1996) evaluated the sorption characteristics of clays for hexavalent chromium and pentachlorophenol using batch sorption experiments to address the contaminant transport through landfill liners. It has been reported that, the simple linear sorption isotherm represents the sorption behaviour of various clays in low concentration regions; however they failed to represent the sorption phenomena at high concentration values. With this in view, authors have suggested to employ the nonlinear sorption isotherm to represent the sorption behaviour of clays over wide range of concentration values.

Pandian *et al* (1996) have studied the sorption and desorption characteristics of fly ashes for heavy metal lead over range of solution pH values. It is reported that the precipitation via hydrolysis and adsorption mechanisms are dominant when the solution pH is above and below 5.5, respectively. As a result precipitation of lead ions in the form of lead hydroxide is quite significant when the solution pH is more than 5.5, which in turn influence the sorption affinity of the fly ashes. It has also been observed that, the leachability of lead ions from the metal laden fly ash is quite insignificant over wide range of pH value.

Gao *et al* (1997) investigated adsorption characteristics of various geomaterials, collected from nine dedicated land disposal units (Dads) located in California State, USA. For this purpose, the study considered composite solution containing heavy metals such as Cd, Cu, Ni, Zn, Pb and Cr and their concentration values ranging from 0 to 50 µmol/L and solid to liquid ratio of 30. It has been observed that, the mass of the contaminant sorbed on geomaterials and the concentration of the contaminant present in the solution is linearly related. It has been reported that, specific surface area of the geomaterials and solution pH influences the sorption behaviour of the geomaterials. Further, the organic content present in the geomaterials enhances its sorption capacity for different heavy metals by forming organic-metal complexes.

Sai and Vesilind (1998) have assessed the hydraulic and sorption characteristics and puncture resistance of synthetic geomaterials fabricated using montmorillonite clay, sand and lime. For this purpose, authors have conducted column sorption experiments using mixture of sand and ten percent montmorillonite clay with variable quantity of lime in it. It has been observed that hydraulic conductivity of geomaterials mixture increases with increasing lime content up to 10 percent and decreases thereafter. This is mainly attributed to pozzolonic reaction between lime and montmorillonite clay, which in turn affects the fabric structure of the geomaterials mixture. On the other hand, sorption characteristics and puncture resistance of the geomaterials mixture increases with lime content in it.

Adamcova (1999) has assessed the sorption characteristics of twelve different clayey geomaterials for various heavy metals such as lead, copper and zinc, with the help of batch sorption experiments, using single as well as composite of heavy metal solutions. The author has suggested that, evaluation of sorption capacity of the geomaterials using composite solution represents the real life scenario in a better passion when compared to that tested with single heavy metal solution. It has been observed that, the sorption capacity of the geomaterials is significantly influenced by its carbonate content and cation exchange capacity as compared to that of grain size distribution, plasticity and percentage of clay.

Palmer *et al* (2000) have evaluated the suitability of synthetic material made up of class F fly ash and various materials such as sand, class C fly ash, and bottom ash as a liner material based on its hydraulic characteristics. For this purpose, the in-situ and laboratory hydraulic conductivity of the compacted synthetic material was determined using sealed double ring infiltrometer & two-stage borehole permeameter and flexible wall permeameter, respectively. It has been observed that, the mixtures made from class F fly ash and class C fly ash; class F fly ash and sand compacted on wet of optimum side satisfies the USEPA hydraulic conductivity criteria.

Mimides and Perraki (2000) have evaluated sorption characteristics of the geo-material to assess its suitability as barrier material. For this purpose, authors have conducted both batch and column experiments with heavy metals such as arsenic, cadmium, chromium, zinc, copper, lead, mercury, nickel and selenium. Using the finite difference technique, authors have developed a trilinear textural diagrams and predictive breakthrough curves for a quick estimation of the sorption characteristics of geomaterials towards different heavy metals.

Prasanth *et al* (2001) have examined three different types of fly ashes as hydraulic barrier based on their shrinkage, compaction, permeability, consolidation, strength and pozzolonic characteristics. It has been observed that, the pozzolonic fly ash exhibited higher strength and lower permeability than that of non pozzolonic fly ash. This is mainly due to the formation of cementitious compounds when the reactive silica present in the pozzolonic fly ash interacts with the free lime, which helps in minimizing the pore space between the individual fly ash grains.

Hequet *et al* (2001) have studied the sorption and desorption characteristics of different fly ashes for heavy metals such as copper and zinc, using batch sorption and leachability experiments. It has been observed that the sorption capacity of the fly ash depends on the amount of free lime, amorphous silica and alumina present in it.

Gomes *et al* (2001) have evaluated the selective order and competitive sorption of various heavy metals on seven geomaterials which are different in their chemical and mineralogical properties. It is reported that the heavy metals copper, chromium and lead were the most preferentially sorbed by all the geomaterials considered in this study when compared to that of other heavy metals such as cadmium, zinc and nickel. It has been reported that, selective order of the different heavy metals with same valence, can be predicted effectively based on their misono softness parameter and hydrolysis properties. Further, it is noticed that sorption capacity of the geomaterials highly depends on their pH, organic content, cation exchange capacity and gibbsite content.

Pandian *et al* (2001) have assessed the sorption capacity of kaolinite, black cotton soil and red soil for the heavy metals lead and zinc. It has been reported that, due to the high cation exchange capacity, black cotton soil exhibited higher retention capacity when compared to the other soils considered in this study. Further the percentage sorption of lead by the geomaterials is significantly greater than that of heavy metal zinc. This may be attributed to the fact that, diameter of hydrated lead ion is smaller than that of zinc and the pH required for precipitation of lead ion is smaller when compared to the zinc.

Vengris *et al* (2001) have evaluated sorption and desorption characteristics of virgin and chemically treated clayey soil with the help of batch and column sorption experiments using nickel, copper and zinc as model contaminants. It has been observed that chemically treated clay has altered its structure, chemical and mineralogical composition. As a result the chemically treated clay exhibited higher sorption capacity for the heavy metals considered in this study. Further, authors have modelled the sorption behaviour of both virgin and chemically treated clay using Langmuir sorption isotherm. In addition to this, it has been observed that, insignificant amount of heavy metals were desorbed from the chemically treated clay when they were leached with acidic water of pH 5.

Coles and Yong (2002) have investigated the sorption behaviour of kaolinite for the heavy metals lead and cadmium over wide range of pH. It has been reported that, the cation exchange is the primary sorption mechanism by which both heavy metals considered in this study get sorbed by the geomaterials. It has been observed that pH and metal concentration increases the sorption capacity of the kaolinite for heavy metal cadmium and becomes almost equal to that of heavy metal lead. This is mainly due to the fact that the increase in pH results in higher sorption of monovalent cadmium by the geomaterials when compared to the monovalent lead. Further the increased concentration of the heavy metals may increase the formation of various species which may potentially reduce the mobility of heavy metals.

Kugler *et al* (2002) have assessed the sorption capacity of barrier material collected from the base of ten year old municipal solid waste landfill by employing diffusion and batch sorption experiments, using different heavy metals. Further, selective sequential extraction technique was employed to quantify the sorption capacities of various solid phases present in the geomaterials. It has been observed that, most of the heavy metals were retained by carbonate and oxide phases present in the geomaterials via precipitation mechanism. Further, it is also noticed that, breakthrough times based on the laboratory diffusion experiments for different heavy metals are found to be shorter than anticipated values based on observed concentration profiles in the field. This may be attributed to sample size effects and the anomalies regarding the heavy metal concentrations present in the real landfill leachate and synthetic leachate used in the experiments.

Sezer *et al* (2003) have assessed effect of mineralogical characteristics of Ankara clay on its sorption characteristics and suitability as barrier material. For this purpose authors have conducted batch sorption experiments using various heavy metals solutions such as lead, copper, zinc, manganese and cadmium. It is reported that the geomaterials exhibits higher sorption capacity for different heavy metals, if the geomaterials contains active clay minerals such as Illite, and smectite. It is also observed that, due to the presence of ferrous oxides in the Ankara clay the sorption affinity of this geo-materials for lead and copper is significantly high when compared to that of other heavy metals considered in this study. Based on the findings authors have concluded that the Ankara clay can be effectively utilized as a barrier material.

Lo et al (1992) studied the influence of organic matter and organic ligands (EDTA, Humic acid) on heavy metal adsorption by the soil. From this experiments the concept of specific adsorption mechanism was also demonstrated and discussed. From these experiments it is observed that, the presence of organic ligands (EDTA and Humic acid) have significant influence than the organic matter. This is mainly due to the formation of ligand like complex structure will reduce the heavy metal adsorption efficiency.

Kim et al (2003) studied the influence of liquid to solid ratio and EDTA on extraction of lead from contaminated soils. From these experiments it is observed that, desorption of lead is not affected with increasing liquid to solid ratio. But with the presence of EDTA has significant influence on lead extraction from contaminated soils. The experiments shows the different extraction efficiencies with the presence of EDTA this mainly due to the competition between other cations present in the contaminated soil.

Zuhairi (2003) studied the sorption capacity of five clayey soils (weathered mud rock, Glacial till and alluvial soil) from UK to be used as a landfill liner. The physico-chemical properties shows that, all the selected soils are suitable for construction of landfill liner. The batch sorption experiments shows that, adsorption capacity increasing with increasing in the pH of the solution. The priority order of soils to be used as lands fill liner is alluvial, glacier till and weathered mud rock respectively.

Reddy et al (2004) have conducted batch and electro-kinetic experiments to investigate the removal of three different heavy metals, chromium (VI), nickel (II), and cadmium (II), from a clayey soil by using ethylene diamine tetra acetic acid (EDTA) as a complexing agent. The batch experiments revealed that high removal of these heavy metals 62–100% was possible by using either a 0.1 M or 0.2 M EDTA concentration over a wide range of pH ranging from 2 to 10. However, the results of the electro kinetic experiments using EDTA at the cathode showed low heavy metal removal efficiency. Using EDTA at the cathode along with the pH control at the anode with NaOH increased the pH throughout the soil and achieved high (95%) Cr^{6+}

removal, but the removal of Ni^{2+} and Cd^{2+} was limited due to the precipitation of these metals near the cathode. Apparently, the low mobility of EDTA and its migration direction, which opposed electroosmotic flow, prevented EDTA complexation from occurring. Overall, this study found that many complicating factors affect EDTA-enhanced electro kinetic remediation, and further research is necessary to optimize this process to achieve high contaminant removal efficiency.

Bellir *et al* (2005) have investigated the sorption capacity of locally available clayey soil for copper heavy metal solution. The study also attempted to quantify the influence of various physico-chemical parameters such as the interaction time, the solution pH, the temperature on the retention of the copper by the clayey soil. It has been reported that, the geomaterials retained the heavy metal via adsorption and ion exchange mechanisms and the obtained results were represented very well with theoretical Langmuir sorption isotherm. It is also noticed that sorption capacity of the selected clayey soil increases with increase in pH of the soil solution, temperature and clay contaminant interaction time.

Malandrino et al (2006) performed feasibility study on utilization of locally available vermiculite for waste water treatment system to remove heavy metals (Cd, Cu, Pb, Mn, Ni and Zn). For this purpose, column studies were adopted. From these it was observed that, adsorption of heavy metals by the soil decreased with increasing heavy metal concentration, decreasing in pH and presence of organic complexing ligand. The decreasing order of metal adsorption is observed to be Mn > Ni > Zn > Cd > Cu > Pb. From these studies, author concluded that, the locally available vermiculite can be used as cost effective alternative to treat waste water.

Du and Hayashi (2006) investigated the influence of geomaterials-contaminant interaction time, geomaterials-solution ratio, and pH of the solution on sorption of heavy capacity of Ariake clay for heavy metal cadmium and lead. Authors have demonstrated the application of batch sorption experiments to assess long-term impact on the surrounding ground water quality using numerical analysis. It has been observed that Ariake clay shows higher retention capacity towards the heavy metal lead as compared of cadmium. It is also noticed that, geomaterials-solution ratio seems to be a crucial factor in controlling the sorption of heavy metals.

Antoniadis *et al* (2007) have assessed the sorption characteristics of London clay for heavy metal copper, nickel and zinc. For this purpose, authors have conducted batch sorption and column experiments under accelerated gravity with the single and composite heavy metal solution. It has been reported that centrifuge column experiments simulates the real field conditions in a better passion as compared to that of laboratory batch sorption experiments. It is also observed that, both batch and column experiments have yielded same degree of mobility of the heavy metals through the geomaterials considered in this study. Further, it is noticed that competitive sorption between the different heavy metals increases the mobility of the heavy metal through the geomaterials.

Jlil and Alsewailem (2009) have studied the sorption behaviour of three different types of virgin and acid treated clays for the heavy metal lead over wide range of pH values. It has been observed that virgin clay exhibits high sorption capacity when compared to acid treated clay, corresponding to solution pH value of 4.3. It is reported that, the sorption behaviour of virgin clays can be represented using theoretical Langmuir sorption isotherm. However, the Langmuir sorption isotherm failed to represent the sorption behaviour of acid treated clays, as their clay mineral structure gets altered upon treatment with hydrochloric acid. This resulted in creation of significant heterogeneous sorption sites in the treated geomaterials, which can only be represented by theoretical Freundlich sorption isotherm.

Shu-li *et al* (2009) have evaluated the influence of solution pH, initial heavy metal ion concentration, and amount of sorbent on the sorption capacity of calcium and sodium bentonite for the heavy metal copper. It has been observed that the heavy metals were retained by dissolution mechanism at pH values less than 3, by the ion exchange or adsorption mechanisms for pH values between 3 and 7 and by precipitation mechanism for pH value equals to 8.3 and more. Based on the observed experimental data, it has been demonstrated that Freundlich sorption isotherm represents sorption mechanism of both sodium and calcium based bentonites. It is also noticed that, the Na-Bentonite exhibited twice the sorption capacity when compared to the Ca-bentonite. Further, it is also observed that retention behaviour of both bentonites was significantly influenced by the solution pH, solution concentration and amount of the sorbent.

Moghal et al (2012) studied the retention characteristics of Cu^{+2}, Pb^{+2} and Zn^{+2} from aqueous solutions by two types of low lime fly ashes. A series of Batch equilibrium tests containing the fly ash samples and heavy metal ion solutions at different pH values were conducted. Adsorption kinetics evaluation was done by conducting Batch experiments for predetermined time intervals. It is seen that the amount of metal ions adsorbed varies with the pH of solution. At low pH values, surface adsorption is predominant as protons are exchanged by metal ions at exchange sites on the mineral surface. At high pH values the surface of fly ash is negatively charged and precipitation reactions, mostly as metal hydroxides dominate. The metals are adsorbed in the fly ash by a strong tendency toward chemical bonding between the metal groups and the oxide surface.

Ghosh et al (2014) evaluated the locally available soil as a compacted clay liner to retain the Cr^{6+}which is coming from the tannery industry. Batch sorption studies were conducted and the results shows that Cr^{6+} removal increases with increase in the temperature. The results shows that, the pseudo second-order kinetic model fitted reasonably well. The use of a clayey soil with a thickness of 600 mm is recommended for effective containment of leachate migration.

Mohammed (2016) evaluated the relative performance of two soils as a sustainable material to attenuate the transport of heavy metal ions, cadmium (Cd^{2+}) and nickel (Ni^{2+}), from aqueous solutions has been evaluated. Red earth soil (RS) and black cotton soil (BCS) originating from India, were selected, and batch equilibrium tests including sorption kinetics and leaching studies were conducted. Langmuir isotherm was found to be more suitable than Freundlich isotherm for both the soils. Kinetic data were fitted on four models namely pseudo first order, pseudo second order, Elovich and intra-particle diffusion. Correlation coefficients obtained by all models fitted well in the following ranking: Based on extensive experimental data, it is concluded that the ranking on sorption was of the order Cd >Ni for both the soils, and BCS exhibited relatively higher retention levels compared to RS. It is further concluded that BCS can be used as a substitute to filter material, RS a substitute to main liner material in attenuating Cd^{2+} and Ni^{2+} from an industrial landfill leachate.

2. 5 Contaminant Diffusion through Soil Medium

2.5.1 General

A review of literature regarding with the effectiveness of suitable landfill liner material on the basis of its metal breakthrough characteristics is reported in this chapter. The concept of breakthrough from the viewpoint of column study, factors affecting the breakthrough behaviour of metals passing through soil, mechanisms involved in the immobilization process of metal ions and mathematical parameter to calculate the diffusion of the contaminant are also presented in this chapter.

2.5.2 Significance of column study

The possible response exhibited by the soil against the transport of heavy metals can be properly depicted through the column leaching test. Real field situation can be simulated in the column experiment which can provide us a good reliable output regarding the heavy metal transport through liner geomaterials. Depending upon the results obtained from the column test, it is possible to predict the long-term stability and effectiveness of the liner installed in the landfill. According to Kosson et al (2002), column test that is designed to simulate releasing of heavy metals under specific environmental condition cannot be able to provide suitable information under condition distinct from the simulated one. The disadvantage lies within its execution process which consumes more time and intensive labour work (Angelica Naka et.al 2016).

2.5.3 Mechanisms involved in immobilization process

There are several mechanisms involved in the process of immobilization of heavy metals which are having further dependency on several factors that have to be considered in association with the mechanisms in order to comprehend almost the total phenomenon acting behind the retardation of heavy metals. Adsorption is one of the mechanisms which involves net accumulation of matter at the interface between a solid phase and an aqueous solution phase (Mohamed and Antia 1998; Ming et al 2005). The heavy metals exist in a cationic form which get attracted by the surface negative charges of clay particles. Mainly inner and outer–sphere surface complex formations are the mechanisms of adsorption process which can be differentiated by considering the role of water molecules that comes into picture in time of complex formations and nature of bonding. Technically it can be referred as specific and non-specific adsorption respectively. In specific adsorption, either covalent or ionic bonds or combination of two takes place between the metal cations and surface functional groups of clay minerals (Madgi and Michael 1997) . But in non-specific adsorption, at least one water molecule is interposed between the surface functional groups and the ion or molecule it binds. Due to involvement of electrostatic bonding in this kind of adsorption, it is somehow less stable than specific adsorption. Another form of adsorption can also be happened if a solvated ion does not form a complex with a charged surface functional group, but instead of neutralizing surface charge, it get adsorbed in the diffused-ion layer. This adsorption mechanism generally involves ions that are fully dissociated from surface functional groups and are free to move in the soil solution.

2.5.4 Mechanisms involved in transport process

The mechanisms mainly responsible for the transport of heavy metal ions through geo-materials are advection and diffusion. Either only one or both can exist in the field depending upon the field conditions prevailing at landfill area. Advection phenomenon can be expected only when the seepage flow specifically indicated by the seepage velocity is high enough to dominate in the process of mass flow. If advection is the only process that control the mass flow, the pore velocity (Darcy velocity divided by soil porosity) becomes a good indicator of the transport of dissolved contaminants (Lakshmi et.al 2000). Another transport mechanism associate with the advection process is diffusion which mainly takes place in presence of concentration gradient. Generally the geo-materials used in constructing landfill liner possess very low co-efficient of permeability, lowering down the seepage velocity by a greater magnitude. Hence, we can expect that diffusion predominantly controls the process of transport of heavy metals through the geomaterials rather than advection. In very special cases where cracking occurs in the surface of the liner due to temperature variation, the seepage velocity increases which in-turn promotes advection flow reducing the long-term stability of the installed liner (Daniel 1993).

2.5.5 Quantification of transport process

Fick's law assumed the one-dimensional mass flow due to existence of concentration gradient and thus derived an equation in order to calculate mass flow in the diffusion process which correlates mass flux (i.e. solute in the chemical solution) directly with the concentration gradient (Shackelford, 1991., 2014; Shackelford and Daniel 1991), may be written as given in equation 2.8

$$J = -D_o \frac{\partial c}{\partial x} \tag{2.8}$$

Where J = the mass flux, c = the concentration of the solute in the liquid phase, x = direction of transport, and D_o = the "free-solution diffusion" co-efficient. Naturally free-solution diffusion cannot be expected in case of mass flux through soil as many factors come into picture which resists the free diffusion process. Factors such as volumetric water content (i.e. porosity multiplied by degree of saturation), tortuosity, viscosity of the liquid etc. affect the diffusion process. The use of “D_o” in the mass flow calculation without considering the factors may cause a sufficient deviation in the obtained result. As it is difficult to measure the tortuosity factor, effective diffusion co-efficient (D^*) has been introduced by combining the free-solution co-efficient with the tortuosity factor (τ) that is represented as shown in equation 2.9 (Shackelford, C. D (1991). The effective diffusion coefficient can be calculated by dividing with retardation factor and this retardation factor is mainly dependent on the distribution coefficient (kd). The relation between retardation factor and distribution coefficient is shown in equation 2.1a.

$$D^* = Do\ \tau \qquad (2.9)$$

Finally the equation turns into a new form that has been shown as:

$$J = -D\ \Theta \frac{\partial c}{\partial x} \qquad (2.10)$$

Where D = Diffusion co-efficient, Θ = Volumetric water content (= $n*S_r$), n = porosity and S_r= degree of saturation (expressed as percentage)

The above equation ultimately follows the conservation of mass equation which can be converted into a partial differential equation considering two independent variables known as space(x) and time (t). The continuity equation is represented as:

For only diffusion case: $\partial c/\partial t = D\ (\partial^2 c/\partial x^2)$ (2.11)

For advective-diffusion case: $\partial c/\partial t = D(\partial^2 c/\partial x^2) - v_s\ (\partial c/\partial x)$ (2.12)

Where, D = Diffusion coefficient, vs = seepage velocity

After imposing the boundary conditions for a constant source concentration for one-dimensional case of diffusion, Crank (1956) proposed a solution which can be stated as:

$$\frac{C(x,t)}{Co} = \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad (2.13)$$

Where, C(x, t) = solute concentration at a specific depth of the medium through which solute diffuse after a certain time‘t’, Co= Initial concentration of solute before passing through the medium

For advection-diffusion case:

$$\frac{C(x,t)}{Co} = \frac{1}{2}\left[erfc\left(\frac{x-vt}{2\sqrt{Dt}}\right) + \exp\left(\frac{vx}{D}\right) * erfc\left(\frac{x+vt}{2\sqrt{Dt}}\right)\right] \qquad (2.14)$$

Where, vs = seepage velocity (= discharge velocity divided by porosity of the medium)

2.5.6 Concept of Breakthrough

Breakthrough refers to the phenomenon of releasing heavy metals through soil. Soil is having its own adsorption capacity and when soil gets saturated with the metal ions, it becomes incapable to prevent the ion migration through it. That points refers to the ‘Exhaustion point’ which can give us the information regarding the soil adsorption capacity. After reaching this point, whatever the influent (i.e. metal ions in a solute form) of certain concentration will enter into the soil, the effluent (i.e. metal ions in a solute form after passing through the soil) having same initial concentration as influent can be obtained from the other side of the soil column in column study. Breakthrough curves (BTC) obtained from column study which can be used to test various models for describing reactive solute transport in soil (Madgi

Selim and Amacher 1997) is shown in Fig 2.5. Breakthrough curves are most conveniently represented in dimensionless parameters between relative concentration (C/C_o) and number of pore volumes (P.V) where ‘C’ and ‘C_o’ represents the effluent concentration & influent initial concentration respectively. Sometime the relative concentration is plotted against time of progression of the experiment.

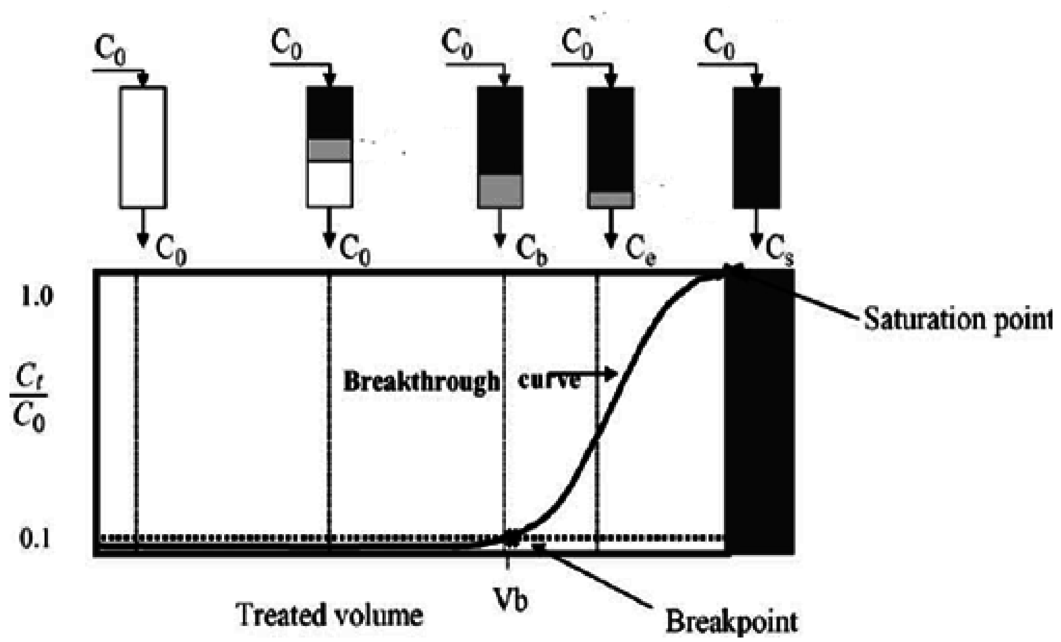


Fig 2.5 Typical diagram of Breakthrough curve (Castodes et al 2003)

In the Fig 2.5, Vb refers to volume of the effluent to the break point and Vx denotes the volume of effluent considered up-to exhaustion point. At break point, the sorption zone reaches to the end of the cylindrical soil specimen. At exhaustion point, all the active sites of the soils get saturated by metal ions and the soil column becomes incapable of retaining heavy metals through sorption process. Ultimately, the concentration of effluent becomes almost equal to the initial concentration of incoming metal solution. Many attempts have been tried in order to reduce the drawback of column experiment related to the excessive time of operation and cost. Lim and Aris (2014) experimentally found the factors that were affecting the operational time of the column experiment such as bed height, initial concentration of influent metal solution and flow-rate. It was found that higher the bed depth, longer time the soil will take to achieve breakthrough. As adsorption increases due to the increased amount of adsorbent in the column and the higher the initial concentration of influent leading to a quick breakthrough curve. In addition to the bed depth and concentration of contaminants, flow rate also had influence on achieving quick breakthrough time. Soil having high cation exchange capacity (CEC) and high specific surface area (SSA) that are associated with their small particle sizes, can be able to adsorb more amount of heavy metal ions making it feasible for constructing liner (Malandrino et. al 2006).

2.5.7 Factors effecting breakthrough of metal ions

There are many factors influencing the transport of heavy metal ions through geo-material. Both the mechanisms of transport i.e. diffusion and advection depend upon the soil properties and environmental conditions. The quantitative parameter named as diffusion coefficient (D) that has been mentioned previously is a quite complicated parameter to be estimated but very useful to predict the breakthrough characteristics of the soil (Shackelford et al 1991). Simply using free solution coefficient (D_o) cannot be able to predict the flow of pollutants through soil due to the presence of soil itself.

The factors that have to be considered along with free solution coefficient (D_o) are explained briefly as follows:

Reduced cross-sectional area

Solutes diffuse at a slower rate in soil than in free solution as soil particles occupy some of the cross sectional area of soil-solution system. Porosity and degree of saturation play important roles in controlling solute flux through soil which can be considered under this category. Maximum flux will occur when the degree of saturation will almost attain 100%.

Effect of Tortuous pathway

The tortuous path of flow existed due to presence of soil particles affect the diffusion of heavy metals. Tortuosity factor (τ) has been included with free solution coefficient for actual determination of effective diffusion coefficient which is very much difficult to calculate.

Chemical interactions with charged soil particles

Soil having high cation exchange capacity can retain more heavy metals leading to quick breakthrough of metal ions.

Besides the above main three influencing factors, some other factors that are having significant contributions in the process of achieving breakthrough. Soils possessing lower hydraulic conductivity is more capable of restricting solute flow through soil. US Environmental Agency (US EPA 1989) has suggested the requirements that can be followed in choosing proper soil to be used as a liner material. The specifications related to the soil properties are given in table 2.1.

Table.2.1 Limiting values of the soil properties used as a liner material (Daniel, 1993)

	Limiting Value
Gravel (%)	< 30
Fine (%)	> 30
Liquid limit (%)	≥ 20
Plasticity Index (Ip)	> 10 and ≤ 35
Cation Exchange Capacity (meq/ 100 gm)	> 10
Co-efficient of hydraulic conductivity (m/s)	$\leq 1\times10^{-9}$

Influence of soil solution pH and presence of organic ligand in the soil affect the metal retention capability of soil which further retards or accelerate the breakthrough process (Abollino et.al 2003). At lower pH, most silanol and aluminol groups are protonated and hence less likely available for metal cations due to competition between hydrogen ion(H^+) and the metal cations for occupying active sites. On contrary i.e. at higher pH, more amount of metal ions get retained due to formation of hydroxyl products and less competition with H^+ for occupying adsorption sites. Organic ligand has the ability to form complex product with the metal ions making it less available for getting adsorbed by soil and thereby increases its mobility. Even the pH of the incoming heavy metal solution reduces the chances of getting retained through precipitation and increase the mobility at higher pH (Yong et.al 1993). Some attempts were made to study the effect of high hydraulic gradients of liquid contaminant on the migration of heavy metals through the soil by performing column study (Zaheer et.al 2013). High hydraulic gradients can give rise to the higher seepage velocity which enhances the advection flow leading to quick breakthrough. Usually smaller the ionic radius and higher the charge of the metal get adsorbed through cation exchange process. But when more than one metal ions with same charge exist in the contaminated solute, the preferential adsorption depends upon the value of ionic radius (Dube et.al 2001). However, it also depends upon the pH of the soil solution. In acidic condition, smaller the ionic radius more electric field will be generated and greater chance of getting adsorbed through cation exchange process. However, with the increment of pH towards basic, the adsorption will depend upon the radius of first hydrolyzed metal product.

2.5.8 Previous Studies

There are several researchers who worked on the area of heavy metals transport through soil for proper understanding chemistry behind the soil- metal interactions based on the obtained experimental results performed in the laboratory. The important findings of the papers that were previously proposed by the researchers based on their observations and knowledge are noted down in this section.

Yong and Phadungchewit (1993) performed batch extraction technique to observe the influence of pH on the selectivity and retention of heavy metals by soils. The paper mainly focused on the study of pH effect on the immobilization of heavy metals present in both single & multi-component heavy metal forms. Seven heavy metals (Pb, Cd, Cu, Zn, Ni, Cr and Hg) were considered for investigation purpose and also four different types of clay soil i.e. Kaolinite, Illite, Montmorillonite and a natural clay obtained from active landfill area situated at 35 km east from Montreal were chosen for identifying the effect of mineralogical property in the presence of varying pH. The results showed the decrease in adsorption in case of composite mix of heavy metals when compared to single one. Further the reduction in the heavy metals retained was explained by the aid of pH-acid titration relationships of the soils. It had been concluded that at lower pH, the competitive effect resulted from the competition with H^+ ion and other metal ions in composite mix for occupying adsorption sites, was lowering down the percentage retention of single heavy metal. Also at higher pH, the shifting to the right of the metal-hydrolysis reaction to maintain chemical equilibrium in case of composite mix, reduced the pH of the soil solution due to the higher yielding of H^+ resulting in the reduction of metal retention through precipitates formation.

Gomes *et al* (2001) conducted experiments following the methods of batch sorption test for evaluating the relative retention and mobility of multiple metals applied together to soils collected from B horizon of a Brazilian Oxisol. Based on the distribution co-efficient obtained from each experiment, the selectivity order of the heavy metal cations had been worked out. Also investigations were done to sort out the relationship between soil properties and adsorption of heavy metals by Brazilian soils with different chemical and mineralogical characteristics. The major findings stated as the competition between the metals considered for the study ultimately leads to the different values of distribution coefficients for different metals thereby changing their order of selectivity. The reasons that were put in support of the observations obtained through experimental results had been correlated to the change in soil solution pH. At higher pH, the phenomenon of adsorption was mainly governed by the characteristics of hydrolyzed product (MOH^+) and at lower pH (acidic), electronegativity of the metal dominated the adsorption of heavy metals. The larger the electronegativity of the metal the easier the dissociation of the H^+ from the functional groups of the soil mineral forming covalent bonding.

