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ENGINEERING APPLICATIONS OF ORGANIC SURFACTANT MODIFIED BENTONITE IN SORPTIVE SOIL BARRIERS

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M.S., K. N. Toosi University of Technology, 2012

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A Dissertation Approved on

April 26, 2017

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To my beloved parents, Gholamreza Javadi and Nasrin Javadi

For their unconditional love and relentless support

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ABSTRACT

ENGINEERING APPLICATIONS OF ORGANIC SURFACTANT MODIFIED BENTONITE IN SORPTIVE SOIL BARRIERS

Sadra Javadi

April 26, 2017

Earthen barriers such as CCLs and GCLs have been employed in geotechnical practices to provide a low permeability hydraulic barrier since long time ago. These types of barriers exhibited satisfactory performance for many applications such as landfills. The performance of low permeability barriers is based on the swelling potential of their component, which is mostly Na-bentonite, in contact with polar fluids such as water. However, the acceptable range of conductivity cannot be achieved by traditional earthen barriers when they are permeated by non-polar fluids such as gasoline. This phenomenon occurs due to the incompatibility of earthen barrier constituent with non-polar compounds. Also, the traditional earthen barriers are not able to retard the contaminant transport due to their negligible reactivity with organic compounds. As a result, the application of low permeability barriers was limited to polar and non-contaminated flows. In this study, the performance of traditional earthen barriers as a hydraulic and chemical barrier was enhanced by introducing an organically modified amendment (HDTMA-bentonite) to traditional earthen barrier's components.

This study was undertaken to examine the sorption characteristics of partitioning organoclays and to evaluate their performances in soil-based barriers. The main goal of this study was to quantify the physicochemical properties of organobentonites for their applications in waste containment and site remediation.

It was observed that the intercalation of organic carbon on the surface of unmodified bentonites increased the organophilicity of sorbents. As a result, organic contaminants exhibited higher affinity toward modified bentonite. It was found that the organophilicity of organoclays increased either by increasing the chain length or number of chains. Consequently, PM-199 exhibited higher sorptivity compared to HDTMA-bentonite because it was synthesized by a double chain surfactant. The effect of grain size on the sorption capacity of organobentonites was also studied. The obtained results suggested no significant difference in sorption capacity of powder PM-199 and granular PM-199.

In addition, the effect of chlorination, and aromatic ring on sorptivity of sorbent was studied. It was observed that the solubility of organic compounds decreased by increasing the chlorinated positions on the aromatic ring. As a result, organophilicity of the organic contaminants increased as chlorination and the number of aromatic rings increased. The affinity of organic contaminants toward the organic phase of sorbents increased which resulted in higher partitioning toward HDTMA-bentonite.

When the effects of co-solvent on the sorptivity of sorbents was examined, it was observed that the Cosolvency of non-polar solvents resulted in higher solubility of organic contaminants in the solution which reduced their affinity toward HDTMA-bentonite. Also, the effect of temperature on the sorption capacity of HDTMA-bentonite was studied. The obtained results indicated that the increase in temperature resulted in higher level of kinetic energy in the solution which facilitate the partitioning of benzene toward HDTMA-bentonite.

The feasibility of using the HDTMA-bentonite as an amendment in compacted clay liners was evaluated by conducting a soil column experiment. The obtained results from swelling experiment suggested that unmodified bentonites have higher swelling tendency in polar liquids while modified bentonites have higher swelling capacity in non-polar liquids. As a result, the permeability of the silty clay column was enhanced with unmodified bentonite when it was permeated by polar solution. On the other hand, the permeability of silty clay column was enhanced with modified bentonite when it was permeated by non-polar solutions. Additionally, it was observed that only 5% HDTMA-bentonite amendment enhanced the retardation capacity of the system while it had no significant effect on the permeability of the compacted silty clay. The obtained results suggested that a small percentage of HDTMA-bentonite can reduce the mass flux of contaminant by 90% which suggested that HDTMA-bentonite has a promising performance as reactive material for Compacted liner barrier for organic and/or low polarity fluids.

Additionally, the feasibility of using HDTMA-bentonite as a reactive amendment for GCL liners were investigated. The swelling behavior of unmodified and modified bentonites were studied as a function of: polarity, ion strength, acidic/basic environment. It was observed that unmodified bentonites had higher swelling tendency in polar liquids while modified bentonites swelled significantly in non-polar liquids. pH and low ionic strength (<0.01 M) did not affect the swelling behavior of studied sorbents. However, the swelling of unmodified bentonites decreased drastically in solutions with higher ionic strength.

The permeability of GCL specimens with different percentage of HDTMA-bentonite permeated by polar and low polarity solutions were studied. It was observed that the permeability of GCL specimens to polar solutions increased by increasing the percentage of HDMA-bentonite in GCL soil. However, the permeability of GCL specimens to low polarity solutions decreased by increasing the percentage of HDMA-bentonite in GCL soil. Also, it was found that a small percentage of PM-199 amendment can provide the minimum permeability for GCL specimens permeated by both polar and non-polar liquids. It was observed that the permeability of GCL specimens increases by increasing the confining stress.

In addition, the breakthrough test was carried out to study the transport mechanism of benzene solution through the GCL specimens. The results suggested that 20% of HDTMA-bentonite enhanced the sorptivity and retardation of the GCL barriers significantly; however, it did not affect the permeability of the liner system. The numerical and analytical approaches were used to estimate the transport parameters of benzene by using experimental results.

Finally, the potential application of HDTMA-bentonite as a reactive component of fast flow rate barriers were evaluated. The acquired results suggested that the retardation capacity of HDTMA-bentonite increased by decreasing the seepage velocity of the column. In addition, the kinetic study and analytical approaches were employed to obtain

the retardation factor of the soil columns at non-equilibrium condition. It was noticed that both methods resulted in a similar value within an acceptable range of error. This result suggested that the non-equilibrium partitioning coefficient measured from kinetic study can be employed to calculate a reliable retardation factor in non-equilibrium condition. The overall results suggested that HDTMA-bentonite can serve as an efficient reactive material in PRBs which not only increased the retardation capacity of the fast flow rate columns, but also did not affect the seepage velocity of the system with fast seepage velocity.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1 CHAPTER ONE INTRODUCTION

1.1 Background

The increasing growth of population in all over the world (near to 70 million growth of population is expected for United States by 2045 (USDOT 2015)) increases the demand of waste containment, contaminated site remediation and sustainable development (Sharma and Reddy 2004). Inappropriate waste disposal practices in the past has caused the contamination of subsurface and groundwater with a variety of environmental pollutants (Gates et al. 2009). These contaminants are detrimental to public health and the environment and lead to costly remediation actions. At the same time, although the land disposal technologies have been developed significant, new materials and improved containment systems still merit examination.

Up until the early 1970s, chemicals used in industrial and municipal activities and their byproducts were disposed without much consideration of their transport and fate in the subsurface, as well as their impact on the human health and the ecosystem. At the time, the collected solid waste was piled up in an open area on the ground surface or they were disposed in the open ditches or pits. Due to the absence of legislation and environmental laws to control this practice, these areas lacked appropriate liner systems, which led to contamination of the surrounding soil.

Records indicated that in the past many coal mining piled up coarse tailing and the wastewater in an impoundment for a long period of time. The contaminants infiltrated into the subsurface and reached to the groundwater table. There are also several reports from army bases that have stored toxic chemical waste in unlined pits which led to the contamination of surrounding groundwater (Lo and Yang 2001). In early 1970s, impermeable caps were constructed over the pits or impoundments to minimize the percolation. However, it was until 1980's that the engineers started to build bottom barriers for landfills and surface impoundments (Sharma and Reddy 2004). Many old underground storage tanks (USTs) have been used to store chemicals and fuels. USEPA estimated that up until 1995, over 400000 sites had been polluted by leakage from underground storage tanks. This led to a remedial operation that cost over $4 million dollars.

There are many other examples in addition to the mentioned case studies, which confirm the necessity of using barrier systems in containment facilities. Additionally, for the remediation of the existing soil/groundwater contaminations, a short-term in-situ barrier system is often required to prevent the spreading of contaminants and also to facilitate the following remediation (Lee et al. 2012). Other long-term in-situ or ex-situ environmental geotechnics may apply in conjunction with short-term containment technologies (Sharma and Reddy 2004).

A waste containment facility can be categorized as either a passive system or an active system. Passive system includes the installation of physical low permeable barriers around the contaminated site. The purpose of passive system is to isolate the potential sources of contamination or contaminated site and minimize the possibility of contaminant spreading to the surrounding environment. Passive system can be used in vadose or saturated zone and includes one or combination of the following barrier types: (1) vertical barriers to limit the lateral spread of contaminants; (2) bottom barriers to prevent the vertical spread of contaminants such as bottom liner for storage tanks and landfills; or (3) cover barrier to isolate the stored waste and minimize the infiltration of surface water to the system such as landfills. An active containment system includes the installation of either pumping well or subsurface drain systems to adjust the hydraulic gradient with the purpose of containing groundwater contaminants. In some scenarios, a combination of active and passive system may be used in order to contain the contaminant plume carried by groundwater flow. Although a passive containment system can be incorporated into an active remediation system, this dissertation is focused on the in-situ containment practices and the performances of soil-based barriers as a part of a passive containment system.

1. Vertical barriers

Vertical barriers are also known as vertical cutoff barriers or vertical cutoff walls. The function of vertical barriers is to contain the contaminated soils/groundwater or block the lateral contaminant flow in subsurface. They can build on the top of a bottom barrier system or extend to a low permeability barrier systems. Most commonly, vertical barriers are used in combination with pump and treat method. The vertical barriers are constructed in different types such as: (1) compacted clay barriers; (2) slurry trench barriers; (3) grouted barriers; (4) mixed-in -place barriers, and (5) steel sheet pile barriers.

One of the most common type of vertical barriers is compacted clay barriers. Compacted clay barriers are constructed by compacting silty or clayey materials on subgrade soil or in a trench to construct a liner with a high dry unit weight. The moisture content and the type of compaction effort should be controlled to provide a soil barrier with the lowest permeability ($k \leq 10^{-7}$ cm/s). The most suitable application of compacted clay barriers is in aquitard layer with shallow depth.

2. Bottom barriers

Typically, bottom barriers are used to contain the waste site when there is no natural stratum with low permeability available at a reasonable depth. Their function is to minimize the diffusive and advective transport of contaminants into the subsurface layers as much as possible. Different techniques can be applied to construct a bottom barriers including grouting or a combination of different methods like tunneling and geomembrane installment, and a mixture of grout with slurry.

3. Covers or caps

Cover barriers are commonly constructed over a buried waste such as landfills to prevent the infiltration of liquid or gases and minimize the leachate generation. Cover barriers are consisted of six major components: (1) surface layer; (2) protection layer; (3) drainage layer; (4) hydraulic barrier layer; (5) gas collection layer; and (6) foundation layer, a detailed sketch of typical landfill cover system can be found in part 1.2.1 (Figure 1-2).

The conclusion of different studies in many cases has confirmed that the compaction of local soils does not provide the sufficient permeability requirements for low permeability barrier systems (Bagchi 2004). For instance, a layer of silty soil from Chaco – Pampean plain in the center and north- east of Argentina could reach to the average hydraulic conductivity of 10^{-8} m/s after the heavy compaction effort (Francisca and Glatstein 2010).

Thus, it is necessary to use amendments combined with local soils to make them useful for liner system.

During the past decade, many researches have been done to evaluate the feasibility of using various amendments to meet the required permeability for low permeability barrier systems. A list of different amendments used in liner system is summarized in Table 1-1 (Widomski et al. 2015). Among the tested geo-materials, bentonite demonstrated a promising performance regarding the permeability for the liner application. Bentonite is defined as a natural clay with high swelling tendency, high ion exchange capacity and very low water permeability. Other significant characteristics of bentonite are high percentage of montmorillonite (60-90%), high water absorption capacity (200-700% weight), high swelling potential(7-30 mL), high range of plasticity (140-380%), and cation exchange capacity of (0.60-0.90 mol/kg) (Egloffstein 2001). Consequently, bentonite-clay barriers have served as the containment systems for a long time.

Table 1-1. Summary of hydraulic conductivity for different amendments

Material	Minimum hydraulic conductivity (m/s)	Sources
Fly ash	3.1×10^{-10}	Palmer et al. (2000)
Quicklime	1.0×10^{-10}	Wiśniewska and Stępniewski (2007)
Silica fume	9.03×10^{-10}	Kalkan and Akbulut (2004)
Cement	8.53×10^{-10}	Kalkan (2006)
Claystone	5.34×10^{-12}	Musso et al. (2010)
Red mud	3.73×10^{-10}	Kalkan (2006)
Bentonite	1.0×10^{-11} to 5.4×10^{-12}	Komine (2010)&Ahn and Jo (2009)

Although different types of barriers can be used individually as the bottom barrier systems, compacted clay liners are frequently used in combination with other geosynthetic materials; such as geomembrane; as a composite liner system. In addition, recent developments in geosynthetics area make it possible to use geosynthetic clay liners (GCLs) as a substitution for compacted clay liners due to their low permeability and cost efficiency.

1.2 Engineering applications

Most commonly, the barrier systems in waste containment facilities are employed to serve as low permeability barrier systems, or fast flow rate barrier systems.

1.2.1 Low permeability soil barriers

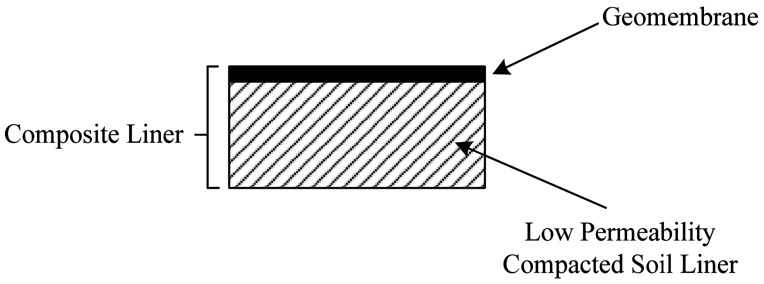
Many waste containment systems are required to have one or several low permeability hydraulic barriers. The liner system is typically a combination of engineered soils and geosynthetic materials and these composite liners must provide a hydraulic conductivity less than 10^{-7} cm/s as bottom barriers and 10^{-5} cm/s as cover barrier. They are frequently used for landfills and underground storage tanks (USTs). the typically layout of the composite barrier or soil barriers are briefly introduced next:

1. Landfill:

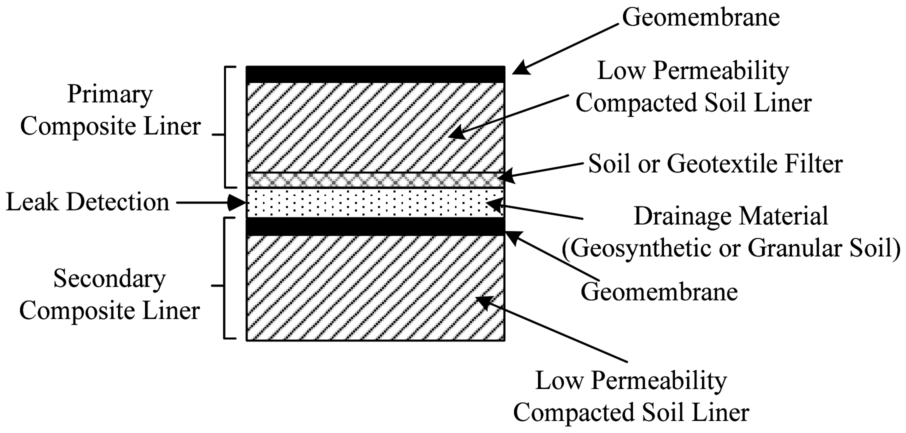
Landfill is the primary containment practice in the United States to dispose the municipal solid waste (MSW). Landfills are categorized to sanitary and secure landfills. Sanitary landfills are employed for disposal of non-hazardous waste while secure landfills are used to dispose the hazardous waste. Hazardous waste is buried in excavated holes or trenches which are lined with barrier systems to minimize the leakage of hazardous substances into the soil and water bodies. The Resource Conservation and Recovery Act (RCRA) in 1976 provided guidelines regarding the management of hazardous, non-hazardous wastes and underground storage tanks. In conclusion, a comprehensive regulation has been developed by USEPA under two major subtitles: subtitle C, and Subtitle D.

Subtitle C provides the minimum requirements for proper management and disposal practices of hazardous wastes. Based on subtitle C, a landfill used for disposal of hazardous wastes should have a leachate collection system, a top flexible membrane liner, a system to collect, detect, and remove the leachate, and a composite liner system. Also, it is required to cover the landfills that are used for hazardous waste disposal with a final cover which minimize the long-term diffusion of liquids through the landfill. The cover system should have a permeability value equal or less than the permeability of bottom liners. A schematic arrangement of bottom liner legislated by subtitle C is presented in Figure 1-1 (b), and Figure 1-2.

Subtitle D provides the guidelines to manage the municipal solid wastes. It is required by subtitle D to employ a leachate collection system and a composite liner system which consisted of a compacted clay liner and flexible membrane liner for a landfill used for non-hazardous wastes. A schematic arrangement of bottom liner legislated by subtitle D is presented in Figure 1-1 (a).



(a)



(b)

Figure 1-1. Schematic figure of bottom barrier system (a) single composite liner (b) double composite liner

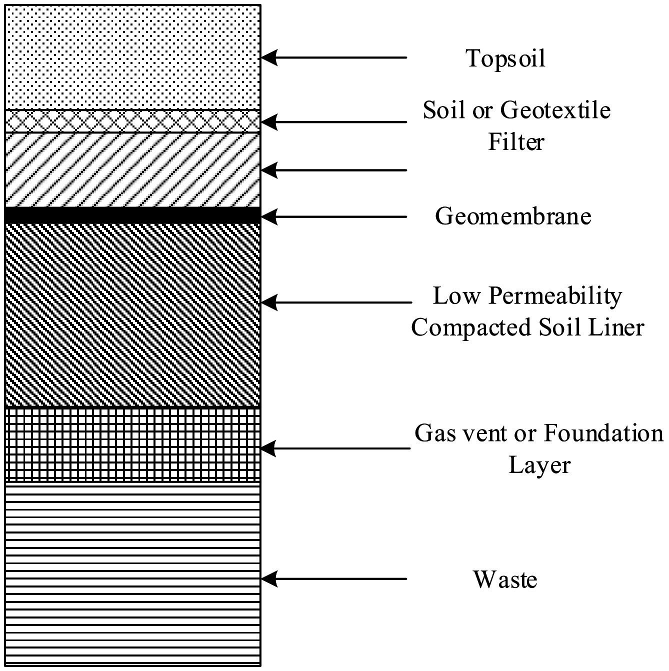


Figure 1-2. Schematic figure of cover system for buried waste

2. Underground storage tanks (USTs):

USTs are referred to a tank and the pipe lines connected to the tank that has at least 10% of their entire system underground. Topically, USTs are used to store the pure phase chemical or petroleum related products as well as other hazardous substances. In 1984, subtitle I of the Solid Waste Disposal Act (SWDA) required the closure of near to 1.7 million active USTs in United States.

- Subtitle I:

Subtitle I encompasses the federal requirement for closure and corrective actions regarding the existing and new underground storage tanks (USTs) used to store the petroleum and other hazardous compounds. This subtitle has been addressed in 40 CFR 264.190 through 264.200. Subtitle I aims to provide guidelines for owners and operators of USTs regarding the maintenance and closure of the USTs. Under this subtitle, different requirements have to be addressed including:

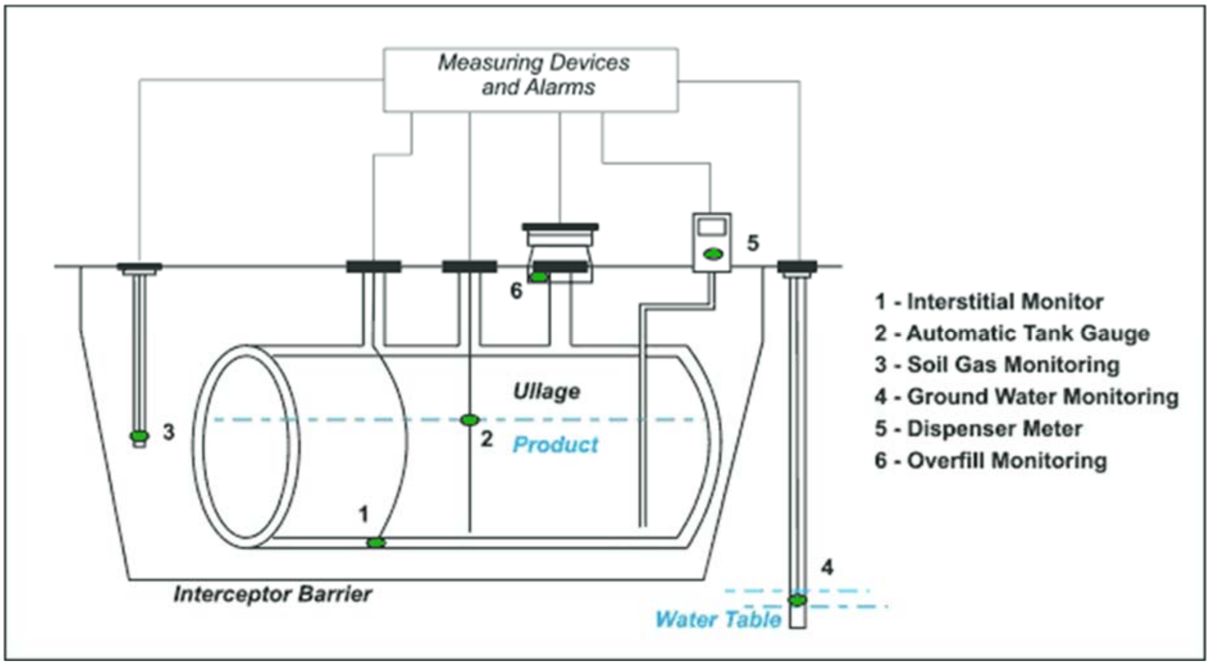


Figure 1-3. Schematic setup of USTs with barrier systems (Musy 2008)

1.2.2 Fast flow rate barrier systems

In addition to low permeability barriers, vertical barriers can be used as fast flow rate barriers in groundwater remediation practices such as permeable reactive barriers (PRBs). PRBs are permeable chemical barriers that designed to degrade or immobilize the constituent contaminant in the groundwater flow while passing through them. Permeable reactive barriers have received significant attention during the past decade due to their considerable capacity for attenuating or removal of a wide range of contaminants. To construct the PBRs, a trench with reactive components will be built perpendicular to the contaminant flow (Figure 1-4). The pollutants carried by the flow will be immobilized or transformed into nontoxic constituents (Vidic and Pohland 1996)

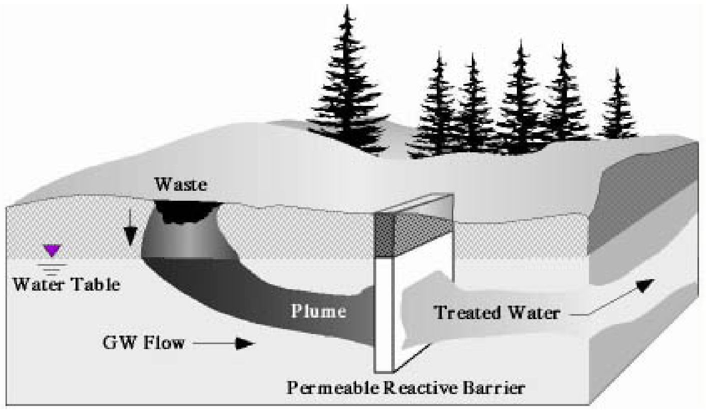


Figure 1-4. Schematic permeable reactive barrier system (Australia. 2012)

The reactive components of PRBs include reactive material to degrade the volatile contaminants, chelators to immobilize the heavy metals, or nutrients and oxygen to enhance the bioremediation (Bowman 1999). To facilitate the groundwater flow through PRBs, the reactive components are often mixed with porous materials such as sand.

Reactive components in the PRB system attenuate the transport of variety of groundwater contaminants including organic and inorganic contaminants. Organic contaminants such as BTEX, TCE, PCBs, PAHs, and TCA can be treated by employing a barrier with reactive material that degrade or sorb the pollutants. Most common reactive materials for organic contaminant degradation are zero-valent iron (ZVI), iron (II) porphyrin, resting-state microorganisms, and dithionite. Other materials to sorb the contaminants include zeolite, organobentonites, and activated carbon. The reactive permeable barriers are suitable to use in sites with permeable soil, with relatively high speed groundwater flow which the contamination zone locates no deeper than 50 ft below ground.

If designed and installed appropriately, the conventional soil barriers exhibited desirable performance and reliability for water with low solute concentrations. However, chemical incompatibility was also observed in conventional soil barriers when they were permeated by organic liquids and fuels. Previous studies indicated that the permeability of natural clay soils increased up to four order of magnitudes when they were permeated with pure hydrocarbons liquids (Brown et al. 1983; Brown et al. 1984). Bowders and Daniel (1987) investigated the permeability of compacted kaolinite and illite when permeated by methanol, acetic acid, heptane, trichloroethylene (TCE), and water. They concluded that the permeability of clay increased when the concentration of methanol exceeded 80%. They also suggested that the increased permeability was due to the shrinkage of the diffuse double layer of the clays in methanol. They also observed that pure heptane and TCE would cause the increased flow in the clay liner.

In addition to significantly increased permeability due to chemical incompatibility, the conventional soil barriers also have limited contaminant retention capacity. Although it would take longer time for the contaminant flow to go through the common soil barriers, the dissolved organic contaminants might migrate through them at a faster pace. From a perspective of barrier performance, they are not very capable of impeding the mass transport of contaminants even if they can minimize the flow. In these situations, an effective "chemical barrier" is also required in addition to the existing hydraulic barrier. Consequently, novel soil barriers with higher chemical compatibility and enhanced the sorption capacity for organic compounds merits examination.

It was suggested that the chemical incompatibility between the organic liquids and clay minerals is due to the differences in polarity of the two (Chiou 1998; Lo and Yang 2001; Smith et al. 1988). Typically, inorganic soils like clays are hydrophilic as their constituents are mainly aluminosilicate sheets, however, most of the organic compounds are non-polar, hydrophobic substances that have lowest affinity to the minerals. Consequently, organic-matter enhancement of liner materials has been suggested to improve the compatibility of soil and organic compounds as they can be compatible with both. The improvement due to the additives could be the stable permeability and increased contaminant retention capacity of soil barriers. The increased contaminant retention capacity is explained in next few paragraphs.

There are three major processes that control the transport of contaminant in porous media: (1) advection, diffusion and dispersion; (2) chemical mass transfer process such as sorption; and (3) biological process. Advection refers to the contaminant transport under a hydraulic gradient while diffusion refers to the contaminant transport under a chemical gradient. The relative importance of advection and diffusion can be quantified by the Peclet number, equation 1-1:

$$P_L = \frac{v_s L}{D} \qquad 1\text{-}1$$

where P_L is the Peclet number, v_s is the seepage velocity (m/s), L is the travel distance for contaminant (m), and D is the diffusion coefficient (m^2/s). The advection process is dominant in contaminant transportation at high flow rate systems (e.i., $P_L \geq 50$) whereas the diffusion controls the contaminant transportation mechanism in low flow rate systems (e.i., $P_L \leq 1$).

The transport of solute through homogeneous soil is typically described by the one-dimensional advection-dispersion equation, equation 1-2.

$$R\frac{\partial C_r}{\partial t} = D\left(\frac{\partial^2 C_r}{\partial x^2}\right) - v\left(\frac{\partial C_r}{\partial x}\right) \tag{1-2}$$

where D is the hydrodynamic dispersion coefficient (m^2/s), v is seepage velocity (m/s), x is microscopic distance in the direction of transport (m), t is time (s), and Cr is the concentration of solute in the pore water of the soil (µg/mL).

The chemical mass transfer is negligible if the solutes have limited reactions with soils. However, if certain chemical reactions (e.g. acid-base reaction; reduction-oxidation reaction; dissolution-precipitation; sorption-desorption) can reduce the aqueous concentration of the solute, the mass of the solute (or contaminant) will be retarded. If sorption of solute molecules by the porous media is the dominant mechanism, the retardation can be described by a retardation factor that is related to the sorptivity of the soil. Assuming the distribution of solute (or contaminant sorbate) in solvent and in soil sorbent is proportional, the retardation factor R can be determined as equation 1-3 (Freeze and Cherry 1979):

$$R = 1 + \frac{\rho_b}{n}K_d \tag{1-3}$$

where ρ_b is dry density of porous media (g/cm^3), n is the porosity of the porous media, and K_d is the distribution coefficient (mL/g). More details of the equations and parameters can be found in chapter 3.

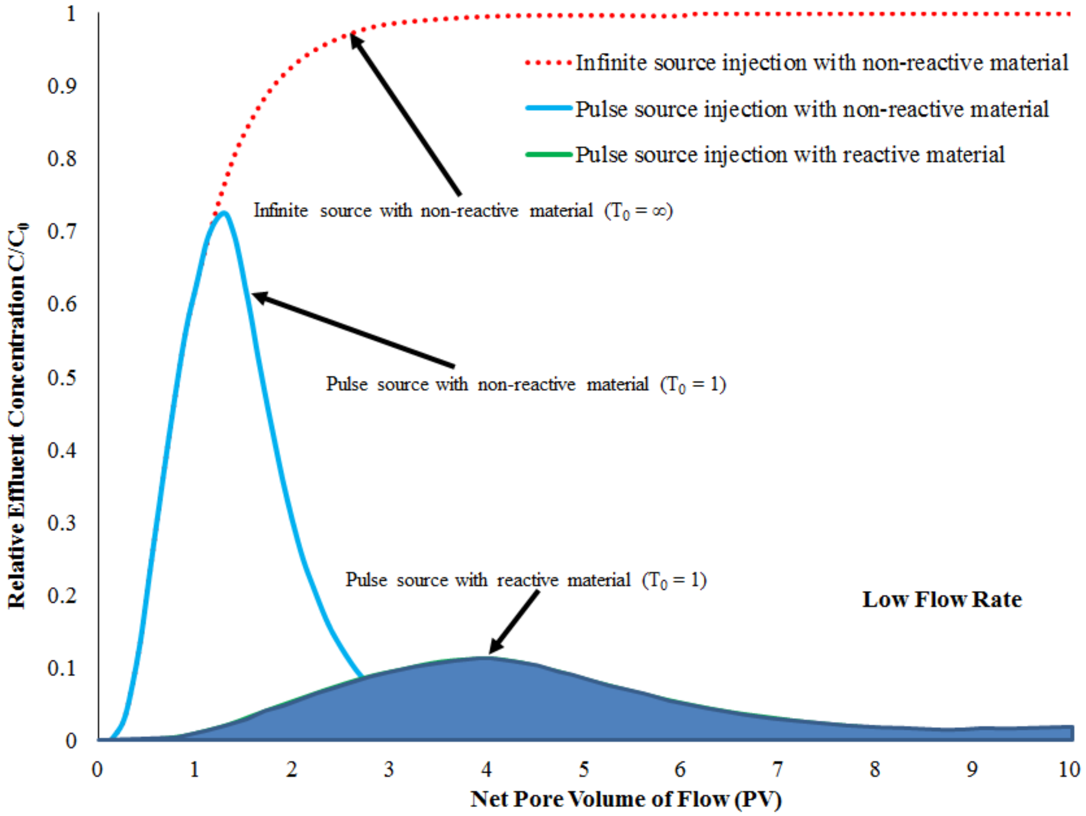


Figure 1-5. Low flow rate breakthrough curve for different type of solute injection

At the laboratory scale, the retardation factor can be estimated from soil column study. the studied contaminants can be introduced to the soil columns through two different injection method. The first one is infinite source injection which the contaminated solution will be injected to the column continuously until the relative concentration (concentration of contaminant in effluent/initial concentration of contaminant) is equal to 1. It results to a s shape breakthrough curve (red curve). Also, the solution can be introduced to the soil column for one pore volume and then it be flushed by water. In this case, pulse source injection results in a bell shape breakthrough curve (blue curve). If the component of soil column consists of sorptive material, the pulse signal injection method results in a flatten belled shape breakthrough curve with considerably low relative concentration at peak followed by a long tail. This phenomenon occurs due to the higher sorption capacity of sorptive materials which sorb the contaminants and release them with a much-attenuated concentration in a long period of time. This mechanism is called retardation.

At the field scale, the retardation of contaminants by the soil barriers would lead to a slower spreading of the contaminants in the subsurface, or a much smaller plume of contaminants within certain time. Pickens and Lennox (1976) demonstrated a solution for contaminant transport considering retardation term. They concluded that the contaminant transport through a large area as a result of advection and dispersion and they simulated the situations when the soil was non-sorptive, slightly sorptive and very sorptive (K_d was 0, 1 and 10, correspondingly). The concluded result is illustrated in Figure 1-6.

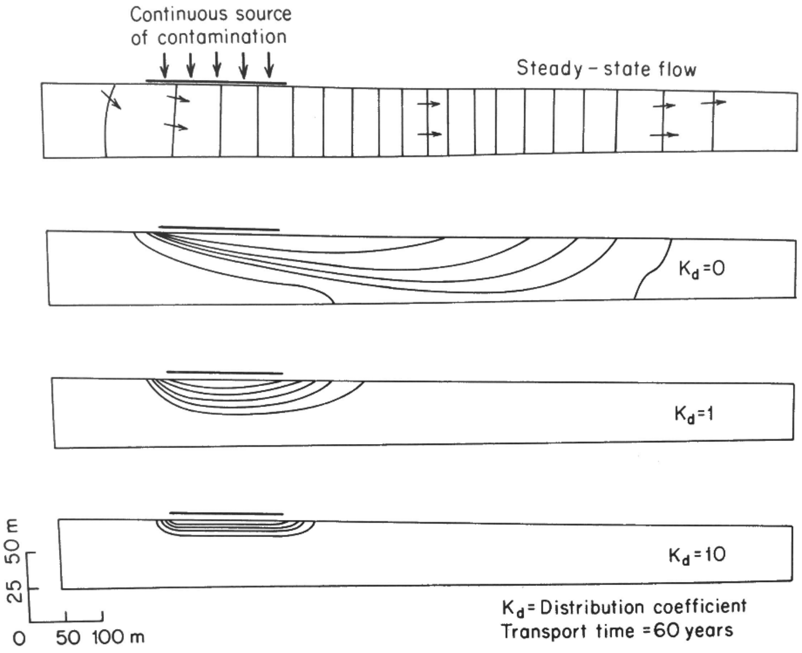


Figure 1-6. The effect of partitioning coefficient on the retardation of contaminant transport (Freeze and Cherry 1979)

For either constant (Figure 1-6) or limited source (Figure 1-7) of contaminants, the sorptive soil would decrease the size of the contamination plume or reduce the contaminant concentration in the subsurface.

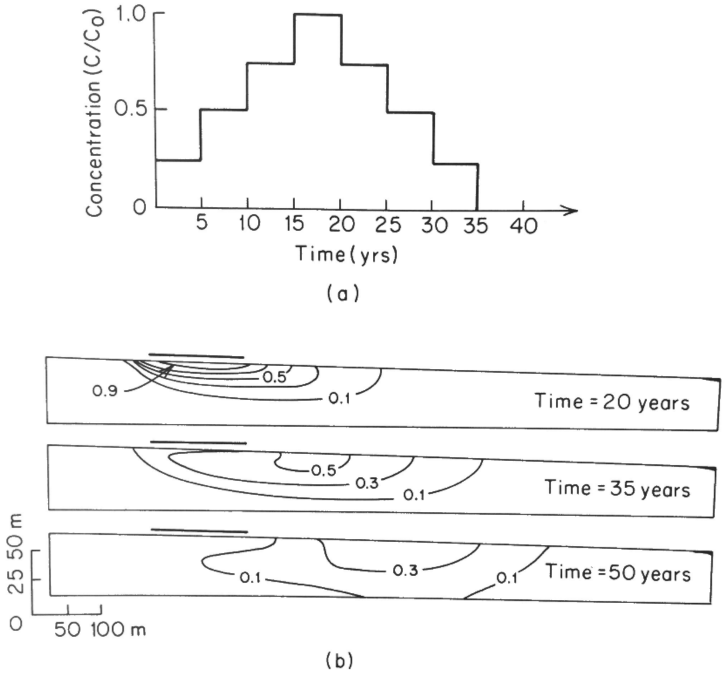


Figure 1-7. (a) the relative concentration of contaminant versus time (b) contaminant distribution during time (Freeze and Cherry 1979)

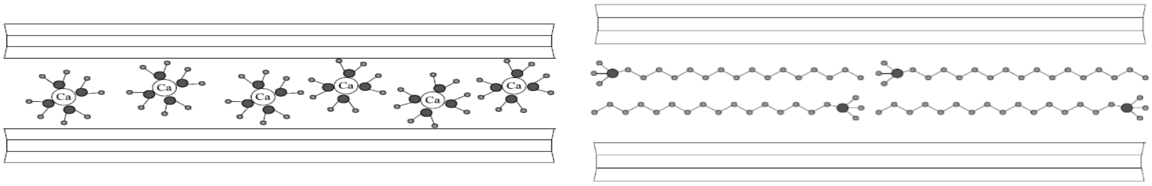
Most naturally occurring soils have low sorptivity of nonpolar organic compounds (NOCs) due to their low organic content (Park et al. 2011). Various types of reactive materials have been proposed as amendments to enhance the sorption/retardation and compatibility of liner materials. The proposed materials are: mixture of bentonite and fly ash, surfactant modified soils, activated carbon, paper industry sludge, organo-sand, zeolite, organo-zeolite, and many other commercial additives. Recently, the surface modification of clay minerals has received a great attention because it can produce a strong and stable sorbent media with favorable sorption of common environmental pollutants (Redding et al. 2002; Richards and Bouazza 2007; Zhao and Burns 2012). Among the surfactant modified soils, organoclays have demonstrated superior performances as a fine-grained soil sorption. This effectiveness of organoclay is due to its considerable characteristics including higher organic carbon, higher thermal stability, organophilicity, hydrophobicity, and higher sorption/retardation capacity (Benson et al. 2015; de Paiva et al. 2008; Gates et al. 2004; Soule and Burns 2001). Consequently, organoclay was chosen as the studied material in this dissertation.

1.3 Organoclay

Organoclays are typically synthesized from naturally occurring aluminum silicates under controlled laboratory conditions. The synthesis of organoclay enriches the base aluminum silicate with organic carbons which often leads to their expanded interlayer spacing and hydrophobicity. In general, organoclays are synthesized from sodium or calcium montmorillonites as they have high cation exchange capacity and desirable interlayer spacing for intercalation. Some other clay minerals such as hectorite, mica, sepiolite, illite, muscovite, clinoptilolite, kaolinite and vermiculite are also possible base clays for the synthesis of organoclays (de Paiva et al. 2008; Soule and Burns 2001).

Several types of organic matters including quaternary ammonium cations (QACs), polymeric quaternary alkylammonium cations and copolymers, alcohols, aldehydes, and biomolecules are often used for the organoclay synthesis (Bate et al. 2014; de Paiva et al. 2008; Lee and Tiwari 2012). Among the available organic surfactants, QAC is the most common cationic surfactant type due to its availability, ease of preparation and stable physicochemical behaviors (Sarkar et al. 2012).

The synthesis of organoclay can be achieved by the cation exchange process in the aqueous phase, which is also known as the “slurry method”. Most of the naturally occurring inorganic cations in montmorillonite (e.g., calcium cation, Figure 1-8) reside in the interlayer spacing of montmorillonite and they tend to hydrate when the soil is soaked in water. The inorganic cations will be substituted by the organic cationic surfactant in they present in the same aqueous phase. This is typically referred as the cation exchange process or primary sorption of organic phase by the clays. After cation exchange, the interlayer calcium/sodium cations and water molecules are replaced by the intercalated organic cations.



(a) (b)

Figure 1-8. microstructure of (a) calcium bentonite (b) HDTMA-bentonite

The structure of polymer/clay composite is categorized based on the microstructure of particle-aggregates of the synthesized clays. Most commonly, the polymer/surfactant modification of clays will lead to separated or exfoliated silica sheets. Based on previous studies, possible patterns of organoclays microstructures are: conventional, intercalated, and exfoliated composites (Alexandre and Dubois 2000; Esfandiari et al. 2008; Giannelis et al. 1999; Lan et al. 1995), Figure 1-9.The method of synthesizing, structure of clay and polymer, and organic modifiers are the controlling factors in determining the morphology of polymer or surfactant/clay composites (Giannelis et al. 1999).

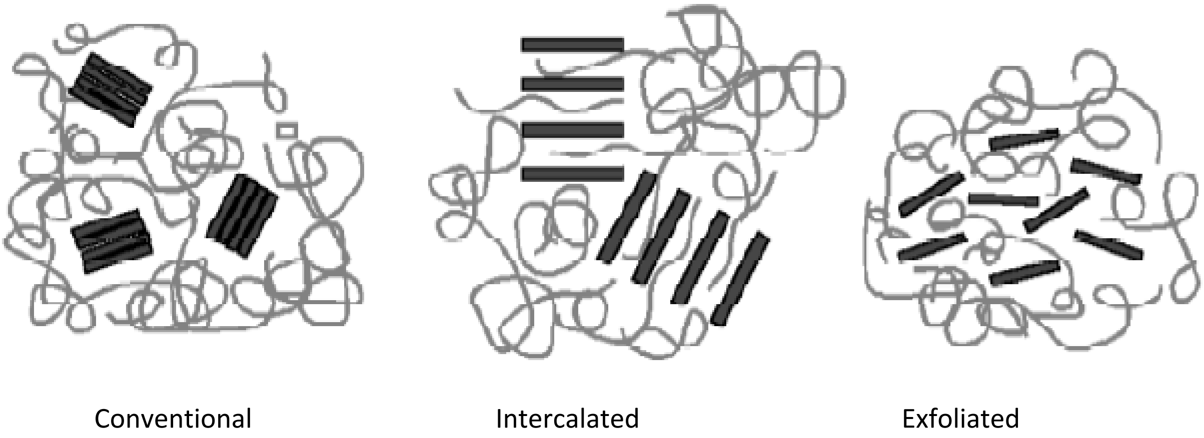


Figure 1-9. Different microstructure morphology of organoclays (Giannelis et al. 1999)

To optimize the structural stability of the surfactant/clay composites, the modifier polymers or surfactants with long carbon chains is often preferred as they can be intercalated in interlayer and interact with both clay platelets (Esfandiari et al. 2008).

Several laboratory characterization techniques can be used to study the microstructure of organoclays at the micro-scale level (Nanos to microns). Most commonly, the basal spacing of intercalated clays is the most important parameter and it can be related to the microstructure of the intercalated surfactants and ultimately, the physicochemical properties of organoclays. The most common techniques that are used to study the microstructures of clays are: X-ray diffraction (XRD) and scanning electron microscope (SEM).

1.3.1 X-ray diffraction (XRD)

The small angle XRD is able to measure the basal spacing of the clay particles. The emitted X-rays diffract in different directions after reflecting from the crystalline atoms of clay minerals. The intensity of the reflected rays can be measured as the function of the reflection angles. The basal spacing of the clay minerals can be measured by plotting the intensity versus the reflection angles of the beams (He et al. 2005). The basal spacing of organoclays usually are detected in the scanning angles (2θ) ranging from 3 to 6˚ (approximately 14.7 to 44.1 Å) (Zhao et al. 2016). Lagaly (1986) proposed an arrangement patterns which can be used to measure the number of organic carbon layers by using the XRD results. The expansion of the interlayer of the unmodified clays after the intercalation of cationic surfactant can be detected by XRD measurement (Xue et al. 2007).

1.3.2 Scanning electron microscope (SEM)

SEM is a non-destructive method to create the surface topography and composition of the particles in microscale by using the electron beams instead of light beams. SEM demagnifies an electron beams generated from a source to scan the surface of the soil in a parallel fashion. The reflected beam from the surface of the soil sample produces different types of emission and captured by multi detectors. The topographical and compositional information can be assessed by analysis of specific type of collected electron(Suga et al. 2014).

1.3.3 Total organic carbon analyzer (TOC)

TOC analyzer measures the quantity of the total organic carbon presents in the soil sample. In this method, the soil sample is combusted at a 680˚ C in an environment enriched with oxygen. As a result, the existing carbons in the soil structure will be decomposed and converted to carbon dioxide (CO_2) in gaseous phase. The CO_2 emission from the combustion procedure will be cooled down and collected by an infrared gas analyzer (Schumacher 2002). The fraction of organic carbon would be determined by analysis of the emission and comparison with the calibration curves.

1.4 Geotechnical testing and engineering properties of soils

The engineering properties of the geo-materials can be evaluated through well-known laboratory soil experiments. For this reason, a series of laboratory experiments were conducted during this study to quantify the physical and chemical properties of geo-materials. The test methods used to evaluate the engineering properties of soils are summarized in Table 1-2.

