

An experimental investigation into the utilisation of organoclay-amended bentonite as a barrier material for waste containment applications

A thesis submitted in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

by

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November 2024

Dedicated to

My Parents

Roy C J & Ponnamma Roy

and

My Husband

Christy K Benny

Declaration

This is to certify that the work contained in this thesis entitled "**An experimental investigation into the utilisation of organoclay-amended bentonite as a barrier material for waste containment applications**" is original and has been carried out by myself and under the supervision of Dr. Anil Kumar Mishra in the Department of Civil Engineering, Indian Institute of Technology, Guwahati, Assam, India. The work reported herein has not been submitted to any other Institute for any degree or diploma. I have given due credit to the people wherever applicable by citing them in the text of the thesis and giving their details in the references.

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CERTIFICATE

This is to certify that the thesis entitled "**An experimental investigation into the utilisation of organoclay-amended bentonite as a barrier material for waste containment applications**", submitted by Ms. Riya Roy (186104107), a research scholar in the Department of Civil Engineering, Indian Institute of Technology, Guwahati, for the award of the degree of Doctor of Philosophy, is a record of an original research work carried out by her under my supervision and guidance. The thesis has fulfilled all requirements as per the institute's regulations and has reached the standard needed for submission. The results embodied in this thesis have not been submitted to any other University or Institute for the award of any degree or diploma.

Date: 30-11-2024

Place: IIT Guwahati



Dr. Anil Kumar Mishra

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Date:

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ABSTRACT

The incorporation of a hydraulic barrier system is indispensable while designing an engineered waste containment facility to avert environmental pollution resulting from hazardous and toxic waste constituents. Bentonite is a widely adopted hydraulic barrier material owing to its distinct characteristics, such as high swelling capacity, extremely low hydraulic conductivity, and high sorption capacity. However, the long-term barrier performance of bentonite liners can be compromised by the permeation of chemicals from the waste. As a consequence, harmful contaminants from the leachate percolate through the failed liner and eventually contaminate the surrounding ecosystem. To enhance the barrier performance and reduce chemical sensitivity, alternative materials should be explored and utilised as amendments to conventional bentonite. Organoclays offer a promising solution due to their superior sorption capabilities and improved hydraulic performance in the presence of organic pollutants.

In this study, commercially available organoclays were utilised as an amendment to Indian bentonite in a 10:90 ratio to evaluate their barrier performance when in contact with various chemicals. The sorption performance of both bentonite and organoclay was initially assessed for their ability to retain heavy metals and phenol. A comprehensive investigation of the geotechnical properties of bentonite and organoclay-amended bentonite (BOC) was conducted in the presence of various leachate constituents to comprehend their chemical sensitivity. Key parameters, such as plasticity, free swelling, swell potential, swell pressure, hydraulic conductivity, consolidation parameters and compressibility characteristics, were evaluated under different concentrations of inorganic salts (NaCl and CaCl₂), heavy metals (cationic: Pb²⁺ and Zn²⁺, anionic: Cr(VI)) and organic pollutants (acetone and phenol).

The results indicate that both clays exhibited superior sorption efficiencies for lead ions. Bentonite demonstrated excellent sorption for cationic heavy metals but was less effective in removing phenol and anionic heavy metal Cr(VI). Conversely, organoclay exhibited excellent removal efficiencies for phenol and Cr(VI), along with a good sorption performance for Zn²⁺. In addition, the research outcomes indicated that the liquid limit, free swelling, swell potential, swell pressure, coefficient of volume change, time for 90% consolidation, and compression index of both bentonite and BOC were found to decline as the concentration of inorganic salts and heavy metals increased. An increase in coefficient of consolidation and hydraulic conductivity was also noted, but none of the samples surpassed the limiting hydraulic conductivity criteria of 10⁻⁹ m/s suggested for the hydraulic barriers. The bentonite samples were substantially affected by divalent cations (Ca²⁺, Pb²⁺ and Zn²⁺), whereas monovalent Na⁺

ions from NaCl and K^+ ions from $K_2Cr_2O_7$ had a relatively lesser impact. Nevertheless, the impact of the pore fluid characteristics, including valency and concentration of inorganic salts and heavy metals, on the geotechnical properties of BOC was less pronounced compared to bentonite samples, suggesting the lower chemical sensitivity of BOC.

Bentonite subjected to the permeation of organic fluids exhibited similar deterioration in barrier performance as observed in inorganic salts and heavy metals. However, in BOC, the swelling, compressibility properties, time for 90% consolidation and coefficient of volume change initially decreased at low organic concentrations and then increased as the concentration exceeded 5%. Additionally, the hydraulic conductivity and coefficient of consolidation initially increased and later decreased at higher organic concentrations. This variation was more pronounced with phenol as the permeant fluid than acetone, owing to the greater interaction between phenol and the organoclay fraction in BOC. The decreased permeability in the presence of organic contaminants and the reduced chemical sensitivity with inorganic pollutants indicate that BOC could function as a more efficient hydraulic barrier in waste containment systems that have significant levels of both organic and inorganic chemicals.

Keywords: Bentonite; Organoclay; Hydraulic barrier; Inorganic Salts; Heavy Metals; Phenol; Leachate; Adsorption; Diffuse Double Layer; Swell Behaviour; Hydraulic Conductivity; Compressibility.

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ABBREVIATIONS

SWM	Solid Waste Management
MSW	Municipal Solid Waste
DGR	Deep Geological Repository
UST	Underground Storage Tank
LCS	Leakage Collection System
LDS	Leakage Detection System
PRB	Permeable Reactive Barrier
CCL	Compacted Clay Liner
GCL	Geosynthetic Clay Liner
DDL	Diffused Double Layer
RMD	Relative Abundance of Monovalent And Divalent Cations
CEC	Cation Exchange Capacity
DPH-GCL	Dense-Prehydrated Geosynthetic Clay Liner
MSB	Multi-Swellable Bentonite
KB	Kaolin-Bentonite Mix
SHMP	Sodium Hexametaphosphate
MIP	Mercury Intrusion Porosimetry
SEM	Scanning Electron Microscopy
BET	Brunauer-Emmett-Teller Method
PAA	Sodium Polyacrylate
CMC	Carboxymethyl Cellulose
SB	Sand-Bentonite
QAC	Quaternary Ammonium Cations
HDTMA	Hexadecyl Trimethyl Ammonium Bromide
DODMA	Dimethyl Distearyl Ammonium Bromide
BTEA	Benzyl Triethylammonium
TMA	Tetramethylammonium
PAH	Polycyclic Aromatic Hydrocarbons
NAPL	Non-Aqueous Phase Liquids
BTEX	Benzene, Toluene, Ethylbenzene, And Xylene
IOC	Inorganic-Organic Hybrid Clay
TMA	Tetramethylammonium
DTMA	Dodecyl Trimethylammonium
PAH	Polycyclic Aromatic Hydrocarbons
TCLP	Toxicity Characteristic Leaching Procedure
UCS	Unconfined Compressive Strength
BPA	Bisphenol A
APS	3-Aminopropyltriethoxysilane
AEAPS	3,2-Aminoethylaminopropyltrimethoxysilane
RSM	Response Surface Methodology
BOC	10:90 Organoclay Amended Bentonite
B	Bentonite

EGME	Ethylene Glycol Monoethyl Ether
MDD	Maximum Dry Density
OMC	Optimum Moisture Content
XRD	X-Ray Diffraction
FTIR	Fourier Transform Infrared Spectroscopy
XRF	X-Ray Fluorescence
FESEM	Field Emission Scanning Electron Microscope
AAS	Atomic Adsorption Spectrophotometer
EDS	Energy Dispersive X-Ray Spectroscopy
LL	Liquid Limit
FSI	Free Swell Index
USEPA	US Environmental Protection Agency
ASTM	American Society for Testing and Materials
rpm	Revolutions per minute
ppm	Parts per million
mL	Milli-Litre
mg	Milli-gram
N	Normality
kg	Kilogram
DI water	Deionised water

NOTATIONS

h	hour
k	Hydraulic conductivity
G	Specific gravity
ΔH_s	Change in sample thickness
Δe_s	Change in void ratio
H_f	Final height of soil sample corresponding to each load increment
H_i	Initial height of soil sample at particular load increment
e_i	Initial void ratio of the soil sample corresponding to each load increment
$\Delta \sigma$	Change in load increment or change in effective stress
m_v	Coefficient of volume change
t_{90}	Time for 90% consolidation
T_v	Time factor for 90% consolidation
H_{dp}	Maximum drainage path for 90% consolidation
e_1	Void ratios corresponding to the effective stress σ_1
e_2	Void ratios corresponding to the effective stress σ_2
c_v	Coefficient of consolidation
k	Coefficient of permeability or hydraulic conductivity
γ_w	Unit weight of the pore fluid
ΔH_T	Total change in sample thickness at the end of the swelling
C_c	Compression index
σ_y	Yield stress
t_{is}	Time taken for completing initial swelling
t_{ps}	Time taken for completing primary swelling
H_o	Initial height of the soil sample
e_o	Initial void ratio of the soil sample
q_u	Unconfined compressive strength
q_e	Sorbed amount per unit mass of sorbent
C_e	Final concentration of heavy metals after adsorption
V_L	Volume of heavy metal solution
C_i	Initial concentration of heavy metals
m_s	Adsorbent mass used for the experiment
ϵ	Dielectric constant
$\text{\AA}$	Angstrom
μm	Micrometer
T	Temperature
E	Permittivity of medium
E_0	Permittivity of vacuum
K	Boltzmann constant
v	Valence of ions
e	Elementary electric charge
n_0	Concentration of ions
σ'	Effective consolidation stress

CHAPTER 1

INTRODUCTION

1.1 General

The uncontrolled generation of waste due to increasing populations, industrialisation, and urbanisation, coupled with unscientific waste management, has become a critical issue in many developing countries, including India. At engineered waste containment facilities such as landfills, tailing impoundments, and nuclear disposal facilities, hydraulic barriers are essential to safeguard the surrounding soil and environment from pollutants percolating from the waste. Leachate, a highly toxic liquid generated from waste, contains a diverse range of contaminants, including hazardous heavy metals and organic pollutants, resulting from its heterogeneous composition. If this highly polluted leachate infiltrates through a failed hydraulic barrier system, it can pose a significant global public health risk, with severe consequences for humans and other living organisms. Thus, ensuring the integrity and performance of these barriers is essential for mitigating the environmental and health risks associated with waste leachate.

Bentonite is commonly used as a barrier material, either as a component in compacted clay liners or in geosynthetic clay liners, to reduce the advection and mass transport of contaminant flow (He et al., 2022; Amadia and Odededeb, 2021; Khalid et al., 2019; Naka et al., 2019). The primary advantages of the bentonite-based barriers include low hydraulic conductivity, reliable performance, effective removal of cationic heavy metals, and relatively low cost (Egloffstein, 2020; Wang et al., 2024). However, the chemical incompatibility between bentonite barriers and leachate constituents can result in shrinkage and crack formation, leading to a rise in hydraulic conductivity (Ray et al., 2022; Özçoban et al., 2022; Du et al., 2015). Additionally, the mass flux of organic contaminants is higher due to the non-interactive nature of conventional bentonite (Javadi et al., 2017). Heavy metal ions, inorganic alkali metal ions, and organics present in the leachate can affect the pore fluid characteristics, causing diffuse double layer (DDL) contraction and consequently impairing the hydraulic barrier performance. To mitigate the chemical sensitivity of bentonite, several natural or engineered materials can be adopted as amendments to enhance the barrier performance of conventional bentonite liners (Yang et al., 2022; Zhao et al., 2017; Katsumi et al., 2008).

Organoclay is one such alternative additive, proven to be an effective sorbent and barrier amendment under various organic contaminants (Lo and Mak, 1998; Lorenzetti et al., 2005;

Lee et al., 2012; Ghavami et al., 2017). Organoclay is a modified clay produced by replacing inherent interlayer metal cations in clay with organic molecules, thereby improving the affinity towards organic pollutants. Organoclay exhibits enhanced hydraulic conductivity, high swelling tendency, high sorptive capacity, high plasticity, and increased strength and stiffness when in contact with organic liquids, especially non-polar or less polar organic contaminants (Zhao et al., 2017). Researchers have suggested several applications for organoclays, including but not limited to (i) hydraulic barrier systems (landfill clay liner, vertical cut-off wall. Slurry wall and cover systems), (ii) secondary compound liner in industrial waste containment facilities, (iii) secondary barrier for underground storage tanks containing fuels and organic solutions (Sreedharan and Sivapullaiah, 2017; Boldt-Leppin et al., 1995) (iv) treatment of wastewater with high organic pollutants (Wang et al., 2021; Moshe and Rytwo, 2018).

A few studies have utilised organoclay as an amendment to clay barriers and assessed the sorption behaviour and barrier performance of organoclay-based liners against organic contaminants (Lo, 2001; Benson et al., 2015; Gitipour et al., 2015; Javadi et al., 2017; Xie et al., 2023). However, the performance of such liners in the presence of heavy metals and inorganic salts remains under-studied. Similarly, the hydraulic and sorption performance of bentonite in the presence of various inorganic and organic solutions have also been extensively studied (Ray et al., 2021; Jadda and Bag, 2020; He et al., 2019; Dutta and Mishra, 2017; Goodarzi et al., 2016; Siddiqua et al., 2011; Alawaji, 1999). Prior research has demonstrated superior sorption capacities of bentonite for cationic heavy metals and better sorption efficiencies of organoclay for organic pollutants (Gupt et al., 2020; Padilla-Ortega et al., 2013; Su et al., 2011). Since leachate generates a wide variety of inorganic elements, heavy metals and organic pollutants at high concentrations, a combination of bentonite and organoclay as a barrier may effectively remove a broad range of contaminants without compromising the hydraulic performance.

1.2 Motivation and the broad objective of the study

A comprehensive understanding of the geochemical and physical behaviour of organoclay-amended bentonite is necessary for its effective use as an amendment to conventional bentonite barriers. As stated in the above section, there are several existing knowledge gaps in adopting bentonite-organoclay mixtures in conventional barriers. With this in view, the proposed study aims to address the existing research gaps by investigating various geochemical and physical properties of organoclay-amended bentonite and comparing its performance with conventional

bentonite under the influence of various leachate constituents, including inorganic salts, heavy metals, and organic pollutants. Key parameters examined include hydraulic conductivity, swelling behaviour, sorption performance, compressibility, and consolidation behaviour. The fundamental mechanisms behind these variations are also explored with the aid of microstructural investigations.

The main objectives that have led to the inception of this research work can be broadly classified as (1) analysing the potential of commercially available clays (bentonite and organoclay) for application in hydraulic barriers by investigating their contaminant retention behaviour. (2) exploring the chemical sensitivity of bentonite barriers under various organic and inorganic contaminants. (3) comparing the hydraulic barrier performance of proposed organoclay-amended bentonite with conventional bentonite under the influence of inorganic salts, heavy metals and organic fluids for potential applications in waste containment. To achieve these objectives, the present study will thoroughly investigate the physical and geochemical characteristics of both bentonite and organoclay-amended bentonite.

1.3 Organisation of the Thesis

The thesis has been arranged into eight chapters. **Chapter 1** presents a general overview of the thesis, the motivation behind this research work, and their importance. **Chapter 2** reviews the literature comprehensively on background research and identifies the gap areas. The objective and scope of the study are addressed based on the research gap. **Chapter 3** presents the details of the materials and methodology adopted in the study to meet the research objectives. Furthermore, the physical characterisation of the parent materials procured commercially from the Indian market was also analysed in detail. **Chapter 4** displays a detailed investigation of the sorption characteristics of parent materials. The study involves the adsorption of commonly found leachate pollutants, including heavy metals and an organic contaminant (phenol). **Chapter 5** analyses the effect of organoclay addition on the physical, hydraulic and mechanical properties of compacted bentonite. This chapter also investigates the impact of inorganic salts (NaCl and CaCl₂) at varied concentrations (0.1 N and 1 N) on the hydraulic barrier performance of bentonite and organoclay-amended bentonite. The basic geotechnical properties such as liquid limit, free swelling, swell pressure, swell potential, compression index, consolidation parameters – time for 90% consolidation, coefficient of consolidation and coefficient of volume change of bentonite and organoclay-amended bentonite were studied in detail. The analysis was aided by microstructural investigation as

well. **Chapter 6** examines the effect of cationic and anionic heavy metals (Zn^{2+} , Pb^{2+} and $Cr(VI)$) at varied concentrations (100, 500 and 1000 mg/L) on the plasticity, swelling, hydraulic and mechanical behaviour of bentonite and organoclay-amended bentonite. This chapter also provides a detailed study of the microstructural investigation of consolidated samples. **Chapter 7** studies the influence of organic solutions (acetone and phenol) at varied concentrations (5, 10 and 20%) on the physical, hydraulic and mechanical characteristics of bentonite and organoclay-amended bentonite. **Chapter 8** summarises the major findings and concluding remarks of the study and the scope for future investigation.



CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 General

Environmental challenges and public health problems are important issues associated with increased waste generation and inadequate waste collection, treatment, and disposal. Systematic and scientific management of solid waste has been identified as one of the requirements for sustainable development. The increasing population, rapidly varying waste characterisation and generation patterns, and growing urbanisation and industrialisation are crucial reasons for the need for solid waste and hazardous waste management. Over the years, many waste management technologies have been developed, including incineration, pyrolysis, landfilling, marine dumping, anaerobic digestion, and bioreactor landfills. Among the various methods, landfilling is considered the widely adopted and cheapest solid waste management (SWM) method in developing countries (Swati, 2018; Agamuthu, 2013). Landfilling is advantageous over alternative methods, such as incineration and recycling, due to its cost-effectiveness and less labour-intensive procedures. Additionally, a centralised landfill operation has the potential to generate revenues by harnessing landfill gas and leachate for energy generation purposes. This multifaceted approach not only proves economically advantageous but also aligns with sustainability objectives, utilising waste by-products to contribute to energy production within the landfill facility. However, the environmental impact posed by the emission of toxic substances, greenhouse gases, and leakage of leachate from landfills is of serious concern.

Landfills can be broadly classified into three: open dumping, controlled dumps, and sanitary landfills. Well-constructed and maintained sanitary landfills are safer than open dumping sites, but they can eventually fill up and may probably start to leak after many years. Therefore, waste should be properly reused, recycled, and treated before dumping it in sanitary landfills for its long-term performance and to reduce the adverse impact on human health and the environment. Despite the various challenges in their planning and construction, sanitary landfills with engineered barriers are considered one of the better waste disposal options for India's urban spaces. It not only allows the safe disposal of MSW on land but also protects ground and surface water from pollution and avoids air emissions, wind-blown litter, odour, fire hazards, problems with animals, birds, and other pests/rodents, and reduces greenhouse gas emissions and slope instability issues. The barriers may be placed at the bottom, top (as cover),

and/or sides (as lateral barriers or walls) of the waste containment systems, and they usually make use of a variety of materials and mechanisms (advection, diffusion, sorption, etc.) to control contaminant transport. Barriers are generally made of natural (e.g., soil, clay) and/or synthetic materials, such as polymeric materials (e.g., geomembranes, geosynthetic clay liners), usually arranged in layers.

2.2 The current waste management scenario in India

Despite significant social, economic, and environmental development, SWM systems in India have remained relatively unchanged. Current SWM systems are inefficient, resulting in uncontrolled waste disposal, which poses significant risks to public health and the environment. Moreover, proper waste management practices contribute to economic growth by promoting resource recovery, recycling, and the development of waste-to-energy initiatives. Adherence to stringent environmental regulations is essential not only to avoid legal consequences but also to foster a positive global image that aligns with international sustainable development goals. In India, it is estimated that daily solid waste generation amounts to roughly 160,000 metric tonnes. Although approximately 95% of this waste is collected, only half undergoes proper treatment, and a mere 18% is disposed of in landfills (CPCB, 2021). Thus, a large portion of solid waste is dumped indiscriminately on the outskirts of towns or cities without any prior treatment. This unauthorised dumping and unscientific handling of municipal solid waste (MSW) lead to environmental pollution, causing a threat to human health and the environment. In an analogous manner, shallow surface disposal facilities or landfills also witness unscientific disposal of low-level radioactive wastes and hazardous wastes. As per the CPCB (2021), 1924 landfill sites have been identified in India, along with 305 landfills constructed, 341 in operation, and 126 in the planning and implementation stage. However, most of the existing landfills are already exhausted and overburdened by improper segregation, lack of treatment, and unauthorised dumping of daily waste disposal. Approximately 3,184 unscientific dumpsites have been identified in India. The inadequate waste management has led to significant environmental and public health concerns in major urban areas of India. In order to address these issues, it is necessary to either rehabilitate existing landfills or construct new engineered sanitary landfills.

2.3 Waste containment facilities

Waste containment facilities are storage facilities designed to securely contain and manage both hazardous and non-hazardous wastes. Properly designed, constructed and maintained waste containment facilities are essential for minimising the adverse effects of waste on human health and the environment. The primary objective of waste containment is to prevent the release of harmful liquid and gases generated from the contained waste into the environment, mitigating potential risks to public health and safeguarding ecosystems from pollution. Wastes generated can be broadly classified into three categories: municipal solid waste, industrial waste, and hazardous waste. Inside a waste containment facility such as a landfill, the rainwater percolated can react with waste constituents and generate a liquid called leachates. This leachate can contain hazardous components that are harmful to the environment if it reaches the surrounding soil and groundwater. In order to prevent this percolation, properly designed landfill liners are provided at the bottom and side of the waste containment facilities. Different waste containment facilities are designed based on the type of waste.

2.3.1 Municipal solid waste and hazardous waste landfills

Municipal solid waste and non-hazardous landfills are landfills that are designated to dispose of municipal solid waste from households and non-hazardous wastes from industries. However, some household items such as paints, cleaners/chemicals, motor oil, batteries and pesticides are not allowed to be disposed of in MSW landfills. Bioreactor landfill is one of the MSW landfill types that operates to transform and degrade organic waste rapidly. A typical cross-section of the MSW landfill is given in Fig. 2.1.

Industrial landfills are specifically engineered landfills to accommodate the disposal of commercial and institutional waste, collectively referred to as industrial waste. This category of waste, originating from commercial enterprises and institutions, constitutes a substantial proportion of solid waste, even in smaller cities and suburban areas. Two examples of industrial landfills include construction and demolition debris landfills and coal combustion residual landfills. Industrial wastes can be broadly classified into three categories: inert waste, non-hazardous waste, and hazardous waste. Inert wastes predominantly consist of demolition and construction debris, characterised by their lack of reactivity or potential harm. The remaining waste constituents are bifurcated into hazardous and non-hazardous categories, contingent upon their toxic contents. Non-hazardous fractions can be dumped in municipal solid waste landfills, whereas hazardous fractions end up in hazardous waste landfills.

Hazardous waste landfills are designed to accommodate hazardous wastes generated from various industrial activities. These wastes are not allowed to be disposed of in MSW landfills. One such example is polychlorinated biphenyl landfills. According to the US Environmental Protection Agency (USEPA), a waste can be classified as hazardous if it has any of the following characteristics – ignitability, reactivity, corrosivity and toxicity (USEPA, 1990). Hazardous wastes predominantly originate from heavy industries, including but not limited to iron and steel production, the dye industry, electronic manufacturing, and the scrap metal industry (Gupt et al., 2020). Like MSW landfills, hazardous landfills are also designed with proper liner systems, slurry trenches, leachate collection and treatment systems and cover systems. Proper design, monitoring practices, and adherence to regulatory requirements are essential to ensure the safe and effective operation of these facilities throughout their lifecycle.

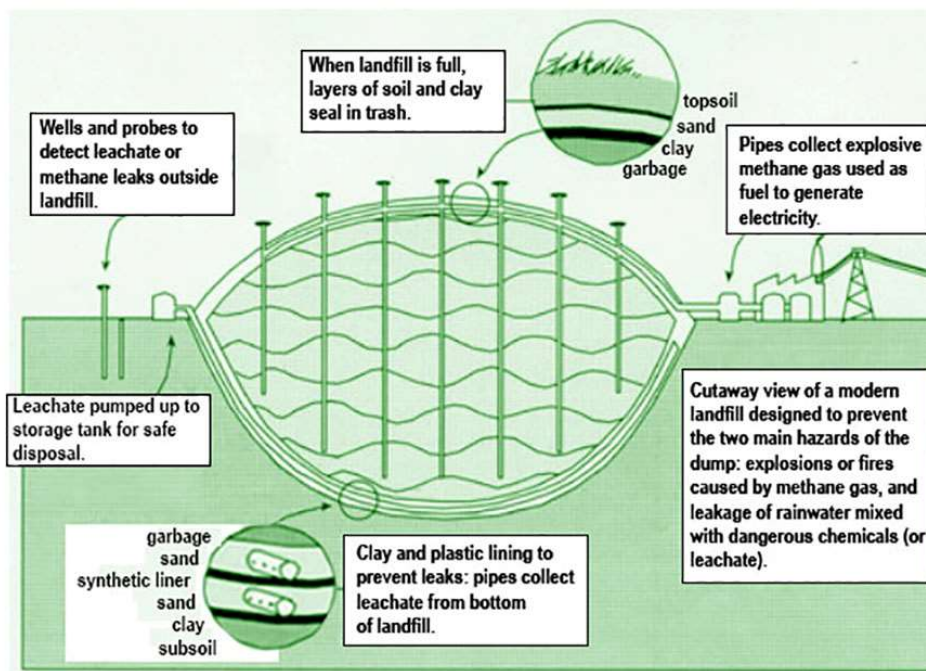


Fig. 2.1 Cross section of a municipal solid waste landfill (USEPA, 2017)

2.3.2 Tailings dams and surface impoundments

Tailing storage facilities are surface-retaining structures used to store and manage waste generated from the mining industries. Tailing dams, embankments, and surface impoundments are part of tailing storage facilities. They are used to manage and contain the residue (valueless mineral) from the mining process, known as tailings, which usually consist of fine ground rock, water, and harmful chemical effluents. Tailings dams can indeed be immense in size, comparable to lakes, with heights reaching up to 300 meters. The primary function of tailings

dams lies in the prolonged storage of tailings in a slurry state, facilitating the separation of water and solid components. Rapid settling of solid particles occurs, giving rise to a "tailing beach" where fine-grained particles migrate from the discharge point. Simultaneously, the separated slurry water moves away from the discharge point, forming a pond within the impoundment. The collected water may undergo disposal or re-utilisation, while the coarse waste material holds potential for application in dam construction. Proper waste containment barriers should be provided for the tailing dams and impoundments because many harmful heavy metals and organic pollutants may be associated with mining and milling wastes. As per the report from the Indian Bureau of Mines (1999), the potential contaminants associated with mining wastes are listed in Table 1.

Table 2.1 Potential contaminants present in the tailing facilities (Indian Bureau of Mines, 1999)

Ore category	Solid waste	Potential contaminants
Cu	Leach heaps and dumps	Pyrites
	Mine drainage tailings	Cu, Fe, Mg, Pb, Sn, Zn, As, pyrites pH, pyrites
Pb, Zn	Tailings	Pb, Zn, Cl, Cr, As, Cu, Ag, Mn, Sb
	Mine drainage	pH, pyrites, trace metals
Hg	Mine drainage	pH, pyrites, Ni
U-Ra-Vn (conventional mining method)	Waste rock	Ra, U, Th
	Mine water	Zn, Ra, U, Th
	Tailings	As, pH, NH ₃
Sb	Tailings	Pb, Zn
Rare earth metals, Pt, Sn	Tailings	Ti, Zr
Be	Tailings	Be, other metals
Au, Ag	Tailings	Cu, Pb, Zn, Hg, NaCN
Al	Red and brown muds	pH, Mn, Fe, Al
Fe	Tailings	pH, Fe
Ti, Zr	Tailings	pH, Fe, Ni, Zn
U (in-situ solution mining method)	Ore body	pH, U, Ra, gross NH ₃ , SO ₄ , Mn, dissolved metals
	Surface impoundment	U, Ra, NH ₃ , pH

Fig. 2.2 depicts the cross-section of a mine tailing storage facility showing different components. The incorporation of barrier systems constitutes a fundamental aspect in the design of tailing storage facilities. To effectively contain hazardous contaminants originating from tailings and associated fluids, it is imperative to employ highly efficient liners. Tailings, when in contact with external factors, may result in acid generation and metal mobilisation, which pose a serious threat to the environment. In order to ensure environmental protection, containment is generally provided in two stages – primary and secondary. The most common liner systems used are a single-composite liner system comprising a prepared foundation, low permeability soil layer (clay or GCL), geomembrane, and drainage layer and a double-composite liner system, where there is an additional secondary geomembrane and a leak collection layer. Compacted clay liners are generally utilised for the installation of liners. However, the vulnerability of clays to acids, bases and salts, along with the poor performance under seismic activity and the possibility of desiccation cracks, necessitates the need for better alternative liners. In addition to liners, embankment barriers such as grout curtains, cut-off trenches, and slurry walls are positioned beneath the impoundments, further enhancing the overall containment efficacy of tailing storage facilities.

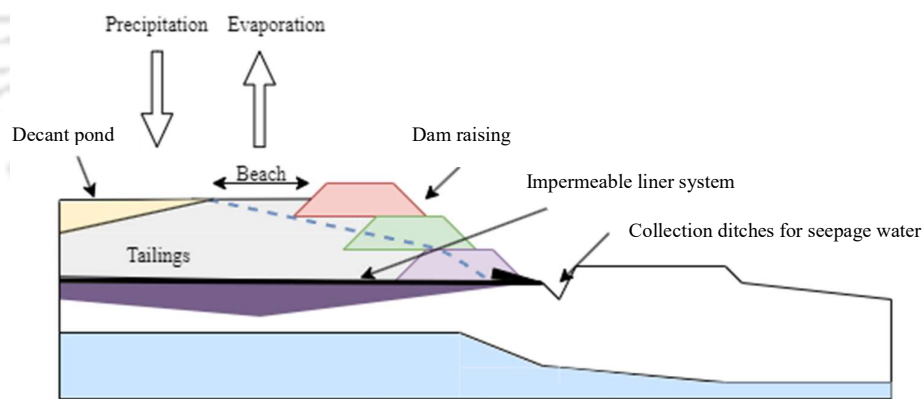


Fig. 2.2 Cross-section of tailings pond in a mine tailing storage facility (Tuomela et al., 2021)

2.3.3 Radioactive waste repositories

Nuclear wastes can be broadly divided into three levels: low level, moderate level, and high level. Since high-level radioactive waste contributes to 99% of the radioactivity, proper care should be given while handling and disposing of such wastes. Therefore, high-level radioactive wastes are disposed of in deep geological waste repositories (DGR) comprising multi-levels of engineered barrier systems. The deep geological repositories help in containing radioactive

waste until the waste decays to safe levels of radioactivity. Figure 2.3 represents the schematic representation of the deep geological repository. The engineered barrier systems in the waste repositories include a host rock and a buffer material, which encapsulates the waste canister. Compacted bentonite or bentonite-sand mixtures are preferred as buffer material due to their favourable thermo-hydro-mechanical performance. Bentonites are prepared as compacted bricks and placed in layers around the radioactive waste canister. This compacted bentonite will be able to swell when in contact with groundwater and provide buffering functions (Du et al., 2022). According to Siddiqua et al. (2011), the composite barrier systems may include five clay-based materials such as highly compacted bentonite, bentonite-sand buffer, dense backfill, light backfill and gap fill.

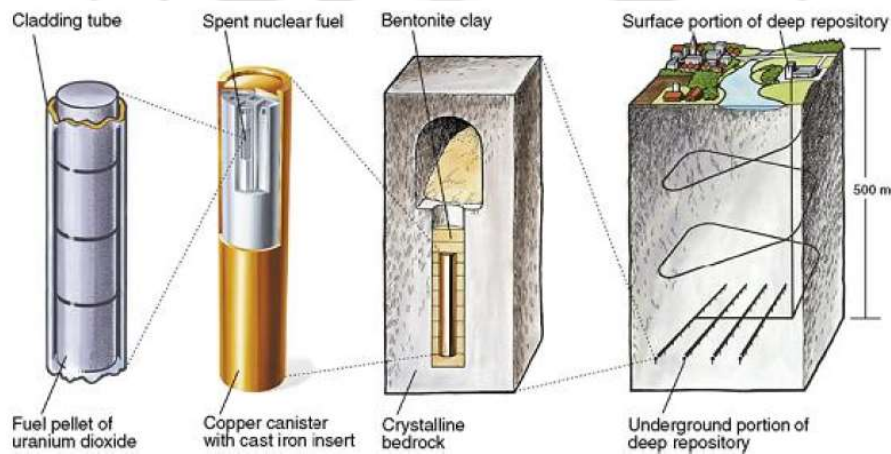


Fig. 2.3 Schematic representation of deep geological repository (King, 2007)

2.3.4 Underground storage tanks

An underground storage tank (UST) system comprises a tank or a combination of tanks along with connected underground piping, with at least 10 per cent of their combined volume situated below the ground surface. The comprehensive UST system encompasses the tank, the interconnected subterranean piping, underground ancillary equipment, and the containment systems designed to confine potential releases or leaks. These USTs are used to store petroleum products and other hazardous substances, which can pose a serious threat to contaminate groundwater and soil if leaks, spills, or overfills occur. Furthermore, fumes and vapours generated have the potential to migrate underground, accumulating in confined spaces such as basements, utility vaults, and parking garages, thereby presenting a significant risk of explosion, fire, and adverse health effects such as asphyxiation. Several environmental protection agencies, such as USEPA, demanded the use of secondary containment in addition

to primary containment for all USTs (Lo and Yang, 2001). Conventional clay liners are generally provided as secondary containment due to their specific hydraulic barrier properties. However, the efficiency of such liners under organic contaminants and petroleum products such as gasoline, petrol, etc., needs detailed investigation. Several researchers have suggested using geosynthetic clay liners, geomembranes, and modified clays to improve the barrier performance of clay liners (Lo, 2001; Moon et al., 2007).

2.4 Leachate and leachate constituents

The management of leachate is a pivotal element in the design and operation of sanitary landfills. Leachate is a hazardous liquid by-product generated when rainfall infiltrates through the wastes and during the decomposition of waste materials within landfills. The leachate naturally migrates towards the landfill's base, carrying potentially harmful contaminants in a soluble and suspended state. Impermeable liners are strategically implemented to mitigate the risk of leachate escaping into the surrounding surface or groundwater. These liners play a crucial role in minimising the likelihood of environmental contamination and promoting the safe containment of leachate within the landfill structure. Depending on the landfill type and other environmental factors, the leachate has a highly variable composition and varied physico-chemical characteristics. Leachates mainly consist of dissolved organic matter, ammonia, inorganic macro compounds, heavy metals and organic contaminants (Nanda and Berruti, 2021). The origin of these contaminants might be personal care products, household chemicals, industrial chemicals, and pharmaceuticals. The mixing and movement of pollutants by percolating through the liners occurs through various mechanisms, including advection, dispersion and diffusion. As a result, soil and groundwater contamination can occur. Therefore, the generated leachate should be collected and treated at the landfill site using proper methods before disposal.

2.4.1 Inorganic elements

The inorganic macro elements in the leachate comprised sodium, potassium, calcium, magnesium, manganese, ammonium, chlorides, nitrates, sulphates and carbonate compounds. The presence, composition and concentrations of these compounds depend on the waste decomposition phase and microbial activity. In addition to this, various factors such as climatic conditions, waste structure, absence or existence of hydrogen and oxygen gases, construction of cover material and retention period of wastes in landfills also affect leachate generation (El-Saadony et al., 2023). The wastes having organic matter with high moisture content tend to

accelerate leachate production. Similarly, landfills in dry and hot areas produce less leachate, while tropical areas generate more leachate.

Literature reported that municipal solid waste leachate contains large concentrations of inorganic metal ions such as sodium (Na^+), potassium (K^+) and calcium (Ca^{2+}) cations relative to other cations in waste leachate (Barone, 1993; Alawaji, 1999). Furthermore, hyper-saline leachates have been reported to be percolated from the mining and mineral processing industrial wastes. Other industrial wastes, abandoned sites, accidental spills, and seawater intrusion can all contribute to salt release and finally affect the clay barriers (Yang et al., 2022). Additionally, in the long-term operation of DGR, buffer materials may be exposed to various electrolyte pore fluids generated due to the degradation of concrete walls or percolation of saline groundwater. The salinity of groundwater could reach 2.0 M or higher based on the field conditions (Arcos et al., 2006; Zhang et al., 2016). The presence of high salinities can pose significant damage to the barrier performance of DGR. It can corrode the repository materials, adversely affect the swelling ability of buffer and backfill, and make the geochemical reactions complex (Siddiqua et al., 2011). Therefore, the effect of high electrolyte solutions such as NaCl and CaCl_2 on the hydro-mechanical performance of compacted bentonite-based barrier is essential.

2.4.2 Heavy metals

Heavy metals such as lead, copper, zinc, cadmium, chromium and nickel are generally present in landfill leachates. Some of these heavy metals are present in low concentrations, but depending on the type of industry and toxicity of hazardous industrial waste, some metals can be detected at high concentrations as well. Thus, elevated concentrations of heavy metal cations may be encountered in various environmental contexts, such as municipal solid waste leachates, hazardous landfills, or tailing impoundments. These concentrations can arise through processes including the percolation of acid rain through waste materials or through in situ generation facilitated by bacteriological activities (Jullien et al., 2002).

Heavy metals are naturally occurring elements in the earth, but most of the environmental contamination is due to various anthropogenic activities (Bedi, 2023; Mukherjee et al., 2020; Njati and Maguta, 2019). Industrial sectors, including chemical manufacturing, petroleum and coal manufacturing, nuclear facilities, waste treatment and disposal sectors, contribute to the majority of hazardous waste globally (Du et al., 2022; Goswami et al., 2017). A large quantity of this hazardous waste containing heavy metals is getting disposed of unscientifically in

landfills, which contributes to the ecological imbalance and health hazards. Heavy metals such as Pb^{2+} , Cu^{2+} and Zn^{2+} are often encountered in MSW and hazardous waste leachates. These heavy metals pose extreme toxicity and are ubiquitous in mine tailings and hazardous wastes. The main sources of lead are batteries, construction, paints, medical equipment, and alloys. If lead enters the body of humans or organisms at quantities more than permissible limits, it can disrupt the metabolism and cause harmful effects on the organism. Copper is another heavy metal required in small amounts for enzyme activities, but it becomes harmful when present in larger quantities. Since copper doesn't break down naturally, it tends to stick to humus substances. This can lead to the movement of copper-loaded humus in water or the build-up of copper in soils by binding to particles. Industries such as agrochemicals, petroleum refining, smelting, brass manufacturing, and mining are probable sources of copper pollution. The presence of copper in high concentrations ($>5 \text{ mg/L}$) may lead to health issues like hemolysis, infections, and vomiting. It is also a very serious concern for the aquatic environment because of the adverse impact on marine life (Ray et al., 2020). Zinc is another crucial heavy metal required for physiological and biochemical functions if present in trace amounts. However, like other heavy metals, exceeding the permissible limit can result in toxicity. Some major sources of zinc contamination in the environment include industries like paints, galvanisation, plastics, and manufacturing of brass and bronze alloys, as well as cosmetics and pharmaceuticals. Other human activities such as mining, wood and metal coating, deodorant use, drug manufacturing, and battery production also contribute to elevated zinc exposure. Excessive exposure to zinc can result in various health problems, typically occurring through three pathways: inhalation, dermal exposure, and oral ingestion.

Chromium is one of the most dangerous, toxic, and highly mobile heavy metal contaminants, and it is ubiquitously found in industrial landfill leachates. The industries such as metallurgical, textile and paper manufacturing, refractory, chemical pigments, electroplating, wood preservation and tanning industries generate significant amounts of chromium-containing effluents and wastes (Rathnayake, 2017). It is a strong oxidising agent that is carcinogenic and mutagenic and diffuses quickly through soil and aquatic environments. Chromium exists in trivalent (Cr^{3+}) and hexavalent (Cr(VI)) states. Unlike other cationic heavy metals, the hexavalent chromium, Cr(VI) exists in an oxy-anionic form such as CrO_4^{2-} , HCrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ in aqueous solutions (Yang et al., 2021). The high concentration of such toxic heavy metals from hazardous waste landfills and tailing impoundments may percolate along

with other leachate constituents and can cause deleterious effects on the proper functioning of landfill barriers, resulting in groundwater contamination.

2.4.3 Organic contaminants

Organic chemicals serve as the cornerstone for various industries, including fuel refining, petrochemical complexes, plastics manufacturing, and the detergent industry. However, the inappropriate handling and accidents related to the use of organic chemicals can contribute to environmental contamination. Additionally, xenobiotic organic compounds such as hydrocarbons, halogenated hydrocarbons, phenols, and aromatic pesticides are also present in trace amounts in landfill leachates, especially in mining wastes and hazardous landfill leachates. Even though they are present in trace amounts, the impact of such contamination on the environment can't be neglected if they diffuse through the clay liners. Organic pollutants are primarily composed of hydrogen and carbon with smaller quantities of sulphur, chlorine, phosphorous and nitrogen. Anthropogenic activities can produce quantities of organic pollutants beyond their permissible limits. Literature showed the occurrence and release of xenobiotic organic contaminants from landfills during its service period (Kjeldsen et al., 2002).

Numerous studies have investigated the presence of xenobiotic organic compounds (XOCs) in landfill leachates, which encompass a range of aromatic hydrocarbons, phenols, chlorinated aliphatics, pesticides, and plasticisers (Varank et al., 2011). Among these compounds, phenol holds particular significance due to its role as a precursor in the synthesis of various organic compounds and its potential for toxicity (Boopathy, 1997). Moreover, phenol and its substituted derivatives are common transformation products of several pesticides. Several substituted phenols, including chlorophenols, nitrophenols, and cresols, have been identified as priority pollutants by regulatory bodies such as the USEPA (Boyd et al., 1983).

2.5 Components of Engineered Landfills

An engineered sanitary landfill necessitates the incorporation of essential components, including a liner system along the bottom and sides, a leachate removal system with associated treatment measures, groundwater monitoring, gas extraction facilities, and a cover system. The primary elements of a sanitary landfill are outlined below and illustrated in Fig. 2.4.

- (i) Bottom and side liners: One of the critical design components provided to restrain the percolation of waste components confined inside the landfills and to prevent the contamination of soil and groundwater. Highly impermeable liners placed at the bottom and side of the engineered landfills help separate and prevent the leakage of leachate. Generally, compacted clay liners are used as liners, along with or without geosynthetic materials.
- (ii) Cells: the area where waste is stored inside the landfills. The waste is dumped in thin layers compacted using heavy rollers and later covered with soil.
- (iii) Leachate collection systems: The leachate generated within the landfills is collected at the bottom by providing a slope to a low point called a sump. The collection system comprises a series of perforated pipes along with a layer of sand and gravel or geonets. Geonets are basically plastic net-like drainage blankets. The leachate thus collected will be pumped to tanks where it can be stored and treated.
- (iv) Gas monitoring and collection systems: During the decomposition process of waste in landfills, bacteria break down the waste materials in anaerobic conditions, resulting in the production of methane gas. A methane gas collection system is installed to harness this methane gas, allowing for its reuse. A landfill gas management system consists of two primary components: a gas collection system and a gas utilisation system. The gas collection system comprises pipes connecting collection wells, which extract gas under vacuum pressure generated by a central blower. While both vertical and horizontal wells can be employed, vertical wells are more commonly used. Landfill gas, if not managed properly, can be flared on-site, though this is not considered a beneficial application of this resource. Alternatively, beneficial energy recovery systems involve converting the gas into electricity or heat or transforming it into chemicals or fuels.
- (v) Stormwater drainage system: A network of ditches is employed to guide stormwater to designated zones referred to as stormwater management ponds. This design is aimed at decelerating the flow of runoff water or retaining it for a sufficient duration, facilitating the settling of suspended soil particles within the ponds. Common measures for controlling stormwater involve the construction of ditches, dikes, or culverts to redirect and manage the flow.
- (vi) Covers: Once the landfill reaches its designed height, a final cap/cover is installed to reduce the infiltration of rainwater, minimise waste dispersal, and facilitate long-term maintenance. A modern landfill cover is composed of multiple layers, each

serving a specific function. The final cover, arranged from top to bottom, includes vegetation and supporting soil, a filler and drainage layer, a hydraulic barrier, a foundation for the hydraulic barrier, and a gas control layer.

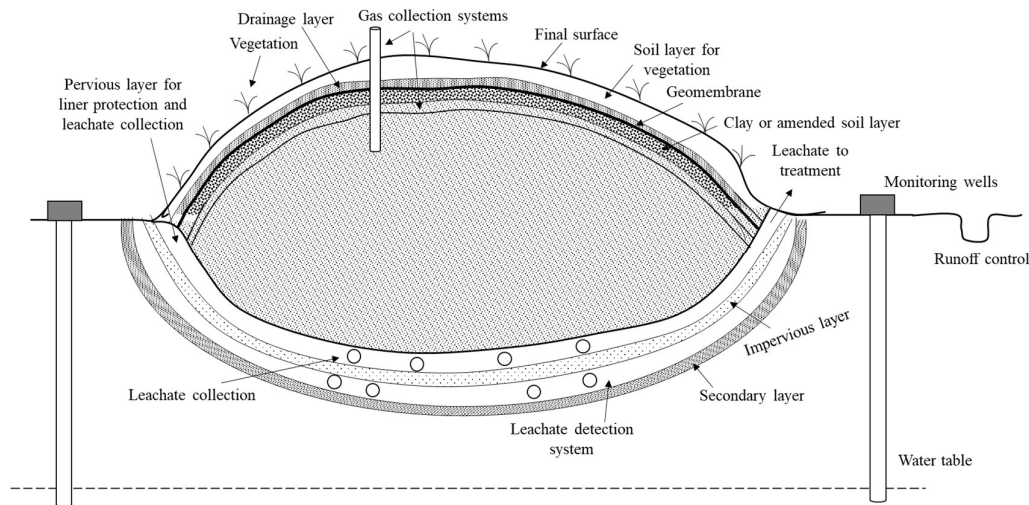


Fig. 2.4 Cross section of a sanitary landfill (Qrenawi, 2006)

2.6 Engineered barrier systems

Hydraulic barrier systems play a critical role in containing waste within the system, aiding in the attenuation of contaminants, and restricting/intercepting the movement of contaminants to prevent their reach into groundwater and surrounding soil. Examples of barrier systems include vertical cut-off walls and liners for waste disposal facilities such as landfills and tailing impoundments, as well as spill protection around underground storage tanks. Depending on the waste type, topography, local conditions and environmental regulations, different barrier configurations such as single-liner systems, double-liner systems, and composite liner systems can be provided. To prevent the advective and diffusive transport of contaminants, liners are generally provided at the bottom and sides of the landfill. In addition to restricting contaminants, the liners also help provide structural support to landfills. While designing, suitable landfill liner material should be selected to ensure pollutant attenuation, structural durability and leachate percolation prevention.

2.6.1 Landfill liners

Depending on the type and composition of waste and the potential threat posed by the waste on the environment, different types of liner systems can be provided. Liners may be classified as single-liners, double-liners and composite liners. Compacted clays, in combination with or

without geosynthetics, are generally used as liner material. Composite barrier systems are comprised of a geomembrane overlying either a compacted soil liner (CSL), geosynthetic clay liner (GCL) or both. Fluet et al. (1992) classified liner systems for landfills into five categories (as illustrated in Fig. 2.5) which are described below.

(i) Single liner systems

A single-liner system consists of only one liner with a leachate collection system (LCS) above the liner. The liner may consist of either a geomembrane or low-permeable soil. Single liners are sometimes used in landfills designed to hold construction and demolition debris.

(ii) Single composite systems

A liner system consisting of two or more different, low-permeable materials placed in direct contact with each other is termed a single composite liner system. The advantages of both geomembranes and low-permeable soils can be utilised in this system. It also comprises an LCS above the composite liner.

(iii) Double liner systems

A double liner consists of two liners with an intervening drainage layer, called a leakage detection system (LDS), placed between the two liners and an LCS at the top. High-permeable materials such as geonets and gravels are used for leachate detection systems. The drainage layer is used to detect, collect, and remove leachate between the two liners. Double-liner systems are used in some municipal solid waste landfills and in hazardous waste landfills.

(iv) Double liner with bottom composite liner systems

A double-liner system with a bottom composite liner consists of a single liner at the top and a composite liner at the bottom. It also includes an LCS above the top liner and an LDS between the liners. A composite liner combines a geomembrane with a low-permeable soil liner. Composite-liner systems are more effective at limiting leachate migration into the subsoil than either a clay liner or a single geomembrane layer. These types of liners are required in hazardous waste landfills.

(v) Double composite liner systems

Double composite liner systems consist of composite liners as top and bottom liners. Both LCS and LDS exist above the top liner and between the liners, respectively. Such systems are usually considered in situations where a high level of environmental protection is required.

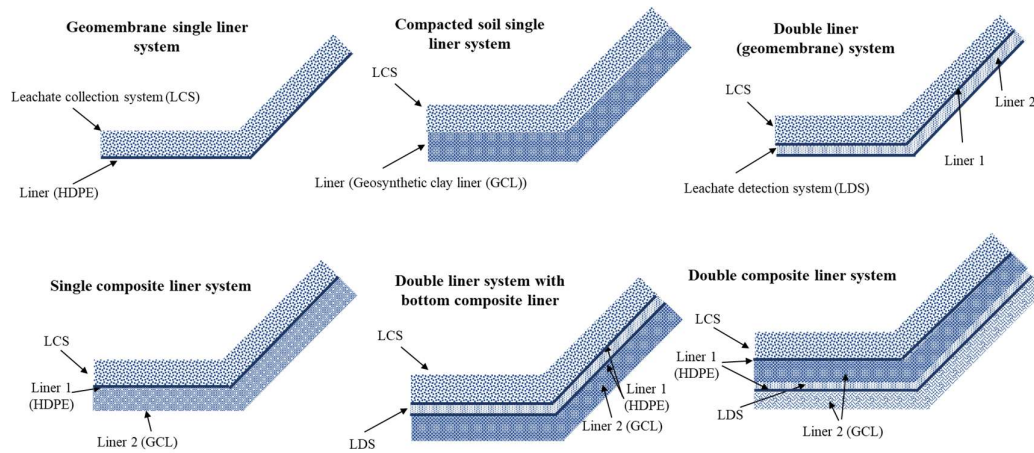


Fig. 2.5 Different types of liner systems (Fluet et al., 1992)

2.6.2 Vertical cut-off walls (Slurry cut-off walls and permeable reactive barriers)

Vertical cut-off walls are hydraulic barriers provided below the ground level to restrict the horizontal movement of groundwater and contaminants. If the objective is to prevent contamination and reroute the flow of groundwater, slurry cut-off walls can be provided, while if the criteria are to minimise the contaminant flow and remediate the contaminated groundwater, then permeable reactive barriers (PRB) are provided.

Slurry cut-off walls are underground walls that function as a barrier to prevent the horizontal flow of water and other fluids. It helps in changing the channel of groundwater from a contaminant plume and helps to increase the retardation time of contaminants. Based on the design, it can be placed before or after the contaminant source. Different materials and combinations of materials such as bentonite, soil-bentonite, red mud-bentonite and cement-bentonite are used as slurry cut-off walls. The construction process for a cut-off wall typically involves two sequential stages. Firstly, a vertical trench is excavated to reach the relative aquiclude in the subsurface soils. Concurrently, the trench is filled with a bentonite-water slurry to ensure the stability of the excavation. Secondly, the excavated soil or alternative materials should be blended with amendments (such as dry bentonite, zeolite, etc.) and slurry to prepare the backfill with optimal workability. Following the filling of the excavated trench, the backfills undergo consolidation over an extended period, influenced by gravity, sidewall friction, and pore water pressure (Zhu, 2020). While using bentonite barriers as cut-off walls, sand is chosen as one of the common amendments to improve the structural integrity and workability of barriers as well as to reduce the shrinkage cracks and cost considerations. Recently, waste materials such as red mud, fly ash, pond ash, tyre fibres, etc., have been

recommended as a solution for pollution control measures (Zhu et al., 2023; Rout and Singh, 2020).