Abollino *et al* (2003) performed continuous column method instead of conventional batch technique to study the adsorption of heavy metals on Na-montmorillonite.

Seven heavy metals chosen for study purpose were Cadmium (Cd), Copper (Cu), Chromium (Cr), Manganese (Mn), Nickel (Ni), Lead (Pb) and Zinc (Zn). This paper focused on the effect of pH ranged from 2.5 to 8 and organic ligands such as nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), oxalic acid, malonic acid, succinic acid, glutaric acid, tartaric acid and citric acid (Concentration of all ligands considered as 1 milimole) on the adsorption of heavy metals. It was observed that the effect of pH on the adsorption of heavy metals were different for each metal. Below pH≤3.5, the ascending order of retention was found in a following manner: $Cu^{2+} < Pb^{2+} < Cd^{2+} < Zn^{2+} \leq Mn^{2+} \approx Cr^{3+} \approx Ni^{2+}$ revealing adsorption decreased with decreasing pH. For Cd^{2+} and Pb^{2+}, the effect of low pH was highly visible due to their large ionic radius (0.97 and 1.20 Ǻ respectively) and lower charge density. Almost in presence of all ligands, the metal adsorption increased in the ascending order: $Cr^{3+} < Cu^{2+} < Ni^{2+} < Zn^{2+} \leq Cd^{2+} \leq Pb^{2+} \leq Mn^{2+}$.

Bernd N (2002) had made an attempt to render an overview on the environmental chemistry of anthropogenic chelating agents of the group of the amino-poly-carboxylates such as EDTA, NTA, DTPA and EDDS with an intense description about exchange reactions conformed to metal-exchange in solution, adsorption to mineral surfaces, dissolution of minerals, and remobilization of adsorbed metals. Besides, the redox reactions involved in maintaining the equilibrium process and the determination of their speciation by analytical techniques were also presented in the paper. One of the notable points that had been mentioned was specifically related to effect of the concentration of EDTA on the adsorption of heavy metal ions by soil minerals. At higher adsorption, EDTA promoted mobilization of metal though the formation of dissolved complexes, but at lower concentration instead of reducing adsorption, it assisted in adsorption process through changes in electrostatic properties of the solid/solution interface or through sorption of the metal-ligand complex on the soil surface under formation of two different ternary surface complexes.

Oviedo and Rodriguez (2003) gathered lots of information regarding with the presence of EDTA which got released into the environment at a higher rate mainly from household and industrial applications. It was also found that EDTA was having poor biodegradability that can create a major problem by increasing the mobility of the heavy metals through metal-EDTA complex formation. The amount of EDTA that was used in the industrial and household works also represented in the paper in a percentage of world market. EDTA can solubilize the radioactive metals and increase their environmental mobility. In case of soil, it can reduce the adsorption of heavy metals which can seriously cause a great trouble in landfill area where liner made of geomaterials is installed in order to restrict the transport of heavy metals through it. By lowering the effectiveness of the liner, EDTA can indirectly contaminate the groundwater by increasing the solubility of the toxic heavy metals (Lo et.al 1992).

Reddy *et al* (2004) conducted batch and electro kinetic experiments to study the remediation of multiple heavy metals by using EDTA. Three heavy metals such as Nickel (II), Cadmium (II) and Chromium (VI) were considered. Experiments were performed under a wide range of pH conditions and two different concentrations of EDTA (0.1 and 0.2 M) were used to study EDTA enhanced electro kinetic remediation. From the results obtained from the batch experiments, certain conclusions had been drawn which rendered probable causes of experimental outcomes. Chromium (VI) showed a sufficient adsorption at lower pH whereas

Nickel and Cadmium got immobilized through precipitation at higher pH. At higher pH, the stability of Ni-EDTA and Cd-EDTA increased but at lower pH, complexation with hydrogen ion (H^+) hindered the effective removal of Nickel and Cadmium.

Malandrino *et a.* (2006) conducted continuous column test on vermiculite supplied by Aldrich to study the effect of pH, particle size and organic ligands on the adsorption of heavy metals (Cd^{2+}, Cu^{2+}, Cr^{3+},Mn^{2+},Ni^{2+}, Pb^{2+} and Zn^{2+}). Vermiculite of three different range of particle sizes i.e. less than 90μm, between 90-300 μm and greater than 300 μm were considered for scrutinizing the effect of particle sizes on the retention of heavy metals by vermiculite. It was observed that with the decrease in particle size, the uptake of heavy metals by vermiculite was increasing due to the generation of high surface area. In case of all heavy metals, percentage adsorption were higher for least particle size (< 90 μm).

Zhang et al (2005) tried to sort out some potential problems concerned with laboratory diffusion ad batch sorption experiments and provide some strategies to come up with the limitations observed in individual tests that can be performed for accurate estimation of distribution co-efficient and effective diffusion co-efficient. The advantages, disadvantages, limitations and probable problems related to the tests were compared and summarized in the paper. They suggested that constant source concentration column test cannot be used to determine the effective diffusion co-efficient and also cannot be used to test specimens with low permeability due to its less replicating capability of simulating exact field condition, cumbersome efforts required to maintain constant source concentration and easy test management. Instead of it, decreasing source concentration test can be adopted in the laboratory. But for determining the effective diffusion co-efficient obtained from the suggested test data, semi-analytical solutions combined with numerical approaches had to be assimilated.

Manouchehri and Bermond (2009) presented a comprehensive review on the use of EDTA (Ethylene diamine tetra acetic acid) in various fields of environmental geochemistry. The application of EDTA as a chelating agent had been pointed out with proper discussions about the chemistry involved in metal-EDTA interactions. The logarithm of conditional stability constant i.e. complexation constant determined the stability of the meta-EDTA complex product against variation of soil solution pH. Even at equal pH, the complexation constants varied for different heavy metals. The metal remediation technique by EDTA chelation was conditioned by numerous factors such as co-dissolution of major cations (Fe and Ca particularly), m_{soil}/v_{EDTA} ratio, source of contamination, soil pH, soil type, cation exchange capacity (CEC), temperature, particle size, dissolved organic matter and kinetic of exchanges. These factors affected widely the extraction of metals. Besides pH, the stability constant of a metal was also affected by the competitive behaviour of other cations in the system, concentration of EDTA and presence of other electrolytes (Ringbom 1967; Norvell and Linsay 1969).

Chotpantarat et al (2011) studied the sorption and transport of heavy metals through soils in the presence of other metals. The competitive sorption and transport of four heavy metals, Pb^{2+}, Ni^{2+}, Zn^{2+}, and Mn^{2+}, were investigated using column experiments with lateritic soil. For multi-metal systems, the estimated retardation factors for the metals from highest to lowest were: $Pb^{2+} > Zn^{2+} \sim Ni^{2+} > Mn^{2+}$, suggesting the mobility of metals through lateritic soil for a multi-metal system would be in the order of $Mn^{2+} > Ni^{2+} \sim Zn^{2+} > Pb^{2+}$. Mass recoveries estimates showed that the sorption of metals was more reversible under competitive multi-metal systems than in single metal systems.

Ghosh et al (2013) have carried out the investigation in field scale in a common tannery effluent treatment plant site near Kolkata for evaluating hexavalent chromium migration through the fine-grained clayey soil, for disposal of chrome sludge emanated from cake filter press. The locally available soil was used in situ as a compacted clay liner material as adsorbing candidate. Laboratory batch adsorption results demonstrated about 70–80 % of hexavalent chromium removed after 120 min of equilibration time. Hydraulic conductivity of the soil was found to be decreased by two decimal place due to permeation of hexavalent chromium laden leachate. Field test results also exhibited 63 % of hexavalent chromium was sorbed after 120 days interval. Experimental results were also validated by mathematical analysis with good agreement to test data.

Aldaeef and Rayahani (2014) conducted Hydraulic conductivity tests on different soil specimens after being exposed to various thermal and dehydration cycles. An increase in the CCL hydraulic conductivity of up to one order of magnitude was recorded after 30 thermal cycles for soils with low plasticity index (PI = 9.5%). Overlaying the CCL with a cover can minimize the effects of daily thermal cycles, and maintained stable hydraulic performance in the CCLs even after exposure to 60 thermal cycles. The study underscores the importance of protecting the CCL from exposure to atmosphere through covering it by a layer of geomembrane or an interim soil layer

Sharmeen *et al* (2015) had made an attempt to study the adsorption performance of continuous fixed bed column for the removal of methylene blue (MB) dye using

Eucalyptus sheathiana bark biomass because of its cost-effectiveness and sustainability. Barks of Eucalyptus species was collected from inside the Curtin University – Bentley campus, Perth, Western Australia for preparing columns of different thickness (10 cm, 12 cm and 15 cm). Also a series of experiments was performed to study the effect of inlet flow rate (10 mL/min, 12mL/min and 15mL/min) and initial MB dye concentration (50, 75 and 100 mg/L) at a fixed solution pH of 7.4. Two mathematical models such as Thomas, Yoon-Nelson and Bed depth service time (BDST) were incorporated in order to predict the dynamic behaviour of the bed in column performance. From the breakthrough curves obtained from the experiments, it were observed that with the increase in adsorbate flow-rate, BTC became steeper indicating swift breakthrough due to lack of time required for reaching adsorption equilibrium. Also in increase in bed depth and the initial adsorbate concentration, the breakthrough time was increasing and decreasing respectively.

Zhang and Huang (2016) conducted the basic experiments on chromium-contaminated soil for finding its physio-chemical properties in order to know whether the properties were changing or not after interaction with chromium. The properties such as pH, water content, maximum dry density (MDD) and corresponding optimum moisture content (OMC), Atterberg limits especially liquid limit & plastic limit, specific gravity and particle size distribution were considered for study purpose. It was observed that in the presence of chromium, certain properties like liquid limit and plastic limit of the contaminated soil were decreased but other properties like specific gravity, maximum dry density and silt content increased. Free swell had also performed on the chromium-contaminated soil for observing the expansion behaviour of the tested soil. The expansion ratio which was expressed as a percentage decreased by a higher amount to be noticeable.

2.6 Cracking Behavior and Contaminant Transport through Cracked Soil

Landfill problems and their remediate solutions have been increased to a point where waste disposal in landfill becomes a technology. Clayey soils are generally used in construction of landfills as liners. The basic criterion for a soil to be used as a liner is that it should have permeability < 1 x 10^{-9} m/sec (Daniel 1993). Generally clayey soils satisfy this condition but the problem occurs when desiccation cracks occur in these soils as it increases the hydraulic conductivity of soils. So, for a soil to be used as a liner material it should sustain low hydraulic conductivity even after desiccation effect so that it can restrain permeation of leachate. There are many researches regarding change in properties of soil contaminated with leachate (Afshin Asadi et al 2011). But the effect of heavy metals on soil upon desiccation has to be verified as heavy metal contamination is highly dangerous to living beings and environment.

2.6.1 Previous Studies

Kleppe and Olson (1985) conducted shrinkage tests on clay and sand mixed with clay varying from 10% to 12%. Cylindrical soil samples were used to find shrinkage of the clay - sand. The severity of cracking for each mixture was determined by preparing flat plates of the clay - sand mixtures and measured the size and number of cracks and gave the ration on point scale from 0 to 4 (4 being the most severely cracked). From the experiments, it is observed that, the soil sample shrinkage decreased with increasing sand content as well as with increasing water content but it was independent of compactive effort.

Morris *et al* (1992) reported that macro cracks were developed and its growth will depend on the negative pore water pressure generated in the soil. The authors also disclosed that, soil cracks produced in fine grained soils than in coarse grained soils due to rapid development of negative pore water pressure. This is due to the fact that, fine grained soils have smaller particle size and hence smaller inter-granular voids. The smaller voids can create high pore water suction. They also reported that the conditions for crack propagation are more positive at the where suction is more.

Othman *et al* (1993) conducted permeability tests on two low plastic clays (Live Oak and Wenatchee clays) subjected to four cycles of wetting and drying. Each soil sample was prepared at ± 3% of optimum water content and at optimum water content. Wenatchee clay compacted dry of optimum and at optimum water content showed no significant increase in permeability when desiccated but the permeability of soil specimen prepared at wet of optimum water content increased by a factor of three. For the Live Oak clay, the permeability of all soil samples increased one order of magnitude within first two wet-dry cycles, but decreased thereafter.

Benson and Trast (1995) conducted permeability tests on thirteen types of clayey soils. The samples were compacted to different water contents and permeability tests were conducted on flexible wall permeameter. Comparisons between index properties and hydraulic conductivities for water contents ±2% wet of optimum for each compactive effort showed that permeability was very sensitive to its composition. Lower permeability was achieved for soils that are having more plasticity. A regression equation was developed from the data to estimate permeability for given initial saturation, compactive effort, plasticity index and clay content.

Miller *et al* (1998) conducted tests to study desiccation cracking of three compacted liner soils obtained from local landfills in southeast Michigan. Surficial dimensions of cracks were quantified using the crack intensity factor (CIF). All of the soils were subjected to a compaction–dry cycle and a subsequent wet–dry cycle. The soil used for the study had low PI and was compacted to dry of optimum. From the experiments, it was observed that, almost 90% of the cracks happened within 19 time period. Upon the second cycle of drying, the cracks have increased significantly when compared to first cycle. In the first cycle the cracking pattern was observed to be linear whereas in the second cycle, the crack pattern shows the polygon network. The variation of CIF with varying in soil moisture suction has been observed and concluded that, the cracking is started suction reached a value about 6 bars pressure.

Kodikara *et al* (2000) studied the effects of soil thickness, initial soil density, base adhesion and desiccation rate. It was considered that desiccating clay soils crack when the tensile stresses developed in the soil due to matric soil suction exceeds the tensile strength of the soil. The samples were prepared in wooden containers (600mm x 840mm x 70mm) having base materials like plain wood, greased wood, sheet of glass and 20mm thick sand in wooden container. The test results indicated that glass base produces smaller cell sizes in comparison to wood base. The adhesion at interface is strongly dependant on the soil moisture content where the value of adhesion gradually rises to a peak as the water content decreases from the initial water content and then decreases rapidly as the soil dries out. Further it is said that the low cracking in samples on sand base was due to the lower shear restraint exerted on the soil by the base.

Rayhani *et al* (2006) studied effect of desiccation induced cracking on hydraulic conductivities of clayey soils from Iran. Specimens prepared from these soils were subjected to wetting and drying cycles. The results showed that the dimension of cracks increased with increasing plasticity index and clay content so the initial hydraulic conductivity increased with increased plasticity index and cycles of wetting and drying. After a long saturation time, the hydraulic conductivity of the soils decreased with an increase in saturation time, which could be associated with a self-healing process that affects the soils by different degrees. To evaluate the effect of soil properties on the cracking and permeability behaviour Kr (ratio of hydraulic conductivity of cracked specimen to that of un-cracked specimen) was used. If the Kr is unity it is considered to be an ideal material for using in construction of liner.

Chalermyanont *et al* (2008) studied about the transport of heavy metals through a compacted sand-bentonite mixture and its chemical compatibility was studied through the batch adsorption test, the column test and the hydraulic conductivity test. Hydraulic conductivity of the compacted sand mixed with as low as 3% sodium bentonite content is less than $1x10^{-7}$ cm/s. A mixed heavy metal solution was used to simulate real leachate, which consists of many heavy metals. One sample was permeated with DI water only whereas another sample was permeated first with DI water and later with the mixed heavy metal solution. When permeated with DI water, the hydraulic conductivity of sand-bentonite mixture was $4x10^{-9}$ cm/s. The hydraulic conductivity increased when permeated with mixed heavy metal solution. The average hydraulic conductivity of the sand-bentonite mixture of $9x10^{-9}$ cm/s was obtained when it was permeated with mixed heavy metal solution for two pore volumes of effluent (PVEs). However, its hydraulic conductivity was still less than

$1x10^{-7}$ cm/s, which was a common regulatory for landfill liners. The chemical compatibility of the hydraulic conductivity of the sand-bentonite mixture samples was assessed by permeating the samples with various concentrations of the chromium solution. It was found that only chromium solutions having concentrations of 0.001 to 0.0001 M were compatible with the sand-bentonite mixture.

Tang *et al* (2011) studied the influence of wetting-drying cycles on the initiation and progression of cracks in clay layer. The wetting and drying influence on soil surface cracking was analysed by image processing. It was found that, with increasing number of wetting and drying cycles resulted in significant rearrangement of specimen structure: the initially homogeneous to aggregated structure with after the second wetting and drying cycle. The image analysis results show that the geometric characteristics of crack pattern were significantly influenced by the increasing number of wetting and drying cycles. Results proved that the image analysis can be used to assess the wetting and drying cycle dependent cracking behaviour.

2.7 Critical Appraisal of Literature review

Based on the literature presented in the previous sections, the following observations are made:

Several studies reported in the literature, suggested the suitability of different geomaterials as landfill liner material based on their hydraulic conductivity characteristics. In addition the researchers have also proposed the methodologies to enhance the hydraulic characteristics of locally available clayey soil using commercially available additive/immobilizing agents such as bentonite and zeolite. However, not many efforts were made by the researchers to highlight the importance of chemical compatibility, sorption characteristics and desiccation cracking behaviour of the clayey soil while selecting the clayey soils as a landfill clay liner. In addition, attempts were not made to understand the influence of sorption characteristics with variation of pH and initial concentration of heavy metal solution (single and multi-heavy metal solution). Similarly, Efforts were not made to understand the change in the diffusion of heavy metals through the soil under the influence of organic chemical and cracking behaviour of soils. The diffusion of the heavy metals through the liner material and cracking characteristics of clay liner material under in the influence of organic contaminants were not addressed in detail and there is a necessity to study these factors before suggesting a suitable material to be used as a compacted clay liner.

CHAPTER – 3
METHODOLOGY

3.1 General

This chapter describes the materials used and the experimental methods adopted to evaluate the suitability of locally available clayey soils as a landfill liner material.

3.2 Soils Considered

For this study, two locally available soils (Black Cotton soil and Red Earth) which are the abundantly available in Warangal region of Telangana state were collected from nearby locations of NIT Warangal. The Index, engineering, chemical and mineralogical characteristics of these two soils were conducted as per IS code of practice.

3.3 Properties of soils

The index and engineering properties of selected soils (Black Cotton soil and Red Earth) are described in the following sections and the results from the these tests are presented in table 3.1.

3.3.1 Specific Gravity:

The specific gravity, *G*, for the soils were obtained by using density bottle method by following the guidelines given in IS 2720 (part I) - 1963.

3.3.2 Grain Size Analysis:

The particle size distribution of the soils were assessed as per IS: 2720 (part IV) 1985.

3.3.3 Atterberg Limits:

The liquid limit (LL), plastic limit (PL) and shrinkage limit (SL) were measured for the by following the guidelines presented in IS: 2720 (Part V) 1970.

3.3.4 Standard compacted test:

To get Optimum Moisture Content (OMC) and Maximum Dry Density (MDD) of the both the soils, standard Proctor compaction test was done according to the guidelines of IS: 2721 (Part VI) 1974.

3.3.5 Hydraulic Conductivity Test:

To determine the coefficient of permeability of both the soil, variable head permeability test was conducted according to IS: 2720 (Part17) 1986.

3.3.6 Free Swell Index (FSI):

Free swell index determined according to guidelines given in IS: 2720 (Part XL) 1977.

3.3.7 Cation Exchange capacity:

The cation exchange capacity, CEC, is the ability of a material to exchange the cations and it depends on the pH, ionic strength of the soil pore solution and presence of dissolved salts in soils. For determining the CEC of soils considered in this study, the guidelines presented in Indian Standard (IS 2720, Part XXIV-1976) were followed.

For this purpose, the sample was treated with hydrogen peroxide (H_2O_2), laboratory reagent grade and boiled thoroughly for 1 hour to eliminate the organic content matter present in the soil. The treated sample was oven dried, and 5 g of the representative soil samples was mixed with 50 ml of 1N sodium acetate, (CH_3COONa) of pH 5 solution and it is incubated in a water bath at 100 °C for 30 -

minutes, with recurrent stirring, and later the samples was centrifuged at 1000 g for 15 minutes. The supernatant liquid was decanted and discarded; filtrate was again washed with 50 ml of 1N Sodium acetate (CH_3COONa) solution and centrifuged. This procedure was repeated for three times, to ensure exchange of all cations present in the soils by sodium ion, (Na^+). Further, this sample was washed with 1N calcium chloride, ($CaCl_2$). This solution, was incubated and centrifuged, similar to sodium acetate of pH 5. The whole process was repeated thrice, to ensure exchange of all sodium ions, (Na^+) that were adsorbed on the geo-material during the previous step, by calcium ions (Ca^{2+}). This sample was again washed with 50 ml 1N sodium acetate (CH_3COONa) solution of pH 7 and was again incubated and centrifuged, and this operation was also performed thrice. The resulting supernatant was collected in a 250 ml volumetric flask, and concentration of calcium ion, Ca^{2+} present in the solution was determined using volumetric analysis. The CEC represented as meq. /100 g of the material was computed using the equation 3.1.

$$\text{CEC (meq/100g)} = \frac{\text{Cation Concentration} * 100 * \text{Vol of Extract (ml)}}{\text{Equivalant weight of cation X 1000 X wt of sample (g)}} \qquad 3.1$$

Table 3.1. Properties of selected soils

Properties	Red Earth	BC Soil
Specific Gravity	2.64	2.76
Gravel (%)	6	0
Sand (%)	27	30
Silt (%)	41	39
Clay (%)	26	31
Liquid limit (%)	38	61
Plastic limit (%)	18	21
Plasticity Index	20	40
Shrinkage limit	12.6	11.67
Soil Classification	CI	CH
Maximum dry density (g/cc)	1.8	1.68
Optimum moisture content (%)	19.7	12.6
Free Swell Index	5	90
Permeability (cm/s)	0.141×10^{-7}	0.505×10^{-7}
Cation Exchange Capacity (meq/100 gm)	42	96
Minerals Present	Quartz Kaolinite Hematite	Quartz Montmorillonite Microcline

3.3.8 Chemical Composition of soils:

The selected soils are assessed for their chemical and mineralogical characteristics by using XRF and XRD. The chemical composition of CH and CI soils are assessed by using XRF are presented in Table 3.2. From table 3.2, it is observed that, oxides of aluminium, silica, iron, magnesium, calcium and titanium are major compounds in both the soils; whereas the compounds of sodium, potassium, phosphorous, manganese and sulphur are in small quantities. The mineralogical characteristics are assessed using XRD test and the results from the test are presented in Fig 3.1.

Table 3.2. Chemical Composition of Soils

Soil /Composition	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	SO_3
CH Soil	43.6	22.8	14.7	7.3	7.5	0.225	0.63	1.71	0.28	0.47	0.14
CI Soil	36.6	22.9	26.8	4.6	4.5	0.079	0.74	2.0	0.22	0.75	0.125

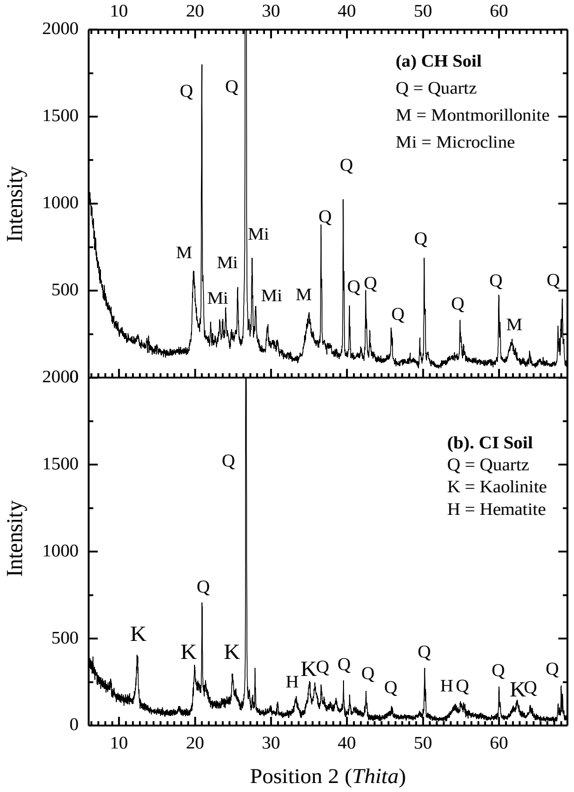


Fig 3.1. XRD Patterns of (a) CH Soil and (b) CI Soil

From the Fig 3.1, it is observed that, Montmorillonite is observed to major mineral in CH soil and Kaolinite is observed to be major mineral in CI soil

3.4 Chemical Composition of model contaminants used

Based on the leachate chemical composition experiment analysis, out of all the heavy metals observed in the Warangal Municipal Solid Waste leachate, there is a maximum concentration value of about 30 ppm in case of Nickel. Hence, in the present experimentation, for the sake of uniformity and by considering the possibility of having such a concentration in the future for the other metals, a maximum concentration value for all the heavy metals considered is maintained as 30ppm.

The synthetic leachate (handling actual leachate is very difficult because of microbial activity in test chambers) resembling the chemical composition of Warangal landfill leachate was prepared from various heavy metal solutions such as Lead, Nickel, and Cadmium in their nitrate form and chromium in its potassium form. The heavy metal salts used and their corresponding chemical formula are given in table 3.3.

Table 3.3 Chemical Composition of Warangal Municipal Solid waste Leachate

Element	Concentration (mg/l)	Element	Concentration (mg/l)
C O D	50800	Mn	67
Cl	500	NH^{4+}	48
So_2^{-4}	72	Ni	30
Na	368	Cd	1.1
K	17	Cr	22
Ca	876	Pb	0.7
Mg	318	pH	6

3.4.1 Preparation of synthetic Heavy metal solution:

Four different heavy metals namely Lead (Pb^{2+}), Nickel (Ni^{2+}), Cadmium (Cd^{2+}) and Chromium (Cr^{6+}) were considered for the present study. The maximum concentration of heavy metals in Warangal municipal solid waste leachate is 30 mg/L. So, for the present experimentation, maximum concentration for all heavy metals maintained as 30 mg/L. For each heavy metal, stock solution of 1000 mg/L was prepared from where the required concentrations of synthetic heavy metal solutions were prepared by using equation 3.2.

$$\text{Amount of salt required (in grams.)} = \frac{\text{Molar mass of the required compound }(\frac{\text{g}}{\text{mole}})}{\text{Atomic mass of the metal} \times \text{purity}} \quad (3.2)$$

Lead (Pb^{2+}):

Solid compound Lead Nitrate {$Pb(NO_3)_2$} was used to prepare 1000 mg/L lead solution. 1.5984 gm of Lead salt was taken after measuring in a highly sensitive weighing machine and diluted with de-ionized water in a 1000 ml capacity graduated bottle.

Nickel (Ni^{2+}):

1000 mg/L of Nickel (II) stock solution was prepared from solid inorganic compound Nickel Nitrate {$Ni(NO_3)_2$} by following the same procedure stated for Lead (II). 4.953 gm of Nickel Nitrate salt was diluted with de-ionized water and filled it up to 1000 ml mark in a graduated reagent bottle.

Cadmium (Cd^{2+}):

2.3285 gm of solid was taken from Cadmium Nitrite {$Cd(NO_3)_2$} to prepare 1000 mg/L Cadmium stock solution. Percentage purity (around 98%) labelled in Cadmium Nitrite bottle was taken into the calculation at the time of estimating solid required.

Chromium (Cr^{6+}):

Potassium Dichromate ($K_2Cr_2O_7$) was utilized for formulating 1000 mg/l of Chromium (VI). 2.829 gm of Potassium Dichromate was diluted with de-ionized water in a graduated reagent bottle of 1000 ml capacity. The heavy metal solution was prepared by mixing the heavy metal salt with double deionised water. Initially, the stock solution of 1000 mg/L concentration of metal was prepared by dissolving required amount of metal salt in 1000 ml of double deionised water by using equation 3.3.

$$C_1 \times V_1 = C_2 \times V_2 \qquad (3.3)$$

Where:

C_1= Concentration of metal in stock solution (1000 mg/L)

V_1= Volume of stock solution required (unknown)

C_2= Concentration required (10, 15, 20, 25 and 30 mg/L)

V_2= Volume of solution required for M_2 concentration of metal.

Ethylene diamine tetra acetic acid (EDTA):

EDTA considered in the study as an organic contaminant. This is mainly because, all detergents and soaps are containing the EDTA chemical. When it disposed in landfill, the EDTA will leached out and causing the environmental related problems. The concentrations of EDTA (0.1 mM, 0.5 mM and 1.0 mM) were considered and this concentration varies from 14 – 1120 micro gram per litre (Abollino et al, (2006)., Oviedo et al (2003).

3.5 Sorption Characteristics of soil:

The sorption behaviour of soils mainly depend on their physical, chemical, mineralogical properties (Harter, 1983; Gray *et al.*, 1986; Yong and Phadungchewit, 1993; Gao *et al.*, 1997; Chotpantarata, et al 2011). Considering these into consideration, batch sorption experiments were conducted over a wide range of pH values such as 2, 4, 6 and 7 at a temperature of, 27±1ºC. The detailed methodology adopted for batch sorption was explained in the following sections.

The soils passing through 2 mm sieve were used to perform batch sorption experiments (Grolimund *et al.*, 1995). To achieve *L*/*S* value of 20, the sample weighing 5 gm was mixed with 100 ml of the corresponding heavy metal solution with the different initial concentration in air tight polypropylene sample bottles (Gao *et al.*, 1997; ASTM D4646, 2004).

The obtained sorption capacity soils, the initial concentration of the solution (C_i) and equilibrium solution concentration (C_e), i.e., the concentration of heavy metal present in the solution after equilibration time. Later, the mass of the heavy metal adsorbed on the soils, q_e (mg/g) and Percentage adsorption, was computed by using Equation 3.4 and 3.5 respectively.

$$q_e = \{(C_i - C_e) / M \}*V \qquad (3.4)$$

$$R (\%) = \{(C_i - C_e) / C_i\}*100 \qquad (3.5)$$

3.5.1 Parameters considered for study

Effect of pH:

Adsorption of various heavy metals by the soils are dependent on pH, since majority of the heavy metals may exhibit the precipitate mechanism by forming compounds such as hydroxides, sulfates, and chlorates (Farrah and Pickering, 1979). The precipitate mechanism is prevails mostly when the pH value is more than 7 for cations. In case of anions the precipitation is prevails when pH is less than 7. Further, the ability of the soils to adsorb heavy metals also depends on its buffer capacity. Hence, this is an important parameter to be considered while evaluating the suitability of soils as liner material (Stumm, 1992; Farrah and Pickering, 1979). With this in view, attempts were made in this study to demonstrate the influence of pH (over range of 2 to 7) on sorption characteristics for a given *L/S* of 20.

Effect of Composite Heavy Metal Solution:

The municipal and industrial wastes from the urban area may contain several heavy metals in it. In such a scenario, various heavy metals present in the solute result in competition. Given the above facts, the present study evaluated the competition and selectivity order of the heavy metals present in the composite solution. For this purpose, the individually prepared single heavy metal solutions were mixed to form the composite heavy metal solution of 10 mg/l to 30 mg/l. Further, the composite heavy metal solution pH is adjusted using NaOH and 0.1M HNO_3, and sorption experiments were conducted corresponding to *L/S* of 20, using the composite solution.

The procedure for sorption test is as explained below.