Table 1-2. Conducted laboratory tests to evaluate the engineering properties of soils

Type of test	Standard	Target engineering properties
Atterberg limit test	ASTM D 4318-05	Liquid limit (LL), Plastic limit (PL), Plastic index (PI)
specific gravity test	ASTM D 854-B	Specific gravity (G_s)
specific surface area test	Santamarina et al. (2002) and Kandhal and Parker (1998)	Specific surface area (SSA)

1.5 Current application of organoclays

Currently, organoclays have been used in various engineering applications such as: drilling, site remediation and waste disposal (de Paiva et al. 2008). Although the field applications of organoclays in conventional earthen barriers is still limited, several studies indicated that they could be very promising amendments in earthen barriers to enhance both the hydraulic and chemical performances. Lo (2001) investigated the potential use of organoclay-bentonite admixture as a barrier for waste containment. He suggested that a small percentage of organoclay (20%) can be mixed with bentonite and used as the material of a soil-based liner. He explained that organoclay enhanced the removal efficiency of the soil liner and maintain the hydraulic conductivity of the barrier at the acceptable range which is required by U.S. Environmental Protection Agency (i.e. 1×10^{-7} cm/s). Lo and Yang (2001) studied the hydraulic barrier performance of a organoclay as the secondary containment for the underground storage tanks. They concluded that organoclays can be efficient barriers for advective transport of gasoline. they stated that organoclays have a fair resistance to desiccation, weathering, and self-healing because of their notable swelling tendency in contact with gasoline. Lo and Mak (1998) studied the feasibility of employing organoclay in compacted liner systems to retard the transport of phenolic compounds. They proposed that using the organoclay in compacted clay liners increased the retardation factor of barrier system to phenolic compounds, significantly.

In addition, organoclays have been used as rheological agent in oil-based drilling fluids. Caenn et al. (2011)clarified that the oil-based drilling fluids have higher lubricity, significant thermal stability, and higher rate of penetration compared to the water-based drilling fluids. Organoclay can be dispersed easily in the organic hydrocarbon liquids like diesel and mineral oils due to their organophilic properties. As a result, organoclay amendments can enhance the physical and chemical properties of oil-based drilling fluids under high pressure and high temperature.

1.6 Scope of this study

Although many studies have been carried out to investigate the geochemical properties of engineered organoclays, their geotechnical behaviors, especially the field performance as a sorptive amendment in earthen barrier still merits examination. The goal of this dissertation is to bridge the laboratory sorption test with the possible geotechnical engineering applications of organoclays in compacted clays, geosynthetic clay liners and permeable reactive barriers by investigating the hydraulic performance and contaminant retention of organoclays under controlled laboratory conditions. Specifically, this dissertation discusses the following topics:

1. The sorptivity of organoclays, especially partitioning clays as a function of: sorbate properties (organic carbon content, surfactant type, grain size); sorbate properties (chlorination, water solubility) and the aqueous environment (temperature, co-solvent). To obtain the results, several series of batch sorption tests were designed and carried out. The details were elaborated in Chapter 2.
2. The mass transport of representative organic contaminants through soil barriers including compacted clay, geosynthetic clay liner and permeable soil admixtures. We proposed a new concept of using the organoclays as the active components to aid the performance of these materials as chemical barriers. The effect of organoclay amendment on the mass flux of contaminants and enhanced retardation capacity of the amended barrier materials were investigated.

Additionally, the “hydraulic” performance of the same materials was studied, with the emphasis being placed on the impact of organoclay additive ion the fluid flow of non-polar liquids. For these reason, flexible-wall permeability tests and column breakthrough tests were carried out and analyzed. The details of these investigations were elaborated in Chapter 3, 4 and 5.

2 CHAPTER TWO SORPTION OF ORGANIC CONTAMINANTS ONTO ORGANOCLAYS

2.1 Background

Sorption process in an aqueous phase defines the distribution of the dissolved contaminants (sorbate) between the solution and sorbent (Sharma and Reddy 2004). For a variety of environmental pollutants (e.g., polychlorinated biphenyls, polycyclic aromatic hydrocarbons, etc.), natural soils typically have very limited sorption unless they are with high natural organic matter (NOC) content. In comparison, the engineered organic surfactant/clay hybrids, or organoclays, typically have their sorptivity hundreds of times greater than their unmodified counterparts (Chiou et al. 1983; Redding et al. 2002; Richards and Bouazza 2007; Upson and Burns 2006). They have significant amount of organic carbon content and are strong sorbents for chlorinated hydrocarbons and petroleum related hydrocarbons (with solubility no greater than a few mg/L). The physical/chemical properties of the synthesized organoclay is a function of the characteristics of the quaternary ammonium cations (QACs) including the molecular structure and quantity, or the morphology of the intercalated QACs. Based on the level of interaction, the sorption mechanism can be categorized into: (1) physical sorption which also is known as the van der Waals sorption (physisorption), and (2) chemical sorption (chemisorption) (Webb 2003).

The physical sorption occurs when a relatively weak van der Waals interaction exists between solid and liquid phase. The level of energy generated during physical sorption is typically under 80 kJ/mole. In addition, it is possible that the sorbate molecules diffuse on the exterior surface of the solid phase and make a weak bond which can be reversed easily. However, the physically sorbed molecules do not have the potential to make a structural disturbance on the sorption site. Physical sorption can result in either a monolayer or a multilayer structure of sorbed molecules on the interaction surfaces which have favorable temperature and pressure condition for the physical bonding.

In contrast, the chemical adsorption is the result of strong chemical bond between sorbate and sorbent. The nature of chemical bonds can be either the covalent (electron sharing) or ionic (electron charge transferring). The released heat energy during the chemical adsorption ranges between 600 kJ/mole to 800 kJ/mole. Because of a strong chemical bond in chemisorption, the nature of adsorbate change and form a new species. Moreover, the structure of top layers in adsorbent can be changed as well. These changes include the relaxation of interlayer spacing and/or the rearrangement of molecular structure in the adjacent top layers to the adsorption site. In this class of adsorption, typically the adsorption process lasts until the adsorbate can make a direct contact with the surface of adsorbent (Webb 2003).

Mostly, organoclays are produced by exchanging the QACs with the existing inorganic cations in interlayer of base clay. The intercalation of QACs into the interlayer space of base clay refers to the primary sorption. However, increasing the QAC loading will result in propping up the interlayer spacing which creates a favorable organophilic phase for sorption of non-polar molecules. This process refers to the secondary sorption.

The relationship between the amount of sorbed contaminant by sorbent (S) and the remained contaminant in the solution phase (C) at equilibrium is known as isotherm (Suzuki 1990). Concentrations in liquid and solid phase are described as a unit mass per volume, and absorbed mass of contaminant per unit mass of sorbent, respectively. The sorption isotherm models are categorized in three major groups: (1) Linear isotherm (2) Langmuir isotherm (3) Freundlich isotherm.

In the linear isotherm, there is a linear relationship between the absorbed amount of contaminant and the remaining concentration of contaminant in the solution defined by equation 2-1.

$$S = K_d \mathrm{C} \qquad 2\text{-}1$$

where S is the mass of adsorbed contaminant by the sorbent (µg/g), K_d is the linear distribution (partitioning) coefficient (mL/g), and C is the concentration of contaminant in the solution at the equilibrium condition (µg/mL). To obtain the K_d value, mass of adsorbed contaminant by the sorbent (S) is plotted versus concentration of contaminant in the solution at the equilibrium condition (C) and the slope of linear fitted line to the data points is defined as distribution coefficient. An example of linear sorption isotherm is shown in Figure 2-1.

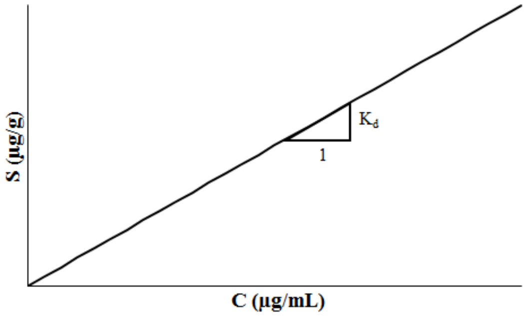


Figure 2-1. Linear sorption isotherm

In the Langmuir isotherm, a non-linear relationship between the absorbed amount of contaminant and the remaining concentration of contaminant in the solution is defined based on the concept that there are finite number of sorption sites available on the solid surface and sorption process depends on the availability of the sorption sites. Langmuir isotherm can be defined mathematically by equation 2-2.

$$S = \frac{\alpha\beta C}{1 + \alpha C} \tag{2-2}$$

where α is a sorption constant that defines the binding energy (1/mg), and β is the maximum mass of contaminant that can be absorbed by sorbent (μg/g). To find the sorption constants, there are four different linear models that can be applied to the Langmuir sorption data, Table 2-1 (Ho 2006).

Table 2-1. Linear models of Langmuir sorption isotherm

Linear model	Plot
$\frac{\beta}{S} = \frac{1}{C}\beta + \frac{1}{\alpha}C$	$\frac{\beta}{S}\ vs.\beta$
$\frac{1}{S} = \left(\frac{1}{\alpha C}\right)\frac{1}{\beta} + \frac{1}{C}$	$\frac{1}{S}\ vs.\frac{1}{\beta}$
$S = C - \left(\frac{1}{\alpha}\right)\frac{S}{\beta}$	$S\ vs.\frac{S}{\beta}$
$\frac{S}{\beta} = \alpha C - \alpha S$	$\frac{S}{\beta}\ vs.S$

An example of Langmuir sorption isotherm is shown in Figure 2-2.

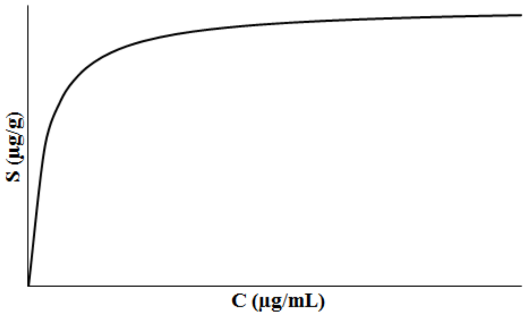


Figure 2-2. Langmuir sorption isotherm

The Freundlich isotherm is used for higher concentrations which represents highly favorable sorption. The Freundlich isotherm model is described mathematically as equation 2-3.

$$S = KC^N \qquad 2\text{-}3$$

where K is the constant of sorption capacity and N is the intensity constant which is always less than 1. An example of Freundlich sorption isotherm is shown in Figure 2-3.

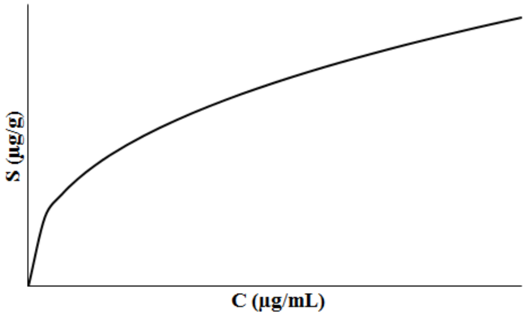


Figure 2-3. Freundlich sorption isotherm

There are many diverse factors which affect the sorption of a sorbate in soil media. The mentioned factors can be classified in three major groups: (1) sorbate characteristics such as water solubility, (2) soil characteristics such as TOC, and (3) fluid media characteristics such as temperature (Sharma and Reddy 2004). The classification of the effective factors on the sorption of organic contaminants by soil media is illustrated in Figure 2-4.

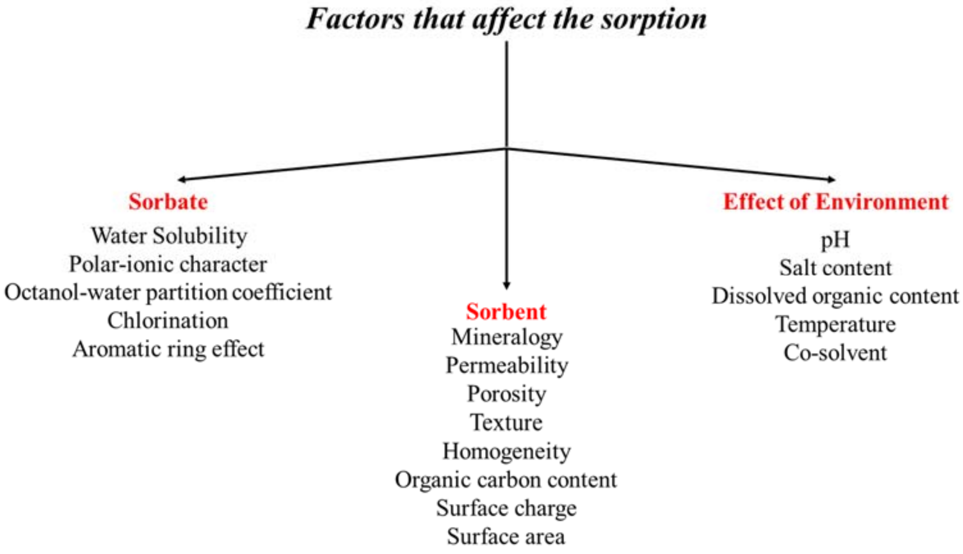


Figure 2-4. Effective factors in the sorption process of sorbates by sorbent

Previous studies indicated that the sorption capacity of partitioning organoclays can be affected by both sorbate and sorbent properties. Specifically, greater amount of intercalated cationic surfactants with larger size (or consequently, higher amount organic carbon loading) would increase the sorptivity of synthesized organoclays while the type, size and functional group could control the affinity of sorbates towards the organoclay sorbents., Additionally, the aqueous environmental including the co-solvent, pH, temperature and ionic strength can also impact the sorption process. Previously, the most common approach to predict the affinity of organic sorbates to the partitioning clays was based on their solubility in octanol-water distribution coefficient (K_{OW}) (Chiou et al. 1998; Di Cesare and Smith 1994; Smith et al. 1988). Chiou et al. (1982) suggested that the water solubility of the organic compounds could be one of the primary indicator of the affinity of organic compounds toward the organically modified clays. It was suggested that the water solubility of sorbate molecule would decrease if the number of aromatic ring and degree of chlorination of the molecule increases and consequently, an increased K_{OW} is often observed (Mortland et al. 1986; Zhao et al. 2016).

The quantity of aliphatic carbon will increase on the surface of organoclays by increasing the total organic carbon (TOC). In a QAC modified clay, typically the entangled bulk aliphatic chains of the QAC play the role of partitioning medium in the sorption process. Many studies have indicated that the sorption capacity of organoclays is directly related to their TOC content, especially the organic carbons that was intercalated into the interlayer of the clays. Lee et al. (1989) used three organic cations: hexadecyltrimethylammonium (HDTMA), dodecyltrimethylammonium (DDTMA), nonyltrimethylammonium (NTMA) to modified soils. They observed that organic cation with longer aliphatic carbon chain demonstrated higher sorption capacity of nonionic organic contaminants (NOCs). Redding et al. (2002) studied the sorption of benzene onto two organoclays as a function of TOC and demonstrated that benzene has higher binding tendency to partitioning organoclays when the TOC increases. For organoclays modified by cationic surfactant with branched carbon chains, Bartelt-Hunt et al. (2003) indicated BTEA-bentonite had higher sorption capacity for TCE, benzene, and 1,2-dichlorobenzene from aqueous phase.

The next few paragraphs discuss the effect of aqueous environment on the organoclay sorptivity. Previous studies indicated that the co-solvent may inhibit the sorption of organic sorbates onto organoclays (Nzengung et al. 1997).The study of Nzengung et al. (1996) evaluated the sorption of naphthalene dissolved in solution with different methanol fraction (f^c) by organobentonites. They concluded that the sorption of naphthalene onto organoclays decreased as the fraction of methanol in solution matrix increased. Rao et al. (1985) presented a solvophobic model to quantify the effect of co-solvent on the sorption capacity of hydrophobic organic chemicals (HOCs) (equation 2-4):

$$ln\left(\frac{K^m}{K^w}\right) = -a\alpha\sigma^c f^c \qquad 2\text{-}4$$

where K^w is the sorption coefficient from water (mL/g), K^m is the partitioning coefficient from mixed solvent (mL/g), a is an empirical constant presenting the interactions between water and co-solvent, α is an empirical constant presenting the interactions between sorbent and solvent, and σ^c is the cosolvency power of the solvent which presents the interaction between solvent and the solution. This model suggests the equilibrium partitioning coefficient (K^m) of HOCs decreases exponentially as the fraction of co-solvent (f^c) in the solution increases. Fu and Luthy (1986) investigated the effect of nonpolar solvents on the sorptivity of hydrophobic solutes onto the silt loam and sandy soil. They concluded that the sorption of hydrophobic solutes decreased semi-logarithmically as the percentage of solvents increased in the aqueous solution.

Also, the effect of temperature on the sorption tendency of sorbents has been studied. Chiou et al. (1979) indicated that the sorption of 1, 1, 1 – trichloroethane increases at higher temperature. In another study, Mirmohamadsadeghi et al. (2012) studied the effect of temperature in the range of 30 to 50° C on the sorption of phenol to HDTMA-bentonite. They concluded that HDTMA-bentonite reached to its maximum sorption capacity at 50° C. Also, Sadeghi Ghari and Shakouri (2016) studied the effect of temperature on the sorption of toluene on organoclay. The reported that the sorption of toluene by organoclay increases when the temperature increases from 25 to 55° C. they stated that the observed increase in the sorption capacity of organoclay is due to the higher level of interaction between organoclay and solvent.

Although many studies were conducted to quantify the sorption capacity of different organoclay sorbents vs organic sorbates, the fundamental sorption process still merits examination. This was due to the complexity of understanding the natures of the sorbents and sorbates as well as the difficulty of taking the aqueous environmental conditions into consideration. In this chapter, a series of batch sorption studies were conducted to quantify the sorption capacity of the organoclay sorbents with known microstructures and physicochemical properties. The impact of sorbate, and aqueous environment were also examined. Two partitioning clays: HDTMA-bentonite and PM-199 were selected as the soil sorbents for the batch sorption tests and benzene, naphthalene, hexachlorobenzene, 1, 2, 4 –trichlorobenzene, and phenanthrene were selected as the dissolved organic contaminants. The major factors involved in sorption study were: (1) sorbate (chlorination, water solubility), (2) sorbent (organic carbon content, surface charge, grain size), and (3) aqueous environment (temperature, co-solvent).

2.2 Materials and methods

2.2.1 PM-199

Organoclay PM-199 in powder format was obtained from CETCO Company (Hoffman Estates, Illinois). PM-199 is a sodium bentonite (Na-bentonite) that modified by bis(hydrogenated tallow alkyl) dimethyl ammonium chloride. The modification was achieved by exchanging the naturally occurring sodium cations in the Na-bentonite interlayer with the dimethylammonium cation (Lee et al. 2012). The physical properties of PM-199 are summarized in Table 2-3. The specific gravity of PM-199 was measured as 1.46 ± 0.2 while the specific gravity of Na-bentonite was around 2.75 (ASTM D854-B). The diffrences between the specific gravity of PM-199 and Na-bentonite was attributed to intercalated organic cations (Burns et al. 2006; Lee et al. 2012; Soule and Burns 2001). The mineralogy of PM-199 is summarized in Table 2-2

Table 2-2. Mineralogy of PM-199 (Lee et al. 2012)

Mineral	(%)
smectite	62
quartz	14
plagioclase feldspar	12
halite	5
potassium feldspar	2

2.2.2 HDTMA modified bentonite

Hexadecyltrimethylammonium (HDTMA) cation ($[(CH_3)_3NC_{16}H_{33}^+]$) was selected as the surfactant to synthesize HDTMA-bentonite because it yields surfactant/clay hybrid with higher structural stability under different environmental conditions. A calcium bentonite (Ca-bentonite) (Panther Creek 200, American Colloid Company) was used as based clay to synthesize the HDTMA-bentonite under a controlled laboratory condition. It was reported that the Ca-bentonite contained about 85% montmorillonite (American Colloid Company) and 2.58% natural organic-carbon content (McCoy & McCoy Laboratories, Incorporated), with a cation exchange capacity (CEC) of 103 meq/100 g (Hazen Research, Incorporated).

The amount of HDTMA cation for the synthesis of HDTMA-bentonite was estimated by:

$$f = \frac{M_{cation}}{CEC.M_{clay}.GMW_{cation}.Z} \qquad 2\text{-}5$$

where f is the desired percentage of CEC that will be satisfied by organic cation, M_{cation} is the mass of the organic cation that is needed to achieve the designed CEC, CEC is the cation exchange capacity of the base bentonite (meq/mol), M_{clay} is the mass of the bentonite that will be used to modify (g), GMW_{cation} is the gram molecular weight of the HDTMA-Br (g/mol), and Z is the number of charge moles per each equivalent.

The weighted salt (Hexadecyltrimethylammonium (HDTMA) bromide ($[(CH_3)_3NC_{16}H_{33}Br]$)) was first dissolved in 500 ml of deionized water at 60º C. Next, 300 g of the calcium bentonite (sieved through #200) was mixed with the prepared solution and the slurry was stirred for 30 min. The slurry was covered and placed at room temperature for 24 hrs. The modified clay was filtered and rinsed with deionized water before it was oven-dried at 110º C for 72 hrs. Finally clay particles was ground and sieved by sieve number 40.

In order to measure the surfactant intercalation, the basal spacing of Ca-bentonite and HDTMA-bentonite were measured using the XRD analysis. The spectra of XRD was recorded for angles between 2° to 20° (2θ) using CuKa radiation (n=1.5406 Å) at the scanning rate of 2°/min. The basal spacing of the Ca-bentonite and HDTMA-bentonite were measured as 15.06 Å and 19.44 Å, respectively. The XRD results are shown in Figure 2-5. Due to the intercalation process, HDTMA cations penetrated into the interlayer of Ca-bentonite and consequently increased the basal spacing of the clay. In addition to Ca-bentonite, a commercially available Na-bentonite was purchased from CECTCO Company and used as a sorbent for comparison. The engineering properties of

Ca-bentonite, HDTMA-bentonite, and Na-bentonite are summarized in Table 2-3. Additionally, SEM and TEM tests were conducted to examine the microstructures of Ca-bentonite and HDTMA-bentonite (Figure 2-6).

Table 2-3. The engineering properties of Ca-bentonite, Na-bentonite, and HDTMA bentonite

Properties	References	Ca-bentonite	HDTMA-bentonite	Na-bentonite	PM-199
Liquid limit (%)	ASTM D4318	88.3	74.9	282.5	50.7
Plasticity index (%)	ASTM D4318	37.3	16.3	221.6	2
Fraction pass through #200 sieve (%)	ASTM D6913	85.5	100	100	100
Specific gravity	ASTM D854-14	2.58	1.75	2.75	1.46
Specific surface area (m^2/g)	Santamarina et al. (2002)	276.28	162.21	628	60.7
Total organic carbon (%)	ASTM D7348	2.58	21.44	< 1	21.7
Basal spacing (Å)	Ye et al. (2014)	15.06	19.44	12.57	35.58

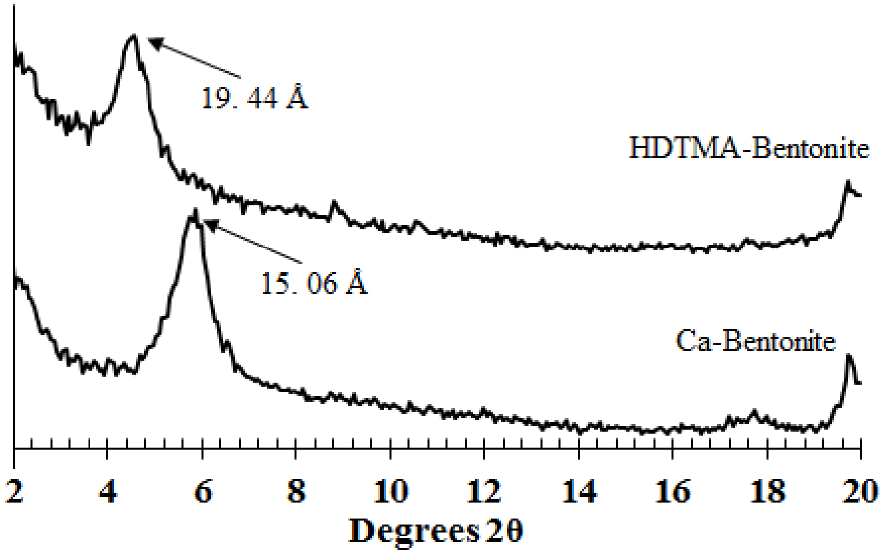
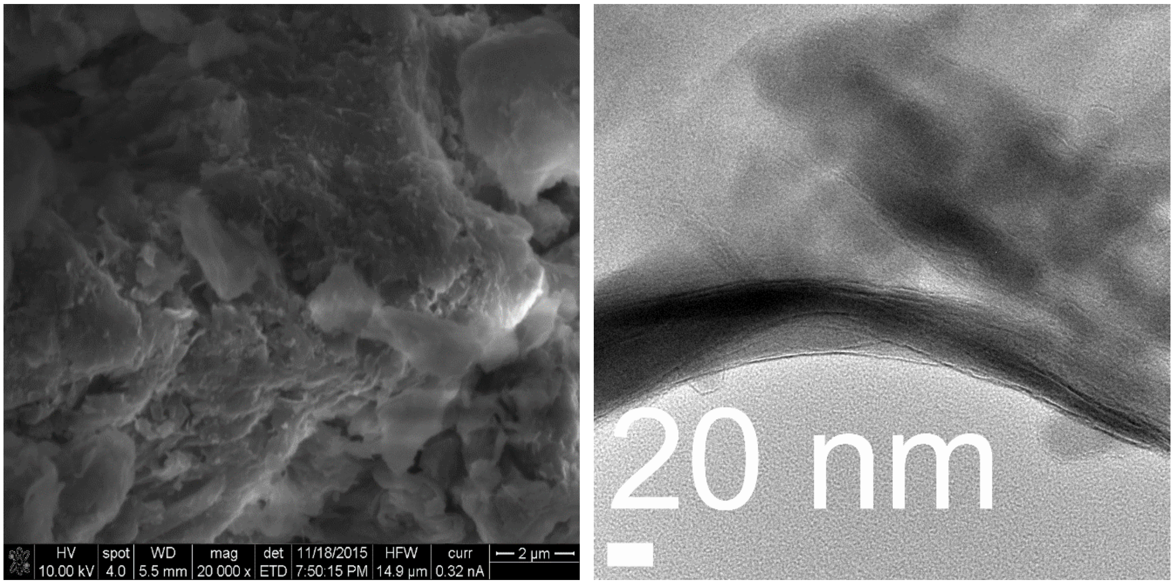


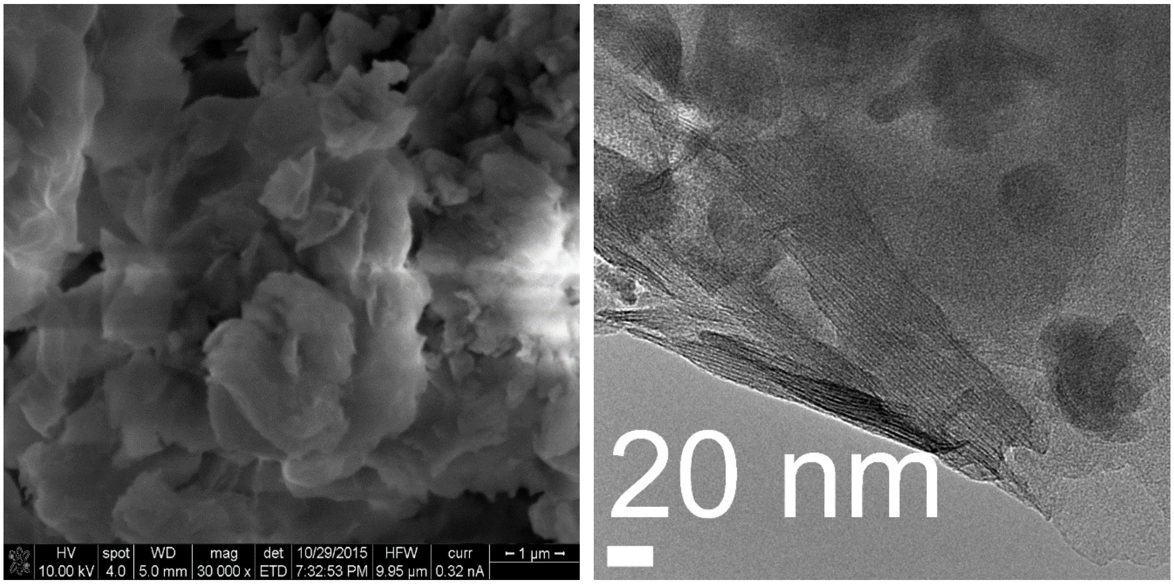
Figure 2-5. XRD result for Ca-bentonite and HDTMA-bentonite



Calcium bentonite

HDTMA-bentonite

(a)



(b)

Figure 2-6. (a) Scanning Electron Microscope (SEM) and Transmission electron microscopy (TEM) test of Ca-bentonite (b) Scanning Electron Microscope (SEM) and Transmission electron microscopy (TEM) test of calcium bentonite HDTMA-bentonite

2.2.3 Organic sorbates

Anhydrous benzene with purity of 99.8%, hexachlorobenzene with purity of 99.1% in acetone solution, and anhydrous 1,2,4-trichlorobenzene with purity of 99% were purchased (Sigma-Aldrich). Also, Phenanthrene and naphthalene in crystal form with purity of 97% were purchased (Fisher Scientific Company). The physical and chemical properties of the studied contaminants are summarized in Table 2-6.

2.2.4 Co-solvents

Acetone (W.M.Barr Co.)and methanol (Carolina Co.) were used as the organic solvent. The physical and chemical properties of the solvents are summarized in Table 2-4 and Table 2-5.

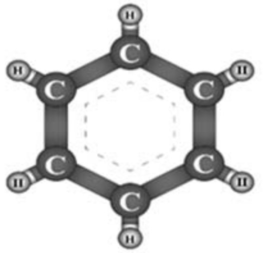
Table 2-4. Physical and chemical properties of acetone

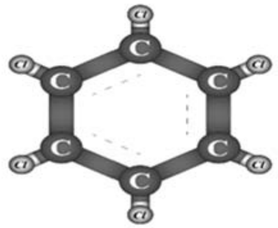
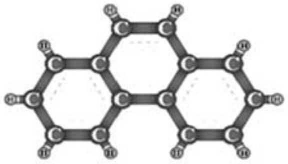
Physical States:	Liquid
Boiling Point:	> 133˚ F
Auto-ignition Point:	869˚ F
Flash Point (according to TAG Closed Cup method):	0˚F
Explosive Limits:	LEL: 2.5 % at 77˚ F, and UEL: 13 % at 77˚ F
Density:	0.7845 g/cm^3 at 77˚ F
Vapor Pressure (vs. Air or mm Hg):	30.6 kPa at 77˚ F
Solubility in Water:	Complete

Table 2-5. Physical and chemical properties of methanol

Physical States:	Liquid
Boiling Point:	> 148.5˚ F
Auto-ignition Point:	878˚ F
Flash Point (according to TAG Closed Cup method):	52˚ to 54˚F
Explosive Limits:	LEL: 6 % at 77˚ F, and UEL: 36 % at 77˚ F
Density:	0.792 g/cm^3
Vapor Pressure (vs. Air or mm Hg):	13.02 kPa at 68˚ F
Solubility in Water:	Complete

Table 2.6. Physical and chemical properties of the studied contaminants

Compound	Density (g/cm^3)	Solubility in water at 25° C (mg/L)	Vapor Pressure at 25° C (mm Hg)	Log Kow	Total benzene ring	Sources	Structure
Benzene	0.8765	1.79×10^3	94.8	2.13	1	combustion processes, industry production, wood burning, petroleum based chemicals inhalation during its manufacture and use, consumption of contaminated drinking water and food	
1,2,4-Trichlorobenzene	1.46	49.0	0.46	4.02	1		

Hexachlorobenzene	2.04	4.7×10^{-3}	1.72×10^{-5}	5.73	1	chlorinated solvents, pesticides, by-product for production of atrazine, propazine, simazine, and mirex, fossil fuel, wastes and sewage sludge incineration emissions from the chemical and primary metals industries, biomass burning,	
Naphthalene	1.162	31.6	0.085	3.30	2	gasoline and oil combustion, tobacco smoking, the use of mothballs, fumigants, and deodorizers	
Phenanthrene	1.18	1.6	1.21×10^{-4}	4.46	2	gasoline and oil combustion, tobacco smoking, the use of mothballs, fumigants, and deodorizers	

2.2.5 Extraction Liquids

American Chemical Society (ACS) grade hexanes (Carolina Co.) and anhydrous dichloromethane (DCM) with purity of 99.8% (Sigma-Aldrich Co.) were used to extract sorbates from the aqueous phase.

2.2.6 Batch sorption test

2.2.6.1 Sample preparation

The sorption capacity of soils sorbents and the effects of sorbents properties (including the grain size, TOC, specific gravity, and specific surface area); sorbates properties (including the water solubility and chlorination of the sorbate molecules), and aqueous environment (co-solvent fraction and temperature) were investigated. The testing matrix of conducted sorption tests is summarized in Table 2-7.

Table 2-7. Test matrix of the lab batch sorption

Test NO.	Sorbate	Co-Solvent	Water	Temperature	Sorbent
1	HCB	Acetone (100%)	0%	25° C	HDTMA-bentonite
2	HCB	Acetone (100%)	0%	25° C	PM – 199 (Powder)
3	1, 2, 4 - Trichlorobenzene	Acetone (100%)	0%	25° C	HDTMA-bentonite
4	Phenanthrene	Acetone (100%)	0%	25° C	HDTMA-bentonite
5	Naphthalene	Methanol (30%)	70%	25° C	HDTMA-bentonite
6	Naphthalene	Methanol (30%)	70%	25° C	Low plasticity silty clay
7	Naphthalene	Acetone (100%)	0%	25° C	HDTMA-bentonite
8	Benzene	Methanol (30%)	70%	25° C	HDTMA-bentonite
9	Benzene	0%	100%	60° C	HDTMA-bentonite
10	Benzene	0%	100%	40° C	HDTMA-bentonite
11	Benzene	0%	100%	25° C	HDTMA-bentonite
12	Benzene	0%	100%	10° C	HDTMA-bentonite
13	Benzene	0%	100%	25° C	Ca - bentonite
14	Benzene	0%	100%	25° C	Na - bentonite
15	Benzene	0%	100%	25° C	PM – 199 (Powder)
16	Benzene	0%	100%	25° C	PM – 199 (Granular)
17	Benzene	Acetone (100%)	0%	25° C	HDTMA-bentonite

As an example, the solution preparation procedure for HCB is described in follow. The HCB stock solution with an initial concentration of 1000 μg/mL was used to generate the HCB solutions with the desired concentrations to investigate the impact of chlorination and water solubility of the sorbate molecules, and also the effect of modifier surfactant on the sorption capacity of the sorbents. For this purpose, acetone was used as the solvent to prepare the HCB solutions with final concentrations of 1, 5, 10, 20, 30, 40, 60, 80, and 100 μg/mL.

Next, a sets of conical centrifuge tubes with teflon coded lid (CORING Co.) with capacity of 15 mL were filled with prepared stock solutions. Next, 0.2 g of sorbent was added to the second set of batch reactors. Then, the batch reactors were agitated for 24 hours before centrifuged at 1500 rpm for 30 min. Next, 8 mL of supernatant in batch reactor was filtered through a 0.2 μm syringe filters (Acrodisc Co.). The filtered samples were extracted with hexane (used for naphthalene) or dichloromethane (used for benzene) at a ratio of 10:1 (v/v) to prepare the samples for analysis. The filtered samples were analyzed with Gas Chromatography equipped with flame ionization detector and electron capture detector (GC-FID/ECD) (Clarus 480, Perkin Elmer Co.). A schematic illustration of the batch sorption procedure is shown in Figure 2-7.

The concentration of the absorbed sorbate by sorbent was measured as:

$$S = \frac{V_m\left(C_0 - C\right)}{M_s} \qquad 2\text{-}6$$

Where S (μg/g) is the concentration of sorbate sorbed by sorbent, C_0 (μg/mL) and C (μg/mL) are the initial and equilibrium concentrations of sorbate in the solution, respectively. V_M (mL) is the volume of the batch reactor, and M_S (g) is the total weight of the sorbent. S was plotted versus C and the slope of the linear fit was determined as the partitioning coefficient, K_d.

In addition, the sorption kinetics of naphthalene and benzene onto HDTMA-bentonite were quantified by a series of non-equilibrium sorption tests. For kinetic study of naphthalene, 16 stock solutions consisted of 200 μg/mL naphthalene in 70% deionized water and 30% methanol were prepared in the batch reactors. For benzene, 32 stock solutions with concentration of 200 μg/mL in deionized water were prepared in the batch reactors. Then 0.2 g of HDTMA-bentonite were added to batch reactor. At 16 preset time periods (starting from 15 secs to 48 h), the supernatant was tested for the naphthalene and benzene concentration.

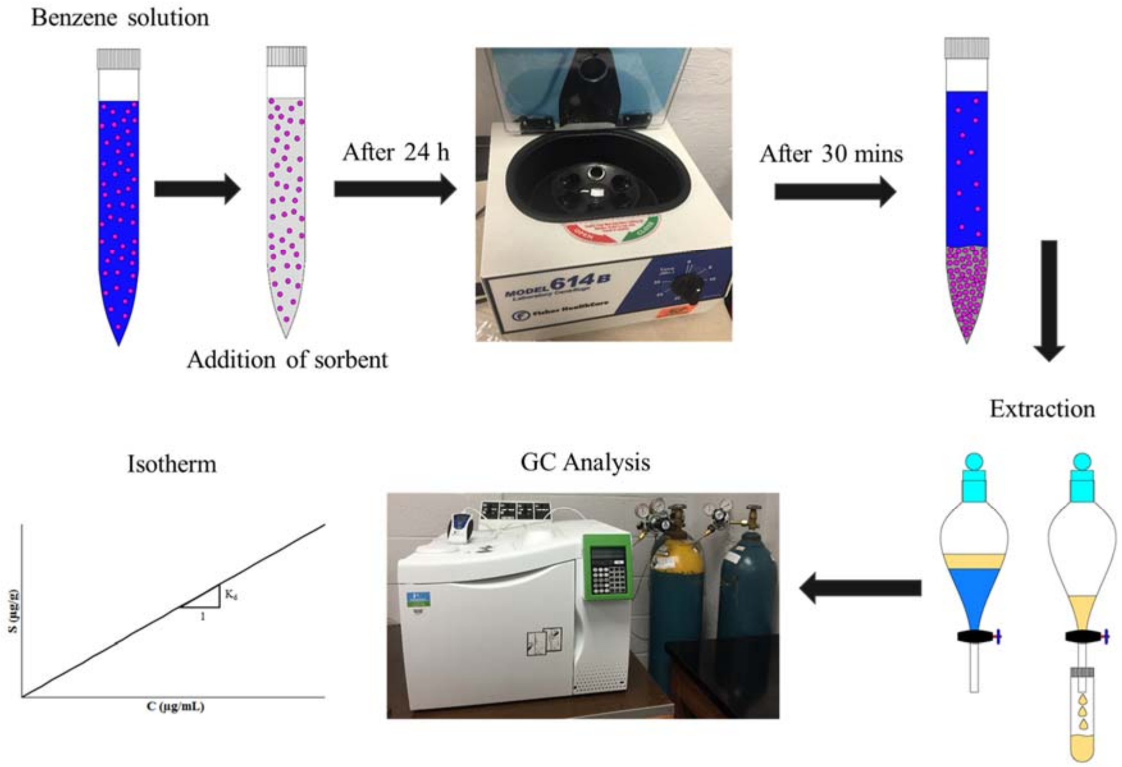


Figure 2-7. Schematic figure of the sorption procedure

2.3 Results and discussion

2.3.1 Overall results

The effect of major factors including (1) sorbate (chlorination, water solubility), (2) sorbent (organic carbon content, surface charge, surface area, grain size), and (3) aqueous environment (temperature, co-solvent) on the sorption characteristics of studied sorbents were studied.

The acquired results suggested that the affinity of dissolved organic contaminants to organobentonites increased when the number of aromatic rings and chlorination increased in organic contaminants. It was observed that the solubility of molecules decreased in the order of (phenanthrene>naphthalene>benzene) as the aromatic ring increased. Likewise, the solubility of molecules decreased in the order of (hexachlorobenzene>1, 2, 4 –trichlorobenzene >benzene) as the chlorinated position on the ring increased. This happened because of the increased hydrophobicity of organic contaminants which resulted in decreased solubility.

The surface modification resulted in expansion of interlayer in the base clay followed by increasing the organic matter loading within the clay interlayer. Consequently, a favorable organophilic phase was created in organobentonite which attributed to higher affinity of dissolved organic contaminants toward organobentonites compared to unmodified sorbents. Also, it was observed that PM-199 showed higher sorption capacity to organic contaminants compared to HDTMA-bentonite. The reason was that PM-199 was synthesized by a double chain surfactant modifier while a single chain surfactant modifier was used to synthesize HDTMA-bentonite. As a result, the percentage of aliphatic carbon in PM-199 was higher than HDTMA-bentonite which resulted in higher sorption capacity of PM-199. In addition, the obtained results suggested that grain size has a negligible impact on the sorption capacity of the sorbents.

Additionally, it was found that the affinity of organic contaminants to organobentonite was decreased by increasing the percentage of solvent in the aqueous solution due to the cosolvency of the co-solvent which increased the solubility and decreased the sorption capacity of hydrophobic organic contaminants. Also, it was observed that the sorption capacity of the organobentonites increased by increasing the temperature due to a higher level of kinetic energy that was induced to the solution and increased the interaction between organobentonite and organic contaminants.

2.3.2 Effect of molecular characteristics of sorbents on sorption capacity

In this section, the effect of molecular characteristics of sorbents on the sorption behavior of organically modified and unmodified sorbents is discussed.

The obtained results from the batch sorption study of dissolved benzene in aqueous solution indicated that the sorption capacity of organobentonites to organic contaminants were significantly higher than unmodified bentonites. The partitioning coefficient of PM-199 and HDTMA-bentonite for benzene solution were measured as 251.4, and 82.97 mL/g respectively. While, the partitioning coefficient of Ca-bentonite and Na-bentonite for benzene solution decreased drastically to 19.83, and 9.75 mL/g respectively. As it mentioned previously, the intercalation of QACs with base clays increases the organic matter loading within the clay interlayer. Many studies have been done on the effect of organic carbon loading on the sorption capacity of sorbents (Bartelt-Hunt et al. 2003;

Boyd et al. 1988; Redding et al. 2002). The natural organic carbons existing on the surface of sorbents has higher affinity to interact with organic compounds. As a result, unmodified bentonites and silty clay presented a negligible sorption capacity to organic contaminants because they have limited percentage of natural occurring carbon in their structure (Redding et al. 2002). However, organobentonites exhibited significant sorption capacity to organic contaminants because the intercalated modifier cations increase the carbon loading on the surface of organobentonites (Boyd et al. 1988; Smith and Jaffe 1994).The effect of TOC on the partitioning coefficient of studied sorbents has been shown in Figure 2-8.