Permeable reactive barriers are another type of vertical cut-off wall, which are designed for remediating polluted groundwater. The contaminants are either immobilised or chemically transformed while passing the contaminated water through the reactive zone of the permeable reactive barrier. One such example of reactive material used in PRB is zerovalent iron. Two types of installation methods are adopted to implement PRB in the field – continuous method and funnel and gate method. The former method consists of only one single reactive zone installed across the contaminant plume, while the latter consists of a permeable gate placed between two impermeable walls, which direct the contaminated flow towards the reactive material. Three contaminant removal mechanisms, namely precipitation, degradation and sorption, are mainly responsible for the removal of pollutants in PRBs.

2.7 Hydraulic barrier materials

Compacted clay liners (CCL) or in association with geosynthetics as geosynthetic clay liners (GCL) have been employed as hydraulic barriers in waste containment facilities. As suggested by various researchers and environmental protection agencies, the barrier material should have a minimum hydraulic conductivity of 10^{-9} m/s (USEPA, 1988). Since clays have very low permeability, they are considered the best liner candidates and have become an integral part of designing a containment facility. Furthermore, clays exhibit better contaminant retention ability for heavy metals and good sealing ability. To ensure environmental protection, clay liner thickness normally ranges from 0.3 to 3 m or more, although typical thickness ranges between 0.6 and 1.2 m. The construction process involves lifts or layers of clay being compacted on top of each other. Adjacent lifts should be bonded well to prevent areas of high conductivity existing between layers. If layers are bonded well, any discontinuities in adjacent lifts get hydraulically disconnected. Care should be taken to prevent drying during the placement because desiccation cracks may form, and the effectiveness of the clay liner gets compromised. The performance of CCL will depend upon (a) clay characteristics, (b) method of compaction and compaction water content and (c) protection against desiccation after construction.

Geosynthetic liners primarily consist of geomembranes, an impermeable membrane crafted from polymeric materials. A GCL is typically a composite liner system consisting of a layer of processed clay (commonly bentonite) supported or enclosed by geotextiles or geomembranes.

Geomembranes are polymeric sheet materials that remain impermeable to liquids as long as their integrity is maintained. On the other hand, geotextiles are woven or non-woven sheet materials that are less impervious to liquids than geomembranes but offer greater resistance to penetration damage. Geotextiles provide durable resistance to physical or chemical degradation in harsh environments, while the high swelling capacity and low permeability of bentonite contribute to an effective hydraulic seal. Traditional GCLs are thin and flexible sheets of sodium bentonite (approximately 4.9 kg/m²) either sandwiched between two geotextiles or glued to a geomembrane. Although GCLs are easy, flexible, and reliable, the structural integrity of the thin GCLs is questionable if the GCL gets punctured or torn. Moreover, the effectiveness of GCL is regulated by various factors such as overall configuration, clay quality, amount of clay used per unit area, and uniformity. Numerous studies have demonstrated that geomembranes exhibit high impermeability to the diffusion of inorganic contaminants. However, organic compounds have been observed to readily penetrate through geomembranes within a relatively short timeframe (Varank et al., 2011; 2017). Composite liners can be used to improve the overall performance of hydraulic barriers by considering the limitations of each barrier. Composite barriers consist of two or more types of liners so that the advantages of each system can be incorporated.

2.7.1 Bentonite and its amendments

Bentonite is a commonly used clay component in engineered hydraulic barriers such as CCL or GCL for various geo-environmental applications. It is a processed clay formed as a volcanic ash deposit consisting mostly of montmorillonite with minor amounts of feldspar, quartz, mica, calcite, gypsum, and other minerals and rock fragments. The properties of bentonite, especially sodium type, including high osmotic swell and low hydraulic conductivity (k) to water (Rowe, 2012; Tong and Sample-Lord, 2022), the limited advective flux of contaminants into the environment (Norrish and Quirk, 1954; van Olphen, 1977; McBride, 1994; Petrov and Rowe, 1997; Shackelford et al., 2000; Jo et al., 2001, 2005) are desirable to be used as a hydraulic barrier. Due to its distinct characteristics, sodium bentonite is one of the most commonly used and preferred barrier materials. However, the limited availability of preferred soils demands the use of locally available soils, waste materials or other modified soils as bentonite amendments to improve the barrier efficacy. The implementation of other less swelling soils such as calcium bentonite, kaolin, zeolite or other waste materials or local soils also displayed better engineering properties and are generally chosen as preferable bentonite amendments for hydraulic barrier applications (Fan et al., 2014; Nath et al., 2023).

2.7.1.1 Structure of montmorillonite

The primary clay mineral present in bentonite is montmorillonite. The basic structure of montmorillonite consists of an octahedral sheet sandwiched between two tetrahedral sheets (2:1 clay mineral). Each tetrahedron in the structure of montmorillonite contains a central silicon atom surrounded by four oxygen or hydroxyl ions arranged in a tetrahedral sheet. These ions are positioned equidistantly from the silicon atom. The tetrahedral sheets are organised in a hexagonal network by sharing oxygen atoms with adjacent tetrahedral sheets. The octahedral unit comprises two layers of closely packed oxygen or hydroxyl ions, with aluminium or magnesium ions embedded within them. These embedded ions are equidistant from six oxygen or hydroxyl ions. The successive layers are bonded by weak van der Waals forces and cations that balance the charge deficiency. Therefore, water or any polar liquids can easily break the bond between layers and result in significant expansion. The specific surface area of bentonite in dry conditions ranges from 600-800 m²/g. The basal spacing of montmorillonite varies from 9.6 to 21 Å.

Montmorillonite often experiences charge imbalances due to isomorphous substitutions and broken bonds. These substitutions create a negative charge deficiency, which is partially compensated by substitutions in the adjacent sheet of the unit layer. The primary occurrence of charge deficiency happens within the octahedral sheet, and the resulting net charge imbalance needs to be addressed at the surface of the unit. A typical example is sodium montmorillonite, where the surface charge is balanced by sodium ions. As sodium ions are weakly bound, sodium montmorillonites exhibit a notable capacity to readily exchange their sodium ions for other cations, particularly those with higher valences. This ion exchange tendency, combined with their larger surface area, grants this group of clay minerals a remarkably high cationic exchange capacity ranging from 80-150 meq/100g.

2.7.1.2 Bentonite – Permeant fluid interaction

The interaction between the surface of bentonite and the surrounding pore fluid is critical for understanding the engineering behaviour of barrier materials. These interactions are primarily governed by physicochemical forces acting on the bentonite, which are influenced by its surface charge characteristics. However, external factors such as temperature, salinity, pH, and the type of exchangeable cations present in the interlayer determine the strength of bonds and the water adsorption capacity of bentonite. When water is added to dry bentonite, it is strongly drawn towards the interlayer space and clay mineral surface. Several mechanisms,

such as hydrogen bonding, hydration of exchangeable cations, and attraction by osmosis, are involved in the process. The surface of bentonite comprises a layer of either oxygen or hydroxyl. Hydrogen bonds form when oxygen attracts the positive corners, or hydroxyl attracts the negative corners of dipolar water molecules. Cation hydration occurs when the negatively charged ends of the water molecules attract towards the positively charged cations in the bentonite. The extent of water adsorption by cation hydration depends upon the type of cation species and its hydration energy. Attraction by osmosis occurs due to the difference in ionic concentration inside and outside the clay system. As a result, more water molecules tend to diffuse towards the clay surface to equalise the concentration.

2.7.1.3 Diffused double-layer behaviour

Water molecules can either be sorbed onto the surfaces of montmorillonite or form hydration shells around interlayer inorganic cations. The capacity of montmorillonite to absorb considerable amounts of water is crucial, as the swelling behaviour differs from one clay to another. In dry conditions, the negative charges on the clay surface are balanced by exchangeable cations such as Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , which are located on the layer surface and are held by electrostatic attraction. When water is added, these compensating cations tend to diffuse away from the layer surface due to their lower concentrations in the bulk solution. However, they are also electrostatically attracted to the charged layer surface. These opposing tendencies lead to the formation of a diffuse double layer. Therefore, the diffused double layer (DDL) can be defined as the layer comprising the charged clay surface and the diffused ions/charges in the adjacent phases. Fig. 2.6 represents the ion distribution in the diffused double layer. The cation concentration will be maximum at the clay surface and decrease as the distance from the clay surface increases. Similarly, the anionic concentration will be lowest at the clay surface, and it increases as the distance increases.

In geotechnical engineering, the Gouy-Chapman model is the most commonly utilised mathematical theory for describing the distribution of ions near the surface of clay particles. The theory explains the distribution of electric potential in the DDL around a clay particle. The theory involves some assumptions: (i) ions in the double layer are point charges, and there is no interaction between them (ii) charges on the particle are uniformly distributed (iii) The particle surface is a plate that is large relative to the thickness of the double layer (iv) The permittivity of the medium adjacent to the particle surface is independent of position.

According to the Gouy-Chapman theory, the thickness of the diffused double layer is given by

$$\text{Debye length, } \frac{1}{\kappa} = \sqrt{\frac{EKT}{2n_0e^2v^2}} = \sqrt{\frac{E_0\epsilon KT}{2n_0e^2v^2}} \quad (2.1)$$

where T is the temperature in Kelvin, E is the permittivity of the medium, E_0 is the permittivity of a vacuum, ϵ is the dielectric constant of the pore fluid, K is the Boltzmann constant, e is the electronic charge, v is the valence of ions, and n_0 is the concentration of ions.

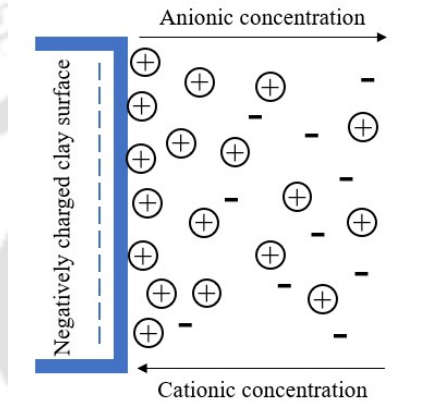


Fig. 2.6 Ionic distribution in the diffused double layer around a clay particle

Hence, both soil properties and fluid properties play a significant role in influencing the thickness of the diffused double layer. Soil parameters, including clay mineralogy, specific surface area, and exchangeable cations, as well as fluid properties such as electrolyte concentration, ion valence, dielectric constant, size of hydrated cations, and anion adsorption, contribute to the DDL thickness. Additionally, external factors like temperature and pH also impact the DDL thickness.

When an electrolytic solution is added to the system, it may penetrate into the interlayer space as well as diffused double-layer space. The factors influencing the thickness of the interlayer space are similar to those affecting the double layer. Under favourable conditions, cations in the double layer and interlayer space can be exchanged with other cations, while molecules of the pore fluid can also be replaced by those of a new fluid. These alterations can impact the thickness of the double layer and modify the behaviour of the clay. The replacing power is the ability of a cation to replace another one and primarily depends on the valence and ion size. Generally, higher valence ions replace lower valence cations, and if the valence is the

same, then one with the smaller radii is less replaceable than larger ones. The order of replaceability is as follows: $\text{Na}^+ < \text{K}^+ < \text{Mg}^{2+} < \text{Ca}^{2+}$. This behaviour is generally quantified by the term “cation exchange capacity (CEC)” and is generally expressed in milli equivalents per 100 grams. Sodium bentonite has the highest cation exchange capacity compared to any other type of bentonite.

Alternative models, such as the Stern model and Grahame model of the double layer, have also been developed to describe the double layer around clay particles. These models were devised to address the limitations of the Gouy-Chapman theory (Gouy, 1910; Chapman, 1913).

2.7.1.4 Swelling behaviour of bentonite

The swelling behaviour of bentonite plays a significant role in barrier applications as it helps in sealing the voids or cracks formed during the functional period of waste containment facilities. According to Norrish and Quirk (1954), the swelling of bentonite takes place in two stages – inner crystalline and osmotic swelling.

(i) Inner-crystalline swelling

In completely dried bentonite, exchangeable cations are located either on the surface of the layers or within the hexagonal holes of the tetrahedral sheets. At this stage, the clay sheets are closely stacked together, with a layer distance ranging from 0.96 to 1 nm. Equilibrium between the negatively charged clay surface and the positively charged interlayer cations is maintained by weak van der Waals attraction.

Inner-crystalline swelling (as seen in Fig. 2.7) occurs when water molecules enter the interlayer region of montmorillonite to hydrate the exchangeable cations. Upon hydration, the cations align themselves on a plane midway between the clay layers, leading to an expansion of the spacing between the layers. This process can cause the volume of montmorillonite to double. The polarity of water molecules is crucial in inner-crystalline swelling, as the negative dipoles of water molecules orient towards the cations, weakening the electrostatic interaction between the negatively charged layers and the interlayer cations. Inner-crystalline swelling, also known as Type I swelling, involves the sequential intercalation of one, two, three, or four discrete layers of water molecules between mineral interlayers. This swelling process is followed by osmotic (Type II) swelling, which is associated with longer-range electrical diffuse double-layer effects.

In inner-crystalline swelling, a balance exists between attractive and repulsive forces acting between adjacent interlayer surfaces. Electrostatic attraction between exchangeable cations and the basal surfaces of the clay primarily governs the net potential energy of interaction, while the hydration energy of exchangeable cations regulates the net potential energy of repulsion. The dominance of either attraction or repulsion forces depends on the saturation conditions and electrolyte concentrations present in the system.

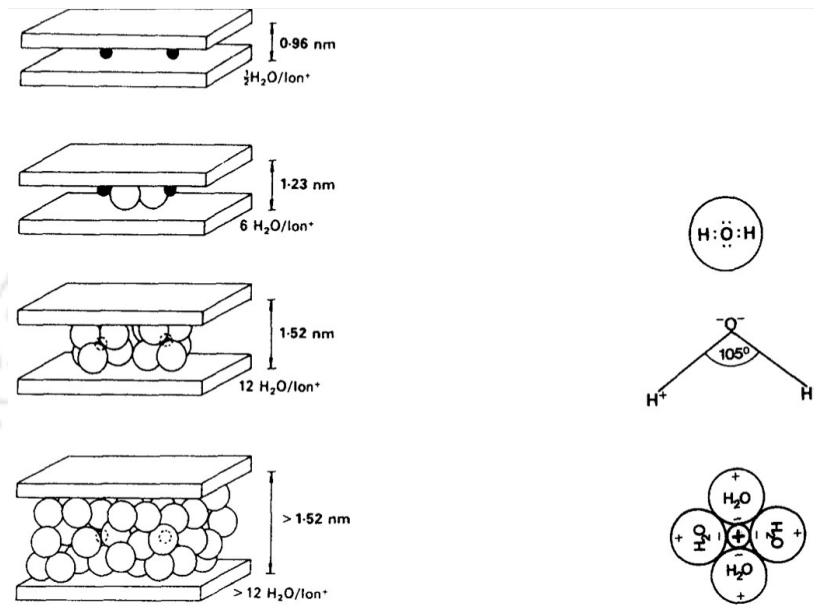


Fig. 2.7 Inner crystalline swelling of sodium bentonite and structure of water molecule (Madsen and Müller-Vonmoos, 1989)

(ii) Osmotic swelling

In contrast to inner-crystalline swelling, which occurs over short distances, osmotic swelling is driven by the repulsion between electric double layers, and it can occur over much larger distances. In soils like sodium bentonite, osmotic swelling may lead to complete separation of the layers. The primary cause of osmotic swelling is the significant concentration gradient between ions electrostatically held near the clay surface and those in the pore water. In short, the diffused electric double layer is responsible for the osmotic swelling.

The osmotic phase of swelling follows the inner crystalline phase but occurs exclusively when the exchange sites contain monovalent cations (Jellander et al., 1988; McBride, 1994; Norrish and Quirk, 1954; Prost et al., 1998). During this phase, the interlayer region retains multiple layers of water molecules, with the number of layers at equilibrium being proportional to the cation concentration in the bulk water (Norrish, 1954; Onikata et al., 1999; Zhang et al.,

1995). For instance, if the bulk water possesses a low concentration of monovalent cations and monovalent cations occupy the exchange sites, a larger portion of the total water becomes bound, resulting in reduced mobility and lower hydraulic conductivity. This scenario is commonly observed in sodium-montmorillonite when hydrated and/or permeated with deionised (DI) water (Alther et al., 1985; Gleason et al., 1997; Lutz and Kemper, 1959; Petrov and Rowe, 1997; Ruhl and Daniel, 1997; Shackelford et al., 2000). Conversely, when polyvalent cations occupy the exchange sites, only the inner crystalline phase occurs, and the interlayer expansion ceases after containing four monolayers of water (Jellander et al., 1988). The absence of an osmotic phase in the presence of polyvalent ions has been experimentally well-documented (McBride, 1994; Norrish and Quirk, 1954; Posner and Quirk, 1964; Prost et al., 1998), particularly evident in calcium-montmorillonite's nominal free swelling, even when hydrated with DI water. In contrast, sodium-montmorillonite typically exhibits substantial free swelling in low ionic strength solution (Egloffstein, 2020; Lin and Benson, 2000).

The driving force behind osmotic swelling lies in the significant concentration disparity between ions electrostatically bound near the clay surface and those in the pore water. This results in an excessively high positive ion concentration near the surface compared to a minimal negative ion concentration. As distance from the surface increases, the positive ion (cation) concentration diminishes while the negative ion (anion) concentration increases. The negatively charged clay surface and the surrounding ion cloud constitute the diffuse electric double layer, wherein a high negative potential exists directly at the clay layer's surface. As distance from the surface increases, this potential diminishes and reaches zero in the pore water. When two such negative potential fields overlap, they repel each other, inducing the observed clay swelling. The profile of the potential curves, and thus the repulsion at a given distance, varies with the valence and radius of the counter-ions in the double layer and the concentration of electrolytes in the pore water. Transformation of sodium montmorillonite into its calcium form or an increase in pore water-electrolyte concentration leads to a decrease in double-layer thickness and a reduction in swelling stress.

2.7.2 Review of published research on bentonite-based barriers

2.7.2.1. Effect of inorganic salts on the engineering behaviour of bentonite and soil-bentonite barriers

Numerous studies have investigated the engineering properties of bentonite-based barriers, including their hydraulic conductivity, swelling behaviour, mechanical stability, and long-term

barrier performance. These studies have utilised laboratory experiments, field trials, and numerical modelling techniques to characterise and optimise the design and construction of bentonite barriers. Key factors influencing barrier performance include bentonite type and quality, barrier thickness, compaction methods, and construction practices.

Previous research has consistently demonstrated the influence of pore fluid composition on the engineering and index properties of soils, particularly clays (di Maio, 1999). Therefore, factors such as ionic concentration, ionic valence and soil properties can significantly impact the barrier performance of clay-based barriers. Many studies have investigated the impact of inorganic salts on the geotechnical characteristics of compacted bentonite in detail. di Maio (1999) investigated the mechanical characteristics of Ponza bentonite when exposed to three different electrolyte solutions, such as NaCl, KCl and CaCl₂, by performing direct shear tests and consolidation tests. The incorporation of inorganic salt ions resulted in ion diffusion and consequently led to strength gain and reduction in deformability. The results also demonstrated that the divalent Ca²⁺ ions and monovalent K⁺ ions impart irreversible ion exchange reactions and permanent reduction in the diffused double layer. In addition to mechanical behaviour, the impact of inorganic salt ions on the consistency limits, sedimentation behaviour, swell-shrink behaviour, consolidation and hydraulic behaviour has also been investigated in the past (He et al., 2020). Yukselen-Aksoy et al. (2008) concluded that the compressibility and consolidation characteristics of soils having a liquid limit of less than 110% were not affected by the intrusion of salinity. The multivalent cations or monovalent cations in the percolating leachates may replace the inherent exchangeable Na⁺ ions from bentonite, resulting in the elimination of osmotic swelling, rise in hydraulic conductivity or increased flux of contaminants across the bentonite barrier. Hence, this chemical intolerance between bentonite and inorganic salts in leachates may impart detrimental effects on the long-term barrier performance of bentonite-based liners. The impact of multivalent ionic species (Li⁺, Na⁺, Ca²⁺ and Mg²⁺) on geosynthetic clay liners was studied by Kolstad et al. (2004), and they introduced a parameter called “relative abundance of monovalent and divalent cations (RMD)” for quantifying the cation concentrations in the system. In dilute solutions, the effect of RMD on the swell and hydraulic behaviour of GCL was superior, whereas ionic strength imparts a significant effect at higher concentrations of inorganic salt solutions. Apart from the experimental investigation from the laboratory, recently, a few research studies have been developed on modelling the hydro-mechanical behaviour of bentonite under saline environments (Du et al., 2022).

Along with the pore fluid chemistry, different factors on the engineering behaviour of bentonites, such as external applied vertical stress, pH, temperature, suction, and initial compaction condition, were also meticulously analysed. The dependency of vertical stress and salinity on 1D-swelling characteristics of GMZ01 bentonite was studied by Chen et al. (2016). The influence of vertical stresses on the swell behaviour of bentonite was found to be substantial at low overburden stresses and low salinity conditions. Similarly, the effect of the concentration of permeants had a significant impact on swell properties at low overburden loads and had a negligible effect at higher vertical stresses. Zhang et al. (2016) studied the influence of the same parameters (vertical stress and salinity) on the volume change behaviour of compacted GMZ01 bentonite. A decline in swelling strain, the elastic compressibility parameter and plastic compressibility parameter, and a rise in yield stress were noted with a rise in concentrations of NaCl solution. However, the elastic compressibility parameter and the plastic compressibility parameter were least affected by the vertical stresses. Zhang and Jia (2016) studied the mechanical strength properties of GMZ07 bentonite under saline conditions by performing a series of direct shear tests and consolidation tests. The shear strength of bentonite was improved upon the salt addition as the friction angle was found to increase while cohesion remained unaffected. The reason was attributed to the changes in surface morphology due to the rise in surface roughness and increase in interaction between soil particles. Similar to GMZ bentonites, many studies have been carried out on MX80 bentonite and FEBEX bentonites, substantiating the important role of inorganic salt solutions on the engineering behaviour of bentonites from various sources (Muurinen and Lehtikoinen, 1999; Herbert et al., 2008; Castellanos et al., 2008; Cui 2017).

The variations in engineering properties of bentonite are dependent on soil mineral composition as well as geological factors. Many geotechnical studies have been carried out on different specific bentonites used across the world, such as GMZ bentonite (China), FEBEX bentonite (Spain), SWy and MX80 bentonite (Wyoming). Dutta and Mishra (2016) evaluated the effect of salt solutions (NaCl and CaCl_2) on the engineering properties of compacted bentonite from Indian origin. The mechanical parameters such as compression index, coefficient of volume change and time taken for 90% consolidation showed a declining trend, while the coefficient of consolidation displayed a rising trend with an increase in salt concentrations. The results also indicated that bentonites with higher CEC and swelling ability exhibited higher changes in consolidation parameters compared to other bentonites with lower values of CEC and swelling. The considerable effect of divalent cations on the diffused double-

layer thickness of bentonite was also substantiated by the results. Jadda and Bag (2020) investigated the influence of NaCl and CaCl₂ on the swell pressure, consolidation behaviour and hydraulic conductivity of commercially available Indian calcium and sodium bentonites. The significant changes in surface morphology, microstructure, and hydro-mechanical characteristics of sodium bentonite due to the inorganic salt permeation were confirmed, whereas minimal influence was observed in calcium bentonite. The crystalline and osmotic swelling of Na-bentonite gets affected by the intrusion of salt permeants and significantly suppresses the diffused double layer thickness, resulting in reduced swelling and increased hydraulic conductivity. However, in the divalent bentonite, the cations were strongly hydrated, and the interlamellar complexes were rigid and stable, thereby restricting the effect of pore fluid chemistry on swelling behaviour. Thus, the results suggested the utilisation of divalent bentonite barriers in high salinity conditions and monovalent bentonite barriers in low salinity conditions. In addition to the pore fluid chemistry, the variations in temperature also have a significant impact on the swelling properties of compacted bentonites. It was observed that the swelling behaviour of Na-bentonite declined with an increase in temperature, and a reverse trend was observed for calcium bentonite. Therefore, for further understanding, the combined effect of temperature and electrolytic solution on divalent and monovalent bentonites was studied by Jadda and Bag (2022). The coupled effect of temperature and salinity substantially reduced the swell pressure of monovalent bentonite; hence, divalent bentonite showed better thermo-chemical endurance.

Due to the above-mentioned chemical incompatibility of sodium bentonite, a few studies have explored the utilisation of amended or enhanced bentonites to address chemical incompatibility issues (Norris et al., 2018). The bentonite enhanced with polyacrylic acid has been utilised and proposed to improve engineering behaviour under different leachates or aggressive chemical solutions. Some researchers also suggested the pre-hydration of geosynthetic clay liners prior to exposure to the electrolytic solution for better chemical compatibility (Katsumi et al., 2008). The barrier performance of two modified bentonites – multi-swellable bentonite (MSB) and a dense-prehydrated geosynthetic clay liner (DPH-GCL) under different electrolytic solutions was investigated by Katsumi et al. (2008). The long-term hydraulic performance (for seven years) of proposed liners was analysed, and results indicated better chemical resistivity under NaCl and CaCl₂ solutions of concentrations less than or equal to 1M. Prongmanee et al. (2018) also found the potential of polymerised (sodium polyacrylate) bentonite to partially prevent cation exchange reaction in the presence of aggressive

electrolytes and subsequently provide better hydraulic barrier properties in aggressive cationic solutions. Tong et al. (2021) studied the diffusion behaviour across polymer (polyacrylic acid) enhanced bentonite (BPC) under dilute and aggressive calcium chloride solution. The results indicated that BPC displayed better barrier performance when compared with conventional sodium bentonite, as the solute flux through the BPC was lower and mainly dominated by diffusion rather than advection. Frankovská et al. (2010) showed that the incorporation of 40% palygorskite into bentonite could potentially improve the swelling ability and hydraulic barrier efficiency of GCL liners permeated with NaCl concentrations up to 1.80 M. The unavailability of bentonite deposits and the structural degradation of bentonite liners paved the way for the utilisation of other soils, such as kaolin, to amend bentonite liners. A few researchers proposed mixes of kaolin and bentonite (KB) for application as hydraulic barriers. Duong and Hao (2020) evaluated KB at different proportions to understand the variation of different consolidation parameters under the permeation of 1N NaCl. The dependency of pore fluid on the compression and swelling behaviour of KB was well established from the results, especially at higher bentonite proportions. However, the effect of NaCl was found to be least for KB having a liquid limit (in distilled water) less than 110% and compression index (in distilled water) less than 1. Das and Bharat (2021) proposed the use of layered kaolin-granular bentonite in GCLs, and the results demonstrated better self-healing and swelling ability under adverse saline conditions and lower overburden pressures. The introduction of the kaolin layer to bentonite liner helped in improving osmotic swelling and resulted in the sealing of voids in underlying bentonite in addition to the better contaminant retardation factors. Being a non-toxic polymer, sodium hexametaphosphate was suggested for modifying calcium bentonite to improve the chemical resistance and dispersibility of bentonite. Fang et al. (2022) investigated the consolidation properties of a mixture of sand and sodium hexametaphosphate (SHMP) modified calcium bentonite backfill when inundated with CaCl_2 solutions. The adverse impact of salt solution on the consolidation behaviour of SHMP-treated Ca-bentonite was observed from the results. However, the studies done by Yang et al. (2022) showed that apart from the adverse impact on swelling and hydraulic behaviour under CaCl_2 solutions, the SHMP-modified Ca bentonite could be effectively employed in cut-off walls as it enhances the attenuation capacity and retardation of the multivalent cations in the cut-off wall. Moreover, investigations into the physico-mechanical behaviour of pond ash-bentonite and sand-bentonite mixtures under various salt solutions have provided insights into their performance and suitability for different applications. Rout and Singh (2020) found that modified bentonites exhibited varying responses to salt concentrations (NaCl , CaCl_2 , and FeCl_3) and permeation times, with pond

ash-bentonite mixtures showing greater resistance to external factors compared to sand-bentonite mixtures. The increase in concentration and permeation time displayed a reduction in free swelling, volumetric shrinkage strain and consistency limits, along with a rise in hydraulic conductivity. In addition to this, an increase in unconfined compressive strength (UCS) was noted at lower concentrations and a decrease in UCS at high concentrations of inorganic salts. Therefore, the results from the above-mentioned research highlighted that the modified bentonite or bentonite amended with various polymers has the potential to withstand salt sensitivity under field conditions.

2.7.2.2 Effect of heavy metals on the engineering behaviour of bentonite-based barriers

Numerous investigations have been conducted by researchers in the field of geotechnical engineering to examine the impact of diverse heavy metals on the engineering characteristics of clay-based barriers. A predominant focus of these studies has been directed towards the evaluation of index properties, swelling, and hydraulic behaviour of barrier materials when subjected to the permeation of heavy metals. The preeminent choice for barrier materials in these investigations was bentonite owing to its recognised hydraulic efficacy. Furthermore, the studies focused mostly on commonly found cationic heavy metal contaminants, such as lead, copper, and zinc, as the metals of interest in these investigations.

Jullien et al. (2002) investigated the role of copper metal ions on the permeability, swell strain, void ratio and retardation factor of calcium smectite by conducting oedometer experiments. The results indicated that there was a slight increase in permeability and a reduction in the swelling strain of calcium smectite upon copper ion percolation. The studies by Ouhadi et al. (2006) showed that the short-term as well as long-term chemical and mechanical properties of bentonite barriers significantly varied upon changes in pH and heavy metal contamination. The infusion of cationic Pb^{2+} and Zn^{2+} ions had the capacity to reduce the system's pH, leading to microstructural modifications and changes in the osmotic equilibrium of the system. All these factors, along with the possibility of metal hydroxide precipitation, collectively contribute to the alterations in the consolidation and compressibility behaviour of bentonite barriers. Souli et al. (2008) analysed the permeability behaviour of compacted montmorillonite mixed with zinc solutions and correlated the changes with soil structure orientation using mercury intrusion porosimetry (MIP), Brunauer-Emmett-Teller (BET) surface area, scanning electron microscopy (SEM) and X-ray diffraction (XRD) results. The addition of 1M zinc ions altered the particle arrangement to an anisotropic flocculated

structure, resulting in an increase in interaggregate pores and an increase in permeability. Dutta and Mishra (2017) evaluated the consolidation behaviour of compacted Indian bentonite in the presence of zinc, lead and copper ions. The results were similar to that of inorganic salts, and the variation in consolidation parameters was ascribed to the diffused double layer contraction due to the permeation of divalent heavy metal ions. Ray et al. (2022) analysed the mechanical behaviour of Indian bentonites under the same heavy metal solutions (Pb, Cu and Zn). The outcomes revealed that there was a considerable decline in swell potential, swell pressure, compression behaviour and unconfined compressive strength with an increase in heavy metal ion concentrations. The hydraulic conductivity of bentonite under the permeation of copper and zinc ions was evaluated with respect to microstructural changes by Nartowska et al. (2019). The ions present in the leachate could lead to changes in interplanar distance depending upon the type of exchangeable cations present in the bentonite and the possibility of an ion exchange mechanism. The results also revealed that different heavy metal ions could possibly exhibit different engineering behaviours depending on the soil properties and chemical properties of the permeant solution. Xiao et al. (2021) utilised the Dose-response logarithmic model for evaluating the swelling and shrinkage behaviour of sodium bentonite liners under the influence of copper ions, which could possibly percolate through hazardous and non-hazardous landfill wastes. The authors concluded that the increase in Cu^{2+} could deteriorate the swelling ability due to the thinning of DDL thickness and reduce the shrinkage rate of bentonite. The ion exchange reaction that occurred between the Cu^{2+} from permeant solution and Na^+ from bentonite led to the reduction in concentrations of Na^+ and Mg^{2+} in the interlayer of sodium bentonite.

Numerous experimental investigations were also carried out on amended bentonite barriers subjected to heavy metal contamination. The sedimentation and hydromechanical characteristics of lead-contaminated kaolin-bentonite (KB) mixture coupled with changes in soil fabric were analysed by Fan et al. (2013). A considerable variation in pH, compressibility, and permeability of the KB mixture was observed due to heavy metal contamination, as well as subsequent DDL compression and alterations in surface charges. Higher concentrations of lead ions induced face-to-face aggregation of particles in KB, which was responsible for the changes in index and engineering properties. Furthermore, Du et al. (2015) extended the research by focusing on the effects of lead contamination on index properties and consolidation behaviour of kaolin-mixed calcium bentonite cut-off walls. It was noted that the compressibility properties and permeability of backfill soil were substantially affected by the

concentration of lead contamination and the proportion of bentonite in the mixture. The authors proposed an equation for predicting the hydraulic conductivity of lead-contaminated clay-bentonite backfills. The results of this chemical compatibility study also confirmed the adverse influence of high Pb^{2+} concentrations on the permeability of the proposed cut-off wall backfill, especially at lower vertical stresses. Similar research was conducted by Du et al. (2014) to understand the effect of zinc contamination on the engineering properties and microstructural behaviour of other types of clayey soils. The outcomes supported the earlier research by substantiating the adverse impact of zinc on the hydraulic barrier performance of proposed clay barriers. He et al. (2021) studied the effect of copper sulphate solutions and sodium chloride solutions on the hydraulic and mechanical behaviour of laterite-bentonite mixtures. The improvement of hydraulic properties and seepage control of the mixtures were identified with an increase in bentonite contents. Furthermore, the chemical contamination was found to improve the compression performance of laterite-bentonite mixtures. Zha et al. (2023) further affirmed the substantial deterioration of soil-bentonite barrier performance when subjected to the permeation of Cu^{2+} ions exceeding 500 ppm. Nazab and Keykha (2021) conducted an in-depth examination of the influence of heavy metal contamination (lead and zinc) on various geochemical properties of sand-kaolinite and sand-bentonite mixtures. This comprehensive laboratory investigation encompassed the assessment of consistency limits, pH levels, direct shear tests, unconfined compression tests, batch adsorption experiments, and electrical resistivity. The findings revealed that heavy metal contamination led to a reduction in cohesion but an increase in friction angle and compressive strength for sand-bentonite mixtures, whereas sand-kaolinite mixtures exhibited an inverse trend. Concurrently, the electrical resistivity decreased in both types of soil mixtures. Despite superior sorption capabilities observed in sand-bentonite mixtures, it was noted that the geotechnical properties of sand-bentonite were more susceptible to the permeation of metals. Additionally, lead ions had a more noticeable impact on the shear strength properties of both clay mixtures than zinc ions. Motlagh et al. (2023) also conducted studies on the adsorption and shear strength behaviour of sand-bentonite and sand-kaolinite mixtures under heavy metal solutions and yielded similar results. In contrast to these findings, Zha et al. (2021) observed a more pronounced impact of zinc contamination as opposed to lead contamination on strength, leaching, and electrical resistivity. In addition to the above-explained studies, several other researchers were also conducted to comprehend the effect of heavy metal contamination in other types of clays, such as kaolinite and locally procured soils, and the results were in conjunction with the studies explained earlier (Negahdar and Nikghalbpour, 2020; Gupt et al., 2021; Zhan et al., 2022).

The response of geotechnical properties of any type of clay barriers under cationic heavy metal contamination was similar to that of inorganic salt permeation. In solutions containing inorganic salts, cations like Na^+ , Ca^{2+} , and Mg^{2+} play a role in contracting the thickness of the diffused double layer. Similarly, in solutions containing heavy metals, divalent metal cations such as Pb^{2+} , Cu^{2+} , and Zn^{2+} have the potential to contract the double-layer thickness of bentonites. This thickness reduction subsequently alters bentonites' hydraulic, swelling and mechanical behaviour. As a result of the significant impact of cationic heavy metal ions on the barrier efficacy of bentonite or soil-bentonite barriers, few researchers proposed amendments to bentonite, such as polymers, waste materials, etc., for improving the hydraulic barrier efficiency under heavy metal permeants. Jia-Kai et al. (2023) proposed the use of locally available smectite as a viable alternative to high-quality Wyoming bentonite in barrier applications. Additionally, they introduced the incorporation of polymer-amended bentonites to enhance chemical compatibility in the presence of Cu^{2+} contaminants. The study examined the effectiveness of two polymers, namely sodium polyacrylate (PAA) and sodium-carboxymethyl cellulose (CMC), added in different proportions to locally available bentonite. The investigation focused on studying the swelling and hydraulic performance under various concentrations of Cu^{2+} and different acidic pH levels. The addition of 5% PAA displayed the lowest value of k due to the pore-filling effects, H-bonding, and limited polymer elution. CMC-modified bentonite also showed the lowest k value at 5% due to the intercalation by cation bridging and pore filling. However, CMC-bentonite showed better chemical compatibility under Cu^{2+} contamination than PAA-bentonite due to the restriction of the cation exchange mechanism and enhanced osmotic swelling. The swelling, hydraulic and adsorption performance of sodium-activated calcium bentonite modified with two polymers, namely acrylic acid and sodium carboxymethyl cellulose, was analysed under different concentrations of Pb^{2+} and Cd^{2+} ions by Zhao et al. (2022). The findings revealed enhanced hydraulic barrier efficiency along with high adsorption ability in polymer-amended bentonites when subjected to high concentrations of heavy metals. This improvement was attributed to the formation of a gel structure by the polymers, effectively blocking pore channels. The authors observed that the conventional correlation between swelling and hydraulic conductivity did not hold true for the proposed polymers under elevated concentrations of heavy metals. Notably, the modified bentonite demonstrated superior adsorption capacity for Pb^{2+} ions and exhibited a more pronounced impact on anti-seepage and hydraulic barrier performance compared to Cd^{2+} ions.

Most of the previous studies primarily focused on the influence of cationic heavy metals. Only limited studies were carried out to understand the impact of anionic heavy metal ions on the engineering properties of bentonite barriers. Yang et al. (2021) explored the effect of Cr(VI) on the hydraulic and consolidation behaviour of sand-calcium bentonite amended with SHMP backfills by performing a series of oedometer and flexible wall permeameter tests. The outcomes of the study revealed a slight variation in short-term permeability and indicated an insignificant impact of Cr(VI) on the consolidation parameters of proposed backfills. Hence, the authors proposed the use of SHMP-amended bentonite in slurry trench walls to improve Cr(VI) containment. He et al. (2023) conducted a numerical simulation on barriers composed of laterite-bentonite, and the outcomes exhibited enhanced retention capabilities against the migration of Cr(VI). However, the study also highlighted a long-term issue concerning the chemical compatibility of the proposed liners, as a substantial reduction in retention ability was observed after a 20-year period.

2.7.2.3 Effect of organic solutions on the engineering behaviour of bentonite-based barriers

The concomitant presence of organic and inorganic pollutants in leachates originating from waste disposal facilities has prompted investigations into the impact of organic solutions on the barrier effectiveness of compacted liners. Early investigations were exclusively based on clayey soils obtained directly from the local study area. Acar and Olivieri (1989) conducted an analysis of the influence of various organic fluids on the swelling, plasticity, and permeability of kaolinite and montmorillonite soils. The findings indicated a substantial reduction in swelling and plasticity, accompanied by rearrangement in soil fabric, resulting in an increase in hydraulic conductivity. The alterations in engineering properties were correlated with the dielectric constant and pH of the permeating organic fluids. Fernandez and Quigley (1985) and Anderson et al. (1985) demonstrated an increase in hydraulic conductivity of compacted clays upon permeation by organic fluids. The observed changes were elucidated by considering fluid properties such as density and viscosity. Evans et al. (1985) further supported these findings by confirming a significant increase in the hydraulic conductivity of soil-bentonite cut-off walls when permeated with concentrated organic solutions, whereas diluted solutions had a less detrimental effect. Meegoda and Ratnaweera (1994) conducted a thorough investigation into the basic geotechnical and compressibility properties of two clays contaminated with glycerol and propanol. The compression indices and index properties of the soil underwent notable alterations due to the significant influence of pore fluid characteristics, including the type and

concentration of chemicals in the pore fluid, as well as the dielectric constant and viscosities of the pore fluid.

Moavenian and Yesrobi (2008), Olgun and Yildiz (2010), and Estabragh et al. (2016) undertook similar studies to affirm the impact of various concentrations of organic pollutants on the index and engineering properties of local clays. The results indicated a substantial decline in swell and compressibility, coupled with an increase in shear strength upon the addition of organic fluids. This variation was particularly noticeable for concentrations exceeding 40%. In contrast, Mosavat and Nalbantoglu (2011) reported a reduction in the shear strength of compacted clay upon contamination with organic fluids, highlighting the dependence of strength behaviour on soil type and pore fluid characteristics.

Apart from studies on local clay soils, research has also been conducted on bentonite. Several researchers (Amarasinghe et al., 2012; Goodarzi et al., 2016; Schanz et al., 2018; Rahman et al., 2024) explored the role of dielectric constant on the permeability, consolidation, and compressibility behaviour of bentonite. The results revealed a significant deterioration in the geotechnical properties of bentonite upon the introduction of organic solutions. Similar to studies in clays, there was a considerable reduction in swelling, plasticity index, and compressibility, accompanied by a significant increase in permeability. Less or non-polar solutions exhibited higher compressibility and consolidation compared to high-polar fluids. The studies confirmed the influence of clay mineralogy, dielectric properties of the pore fluid, initial compaction conditions, and applied stress on the geotechnical properties of bentonite.

Li et al. (2015) emphasised the limited barrier performance efficiency of sand-bentonite barriers percolated with perfluorinated compounds (PFC) when compared to bentonite. However, the adsorption of PFCs onto bentonite was found to be ineffective, even though the permeability properties were not compromised. Similar poor barrier efficiency of sand-bentonite under alcohol-water mixtures was also reported by Rahman and Sharma (2023).

2.7.2.4 Effect of metal ions and organic solutions on the adsorption behaviour of bentonite barriers

Within the context of hazardous or radioactive waste containment within an engineered clay barrier, studies have been undertaken to explore the adsorption, diffusion or retention mechanisms of different metal ions or organic molecules, in addition to the assessment of the engineering properties. The contaminant migration through diffusion and advection mechanisms was investigated using laboratory experiments and numerical modelling.

Bentonite has demonstrated remarkable adsorption capacity for cationic heavy metals, including Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Co^{2+} , and Ni^{2+} (Bereket et al., 1997; Anna et al., 2014; Vhahangwele and Mugera, 2015). Bentonite showed selective adsorption of metals in multiple ionic species environments based on the strong competitive adsorption among the cations. Factors such as pH, contact time, dose of bentonite, initial metal concentration, temperature and ionic strength significantly affected the heavy metal removal (Kaya and Oren, 2005). Glatstein and Fransicsa (2015) noted the minimal influence of ionic strength on the removal of lead and copper compared to cadmium removal. Adsorption mechanisms include ion exchange, precipitation and surface complexation depending on the type of heavy metal ions. Acid activation using HCl and sodium activation have been explored as potential methods to enhance the sorption efficiency of heavy metals onto bentonite (Mohammed Azizi and Boufatit, 2013; Álvarez-Ayuso and García-Sánchez, 2003). Studies have also investigated the sorption efficiency of locally available clayey soils for potential use in landfill barriers (Zaki et al., 2017; Wang and Zhang, 2021).

In addition to individual clay soils, bentonite amended with locally available soils or waste products has also been evaluated for sorption performance (Tahervand and Jalali, 2017). The impact of metal ionic valency (K^+ , Ca^{2+} and Fe^{3+}) on the adsorption and hydraulic performance of a soil-bentonite barrier was explored by Lv and Zhao (2013). Higher valence (Fe^{3+}) was found to exhibit better adsorption, but it resulted in a higher speed of permeation through the soil-bentonite barrier. He et al. (2023) investigated the retention performance of soil-bentonite in the presence of Zn^{2+} and Cr(VI) under binary and ternary systems, considering both individual effects and combined influences of ionic strength (NaCl) and heavy metal ions. Under binary systems, Zn^{2+} showed better retention efficiency than Cr(VI) , and in ternary solutions, the ion bridge role of $\text{Cr(VI)}/\text{Zn}^{2+}$ was observed to enhance the adsorption ability of soil-bentonite.

Tahervand and Jalali (2017) analysed the sorption and desorption performance of Cu, Ni, Cd, and Zn onto locally available soil amended with bentonite, calcite, and zeolite using batch studies and geochemical modelling. The soil amended with bentonite and calcite exhibited maximum sorption, while zeolite-amended soil showed the highest desorption. The majority of these investigations involved batch adsorption studies, with a limited number of column studies, collectively highlighting the favourable sorption capacity of bentonite for cationic heavy metal ions.

2.7.3 Organoclay

While bentonite exhibits superior hydraulic performance and effective retention of cationic heavy metals, the chemical compatibility of bentonite liners under aggressive chemicals and environmental conditions remains a subject of concern. Various researchers have proposed alternative materials or modifications to bentonite to address the aforementioned issue. Several classes of modified clays are used for a variety of geo-environmental applications such as immobilisation of contaminants, enhanced degradation of toxic organic chemicals, purification of wastewater, and protection of groundwater from pollution. Modified clays can be grouped into several categories, viz., organoclays, nanocomposites, pillared layered clays, acid and salt-modified clays, and thermally and mechanically modified clays (Prost and Yaron, 2001). The use of other additive barrier materials, such as zeolites, high-carbon fly ash, and tyre chips, has been proposed to enhance the attenuation capacity of waste containment liners (Shackelford, 1999).

Modifications such as chemical modification, particularly through surfactants or polymers, have recently garnered considerable attention to enhance the inherent properties of clays. These modifications enable the development of clay-polymer or clay-surfactant hybrids with improved engineering behaviours. The organoclays are organically modified clays, which are composed of base clay and organic matter. Montmorillonite has been extensively utilised in the production of organoclays due to its favourable properties, which include high cation exchange capacity, high specific surface area, good adsorption capabilities, and significant swelling behaviour. Organic matter employed in the synthesis of organoclays encompasses a variety of compounds, including quaternary ammonium cations (QACs), a type of surfactant, as well as numerous other organic substances such as polymeric quaternary alkylammonium salts and copolymers, alcohols, aldehydes, biomolecules like proteins, enzymes, amino acids, peptides, and proprietary agents found in commercial products (de Paiva et al., 2008; Bate et al., 2014; Lee et al., 2012). Among these, QACs stand out as the most widely utilised organic compounds for the modification of organoclays (de Paiva et al., 2008; Sarkar et al., 2012).

QACs are comprised of a nitrogen head group and four exchangeable positions that can be occupied by organic functional groups of varying structures and sizes. There are two common types of cationic surfactants: long-chain amines and quaternary amine salts. Long-chain amines are made from natural fats and oils or synthetic amines. Depending on the length of the alkyl chain and the number of carbon (C) atoms, QACs can be classified as long (if $C > 12$) and short.

Some examples of long-chain groups are hexadecyl trimethyl ammonium bromide (HDTMA) and dimethyl distearyl ammonium bromide (DODMA), while benzyl triethylammonium (BTEA) and Tetramethylammonium (TMA) belongs to short chain alkyl groups. The process of introducing QAC cations onto the surface of bentonite by replacing its exchangeable inorganic cations is referred to as the primary sorption of organic cations. The interlayer of unmodified clay is relatively small, and its environment is hydrophilic due to the presence of inorganic cations. However, the intercalation of organic surfactants within the clay interlayers not only alters the hydrophilic environment to hydrophobic but also significantly increases the interlayer spacing (Lagaly, 1981). This expansion of the interlayer space is quantified by the basal spacing (Ghavami, 2017). The enhanced hydrophobicity of organoclays is attributed to the structure of quaternary amines. Quaternary amines possess both polar and nonpolar characteristics. The ionic part of these substituted ammonium salts is drawn to the negatively charged clay surface, while the nonpolar hydrocarbon chains have an affinity for nonpolar organic contaminants (Sell et al., 1992).

Surfactant-intercalated clay minerals are characterised by enhanced sorption properties, thermal stability, and compatibility with non-polar fluids. Therefore, they are highly favourable for practical applications such as wastewater treatment, environmental remediation, soil liner construction, waste containment, and oil well drilling operations (Caenn et al., 2011; Lo and Yang, 2001; Lorenzetti et al., 2005; Redding et al., 2002; Sheng and Boyd, 2000). The sorption capacity of the clay/surfactant hybrid is typically highest when long carbon-chain surfactants are intercalated into the interlayer of montmorillonites, as these intercalated surfactants promote the partitioning of organic compounds (Zhao and Burns, 2012).

In recent decades, the rapid expansion of chemical and petroleum industries has raised significant public concern regarding the extensive contamination of surface water, groundwater, and soil with various organic compounds (Zhu et al., 2015). Consequently, the remediation of contaminated sites has emerged as a pressing priority. To address this challenge, considerable research efforts have been directed towards identifying innovative and efficient materials for site remediation. Notably, recent studies have highlighted the potential of organoclays as effective binders or stabilisers for waste materials and contaminated soils. Stabilisation mechanisms involve chemical alterations in contaminants and their surrounding environment, resulting in reduced toxicity or mobility of the contaminants. Previous research indicates that organoclays serve as effective intermediates in the immobilisation of hazardous

contaminants such as polycyclic aromatic hydrocarbons (PAH) and non-aqueous phase liquids (NAPL) (Lee et al., 2012).

2.7.3.1 Synthesis of organoclays

Organoclays can be synthesised by two methods – cation exchange reaction and solid-state reaction (de Paiva et al., 2008). The cation exchange reaction involves the exchange of bentonite's interlayer cations by alkyl ammonium cation in aqueous solution. However, in a solid-state reaction, the organic molecules are intercalated in the interlayer space in dry conditions by mixing manually without any solvent addition. At low organic cation loading, the interlayer water gets displaced by polar organic molecules. When the loading increases, the added surfactants get adsorbed through both cation exchange and hydrophobic bonding. If organic loading is above the CEC of clay, then hydrophobic bonding, i.e. attraction between the alkyl chains of organic cation molecules, becomes the predominant adsorption mechanism. The excessive hydrophobic loading may cause a charge reversal on the clay surface, resulting in the build-up of a positively charged clay surface. This positive charge formation helps in the adsorption of toxic anions. The sorbed organic cations can be arranged in three different forms, including (i) organic cations intercalated into the interlayer spaces through cation exchange and bound to surface sites through electrostatic attraction, (ii) surfactant molecule physically adsorbed on the external surfaces of clays (iii) surfactant molecules present in the clay interlayer bound to their neighbouring surfactant molecules. Similarly, organic compounds can also be sorbed onto clay surfaces through hydrogen bonding, ion-dipole interaction, coordination bonds, hydrophobic interactions, acid-base reactions, charge transfer and van der Waals forces.

2.7.3.2 Arrangement of organic cations in the interlayer

The chain length of organic cations and the layer charge of clays decide the arrangement of organic cations in the interlayer of organoclay. The alkylammonium cations can align in different possible arrangement patterns, such as lateral monolayers, bilayers, pseudo trimolecular layers and paraffin layers (Lagaly, 1986).

In monolayer arrangement, the packing density of chains is low, and the chain arrangement is parallel to the silicate surfaces. The basal spacing is typically in the range of 13-15 Å. In bilayer arrangement, parallel conformations are seen, but there will be two carbon layers in the interlayer. The basal spacing ranges from 17-19.8 Å. The head groups of the alkylammonium

ions stay attached to the layers in the pseudo-trimolecular structure. The formation of curves causes the non-polar chain ends to be relocated to lie above one another. The thickness of the three alkyl chains causes interlayer separation (Lagaly, 1994). In the paraffin structure, the ammonium groups (the head group of alkylammonium) remain adhered to the silicate layer, whereas the chains in all-trans conformation face away from the surface, as seen in Fig. 2.8(d). The basal spacings of pseudo trimolecular and paraffin arrangements normally range above 22 Å (Lagaly, 1986).