1. 200 ml of heavy metal solution with a particular initial concentration (say 10, 15, 20, 25 and 30 mg/L) was taken in a 250 ml conical flask as shown in Fig. 3.2

Fig. 3.2 Conical Flask with 250 ml of Heavy Metal Solution

2. 5g of air-dried soil passing through 425µ sieve was taken and mixed with the solution in conical flask to maintain a liquid to solid ratio of 20.
3. pH of the soil solution matrix was then stabilized using a pH meter to a required value (2, 4, 6 and 7) by adding 0.1 N HNO_3 or 0.1N NaOH solutions as shown in Fig. 3.3.

Fig. 3.3 pH stabilization of soil solution matrix

4. Conical flask was closed with tin foil and kept in an orbital shaker which gently agitates the soil solution matrix continuously for 24±0.5 h at 29±2 r/min at room temperature as shown in Fig. 3.4

Fig. 3.4 Soil solution matrix under agitation in Orbital Incubator Shaker

5. After 24 hours, the conical flask was taken out from the orbital shaker, opened and the solution was filtered by Whatman filter paper of grade 42 (ASTM D 4646 -3) having a pore siaze of 2.5µm as shown in Fig. 3.5

Fig. 3.5 Filtration of Sample using Whatman filter paper no.42

6. Similar procedure was followed for both soils (CH and CI) and all four heavy metals (Pb, Ni, Cd and Cr) with different initial concentrations (10, 15, 20, 25 and 30 mg/L).

7. The clear solution which is obtained from the soil – solution matrix after filtration was chemically analyzed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) as shown in Fig.3.6.

Fig. 3.6 ICP-OES instrument for checking metal concentration in the effluent

3.6 Column Flow experiments:

Unlike batch sorption studies, column flow studies are more reliable to be adopted in the laboratory because of its capability to simulate the field arrangement of landfill liner and to sort out the kinetic behaviour of heavy toxic metals when passing through liner under field conditions. The column studies are conducted based on the results obtained from the batch sorption experiments. The column studies are very helpful to study the contaminant transport behaviour through the soil media. For that, different parameters needed to be considered for proper understand the transport of heavy metals under (i) pH of the influent solution, (ii) the presence of organic chemical and (iii) concentration of the metal solution. To consider all the effects on the transport of heavy metals and finally come up with a strong conclusion with reasonable explanations, firstly it is necessary to understand the consequences of every single parameter separately. Several types of research works have been carried out by taking single or multiple parameters to comprehend the soil-metal interactions affecting the breakthrough characteristics of soil against different heavy metals. Parameters obtained from the breakthrough curves help to foresee the effectiveness of the locally available soil as a liner material.

Several approaches have been made for simulating the field conditions into an experimental model. Different approaches showed different outcomes, but ultimately some common points were drawn from those outcomes by the researchers to accommodate it into a single frame of analysis. The effect of organic chemical complexation behaviour by the presence of other electrolytes needs special investigations in the form of extensive research works as in maximum cases where more than one type of contaminant in the landfill leachate along with organic chemical. Batch sorption tests in association with column leaching test can give a quite clear idea about how the adsorption and migration behaviour of soils are influenced by other contaminant with different pH values of influent.

3.6.1 Column Specifications:

Hollow plexi-glass cylinders of specific dimensions (14 cm Height, 6.7 cm inner diameter with wall thickness of 0.5 cm (Shakelford C D., 1991)) were utilized for the experimental purpose. The experimental setup used for these studies is shown in Fig 3.7. Seven numbers of cylinders were engaged to conduct the experiments simultaneously in the laboratory. The small soil sample thickness of 2 cm is used primarily to reduce the time required for soaking the samples prior to diffusion testing. The technical information regarding this is observed from the research article by Shackelford C D., 1991 and Lim and Aris, 2014. The soil is compacted to achieve the maximum dry density of soil using standard proctor compaction method. Two circular caps made of same material as of cylinder were used to cover bottom and above portions of hollow column. Each cap was having a central hole where notch was fixed. The prepared synthetic heavy metal solution was poured from the above notch, and after passing through the soil, effluents were emitting out from the bottom notch. Conical flasks of 250 ml capacity were placed under the columns to collect effluents for varying intervals of time.

3.6.2 Synthetic solution Specifications:

An initial concentration of 30 mg/L was chosen as an influent solution mainly because, the maximum heavy metal concentration was observed in the landfill leachate is 30 mg/L.

3.6.3 Experimental Methodology for Column study:

The flow procedure adopted in the flow process of contaminants is explained below.

1. The soil was compacted to 2 cm thick at its OMC and MDD using light compaction technique inside the plex-iglass cylinder (Lim and Aris, 2014).
2. Before placing the soil, silicon grease was applied around the inner surface of the cylinder to ensure that solution would not leak out from the space between the soil and inner perimeter of the cylinder. Whitman Filter paper grade 42 was placed below and above the soil column to avoid loss of soil particles due to the flow of liquid through the soil.

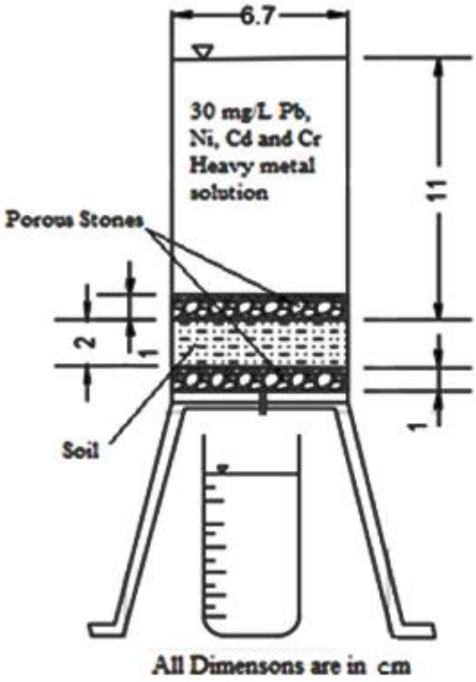


Fig 3.7 Column experimental setup (Shakelford C D., 1991)

3. After placing filter paper above the compacted soil column, a porous stone made of Teflon having 6.7 cm diameter and 2 cm thickness was positioned above it for distribution of liquid throughout the soil sample evenly so that every portion of the sample could be able to participate in adsorption of heavy metals.
4. The rest vacant portion of the hollow cylinder after placing soil column was filled up with the heavy metal solution of known concentration. pH of the metal solution was then adjusted to 2 and 7 by adding 0.1 N HNO_3 or 0.1N NaOH solutions as shown in Fig 3.8.
5. The hydraulic gradient adopted in the experiment was around 6 based on the hydraulic conductivity of the soil obtained from variable head permeability test (ASTM D5856-15) as shown in Fig. 3.9. Head above the soil column was maintained during the whole period of experiments by pouring the required single, or multi-metal solution based on the head drop observed periodically

neglecting the minor variations in the initial metal concentration of 30 mg/L. The velocity of leachate through the soil is maintained as 3.5 x 10^{-12} cm/sec.

Fig 3.8 pH stabilization of influent heavy metal solution

6. Effluents coming out from the column were collected at varying intervals of time and finally made it available for checking the metal concentration by the using of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) instrument shown in Fig 3.5.

Fig 3.9 Column Experiment with heavy metal as influent solution

7. The quantity of flow collected at varying intervals of time was used to plot breakthrough curves. This can be adopted to avoid the problem regarding with the acquirement of readings in the specified time. Number of pore

volumes (P.V) can be calculated as the ratio of cumulative volume of effluent to the volume of voids of the soils as given in equation 3.6.

$$\text{Number of pore volumes (P.V)} = V_T/V_V \qquad (3.6)$$

3.6.4 Calculations of Diffusion Coefficients:

The concentration of each sample collected at different time intervals was obtained. By knowing the effluent concentration, seepage velocity, thickness of the soil sample and the time for achieving 50% breakthrough (t_{50}) the diffusion coefficient (D) was calculated for each case by using the advection-diffusion equation as shown in the equation 3.7 (Mohamed and Anetia., 1998., Shackelford 1991).

$$\frac{C(x,t)}{Co} = \frac{1}{2}\left[erfc\left(\frac{x-vt}{2\sqrt{Dt}}\right) + \exp\left(\frac{vx}{D}\right) * erfc\left(\frac{x+vt}{2\sqrt{Dt}}\right)\right] \qquad (3.7)$$

In the above equation, ‘v.' refers to the seepage velocity,‘t’ referees to the time to achieve 50% breakthrough of contaminant through column and ‘x’ referrers to the thickness of the soil medium. The expressions that were sequentially used for calculating seepage velocity. For 50% breakthrough, C(x, t)/Co will be 0.5 where C(x, t) refers to the effluent concentration after a specific time‘t’, x = thickness of the sample taken as 2 cm and C_0 denotes the initial concentration of the synthetic metal solution (30 mg/L for all case).

The chart given below in Table 3.4 provides the values of complementary error function (erfc). This value was used for calculating the effective diffusion co-efficient from the above-mentioned advection-diffusion equation which contains both error complementary function (erfc) and exponential function (exp). The argument ‘ξ’ given in the chart is equal to the total term mentioned under erfc functions which are expressed as $\xi = \frac{x-vt}{2\sqrt{Dt}}$ (associated with the first term of erfc function) and $\xi = \frac{x+vt}{2\sqrt{Dt}}$ (associated with the second term in the above-mentioned equation)

Table 3.4 Complementary error function (erfc (ξ)) (Mohamed and Anetia 1998)

ξ	erf(ξ)	erfc (ξ)	ξ	erf(ξ)	erfc (ξ)
0	0	1	1.1	0.880205	0.119795
0.05	0.056372	0.943628	1.2	0.910314	0.089686
0.01	0.112463	0.887537	1.3	0.934008	0.065992
0.15	0.167996	0.832004	1.4	0.952285	0.047715
0.2	0.222703	0.777297	1.5	0.966105	0.033895
0.25	0.276326	0.723674	1.6	0.976348	0.023652
0.3	0.328627	0.671373	1.7	0.98379	0.01621
0.35	0.379382	0.620618	1.8	0.989091	0.010909
0.4	0.428392	0.571608	1.9	0.99297	0.00721
0.45	0.475482	0.524518	2	0.995322	0.004678
0.5	0.5205	0.4795	2.1	0.997021	0.002979
0.55	0.563323	0.436677	2.2	0.998137	0.001863
0.6	0.603856	0.396144	2.3	0.998857	0.001143
0.65	0.642029	0.357971	2.4	0.999593	0.000407
0.7	0.677801	0.322199	2.5	0.999764	0.000236
0.75	0.711156	0.288844	2.6	0.999866	0.000134
0.8	0.742101	0.257899	2.7	0.999866	0.000134
0.85	0.770668	0.229332	2.8	0.999925	0.000075
0.9	0.796908	0.203092	2.9	0.999959	0.00041
0.95	0.820891	0.179109	3	0.999978	0.000022
0.1	0.842701	0.157299			

Based on the available data, the argument 'ξ' value is calculated and the value of erf (ξ) and erfc (ξ) were obtained. Using the value of erfc (ξ) and other parameters the value of effective diffusion coefficient was calculated.

3.7 Crack Intensity Factor, Permeability Ratio and Breakthrough of Cracked Soils:

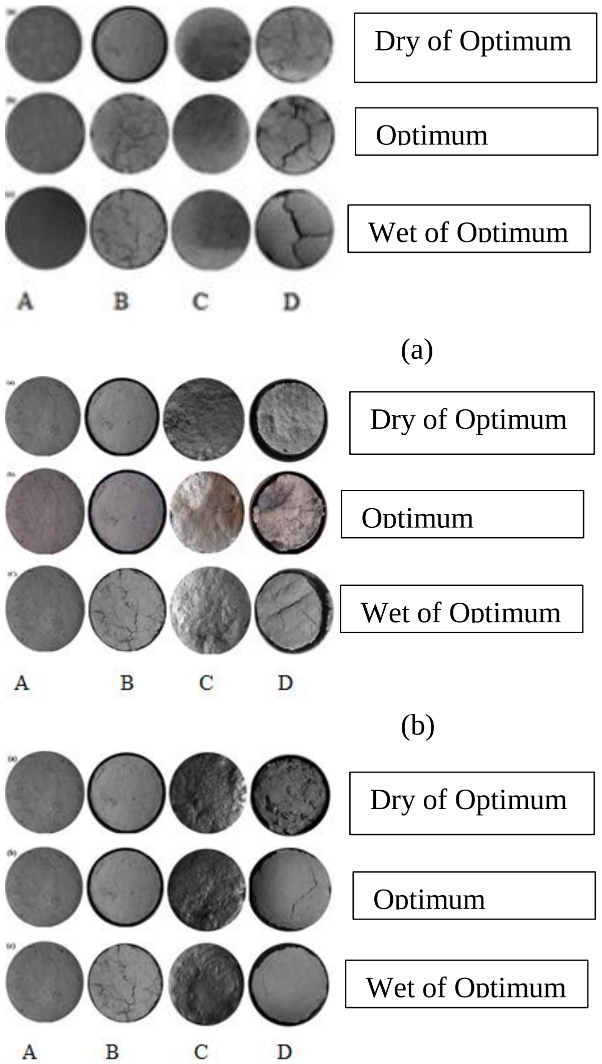
3.7.1Crack Intensity Factor

The crack intensity factor (CIF) was introduced (Mi, H 1995 and Miller et al., 1998; Herve et al 2009) as a descriptor for determining the extent of surface cracking. The soil samples were tested for the crack intensity factor and its hydraulic conductivity by using deionized water and synthetic heavy metal solutions under different pH conditions of pH 2 and 7. The soils were compacted at three different water contents (the dry side of the optimum, optimum and wet side of optimum). Then the soil samples were dried in the oven at a temperature of 65 degrees centigrade (Zhou and Rowe 2005), and the surface images were captured for both CH and CI soils with the help of a high-resolution camera during the process of wetting and drying, and these images were converted to gray scale and presented in Fig 3.10 and 3.11.

These two Figures show the images of compacted CH and CI soil at water contents of ± 2 % of optimum (dry of optimum, optimum and wet of optimum moisture contents). After compacting at three different water contents, the samples were placed in a humidity chamber with a relative humidity of 10% to simulate Warangal weather conditions, especially in summer. Image A shows the soil specimen immediately after compaction and B shows the image of the soil sample in dried-up condition at 65^{o}C while image C represents the image of the dried soil sample which was saturated with either water or chemical solution. After the stage of saturation, the soil sample was dried up by placing it in the humidity chamber for 24 hours. The image named as D shows the condition of the dried soil after the wetting – drying cycle.

All the images were converted to grayscale and were uploaded into crack intensity factor program developed at our institute of NIT Warangal using Java software. The results from this program are displayed regarding the number of dark and bright pixels, where the dark pixels indicate the uncracked portion of the soil while the bright ones indicate cracked portion on the soil surface. The cracked intensity factor was calculated using the equation 3.8.

$$\text{Crack Intensity Factor (CIF)} = \frac{\text{Total Number of Bright Pixels}}{\text{Total Number of Pixels}}\ X\ 100 \qquad (3.8)$$

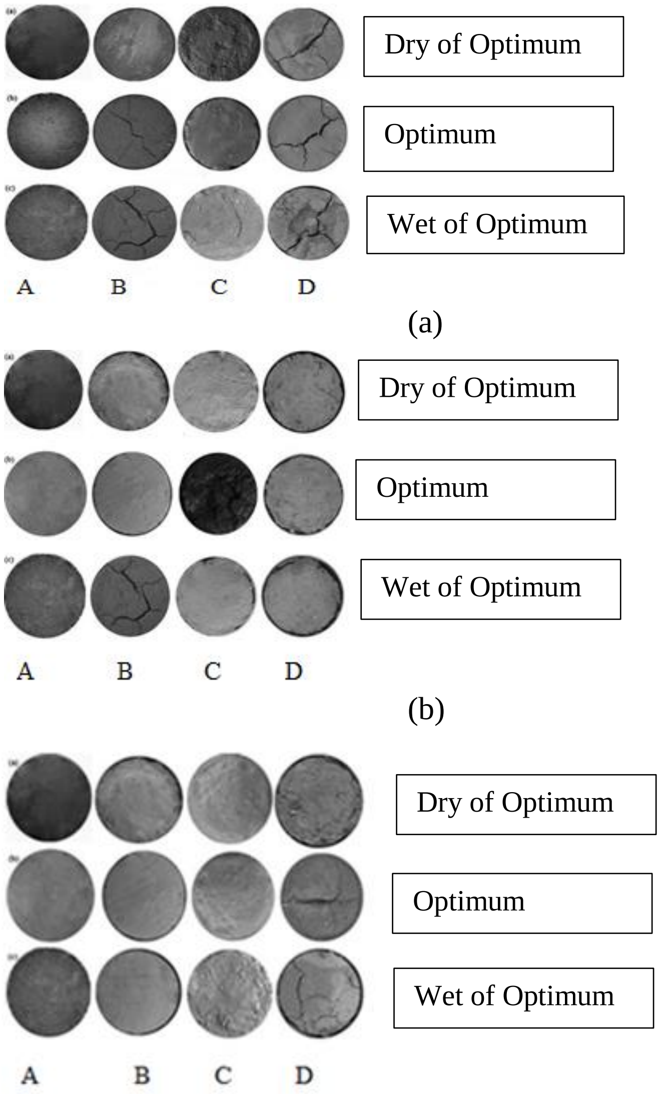


(a)

(b)

(c)

Fig 3.10. Cracked Images of CH soil: (a) CH soil with water, (b) CH soil with MHMS pH 2, (c) CH soil with MHMS pH 7



(a)

(b)

(c)

Fig 3.11. Cracked Images of CI soil: (a) CI soil with water, (b) CI soil with MHMS pH 2, (c) CI soil with MHMS pH 7

3.7.2 Permeability ratio:

In the present study, experiments were conducted to understand the influence of contaminants on the permeability of soils before and after desiccation. For this purpose, laboratory permeability test was conducted by using fixed wall permeameter as per IS code of practice IS 2720 – 24, 2010. To prevent side wall leakage, silicon grease applied to side walls of the mould.

3.7.3 Column Studies on desiccated soil:

Column tests were conducted to determine the transport parameters of the CH and CI soil. The soil samples were prepared by adding deionized water to the air dried soils to achieve water content 2% wetter than the optimum water content in order to obtain the lowest hydraulic conductivity of soil sample (Benson et al 1999; Daniel, 1994). The soil was cured in plastic bags for 24 hours. Substantially, the samples were compacted in accordance with an adaptation of the standard proctor compaction method using a mould of 6.74cm diameter and 2 cm height. The sample was permeated initially with deionized water in order to achieve the first exposure effect and hence reduce the hydraulic conductivity of the samples (Shakelfold, 1994; Quaranta et al., 1996; Gelason et al., 1997). The flow was induced by maintaining the constant head throughout the experiment. The effluent was collected periodically and the volume of effluent was used to calculate the hydraulic conductivity of the soil sample using the constant head test method (ASTM D 5084). After terminating the permeation with the deionized water, heavy metal solutions were introduced and then heavy metal effluents concentration were periodically analysed by using ICP – OES.

CHAPTER – 4
RESULTS AND DISCUSSIONS

4. 1 General:

This chapter deals with the results obtained from the experiments like sorption characteristics, diffusion parameters and cracking patterns of the selected two soils, whose details are given in previous chapter.

4.2 Sorption Capacity of Soils:

The percentage adsorption of heavy metals by the soils and sorption capacity of soils to retain various heavy metals are calculated based on the methodology adopted and explain in the previous chapter.

4. 2. 1 Lead adsorption capacity:

The percentage adsorption of lead metal ion by the CH soil under different pH (2, 4, 6 and 7) values at 10mg/L initial concentration of the solution and for varying concentrations of EDTA is shown in Fig. 4.1

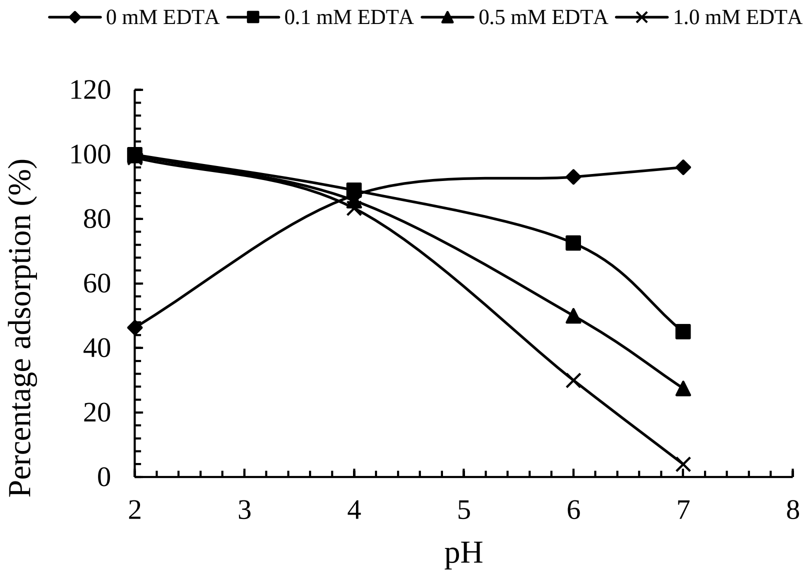


Fig. 4.1. Percentage adsorption of Lead by CH soil with varying concentrations of EDTA under different pH values

It can be observed from this figure that, for the condition of no EDTA the percentage adsorption of lead by the CH soil increased with increase in the pH of the soil solution (Maliou et al 1992; Chulsung et al 2003; Grcman et al 2001). The rate of increase in the percentage adsorption is more from pH 2 to 4 and later; this rate is less from pH 4 to 7. At pH 2, the percentage adsorption is observed to be 46% whereas it is increased to 87% at pH 4. From pH 4 to pH 7 the percentage adsorption is observed to increase only by 8%. With increase in pH from 4 to 7, there is a slow decrease in the adsorption of metal ions. At pH ≤ 2, Hydrogen (H^+) ions may be competing with Pb^{2+} for adsorption onto the active sites, resulting in a decrease in adsorption capacity and percentage adsorption. As pH increase more than 6, the surface charge on the soil remains negative; this is also helpful for adsorption due to clay surface attraction. Contradictory to the above observation, the Percentage adsorption is found to decrease with increase in pH from 2 to 7 with the presence of EDTA in solution. The percentage adsorption decreased from 99% to 45% for 0.1mM EDTA, whereas it decreased from 99% to 27% for 0.5mM EDTA, while it decreased from 99% to 4% for 1mM EDTA with increase in pH from 2 to 7. The decrease in the percentage adsorption is mainly because of the ligand type adsorption, i.e., adsorption of heavy metal on the surface of the soil due to the formation of a metal complex with EDTA. This EDTA ligand may form a bridge between the clay surface and metal ion as stated in equation 4.1. Adsorption through a ligand bridge classified as ‘ligand like’ occurs probably at low pH condition.

$$S - OH + M\,e^{n} + H_{m}\,Lig \rightarrow S - Lig - M\,e^{(n-m-1)+} + (m+1)\,H^{+} + H_{2}O \quad (4.1)$$

Adsorption of metal ions does not only depend on the pH of the soil solution but also on the concentration of heavy metals present in soil solution. In order to consider the initial concentration effect on heavy metals adsorption by the soil, batch sorption experiments were conducted with varying heavy metal concentration from 10 mg/L to 30 mg/L. The Fig 4.2 shows the influence of initial concentration of lead metal ion soil solution at pH 7 on the percentage adsorption of CH soil with a variation in the concentration of EDTA.

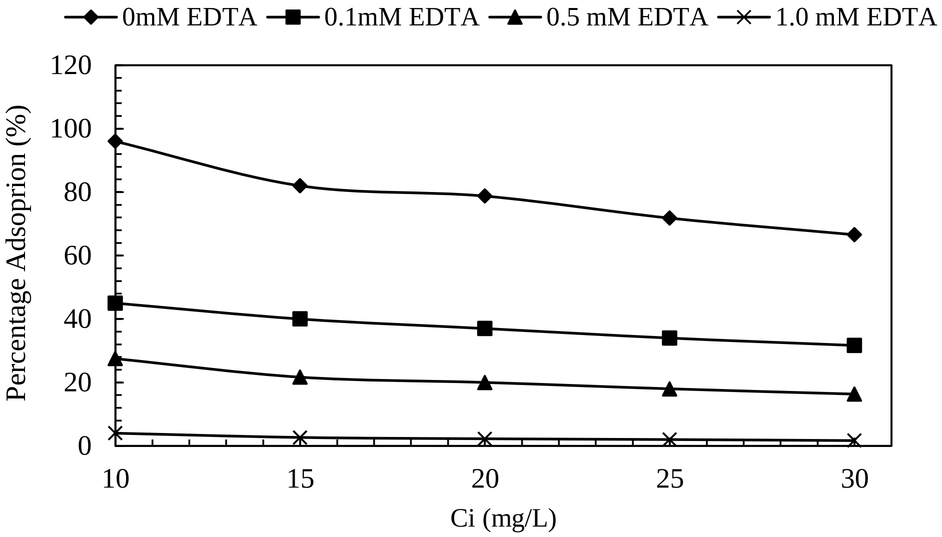


Fig 4.2. Variation of percentage adsorption of lead by CH soil with initial concentration (Ci) at pH 7

From this figure it is observed that, with increase in initial concentration from 10 mg/L to 30 mg/L, the percentage adsorption is decreased from 96% to 45% without EDTA present. Even with the presence of EDTA, the percentage adsorption decreased. The decrease is observed to be 45 % to 31 % for 0.1mM EDTA, 27.5% to 16.3% for 0.5mM EDTA and 4 % to 1.6 % for 1mM of EDTA. This is mainly because, with increase in the concentration of heavy metal in the soil solution, there is shortage of adsorption sites present on the surface of the soil. From the above figure it is also observed that, the percentage adsorption is decreased with increase in the concentration of EDTA. This is due to the formation of more metal EDTA complex.

The lead metal ion adsorbed by the CI soil with varying pH of the solution is presented in the Fig 4.3. From this figure, it is observed that, the percentage adsorption is increasing with increase in pH of the solution (Cynthia and Raymond 2002).

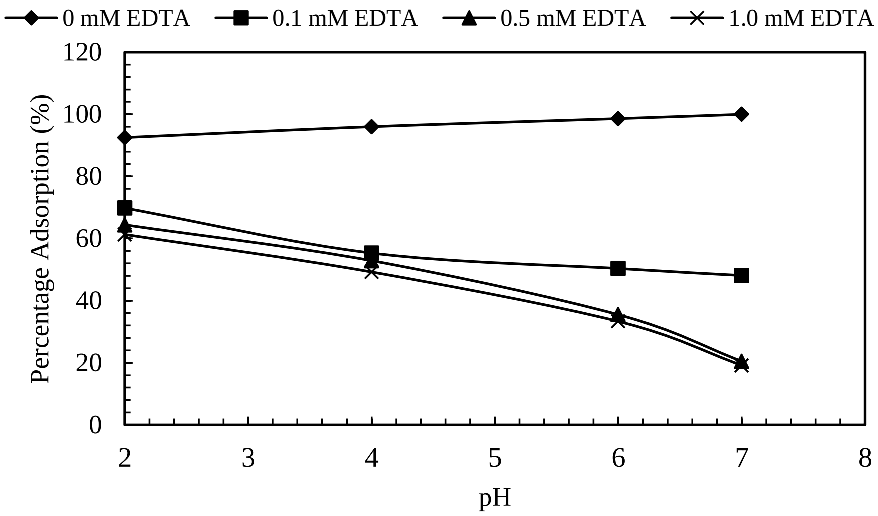


Fig. 4.3 Percentage adsorption of Lead by CI soil with varying concentrations of EDTA under different pH values

The percentage adsorption by CI is more when compared to CH soil this is due to the fact that, the formation Pb – Fe complex without EDTA in the solution. With the presence of EDTA in the solution, the percentage adsorption is significantly reduced. The percentage adsorption is observed to be decreased from 69% to 48% for 0.1mM EDTA, 64% to 20% for 0.5mM and 61% to 19% for 1.0mM EDTA with increase in pH of the solution from pH 2 to 7. This may be due the formation of $PbEDTA^{2-}$ complex which is repulsed by the surface of the soil.

Influence of initial concentration of soil solution (Ci) varying from 10 mg/L to 30 mg/L on the percentage adsorption of Lead metal ion at pH 7 with varying concentration of EDTA by CI soil is shown in Fig 4.4. From this figure it is observed that, with increase in initial concentration from 10 mg/L to 30 mg/L, the percentage adsorption is decreased from 99.98% to 99.43% without EDTA present. Even with the presence of EDTA, the percentage adsorption decreased.

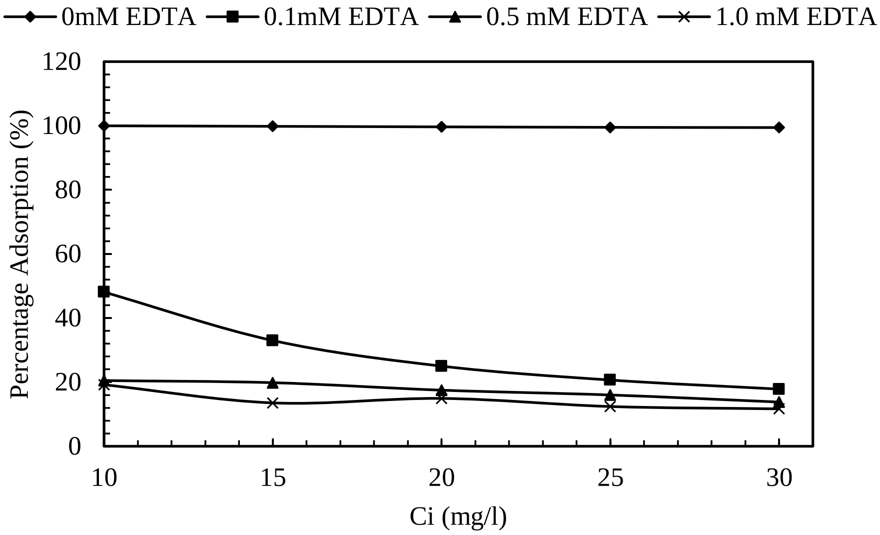


Fig. 4.4 Variation of percentage adsorption of lead by CI soil with initial concentration (Ci) at pH 7

The decrease is observed to be 48 % to 17.83 % for 0.1mM EDTA, 20.5% to 13.80% for 0.5mM EDTA and 19.20 % to 11.6 % for 1mM of EDTA. This is mainly due to the formation of EDTA complex.

4.2.1.1 Adsorption Isotherms

The sorption isotherms represent the soil – heavy metal interaction in terms of their sorption characteristics which are assessed using the results obtained from batch sorption experiments. For this purpose, the amount of heavy metal adsorbed by the soils, q_e, and the final equilibrium concentration of the solute C_e, are used as model parameters. With this in view, the sorption isotherms are modelled for selected geo-materials. The sorption parameters such as K, K_f, n, K_L and q_m along with regression coefficient, R^2, for different isotherms are presented in Table 4.1.