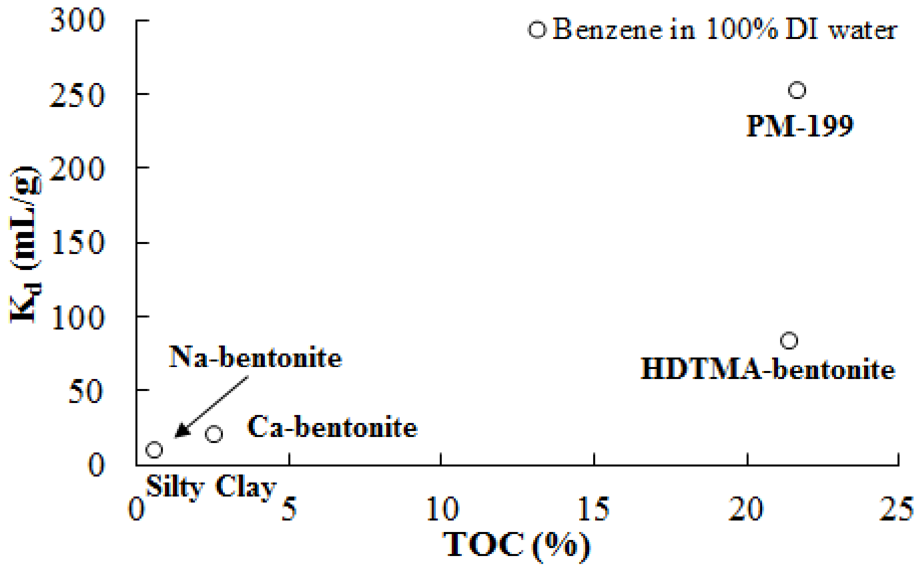
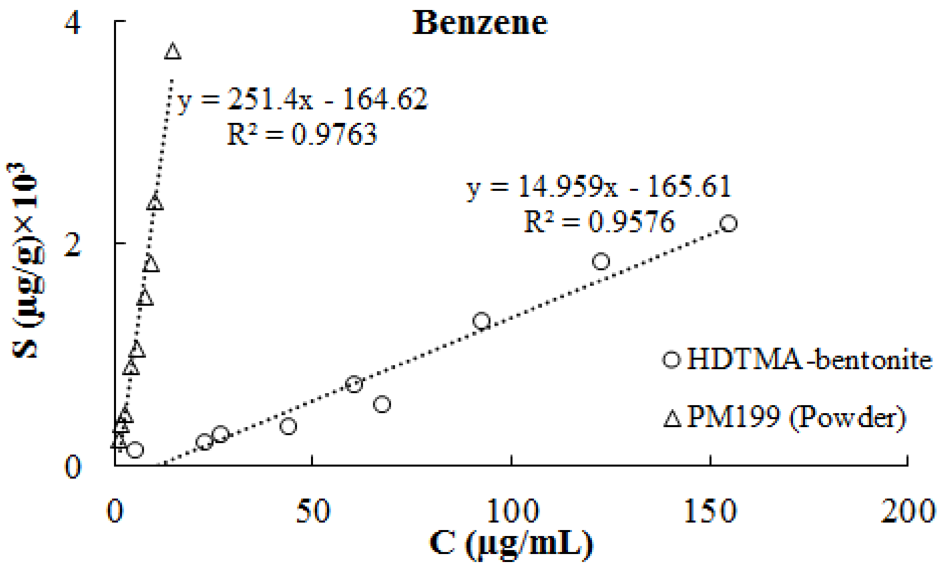
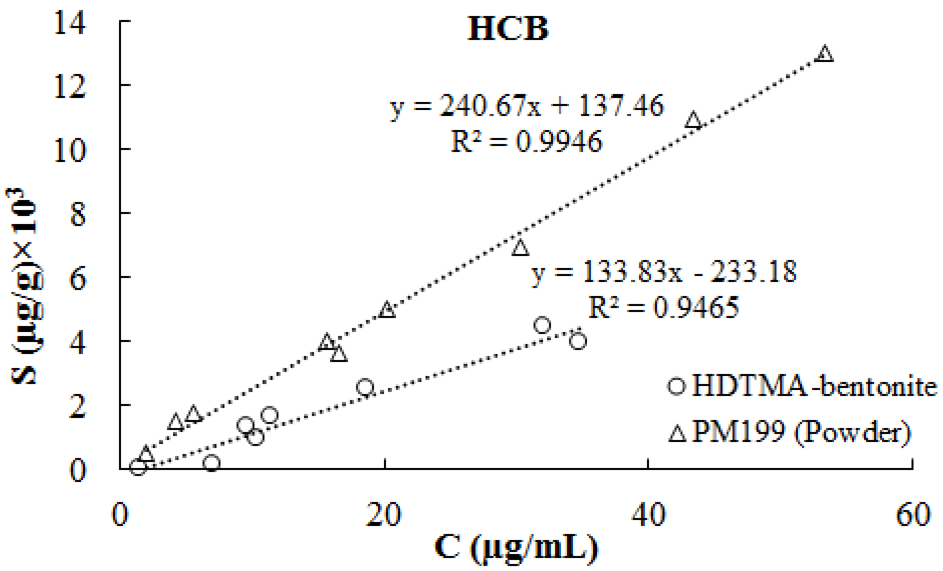


Figure 2-8. Effect of TOC on the partitioning coefficient

In addition, it was noticed that PM-199 exhibited much higher sorption capacity for organic contaminant compared to HDTMA-bentonite. This result was validated using two sets of sorption study including the sorption of benzene from aqueous solution and HCB from 30% acetone + 70% DI water solution to PM-199 and HDTMA-bentonite. The partitioning coefficient of PM-199 and HDTMA-bentonite for HCB were measured as 240.67, and 133.83 mL/g respectively. It was found that the higher sorption capacity of PM-199 compared to HDTMA-bentonite was due to the higher number of aliphatic carbons in PM-199 compared to HDTMA-bentonite. The number of intercalated aliphatic carbons can be increased either by increasing the length of carbon chain or the number of organic chains, which results in higher sorption of organic compounds (Burns et al. 2006). Due to the mentioned reason, it was anticipated that PM-199 exhibits higher sorptivity compared to the HDTMA-bentonite because PM-199 was synthesized by a double chain surfactant compared to HDTMA-bentonite that was synthesized by a single chain surfactant. The obtained results are demonstrated Figure 2-9.



(a)



(b)

Figure 2-9. Sorption capacity of PM-199 and HDTMA-bentonite as a function of organic cation types for (a) benzene in aqueous solution[1], and (b) HCB in 30% acetone + 70% DI water solution

Also, the sorption capacity of PM-199 in the form of powder and granular for dissolved benzene in aqueous solution was investigated to study the effect of particle size as a physical property of sorbent on the sorption capacity of sorbent. The results are presented in Figure 2-10. The partitioning coefficient of powder PM-199 and granular PM-199 for benzene were measured as 251.4, and 231.37 mL/g respectively. As a result, no significant differences between the partitioning coefficient of powder and granular PM-199 was observed. It can be concluded that the particle size has a negligible impact on the sorptivity of sorbents.

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[1] The isotherm for benzene sorption by HDTMA is scaled down by 10.

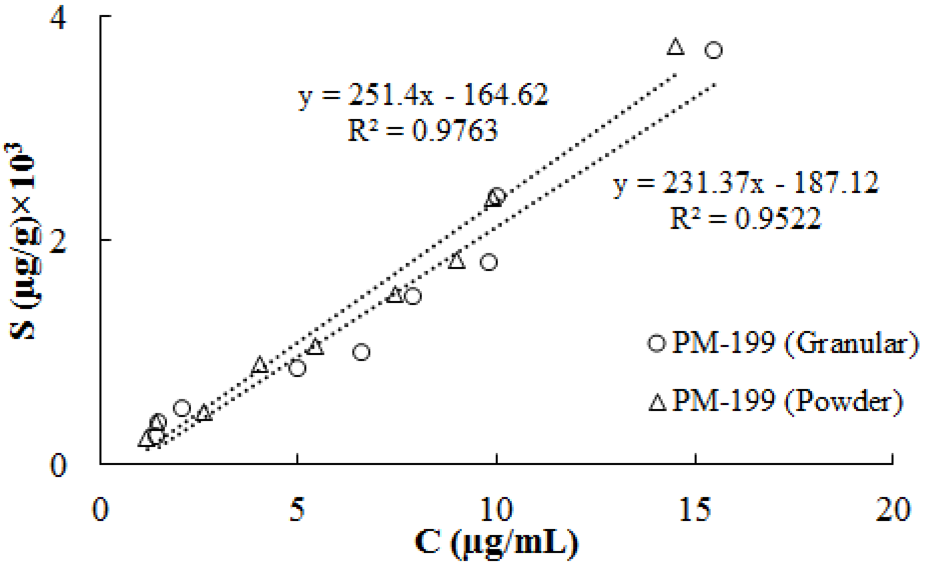

Figure 2-10. Effect of particle size on the sorption capacity of PM-199

2.3.3 Effect of the characteristics of sorbates on sorption capacity

Although the molecular characteristics of sorbents has significant impact on their sorption capacity, the molecular structure of sorbates can directly affect the sorption capacity of geo-material. In this section, the effect of sorbate structure on the sorption capacity organic compounds onto HDTMA-bentonite has been investigated. The sorption capacity of HDTMA-bentonite as a function of two variable factors including the chlorination and the number of aromatic rings has been quantified by conducting a series of batch sorption tests.

Benzene, 1,2,4-Trichlorobenzene, and HCB were selected as the organic contaminants to study the impact of chlorination on the sorption capacity of HDTMA-bentonite. For this reason, a set of batch sorption test for each organic compound was conducted using acetone as co-solvent. The sorption data for each component was fitted with a linear isotherm which confirmed that the sorption of studied organic contaminants onto the

HDTMA-bentonite occurred due to the partitioning mechanism. The obtained isotherms are illustrated in Figure 2-11.

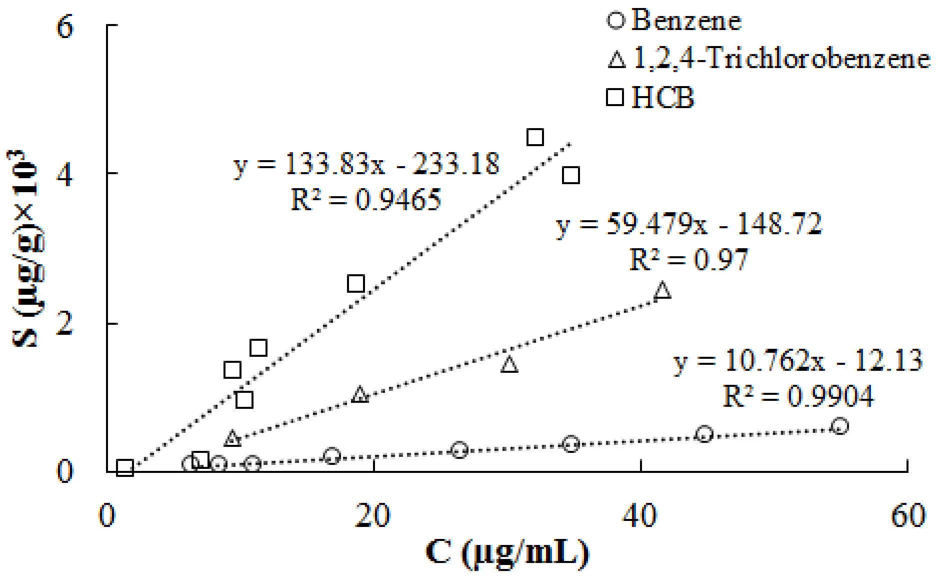

Figure 2-11. Chlorination effect on the sorption capacity of HDTMA-bentonite[2]

The partitioning coefficient of HDTMA-bentonite for benzene, 1,2,4-Trichlorobenzene, and HCB were measured as 10.76, 59.47, and 133.83 mL/g, respectively. For the sorption of three studied compounds to HDTMA-bentonite, the sorption capacity increased as the compound chlorinated. It can be said that the chlorination decreases the solubility of compounds. In benzene, hydrogen atoms facilitate the hydrogen bonding of benzene with acetone which demonstrates a weak partitioning to the HDTMA-bentonite compared to the HCB with relatively lower solubility in acetone. As a result, the partitioning coefficient of studied compounds decreases in the order of HCB>1,2,4-trichlorobenzene>benzene, respectively.

Additionally, benzene, naphthalene, and phenanthrene were selected to study the effect of aromatic rings on the sorption capacity of HDTMA-bentonite. Therefore, a set of batch

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[2] The isotherm for 1,2,4-Trichlorobenzene is scaled down by 10

sorption test for each organic compound was carried out using acetone as co-solvent. The sorption data for each component was fitted with a linear isotherm. The isotherm parameters are illustrated in Figure 2-12.

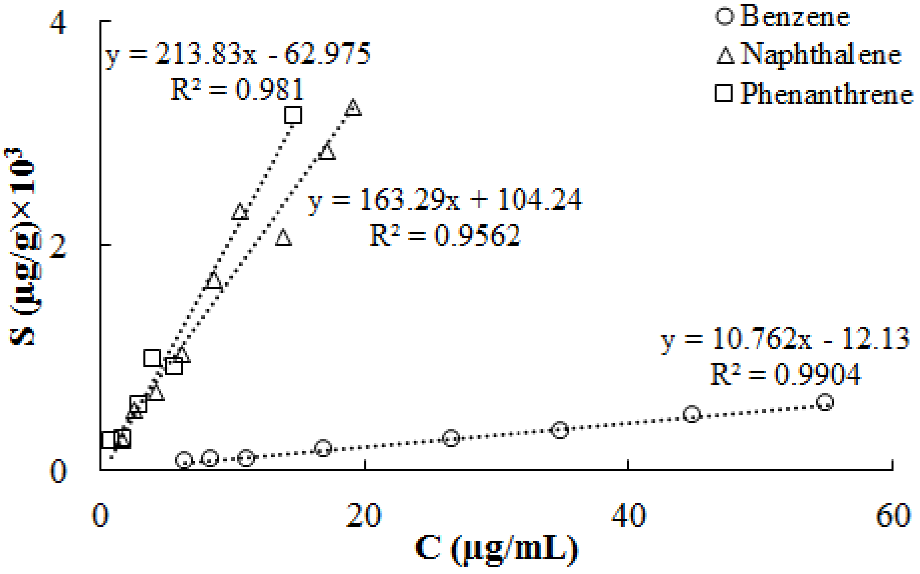

Figure 2-12. Aromatic benzene ring effect on the sorption capacity of HDTMA-bentonite[3]

The partitioning coefficient of HDTMA-bentonite for benzene, naphthalene, and phenanthrene were measured as 10.76, 163.29, and 213.83 mL/g, respectively. It was observed that the sorption capacity of HDTMA-bentonite increased when the number of aromatic rings increased in the compound structure. The partitioning coefficient of benzene is much lower than naphthalene and phenanthrene. It can be attributed to higher solubility of benzene in acetone compared to naphthalene and phenanthrene. It suggests that organic compounds with higher solubility have lower sorption into sorbent due to the partitioning mechanism compared to the organic compounds with lower solubility

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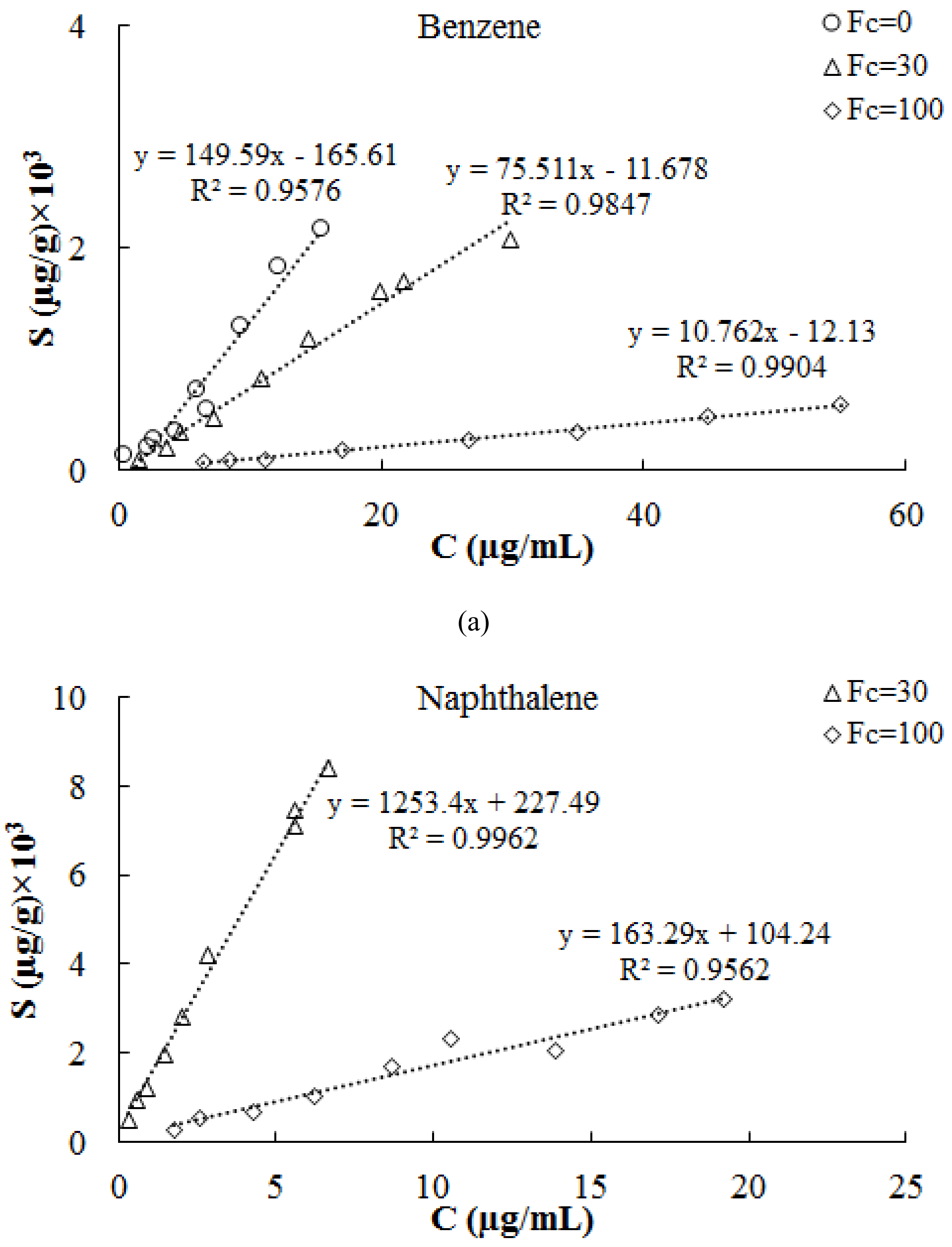
[3] The isotherm for Naphthalene is scaled down by 10 & the isotherm for Phenanthrene is scaled down by 100

(Changchaivong and Khaodhiar 2009). In conclusion, the K_d values decrease in the order of phenanthrene>naphthalene>benzene, respectively.

2.3.4 Effect of aqueous environment

Additionally, the effect of co-solvent on the sorption behavior of organobentonite (HDTMA-bentonite) was studied. The stock solutions were prepared by using acetone as the non-polar co-solvent and DI water as polar solvent. Benzene and naphthalene were selected as organic sorbates. It was observed that the partitioning coefficient of benzene in water is 149.59 mL/g and decreased to 75.51 mL/g and 10.76 mL/g by increasing the percentage of acetone from 30% to 100%, respectively. it was concluded that the dissolved benzene in water has 13 times higher affinity to HDTMA-bentonite compared to dissolved benzene in acetone. The acquired results are shown in Figure 2-13 (a). Likewise, it was observed that the sorption capacity of HDTMA-bentonite to naphthalene dissolved in a aqueous solution consisted of 30% acetone was 1253.4 mL/g and decreased to 163.29 mL/g when the naphthalene dissolved in 100% acetone. The acquired results are shown in Figure 2-13 (b). This result showed that the capacity of HDTMA-bentonite to sorb naphthalene decreased drastically (by 86%) when the solvent for naphthalene changed from aqueous solution with 30% acetone to 100% acetone. As a result, the partitioning coefficient increases when the co-solvent fraction in the solution decreases. Increasing the co-solvent percentages in the solution will be accompanied by higher water solubility of organic components which results in lower affinity to the sorbents (Nzengung et al. 1996). Rao et al. (1990) concluded a similar result. They explained that the cosolvency of the co-solvent increased the solubility and decreased the sorption capacity of hydrophobic organic chemicals.



(a)

(b)

Figure 2-13. Sorption capacity of HDTMA-bentonite as a function of co-solvent for (a) benzene[4], and (b) naphthalene[5]

Moreover, the sorption of benzene onto HDTMA-bentonite was characterized as a function of temperature variation. The obtained results are presented in Figure 2-14.

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[4] The isotherms for benzene sorption (F^c=0 & 30) are scaled down by 10.

[5] The isotherm for naphthalene sorption (F^c=100) is scaled down by 10.

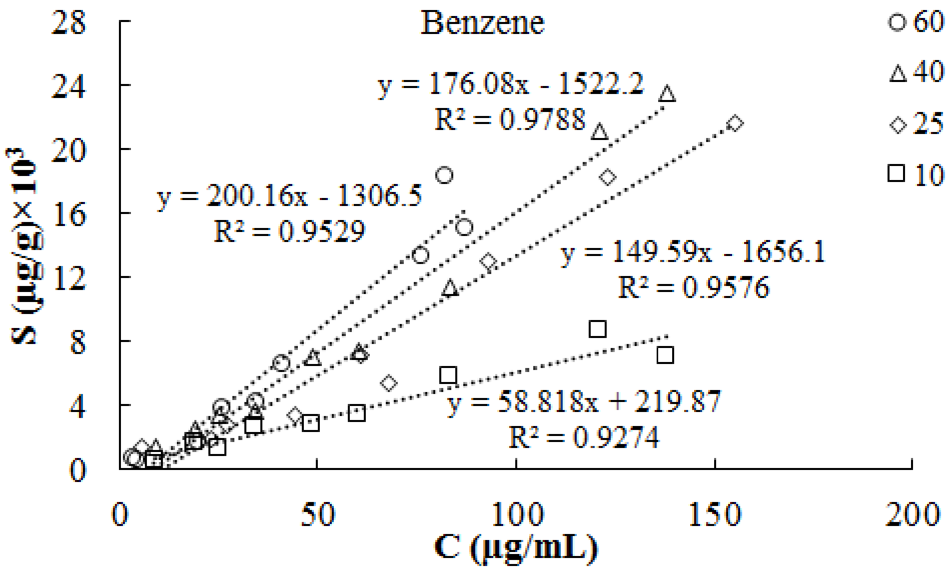
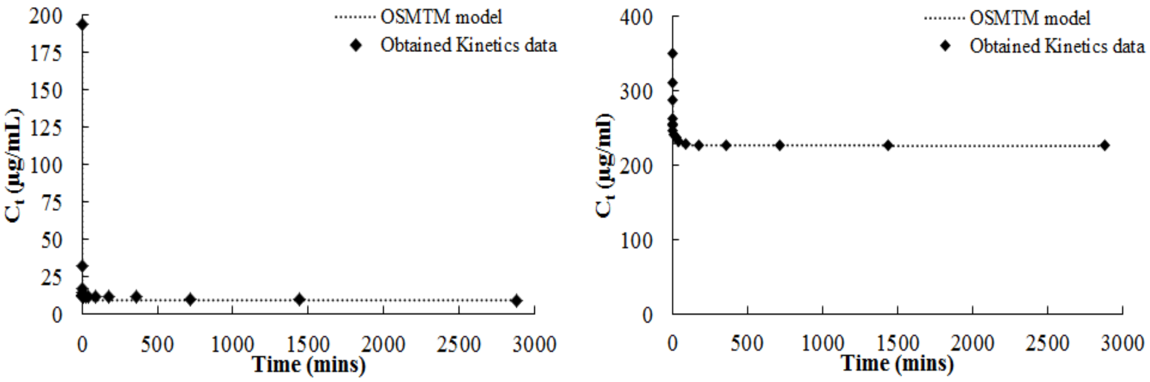


Figure 2-14. Effect of temperature variation on the sorption capacity of HDTMA-bentonite

The sorption isotherm displayed a linear behavior for the entire range of studied temperature. This indicated that the governing reaction process between benzene and HDTMA-bentonite in various temperatures was partitioning. The partitioning coefficient of HDTMA-bentonite at 60˚ C was measured as 200.16 mL/g and decreased to 176.08, 149.59, and 58.81 mL/g by lowering the temperature from 40˚ C to 25˚ C and 10˚ C, respectively. the results suggested that the sorptivity of benzene in aqueous solution to HDTMA-bentonite increases by increasing the temperature. The reason may attribute in the higher kinetics energy that will be induced to the solution by increasing the temperature. As a result, the kinematic energy of dissolved contaminant compounds increases which increases the level of interaction between sorbent and sorbate. Rowe et al. (2005) derived the same conclusion for the sorption of benzene to Na-bentonite.

2.3.5 Kinetic sorption test

The results of sorption kinetic are shown in Figure 2-15. The kinetic study revealed that the uptaking of naphthalene by HDTMA-bentonite occurred quicker (20 s) when compared with the uptaking benzene (20 min). It was observed that approximately 85% of sorbed concentration of naphthalene at equilibrium were uptaken by the HDTMA-bentonite within first 20 seconds while only 5% of benzene was sorbed to the HDTMA-bentonite in first 20 seconds. These results suggested that the rate of sorption for benzene is 17 times lower than naphthalene. After the initial rapid sorption stage, the rest of ultimate sorption for both sorbents were attained in a slow sorption stage that was completed in 12 hours.



(a) (b)

Figure 2-15. Sorption kinetic of (a) naphthalene (b) benzene on HDTMA-bentonite

The kinetic parameters for both studies were estimated by applying the on-site transfer model described by the following equation (Nzengung et al. 1997):

$$C_t = C_e + [C_0 - C_e]exp\left[-\left(\frac{\varepsilon C_0}{C_e}\right)t\right] \qquad 2\text{-}7$$

where C_t is the solution concentration at time (t) (µg/mL), C_e is the solution concentration at equilibrium (µg/mL), C_0 is the initial solution concentration (µg/mL), t is time (min), and ε is mass transfer coefficient (1/min). As a result, the mass transfer coefficient (ε) was optimized using the partitioning coefficient constant (K_P) obtained from batch sorption study for studied sorbates, naphthalene and benzene. The measured kinetic parameters are summarized in Table 2-8.

Table 2-8. Sorption kinetics and equilibrium sorption parameters

Sorbate-Sorbent	K_P (K_d) (mL/g)	R^2	ε (1/min)	Equilibrium time (h)
Naphthalene/HDTMA-bentonite	1355.50	0.98	0.45	12
Naphthalene/Silty clay	4.53	0.95	N. A.	N. A.
Benzene/HDTMA-bentonite	149.59	0.95	0.39	12
Benzene/PM-199	251.4	0.97	N. A.	N. A.

The obtained results are in good agreement with previous researches and indicated that the equilibrium sorption governed the transport of naphthalene and benzene in soils when given the low flow rate or long detention time. Also, it was assumed that the desorption of naphthalene and benzene occurs fast as well and the one-dimensional mass transport model is valid for the contaminant transport modeling in the next few chapters (Freeze and Cherry 1979).

2.4 Conclusions

In this chapter, the sorption characteristics of two representative organobentonites were studied by examining the effects of sorbate properties, sorbents properties and the aqueous conditions. It was observed that the surface modification increased the organic carbon content of Ca-bentonite from 2.58% to 21.44% for HDTMA-bentonite. The increasing of the organic carbon content crated a organophilic phase which increased the affinity of organic contaminants toward organobentonite. As a result, the sorption capacity of organobentonites to organic contaminants were considerably higher than unmodified bentonite. Also, the result from the sorption study of benzene solution confirmed that the partitioning coefficient of PM-199 and HDTMA-bentonite for benzene solution were much higher compared to the partitioning coefficient of Ca-bentonite and Na-bentonite. In addition, the results from sorption study suggested that PM-199 exhibited much higher sorption capacity for organic contaminant compared to HDTMA-bentonite. In addition, the obtained results suggested that grain size has a negligible impact on the sorption capacity of the sorbents.

In addition, the effect of chlorination and water solubility of sorbates on the sorption characteristics of HDTMA-bentonite was investigated. The acquired results suggested that the affinity of dissolved organic contaminants to organobentonites increased when the number of aromatic rings and chlorination increased in organic contaminants. This happened because the chlorination and increased aromatic rings result in increased hydrophobicity of organic contaminants and result in decreased solubility. It was observed that the solubility of molecules decreased in the order of (phenanthrene>naphthalene>benzene) as the aromatic ring increased. Likewise, the solubility of molecules decreased in the order of (hexachlorobenzene>1, 2, 4 – trichlorobenzene >benzene) as the chlorinated position on the ring increased. The organic contaminants with lower solubility have higher organophilicity which results in higher affinity toward organobentonite.

Finally, the effect of aqueous condition on the sorption characteristics of HDTMA-bentonite was investigated. The results of this study suggested that the sorption capacity of HDTMA-bentonite to the organic contaminants decreased when the fraction of co-solvent increased in the solution because the cosolvency of the co-solvent increased the solubility and decreased the sorption capacity of hydrophobic organic contaminants. Moreover, the effect of temperature on the sorptivity of HDTMA-bentonite was evaluated. It was found that the sorption capacity of sorbents to the organic contaminants increases when the environment temperature increases. The reason may attribute in the higher kinetics energy that will be induced to the solution by increasing the temperature. As a result, the kinematic energy of dissolved contaminant compounds increased which increases the level of interaction between sorbent and sorbate.

3 CHAPTER THREE ENGINEERING BEHAVIORS OF COMPACTED CLAY AMENDED WITH ORGANOCLAYS

3.1 Introduction

Compacted clay liner (CCL) is the most common soil liner for landfills or underground storage tanks. CCLs are mechanically modified soils to reduce the fluid flow and mass transport in the subsurface (Broderick and Daniel 1990). Most commonly, CCLs are compacted to a thickness of 600 mm (2ft) or 900 mm (3ft). However, their thickness can reach to 1.2 to 3 m or higher, especially for the applications in vertical barriers (or vertical cutoff walls). There are several major types of CCL materials: natural soils, soil-bentonite mixtures and others. Naturally occurring clays are the most common components in CCLs. This group of soil consists of significant amount of clay including lean clay (CL), fat clay (CH), or clayey sand (SC). A mixture of natural soil and bentonite is typically used when the excavated soil from vicinity borrows does not contain significant percentages of clay content. Bentonites, mainly composed of sodium or calcium smectites are ideal amendments in CCLs to provide low permeability and to assure barriers performances (Boynton and Daniel 1985; Rowe et al. 2004).

The CCLs are typically designed to have a low hydraulic conductivity at the field. Daniel and Benson (1990) demonstrated that the hydraulic conductivity of a CCL would decrease if (1) the level of energy in compaction effort increased; (2) the water content slightly increased from the optimum water content (Figure 3-1). For the CCL application in a horizontal or a vertical barrier, two factors must be considered and it yields an acceptable zone on the compaction curve: (1) the CCL must have its hydraulic conductivity lower than 10^{-7} cm/s. A good example is illustrated in Figure 3-1: for the reduced proctor test, the compacted soil must have a water content between W_1 and W_2 such that the resultant hydraulic conductivity of the soil will be lower than 10^{-7} cm/s (2) density. Typically, the soil must be compacted at a dry density γ_d greater than 90~95% of its maximum dry density γ_{max} such that the soil will be stronger and less compressible. Most commonly, the requirement of the hydraulic performance of the CCL defines the range of water content in which the soil should be compacted while the requirement of strength and deformation defines the lower bound of the dry density of the compacted CCL. To meet both requirements, the combination of water content and dry density is required to be situated in the acceptable zone, as illustrated in Figure 3-2.

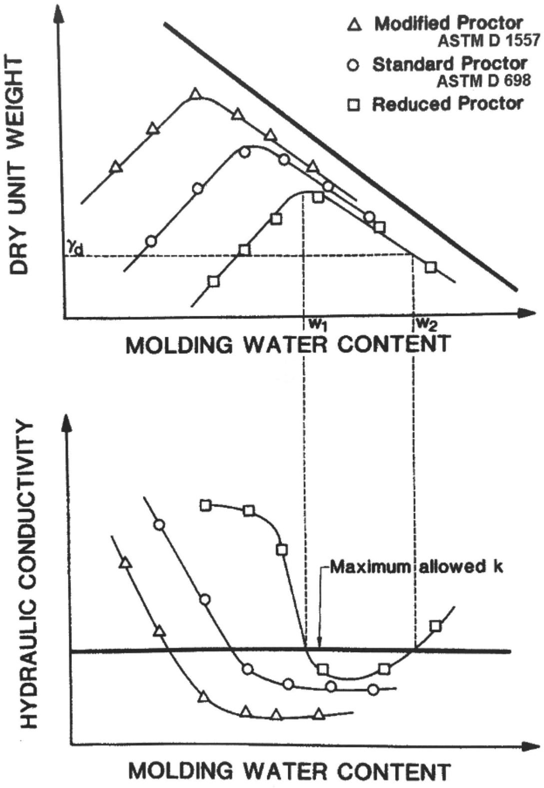


Figure 3-1. Recommended design criteria for the compaction of CCLs (Sharma and Reddy 2004)

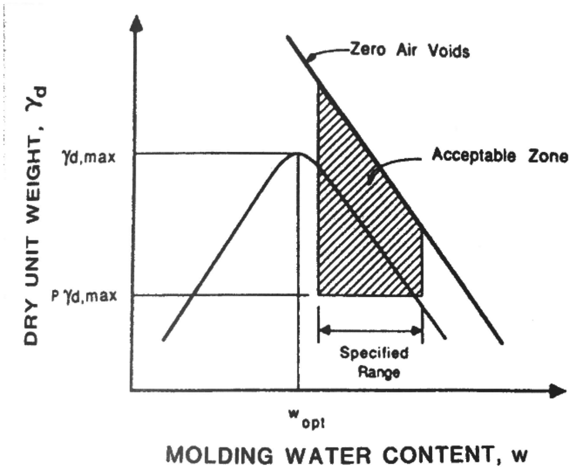
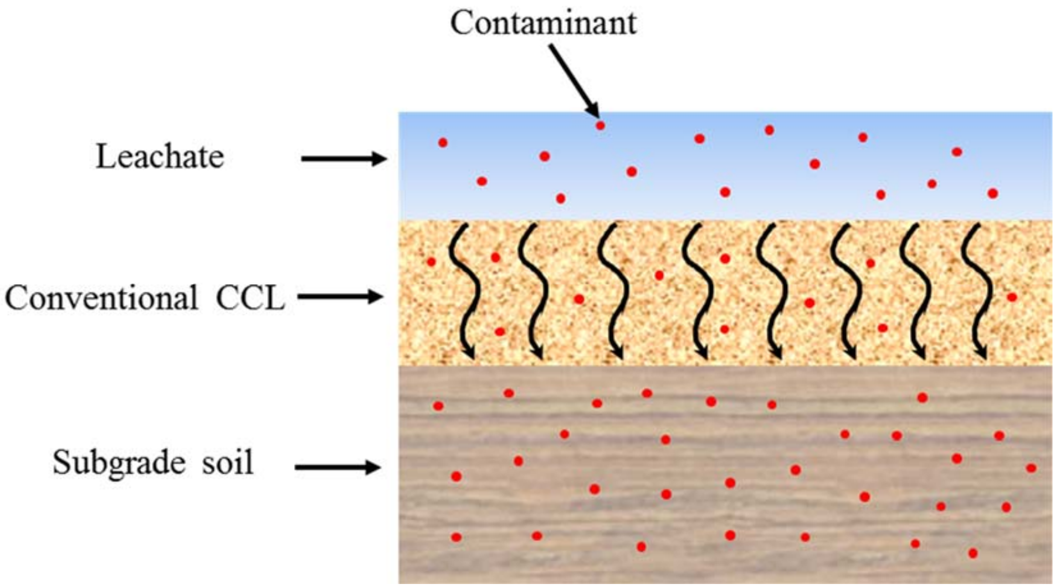


Figure 3-2. Acceptable range of water content and dry unit weight for CCLs (Sharma and Reddy 2004)

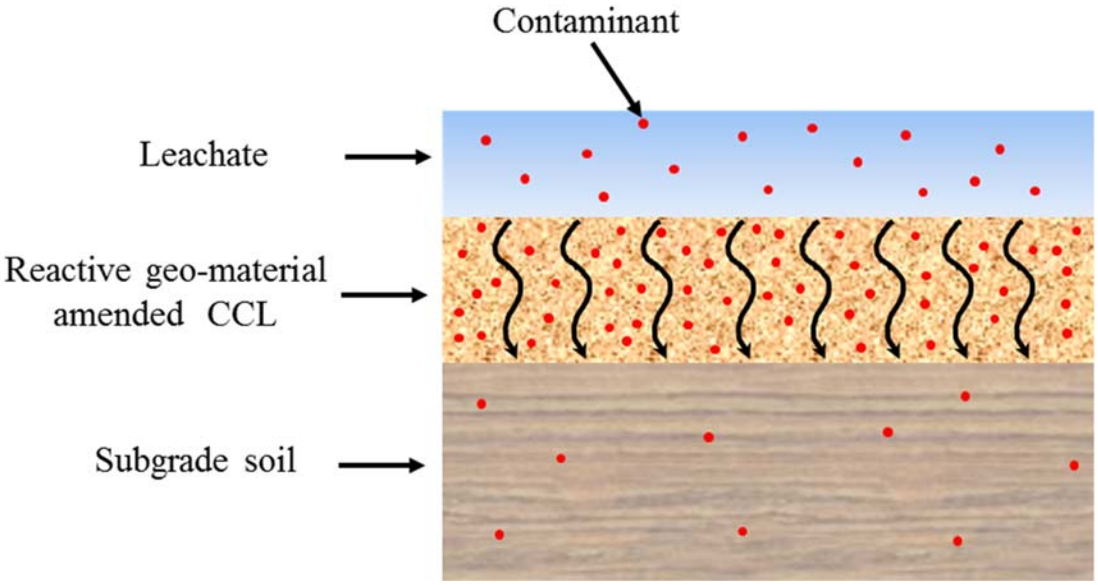
Although the CCLs are designed to provide a low rate of permeability, the previous studies indicated that the permeability of CCLs to the certain organic contaminants could increase significantly due to the chemical incompatibility. For instance, it was observed that the CCL materials shrink in contact with pure phase organic compounds or petroleum-related products and cracks are developed in entire CCL profile which cause higher hydraulic conductivity (Bowders and Daniel 1987; Broderick and Daniel 1990; Fernandez and Quigley 1985).

Also, the mass flux of contaminant through CCLs can be significant even though the low flow rate regime governs the advection of contaminants through CCLs because the filling materials in conventional CCLs have non-interactive nature and low sorption capacity (Bright et al. 2000; Brown and Burris 1996). The advection-dispersion mechanism controls the contaminant mass transport through CCLs with non-interactive components because no chemical or biochemical reactions take place in the pore volumes of fillings that uptake or reduces the concentration of contaminants (Shackelford 1994).This indicates that a low level of pure organic or petroleum derivative contaminants can raise a great concern regarding the long term performance of CCL systems (Ma et al. 2015). Therefore, additional investigation on the behavior of CCLs in contact with certain chemical contaminants is required to enhance the long-term performance of CCL system.

The obtained results from the recent investigations have proposed the possibility of using the chemically reactive geo-materials as an additive in CCL soil to enhance the chemical compatibility and the contaminant attenuation capability of CCLs. Consequently, the concept of low permeability reactive barrier with reactive geo-material amendments has been proposed for the clay liner applications(Lo et al. 1997; Wiles et al. 2005). .The advantages of the proposed reactive barriers over the conventional CCLs is their ability to uptake, immobilize and/or degrade the contaminant transport (Figure 3-3) while maintaining the hydraulic conductivity of the barrier in a satisfactory range (Crocker et al. 1995; Lo and Yang 2001; Wagner et al. 1994). Many different studies have been conducted to identify suitable natural or engineered geo-material candidates as reactive amendment in CCLs (LaGrega et al. 1994). Other than bentonite, mixture of bentonite and fly ash, modified soils, activated carbon, paper industry sludge, and many other commercial additives can be used as a CCL component under certain circumstances. By all of the studied geo-materials, fly ash, zeolite, organo-zeolite, coated sand and organoclays have shown promising potential as reactive amendment in order to improve the soptivity of CCLs (Lo and Liljestrand 1996; Prasad et al. 2012; Varank et al. 2011; Younus and Sreedeep 2012).Among the proposed amendments, organoclays have demonstrated the most effective sorption capacity of organic contaminants (Benson et al. 2015; de Paiva et al. 2008; Gates et al. 2004; Soule and Burns 2001).



(a)



(b)

Figure 3-3. Contaminant transport through (a) conventional CCL (b) reactive geo-material amended CCL

Organoclays are suitable sorbents to uptake nonpolar or low-polarity compounds from aqueous phase. The organic surfactant/clay hybrids also have increased swelling tendency and plasticity in organic liquids and decreased permeability for non-polar liquids.

Based on previous studies, organoclays are efficient to enhance the retention capacity of organic liquids or petroleum products by the CCLs (Lo and Yang 2001; Moon et al. 2007; Smith et al. 2003; Yang and Lo 2004). It was observed that the permeability of organoclays amended CCLs to gasoline decreased two to four orders of magnitude compared to the hydraulic conductivity of same system permeated by water (Smith et al. 2003). Although the organoclays increase the hydraulic conductivity of barrier system when permeated with water, a low dosage of organoclay in the CCL soil has limited impact the overall permeability of the CCLs (Yang and Lo 2004). However, a small fraction of organoclays in GCL soil increases significantly the attenuation capability of non-polar organics, chlorinated organics, polycyclic hydrocarbons and pesticides from aqueous phase (Boyd et al. 1988; Jaynes and Boyd 1990; Jaynes and Boyd 1991; Larsen et al. 1992; Montgomery et al. 1991; Owabor et al. 2010; Qu et al. 2008; Smith et al. 1990). Nzengung et al. (1996)proposed that the organic contaminants can be absorbed by organically modified clays through the partitioning process, which mostly the partitioning coefficient of organoclays may be hundreds of thousands of times greater than those of natural soils.

Many studies have been conducted to assess the barrier performance of low flow rate (CCLs) and the corresponding contaminant transport parameters (Acar and Haider 1990; Crooks and Quigley 1984; Lai and Lo 2006; Lai et al. 2006). However, relatively limited researches have been conducted to evaluate the feasibility of using organoclays as an amendment in CCLs for the purpose of attenuating the mass transport of waste contaminant (Lee et al. 2012; Lo and Mak 1998). This is because of difficulties in controlling the properties of flow and the contamination and long duration of breakthrough test in low flow rate systems. The scope of this study is to produce barrier systems with new reactive components. The objectives of studying low flow rate barrier (CCL) are to quantify the transport parameter when permeating by naphthalene and evaluate the attenuation capacity of the system consisting of 95% silty clay and 5% HDTMA-bentonite. HDTMA-bentonite was selected as a reactive component of CCL because it has relatively high percentage of organic carbon and high sorption capacity to absorb organic compounds (organophilicity). The barrier performance of silty clay with

HDTMA-bentonite amendment permeating with gasoline (as a representative of petroleum product) and PAH (as a representative of NAPLs which are the most common pollution in groundwater) was assessed. Initially, the permeability of saturated CCLs specimens consisted of silty clay with HDTMA-bentonite amendment were evaluated in the flexible wall permeameter. Also, the free swelling experiment to measure the swelling index of the clay/HDTMA bentonite in water and gasoline were carried out. Finally, the retardation factor and diffusion coefficient of naphthalene in compacted clay/HDTMA bentonite soil were quantified using batch sorption study and soil column laboratory test.

3.2 Materials and methods

Three different soil media including natural low plasticity silty clay, HDTMA-bentonite, and Ca-bentonite were used in this study. The low plasticity silty clay (Nugent Sand Co.) consisted of 1% gravel, 12% sand, and 87% fine particles (ASTM D422). The physical properties of the low plasticity silty clay is summarized in Table 3-1.

Table 3-1. Engineering properties of the natural low plasticity silty clay

Properties	Low plasticity silty clay
Liquid limit (%)	26
Plasticity index (%)	4.5
Fine content % (<#200 sieve)	87
Specific gravity	2.62
Specific surface area (m^2/g)	33.5
Total organic carbon (%)	<1

3.2.1 Standard proctor compaction test

To determine the optimum water content and the maximum dry density, the standard proctor test was carried out for each soil specimen in accordance with ASTM D698, Method A. The specification of standard proctor testis summarized in Table 3-2.

Table 3-2. The specification of standard proctor test

Method	Mold diameter	Rammer weight	Rammer free-fall height	Number of layers (and blows per layer)	Equivalent compaction energy
Standard effort (ASTM D698)	4 in (101.6 mm)	5.5 lbf (24.4 N)	12 in (305 mm)	3 (25)	12400 ft-lbf/ft^3 (600 kN-m/m^3)

First, the synthesized HDTMA bentonite, calcium bentonite, and silty clay were oven dried for 24 hrs. The compaction test was conducted on 4 soil admixtures of: 100% silty clay; 90% silty clay + 10% Ca-bentonite; 90% silty clay + 10% HDTMA-bentonite; and 95% silty clay + 5% HDTMA-bentonite (by weight). Approximately 2 kg of the designed oven dried soil admixtures was weighted and spread out on the pan to cool down. For each soil admixture, six specimens with different water content ranging from 10% to 16% (with increment of 1%) were prepared and standard proctor test was carried out on each specimen. Approximately 2kg of prepared soil was placed into a compaction mold. Next, a 5.5 lbf rammer was dropped from the height of 12 inches and transfer the total compaction energy (12400 ft-lbf/ft^3) to the soil (Figure 3-4(a)). After compaction, the collar was removed and the soil was trimmed. Next, the compacted soil was weighted and

3 samples were taken from the top, middle, and bottom of the soil column (~100 g) for a water content determination, Figure 3-4(b).