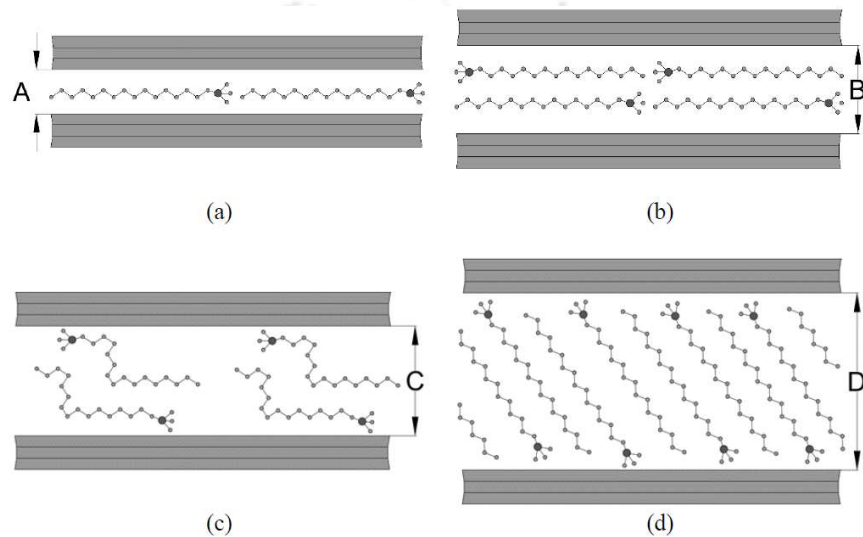


Fig. 2.8 Different interlayer organic cation arrangements of organoclay (a) monolayer (b) bilayer (c) pseudo trimolecular (d) paraffin structure (Lagaly, 1994)

2.7.3.3 Engineering properties of organoclay

After organic modification, organoclay is expected to undergo changes in surface charges and geotechnical properties compared to pristine clay. Intercalation of organic cations into the clay significantly reduces the water adsorption capacity or liquid limit of the clay mineral when exposed to polar liquids such as water. However, when mixed with non-polar organic liquids, organoclay exhibits a higher liquid limit than pristine clay. This reduction in liquid limit in water can be attributed to the hydrophobic nature of organoclay and the inability of surface cations to hydrate. Organoclay demonstrates hydrophobicity, resulting in minimal swelling tendency and low hydraulic conductivity in water. Conversely, they exhibit high swelling ability in the presence of organic liquids, as the interlayer can accommodate permeant organic liquids and expand. This interlayer expansion, along with particle dispersion, leads to a reduction in soil pore volume under fixed confining stress and volume. Therefore, the organic modification led to the reduction in specific gravity, specific surface area, liquid limit and

compressibility in water while increasing the hydrophobicity. The structural, textural, thermal and surface properties of pristine clay were altered due to the organic modification. Various studies confirmed the better removal of organic impurities and better barrier performance of organoclays in organic fluids, owing to their hydrophobic and organophilic characteristics. Moreover, organoclays display higher shear strength due to strong electrostatic bonding between organic surfactant head groups and clay surfaces (Bate et al., 2014). Further sections will provide detailed literature on the variation in engineering properties of organoclays.

2.7.4 Review of published research on Organoclay barriers

2.7.4.1 Effect of organic fluids on the engineering behaviour of organoclays

Organoclays are effective barrier modifications for engineering applications, including horizontal cut-offs, grout mixes, cut-off slurries, soil mortars, and landfill liners in the presence of organic pollutants and fuels (Lo, 2003; Benson et al., 2015; Heidarzadeh and Parhizi, 2020). The majority of the research has focused on examining the impact of surfactant type and organic fluids on the fundamental geotechnical characteristics of organoclays (Akbulut et al., 2010; Javadi et al., 2017; He and Zhu, 2017). The increase in alkyl chain length and chain number of surfactants increased the basal spacings of the clay and also increased the hydrophobicity (Lazorenko et al., 2020). Sodium montmorillonites were chosen as the best base clay option for modifying with surfactants due to their excellent adsorption and high cation exchange capacity (de Paiva et al., 2008; Zhao et al., 2017).

Lo (2001) conducted compaction, adsorption, and hydraulic conductivity tests on soil samples containing different percentages of bentonite, organoclay, and locally available soil. The results indicated that the organoclay fraction contributed to the retardation of leachate pollutants, while the bentonite fraction significantly reduced hydraulic conductivity. As a result, the thickness of the compacted liner could be significantly reduced, and the barrier performance could be improved. Gates (2004) investigated the crystalline swelling behaviour of organoclays in ethanol-water solutions. It was found that total layer charge density and the ratio of octahedral to tetrahedral layer charge affect the crystalline swelling in ethanol solutions. He et al. (2006) analysed the geotechnical behaviour and sorption ability of *p*-nitrophenol onto HDTMA-modified bentonites. This study substantiated the role of surfactant arrangement in the interlayer on the sorption and engineering properties of organoclays. Burns et al. (2006) explored the chemical and physical behaviour of two modified bentonites, HDTMA and BTEA modified bentonites, and concluded that cation packing density and

organic content influenced geotechnical properties. Lee et al. (2012) studied the effectiveness of organoclays as a variable permeable reactive barrier media for managing non-aqueous-phase liquid (NAPL). The hydraulic conductivity of mixtures comprising organoclay and sand, with a minimum of 25% organoclay content, exhibited NAPL conductivities on the order of 10^{-10} m/s. However, it is important to note that the hydraulic conductivity to water in these mixtures remained in the range of 10^{-3} m/s, allowing the easy flow of water while impeding NAPL advection. Akbulut et al. (2013) investigated the geotechnical properties of organoclays treated with cationic and anionic surfactants, observing alterations in specific gravity, unconfined compressive strength, and maximum dry density.

Boldt-Leppin et al. (1996) investigated the long-term barrier performance of sand-bentonite (SB) mixtures contaminated with diesel fuel after incorporating different percentages of organoclay. The desiccation cracking induced in the petroleum-permeated SB liner was effectively reduced by the addition of 3% of organoclay. However, the authors advised attention when adding higher fractions of organoclays, as it may lead to an increase in permeability to water. Benson et al. (2015) evaluated the geo-environmental characteristics (sorption capacity, hydraulic conductivity and swelling) of organoclay and organoclay-sand mixtures in various organic fluids and fuels. They proposed that a minimum of 50% organoclay is necessary for organoclay–uniform sand combinations to achieve lower hydraulic conductivity to jet fuel and gasoline, while at least 75% organoclay was necessary for diesel and fuel oil. Gitipour et al. (2015) suggested the use of organoclays for hydraulic barrier applications in petroleum-contaminated sites, demonstrating a significant reduction in hydraulic conductivity and higher adsorption of organic contaminants. Javadi et al. (2017) conducted laboratory tests on organoclay-amended compacted silty clay to study the advection and retardation of gasoline and naphthalene solution through the proposed barrier. They concluded that adding more than 10% organoclay (HDTMA-modified bentonite) reduced the hydraulic conductivity of the barrier to gasoline but slightly increased the hydraulic conductivity to the water. The results from the column tests also revealed better retardation capacity of the proposed barrier for naphthalene. Heidarzadeh and Parhizi (2020) investigated the influence of phenol on the hydraulic conductivity and adsorption behaviour of sand, bentonite, and organoclay combinations. They proposed a cost-effective sample with 87% sand, 10.2% bentonite and 2.8% organoclay as the optimal choice for clay liners when in contact with phenol.

Nevertheless, it is crucial to acknowledge that, despite their organic sorption benefits, the introduction of organoclays into the proposed liners may lead to a noteworthy compromise in hydraulic conductivity. In the investigation conducted by Lorenzetti et al. (2005), it was observed that the k of modified GCL, which comprised of bentonite and organoclay, exhibited a substantial increase in k when the proportion of organoclay exceeded 20% by weight. This notable change was attributed to various physico-chemical reactions arising from the interaction between the clay and the permeant. Therefore, the degree of organic modification and the proportion of organoclays in the mixture play a significant role in affecting the barrier performance.

In addition to barrier applications, organoclays could also be utilised to remediate contaminated soils, particularly through stabilisation and solidification processes (Nasrollahpour et al., 2019). Sell et al. (1992) demonstrated the potential of organoclays to remove phenol and chlorophenols from aqueous solutions. Moreover, they suggested the use of an optimal proportion of cement and organoclay for remediating chlorinated phenol-contaminated soils because they exhibited good shear strength and better contaminant immobilisation. Gitipour et al. (1997) investigated and confirmed the ability of organoclays to remove benzene, toluene, ethylbenzene, and xylene (BTEX) compounds from contaminated soils, suggesting its potential application as an adsorbent in petroleum spills, oil spills, slurry barriers, and landfill liners. Rathnayake et al. (2017) investigated and compared the remediation potential of organoclay and inorganic-organic hybrid clay (IOC) for Cr(VI) contaminated soil. The better Cr(VI) adsorption of IOC than organoclay was observed, and it also performed better in the simultaneous adsorption of Cr(VI) and bisphenol. In a study conducted by Yu et al. (2017), the stabilisation of various heavy metals on two modified bentonites (tetramethylammonium (TMA) and dodecyl trimethylammonium (DTMA) modified bentonites) was investigated. The efficiency and mechanisms of stabilisation varied depending on the metal species and the characteristics of the modified clay. The stabilisation efficiency of cationic metals such as copper, zinc, and cadmium onto modified bentonites exhibited a declining trend, whereas non-ionic mercury showed better efficiency. DTMA-modified bentonites were effective in immobilising chromium and arsenic through electrostatic attraction, while TMA-modified bentonite did not yield improved results. Consequently, the authors suggested that the selection of suitable modification should be based on the specific characteristics of the contaminated sites. Yang et al. (2017) conducted a similar study for stabilising Cr(VI) contaminated soil using two organoclays – TMA-modified and HDTMA-

modified bentonites. Both organoclays displayed reasonable stabilisation ability, whereas the adsorption mechanism behind each one remains different. TMA-modified bentonites immobilise contaminants by specific adsorption, while HDTMA-modified bentonites involve non-specific adsorption. Shahidi et al. (2019) demonstrated the feasibility of using hydrophilic nanoclay and hydrophobic organoclay to improve the stability and durability of gasoil-contaminated clayey sands. It was also noted that the addition of clay nanoparticles helped to improve the plasticity properties of contaminated soil. The remediation of PAH (polycyclic aromatic hydrocarbons) contaminated soil using a cement-organoclay mixture was examined by Ghavami et al. (2019). The study was conducted up to an organoclay fraction of 10%, and experiments such as toxicity characteristic leaching procedure (TCLP), UCS and permeability were conducted on different mixes. The results indicated a significant reduction in organic contaminant leaching along with satisfied strength and permeability.

2.7.4.2 Effect of organic fluids and heavy metals on the adsorption behaviour of organoclays

The introduction of organic modifications has led to the expansion of interlayer spaces and enhancements in the organophilicity and hydrophobicity of clays. These improvements facilitate the sorption of organic contaminants onto the interlayer space or surface of the modified clay, thereby enhancing its effectiveness in removing contaminants. Numerous studies have demonstrated the superior organic sorption capacity of organoclays compared to their unmodified counterparts, suggesting their potential as alternatives to traditional bentonite or soil-bentonite barriers. However, the efficacy of sorption depends on various factors, including the specific organic cations used for modification, the types of organic contaminants considered, and the interaction mechanisms involved.

Several studies have investigated the sorption of organic pollutants by organoclays, with a focus on adsorption studies involving phenol (Senturk et al., 2009; Su et al., 2011; Park et al., 2011; Garikoé et al., 2022). Stockmeyer (1991) explored the adsorption efficiencies of two organoclays for organic contaminants such as phenol, aniline, nitroethane, diethyl ketone, ethoxy acetic acid, maleic acid and hexadecyl pyridinium bromide. Out of the different organic pollutants considered, the best-adsorbed compounds were phenol, aniline and nitroethane. The phenol adsorption could be attributed to various mechanisms, including van der Waals interaction/organophilic interactions and hydrogen bonding. Rawajfih and Nsour (2005) investigated the sorption performance of phenol, *p*-chlorophenol, and 2,4-dichlorophenol onto an HDTMA-modified bentonite. The sorption capacity was noted to be a function of the

hydrophobicity and chlorine content of phenolic compounds. However, the sorption efficiency depends upon the type of organoclays, the quantity of surfactants, the properties of organic compounds, and the interactions between the organic molecules and organoclays. It was also observed that the adsorption mechanism at lower concentrations dominated the phenol sorption while partitioning mechanisms came into action at high concentrations. Ko et al. (2007) examined the utilisation of commercially available organoclays (Cloisite-10A, Cloisite-15A, Cloisite-30B and Cloisite-93A) for removing phenols, *p*-nitrophenol and aniline. The authors suggested that the phenol adsorption was mainly due to hydrophobic-hydrophobic chemical interaction and the sorption ability depends upon the concentration, solubility and log K_{ow} of sorbates, temperature, kinetic reaction time, and steric contour of organics, whereas sorption efficacy was found to be independent on solution pH. He et al. (2006) suggested that the adsorption performance of organic pollutants onto organoclays was mainly dependent upon the distribution of surfactant and the arrangement of the surfactant in the interlayer. If the surfactant loading is less than the CEC of soil, the adsorption mechanism involves surface adsorption and partitioning, but when the surfactant loading increases beyond the CEC, the adsorption mechanism involves partitioning only. The significance of the alkyl chain length of surfactant on the removal efficiency of phenol from aqueous solutions was investigated by Liu et al. (2008). The outcomes revealed that the increase in alkyl chain length in surfactant molecules and the CEC improved the phenol removal efficacy. Park et al. (2013) analysed the adsorption behaviour of *p*-nitrophenol and *p*-chlorophenol onto HDTMA-modified bentonites under different environmental conditions (pH and temperature). The results demonstrated good sorption capacity for both phenolic compounds due to the partitioning mechanism; however, more efficiency was observed for *p*-nitrophenol than the latter.

Further research has explored the sorption performance of organoclays for organic contaminants in conjunction with heavy metals in multi-contaminant environments (Liu et al., 2018; Guo et al., 2023). The interaction between heavy metals, organic contaminants and microorganisms in multiple contaminant environments and their adsorption onto organo-bentonite was analysed by Yoo et al. (2003). The results suggested the utilisation of organo-bentonite as a reactive medium for immobilisation and biodegradation of organic contaminants in the presence of heavy metals in the subsurface soil. Wang et al. (2017) explored the adsorption mechanism of organo-montmorillonites on multiple contaminant systems containing phenol and zinc ions. The presence of one contaminant did not affect the adsorption of the other contaminant. Partitioning helped in adsorbing phenol, and mechanisms such as ion

exchange, formation of complexes and/or precipitation helped in Zn^{2+} adsorption onto organoclays. Xie et al. (2023) studied the adsorption mechanism of bisphenol A (BPA) onto organoclay-amended loess liners in single-species systems and binary systems along with Pb^{2+} ions. The outcomes revealed an increase in the adsorption capacity of the proposed liner without compromising the required hydraulic conductivity of the liner. Modelling transport behaviour studies were also done, and the results showed an increase in the breakthrough time of BPA through the proposed liner. The polymers possessing functional groups such as hydroxyl and carboxyl have the capability to create a spatial three-dimensional cross-linking structure on the bentonite surface. This structure facilitates the formation of additional adsorption sites for heavy metal ions (Guo et al., 2023).

In a nutshell, the efficacy of sorption capacities of organoclays varies with factors, including the nature of sorbates, solvent properties, pH, contact time, and temperature (Guerra et al., 2014; Zhao et al., 2017). The intercalation of organic compounds in organoclay increases the interlayer spaces and changes the surface properties. As a result of these changes, new adsorption sites are opened up, which could potentially increase the sorption capacity. Batch adsorption and column tests have identified surface adsorption and partitioning mechanisms as key processes. The studies concluded that the sorption of organic contaminants onto organoclays with long carbon chains involves partitioning, while organoclays with short chain lengths exhibit surface adsorption mechanisms. In most cases, the equilibrium was attained quickly, within 10 minutes, and higher adsorption of phenol was found in an alkaline environment. Additionally, higher temperature, higher initial ion concentration also improved the adsorption efficiency (Wang et al., 2017).

The inherent negative surface charges on the bentonite may not be suitable for the adsorption of anionic heavy metals. Organic modification of clays can reverse inherent negative surface charges, thereby improving the adsorption of anionic heavy metals. Research is available on evaluating the adsorption of various organic pollutants and anionic heavy metals onto organoclays. Guerra et al. (2014) studied the Cr(VI) adsorption capacity on two different modified bentonites. The raw bentonite was a calcium type, and the modifiers used for the study were 3-aminopropyltriethoxysilane (APS) and 3,2-aminoethylaminopropyltrimethoxysilane (AEAPS). The conclusion from the study revealed that the adsorption of Cr(VI) was pH-dependent, and a substantial improvement in sorption ability was observed by the organo-functionalisation of calcium bentonite. A few researchers utilised response surface methodology (RSM) to optimise the conditions and enhance adsorption capacities. The

outcomes from the RSM studies conducted by Castro-Castro et al. (2020) showed that stirring speeds above 200 rpm, contact times greater than 120 min, and the addition of NaCl (0.1 to 2.0 mM) did not have a significant effect on Cr(VI) removal by HDTMA modified bentonite.

Additionally, investigations have expanded to include pharmaceutical contaminants such as amoxicillin and diclofenac, with studies demonstrating the efficacy of organoclays in their removal from contaminated water (Guegen and Forstier, 2021). The simultaneous adsorption of amoxicillin and Cu^{2+} from wastewater onto organoclays was analysed by Jin et al. (2014). The adsorption of amoxicillin was better than that of bentonite, and Cu^{2+} adsorption was comparable to that of bentonite. They concluded the removal mechanism for amoxicillin was partitioning, while Cu^{2+} adsorption was due to ion exchange. Sun et al. (2017) studied the uptake of diclofenac and chloramphenicol drugs from contaminated water onto an organo-kaolin. The rise in hydrophobicity and the generation of more positively charged surfaces on the modified kaolin helped to improve electrostatic interactions between anionic diclofenac and positively charged organo-kaolin. The outcomes suggested the utilisation of organo-kaolin as a good sorbent for the uptake and removal of anionic pharmaceutical compounds. The adsorption kinetics, equilibrium and thermodynamics of diclofenac sodium onto a commercial organoclay was investigated by Maia et al. (2019). The results showed that there were no structural changes in organoclay due to the permeation of pharmaceutical pollutants. The effectiveness of organoclays in removing pharmaceutical contaminants from polluted water was reaffirmed from the results.

2.8 Summary of the literature review and research challenges

Bentonite is commonly considered the better option for hydraulic barriers due to its distinct properties, such as very low hydraulic conductivity, high cation exchange capacity, high pollutant retention ability and semi-permeable membrane behaviour. These beneficial properties can be adversely affected by chemical compatibility issues, i.e. by environmental conditions that promote ion exchange of multivalent cations for monovalent cations. Such cation exchange in bentonite can cause a collapse of the diffused double layer, thereby increasing the hydraulic conductivity and decreasing the membrane behaviour, which are the two important parameters in hydraulic barrier applications (Bohnhoff and Shackelford, 2010). The susceptibility of bentonite and soil-bentonite liners to alterations in hydraulic conductivity upon exposure to chemical solutions, coupled with the limited organic contaminant removal efficiencies of bentonite, imposes constraints on their utility as effective hydraulic and

chemical barriers for waste containment. The limited adsorption capacity for organic liquids observed is attributed to the hydrophilic nature of bentonite and the substantial molecular size of the organic compounds involved. Consequently, there exists a need for the development of superior materials that not only demonstrate the capacity to eliminate organic compounds from leachate but also mitigate or restrict the impact of leachate on the geochemical behaviour of bentonite while preserving its intrinsic low permeability.

By considering the limitations of conventional bentonite liners, it is of prime importance to research new materials for liner construction without compromising the primary objective of efficient waste containment. From the literature review, it was highlighted that organoclays are one such material that researchers have used for various applications in recent years, especially while dealing with the pressing issue of organic pollutant contamination in various environmental matrices. Organoclays formed through the modification of natural clays with organic compounds exhibit enhanced sorption capacities for organic contaminants compared to unmodified clays, making them promising materials for remediation and hydraulic barrier applications in waste containment facilities. Studies have demonstrated the effectiveness of organoclays, particularly in adsorbing organic pollutants such as phenols, BTEX compounds, and dyes from aqueous solutions, along with other pollutants such as heavy metals and pharmaceuticals (Sun et al., 2017; Choi et al., 2023).

By combining the advantages of both barrier materials and addressing the coexistence of organic and inorganic contaminants in the leachates, a mixture of bentonite and organoclay may offer superior performance as a hydraulic barrier in environments with multiple contaminants. This composite liner system is expected to more effectively contain a range of pollutants, including organic compounds, heavy metals, and inorganic salts, compared to conventional bentonite alone. While numerous studies have explored the sorption and hydraulic performance of bentonite liners and organoclay individually, the geotechnical behaviour and barrier efficacy of organoclay-amended bentonite require further detailed investigation. Moreover, to the author's knowledge, there has been no comprehensive study on the performance of organoclay-amended bentonite liners in the presence of inorganic salts and heavy metals. Therefore, this research aims to thoroughly examine the geotechnical and geochemical performance of organoclay-amended bentonite liners under the influence of various leachate constituents, including inorganic salts, cationic and anionic heavy metals, and organic contaminants. Furthermore, the existing literature has not extensively documented

detailed material characterisation, surface charge analysis, and sorption efficacy of commercially available organoclay and bentonite.

2.9 Objectives of the study

The critical appraisal of the reviewed literature showed that the suitability of organoclay-bentonite mixture for hydraulic barrier applications under the effect of various pollutants was not investigated in detail. With this in view, a mixture of commercially available organoclay and bentonite was considered for performing various geotechnical experiments to understand the variation in geochemical properties in the context of a liner material which can retard both organic and inorganic contaminants. The primary goal of the present study is the detailed geotechnical investigation of organoclay-amended Indian bentonite (BOC) as a liner under the influence of different types of pollutants such as inorganic salts (NaCl and CaCl₂), heavy metals (Pb²⁺, Zn²⁺ and Cr(VI)) and organic contaminants (Phenol and Acetone). Furthermore, the barrier efficiency of the BOC was compared to that of conventional bentonite under these leachate constituents. The proposed scope and objective of the study are discussed.

- ✓ Material characterisation of commercially procured parent materials and investigation into the sorption behaviour of phenol and heavy metals onto commercial bentonite and organoclays.
- ✓ To investigate the effect of organoclay addition on the physical, hydraulic, and mechanical properties of bentonite in the presence of DI water.
- ✓ To analyse the variations in plasticity, swelling, hydraulic and mechanical characteristics of organoclay-amended bentonite under the influence of inorganic salts.
- ✓ To carry out a detailed study on the geotechnical and geochemical properties of organoclay-amended bentonite when subjected to anionic and cationic heavy metals.
- ✓ To assess the impact of organic contaminants on the physical, hydraulic and mechanical behaviour of organoclay-amended bentonite.

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 General

This chapter encompasses the details of the materials used as well as the experimental methodologies followed to complete the study. The research work was carried out in different stages to complete the proposed objectives by utilising the materials and methodologies described in this chapter.

3.2 Layout of the research work

The entire research work was completed in six different phases.

In phase I, the parent materials (i.e. bentonite and organoclay) were procured from the Indian commercial market. Figure 3.1 shows the summarised objectives and their distribution in different stages. The material was characterised initially by carrying out laboratory experiments to determine its physical and chemical characteristics.

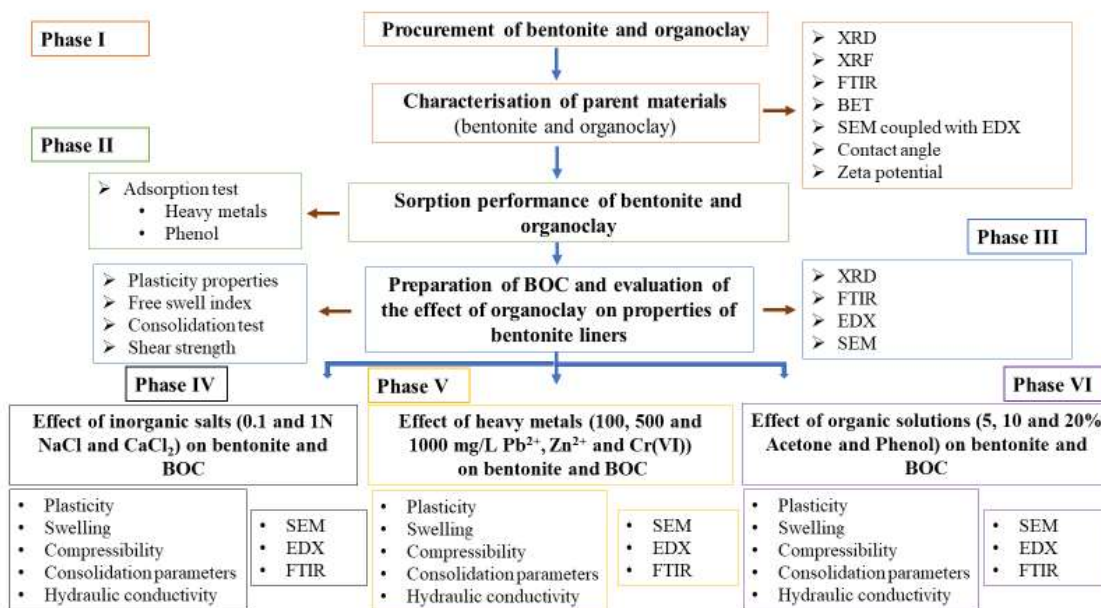


Fig. 3.1 Work flow of the research work

In phase II, the adsorption capacity of parent materials for retaining heavy metals (Pb²⁺, Zn²⁺, Cr(VI)) and organic contaminants (phenol) was investigated. The sorption capacity of parent materials at different pH and at varied adsorbate concentrations was analysed.

Phase III provides an idea about the effect of organoclay amendment on compacted bentonite. Various geotechnical characteristics such as liquid limit, free swell index, swell behaviour, compressibility properties, consolidation parameters, and shear strength behaviour of bentonite and organoclay-amended bentonite (BOC) in DI water were studied. The hydraulic conductivity of the samples was indirectly measured using consolidation test results.

The influence of two commonly found inorganic salts – NaCl and CaCl₂ (at 0.1 and 1N concentrations) on the hydraulic barrier performance of compacted bentonite and BOC was analysed in detail in Phase IV. Liquid limit, free swell index, and consolidation tests were performed on bentonite and BOC at varied concentrations of inorganic salts.

Phase V describes the effect of two cationic heavy metals (Pb²⁺ and Zn²⁺) and an anionic heavy metal (Cr(VI)) on the various geotechnical and chemical properties (pH, plasticity, swelling, compressibility, and consolidation behaviour) of compacted bentonite and BOC.

Finally, in Phase VI, a detailed geotechnical investigation of bentonite and BOC was carried out in the presence of two organic contaminants – acetone and phenol at varied concentrations (5, 10 and 20%).

3.3 Procurement of parent materials

3.3.1 Bentonite

Bentonite used in this study was procured commercially from the Barmer district, Rajasthan, India (Fig. 3.2). The soil was in powdered form, light brown in colour, and smooth in texture. The soil was mixed thoroughly and sieved through 425-micron sieves and stored in a drum for further testing. The physico-chemical and hydro-mechanical properties of bentonite were determined using standard laboratory procedures and are reported in Table 3.1.

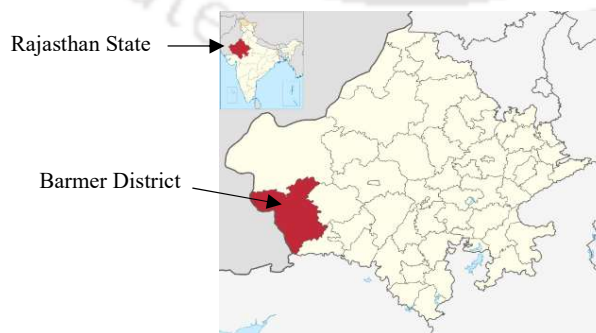


Fig. 3.2 Location of bentonite source

Table 3.1 Properties of bentonite

Property	Value
Specific gravity	2.68
Liquid limit (%)	310
Plastic limit (%)	38
Plasticity index	272
Free swell index(mL/2g)	36
CEC (meq/100g)	49.50
Na ⁺	31.8
Ca ²⁺	14.7
K ⁺	0.7
Mg ²⁺	2.3
Specific surface area (m ² /g)	340.4
BET specific surface area (m ² /g)	32.26
Optimum moisture content (%)	35.0
Maximum dry density (g/cc)	1.36
XRD d ₀₀₁ (nm)	1.05
pH (L/S = 20)	9.43
Electrical conductivity (mS/cm ²) (L/S = 20)	2.11
Clay content (%)	61
Silt content (%)	39

The physical, chemical and mineralogical characteristics of procured bentonite were determined using standard laboratory procedures. The specific gravity of parent soils was found using the procedure described in ASTM D854 (2014). ASTM D4318(2017) was adopted to determine the plasticity properties such as liquid limit, plastic limit and shrinkage limit. The procedure given in ASTM D5890 (2009b) was used to measure the free swell index of soils. The total specific surface area and cation exchange capacity (CEC) were determined by the Ethylene glycol monoethyl ether (EGME) method (Cerato and Lutenegeger, 2002) and the Ammonium replacement method (Chapman, 1965), respectively. The nitrogen adsorption-desorption isotherms were used to determine Brunauer–Emmett–Teller (BET) specific surface area. The compaction characteristics – maximum dry density (MDD) and optimum moisture content (OMC) of soil samples were found out by performing a mini compaction test described in Sridharan and Sivapullaiah (2005). The pH and electrical conductivity of soil samples at a liquid-to-solid ratio (L/S) of 20 were measured by using a standard pH meter and conductivity meter, respectively.

3.3.2 Organoclay

The organoclay (Fig. 3.3) used in the study was commercially available and was obtained from Ultrananotech Private Limited, Bangalore. It is organically modified based on natural bentonite and is off-white in colour. The primary surfactant used for the treatment is dimethyl di (hydrogenated tallow) alkylammonium salt. The organoclay is generally used as an additive for plastics to improve various physical properties, such as reinforcement, synergistic flame retardant and barrier for polymer applications. The basic properties of the organoclay, as given by the manufacturer, are listed in Table 3.2.

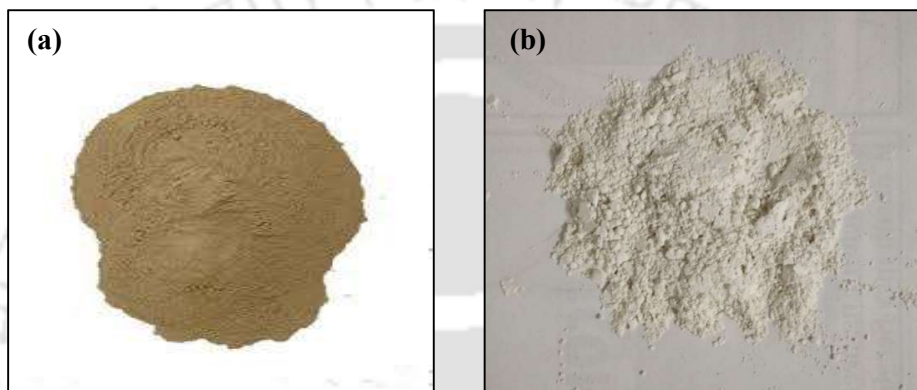


Fig. 3.3 Images of (a) bentonite and (b) organoclay

Table 3.2 Properties of organoclay (as per the manufacturer)

Property	Value
Specific gravity	1.7
Product form	Powder
Colour	Off white
Bulk density (g/cc)	0.450
Median particle size, d_{50} (μm)	<10
Moisture content (%)	<1
500 mesh pass rate (%)	>95
XRD d_{001} (nm)	3.3

3.4 Characterisation of parent materials

Material characterisation of procured materials is essential to understand the physical and chemical properties of the soils and soil mixture. To understand this, several microstructural investigations were conducted on both bentonite and organoclay, as shown in Figs. 3.4 and 3.5. The experiments performed were X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Fluorescence (XRF) and Field Emission Scanning Electron

Microscope (FESEM). The XRD test (SmartLab, Rigaku Technologies, Japan) was conducted on both soils by choosing a 2θ angle between 2 to 70° with a step size of 0.02° . The presence of montmorillonite mineral, basal spacings and crystallinity of both bentonite and organoclay were identified from the XRD peaks shown in Fig. 3.4(a). The basal spacings of bentonite and organoclay were found to be $10.53 \text{ \AA}$ and $32.60 \text{ \AA}$, respectively. The basal spacing of $32.60 \text{ \AA}$ for organoclay displays the pseudo trilayers or paraffin arrangement of organic molecules in its interlayer (Lagaly, 1986). The FTIR analysis (Perkin Elmer Spectrum Two FT-IR Spectrometer, UK) was conducted for both parent materials and possible interactions between particles were identified (Fig. 3.4 b). In the case of organoclay, the modification of bentonite by organic cations was confirmed by the presence of peaks at 1469 and 720 cm^{-1} . Unlike bentonite, the absence of a peak at 3400 cm^{-1} and a reduction in peak at 1643 cm^{-1} validated the loss of interlayer water and the hydrophobic nature of organoclays (Khenifi, 2007; Sreedharan, 2013). Furthermore, the hydrophobic nature of organoclay was confirmed with the help of contact angle measurement using a goniometer (Holmarc Contact angle meter, model: HO-IAD-CAM-01B). The measured average contact angles for bentonite and organoclay samples were 36.8° and 133.6° , respectively (Fig. 3.5). Thus, the higher contact angle obtained for organoclay reaffirms the hydrophobicity of organoclay. The FESEM images shown in Fig. 3.4 (c) and (d) confirmed the presence of plate-like particles in both bentonite and organoclay. The elemental composition of bentonite and organoclay was determined using the X-ray fluorescence (XRF) (Zetium XRF Spectrometer, PANalytical, Malvern, UK), and the data is displayed in Table 3.3. From CHNS/O (Carbon, Hydrogen, Nitrogen, Sulphur, Oxygen) elemental analysis (Elementar, Vario MACRO Cube), the percentage of nitrogen was found to be 0.43 and 11.41% in bentonite and organoclay, respectively. The amount of nitrogen in organoclay represents the intercalation of quaternary ammonium salts.

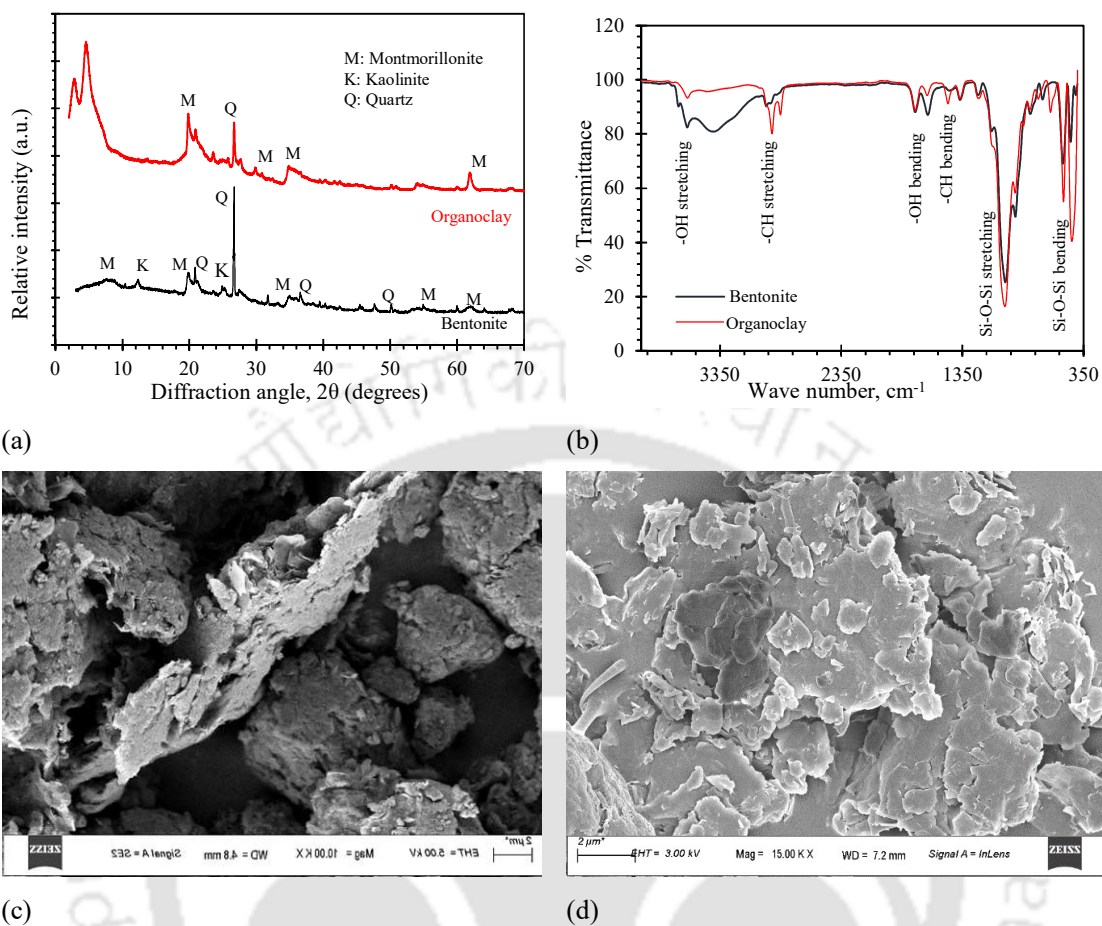


Fig. 3.4 (a) XRD of bentonite and organoclay (b) FTIR of bentonite and organoclay (c) FESEM image of dry bentonite (d) FESEM image of dry organoclay

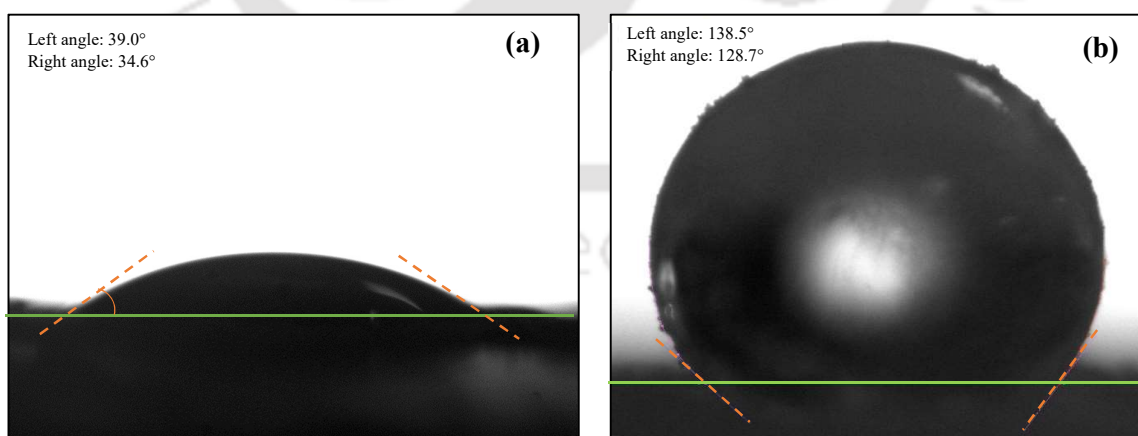


Fig. 3.5 Contact angles of (a) bentonite and (b) organoclay samples measured using a goniometer

Table 3.3 Elemental composition of bentonite and organoclay from XRF results

Elemental oxides	Composition (%)	
	Bentonite	Organoclay
SiO ₂	47.28	39.93
Al ₂ O ₃	16.23	12.56
Fe ₂ O ₃	13.09	1.23
MnO	0.34	0.02
MgO	1.56	2.37
CaO	0.53	0.27
Na ₂ O	2.53	0.07
K ₂ O	1.11	1.1
TiO ₂	2.26	0.11
P ₂ O ₅	0.14	0.01
SO ₃	0.2	0.02

The zeta potential of both bentonite and organoclay was measured automatically with the aid of the Dynamic Light Scattering System (Anton Paar GmbH- Austria, Litesizer 500), which uses the electrophoretic light scattering method or Doppler electrophoresis. The soil suspensions were prepared using milli-Q water at a solid-to-liquid ratio of 0.1wt%. The analyses were carried out by varying initial pH ranging from 2 to 9, and the results are shown in Fig. 3.6. The zeta potential of bentonite showed a drastic change in magnitude with a decrease in pH, whereas organoclay showed comparatively less variation. The high negatively charged surface of bentonite and the comparatively lower negatively charged surface of organoclay can be interpreted from these results.

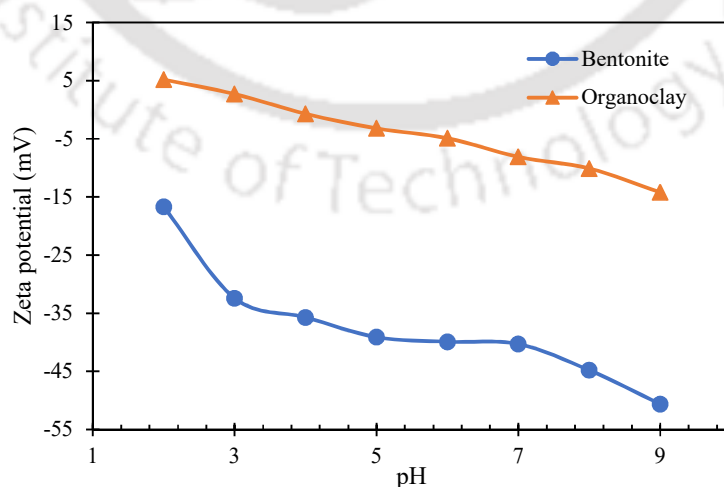


Fig. 3.6 Zeta potential distribution of bentonite and organoclay

3.5 Preparation of organoclay-amended bentonite (BOC)

Considering the advantages of both bentonite and organoclay observed from literature studies, the current study proposes the utilisation of organoclay-amended bentonite for hydraulic barrier applications. A mixture of bentonite and organoclay in a dry weight proportion of 90:10 was adopted for the current experimental investigation. The determination of the optimal proportion of bentonite and organoclay for utilisation in landfill liner applications was established through a comprehensive review of prior research studies undertaken within analogous contexts (Ghavami, 2017; Javadi et al., 2017). Previous researchers noted that the addition of more than 10% organoclay could significantly increase the hydraulic conductivity in DI water, which may affect the hydraulic performance of landfill liners. The term BOC will be used further to refer to a 90:10 mixture of bentonite and organoclay.

A dry mixing procedure was adopted for the analysis as follows: the required amount of oven-dried bentonite and organoclay was weighed and spread over a glass plate. The mixture was thoroughly blended in its dry state until a uniform mixture was attained (Fig. 3.7). After achieving uniform dry mixing, the required amount of respective solution was added using a spray and mixed uniformly until the optimum moisture content was obtained. The samples were then transferred to a polythene bag and kept in a humidity-controlled desiccator for a minimum time period of 24 hours to attain moisture equilibrium.



Fig. 3.7 Bentonite-organoclay mixture

3.6 Permeant liquids

The composition of municipal and industrial hazardous waste leachates significantly varies based on the waste type as well as other geological and environmental factors. However, prior studies concluded that high concentrations of inorganic macro compounds, heavy metals and

organic pollutants coexist in various leachates (Dutta and Mishra, 2016; Ray et al., 2021; Gupta et al., 2020). To understand the effect of various leachate constituents on the proposed landfill barrier material, two inorganic salts - NaCl and CaCl₂, three heavy metals - Pb²⁺, Zn²⁺ (cationic) and Cr(VI) (anionic), and two organic contaminants – acetone and phenol were selected for this investigation. Since high amounts of Na⁺ and Ca²⁺ are found in waste leachates, the inorganic salts of NaCl and CaCl₂ were prepared at a concentration of 0.1N and 1N for the analysis. As a representative of cationic heavy metal, stock solutions (1000 mg/L) of Pb²⁺ and Zn²⁺ were prepared by dissolving precalculated quantities of lead nitrate (Pb(NO₃)₂) and zinc nitrate (Zn(NO₃)₂·6H₂O) in DI water. The nitrate anion was chosen for the study because of the insignificant effect of nitrate ion on the geotechnical properties of bentonite (Barbier et al., 2002; Du et al., 2015). Chromium (VI) was selected as an anionic heavy metal, and different concentrations (100, 500 and 1000 mg/L) of Cr(VI) were prepared by dissolving a predetermined amount of potassium dichromate salt in DI water. This study employed a maximum heavy metal concentration of 1000 mg/L owing to the detection of such elevated concentrations in waste leachates and their reporting in prior research papers (Yang et al., 2021; Gupta et al., 2020; Ray et al., 2021; Dutta and Mishra, 2017; Bancchor et al., 2020). Stock solutions of 1000 mg/L were prepared initially, and it was further diluted to obtain other concentrations (100 and 500 mg/L) of Pb²⁺, Zn²⁺ and Cr(VI). In most municipal solid waste leachates, organic contaminants are present in trace amounts. However, their presence might be high in industrial leachates. Since pure organic fluids are not encountered in leachates, the maximum concentration of organic pollutants was fixed at 20%. Phenol and Acetone were chosen as representative of organic pollutants and were prepared at a concentration of 5, 10 and 20% (volume to volume basis). All salts were purchased from Merck, India, and the purity was observed to be around 99%.

3.7 Experimental Methodology

3.7.1 Plasticity properties

Plasticity properties such as liquid limit, plastic limit and shrinkage limit are essential for understanding the engineering behaviour of clays. In this study, Casagrande's method and thread rolling method were adopted for the determination of liquid limit and plastic limit, respectively. The detailed experimental procedure is given in ASTM D4318 (2017). Approximately 150 to 200 g of soil was sieved through a 425 µm sieve and mixed thoroughly with sufficient quantities of the respective solutions on a glass plate. The samples were sealed

in a polyethylene cover and kept in a humidity-controlled desiccator for at least 24 hours to attain moisture equilibrium.

After attaining equilibrium, the samples were thoroughly remixed. A portion of the soil sample was placed over the Casagrande's cup and spread it over. Necessary precautions were taken to reduce air bubbles in the soil. A groove was created in the central portion of the soil using the standard grooving tool. The cup was lifted and dropped at a rate of 1.9 to 2.1 drops per second until the two halves joined at the bottom of the groove along a distance of 13 mm. The number of drops required to close the groove was recorded, and a portion of the sample was taken for moisture content determination. The procedure was repeated until enough data points were obtained within the range of 15 to 35 number of drops.

The relationship between water content and the number of drops was plotted on a semi-logarithmic graph with water content on the arithmetical scale (ordinate) and the number of drops on a logarithmic scale (abscissa). The best-fitting straight line was drawn, and the liquid limit was determined as the water content corresponding to the intersection of the line with the 25-drop abscissa, rounded to the nearest whole number.

The thread rolling method was used to determine the plastic limit of soils. A few grams of soil were taken and sufficiently dried from the sample taken for liquid limit determination. The soil was rolled using the hand-rolling method until the thread diameter reached 3.2 mm. If the thread could be further rolled without breaking, it was broken into pieces and rerolled. The procedure was repeated until the soil crumbled before the thread reached a diameter of 3.2 mm, and the corresponding water content was noted as the plastic limit. The reported Atterberg's limit value represents the average value obtained by conducting the experiment thrice.

3.7.2 Free Swell Index

The free swell index measures the extent to which clay swells when submerged in DI water or any other fluid without any external confining pressure. The test provides an easy and simple procedure for assessing the swelling ability of clays in various liquids. The procedure described in ASTM D5890 (2009b) and Lo et al. (1997) was adopted to determine clays' free swell index.

Two grams of oven-dried sample were slowly added to approximately 40 ml of the respective fluids taken in a 100 ml graduating cylinder. The contents of the cylinder were then thoroughly shaken to obtain a suspension. The suspension was then topped up to 100 ml by adding more fluid. The mixture was stirred to ensure full contact of the clay with the test liquid.

The cylinders were sealed and left undisturbed for a minimum time period of 24 hours. The sediment volume was then noted and reported as the free swell index in mL per 2 g (Fig. 3.8).



Fig. 3.8 Free Swelling Test

3.7.3 Consolidation Properties

The swelling, compressibility, consolidation parameters and hydraulic behaviour were estimated through a series of one-dimensional oedometer tests. The experiment was performed on bentonite and BOC under different inundating fluids, including DI water, inorganic salt permeants, heavy metal solutions and organic solutions. Figure 3.9 depicts the schematic diagram and set up used for consolidation tests.

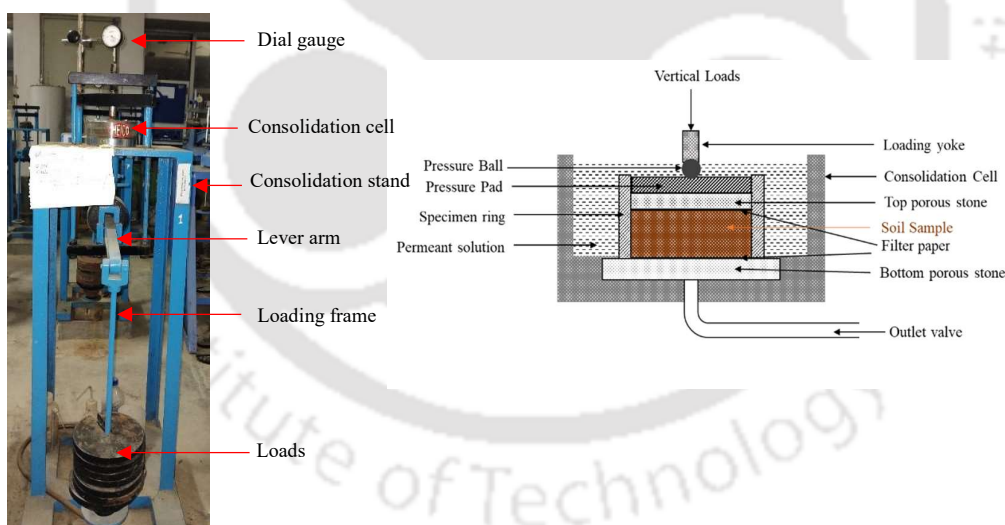


Fig. 3.9 Consolidation setup and its schematic diagram

Prior to the oedometer tests, the compaction characteristics of both bentonite and BOC in DI water were determined using a mini-compaction test, following the methodology explained by Sridharan and Sivapullaiah (2005). The obtained compaction parameters, OMC and MDD in DI water, were utilised for the preparation of oedometer samples. This approach was chosen because the permeation of inorganic and organic contaminants will only manifest during the

functional period of the soil barrier. The detailed procedure for conducting the oedometer tests is outlined in ASTM D2435 (2011).