Table 4.1. Adsorption isotherm coefficients values for CH and CI soils

[For different pH values with varying EDTA concentration and initial concentrations of Lead solution]

pH 2									
Material	EDTA Conc (milli Molar)	K_d	K_f	n	K_l	q_m	R^2		
							Linear	Freundlich	Langmuir
Black Cotton soil (CH)	0	0.0009	0.2916	7.9872	0.7806	0.0901	0.9369	0.8061	0.6601
	0.1	0.4890	0.7768	4.2699	80.9004	0.4399	0.9808	0.9566	0.8447
	0.5	0.3730	0.7464	3.4638	26.5554	0.4441	0.9738	0.9123	0.8217
	1	0.0165	0.5578	7.3801	15.3661	0.3251	0.9455	0.9469	0.8070
Red earth (CI)	0	0.0336	0.5027	2.6874	0.8883	0.4520	0.9261	0.9876	0.9509
	0.1	0.0146	0.3298	1.9810	0.1770	0.3899	0.9836	0.9815	0.9543
	0.5	0.0153	0.2968	1.6827	0.1001	0.4862	0.9904	0.9970	0.9952
	1	0.0150	0.2781	1.5873	0.0827	0.5025	0.9922	0.9926	0.9902
pH 7									
Material	EDTA Conc (milli Molar)	K_d	K_f	n	K_l	q_m	R^2		
							Linear	Freundlich	Langmuir
Black Cotton soil (CH)	0	0.0218	0.5230	4.4072	3.0428	0.3439	0.9553	0.9313	0.7993
	0.1	0.0066	0.2307	1.7479	0.0740	0.3082	0.9862	0.9987	0.9966
	0.5	0.0025	0.1857	2.0730	0.0892	0.1364	0.9866	0.9876	0.9635
	1	0.0001	0.0961	4.2735	0.2261	0.0113	0.8992	0.8616	0.7747
Red earth (CI)	0	2.2398	0.9063	4.2790	407.0179	0.4387	0.9850	0.9416	0.8216
	0.1	0.0005	0.3446	16.0000	1.6508	0.1065	0.9672	0.8847	0.7571
	0.5	0.0023	0.1493	1.6647	0.0404	0.1725	0.9186	0.9573	0.9827
	1	0.0018	0.1445	1.8345	0.0684	0.1023	0.9083	0.8864	0.8301

From this table 4.1, a comparison of regression coefficient is made, to find the best suitable isotherms for the geo-materials and it is found that both geo-materials (CH & CI soil) are following Freundlich isotherm. The isotherm model for CH soil at a pH value of 7 is shown in the Fig 4.5. From this figure, the distribution coefficient is observed to be 0.0961 L/g.

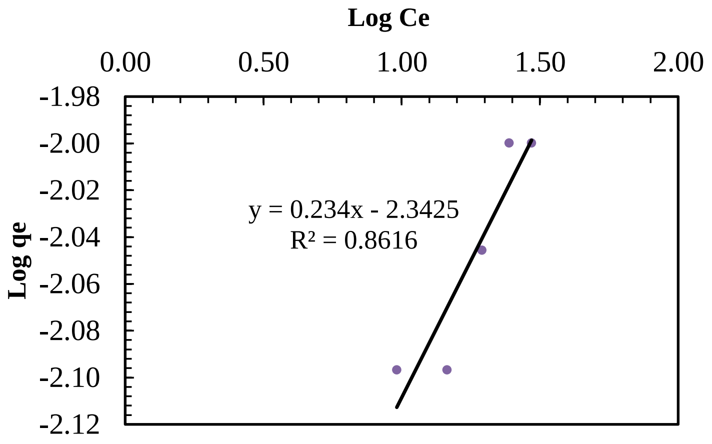


Fig. 4.5. Freundlich isotherm for adsorption of Lead on CH soil at pH 7

Hence adsorption of lead onto CI soil is also fitting into the Freundlich isotherm model, thus allowing multiple layers of adsorption to happen. The Freundlich isotherm modelled at a maximum pH value 7 is shown in Fig 4.6

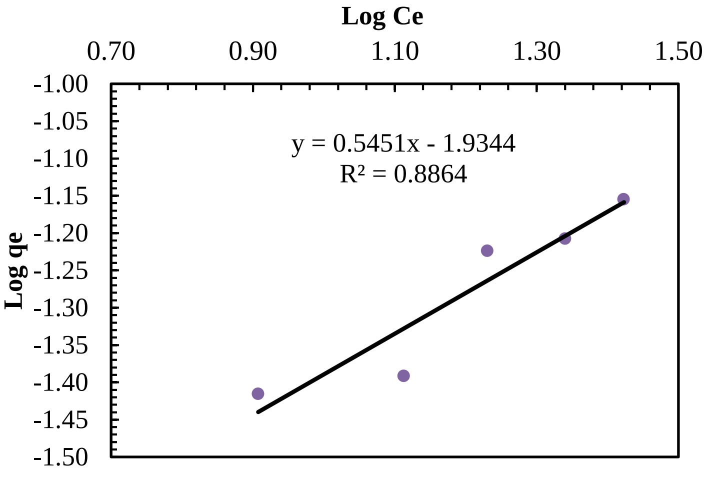


Fig. 4.6. Freundlich isotherm for adsorption of Lead on CI soil at pH 7

It can be observed from figure that, the value of the exponent (n) and Freundlich isotherm constant are calculated by comparing the best fit equation obtained, with the linearized equation form of Freundlich isotherm and value of the Freundlich isotherm constant obtained is $K_f = 0.1445$ L/g.

4.2.2 Nickel Adsorption capacity

The percentage adsorption of Nickel by CH soil with varying pH is shown in the Fig 4.7. From this figure, it is observed that, the Percentage adsorption in absence of EDTA is found to increase by 26% as pH is increasing from 2 to 7 (Marcio et al 2011). While the Percentage adsorption is found to be decreasing with the increase in pH under the influence of EDTA.

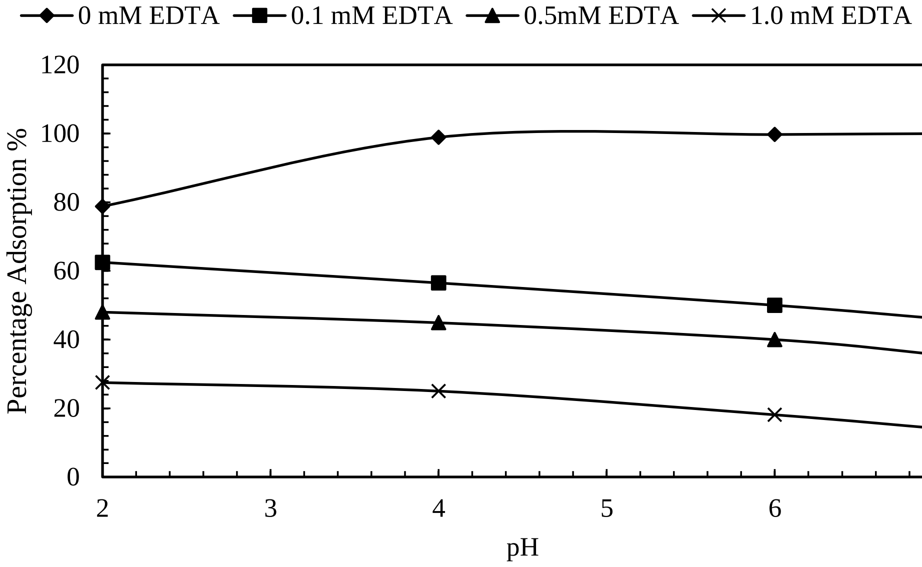


Fig. 4.7 Variation of percentage adsorption of Nickel by CH soil with varying concentration of EDTA under different pH values

With the presence of EDTA, Percentage adsorption decreased to 62.5% to 46% for 0.1mM EDTA, 48% to 35% for 0.5mM EDTA and 27.5% to 14% for 1mM EDTA with increase pH from 2 to 7. This is due to the fact that, the occurrence of Ni –

EDTA complex decreases Ni adsorption with increase in pH values and also formation of surface – ligand – metal ternary surface complex (Kent. 2008).

The influence of initial concentration on percentage adsorption of nickel metal ion by the CH soil is shown in the Fig 4.8. From this figure, it can be observed that the Percentage adsorption decreases with the increase in initial concentration. This behaviour is due to the insufficient adsorption of soil sites with increase in the metal ion concentration.

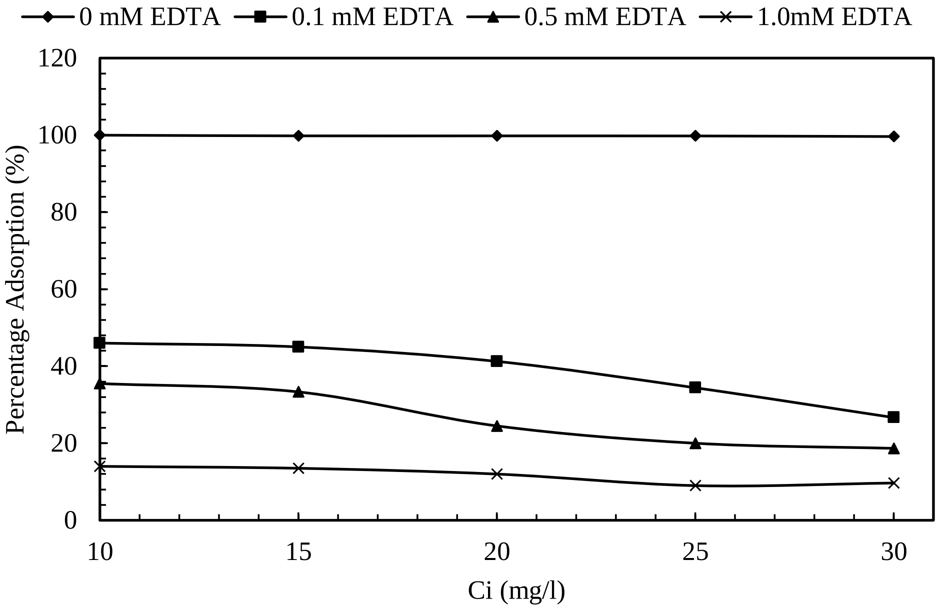


Fig. 4.8 Variation of percentage adsorption of Nickel by CH soil with initial concentration (Ci) at pH 7

The percentage adsorption is less significant for without EDTA in the solution. This is mainly due to the fact that, at pH > 6 the metal ions are adsorbed by the formation of the outer sphere complex on the surface of the soil. With the presence of EDTA in the solution, the Percentage adsorption decreases due to the formation of Ni $EDTA^{2-}$. The decrease in the adsorption is observed to be 46% to 26.6% for 0.1mM

EDTA, 35.5% to 18% for 0.5mM EDTA and 14 to 9.67% for 1.0 mM EDTA under the varying initial concentration 10 mg/L to 30 mg/L.

The variation in percentage adsorption of Nickel by CI soil with varying pH values is presented in the Fig 4.9.

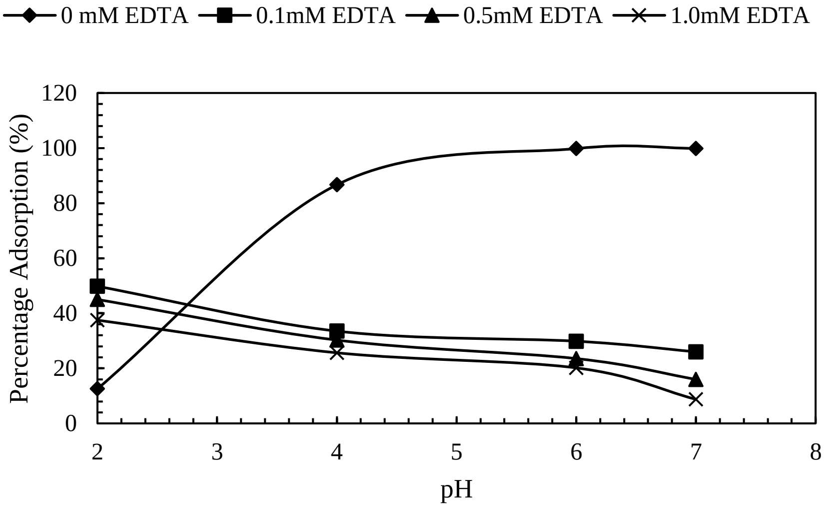


Fig. 4.9 Variation of Percentage adsorption of Nickel by CI soil with varying pH

From this figure, it is observed that, the percentage adsorption of Nickel by the CI soil is less when compared to the CH soil. This is due to the fact that, the presence of prior existence of Nickel traces in the CI soil in the form of sodium Nickel sulphate hydrate [$Na_2Ni(SO_4)_2.4H_2O$] the adsorption sites are less for Nickel metal ion and repulsive surface forces created by the H^+ ion result less adsorption of Nickel metal ion at pH 2.

As in the pH value of the solution increases from 2 to 7, the percentage adsorption is increased. This is due to the availability of OH^- surface functional at pH > 6 on the surface of the soil which leads to the increases the adsorption on the surface of the soil. For the condition of without EDTA with the increase in pH of the solution, the percentage adsorption is increases from 12% at pH 2 to 99% at pH 7. This can be due to the formation of metal hydroxide compounds at pH 7 when compared to pH 2. In the presence of EDTA the percentage adsorption pattern is totally different when there is no EDTA. In the presence of EDTA, the percentage adsorption is significantly reduced due to the formation of Metal EDTA complex. These metal EDTA complex will be more soluble with an increase in pH from 2 to 7 and as a result, the adsorption of metal ion is decreased with increase in the pH of the solution. The decrease increase in percentage adsorption is observed to be 49% to 26% for 0.1mM EDTA, 45% to 16% for 0.5mM EDTA and 37% to 8.75% for 1mM EDTA.

The influence of initial concentration on percentage adsorption of nickel metal ion by the CI soil is shown in the Fig 4.10.

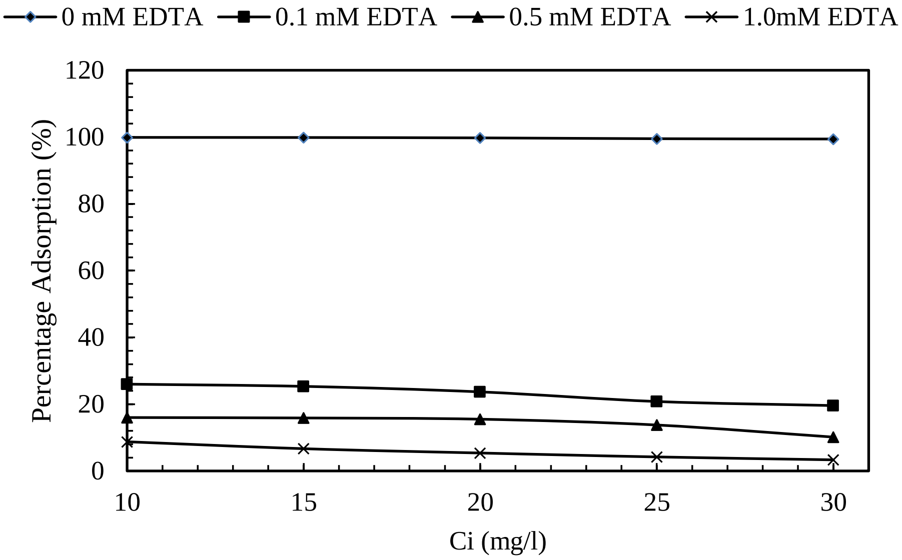


Fig. 4. 10 Variation of percentage adsorption of Nickel by CI soil with initial concentration (Ci) at pH 7

From this figure, it can be observed that there is a slight decrease in the Percentage adsorption with the increase in initial concentration from 10 to 30 mg/L. This behaviour is due to insufficient adsorption soil sites on the surface of the soil with increase in the concentration of heavy metal solution. With the presence of EDTA, the percentage decrease is observed to be 26 % to 19.5% for 0.1mM EDTA, 16% to 10.1% for 0.5mM EDTA and 8.7% to 3.3% for 1.0 mM EDTA under the varying initial concentration from 10 mg/L to 30 mg/L.

4.2.2.1 Adsorption Isotherms

The interaction of nickel solution with both the soils are modelled using he various sorption isotherms such as liner, Langmuir and Freundlich isotherm. The sorption parameters such as K, K_f, K_l, n and q_m along with the regression coefficient R^2 for different isotherms are presented in Table 4.2. From this table, a comparison of regression coefficient is made, to find the best suitable isotherms for both the soils and it is found that the adsorption of Nickel on CH and CI soil was found to follow Langmuir isotherm.

Table 4.2 Adsorption isotherm coefficients values for CH and CI soil

[For different pH values with varying EDTA concentration and initial concentrations of Nickel solution]

<table>
<tr><th colspan="10">pH 2</th></tr>
<tr><th rowspan="2">Material</th><th rowspan="2">EDTA Conc (milli Molar)</th><th rowspan="2">K_d</th><th rowspan="2">K_f</th><th rowspan="2">n</th><th rowspan="2">K_l</th><th rowspan="2">q_m</th><th colspan="3">R^2</th></tr>
<tr><th>Linear</th><th>Freundlich</th><th>Langmuir</th></tr>
<tr><td rowspan="4">Black Cotton soil (CH)</td><td>0</td><td>0.0029</td><td>0.4239</td><td>9.1996</td><td>2.1277</td><td>0.1880</td><td>0.8702</td><td>0.6649</td><td>0.4544</td></tr>
<tr><td>0.1</td><td>0.0248</td><td>0.2467</td><td>1.1975</td><td>0.0039</td><td>0.9670</td><td>0.9956</td><td>0.9896</td><td>0.9829</td></tr>
<tr><td>0.5</td><td>0.0127</td><td>0.2062</td><td>1.2657</td><td>0.0284</td><td>0.7463</td><td>0.9972</td><td>0.9979</td><td>0.9981</td></tr>
<tr><td>1</td><td>0.0040</td><td>0.1612</td><td>1.4603</td><td>0.0293</td><td>0.3194</td><td>0.9019</td><td>0.9550</td><td>0.9849</td></tr>
<tr><td rowspan="4">Red earth (CI)</td><td>0</td><td>0.0010</td><td>0.1204</td><td>2.0969</td><td>0.1134</td><td>0.0450</td><td>0.7889</td><td>0.6527</td><td>0.4845</td></tr>
<tr><td>0.1</td><td>0.0028</td><td>0.2440</td><td>2.7824</td><td>0.1672</td><td>0.1460</td><td>0.9028</td><td>0.8859</td><td>0.8778</td></tr>
<tr><td>0.5</td><td>0.0034</td><td>0.3002</td><td>3.1606</td><td>0.1898</td><td>0.2033</td><td>0.7431</td><td>0.7745</td><td>0.8312</td></tr>
<tr><td>1</td><td>0.0039</td><td>0.3004</td><td>2.9028</td><td>0.1671</td><td>0.2280</td><td>0.7984</td><td>0.8528</td><td>0.9118</td></tr>
<tr><th colspan="10">pH 7</th></tr>
<tr><th rowspan="2">Material</th><th rowspan="2">EDTA Conc (milli Molar)</th><th rowspan="2">K_d</th><th rowspan="2">K_f</th><th rowspan="2">n</th><th rowspan="2">K_l</th><th rowspan="2">q_m</th><th colspan="3">R^2</th></tr>
<tr><th>Linear</th><th>Freundlich</th><th>Langmuir</th></tr>
<tr><td rowspan="4">Black Cotton soil (CH)</td><td>0</td><td>3.6982</td><td>0.9888</td><td>3.7580</td><td>401.2679</td><td>0.4450</td><td>0.9082</td><td>0.8927</td><td>0.8122</td></tr>
<tr><td>0.1</td><td>0.0037</td><td>0.2798</td><td>2.4894</td><td>0.1060</td><td>0.2665</td><td>0.5726</td><td>0.7496</td><td>0.8856</td></tr>
<tr><td>0.5</td><td>0.0017</td><td>0.2624</td><td>3.5920</td><td>0.1890</td><td>0.1349</td><td>0.6851</td><td>0.7560</td><td>0.8376</td></tr>
<tr><td>1</td><td>0.0014</td><td>0.1294</td><td>1.8005</td><td>0.0477</td><td>0.0989</td><td>0.8454</td><td>0.8850</td><td>0.9286</td></tr>
<tr><td rowspan="4">Red earth (CI)</td><td>0</td><td>2.1043</td><td>1.0512</td><td>2.7480</td><td>43.9380</td><td>0.6135</td><td>0.9249</td><td>0.9721</td><td>0.9922</td></tr>
<tr><td>0.1</td><td>0.0038</td><td>0.1573</td><td>1.4795</td><td>0.0312</td><td>0.2824</td><td>0.9568</td><td>0.9752</td><td>0.9897</td></tr>
<tr><td>0.5</td><td>0.0017</td><td>0.1334</td><td>1.6404</td><td>0.0309</td><td>0.1614</td><td>0.6821</td><td>0.8227</td><td>0.9191</td></tr>
<tr><td>1</td><td>0.0001</td><td>0.1556</td><td>7.7580</td><td>0.3705</td><td>0.0232</td><td>0.3628</td><td>0.5420</td><td>0.7068</td></tr>
</table>

This is indicating that, the adsorption of Nickel by CH and CI soil happened through the chemisorption by forming the covalent bonds nickel metal ions. The modelled isotherm is shown in Fig 4.11.

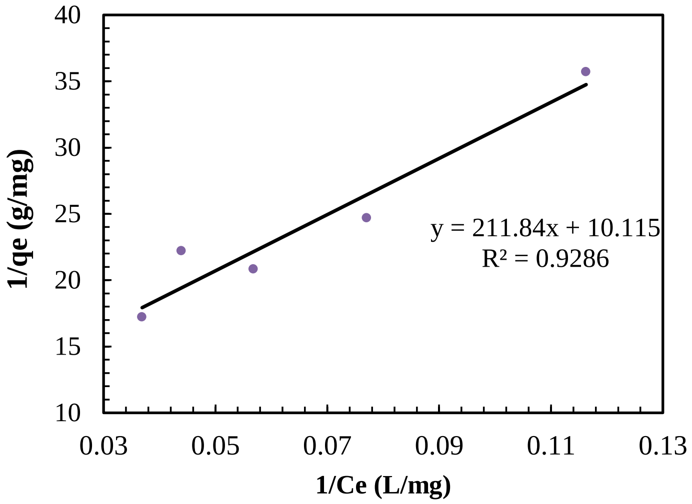


Fig. 4. 11 Langmuir isotherm for adsorption of Nickel on CH soil at pH 7

From the above figure, the value of the Langmuir isotherm constant (K_L) and maximum adsorption capacity (q_m) obtained for CH soil are 0.0477L/g and 0.0989 mg/g. Hence adsorption of lead onto CI soil is also fitting into the Langmuir isotherm model, thus allowing mono layer adsorption to happen. The Langmuir isotherm modelled at a maximum pH value 7 is shown in Fig 4.12. As can be observed from figure, the value of Langmuir isotherm constant is 0.0232 mg/g.

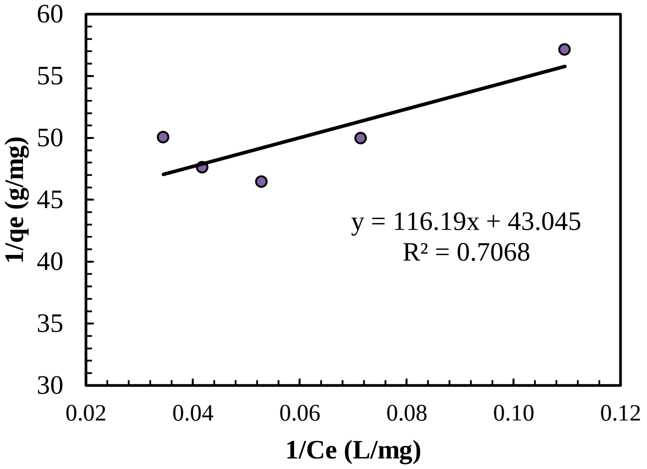


Fig. 4.12 Langmuir isotherm for adsorption of Nickel on CI soil at pH 7

4.2.3 Cadmium adsorption capacity

The percentage adsorption of cadmium metal ion by the CH soil with varying concentrations of EDTA under different pH values is presented in Fig 4.13.

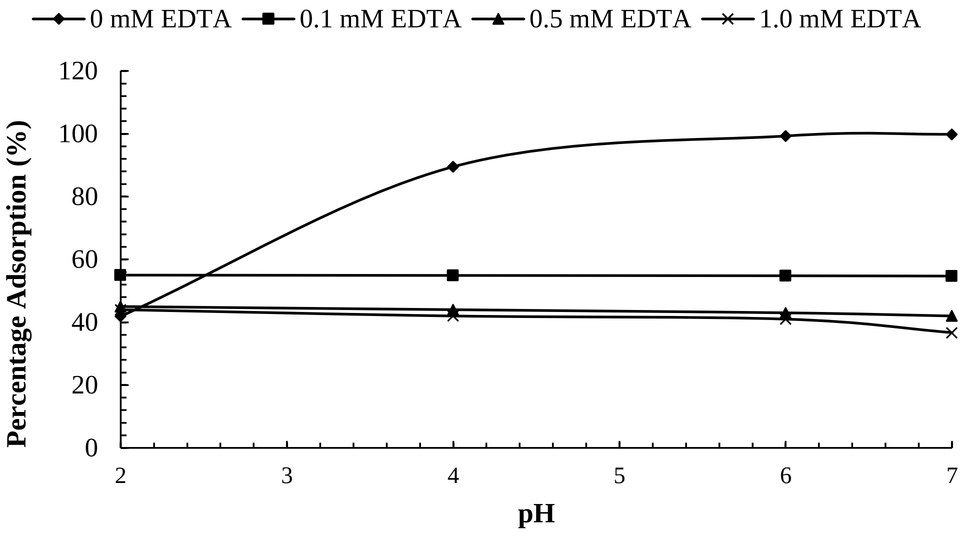


Fig. 4. 13 Variation of Percentage adsorption of Cadmium by CH soil with varying concentrations of EDTA under different pH values

From this figure, it is observed that, the percentage adsorption of Cadmium by CH soil is found to increase from 44% to 100% as pH is increasing from 2 to 7 when there is no EDTA. While the percentage adsorption is found to be marginally decreasing with the increase in pH under the influence of EDTA. The Percentage adsorption decreases by from 55% to 54% for 0.1mM EDTA, 45% to 42% for 0.5mM EDTA and decreases from 44% to 36% for 1mM EDTA concentration. The presence of EDTA increased the dissolution of sorbent and decreases amounts of metal ions adsorbed because of the formation of Cd EDTA^{2-} complexes. It was found that the CdEDTA^{2-} complex do not adsorbed on the soil surface at any measurable amounts. This is because, the possible amount of Cd metal ions bond with soil in solution depends also on the EDTA concentration and more over these proton – and – ligand EDTA promoted the surface phase transmissions in the presence of Cd^{2+} and CdEDTA^{2-}.

The variation of percentage adsorption with varying the metal ion concentration is presented in Fig 4.14.

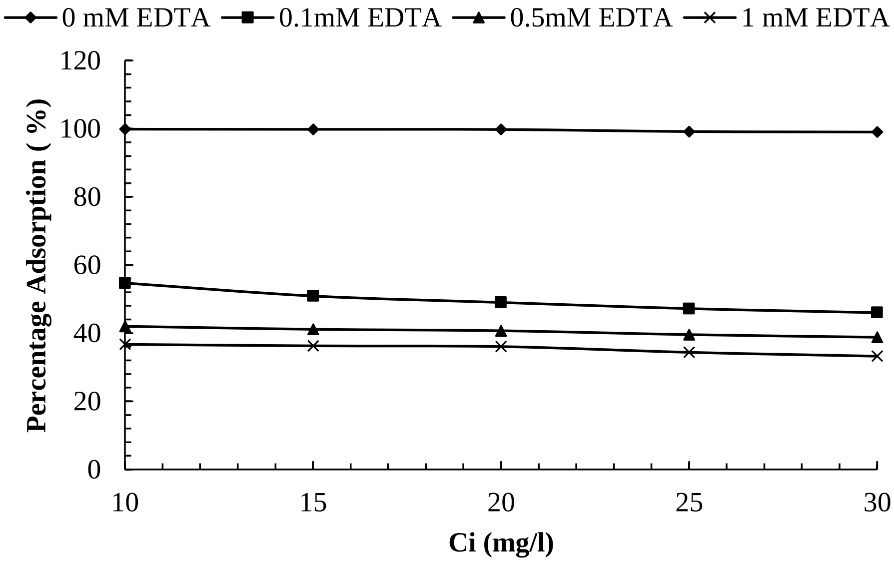


Fig. 4. 14 Variation of percentage adsorption of Cadmium by CH soil with initial concentration (Ci) at pH 7

From this figure, it can be observed that, the percentage adsorption decreases with the increase in initial concentration because of insufficient adsorption soil sites presents on the surface of the soil. The Percentage adsorption decrease from 54.7% to 46% for 0.1mM EDTA, 41% to 33.23% for 0.5mM EDTA and from 36% to 33% for 1.0 mM EDTA under the varying initial concentration from 10 mg/L to 30 mg/L.

The percentage adsorption of cadmium metal ion by CI soil with varying pH is presented in Fig 4.15. From this figure, it can be observed that, with increase in the pH of the solution, the percentage adsorption is increased when there is no EDTA. At pH 2 the concentration of H^+ is more which competes with the positively charged cations and as a result, the percentage adsorption is decreased. As increase in the pH of the solution is more than 6, cadmium metal ions are attached to the OH^- soil functional groups and as a result, the adsorption percentage is increased with increase in pH. The percentage adsorption is increased from 21% to 99% from the varying pH 2 to 7 without the presence of EDTA in the solution.

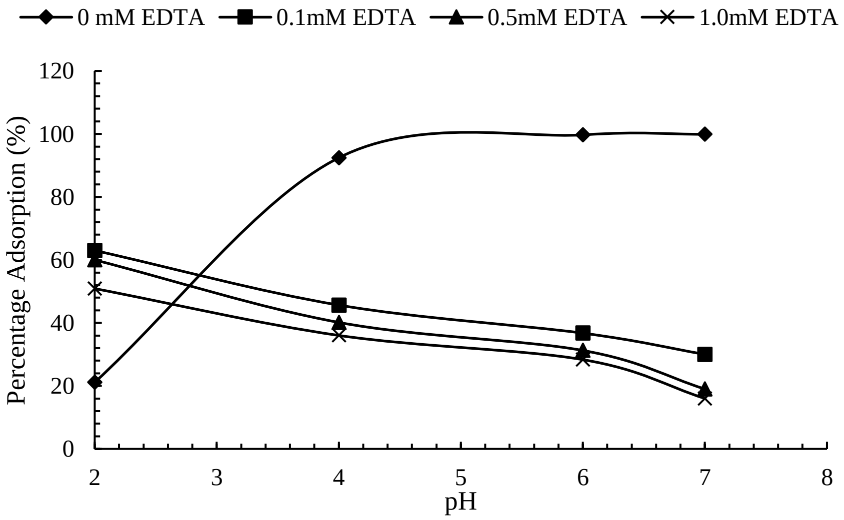


Fig. 4.15 Variation of Percentage adsorption of Cadmium by CI soil with varying pH

With the presence of EDTA in the solution, the parentage adsorption is observed to be decreasing significantly. The decrease is observed to be 62% to 30% for 0.1mM EDTA, 60% to 19% for 0.5mM and 50% to 16% for 1mM EDTA. From this figure, it can also observed that, when compared with CH soil the percentage adsorption of cadmium by CI soil is less. This is due to the lesser affinity of mineral Kaolinite present in CI soil which is having less adsorption towards Cadmium ions (Farrah and Pickering, 1979).

The initial concentration influence of cadmium on percentage of adsorption is presented in Fig 4.16. From this figure, it is observed that, with increase in initial concentration of metal solution, the percentage adsorption is decreased by small amount due to the insufficient adsorption sites on the surface of the soil. The decrease in the percentage adsorption is very less without EDTA in the solution.