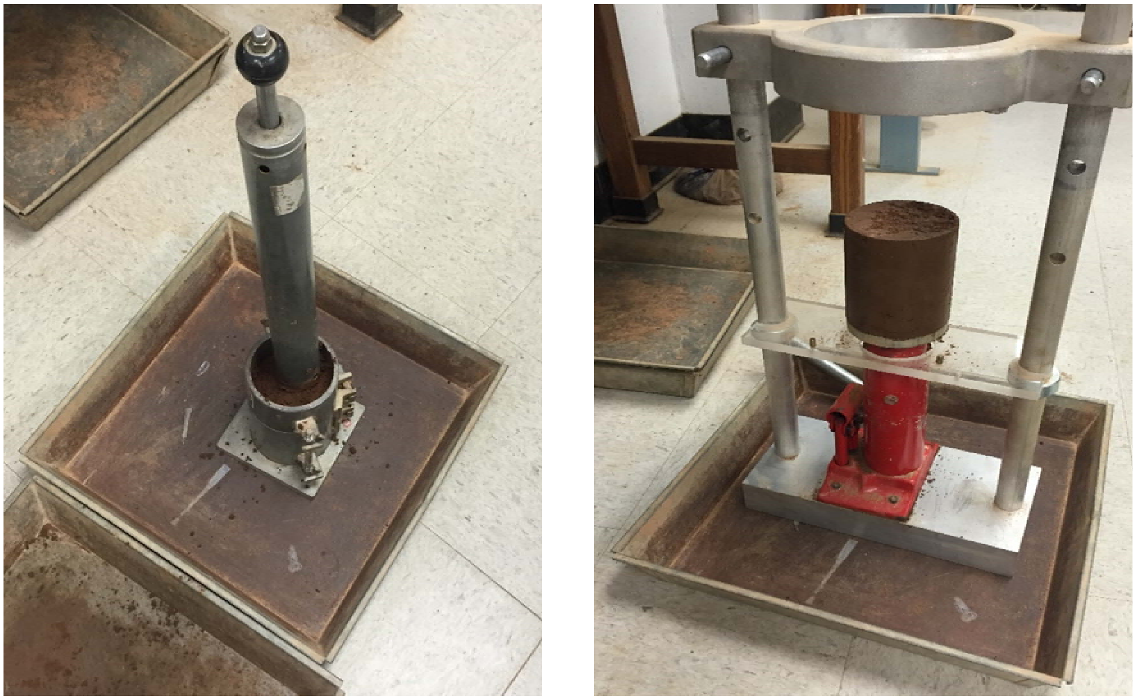

(a) (b)

Figure 3-4. (a) Compaction of soil layer (b) Extruded soil from compaction mold

To measure the water content of moist samples, their weight was recorded right after sampling. Then, soil samples were oven-dried for 24 hours. Finally, the weight of dried samples was recorded. The water content of the samples was calculated by using equation 3-1.

$$w = \frac{w_w}{w_s} \times 100 \qquad 3\text{-}1$$

Where w is the water content of the soil sample (%), w_w is the weight of water which is also the difference between the weight of moist soil (w_T) and the weight of the oven-dried soil (w_s). Initially, the moist density of the compacted soil was determined using equation 3-2.

$$\rho_m = \frac{(M_t - M_{md})}{1000V} \tag{3-2}$$

where ρ_m is the moist density of the compacted soil, M_t is the total weight of soil specimen and mold, M_{md} is the weight of mold, and V is the volume of compaction mold (944 cm^3 for the standard effort).

The dry density ρ_d of the compacted soil specimen was by:

$$\rho_d = \frac{\rho_m}{1 + \frac{w}{100}} \tag{3-3}$$

The dry unit weight (γ_d) was calculated as:

$$\gamma_d = 9.807 \rho_d \left({}^{kN}\!/_{m^3} \right) \tag{3-4}$$

The relationship between water content and dry density of each compacted specimen was obtained with sufficient numbers of repeated tests. The maximum dry density and the optimum water content of each admixture were determined and shown in Figure 3-5 and Table 3-3.

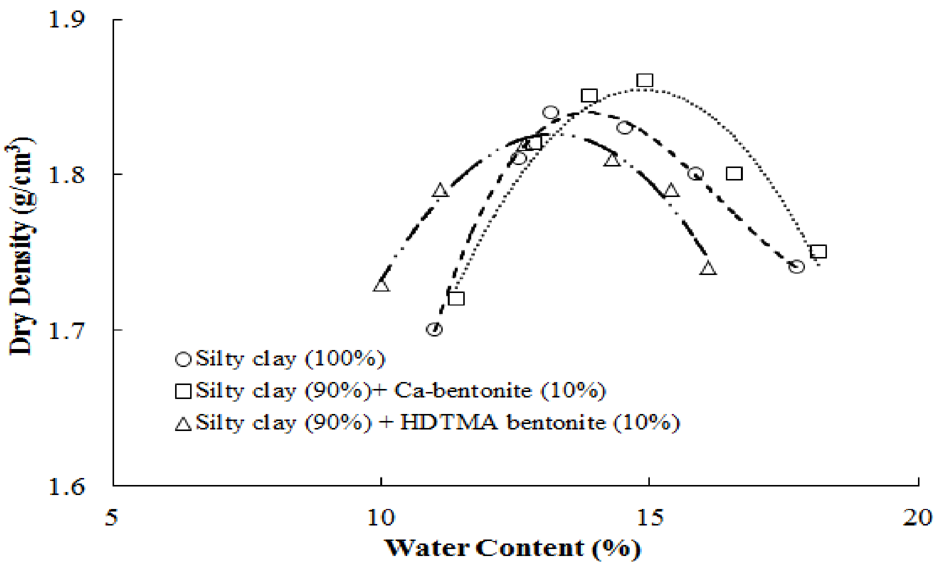


Figure 3-5. Compaction curve for the studied soil admixtures

Table 3-3. Compaction test results

Soil admixture	W (%)	γ_d (g/cm^3)
Silty clay (100%)	13.6	1.85
Silty clay (90%) + Ca-bentonite (10%)	14.83	1.86
Silty clay (90%) + HDTMA-bentonite (10%)	13.04	1.82

3.2.2 One-dimensional swell test

The one-dimensional swell test was carried out for the three soil admixtures including 100% silty clay, 90% silty clay + 10% Ca-bentonite, and 90% silty clay + 10% HDTMA-bentonite according to ASTM D4546. First of all, the three soil admixtures were oven dried for 24 h. Next, the water content of the oven dried specimens was adjusted to 13 to 14%. The soil specimens were mixed and placed into a ring with diameter of 66 mm and height of 20 mm, respectively. The surface of the filled soil into the ring was smoothened and the ring was placed into the oedometer apparatus. An overburden pressure of 1 kPa was applied to each of the soil specimen. Then water or gasoline was added to the soil specimen in the ring. The vertical deformation of the soil specimen was recorded versus time. It was observed that the vertical deformation typically stabilized after 24 hours.

3.2.3 Permeability test

The hydraulic conductivity of three compacted soils: 100% silty clay, 90% silty clay + 10% Ca-bentonite, and 90% silty clay + 10% HDTMA-bentonite were measured using flexible wall permeameter (Trautwein Soil Testing Equipment) following the ASTM standard D5084. First each soil specimen was compacted at the determined optimum water content following the compaction procedure explained in section 3.2.1. After extruding the compacted specimens from the compaction mold, a cylindrical trimming mold with 5.08 cm diameter and 10.16 cm in height was used to obtain a compacted soil sample with desirable dimensions for the permeability test. Two pairs of porous stone and filter paper were saturated before placed on top and below the trimmed soil specimen. Next, a membrane stretcher was used to stretch a latex membrane before it wrapped around the soil specimen. Next, a Finally, the inflow and outflow tubes were connected to the top cap and the chamber was mounted on the base of permeameter (Figure 3-6).

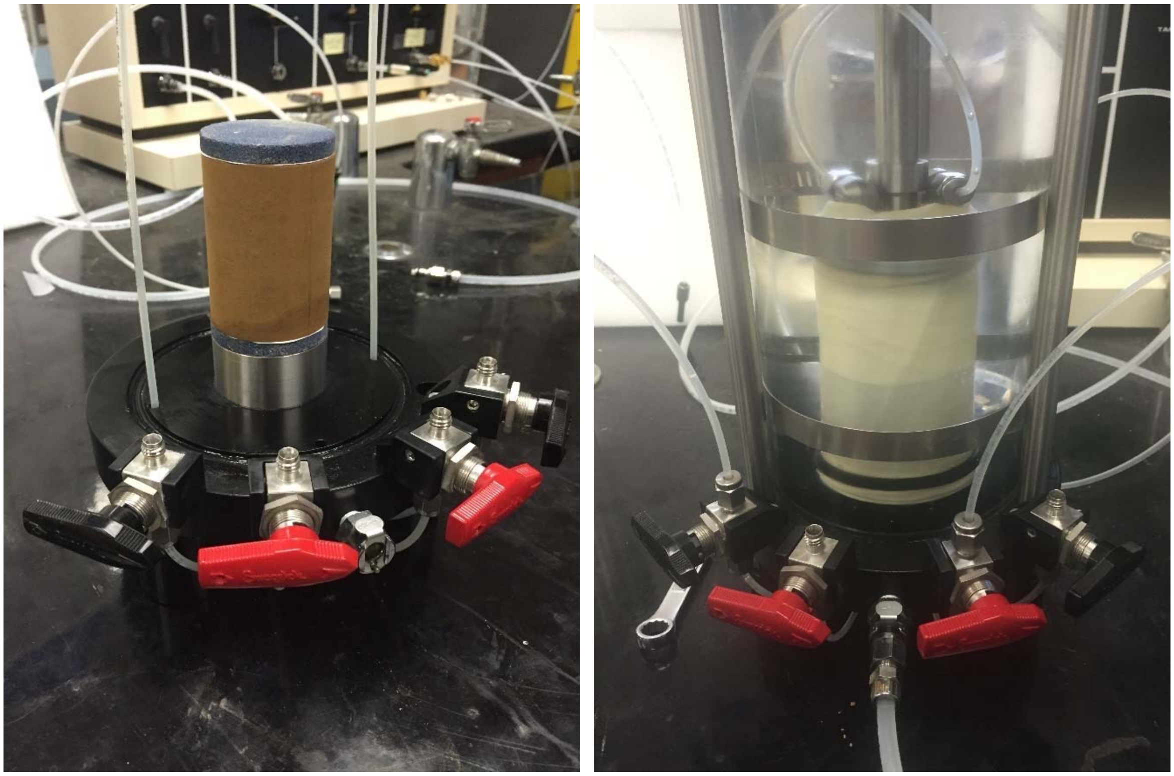

(a) (b)

Figure 3-6. (a) Soil column arrangement for hydraulic conductivity (b) Sealed soil column in the pressure chamber

After the chamber was filled with de-aired water, the chamber pressure (cell pressure) was set at13.7kPa and the water was fed into the soil column from the bottom to the top. To increase the saturation of the soil specimen, back pressure was applied to the specimen. The back pressure and cell pressure were increased simultaneously with same increment of13.7 kPa each time and the Skempton's B-value was examined. Typically, B-value greater than 95% was achieved for hydraulic conductivity test at the back pressure of 192kPa and the cell pressure of 206kPa.

Initially, the hydraulic conductivity of three specimens was measured using the falling head, rising tailwater method (Method C). In addition, the permeability of soil specimen with of 90% silty clay and 10% HDTMA-bentonite to the gasoline was measured using the same method. The fluid conductivity of compacted soil sample to the permeant fluid k was determined by:

$$k = \frac{a.L}{2A.\Delta t} ln\left(\frac{h_1}{h_2}\right) \tag{3-5}$$

The falling head, constant tailwater pressure (Method B) was used to measure the hydraulic conductivity k of soil column comprised of 95% silty clay and 5% HDTMA-bentonite which permeated by benzene solution for the breakthrough test:

$$k = \frac{a.L}{A.\Delta t} ln\left(\frac{h_1}{h_2}\right) \tag{3-6}$$

where k is the hydraulic conductivity (m/s), a is the cross-sectional area of the reservoir containing the influent liquid (m^2), L is the length of specimen (m), A is the cross-sectional area of specimen (m^2), Δt is the time interval between h_1 and h_2 (s), h_1 is the head loss across the specimen at t_1 (m), and h_2 is the head loss across the specimen at t_2 (m).The physicochemical properties of the permeant fluids are summarized in Table 3-4.

Table 3-4. Physicochemical properties of the permeant fluids

Fluids	Type	Polarity	Density (kg/L) at 20° C	Dynamic viscosity (cP)
Water	Deaired	10.2	1	1
Gasoline	Unleaded #87	<3	0.76	0.55
Naphthalene/methanol	Crystal/reagent grade	5.1	0.791	0.56

The fluid conductivity of each soil specimen was measured when the steady state was reached. Typically, the results of three trials were recorded for each test and the average was chosen as the reported value.

3.2.4 Breakthrough test

A compacted soil column specimen consisted of 5% of HDTMA-bentonite and 95% of silty clay was constructed to evaluate the efficiency of HDTMA-bentonite amended CCL in retention of organic contaminants. The compaction and sample preparation procedure were conducted as it was explained in section 3.2.1. The compaction test results confirmed that the optimum water content of silty clay remained the same after 10% HDTMA-bentonite was added. Consequently, the soil admixture for breakthrough test was compacted at the optimum water content of 13% to 14% following ASTM D698 (Method A). The standard proctor compaction effort resulted in compacted soil column with bulk density ranging between 1.78 to 1.85 g /cm^3.The soil specimen was wrapped with Teflon tape before wrapped with latex membrane to minimize the sorption of dissolved naphthalene by the latex membrane.

Table 3-5. Specification of compacted soil column

Column Component	95% Silty clay + 5% HDTMA bentonite
Diameter (mm)	50
Length (mm)	68
G_s	2.57
Unit weight (g/cm^3)	2.02
Porosity	0.3

Pore volume (cm^3)	42

Prior to the saturation stage, the soil column was flushed with de-aired water for approximately 4 pore volume. Then, the saturation stage started which took near to 2 pore volumes to complete till the steady state was attained at effluent. The flow rate of effluent at steady state stage was measured as approximately 1 mL/hr. To prepare the permeant solution, 0.13 g of naphthalene in solid phase was dissolved in 300 mL of methanol and diluted with 700 mL of deionized water to acquire a solution with naphthalene concentration of 130 µg/mL. Naphthalene was selected as the organic contaminant because of its relatively simple structure (Chen et al. 2005) and the frequent presence in the wastewater of landfill (Javadi et al. 2016; Wolfe et al. 1986). A bladder accumulator with viton membrane was used to feed the solution into the soil column. The bladder accumulator was filled with the naphthalene solution and 1 pore volume of pulse-type contaminant solution (~42 cm^3) was injected to the soil column. Next, the inflow was switched back to the de-aired water right away. At the same time, samples were taken from effluent in vials with capacity of 8 mL. The de-aired water was injected into the soil column for additional 12 pore volumes (approximately 30 more days) until the concentration of naphthalene in the effluent was below the detection limit. The collected effluent samples were extracted from aqueous phase by hexane and analyzed for naphthalene concentration by GC, as described in chapter 2. The experimental setup is illustrated in Figure 3-7.

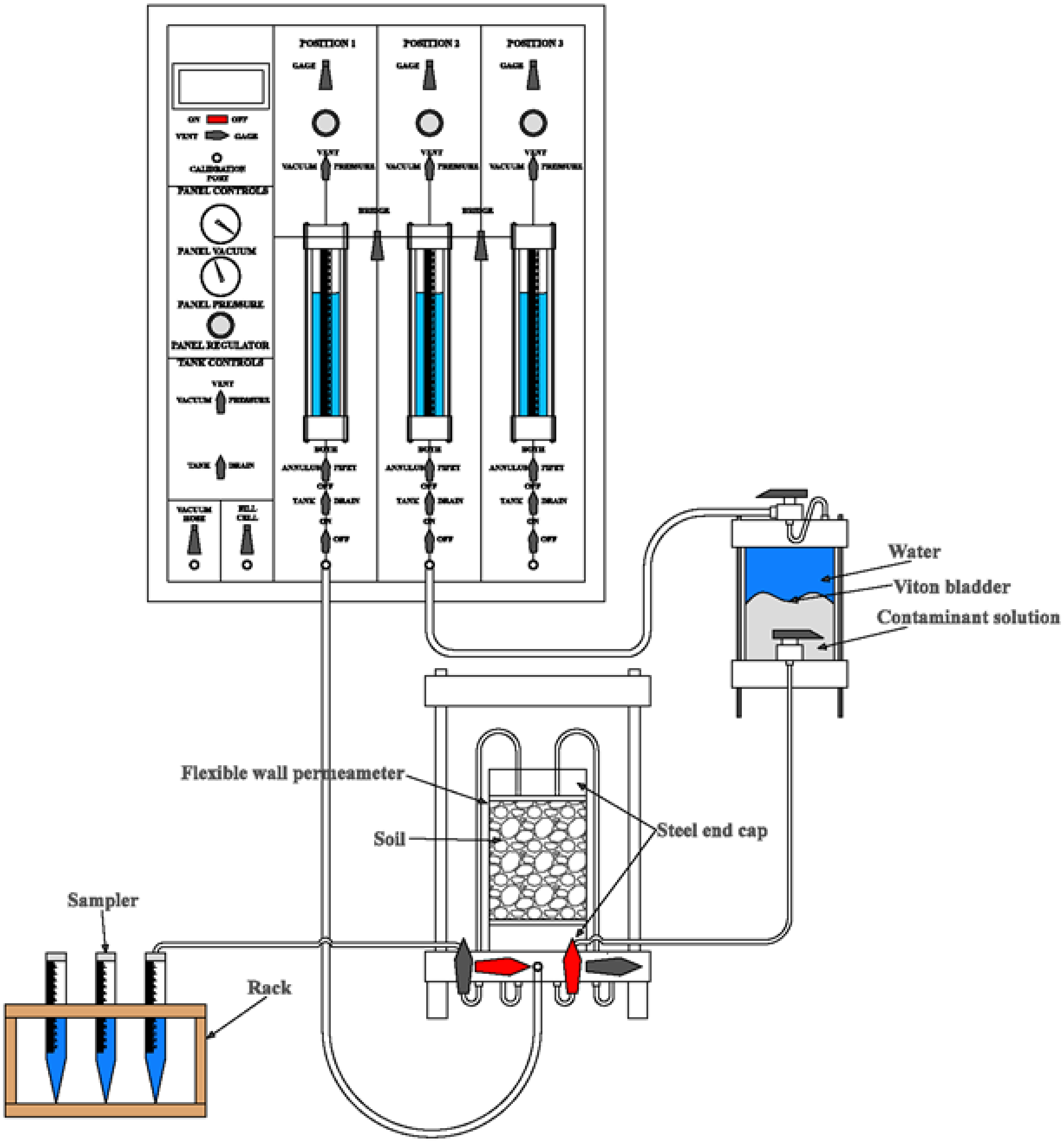
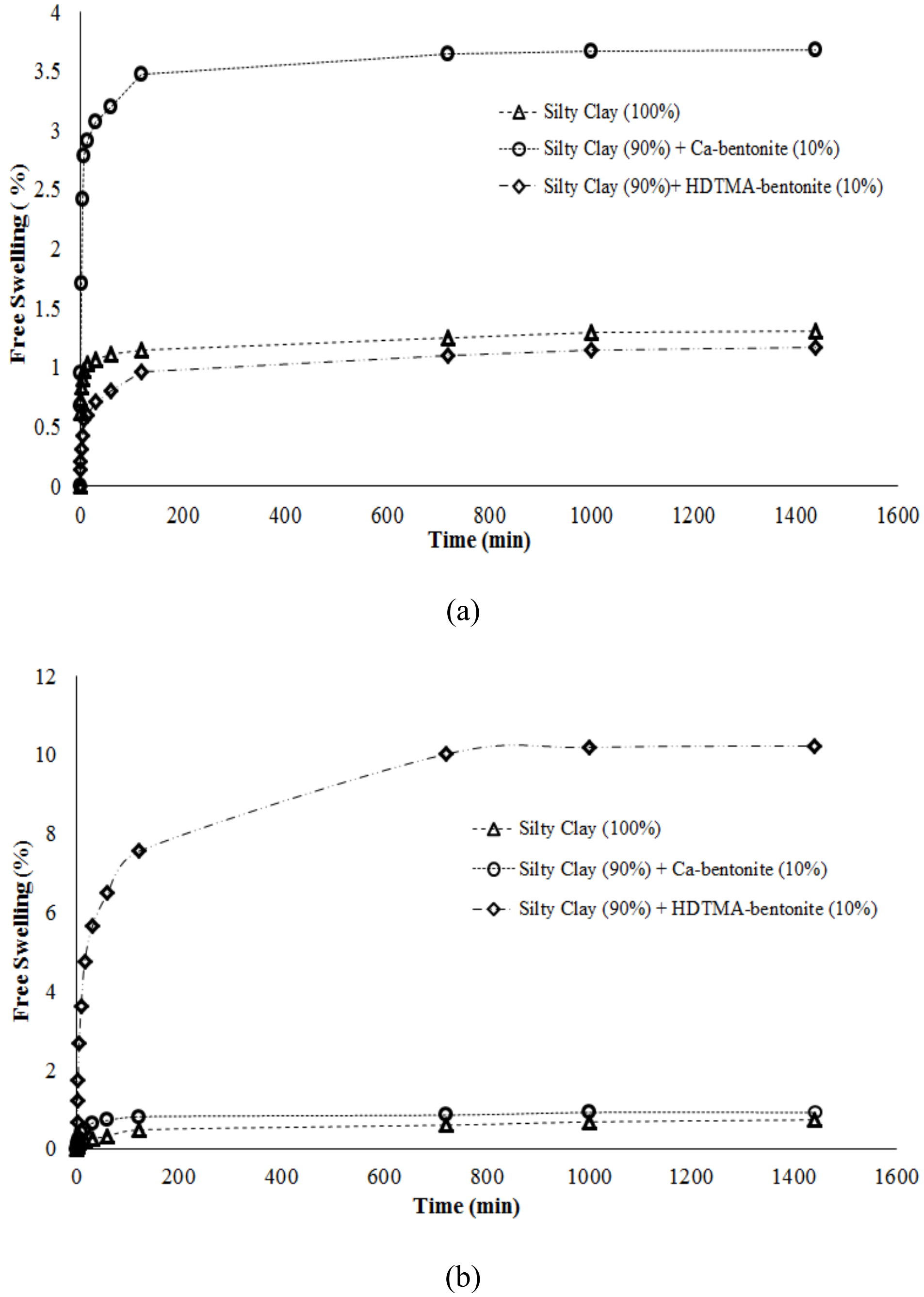


Figure 3-7. Experimental setup for breakthrough test

3.3 Result and discussion

3.3.1 One-dimensional swell test

The swelling tendency of three studied soil admixtures including silty clay, silty clay + 10% Ca-bentonite, silty clay + 10% HDTMA-bentonite in the water and gasoline are presented in Figure 3-8.



(a)

(b)

Figure 3-8. Free swelling results for the three studied soil admixture in (a) water (b) gasoline

It was observed that adding 10% of Ca-bentonite to the silty clay soil increased the free swelling of the admixture significantly and the hydration of Ca-bentonite is the main reason of the notable swelling tendency of the admixture (Chapuis 1990; Sun et al. 2009). In comparison, silty clay with 10% of HDTMA bentonite exhibited very limited swelling in water as both components had very low hydration in water and also low plasticity. (Benson et al. 2015; Sreedharan and Sivapullaiah 2014). However, the admixture of silty clay and HDTMA-bentonite demonstrates a considerable swelling tendency in nonpolar organic liquids such as gasoline. Tests results (Figure 3-8 (b)) suggested that 10% of HDTMA-bentonite + 90% of silty clay had 10 times of swelling in gasoline when compared to the 100% silty clay. The above observations can be explained by the hydrophobic interactions between non-polar species and intercalated aliphatic carbon chains in HDTMA bentonite (Slade and Gates 2004).As naturally occurring clay minerals, the pure silty clay or Ca-bentonite had demonstrated a little or negligible swelling in gasoline because the mineral hydration and cation hydration were predominant interactions between the two and water. However, the HDTMA bentonite, with modified and hydrophobic characteristics were able to interact with aliphatic aromatic hydrocarbons. Consequently, it appeared that organoclays could be superior materials for the containment of petroleum related products or other non-polar fluids when compared to natural clays. It is important to note most of the earthen barrier materials are under certain overburden stresses other than 1kPa. The effect of confining stress on the swelling tendency of the studied soil admixtures was not investigated here. It was expected that the higher swelling potential could lower the permeability the admixtures in the same liquid but the overburden stress would also lower the permeability as well.

3.3.2 Permeability

The hydraulic conductivity of three soils including silty clay, 90% silty clay + 10% Ca-bentonite admixture, and 90% silty clay + 10% HDTMA-bentonite admixture were measured. In addition, the permeability of 90% silty clay + 10% HDTMA-bentonite to gasoline was measured and the obtained results are summarized in Table 3-6.

Table 3-6. Average fluid conductivities of three compacted soils with varying permeants

Materials	Soil preparation	Void ratio	Permeant liquid	Liquid limit	Plasticity index	Fluid conductivity (m/s)	Intrinsic permeability (m^2)
Silty clay (100%)	Compacted (ρ_d=1.85g/cm^3)	0.42	Water	26	4.4	5.04×10^{-9}	5.16×10^{-16}
Silty clay (90%) + Ca-bentonite (10%)	Compacted (ρ_d=1.82g/cm^3)	0.43	water	32	10	7.70×10^{-10}	7.78×10^{-17}
Silty clay (90%) + HDTMA-bentonite (10%)	Compacted (ρ_d=1.78g/cm^3)	0.42	water	30	6.6	1.57×10^{-8}	1.61×10^{-15}
		0.42	Gasoline	-	-	9.20×10^{-10}	6.7×10^{-17}

The hydraulic conductivity of compacted silty clay was 5.04 $\times10^{-9}$ m/s while adding 10% Ca-bentonite to the component of compacted soil specimen decreased the hydraulic conductivity of the compacted admixture to 7.70×10^{-10} m/s. This was explained as the swelling of Ca-bentonite resulted in deceased pores volumes in the soil admixture and consequently, lower hydraulic conductivity. However, the hydraulic conductivity of compacted soil admixture consisted of silty clay and 10% HDTMA-bentonite was 1.57×10^{-8} m/s, approximately 1 order of magnitude higher than the hydraulic conductivity of the compacted silty soil. This can be explained by the increased hydraulic conductivity of the HDTMA-bentonite as a results of its hydrophobic surface characteristics(Li et al. 1996; Lorenzetti et al. 2005; Moon et al. 2007).

This occurred because the plasticity index of the soil admixture increased from 4.4 for the pure silty clay to 10 for 90% silty clay + 10% Ca-bentonite (Benson et al. 1994; Lo and Yang 2001). It was noted that the hydraulic conductivity of silty clay with 10% HDTMA-bentonite to water increased by approximately 1 order of magnitude compared to 100% silty clay which is. HDTMA-bentonite increases the hydrophobicity of the soil specimen, and as expected the conductivity of the water through soil pores increases when the hydrophobicity of complex increases.

Previous studies confirmed that organoclays have the swelling potential in non-polar liquids similar to natural bentonites in water(Benson et al. 2015).Some other studies also suggested that organoclays had very low plasticity in water but could exhibit high consistency in non-polar liquids (Soule and Burns 2001). Lo and Yang (2001) explained that the soils with higher liquid limit and plasticity index in a certain liquid expressed higher swelling capacity which resulted in lower fluid permeability. The permeability of compacted soil specimen consisted of 90% silty clay with 10% HDTMA-bentonite to gasoline was measured as 9.20×10^{-10} m/s while the permeability of the same compacted soil specimen to water was as high as 1.57×10^{-8} m/s. The same trend in permeability of different soil specimen to water and gasoline was reported by several previous studies (Lo and Yang 2001; Moon et al. 2007; Smith et al. 2003).Smith et al. (2003)investigated the permeability of compacted BTEA-bentonite and HDTMA-bentonite to water and unleaded gasoline. They observed that the permeability of compacted organoclays decreased approximately by an order of 2in magnitude when permeated with unleaded gasoline instead of water. Yang and Lo (2004)noted that the permeability of compacted BB-40 to gasoline (10^{-9} cm/s) was four orders of magnitude lower than the permeability of Na-bentonite to gasoline (10^{-5} cm/s). All these studies indicated that compared to the naturally occurring bentonite, HDTMA-bentonite has a higher permeability to water, but much lower permeability to petroleum related products like unleaded gasoline. It was explained that the higher swelling tendency of HDTMA-bentonite in non-polar liquids and the increased drag force on the gasoline caused the decreased permeability of gasoline in organoclay. Consequently, the permeability of compacted soil specimen consisted of 90% silty clay with 10% HDTMA-bentoniteto gasoline was lower than its permeability to water.

It was concluded that small dosage oforganoclayhave a low impact on the overall hydraulic conductivity of soil admixtures when used as additives(Bate 2010; Ghavami et al. 2016). However, our results suggested that the permeability of compacted silty clay and only 10% of organobentonite to gasoline was decrease by half.For the unsaturated flow in the same compacted soil admixture, the permeability could be even lower for the low-polarity fluids. This suggests that organoclays, especially organobentonitesare promising amendment in compacted soils to reduce the advection rate of organic contaminant flow. Also, it was not investigated in this study but it was expected that combinations of Na-bentonite and organoclay could be effective amendments to reduce the advection of water and organic fluids in compacted soil barriers.

3.3.3 Breakthrough test

From the obtained results in chapter 2, the equilibrium sorption isotherms of naphthalene onto HDTMA-bentonite/silty clay is presented in Figure 3-9.

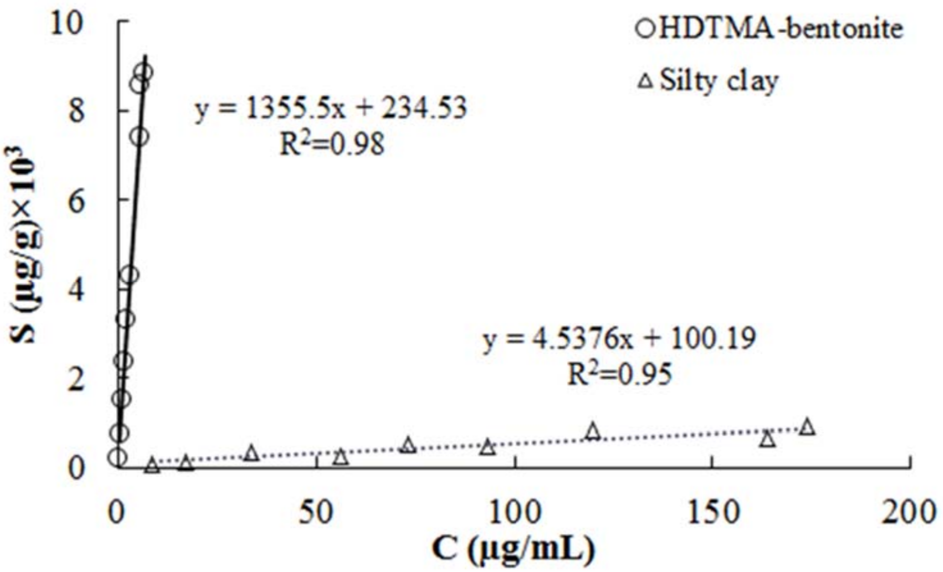


Figure 3-9. equilibrium sorption isotherms of naphthalene onto HDTMA-bentonite/silty clay

Linear isotherms were observed for the sorption of naphthalene onto two studied soils. The measured partitioning coefficient (K_d) of silty clay and HDTMA-bentonite for naphthalene were 4.53 and 1355.5 mL/g, respectively.

The transport of naphthalene through the compacted clay column was performed under the low flow rate condition to stimulate the mass transport of organic contaminants through the low permeability earthen barriers. The average seepage velocity of the effluent permeated solution was monitored during the breakthrough test to assure that the steady state condition was available during the experiment. The recorded average seepage velocity is presented in Figure 3-10. The average hydraulic conductivity of the naphthalene solution was also measured during the breakthrough test as 8.84×10^{-9} m/s following ASTM D5084, method B.

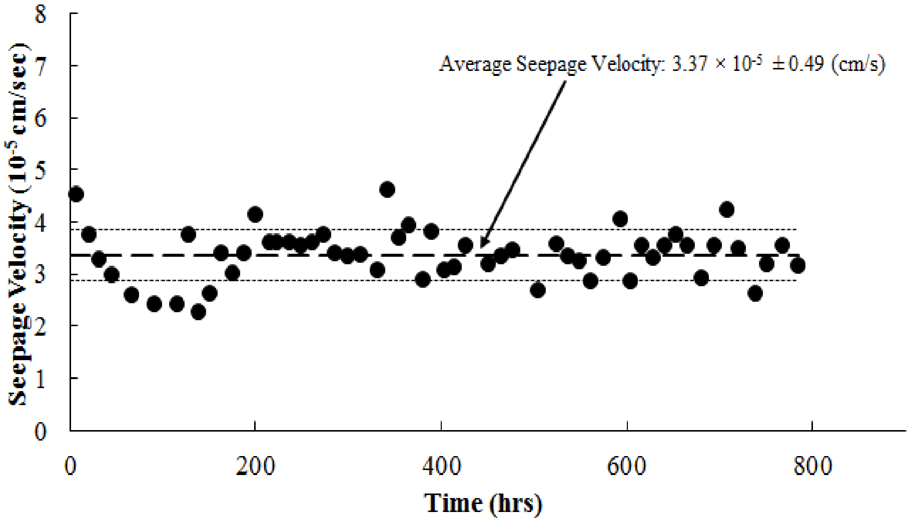


Figure 3-10. Average seepage velocity of naphthalene solution during the breakthrough study

The breakthrough of naphthalene solution in compacted soil column consisting of 95% silty clay and 5% HDTMA-bentonite is shown in Figure 3-11.The maximum concentration of naphthalene breakthrough curve in compacted silty clay/HDTMA-bentonite column appeared after 142 hours which was approximately 9 times lower than initial introduced concentration to the column. The high sorption capacity of HDTMA-bentonite to adsorb naphthalene from aqueous phase resulted in significant low naphthalene concentration in effluent. Because a relatively low advection rate mechanism governed the mass transport of naphthalene through the compacted soil column, the retardation factor for the pulse-type injection was measured from the first moment analysis(Shackelford and Redmond 1995; Valocchi 1985). Using the first moment method analysis, the retardation factor of naphthalene solution passing through compacted silty clay/ HDTMA bentonite soil column was measured as 6.98. For the retardation calculation, the initial introduced naphthalene concentration into the column (C_0) was 130 µg/mL and the pore volume of introduced naphthalene solution into the column (PV_0) was 1. The calculated retardation factor was compared with the retardation coefficient derived from the partitioning coefficient (Freeze and Cherry 1979), equation 3-7:

$$R = 1 + \frac{\rho_b}{n}.K_d = 1 + \frac{2.02}{0.3}.(0.05\times1355.5 + 0.95\times4.5376) \cong 486 \qquad 3\text{-}7$$

The latter calculation disclosed a notable difference between the retardation factor calculated from first moment analysis and derived from partitioning coefficient. Shackelford (1994) explained that the retardation factor equation proposed by Freeze and Cherry may be applicable for the fast flow rate regimes which the advection is the dominant transport mechanism. However, the retardation factor should be calculated from the breakthrough curve for the cases of (1) an infinite constant contaminant source with continuous contaminant injection method, or (2) a finite constant contaminant source with pulse-signal type contaminant injection method. For the first scenario, the retardation factor is equal to the pore volume corresponds to the relative effluent concentration of 0.5. For the second scenario, the first moment analysis should be applied to estimate the retardation factor (Daniel 1993). Although previous works including the research conducted by Shackelford and Redmond (1995) did not consider the organoclays as amendment in the compacted soil matrix, the obtained results suggest that the same conclusion can be drawn on the breakthrough experiment of naphthalene in HDTMA-bentonite amended soil column.

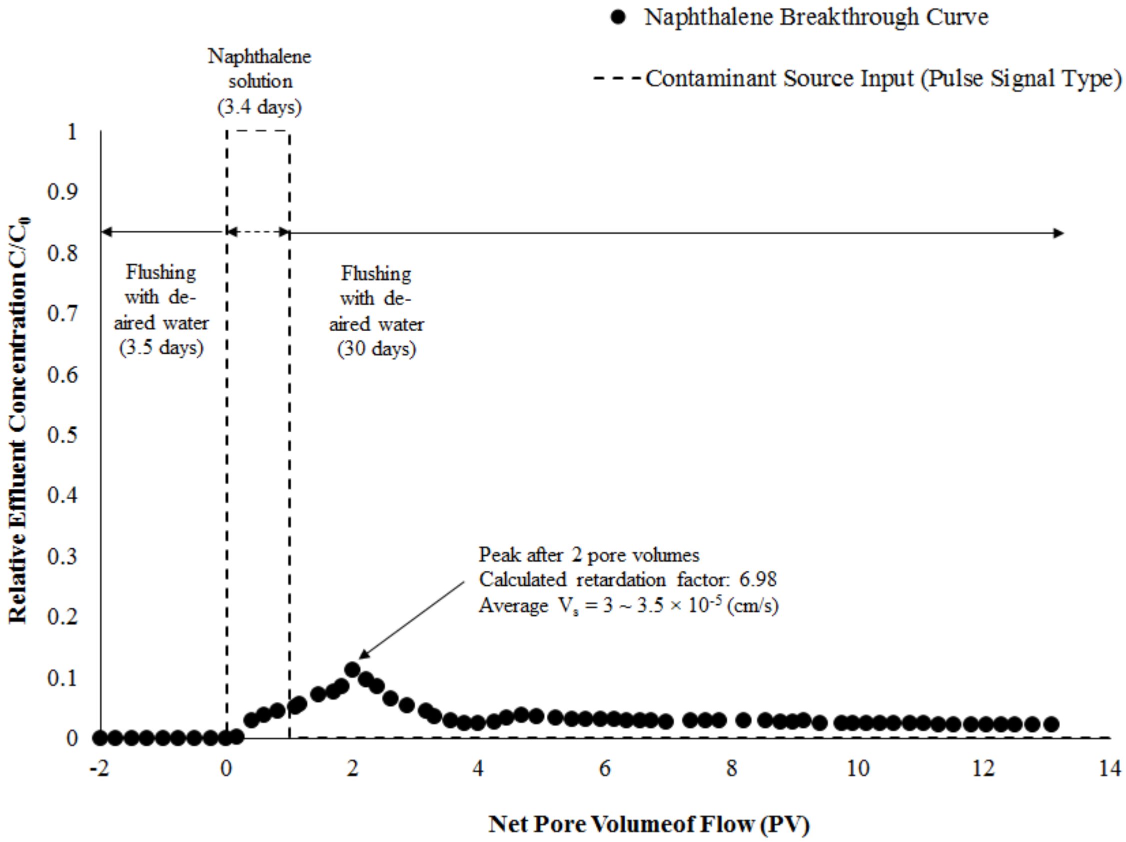


Figure 3-11. Breakthrough curve of naphthalene transport in 95% silty clay + 5% HDTMA-bentonite compacted soil column

Moreover, the breakthrough curve revealed that even a small fraction of HDTMA-bentonite (only 5% by weight) as an amendment to silty clay decreases the mass flux of naphthalene in the effluent, significantly. Also, the reduction of mass flux in the effluent increases as the percentages of HDTMA-bentonite in soil matrix increases. The mass flux of introduced naphthalene solution into the compacted soil column was 0.113 $mg/cm^2 \times day$ while the retardation process decreased the mass flux of naphthalene to 0.004 $mg/cm^2 \times day$ in the effluent (approximately reduced 29 times). In addition, the mass balance calculation indicated that only 5% of HDTMA-bentonite exhibited such a high sorption capacity that 54% of total introduced naphthalene to the soil column was still uptaken by the column after 33 days and was releasing gradually. Using numerical modeling, a transport model for equation 1-3 was developed to estimate the diffusion coefficient of naphthalene. By curve fitting of the developed model to the breakthrough curve, it was concluded that the diffusion coefficient of naphthalene was in the order of 10^{-6} cm^2/s for the HDTMA-bentonite amended silty clay which was comparable with the results from previous researches on the retardation performance of soil barriers (Headley et al. 2001). A summary of previous studies on contaminant transport in fast/low flow rate systems is presented in Table 3-7.

Table 3-7. Summary of contaminant transport parameters for fast and slow flow rate condition

Study	Contaminants	Soil Matrix	Velocity (cm/s)	Retardation Factor	Diffusion Coefficient (cm2/s)
	High Flow Rate				
Liu et al. (1991)	Naphthalene	Lincoln - sand	2×10^{-3}	5	N.A.
		Eustis - sand		12	
Thierrin et al. (1995)	Benzene	Sandy aquifer	2.5×10^{-2}	1.02	N.A.
	Toluene			1.04	
	p-Xylene			1.12	
	Naphthalene			1.32	
Owabor et al. (2010)	Naphthalene	Sandy soil	2×10^{-3}	25.77	N.A.
Larsen et al. (1992)	Naphthalene	Aquifer material	N.A.	1.61	N.A.
	Low Flow Rate				
Lo et al. (1997)	benzene, toluene, o-xylene, ethyl-benzene, phenol, 2-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol	BB-40	4.93×10^{-6}	N.A.	N.A.
Li et al. (2002)	Chromate	HDTMA-modified illite	1×10^{-4}	N.A.	N.A.
Shackelford et al. (1991)	Cl-	Kaolinite & Lufkin clay	N.A.	N.A.	4.4 to 6×10^{-6}
	Br-				4.8 to 6.5×10^{-6}

Shackelford (1995)	Cl-	Kaolin	7×10^{-7}	1.4	3.75 × 10-6
	Na+			2.4	5.8×10^{-6}
Lo (2003)	Total organic carbon of landfill leachate	Mixture of BB-40, bentonite, and decomposed volcanic rock	N.A.	8.92	2.3×10^{-6}
Shackelford and Redmond (1995)	Cl-	Kaolin	7×10^{-7}	2.336	2.84×10^{-6}
	Na+			9.53	8.78×10^{-6}
Rodriguez-Cruz (2007)	Linuron	Modified sandy loam with ODTMA-montmorillonite	N.A.	69.5	N.A.
	Atrazine			9	
	Metalaxyl			10	
This Study	Naphthalene	HDTMA-bentonite	3.4×10^{-5}	6.98	$\sim9\times10^{-6}$

This study suggests that a small fraction of HDTMA-bentonite amendment (5% by weight) in soil matrix have negligible impact on total hydraulic conductivity and diffusion coefficient of soil admixture. However, even a small fraction of HDTMA-bentonite amendment can increase the sorption capacity and enhance the retardation of naphthalene in compacted soil and it may enhance the sorption characteristics of the compacted clay for other organic contaminants as well. As a result, organoclay amendments can enhance the sorption capacity of the barrier systems and decrease the mass flux of contaminant through the barriers while they do not impose a considerable change to the advection and diffusion rate of contaminants.

3.4 Conclusion

In this chapter, the permeability of compacted soil barrier consists of silty clay and HDTMA-bentonite. Obtained results suggested that 10% of HDTMA-bentonite additive has a negligible impact on the free swelling behavior of silty clay in water. However, the HDTMA-bentonite amended silty clay demonstrated a significant swelling tendency to gasoline because of the interaction between the organophilic surfactants in the HDTMA bentonite and non-polar liquid. Although the 10% HDTMA-bentonite as an amendment to compacted silty clay increased the hydraulic conductivity of the system to water, slightly (5.04×10^{-9} m/s to 1.57×10^{-8} m/s), but it decreased the permeability of the compacted clay system to gasoline approximately 1 order of magnitude (9.20×10^{-10} m/s). the acquired results from this study in conjunction with previous studies suggest that a small fraction of organoclay amendments have a limited impact on the hydraulic conductivity of compacted silty clay while they enhance the capability of the barrier system to confine the transport of organic or low-polarity fluids. The breakthrough study revealed that a small percentage of HDTMA-bentonite additive (~5%) to the compacted silty clay enhances the retardation capacity (approximately 7) of the system to the mass transport of organic contaminant (naphthalene). Although the breakthrough rate of the naphthalene through compacted HDTMA-bentonite amended silty clay did not increase significantly, the absorbed mass of naphthalene by HDTMA-bentonite was released in a considerably low paste (average of 0.004 $mg/cm^2\times day$ and peak of 0.011 $mg/cm^2\times$ day compared to the source of 0.113 $mg/cm^2\times day$). The overall results in this study suggest that HDTMA bentonite or other organophilic clays hold the promise of being the amendment material in a CCL barrier for organic and/or low polarity fluids.

4 CHAPTER FOUR ENGINEERING BEHAVIORS OF GEOSYNTHETIC CLAY LINERS (GCLs) AMENDED WITH ORGANOCLAYS

4.1 Introduction

Conventional Geosynthetic Clay Liners (GCLs) consists of a layer of sodium or calcium bentonite sandwiched between two layers of woven/nonwoven geotextiles (Bouazza 2002). GCLs have been used as low permeability components in composite hydraulic barriers in the United States since 1980, and their design and applications have gained increasing popularity due to their reliable performances. Most commonly, GCLs have been used in composite liner systems; capping of landfills; liquid waste ponds; barrier system for the hydrocarbon spills; liners of underground storage tanks; containment systems of gas and fluids in mining industry and transportation facilities (Lorenzetti 2005; Nathalie Touze-Foltz 2012; Touze-Foltz et al. 2012).Compared to the conventional low-permeability barriers (e.g. compacted clay), GCLs have significant advantages such as availability, consistent low hydraulic conductivity ($k_w < 10^{-10}$ m/s), low cost, limited thickness, and easy installation (Bouazza 2002).Detailed comparison of advantages and disadvantages of GCL is summarized in Table 4-1 (Bouazza 1997). These advantages were recognized and consequently, increased the interest of GCL application in environmental geotechnics

Table 4-1. Advantages and disadvantages of GCL

Advantages	Disadvantages
Rapid installation/less skilled labor/low cost	Low shear strength of hydrated bentonite (for unreinforced GCLs)
Very low hydraulic conductivity to water if properly installed	GCLs can be punctured during or after installation
Can withstand large differential settlement	Possible loss of bentonite during placement
Excellent self-healing characteristics	Low moisture bentonite permeable to gas
Not dependent on availability of local soils	Potential strength problems at interfaces with other materials
Easy to repair	Smaller leachate attenuation capacity
Resistance to the effects of freeze/thaw cycles	Possible post-peak shear strength loss
More airspace resulting from the smaller thickness	Possible higher long term flux due to a reduction in bentonite thickness under an applied normal stress
Field hydraulic conductivity testing not required	Possible increase of hydraulic conductivity due to compatibility problems with contaminant if not prehydrated with compatible water source
Hydrated GCL is an effective gas barrier	Higher diffusive flux of contaminant in comparison with compacted clay liners
Reduce overburden stress on compressible substratum (MSW)	Prone to ion exchange (for GCLs with sodium bentonite)
	Prone to desiccation if not properly covered (at least 0.6m of soil)

Typically, the common range of hydraulic conductivity of GCLs under the different confining stresses is in the range of 2×10^{-12} to 2×10^{-10} m/s (Figure 4-1).Petrov et al. (1997) suggested that the higher confining stress decreases the bulk void ratio of the GCL. Consequently, the hydraulic conductivity of the GCL tendto decrease asthe confining stress increases.