According to the standard procedure, soil samples were mixed thoroughly with DI water at their corresponding OMC and stored in a polythene cover. The samples were kept in a humidity-controlled desiccator for at least 24 hours to achieve moisture equilibrium. A sufficient quantity of samples was then statically compacted in the oedometer ring at their respective MDD up to a height of 15 mm. The initial height and weight of samples were noted for further calculations. Soil samples with dimensions of 60 mm in diameter and 15 mm in height were compacted in an oedometer ring and assembled in a consolidation cell. On either side of the soil sample, filter papers and porous stones were kept. Filter papers were placed to avoid the clogging of porous stones due to the probable intrusion of soil particles, whereas porous stones were used to allow the double drainage of soil samples. The components of the oedometer cell were carefully placed and mounted on a consolidation stand. Dial gauges were attached to the consolidation cell to note down the changes in the height of soil samples. Loading frames attached to the consolidation stand help in transferring vertical loads to the soil through lever arms. Initially, a seating load of 5 kPa was added, and respective solutions were poured into the consolidation cell. Once the swelling ceased, extra loads were applied at a load increment ratio of one. Each load was kept for a sufficient period to complete the deformation, and dial gauge readings were noted at regular intervals. Time-deformation curves were plotted for each load increment, and corresponding consolidation parameters were found by employing the square root of the time-fitting method (Taylor, 1942). From the consolidation test results, the following parameters were found;

- From the dial gauge readings, changes in sample thickness (ΔH_s) and changes in the void ratio (Δe_s) were found for each load increment using the following equations:

$$\Delta H_s = H_f - H_i \quad (3.1)$$

$$\Delta e_s = \frac{\Delta H_s}{H_i} \times (1 + e_i) \quad (3.2)$$

where H_f = Final height of soil sample corresponding to each load increment

H_i = Initial height of soil sample at particular load increment

e_i = Initial void ratio of the soil sample corresponding to each load increment

- From the time-settlement curve, the time for 90% consolidation (t_{90}) was found out for each load increment using the procedure explained by Taylor (1942), as shown in Fig. 3.10.
- The coefficient of volume change (m_v) was determined by the ratio of unit volume change to change in effective stress, which is given by

$$m_v = \frac{\Delta e_s}{(1 + e_i) \Delta \sigma} \quad (3.3)$$

where $\Delta \sigma$ is the change in load increment or change in effective stress

- The coefficient of consolidation (c_v) is a laboratory parameter that gives a measure of the compressibility of soil. It can be found out by using the following equation:

$$c_v = \frac{T_v H_{dp}^2}{t_{90}} \quad (3.4)$$

where T_v = time factor for 90% consolidation = 0.848

H_{dp} = maximum drainage path for 90% consolidation = $0.5 \times$ average height of soil sample for double drainage

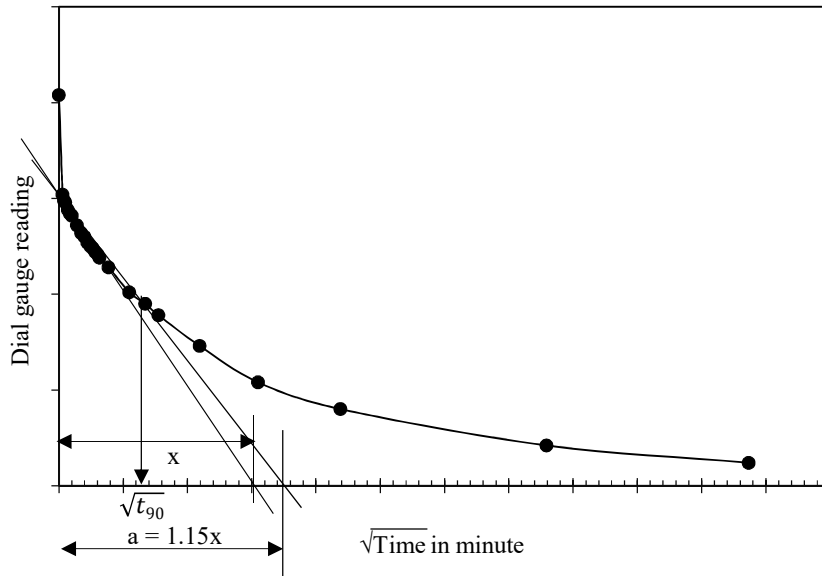


Fig. 3.10 Square root of time method for the determination of time for 90% consolidation

- The compressibility property, compression index (C_c) and the consolidation characteristic - yield stress (σ_y) of compacted samples were obtained with the help of the void ratio-overburden pressure ($e - \log \sigma$) curve.
 - C_c for all samples was found by measuring the slope of the straight-line portion of the void ratio - overburden pressure ($e - \log \sigma$) curve under the virgin loading path.

$$C_c = \frac{\Delta e}{\Delta \sigma} = \frac{e_1 - e_2}{\log \frac{\sigma_2}{\sigma_1}} \quad (3.5)$$

where e_1 and e_2 are the void ratios corresponding to the effective stress σ_1 and σ_2 , respectively.

- The yield stress of bentonite and BOC under various permeants was determined based on Casagrande's method (Casagrande, 1936).
- Coefficient of permeability or hydraulic conductivity (k)

The coefficient of permeability or hydraulic conductivity of soil (k) is a crucial factor in designing landfill covers and liners (Daniel, 1984). Based on the USEPA (1988) recommendations, the material should be used as a compacted soil liner if the hydraulic conductivity falls below 1×10^{-9} m/s. In the current study, the hydraulic conductivity of each sample was computed indirectly by using the equation proposed by Terzaghi (1965). Various researchers have utilised this method for determining k because it has been proven to yield results similar to direct methods (Mesri and Olson, 1971; Ray et al., 2022; Sivapullaiah et al., 2000). According to Terzaghi (1965), the k value is given by

$$\text{Hydraulic conductivity, } k = m_v \cdot C_v \cdot \gamma_w \quad (3.6)$$

where γ_w is the unit weight of the pore fluid

- Swell potential and Swell pressure

From the consolidation test results, the swell potential and swell pressure were determined for each sample. The compacted soil samples saturated with respective solutions were allowed to swell under an initial seating load of 4.9 kPa, and the variation of swelling with time was recorded using dial gauges. The measurements were continued till negligible variation in swelling values was obtained.

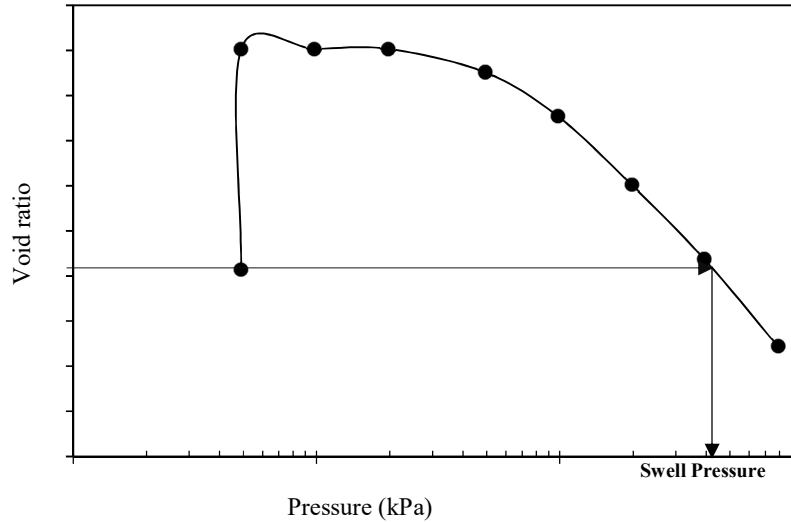


Fig. 3.11 Determination of swell pressure

The swell percentage or swell potential for each sample was obtained by the following equation;

$$\text{Swell potential (\%)} = \frac{\Delta H_T}{H_0} \times 100 \quad \text{or} \quad \frac{\Delta e}{1+e_0} \times 100 \quad (3.7)$$

where ΔH_T = Total change in sample thickness at the end of the swelling

H_0 and e_0 represent the initial height and initial void ratio of the sample before commencing the experiment

The pressure needed to compress the specimen to its initial void ratio after saturating with inundating fluid is known as swelling pressure. The void ratio – overburden pressure curve was used to evaluate the swelling pressure. Sridharan et al. (1986) and Sridharan and Gurtug (2004) explained this method for determining swelling pressure in detail (Fig. 3.11).

- Stages of swelling

The addition of permeant solution increased the swelling of bentonite and BOC with time. Irrespective of the soil type and pore fluid characteristics, the time – swelling plot displayed an S-shaped curve, and the entire swelling can be divided into three phases – initial, primary and secondary swelling (Sridharan and Gurtug, 2004). When solutions are added, initially, the soil swells slowly in the “initial swelling” stage, then increases steeply in the “primary swelling” stage, then shows a marginal increase in swelling and reaches an asymptotic value in the “secondary swelling stage” (Dutta and Mishra, 2016; Rao and Thyagaraj, 2007). The procedure

for calculating the initial and primary swelling time was based on Fig. 3.12, as described by Sridharan and Gurtug (2004). The time taken for completing initial swelling and primary swelling are denoted as t_{is} and t_{ps} , respectively.

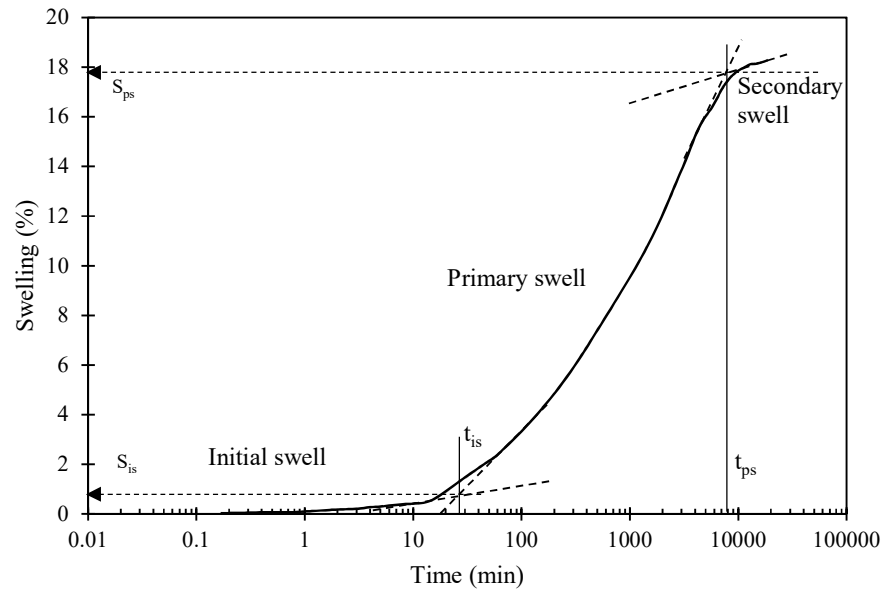


Fig. 3.12 Representation of different stages of swelling (Sridharan and Gurtug, 2004)

3.7.4 Strength properties

The shear strength of the barrier is a crucial criterion in the design of an engineered landfill. The liner material should possess sufficient strength to withstand the static load exerted by the overlying waste (Kenny et al., 1992). Researchers suggested a minimum UCS value of 200 kPa as a minimum criterion for liner (Daniel and Wu, 1993). The strength characteristics (undrained shear strength) of the samples were determined using the UCS test according to ASTM D2166 (2006). The UCS test is a simple and quick experiment used to obtain the shear strength of soils with sufficient cohesion to permit testing in the unconfined state. The soil samples were premixed with respective permeants at a moisture content equal to OMC of DI water and stored in a desiccator for 24 hours. Cylindrical soil samples of 38 mm diameter and 76 mm height were prepared at MDD corresponding to DI water (Fig. 3.13). Once the samples were prepared, they were loaded under a constant strain of 1.25 mm/min to simulate the undrained condition during the testing. The proving ring readings corresponding to the dial gauge readings were noted at regular intervals. The load was continued until the load values decreased with an increase in strain or until a 15% strain was achieved. The axial strain (ϵ_o in %) was determined

by calculating the ratio of the change in length to the initial length of the specimen. If the initial cross-sectional area of the specimen is A_0 (mm^2), then the average cross-sectional area (A) for a given load can be calculated by

$$A (\text{mm}^2) = \frac{A_0}{1 - \varepsilon_0} \quad (3.8)$$



Fig. 3.13 Sample preparation and apparatus for UCS test

The ratio of the applied load to the corresponding average cross-sectional area provides the unconfined compressive stress of soil. Furthermore, a graph was plotted between compressive stress on the ordinate and axial strain on the abscissa. The peak value of compressive stress or the compressive stress at 15% axial strain, whichever was secured first, was reported as the unconfined compressive strength, q_u . The test was repeated at least thrice, and the average value was reported as the unconfined compressive strength. The undrained shear strength of the soil was determined to be half of the unconfined compressive strength.

3.7.5 Adsorption properties

Adsorption efficiencies of heavy metals (Pb^{2+} , Zn^{2+} and Cr(VI)) and organic contaminant (phenol) onto commercially procured bentonite and organoclay were investigated by using batch procedures based on ASTM 4646 (2008). A separate kinetic study was not conducted in bentonite and organoclay because prior studies confirmed that equilibrium was achieved within 2 to 3 hours (Anna et al., 2015; Dinh et al., 2022; Gupt et al., 2022). Therefore, a time period of 24 hours was considered for the batch adsorption tests as per the ASTM code. The stock solutions of Pb^{2+} and Zn^{2+} were prepared using DI water, and the required concentrations of heavy metals or phenol were prepared by diluting them. Initially, the effect of pH on the adsorption behaviour was analysed by varying the pH from 2 to 9 by adding required quantities of HNO_3 and NaOH (0.01 and 0.1 M) buffer. For low pH, a few drops of concentrated HNO_3

were used. To understand the possibility of heavy metal or phenol precipitation, the study was initially carried out on heavy metal solutions at varied pH levels without adding adsorbents. The results demonstrated that the Pb^{2+} ions and Zn^{2+} ions precipitated beyond a pH of 6 and 8, respectively. In the case of Cr(VI) and phenol, no precipitation was identified in the pH range of 2 to 9. Later, a known amount of adsorbent (bentonite or organoclay was added), at a liquid-to-solid ratio of 20, to 100 mL of 500 mg/L adsorbate (Pb^{2+} or Zn^{2+} or Cr(VI) or Phenol) taken in 250mL conical flasks. The procedure for the addition of clay adsorbent to cationic heavy metals was based on Gupt et al. (2020), as the high pH of adsorbents may result in immediate precipitation when it comes in contact with heavy metal solutions. After the addition of adsorbent, the conical flasks were shaken continuously in a rotary shaker at 180 rpm for 24h at room temperature ($28 \pm 1^\circ\text{C}$). Later, the solutions were vacuum filtered, and the cationic heavy metals in the filtrate were analysed using an Atomic Adsorption Spectrophotometer (AAS), while anionic Cr(VI) and phenol were analysed using a UV-vis-Spectrophotometer. The sequential procedure adopted for the adsorption test is shown in Fig. 3.14.

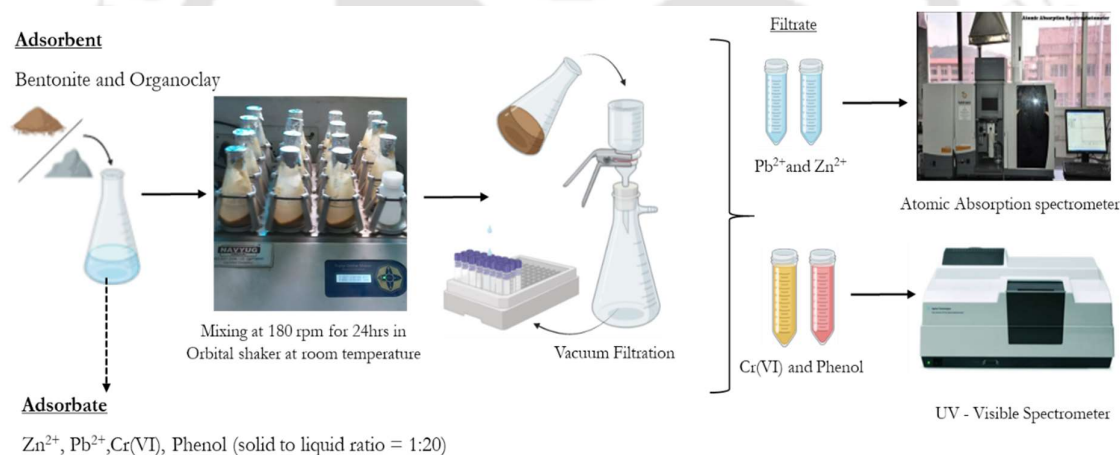


Fig. 3.14 Step-by-Step Procedure for Adsorption test

In addition to this, the sorption capacity or retention capacity of contaminants onto bentonite and organoclay at varied adsorbate concentrations was also investigated. This study is important as the concentration of heavy metal or organic pollutants in various leachates varies from time to time and also varies based on the type of waste. An initial adsorbate concentration of 50, 100, 250, 500, 750, 1000 and 2000 mg/L were prepared from the stock solutions. The pH of the solution was adjusted to 5 ± 0.2 by adding small amounts of NaOH and HNO_3 . This pH was pre-fixed in order to avoid the precipitation of heavy metal ions and to simulate the pH of leachate as reported in the literature (Wdowczyk and Szymańska-

Pulikowska, 2021; Parvin and Tareq, 2021; Gupta, 2023). Five grams of adsorbent was added to a 250mL conical flask containing 100 mL of varied adsorbate concentrations. After the addition of adsorbent, the conical flasks were shaken continuously at 180 rpm in a rotary shaker for 24 hours at room temperature ($28 \pm 1^\circ\text{C}$). Later, the solutions were vacuum-filtered. The heavy metals and phenol in the filtrate were analysed using an Atomic Adsorption Spectrophotometer (AAS) and UV visible spectrophotometer.

The adsorbed amount of heavy metals onto the adsorbent surface and the percentage removal was determined using the following equations:

$$q_e = [(C_i - C_e) \times \frac{V_L}{m_s}] \quad (3.9)$$

$$\text{Percentage removal (\%)} = \left[\left(\frac{C_i - C_e}{C_i} \right) \times 100 \right] \quad (3.10)$$

where q_e is the sorbed amount per unit mass of sorbent in (mg/g); C_i is the initial concentration of adsorbate (i.e. heavy metals or phenol) (mg/L); C_e is the final concentration of adsorbate after adsorption (mg/L); V_L is the volume of heavy metal/phenol solution (mL); m_s is the adsorbent mass used for the experiment (g)

3.7.6 Microstructural analysis

The surface morphological and topographical variations on the bentonite and BOC due to the permeation of various solutions were identified using the images obtained from FESEM. The elemental information of the samples was analysed using a FESEM coupled with an element EDS detector (Sigma 300 model, Zeiss). After performing the consolidation tests, each sample was dried and carefully cut into two halves. A representative soil from the mid portion of the consolidated sample was carefully retrieved to conduct the microstructural analysis, such as Energy Dispersive X-ray Spectroscopy (EDS), FESEM, XRD, and FTIR. For FESEM and EDS analysis, the dried samples were powdered using a mortar and pestle. The obtained fine fraction was sieved through a 75 μm Indian standard sieve. A small quantity of this powdered sample was placed on carbon tape, which was mounted on an aluminium stub. Before placing the sample in the FESEM machine, a thin layer of gold was coated over the stub using a gold sputter coating machine. Each soil sample was examined by taking images at different magnifications ranging from 1kX to 20kX. Selected images are presented in the results to compare the morphological changes due to the permeation of leachate constituents.

The surface functional groups of the samples were identified from the FTIR spectroscopy data (PerkinElmer, Singapore, Model: Spectrum two). For FTIR analysis, the powdered samples were mixed with potassium bromide (KBr) to form pellets, as KBr is transparent to infrared radiation. These pellets were then placed in a pellet holder, and the spectra were recorded across a wavelength range spanning from 400 to 4000 cm^{-1} . During the process, an infrared beam was directed through the sample within the specified wavelength range, resulting in the sample adsorbing some of the IR energy depending on the functional group present in it.

X-ray diffraction (XRD) tests were employed to identify the presence of predominant clay minerals in the soil samples. Additionally, crystallinity, basal spacings, and mineralogy in the soil were obtained. For the analysis, a powder X-ray diffractometer (SmartLab, Rigaku Technologies, Japan) consisting of a 9 kW rotating anode X-ray source coupled with an X-ray detector was used. The test was performed on powdered soil samples at a step size of 0.02° , scanning speed of 20° $2\theta/\text{min}$ and 2θ range between 2° and 70° . The obtained diffractograms were analysed using X'Pert Highscore software, and the d-spacings were determined using Bragg's equation.

CHAPTER 4

Adsorption of Heavy metals and Phenol onto Bentonite and Organoclay

4.1 General

This chapter examines the contaminant retention capacities of commercially procured bentonite and organoclay, intended for use as barrier material in highly contaminated hazardous waste containments. Lead and Zinc were selected as representative cationic heavy metal contaminants, while Cr(VI) was chosen as the model anionic heavy metal contaminant. Phenol was selected to represent commonly found organic contaminants in waste containment facilities. Batch adsorption studies were conducted to evaluate the adsorption capacities of the parent materials.

4.1.1 Background

Waste containment facilities often contain a wide variety of contaminants in high proportions due to the highly heterogeneous nature of the waste. The effective retention of these pollutants within the facility is crucial to protect the surrounding environment. Therefore, the barrier material must be capable of effectively retaining the pollutants present in percolated leachates. Various methods, including chemical precipitation, membrane filtration, ion-exchange, solvent extraction, electrochemical treatments, reverse osmosis, and adsorption, are found to be effective in removing organic and inorganic contaminants from aqueous solutions. Among these methods, adsorption by clay minerals is an economical and effective solution for the removal of highly toxic heavy metals or organic contaminants due to their easy synthesis, versatility, and abundant natural occurrence. Consequently, clays with high retention or sorption capacity are preferable for use as a hydraulic barrier.

Bentonite, a commercially available clay, has been proven to be an efficient adsorbent due to its high cation exchange capacity and specific surface area (Chu et al., 2019). Researchers have recommended the use of bentonite as a buffer and backfill material in deep geological repositories and as a liner for hazardous/non-hazardous landfills. The high negative charge density at the bentonite surface facilitates the adsorption of cationic heavy metals, though it reduces the affinity for anionic heavy metals and organic pollutants. Clays such as bentonite are often organically modified to produce organoclays, which enhances the adsorption efficiency of organic pollutants.

Numerous studies have examined the sorption performance of bentonite under the effect of cationic heavy metals such as Pb^{2+} , Zn^{2+} , Cd^{2+} and Cr^{3+} . Similarly, research has been conducted on the adsorption capacities of organoclay for organic pollutants. However, the adsorption performance of bentonite in the presence of anionic heavy metals (Cr(VI)) and organic contaminants still requires examination. Additionally, a comprehensive analysis is required to evaluate the adsorption performance of organoclays for both cationic and anionic heavy metals.

The objective of this research is to investigate the sorption capacities of bentonite and organoclay for heavy metals and phenol through a series of batch adsorption experiments in single contaminant systems. It is important to note that the sorption studies of parent materials are essential as the behaviour of commercially procured clays can vary significantly depending on factors such as the source of the clay and the type of organic modification. The adsorption studies were carried out by varying two important parameters: initial pH and initial adsorbate concentration. An isotherm study was also carried out based on the results to understand the adsorption mechanism. This investigation will be useful in designing an engineered barrier system for highly polluted waste containment facilities and understanding the contaminant removal performance of these systems.

4.2 Results and Discussions

4.2.1 Effect of initial pH on the adsorption performance of bentonite and organoclay

The pH of the solution is a critical parameter influencing the sorption performance of clays because it can affect the surface charge of the adsorbents and metal speciation or ionisation degree of the adsorbate. The removal efficiencies of heavy metal ions and phenol as a function of pH, within the range of 2 to 8, are illustrated in Figs. 4.1 to 4.4. All experiments were performed at an initial concentration of 500 mg/L and a solid-to-liquid ratio of 1:20. The figures demonstrate the comparative removal percentages of Pb^{2+} , Zn^{2+} , Cr(VI) and phenol by bentonite and organoclay.

4.2.1.1 Effect of pH on cationic heavy metal sorption by bentonite

Figures 4.1 and 4.2 presented the cationic heavy metal removal efficiencies of bentonite, which increased with an increase in the initial pH of the solution. At highly acidic pH ($\text{pH} = 2$), bentonite displayed a percentage removal of 72% for Pb^{2+} and 38% for Zn^{2+} . However, the removal of Pb^{2+} increased drastically with a further rise in pH, showing nearly 100% removal beyond a pH of 4. In the case of Zn^{2+} , the removal efficiency was over 95% beyond a pH of 6.

The isomorphous substitution in tetrahedral and octahedral sheets of bentonite resulted in high negative charge density on the surface of bentonite. This negatively charged surface of bentonite is desirable for the adsorption of cationic heavy metals such as Pb^{2+} and Zn^{2+} .

Various mechanisms, such as cation exchange, outer sphere complexation, inner sphere complexation, and precipitation, can contribute to the adsorption ability of bentonite at varied pH levels. At lower pH levels, a scenario of competitive adsorption arises, where H^+ or H_3O^+ ions and Pb^{2+} or Zn^{2+} ions strive for available adsorption sites on the bentonite surface. This competition is a consequence of the protonation of the hydrated bentonite surface. Therefore, cationic heavy metal sorption onto the bentonite showed a declining trend as the pH changed from alkaline to acidic. However, at higher pH levels, the concentration of H^+ in the solution decreases as well as the deprotonation of the bentonite surface occurs, leading to a rise in electrostatic attraction between the $\text{Pb}^{2+}/\text{Zn}^{2+}$ ions and the highly negatively charged bentonite surfaces (Chu et al., 2019). As a result, the adsorption capacity of bentonite improved with a rise in pH. These results are consistent with the trends observed in previous literature (Kubilay et al., 2007; Anna et al., 2015; Chu et al., 2019; Gupt et al., 2020). The electrostatic interaction between cationic heavy metal ions and negative surface charges contributes to the outer sphere complexes, whereas inner sphere complexes were formed between metal ions and aluminol or silanol groups at the edges of bentonite particles (Dinh et al., 2022). In the pH range of 3 to 6, the major adsorption mechanism may be due to the surface complexation. At $\text{pH} < 6$, the predominant lead species will be Pb^{2+} and beyond a pH of 6, lead species exist in the insoluble precipitate form, such as $\text{Pb}(\text{OH})_2$. Similarly, at a $\text{pH} > 8$, zinc species get precipitated in the form of metal hydroxyl complexes. Therefore, the nearly complete removal of Pb^{2+} and Zn^{2+} beyond the mentioned pH ($\text{pH} > 6$ for lead and $\text{pH} > 8$ for zinc) might be mainly attributed to the precipitation mechanism.

As illustrated in Figs. 4.1 and 4.2, regardless of the pH, bentonite demonstrated superior removal of lead ions compared to zinc ions. Specifically, the removal efficacy of Pb^{2+} by bentonite at a pH of 5 was noted as 99.3%, whereas the removal efficacy for Zn^{2+} was observed to be 86.6%. According to Coulomb's law, the attraction between two ions is directly proportional to the product of their charges and inversely proportional to the distance between their centres. Since both Pb^{2+} and Zn^{2+} possess the same charge (+2), the variation in adsorption capacity can be linked to the difference in their hydrated radii. Cations with smaller hydrated radii can pack closer together, resulting in a stronger attraction energy to the sorbent. Additionally, the hydrated radii of cations are inversely proportional to their ionic radii. The

ionic radius of Pb^{2+} ($1.19 \text{ \AA}$) is higher than that of interlayer Na^+ ($0.95 \text{ \AA}$) as well as Zn^{2+} ($0.74 \text{ \AA}$). Consequently, the interlayer spaces of clays can accommodate more Pb^{2+} ions, which have smaller hydrated radii. Hence, bentonite showed better removal of Pb^{2+} ions compared to Zn^{2+} .

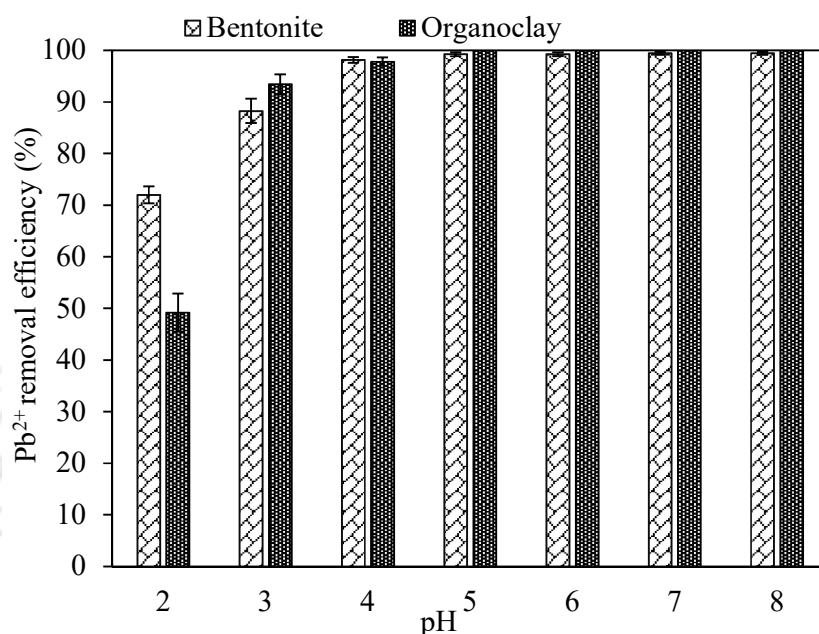


Fig. 4.1 Effect of pH on the Pb^{2+} removal efficiency of bentonite and organoclay (at a fixed initial concentration of 500 mg/L and S/L of 1:20)

4.2.1.1 Effect of pH on cationic heavy metal sorption by organoclay

From the Figs. 4.1 and 4.2, it was noted that organoclay exhibited poor removal efficiency for cationic heavy metals, particularly in strongly acidic solutions. For instance, at a pH of 2, organoclay achieved a removal efficacy of 49.2% for Pb^{2+} and 23.8% for Zn^{2+} . As the pH of lead and zinc nitrate solutions increased, the removal efficacy of cationic heavy metals by organoclay also increased, with Pb^{2+} showing substantially higher removal performance. In strongly acidic conditions, the hydrated surface of organoclay becomes protonated, and excess H^+ ions and divalent cations compete to occupy the available adsorption sites. The rise in pH causes deprotonation, resulting in a more negatively charged surface, which enhances the electrostatic attraction between cationic heavy metals and the negatively charged organoclay surface at higher pH, as seen from zeta potential data (Chu et al., 2019).

Irrespective of the pH, organoclay consistently demonstrated lower cationic removal efficiency than bentonite. This difference is attributed to the high negative charge density of bentonite compared to organoclay, which increased the electrostatic attraction between clay

surface and divalent cations. Within the pH range of 2 to 8, organoclay showed poor Zn^{2+} removal efficacy, ranging between 24% and 55%, whereas bentonite's removal efficiency ranged between 38% and 100%.

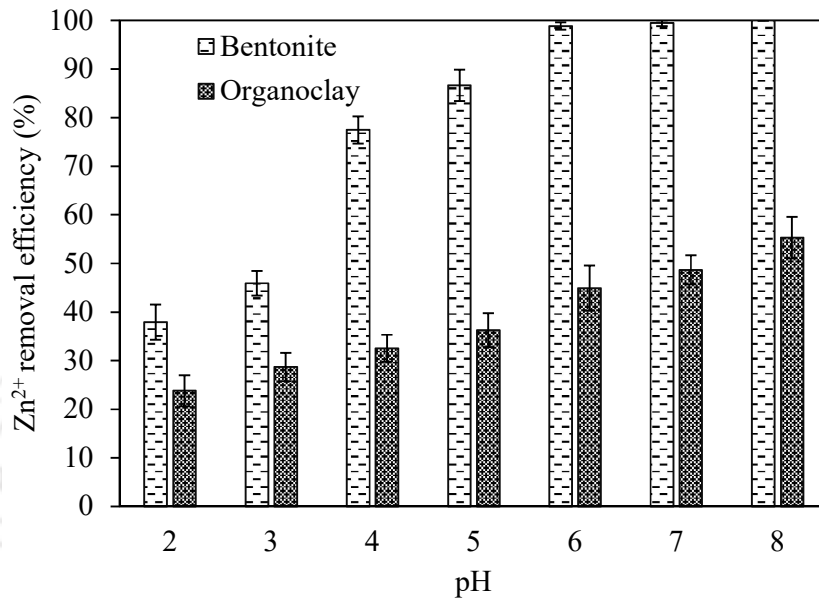


Fig. 4.2 Effect of pH on the Zn^{2+} removal efficiency of bentonite and organoclay (at a fixed initial concentration of 500 mg/L and S/L of 1:20)

The interlayer cations of the organoclay are primarily occupied by cationic surfactants such as quaternary ammonium cations (QAC), along with a limited amount of inherent interlayer cations, Na^+ or Ca^{2+} (as shown in Table 3.3). The presence of a smaller fraction of Na^+ and Ca^{2+} in organoclay might be due to the incomplete organic modification during manufacturing. These residual interlayer exchangeable cations may participate in ion exchange interactions with cationic heavy metals. The interlayer cationic surfactants have a positively charged hydrophilic head group and hydrophobic tail end composed of hydrocarbons. As a result of the organic modification, the hydrophilic characteristics of the clay surface were converted into hydrophobic surfaces, significantly reducing the negative charge density on the clay surface. Generally, due to the positively charged surface, organoclays exhibit poor affinity towards cationic heavy metals, as these metals cannot undergo cation exchange with QACs (Perelomov et al., 2024). However, Pb^{2+} ions have the tendency to form chelates with alkyl ammonium surfactants available in the interlayer space of organoclay (Xie et al., 2023). This might be the reason for better Pb^{2+} removal by organoclay compared to Zn^{2+} .

Beyond a pH of 6, there are chances of precipitate formation for lead ions in the form of lead hydroxides or carbonates, whereas, beyond a pH of 8, zinc ions get precipitated in the form of zinc hydroxides. Therefore, the higher removal efficacy of adsorbents beyond this pH value might be ascribed to the precipitation mechanisms. In summary, the adsorption mechanism for the removal of cationic heavy metals by organoclay involves cation exchange, surface complexation, chelation with surfactant molecules and precipitation.

4.2.1.2 Effect of pH on Cr(VI) sorption by bentonite and organoclay

The adsorption of hexavalent chromium onto the bentonite and organoclay surfaces as a function of pH is shown in Fig. 4.3. The influence of pH on the Cr(VI) sorption capacity of bentonite and organoclay was investigated by varying the pH from 2 to 8 at room temperature. The data indicated that bentonite showed negligible Cr(VI) removal, while organoclay exhibited better removal efficacy. The removal percentage of Cr(VI) by organoclay remained relatively constant up to a pH of 6, after which it displayed a slight decrease in removal efficiency. At pH 8, the organoclay achieved almost 53% removal, whereas at pH of 2, it indicated nearly 68% Cr(VI) removal.

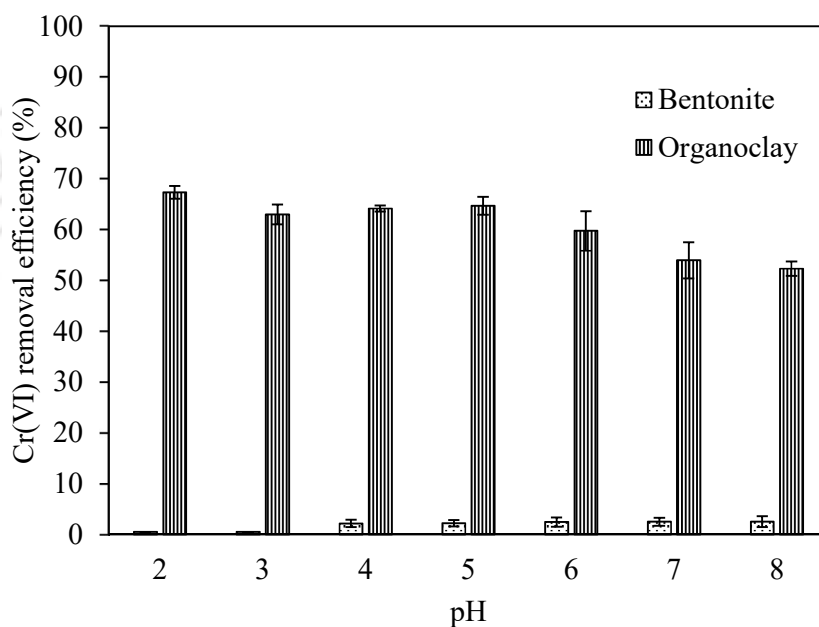


Fig. 4.3 Effect of pH on the Cr(VI) removal efficiency of bentonite and organoclay (at a fixed initial concentration of 500 mg/L and S/L of 1:20)

The reduction in sorption efficiency with increasing pH can be explained by using different forms of Cr(VI) in the aqueous phase. The solution pH determines the degree of ionisation and

speciation of chromium in the aqueous solution. The predominant chromium species in the pH range of 2 to 6 are HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$. At $\text{pH} > 6$, chromium is mainly available in the form of CrO_4^{2-} . At low pH, the surface of organoclay displays positive surface charges due to strong protonation, increasing the electrostatic attraction between the positively charged organoclay surface and the negatively charged Cr(VI) anions. The interaction between organic surfactant in the interlayer and Cr(VI) anionic species also contributes to an increased sorption efficiency. However, when pH is increased beyond 6, competition arises between CrO_4^{2-} ions and OH^- ions for the adsorption sites, leading to a slight decline in removal efficiency. Furthermore, oxyanions can also be adsorbed into organoclay by replacing the counter anion of the cationic surfactant (i.e. halides) via anion exchange reactions (Rathnayake et al., 2017; Sarkar et al., 2010). Therefore, the primary adsorption mechanism for Cr(VI) removal by organoclay can be identified as electrostatic interactions and anion exchange.

On the other hand, bentonite adsorbs almost negligible amounts of Cr(VI) due to its distinct surface charge attributes. The zeta potential results indicated a high negative charge density in the bentonite surface throughout the pH range of 2 to 8. The anionic species of Cr(VI) gets repelled by the highly negatively charged surfaces of bentonite, resulting in a negligible percentage of Cr(VI) removal by bentonite. The findings are in accordance with the findings of previous research (Akar et al., 2009).

4.2.1.3 Effect of pH on Phenol sorption by bentonite and organoclay

The percentage phenol removal by bentonite and organoclay was studied by varying the pH from 2 to 8, and the results are shown in Fig. 4.4. As the pH increased from 2 to 6, the removal efficiency by bentonite declined from 41.7% to 15.6%, followed by a slight increase to 19.8% when the pH was further increased to 8. Conversely, the removal percentage by organoclay remained consistent, ranging from 85 to 87% across the specified pH range. The phenol removal by organoclay was significantly higher than that by bentonite. For example, at a pH of 5, the removal percentage for bentonite was only 16.7%, while organoclay exhibited 85.9% removal.

In the case of bentonite, the percentage of phenol removal was highly dependent on the solution pH. The removal efficacy of phenol by the bentonite surface declined with increasing pH. One important reason for this reduction can be ascribed to the effect of pH on phenol ionisation. Most phenols are present as weak acids in aqueous solutions, and their dissociation of the solutes and their derivative molecules are strongly dependent on pH (Park et al., 2013).

In aqueous solutions, phenol can exist either as neutral undissociated molecules or as anionic phenolate form (dissociated). The ionic fraction of phenolate ion (ϕ) can be determined from the following equation (Banat et al., 2000):

$$\phi = \frac{1}{1 + 10^{(pK_a - \text{pH})}} \quad (4.1)$$

Where pK_a is the acid dissociation constant of phenol and pH is the pH of the solution.

Therefore, the ionic phenolate fraction decreases with the decline in pH. Furthermore, the acidic pH reduces the negative charge density at the clay surface due to protonation, which increases electrostatic attraction between the clay surface and phenol molecules. As the pH increases, phenol undergoes deprotonation, which increases its ionisation degree. As a result, an increase in electrostatic repulsion between the clay surface and phenolate ion occurs, hindering the diffusion of phenol and resulting in reduced adsorption capacity. Similar trends were observed in studies conducted on bentonites by Banat et al. (2000) and Asnaoui et al. (2022). Furthermore, van der Waals forces and π - π interaction between the phenyl rings and siloxane oxygens of the bentonite can also contribute to the adsorption in the pH range of 3 to 6.5 (Gładysz-Płaska et al., 2012)

The rise in pH only slightly influenced the phenol removal efficiency by organoclays within the specified pH range. As explained earlier, the share of phenolate anions increases as the pH exceeds 7. The negatively charged phenolate anions can be electrostatically attracted to the positively charged organoclay surface. From the literature, it was noted that the dissociation constant (pK_a) for phenol is around 9.96 (Jacobo-Azuara et al., 2006). At $\text{pH} < pK_a$, phenols exist in the molecular form, and the molecular phenol gets better adsorbed on organoclays than the anionic species. Therefore, the partitioning mechanism is prevalent when the phenols exist in molecular form. During organoclay preparation, the organic surfactants are adsorbed on the exterior surface and are intercalated into the interlayer of clay particles. This configuration creates an effective organic environment and enhances the hydrophobicity of the organoclays, resulting in a strong affinity for organic compounds such as phenols. In particular, the surfactant molecules in the interlayer space of the organoclays tend to act as an efficient partition medium for the removal of phenolic compounds via hydrophobic interaction and Van der Waals interaction under acidic environmental conditions (Park et al., 2013). Therefore, at low pH, the partitioning mechanism might be the primary removal mechanism, whereas electrostatic interactions along with partitioning might be the removal mechanism at highly alkaline conditions. It should also be noted that the solution pH (in the range of 2 to 8) only

has a limited influence on the phenol removal by organoclays. Studies by Ko et al. (2007) and Senturk et al. (2009) on the sorption performance of phenolic compounds by organoclays also demonstrated pH independence within the specified pH range. Park et al. (2013) also concluded that organoclays with higher surfactant loadings and those prepared with di-alkyl surfactants were less influenced by pH environments compared to the organoclays with lower surfactant loading and those intercalated with mono-alkyl surfactants.

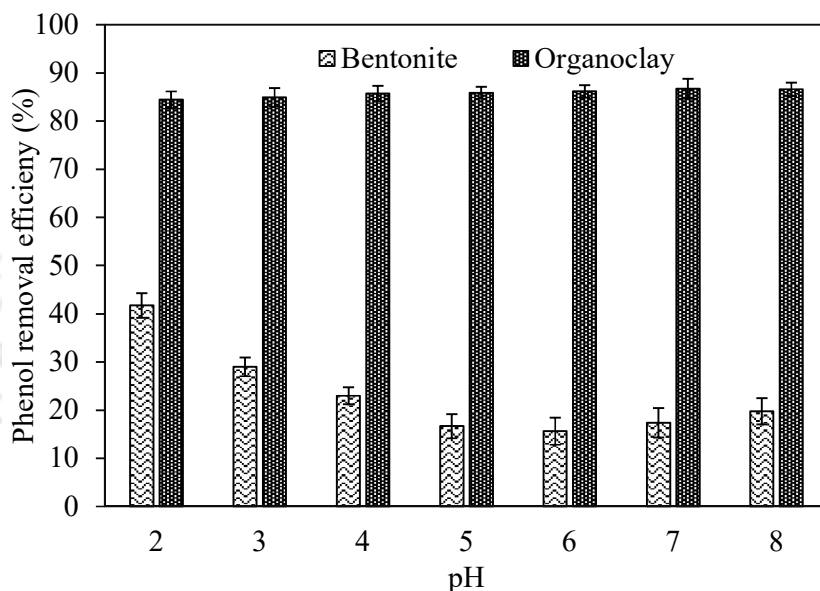


Fig. 4.4 Effect of pH on the phenol removal efficiency of bentonite and organoclay at an initial concentration of 500 mg/L

By analysing the adsorption capacities of bentonite and organoclay for heavy metals and phenols, we can conclude that there is a potential for precipitate formation beyond a pH of 6 for lead precipitate and beyond a pH of 8 for zinc precipitate. Therefore, in order to avoid the chance of precipitation of heavy metals, a fixed pH of 5 ± 0.2 was chosen for further batch experiments. Additionally, this pH is within the range of leachate pH commonly encountered in waste containment facilities.

4.2.2 Effect of initial adsorbate concentration on the adsorption performance of bentonite and organoclay

Initial adsorbate concentration can significantly influence the sorption capacity and removal efficiencies of clay adsorbents. The effect of initial adsorbate concentration on the removal efficiencies and adsorption capacities of bentonite and organoclay for various heavy metals and phenol is illustrated in Fig. 4.5 to 4.12. All these batch-type experiments were

performed by varying concentrations of Pb^{2+} , Zn^{2+} , Cr(VI) and phenol solutions, ranging between 0 to 2000 mg/L, at an initial pH of 5 ± 0.2 and S/L of 1:20.

4.2.2.1 Cationic heavy metals (Pb^{2+} and Zn^{2+})

The removal efficiency for Pb^{2+} and Zn^{2+} by bentonite and organoclay is demonstrated in Figs. 4.5 and 4.6, respectively. Similarly, Figs. 4.7 and 4.8 depict the sorption capacity or sorbed amount of adsorbate, q_e (mg/g), of both clays for cationic heavy metals at varied initial metal ion concentrations. As the initial concentration increased, both clay materials displayed a decrease in the removal efficiency and an increase in the sorption capacity.

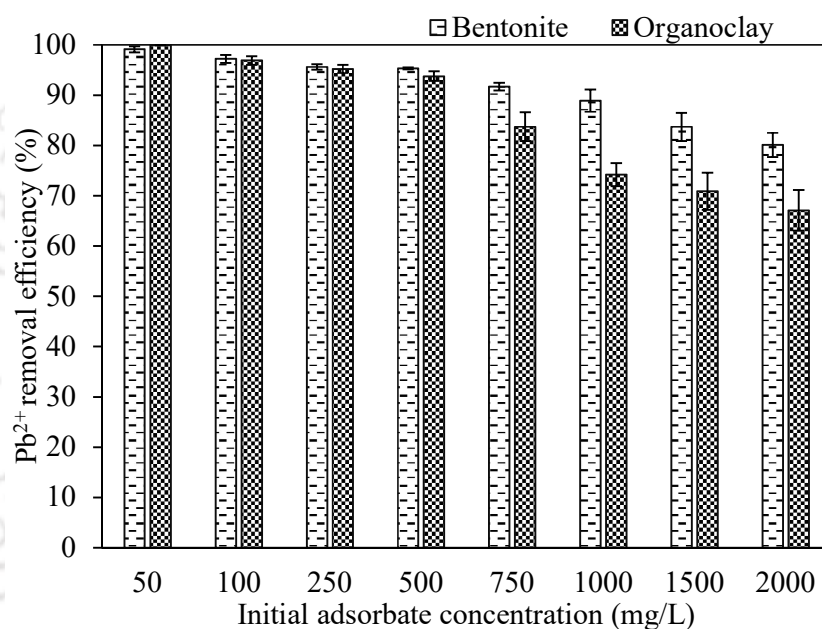


Fig. 4.5 Effect of initial adsorbate concentration on the Pb^{2+} removal efficiency of bentonite and organoclay (at a fixed initial pH of 5 ± 0.2 and S/L of 1:20)

As depicted in Fig. 4.5, both bentonite and organoclay indicated a marginal reduction in percentage Pb^{2+} removal up to an initial concentration of 500 mg/L. Beyond this concentration, a notable reduction in removal efficiency was observed for bentonite and organoclay, with organoclay showing a more pronounced decrease. In contrast, both clay adsorbents showed lower removal efficiency for zinc ions than lead ions, particularly at higher initial metal ion concentrations. The lower Zn^{2+} removal could be due to the larger hydrated radius of zinc ions, resulting in faster saturation of available adsorption sites (Wang and Zhang, 2021). At an initial metal ion concentration of 1000 mg/L, bentonite removed 88.9% of Pb^{2+} ions and 43.3% of Zn^{2+} ions, whereas organoclay showed a removal efficiency of 74.2% for lead ions and 28.8%

for zinc ions. Moreover, organoclay exhibited consistently lower removal efficacies for zinc ions, even at lower metal ion concentrations. However, at zinc concentrations greater than 1000 mg/L, organoclay presented better removal efficiencies than bentonite, suggesting superior performance of organoclay at higher concentrations.

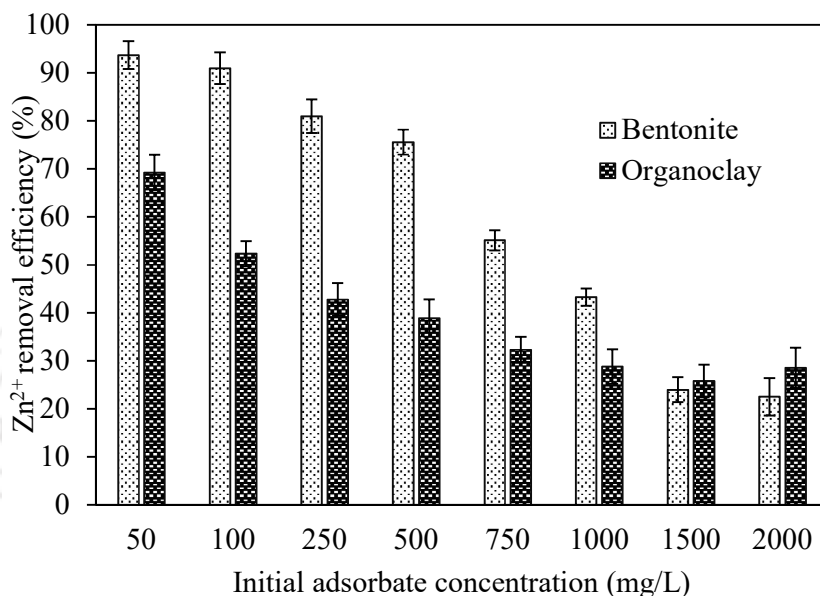


Fig. 4.6 Effect of initial adsorbate concentration on the Zn²⁺ removal efficiency of bentonite and organoclay (at a fixed initial pH of 5±0.2 and S/L of 1:20)

From the Fig. 4.7, it was observed that increasing the Pb²⁺ concentration from 0 to 2000 mg/L increased the Pb²⁺ adsorption capacity of bentonite from 0 to 32.06 mg/g, while organoclay showed an increase from 0 to 26.84 mg/g. The sorption capacity of both bentonite and organoclay for zinc ions was considerably lower when compared to lead ions. At lower initial metal ion concentrations, organoclay displayed lower sorption capacity than bentonite. However, beyond 1500 mg/L, the zinc sorption was higher for organoclay than bentonite. For instance, at 2000 mg/L, the maximum sorbed amount of Zn²⁺ on bentonite and organoclay surfaces was 9 mg/g and 11.37 mg/g, respectively.

The affinity of clays for heavy metal ions depends on several factors, such as ionic radius, hydrated ionic radius, and electronegativity. Since the ionic radius and electronegativity of Pb²⁺ is higher than that of Zn²⁺, more Pb²⁺ ions were sorbed onto the clay surfaces. The smaller hydrated radii of Pb²⁺ ions can easily pass through the inner pores of bentonite and organoclay surfaces, leading to higher sorption.

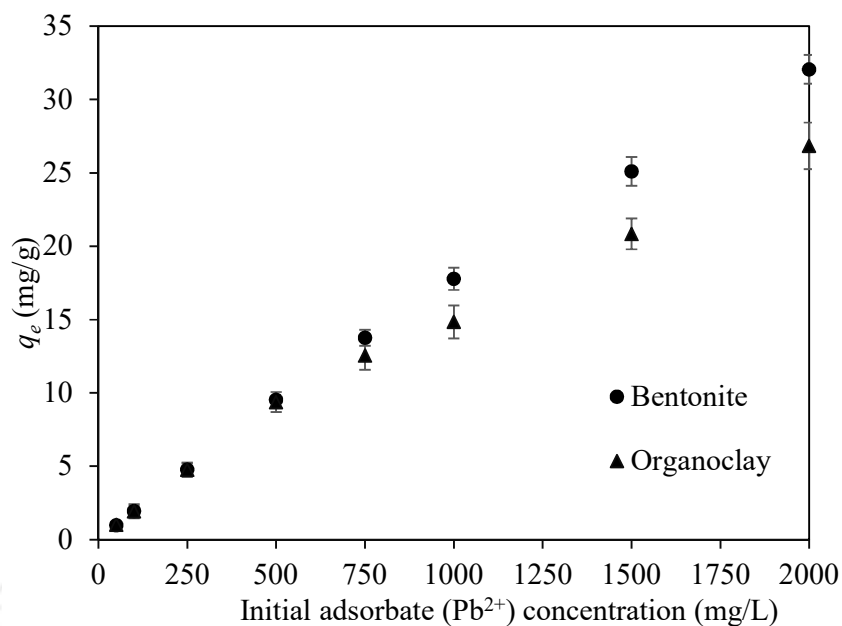


Fig. 4.7 Effect of initial adsorbate concentration on the sorption capacity of Pb^{2+} on bentonite and organoclay (at a fixed initial pH of 5 ± 0.2 and S/L of 1:20)

The distinct surface charge characteristics of the bentonite might be responsible for the higher amount of cationic metal ions sorbed onto the bentonite surface. The isomorphous substitution in tetrahedral and octahedral sheets of bentonite resulted in high negative charge density on the surface of bentonite. These negative charges are counterbalanced by alkali or alkaline earth metals (Na^+ in this study), which are found in the interlayer space of bentonite. The interlayer cations have the ability to undergo cation exchange with the Pb^{2+} ions present in the permeant solutions. Fewer Pb^{2+} or Zn^{2+} ions are available at low initial metal ion concentrations to bind the bentonite surface, leading to a lower sorbed amount. As the concentration increases, the concentration gradient between permeant solutions and the solid surface increases. Hence, more metal cations occupy the available binding sites, leading to increased adsorption per unit mass (Gupt et al., 2020). Akpomie and Dawodu (2015) also demonstrated a similar variation for contaminant removal by bentonite with a change in adsorbate (Ni^{2+} and Mn^{2+}) concentration. However, studies have reported that beyond a certain concentration threshold, a further rise in metal ion concentrations does not enhance the adsorption capacity of bentonite, as all active sites on the adsorbent surface are already saturated with the adsorbate ions (Guan et al., 2022; Chang et al., 2020). Therefore, the saturation of active sites in bentonite might be the reason for a steady adsorbed amount of 8 ~ 9 mg/g for Zn^{2+} beyond an initial concentration of 1000 mg/L.