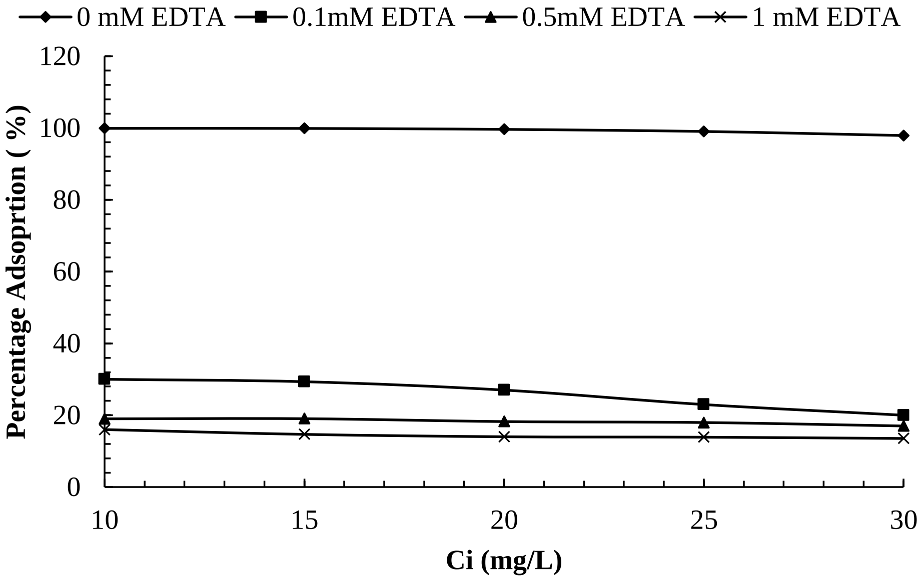


Fig. 4. 16 Variation of Percentage adsorption of Cadmium by CI soil with initial concentration (Ci) at pH 7

With the presence of EDTA in the solution, the percentage adsorption is significantly reduced when compared to that without EDTA present in the solution. The decrease in the percentage adsorption is observed to be 30% to 20% for 0.1mM EDTA, 19% to 17% for 0.5mM EDTA and 16% to 13.5 % for 1.0mM EDTA with varying initial concentrations from 10 mg/L to 30 mg/L.

4.2.3.1 Adsorption Isotherms

Interaction of Cadmium solution with both the geo-materials were modelled using the various sorption isotherms such as Linear, Langmuir and Freundlich isotherm. The sorption parameters of different isotherms are presented in Table 4.3. From the table, a comparison of regression coefficient is made, to find the best fitted isotherms for CH soil, the beat fitted isotherm is Langmuir isotherm and for CI soil is the best fitted isotherm is Freundlich.

Table 4.3 Adsorption isotherm coefficients values for CH and CI soil

[For different pH values with varying EDTA concentration and initial concentrations of Cadmium solution]

pH 2									
Material	EDTA Conc (milli Molar)	K_d	K_f	n	K_l	q_m	R^2		
							Linear	Freundlich	Langmuir
Black Cotton soil (CH)	0	0.0051	0.2287	1.9512	0.0952	0.2303	0.9862	0.9876	0.9722
	0.1	0.0050	0.3000	2.7988	0.2260	0.2122	1.0000	0.9805	0.9291
	0.5	0.0031	0.2736	3.1279	0.2299	0.1566	0.9968	0.9635	0.9004
	1	0.0020	0.2138	2.7233	0.1485	0.1145	1.0000	0.9871	0.9502
Red earth (CI)	0	0.0051	0.1552	1.8664	0.0680	0.1183	0.9995	0.9946	0.9765
	0.1	0.0168	0.2013	1.1353	0.0170	1.3134	0.9997	0.9997	0.9986
	0.5	0.0195	0.2592	1.3287	0.0434	0.8439	0.9929	0.9972	0.9994
	1	0.0200	0.2674	1.3493	0.0475	0.8297	0.9837	0.9939	0.9977
pH 7									
Material	EDTA Conc (milli Molar)	K_d	K_f	n	K_l	q_m	R^2		
							Linear	Freundlich	Langmuir
Black Cotton soil (CH)	0	1.1347	0.9476	3.1250	31.3814	0.6298	0.8637	0.9173	0.9912
	0.1	0.0143	0.2365	1.3742	0.0478	0.6064	0.9987	0.9995	0.9953
	0.5	0.0118	0.1739	1.1275	0.0117	1.3214	0.9975	0.9991	0.9998
	1	0.0092	0.1616	1.1481	0.0109	1.1395	0.9909	0.9953	0.9984
Red earth (CI)	0	0.5210	0.8525	4.1356	54.5495	0.5505	0.7784	0.9339	0.9660
	0.1	0.0034	0.1904	1.7870	0.0499	0.2393	0.8551	0.9183	0.9645
	0.5	0.0038	0.1093	1.1313	0.0077	0.6533	0.9928	0.9962	0.9983
	1	0.0028	0.1036	1.2063	0.0161	0.2656	0.9995	0.9981	0.9952

The best fitted isotherm models are shown in Fig 4.17 and Fig 4.18. The value of the maximum amount of metal ions required to form a monolayer (qm) is calculated as 1.1395 mg/g and the Langmuir coefficient (Kl) is 0.0109 l/g.

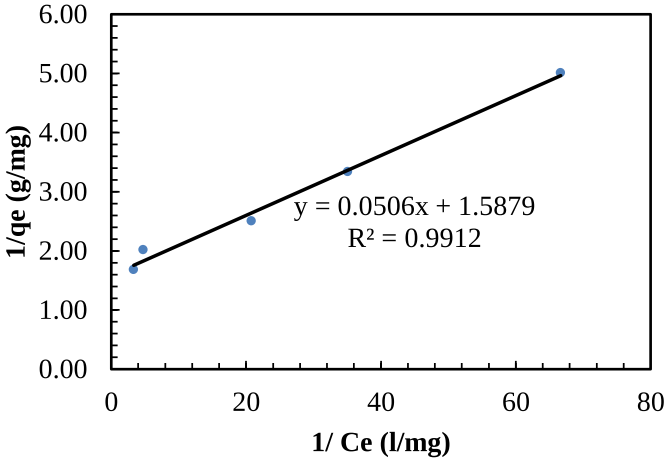


Fig. 4. 17 Langmuir isotherm for adsorption of Cadmium on CH soil at pH 7

Also from the table 4.3, it is observed that, the value of qm obtained was decreasing with increase in pH value, thus indicating that the amount of cadmium ions adsorbed by the CH soil has decreases as the pH value is increasing.

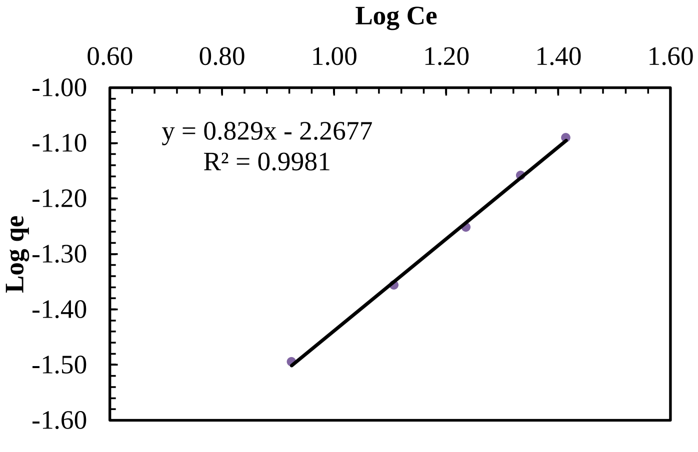


Fig. 4. 18 Freundlich isotherm for adsorption of Cadmium on CI soil at pH 7

From the above figure, the value of the Freundlich isotherm constant (K_f), obtained from the best fit equation is 0.1036 L/g.

4.2.4 Chromium Adsorption capacity

The percentage adsorption of Chromium metal ion by the CH and CI soils are shown in Fig 4.19 and 4.21 respectively. From these figures for both without and with EDTA conditions, the percentage adsorption of chromium by CH soil is found to decrease with increase in pH of the solution. This is due to the fact that, as chromium being in an anion form, reverse behaviour is observed when compared to that of other metal ions. The decrease in percentage adsorption is found to be 91% from pH 2 to pH 7 for without EDTA condition.

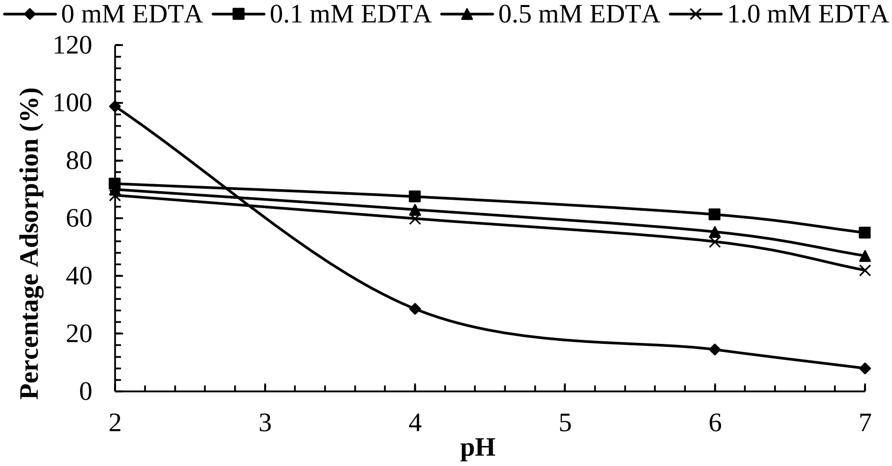


Fig. 4. 19 Variation of Percentage adsorption of Chromium by CH soil with varying concentrations of EDTA under different pH values

With the presence of EDTA in the solution, the amount of percentage adsorption is found to decrease at pH 2 and increase at pH 7. The decreased percentage adsorption is observed to be 72% to 55 % for 0.1mM EDTA, 70% to 47% for 0.5mM EDTA and 68 % to 42 % for 1mM EDTA from pH 2 to pH 7. This is mainly due to the reason that, (1) the direct reduction of Cr(VI) to Cr(III) with organic ligands in solution and (2) catalytic Cr(VI) reduction by surface-bound natural organic matter (NOM), surface minerals (e.g., clays, Fe oxides, TiO_2) or dissolved metals (e.g., Fe(II; III). NOM can reduce Cr (VI) to Cr (III) in solution since it contains certain functional groups (e.g., carboxyl (COOH)) that represent a significant reservoir of electron donors for the reduction of Cr (VI) to Cr (III) as shown in the equation below.

$$3C + 4\,CrO_4^{2-} + 20H^+ \leftarrow\!\!-\!\!-\!\!-\!\!\rightarrow 4\,Cr^{3+} + 3CO_2 + 10H_2O$$

Sorption experiments suggest that most of total chromium (>90%) in solution was in the hexavalent form, Cr(VI), indicating that surface-bound organic matter/Fe oxides or dissolved metal ions such as Fe may be responsible for the enhanced Cr (VI) uptake by soil under neutral pH conditions. The term “uptake” will be used in the text to describe the sorption of both Cr (VI) and reduced Cr (VI) [e.g., Cr (III)] in the presence of organic ligands hereafter. Kantar, (2008) found that while the Cr (VI) reduction by organic ligands occurs very fast under acidic conditions, the reaction rate decreases with increase in pH value. Deng et al. (2003) found that clays such as Smectite and Illite catalyzed Cr (VI) reduction by organic ligands.

The variation of percentage adsorption of chromium by CH soil with different initial concentration values from 10 mg/L to 30 mg/L at pH 7 is shown in Fig 4.20.

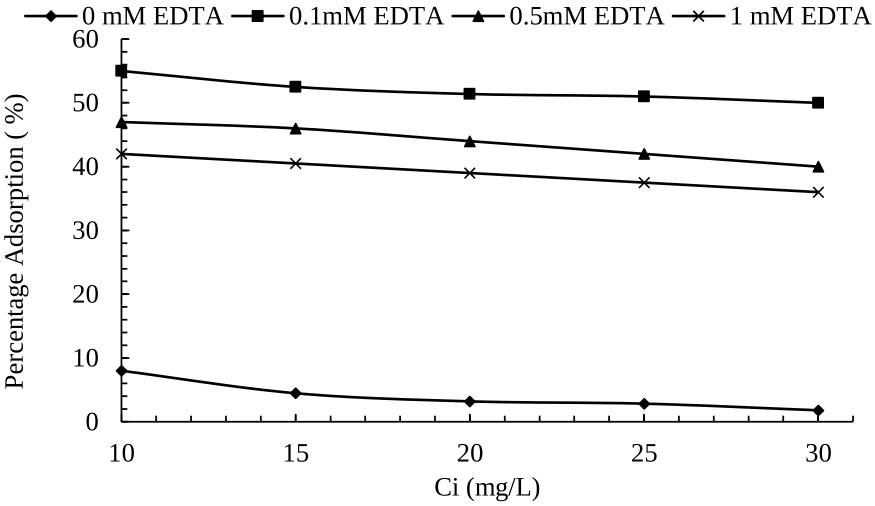


Fig. 4. 20 Variation of percentage adsorption of Chromium by CH soil with different initial concentrations (Ci) at pH 7

The percentage adsorption of chromium is observed to decrease with an increase in the initial concentration of chromium. From this figure, it can be seen that, in the absence of EDTA in the solution, the percentage observed to be decreased from 8% to 1.8% with increase in the initial concentration from 10mg/L to 30 mg/L. Even with the presence of EDTA in the solution, the percentage adsorption is observed to get decreased with an increase in the concentration of EDTA. This is mainly due to the insufficient adsorption sites present on the surface of soil. The Percentage adsorption decrease from 55% to 50% for 0.1mM EDTA, 46% to 40% for 0.5mM EDTA and 40.5% to 36% for 1.0 mM EDTA under the varying initial concentration from 10 mg/L to 30 mg/L.

The variation of percentage adsorption of chromium by CI soil for different pH values are shown in Fig 4.21.

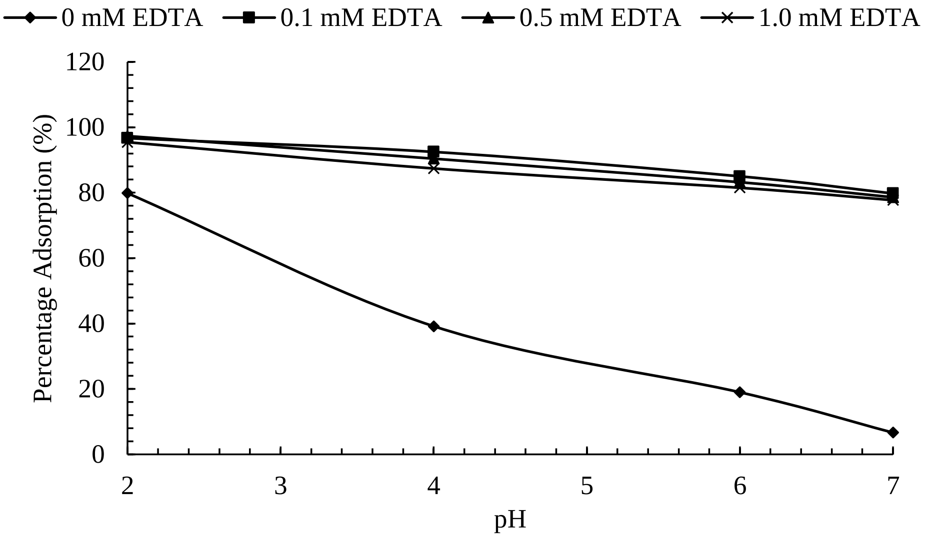


Fig. 4. 21 Variation of percentage adsorption of Chromium by CI soil with varying concentrations of EDTA under different pH values

The percentage adsorption is showing the similar trend as observed in case of CH soil with varying pH of the solution. The decrease in percentage adsorption with increase in the pH of the solution is observed to be more significant and the percentage adsorption decreased from 79% to 6.6% with increase in pH of the solution from 2 to 7 in the absence of the EDTA. From the above figure, it can observed that, the percentage adsorption is increased with the presence of EDTA. This is mainly due to the fact that, most of the total chromium, in the solution was bound to Fe oxides in soil and Organic chemicals in the solution which is responsible for the enhancement of chromium adsorption. These Fe oxides present in the soil and carboxyl functional groups are responsible for reduction of hexa-valent chromium to the Tri valent Chromium play a significant role in metal oxidation and reduction reactions. These trivalent chromium will react with the EDTA ions and forms Cr EDTA complex as a result, the percentage adsorption is decreased with increase in pH of the solution. The percentage adsorption decreased from be 97% to 79% for 0.1mM EDTA, 96% to 78% for 0.5mM EDTA and 95% to 77% for 1mM EDTA from pH 2 to 7.

The percentage adsorption of Chromium metal ion with increase in the initial concentration of chromium with and without EDTA is shown in the Fig 4.22.

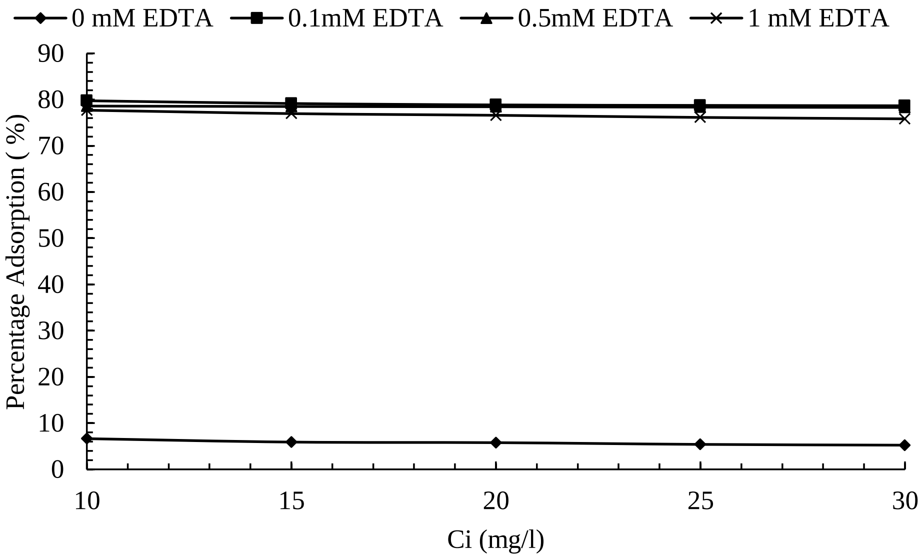


Fig 4. 22. Variation of percentage adsorption of Chromium by CI soil with initial concentration (Ci) at pH 7

From this figure, it is observed that with increase in the concentration of metal ion, the percentage adsorption is reduced very marginally due to decrease in the adsorption sites on the surface of the soil. The decrease in the percentage adsorption is observed to be less significant even with increase in the concentration of chromium metal ion. The percentage adsorption of chromium is observed to be decreased from 6.5 % to 5.2%, with variation in initial concentration from 10 mg/L to 30 mg/L in the absence of EDTA. With the presence of EDTA, the decrease in percentage adsorption is from 79% to 78% for 0.1mM EDTA, 78.5% to 78% for 0.5mM EDTA and 77% to 75% for 1 mM EDAT with change in concentrations from 10 mg/L to 30 mg/L.

4.2.4.1 Adsorption Isotherms

The adsorption of Chromium metal ion on the surface of the geo-materials is modelled using the various sorption isotherms such as Linear, Langmuir and Freundlich isotherm. The sorption parameters such as K, K_f, n, K_L and q_m along with regression coefficient, R^2, for different isotherms are presented in Table 4.4. From the table, a comparison of regression coefficient is made, to find the best suitable isotherms for the geo-materials and it is found that CH soil data fitting with Langmuir isotherm and for CI sol, the adsorption of is best fitting available with chromium Black cotton soil (CH) was found to follow Langmuir isotherm.

Table 4.4 Adsorption isotherm coefficients values for CH and CI soils
[For different pH values with varying EDTA concentration and initial concentrations of Chromium solution]

pH 2									
Material	EDTA Conc (milli Molar)	K_d	K_f	n	K_l	q_m	R^2		
							Linear	Freundlich	Langmuir
Black Cotton soil (CH)	0	0.0145	0.6028	7.3475	8.8768	0.4060	0.5111	0.8081	0.9253
	0.1	0.0224	0.3355	1.6480	0.1075	0.6322	0.9733	0.9826	0.9891
	0.5	0.0222	0.3138	1.5415	0.0923	0.6407	0.9889	0.9984	0.9980
	1	0.0225	0.2943	1.4658	0.0875	0.6082	0.9996	0.9936	0.9819
Red earth (CI)	0	0.0177	0.3871	2.4266	0.3946	0.3480	0.9223	0.8878	0.8297
	0.1	0.1545	0.6093	2.0016	1.4399	0.5800	0.9999	0.9825	0.9408
	0.5	0.1567	0.6123	2.2810	2.2613	0.5028	0.9739	0.9246	0.8790
	1	0.1037	1.7725	2.0653	1.0923	0.5574	0.9982	0.9871	0.9442
pH 7									
Material	EDTA Conc (milli Molar)	K_d	K_f	n	K_l	q_m	R^2		
							Linear	Freundlich	Langmuir
Black Cotton soil (CH)	0	0.0002	0.1026	3.1566	0.1394	0.0188	0.9508	0.9519	0.9472
	0.1	0.0183	0.2204	1.1903	0.0262	1.0310	0.9993	0.9990	0.9968
	0.5	0.0114	0.2083	1.3060	0.0285	0.7218	0.9864	0.9942	0.9987
	1	0.0098	0.1876	1.2639	0.0241	0.6842	0.9936	0.9983	1.0000
Red earth (CI)	0	0.0010	0.0716	1.2837	0.0189	0.0874	0.9974	0.9979	0.9947
	0.1	0.0714	0.3367	1.0609	0.0196	4.1545	1.0000	0.9998	0.9995
	0.5	0.0715	0.3235	1.0160	0.0042	17.4520	1.0000	1.0000	1.0000
	1	0.0597	0.3242	1.0966	0.0251	2.9172	0.9997	1.0000	0.9998

The modelled isotherms are shown in Fig 4.23 ad 4.24, from the table 4.4 the value of the maximum amount of metal ions required to form a monolayer (q_m) is calculated as 0.6842 mg/g and the Langmuir coefficient (Kl) is 0.0241 l/g.

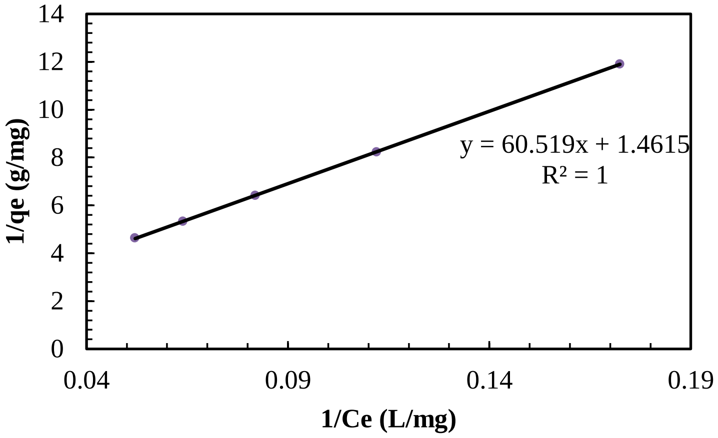


Fig 4. 23 Langmuir isotherm for adsorption of chromium on CH soil at pH 7

From the Fig 4.24, the value of the Freundlich isotherm constant (K_f), obtained from the best fit equation is 0.3242 L/g.

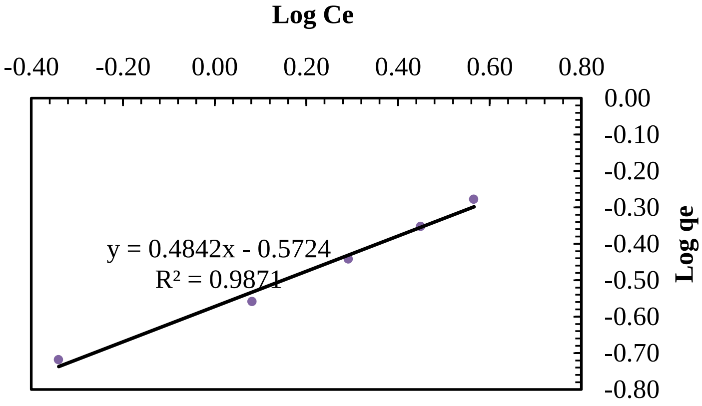


Fig 4. 24. Freundlich isotherm for adsorption of chromium on CI soil at pH 7

4.2.5 Competitive effect on adsorption capacity of soils

Competitive batch sorption studies are being conducted on both the soils (CH and CI) with composite heavy metal solutions in order to determine the pH – dependent adsorption of Lead, Nickel, Cadmium and. The major objective was to determine the metal retention sequence for each soil. The results obtained from the series of competitive batch sorption experiments are discussed in the following sections.

4.2.5.1 Lead adsorption capacity of soils

The competitive effect on adsorption capacity of CH soil for lead metal ion is shown in Fig 4.25. From this figure, it is observed that, under competitive influence the heavy metal lead got adsorbed almost by 100% when pH increasing from 2 to 7 under the absence of EDTA. This may be due to the fact that, there is formation of lead oxides.

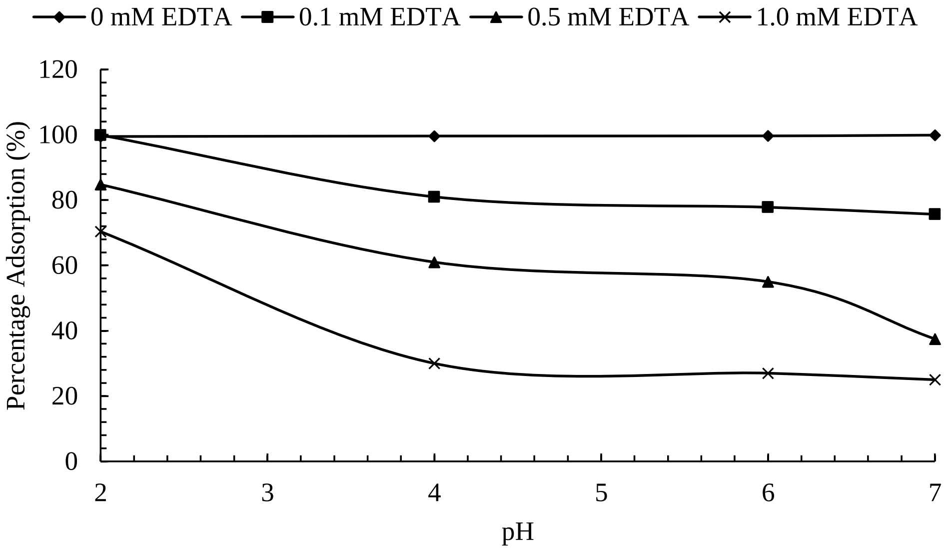


Fig. 4. 25 Variation of percentage adsorption of lead by CH soil with varying pH

The percentage adsorption is found to be decreasing with the increase in pH under the influence of EDTA. This due to the fact that, with the presence of EDTA in the solution, there is a formation of PbEDTA^{2-} complex and this complex forms covalent bonds more effectively at pH> 6 when compared to pH 2. As a result of this the percentage adsorption is decreasing with increasing pH from 2 to 7. The Percentage adsorption decrease from 100% to 75% for 0.1mM EDTA, 84% to 37% for 0.5mM EDTA and 70% to 25% for 1mM EDTA concentration.

The percentage adsorption of lead metal ion by the CI soil under composite heavy metal interaction is shown in Fig 4.26. from this figure it is observed that, with increasing pH of the soil from 2 to 7 it is following the same trend as in case of CH soil reaching almost 100% percentage adsorption in the absence of EDTA in the solution.

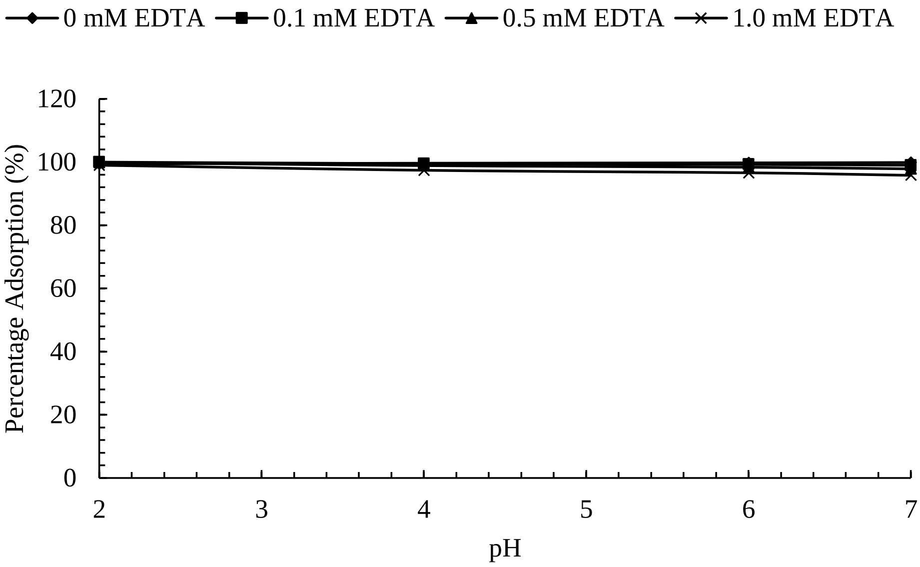


Fig. 4. 26 Variation of percentage adsorption of lead by CI soil with varying pH

While the percentage adsorption is found to be decreasing in very small amounts with the increase in pH under the influence of EDTA due to the formation of Metal EDTA complex. The percentage adsorption decrease from 99% to 98% for 0.1mM EDTA, 99% to 97% 0.5mM EDTA and 99% to 96% for 1mM EDTA concentration.

4. 2. 5. 1.1 Adsorption Isotherms

The suitability of sorption isotherms to represent the geo-materials – heavy metal interaction in terms of their sorption characteristic are assessed using the results obtained from batch sorption experiments. For this purpose, amount of heavy metal sorbed by the geo-materials, q_e, and the final equilibrium concentration of the solute C_e, are used as model parameters. With this in view, the sorption isotherms are modelled for selected geo-materials. The sorption parameters such as K, K_f, n, K_L and q_m along with regression coefficient, R^2, for different isotherms are presented in table 4. 5

Table 4.5. Adsorption isotherm coefficients values for CH and CI soils

[For different pH values with varying EDTA concentration and initial concentrations of Lead from multi heavy metal solution]

pH 2									
Material	EDTA Conc (milli Molar)	K_d	K_f	n	K_l	q_m	R^2		
							Linear	Freundlich	Langmuir
Black Cotton soil (CH)	0	2.0136	1.2156	1.4008	4.0009	1.0977	0.9997	0.9982	0.9910
	0.1	0.0414	0.5967	9.8328	142.0242	0.3401	0.9557	0.6568	0.6297
	0.5	0.0450	0.4074	1.6872	0.2547	0.5892	0.9980	0.9831	0.9587
	1	0.0335	0.2923	1.2170	0.0351	1.4972	0.9839	0.9944	0.9991
Red earth (CI)	0	0.6951	0.8640	2.2676	7.8146	0.6276	0.9799	0.9796	0.9792
	0.1	0.2639	0.7022	5.3163	93.2077	0.4126	0.9989	0.8458	0.7796
	0.5	0.2204	0.6903	5.5804	95.2257	0.4086	0.9988	0.8372	0.7747
	1	0.1389	0.6477	3.3434	8.0965	0.4349	0.9988	0.9345	0.8378
pH 7									
Material	EDTA Conc (milli Molar)	K_d	K_f	n	K_l	q_m	R^2		
							Linear	Freundlich	Langmuir
Black Cotton soil (CH)	0	10.6790	2.2142	1.2923	11.9504	1.5969	0.9950	0.9980	0.9989
	0.1	0.0241	0.3507	1.7510	0.1651	0.5175	0.9984	0.9950	0.9810
	0.5	0.0082	0.1736	1.2642	0.0235	0.5848	0.9942	0.9974	0.9987
	1	0.0007	0.2285	5.2854	0.3580	0.0671	0.9854	0.9319	0.8451
Red earth (CI)	0	7.8002	1.9159	1.3912	11.7813	1.4170	0.9784	0.9912	0.9987
	0.1	0.0590	0.6040	4.4267	9.9703	0.3919	0.9808	0.9348	0.8109
	0.5	0.0100	0.5584	6.5232	5.8363	0.3485	0.5100	0.8823	0.9355
	1	0.0089	0.5264	6.2775	3.2016	0.3247	0.6951	0.9578	0.9728

From Table 4.5, a comparison of regression coefficient is made, to find the best fitted isotherms for the geo-materials and it is found that CH soil is following Freundlich isotherm. The Freundlich isotherm model is shown in the Fig 4.27.