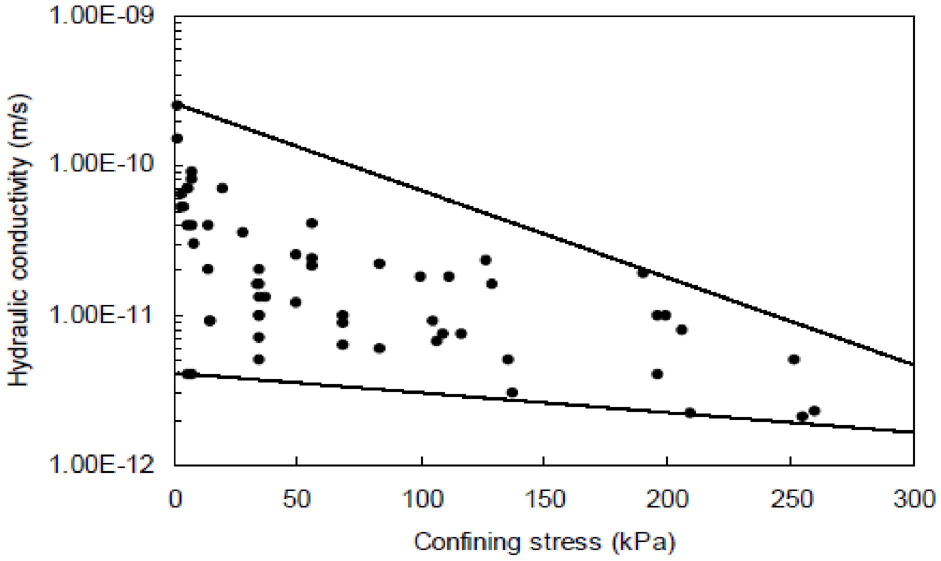


Figure 4-1. Variation of hydraulic conductivity with different confining stress (Bouazza 2002)

A higher hydraulic gradient is commonly used when examining the hydraulic performance of low flow rate systems because it would reduce the duration of the tests. However, exceeding a certain level of hydraulic gradient will cause the consolidation of the specimen due to seepage force and possibly result in a lower hydraulic conductivity (Shackelford et al. 2000).Typically, the acceptable range of hydraulic gradient for GCL layers lays is in the range of 50 and 500 (Daniel et al. 1993; Petrov et al. 1997; Shan and Daniel 1991). Petrov et al. (1997) investigated the effect of hydraulic gradient on the conductivity of a GCL permeated with deionized water, and 0.6/2 M NaCl solutions. The retrieved results are presented in Figure 4-2.

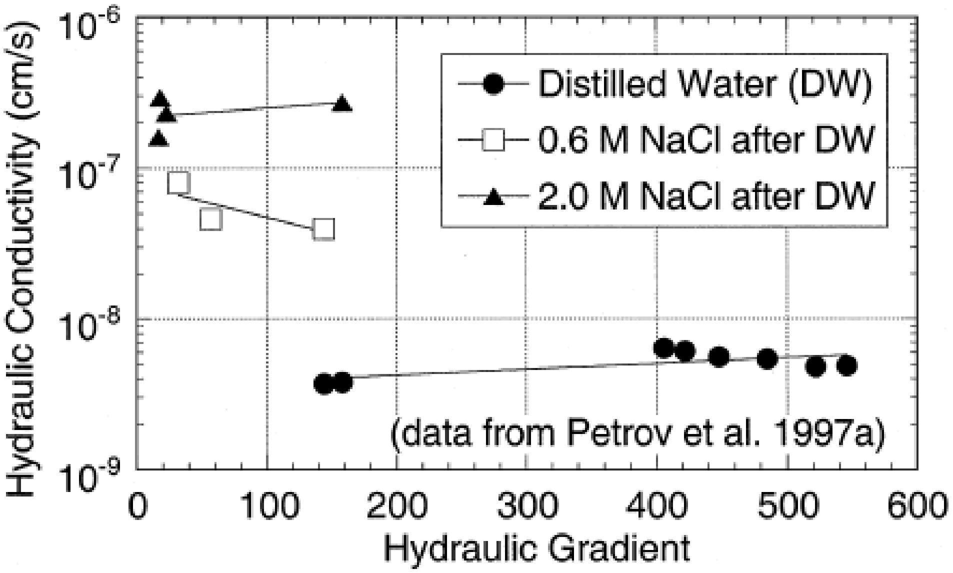


Figure 4-2. effect of hydraulic gradient on the conductivity of a GCL permeated with different liquids(Shackelford et al. 2000)

Petrov et al. (1997) proposed that the hydraulic gradient has a negligible effect on the hydraulic conductivity of GCLs (<factor of 2). Previously, Rad et al. (1994)suggested the same concept.

Although GCLs have a long history of successful engineering applications and have demonstrated reliable hydraulic performance to decrease the advective flow, the following limitations were observed in the field, including: (1) possible defects due to manufacture, transportation and installation (2) susceptibility and incompatibility (e.g. increased permeability, shrinkage) with certain chemicals, especially organic liquids (3) significant diffusive transport of contaminants even the advection is low. The above-mentioned limitations, especially the chemical impartibility of conventional Na-bentonite GCL or Ca-bentonite GCL with organic fluid may directly impair their performance in soil barriers (e.g. liners of underground storage tank), which may raise short-term or long-term concerns. Specifically, it has been reported that the organic compounds with higher concentration or low-polarity organic fluids may dehydrate the clay minerals and consequently increase the hydraulic conductivity of the liner systems due to desiccation (Ruhl and Daniel 1997). In addition, the clay materials exposed to organic liquids tends to shrink considerably which results in different levels of cracks and increases the hydraulic conductivity of barrier system (Bowders and Daniel 1987; Lake and Rowe 2004). Ruhl and Daniel (1997) investigated the hydraulic performance of GCLs permeating with simulated municipal solid wastes. They discovered that the permeability of studied GCLs to the leachates of the solid wastes was about four orders of magnitude higher than the permeability of GCLs to the tap water. Additionally, Daniel et al. (1993) and Shan and Daniel (1991) evaluate the permeability of a GCL permeated with varying fluids. Their results suggested the GCL used to have a permeability for water as low as 10^{-9} cm/s, however, when permeated with organic liquid(s), the permeability of GCL increased drastically to 10^{-5} cm/s.

Other fluid properties, including ionic strength and pH could affect the hydraulic performance of GCL as well. Jo et al. (2001) studied the impact of ionic concentration on the swelling tendency and hydraulic conductivity of non-prehydrated GCLs. They noted that the GCLs permeated by solutions with higher ionic concentration or with high-valence cations exhibited higher hydraulic conductivity compared to solutions with monovalent cations or water. Shackelford et al. (2000) investigated the hydraulic performance of GCLs permeated by non-standard solutions and they draw similar conclusions. Bradshaw et al. (2016)conducted tests to evaluate the effect of pH on the saturated hydraulic conductivity of studied GCL. They suggested that the hydraulic conductivity decreased when the pH of the permeant solution increased.Ye et al. (2014)

explored the effect of pH on the hydraulic conductivity of compacted bentonite and concluded that compacted bentonite has higher hydraulic conductivity in the basic solution.

Most commonly, the chemical incompatibility observed for the GCL field applications are due to the contact with petroleum-related products, landfill leachate, fuels, and industrial wastewater (Bradshaw et al. 2016). Typically, the organic compounds, or the organic liquids in the waste or wastewater are the components that are not compatible with inorganic soils like Na-bentonite or Ca-bentonite. Additionally, although the conventional Na-bentonite or Ca-bentonite based GCLs exhibited lower permeability for aqueous solutions, they also had a much lower contaminant retention capacity for dissolved organics(Broderick and Daniel 1990). Because of the above reasons, the performance of conventional GCL as both hydraulic barrier and chemical barrier can be fair or poor. Different sorptive/reactive geo-materials have been suggested as an amendment in compacted soil liners (Lo et al. 1997).. Similarly, certain amendments with enhanced reactivity with organic solute and/or organic fluid could enhance the chemical compatibility of the conventional GCLs Many studies have been carried out to investigate the feasibility of using fly ashes, zeolites, organo-zeolites, coated sands and organoclays as reactive amendments to the GCLs(Lo and Liljestrand 1996; Prasad et al. 2012; Varank et al. 2011; Younus and Sreedeep 2012).

Recent studies suggested that the permeability of organobentonites decreases by decreasing the polarity of the permeant fluid. For instance, the permeability of organoclays to non-polar liquid like fuels is much lower compared to polar or semi-polar liquids(Ghavami et al. 2016). Lorenzetti et al. (2005) studied the effect of different percentages of organoclays amendment on the hydraulic conductivity of GCLs. They indicated that the hydraulic conductivity of GCLs can be affected significantly by different fraction of organoclays, especially when the fraction of organoclay amendment is greater than 20% of total weight of filling material in GCLs. Their results showed that the hydraulic conductivity of GCL permeated by water increases as the percentages of organoclay amendment increases. However, it was observed that a small fraction of organoclays (less than 10% by weight) has limited impact on the hydraulic conductivity of GCLs while it can reduce the permeability of the GCL to organic liquids and may retard the mass transport of organic contaminants significantly. Although organoclays increase the hydraulic conductivity of the compacted clay systems, the bentonite component compensates the defect of hydraulic conductivity and maintains the conductivity of the system at a low rate. It was proposed that a combination of organoclay and bentonite could be used as earthen barrier materials because they can enhance the sorption and retardation capacity of the barrier systems to organic contaminants while they can provide a relatively low hydraulic conductivity for waste disposal practices.

Although previous studies yield great insights into the interactions between bentonites, permeant fluids and ions, the organic compounds retention of GCLs under a slow advective flow condition remained relatively unknown. This was due to: (1) the time required to perform the study of organic contaminant mass transport through a low flow rate GCL is too long (more than weeks); (2) the difficulty to control the organic contaminant source during the test; (3) the lack of analytical solution to interpret the observed retention or retardation of organic contaminants in GCLs; and also (4) the limited chemical interactions between conventional GCLs and the organic compounds.

In this study, the permeability of conventional Ca-bentonite/Na-bentonite GCLs and Ca-bentonite/Na-bentonite GCLs amended with organobentonite were investigated. Water, benzene solution, methanol, and gasoline were chosen as the permeant liquids and the effects of confining stress, pH, and ionic strength on the permeability of GCLs were studied. Lab batch sorption test and contaminant breakthrough in the GCLs were carried out and benzene was selected (a representative of BTEX) as the organic contaminant. The retarded transport of benzene through Ca-bentonite/Na-bentonite GCL with different fraction of organobentonites was observed and analyzed.

4.2 Material and methods

4.2.1 GCL specimen

A roll of Bentomat 200R GCL was provided by CETCO Co. (Figure 4-3). The Bentomat 200R consists of a layer of granular bentonite sandwiched between a nonwoven and woven geotextile layers. The geotextile layers and granular bentonite as the middle layer are needle punched together. The properties of Bentomat 200R is summarized in Table 4-2 (CETCO 2014):

Figure 4-3. The base GCL, Bentomat 200R

Table 4-2. Properties of Bentomat 200R

Material property	**Test method**	**Required values**
Bentonite Swell Index	ASTM D 5890	24 mL/2g min.
Bentonite Fluid Loss	ASTM D 5891	18 mL max.
Bentonite Mass/Area	ASTM D 5993	0.75 lb/ft^2 (3.6 kg/m^2) min.
GCL Tensile Strength	ASTM D 6768	30 lb/in (53 N/cm) MARV
GCL Peel Strength	ASTM D 6496	1 lb/in (1.75 N/cm) min.
GCL Index Flux	ASTM D 5887	1 × 10^{-8} m^3/m^2/sec max.
GCL Hydraulic Conductivity	ASTM D 5887	5 × 10^{-9} cm/sec max.
GCL Hydrated Internal Shear Strength	ASTM D 5321 ASTM D 6243	150 psf (7.2 kPa) typical

The entire surface of GCL was inspected for any damages or defects. A porous stone was used as a base to cut a circular sample of GCL, which matches to the exact size of the base and cap used in the column study. In this study, GCL specimens were carved from the base GCL with the dimension of 4 inches (101.6 mm) in diameter, Figure 4-4.

Figure 4-4. Carved GCL specimen from the base GCL

The original soil filling in the Bentomat 200R was replaced by a certain weight of desired soil filling. A mixture of calcium and sodium bentonite and desired percentages of HDTMA bentonite was used as the filling (D6766). The edges of the specimens were moisturized by a squirt bottle to prevent the filling lost at the edges (Rowe et al. 2000), Figure 4-5.

Figure 4-5. Filling the soil mixture in the GCL specimen

To have an even flow distribution through the sample, a pair of porous stone were placed at top and bottom of each specimen. The initial thickness of constructed GCL specimens were typically measured between 7 and 8 mm, Figure 4-6.

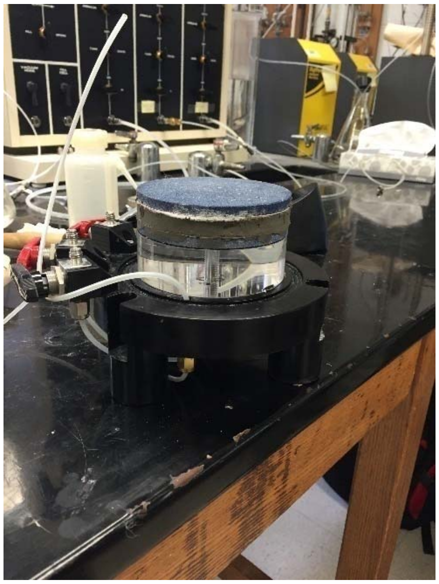


Figure 4-6. Assembled GCL specimen for column test

To ensure the compatibility with the permeant fluids, polytetrafluoroethylene (PTFE) tubes were used in the entire flow-through system. Also, the GCL specimens were wrapped finally by the Teflon tape to prevent the decay of initial concentration of benzene due to the sorption by the latex membrane, Figure 4-7.

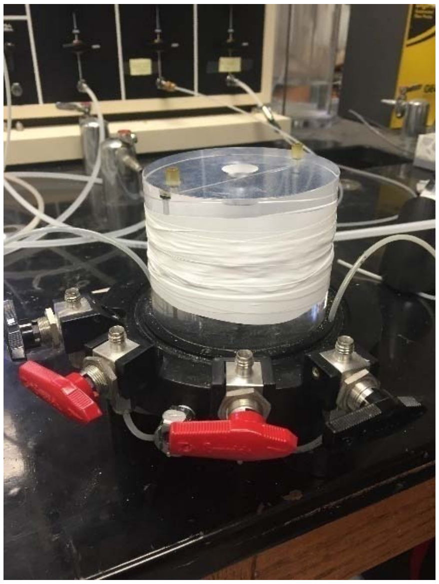


Figure 4-7. GCL specimen wrapped by Teflon tape

At the final step, the GCL specimens were wrapped by latex membrane. to seal the membrane to the top cap and the base, a pair of O-ring was placed around the specimen. The physical properties of GCL specimens are summarized in Table 4-3 and Table 4-4.

Table 4-3. The physical parameters of calcium based GCL specimens

Column Component	100% Ca-bentonite	90% Ca-bentonite + 10% HDTMA-bentonite	80% Ca-bentonite + 20% HDTMA-bentonite
Diameter (mm)	101.6	101.6	101.6
Height (mm)	7.8	8	7.9
Specific gravity of soil filling (G_s)	2.62	2.53	2.44
Porosity	0.64	0.69	0.67
Pore volume (cm^3)	40	37	33

Table 4-4. The physical parameters of sodium based GCL specimens

Column Component	100% Na-bentonite	90% Na-bentonite + 10% HDTMA-bentonite	80% Na-bentonite + 20% HDTMA-bentonite
Diameter (mm)	101.6	101.6	101.6
Height (mm)	7.5	7.7	7.8
Specific gravity of soil filling (G_s)	2.63	2.54	2.45
Porosity	0.68	0.67	0.64
Pore volume (cm^3)	37	40	40

4.2.2 Permeant liquids

Anhydrous benzene with purity of 99.8% was diluted by deionized water to reach to the target concentration for this study, which was 300 to 400 μg/mL. To achieve the desired concentration, 0.3 to 0.4 g of liquid benzene was extracted by a 10 μL glass syringe (Hamilton Co.) from the source and placed into a flask (Fisher scientific Co.) with the capacity of 2 L. one liter of deionized water was added to the flask and stirred in an Ultrasonic Bath (VWR Co.) for 30 mins. The obtained stock solutions were stored at room temperature for less than 1 hour before the tests. Additionally, pure methanol (Carolina Biological Supply Co.) and unleaded gasoline (grade 87) were used as low polarity liquids for the permeability tests.

4.2.3 Swell index test of GCL soil components

Previous studies indicated that the permeability of GCL is typically related to the swelling tendency of the filling soil in the permeant liquid (Jo et al. 2001). The swell index tests were conducted to evaluate the swelling tendency of studied soils ,following the ASTM standard D5890-11.Initially, the studied soils were oven dried at 90 ºC for 24. Next, the soils were sieved through the No. 100 sieve (Phanikumar and Shankar 2016). 2 g of sieved dry soil grains was then added to a 100mL graduated glass cylinder filled with 90 mL of one of the selected liquids (DI water, methanol, gasoline, sodium chloride (NaCl) solution, and basic/acidic solutions). Additional liquid was then added to the cylinder until the 100 mL mark was reached. NaCl solutions with ionic concentrations of 0.01 M, 0.1 M, and 1 M were prepared and used for the swelling tests. the volume of suspended soil was measured for the first 24 hours.

4.2.4 Permeability test

To investigate the impact of the polarity of the fluids on the permeability of organobentonite amended GCLs, 16 GCL specimens were constructed following the method described in 4.2.1. 6 GCL specimens were filled with Ca-bentonite, Na-bentonite, 10% HDTMA-bentonite + 90% Ca-bentonite, 10% HDTMA-bentonite + 90% Na-bentonite, 20% HDTMA-bentonite + 80% Ca-bentonite, and 20% HDTMA-bentonite + Na-bentonite. and three permeant liquids with high polarity (water), intermediate polarity (methanol) and low polarity (gasoline) were used. Additionally, 10 Na-bentonite GCL specimens with different percentage of HDTMA-bentonite and PM-199 were constructed to examine the effect of organobentonite amendments. The physical properties of GCL specimens are summarized in Table 4-5.

Table 4-5. Physical properties of GCL specimens for permeability study

GCL specimen	Water content (%)	Average dry density (g /cm^3)	Mass per unit area (g /cm^2)
Ca-Bentonite	8%	1.26	0.95
Na-Bentonite	8%	1.10	0.83
10% HDTMA-Bentonite + 90% Ca-Bentonite	10%	0.93	0.75
20% HDTMA-Bentonite + 80% Ca-Bentonite	9%	1.00	0.77
10% HDTMA-Bentonite + 90% Na-Bentonite	10%	1.03	0.80
20% HDTMA-Bentonite + 80% Na-Bentonite	9%	1.26	0.90
30% HDTMA-Bentonite + 70% Na-Bentonite	9%	1.05	0.89
50% HDTMA-Bentonite + 50% Na-Bentonite	10%	1.11	0.84
70% HDTMA-Bentonite + 30% Na-Bentonite	10%	1.00	0.75
10% PM-199 + 90% Na-Bentonite	9%	1.18	0.83
20% PM-199 + 80% Na-Bentonite	9%	1.15	0.84
30% PM-199 + 70% Na-Bentonite	10%	1.12	0.81

50% PM-199 + 50% Na-Bentonite	8%	1.06	0.77
70% PM-199 + 30% Na-Bentonite	9%	1.08	0.79
HDTMA-Bentonite	8%	1.15	0.98
PM-199	8%	1.09	0.95

The permeability of studied GCLs were carried out in a flexible wall permeameter following ASTM D6766. The conductivity (k) of permeant liquids based on the falling head test method can be measured as follow:

$$k_t = \frac{aL}{At} ln\left(\frac{h_1}{h_2}\right) \quad 4\text{-}1$$

where k_t is hydraulic conductivity (m/s), a is cross-sectional area of the reservoir containing the influent liquid (m^2), L is length of the specimen (m), A is cross-sectional area of the specimen (m^2), $h_1$is the head loss (m) across the specimen at time t_1 (s), $h_2$is the head loss (m) across the specimen at time t_2 (s), and t is the elapsed time (s) between determination of h_1 and h_2.

Also, the intrinsic permeability was calculated for each GCL specimen. The intrinsic permeability is independent of the fluid properties and represents the pore distributions and connectivity in the porous media. The intrinsic permeability is defined as:

$$k_i = \frac{\mu k_t}{g} \quad 4\text{-}2$$

where k_i is intrinsic permeability (m^2), μ is kinematic viscosity of the permeant fluid (m^2/s), k_t is hydraulic conductivity (m/s), and g is the gravitational acceleration (m/s^2).

After the assembly of the GCL specimens, de-aired water was flushed through the specimens under a relatively high hydraulic gradient (100) to flush two pore volumes of water in a short period of time. A relatively lower hydraulic gradient (25) was applied to the GCL specimens when permeated with organic liquids (methanol and gasoline). This was similar to the procedure by Ruhl and Daniel (1997). The GCL specimens were saturated for 4 days until the flow reached steady state. For each specimen, the confining pressure (cell pressure) was kept constant at 34.47 kPa during entire test. The steady state flow was at 1.1±0.2 mL/hour and 0.9±0.2 mL/hour for Na-bentonite and Ca-bentonite based GCL specimens, respectively.

4.2.5 Breakthrough test

Breakthrough test was conducted to evaluate organic contaminant transport through the compacted soils, certain volume of the contaminant solution was introduced to each soil column with known soil constituents. Effluent was collected and analyzed for the concentration of the contaminant remained in the flow. Finally, the breakthrough curve was obtained by plotting the concentration of contaminant (or the relative concentration, the ratio of the effluent concentration to the source concentration) in the effluent versus time. Also, the collected pore volumes of effluent samples were recorded during the sampling. In this study, the mass transport of benzene through the GCL specimens with/without sorptive amendments (HDTMA-bentonite) was recorded during the breakthrough test. As explained in permeability test, the GCL specimens were flushed with de-aired water prior to the breakthrough test. The benzene solution with initial concentration of 300 to 400 μg/ml was fed to the GCL specimens using a bladder accumulator. The pulse-type contaminant injection method was selected as one pore volume of benzene solution was injected into the each GCL specimen, followed by the de-aired water until the test was completed. The breakthrough tests were terminated after the concentration of benzene in effluent was lower than the detection limit. For all specimens, the flow rate of benzene solutions was monitored during the breakthrough test. The effluent samples were collected in10 mL conical centrifuge tubes (CORING Co.) and filtered through 0.2 μm syringe filters (Acrodisc Co.). The liquid-liquid extraction was performed to extract the dissolved benzene from the filtered solution. Dichloromethane (DCM) was choose as the extraction liquid and it was mixed with the filtered solution in using a separatory funnel at a ratio of 10:1 (v/v). Then the separatory funnel was shaken gently and left at rest until the two separate phases were observed. The DCM liquids were analyzed in Gas Chromatography equipped with Flame Ionization Detector (Clarus 480, Perkin Elmer Co.). As explained in chapter 3, the retardation factor R_d of contaminant transport under low-flow rate condition was estimated as (Valocchi 1985):

$$R_d = \frac{\sum(C/C_0)PV\Delta PV}{\sum(C/C_0)\Delta PV} - 0.5PV_0 \qquad 4\text{-}3$$

where R_d is the dimensionless retardation factor, C_0 (μg/mL) and C (μg/mL) are the initial and equilibrium concentrations of naphthalene in aqueous phase, respectively; PV (mL) is the corresponding pore volume to each measured concentration, ΔPV (mL) is the differential pore volume between each sampling step, and PV_0 (mL) is the initial injected pore volume of the solution into the soil column.

In addition, the diffusion coefficient and the retardation factor were estimated by the numerical and analytical solutions. Assuming the steady state flow and equilibrium sorption, the contaminant transport through the porous media can be described by a one-dimensional advection-dispersion-retardation equation (equation 1-3). To determine the soil parameter including retardation factor and diffusion coefficient, an implicit finite difference scheme was employed to fit the laboratory data. as following:

$$C_j^{k+1} = C_j^k + \left(\frac{D.\Delta t}{R_d.\Delta x^2}\right)\left(C_{j-1}^k - 2C_j^k + C_{j+1}^k\right) - \left(\frac{v.\Delta t}{2.R_d.\Delta x}\right)\left(C_{j+1}^k - C_{j-1}^k\right) \tag{4-4}$$

where k corresponds to the distance dimension, j corresponds to the time dimension, C is the concentration of the effluent in time j and location of k (μg/mL), D is the diffusion coefficient (cm^2/s), R_d is the retardation factor, Δt is the time step (s), and Δx is the distance step (cm). Two criteria have to be met to assure the convergence of the solution.

$$\begin{cases} 1.\left(\frac{D.\Delta t}{R_d.\Delta x^2}\right) \leq 0.5 \\ 2.\left(\frac{v.\Delta t}{R_d.\Delta x}\right)^2 \leq \left(\frac{2.D.\Delta t}{R_d.\Delta x^2}\right) \end{cases}$$

The convergence criteria was met by setting the time step to 0.1 and the distance step to 0.1. Two parameters were determined by finding the best fit: (1) the retardation factor (R_d), and (2) the diffusion coefficient (D). An initial value for D was assumed based on the common range of D reported in previous studies (~10^{-6} cm^2/s) and the best fitted curve was attained by changing D and R_d, simultaneously.

In addition, the laboratory results were compared with an analytical solution to equation 1-3 considering the pulse-type injection method (Genuchten et al. 2013). The pulse-type injection can be defined as:

$$g(t) = \begin{cases} C_0 & 0 < t \leq t_0 \\ 0 & t > t_0 \end{cases} \tag{4-5}$$

And the solution to equation 1-3 can be obtained as follow:

$$C(x,t) = \begin{cases} C_i + (C_0 - C_i)A(x,t) & 0 < t \leq t_0 \\ C_i + (C_0 - C_i)A(x,t) - C_0A(x,t-t_0) & t > t_0 \end{cases} \tag{4-6}$$

where,

$$A(x,t)=\frac{1}{2}erfc\left[\frac{R_d x-vt}{\sqrt{4DR_d t}}\right]+\sqrt{\frac{v^2t}{\pi DR_d}}exp\left[\frac{(R_d x-vt)^2}{4DR_d t}\right] \\ -\frac{1}{2}\left(1+\frac{vx}{D}+\frac{v^2t}{DR_d}\right)exp\left(\frac{vx}{D}\right)erfc\left[\frac{R_d x+vt}{\sqrt{4DR_d t}}\right] \qquad 4\text{-}7$$

where C(x,t) is the solute concentration (µg/mL), C_0 is the initial concentration of injected pulse (µg/mL), C_i is the initial concentration of studied semi-infinite domain (µg/mL), v is the longitudinal fluid flow velocity (cm/s), t is the time of breakthrough (s), and D is longitudinal diffusion coefficient (cm^2/s). Likewise, both R_d and D were changed simultaneously to find the best curve fitting in this solution.

4.3 Result and discussion

4.3.1 Swelling index

The results of swell index test are shown in Figure 4-8. It can be noticed that the unmodified bentonites, especially Na-bentonite, exhibit a significant swelling in water because of strong hydration of inorganic cations in the interlayer. When sodium or calcium bentonites are dry, the interlayer spacing are typically 9~10Å as the cations formed surface complex on the sillica sheets. However, the bonding between the inorganic cations and montmorillonite sheets are very week and can be easily interrupted by polar fluids such as water (Oweis and Khera 1998). The water molecules would form hydration shells around the Na^+ and Ca^{2+} cations and prop open the interlayer spacing (from 14 Å ~16 Å) (Ayral-Cinar et al. 2016; Doh and Cho 1998). Additionally, the hydration of Na^+ in water is the highest because it has a strong dipole polarity, 1.854 (Lo and Yang 2001). Consequently, the volume of particle aggregates increases as the hydration prevails in the interlayer of the bentonites.

In comparison, the swelling index of HDTMA-bentonite and PM-199 in water are significantly lower (5 mL/2g). Because the naturally occurring interlayer cations (Na^+ or Ca^{2+}) of bentonite were replaced by quaternary ammonium cations, the surfactant-coated surfaces of modified bentonite became hydrophobic. The cation hydration was no longer the prevailing mechanism of organobentonite swelling in water. The swelling of Na-bentonite and HDTMA-bentonite admixture or Na-bentonite and PM-199 admixture decreased slightly from 24 mL/2g for 100% Na-bentonite to 21 mL/2g for 80% Na-bentonite + 20% HDTMA-bentonite, and 22 mL/2g for 80% Na-bentonite + 20% Pm-199.

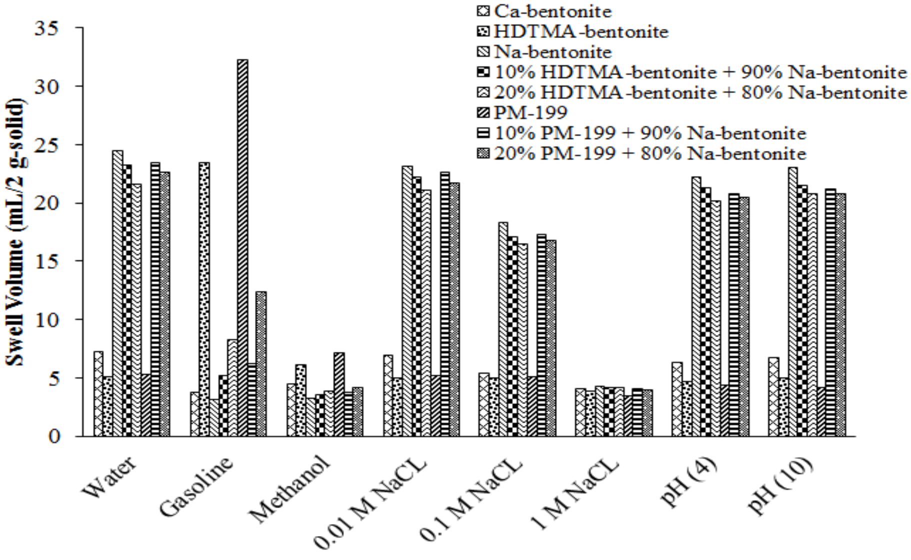


Figure 4-8. Swell index result for studied soil matrixes

The swelling of Na-bentonite in gasoline and methanol were inherently low (3.2 and 3.3, respectively). Similarly, Ca-bentonite swelled much less in gasoline and methanol as well

(3.8 and 4.5, respectively). This because the dominant constituents of the gasoline or methanol such as normal alkanes, benzene, and p-xylene have symmetric molecular structures which result in the dipole polarity of zero or near zero (Lo and Yang 2001). Because of this reason, the adsorption of gasoline or methanol molecules by the interlayer of Na^+ or Ca^{2+} bentonites was minimum and the interlayer swelling of the two were inhibited. The low swelling capacity of the unmodified bentonite can also be interpreted from the dielectric constant of the solution (ε).Graber and Mingelgrin (1994) explained that the swelling of bentonite decreases steadily when the dielectric constant of the solution decreases. They indicated that the maximum volumetric swelling of bentonite was in the water as it has the highest value of dielectric constant (ε = 80.20).

In contrast, HDTMA-bentonite and PM-199 had significant swelling in gasoline, Figure 4-9. The swelling indices of HDTMA-bentonite and PM-199 in gasoline were 23.5 and 32.2, respectively. Also, a slight swelling of HDTMA-bentonite and PM-199 in methanol were observed (6.1 and 7.2, respectively). Previous studies suggested that the swelling tendency of organobentonite in organic liquid is related to the TOC of the liquid (Benson et al. 2015). Typically, the TOC of gasoline and methanol are higher than 10000 ppm (Lo and Yang 2001). Because of the hydrophobic interactions between the intercalated surfactants and the non-polar solvent molecules, the modified clay minerals show higher tendency to adsorb organic liquids. Additionally, PM-199 exhibited higher swelling capacity in gasoline/methanol compared to the HDTMA-bentonite. This was due to the fact that PM-199 had a double chain quaternary ammonium cation while HDTMA-bentonite was modified by a single chain quaternary ammonium cation.

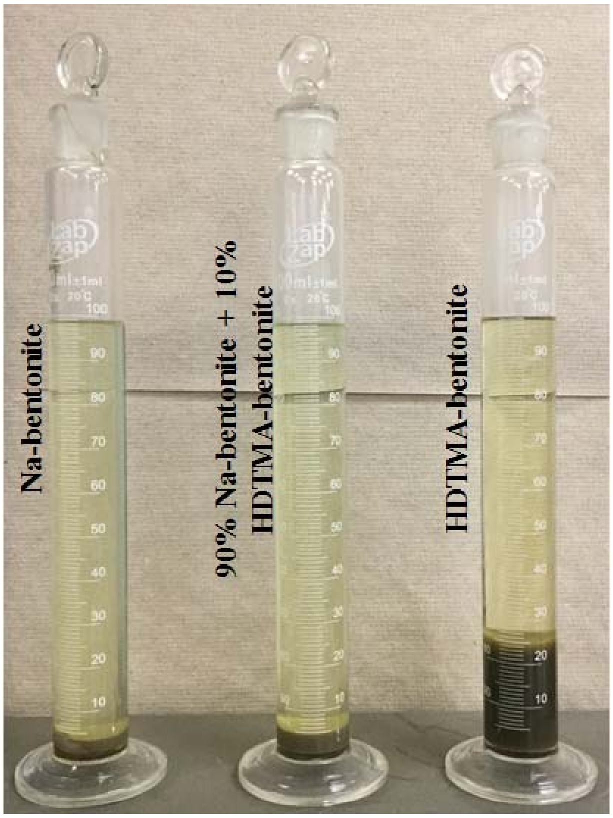


Figure 4-9. Swell index experiment for three studied soil specimens in gasoline

The results of swelling tests indicated that the organoclays and unmodified clays may exhibit very different swelling tendency in different liquids. The swelling tendency of unmodified bentonite increased when the polarity of the solution increased while organobentonites exhibited a lower swelling capacity when the polarity of solution increased. Notably, the organobentonites had increased swelling when the soaked in gasoline, which indicated both had a higher compatibility with gasoline, or other petroleum products.

The lower ionic concentration of 0.01 and 0.1 M of NaCl had limited impact on the swelling index of Na and Ca-bentonites. However, the swelling of Na-bentonite decreased to 4.3 mL/2 g at very high ionic strength (1M) (Figure 4-10). This was because the free energy gradient that induced by the elevated ionic concentration in the bulk solution dragged the water out of the interlayer of Na and Ca-bentonites (McBride 1994; Sposito 1981). Because of the same reason, it was observed that the permeability of GCL increases significantly when the ionic concentration of the fluid is very high (Jo et al. 2001). PM-199 and HDTMA-Bentonite had limited and consistent swelling in the NaCl solution with varying ionic strength. It can be concluded that although the organobentonites swell inherently less in aqueous solution, they are also less susceptible to the ionic concentration. The low percentage of organobentonites (10% and 20%) in the admixture with Na-bentonite did not affect the overall swelling tendency of Na-bentonite.

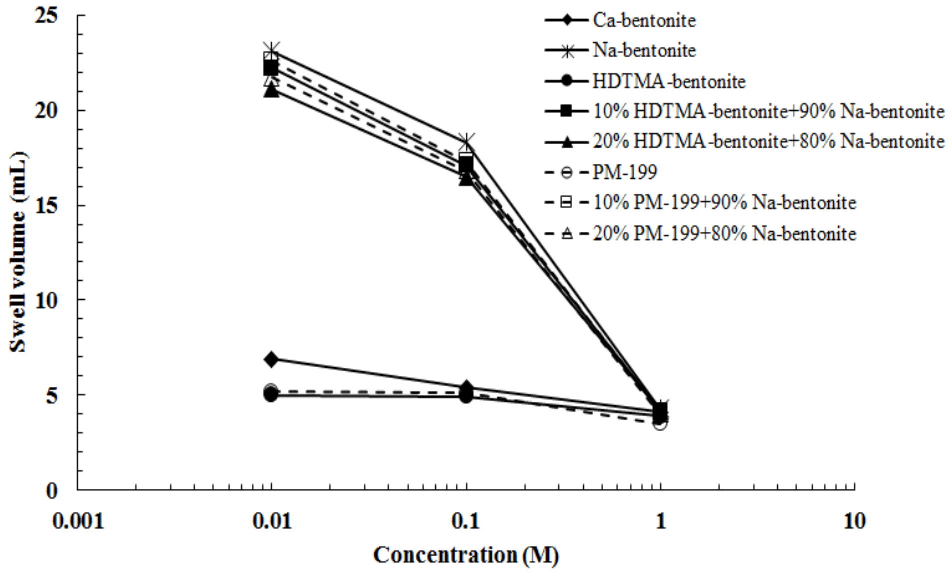


Figure 4-10. The effect of ionic concentration on the swelling tendency of the proposed soil combinations

In addition, the effect of pH on the swelling tendency of the soils were examined and results are presented in Figure 4-11. It was observed that the pH had limited effect on the swelling tendency of the all soils (in the range of 4-10). The observation in this study was similar to the results of a sedimentation experiment of sodium bentonite in the HCl and NaOH solutions (Shackelford (1994). However, previous studies have also indicated that the swelling of Na-bentonite can be significantly affected when the pH level of the solution is greater than 12 or less than 3 (Jo et al. 2001).The effect of pH on the swelling volume of the Na-bentonite in combination with different percentage of HDTMA-bentonite and PM-199 in presented in Figure 4-12. Organobentonites have a limited swelling capacity in aqueous solutions with different pH level (4,7, and 10). Thus, the small dosage of organobentonites (10% and 20%) mixed with Na-bentonite did not affect the overall swelling tendency of Na-bentonite (Figure 4-12).

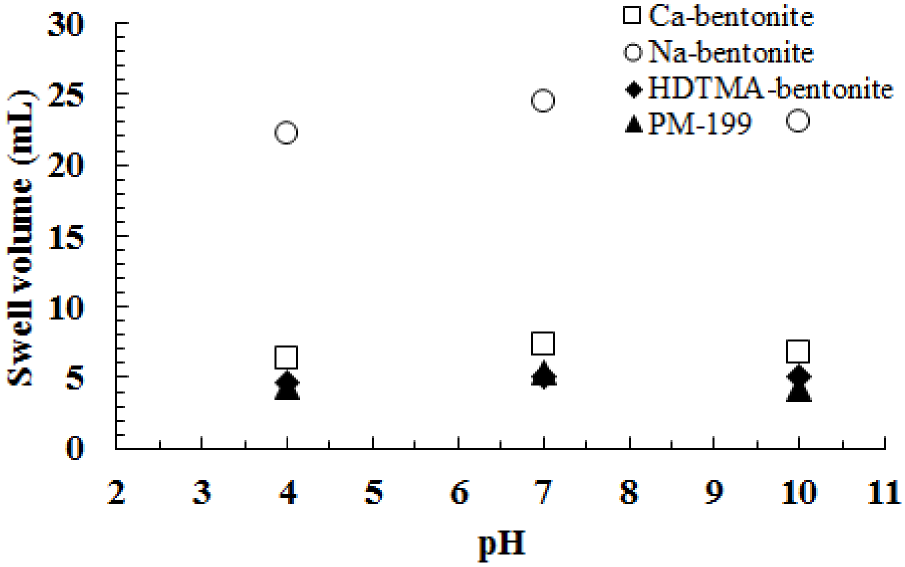


Figure 4-11. Effect of pH on the swelling of studied sorbents

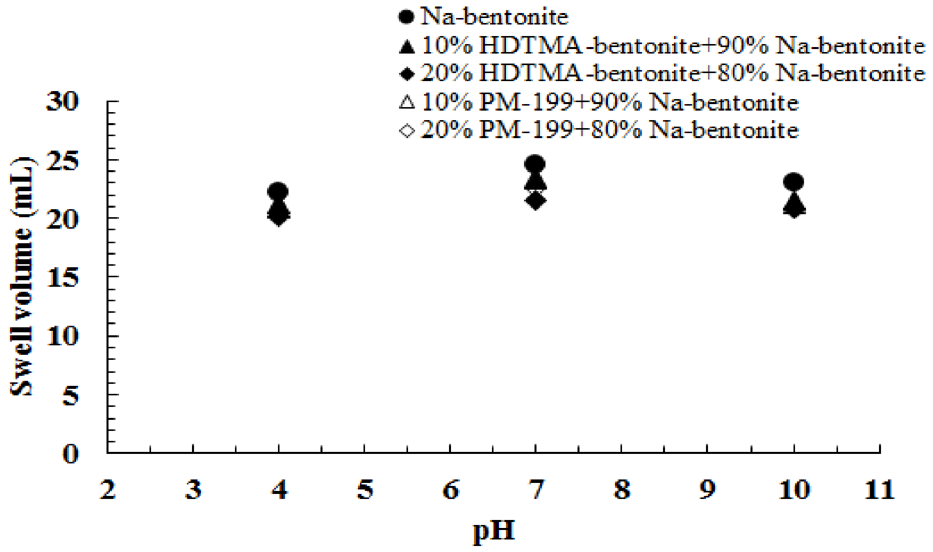


Figure 4-12. Effect of pH on the swelling volume of the Na-bentonite mixture with PM-199 and HDTMA-bentonite

Although the free-swelling tests directly compared the stability of suspended particles in aqueous phase, soil swelling in GCL could be under a partially saturated, confined environment. During the permeability and breakthrough tests, the thickness of dry and hydrated GCL specimens were measured to yield better insights into the swelling of soils confined between geotextiles. The GCL specimens were subjected to the isotropic confining stress of 34.47 kPa during the entire experiment and no additional overburden stress were applied to the GCLs. The initial thickness (H_i) and the final thickness (H_f) of GCL specimens were measured before and after the tests. the ratio of H_f to H_i was determined as the swelling ratio of the GCL specimen (Lorenzetti et al. 2005). The measured swelling ratio of the five studied specimens are summarized in Table 4-6.

Table 4-6. Swelling ratio of studied GCL specimens

GCL specimen components	Swelling ratio
Ca-bentonite	1.25
10% HDTMA-bentonite +90%Ca-bentonite	1.21
20% HDTMA-bentonite + 80% Ca-bentonite	1.19
Na-bentonite	2.05
10% HDTMA-bentonite + 90% Na-bentonite	2.00

20% HDTMA-bentonite + 80% Na-bentonite	1.87

It was observed that GCL specimens exhibited considerable swelling in vertical direction ranging from 20~30% for calcium amended GCLs and around 100% for sodium bentonite amended samples. It was believed that the excessive swelling of several GCL specimens occurred because the geotextiles of GCL specimens were not stitched together. In general, it is expected that the swelling tendency of GCL specimens decreases when the percentage of organoclays increases. However, no significant differences were detected between the swelling ratio of calcium/sodium bentonite amended GCLs and HDTMA-Bentonite amended GCLs due to the small fraction of HDTMA-bentonite in the filling matrix (maximum 20% by weight).

4.3.2 Permeability test

The fluid conductivities (k) and intrinsic permeability of constructed GCL specimens to different liquids are summarized in Table 4-7.