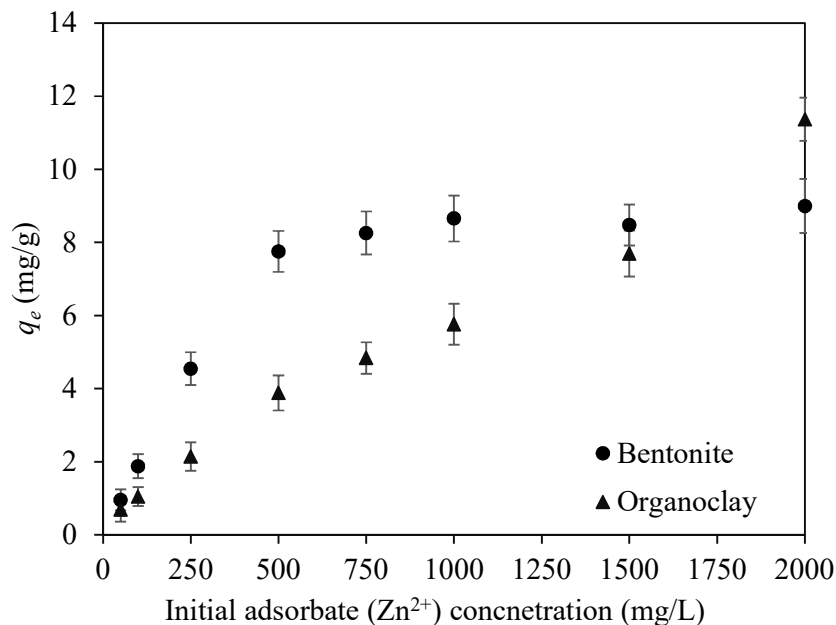


Fig. 4.8 Effect of initial adsorbate concentration on the sorption capacity of Zn²⁺ on bentonite and organoclay (at a fixed initial pH of 5±0.2 and S/L of 1:20)

During organic modification, the interlayer cations are replaced by organic cationic surfactants and are strongly attached by covalent bonding. Therefore, it cannot be replaced further by the cationic metal ions present in the permeant solution. Thus, the cation exchange mechanism, which is the primary adsorption mechanism found in bentonite, cannot occur in organoclays (Guo et al., 2022). Additionally, the organic modification process generated positive surface charges on the organoclay surfaces. The zeta potential data of the parent materials (Refer Fig 3.6) also confirmed positive surface charges on the organoclay surface. Therefore, the positively charged organoclay surface reduced the electrostatic attraction between the surface and cationic metal ions. The reduced electrostatic attraction impeded the sorption efficiency of organoclay for cationic heavy metal ions, particularly zinc ions. This is the reason for the lower sorption capacity displayed by organoclay than bentonite. However, at higher zinc ion concentrations (>1000 mg/L), more zinc ions were sorbed onto the organoclay surface than bentonite, indicating that organoclays' active surface sites were not exhausted even at very high Zn²⁺ concentrations.

4.2.2.2 Anionic heavy metal (Cr(VI))

The Cr(VI) removal efficacy and adsorption capacity of organoclay and bentonite as a function of initial adsorbate concentration is depicted in Figs. 4.9 and 4.10. Organoclay consistently exhibited significantly higher sorption of anionic hexavalent chromium compared

to bentonite. This superior performance of organoclay can be attributed to its more positively charged surfaces and increased hydrophobicity, which provide more reactive sites for Cr(VI) adsorption. On the other hand, bentonite displayed poor Cr(VI) removal due to its inherently negative surface charges, which result in the electrostatic repulsion between anions and negatively charged bentonite surface.

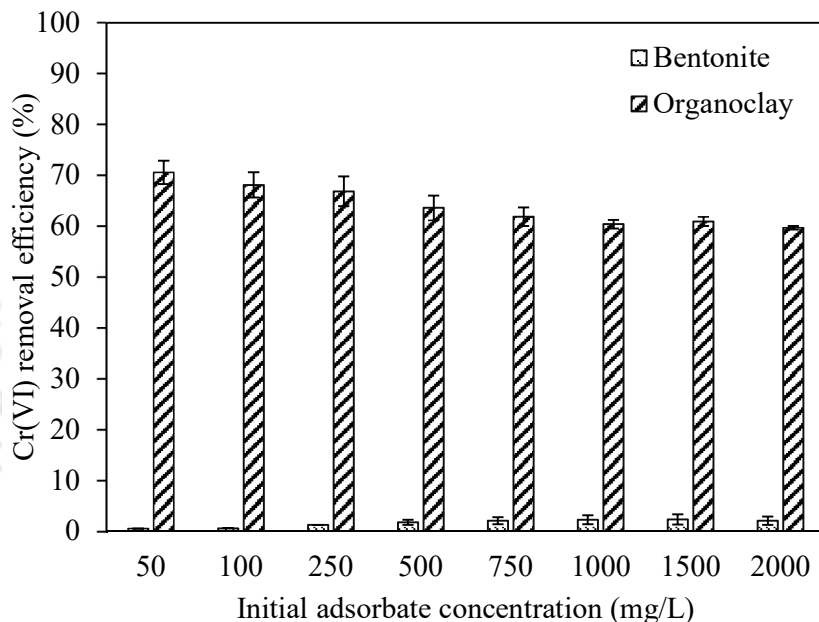


Fig. 4.9 Effect of initial adsorbate concentration on the Cr(VI) removal efficiency of bentonite and organoclay (at a fixed initial pH of 5 ± 0.2 and S/L of 1:20)

The rise in initial Cr(VI) concentration slightly decreased the removal percentages by organoclay and increased the sorbed amount. For example, as the initial metal ion concentration increased from 50 mg/L to 2000 mg/L, the percentage of Cr(VI) removal by organoclay declined from 70.6% to 59.7%. At low metal ion/adsorbent ratios, metal ion adsorption involves higher adsorption energy sites. As the metal ion/adsorbent ratio increased, the higher energy sites were saturated, and adsorption started to occur in lower energy sites, decreasing adsorption efficiency. Studies by Bhattacharya et al. (2008) on low-cost adsorbents have also shown similar trends of decreased percentage Cr(VI) removal with increasing initial metal ion concentrations. On the contrary, the q_e increased from 0.71 to 23.9 mg/g when the concentration rose from 50 mg/L to 2000 mg/L. The increase in initial metal ion concentration improved the driving force of heavy metals to the adsorption site and consequently enhanced q_e . At low initial metal ion concentrations, the ratio of heavy metals to the available adsorption sites is low. However, as the concentration increases, the competition for the remaining

adsorption sites becomes fierce due to the saturation of most adsorption sites. Since the adsorbed amount on organoclay was consistently increasing, it indicated that the active sites were not saturated even at 2000 mg/L concentration. The high affinity of organoclay for Cr(VI) might be ascribed to the presence of positively charged surfaces and increased hydrophobic surfaces, which provided more reactive sites.

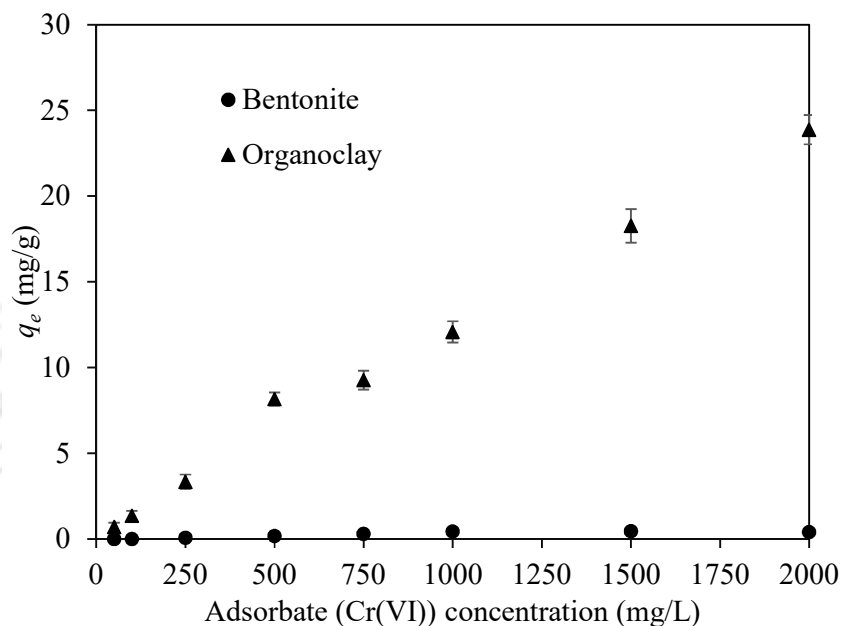


Fig. 4.10 Effect of initial adsorbate concentration on the sorption capacity of Cr(VI) on bentonite and organoclay (at a fixed initial pH of 5 ± 0.2 and S/L of 1:20)

4.2.2.3 Phenol

Figures 4.11 and 4.12 illustrate the removal efficiency and adsorption amount of phenol on bentonite and organoclay as a function of initial adsorbate concentration. Both removal percentage and adsorption capacity increased with rising initial phenol concentration. Compared to bentonite, the removal efficiency and sorption capacity of organoclay were significantly higher due to its hydrophobic and organophilic characteristics. The presence of alkyl ammonium compounds in the interlayer and surface might be conducive to the adsorption of phenol by organoclays.

When the initial concentration increased from 50 mg/L to 100 mg/L, the removal percentages for organoclay rose significantly from 71.5% to 89.7%, while bentonite showed an increase from 24.1% to 29.8%. Similarly, for the same change in initial concentration, the adsorption capacity for organoclay increased from 0.7 to 1.8 mg/g, and for bentonite, it increased from 0.2 to 0.6 mg/g. Furthermore, at a fixed pH and initial phenol concentration of

1000 mg/L, the adsorbed amounts of phenol onto bentonite and organoclay were 9.6 mg/g and 18 mg/g, respectively. At the same initial concentration level, bentonite displayed a percentage removal of 47.9%, whereas organoclay achieved 89.9%.

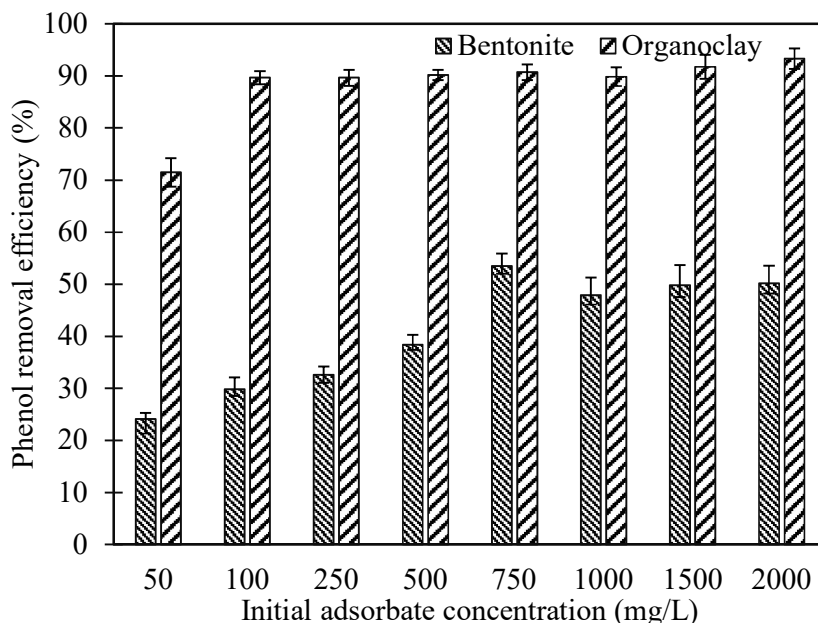


Fig. 4.11 Effect of initial adsorbate concentration on the phenol removal efficiency of bentonite and organoclay (at a fixed initial pH of 5 ± 0.2 and S/L of 1:20)

The initial phenol concentration serves as a driving force between the solution and the surface of the clay. Increasing initial phenol concentration enhances the mass transfer driving forces, resulting in more phenol molecules attaching to the clay surface from the solutions. With the addition of more phenol molecules, the adsorption sites become occupied by the adsorbate molecules, thus increasing the adsorption capacity, q_e . The studies conducted by Banat et al. (2000) also displayed similar trends for the relationship between initial phenol concentration and sorption capacity of bentonite. However, at higher concentrations, the phenol molecules available in the solutions may not be able to interact with the active sites of clays due to the saturation of the active sites (Senturk et al., 2009).

The possible mechanisms for phenol removal by bentonite include hydrogen bonding, where the polar hydroxyl group of phenol molecule forms hydrogen bonding with the hydrophilic clay surface. The polar phenol molecules can interact with exchangeable Na^+ in the interlayer through water bridges, or the adsorbate molecules directly form shells around the counter ions. The phenol adsorption on the negatively charged bentonite surface can occur through the polarization of π electrons and phenolate on the edges of bentonite through the ion

exchange. At higher pH, the adsorption was even less due to the deprotonation of phenol and limited anion adsorption sites on the bentonite surface.

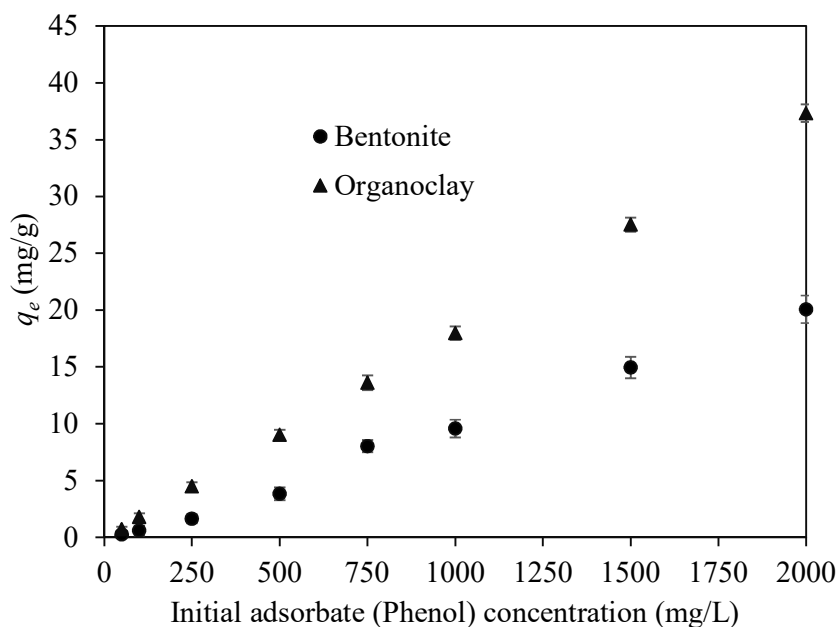


Fig. 4.12 Effect of initial adsorbate concentration on the sorption capacity of phenol on bentonite and organoclay (at a fixed initial pH of 5 ± 0.2 and S/L of 1:20)

In organoclay, phenol removal mechanisms include hydrogen bonding, electrostatic interactions and the formation of coordination compounds (Xie et al., 2023). The surface of organoclay contains several hydroxyl groups, which can form hydrogen bonds with phenol molecules. The positively charged organoclay surface experiences electrostatic attraction towards negatively charged phenolate anions. Van der Waals interactions also occur between organic cations in organophilic bentonite and the phenyl group. However, the hydrophobic interaction or the partitioning mechanism was identified as the main adsorption mechanism for organic pollutants such as phenol in organoclays.

4.2.3 Isotherm study

Understanding the adsorption isotherm is crucial for elucidating the mechanism of adsorption, the nature of the adsorbent surface, and the sorbent's affinity for contaminants (Nayak and Singh, 2006). In order to achieve this, the experimental data could be fitted to various adsorption isotherm models, including the Langmuir model, Freundlich model, Sips isotherm model, and Elovich isotherm. Among these, the Langmuir and Freundlich isotherm models are commonly used due to their simplicity. Consequently, this research focused on

analysing the relationship between the amounts of contaminants adsorbed onto both clays and their equilibrium concentration using Langmuir and Freundlich isotherm models. The adsorption isotherms obtained for Pb^{2+} , Zn^{2+} , Cr(VI) and phenol onto bentonite and organoclay at a constant pH of 5 ± 0.2 and at room temperature are illustrated in Figs. 4.13 to 4.20.

(a) Langmuir isotherm

Langmuir model (Langmuir, 1918) represents the relationship between the adsorption of adsorbate and the surface of adsorbent. The model assumes that the adsorption of adsorbate takes place as monolayer adsorption at specific homogeneous sites on the adsorbent surface. Once the adsorption site is occupied, no further adsorption can occur at this site. Therefore, the adsorption to the surface is strongly related to the driving forces and surface area. The Langmuir isotherm model can be expressed by the following relationship:

$$q_e = \frac{x}{M} = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4.2)$$

where q_e (mg/g) is the amount of adsorbate sorbed onto the adsorbent surface at equilibrium, x is the equilibrium concentration of the adsorbate in solid phase (mg/L), M is the mass of adsorbent in the free volume (mg/L), the q_m (mg/g) represents the theoretical monolayer capacity, K_L (L/mg) is the Langmuir equilibrium constant related to the affinity of binding sites and the energy of adsorption, C_e (mg/L) is the equilibrium concentration of the adsorbate remaining in the solution.

R_L is a dimensionless separation factor, which helps to understand whether Langmuir adsorption is favourable or not.

$$R_L = \frac{1}{1 + K_L C_0} \quad (4.3)$$

where C_0 is the initial concentration of adsorbate.

Based on the R_L value, the adsorption process can be considered favourable (when $0 < R_L < 1$), unfavourable (when $R_L > 1$), linear (when $R_L = 1$) and irreversible (when $R_L = 0$).

(b) Freundlich isotherm

The Freundlich isotherm model (Freundlich, 2002) assumed that the adsorption occurs at heterogeneous surfaces or surfaces supporting sites of varied affinities. The model represents the exponential distribution of active adsorption sites and their energies. It is applicable when the adsorption takes place in multilayers. The Freundlich equation is expressed as:

$$q_e = K_F C_e^{1/n} \quad (4.4)$$

where K_F (L/mg) and n are the Freundlich constants, which are related to the relative retention capacity of adsorbent and adsorption intensity, respectively.

4.2.3.1 Adsorption isotherm study of cationic heavy metals on bentonite and organoclay

Figures 4.13 and 4.14 demonstrate the data fitted to the linear form of Langmuir and Freundlich isotherm models for Pb^{2+} sorption on bentonite and organoclay. Similarly, Figs. 4.15 and 4.16 represent the Langmuir and Freundlich isotherm fitted for Zn^{2+} sorption on bentonite and organoclay. The isotherm coefficients for each model were computed, and the values are shown in Tables 4.1 and 4.2. The data indicated that the experimental results for lead and zinc adsorption onto bentonite and organoclay fit with both Langmuir and Freundlich isotherm models. However, the lead and zinc adsorption by bentonite were best fitted with Langmuir isotherm, as the regression coefficients (R^2) were higher for Langmuir isotherm than for Freundlich isotherm. This indicated that the adsorption onto bentonite was monolayer adsorption, with the adsorption sites having identical energy and no trans-migrations. For organoclay, the sorption of both heavy metals fits well with both isotherms, with R^2 values greater than 0.98, indicating that adsorption can be either monolayer or multilayer.

Table 4.1 Adsorption Isotherm fitting parameters for Pb^{2+} on bentonite and organoclay

Adsorbents	Langmuir model			Freundlich model		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
Bentonite	21.19	0.047	0.987	1.4048	1.872	0.988
Organoclay	17.09	0.041	0.989	1.4651	2.246	0.979

Table 4.2 Adsorption Isotherm fitting parameters for Zn^{2+} on bentonite and organoclay

Adsorbents	Langmuir model			Freundlich model		
	q_m (mg/g)	K_L	R^2	K_F	n	R^2
Bentonite	8.57	0.029	0.97	0.854	2.83	0.88
Organoclay	5.98	0.008	0.98	0.113	1.64	0.99

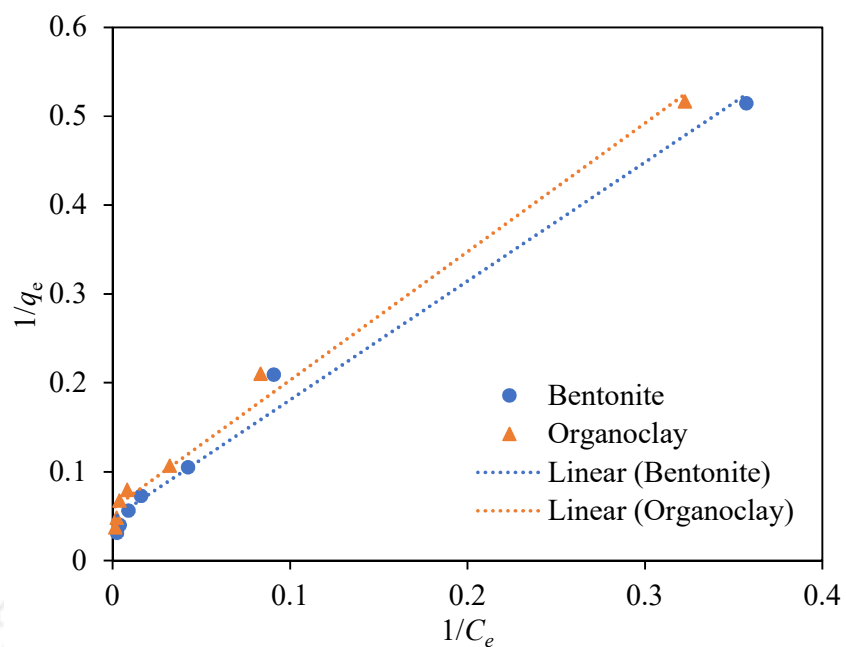


Fig. 4.13 Linear fits for adsorption isotherms for Pb^{2+} on bentonite and organoclay with Langmuir model

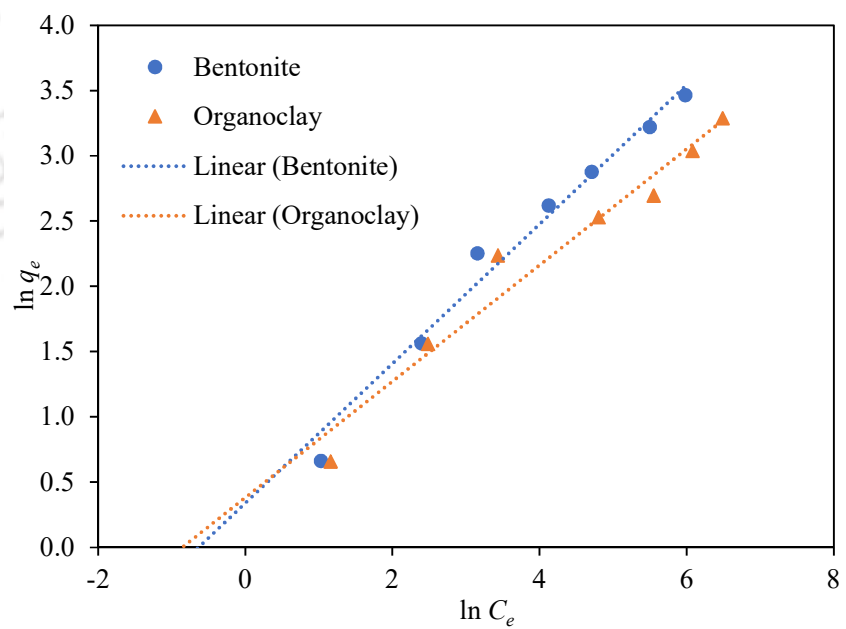


Fig. 4.14 Linear fits for adsorption isotherms for Pb^{2+} on bentonite and organoclay with Freundlich model

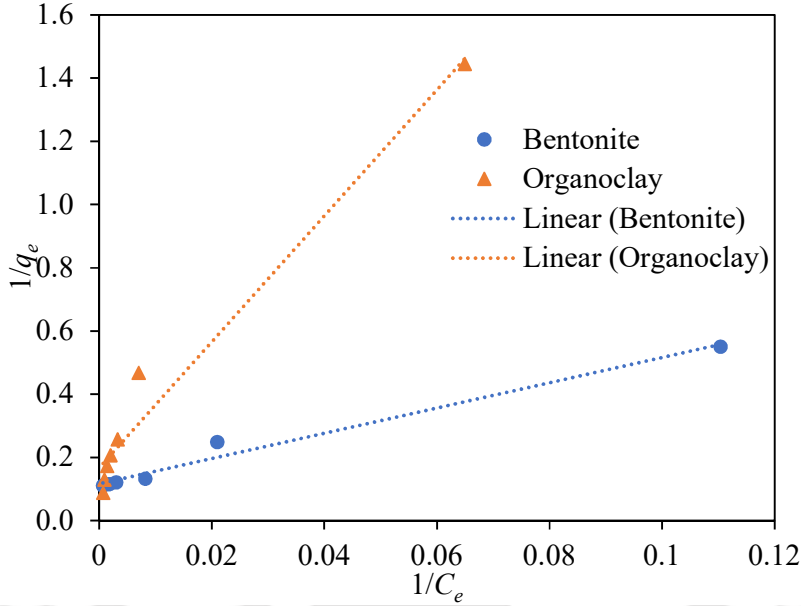


Fig. 4.15 Linear fits for adsorption isotherms for Zn^{2+} on bentonite and organoclay with Langmuir model

From the Langmuir parameters, it was observed that bentonite exhibited a maximum monolayer adsorption amount (q_m) of 21.2 mg/g for Pb^{2+} and 8.57 mg/g for Zn^{2+} . Similarly, organoclay showed a q_m value of 17.09 mg/g for lead and 5.98 mg/g for zinc. The difference in the sorption performance may be due to the variations in hydrolysis constants, ionic radius, electrode potential, and solubility of these ions (Wang and Zhang, 2021). From the isotherm fitting, the Langmuir constant, R_L , for bentonite ranged from 0.01 to 0.36 for lead and from 0.001 to 0.41 for zinc ions. The R_L of organoclay also ranged between 0 and 1, indicating that the sorption of cationic heavy metals is favourable for both adsorbents.

The Freundlich adsorption constant (n) for Pb^{2+} adsorption on bentonite and organoclay was noted as 1.87 and 2.25, respectively. For Zn^{2+} adsorption on bentonite and organoclay, n values were 2.83 and 1.64, respectively. Therefore, the $1/n$ value for all these cases is between 0 and 1, suggesting that these adsorbents are preferred for adsorption in the considered metal ion concentration range. The $1/n$ value shows the intensity of adsorption, and the adsorption is preferable if the $1/n$ value is between 0 and 1. On the other hand, the value of K_F was higher for lead compared to zinc, indicating greater Pb^{2+} sorption onto the adsorbents. Since K_F is the measure of the adsorption capacity of the adsorbent, it indicates the improvement of Pb^{2+} adsorption by these clay adsorbates.

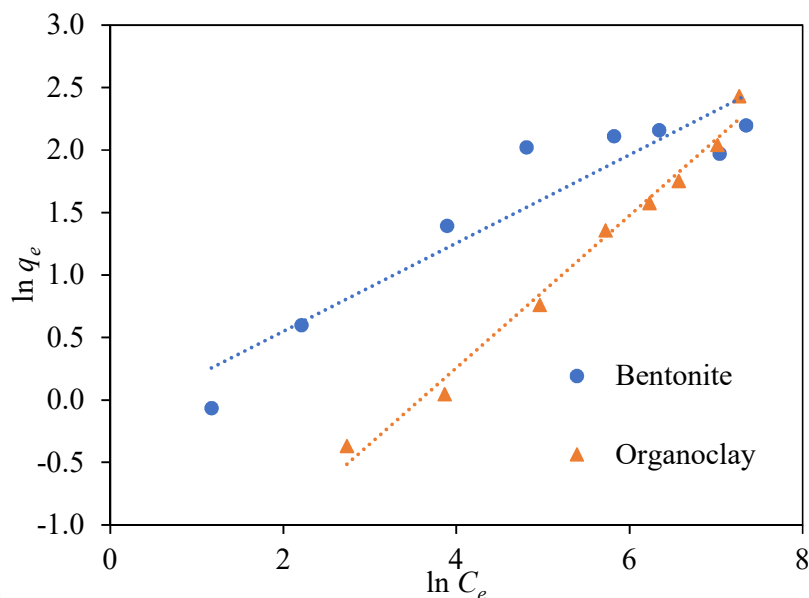


Fig. 4.16 Linear fits for adsorption isotherms for Zn^{2+} on bentonite and organoclay with Freundlich model

4.2.3.2 Adsorption isotherm study of Cr(VI) on bentonite and organoclay

The experimental data of Cr(VI) adsorption on organoclay fitted to Langmuir isotherm model and Freundlich isotherm model are shown in Figs. 4.17 and 4.18, respectively. Due to the very low adsorption capacity of bentonite for Cr(VI), the experimental data were not fitted to isotherm models. Both isotherm models displayed an excellent fit to the experimental data for organoclay, with regression coefficients greater than 0.99. According to the Langmuir isotherm, the maximum sorbed Cr(VI) amount was noted to be 32.36 mg/g. The dimensionless constant R_L provides an indication of whether the Langmuir adsorption is favourable or not. The R_L values ranged between 0.25 and 0.93, depending on the initial concentration. Since the R_L values ranged between 0 to 1, suggesting that the adsorption is favourable (Zhang et al., 2022). The best-fit retention intensity (n) of the Freundlich model for organoclay was found to be 1.14. Thus, the value of $1/n$ was 0.71, which is less than unity, indicating a favourable retention of Cr(VI) onto the organoclay surface (Yang et al., 2019). Hence, it can be deduced that the adsorption onto the organoclay surface can be either monolayer adsorption or multilayer adsorption. Various mechanisms such as van der Waals interaction, hydrophobic interaction, and electrostatic interactions may contribute to the Cr(VI) adsorption onto organoclay.

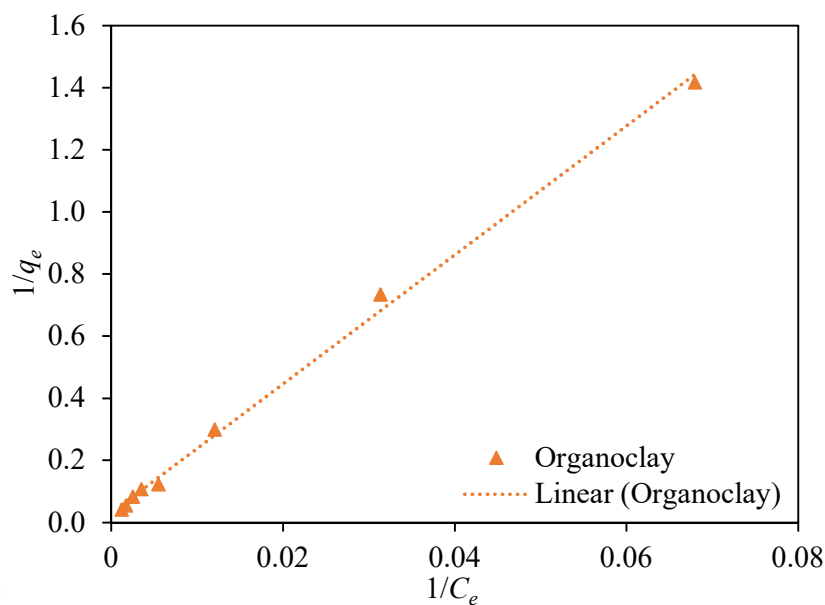


Fig. 4.17 Linear fits for adsorption isotherms for Cr(VI) on organoclay with Langmuir model

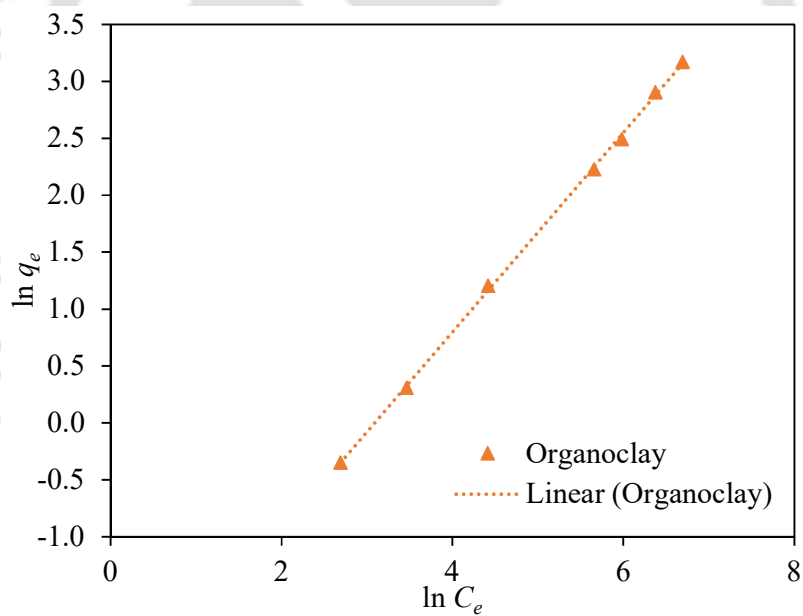


Fig. 4.18 Linear fits for adsorption isotherms for Cr(VI) on organoclay with Freundlich model

Table 4.3 Adsorption Isotherm fitting parameters for Cr(VI) on bentonite and organoclay

Adsorbents	Langmuir Model			Freundlich model		
	q_m (mg/g)	K_L	R^2	K_F	n	R^2
Bentonite	-	-	-	-	-	-
Organoclay	32.36	0.001	0.997	0.067	1.141	0.9995

4.2.3.3 Adsorption isotherm study of phenol on bentonite and organoclay

The experimental adsorption equilibrium data for phenol on bentonite and organoclay were fitted to standard Langmuir and Freundlich isotherms. The constants of these isotherms were determined using linear equations and are shown in Table 4.4. The isotherm parameters indicated that the data were better fitted into the Freundlich isotherm than Langmuir isotherm. The intercept of Langmuir isotherm showed a negative value, indicating no physical significance for monolayer adsorption. Since the adsorption equilibrium obtained from Freundlich is quite close to the experimental data, the adsorption of phenol onto both clays involves multilayer adsorption rather than monolayer adsorption. In both cases, the n value was less than 1, indicating that the adsorption system was more favourable at high concentrations of phenol (Park et al., 2013). A higher K_F value was noted for organoclay than bentonite.

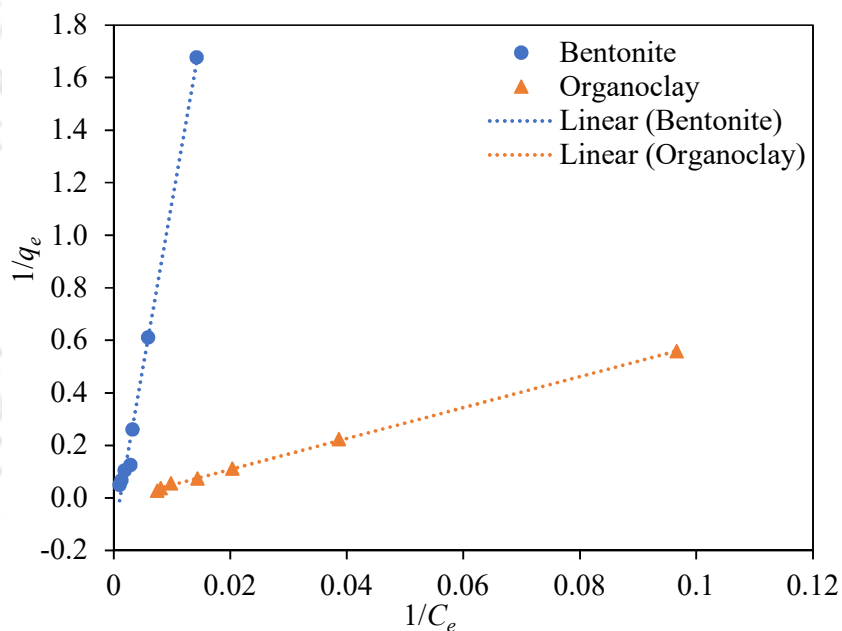


Fig. 4.19 Linear fits for adsorption isotherms for phenol on bentonite and organoclay with Langmuir model

Therefore, we can conclude that several adsorption mechanisms, including hydrophobic interactions/partitioning, hydrogen bonding and electrostatic interactions, might be responsible for the sorption of phenol onto organoclays. During modification, surfactants were adsorbed on the exterior surface as a monolayer and intercalated into the interlayer of clay particles. An organic medium was constructed on the exterior surface and interlayer due to these surfactants, and as a result, hydrophobicity increased (Zhang et al., 2015). The surfactant molecules present in the interlayer space and external surface of organoclays strongly attract the undissociated

phenolic molecules through hydrophobic interactions. Additionally, the dissociated phenolic anions tend to interact with the surfactant cations through electrostatic attraction. On the other hand, the phenol sorption onto bentonite could be mainly attributed to mechanisms such as hydrogen bonding and electrostatic interactions.

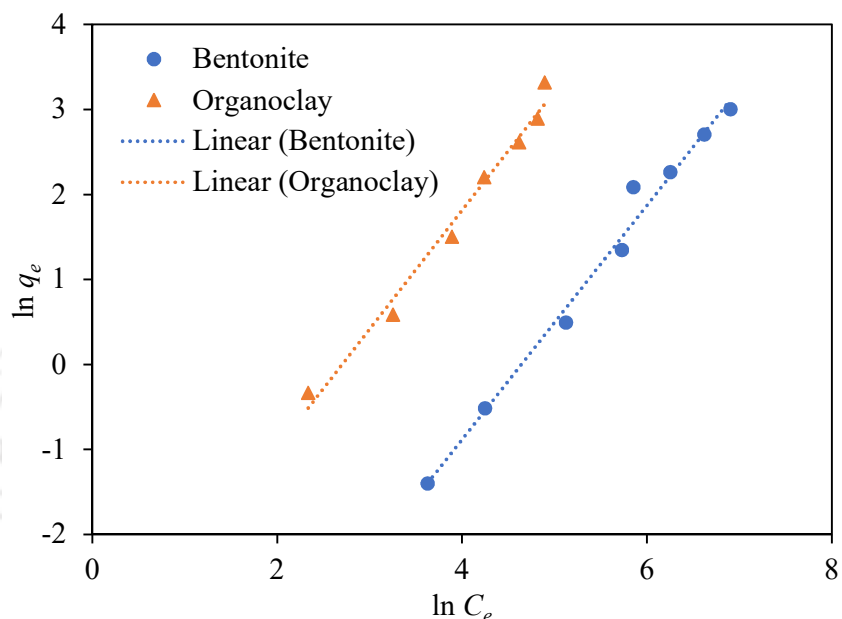


Fig. 4.20 Linear fits for adsorption isotherms for phenol on bentonite and organoclay with Freundlich model

Table 4.4 Adsorption Isotherm fitting parameters for phenol on bentonite and organoclay

Adsorbents	Langmuir model			Freundlich model		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
Bentonite	-7.27	-0.001	0.993	0.0463	0.7496	0.919
Organoclay	-103.09	-0.002	0.999	3.963	0.0017	0.986

4.3 Summary

This chapter examines the sorption performance of bentonite and organoclay for two cationic heavy metals (Pb^{2+} and Zn^{2+}), an anionic heavy metal ($Cr(VI)$) and an organic pollutant, phenol. A series of batch adsorption studies were conducted by varying the initial pH (2 to 8) and initial adsorbate concentrations (0 to 2000 mg/L). Additionally, isotherm studies were also carried out using the Langmuir model and Freundlich model to understand

the adsorption mechanisms of both adsorbents. Based on the experimental outcomes, the following conclusions were drawn:

- The initial pH and initial adsorbate concentration significantly influence the sorption of heavy metals and phenol on both bentonite and organoclay.
- Bentonite exhibited superior sorption performance for removing cationic heavy metal compared to organoclay. The rise in pH from 2 to 8 increased the percentage removal from 72% to 100% for Pb^{2+} and from 37.9% to 100% for Zn^{2+} by bentonite. Similarly, for organoclay, the increase was from 49.2% to 100% for Pb^{2+} and from 23.8% to 55.3% for Zn^{2+} .
- The primary mechanisms for cationic heavy metal removal by bentonite include cation exchange, outer and inner sphere complexation and precipitation. The main adsorption mechanisms for cationic removal by organoclay are surface complexation, chelation with organic surfactants, precipitation, and limited cation exchange.
- The anionic Cr(VI) removal by organoclay was significantly higher compared to bentonite. In the pH range of 2 to 8, organoclay removed almost 70 to 80% Cr(VI) from the solution, while bentonite removed only negligible amounts. Superior sorption performance by organoclay is due to electrostatic attraction between positively charged organoclay surface and anionic Cr(VI). The poor sorption performance of bentonite may be ascribed to the high negative charge surfaces on bentonite, which get electrostatically repelled by anionic Cr(VI).
- The organic contaminant phenol was removed by both organoclay and bentonite. However, when the pH varied from 2 to 8, organoclay exhibited almost 80 to 90% phenol removal, while bentonite only showed less than 40% removal. The superior organic sorption by organoclay may be due to the partitioning through hydrophobic interactions, electrostatic interactions and hydrogen bonding. Hydrogen bonding and electrostatic interaction might be the reason for phenol adsorption by bentonite.
- The rise in initial adsorbate concentration decreased the heavy metal removal efficiency for both bentonite and organoclay while increasing the adsorption capacity for heavy metals and phenol.
- From the isotherm models, it was noted that the cationic heavy metal sorption on bentonite was best fitted with the Langmuir model, while organoclay was best fitted with both Langmuir and Freundlich models. Similarly, Cr(VI) sorption onto organoclay fit well with both isotherm models, with a maximum Langmuir sorption capacity of

32.4 mg/g. However, phenol sorption onto both adsorbents fits well with the Freundlich isotherm compared to the Langmuir model.

- Therefore, it can be concluded that the bentonite showed poor removal for anionic heavy metals and phenol but exhibited superior sorption efficiency for cationic heavy metals. In the case of organoclays, the sorption of Pb^{2+} , Cr(VI) and phenol was superior, with a comparable removal efficiency for Zn^{2+} . Hence, organoclay could act as a better sorbent than bentonite in a multiple-contaminant environment.



CHAPTER 5

Geotechnical properties of organoclay-amended bentonite (BOC) in the presence of inorganic salts

5.1 General

Landfilling has become the world's most widely used waste management practice due to its low cost and energy-generating potential (Swati et al., 2018). However, the lack of proper management of landfills and the associated risks are worrisome. Engineered landfills with effective liner systems are essential for preventing harmful leachate components from entering the surrounding environment and groundwater.

Compacted bentonite is a frequently used engineered barrier material in waste containment systems due to its large specific surface area, low hydraulic conductivity, high swelling tendency, and high cation exchange capacity. Bentonite's ability to form interlayer and diffused double layers when in contact with water adds to its suitability for use as a hydraulic barrier (Mesri and Olson, 1971). Several chemical compatibility studies on bentonite have been conducted in the past (Fu et al., 2022; Ray et al., 2022; Gupt et al., 2020; Du et al., 2015). The results from these studies indicated that the efficiency of such liners significantly deteriorates in the presence of organic and inorganic pollutants due to the alterations in geotechnical properties (Guarena et al., 2024; Erdogan et al., 2023). In order to improve the barrier performance under chemical conditions, various engineered and natural materials were employed to amend conventional bentonite barriers (Jia-Kai et al., 2023; Beryl and Xavier, 2021; Di Emidio et al., 2017). Among various materials, organoclays can be considered a potential amendment to the bentonite barrier because of their excellent sorption capacity for toxic heavy metals and organic contaminants, as shown in Chapter 4. The improved hydraulic performance of organoclay-based barriers under the influence of organic contaminants was also confirmed in previous literature (Ni et al., 2024; Keerthana and Arneppali, 2022; Ghavami, 2017; Benson et al., 2015; Andini et al., 2006). Furthermore, these organoclays are processed from natural resources, i.e. clays, making them a sustainable and environmentally safe option for liner amendment (Carroccio et al., 2021). However, due to the relatively high cost of organoclay, it cannot be used alone as a barrier material; instead, it can be added in small quantities as an amendment to conventional bentonite. Therefore, a combination of organoclay and bentonite is used to ensure the effective sorption of both organic and inorganic contaminants.

While selecting a liner material, along with the sorption performance, various geotechnical properties such as hydraulic conductivity, swelling, compressibility, and shear strength are of prime importance. The analysis of the barrier performance of compacted bentonite under the effect of inorganic salts and heavy metals have been reported in the literature (Gastelo et al., 2023; Norris et al., 2022; Ishimori et al., 2020; Rout and Singh, 2020; Jadda and Bag, 2020; Dutta and Mishra, 2016). Similarly, organoclays were studied for the hydraulic barrier performance in the presence of organic contaminants. However, limited studies have been available on the hydraulic barrier performance of organoclay-amended bentonite, especially in the presence of different leachate constituents – inorganic salts, heavy metals and organic contaminants. Furthermore, the majority of the prior research focused on the swelling and hydraulic behaviour of barrier materials. Apart from hydraulic properties, consolidation and compressibility characteristics are two critical parameters to understand the usability of a material for hydraulic barriers. To the best of the authors' knowledge, limited studies were undertaken in the past regarding the compressibility and consolidation performance of an organoclay-amended bentonite barrier under aggressive electrolytic solutions. In India, approximately 55.5% of the total 4.5 metric tonnes of hazardous waste produced is landfilled annually (Soni et al., 2022), necessitating large hazardous landfills. As a result, the landfill height dramatically increases. The placement of the waste in landfills occurs in several stages, and the barrier components experience significant vertical pressure during and after placement operations. This substantial amount of vertical stress exerted on the barrier system results in the consolidation and compression of barrier material. Furthermore, the consolidation of the barrier system may reduce the breakthrough time for contaminants and may allow quick contaminant transport through the barrier system (Yan et al., 2021). Therefore, it is crucial to understand how landfill leachate constituents affect the compressibility and consolidation properties of hydraulic barriers to comprehend the overall performance of barrier materials and to design an effective landfill barrier system.

Therefore, this research aims to comprehend the geotechnical properties, including swelling, hydraulic conductivity, compressibility and consolidation behaviour of conventional bentonite and the proposed organoclay amended bentonite under the effect of aggressive inorganic salt solutions. In this research, a 90:10 mixture of bentonite and organoclay was adopted to analyse and compare the barrier performance with conventional bentonite. The determination of the optimal proportion of bentonite and organoclay (90:10 by dry weight) for utilisation in landfill liner applications was established through a comprehensive review of

prior research studies undertaken within analogous contexts. Since the leachates contain high concentrations of inorganic salts, two commonly found inorganic salts, NaCl and CaCl₂, were utilised in this study at varied concentrations ranging between 0 and 1N. Additionally, a comprehensive microstructural investigation was also carried out on consolidated samples to comprehend the hydraulic behaviour of barrier materials in the presence of inorganic salts.

5.2 Effect of 10% organoclay addition on the geotechnical behaviour of bentonite

The incorporation of 10% organoclay altered the geotechnical behaviour of bentonite. The pre-calculated amounts of bentonite and organoclay were mixed in a ratio of 90:10 on a dry-weight basis. The basic geotechnical properties of BOC determined using standard laboratory procedures are listed in Table 5.1. In all these experiments, DI water was used as the permeant solution.

Table 5.1 Physical properties of BOC

Properties	BOC	Methods
Specific gravity	2.56	ASTM D854 (2014)
d ₀₀₁ spacing (nm)	1.32	X-ray diffraction
Liquid limit, LL (%)	180.0	ASTM D4318 (2017)
Plastic limit, PL (%)	46.0	ASTM D4318 (2017)
Free Swell Index, FSI (mL/2g)	18.0	ASTM D5890 (2009b)
Maximum dry density, MDD (g/cc)	1.33	Sridharan and Sivapullaiah (2005)
Optimum moisture content, OMC (%)	33.6	Sridharan and Sivapullaiah (2005)
Unconfined compressive strength (kPa)	402	ASTM D2166 (2006)

The specific gravity reduced marginally from 2.65 to 2.56 when 10% organoclay was incorporated into the bentonite. This reduction may be due to a lower specific gravity of organoclay ($G_{oc}=1.7$). The lower specific gravity of organoclay was reported by various researchers (Sreedharan, 2013; Soul and Burns, 2001), and the reason can be attributed to the low mass per volume due to the intercalation of organic cations. It was believed that the hydrophobic interlayer created by the presence of the organic cations excluded a disproportionate quantity of solution during the specific gravity tests (Burns et al., 2006; Bate, 2010).

The optimum moisture content (OMC) and maximum dry density (MDD) for bentonite and BOC in DI water were determined using a mini-compaction apparatus. The MDD and OMC

were found to be 1.324 g/cc and 34% for BOC and 1.355 g/cc and 35.0% for bentonite, respectively. The replacement of 10% bentonite with organoclay slightly reduced the OMC and MDD of bentonite. The presence of organic cation in the organoclay fraction of BOC reduces the repulsive forces in the clay structure and imparts more hydrophobicity. Thus, the addition of highly hydrophobic organoclay may be responsible for the reduced optimum moisture content.

The liquid limit and plasticity index of BOC showed a significant reduction compared to bentonite, with a percentage decline of 41.9% and 50.7%, respectively. This reduction may be attributed to the hydrophobic nature of organoclays, which reduces the water-holding capacity of the soil mixture. The organic surfactants (e.g. quaternary ammonium salts) may be incapable of hydration in the presence of water compared to the interlayer exchangeable inorganic cations in the bentonite (Ghavami, 2017). As a result, the plasticity and swelling declines.

The free swell index (FSI) value of the BOC in DI water was found to be 18 mL/2g, while bentonite exhibited an FSI value of 36 mL/2g. A substantial reduction in free swell value was noted when the bentonite was mixed with 10% organoclay and inundated with distilled water. The organoclays exhibit high hydrophobicity when it is mixed with water. The free swell value of the bentonite-organoclay mixture depends on the amount of organoclay added and the type of permeant fluid (Sreedharan and Sivapullaiah, 2017). Since BOC contains 90% bentonite, a significant swelling is observed due to the sodium bentonite, which has large amounts of montmorillonite. However, increasing the proportion of organoclay increases the hydrophobicity of the mixture, which can deteriorate its sealing ability.

The unconfined compressive strength (UCS) of bentonite and BOC were noted as 336 kPa and 402 kPa, respectively. A notable strength improvement (19.6% increase) was observed with the incorporation of a 10% organoclay fraction into the bentonite. There is literature reporting the increase in undrained shear strength associated with the reduction in plasticity index and liquid limit. The decrease in plasticity can impart greater resistance to external forces and hence improve shear strength (Sreedharan, 2013). A minimum unconfined compressive strength of 200 kPa was recommended by Daniel and Wu (1993) for a liner material to maintain the integrity of the liner against the overburden stresses, which is satisfied by BOC.

5.3 Impact of inorganic salts (NaCl and CaCl₂) on the hydraulic barrier performance of compacted bentonite and BOC

5.3.1 Influence of inorganic salts on the Atterberg limits and free swell index of bentonite and BOC

(a) Atterberg limits

The Atterberg limits, comprising the liquid limit, plastic limit, and shrinkage limit, play a vital role in comprehending various geotechnical properties of fine-grained soils, encompassing swelling, compression, shear strength, and shrinkage. The replacement of 10% bentonite with organoclay significantly decreased the liquid limit and plasticity index of bentonite, with water as the pore medium. When inorganic salts replaced the pore medium, significant reductions in plasticity properties were observed for both bentonite and BOC, although the percentage reduction in plasticity was less for the latter. Figs. 5.1 and 5.2 indicate the effects of inorganic salt addition on the liquid limit, as well as the plasticity index of bentonite and BOC. Permeation with DI water resulted in liquid limits of 310% and 180% for bentonite and BOC, respectively. The organoclay fraction in the BOC reduced the electrostatic repulsion between the particles due to the rise in the hydrophobicity of the mixture, thereby decreasing its water-holding capacity. As the liquid limit indicates the soil's water-holding ability, the liquid limit of organoclay-amended bentonite displayed a lower liquid limit value. Furthermore, organoclay-modified bentonite demonstrated a modest rise in plastic limit in DI water due to its increased hydrophobicity compared to bentonite. These trends are in concordance with the results obtained by Sreedharan and Sivapullaiah (2011).