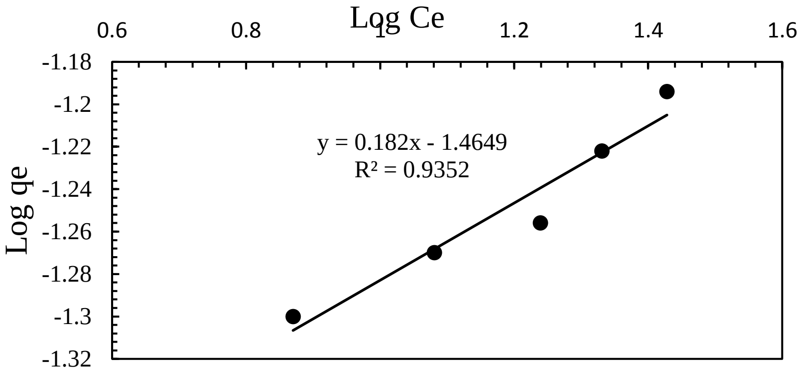


Fig. 4. 27 Freundlich isotherm for adsorption of Lead on CH soil at pH 7

From the above figure 4.27, the value of the Freundlich isotherm constant (K_f), obtained from the best fit equation is 0.2285 L/g, while the adoption of lead by CI soil is fitting in to the Langmuir Isotherm model and it is shown in the Fig 4.28.

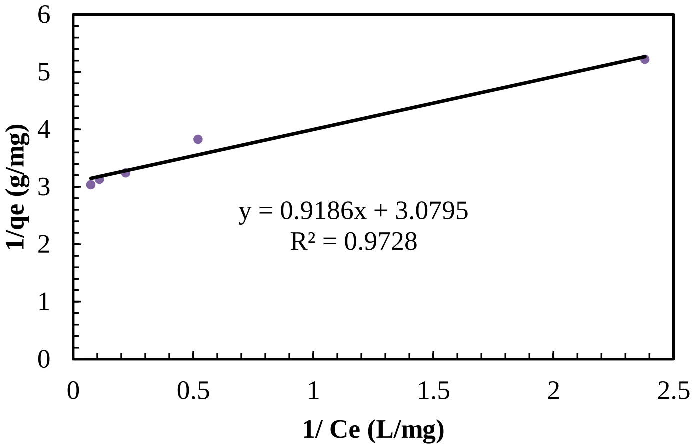


Fig. 4. 28 Langmuir isotherm for adsorption of lead on CI soil at pH 7

The value of the maximum amount of metal ions required to form a monolayer (qm) is calculated as 0.3247 mg/g and the Langmuir coefficient (Kl) is 3.2016 l/g.

4.2.5.2 Nickel Adsorption capacity of soils

The percentage adsorption of nickel metal ion by the CH soil under the influence of composite heavy metal solution is shown in Fig 4.29.

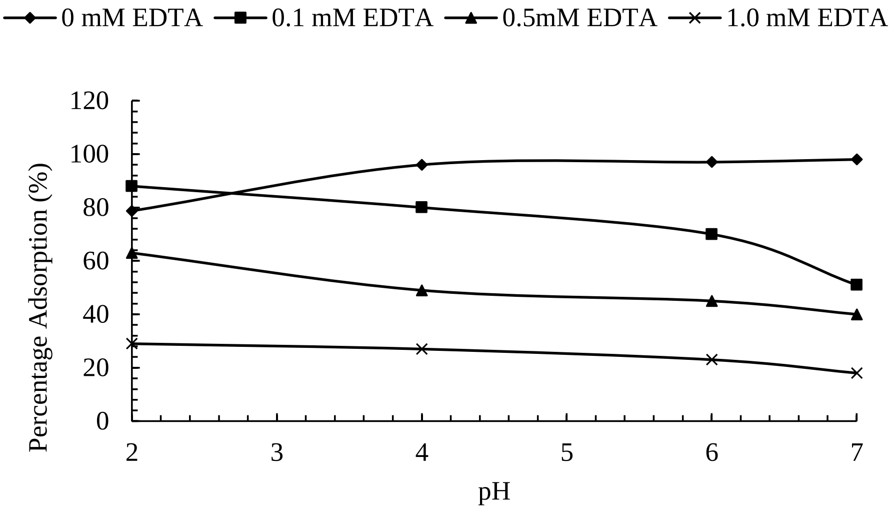


Fig. 4. 29 Variation of percentage adsorption of Nickel by CH soil with varying pH

From this figure it is observed that, the percentage adsorption is increasing with increase in the pH of the solution from 2 to 7 in absence of EDTA. This is due to the fact that, at pH 2 the negatively charged soil surface is occupied by the H^+ ions as a result, the heavy metal adsorption is less. As pH increases from 2 to 7, the negatively charged soil surface is attracts the positively charged cations to the surface of the soil. The increase in the percentage adsorption is observed to be 25% from pH 2 to 7.

However, with the presence of EDTA in the solution, the percentage adsorption is decreasing with an increase in the pH from 2 to 7. This can be due to the formation of Ni $EDTA^{2-}$ metal complex. Under composite heavy metal interaction, the percentage adsorption is little more when compared to the percentage adsorption under single metal interaction. This is due to the fact that, under composite metal interaction, EDTA is in coordination with all the heavy metals as a result, the Ni EDTA coordination is less in the composite heavy metal interaction when compared to single metal interaction. From Fig 4.29, it is also observed that, the percentage adsorption decrease from 88% to 51% for 0.1mM EDTA, 63% to 40% for 0.5mM EDTA and decreases from 29% to 18% for 1mM EDTA concentration.

The percentage adsorption of Nickel by the CI soil with varying pH of the solution is shown in the Fig 4.30.

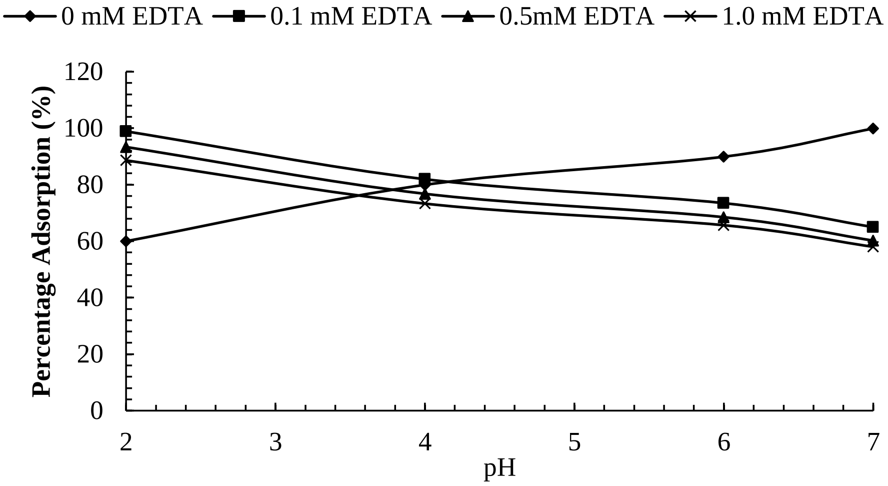


Fig. 4. 30 Variation of Percentage adsorption of Nickel by CI soil with varying pH

From this figure, it is observed that, the percentage adsorption is following the same trend as CH soil with change in the pH of the solution. But the percentage adsorption is less at pH 2 when compared to the CH soil. This is mainly due to the fact that, there is a prior existence of Ni in the CI soil decrease the adsorption sites for fresh nickel metal ins as a result the percentage adsorption is decreased at pH 2. In case of EDTA present in the heavy metal solution, the percentage adsorption is found to be decreasing with the increase in pH under the influence of EDTA. The percentage adsorption decrease from 98% to 65% for 0.1mM EDTA, 93% to 60% for 0.5mM EDTA and 88% to 58% for 1mM EDTA concentration.

4.2.5.2.1 Adsorption Isotherms

Interaction of Nickel solution with the geo-materials are modelled using the various sorption isotherms such as Linear, Langmuir and Freundlich isotherm. The sorption parameters such as K, K_f, n, K_L and q_m along with regression coefficient, R^2, for different isotherms are presented in Table 4.6.

Table 4.6 Adsorption isotherm coefficients values for CH and CI soils

[For different pH values with varying EDTA concentration and initial concentrations of Nickel from multi heavy metal solution]

pH 2									
Material	EDTA Conc (milli Molar)	K_d	K_f	n	K_l	q_m	R^2		
							Linear	Freundlich	Langmuir
Black Cotton soil (CH)	0	0.0365	0.3512	1.4919	0.1482	0.6348	0.9637	0.9511	0.9222
	0.1	0.0144	0.2137	1.2450	0.0275	0.8543	0.9959	0.9989	0.9992
	0.5	0.0067	0.2001	1.5427	0.0545	0.3183	0.9991	0.9970	0.9866
	1	0.0036	0.1779	1.6756	0.0477	0.2317	0.9474	0.9768	0.9944
Red earth (CI)	0	0.0132	0.2696	1.6739	0.1140	0.3671	0.9803	0.9468	0.9056
	0.1	0.0099	0.5482	8.6655	15.9107	0.3084	0.7767	0.9566	0.8408
	0.5	0.0053	0.4783	11.4943	7.1380	0.2232	0.7785	0.4748	0.2881
	1	0.0049	0.4666	7.0423	1.9838	0.2523	0.8730	0.9799	0.8997
pH 7									
Material	EDTA Conc (milli Molar)	K_d	K_f	n	K_l	q_m	R^2		
							Linear	Freundlich	Langmuir
Black Cotton soil (CH)	0	0.0038	0.5047	18.9036	26.4260	0.2323	0.9662	0.6858	0.4761
	0.1	0.0675	0.4553	1.5352	0.1914	0.9478	0.9665	0.9890	0.9993
	0.5	0.0027	0.3715	5.1177	0.4782	0.1997	0.7815	0.8980	0.9724
	1	0.0031	0.1125	1.2366	0.0176	0.2836	0.9995	0.9998	0.9982
Red earth (CI)	0	1.4795	0.9750	3.0637	47.5699	0.5759	0.9141	0.9738	0.9890
	0.1	0.0096	0.3208	2.2978	0.2057	0.3017	1.0000	0.9837	0.9419
	0.5	0.0049	0.3260	3.3535	0.3524	0.1989	0.9657	0.8908	0.7930
	1	0.0019	0.3520	7.8370	1.2091	0.1335	0.6147	0.3989	0.2236

From the above table 4.6, a comparison of regression coefficient is made, to find the best fitted isotherms for the geo-materials and it is found that CH Soil and CI Soil both are fitting in to the Freundlich isotherm model and shown in the Fig 4.31 for CH soil and Fig 4.32 for CI soil.

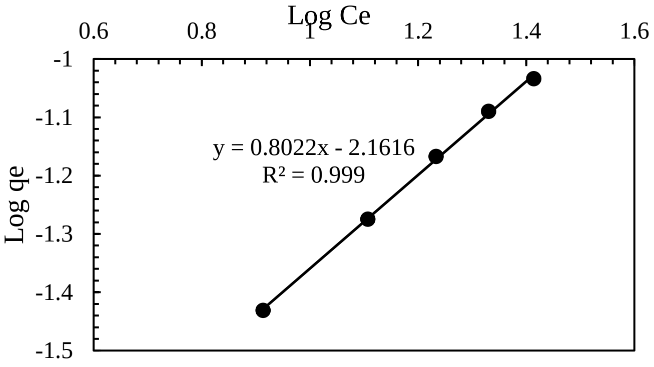


Fig. 4.31 Freundlich isotherm for adsorption of Nickel on CH Soil at pH 7

From the above figure, the value of the Freundlich isotherm constant (K_f), obtained from the best fit equation is 0.1125 L/g.

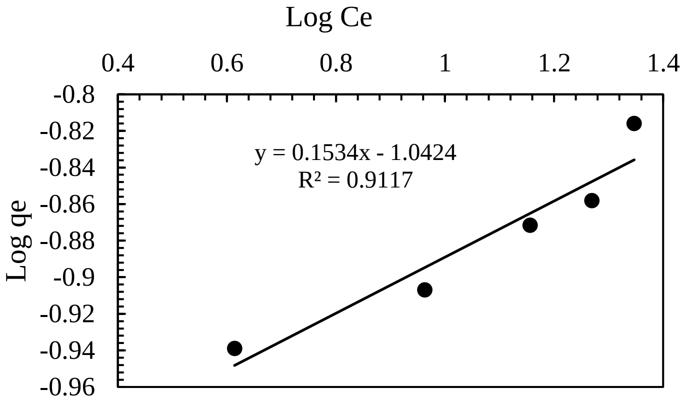


Fig. 4. 32 Freundlich isotherm for adsorption of Nickel on CI soil at pH 7

From the above figure, the value of the Freundlich isotherm constant (K_f), obtained from the best fit equation is 0.3520L/g.

4. 2.5.3 Cadmium Adsorption capacity of Soils

The percentage adsorption of Cadmium by the CH soil is shown in the Fig 4.33.

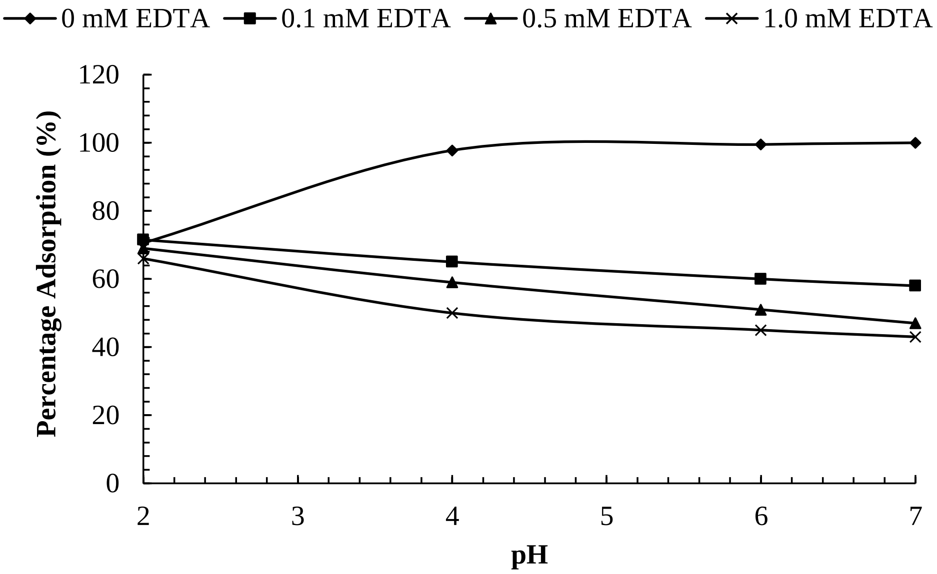


Fig. 4. 33 Variation of percentage adsorption of Cadmium by CH soil with varying pH

From the above figure, the percentage adsorption of Cadmium by CH soil in absence of EDTA is found to be increasing from 66% to 100% when pH is increasing from 2 to 7. The percentage adsorption is found to be decreasing with the increase in pH under the influence of EDTA. The percentage adsorption decrease from 71% to 58% for 0.1mM EDTA, 69% to 47% for 0.5mM EDTA and 66% to 43% for 1mM EDTA concentration.

The percentage adsorption of Cadmium by the CI soil with varying pH of the solution is shown in the Fig 4.34. From this figure, it is observed that the percentage adsorption of Cadmium by CI soil in absence of EDTA is found to be increasing from 55% to 100% when pH is increasing from 2 to 7.

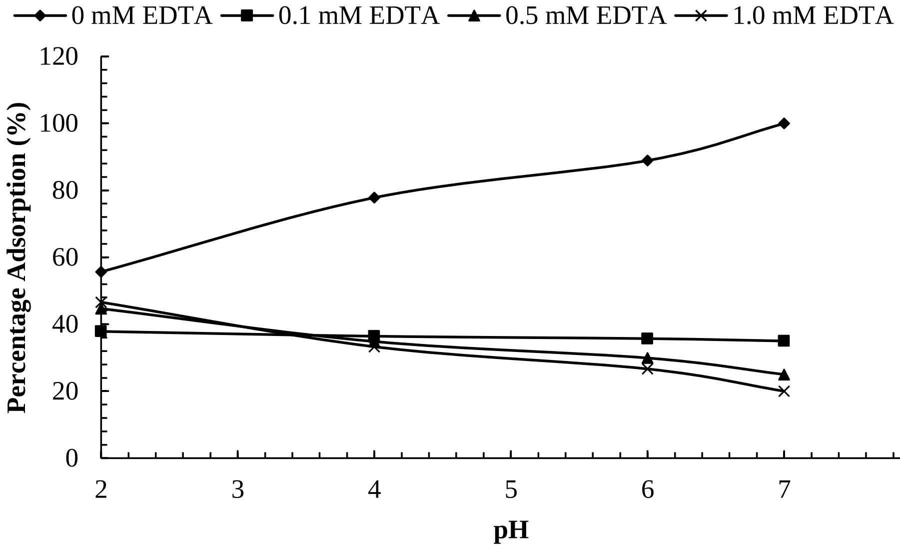


Fig. 4. 34 Variation of percentage adsorption of Cadmium by CI soil with varying pH

The Percentage adsorption is found to be decreasing with the increase in pH under the influence of EDTA. The percentage adsorption decrease from 35% to 37 % for 0.1mM EDTA, 44% to 25% for 0.5mM EDTA and 46% to 20% for 1mM EDTA concentration.

4.2.5.3.1 Adsorption Isotherms

Interaction of Cadmium solution with all the geo-materials were modelled using the various sorption isotherms such as Linear, Langmuir and Freundlich isotherm. The sorption parameters such as K, K_f, 1/n, K_L and q_m along with regression coefficient, R^2, for different isotherms are presented in Table 4.7

Table 4.7 Adsorption isotherm coefficients values for geo-materials

[For different pH values with varying EDTA concentration and initial concentrations of Cadmium from multi heavy metal solution]

pH 2									
Material	EDTA Conc (milli Molar)	K_d	K_f	n	K_l	q_m	R^2		
							Linear	Freundlich	Langmuir
Black Cotton soil (CH)	0	0.0373	0.2777	1.2009	0.0772	0.7324	0.8039	0.7645	0.7450
	0.1	0.0316	0.3005	1.3060	0.0653	0.8942	0.9862	0.9903	0.9864
	0.5	0.0192	0.3187	1.6173	0.0885	0.6453	0.9443	0.9768	0.9953
	1	0.0066	0.3648	2.7609	0.1749	0.3721	0.5480	0.7351	0.8919
Red earth (CI)	0	0.0172	0.2303	1.2513	0.0312	0.9117	0.9953	0.9991	0.9992
	0.1	0.0052	0.2060	1.6875	0.0571	0.2889	0.9595	0.9859	0.9811
	0.5	0.0074	0.2195	1.6364	0.0719	0.3060	0.9983	0.9878	0.9696
	1	0.0080	0.2298	1.6005	0.0553	0.4103	0.9546	0.9822	0.9963
pH 7									
Material	EDTA Conc (milli Molar)	K_d	K_f	n	K_l	q_m	R^2		
							Linear	Freundlich	Langmuir
Black Cotton soil (CH)	0	1.2525	0.8427	6.0314	1354.7059	0.4342	0.8915	0.9732	0.8332
	0.1	0.0169	0.2484	1.3335	0.0395	0.8171	0.9838	0.9940	0.9989
	0.5	0.0038	0.2722	2.8458	0.2161	0.1698	0.9780	0.9265	0.8541
	1	0.0031	0.2619	2.9612	0.2149	0.1508	0.9781	0.9262	0.8527
Red earth (CI)	0	0.8476	0.8675	4.1806	188.4915	0.4496	0.8548	0.9867	0.8521
	0.1	0.0042	0.2036	1.7947	0.0612	0.2473	0.9283	0.9703	0.9927
	0.5	0.0042	0.1415	1.3189	0.0222	0.3512	0.9837	0.9935	0.9986
	1	0.0022	0.1442	1.7039	0.0550	0.1283	1.0000	0.9950	0.9811

From the above table 4.7, a comparison of regression coefficient is made, to find the best fit isotherms for CH and CI soils are fitting in to the Freundlich isotherm model and these models are shown in Fig 4.35 for CH soil and Fig 4.36 for CI soil. From the figure 4.35, the value of the Freundlich isotherm constant (Kf), obtained from the best fit equation is 0.2619 L/g.

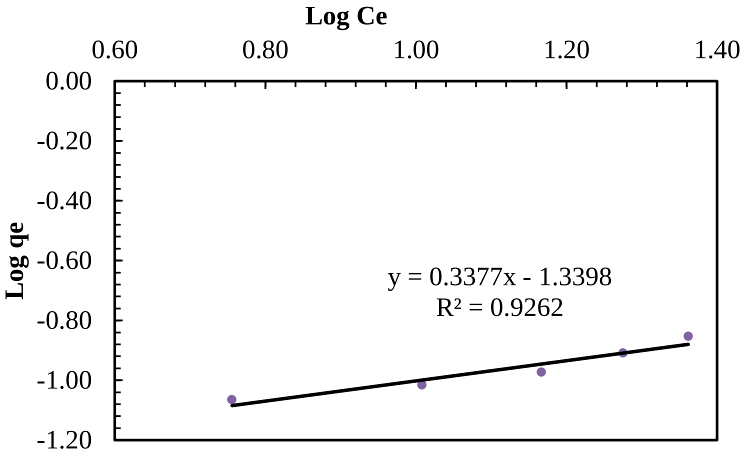


Fig. 4. 35 Freundlich isotherm for adsorption of Cadmium by CH soil at pH 7

The Fig 4.36 shows the, the value of the Freundlich isotherm constant (Kf), obtained from the best fit equation is 0.1442 L/g.

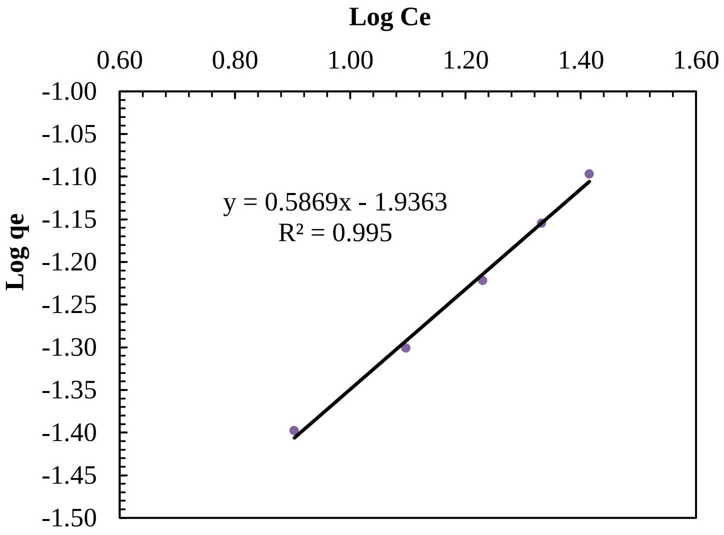


Fig. 4. 36 Freundlich isotherm for adsorption of Cadmium on CI soil at pH 7

4.2.5.4 Chromium Adsorption capacity of Soils

The percentage adsorption of Chromium by the CH soil is shown in the Fig 4.37. From the Fig 4.37, it is observed that, the percentage adsorption of Chromium by CH soil in absence of EDTA is found to be decreasing from 85% to 34% when pH is increasing from 2 to 7. The increase in percentage adsorption with increase in case of composite heavy metal solution is due to the the formation of cation-anion complex. As a result of that, the percentage adsorption is increased when compared to the single metal solution.

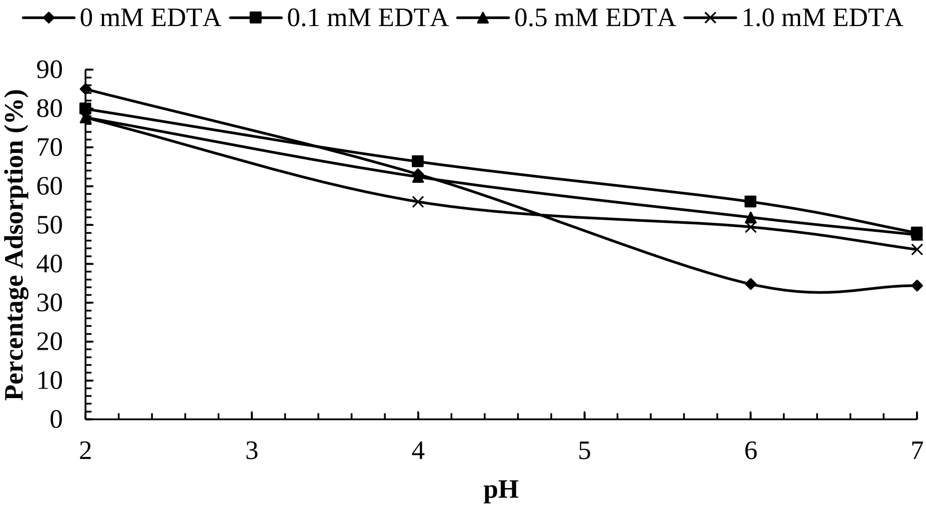


Fig. 4. 37 Variation of percentage adsorption of Chromium by CH soil with varying pH

With the presence of EDTA in the solution, the percentage adsorption is found to be decreasing with the increase in pH but the decrease in the percentage adsorption is little more when compared to the single metal interaction. This is mainly due to the formation of Cr-EDTA metal complex and the EDTA is effectively coordinated with the EDTA by donating the oxygen atoms. The Percentage adsorption decrease from 77% to 47% for 0.1mM EDTA, 77% to 47.5% for 0.5mM EDTA and 76% to 43% for 1mM EDTA concentration.

The percentage adsorption of Chromium by the CI soil is shown in the Fig 4.38. From the Fig 4.38, it is observed that, the percentage adsorption of Chromium by CI soil in absence of EDTA is found to be decreasing from 77% to 25% when pH is increasing from 2 to 7.

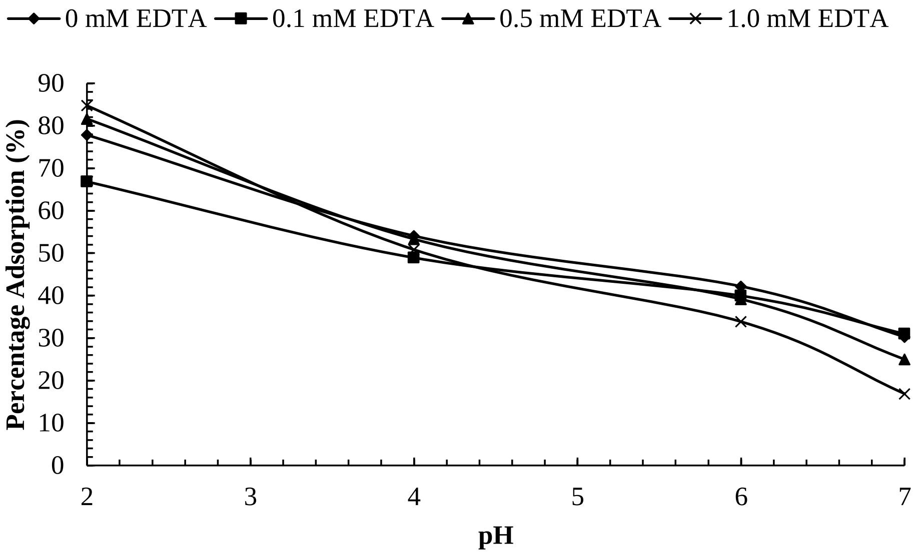


Fig. 4. 38 Variation of percentage adsorption of Chromium by CI soil with varying pH

The percentage adsorption is found to be decreasing with the increase in pH under the influence of EDTA. The percentage adsorption decrease from 66% to 25% for 0.1mM EDTA, 81% to 25% for 0.5mM EDTA and 84% to 17% for 1mM EDTA concentration.

4.2.5.4.1 Adsorption Isotherms

The adsorption behaviour of Chromium solution with all the geo-materials is modelled using the various sorption isotherms such as Linear, Langmuir and Freundlich isotherm parameters are presented in Table 4.8. From this table, it is found that, Freundlich isotherm model is best fitted for CH and Langmuir isotherm for CI soil.

Table 4.8 Adsorption isotherm coefficients values for geo-materials

[For different pH values with varying EDTA concentration and initial concentrations of Chromium from multi heavy metal solution]

pH 2									
Material	EDTA Conc (milli Molar)	K_d	K_f	n	K_l	q_m	R^2		
							Linear	Freundlich	Langmuir
Black Cotton soil (CH)	0	0.0390	0.4345	18.3117	0.2152	0.7069	0.9111	0.9475	0.9830
	0.1	0.0674	0.3445	1.1006	0.0237	3.5286	0.9966	0.9983	0.9995
	0.5	0.0647	0.3201	1.0443	0.0097	7.3746	0.9993	0.9997	0.9999
	1	0.0523	0.3321	1.1816	0.0445	1.7120	0.9980	0.9997	0.9996
Red earth (CI)	0	0.0221	0.3652	2.0068	0.2670	0.4041	0.9838	0.9448	0.8967
	0.1	0.0310	0.2680	1.1673	0.0271	1.6189	0.9973	0.9993	0.9998
	0.5	0.0271	0.3918	2.0284	0.3059	0.4410	0.9795	0.9562	0.9270
	1	0.0300	0.4453	2.0450	0.2289	0.6760	0.8360	0.9076	0.9700
pH 7									
Material	EDTA Conc (milli Molar)	K_d	K_f	n	K_l	q_m	R^2		
							Linear	Freundlich	Langmuir
Black Cotton soil (CH)	0	0.0177	0.0992	0.7188	0.0257	0.3364	0.9710	0.9813	0.9906
	0.1	0.0152	0.1927	1.1203	0.0102	1.9198	0.9920	0.9955	0.9982
	0.5	0.0133	0.1988	1.1969	0.0186	1.0693	0.9911	0.9961	0.9991
	1	0.0120	0.1825	1.1623	0.0157	1.0749	0.9962	0.9990	0.9998
Red earth (CI)	0	0.0063	0.1480	1.2067	0.0155	0.6210	0.9899	0.9962	0.9990
	0.1	0.0032	0.1941	1.9186	0.0729	0.1841	0.9698	0.9926	0.9967
	0.5	0.0032	0.1585	1.5630	0.0369	0.2330	0.9340	0.9688	0.9903
	1	0.0024	0.1194	1.3879	0.0253	0.1950	0.9830	0.9939	0.9988

The adsorption isotherm plot for CH soil is shown in Fig 4.39. From this figure, the value of the Freundlich isotherm constant (Kf), obtained from the best fit equation is 0.2285 L/g.

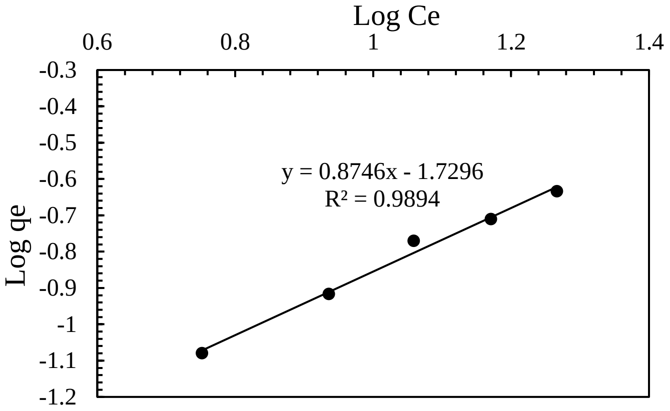


Fig. 4. 39 Freundlich isotherm for adsorption of Chromium by CH soil at pH 7

The Langmuir isotherm model which is best fitted for CI soil is shown in Fig 4.40 The adsorption of chromium by the CI soil happened by forming covalent bonds. The value of the maximum amount of metal ions required to form a monolayer (qm) is calculated as 0.1950 mg/g and the Langmuir coefficient (Kl) is 0.0253 l/g

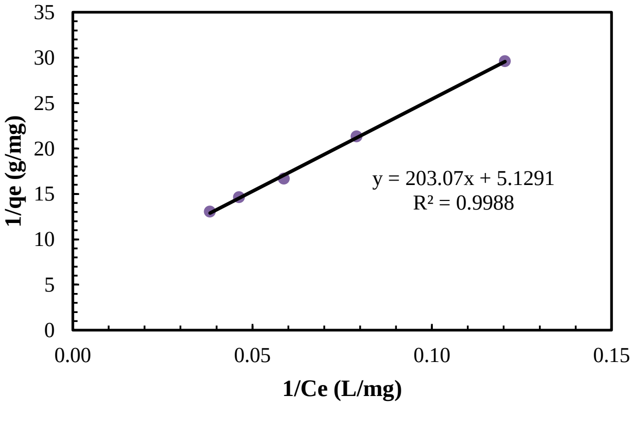


Fig.4.40 Langmuir isotherm for adsorption of Chromium by CI soil at pH 7

4.2.6 Inference from the sorption experiments

1. The adsorption of heavy metals such as Pb, Ni and Cd is increasing with increase in the pH of the solution. Whereas for Cr the percentage adsorption is decreasing with increase in the pH of the solution. The amount of metal ion adsorption decreases with the increase in the initial concentration of the heavy metal solution due to the insufficient adsorption sites.