Table 4-7. Average conductivity of studied GCL specimens permeated by different liquids

GCL component	Permeant Liquid	k (m/s)	Intrinsic permeability (m^2)
Ca-bentonite	water	3.0×10^{-10}	2.16×10^{-17}
	benzene solution ($C_0 = 300$ to 400 μg/mL)	3.1×10^{-10}	2.23×10^{-17}
10% HDTMA-bentonite + 90% Ca-bentonite	water	4.6×10^{-10}	4.5×10^{-17}
	benzene solution ($C_0 = 300$ to 400 μg/mL)	$3. 5 \times 10^{-10}$	3.42×10^{-17}
	methanol	2.75×10^{-8}	2.1×10^{-15}
20% HDTMA-bentonite + 80% Ca-bentonite	water	8.6×10^{-10}	7.82×10^{-17}
	benzene solution ($C_0 = 300$ to 400 μg/mL)	8.1×10^{-10}	7.37×10^{-17}
	methanol	7.7×10^{-8}	5.49×10^{-15}
Na-bentonite	water	1.7×10^{-11}	1.49×10^{-18}
	benzene solution ($C_0 = 300$ to 400 μg/mL)	1.8×10^{-11}	1.48×10^{-18}
	methanol	5.4×10^{-8}	3.5×10^{-15}

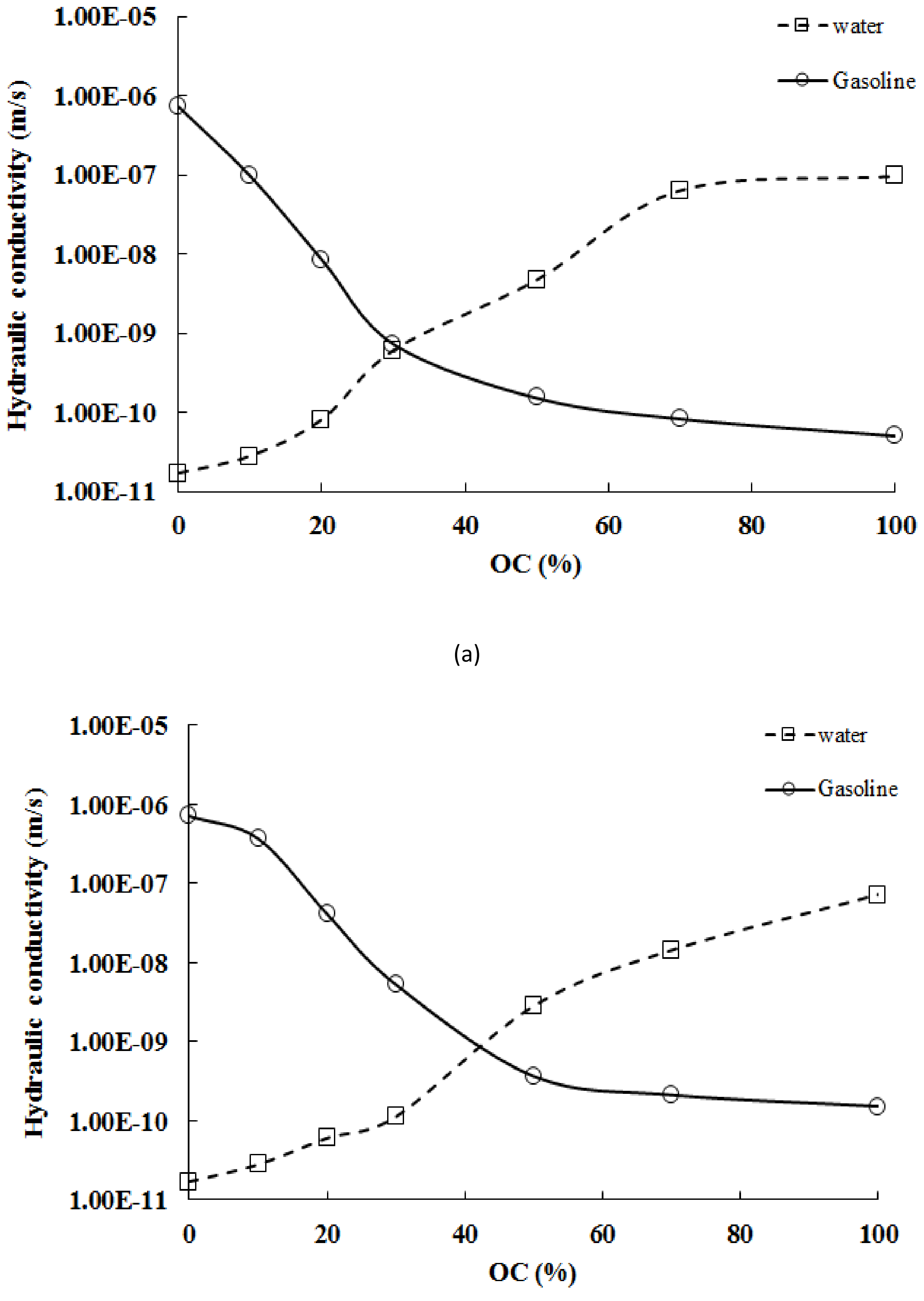
	gasoline	7.2×10^{-7}	4.27×10^{-14}
10% HDTMA-bentonite + 90% Na-bentonite	water	2.8×10^{-11}	2.47×10^{-18}
	benzene solution (C_0 = 300 to 400 µg/mL)	2.73×10^{-11}	2.41×10^{-18}
	methanol	2.62×10^{-8}	1.81×10^{-15}
	gasoline	2.72×10^{-7}	1.72×10^{-14}
20% HDTMA-bentonite + 80% Na-bentonite	water	5.7×10^{-11}	4.11×10^{-18}
	benzene solution (C_0 = 300 to 400 µg/mL)	5.62×10^{-11}	4.05×10^{-18}
	methanol	1.52×10^{-8}	8.6×10^{-16}
	gasoline	4.12×10^{-8}	2.13×10^{-15}
HDTMA-bentonite	water	4.5×10^{-8}	3.56×10^{-15}
	methanol	6.7×10^{-9}	4.15×10^{-16}
	gasoline	1.5×10^{-10}	8.5×10^{-18}

The hydraulic conductivity of Ca-bentonite and Na-bentonite GCLs were measured as 3.0×10^{-10} and 1.7×10^{-11} m/s, respectively. The hydration of inorganic cations (Na^+ or Ca^{2+}) leads to the interlayer expansion of the bentonite particle aggregates and consequently, the expansion of the bulk volume. Since bentonite soil filling in GCL was confined between two layers of geotextile, the volume expansion of soil filling was inhibited and instead, the bentonite ended up with a lower pore volume and decreased size of meso-pores. This process controls the permeability of water in the GCL as hydrated GCL tend to have much lower hydraulic conductivity. Mesri and Olson (1971) demonstrated that the higher plasticity of clayey soils is related to their higher swelling and lower hydraulic conductivity. They explained that the clay, especially colloidal particles typically have thicker double layer which resulted in stronger interactions with water molecules. Benson et al. (1994) suggested that the hydraulic conductivity of the geo-materials decreases when the plasticity index or swelling potential increases. The dissolved organics had no or low impact (e.g. 5% of difference) on the hydraulic conductivity of the Ca-bentonite and Na-bentonite GCLs.

Previous study indicated that the hydraulic conductivity of calcium or sodium bentonite GCL increases as the mass ratio of organoclay additives increases (Lorenzetti et al. 2005). The increased hydraulic conductivity is attributed to the hydrophobic characteristics of organoclays surfaces, which tends to impose decreased drag forces on water in the pore space. As a result, the hydraulic conductivity of Na-bentonite GCL specimen with 20% of HDTMA-bentonite was reported to be 5.7×10^{-11} m/s, approximately three times higher than the hydraulic conductivity of 100% Na-bentonite GCL. The same trend was observed for the Ca-bentonite based GCLs. The hydraulic conductivity of Ca-bentonite GCL was measured as 3.0×10^{-10} m/s and it increased to 8.6×10^{-10} m/s by adding 20% HDTMA-bentonite to the Ca-bentonite.

The interaction between sodium or calcium bentonite and low polarity liquids are very limited as the inorganic cations cannot be solvated or hydrated by the larger, non-polar organic molecules. Consequently, the swelling of Na-bentonite and Ca-bentonite were inhibited in the low polarity fluids like gasoline or methanol. The permeability of methanol and gasoline were at 5.4×10^{-8} m/s and 7.2×10^{-7} m/s (almost 3 orders of magnitude higher water) in the Na-bentonite GCL, respectively.

The correlations of the permeability (to water and gasoline) of GCL specimens and the mass percentages of PM-199/HDTMA-bentonite amendments are illustrated in Figure 4-13. The obtained results for the GCL specimens with HDTMA-bentonite amendment suggest that the GCL soil should have at least 43% HDTMA-bentonite in order to obtain a low permeability (1×10^{-9} m/s) to gasoline and water at the same time. However, the acquired results for GCL specimens with PM-199 amendments suggest that 28% PM-199 amendment in Na-bentonite GCLs can provide a permeability of 6×10^{-10} m/s for gasoline and water at the same time. Moon et al. (2007) evaluated the permeability of a compacted HDTMA-bentonite specimen to gasoline. They suggested that a compacted specimen consisted of 100% HDTMA-bentonite could provide the permeability to gasoline as low as 2.53×10^{-10} m/s. in another study, Yang and Lo (2004) investigated the permeability of a compacted organoclay (BB-40) specimen to gasoline. Their result suggested that the organoclay compacted specimen could reach to a permeability as low as 6×10^{-11} m/s for gasoline. The obtained results in this study suggested that a GCL specimen with 100% HDTMA-bentonite/PM-199 could provide such a low permeability to gasoline that was reported for compacted organoclay specimen. However, it can be concluded that PM-199 is more efficient amendment for the GCL specimen compared to HDTMA-bentonite. Because a lower percentage (10~20%) of PM-199 not only maintained a low permeability of GCL to water (less than 10^{-10} m/s) but also decreased the permeability of GCL to gasoline by approximately two orders of magnitude (10^{-6} m/s to 10^{-8} m/s).



(a)

(b)

Figure 4-13. Permeability of Na-bentonite GCL specimens with different percentages of (a) PM-199 (b) HDTMA-bentonite permeated by water and gasoline

Previous studies indicated that increasing the confining stress in the permeameter would decrease the void ratio of GCL soil, which typically leads to lower hydraulic conductivities (Shackelford et al. 2000; Shan and Daniel 1991).The effect of confining stress on the hydraulic conductivity of Na-bentonite GCL and GCL with 10% and 20% HDTMA-bentonite amendment is presented in Figure 4-14. The fluid confining pressure applied to the GCL specimens were 34.47, 68.94, 137.89, 206.84, and 275.79 kPa. It was observed that the hydraulic conductivity of Na-bentonite GCL and GCL with 10% HDTMA-bentonite + 90% Na-bentonite decreased as the confining stress increased from 5 to 20 kPa.

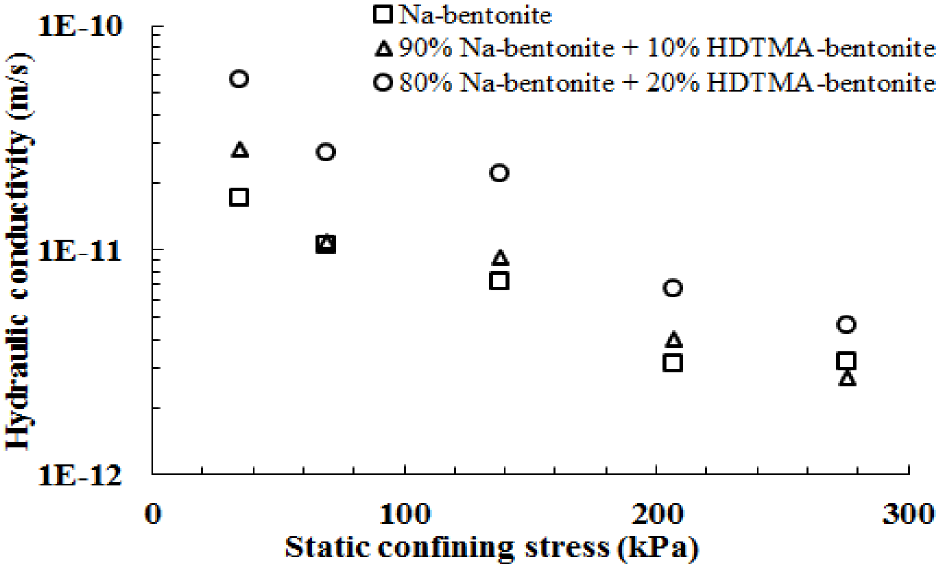


Figure 4-14. Effect of confining stress on the hydraulic conductivity of Na-amended GCLs

The quantity of solution that permeates through a certain area of the liner system (GCL) during a certain period of time under a specific hydraulic gradient is defined as permittivity. The permittivity is determined as the ratio of the permeability to the thickness of the GCL specimen:

$$\psi = \frac{k}{t} \tag{4-8}$$

where ψ is permittivity (1/s), k is the permeability of GCL specimen (cm/s), and t is the thickness of the GCL specimen (cm).

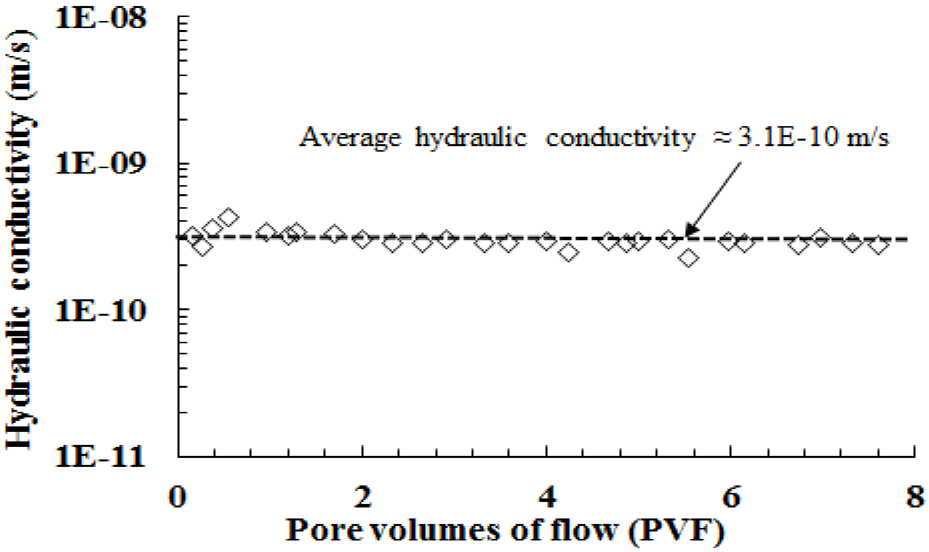
The average permittivity of the studied GCL specimens permeated by water and benzene solution are summarized in Table 4-8. It was observed that the permittivity of Na-bentonite/Ca-bentonite based GCLs are comparable with the permittivity of conventional compacted clays (1.6 × 10^{-9} s^{-1}).

Table 4-8. The average permittivity of GCL specimens

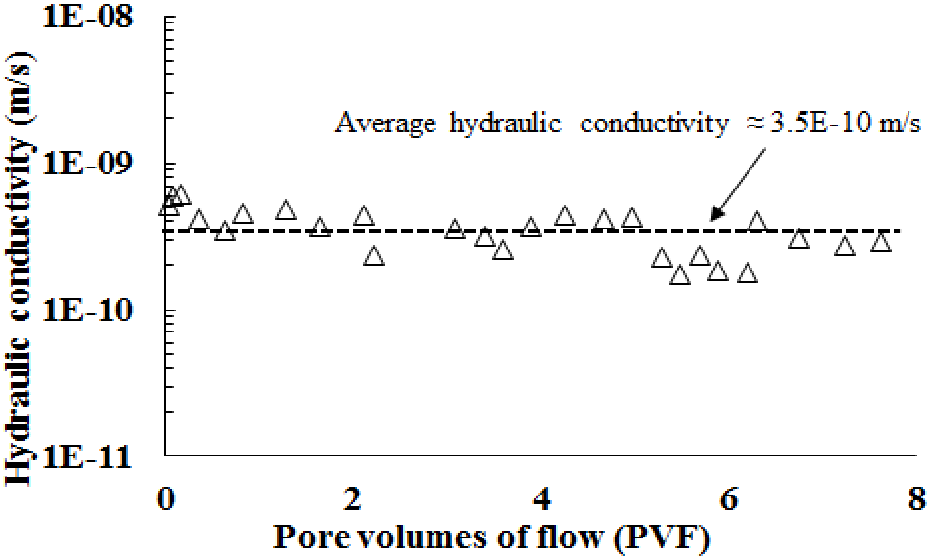
GCL component	Permeant liquid	Permeability (m/s)	Thickness (cm)	Permittivity (1/s)
Ca-bentonite	water	3.0×10^{-10}	0.8	3.75×10^{-8}
	benzene solution	3.1×10^{-10}		3.875×10^{-8}
10% HDTMA-bentonite + 90% Ca-bentonite	water	4.6×10^{-10}	1.2	3.83×10^{-8}
	benzene solution	3.5×10^{-10}		2.91×10^{-8}
20% HDTMA-bentonite + 80% Ca-bentonite	water	8.6×10^{-10}	1.3	6.61×10^{-8}
	benzene solution	8.1×10^{-10}		6.23×10^{-8}
Na-bentonite	water	1.7×10^{-11}	0.75	2.26×10^{-9}
	benzene solution	1.8×10^{-11}		2.4×10^{-9}
10% HDTMA-bentonite + 90% Na-bentonite	water	2.8×10^{-11}	0.77	3.63×10^{-9}
	benzene solution	2.73×10^{-11}		3.54×10^{-9}
20% HDTMA-bentonite + 80% Na-bentonite	water	5.7×10^{-11}	0.78	7.3×10^{-9}
	benzene solution	5.62×10^{-11}		7.2×10^{-9}

Based on the measured fluid conductivities, it was estimated that the advective breakthrough in the Ca-bentonite GCL, GCL with 10% HDTMA-bentonite + 90% Ca-bentonite, and GCL with 20% HDTMA-bentonite + 80% Ca-bentonite would require 308, 297, and 185 days (thickness divided by conductivity) under a hydraulic gradient of 1. However, the advective breakthrough time for the fluid flow to transport along Na-bentonite GCL and GCL with 10% HDTMA-bentonite + 90% Na-bentonite would require 4823 and 3392 days under a gradient of 1. Furthermore, around 7233 days is needed for the advection of the solution through a compacted clay layer.

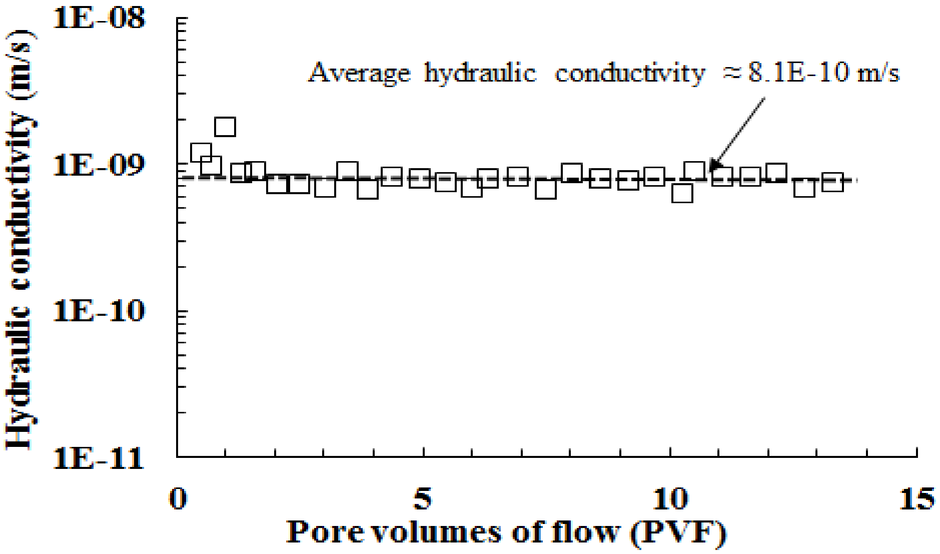
The advection of benzene solution through GCL specimens were monitored during the breakthrough test and the calculated fluid conductivities as a function of time were shown in Figure 4-15. Also, the acquired data for hydraulic conductivity was used to determine the average seepage velocity of the contaminant flow. The measured average seepage velocities during the breakthrough of the benzene solution are illustrated in Figure 4-16.



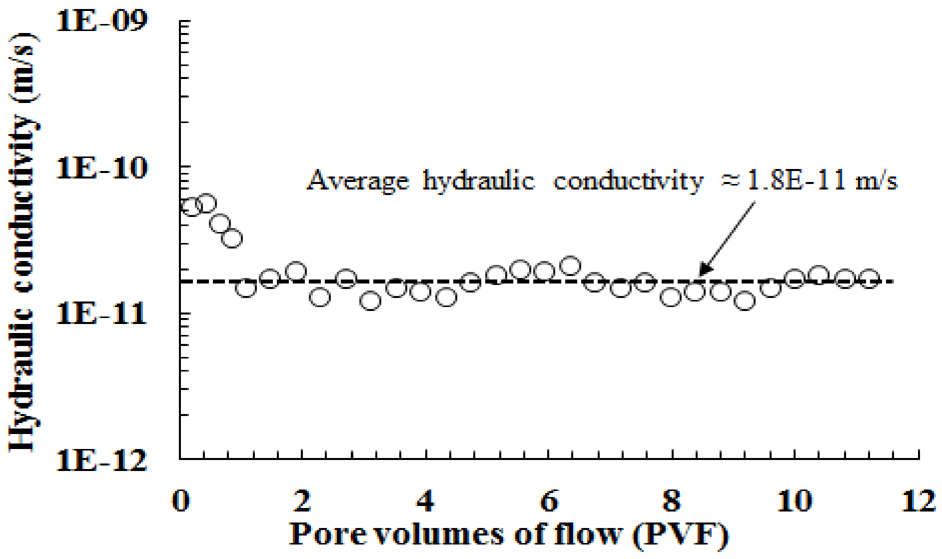
(a)


1E-08
1E-09
1E-10
1E-11
Hydraulic conductivity (m/s)
Average hydraulic conductivity ≈3.5E-10 m/s
0
2
4
6
8
Pore volumes of flow (PVF)

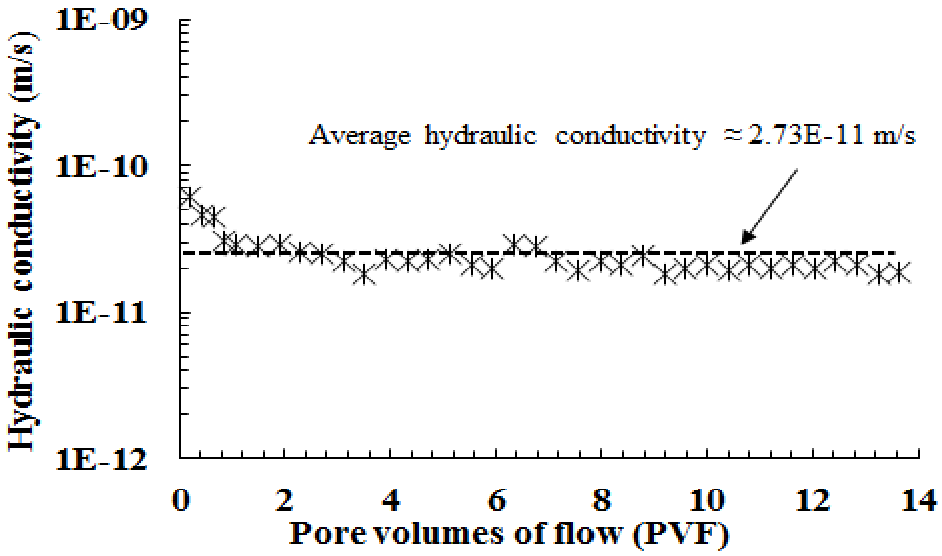
(b)


1E-08
1E-09
1E-10
1E-11
Hydraulic conductivity (m/s)
Average hydraulic conductivity ≈8.1E-10 m/s
0
5
10
15
Pore volumes of flow (PVF)

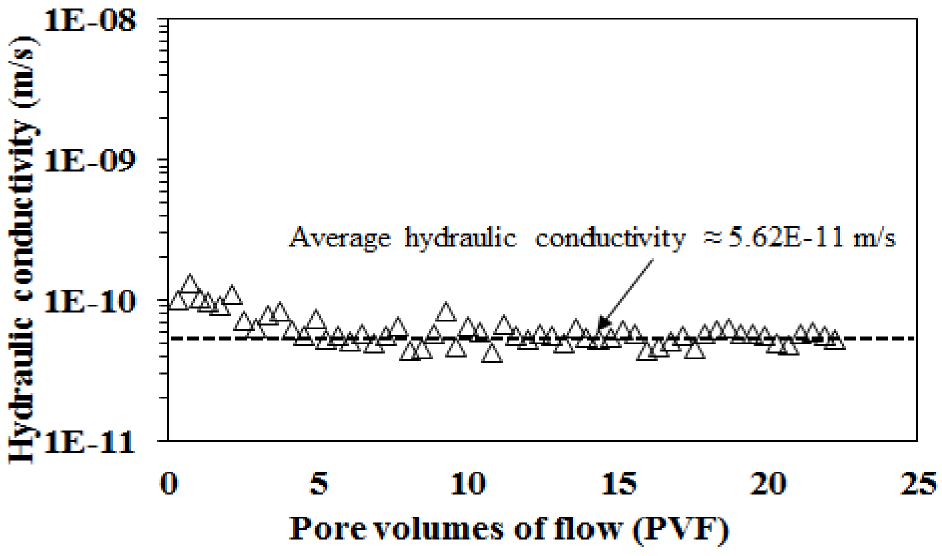
(c)


Hydraulic conductivity (m/s)
1E-09
1E-10
1E-11
1E-12
Average hydraulic conductivity ≈ 1.8E-11 m/s
0
2
4
6
8
10
12
Pore volumes of flow (PVF)

(d)

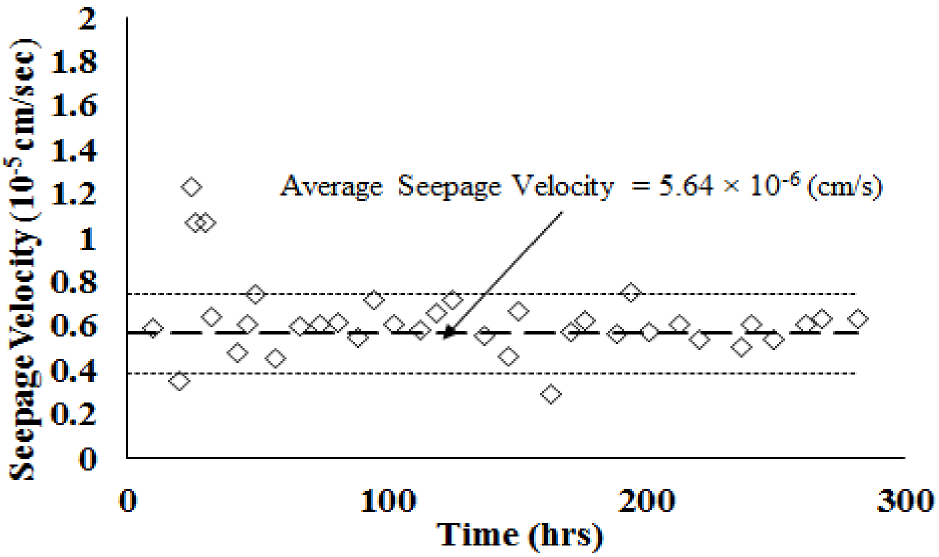

Hydraulic conductivity (m/s)
1E-09
1E-10
1E-11
1E-12
Average hydraulic conductivity ≈ 2.73E-11 m/s
0
2
4
6
8
10
12
14
Pore volumes of flow (PVF)

(e)

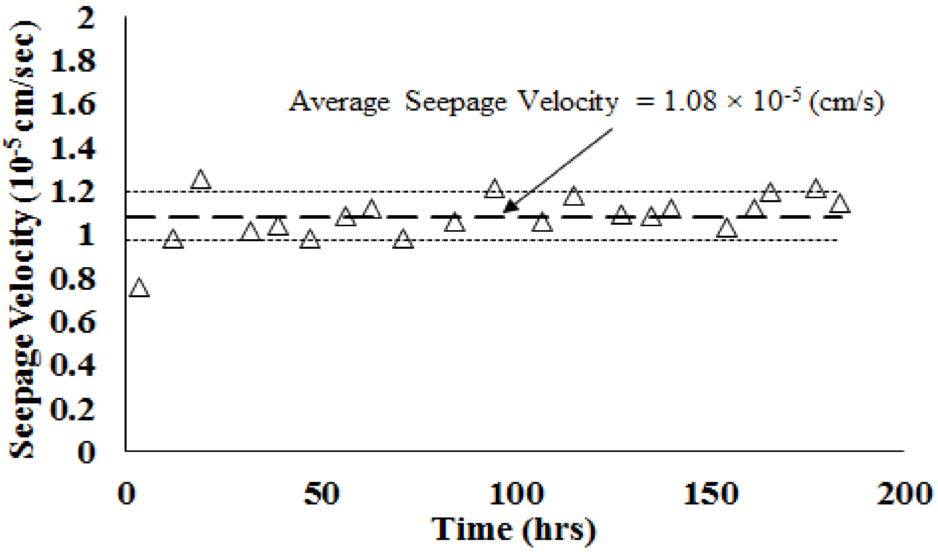


(f)

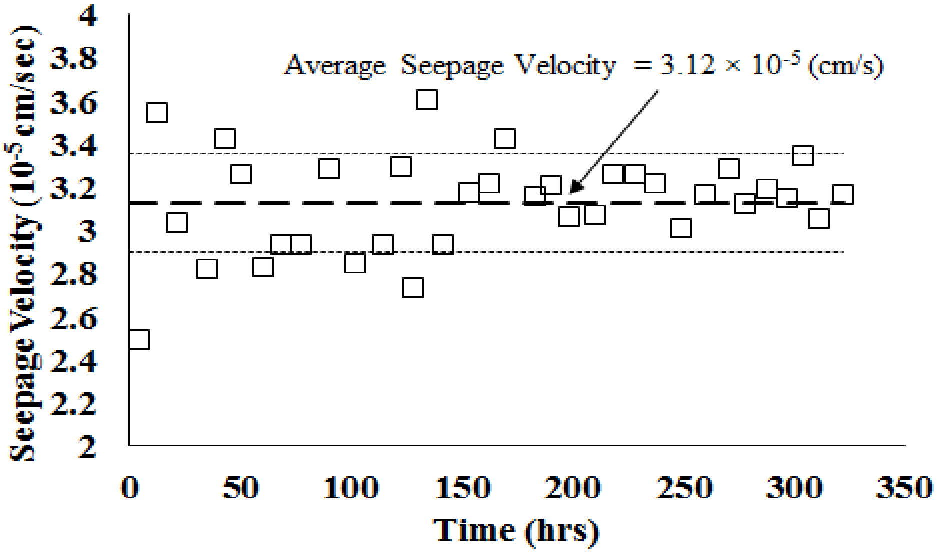
Figure 4-15. Measured hydraulic conductivity during breakthrough test for GCL with (a) Ca-bentonite (b) 10% HDTMA-bentonite + 90% Ca-bentonite (c) 20% HDTMA-bentonite + 80% Ca-bentonite (d) Na-bentonite (e) 10% HDTMA-bentonite + 90% Na-bentonite (f) 20% HDTMA-bentonite + 80% Na-bentonite



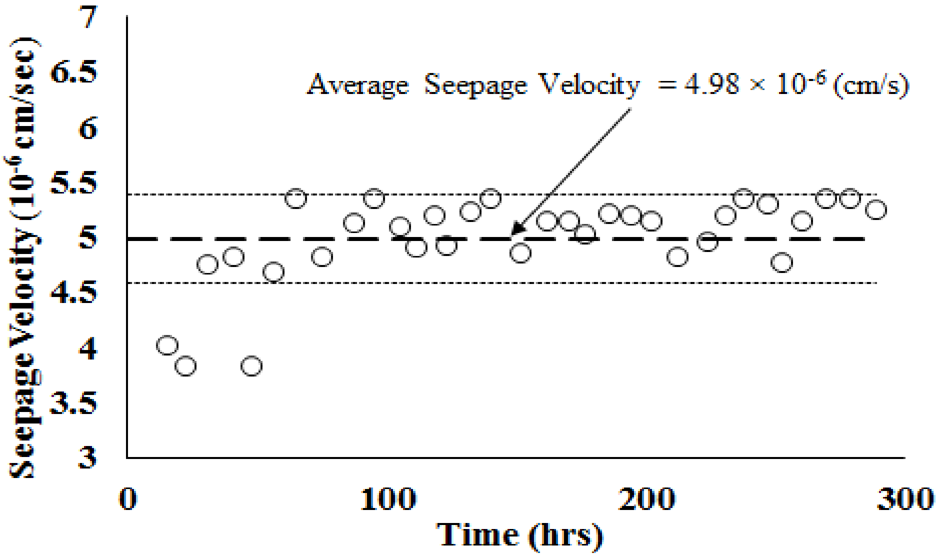
(a)


Seepage Velocity (10-5 cm/sec)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Average Seepage Velocity = 1.08 × 10-5 (cm/s)
0
50
100
150
200
Time (hrs)

(b)

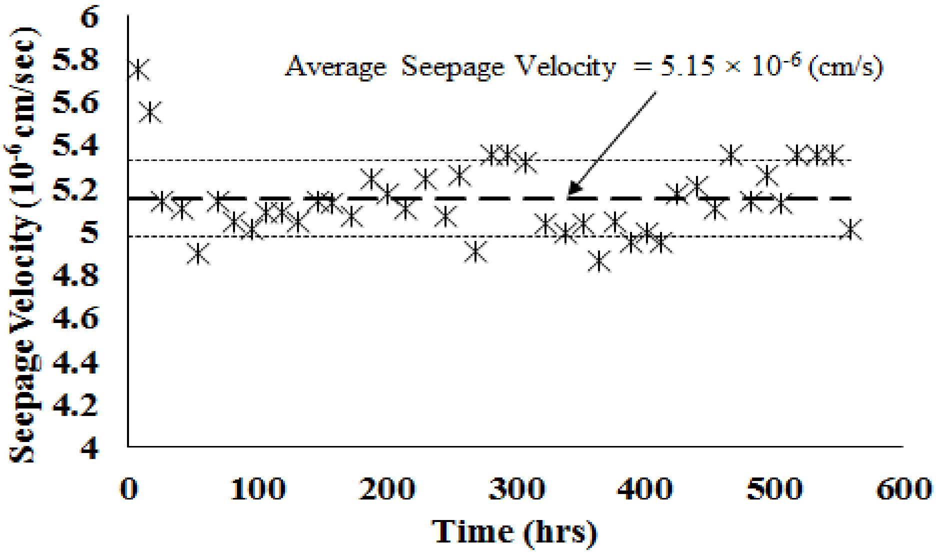

Seepage Velocity (10-5 cm/sec)
4
3.8
3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
2
Average Seepage Velocity = 3.12 × 10-5 (cm/s)
0
50
100
150
200
250
300
350
Time (hrs)

(c)



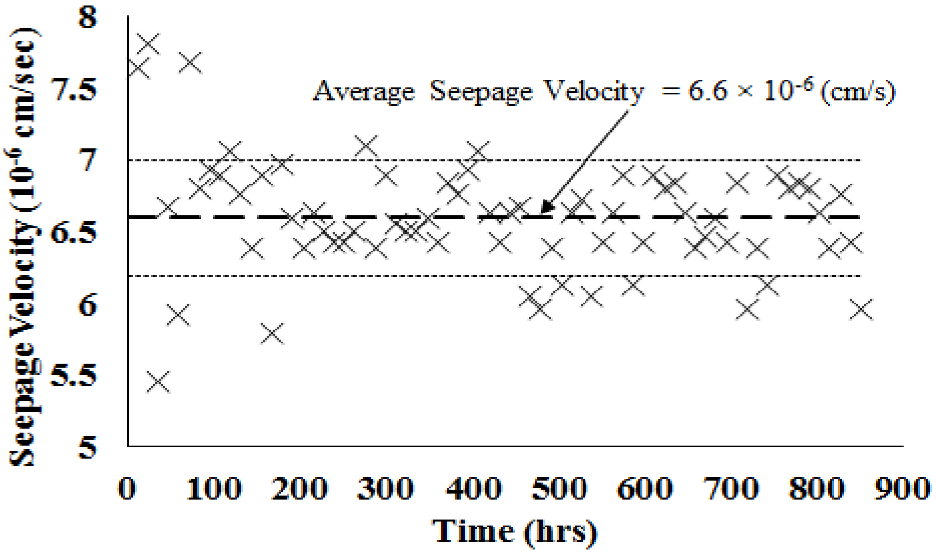
Seepage Velocity (10-6 cm/sec)
7
6.5
6
5.5
5
4.5
4
3.5
3
0
100
200
300
Time (hrs)
Average Seepage Velocity = 4.98 × 10-6 (cm/s)

(d)



Seepage Velocity (10-6 cm/sec)
6
5.8
5.6
5.4
5.2
5
4.8
4.6
4.4
4.2
4
0
100
200
300
400
500
600
Time (hrs)
Average Seepage Velocity = 5.15 × 10-6 (cm/s)

(e)

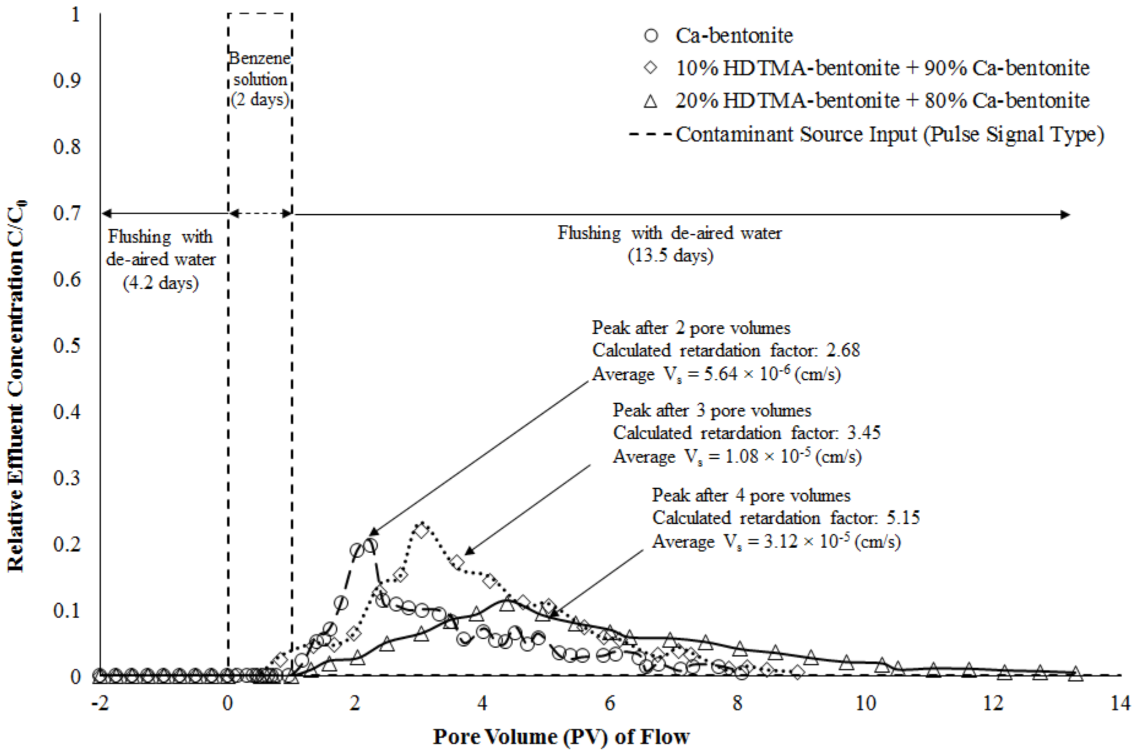


(f)

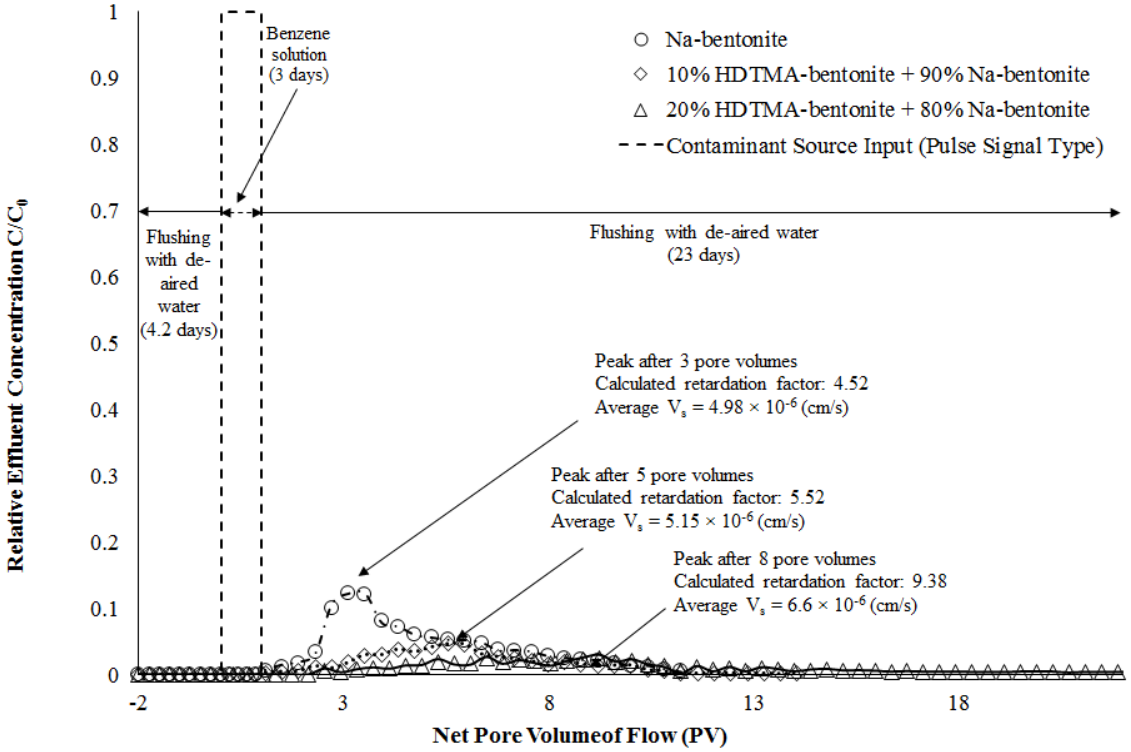
Figure 4-16. Average seepage velocity of GCLs with (a) Ca-bentonite (b) 10% HDTMA-bentonite + 90% Ca-bentonite (c) 20% HDTMA-bentonite + 80% Ca-bentonite (d) Na-bentonite amended GCL (e) 10% HDTMA-bentonite + 90% Na-bentonite (f) 20% HDTMA-bentonite + 80% Na-bentonite

4.3.3 Breakthrough test

Two series of breakthrough tests on the Ca-bentonite based and Na-bentonite based GCL specimens were conducted to examine the mass transport of benzene through the GCL when subjected to sorption and retardation. The acquired breakthrough curves for both types of GCL specimens are presented in Figure 4-17.


Ca-bentonite
10% HDTMA-bentonite + 90% Ca-bentonite
20% HDTMA-bentonite + 80% Ca-bentonite
Contaminant Source Input (Pulse Signal Type)
Benzene solution (2 days)
Flushing with de-aired water (4.2 days)
Flushing with de-aired water (13.5 days)
Peak after 2 pore volumes
Calculated retardation factor: 2.68
Average $V_s = 5.64 \times 10^{-6}$ (cm/s)
Peak after 3 pore volumes
Calculated retardation factor: 3.45
Average $V_s = 1.08 \times 10^{-5}$ (cm/s)
Peak after 4 pore volumes
Calculated retardation factor: 5.15
Average $V_s = 3.12 \times 10^{-5}$ (cm/s)
Relative Effluent Concentration C/C_0
Pore Volume (PV) of Flow
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
-2
0
2
4
6
8
10
12
14

(a)


Na-bentonite
10% HDTMA-bentonite + 90% Na-bentonite
20% HDTMA-bentonite + 80% Na-bentonite
Contaminant Source Input (Pulse Signal Type)
Benzene solution (3 days)
Flushing with de-aired water (4.2 days)
Flushing with de-aired water (23 days)
Peak after 3 pore volumes
Calculated retardation factor: 4.52
Average $V_s = 4.98 \times 10^{-6}$ (cm/s)
Peak after 5 pore volumes
Calculated retardation factor: 5.52
Average $V_s = 5.15 \times 10^{-6}$ (cm/s)
Peak after 8 pore volumes
Calculated retardation factor: 9.38
Average $V_s = 6.6 \times 10^{-6}$ (cm/s)
Relative Effluent Concentration C/C_0
Net Pore Volumeof Flow (PV)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
-2
3
8
13
18

(b)

Figure 4-17. Benzene breakthrough curves through (a) Ca-bentonite based (b) Na-bentonite based GCL specimens without/with HDTMA-bentonite

The breakthrough experiments typically lasted more than 2 weeks (~8 to 13 pore volumes) for the Ca-bentonite based GCL specimens while it took more than 3 weeks (~13 to 15 pore volumes) for the Na-bentonite based GCL specimens. The sampling was continued until the concentration of benzene in the effluent was below the detection limit of GC equipment.

The seepage velocity of benzene solution permeating Na-bentonite and Ca-bentonite GCL specimens were measured as 4.98×10^{-6} and 5.64×10^{-6} m/s which were at the same range. However, the seepage velocity of GCL specimen with 20% HDTMA-bentonite + 80% Na-bentonite to benzene solution remained at the range of 6.6×10^{-6} m/s and addition of 20% HDTMA-bentonite did not change the seepage velocity of Na-bentonite amended GCL significantly. As mentioned previously, it is because of strong hydration of Na-bentonite with polar liquids with resulted in such low permeability. In contrast, the seepage velocity of GCL specimen with 20% HDTMA-bentonite + 80% Ca-bentonite to benzene solution was measured as 3.12×10^{-6} m/s which was about one order of magnitude higher than the he seepage velocity of Ca-bentonite GCL specimen. The peak of mass flux in Na-bentonite GCL occurred at approximately 3 pore volumes, one pore volume later when compared to Ca-bentonite GCL. This happened because of lower hydraulic conductivity of Na-bentonite compared to Ca-bentonite and longer advective breakthrough of benzene solution in Na-bentonite GCL.