The permeation of 0.1N NaCl and CaCl₂ further reduced the liquid limit to 145% and 121% for bentonite and 128% and 113% for BOC, respectively. At any given concentration, the decrease in the liquid limit was more evident for the calcium chloride solution than for the sodium chloride solution. The presence of inorganic salt solutions minimises the interparticle repulsion, allowing the particles to approach each other at a lower water content and thus lowering the liquid limit. Even though the experimental results demonstrated variations in the plasticity characteristics of BOC with salt concentration and valency, the effect of such aggressive salt solutions was less pronounced in BOC liners compared to bentonite liners.

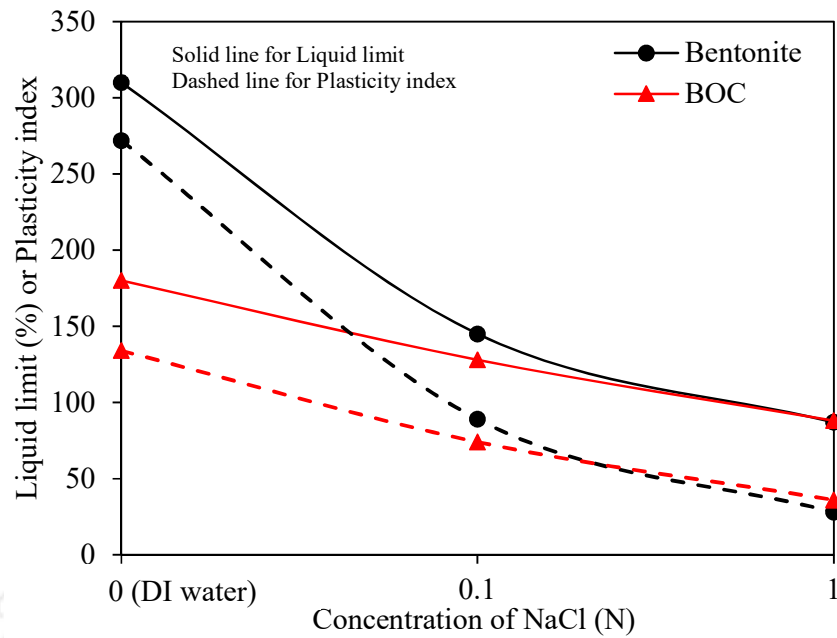


Fig. 5.1 Atterberg limits of bentonite and organoclay amended bentonite (BOC) when mixed with sodium chloride

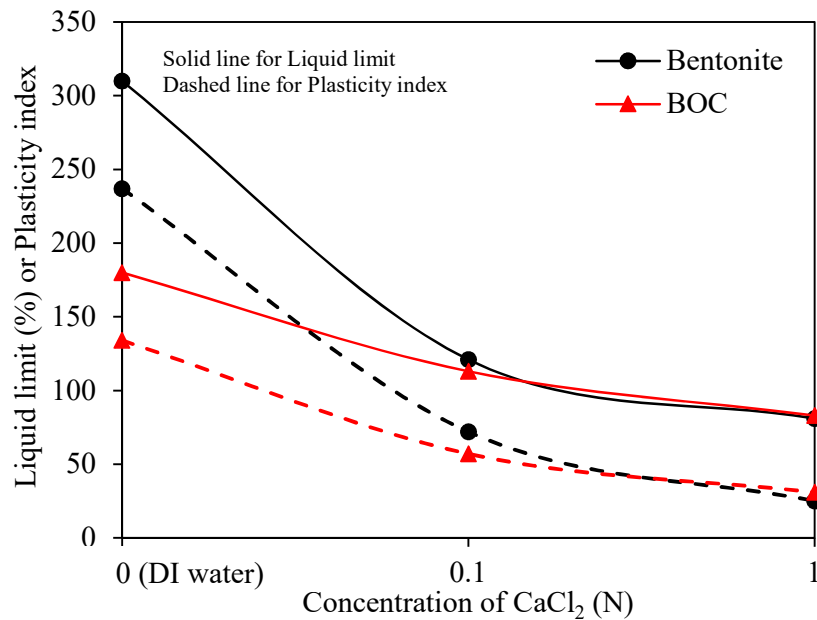


Fig. 5.2 Atterberg limits of bentonite and BOC when mixed with calcium chloride

(b) Free swell index

The term "free swelling" refers to the volumetric expansion experienced by the soil when submerged in DI water or any permeant solution without any external overburden pressure or

constraints. Figure 5.3 demonstrates the effect of NaCl and CaCl₂ concentrations on the free swelling of bentonite and BOC samples. The experimental data showed that the rise in salt concentration led to a reduction in free swelling for both samples. During the organic modification process, naturally occurring interlayer cations (sodium ions in this case) in bentonite were replaced by organic quaternary ammonium cations, altering the surface characteristics. As a consequence, the presence of organic hydrophobic surfaces in the organoclays led to minimal or negligible swelling in DI water (Sreedharan and Sivapullaiah, 2011). In this study, the organoclay fraction in BOC restricted the cation hydration and diffused double-layer formation in DI water, leading to a substantial reduction in swelling.

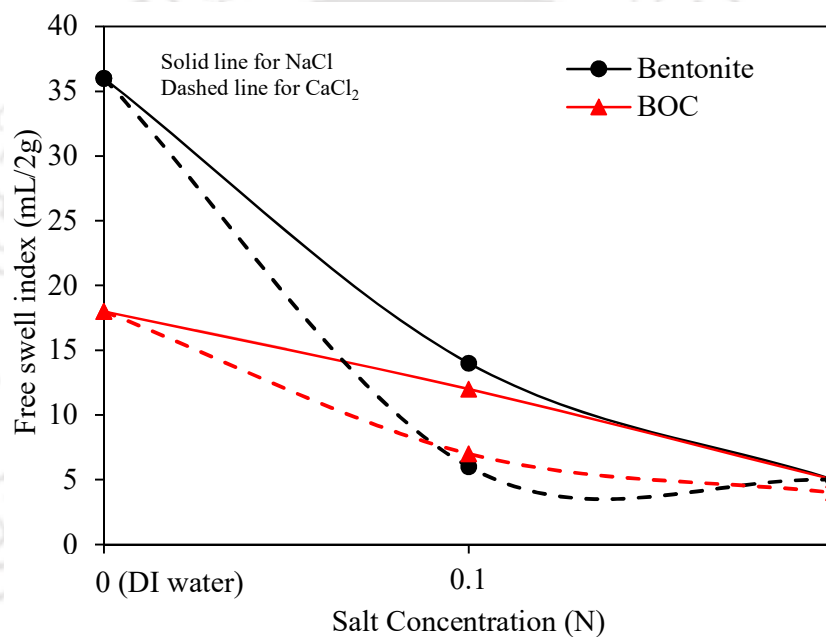


Fig. 5.3 Free swelling values of bentonite and BOC when inundated with inorganic salt solutions

Subsequently, when inorganic salts replaced DI water as the permeant, the decrease in cation hydration and diffused double-layer thickness significantly lowered the free swelling of both bentonite and BOC samples. Nonetheless, as ionic concentration and valency increased, the reduction of free swelling was more pronounced in bentonite samples than in BOC samples. For instance, when changing the permeant solution from DI water to 0.1N NaCl, the free swelling percentage reduction for bentonite and BOC was 61.11% and 33.33%, respectively. Similarly, when exposed to 0.1N CaCl₂ solutions, the reduction percentages for bentonite and BOC were 83.33% and 61.11%, respectively. Regardless of the ionic concentration and valency, BOC consistently exhibited relatively less swelling than bentonite. The conclusion is

that organoclay fraction in BOC samples must be responsible for intrinsically lower swelling in DI water and reduced reactivity to inorganic ionic concentration (Javadi et al., 2017). Even a small quantity (10%) of organoclay in BOC was sufficient to mitigate the adverse effect of aggressive electrolytic solutions on bentonite's swelling behaviour.

5.3.2 Swell pressure and swell potential of bentonite and BOC under the influence of inorganic salts

The pressure required to compress a saturated soil specimen to its initial configuration is referred to as swelling pressure (Sridharan et al., 1986). Seed et al. (1962) provided a definition of swelling potential as the percentage expansion observed in a laterally confined soil specimen compacted to its MDD and OMC subsequent to full saturation in water or any permeating fluid under minimum confining pressure. The data in Table 5.2 and Table 5.3 depict the swelling pressures and swelling potential of bentonite and BOC under the permeation of DI water and inorganic salt solutions. The results indicated that the rise in salt concentrations led to a decline in swelling pressure and swelling potential for both samples. Specifically, when the NaCl and CaCl₂ concentration was increased from 0 to 1 N, swelling pressure displayed a percentage reduction of 40% and 51.1% for bentonite and 31.4% and 37.1% for BOC, respectively. The drop in swell pressure and swell potential in bentonite can be considered as a consequence of the reduced diffused double layer (DDL) thickness upon salt permeation. With water as the permeant, the exchangeable cations initially attached firmly to the negatively charged bentonite surface tended to diffuse away from the clay surface. The charged clay surface, along with the diffused ions, resulted in the formation of the diffused double layer, which caused the swelling of bentonite particles. In contrast, when inorganic salt solutions replaced DI water, the Na⁺ and Ca²⁺ ion concentrations at the soil-water interface increased. As a result, the concentration gradient was reduced, which resulted in the inhibition of the cation diffusion, and subsequently, the diffused double-layer formation was impeded. Moreover, the increase in the valency of cations further contributed to the reduction in the DDL thickness and a significant drop in swelling was observed. Hence, at any given concentration, monovalent cations (Na⁺) exhibited more swelling pressure for both soils compared to divalent cations, owing to their higher DDL thickness (Dutta and Mishra, 2016).

For the organoclay-bentonite mixture permeated with DI water, lesser swelling was observed due to the hydrophobic surface characteristics of the organoclay fraction (Sreedharan, 2013). The 10% organoclay in the BOC restrained the complete DDL expansion of the

remaining 90% bentonite in the mixture. In addition, the presence of hydrophobic organic cations in the interlayer space of organoclays doesn't undergo hydration in water or inorganic salts and doesn't contribute to the overall swelling of BOC. However, at higher concentrations of inorganic salt solutions, equilibrium was attained, and swelling will be independent of ionic valency for both bentonite and BOC samples. This is the reason why almost similar values for swelling parameters were noted for both bentonite and BOC at 1N salt concentrations. It was also noted that the free swell and oedometer swell followed a similar trend irrespective of their methodologies, indicating that swell potential under both inorganic pore fluids can be correlated to their free swell index.

Table 5.2 Swelling pressure of bentonite and BOC at different concentrations of NaCl and CaCl₂

Salt concentrations (N)	Swelling pressure (kPa)			
	Bentonite		BOC	
	NaCl	CaCl ₂	NaCl	CaCl ₂
0 (DI water)	450	450	350	350
0.1	420	350	270	235
1	270	220	240	220

Table 5.3 Swelling potential of bentonite and BOC at different concentrations of NaCl and CaCl₂

Salt concentrations (N)	Swelling Potential (%)			
	Bentonite		BOC	
	NaCl	CaCl ₂	NaCl	CaCl ₂
0 (DI water)	36.78	36.78	17.36	17.36
0.1	20.93	18.17	9.82	7.48
1	10.91	9.14	6.72	7.05

5.3.3 Time-swelling variation of bentonite and BOC under the influence of inorganic salts

The curves shown in Figs 5.4 and 5.5 illustrate how the addition of various concentrations of NaCl and CaCl₂ affects the swelling percentage of bentonite and BOC with time. Regardless of the type of permeating fluid, the time-swelling curves for both soil samples displayed an "S" shaped curve. The plot showed different phases of swelling, i.e. initial swelling, primary swelling and secondary swelling (Sridharan and Gurtug, 2004). Upon the addition of solutions,

the soil undergoes a progressive swelling process. Initially, it showed gradual swelling during the initial swelling stage, followed by a sharp increase during the primary swelling stage. Subsequently, the swelling rate shows only a marginal increase, eventually reaching an asymptotic value during the secondary swelling stage (Dutta and Mishra, 2016; Rao and Thyagaraj, 2007). The initial and primary swelling time was calculated based on the procedure described by Sridharan and Gurtug (2004), which was explained earlier in Fig. 3.12. The time taken for completing initial swelling (t_{is}) and primary swelling (t_{ps}) of bentonite and BOC at varied inorganic salt concentrations are listed in Tables 5.4 and 5.5. The time required to complete the initial and primary swelling of bentonite and BOC declined as the salt concentration increased. The "S" shaped curve for bentonite inundated with DI water and inorganic salt solutions was more pronounced than that of BOC. Tables 5.6 and 5.7 depict the distribution of swelling potential during each phase of swelling. When inundated with DI water, almost 95.98% and 88.13% of total swelling was completed in the primary swelling region for bentonite and BOC, respectively. Similarly, in the presence of inorganic salt solutions, the maximum amount of swelling was observed during the primary swelling stage for both bentonite and organoclay-bentonite mix.

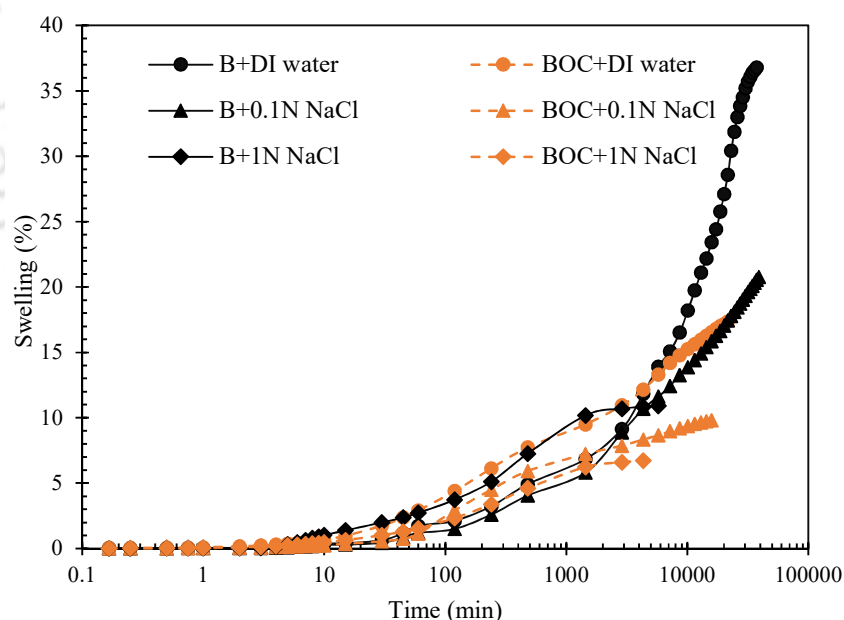


Fig. 5.4 Time-swelling plot of bentonite (B) and organoclay amended bentonite (BOC) when inundated with sodium chloride solutions

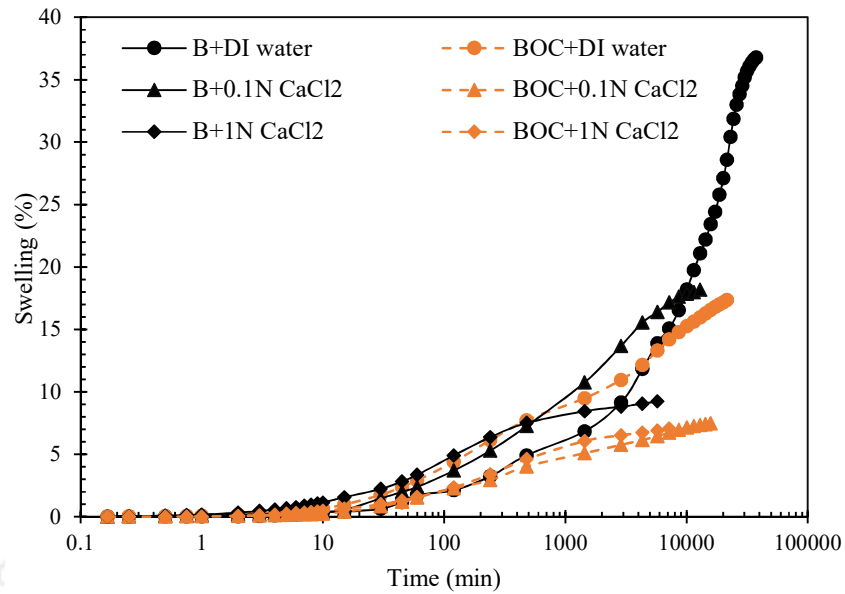


Fig. 5.5 Time-swelling plot of bentonite and BOC when inundated with calcium chloride solutions

Table 5.4 Time required for completion of initial swelling of bentonite and BOC under various concentrations of NaCl and CaCl₂

Salt concentrations (N)	Time taken for initial swelling, t_{is} (minutes)			
	Bentonite		BOC	
	NaCl	CaCl ₂	NaCl	CaCl ₂
0 (DI water)	120	120	40	40
0.1	50	27	40	19
1	15	17	12	13

Table 5.5 Time required for completion of primary swelling of bentonite and BOC under various concentrations of NaCl and CaCl₂

Salt concentrations (N)	Time taken to complete primary swelling, t_{ps} (minutes)			
	Bentonite		BOC	
	NaCl	CaCl ₂	NaCl	CaCl ₂
0 (DI water)	31700	31700	15500	15500
0.1	37000	7200	12500	10500
1	1550	900	1200	2100

As the concentration of salt solutions increases, the swelling decreases for both bentonite and BOC. These results are consistent with the free swelling value obtained earlier. In the presence

of NaCl concentrations, bentonite exhibited higher swelling compared to CaCl₂ solutions, primarily attributed to the increased thickness of the DDL and interlayer expansion in NaCl solution (Dutta and Mishra, 2016). On the other hand, owing to the hydrophobic nature of the organoclay fraction, BOC expanded less in DI water and inorganic salt solutions.

Table 5.6 The contribution to swelling potential in each stage of swelling for bentonite and BOC at different concentrations of NaCl

Salt concentrations (N)	Bentonite			BOC		
	Contribution to swell potential (%)			Contribution to swell potential (%)		
	Initial swelling	Primary swelling	Secondary swelling	Initial swelling	Primary swelling	Secondary swelling
0 (DI water)	1.20	35.30	0.28	1.50	15.30	0.56
0.1	0.75	20.15	0.03	0.45	9.25	0.12
1	0.60	9.90	0.41	0.40	5.95	0.37

Table 5.7 The contribution to swelling potential in each stage of swelling for bentonite and BOC at different concentrations of CaCl₂

Salt concentrations (N)	Bentonite			BOC		
	Contribution to swell potential (%)			Contribution to swell potential (%)		
	Initial swelling	Primary swelling	Secondary swelling	Initial swelling	Primary swelling	Secondary swelling
0 (DI water)	1.20	35.30	0.28	1.50	15.30	0.56
0.1	0.70	17.10	0.37	0.30	6.90	0.28
1	0.60	8.2	0.34	0.20	6.50	0.35

5.3.4 Variation of hydraulic conductivity with void ratio for samples permeated with different concentrations of inorganic salts

While designing landfill covers and liners, the coefficient of permeability (k) or hydraulic conductivity of the soil barrier is crucial (Daniel, 1984). The material could be used as a compacted soil liner only if the hydraulic conductivity falls below 1×10^{-9} m/s, as recommended by USEPA (1988). This study estimated the hydraulic conductivity of bentonite and an organoclay-bentonite mix by an indirect method using an oedometer test. Despite the limitations associated with this indirect method, the authors chose to use this approach to determine the k of fine-grained soils, given the time constraints and its widespread acceptance

among researchers (Mesri and Olson, 1971; Sivapullaiah et al., 2000; Demdoun, 2020; Owino and Hossain, 2023; Ray et al., 2022).

The variations in hydraulic conductivity of bentonite and BOC at different void ratios and electrolyte solutions are depicted in Figs. 5.6 and 5.7. The hydraulic conductivities of bentonite and BOC increased as the concentration of inorganic salts increased. The deviations in hydraulic conductivity may be attributable to the pore fluid-induced changes in the soil structure. Although BOC possesses a higher hydraulic conductivity compared to bentonites, it is noteworthy that none of the samples surpassed the limiting value of hydraulic conductivity acceptable for landfill liners. In BOC, the hydrophobic surface properties of organoclay account for the higher hydraulic conductivity (Javadi et al., 2017; Moon et al., 2007). According to previous research, adding organoclay increases the hydraulic conductivity of the soil mixture when it comes into contact with DI water, but it decreases when it is permeated with organic contaminants and petroleum chemicals (Javadi et al., 2017; Smith et al., 2003). Since landfill leachate contains a variety of contaminants, an organoclay-modified bentonite liner can potentially perform better as a barrier material to retain all types of pollutants.

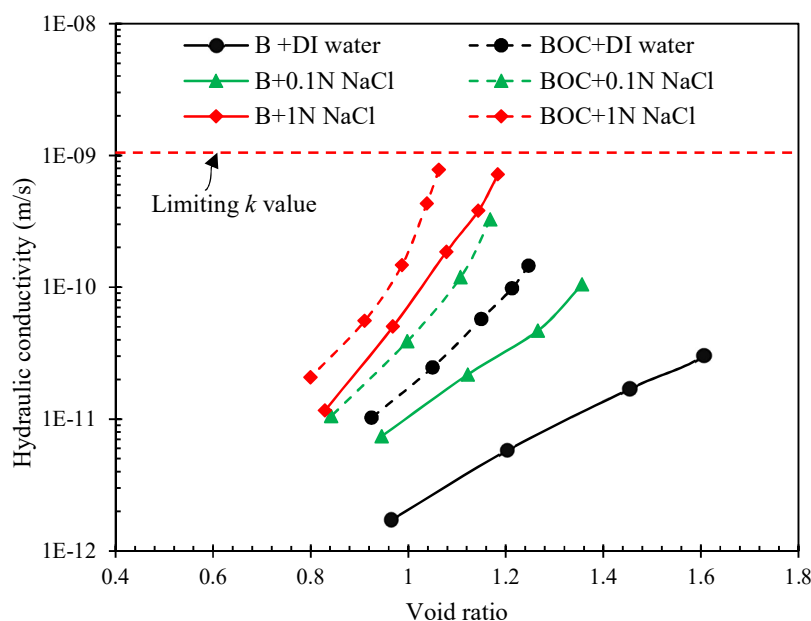


Fig. 5.6 Hydraulic conductivity - void ratio plot for bentonite (B) and BOC at various concentrations of NaCl solutions

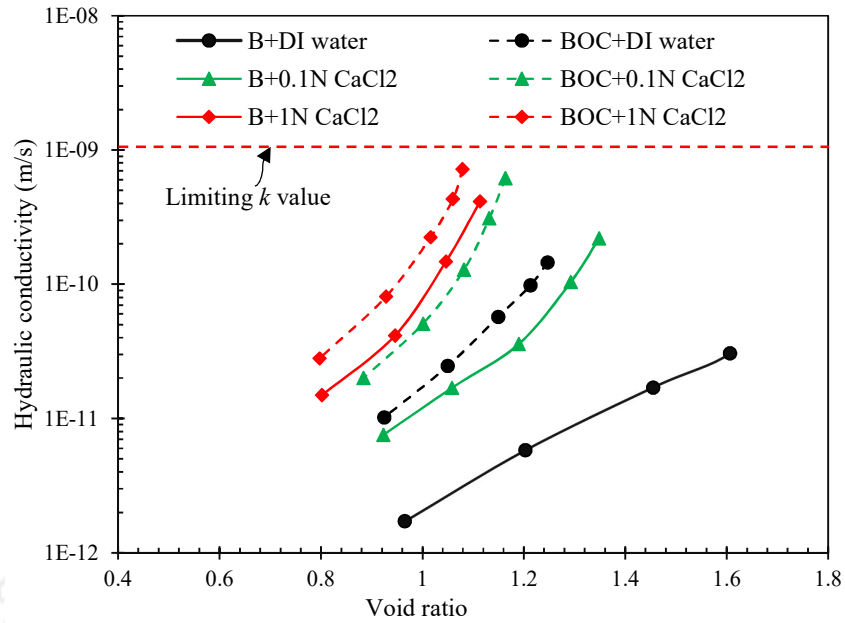


Fig. 5.7 Hydraulic conductivity - void ratio plot for bentonite (B) and BOC at various concentrations of CaCl_2 solutions

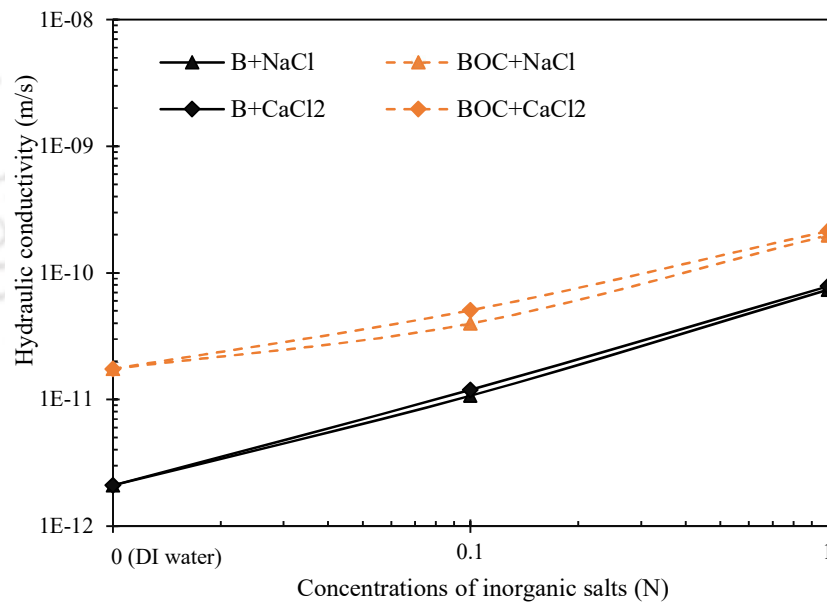


Fig. 5.8 Variation of hydraulic conductivity of bentonite (B) and BOC at a void ratio of 1.0 when permeated with different concentrations of inorganic salts

Figure 5.8 illustrates the variation in the k value of bentonite and BOC permeated with different inorganic salt concentrations at a fixed void ratio of 1.0. When inundated with DI water, the addition of organoclay raised the hydraulic conductivity of bentonite at a void ratio of 1.0 from 2.1×10^{-12} m/s to 1.74×10^{-11} m/s (i.e. increased by 8.32 times). As the concentration

of NaCl increased from 0 to 1 N, the hydraulic conductivity of bentonite and BOC increased by 35.1 and 11.4 times, respectively, while it increased by 37.4 and 12.3 times for CaCl_2 . It was clear from the data that the increase in hydraulic conductivity of BOC was significantly less in the presence of aggressive inorganic salt conditions. For both soil samples, the effect of calcium chloride was observed to be higher than that of sodium chloride. Consequently, it can be inferred that even though the presence of inorganic salts increases, the hydraulic conductivity of organoclay-amended bentonite due to the permeation of aggressive electrolyte conditions had a relatively minimal effect when compared to bentonite.

5.3.5 Mechanism behind the variations in swelling and hydraulic conductivity under inorganic salt permeation

The mechanism underlying the increased hydraulic conductivity and decreased swelling of bentonite and BOC upon salt permeation is elucidated here. The bentonite used in this study contained sodium ions as exchangeable cations. The permeation with DI water resulted in two types of swelling in bentonite, i.e. inner-crystalline and osmotic swelling (Norrish and Quirk, 1954). Inner-crystalline swelling occurred at the clay mineral surface and was mainly attributed to the hydration of exchangeable Na^+ ions in the clay system. This type of swelling can adsorb up to several layers of water, but beyond the formation of the maximum number of hydrates, surface hydration becomes less prominent. Osmotic swelling, on the other hand, was mainly due to diffuse double-layer swelling as a consequence of the cation concentration gradient created inside and outside the individual clay-pore fluid system. The osmotic swelling of bentonite significantly contributes to the total swelling and can extend for several days when permeated with DI water (He et al., 2019; Rout and Singh, 2020).

The permeation of the NaCl solution allowed both inner-crystalline and osmotic swelling in bentonite. However, the extent of osmotic swelling was less than that observed in DI water because of the higher concentration gradient in the pore fluid compared to the clay interlayer space. As a result of the concentration gradient, more Na^+ cations were transported into the diffused layer, resulting in the expulsion of water from the diffused double layer. In the case of the calcium chloride permeant, only inner-crystalline swelling will be predominant, followed by the cation exchange of interlayer Na^+ ions with Ca^{2+} ions from the pore solution. As a result of ion exchange, the interlayer space collapses, and the particles tend to flocculate. At higher concentrations of CaCl_2 , more Ca^{2+} ions are available for replacement, possibly leading to almost complete replacement of exchangeable Na^+ with Ca^{2+} ions. Owing to this replacement, the osmotic component of the swell diminished, and it was reflected in the free swell, swell

pressure, and swell potential values. Furthermore, the collapse of the diffused double-layer thickness of bentonite and the subsequent reduction in swelling resulted in particle flocculation and the formation of intra-aggregate voids in the presence of inorganic salt solutions (Malusis and McKeehan, 2013; Yang et al., 2022). The formation of intra-aggregate pores and increased hydraulic conductivity in salt solutions can be observed in the FESEM images (discussed in the coming sections).

In the case of BOC, where 10% of bentonite was replaced with organoclay, there was a significant reduction in the swelling characteristics. Organic alkyl ammonium ions were present in the interlayer space of organoclay instead of exchangeable inorganic cations, such as Na^+ or Ca^{2+} ions. The hydrophobic nature of organic ions prevented inner-crystalline swelling because of the inability to hydrate organic cations. Additionally, in organoclay fraction, the formation of diffused double-layer and hydrogen bonding of adsorbed water might have been hindered due to the specific hydrophobic and organophilic properties of organoclay (Shah et al., 2013). Furthermore, the complete DDL expansion of the remaining 90% of bentonite particles might have been restricted due to the nearby hydrophobic organoclay particles. Therefore, compared to bentonite, a significant reduction in swelling was observed in BOC mixed with DI water, and the total swelling of BOC might have been contributed by the bentonite fraction alone.

When the permeant solution was replaced from DI water with high concentrations (1N) of inorganic salt solutions, BOC exhibited less percentage variation in plasticity, swelling, and hydraulic conductivity compared to bentonite. This is likely due to the strong covalent bond between the interlayer organic cations and the clay surface, which prevents the cation hydration as well as the cation exchange reaction between the interlayer cations and permeant Ca^{2+} ions (de Paiva et al., 2008). However, a cation exchange reaction may occur between the permeant ions and exchangeable sodium ions present in the interlayer of the remaining bentonite fraction, leading to a reduction in repulsive forces and DDL thickness in BOC and subsequent particle aggregation. This particle aggregation might explain the higher hydraulic conductivity displayed by BOC compared to bentonite.

5.3.6 Impact of inorganic salts on the compressibility characteristics of bentonite and BOC

(a) *Compressibility behaviour (e - $\log \sigma'$ plots)*

The influence of various electrolyte concentrations (0, 0.1N and 1N) and valency (monovalent- Na^+ and divalent- Ca^{2+}) on the void ratio (e)-consolidation pressure (σ') relationship of bentonite and BOC are presented in Figs. 5.9 and 5.10. The consolidation pressure discussed here represents the field overburden stress that may be exerted on the liner due to the placement of waste within the waste containment facility. The e -log σ' relationship provides an indication of the compressibility characteristics of the soil. Therefore, the compressibility behaviour of both bentonite and BOC under the influence of various permeants can be studied from these figures. The curves illustrated that the void ratio of all compacted samples decreases with the increase in consolidation pressure. However, the reduction in the void ratio was not significant when the consolidation pressure was less than 50.0 kPa. As the pressure increases, the applied pressure can overcome the interparticle repulsion between particles, and a closer particle arrangement occurs, thereby reducing the void ratio. At an consolidation pressure of 4.9 kPa, the void ratio of bentonite changes from 1.72 for DI water to 1.21 and 1.17 for 1N NaCl and 1N CaCl_2 solutions, respectively. Similarly, for BOC, it decreased from 1.25 for DI water to 1.08 and 1.09 for 1N NaCl and 1N CaCl_2 , respectively.

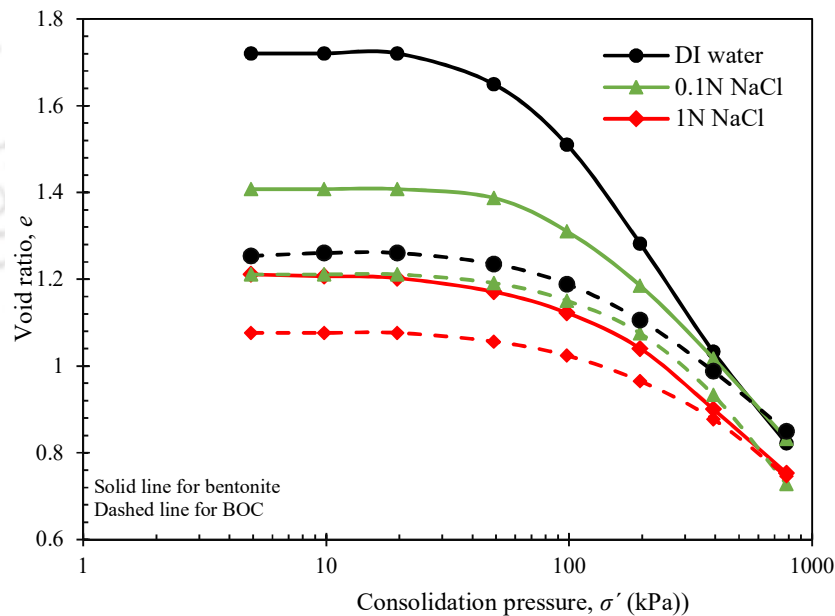


Fig. 5.9 Void ratio-consolidation pressure plots for bentonite and BOC inundated with sodium chloride solutions

The e -log σ' curve of both bentonite and BOC showed a downward shift when the permeant solution changed from DI water to inorganic salt solutions, which implied that the compressibility of both the compacted samples reduced with the permeation of inorganic salt solutions. The change in void ratio at any given pressure indicates the repulsive forces acting

on the soil matrix due to the interaction between soil particles and inundating fluid (Sridharan and Rao, 1973; Alawaji, 1999). When the concentration and valence increase, the repulsive forces acting on the adjacent bentonite particles decrease due to the reduction in DDL thickness, and hence, compressibility reduces.

When compared to bentonite, BOC samples showed a moderate downward shift in the curve with an increase in both the concentration and valency of electrolytes. This is due to the reduced water affinity of the hydrophobic organoclay fraction available in the mixture. Consequently, there will be a restriction in the DDL formation. Thus, the effect of double-layer contraction will be comparatively lesser in BOC samples upon inundation with various inorganic salt permeants. Therefore, the compressibility of BOC samples was significantly less due to the permeation of higher concentrations and higher valency of inorganic salts. However, at higher pressures, all the samples displayed a converging trend, which indicated that the compressibility behaviour was independent of the pore fluid characteristics and quantity of organoclay at higher consolidation pressure (Sreedharan, 2013).

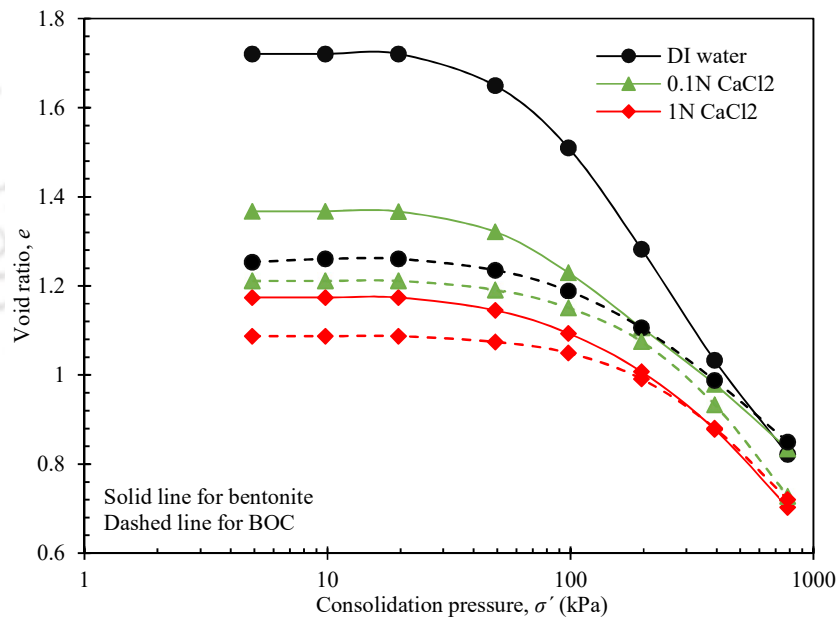


Fig. 5.10 Void ratio-consolidation pressure plots for bentonite and BOC inundated with calcium chloride solutions

(b) Compression index

The compression index (C_c) of each sample was found from the slope of the straight-line portion of the virgin e - $\log \sigma'$ plot. The C_c values of bentonite and BOC, when inundated with various permeant solutions, are shown in Table 5.8. For the compacted bentonite inundated

with DI water, a larger compression index was observed due to the predominant interparticle repulsive forces as a consequence of the increased thickness of the DDL (Duong and Hao, 2020). The compression index of bentonite reduced from 0.762 to 0.477 and 0.461 when the permeant was replaced from DI water to 1N NaCl and 1N CaCl₂, respectively. Due to the presence of aggressive electrolyte concentration, more cations were diffused in the double layer, which resulted in the reduction of repulsive forces and hence, a considerable decrease in compression index was observed. As a result, the soil structure also changed from a dispersed state to a flocculated state (Dutta and Mishra, 2016; Jadda and Bag, 2020). This change in soil structure may increase the permeability coefficient in the presence of inorganic salts (Mishra et al., 2015).

In DI water, the addition of 10% organoclay to bentonite reduced the compression index from 0.762 to 0.526. This reduction in C_c was due to the hydrophobic nature of organoclay, which considerably reduced the amount of water adsorbed in the interlayer surface. From Table 5.8, it was noted that the influence of concentration and valency of inorganic salts was minimal for BOC samples. For instance, when the concentration changed from 0 (DI water) to 1N of NaCl and CaCl₂, a percentage C_c reduction of 37.4% and 39.5% was observed for bentonite and 23.9% and 25.5% for BOC, respectively.

Table 5.8 Compression index and Yield stress of bentonite and BOC samples inundated with different permeants

Permeant Solutions	Compression Index (C_c)		Yield Stress, P_o (kPa)	
	Bentonite	BOC	Bentonite	BOC
DI water	0.762	0.526	75.5	161.9
0.1N NaCl	0.587	0.496	107.9	166.8
1N NaCl	0.477	0.400	157.0	186.4
0.1N CaCl ₂	0.510	0.472	122.6	171.7
1N CaCl ₂	0.461	0.392	191.3	215.8

(c) *Yield stress or Pre-consolidation stress*

Using Casagrande's method, yield stress or pre-consolidation stress (P_o) was determined from the e -log σ' curve. The value of P_o for bentonite and BOC inundated with different pore fluids is illustrated in Table 5.8. From the values, it can be noted that the yield stress displayed an increasing trend with an increase in salt concentration and valency. A significant rise in P_o was observed for BOC samples when inundated with aggressive salt solutions. When the

permeating fluid changes from DI water to 0.1N and 1N NaCl, the P_o value increased from 75.5 kPa to 107.9 kPa and 157.0 kPa for bentonite and from 161.9 kPa to 166.8 kPa and 186.4 kPa for BOC. Similarly, for 0.1N and 1N CaCl_2 , the P_o attained a value of 122.6 kPa and 191.3 kPa for bentonite and 171.7 kPa and 215.8 kPa for BOC, respectively. This rise in P_o was due to the lesser swelling of samples upon salt permeation, which resulted in more dense packing and higher yield stress (Zhang et al., 2016).

5.3.7 Impact of inorganic salts on the consolidation parameters of bentonite and BOC

(a) Time for 90% consolidation

Figure 5.11 displays the effect of consolidation pressure on the time for 90% consolidation (t_{90}) for compacted soil specimens under the influence of various permeants. For all compacted specimens, the t_{90} value increased with an increase in consolidation pressure. At maximum consolidation pressure (784 kPa), the sample with maximum swelling potential exhibited more time for 90% consolidation. Consequently, the bentonite samples displayed a substantial t_{90} value in DI water and showed a considerable t_{90} reduction when permeated with inorganic salt solutions. At consolidation stress of 784 kPa, the permeation of 0.1N NaCl and CaCl_2 reduced the t_{90} of bentonite from 1156.0 minutes (for DI water) to 282.2 minutes and 174.2 minutes, respectively. Similarly, at 1N NaCl and CaCl_2 , t_{90} was further reduced to 110.2 and 100.0 minutes, respectively. This reduction in t_{90} of bentonite under aggressive salt solutions could be due to the decrease in interparticle repulsive forces and DDL thickness (Dutta and Mishra, 2016).

However, for BOC specimens, the effect of concentration and valency of inorganic salts was significantly lesser. Figure 5.11 concluded that there was a comparatively minimal reduction in the t_{90} value of BOC from 132.2 minutes (for DI water) to 56.3 minutes and 50.4 minutes for 1N NaCl and CaCl_2 , respectively. Due to the lesser swelling of BOC samples in both DI water and inorganic solutions, the rate of reduction in the void ratio will be considerably lesser when compared to bentonite, which in turn reduces the compressibility and t_{90} of BOC samples.

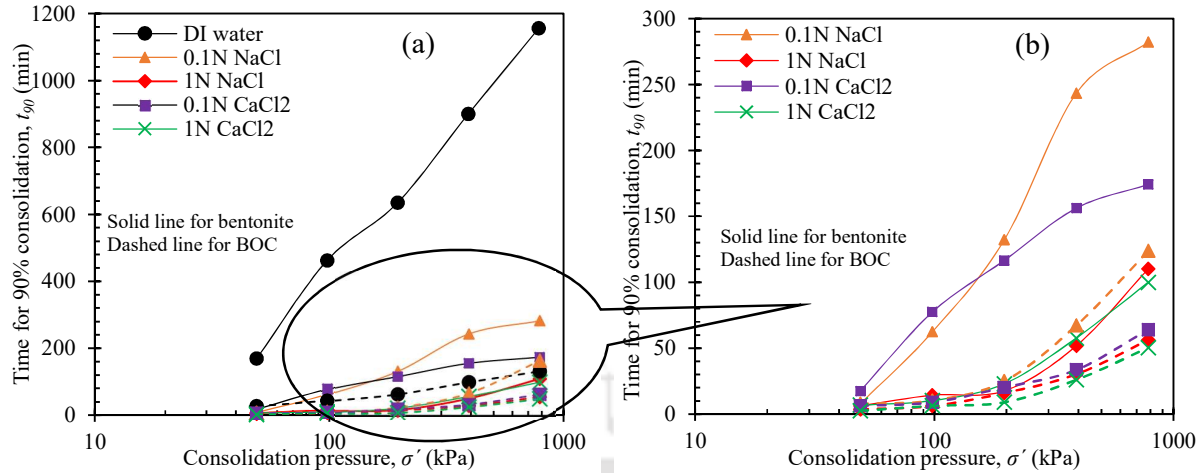


Fig. 5.11 Variation of t_{90} – consolidation pressure for samples (a) inundated with different permeants and (b) inundated with inorganic salt solutions

Further, to understand the variation of t_{90} with liquid limit and free swell index, the relationship between t_{90} versus LL and t_{90} versus free swell index of bentonite and BOC at different consolidation pressures was plotted (Fig. 5.12). The results showed that the t_{90} of all specimens varies with the liquid limit and free swell index as t_{90} depends on the clay-pore fluid interactions (Dutta and Mishra, 2016). From these figures, it should be noted that irrespective of the consolidation pressure, the increase in liquid limit raises the t_{90} for both bentonite and BOC. Also, the variation in the t_{90} value with LL was maximum when the vertical consolidation pressure was highest. This variation is significantly noticeable only when the liquid limit increases beyond 125.0%. At lower liquid limits, the immobile water around the clay particles will be lesser, and the loosely held double-layer water can quickly dissipate when an external consolidation pressure is applied. This dissipation can lead to a substantial reduction in the t_{90} value (Jadda and Bag, 2020). When permeated with monovalent cations, the t_{90} value of bentonite at 784 kPa decreases from 1156.0 minutes (for DI water) to 110.3 minutes (for 1N) as the liquid limit decreases from 310.0% to 87.0%, whereas for divalent cations, it decreases to 100.0 minutes with a comparable change in LL. Hence, it can be concluded that irrespective of the permeant type and soil type, the t_{90} versus LL curve displays an identical trend. However, the variation in t_{90} with consolidation pressure was significantly lower for BOC samples. The hydrophobic nature of organoclays in BOC is attributed to the lesser swelling of the mixture, which could be the possible reason for the reduced t_{90} values.

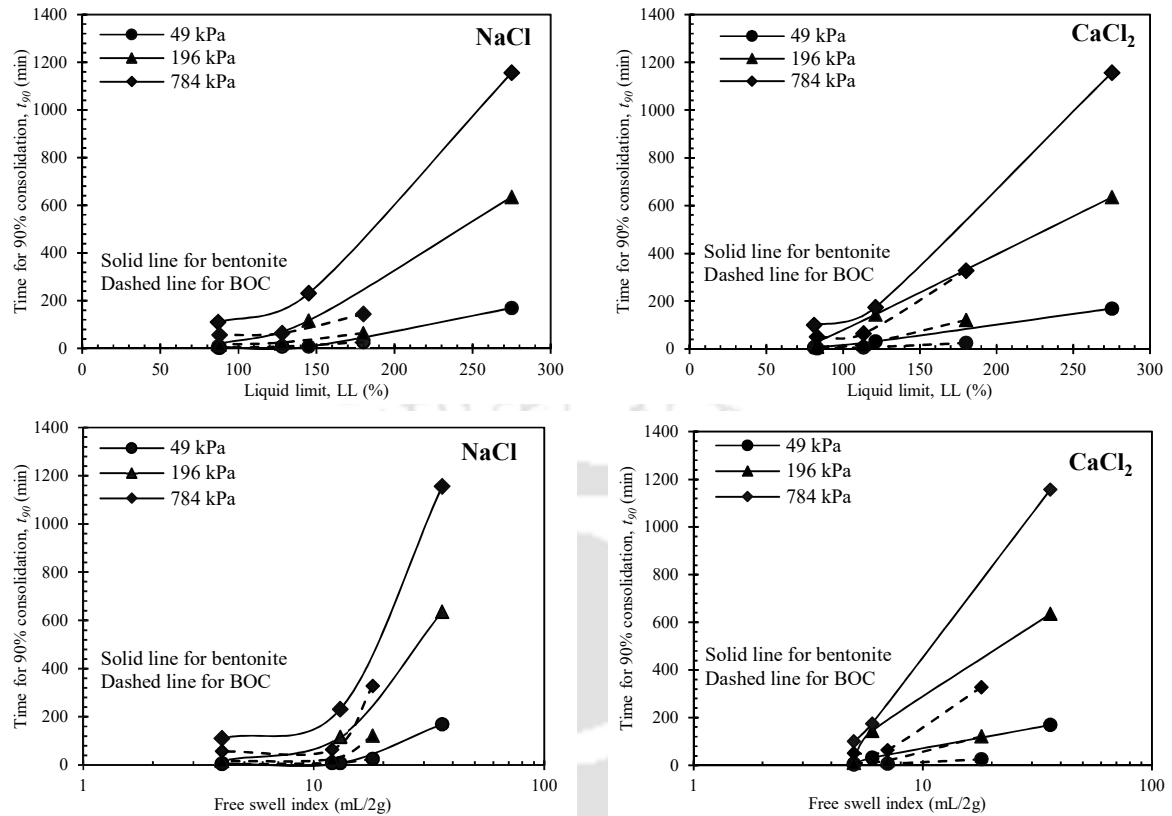


Fig. 5.12 Variation of time for 90% consolidation with liquid limit and free swell index of bentonite and BOC under the influence of NaCl and CaCl_2 permeants

The influence of free swelling on the t_{90} of bentonite and BOC at various vertical consolidation pressures is shown in Fig. 5.12. Irrespective of the permeating fluid and soil type, the t_{90} decreased with a decline in the free swell index. Also, as the consolidation pressure increased, the effect of free swelling on the t_{90} increased. For example, when the permeant solution was changed from DI water to 1N CaCl_2 , the free swell index of bentonite and BOC changed from 36.0 to 5.0 mL/2g (a reduction of 86.1%) and 18.0 to 5.0 mL/2g (a decrease of 72.2%), respectively. Corresponding to these solutions, at an consolidation pressure of 784 kPa, there was a maximum percentage t_{90} reduction of 91.3% and 84.6% for bentonite and BOC, respectively. In addition, the plot also demonstrated that the fluctuation in the t_{90} due to the presence of inorganic salts was minimal for BOC because it was least affected by the salt concentration and valency. Hence, it can be concluded that the external aggressive electrolytic environment doesn't significantly affect the t_{90} of BOC.

(b) Coefficient of consolidation

The coefficient of consolidation (c_v) indicates a soil's rate of consolidation when pressure acts on it. Studies from previous research have shown that the c_v depends on the mineral

composition and pore fluid chemistry (Dutta and Mishra, 2016; Duong and Hao, 2020). In this study, the main mineral present in both bentonite and organoclay was identified as montmorillonite (as evident from XRD images), and hence, all the samples showed a similar variation of c_v with consolidation pressure. As seen from Fig. 5.13, when the pressure increases, the c_v of all specimens decreases. When more load acts on the soil, the particles try to align in a more densely packed manner, resulting in a decrease in the rate of consolidation and a reduction in compressibility. Those soils whose compressibility was controlled by mechanical factors such as soil fabric, properties of soil grains, particle gradation, etc., showed a rise in the c_v with increased pressure. However, the soils whose compressibility was affected by the attractive and repulsive forces showed a decreasing trend in the c_v value with a rise in pressure (Sridharan and Rao, 1973; Dutta and Mishra, 2016). Since the interparticle attractive and repulsive forces govern the compressibility nature of bentonite and BOC, the c_v decreases with the increase in pressure. Furthermore, the influence of the saline environment on the c_v of soils was also studied and displayed in Fig. 5.13. The presence of salts significantly increased the c_v of bentonite and BOC samples. The effect of salinity on the c_v of BOC samples was comparatively lesser, resulting in a faster rate of consolidation in BOC specimens than in bentonite. At any given pressure, the rise in concentration and valency exhibited higher c_v . At a pressure of 784 kPa, the permeation of 1N NaCl and CaCl₂ increased the c_v of bentonite from 6.712×10^{-6} cm²/s to 6.071×10^{-5} (9.1 times) and 6.521×10^{-5} cm²/s (9.7 times), respectively. Similarly, for BOC samples, the replacement of permeant fluid from DI water with 1N NaCl and CaCl₂ showed an increase in c_v from 5.271×10^{-5} cm²/s to 1.209×10^{-4} (2.3 times) and 1.342×10^{-4} cm²/s (2.5 times), respectively.

For a better understanding of the compressibility nature, a graph was plotted between the void ratio and c_v for specimens inundated with different solutions (Fig. 5.14). When the void ratio of compacted soil decreased, a closer particle arrangement was attained. Due to this compacted particle alignment, there will be an increase in interparticle repulsive forces, which further prevents the consolidation rate of bentonite (Dutta and Mishra, 2016). The void ratio of BOC samples was lower than that of bentonite because of its less swelling nature in DI water and inorganic salts. Hence, the effect of the void ratio on the c_v of BOC samples was also lower. Under an aggressive electrolytic environment, the DDL thickness of bentonite decreases considerably; thus, the bentonite samples showed a significant increase in the coefficient of consolidation.