2. The adsorption isotherms of tested soils are obtained from the test and they appear to be non-linear shape of two physical models which describes a quantitative relationship between the experimental data and batch test, the Freundlich model is fits better to the experimental data than the Langmuir model, based on the regression coefficient.
3. With the presence of EDTA in the solution the percentage adsorption is decreasing with increasing pH of the solution for both CH and CI soils. With the presence of EDTA in the solution, CH soil has good adsorption capacity for Nickel and Cadmium and CI soil having good adsorption capacity towards Lead and Chromium.
4. Under the multi heavy metal interaction with organic chemical presence CH soil is showing good percentage adsorption for Cadmium and Chromium and CI soil having good adsorption capacity for Nickel and Lead. Based on the above test results it is found that both CH and CI soil are having good adsorption affinity for different types of heavy metals.

4.3. Heavy Metal Diffusion through Soils under the Influence of Organic Ligands

4.3.1 General

The Batch Sorption experiments were commonly employed to determine sorption characteristics of soils as these experiments are simple and easy to conduct. However, batch Sorption experiments fail to simulate the realistic soil – heavy metal interaction effectively. With this in view, laboratory column flow through experiments were planned and conducted to observe the diffusion of heavy metals through the soil. The diffusion is a contaminant migration process through the soil media from higher concentration region to lower concentration region. Diffusion is one of the dominant transport phenomenon of contaminants through compacted clay liner (Shackelford 1989). The column methods are generally used to study the contaminant transport through the soil (Freeze and Cherry, 1979; Karl and Kurt, 1998).

This section mainly deals with the breakthrough characteristics of CH and CI soils that are obtained for heavy metals (Lead, Nickel, Cadmium and Chromium) with and without organic chemical (EDTA) through column experiments. The column studies were conducted for least sorption conditions observed from batch experiments. For Lead, Nickel and Cadmium, a pH value of 2 is maintained and for chromium pH value of 7 is maintained for single heavy metal interaction. In case of multi heavy metal interaction, pH values of 2 and 7 are maintained.

The required concentration of heavy metal was prepared from the 1000 mg/L stock solution for each heavy metal (Pb (II), Ni (II), Cd (II) and Cr (VI)). The required concentration of 30 mg/L was maintained in all the column experiments. This is because of the fact that, the maximum concentration of metal ions observed in the municipal solid waste leachate is 30 mg/L. After constructing the soil columns of both CH soil and CI soil in the hollow cylinders separately, saturation was done by filling the vacant portion with distilled water and allowing it to flow through the soil columns up-to a quantity of 3 to 4 number of pore volumes, the remaining water was taken out from each cylinder and in place of it, each heavy metal solution of 30mg/L concentration was added. The heavy metal transported through the soil columns was collected and analysed for effluent concentration. Based on the concentration of effluent, the breakthrough curves are plotted where a new dimensionless parameter "relative concentration(C/C_o)" has been introduced in the ordinate. In the parameter, C refers to the effluent concentration collected at different times and C_o denotes the initial concentration of incoming heavy metal solution.

4.3.2 Lead (II) solution as an influent:

The breakthrough curves are shown in Fig 4.41 respectively for both CH and CI soil when Pb solution was used as an influent solution for the pH value of 2. As can be observed from these figures that, for CH soil the time to achieve breakthrough time is 3600 hr and for CI soil it was observed to be 1300 hr. The time required to achieve breakthrough time for CH soil in case of lead solution is about 2.7 times more than that of CI soil.

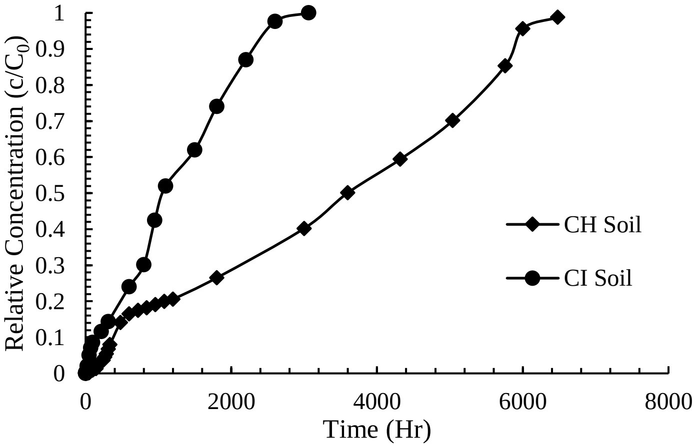


Fig. 4.41 Breakthrough curve of Pb (II) for CH and CI soil @pH 2

From these figures it can also be observed that there is a delayed breakthrough found for CH soil compared to CI soil.

4.3.3 Nickel solution as an influent:

Breakthrough curve is drawn based on the effluent concentration obtained from column experiment conducted with nickel metal solution with respect to time for both CH and CI soils. Fig. 4.42 shows these curves considering only Ni solution as an effluent solution at pH value of 2.

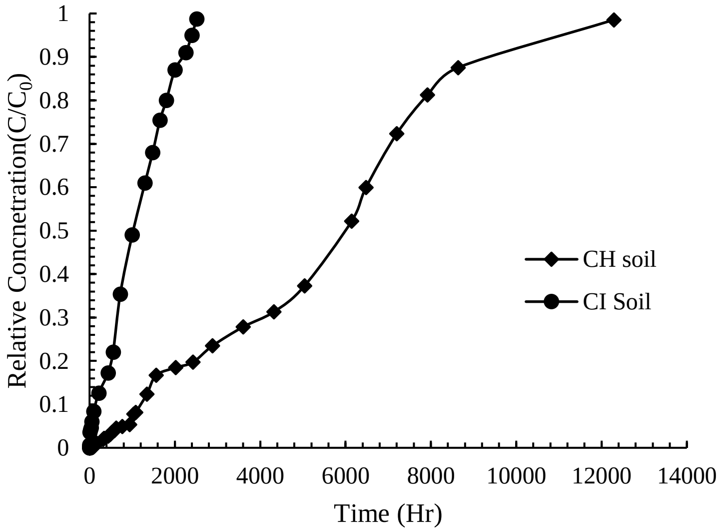


Fig. 4.42 Breakthrough curve of Ni (II) for CH and CI soil @ pH 2

It can be observed from the above curves that the breakthrough time required for achieving 50% breakthrough of Ni in case of CH soil is 6000 hr and for CI soil it is observed to be 1200 hr. the time for CH soil is around 5 times higher than that of CI soil, this is because of the fact that CH soil exhibit higher cation exchange capacity when compared to that of CI soil, which hinders the migration of contaminants through the soil column by means of its higher adsorption capacity.

4.3.4 Cadmium (II) solution as an influent:

The breakthrough curves of cadmium at a pH value of 2 for both CH and CI soils are shown in Fig. 4.43 respectively. From these figures, it is observed that, the breakthrough patterns were followed same as the other heavy metals (Pb and Ni). For CH soil the time to achieve breakthrough time is 3200 hr and for CI soil it was observed to be 600 hr indicating that the breakthrough time for CH soil is around 5 times more when compared to the CI soil.

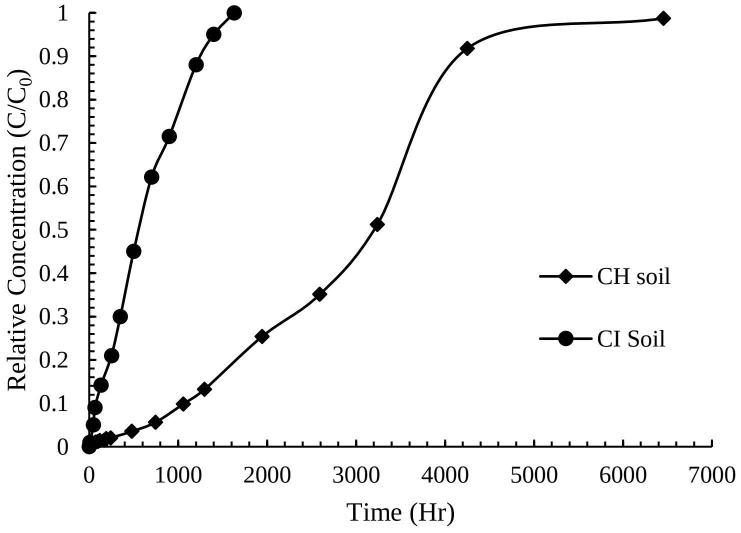


Fig. 4.43 Breakthrough curve of Cd (II) for CH and CI soil @ pH 2

4.3.5 Chromium solution as an influent

Unlike other three heavy metals, pH considered for the hexavalent chromium ion was 7 which is nearer to basic condition. The breakthrough curves obtained for both CH and CI soil and the corresponding figures are shown in Fig. 4.44. Time required to achieve 50% breakthrough for CI soil 1.6 times more when compared to the CH soil.

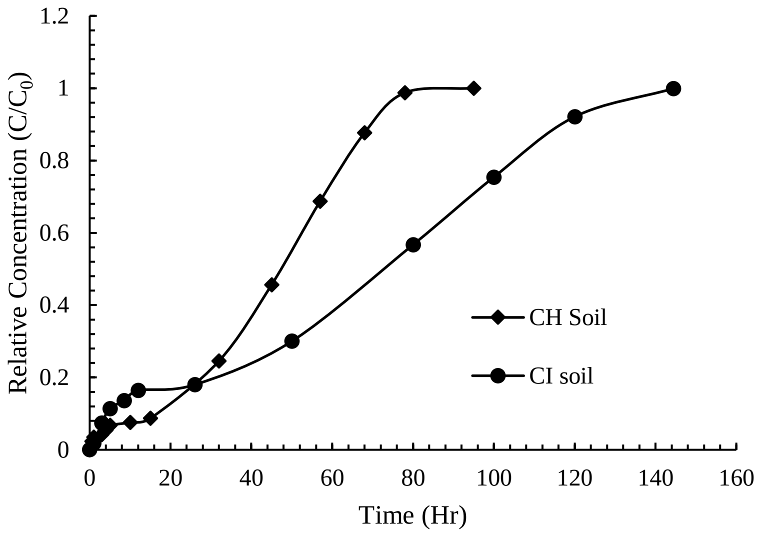


Fig. 4.44 Breakthrough curve of Cr (VI) for CH and CI soil @ pH 7

The Fig 4.44 shows the higher mobility of Cr (VI) at pH 7 when compared to other metals (Pb, Ni and Cd). By considering all the above results shown in the term of breakthrough curves for all four heavy metals separately present in a single metal system, it can be finally concluded that at pH 2, the increasing order of mobility for four heavy metals chosen for study can be expressed as Cr> Cd> Pb> Ni for CH and CI soil Cr> Cd> Ni> Pb. At lower pH, electronegativity of the metal ion plays an important role in getting adsorbed by soil active sites. Higher the electronegativity of metal, the greater chance to get adsorbed by the soil through easier dissociation of H^+ ion from the functional groups of the soil minerals (Gomes et.al. 2001). At pH 2, the adsorption of Cd is more affected by the protonation of silica and alumina group i.e. Si - O^- and Al - O^- respectively (Abollino et.al. 2003) due to its lower charge density. On the other hand, the adsorption of Cr (VI) decreases with increase in pH. This is due to increase of negative charge in the soil solid phase (Sherene, 2010). The greater mobility in case of Cr (VI) for both soils is expected to be enhanced by probable decrease in the plastic limit of the soil. Hence, it increases the hydraulic conductivity of the tested soils due to decrease in the thickness of diffused double layer (Zhang and Huang 2016).

4.3.6 Multi Heavy Metals as an Influent:

In case of composite metal system, all the four heavy metals (Pb, Ni, Cd and Cr) have been considered together for the study. From each stock solution (concentration: 1000 mg/L) prepared previously for each heavy metal, 30 mg/L of each heavy metal was taken for preparing the composite heavy metal solution. The pH of the final solution was set at 2 by adding 0.1N HNO_3. The composite solution was then transferred to prepared column of CH and CI soil separately for further study. The breakthrough curves are plotted based on the results obtained from column tests performed on both CH and CI soils. The breakthrough curves along with time required for 50% breakthrough are presented in Fig 4.45 and 4.46 for both CH and CI soil.

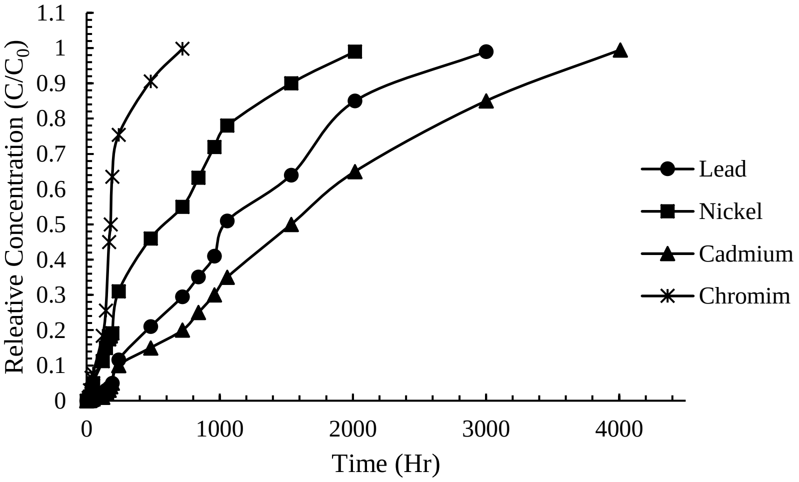


Fig 4.45 Breakthrough curve for Composite heavy metal system for CH soil @pH 2

The results show that the time required for achieving 50% breakthrough for each heavy metal is very less in case of multi metal system when compared to single metal system.

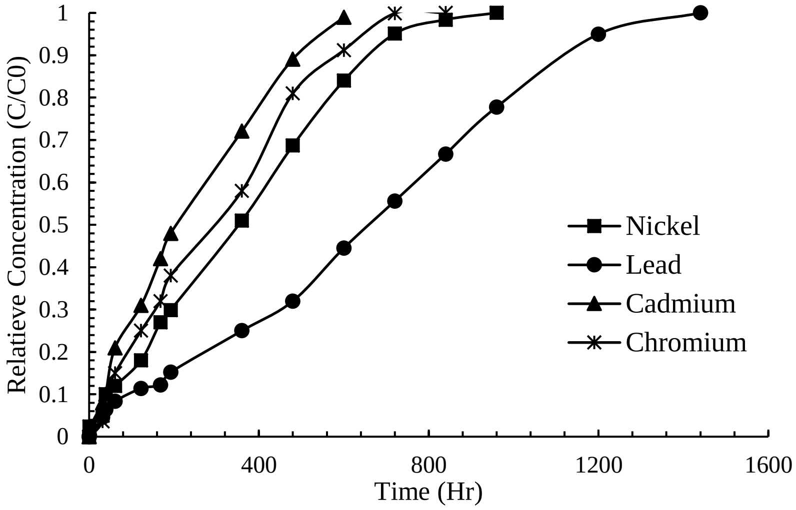


Fig. 4.46 Breakthrough curve for Composite heavy metal system for CI soil @pH 2

Although it has been observed that the time required to accomplish 50% breakthrough for multi metal system is more for CH soil than CI soil, the required time is less for multi metal system when compared to single heavy metal system for both CH and CI soils. The reduction in breakthrough time can be specially observed for three bivalent metal ions i.e. Ni (II), Cd (II) and Pb (II) except for Cr (VI), where the breakthrough time increases when compared to the result obtained in case of single metal system. The probable cause for the reduction in adsorption for three heavy metals can be stated by considering the competitive effect between the metals with hydrogen ion (H^+) for occupying adsorption sites of the soil. At lower pH, due to abundance of hydrogen ion (H^+) presence in the soil solution the competition occurs between H^+ ions and the other three bivalent metals for occupying adsorption sites (Yong and Phadungchewit, 1993). As a result, the mobility of three bivalent ions (Pb, Ni and Cd) are increasing resulting in quick breakthrough of oxy-anionic in case of multi heavy metal system. But in case of Cr (VI) which is present in form, the reverse behaviour can be explained by the transformation of Cr (VI) ion into Cr (III) ion in presence of H^+ ion (Adejo et al 2014).

The equilibrium equation for the yielding of trivalent chromium ion at lower pH is given below (Li et. al 2009):

$$Cr_2O_7^{2-}\,(aq) + 14H^+\,(aq) + 6e^- \longrightarrow 2Cr^{3+}\,(aq) + 7H_2O \qquad (4.1)$$

The newly formed Cr (III) ion can be retained by the soil through cation exchange process due to its higher positive charge ultimately resulting in greater adsorption of Cr (VI) present in multi metal system at pH 2.

4.3.7 Heavy Metal Breakthrough under the Influence of Organic Ligand EDTA

The next stage of the study was accomplished by introducing EDTA in the single heavy metal system. A stock solution of EDTA with a concentration of 0.5M was prepared and kept in a reagent bottle of 1 litre capacity. To find the effect of synthetic organic compound i.e. EDTA on the mobility of heavy metals passing through different soils, a certain concentration of 1 mM of EDTA has been considered for all experiments due to the reason that, the adsorption of heavy metals by the CH and CI soil is less at 1 mM EDTA concentration. By taking calculated volume of EDTA from the stock solution, 1mM of EDTA was prepared and added to each heavy metal influent solution where the concentration of each metal was 30 mg/L. The breakthrough curves obtained based on the experimental data for each of the heavy metal in the presence of EDTA are represented in the following sub-sections. All the curves are drawn between relative concentrations(C/C_o) versus the time of progression starting from the initiation of each experiment. In the relative concentration term, 'C' refers to the effluent concentration collected at specific time of ongoing experiment and 'C_o' denotes the initial influent concentration which is considered here as 30 mg/L.

4.3.7.1 Lead (II) and EDTA as an influent:

The breakthrough curve for Lead (II) in the presence of EDTA is represented in this context. The time required for attaining half breakthrough is also approximately mentioned by sorting it out from the breakthrough curve. The breakthrough curves for both CH and CI soil are shown in Fig 4.47.

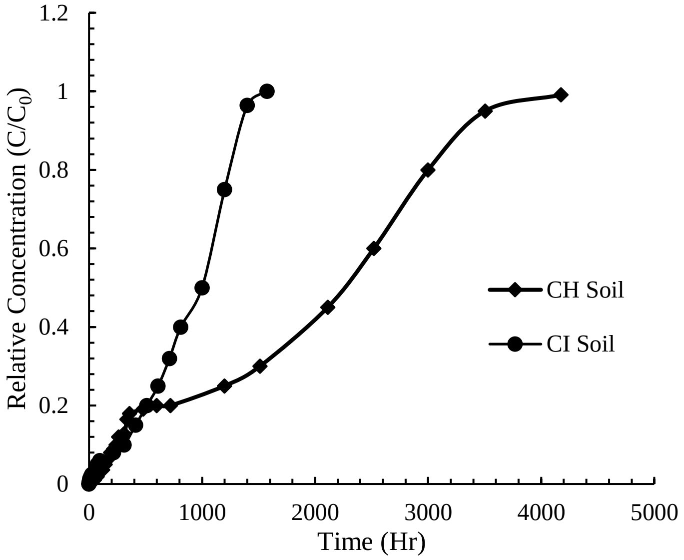


Fig. 4.47 Breakthrough curve for Pb (II) in presence of EDTA for CH and CI soil @pH 2

The same phenomenon of increasing mobility has been observed in case of Pb (II) in the presence of EDTA. The effect of EDTA complexation with metal ion can be presumed based on the obtained breakthrough data. The time required to achieve 50% breakthrough is 1.35 times more for CH soil when compared to the CI soil.

4.3.7.2 Nickel (II) and EDTA as an influent

Based on the effluent concentration obtained, breakthrough curve is plotted with respect to time calculated from the starting of experiment to the point of collection expressed in hours for both CH and CI soil. The breakthrough curves are shown in Fig 4.48 for both CH and CI soils considering only Ni solution in the presence of EDTA as an incoming synthetic pollutant.

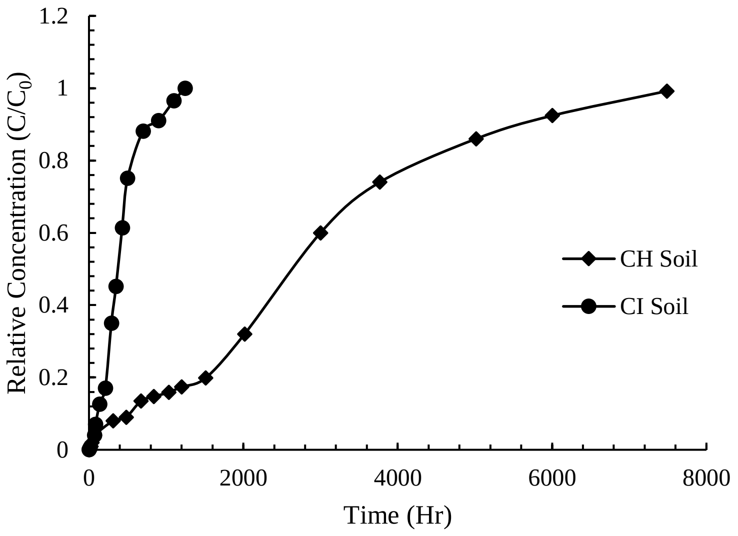


Fig. 4.48 Breakthrough curve for Ni (II) in presence of EDTA for CH and Ci soil @pH 2

The observations reveal that in presence of EDTA, the time for achieving 50% breakthrough is getting reduced compared to the absence of EDTA in single metal system. It is due to the fact that the chelating ability of EDTA increase the solubility of Ni by forming complex product (Kim et.al. 2003). From above shown figures, it is observed that, to achieve 50% breakthrough time is 6.5 times more for CH soil when compared to the CI soil.

4.3.7.3 Cadmium (II) and EDTA as an influent

In presence of EDTA, the mobility of Cd (II) can be depicted from the breakthrough curve plotted on the basis of the results obtained from column test. The time for acquiring 50 % breakthrough along with the curves are shown in Fig. 4.49 for both CH and CI soil.

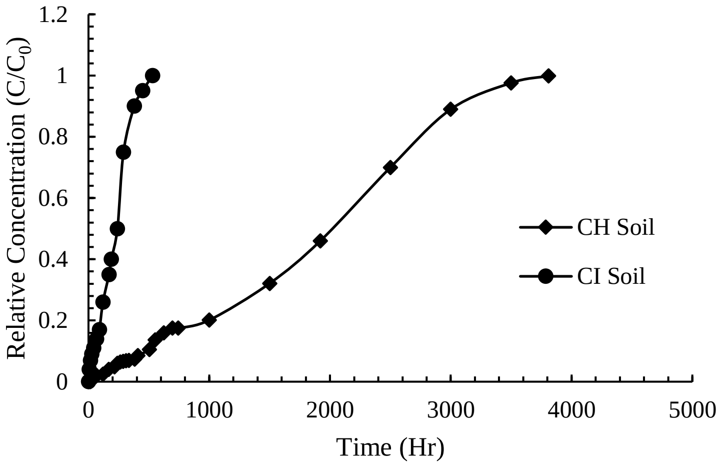


Fig. 4. 49 Breakthrough curve for Cd (II) in presence of EDTA for CH and CI soil @pH 2

Cd (II) is also not an exception case from the other two bivalent metal ions (Pb and Ni). But the reduction in time for achieving half breakthrough due to increase in mobility of metal ion through the formation of soluble metal- EDTA complex product is less pronounced in case of Cd (II) compared to Ni (II) and Pb (II). From above shown figures, it is observed that, the time required for 50% breakthrough is 8.5 times more for CH soil when compared to the CI soil. In the presence of EDTA, the increasing order of mobility are obtained as: Cr> Pb> Cd> Ni for CH soil and Cr> Cd> Ni> Pb for CI soil respectively

The observed behaviour of the three bivalent metals Pb, Ni and Cd can be explained by employing of complexation constant which determines the stability of metal- EDTA complex product. The complexation constant can be compared to the equilibrium rate constant of the complexation reaction. The higher the value of complexation constant, the greater will be the chance of forming more stable metal- EDTA complex product. The ascending order of the stability constant in case of three bivalent heavy metal ions is as follow: Cd (II) < Pb (II) < Ni (II) (Nastaran and Alain 2009).

4.3.7.4 Chromium (VI) and EDTA as an influent

The breakthrough curves for hexavalent chromium solution in the presence of EDTA are shown in Fig 4.50 at pH 7 has been considered to study the transport of Cr (VI) through soils under the influence of EDTA.

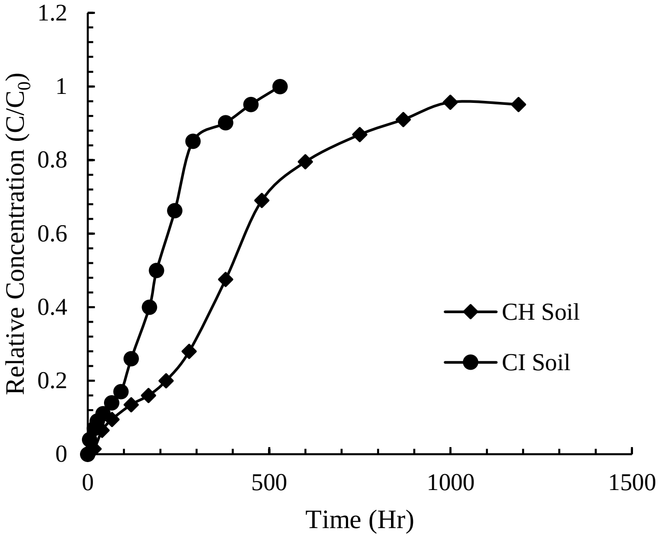


Fig. 4.50 Breakthrough curve for Cr (VI) in presence of EDTA for CH and CI soil @pH 7

It was observed that at pH 7, the mobility of Cr (VI) is decreased with the presence of EDTA in case of both CH and CI soil. From above shown figures, it is observed that, the breakthrough time to achieve 50% breakthrough is 2.1 times more for CI soil when compared to the CH soil. The possible reason can be given on the basis of size of metal ion, which states that smaller the metal ion, the greater chance to form stable complexes with EDTA. The inverse relationship exists between the complexation capacity and the size of metal ion as a result the mobility is decreased.

4.3.7.5 Multi heavy metal system and EDTA as an influent

Previously the multi metal column study was performed without considering the effect of EDTA. With the idea to understand the breakthrough characteristics of four heavy metals present in a composite metal system under the influence of EDTA has been taken granted for study. The column tests were performed on composite heavy metal system in the presence of EDTA at pH of 7 for both soils (CH and CI) for knowing the breakthrough behaviour of heavy metals at a wider range of pH considered. All the results obtained from each test are represented in the form of breakthrough curves which are plotted against the time calculated from the initiation of the test to the point of collection of effluents.

4.3.7.5.1 Composite heavy metals with EDTA at pH 7

On the basis of the experimental data related to the effluent concentration, breakthrough curves are plotted and represented in the context for the case of multi heavy metal system in the presence of EDTA for both CH and CI soils. The initial pH of the influent has been chosen as 7 and the breakthrough curves are shown in Fig 4.51 and Fig 4.52.

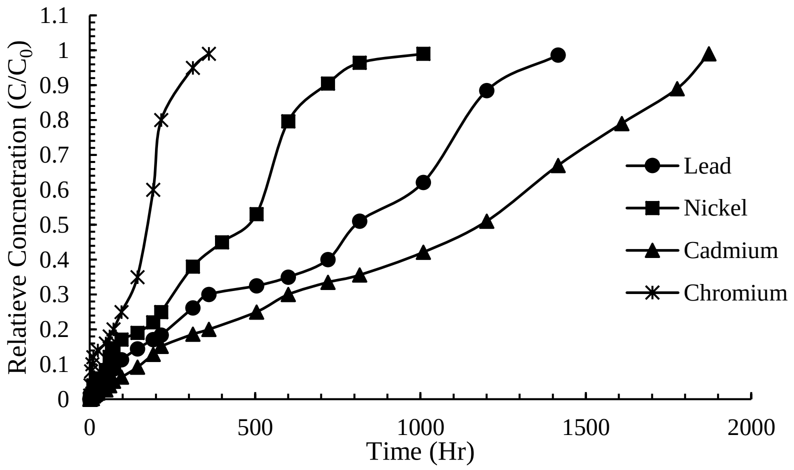


Fig. 4.51 Breakthrough curve for Composite heavy metal in the presence of EDTA for CH soil @ pH 7

At the end, comparative analysis has been performed based on the results obtained at two different pH values with supporting expectable reasons which more or less conform to the explanations provided by the researchers.

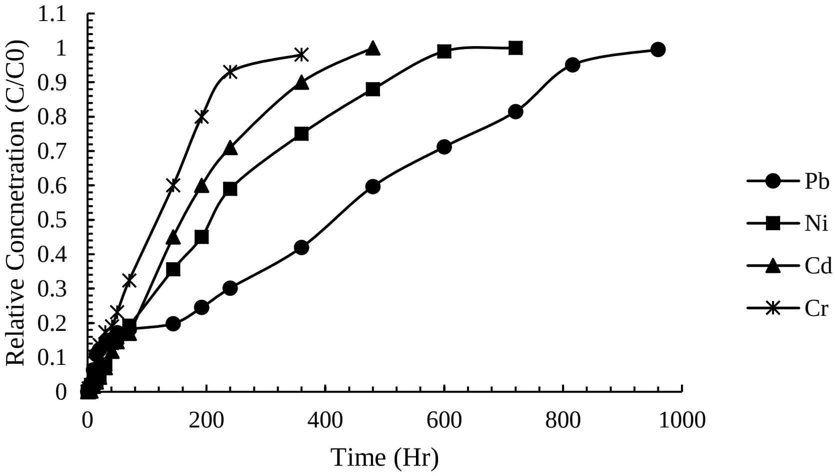


Fig. 4.52 Breakthrough curve for Composite heavy metal in the presence of EDTA for CI soil @ pH 7

It has been observed that from the Fig 4.51 and 4.52 it can be observed that, time to achieve 50% breakthrough time CH soil is more when compared to CI soil and the break through time is reduced significantly in the presence of EDTA at pH 7 condition when compared with Multi heavy metal at pH 2 condition. This is probably due to the formation of metal EDTA complexes that exist in the solution in the form of negative charged molecule (Bradl 2004). As a result of it, the negative charged soil surface is competing with the metal EDTA complex leads to the early migration of heavy metals through the soil.

4.3.8 Diffusion Coefficient (D)

The diffusion co-efficient (D) is calculated on the basis of T_{50} (time required to achieve 50 % breakthrough) obtained from breakthrough curve for the corresponding case (Ramakrishna et.al. 2011). By using advection-diffusion equation (Eq.3.7) and following table 3.4 of complementary error function, effective diffusion coefficients are calculated and expressed in m^2/sec. The parameter D is having greater significance in designing and checking the effectiveness of the landfill liner. The value of diffusion coefficient (D) is calculated based on half breakthrough time for each case of soil column considered in this study and the results are discussed in the following sections.