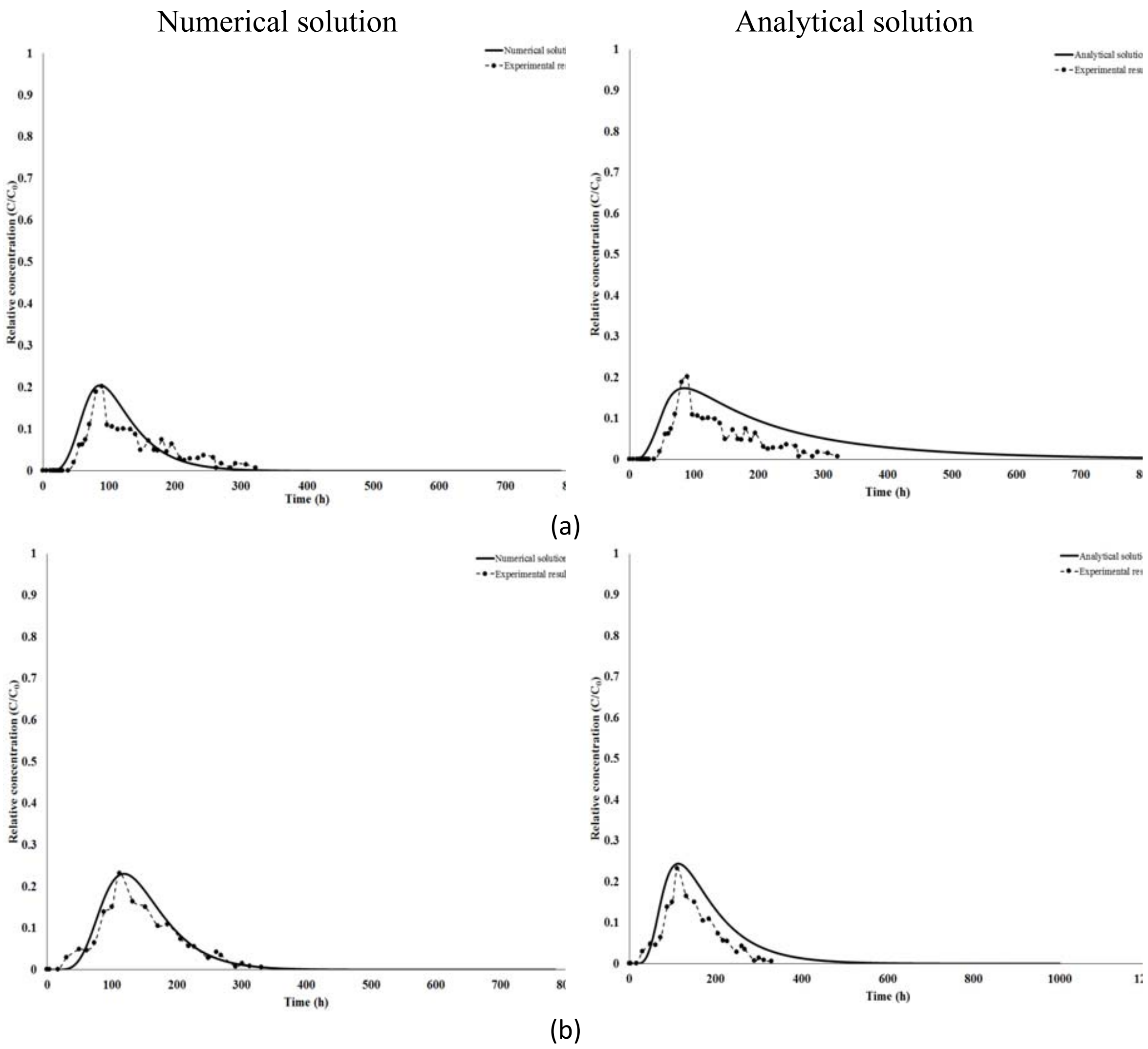
The required time for breakthrough, or retarded transport of benzene in Na-bentonite GCL with 10% of HDTMA-bentonite was significantly longer than what required for Na-bentonite GCL. However, this difference was not observed between GCLs with Ca-bentonite GCL and Ca-bentonite + 10% HDTMA-bentonite.

In the HDTMA-bentonite amended GCL specimens, organic contaminants are absorbed by the HDTMA-bentonite and the absorbed mass of contaminants releases with a lower rate of mass per unit time (quantified by the mass flux). The peak corresponding to the maximum relative concentration of effluent in Ca-bentonite based GCL specimens with 0%, 10%, and 20% of HDTMA-bentonite were detected after approximately 2, 3, and 4 pore volumes, respectively. In comparison, the peak corresponding to the maximum relative concentration of effluent in Na-bentonite based GCL specimens with 0%, 10%, and 20% of HDTMA-bentonite were detected after 3, 5, and 8 pore volumes, respectively. The decreased peak concentration was accompanied with the possible breakthrough within the first pore volume due to the diffusion of contaminant molecules (Shackelford 1994).

It was observed that 10% of HDTMA-bentonite amendments in Ca-bentonite GCL did not make a notable difference in reducing the mass flux of benzene. This could be the result of (1) lower dosage of HDTMA-bentonite (2) the diffusive transport of benzene through the shorter path (8~10 mm, compared with 2~3 ft of compacted clays) overcame the retardation mechanism. In contrast, the 20% of HDTMA-bentonite amendments in Ca-bentonite GCL caused the delayed occurrence of the max mass flux of benzene (two pore volumes compared to Ca-bentonite GCL) and also decreased the magnitude of the relative concentration at peak. The peak mass flux of benzene through Ca-bentonite GCL was decreased by 5 times when 10% HDTMA-bentonite was added and further decreased to 10 times when 20% of HDTMA-bentonite amendments were added.

Interpretation of the breakthrough test results

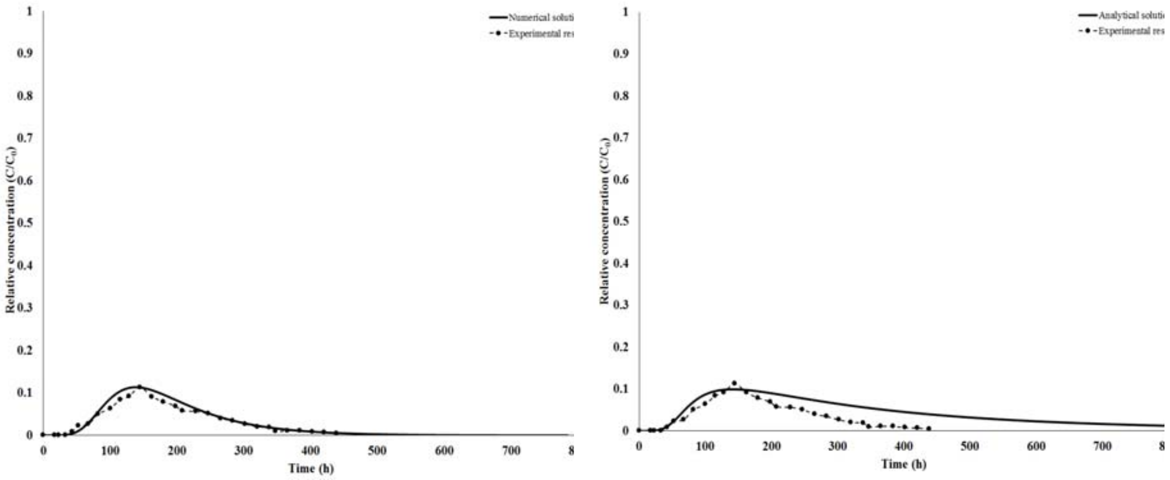
Initially, the retardation factor of benzene transport through the GCL specimens was determined using the first-moment equation. However, it yielded underestimated retardation factors as less than 100% of the introduced mass of benzene was collected in the effluent. Consequently, both numerical and analytical solution was employed to estimate the retardation factor and diffusion coefficient of the benzene transport in GCL specimens (Figure 4-18).


Numerical solution

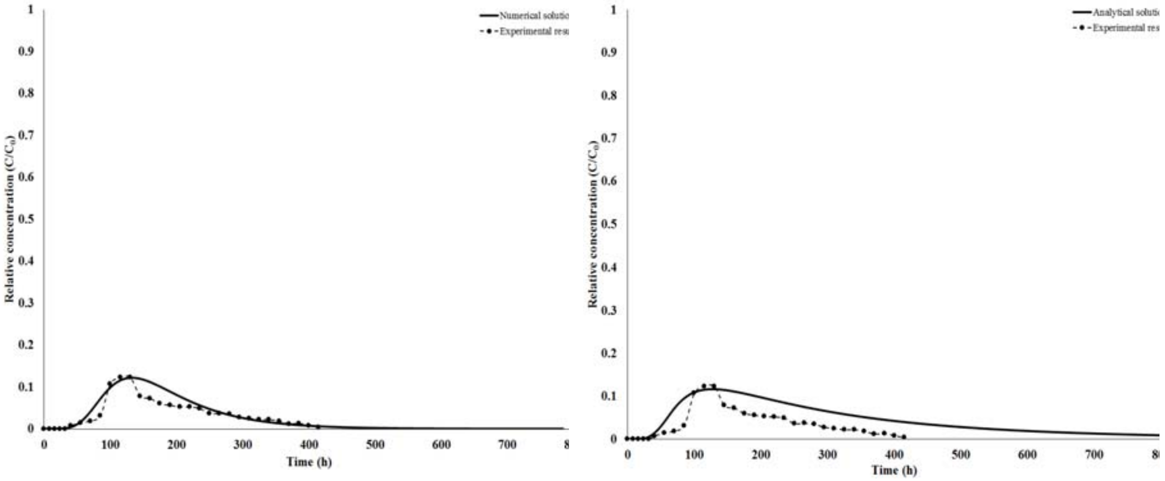
Analytical solution

(a)

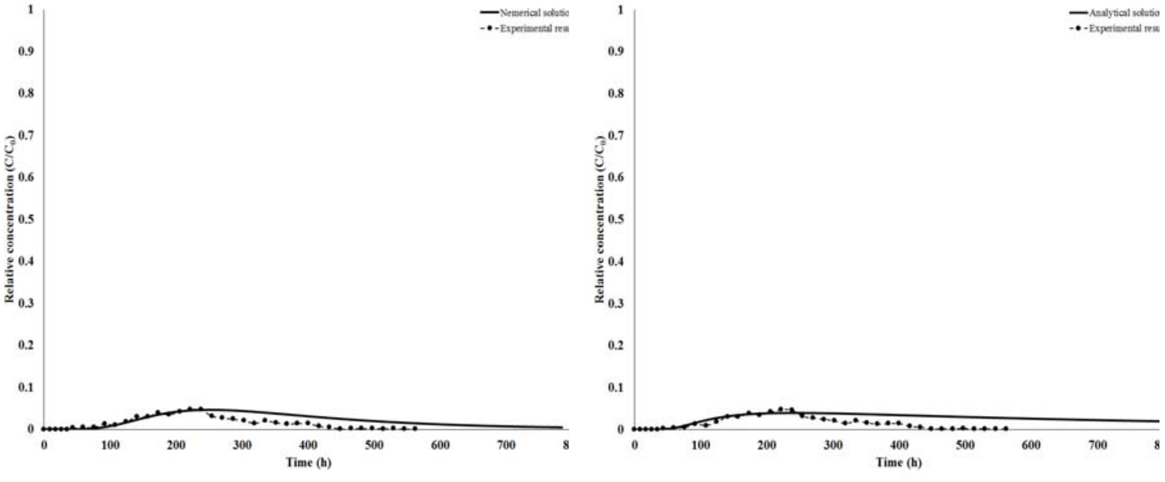
(b)


Relative concentration (C/C0)
Time (h)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
100
200
300
400
500
600
700
8
Numerical soluti
Experimental res
Analytical soluti
Experimental res

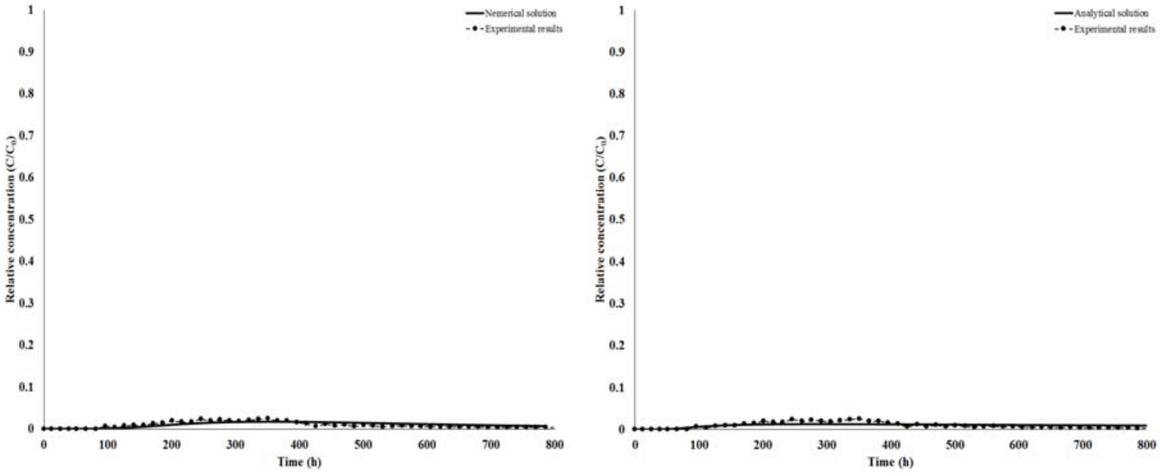
(c)


Relative concentration (C/C0)
Time (h)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
100
200
300
400
500
600
700
8
Numerical solutio
Experimental resu
Analytical soluti
Experimental res

(d)


Relative concentration (C/C0)
Time (h)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
100
200
300
400
500
600
700
8
Nemerical solutio
Experimental resu
Analytical solutio
Experimental resu

(e)



(f)

Figure 4-18. Fitted curve applying numerical and analytical solution for (a) Ca-bentonite GCL (b) Ca-bentonite GCL with 10% HDTMA-bentonite amendment (c) Ca-bentonite GCL with 20% HDTMA-bentonite amendment (d) Na-bentonite GCL (e) Na-bentonite GCL with 10% HDTMA-bentonite amendment (f) Na-bentonite GCL with 20% HDTMA-bentonite amendment

The retardation factors and diffusion coefficients for all breakthrough tests were obtained and compared with the calculated retardation factors from the first-moment equation (Table 4-9).

Table 4-9. Retardation factor and diffusion coefficients for six GCL specimens obtained from analytical and numerical methods and the first-moment equation

GCL component	first-moment analysis	Numerical solution		Analytical solution	
	Retardation factor	Retardation factor	Diffusion coefficient (cm^2/s)	Retardation factor	Diffusion coefficient (cm^2/s)
Ca-bentonite	2.68	6.9	1.8×10^{-6}	5	7.1×10^{-6}
90% Ca-bentonite + 10% HDTMA-bentonite	3.45	14	2.0×10^{-6}	9	1.5×10^{-6}
80% Ca-bentonite + 20% HDTMA-bentonite	5.15	68	5.8×10^{-6}	52	4.6×10^{-6}
Na-bentonite	4.52	10	1.5×10^{-6}	7	6.3×10^{-6}
90% Na-	5.52	26	2.0×10^{-6}	20	7.0×10^{-6}

bentonite + 10% HDTMA-bentonite					
80% Na-bentonite + 20% HDTMA-bentonite	9.38	85	5.0×10^{-6}	73	2.0×10^{-6}

The calculated retardation factors from numerical and analytical solutions suggested that these two methods result in results within a same range. the mathematical models resulted in retardation factors of (5 to 7) and (7 to 10) for Ca-bentonite and Na-bentonite GCLs, respectively. For unmodified bentonites, the calculated retardation factors from mathematical modeling were reletively close to the acquired results from the first moment analysis. The retardation factors calculated from the first moment analysis were 2.68, and 4.52 for Ca-bentonite and Na-bentonite GCL specimens, respectively. However, the mathematical modeling resulted in significantly higher retardation factors compared to the first moment analysis method as the percentages of HDTMA-benotnite increased in the GCL soil. It was observed that the retardation factors obtained from the first moment analysis method increased linearly by increasing the percentage of HDTMA-bentonite. In contrast, the obtainde results from mathematical solutions showed a significant sharp increase in retardation factor by increasing the percent of HDTMA-bentonite in the GCL soil.

The higher retardation factors indicated lower mass flux of benzene throught the GCLs and longer time of benzene breakthrough. Specifically, the peak mass flux of benzene was at 0.007mg/cm^2×day in Ca-bentonite GCL and it decreased by almost half to the 0.004 mg/cm^2×day for Ca-bentonite GCL with 20% HDTMA-bentonite amendment. For

Na-bentonite GCL, the peak mass flux of benzene was approximately 0.005mg/cm^2×day and it decreased to the 0.002 mg/cm^2×day in Na-bentonite GCL amended with 20% HDTMA-bentonite. Also, the average mass flux of benzene at source for Ca-bentonite based GCL specimens was at the range of 0.1658 mg/cm^2×day while it decreased to 0.1132 mg/cm^2×day for the Na-bentonite based GCL specimens. Therefore, it is recommended to employ either numerical or analytical solution to measure the retardation factor when 100% of mass does not retrived in effluent.

4.4 Conclusion

In this chapter, the swelling capacity of studied soils including Ca-bentonite, Na-bentonite, HDTMA-bentonite, PM-199, and soil admixtures including 10%/20% HDTMA-bentonite, and 10%/20% PM-199 with Na-bentonite exposed to different solutions were evaluated. It was observed that Ca-bentonite and Na-bentonite had higher swelling capacity in water due to strong hydration of Ca^{2+} and Na^+. However, their swelling capacity decreased drastically in low polarity liquids (gasoline and methanol) because of symmetric molecular structure of low polarity liquids which resulted in the dipole polarity of zero or near zero and lower adsorption of their molecules by Ca-bentonite and Na-bentonite. In contrast, organobentonites exhibited higher swelling tendency in low polarity liquids because the intercalated surfactants increased the organophilicity/hydrophobicity of the organobentonite followed by higher adsorption of low polarity compounds. Because of the mentioned reason, the swelling capacity of the soil admixtures in gasoline increased as the percentage of organobentonite increased while the reverse trend was detected for the swelling tendency of soil admixtures in water. In addition, the effect of ionic strength on the swelling capacity of the studied soils were evaluated. It was observed that the swelling capacity of the organobentonites did not change as a function of ionic strength and they did not exhibit a notable swelling in the solutions with different ionic strength. In contrast, bentonite soils showed a significant swelling capacity in solution with low ionic concentration (0.01 M NaCl). However, the swelling tendency of bentonite soils decreased by increasing the concentration of ionic solution because the higher ionic concentration dragged water molecules out of bentonite interlayers and resulted in lower swelling capacity. Additionally, the effect of basic and acidic solution was investigated on the swelling capacity of the studied soils. It was observed that basic and acidic solution ($4<pH<10$) did not affect the swelling capacity of studied soils. However, it is expected that the swelling tendency of the bentonites decrease in strong acidic and basic solutions.

Also, the hydraulic performance of GCL with organobentonite amendment for different fluids were evaluated. It was observed that the permeability of bentonite GCL specimens to water was 3.0×10^{-10} for Ca-bentonite and 1.7×10^{-11} m/s for Na-bentonite. The hydration of inorganic cations resulted in the interlayer expansion due to the adsorption of water molecules by inorganic cations. Consequently, the bentonite ended up with a lower pore volume and decreased size of meso-pores which resulted in lower permeability of bentonite GCL specimens to water. However, Na-bentonite and Ca-bentonite had limited interaction with low polarity liquids (gasoline and methanol) and the inorganic cations could not hydrate by the larger, non-polar organic molecules. Consequently, the permeability of the Na-bentonite GCL specimens to gasoline and methanol increased to 7.2×10^{-7} m/s and 5.4×10^{-8} m/s, respectively. In contrast, HDTMA-bentonite exhibited low permeability to low polarity liquids. The low permeability of HDTMA-bentonite to gasoline and methanol is attributed to the inherited organophilic characteristics of organobentonites. As a result, the organobentonites have higher solvation in low polarity liquids. The higher adsorption of large molecules of methanol and gasoline by the intercalated surfactant in the interlayer of organobentonites results in the interlayer expansion of organobentonites. Consequently, the organobentonites molecules swell and fill the available pores in the structure of GCL specimens. As a result, the permeability of GCL specimen with 100% HDTMA-bentonite was as low as 1.5×10^{-10} m/s. Based on the mentioned reason, the permeability of GCL specimens to low polarity liquids decreased by increasing the percentage of HDTMA-bentonite in the GCL soil. In conclusion, the permeability of Na-bentonite GCL specimen with 20% of HDTMA-bentonite was measured as 4.12×10^{-8} m/s which was lower than the permeability of Na-bentonite GCL specimen to gasoline.

In addition, the permeability of Na-bentonite based GCL specimens with different percentage of HDTMA-bentonite/PM-199 to both polar (water) and non-polar (gasoline) liquids was measured. It was found that the minimum permeability of 1×10^{-9} m/s for gasoline and water could be achieved for Na-bentonite GCL with HDTMA-bentonite amendment by using 43% HDTMA-bentonite in the GCL soil. While, it was observed that only 28% PM-199 amendment in Na-bentonite GCLs can provide an approximate permeability of 6×10^{-10} m/s to gasoline and water. Other studies reported that the permeability of compacted organobentonite specimens to gasoline was in order of 10^{-10} m/s. The same range of permeability to gasoline and water was achieved by adding 28% PM-199 amendment to the Na-bentonite GCL specimen. For this reason, it was concluded that PM-199 could serve more efficiently than HDTMA-bentonite as an amendment to Na-bentonite GCLs because it could provide a lower permeability for both polar and non-polar liquids.

Moreover, the effect of confining stress on the hydraulic conductivity of three GCL specimens including Na-bentonite, 10% HDTMA-bentonite + 90% Na-bentonite, and 20% HDTMA-bentonite + 80% Na-bentonite was investigated. It was observed that the hydraulic conductivity of GCL specimens decreased when the confining stress increased from 34.47kPa to 275.79 kPa. This phenomenon happened because the void ratio in GCL specimens decreased by increasing the confining stress.

Only slight increases in retardation of benzene through GCL specimens with 10%/20% of HDTMA-bentonite amendment was observed, due to the lower fraction of HDTMA-bentonite and their relatively lower sorption capacity for benzene. However, Na-bentonite GCL specimens exhibited relatively higher retardation factor compared to Ca-bentonite based GCL specimens. The reason could be because of lower permeability of Na-bentonite GCL specimens to benzene solution which increased the interaction time between HDTMA-bentonite and benzene solution. The average effluent mass flux of benzene at peak started from 0.007mg/cm^2×day for Ca-bentonite GCL and decreased by half to the 0.004 mg/cm^2×day for Ca-bentonite GCL with 20% HDTMA-bentonite. However, the average effluent mass flux of benzene at peak started from 0.005mg/cm^2×day for Na-bentonite GCL and decreased to the 0.002 mg/cm^2×day for Na-bentonite GCL with 20% HDTMA-bentonite. The breakthrough of benzene lasted 13 and 23 days in Ca-bentonite and Na-bentonite GCL specimens with HDTMA-bentonite amendment, respectively. It suggested that 100% of benzene mass breakthrough would take much longer time in HDTMA-bentonite amended GCLs. In addition, a numerical model and analytical solution were employed to calculate the retardation factor and diffusion coefficient corresponding to 100% of benzene mass breakthrough. The analytical solution revealed that the corresponding retardation factors to 100% mass of benzene were much higher compared to the experimental results, especially for GCL specimens with higher percentage of HDTMA-bentonite. However, the obtained results from numerical modeling approach were slightly higher than those from the analytical solution. The mentioned difference was anticipated because of the discretization error in the numerical modeling procedure. The obtained diffusion coefficient from both procedures were in good agreement with previous studies. Overall, this study suggests that using HDTMA-bentonite or other organically modified clay amendments may enhance the attenuation of organic compounds but also decrease the permeability of low polarity fluids in GCL.

5 CHAPTER FIVE NON-EQUILIBRIUM SORPTION AND RETARDATION OF ORGANIC CONTAMINANTS IN PERMEABLE REACTIVE BARRIERS (PRBs) AMENDED WITH ORGANOCLAYS

5.1 Introduction

Permeable reactive barriers (PRB) is an in-situ technology that is mostly used in fast flow rate conditions such as groundwater to remediate the contaminants carried by the flow using reactive barrier components. PRBs consist of a permeable vertical curtain of reactive materials which is constructed perpendicular to the groundwater flow. When the contaminant plume flows through the PRB under the natural hydraulic gradient, the reactive materials interact with the plume and retard the mass transport of the contaminant and immobilize the contaminants or transform them to the non-toxic compounds (Carey et al. 2002; Powell et al. 1998; Skinner and Schutte 2006). A schematic illustration of PRB system is shown in Figure 5-1.

In addition, it is possible to employ the PRB system in horizontal orientated filter layer to control the downward migration of contaminants (Technologies 2017). In most cases, groundwater flow pass through the PRB system naturally under the existing hydraulic gradient. However, sheet piles or low permeability slurry walls may be required in other cases to conduct the groundwater flow toward the PRBs. PRBs can be constructed in a single layer, in combination with low permeability barriers (e.g. sheet pile), or in a series to remediate individual contaminants.

A summary of different common treatment media that have been considered for PRB application are listed in Table 5-1.

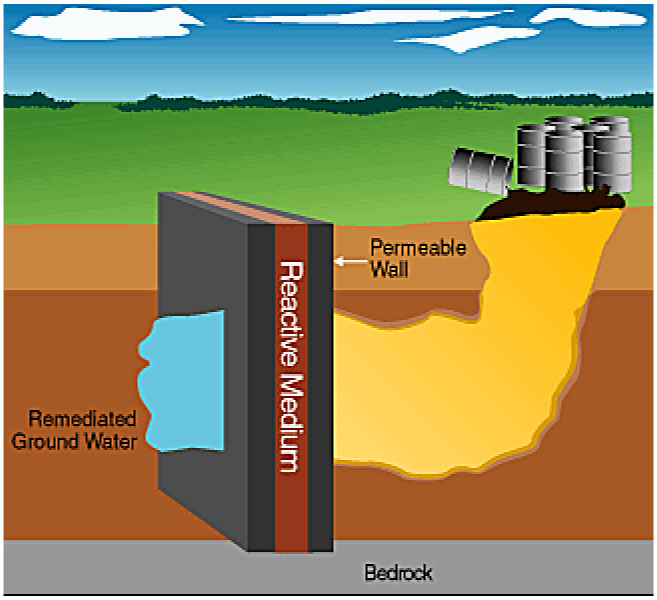


Figure 5-1. Schematic figure of PRB system (DOE-sites 1999)

Table 5-1. Common treatment medium and targeted contaminants in PRBs

Common treatment medium	Targeted contaminants
zero valent iron	Halocarbons, reducible metals
limestone	Metals, acid waters
precipitation agents (gypsum, hydroxyapatite)	Metals
sorptive agents (Fe hydroxide, granular activated carbon, zeolites, organoclay, coal)	Metals (such as Ni, Pb, Cd, Cr, Hg) and organics (such as benzene, toluene, ethylbenzene, xylene, nitrobenzene,

	dichloroethane, trichloroethane, perchloroethylene, petroleum hydrocarbons
reducing agents (organic compost, dithionite, hydrogen sulfide)	Reducible metals, Trichloroethylene
metal couples	halocarbons
biologic electron acceptors (oxygen release compound -oxygen source, nitrate)	benzene, toluene, ethylbenzene, xylene

To attain an efficient PRB in the field, three major factors must be taken into considerations. First, the required time for a desired cleanup should be less than the detention time of the flow in the PRB system. In the case that the reaction rate is slow, partial interaction between reactive material and contaminants could happen. The second requirement is to employ economical efficient materials as reactive components as in some scenarios, the replacement or regeneration of the materials must be affordable. Most importantly, it is required that the reactive components do not cause contamination to the groundwater themselves.

In addition, a detailed site characterization and site assessment must be conducted prior to the installment of barrier system to ensure the efficiency of the PRB system in removing the contaminants in the groundwater flow. Typically, the geological and hydrogeological information, the existing contaminants, and the geochemistry are evaluated before the implementation (Gavaskar et al. 2000). The advantages and disadvantages of PRB system has been summarized in Table 5-2 (Carey et al. 2002; Henderson and Demond 2007; Powell et al. 1998; Puls 2006).

Table 5-2. Advantages and disadvantages of PRB system (Obiri-Nyarko et al. 2014)

Advantages	Disadvantages
Relatively cheap passive technology, low maintenance cost, and negligible cost for disposal of treated contaminants	Only the contaminants passing through PRBs can be treated
Applicable for multi contaminates	Detail site characterization and site assessment is required prior to the barrier installation
Able to remediate a wide range of contaminants	Efficient for the plumes no deeper than 20 m beneath ground surface
The contaminated site can be running while the remediation is ongoing	Lack of data regarding the longevity of the PRBs
No surface contamination causing from PRBs	Possible difficulties in construction and performance
Occasional monitoring to assure the functionality of the system	Possibility of reactive material replacement in long term
No groundwater loss during the treatment process	Require monitoring especially in the case of persistent contaminants or low groundwater flow

The selection of suitable reactive component for PRB depends on the type of target contaminants in groundwater flow. The treatment mechanism can be based on organic, inorganic, or combined reaction scheme. A multiple phase contaminants can be remediated by employing a single or combined treatment procedure, or using single/multi-media. Particularly, some hydrocarbons and certain heavy metals can be treated through the sorption mechanism using fine-grained soils. The possible treatment mechanisms include chemical precipitation mechanism, Oxidation-reduction mechanism, zero-valent metal reaction, and sorption reaction which are explained in following paragraphs.

In *chemical precipitation mechanism*, slightly soluble compounds that contain ions are used to interact and precipitate the dissolved inorganic species like heavy metals and result in an insoluble salt such as sulfate, or carbonate metal salts containing the contaminants. *Oxidation-reduction mechanism* which also is known as "redox" attenuate the dissolved inorganic contaminants through the precipitation process by changing the valance state of contaminants during the redox process. In *zero-valent metal reaction*, metal provide the electron for reduction of chlorocarbons by removing the chlorine from the structure of chlorocarbons and releasing it to the solution as a combination of chloride and ferrous iron (Fe^{2+}).

The *sorption reaction* can be categorized in three groups including hydrophobic, hydrophilic, and ion exchange type. Many different materials have been used to sorb the organic and inorganic compounds from arouse phase. The sorption media are suitable for PRB application because the equilibrium sorption process occurs in a short amount of time. However, the sorption materials have a specific sorption capacity. The breakthrough of contaminants starts as soon as the sorption materials reach to their maximum capacity. In conclusion, an additional means is required in conjunction with sorptive material which remove or replenish the sorption medium.

The sorption reaction has been studied well for the strong organic sorbents which have very low water solubility, strongly hydrophobic, and highly stable for biodegradation. These compounds transfer from the water phase to the available organic carbon in the solid phase geo-materials through the partitioning process. Consequently, it can be concluded that the contaminants carried by groundwater flow can be removed efficiently from the aquifer system by increasing the organic carbon content of aquifer materials.

However, the sorption capacity of the selected materials is one of the most important characteristics which needs to be considered before selecting the treatment materials. The organically modification of sorptive materials can increase their sorption capacity and makes them favorable sorptive material for different scenarios.

Most commonly, zero-valent iron (ZVI), natural zeolites, activated carbon (AC), lime and other alkaline materials, apatite, transformed red mud (TRM), oxide, and sodium dithionite have been employed as the reactive component of PRB system (Liao et al. 2010; Nakagawa et al. 2003; Peric et al. 2004; Simon and Meggyes 2000; Triay et al. 1989). Among the possible options for PRB reactive materials, organoclays have gained more attention because of their higher sorption capacity to the common groundwater contaminants such as aromatic hydrocarbons (Guerin et al. 2002; Lee et al. 2012). In addition, organoclays demonstrated that they uptake contaminants from groundwater through the sorption process. As mentioned previously, the equilibrium sorption process occurs in a fast rate which makes it a favorable mechanism for the fast flow rate systems such as PRBs. The sorption mechanism can be used in aquifers with low organic carbon by utilizing organoclay complex as reactive material for PRBs. In this case, the organoclay can make a mineral complex with aquifer minerals which increase the sorption capacity of the minerals. Various surfactant can be utilized to create the organo complex with aquifer solid minerals. However, the interaction time between organoclays and dissolved contaminant should be enough to let the organo complex adsorb the contaminants. Otherwise, the non-equilibrium sorption mechanism would be dominant and the introduced contaminants would be attenuated partially. Lee et al. (2012) investigated the feasibility of using organoclays to remove PAHs from groundwater flow.

They suggested that organoclays can be employed efficiently for fast flow rate systems. They observed that organoclays blocked the advective transport of non-aqueous-phase liquid (NAPL) while they allowed the water with dissolved PAHs to pass through the PRB system and sorbed the dissolved PAHs.

In a fast flow rate permeable systems, the level of interaction between groundwater contaminants and PRB materials is typically relied on both the sorptivity of the PRB materials and the contact time between the contaminants and PRB materials (Carey et al. 2002; Chen et al. 2011; Henderson and Demond 2007; Puls 2006; Wilkin and Puls 2003).A non-equilibrium condition often exists in such a scenario, even if the sorption of organics onto organoclays are relatively fast (Chapter 2). Consequently, kinetic study is required to understand the sorption capacity of the system at non-equilibrium condition. The scope of this study is to investigate the potentials of using organobentonites as reactive amendment in PRB materials and also provides quantitative results to aid design and possible implementation of such applications Two sets of soil columns with of 10% of organobentonites (HDTMA-bentonite and PM-199) with different hydraulic conductivities (ranging from 10^{-4} to 10^{-7} m/s) were prepared and the impact of or seepage velocity on the sorption and retardation of the organic contaminants were examined. In addition, a model was established to relate the non-equilibrium partitioning coefficients and retardation factors as a function of time.

5.2 Materials and methods

Six different soils (low plasticity silty clay, HDTMA-bentonite, ASTM 20-30, coarse sand, fine sand, and PM-199 powder) were used to prepare the binary soil admixtures for this study. Coarse sand and medium sand were classified as SP (poorly graded sand) according to ASTM D422 and their grain size distribution curves are illustrated in Figure 5-2. The physical properties of the ASTM 20-30, coarse and fine sand are summarized in Table 5-3.

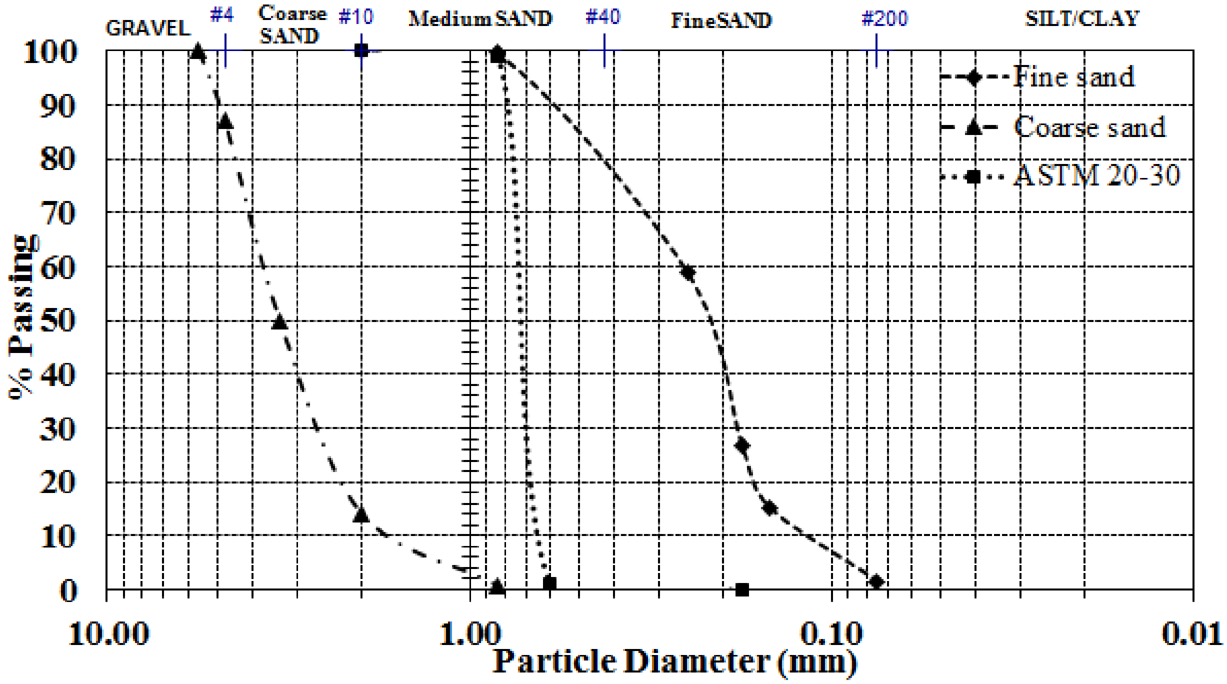


Figure 5-2. grain size distribution curve for coarse and fine sand

Table 5-3. physical properties of the coarse and fine sand

Properties	Coarse sand	Fine sand	ASTM 20-30
C_c	1.14	1.06	1.15
C_u	2.2	2	1
Type of gradation	Poorly graded	Poorly graded	Poorly graded
Specific gravity	2.67	2.65	2.65
Total organic carbon (%)	<1	<1	<1

For this study, pure benzene was dissolved in deionized water to prepare the permeant stock solution with approximate concentration of 100 µg/mL following the procedure explained in chapter 2. The stock solutions were stored at room temperature for less than 1 hour before the tests.

5.2.1 Column preparation

To study the effect of seepage velocity on the contaminant sorption and transport mechanisms, two sets of soil columns were designed. The first set of tests were performed in 4 packed columns with 10% HDTMA-bentonite and 90% of (1) coarse sand, (2) ASTM 20-30 sand, (3) silty clay, and (4) silty clay (slightly compacted). The second set of tests were performed in 3 packed columns with 10% PM-199 (powder) and 90% of (1) ASTM 20-30 sand, (2) fine sand, and (3) silty clay (loose). The percentages of organoclays were kept constant at low ratio of 10% (by weight) because the high sorption capacity of the studied organoclays could yield low effluent concentration that can't be easily tested in GC. The physical properties of the soil columns are summarized in Table 5-4.

Table 5-4. Properties of packed columns

Column NO.	Soil component	Soil mass (g)	Specific gravity	Pore volume (mL)	Dry density (g/cm^3)	Porosity
Column 1	10% HDTMA+90% coarse sand	110	2.53	44	1.49	0.6
Column 2	10% HDTMA+90% ASTM 20-30 sand	110	2.58	30	1.02	0.52
Column 3	10% HDTMA+90%	75	2.53	30	1.02	0.42

	silty clay					
Column 4	10% HDTMA+90% silty clay (slightly compacted)	90	2.53	38	1.22	0.41
Column 5	10% PM-199 (POWDER)+90% ASTM 20-30 sand	110	2.58	31	1.49	0.6
Column 6	10% PM-199 (POWDER)+90% Fine sand	110	2.58	31	1.49	0.42
Column 7	10% PM-199 (POWDER)+90% silty clay	75	2.53	44	1.02	0.4

Cylindrical glass columns with length of 15 cm and diameter of 2.5 cm with Teflon coded caps (Kimble Chase Co.) were used for the column studies. Columns were first cleaned with methanol and deionized water. Teflon tubing was used in this experiment for inlet and outlet flow lines to minimize the sorption of benzene to the wall of tubing.

5.2.2 Hydraulic conductivity test

The hydraulic conductivity of seven soil columns were measured using constant head method following ASTM D 2434. The prepared columns were fixed on a stand and connected to the water reservoir. To saturate and squeeze the trapped air pockets out of the columns, the water was flushed through the columns from bottom to top until the stable water head at water reservoir and steady state at effluent was achieved. The effluent was collected in a container. Meanwhile the required time to collect the effluent and the water head were recorded for each column. The hydraulic conductivity was measured using equation 5-1:

$$k = \frac{QL}{Ath} \qquad 5\text{-}1$$

where k is the hydraulic conductivity (cm/s), Q is the quantity of water discharge (cm^3), L is the length of column (cm), A is the cross-section area of column (cm^2), t is the total time for water discharge (s), and h is the water head difference.

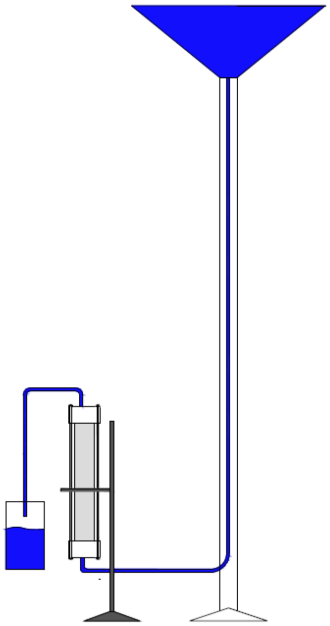


Figure 5-3. Hydraulic conductivity test setup with constant head

5.2.3 Breakthrough test

The breakthrough tests were carried out to obtain the retardation capacity of each binary soil admixture in the seven packed columns. This part of experiment was designed to evaluate the sorptivity of benzene by the organoclay amendments when given a fast seepage velocity and possibly, a non-equilibrium sorption scenario in PRBs.

The pre-saturated columns from the hydraulic conductivity experiment were used for the breakthrough study. A bladder accumulator with viton membrane was used to feed the benzene solution into the soil columns. For this reason, pressure control panel was used to inject the solution. Initially, bladder accumulator was filled with benzene solution and 1 pore volume of pulse-type contaminant solution was injected to the soil columns. Then, the flow was switched to the deionized water. Following the test procedure explained in chapter 4, The effluent samples were collected and analyzed for the concentration of benzene. The columns were flushed with deaired water until the concentration of benzene in effluent was reached below the detection limit. The breakthrough curve for benzene solution was obtained by measuring the concentration of benzene in the effluent. The schematic setup of breakthrough experiment is presented in Figure 5-4.

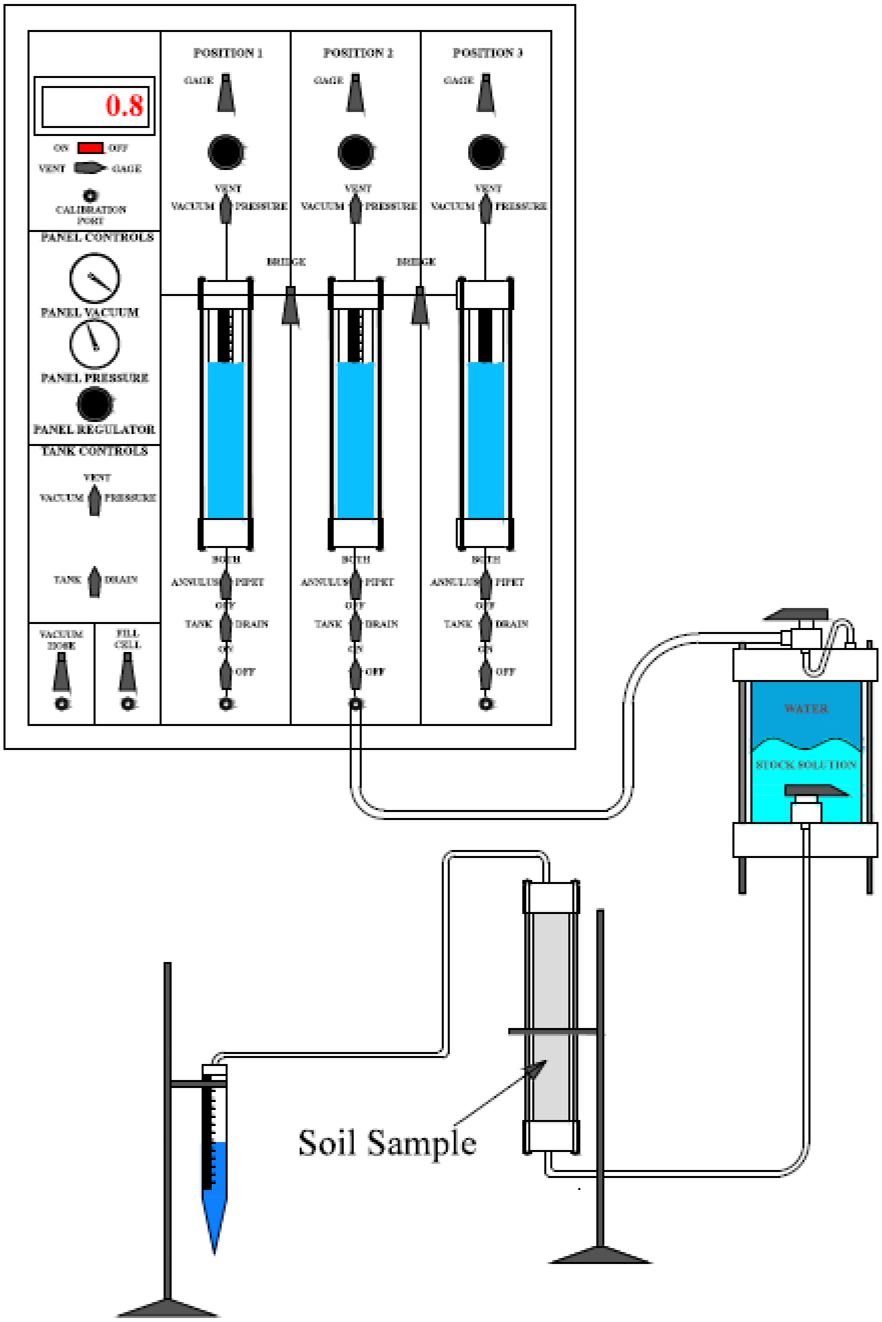


Figure 5-4. Schematic setup of breakthrough test

To analyze the breakthrough test results, the non-equilibrium partitioning coefficient of benzene was estimated from the kinetic study (chapter 2). Also, the numerical and analytical solutions were obtained to estimate the contaminant transport parameters following the same procedure explained in chapter 4. The obtained results from mathematical modeling was compared with the non-equilibrium partitioning coefficient of benzene to verify the accuracy of models.