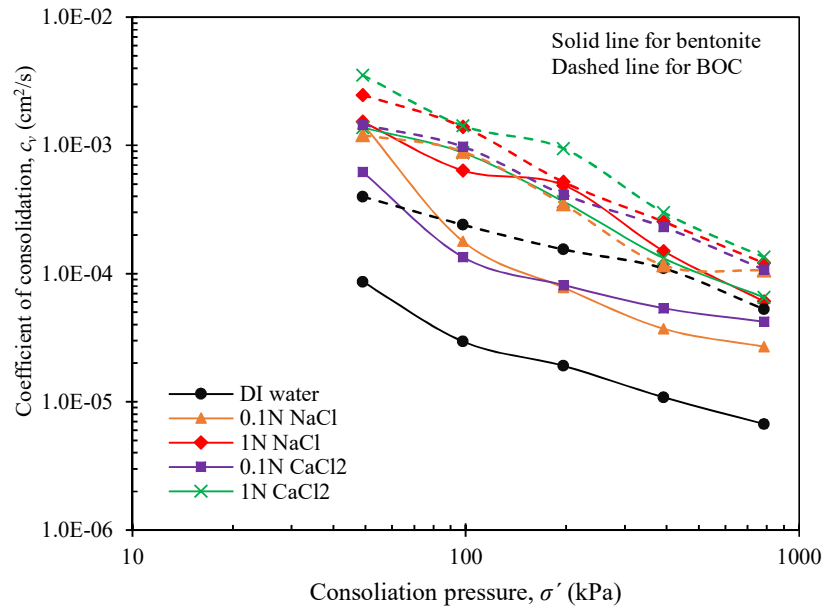


Fig. 5.13 Variation of coefficient of consolidation of bentonite and BOC with consolidation pressure under different inorganic salt permeants

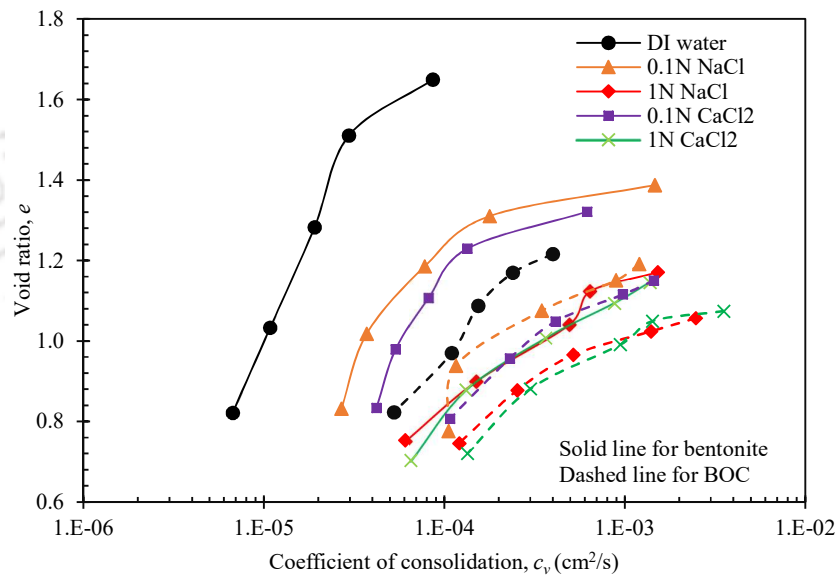


Fig. 5.14 Graph between void ratio and coefficient of consolidation of bentonite and BOC under the influence of various inorganic salt solutions

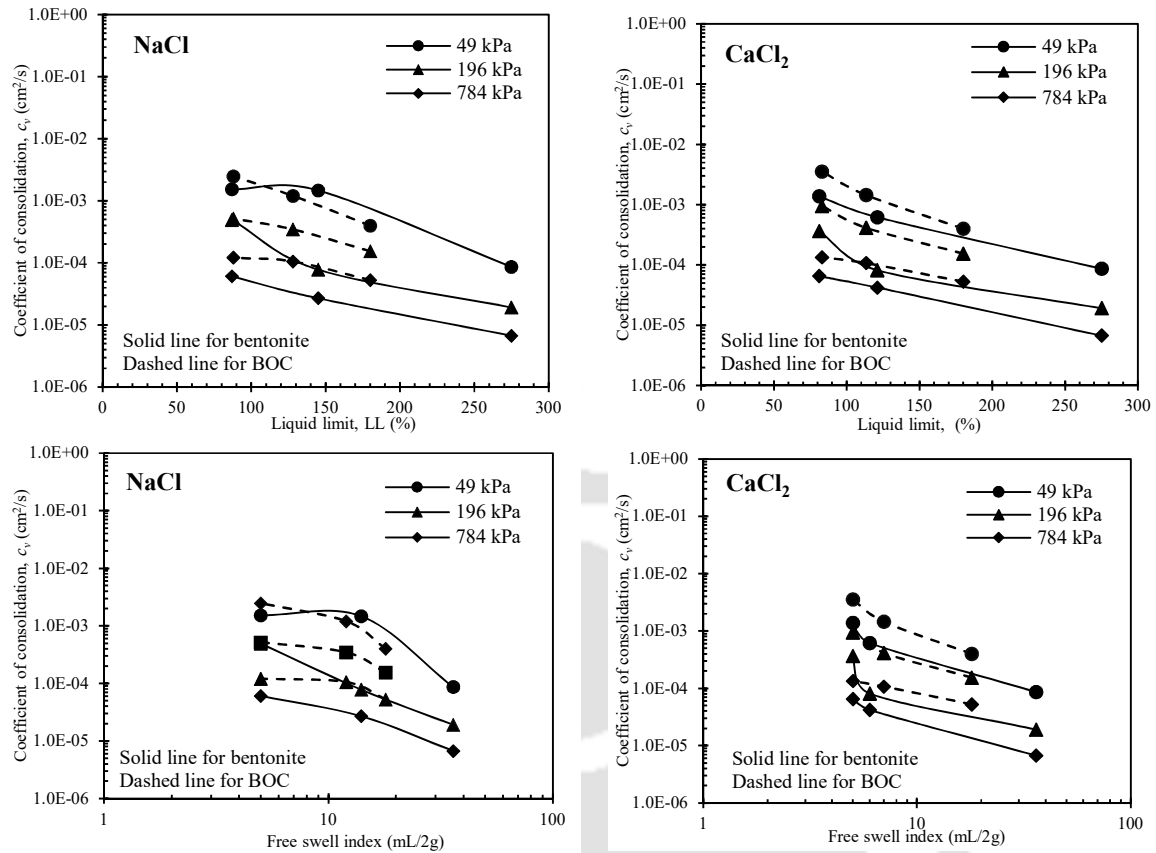


Fig. 5.15 Variation of coefficient of consolidation with liquid limit and free swell index under the influence of NaCl and CaCl₂ permeants

Figure 5.15 illustrates the variation of c_v with liquid limit (LL) and free swell index of samples inundated with different inorganic salt permeants at three different consolidation pressures (49, 196 and 784 kPa). As explained earlier, the LL and free swell index affect the compressibility and consolidation characteristics of soil as it is controlled by the interparticle repulsive forces and DDL thickness (Sridharan and Rao, 1975; Dutta and Mishra, 2017). At higher concentrations of inorganic salts, LL and free swelling were measured to be minimal. At this point, the surface potential will be the least. Consequently, the interparticle repulsive force decreases, resulting in a higher consolidation rate (Mitchell and Soga, 2004; Dutta and Mishra, 2016).

For BOC samples, the effect of inorganic salts on the LL and free swell index was significantly lesser. Hence, the variation in c_v was also less noticeable in the case of BOC. The replacement of DI water with 1N NaCl and CaCl₂ decreased the LL of BOC from 180.0% to 88.4% and 83.2% and dropped the free swell index from 18.0 mL/2g to 5.0 mL/2g and 5.0 mL/2g, respectively. At an consolidation pressure of 49 kPa, the same order of salt permeants increased the c_v of BOC from 3.988×10^{-4} cm²/s to 2.476×10^{-3} (6.2 times) and 3.536×10^{-3} cm²/s

(8.9 times), respectively. Meanwhile, for bentonite at the same pressure and the same change in salt concentrations, the increase in c_v was observed to be 17.7 and 15.9 times, respectively. The comparison of the c_v values of bentonite and BOC samples indicated that BOC attained a faster rate of consolidation, and the c_v of BOC samples was least affected by the presence of aggressive electrolytic conditions.

(c) Coefficient of volume compressibility

The relationship between the coefficient of volume compressibility (m_v) and consolidation pressure for bentonite and BOC samples permeated with different solutions is shown in Fig. 5.16. As noticed by previous researchers, when the permeant is DI water, the m_v of bentonite increases initially, reaches a maximum value and then decreases with an increase in consolidation pressure (Duong and Hao, 2020; Fang et al., 2022). This trend holds true even in the presence of other salt solutions and heavy metals (Dutta and Mishra, 2016; Ray et al., 2019). When pressure acts on the soil, initially, soil particles which were at a higher void ratio tend to consolidate at a faster rate, resulting in an increase in volume compressibility. When the pressure was increased further, the rate at which soil gets compressed decreased and m_v reduced. The samples having a higher DDL were able to consolidate more due to their larger void ratio. Hence, bentonite samples showed higher m_v regardless of the nature of the pore fluid. Due to the addition of salts, bentonite's DDL thickness reduced considerably; thus, the volume change rate also decreased (Duong and Hao, 2020). Figure 5.16 displays that the rate of volume change was significant for bentonite samples permeated with DI water and low concentrations of inorganic salts. However, at maximum consolidation stress (784 kPa), the m_v for all the samples converged to a minimum value ($0.026 \sim 0.017 \text{ kPa}^{-1}$) because of the compact arrangement and minimal DDL thickness at higher consolidation stresses.

For BOC samples, the variation of m_v with consolidation pressure was minimal. For example, at 196.1 kPa, the m_v of bentonite and BOC under the influence of DI water, 1N NaCl and 1N CaCl_2 were found to be 0.091, 0.039 and 0.041 kPa^{-1} , and 0.038, 0.029 and 0.029 kPa^{-1} , respectively. The addition of NaCl and CaCl_2 doesn't significantly vary the DDL thickness of BOC samples due to the presence of the water-repellent organoclay fraction. Due to this negligible variation in DDL thickness, the rate of volume change doesn't change much for BOC under aggressive electrolytic conditions.

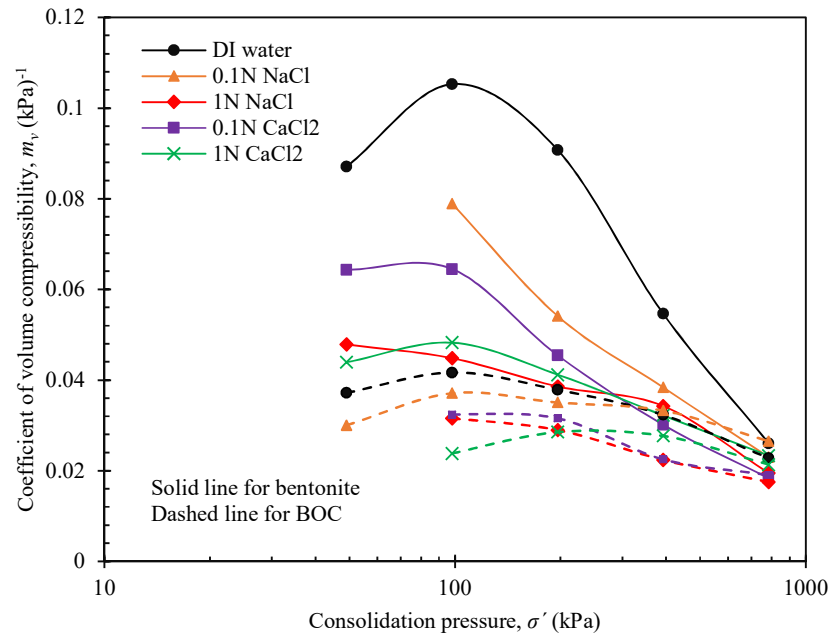


Fig. 5.16 Variation of coefficient of volume change with consolidation pressure of bentonite and BOC under the influence of different inorganic salt permeants

5.3.8 Effect of inorganic salt addition on the surface morphology of the compacted bentonite and BOC

The alterations in soil structure following the permeation of electrolytic pore fluids are reflected in the microscopic images obtained from FESEM analysis. The FESEM analysis carried out on representative samples obtained from the consolidated soil samples is shown in Fig. 5.17. The soil particles are more uniformly distributed in bentonite and BOC mixed with DI water. However, in the case of BOC, the presence of small cracks can be observed, which may contribute to the generation of micropores, potentially accounting for the higher hydraulic conductivity observed.

At higher electrolytic concentrations, the structure of bentonite particles undergoes rearrangement, leading to the formation of a more flocculated soil structure. These flocculated lumps form more open channels, facilitating fluid flow and consequently increasing hydraulic conductivity. Furthermore, at high concentrations (1N) of calcium chloride solutions, there is a chance of bentonite particle disintegration and formation of anisotropic soil fabric (Jadda and Bag, 2020).

In the case of BOC samples, the permeation of higher concentrations of NaCl and CaCl₂ resulted in the formation of flocculated aggregates (as seen in Fig. 5.17). However, upon inundation with monovalent cations, the variation in surface charges and contraction of the

diffused double layer in BOC was nominal compared to divalent cations. As a result, a less flocculated structure was seen in BOC inundated with 1N NaCl. In addition, the impact of inorganic salt permeation on the surface morphology of BOC showed a comparatively smaller distinction than bentonite. This also implied the lower chemical sensitivity of BOC under adverse electrolyte environments than bentonite.

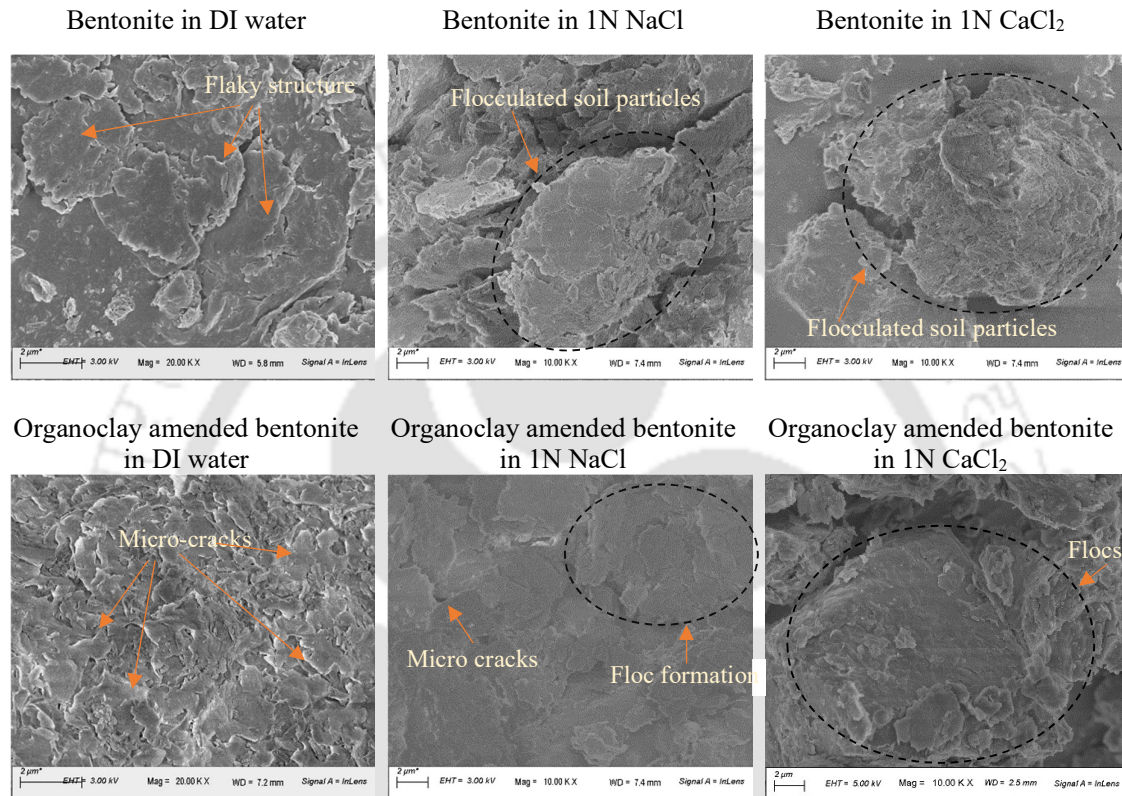


Fig. 5.17 FESEM images of bentonite and BOC permeated with different pore fluids

5.4 Summary

This chapter examines the variations in geotechnical properties of two liner materials – bentonite and organoclay-amended bentonite (BOC) under permeation by 0 (DI water), 0.1, and 1N concentrations of NaCl and CaCl₂. This chemical compatibility analysis involved a series of Atterberg's limit tests, free swell index tests, oedometer tests, and FESEM analysis on both bentonite and BOC in the presence of these inorganic salts. The conclusions derived from the test results are as follows:

The plasticity, free swell, swell potential, and swell pressure of both bentonite and BOC decreased with increasing NaCl and CaCl₂ concentrations. Additionally, the presence of inorganic salt ions increased the hydraulic conductivity of both liner materials. However, the

experimental outcomes indicated that the addition of organoclay to bentonite substantially controlled the adverse effects of salts on the index and engineering properties of bentonite. The hydrophobic nature of the organoclay fraction in BOC did not significantly contribute to inner-crystalline and osmotic swelling. Consequently, the swelling characteristics of BOC were reduced when exposed to DI water. Furthermore, the organoclay fraction inhibited the double layer (DDL) formation and swelling of the remaining bentonite fraction, leading to increased hydraulic conductivity in the presence of inorganic salts and DI water. Upon salt permeation, the soil structure of both bentonite and BOC altered, forming a flocculated structure at higher salt concentrations, which resulted in formations of wider flow paths. Nevertheless, the salt effect was less pronounced in the geotechnical properties of BOC, and none of the samples exceeded the hydraulic conductivity threshold of 1×10^{-9} m/s for barrier applications.

The compression index (C_c) and consolidation parameters – time for 90% consolidation (t_{90}) and coefficient of volume compressibility (m_v) of bentonite decreased significantly with the permeation of inorganic salts. In contrast, the compressibility and consolidation characteristics of BOC samples were less affected by inorganic salts due to the water-repellent nature of the organoclay in the mixture. In aggressive electrolytic environments, the yield stress of bentonite exhibited a significant increase compared to DI water, whereas BOC showed a nominal increase. Specifically, when the inundating fluid changed from DI water to 1 N NaCl and CaCl₂, bentonite displayed a percentage yield stress increase of 107.8% and 153.3%, respectively, whereas BOC showed a minimal increase of 15.2% and 33.3%, respectively. The coefficient of consolidation (c_v) for both bentonite and BOC increased with the addition of inorganic salts and declined with a rise in consolidation pressure. The c_v value also depended on soil mineral composition, salt concentration, and ion valency. Regardless of consolidation pressure, c_v decreased with increasing liquid limit and free swell index for all samples. However, t_{90} values showed a direct relationship with increasing liquid limit and free swell index. Higher salt concentrations (1N) and divalent ions (Ca²⁺ ions) had a greater impact on the geotechnical properties of bentonite compared to lower concentrations (0.1N) and monovalent ions (Na⁺ ions). Nonetheless, the effect of ionic concentrations and valency was significantly lower on the geotechnical characteristics of BOC.

Therefore, the results indicated a lower chemical sensitivity of the organoclay-amended bentonite liner, even in aggressive salt permeants. Hence, BOC may be recommended for barrier applications in waste containment facilities as it is more stable in aggressive electrolytic conditions compared to conventional bentonite.

CHAPTER 6

The impact of cationic and anionic heavy metals on the hydraulic barrier performance of organoclay-amended bentonite

6.1 General

The rapid industrial expansion in developing countries poses a significant threat to environmental sustainability due to the improper disposal of toxic heavy metals and organic pollutants. According to a report from the Central Pollution Control Board (CPCB, 2021), hazardous waste generation in India is increasing at an alarming rate of 5% annually. Heavy metal contamination has become one of the most daunting issues, contributing to severe health hazards such as lead poisoning (Bedi, 2023; Mukherjee et al., 2020; Njati and Maguta, 2019). Toxic cationic heavy metals, including Pb^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+} and Ni^{2+} , are prevalent in mine tailings as well as hazardous and non-hazardous waste landfills (Zeng et al., 2021; Arranz-González et al., 2021; Chen et al., 2020). Chromium is another dangerous and toxic heavy metal ubiquitously found in industrial landfill leachates. Chromium exists in trivalent (Cr^{3+}) and hexavalent (Cr(VI)) states. Unlike other cationic heavy metals, the hexavalent chromium, Cr(VI) exists in an oxy-anionic form such as CrO_4^{2-} , HCrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ in aqueous solutions (Yang et al., 2021). Industrial sectors, such as chemical manufacturing, petroleum and coal manufacturing, nuclear facilities, waste treatment and disposal, contribute substantially to global hazardous waste production (Du et al., 2022; Goswami et al., 2017). The unscientific disposal of this waste in landfills exacerbates ecological imbalance and health hazards (Ravindra and Mor, 2019). The high concentration of toxic heavy metals and organic contaminants in landfills and tailing impoundments can percolate along with other leachate constituents into the surrounding environment, undermining the functionality of landfill barriers. The engineered impermeable barrier system is frequently installed to prevent the probable percolation of toxic constituents from landfills into the surrounding soil and groundwater (Touze-Foltz et al., 2021; Rowe and Barakat, 2021).

Compacted clay liners are the most common soil liners used for waste containment facilities or underground storage tanks. Bentonites, mainly comprised of sodium montmorillonite, are the ideal candidates for amendments in CCLs due to their high swelling ability, low hydraulic conductivity, high cation exchange capacity and high sorption capacity (Gupt et al., 2020). However, its performance can degrade when exposed to aggressive leachate constituents and extreme pH conditions (Keerthana and Arnepalli, 2022). Heavy metals in leachates

significantly affect bentonite's geotechnical performance. Numerous studies have investigated how heavy metals alter the physicochemical properties of bentonite (Du et al., 2014, 2015; Nartowska et al., 2019; Ray et al., 2021). The majority of these studies focused on parameters such as hydraulic conductivity, adsorption, and shear strength when permeated with cationic heavy metals (Fan et al., 2013; Fu et al., 2022; Yang et al., 2021; Ray et al., 2022; Gupt et al., 2020; Du et al., 2015). The results concluded that the permeation of cationic heavy significantly compresses the diffuse double-layer thickness of bentonite, adversely affecting its microstructural and macrostructural properties. However, bentonite exhibited superior cationic heavy metal retention capacity through mechanisms such as ion exchange, surface complexation, precipitation/coprecipitation, and diffusion into particle micropores (Wang and Zhang., 2021; Ouhadi et al., 2006; Naka et al., 2019; Barbier et al., 2000; Liu et al., 2016; Alexander et al., 2017). In addition to adsorption and hydraulic properties, other geotechnical properties of liner materials, such as consolidation and compressibility, are crucial for hydraulic barrier applications. Waste placement in disposal facilities occurs in several stages, causing fluctuating consolidation stresses that can affect the underlying liner material. Hence, the study on consolidation parameters is equally important as hydraulic properties in determining the suitability of a material for hydraulic barrier applications.

Furthermore, the influence of anionic heavy metals on the geotechnical properties of bentonite barriers remains under-examined. The negatively charged surface on the bentonite particles, which are formed due to the isomorphous substitution of Si^{4+} by Al^{3+} , might not be effective for adsorbing anionic heavy metals (chromate ions) onto its surface. The permeation of chemicals reduces bentonite's diffused double-layer thickness, limiting its swelling ability, causing particle flocculation, and forming wider channels that increase hydraulic conductivity. Therefore, suitable amendments to bentonite are needed to enhance barrier efficiency under these chemical conditions. The low sorption capacity of bentonite for anionic metal ions also necessitates exploring alternative solutions for liner material.

Organically modified clays or bentonites were prepared to improve the chemical compatibility of conventional bentonite (Jia-Kai et al., 2023; Beryl and Xavier, 2021; Di Emidio et al., 2017). These hydrophobic organoclays effectively adsorb organic contaminants as well as anionic contaminants (Ma et al., 2016; Yoo et al., 2004). The cationic surfactant modification creates a positively charged clay surface, enhancing interactions between anionic heavy metals and the modified clay surface (Kaya and Yukselen, 2005). Additionally, organoclays also exhibit low hydraulic conductivity in organic solutions, making them suitable

for hydraulic barrier materials in environments with high organic pollutants (Guégan, 2019; Benson et al., 2015; Ni et al., 2024; Keerthana and Arneppali, 2022; Andini et al., 2006). Most studies (Xie et al., 2023; Zhao et al., 2017) have focused on the sorption capacity and hydraulic conductivity of organoclay barriers under organic pollutants. However, the impact of heavy metals on the hydraulic barrier performance of organoclay-amended soil barriers remains unexplored in the literature. This research is crucial as the hazardous industrial leachates and tailings often contain a concomitant mix of inorganic salts, heavy metals, and organic contaminants (Chen et al., 2023; Zhang et al., 2020; Rachwał et al., 2015).

Few studies have investigated the hydraulic barrier performance of Indian bentonite amended with commercial organoclay. This chapter explores the comprehensive physico-chemo-mechanical behaviour and microstructural changes of organoclay-amended bentonite when exposed to different concentrations (0 to 1000 mg/L) of various heavy metal ions (Pb^{2+} , Zn^{2+} and Cr(VI)). The study focused on geo-environmental properties such as consistency limits, pH studies, swelling behaviour, consolidation parameters, compressibility parameters, and hydraulic conductivity of bentonite and organoclay-amended bentonite by conducting a series of laboratory experiments. Microstructural investigations were also carried out using FESEM, EDS, and FTIR tests to elucidate the mechanism behind the variation in geotechnical properties. All these parameters play an inevitable role in understanding the barrier performance of the proposed liner material. The outcomes of this study will be invaluable for the field implementation of commercially available clays (bentonite and organoclay) as barriers in hazardous waste containment and tailing impoundments in India.

6.2 Impact of cationic (Pb^{2+} and Zn^{2+}) and anionic heavy metal (Cr(VI)) on the hydraulic barrier performance of compacted bentonite and BOC

6.2.1 Variation in pH

The pH of all heavy metal solutions ($\text{Zn(NO}_3)_2$, $\text{Pb(NO}_3)_2$, and $\text{K}_2\text{Cr}_2\text{O}_7$) decreases as the concentrations of Pb^{2+} , Zn^{2+} , and Cr(VI) increase, as shown in Table 6.1. Specifically, the pH reduces from 6.81 for DI water to 6.04 for 1000 mg/L Zn^{2+} , 4.70 for 1000 mg/L Pb^{2+} , and 4.28 for 1000 mg/L $\text{Cr}_2\text{O}_7^{2-}$ solutions. This reduction in pH is attributed to the hydrolysis of aqueous heavy metal ions, which results in higher H^+ concentrations in the solutions, as shown in the following equations (Du et al., 2013).





Table 6.1 pH values of heavy metal solutions

Heavy metal ions Concentrations →	pH value of heavy metal solutions			
	0 mg/L	100 mg/L	500 mg/L	1000 mg/L
Zn ²⁺	6.81	6.64	6.32	6.04
Pb ²⁺	6.81	5.24	4.87	4.70
Cr(VI)	6.81	4.69	4.41	4.28

Table 6.2 pH values of soil suspensions at a liquid-to-solid ratio of 20

Concentration of heavy metals (mg/L)	pH value of soil suspensions (L/S =20)					
	Zinc		Lead		Cr(VI)	
	Bentonite	BOC	Bentonite	BOC	Bentonite	BOC
0	9.43	9.28	9.43	9.28	9.43	9.28
100	8.51	7.87	9.20	9.14	8.56	8.13
1000	6.49	6.45	6.41	6.08	6.19	6.14

The pH of both bentonite and BOC suspensions at different heavy metal concentrations was measured at a liquid-to-solid ratio of 20, as tabulated in Table 6.2. It was observed that increasing heavy metal concentrations led to a decrease in the pH of the soil suspensions. The initial pH of bentonite in DI water was 9.43, while that of BOC was 9.28. At a heavy metal concentration of 1000 mg/L, the pH for lead ions and zinc ions reduced to 6.41 and 6.49 for bentonite and 6.08 and 6.45 for BOC, respectively. Similarly, for Cr(VI) ions, the pH was reduced to 6.19 for bentonite and 6.14 for BOC.

This pH reduction is attributed to the neutralisation of the negative charges on the bentonite surface by H⁺ ions from the heavy metal solutions, which reduces the concentration of H⁺ in the pore water and consequently lowers the pH of the bentonite-heavy metal mixtures. In BOC samples, the presence of a hydrophobic organoclay fraction results in fewer net negative

charges on the soil surfaces, requiring fewer H^+ ions from the solution. Thus, the pH of BOC samples was observed to be slightly lower than that of bentonite in the respective heavy metal solutions.

6.2.2 Influence of heavy metals on the Atterberg limits and free swell index of bentonite and BOC

(a) Liquid Limit (LL)

Figures 6.1 to 6.3 indicate the effect of various concentrations of Pb^{2+} , Zn^{2+} , and $Cr(VI)$ on the liquid limit of bentonite and BOC, respectively. The results revealed that the liquid limit of bentonite decreased significantly with increasing heavy metal ion concentration. Although BOC exhibits a similar trend, the impact of metal ions on its plasticity behaviour is relatively less pronounced. For instance, the liquid limit of bentonite decreased from 310% to 225%, 230% and 231% when the permeant solution was changed from DI water to 1000 mg/L Pb^{2+} , Zn^{2+} , and $Cr(VI)$, respectively. Similarly, for the same change in metal ion concentrations, BOC exhibited a liquid limit reduction from 180% to 142%, 151% and 108%, respectively. The influence of heavy metals on the liquid limit follows a similar trend to that observed with inorganic salts (as discussed in Chapter 5). The reduction in LL upon mixing with cationic heavy metal ions is attributed to the presence of divalent Pb^{2+} or Zn^{2+} ions, which compressed the diffused double layer (DDL) thickness of bentonite, reducing water adsorption and subsequently lowering the LL. However, in the case of anionic heavy metal solution, the anionic $Cr(VI)$ was added via potassium dichromate solution, thereby introducing K^+ ions into the system. These K^+ ions can also affect the liquid limit and swelling properties of both bentonite and BOC. As discussed in Chapter 5, the inorganic monovalent K^+ ions can significantly influence the diffused double-layer thickness and plasticity of bentonite while showing comparatively lesser impact on BOC. Consequently, the reduction in plasticity of bentonite in the presence of $Cr(VI)$ is likely primarily due to the influence of K^+ ions, with $Cr(VI)$ playing a minimal role. However, in BOC, although the impact of potassium dichromate on the liquid limit is minimal, the resulting changes might be due to the combined effect of K^+ and $Cr(VI)$.

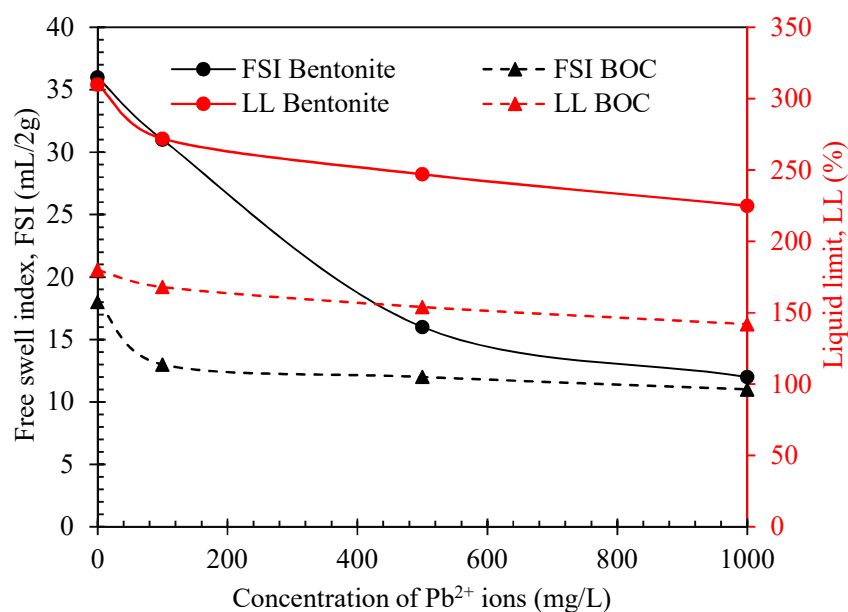


Fig. 6.1 Variation of free swell index and liquid limit of bentonite and BOC with different concentrations of Pb^{2+} ions

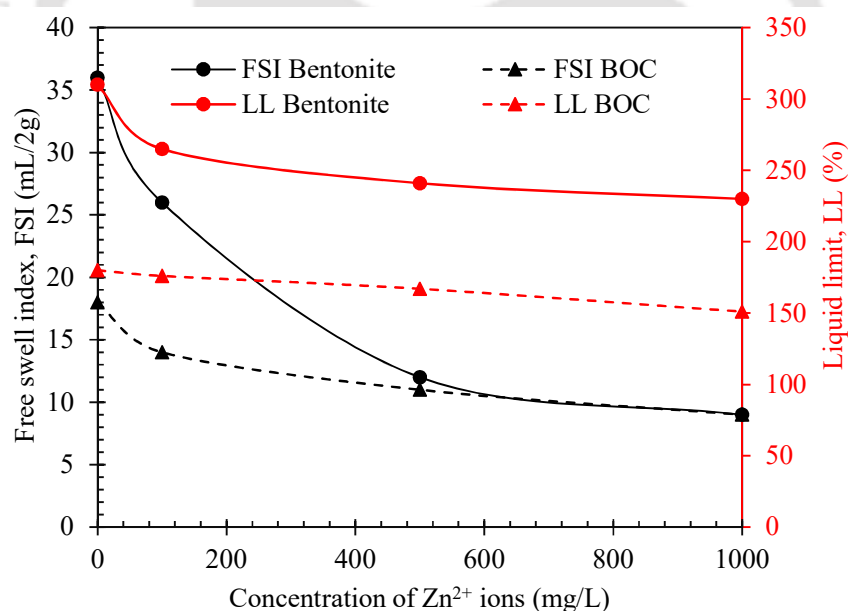


Fig. 6.2 Variation of free swell index and liquid limit of bentonite and BOC with different concentrations of Zn^{2+} ions

Similar trends for LL under the influence of heavy metal solutions have been observed in previous studies conducted on various clays (Ray et al., 2022; Babu et al., 2023). At higher concentrations of heavy metal ions (≥ 500 mg/L), the pH of both bentonite and BOC shifted to a more acidic range. This alteration in pH caused the soil suspensions to transition from a

dispersed state (observed in DI water or at lower heavy metal ion concentrations) to a flocculated state (at higher concentrations). Consequently, this shift reduced the negative charges on the bentonite surface, resulting in a significant decrease in the DDL thickness, which subsequently reduced water adsorption and LL.

For BOC, the hydrophobic nature of organoclay fraction (10%) mitigated the effect on the DDL thickness, resulting in a lower LL compared to bentonite. Some studies have reported that, unlike bentonite, low plasticity clays exhibit opposite behaviour, such as an increase in LL with rising concentration or valency or with lower pH (Gratchev and Towhata, 2016; Ike et al., 2023). This contradictory behaviour may be attributed to the changes in the physical and chemical properties of soils used for the experimental analyses.

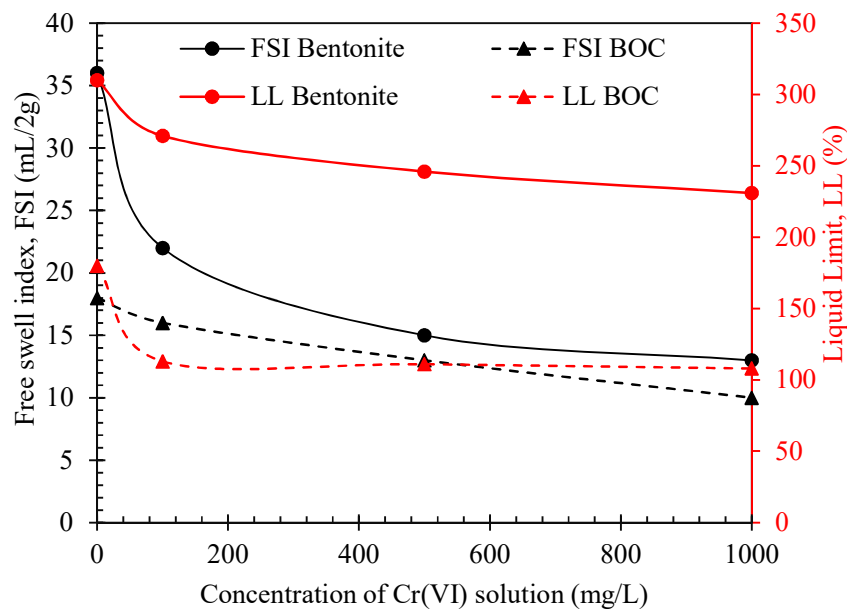


Fig. 6.3 Variation of free swell index and liquid limit of bentonite and BOC with different concentrations of Cr(VI) ions

(b) Free swell index

The free swell index (FSI) results under varying metal ion concentrations align with the previously discussed LL data. The free swelling indices of bentonite and BOC in DI water and various concentrations of Pb^{2+} , Zn^{2+} , and Cr(VI) are presented in Figs. 6.1 to 6.3. The incorporation of 10% organoclay into the bentonite considerably decreased the free swelling tendency in the presence of heavy metals. For example, when the concentration of Pb^{2+} and Zn^{2+} increased from 0 (DI water) to 100 mg/L, free swelling of bentonite decreased from 36 mL/2g to 31 mL/2g and to 26 mL/2g, respectively. Similarly, with the same change in

concentrations of Cr(VI), the FSI of bentonite decreased to 22 mL/2g. In the case of BOC, the FSI reduction was from 18 mL/2g (DI water) to 13 mL/2g for Pb^{2+} , 14 mL/2g for Zn^{2+} and 16 mL/2g for Cr(VI). As seen from the data, the decrease is more pronounced in bentonite, underscoring its chemical sensitivity to heavy metal solutions compared to the relatively stable behaviour of BOC under similar metal ion concentrations.

In DI water, bentonite particles exhibited a dispersive behaviour due to the dominance of repulsive forces over attractive forces among the soil particles. However, the increase in metal ion concentration significantly contributed to a reduction in the DDL thickness of bentonite, resulting in particle flocculation and, subsequently, lower FSI values. Additionally, the cation exchange reaction between Pb^{2+} or Zn^{2+} ions from the solution and Na^+ ions from bentonite also played a role in the formation of flocs and reduction in FSI. In BOC, the relatively lower reduction in FSI can be attributed to the presence of quaternary ammonium cations within the interlayer of the 10% organoclay fraction and its inherent hydrophobic behaviour. These covalently bonded organic cations may not undergo ion exchange with ions from the permeant solution. Thus, changes in the free swelling of BOC might be primarily ascribed to the contribution of the DDL compression on the remaining 90% bentonite fraction.

In potassium dichromate solutions, both the cation (K^+) and anion (Cr(VI)) can influence the geotechnical properties of bentonite and BOC. Conversely, in lead nitrate and zinc nitrate solutions, existing literature indicates that nitrate anions do not significantly alter the geotechnical properties of clays (Du et al., 2013; Barbier et al., 2000). The inorganic K^+ ions can considerably compress the diffuse double layer (DDL) thickness of bentonite, and as the concentration of Cr(VI) increases from 0 to 1000 mg/L, the concentration of K^+ also increases in the solution. Therefore, the reduction in the free swelling of bentonite can be primarily attributed to the K^+ ions. However, in BOC, as discussed in Chapter 5, the impact of inorganic alkali metal cations, such as Na^+ , K^+ and Ca^{2+} , on the compression of DDL thickness is comparatively lesser, thereby minimising the impact on the plasticity and swelling behaviour of BOC. Consequently, the decline in the free swelling of BOC may be partially due to the interaction of K^+ ions with the bentonite fraction and partially due to the interaction between Cr(VI) anions with the 10% organoclay fraction.

As the heavy metal ion concentration increased from 0 to 500 mg/L, a substantial reduction in FSI was observed for bentonite. Beyond this concentration, there were less pronounced changes in FSI. The higher concentrations of heavy metals (> 500 mg/L) induced an acidic

environment in bentonite suspensions, leading to face-to-face flocculation and attained stability. This phenomenon accounts for the diminished variation in FSI beyond the 500 mg/L concentration range. The relatively lower influence of metal ions on the DDL thickness of BOC may account for the reduced effect of heavy metals on their free swelling behaviour.

6.2.3 Swell pressure and swell potential of bentonite and BOC under the influence of heavy metals

(a) Swell Potential

The data in Table 6.3 represents the effect of metal ion concentrations on the swell potential of bentonite and BOC compacted at OMC-MDD. The rise in Pb^{2+} concentration from 0 to 1000 mg/L decreased the swell potential of bentonite from 36.8% to 11.3%, whereas for 1000 mg/L Zn^{2+} and Cr(VI), it decreased to 11.1% and 16.7%, respectively. The swell potential of BOC showed a decline from 17.4% in DI water to 6.4% in 1000 mg/L Pb^{2+} , to 7.5% in 1000 mg/L Zn^{2+} and to 7.6% in 1000 mg/L Cr(VI). A substantial reduction in swell potential was observed in bentonite because high concentrations of cationic divalent Pb^{2+} and Zn^{2+} ions suppressed the DDL thickness, resulting in a decline in swelling properties. The reduction in swelling behaviour of BOC in heavy metal solutions can be attributed to the DDL suppression of 90% bentonite proportion. In potassium dichromate solutions, the K^+ ions impart DDL compression of bentonite and might be the main reason for the decline in swelling properties.

(b) Swell Pressure

From the data in Table 6.4, it was observed that the swell pressure of bentonite and BOC compacted at OMC-MDD also displayed an inverse relationship with metal ion concentration. The swell pressure and swell potential results are consistent with the liquid limit and free swell index of bentonite and BOC. Similar to the liquid limit and free swell index, more influence of heavy metal ions was observed for the swell behaviour of bentonite than BOC. For bentonite compacted at OMC-MDD, a decline in swell pressure was noted from 450 kPa in DI water to 360 kPa in 500 mg/L of Pb^{2+} , to 340 kPa in 500 mg/L Zn^{2+} and to 330 kPa in 500 mg/L of Cr(VI). Similarly, at OMC-MDD conditions, BOC exhibited a swell pressure value of 350 kPa in DI water, 275 kPa in 500 mg/L of Pb^{2+} , 250 kPa in 500 mg/L of Zn^{2+} and 325 kPa in 500 mg/L of Cr(VI).

Table 6.3 Swell potential of bentonite and BOC permeated with different concentrations of heavy metals

Swell Potential (%)	Bentonite			BOC		
	Pb ²⁺	Zn ²⁺	Cr(VI)	Pb ²⁺	Zn ²⁺	Cr(VI)
0 (DI water)	36.78	36.78	36.78	17.36	17.36	17.36
100 mg/L	26.71	24.07	22.62	11.32	11.19	11.50
500 mg/L	18.46	18.13	18.68	6.80	9.55	10.68
1000 mg/L	11.32	11.05	16.68	6.42	7.52	7.55

Table 6.4 Swell pressure of bentonite and BOC permeated with different concentrations of heavy metals

Swell Pressure (kPa)	Bentonite			BOC		
	Pb ²⁺	Zn ²⁺	Cr(VI)	Pb ²⁺	Zn ²⁺	Cr(VI)
0 (DI water)	450	450	450	350	350	350
100 mg/L	420	370	410	280	300	335
500 mg/L	360	340	330	275	250	325
1000 mg/L	310	310	295	280	220	210

The considerable drop in the swelling characteristics of bentonite with increasing heavy metal ion concentrations could be ascribed to various reasons: (i) the contraction of the diffuse double layer (DDL) thickness of bentonite particles, as the DDL thickness is related to the concentration and valency of ions present in the pore fluid. (ii) pH reduction with increasing metal ion concentrations. According to the Gouy-Chapman theory (Chapman, 1913), DDL thickness is inversely related to the concentration and valency of ions and directly proportional to the pH of the system and inversely varies with the size of the hydrated cations (iii) Possible microstructural and mineralogical changes in soil (di Maio, 1996; Li et al., 2015; Du et al., 2015). Therefore, the increased concentration of Pb²⁺ or Zn²⁺ ions, the divalent nature of Pb²⁺ or Zn²⁺ ions, and the presence of an acidic pH combinedly contribute to a significant reduction in DDL thickness, leading to a substantial decrease in swelling characteristics. In the case of BOC, the 10% hydrophobic nanoclay may not hydrate in water and may not contribute to the diffuse double-layer expansion of the mixture. This might be responsible for the reduced swelling value of the BOC compared to that of bentonite in all solutions. Therefore, the impact

of the heavy metal ion concentration on the BOC swelling characteristics was relatively minimal compared to bentonite.

In the case of the potassium dichromate solution, the existence of K^+ ions contribute to the majority of swelling reduction because the K^+ ions in pore water replace the Na^+ ions in the interlayer through the ion exchange process. The $Cr(VI)$ in the pore water exists as anionic complexes, and hence, it gets less adsorbed to the negatively charged bentonite particles; therefore, anionic $Cr(VI)$ will be less reactive with the bentonite (Yang et al., 2021). Hence, the electrolytic properties of the solution are attributed to the changes in the swelling properties of bentonite.

Irrespective of the heavy metal ion concentration, lead ions exhibited higher values for plasticity and swelling parameters of bentonite compared to zinc ions. The differences in the geotechnical properties under these cationic metal ions, despite having the same valency, can be attributed to variations in solution chemistry such as hydrolysis constants, solubility, electronegativity, and hydrated radius of the ions (Wang and Zhang, 2021). Additionally, the higher swelling of bentonite in the presence of lead ions could be primarily due to the insufficient interaction between lead ions and the bentonite surface, caused by the precipitation of Pb^{2+} that occurs at higher pH levels. As explained in Chapter 4, lead ions can precipitate when the pH is greater than 6, while zinc ions precipitate at a pH greater than 8. Consequently, more interaction occurs between Zn^{2+} ions and bentonite particles in the pH range of 6 to 8, leading to a greater decrease in repulsive forces and more pronounced compression of the diffuse double layer (DDL). As a result, the swelling of bentonite in the presence of Zn^{2+} exhibited lower values. However, a few studies performed on other types of soils have shown that the smaller hydrated radius of lead would result in a greater reduction in DDL thickness and thus have a greater impact on geotechnical properties (Negahdar and Nikghalbpour, 2020). The higher pH of bentonite suspensions and the resultant precipitate formation might be the reason for this discrepancy in results. In the case of BOC samples, swelling parameters exhibited higher values in the presence of zinc ions. The adsorption of zinc onto the organoclay fraction is considerably lower compared to lead adsorption, which results in a lesser impact on the reduction of DDL thickness in the presence of zinc ions, thereby indicating higher swell potential than with lead ions. Additionally, the relatively lower pH of BOC suspensions could reduce the extent of precipitate formation, facilitating improved interaction between lead ions and the BOC surface.

6.2.4 Time–swelling variation of bentonite and BOC under the influence of heavy metals

The temporal oedometer swelling of both bentonite and BOC, when permeated with different Pb^{2+} , Zn^{2+} and Cr(VI) concentrations, are presented in Figs. 6.4 to 6.6, respectively. The highest swelling for both bentonite and BOC was observed when permeated with DI water. The higher swelling is contributed by the bentonite particles, which have montmorillonite clay mineral and high cation exchange capacity. However, with the introduction of divalent cation heavy metal ions, the swelling of both liner materials exhibited a declining trend.

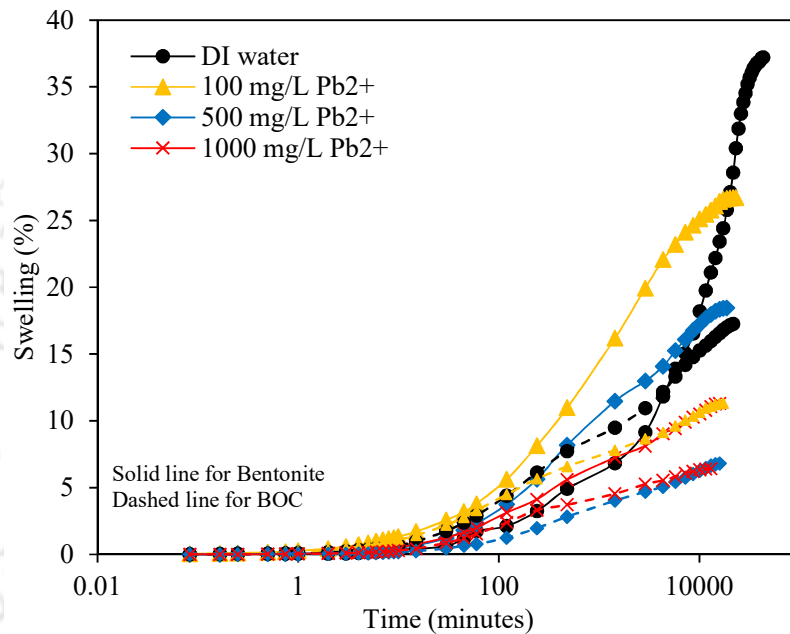


Fig. 6.4 Temporal variation of swelling for bentonite and BOC under the permeation of various concentrations of Pb^{2+} ions

For instance, the maximum swelling percentage reached 37.2% for bentonite and 17.4% for BOC when permeated with DI water under a surcharge load of 4.9 kPa. The addition of heavy metal ions reduced the swelling of bentonite and BOC. For instance, when this permeant solution was substituted with 1000 mg/L heavy metal ions, the swelling of bentonite notably decreased to 11.3% and declined to 6.4% for BOC. In the case of bentonite, the exchangeable Na^+ ions in the interlayer could be readily replaced by the divalent lead or zinc ions from the solution through the process of ion exchange. This can be ascribed to the larger hydrated radius of Pb^{2+} or Zn^{2+} ions, which facilitates the displacement of Na^+ ions from the bentonite interlayer. It's important to note that this ion exchange process is contingent upon factors such as the type of interlayer cation in bentonite and the permeant fluid's concentration, valency, and dielectric constant.

In accordance with Figs. 6.4 to 6.6, regardless of the concentration of metal ions, all time-swelling curves displayed a characteristic *S*-shape. In comparison to BOC, bentonite samples exhibited a prominent *S*-curve distribution of swelling. Initially, the curve exhibits a gradual increase, followed by a sharp rise, and then reaches an asymptotic curve. Consequently, this entire swelling curve can be subdivided into three swelling phases – initial, primary and secondary swelling phases (Sridharan and Gurtug, 2004). The allocation of swelling in these stages for each sample and the time taken to complete each stage is documented in Tables 6.5 to 6.7. This trend aligns with the observations for inorganic salts discussed in Chapter 5. The initial swelling denotes the inter-void (i.e. macro-pores) swelling of the soil samples, primary swelling represents the swelling caused by the hydration of exchanged cations in the interlayer, whereas secondary swell occurs due to the microstructural particle rearrangement (Jain et al., 2022; Alzamel et al., 2022). Depending on the concentration of heavy metal ions, the initial swelling of both bentonite and BOC accounted for around 4 to 12% of the total swelling. The primary swelling stage constituted the majority of total swelling, ranging from 87 to 95%, with less than 2% of swelling occurring in the secondary swelling stage. This *S*-shaped swelling distribution could be linked to the hydration mechanism of montmorillonite, encompassing inner crystalline swelling and osmotic swelling. Inner crystalline swelling corresponds to the expansion of the interlayers within bentonite particles, while osmotic swelling indicates the double layer swelling, occurring between quasi-crystals due to the concentration gradients in the clay-pore fluid system (Alzamel et al., 2022).

As the concentration of heavy metal ions increases, both the percentage of swelling and the time required to complete it decreases across all three stages, especially during the primary swelling stage. At lower concentrations, the cation exchange between Na^+ and Pb^{2+} or Zn^{2+} led to a decline in double-layer swelling. However, at higher concentrations, further ion exchange may not occur due to the complete replacement of Na^+ by Pb^{2+} or Zn^{2+} ions. Consequently, significant reductions in swelling were observed due to the complete disappearance of double-layer or osmotic swelling and the potential dissolution of montmorillonite (Shao et al., 2023; Karnland et al., 2007). Furthermore, in the case of BOC samples, the organic cations present in the interlayer do not participate in ion exchange or hydration mechanisms. This leads to a reduced amount of swelling in all stages, compared to bentonite.