4.3.8.1 Diffusion coefficient (D) of CH Soil

The Diffusion coefficient (D) calculated for all cases including with EDTA in for both single and multi-metal system are given in the following tables 4.9 and 4.10 for CH soil. The table 4.9 presents the diffusion coefficients of heavy metals which are considered for this study under single metal interaction.

Table 4.9. Diffusion coefficient of Single metal system for CH soil

S.No	**pH**	**Heavy Metal**	**Effective Diffusion Coefficient (D*) (m^2/sec)**
1	2	Lead (II)	8.99×10^{-11}
2	2	Nickel (II)	2.897×10^{-11}
3	2	Cadmium (II)	9.56×10^{-11}
4	7	Chromium (VI)	4.78×10^{-8}

From the above table it is observed that, the diffusion of heavy metal Pb, Ni and Cd have less diffusion coefficient when compared to the chromium metal. This is mainly due to the fact that, as Pb, Ni and Cd is present in the form of metal cations, these metal cations adsorbed by the soil as a result the diffusion is decreased. In case of the chromium metal ion the diffusion coefficient is more when compared to the other heavy metals. This is mainly due to the fact that, the Cr is in the form of $K_2Cr_2O_7^-$ which is not adsorbed on the surface of the soil and as a result, the diffusion is increasing through the CH soil.

In order to consider the multi metal interaction effect on diffusion of contaminants, the column test was conducted with the combination of all heavy metals present in the solution. The diffusion coefficients obtained from the breakthrough curves are presented in the table 4.10.

Table 4.10 Diffusion coefficient for Multi-metal system @pH 2

pH	**Heavy Metal**	**Effective Diffusion Coefficient (D*) (m^2/sec)**
2	Lead (II)	5.1×10^{-10}
	Nickel (II)	5.78×10^{-10}
	Cadmium (II)	$4.173 \text{ x } 10^{-10}$
	Chromium (VI)	2.15×10^{-8}

From the above table 4.10, it is observed that, the diffusion of heavy metals Pb, Ni and Cd have increased slightly from the range of 10^{-11} to 10^{-10} m^2/sec. This is because of the competition between the metal ions present in the solution to get adsorbed by the soil. In case of Cr, the diffusion is reduced slightly when compared to single metal interaction. This is because of the fact that, the Cr will form complexes with other heavy metals when leading to decrease in the migration of diffusion. Under the multi metal interaction, the diffusion is increased by 5.6, 19 and 4.3 times respectively for Pb, Ni and Cd when compared to the diffusion of heavy metals under single metal interaction. Under multi metal interaction, the diffusion of Chromium metal decreased by 76% when compared to the single metal interaction.

In order to study the heavy metal diffusion under the influence of organic chemical, the EDTA is used in the column studies, and the diffusion coefficients obtained from these column studies are presented in the table 4.11.

Table 4.11 Diffusion coefficient for Single metal system with EDTA

S. No	**pH**	**Heavy Metal**	**Effective Diffusion Coefficient (D*) (m^2/sec)**
1	2	Lead (II)	1.668×10^{-10}
2	2	Nickel (II)	2.1×10^{-10}
3	2	Cadmium (II)	3.5×10^{-10}
4	7	Chromium (VI)	1.195×10^{-9}

From the above table 4.11, it is observed that, with the presence of EDTA in the heavy metal solution, the diffusion of metals Pb, Ni and Cd is increased and the diffusion of Cr with the presence of EDTA is decreased when compared to the EDTA absence in heavy metal solution. The increase in the diffusion of heavy metals (Pb, Ni and Cd) through the soil is mainly because of the formation of Metal EDTA complex and these metal EDTA complex will carry a negative charge which is repelled by the functional groups present in the soil. For chromium the decrease in the diffusion is due to the conversion of Cr^{6+} to Cr^{3+} with the presence of organic chemical EDTA in the solution and it gets adsorbed on the surface of the soil and as a result the diffusion is decreased. The table 4.12 presents the diffusion coefficients of heavy metals under multiple interaction with the presence of EDTA in the solution.

Table 4.12 Diffusion coefficient for Multi-metal system with EDTA @pH 7

pH	**Heavy Metal**	**Effective Diffusion Coefficient (D*) (m^2/sec)**
7	Lead (II)	6.483×10^{-10}
	Nickel (II)	7.174×10^{-10}
	Cadmium (II)	5.17×10^{-10}
	Chromium (VI)	9.795×10^{-9}

From the table 4.12, it is observed that, in the presence of EDTA, under multi metal interaction, the diffusion of metal ions are further increased. The increase in the diffusion is by 3.8, 3.4 and 1.47 times respectively for Pb, Ni and Cd when compared with the single heavy metal interaction with the presence of EDTA. This is mainly due to the fact that, the EDTA in the solution coordinated with all the metal ions and leads to formation of metal EDTA complex. These metal complexes are carrying a negative charge which will get repelled by the surface functional groups of the soil and as result of this the diffusion of heavy metals are increased. The increase in the diffusion under multi metal interaction along with the EDTA present in the solution is mainly due to the combined effect of EDTA metal complex formation and competition between the metals. The increase in diffusion is observed to be 1.2, 1.24, 1.23 and 4.5 times more respectively for Pb, Ni, Cd and Cr.

4.3.8.2 Diffusion coefficient (D) for CI soil

The diffusion coefficient (D) for CI soil calculated for the conditions of with and without the presence of EDTA in both single and multi-metal system are given in the following tables.

The diffusion coefficients of heavy metals through the CI soil is presented in the table 4.13. From this table 4.13, it is observed that the diffusion of heavy metals are increased through the CI soil when compared to the CH soil. This is mainly due to the fact that, CI soil is having more permeability when compared to the CH and when heavy metal solution passes through the soil column there is a less sorption sites are available to sorb the heavy metal on the surface of the soil.

Table 4.13. Diffusion coefficient for Single metal system

S. No	**pH**	**Heavy Metal**	**Effective Diffusion Coefficient (D*) (m^2/sec)**
1	2	Lead (II)	1.96×10^{-10}
2	2	Nickel (II)	2.2×10^{-10}
3	2	Cadmium (II)	1.3×10^{-9}
4	7	Chromium (VI)	7.17×10^{-8}

From the above table it is observed that, the diffusion of heavy metals (Pb, Ni and Cd) got decreased when compared to the Chromium metal ion. This is mainly due to the fact that the heavy metal cations have more affinity to get adsorbed on to the surface of the soil. For chromium metal ion, the diffusion is increased when compared to the other heavy metals (Pb, Ni and Cd). This is because, as Cr is in anionic from, it gets repelled by the surface of the soil.

In order to consider the multi metal interaction, the column tests were conducted on CI soil to study the combined influence of heavy metals on diffusion of each heavy metals through the soils. The results obtained from these test are presented in table 4.14.

Table 4.14. Diffusion coefficient for Multi-metal system @pH 2

pH	**Heavy Metal**	**Effective Diffusion Coefficient (D*) (m^2/sec)**
2	Lead (II)	7.158×10^{-10}
	Nickel (II)	1.63×10^{-9}
	Cadmium (II)	1.877×10^{-9}
	Chromium (VI)	1.234×10^{-9}

From the above table 4.14, it is observed that, the diffusion of heavy metals have increased. This is because of the competition between the metal ions present in the solution to get adsorbed by the soil. In case of Cr the diffusion is reduced when compared to single metal interaction. This is because of the fact that, the Cr will form complexes with other heavy metals which leads to decrease in the migration of diffusion. The increase in diffusion of heavy metals is by 3.6, 7.4 and 1.3 times respectively for Pb, Ni and Cd. For chromium the diffusion in decreased by 86% when compared to the single metal interaction.

In order to study the heavy metal diffusion under the influence of organic chemical, the EDTA used in the column studies. The diffusion coefficients obtained from these column studies are presented in the table 4.15.

Table 4.15. Diffusion coefficient for Single metal system with EDTA

S. No	**pH**	**Heavy Metal**	**Effective Diffusion Coefficient (D*) (m^2/sec)**
1	2	Lead (II)	3.244×10^{-10}
2	2	Nickel (II)	4×10^{-10}
3	2	Cadmium (II)	2.5×10^{-9}
4	7	Chromium (VI)	2.48×10^{-9}

The diffusion coefficient (D) mentioned in both Table 4.14 and 4.15 for CI soil, it is observed that, with the presence of EDTA in the single metal system, the mobility for Lead, Nickel and Cadmium increased by 1.65, 1.81, 2.96 times and whereas for chromium the diffusion is decreased. This is mainly due to the fact that under the presence of EDTA, the chromium metal ion is coordinated with the EDTA and forms the covalent bonds as a result this the diffusion is decreased.

The table 4.16 presents the diffusion coefficients of heavy metals under multiple interaction with the presence of EDTA in the solution.

Table 4.16. Diffusion coefficient for Multi-metal system with EDTA @pH 7

pH	**Heavy Metal**	**Effective Diffusion Coefficient (D*) (m^2/sec)**
7	Lead (II)	1.235×10^{-9}
	Nickel (II)	2.2×10^{-9}
	Cadmium (II)	3.5×10^{-9}
	Chromium (VI)	7.17×10^{-9}

From the above table, it is observed that diffusion of Pb, Ni, Cd and Cr through CI soil is increased by 3.8, 5.5, 1.4 times when compared to single heavy metal interaction with the presence of EDTA. And the diffusion also increased by 1.72, 1.34 and 1.9 times respectively for Pb, Ni and Cd when compared to the heavy metal diffusion through CI soil without the presence of EDTA. This is mainly due to the fact that, the combined influence of metal EDTA complex formation and competition between metal ions present in the soil.

4.3.9 Inference from the Study:

In this section, the breakthrough characteristics of CH and CI soils are obtained for heavy metals (Lead, Nickel, Ccadmium and Chromium) with and without organic chemical (EDTA) by conducting the column experiments. The conclusions obtained from these experiments are as follows.

1. In single metal system, Chromium shows more diffusion when compared with other heavy metals (Lead, Nickell, and Cadmium). As chromium exists in anionic ($Cr_2O_7^-$) form, it was repelled by negatively charged soil surface; as a result the mobility of Cr is increased.
2. In presence of EDTA, the diffusion of contaminants through soil is increased due to soluble metal-EDTA complex formation. At pH 2, the average diffusion of heavy metals (Pb, Ni, and Cd) are in the order of 3.41×10^{-10} m^2/sec for CH soil and 5.72

x 10^{-9} m^2/sec for CI soil. Whereas the diffusion of chromium is 1.195 x 10^{-9} m^2/sec for CH soil and for CI soil the diffusion is observed to be 2.48 x 10^{-9} m^2/sec.

3. In multi metal interaction, diffusion of heavy metals through the soil is more when compared to the single metal interaction. This can be explained by the competitive effect between the heavy metal ions, the average diffusion of heavy metals (Pb, Ni, and Cd) are in the order of 5.01 x 10^{-10} m^2/sec for CH soil and 1.38 x 10^{-9} m^2/sec for CI soil. Whereas the diffusion of chromium is 2.15 x 10^{-9} m^2/sec for CH soil and for CI soil the diffusion is observed 1.234 x 10^{-10} m^2/sec.
4. In presence of EDTA, at pH 7, the diffusion of heavy metals further increased when compared to pH 2 without EDTA. The diffusion of heavy metals is in the order of 4.377 x 10^{-9} m^2/sec for CH soil and 3.526 x 10^{-9} m^2/sec for CI soil. This is probably due to the formation of metal EDTA complexes that exists in the solution in the form of negatively charged complex and it get repelled by negatively charged soil as a result of this mobility of heavy metals through the soil increases.

4.4 CRACK INTENSITY FACTOR AND PERMEABILITY RATIO OF SOIL

The crack intensity factor (CIF) was introduced (Miller et al, 1998) as a descriptor for determining the extent of surface cracking. In the present study, an attempt is made to understand the influence of leachate on the cracking behaviour of soils from the breakthrough time observed from column flow experiments. The soil samples were tested for the crack intensity factor and its hydraulic conductivity by using water and heavy metal solution under different environmental conditions (pH 2 and 7). Further, to understand the influence of cracks of soils on the performance of clay liners, the permeability ratio (Kr) which is defined as the ratio of cracked permeability to the un-cracked permeability of clay bed is considered. This parameter is used to explain the two key criteria of good barrier: low cracking potential and high self-healing potential. For testing purpose, the soils were compacted at three different water contents (dry side of optimum, optimum and wet side of optimum). Then the soil samples were dried in the oven at a temperature of 65 degrees centigrade (Zhou and Rowe 2005) and the surface images were captured with the help of a high resolution camera during the process of wetting and drying and these images were converted to gray-scale. The gray scale images were already shown in Figures 3 (10) and 3 (11) of chapter 3.

4.4.1 Variation of crack intensity factor (CIF) of soils with water content:

The crack intensity factor of CH and CI soils obtained for different compaction water contents and with synthetic heavy metal solution (pH 2 and pH 7) are presented in table – 4.17. From this table it is observed that, the CIF is increasing with increasing in compaction water content as well as increasing in number of wetting and drying cycles. For CH soil the CIF value observed to be 2.24, 3.22 and 4.43 respectively for soil compacted at DOMC, OMC and WOMC. And at the end of second drying cycle for the condition of water at pH 7, the increase in CIF value was also observed to be around 1.3 times more when compared to the CIF value at the end of the first drying cycle. For CI soil the CIF value is observed to be 0.43, 0.64 and 2.79 respectively for soil compacted at DOMC, OMC and WOMC. At the end of second drying cycle, the average increase in the CIF was observed to be around 1.3 times more when compared to the CIF value at the end of first drying cycle.

The increase in CIF observed for DOMC and OMC had little variation when compared with soil compacted at WOMC. This is because during the drying process, suction produced in the soil sample may increase the tensile stress. If the increased tensile stress is higher than the tensile strength of the sample it may form cracks in weaker zones (Kodikara et al 2000 and 2004). Therefore, the soil behavior towards cracking depends on the water content, rate of evaporation, humidity and also mineralogy of the soil (Uday and Singh. 2013). Therefore, soil compacted at WOMC showed more crack intensity factor when compared with DOMC and OMC. Here, CH soil showed more crack intensity factor when compared to CI soil during the first drying cycle because of the higher clay content present in the CH soil.

4.4.2 Influence of chemical solution on crack intensity factor (CIF)

Clayey soils are very sensitive towards the aggressive chemical environment and further, concentrated organic chemicals and divalent cations can cause shrinkage cracks in the soil mass (Anderson et al 1985). The crack intensity factor (CIF) of soils was studied by saturating the soil sample with a synthetic heavy metal solution having two different pH conditions such as 2 and 7 after first drying cycle. Table – 4.17 shows the variation of crack intensity factor of a soil after permeating with the synthetic heavy metal solution. From this table the CIF value was increased in case of synthetic heavy metal solution when compared to water.

The average increase in CIF values of CH and CI soils at pH 2 are 1.85 and 3.36 times more when compared to water. CH and CI soils permeated with pH 7 synthetic heavy metal solution, the average increase are CIF values are 1.57 and 2.56 times more when compared to water. The CH and CI soils permeated with pH 2 the observed CIF values are 1.2 and 1.3 times more for CH and CI soil when compared to soil permeated with pH 7 solution. From the above observations, the CIF of soil was more after the soil sample was permeated with synthetic heavy metal solution, which is mainly due to an increase in cation concentration in the synthetic heavy metal solution. This leads to reduction in the interaction between electrical double layers associated with the hydrated clay particle, reducing the repulsive stress and increasing the effective stress (Hettiaratchi et al 1998). This increase in the effective stress can cause the shrinkage of soil sample and this shrinkage of soil sample leads to the cracking of weaker zones in the soil specimen (Kodikara et al, 2004).

Table 4.17 Variation of CIF with different water content and contaminants

Crack Intensity factor for CH Soil									
STAGE	Dry of OWC			OWC			Wet of OWC		
	Water pH 7	MHMS pH-2	MHMS pH-7	Water pH 7	MHMS pH-2	MHMS pH-7	Water pH 7	MHMS pH-2	MHMS pH-7
Compaction	0	0	0	0	0	0	0	0	0
drying	2.24	2.24	2.24	3.22	3.22	3.22	4.43	4.43	4.43
wetting	0.03	0.26	0.18	0.04	0.30	0.28	0.08	0.37	0.29
drying	3.08	5.27	4.61	4.34	7.65	6.42	4.79	9.97	8.31
STAGE	**Crack Intensity factor for CI Soil**								
	Dry of OWC			OWC			Wet of OWC		
	Water pH-7	MHMS pH-2	MHMS pH-7	Water pH-7	MHMS pH-2	MHMS pH-7	Water pH-7	MHMS pH-2	MHMS pH-7
Compaction	0	0	0	0	0	0	0	0	0
Drying	0.43	0.43	0.43	0.64	0.64	0.64	2.79	2.79	2.79
Wetting	0.04	0.20	0.15	0.05	0.23	0.16	0.09	0.28	0.17
Drying	0.63	2.63	1.97	0.78	2.81	2.21	3.68	8.82	6.2

4.4.3 Influence of Heavy Metal Solution on Permeability Ratio (Kr)

Permeability ratio (Kr) of CI and CH soils for the condition of synthetic heavy metal solution are presented in Table – 4.18. From this table, it is observed that permeability of soil is influenced by clay content, plasticity index and the number of wetting and drying cycles. CI soil compacted at optimum water content shows the permeability of cracked and un-cracked soil specimens, as respectively $0.505\text{x}10^{-7}$ to $7.17\ \text{x}10^{-7}$ cm/sec with the permeability ratio as 14.2. The permeability ratio of the soil specimen, when compacted at wet side of optimum water content, was observed to be 15.74 and at dry side of optimum moisture content, the Kr value was observed to be 12.1. For the CH soil, the permeability ratio was 13.87 at WOMC while it is 12.83 at OMC, whereas it is 9.4 at DOMC. The above results indicated that with an increase in water content from the dry side of optimum to the wet side of optimum, the permeability ratio (Kr) was observed to be increased. This is mainly because, soil sample compacted at wet of optimum moisture content permits greater refolding of clods, elimination of large inter-clod voids and preferential re-orientation of clay particles, all which result in lower hydraulic conductivity (Daniel, 1993). Whereas in the case of soil compacted at dry of the optimum condition, the clods are stiff and difficult to remold and the clay particles are flocculated; consequently large inter-clod pores exist as well as a more permeable microstructure may form which results in higher hydraulic conductivity (Boynton and Daniel, 1985).

From Table 4.18, it is observed that permeability ratio of CI was more when compared with CH when permeated with water. And it also shows that, when permeated with synthetic heavy metal solution, having different pH values such as pH 2 and 7, for CI soil Kr was observed to be 14.21and 18.44 when soil compacted at DOMC, at OMC the Kr was 16.8 and 19.78 whereas for WOMC Kr was observed to be 20.81 and 26.52. While the Kr values for CH soil at these pH values are 24.51 and 26.52 for soil compacted at DOMC, for OMC it was observed to be 28.8 and 28.84 whereas soil compacted at WOMC the Kr was observed to be 30.35 and 31.59. Permeability ratio (K_r) and CIF was less for CI soil when compared to CH soil when permeated with synthetic heavy metal solution. Among the two locally available soils (CI and CH) that were tested under the presence of multi heavy metal system, the CI soil showed less cracking potential as well as less permeability ratio when compared to CH, especially under multi heavy metal solution condition.

Table 4.18. Permeability ratio of soils at different compaction water contents and multi heavy metal solutions

Variation of Permeability ratio with water									
	Dry of Optimum			Optimum water content			Wet of optimum		
Soil	K_0 (10^{-7} cm/s)	K_1 (10^{-7} cm/s)	K_r	K_0 (10^{-7} cm/s)	K_1 (10^{-7} cm/s)	K_r	K_0 (10^{-7} cm/s)	K_1 (10^{-7} cm/s)	K_r
CH	0.21	1.97	9.4	0.141	1.81	12.83	0.095	1.317	13.87
CI	0.751	9.087	12.1	0.505	7.17	14.2	0.332	5.227	15.74
Variation of Permeability ratio with MHMS pH= 2									
CH	3.213	78.754	24.51	2.066	59.5	28.8	0.99	30.05	30.35
CI	0.75	10.66	14.21	0.4062	6.83	16.8	0.234	4.87	20.81
Variation of Permeability ratio with MHMS pH= 7									
CH	2.512	66.638	26.52	1.898	54.75	28.84	0.889	28.09	31.59
CI	0.55	13.835	18.44	0.331	6.55	19.78	0.155	4.131	26.52

4.4.4 Break Through of heavy metals through cracked soils:

4. 4.4.1 Sample preparation:

The column experiments were conducted to study the breakthrough behaviour of desiccated soil. These experiments were conducted by using soil column which is shown in Fig 3.7 of Chapter – 3. These soil samples were prepared by adding optimum moisture content to the air dried soils and compacted to its maximum dry density in a column mould which is shown in Fig 3.5 of Chapter – 3 (Daniel, 1994). The soils were equilibrated in plastic bags for 24 hours. And permeated initially with deionised water in order to achieve the first exposure effect and hence reduce the hydraulic conductivity of the samples (Shackelford, 1994; Quaranta et al., 1997). The flow was induced by maintaining the constant head throughout the experiment. The effluent was collected periodically and the volume of effluent was used to calculate the hydraulic conductivity of the soil sample using the constant head test method (ASTM D 5084). Permeation with the deionised water was terminated and heavy metal solutions were introduced instead and then the heavy metal effluents were collected periodically. The concentrations of these effluents were analysed by using ICP – OES as explained in Chapter -3.

4. 4.4.2 Breakthrough of heavy metals through cracked soils:

In case of composite metal system, four heavy metals (Pb, Ni, Cd and Cr) have been considered for the study. From each stock solution (concentration: 1000 mg/L) prepared previously for each heavy metal, certain volume of heavy metal was taken for preparing 30 mg/L of composite heavy metal solution in which each heavy metal concentration was 30 mg/L. The pH of the final solution was set at 2 by adding 0.1N HNO_3. The composite solution was then transferred to prepared column of CH and CI soil separately for further study. The value of pH has been chosen to eliminate the possibility of getting immobilization through hydroxide compound formation. The breakthrough curves are plotted based on the results obtained from column tests performed on both CH and CI soils and are shown in Fig 4.53 and 4.54 respectively.

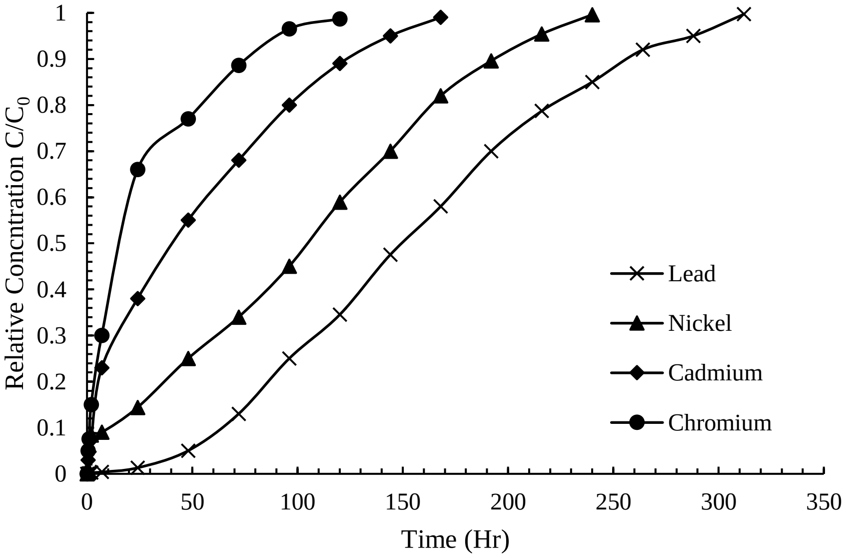


Fig. 4.53 Breakthrough curve for Composite heavy metal system for CH soil

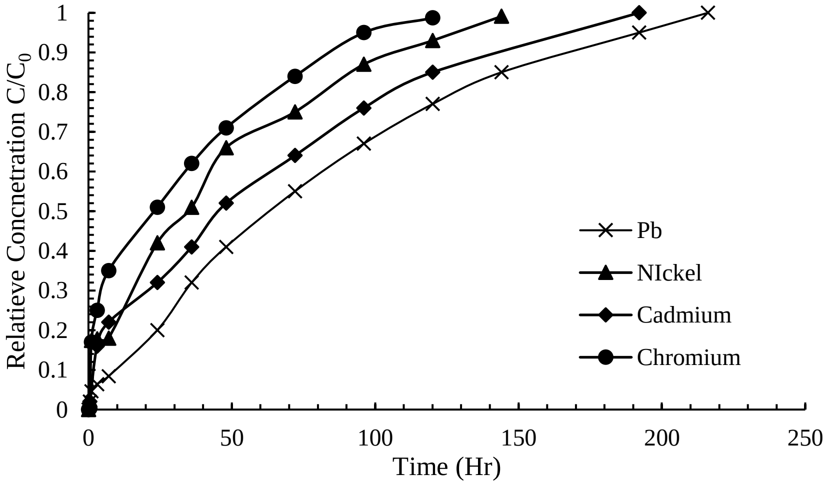


Fig. 4.54 Breakthrough curve for Composite heavy metal system for CI soil

From these figures, it is observed that, for both the soils (CH and CI) the time required to achieve breakthrough of heavy metal through the desiccated soil is less when compared to the un-desiccated soil, may be because of the poor self – healing capacity after interaction with the heavy metal solution. The time required to achieve breakthrough time is more for CH soil when compared to the CI soil due to its self-healing and good adsorption capacity. The diffusion coefficients obtained from these column experiments are shown in table 4.19.

Table 4.19 Diffusion coefficients of Heavy Metals through the cracked soil

S. No	**Heavy Metal**	**Diffusion Coefficients (m^2/sec)**	
		CH soil	**CI Soil**
1	Lead	2.01×10^{-6}	3.06×10^{-6}
2	Nickel	3.21×10^{-6}	6.95×10^{-6}
3	Cadmium	4.50×10^{-6}	6.30×10^{-6}
4	Chromium	5.90×10^{-6}	9.9×10^{-6}
Average Diffusion		3.8775×10^{-6}	8.73×10^{-6}

The migration of contaminants is increasing through both the soils due to the formation of cracks, the time to achieve breakthrough for the CH soil is more when compared to the CI soil. The migration of heavy metals through the CI soil is more when compared to CH soil indicating high retention capacity of CH soil over CI soil.

4.5 Inference from the Study:

The following conclusions are drawn based on the experimental column studies.

1. Cracks are developed more when soil is compacted at wet of optimum water content and then allowed to dry, compared to the soils compacted at optimum moisture content and dry of optimum and allowed to dry. This is because during drying process, the matrix suction produced on soil surface increases the tensile stresses leading to development of cracks in the soil sample.
2. The permeability ratio is increased with increase in the compaction water content and with the presence of the contaminant in the solution. CH and CI soils are having

1.3 times more permeability ratio at wet of optimum when compared to soil compacted at dry of optimum.

3. The migration of heavy metals through the CI soil is 2 times more when compared to CH soil indicating high retention capacity of CH soil over CI soil. The diffusion of heavy metals through desiccated soils is in the range of 2.01×10^{-6} to 5.90×10^{-6} m^2/sec for CH soil and 3.06×10^{-6} to 9.9×10^{-6} m^2/sec for CI soil.

CHAPTER 5

CONCLUSIONS

The following are the conclusions drawn based on the experimental investigations carried out in the present work.

1. The adsorption of metal ions by the both the soils considered for the present study is observed to increase with increase in the pH of the soil-solution; whereas the amount of metal ions adsorbed by these soils decreases with the increase in the pH of the solution in the presence of organic chemical (EDTA). Out of the four heavy metals investigated, the percentage adsorption of three heavy metals (Pb, Ni and Cd) is increasing with increase in the pH of the solution; whereas in case of Cr the percentage adsorption is decreasing with increase in the pH of the solution.
2. Under single heavy metal and multi heavy metal interaction, with the presence of organic chemical, adsorption of heavy metals by both the soils reduced significantly at pH 7 when compared to pH 2.
3. The adsorption isotherms obtained from the batch sorption tests are befitting to the two non-linear isotherm models such as Freundlich and Langmuir. Out of these models, the Freundlich model is best fitting to the experimental data from the present study.
4. The average percentage adsorption of the three heavy metals (Pb, Ni and Cd) at pH 2 is around 54% for CH soil and 41% for CI soil. The percentage adsorption at pH 7 is around 90% for both CH and CI soils. At pH value of 2, the H^+ ion concentration is more in the solution and bivalent heavy metal ions (Pb, Ni and Cd) will have competition between H^+ ions and the metal ions which leads to the lesser adsorption efficiency. At pH value of 7, the adsorption efficiency is increased due to the negative surface charge of soil. Whereas in the case of Chromium, the adsorption efficiency is

about 98% and 79% respectively for CH and CI soils at pH 2 and is about 8% and 6% respectively for CH and CIs soil at pH of 7.

5. With the presence of organic chemical (EDTA) at pH 2, the average adsorption efficiency of CH soil is around 52% for 3 heavy metals (Pb, Ni and Cd) and 68% for chromium; whereas at pH 7 the average adsorption efficiency of CH soil is around 18% for 3 heavy metals and 42% for chromium. The percentage adsorption of CI soil at pH 2 is around 57% for 3 heavy metals and 95% for chromium; whereas at pH 7 the adsorption efficiency of CI soil is around 14% for 3 heavy metals and 77% for pH 7.
6. Under multi metal interaction, for both the conditions of with and without EDTA, the percentage adsorption is further reduced when compared to single metal interaction due to the competition among the heavy metals present in the solution to form metal complexes with the available hydroxyl group, which leads to reduction of the sorption affinity of the soil towards the multi heavy metal solution.
7. In single metal system, Chromium shows more mobility when compared with other heavy metals (Lead, Nickel, and Cadmium). As Chromium exists in anionic ($Cr_2O_7^-$) form, it was repelled by negatively charged soil surface and as a result, the mobility of Chromium is increased when compared to others.
8. In the absence of EDTA, under multi metal interaction at pH 2, the diffusion of heavy metals through the soil is more when compared to the single metal interaction, may be due to the competitive effect between the heavy metal ions. And in the influence of EDTA, under multi metal interaction, the diffusion of heavy metals increased at pH 7 when compared to pH 2. This is probably due to the formation of metal EDTA complexes that exists in the solution as negatively charged EDTA complex and gets repelled by negatively charged soil which will result in increased mobility of heavy metals through the soils.

9. The crack intensity factor and permeability ratio values are increasing with increase in the compaction water content, number of wetting-drying cycles and with the presence of contaminants. With increase in the compaction water content from dry of optimum to wet of optimum, the CIF is increasing by1.55 for CH soil and by 5.8 times for CI soil. The crack intensity factor values are further increased after soil permeated with heavy metal solution. For multi metal interaction, at wet of optimum, the increase in CIF values at pH 2 and pH 7 is observed to 2 and 1.73 respectively for CH when compared to soil permeated with water. For CI soil the increase in the CIF under this condition at pH 2 and pH 7 is observed to be 2.39 and 1.68 respectively when compared to soil permeated with water at wet of optimum moisture content.
10. The permeability ratios of both the soils are more with the presence of heavy metals when compared to water. Under the presence of heavy metals, the permeability ratio values are high at pH 7 when compared to pH 2. Although the migration of contaminants is increasing through both the soils due to the formation of cracks, the time to achieve breakthrough for the CH soil is more when compared to the CI soil. The average diffusion coefficient of all the four heavy metals through the CI soil is around 2 times more when compared to the average diffusion coefficient of CH soil.
11. Based on adsorption studies, crack intensity and permeability ratio values, it is found that, CH soil shows good heavy metal retention capacity because of its good adsorption capacity and exhibiting more self-healing tendency when compared to that of CI soil.

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PUBLICATIONS RELATED TO THE WORK

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