5.3 Result and discussion

5.3.1 Hydraulic conductivity test

The hydraulic conductivity (k) and corresponding seepage velocities (v_s) for seven studied columns were measured and the obtained results are summarized in Table 5-5.

Table 5-5. The measured hydraulic conductivity

Column components	Void ratio (e)	V_s (m/s)	k (m/s)
Column 1	1.5	1.36×10^{-3}	1.33×10^{-4}
Column 2	1.08	2.83×10^{-4}	4.61×10^{-5}
Column 3	0.72	3.29×10^{-5}	2.25×10^{-6}
Column 4	0.69	3.17×10^{-6}	4.07×10^{-7}
Column 5	1.5	1.15×10^{-3}	1.12×10^{-4}
Column 6	0.72	4.13×10^{-4}	2.83×10^{-5}
Column 7	0.66	1.77×10^{-5}	3.32×10^{-6}

The hydraulic conductivity of soil columns with HDTMA-bentonite amendment was at 1.33×10^{-4} m/s for column 1 and decreased to 4.07×10^{-7} m/s for slightly compacted soil column 4. The same trend was observed regarding the hydraulic conductivity of soil columns with PM-199 amendment. The hydraulic conductivity of column 5 was measured as 1.12×10^{-4} m/s while it decreased to 3.32×10^{-6} m/s for column 7. It was observed that the hydraulic conductivity of soil columns were function of void ratio.

Taylor (1948) suggested an equation for coefficient of permeability which considered the properties of both soil medium and permeant fluid, equation 5-2.

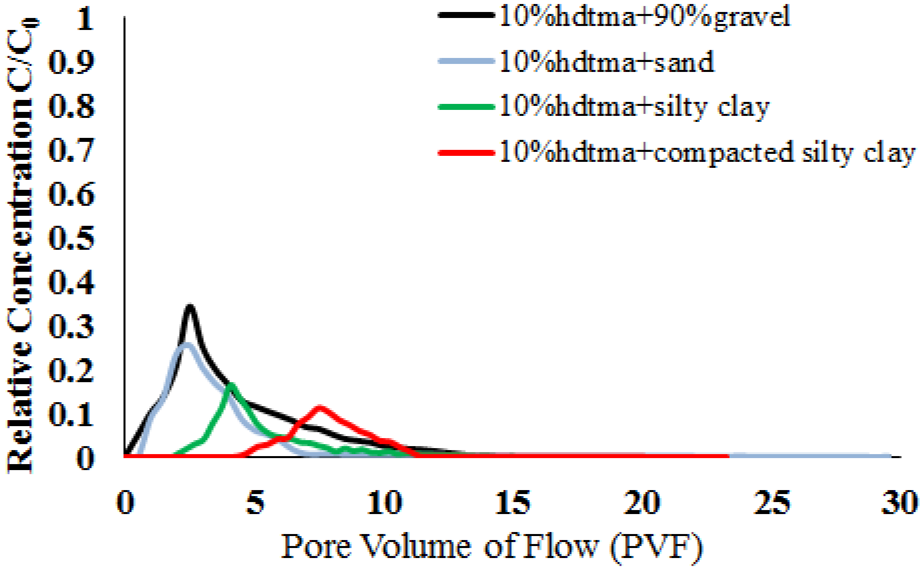
$$k = C{D_s}^2 \frac{\mu}{\gamma} \frac{e^3}{(1+e)} S^3 \qquad 5\text{-}2$$

where C is the shape factor, D_s is the effective particle diameter, e is the void ratio, μ is the viscosity of the permeant fluid, γ is the unit weight of the soil, and S is the degree of saturation. It was observed that the void ratio of packed columns with HDTMA-bentonite amendment started from 1.5 for the column with highest flow rate (column 1) and decreased to 0.69 for the column with lowest flow rate (column 4). Consequently, the hydraulic conductivity in HDTMA-bentonite amended columns started at higher end for column 1 as 1.33×10^{-4} m/s and decreased to 4.07×10^{-7} m/s for column 4 at the lowest end. Likewise, the void ratio of packed columns with PM-199 amendment started from 1.5 for the column with highest flow rate (column 5) and decreased to 0.66 for the column with lowest flow rate (column 7). As a result, the hydraulic conductivity in PM-199 amended columns started at higher end for column 5 as 1.12×10^{-4} m/s and decreased to 3.32×10^{-6} m/s for column 7 at the lowest end.

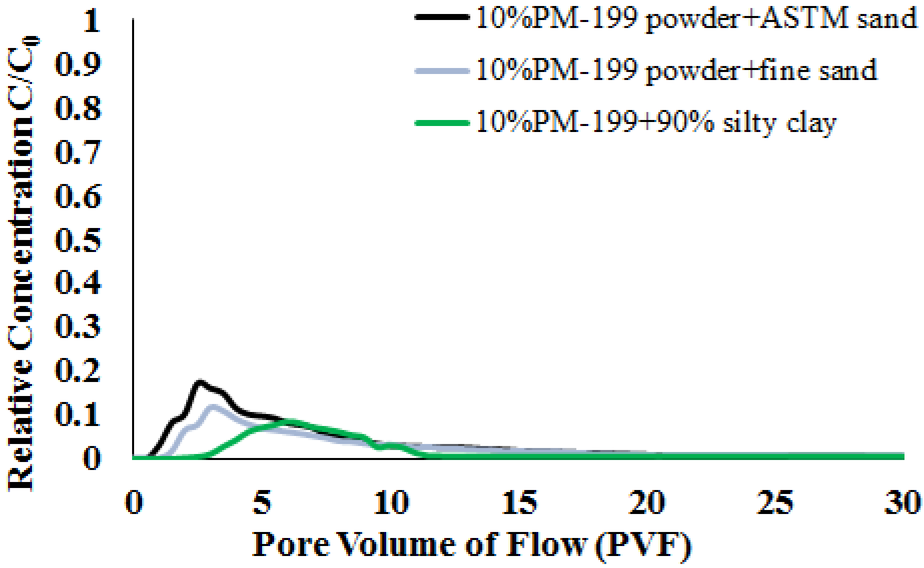
In this study, the obtained results suggested that the void ratio decreased by decreasing the particle size of soil column constituent. As it was anticipated, the hydraulic conductivity of soil columns decreased by mean particle sizes.

5.3.2 Breakthrough test

The breakthrough time increased as the coarse particle fraction decreased in the soil columns. For columns 1, 2, 5, and 6 the tests typically lasted about 20 to 30 minutes (for 25 to 30 pore volumes). However, columns 3, 4, and 7 lasted more than 2 weeks (for 20 to 25 pore volumes). The seepage velocity started from 1.3 × 10^{-3} m/in soil columns s filled with admixture of HDTMA-bentonite and coarse sand and it decreased to 3.17 × 10^{-6} m/s for soil column with HDTMA-bentonite and silty clay. Similar trend was observed as the seepage velocity in PM-199 ASTM with 20-30 sand was measured at 1.15 × 10^{-3} m/s and it decreased to 1.77 × 10^{-5} m/s in PM199 and silty clay. The peak of mass flux in both columns of HDTMA-bentonite + coarse sand and PM-199 + ASTM 20-30 sand appeared after 3 pore volumes. However, the peak of mass flux in HDTMA-bentonite + silty clay occurred 2 pore volumes earlier than PM-199 + silty clay. This was explained as a result of higher sorption capacity of PM-199 compared to HDTMA-bentonite. The obtained breakthrough curve for columns with 10% organoclay amendments are illustrated in Figure 5-5.



(a)



(b)

Figure 5-5. Breakthrough curve of benzene transport in column with (a) 10% HDTMA-bentonite amendment (b) 10% PM-199 amendment

The delayed arrival and decrement of the peak mass flux was attributed to the sorption of benzene by the soils. A retardation factor is typically used to describe such a hindered transport of organic contaminant. Most commonly, the retardation factor is determined by the sorptivity of the soil sorbent ($R = 1 + \frac{\rho}{n} k_d$) and the partitioning coefficient K_d in this equation indicates the affinity of contaminant sorbate towards soil sorbent. However, the partitioning coefficient K_d is typically determined by batch sorption tests and it represents a distribution of contaminants between soil sorbent and aqueous phase under the equilibrium condition. In the PRBs, because the breakthrough time of contaminant through the reactive materials could be less than the time required for equilibrium sorption, the equation tends to yield overestimated K_d and consequently, overestimated retardation factor. It is necessary to investigate the non-equilibrium sorption and the resultant retardation factor given the fast flow situation.

Table 5-6. Required time for seepage of benzene solution through the soil columns

Column components	V_s (m/s)	Time (min)
10% HDTMA + 90% coarse sand	1.36×10^{-3}	1.83
10% HDTMA + 90% ASTM 20-30 sand	2.83×10^{-4}	8.81
10% HDTMA + 90% silty clay	3.29×10^{-5}	75.93
10% HDTMA + 90% silty clay (slightly compacted)	3.17×10^{-6}	786.88
10% PM-199 (POWDER) + 90% ASTM 20-30 sand	1.15×10^{-3}	2.16
10% PM-199 (POWDER) + 90% Fine sand	4.13×10^{-4}	6.05
10% PM-199 (POWDER) + 90% silty clay	1.77×10^{-5}	14.08

Initially, breakthrough time of contaminant flow in each column was calculated based on the seepage velocity (Table 5-6):

$$t = \frac{L}{V_s} \qquad 5\text{-}3$$

Where t is the breakthrough time (s), L is the length of the column (cm), and V_s is the seepage velocity (cm/s). The obtained breakthrough time was then used to estimate the non-equilibrium partitioning coefficient through the aqueous concentration of benzene from the kinetic study (chapter 2).

$$C_t = C_e + [C_0 - C_e]exp\left[-\left(\frac{\varepsilon C_0}{C_e}\right)t\right] \qquad 5\text{-}4$$

For kinetic study, the concentration of dissolved benzene in the solution as a function of time (C_t) was recorded. In addition, the initial concentration of the benzene in the solution was measured as (C_0). Also, the equilibrium concentration of benzene in the solution was measured as (C_e). An initial value for the mass transfer coefficient (ε) was chosen and the resultant curve from equation 5-4 was plotted. The value of ε was altered to fit a curve to the experimental results. Consequently, the suitable value of ε was found and the concentration of benzene as a function of time was calculated by using equation 5-4. the partitioning coefficient of HDTMA-bentonite as a function of time was calculated by dividing the absorbed mass of benzene to the solid phase over the remained concentration of benzene in the solution for each time step. The calculated partitioning coefficient of HDTMA-bentonite for benzene as a function of time is presented in Figure 5-6.

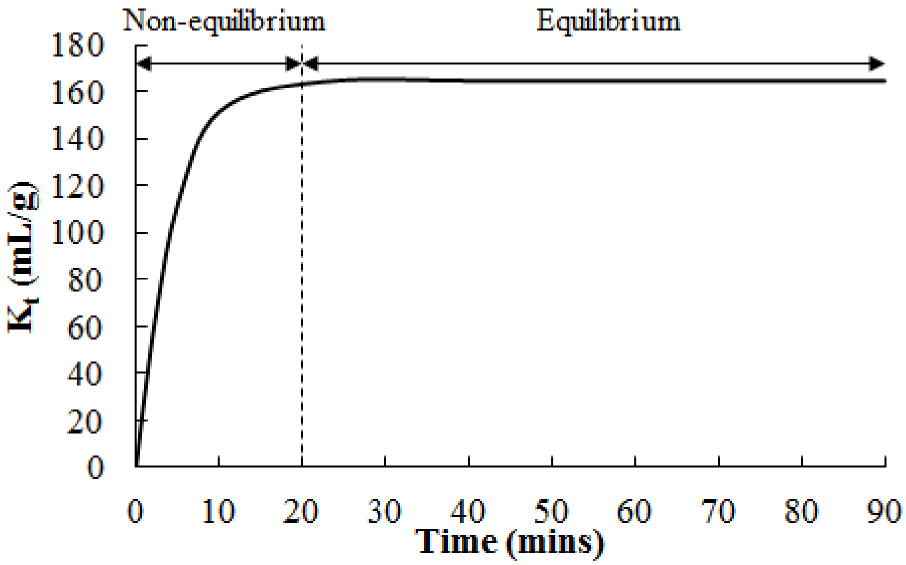


Figure 5-6. partitioning coefficient of HDTMA-bentonite for benzene as a function of time

Based on the results in Figure x, it can be concluded that approximately 20 minutes is needed for the equilibrium sorption of benzene onto HDTMA-bentonite. Consequently, the partitioning coefficient obtained from equilibrium batch sorption test is not valid anymore for non-equilibrium sorption condition with the breakthrough time less than 20 mins. Specifically, out of the 7 packed columns, the benzene transport and retardation in

5 columns (column 1,2,5,6,7,Table 5-7) must be considered as non-equilibrium sorption case.

Table 5-7. Non-equilibrium partitioning coefficient of HDTMA-bentonite for benzene

Column number	Column components	Breakthrough Time (min)	K (mL/g)	
			K_t	K_d
1	10% HDTMA + 90% coarse sand	1.83	13	---
2	10% HDTMA + 90% ASTM 20-30 sand	8.81	110	---
3	10% HDTMA + 90% silty clay	75.93	---	149.59
4	10% HDTMA + 90% silty clay (slightly compacted)	786.88	---	149.59
5	10% PM-199 (powder) + 90% ASTM 20-30 sand	2.16	N.A.	
6	10% PM-199 (powder) + 90% Fine sand	6.05	N.A.	
7	10% PM-199 (powder) + 90% silty clay	14.08	N.A.	

The calculation to determine the overall sorptivity and retardation factor of the soil admixture is illustrated below:

Considering negligible sorptivity of coarse sand, the overall distribution coefficient (K_a) can be calculated as:

$$K_a = \frac{\sum_{i=1}^{n} K_i W_i}{W_i} \qquad 5\text{-}5$$

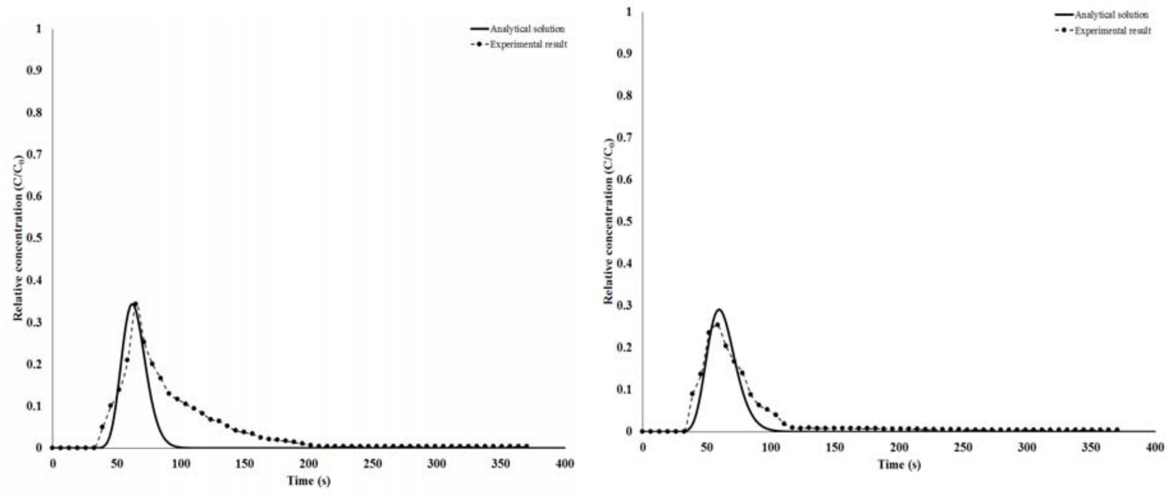
where K_i is the partitioning coefficient of each sorbent (at equilibrium or non-equilibrium condition), and W_i is the mass percentage of each sorbent in the column soil.

Following the mentioned procedure, the distribution coefficients was measured for studied columns. Then, the retardation factor was calculated using equation 5-6.

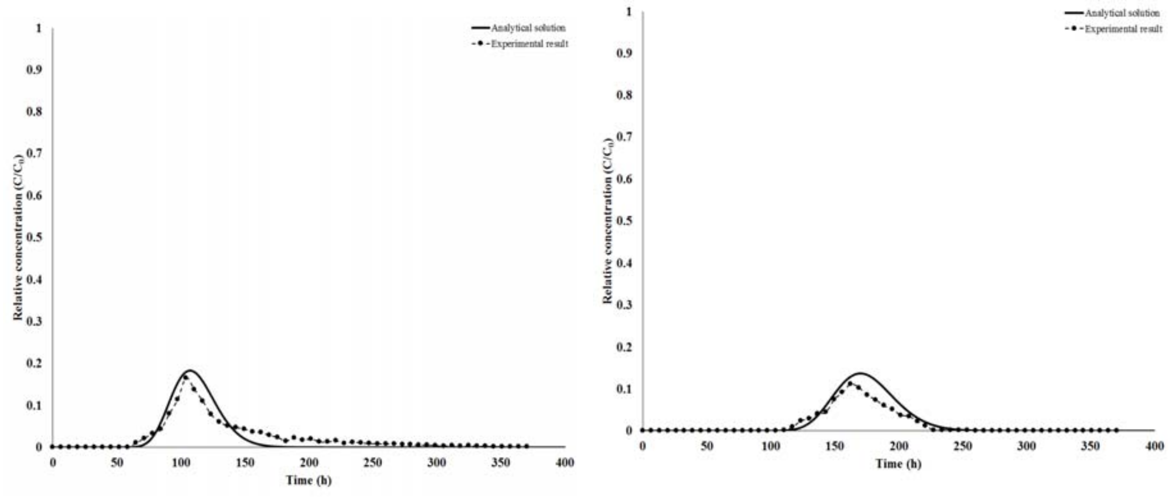
$$R = 1 + \frac{\rho}{n} K \qquad 5\text{-}6$$

the K value used for column 1 and 2 were the non-equilibrium distribution coefficients that was measured through the kinetic study while the retardation factor for column 3, and 4 were measured using the equilibrium distribution coefficients (K_d). The calculated partitioning coefficient and retardation factors for the studied columns are summarized in Table 5-8.

Analytical solution was employed to calculate the retardation factor corresponding to 100% mass of benzene in effluent, Figure 5-7. The acquired results are summarized in Table 5-8.



(a) (b)



(c) (d)

Figure 5-7. Fitted curve applying analytical solution for column (a) 1 (b) 2 (c) 3 (d) 4

Table 5-8. Retardation factor and diffusion coefficients for seven soil columns obtained from analytical and numerical methods and the first-moment equation

Column number	Calculated from kinetic study		Experimental results fitted by analytical solution	
	K (mL/g)	Retardation factor	Retardation factor	Diffusion coefficient (cm^2/s)
1	1.3	4.23	4	2.4×10^{-6}
2	11.0	22.57	19.2	1.2×10^{-6}
3	14.59	37.33	41.1	6.2×10^{-6}
4	14.59	45.51	58.6	1.8×10^{-6}

The retardation factor calculated from the non-equilibrium partitioning coefficient and estimated from analytical solution was 4.23, and 4 for soil columns 1, respectively. Also, the retardation factor for column 2 was obtained from the non-equilibrium partitioning coefficient and the analytical solution as 22.57, and 19.2, respectively. The retardation factor obtained from analytical solution and kinetic study showed only a 5% difference in column 1 whereas in column 2 there was a 15% difference. These results suggested that the kinetic study was a suitable method to calculate the non-equilibrium partitioning coefficient and yield a reasonable retardation factor for non-equilibrium condition.

Additionally, the estimated diffusion coefficient for all columns were at the range of 10^{-6} cm^2/s which were at an acceptable range compared to previous studies.

5.3.3 Effect of seepage velocity on the retrieved percentage of benzene mass in effluent

The retrieved percentage of benzene mass was defined as equation 5-7.

$$R_{mass} = \frac{M_{out}}{M_{in}} \times 100 \qquad 5\text{-}7$$

where R_{mass} is the retrieved percentage of benzene mass (%), M_{in} is the initial mass of benzene which was introduced to the packed column (μg), and M_{out} is the mass of benzene which was collected in effluent (μg). By using the mass balance analysis, R_{mass} were measured as 80%, 71%, 45%, and 31% for column 1 to 4, respectively. R_{mass} is plotted versus the seepage velocity in Figure 5-8.

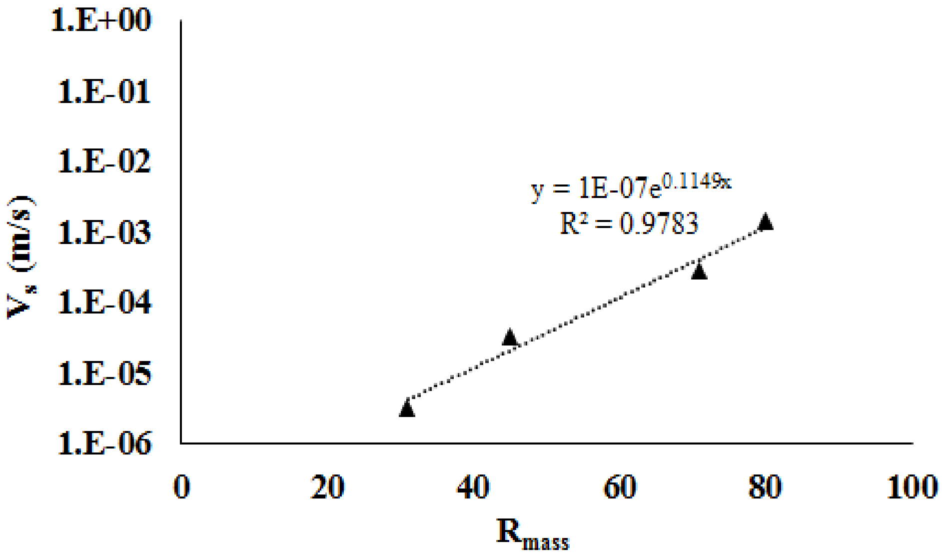


Figure 5-8. R_{mass} versus seepage velocity

It was observed that R_{mass} decreased exponentially from 80% for column 1 with seepage velocity of 1.36×10^{-3} m/s to 31% for column 4 with seepage velocity of 3.17×10^{-6} m/s. The R_{mass} in column 1, and 2 were measured as 80% and 71% respectively, which had higher seepage velocity compared to column 3, and 4. However, R_{mass} decreased to 45% and 31% for column 3, and 4 respectively. It suggested that the sorbed mass of benzene by HDTMA-bentonite needed longer breakthrough time by decreasing the permeability of the system. The acquired results suggested that the HDTMA-bentonite amended PRBs could have promising performance as permeable reactive barriers. Because they have a reasonable range of permeability between 4.07×10^{-7} m/s to 1.33×10^{-4} m/s as a permeable barrier. In addition, it was observed that the dissolved organic contaminants (benzene) required a long breakthrough time (~787 min) with a significantly low mass flux in column with lowest seepage velocity (column 4).

5.4 Conclusion

In this chapter, the transport of benzene through the fast flow rate columns at different seepage velocity was investigated. It was observed that the permeability of the packed columns decreased as the void ratio decreased. This happened because the soil grains with finer particle size occupied the pores within the soil structure and reduced the advective transport of the fluid (water) through the packed column. In addition, the barrier performance of HDTMA-bentonite and PM-199 as reactive amendment to the PRBs were explored. It was observed that the breakthrough of benzene in PM-199 amended soil columns occurred 3 pore volumes later than the HDTMA-bentonite amended columns. Also, the mass flux of benzene through the PM-199 amended columns was much lower than the HDTMA-bentonite amended columns. This happened because of higher affinity of benzene to PM-199 compared to HDTMA-bentonite.

It was noticed that the non-equilibrium condition was dominant in columns with high rate of seepage velocity (1.36×10^{-3} to 2.83×10^{-4} m/s). For this condition, the retardation factor was obtained from two approaches (1) kinetic study; (2) analytical solution. The results of retardation factor for non-equilibrium condition showed a good agreement between the calculated results from kinetic study and estimated result from analytical solution. This result suggested that the non-equilibrium partitioning coefficient measured from kinetic study can be employed to calculate a reliable retardation factor in non-equilibrium condition. Also, the acquired results suggested to employ the analytical solution to estimate the retardation factor for equilibrium condition.

Moreover, it was observed that the R_{mass} decreased by decreasing the seepage velocity of the soil column which assured the promising performance of HDTMA-amendment as reactive material in PRBs. Because not only they provide the required range of permeability for permeable barriers, but also, they decrease the mass flux of benzene which resulted in longer required breakthrough time. The overall results in this chapter suggest that HDTMA-bentonite or other organophilic clays are efficient reactive materials for PRB barriers to uptake the dissolved aromatic hydrocarbons from groundwater flow.

6 CHAPTER SIX SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Earthen barriers such as CCLs and GCLs have been employed in geotechnical practices to provide a low permeability hydraulic barrier since long time ago. These types of barriers exhibited satisfactory performance for many applications such as landfills. The performance of low permeability barriers is based on the swelling potential of their component, which is mostly Na-bentonite, in contact with polar fluids such as water. However, the acceptable range of conductivity cannot be achieved by traditional earthen barriers when they are permeated by non-polar fluids such as gasoline. This phenomenon occurs due to the incompatibility of earthen barrier constituent with non-polar compounds. Also, the traditional earthen barriers are not able to retard the contaminant transport due to their negligible reactivity with organic compounds. As a result, the application of low permeability barriers was limited to polar and non-contaminated flows. In this study, the performance of traditional earthen barriers as a hydraulic and chemical barrier was enhanced by introducing an organically modified amendment (HDTMA-bentonite) to traditional earthen barrier's components.

This research studied the geotechnical behavior and field performance of an engineered organobentonite (HDTMA-bentonite) as an amendment for sorptive soil barriers. The HDTMA-bentonite was synthesized under a controlled laboratory condition and the sorptivity of HDTMA-bentonite in along with other sorbents including a commercially available partitioning clay (PM-199), Ca-bentonite, and Na-bentonite were investigated as a function of: sorbate properties (organic carbon content, surfactant type, grain size); sorbate properties (chlorination, aromatic ring) and the aqueous environment (temperature, co-solvent). To quantify the sorptivity of the studied sorbents, a series of equilibrium batch sorption test were conducted. The obtained results were analyzed and summarized in Table 6-1.

Table 6-1. Results for equilibrium batch sorption study

Studied sorbents	Studied Sorbate	Solvent solution	Function of Sorbate/sorbent/ aqueous environment	Results
PM-199, HDTMA-bentonite, Na-bentonite, Ca-bentonite	benzene	DI water	TOC	The natural or intercalated organic carbons on the surface or interlayer of unmodified soil/organobentonite increase the organophilicity of the sorbents. As a result, the sorptivity increased by increasing the organic carbon content. Organobentonites exhibited much higher sorptivity to organic contaminants compared to unmodified soils.
PM-199, HDTMA-bentonite	Benzene	DI water	Surfactant type	Sorptivity of PM-199 is higher than HDTMA-bentonite. The intercalated surfactant in PM-199 is a double chain surfactant. Consequently, PM-199 has higher aliphatic carbon compare to the HDTMA-bentonite which has a single chain intercalated surfactant
	HCB	30% acetone + 70% DI water		
PM-199 (powder),	Benzene	DI water	Particle size	No significant differences were

PM-199 (granular)				observed
HDTMA-bentonite	Benzene, 1,2,4-trichlorobenzene, HCB	acetone	chlorination	The solubility of organic compounds decreased by increasing the chlorinated positions on the aromatic ring. As a result, organophilicity of the organic contaminants increased as chlorination increased. The affinity of organic contaminants toward the organic phase of sorbents increased which resulted in higher partitioning to HDTMA-bentonite (hexachlorobenzene>1, 2, 4 –trichlorobenzene >benzene).
HDTMA-bentonite	Benzene, naphthalene, phenanthrene	acetone	aromatic ring	The solubility of organic compounds decreased by increasing the aromatic ring. As a result, organophilicity of the organic contaminants increased as the number of aromatic rings increased. The affinity of organic contaminants toward the organic phase of sorbents increased which resulted in higher partitioning to HDTMA-bentonite (phenanthrene>naphthalene>benzene)
HDTMA-bentonite	benzene	DI water, acetone, 30% acetone + 70% water	Co-solvent	The sorption capacity decreased as the co-solvent percentage increased. Cosolvency of co-solvent increased the solubility and decreased the sorption capacity of hydrophobic organic contaminants.
	naphthalene	acetone, 30% acetone + 70% water		

HDTMA-bentonite	benzene	DI water	Temperature (10, 25, 40, 60˚ C)	The sorptivity of HDTMA-bentonite to

The hydraulic performance, and transport of naphthalene as a representative of NAPL was studied through the compacted soil column which consisted of 5% HDTMA-bentonite and 95% silty clay. The obtained results showed that a small percentage of HDTMA-bentonite (< 10%) does not affect the swelling tendency of the silty clay in water while it leads to significant swelling of the HDTMA-bentonite amended silty clay in gasoline. The significant swelling of HDTMA-bentonite in gasoline can be explained as the high interaction of organophilic surfactants in the HDTMA bentonite and non-polar liquid. On the other hand, a small percentage of HDTMA-bentonite (< 10%) amendment in compacted silty clay slightly increased the permeability of column to water while it decreased the permeability of column to gasoline significantly. In addition, it was observed that only 5% HDTMA bentonite amendment enhanced the retardation capacity of the system while it had no significant effect on the permeability of the compacted silty clay. The obtained results suggested that a small percentage of HDTMA-bentonite can reduce the mass flux of contaminant by 90% which suggested that HDTMA-bentonite has a promising performance as reactive material for Compacted liner barrier for organic and/or low polarity fluids.

Additionally, the feasibility of using HDTMA-bentonite as a reactive amendment for GCL liners were investigated. The swelling behavior of Na-bentonite as the major component of GCL, CA-bentonite, HDTMA-bentonite, PM-199, soil admixtures including 10%/20% HDTMA-bentonite + Na-bentonite, and 10%/20% PM-199 + Na-bentonite were studied as a function of: polarity, ion strength, acidic/basic environment.

It was observed that Na-bentonite had the maximum swelling in water due to the strong hydration of Na^+ with polar liquids. In addition, Ca-bentonite exhibited a medium swelling in contact with water due to weaker hydration of Ca^{2+} compared to Na^+ with polar liquids. In contrast, it was observed that organobentonites did not show any significant swelling in polar liquid (water) due to their hydrophobic characteristics. Consequently, the swelling of soil admixtures decreased by increasing the percentage of organobentonite.

Unmodified bentonite showed a negligible swelling tendency in low polarity liquids such as methanol and gasoline (Gheibi et al. 2016). The acquired result suggested that Ca^{2+} and Na^+ did not hydrate in low polarity liquids due to the incompatibility of unmodified bentonites with low polarity liquids. In contrast, organobentonites swelled significantly as the polarity of the liquid decreased (Khabiri et al. 2016). Consequently, the swelling of soil admixtures increased by increasing the percentage of organobentonite.

It was also observed that the solution with low ionic concentration (0.01 M NaCl) and pH level in the range of 4 to 10 did not affect the swelling tendency of studied soils and soil admixtures. However, the swelling tendency of unmodified bentonites decreased drastically by increasing the concentration of ionic strength due to the drag force of ions which pull the water molecules out of clay interlayer.

The study on the permeability of GCLs revealed that Na-bentonite GCLs demonstrated lower permeability to polar liquids compared to Ca-bentonite GCLs. Also, the permeability of GCL specimens to polar liquids increased slightly by increasing the percentage of HDTMA-bentonite in the GCL soil. However, the obtained results suggested that the permeability of Na-bentonite and Ca-bentonite increased significantly when permeated by low polarity liquids such as methanol and gasoline. It was because of the chemical incompatibility of unmodified bentonites with low polarity liquids. In contrast, the chemical compatibility of GCL soils with low polarity liquids enhanced by increasing the percentage of HDTMA-bentonite to the GCL soils.

The permeability of Na-bentonite GCL with different percentage of PM-199 and HDTMA-bentonite to polar (water) and non-polar (gasoline) liquids were also studied (Gheibi and Bagheripour 2010; Gheibi and Bagheripour 2011; Gheibi and Bagheripour 2011; Gheibi et al. 2011). It was observed that the minimum permeability of the GCL when is permeated by both liquids can be obtained by adding 28% of PM-199 to the Na-bentonite GCL soil. Also, the permeability of the GCL specimens decreased by increasing the confining stress due to confinement of existing pores within GCL soil.

The transport of benzene as a representative of BTEX through the GCL specimens which consisted of (0, 10, 20%) HDTMA-bentonite + Na-bentonite and (0, 10, 20%) HDTMA-bentonite + Ca-bentonite were also studied. The column tests were performed to obtain the breakthrough curve for benzene transport. It was observed that 20% HDTMA-bentonite amended GCL decreased the mass flux of benzene by half compared to unmodified GCL specimens while its effect on the permeability of the unmodified GCL specomens was insignificant (Gheibi and Gassman 2014; Gheibi and Gassman 2014; Gheibi et al. 2014). Due to the retardation mechanism, 100% of introduced mass was not received in effluent and a long breakthrough time was required for the sorbed benzene (Gheibi and Gassman 2015). As a result, an analytical and numerical approach was employed to estimate the retardation factor and diffusion coefficient of benzene transport through the column because the retardation factor obtained from the experimental data did not account for 100% of benzene mass. The acquired results suggested that Na-bentonite with a small percentage of HDTMA-bentonite (20%) can enhance the retardation factor and chemical compatibility of the GCL liners under a low advective flow condition.

Finally, two soil columns with of 10% of organobentonites (HDTMA-bentonite and PM-199) with different seepage velocities were prepared to investigate the potentials of using organobentonites as reactive amendment in PRB materials. The results of permeability experiments suggested that the seepage velocity decreased by decreasing the void ratio. This happened because the soil grains with finer particle size occupied the pores within the soil structure and reduced the advective transport of the fluid (water) through the packed column. Also, the peak mass flux of benzene through the PM-199 amended columns was much lower than the HDTMA-bentonite amended columns. It was observed that the partitioning of benzene onto HDTMA-bentonite in columns with fast seepage velocity did not reach equilibrium condition (Gheibi and Gassman 2016; Gheibi et al. 2017). To obtain the transport parameters of benzene under non-equilibrium condition, two approaches including kinetic study and analytical solutions were employed. The results of retardation factor for non-equilibrium condition showed a good agreement between the calculated results from kinetic study and estimated result from analytical solution (Niaki and Jahani 2012; Niaki and Jahani 2013). This result suggested that the non-equilibrium partitioning coefficient measured from kinetic study can be employed to calculate a reliable retardation factor in non-equilibrium condition. In addition, the obtained results suggested that the retardation capacity of the PRBs increased by decreasing the seepage velocity. The overall results suggested that HDTMA-bentonite can serve as an efficient reactive material in PRBs which not only increased the retardation capacity of the fast flow rate columns, but also did not affect the seepage velocity of the system with fast seepage velocity.

This obtained results from this study showed the promising application of organoclays as an amendment for CCL and GCL barriers (Ebrahimi et al. 2017; Ebrahimi et al. 2016; Ebrahimi et al. 2016; Mirbagheri et al. 2014). Also, it was concluded that organoclays are sufficient sorbents to uptake the dissolved contaminants in the fast flow rate barriers such as PRBs. There are several areas or directions of future study, which we could further enhance the work presented in this dissertation.

1. Feasibility of using organoclays as a sorbent of common runoff contaminants for permeable pavement (PP) systems.
2. Feasibility of using organoclays as a sorbent of common runoff contaminants for permeable pavement (PP) systems.
3. Feasibility of using organoclays as a sorbent of common runoff contaminants for permeable pavement (PP) systems.
4. Feasibility of using organoclays as a sorbent of common runoff contaminants for permeable pavement (PP) systems.

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EDUCATION

- **Ph.D.** Civil Engineering – Geotechnical, University of Louisville, Louisville, KY (GPA: 4.0/4.0)
  Dissertation Title: Interaction between organic contaminant and organic surfactant with modified bentonite
- **M.Sc.** Geotechnical Engineering, K.N.Toosi University of Technology, Tehran, Iran (GPA: 4.0/4.0)
  Thesis Title: Experimental investigation on uplift behavior of belled pile supported on Geocell reinforced-soil
- **B.Sc.** Civil and Environmental Engineering, University of Tabriz, Tabriz, Iran

EMPLOYMENT

- **Ph.D. researcher** (2013-Current), University of Louisville, Louisville, Kentucky.
  - Led the Ph.D. Geomechanics Laboratory research group under the supervision of Dr. Zhao
  - Trained fellow students on the knowledge and operation of Gas Chromatography (GC). The GC was new equipment within the geotechnical engineering laboratory.
  - Mastered the knowledge of contaminant attenuation mechanisms in liner and barrier systems (CCL, GCL, and PRB)
  - Modeled the organic contaminant transport through landfill systems using GEO-STUDIO
- **Teaching Assistant** (2014-Current), University of Louisville, Louisville, Kentucky.
  - Geomechanics – University of Louisville (Instructed by: Dr. Qian Zhao)
  - Environmental Geotechnics – University of Louisville (Instructed by: Dr. Qian Zhao)
  - Foundation Engineering – University of Louisville (Instructed by: Dr. Thomas Rockaway)
  - Structural Analysis – University of Louisville (Instructed by: Dr. Zhihui Sun)
  - Mechanics 1: Statics – University of Louisville (Instructed by: Dr. Mark French and Dr. Qian Zhao)
- **Senior Geotechnical Engineer** (2010-2012), GRANTEEN Consultant and Corporation Company, Tehran, Iran.
  - Led multi-disciplinary teams of individuals investigating geotechnical integrity of client sites
  - Supervised field exploration including CPT and SPT, soil sampling, and in situ testing
  - Conducted geotechnical laboratory analyses and interpreted results for meaningful recommendations
  - Prepared geotechnical reports, sharing key recommendations with clients for an estimated cost savings of approximately $10,000 to $15,000 per site
  - Visited 5 to 8 sites per week, maintaining a highly productive schedule across GRANTEEN's various clients
  - Traveled to other cities to cover the requests from non-local clients
  - Performed geotechnical analyses such as bearing capacity, slope stability, lateral earth pressures, pile design, etc.
  - Supervised field operations including soil stabilization, foundation construction and cut-and-fill operations
  - Worked to find practical and economical solutions for site specific geotechnical conditions
  - Performed stabilization operation using nail-anchorage and soldier pile systems for
  - Worked on many high profile projects including the Atlas Mall Project, a colossal excavation project in Iran which required a 120-foot-deep excavation over a 2.5-acre site
- **Geotechnical Engineer** (2009-2012), Soil Mechanics Industries (SMI), Tehran, Iran.
  - Performed field soil sampling. Worked with the drillers to modify procedures to improve the reliability and quality of testing data
  - Prepared geotechnical reports and client recommendation to optimize site development
  - Performed geotechnical laboratory tests including consolidation, triaxial, atterberg limits, etc.
- **Teaching Assistant** (2009-2011), K. N. University of Technology, Tehran, Iran.

  - Advanced Engineering Mathematics – K. N. Toosi University of Technology (Instructed by: Dr. Naser Maghaddas Tafreshi)
  - Foundation Engineering – K. N. Toosi University of Technology (Instructed by: Dr. Naser Maghaddas Tafreshi)
- **Internship** (Summer 2008), Sazehaye Pol CO., Tehran, Iran.
  - Controlled the structural drawings based on the original design, and developed at least 15% of accuracy
  - Estimated the required steel for different projects under the supervision of senior structural engineer
  - Collected and consolidated daily reports from different construction teams working in other cities

Computer Skills

- Revit
- GEO-STUDIO
- AUTOCAD
- SAFE
- ABAQUS
- ETABS
- MATLAB
- SAP
- Microsoft Office Suite (Access, Excel, FrontPage, PowerPoint, Visio, Word)

PROFESSIONAL ACTIVITIES

- Student Member of American Society of Civil Engineering (ASCE)
- Student Member of Computational Geotechnics, Geo-Institute of ASCE
- Reviewer of “Journal of Environmental Chemical Engineering,” 2015- present
- Registered in Civil Engineer committee of Sharif University of Tehran, Iran, 2009- present

HONORS AND AWARDS

- Nominated for outstanding Ph.D. student– University of Louisville - (2015 – 2016)
- Selected Ph.D. student – Department of Civil & Environmental Engineering – University of Louisville - (2015 – 2016)
- The Geosynthetic Institute Fellowship – Geosynthetics Institute – (2015 – 2016)
- Graduate Student Council Scholarship – University of Louisville – Spring 2014
- Grosscurth Scholarship – University of Louisville – (2013 – 2015)

ADDITIONAL RESEARCH PROJECTS

- Investigation on interlocking effect on bending plate
- Numerical modeling of Escherichia Coli (E.Coli) propagation in soil
- Numerical modeling of Geogrid-reinforced rail tracks
- Physical modeling of pile-soil-pile interaction

PUBLICATIONS

- **Javadi, S.,** Abonoori, A.(2011). “Numerical and analytical solutions of partial differential equations.” In the Persian language. BOOK ISBN No. 978-964-04-7735-9.
- **Javadi, S.**, Shabanzad, H.(2011). “Principals of Geosynthetics Engineering.”In the Persian language. BOOK ISBN No. 978-964-04-7736-6.
- **Sadra Javadi**, Seyed Naser Moghaddas Tafreshi “Laboratory investigation of the uplift behavior of belled piles in reinforced sand.” 3rd International Conference on New Developments in Soil Mechanics and Geotechnical Engineering, 28-30 June 2012, Near East University, Nicosia, North Cyprus.
- Boudaghpour, S., Javadi, S., Ebrahimi, M.,“Application of Prefabricated Materials in Building Construction on the basis of Green Construction Approaches in order to Improve Construction Safety and Decrease Adverse Environmental Effects.” Accepted for oral presentation at 2nd National Congress on Building Safety (Design, Building, Operation), Iran, November 2010
- Boudaghpour, S., Javadi, S., Ebrahimi, M., “Air Pollution Forecasting of Tehran’s District 12 by Using Artificial Intelligence Neural Network Software”. Accepted for oral presentation at 6th National Congress on Civil Engineering, Iran, April 2011.
- Moghaddas Tafreshi, S., Javadi, S., & Dawson, A. R. (2014, June). Influence of geocell reinforcement on the uplift response of belled piles. Acta Geotechnica, Volume 9 (Issue3), 513-528.
- Javadi, S., Abdollahian, S., Ghavami, M., Rockaway, T., Zhao, Q., (2016) “Effectiveness of heavy metal removal in Urban Permeable Pavement Systems.” Accepted for publication and presentation in ASCE, GEO-CHICAGO August 14 – 18 2016.
- Ghavami, M., Javadi, S., Zhao, Q., (2016) “Laboratory Characterization of Saturated Conductivities of Compacted Clay- Organobentonite mixtures.” Accepted for publication and presentation in ASCE, GEO-CHICAGO August 14 – 18 2016.
- Javadi, S., Ghavami, M., Zhao, Q., Bate. B, S., (2016) “Advection and Retardation of non-polar contaminants in Compacted Clay Barrier material with Organoclay amendment,” under review in Journal of Applied Clay Science.
- Javadi, S., Ghavami, M., Zhao, Q., (2017) “Sorption and transport of benzene through reactive geosynthetic clay liner (GCL).” Submitted to ASCE, Geotechnical Frontiers March 12 – 15 2017.
- Shang, H., Javadi, S., Zhao, Q., (2017) “Organic surfactant modified zeolite as permeable reactive barrier component-a laboratory study.” Submitted to ASCE, Geotechnical Frontiers March 12 – 15 2017.

- Ghavami, M., Zhao, Q., Jangam, J. S. D., Jasinski, J. B, Saraei, N., Javadi, S., (2016) “Change of Organobentonite Interlayer Microstructure Induced by Sorption of Aromatic Hydrocarbon and Petroleum Hydrocarbons – A Combined Study of Laboratory Characterization and Molecular Dynamics Simulations”, under review in Journal of Langmuir.
- Ghasemzade, H., Abdollahian, S., Shabanzad, H., Javadi, S., (2016) “Experimental investigation on the effect of added fractions of favorable minerals on the transport of E. coli in saturated porous media”, under review in Journal of Contaminant Hydrology.
- Ghavami, M., Mohd Nayan, K., A., Kadir, M., I., Javadi, S., (2016) “Determination of Allowable Bearing Capacity of Shallow Foundation Using a Modified Hyperbolic Stress-Strain Model,” under review in European Journal of Environmental and Civil Engineering.