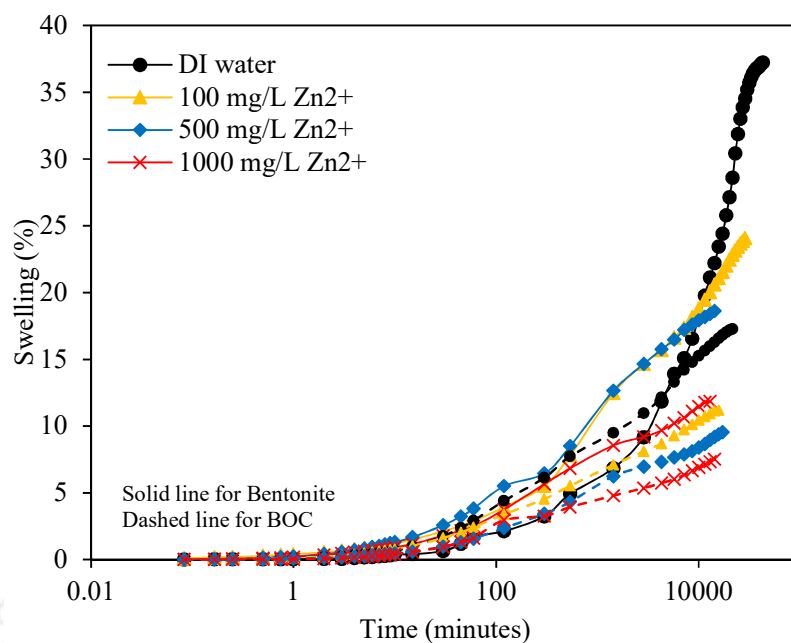


Fig. 6.5 Temporal variation of swelling for bentonite and BOC under the permeation of various concentrations of Zn^{2+} ions

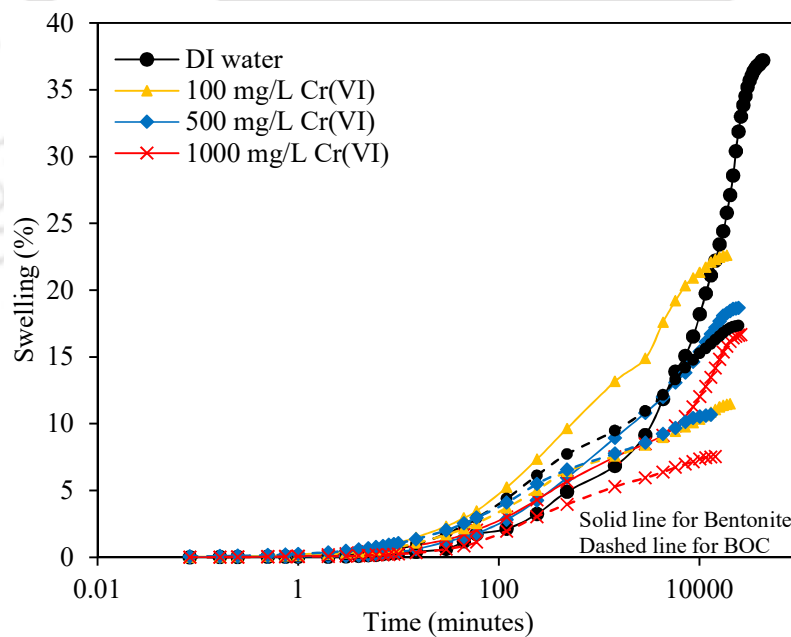


Fig. 6.6 Temporal variation of swelling for bentonite and BOC under the permeation of various concentrations of Cr(VI) ions

Table 6.5 The distribution of total swell potential of bentonite and BOC in each stage of swelling (%) at different concentrations of Pb^{2+}

Concentration (mg/L)	Bentonite			BOC		
	Distribution of total swelling in various stages of swelling (%)					
	Initial swelling	Primary swelling	Secondary swelling	Initial swelling	Primary swelling	Secondary swelling
0	1.20	35.30	0.28	1.50	15.30	0.56
100	1.90	23.40	0.21	1.30	9.90	0.12
500	0.80	17.50	0.06	0.30	6.40	0.10
1000	1.00	10.20	0.06	0.40	5.90	0.12

Table 6.6 The distribution of total swell potential of bentonite and BOC in each stage of swelling (%) at different concentrations of Zn^{2+}

Concentration (mg/L)	Bentonite			BOC		
	Distribution of total swelling in various stages of swelling (%)					
	Initial swelling	Primary swelling	Secondary swelling	Initial swelling	Primary swelling	Secondary swelling
100	3.10	23.40	0.21	1.30	9.90	0.12
500	0.80	17.50	0.06	0.30	6.40	0.10
1000	1.00	10.20	0.06	0.40	5.90	0.12

Table 6.7 The distribution of total swell potential of bentonite and BOC in various stages of swelling (%) at different concentrations of $Cr(VI)$

Concentration (mg/L)	Bentonite			BOC		
	Distribution of total swelling in various stages of swelling (%)					
	Initial swelling	Primary swelling	Secondary swelling	Initial swelling	Primary swelling	Secondary swelling
100	2.30	20.30	0.02	1.20	10.20	0.10
500	1.40	17.00	0.28	1.20	9.30	0.18
1000	1.20	15.40	0.08	0.50	7.00	0.05

6.2.5 Variation of hydraulic conductivity with void ratio for samples permeated with different concentrations of heavy metals

The impact of cationic and anionic heavy metal ion permeation on the hydraulic conductivity (k) of compacted bentonite and BOC is depicted in Figs. 6.7 to 6.9. The bentonite showed a permeability coefficient in the range of 10^{-10} to 10^{-12} m/s and exhibited significant variations depending upon the applied vertical consolidation stress and the concentration of the permeating solution. When the applied vertical consolidation stress changed from 49 to 784 kPa, the void ratio of bentonite permeated with DI water drastically reduced from 1.65 to 0.82, and the k value decreased from 7.4×10^{-11} to 1.7×10^{-12} m/s. Similarly, for BOC under the same conditions, the void ratio changed from 1.23 to 0.78 and the corresponding k from 1.57×10^{-10} m/s to 9.29×10^{-12} m/s. The rise in vertical consolidation stress reduced the void ratio, minimised the individual pore spaces and resulted in an increase in the tortuosity of the seepage path (Du et al., 2015). The bentonite sample displayed excellent swelling capacity in DI water, which led to very small and intricate flow paths in hydrated bentonite. As a result, it demonstrated very low hydraulic conductivity. But BOC exhibited a higher k value, which was ascribed to the limited hydration of organoclay fraction in DI water due to its hydrophobic behaviour and leading to the formation of micro-cracks (Ni et al., 2024; Lorenzetti et al., 2005). The studies by Javadi et al. (2017) and Benson et al. (2015) also indicated a significant increase in the permeability coefficient of organoclay-amended soils in DI water. However, they showed that the hydraulic performance of organoclay-amended soils exhibited better efficiency under the permeation of organic solutions and fuels.

The high chemical sensitivity of bentonite under the influence of heavy metals was evident from the permeability results as k drastically rises with an increase in the metal ion concentrations. At a fixed void ratio of 1.0, the replacement of permeant fluid from DI water to 1000 mg/L Pb^{2+} ions increased the k value of bentonite by 11.3 times, whereas for BOC, it increased only by 3.9 times. Similarly, under the same void ratio and the same change in concentrations, the k value of bentonite under 1000 mg/L Zn^{2+} ions increased by 9.0 times, while the k of BOC increased by 3.6 times. The replacement of pore fluid from DI water to cationic heavy metal ions resulted in an ion exchange reaction between exchangeable Na^+ from bentonite and Pb^{2+} or Zn^{2+} from permeant solution. As a result, the DDL of bentonite progressively collapsed, and the soil particles tended to change their orientation and started to flocculate. Consequently, inter-aggregate pore spaces increased, and several shorter flow paths were created, which led to the drastic increase in k . The compact face-to-face dispersed

arrangement of bentonite particles in DI water changed to a face-to-face aggregated arrangement at high concentrations of cationic heavy metal ions (Souli et al., 2008).

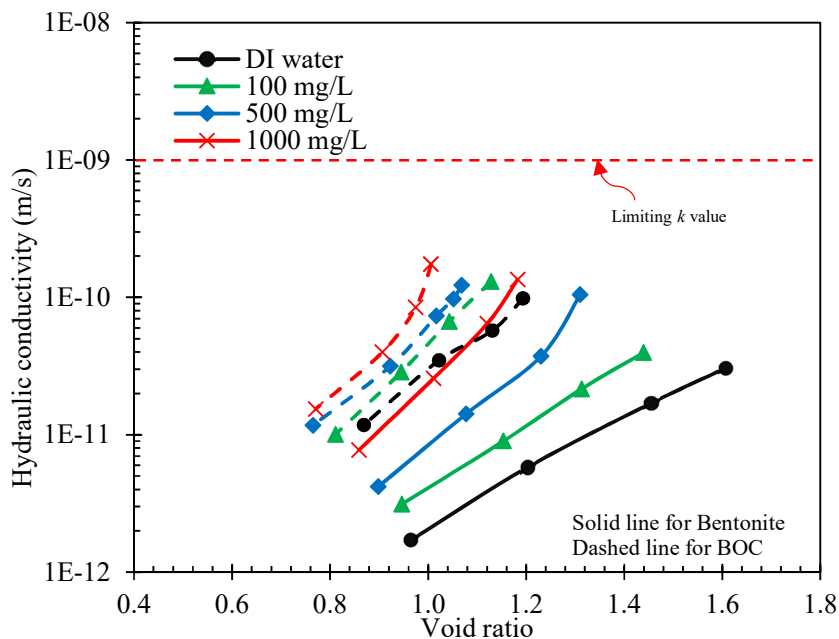


Fig. 6.7 Hydraulic conductivity vs void ratio plots for bentonite and BOC permeated with different Pb^{2+} concentrations

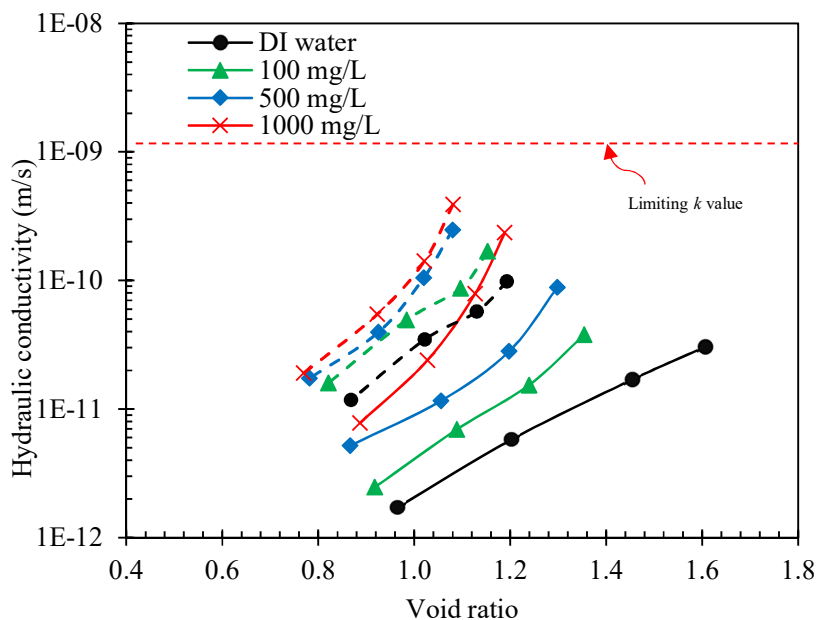


Fig. 6.8 Hydraulic conductivity vs void ratio plots for bentonite and BOC permeated with different Zn^{2+} concentrations

The organic cations in the interlayer of organoclay may not undergo an ion exchange reaction between interlayer cations and Pb^{2+} or Zn^{2+} from the solution (Yoo et al., 2004).

Additionally, the presence of the 90% bentonite component in BOC could potentially influence its hydraulic behaviour in the presence of heavy metal ions. The interaction between bentonite particles in BOC and the permeating fluid may induce microstructural alterations within the soil mixture, leading to flocculation. The remaining 10% organoclay fraction hinders the chemical reactivity of BOC by reducing the extent of flocculation induced by the Pb^{2+} or Zn^{2+} ions. Hence, the results indicated that the effect of pore fluid chemistry had less significance in the hydraulic performance of BOC compared to bentonite.

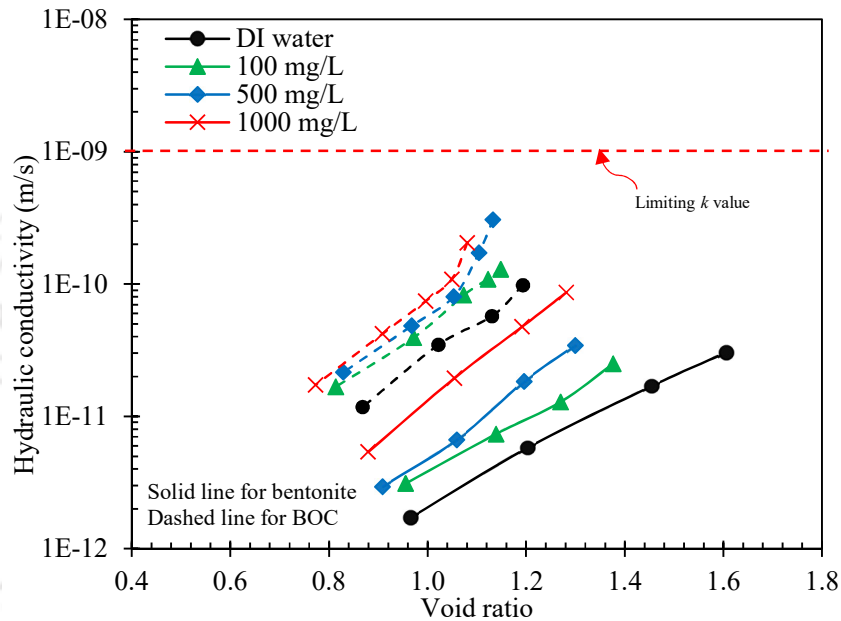


Fig. 6.9 Hydraulic conductivity versus void ratio plots for bentonite and BOC under the effect of Cr(VI) permeants

The anionic heavy metal solutions also displayed a similar relationship between void ratio and hydraulic conductivity as displayed by cationic heavy metals. The variation in hydraulic conductivity of bentonite under anionic heavy metals could be mainly due to the ion exchange reaction between K^+ ions from the solution and exchangeable Na^+ cation from the interlayer. When the concentration of alkali metal ions increases, the swelling of the soil decreases, and particle aggregation can occur. This can form new flow paths and increase hydraulic conductivity. Irrespective of the heavy metal concentration, the hydrophobic surface properties of organoclays account for the higher hydraulic conductivity of the organoclay-bentonite mixture (Moon et al., 2007; Javadi et al., 2017). Compared to bentonite, the lower percentage rise in hydraulic conductivity of BOC with a rise in Cr(VI) concentration might be due to the reduced chemical sensitivity of K^+ ions with BOC.

However, under all circumstances, no soil samples exceeded the limiting criteria for application as landfill liners (i.e. $k \leq 10^{-9}$ m/sec) suggested by various environmental protection agencies (USEPA, 1988). Based on previous studies, the addition of organoclay increased hydraulic conductivity when interacting with DI water but decreased it when interacting with organic pollutants and petroleum compounds (Smith et al., 2003; Javadi et al., 2017). Because landfill leachate contains a variety of contaminants, an organoclay-modified liner can potentially act as a better barrier material to keep all pollutants contained.

6.2.6 Impact of heavy metals on the compressibility characteristics of bentonite and BOC

(a) Compressibility behaviour (e -log σ' plots)

The oedometer experimental data was used to depict the compression curves (in a semi-logarithmic plot) for bentonite and BOC. The pressure-void ratio curves for bentonite and BOC permeated with 0 to 1000 mg/L Pb^{2+} , Zn^{2+} and Cr(VI) ions are illustrated in Figs. 6.10 to 6.12. As the e -log σ' relationship provides an indication of the compressibility characteristics of soil, the compressibility properties of both bentonite and BOC under the influence of various permeants can be studied from this relationship. As illustrated, the void ratio declined with an increase in the consolidation pressure because of the drainage of excess pore pressure and closer particle arrangement attained at higher pressures. As the pressure increased, the interparticle repulsion decreased, and a closer particle arrangement occurred; therefore, a reduction in the void ratio was observed. All samples exhibited minimal changes in void ratio at a stress range of 4.9 to 98.1 kPa, with the exception of bentonite permeated with DI water and 100 mg/L heavy metal ions. In the case of bentonite permeated with DI water and low metal ion concentrations (up to 500 mg/L), a reduction in the void ratio or compressibility was noted even at relatively lower consolidation pressures ranging from 19.6 to 98.1 kPa. In contrast, all BOC samples displayed more stability in terms of compressibility up to consolidation stress of 196.1 kPa, except for samples permeated with DI water and 100 mg/L heavy metal ions, which remained stable up to 98.1 kPa. Thus, the presence of heavy metal ions had a lesser impact on the compression index and void ratios of BOC samples.

With the addition of heavy metal ion concentration, the e -log σ' curve shifts downwards for both bentonite and BOC. For instance, at a consolidation pressure of 4.9 kPa, the void ratio of bentonite changes from 1.72 for DI water to 1.34 for 1000 mg/L Cr(VI) solutions. Similarly, for BOC, it decreases from 1.23 for DI water to 1.11 for 1000 mg/L Cr(VI) . The change in void ratio at any given pressure indicates the repulsive forces acting on the soil matrix owing to the

interaction between soil particles and the inundating fluid (Sridharan and Rao, 1973; Alawaji, 1999). When the concentration increases, the repulsive forces acting on the adjacent bentonite particles decrease because of the compression in the diffuse double-layer thickness; hence, the compressibility decreases.

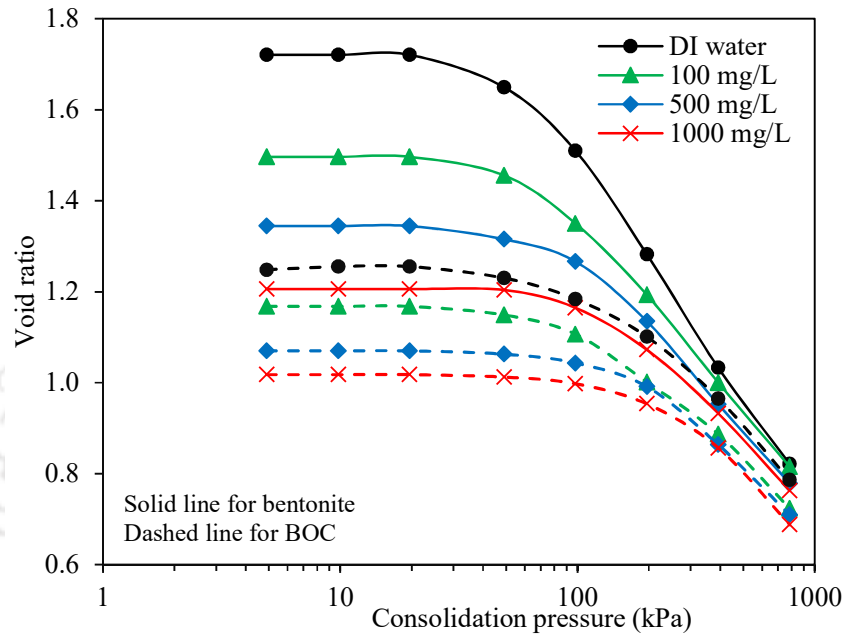


Fig. 6.10 Void ratio-pressure relationship for bentonite and BOC at different Pb^{2+} concentrations

Even though both bentonite and BOC displayed similar trends in e -log σ' variation, the effect of permeant ion concentration on e -log σ' was nominal for BOC compared to bentonite. This less variation might be due to the reduced water affinity of the hydrophobic organoclay fraction available in the BOC mixture (Sreedharan, 2013). Consequently, there will be a restriction in the diffuse double-layer formation. Thus, the effect of double-layer repulsion will be comparatively less in BOC upon inundation with various permeants. Hence, the compressibility of the BOC samples was significantly lower, even at lower concentrations of heavy metal ions.

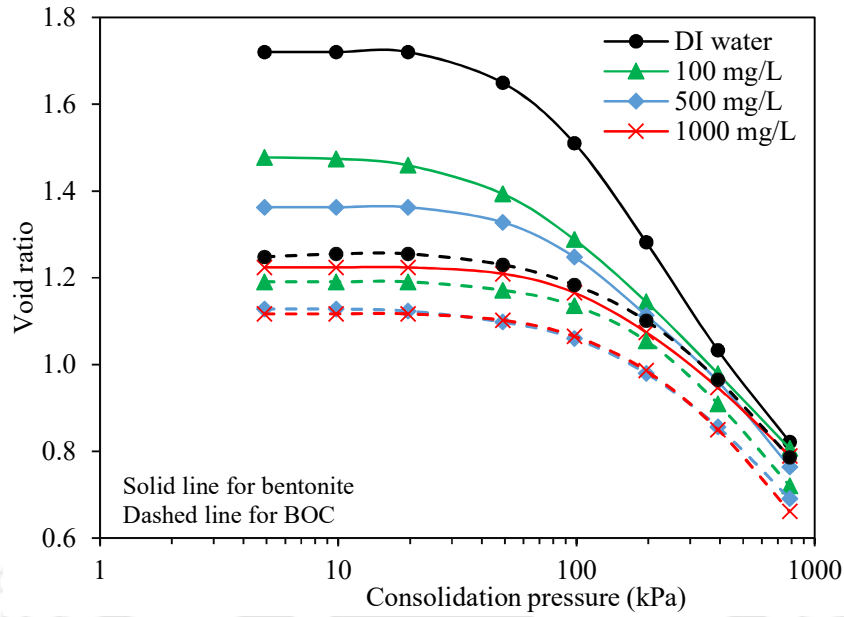


Fig. 6.11 Void ratio-pressure plots for bentonite and BOC at different Zn^{2+} concentrations

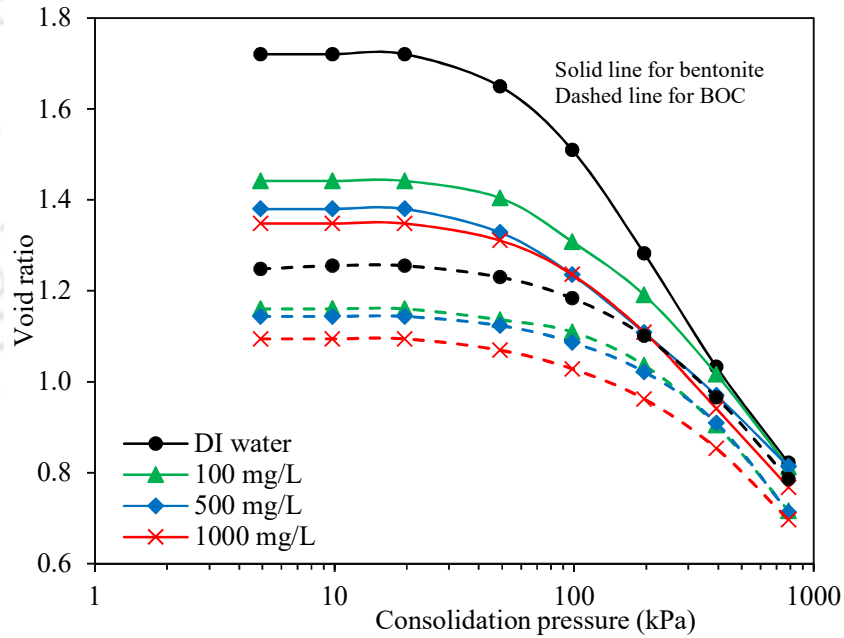


Fig. 6.12 Void ratio-pressure plots for bentonite and BOC at different Cr(VI) concentrations

(b) Compression index, C_c

The influence of cationic and anionic heavy metal ion concentrations (0, 100, 500, and 1000 mg/L) on the C_c of bentonite and BOC are presented in Figs. 6.13 to 6.15. For compacted bentonite inundated with DI water, a larger compression index was observed because of the

predominant interparticle repulsive forces as a consequence of the higher thickness of the diffuse double layer (Duong and Hao, 2020). The compression index of bentonite reduced from 0.76 to 0.52 (~32% decrease), 0.47(~38% decrease), and 0.52(~32% decrease) when the permeant was replaced with DI water to 1000 mg/L of Pb^{2+} , Zn^{2+} , and Cr(VI) , respectively. On account of the presence of aggressive heavy metal concentration, more cations were diffused in the double layer, which resulted in the reduction of repulsive forces; hence, a considerable decline in the compression index was observed.

The addition of 10% organoclay to bentonite reduced the compression index from 0.76 to 0.52. This reduction in C_c was due to the hydrophobic nature of the organoclay, which considerably reduced the quantity of water adsorbed on the interlayer surface. From the results, it was also noted that the influence of the heavy metal ion concentration of pore fluid on C_c was minimal for BOC samples when compared to bentonite. For instance, when the permeant solution was replaced from DI water to 1000 mg/L concentrations of Pb^{2+} and Cr(VI) , a percentage C_c reduction of ~15% and ~15% were observed for BOC samples, respectively.

At lower metal ion concentrations, specifically at 100 mg/L, the osmotic pressure within the soil-pore fluid system was observed to be relatively less. As a result, external stresses may potentially induce deformation in order to establish an equilibrium between the external applied stresses and the internal osmotic pressure (Ouhadi et al., 2006). Therefore, the C_c of bentonite at 100 mg/L metal ions exhibited a notably higher magnitude compared to the C_c values obtained at 500 mg/L and 1000 mg/L concentrations. Increased concentrations of heavy metals enhanced the osmotic pressure within the soil system, and the application of external stress may not significantly impact the C_c value, as the external load could not effectively disrupt the equilibrium osmotic pressure of the system. Thus, higher heavy metal concentrations ultimately led to a reduced change in settlement, aligning with the observations made by the previous research (Li et al., 2015).

The incorporation of 10% organoclay into bentonite substantially reduced the compressibility, improving the barrier's ability to withstand the weight of the landfill's overburdened materials and reducing subsidence over time. Also, it could be less susceptible to changes in pore fluid chemistry, as demonstrated by its stable compressibility behaviour when exposed to heavy metal concentrations. The reduced reactivity of BOC when subjected to high concentrations of heavy metal contaminants suggests that it may better maintain its structural integrity, thereby minimising the risk of breaches and environmental contamination.

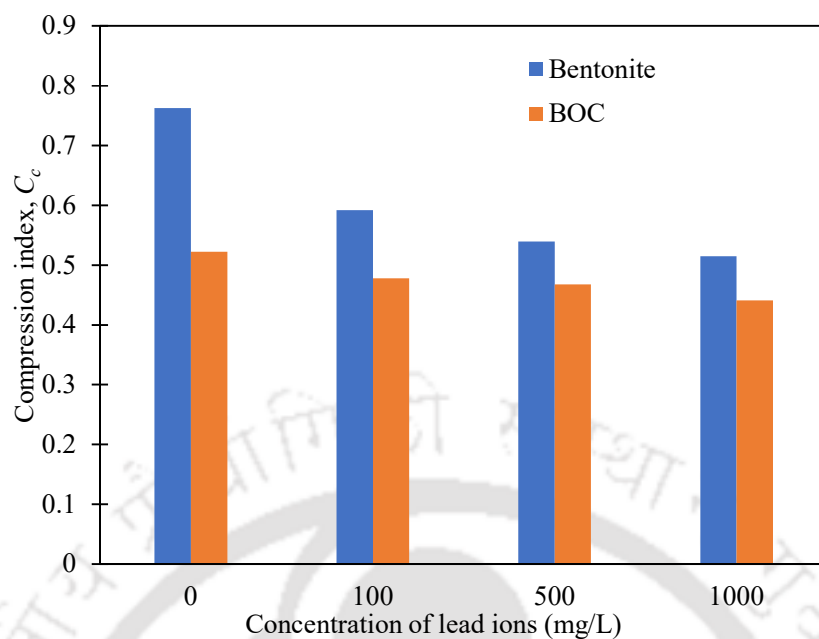


Fig. 6.13 Variation of C_c for bentonite and BOC at different Pb^{2+} concentrations

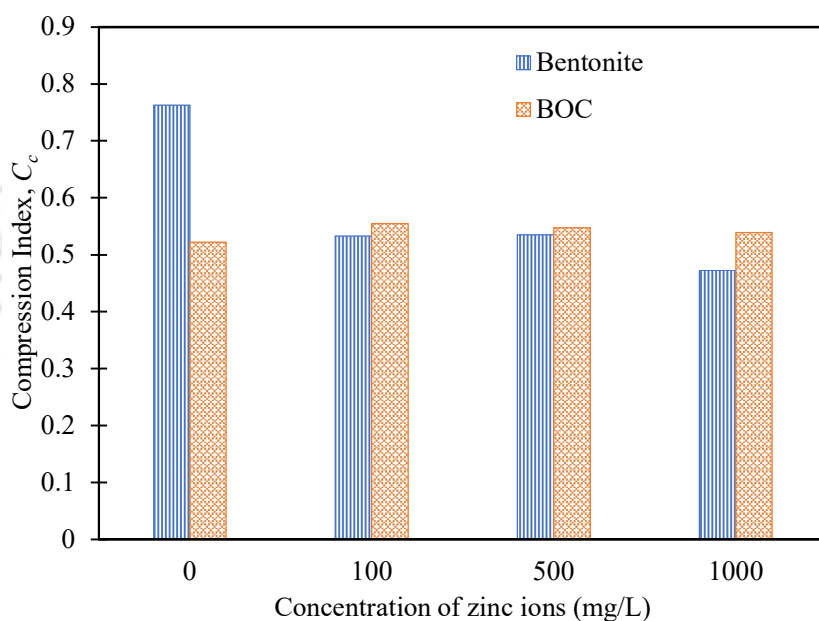


Fig. 6.14 Variation of C_c for bentonite and BOC at different Zn^{2+} concentrations

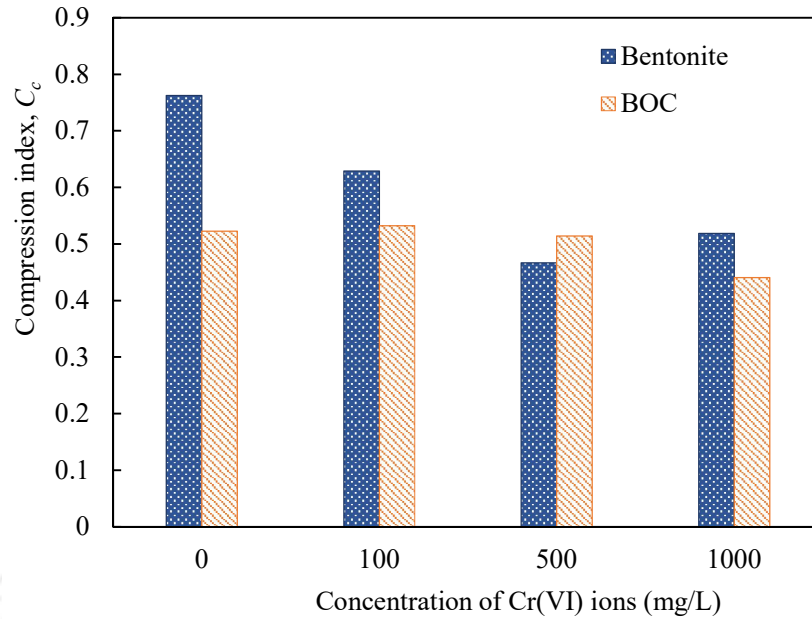


Fig. 6.15 Variation of C_c for bentonite and BOC at different Cr(VI) concentrations

6.2.7 Impact of heavy metals on the consolidation parameters of bentonite and BOC

The consolidation parameters, namely the time for 90% consolidation (t_{90}), coefficient of consolidation (c_v) and coefficient of volume compressibility (m_v), provide critical insights into the rate of settlement, the long-term containment effectiveness, and the structural integrity of barrier components. The t_{90} , c_v and m_v values were measured using Taylor's root of time method. All consolidation parameters were represented as a function of vertical consolidation stress ranging from 49 to 784 kPa. Even though the stress was incremented from 4.9 to 784 kPa, the consolidation parameters were unable to be determined at low consolidation stresses (below 49 kPa) due to the negligible settlement obtained throughout the time. This can be due to the fact that the entire applied consolidation stress was taken up by the pore water at lower consolidation pressures, whereas as the applied stress escalates, pore water dissipates, transferring the load to the soil grains and leading to settlement. The nature and concentration of pore fluid affect the consolidation properties of soil because the repulsive forces acting on the soil are influenced by the pore fluid characteristics (Mesri and Olson, 1971; Ray et al., 2019).

(a) Time for 90% consolidation (t_{90})

Figs. 6.16 to 6.18 illustrate the effect of the consolidation pressure on the time for 90% consolidation (t_{90}) for bentonite and BOC specimens inundated with different concentrations

of Pb^{2+} , Zn^{2+} and Cr(VI) , respectively. For all compacted specimens, the t_{90} value increased with a rise in consolidation pressure. Irrespective of the applied pressure, the sample with more swelling potential required more time for 90% consolidation. Consequently, the bentonite samples displayed a substantial t_{90} value in DI water and showed a considerable t_{90} reduction when permeated with heavy metal solutions. The higher cation exchange capacity and montmorillonite content of bentonite allow it to undergo hydration and adsorb a significant quantity of bound water (Jadda and Bag, 2020; Dutta and Mishra, 2016). Therefore, adequate time is required for bentonite to dissipate it. At higher concentrations of heavy metal ions, the ability to adsorb bound water decreases, and hence, the adsorbed water dissipates quickly. At a consolidation stress of 784 kPa, the permeation of 100 mg/L of Cr(VI) reduced the t_{90} of bentonite from 1156 min (for DI water) to 576 min. Similarly, at 1000 mg/L concentrations of Cr(VI) , t_{90} was further reduced to 506 min. This reduction in the t_{90} of bentonite under aggressive heavy metal solutions could be attributed to the decline in interparticle repulsive forces and diffuse double-layer thickness (Dutta and Mishra, 2016). As explained earlier, the presence of higher concentrations of K^+ ions likely accounts for the ion exchange reaction, reduced swelling and decreased t_{90} value of bentonite in potassium dichromate solutions. In contrast, cationic heavy metals significantly reduce the DDL thickness and are solely responsible for the reduction in t_{90} of bentonite in lead nitrate and zinc nitrate solutions.

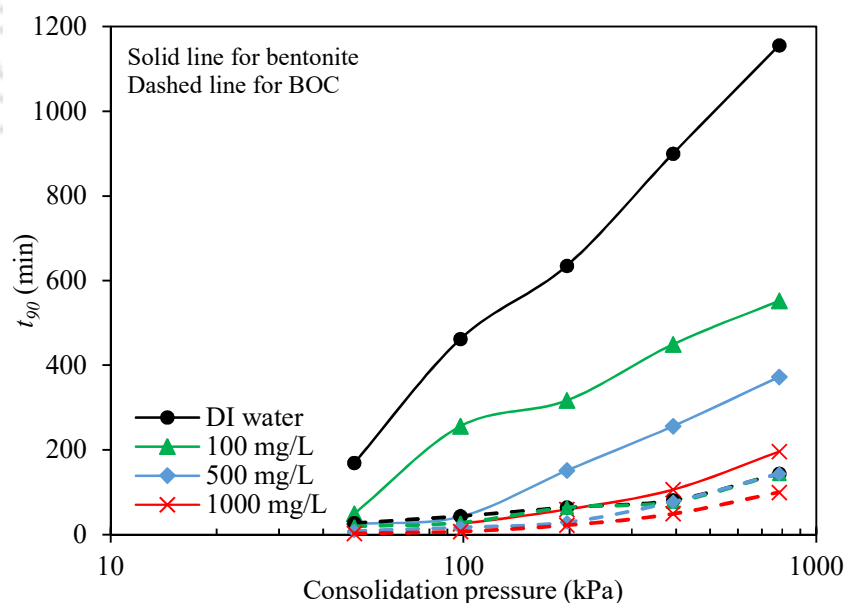


Fig. 6.16 Relationship between time for 90% consolidation (t_{90}) and consolidation pressure for bentonite and BOC permeated with different Pb^{2+} concentrations

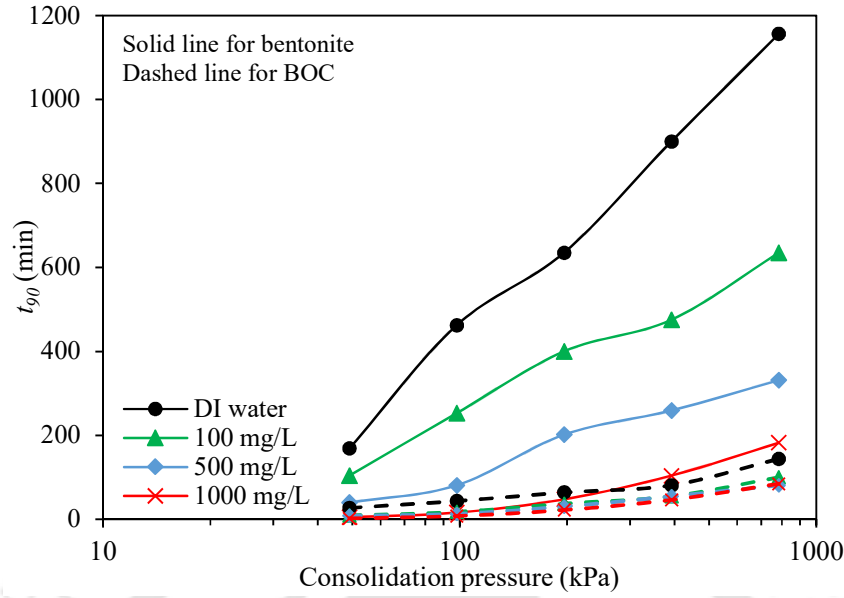


Fig. 6.17 Relationship between time for 90% consolidation (t_{90}) and consolidation pressure for bentonite and BOC permeated with different Zn^{2+} concentrations

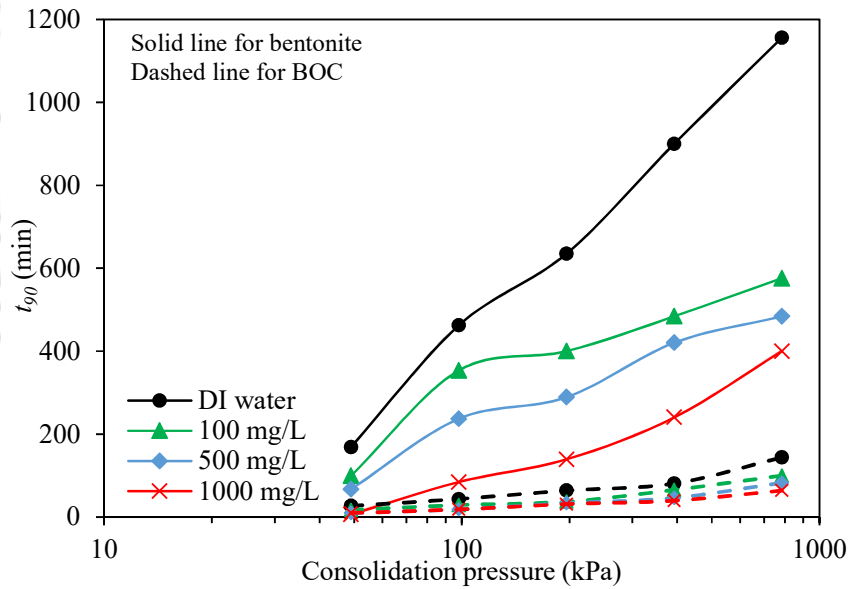


Fig. 6.18 Relationship between time for 90% consolidation (t_{90}) and consolidation pressure for bentonite and BOC permeated with different Cr(VI) concentrations

For the BOC specimens, the effect of heavy metal ion concentration was significantly lower, as indicated in Figs 6.16 to 6.18. The replacement of permeant solution from DI water to 1000 mg/L of Cr(VI) decreased the t_{90} value of BOC from 144 min to 64 minutes. The presence of organic ammonium cations in the organoclay fraction reduced the overall Na^+ cations and surface charge in the soil matrix, resulting in a lower intake of bound water around

the clay particles. This loosely held water dissipates quickly with externally applied loads, and rapid settlement occurs. Hence, the reduction rate in the void ratio is considerably lower for BOC when compared to bentonite, which in turn reduces the compressibility and t_{90} of the BOC samples (Jadda and Bag, 2020).

(b) Coefficient of consolidation (c_v)

The rate at which consolidation of soil progresses can be understood from the coefficient of consolidation (c_v), which is an essential parameter when designing a geotechnical structure on expansive soil (Sridharan and Rao, 1981; Mittal et al., 2021). This value depends on the nature of the soil, the pore fluid chemistry, and the loading conditions. The c_v values of compacted bentonite and BOC samples under the permeation of various Pb^{2+} , Zn^{2+} and Cr(VI) concentrations are shown in Fig. 6.19 to 6.21, respectively. As illustrated, c_v subsided with a rise in the consolidation pressure and increased with a rise in heavy metal concentrations. At lower applied pressure, more void spaces are available, and the soil specimens are consolidated at a rapid rate. However, as the pressure increases, the samples become compacted, the particles come closer, and the interparticle repulsive forces increase. As a result, there might be a substantial reduction in the consolidation rate at higher consolidation pressures; hence, a lower c_v value was attained.

The lowest c_v value was observed for the bentonite sample permeated with DI water. At higher consolidation stress levels, the consolidation rate decreased due to the complete dissipation of pore water. Consequently, the c_v decreased with increasing external consolidation stress. Regardless of heavy metal ion concentration, the c_v of all samples exhibited a consistent trend similar to that observed with DI water when subjected to changes in consolidation stress. However, the magnitude of these values varied depending on the presence of organoclay and the concentration of heavy metals. The higher metal ion concentrations accelerated the consolidation rate of bentonite and increased the c_v value. Therefore, the chemical properties of the permeant fluid, the physical attributes of soil constituents, and external stress factors could influence the consolidation parameters of bentonite and BOC. Owing to the compression in the DDL thickness due to the introduction of Pb^{2+} and Zn^{2+} ions, the repulsive forces between the particles decrease, and the samples become consolidated at a quicker rate. In the presence of a potassium dichromate solution, the K^+ ions may suppress the DDL thickness; hence, there will be an increase in the c_v value owing to the faster rate of settlement. Ray et al. (2019) and Dutta and Mishra (2016) showed similar changes

in c_v for bentonite under the influence of cationic heavy metals and inorganic cations, and the reason was attributed to the change in DDL thickness of bentonite.

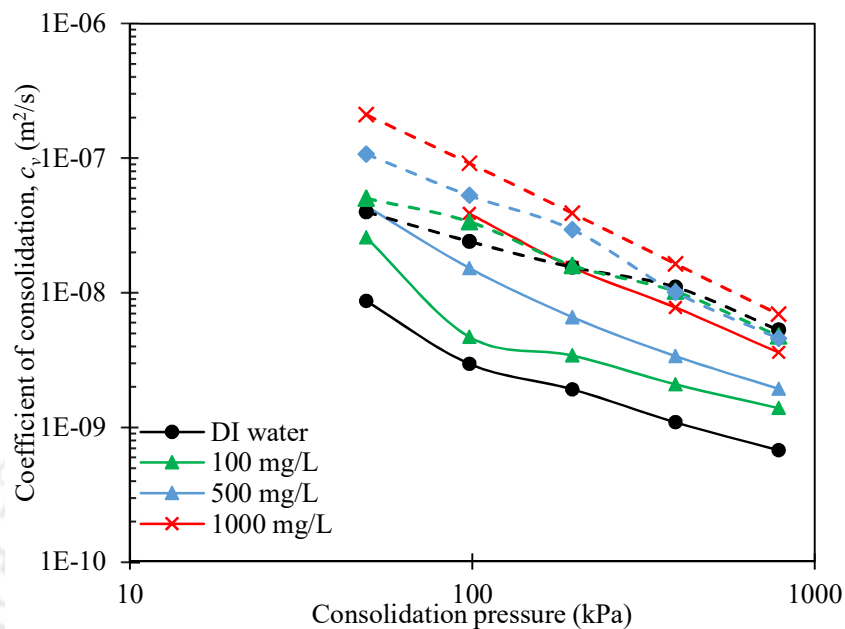


Fig. 6.19 Variations in c_v for bentonite and BOC with change in consolidation pressure and Pb^{2+} concentrations

The BOC samples also displayed similar variations in the c_v value with a change in the consolidation pressure and heavy metal ion concentrations. The incorporation of 10% organoclay to bentonite, at any fixed consolidation stress, resulted in an increase in c_v values as compared to bentonite. This may be attributed to the increased hydraulic conductivity due to the presence of the hydrophobic organoclay fraction and the formation of microcracks within the mixture. Also, the BOC displayed reduced swelling, leading to faster pore water dissipation compared to bentonite. The increase in c_v with higher hydraulic conductivity aligns with findings in previous literature (Ray et al., 2022). It is also important to note that, at lower vertical consolidation stresses, the impact of heavy metal concentration on BOC's c_v properties was more pronounced, similar to bentonite. However, unlike bentonite, at higher consolidation stresses (beyond 196.1 kPa), heavy metal ions had only negligible influence on the c_v of BOC.

The rise in heavy metal ion concentrations exhibited a relatively lower impact on the c_v value of BOC. As discussed earlier, the DDL compression of BOC due to cationic heavy metals was relatively lesser. Similarly, the impact of K^+ and $Cr(VI)$ ions on the reduction in DDL thickness is also minimal for BOC samples. Thus, BOC samples exhibited minimal variation in the c_v value with changes in heavy metal ion concentrations. For example, at 196 kPa, the c_v

of BOC increased from $1.54 \times 10^{-8} \text{ m}^2/\text{s}$ for DI water to $2.66 \times 10^{-8} \text{ m}^2/\text{s}$ for 1000 mg/L Cr(VI) (1.73 times), whereas for bentonite, c_v decreased from $1.91 \times 10^{-9} \text{ m}^2/\text{s}$ for DI water to $6.76 \times 10^{-9} \text{ m}^2/\text{s}$ for Cr(VI) (3.54 times).

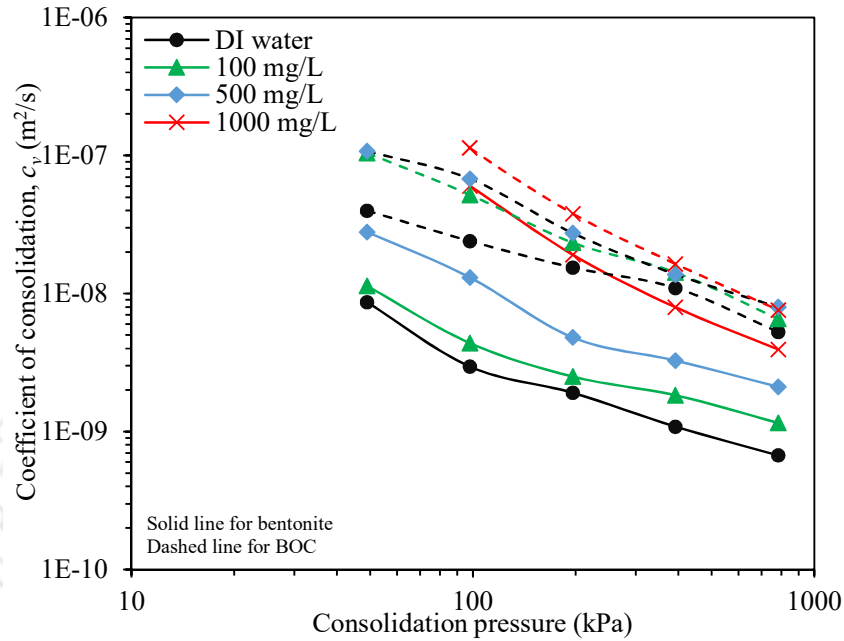


Fig. 6.20 Variations in c_v for bentonite and BOC with change in consolidation pressure and Zn^{2+} concentrations

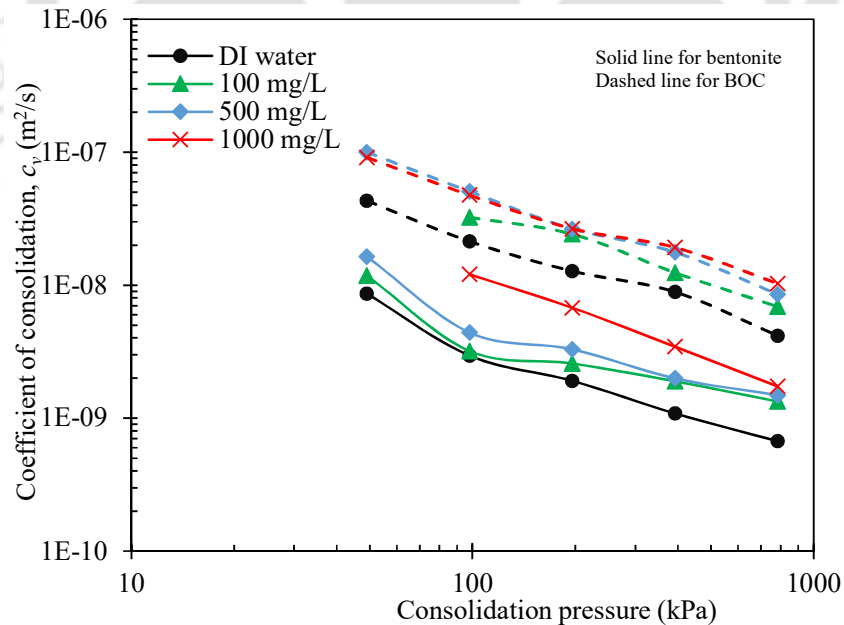


Fig. 6.21 Variations in c_v for bentonite and BOC with change in consolidation pressure and Cr(VI) concentrations

(c) Coefficient of volume compressibility (m_v)

The coefficient of volume change (m_v) is another crucial parameter for evaluating consolidation settlement. The m_v is defined as the ratio of volumetric strain to the corresponding increase in effective stress. For expansive clays such as bentonite, compressibility behaviour is highly influenced by pore water chemistry. The plot in Figs. 6.22 to 6.24 display the variations in m_v value with a change in consolidation pressure for bentonite and BOC samples inundated with different concentrations of heavy metal ions. Both bentonite and BOC in DI water exhibited an increase in m_v with an increase in applied consolidation stress, which subsequently reached a peak value and then declined. A similar trend was observed even in the presence of cationic heavy metals and inorganic salts (Dutta and Mishra, 2016; Duong and Hao, 2020). When pressure acts on the swollen soil, soil particles with a higher void ratio tend to consolidate at a faster rate, resulting in an increase in volume compressibility. A further rise in pressure resulted in a slower pace of soil compression, thereby enhancing bonding forces and yield stress, which leads to reduced m_v . The samples with a higher diffuse double layer were able to consolidate more because of their larger void ratios. Hence, the bentonite samples showed a higher m_v regardless of the pore fluid concentration. On the other hand, Jadda and Bag (2022) reported a decrease in m_v with increasing consolidation pressure for both calcium and sodium bentonite in its slurry condition. This discrepancy is primarily due to the large amount of bound water present in the slurry state, which subsequently gets expelled under applied stresses.

Owing to the addition of permeant solution, the DDL thickness of bentonite was considerably reduced; thus, the volume change rate also decreased (Ray et al., 2019). Irrespective of the permeant solution, BOC exhibited a lower m_v value than bentonite due to the formation of marginal DDL thickness and limited bound water. It is also noted from the figures that the rate of volume change was significant for bentonite samples permeated with heavy metal solutions. For example, at 196 kPa, the m_v of bentonite and BOC under the influence of DI water and 1000 mg/L Cr(VI) was found to be 0.091 and 0.056 kPa⁻¹, and 0.037 and 0.033 kPa⁻¹, respectively. Similar results were observed in samples permeated with Pb²⁺ and Zn²⁺ ions. The presence of permeant solution did not significantly vary the DDL thickness of the BOC samples due to the presence of the water-repellent organoclay fraction. Due to this restricted variation in DDL thickness, the rate of volume change doesn't change much for BOC under aggressive heavy metal concentrations. However, at the maximum consolidation stress (784 kPa), the m_v for all samples converged to a minimum value (0.03 ~ 0.02 kPa⁻¹) because

of the lower void ratio and compacted particle arrangement at this stress. It is crucial to note that the effect of monovalent K^+ ions on the DDL thickness of bentonite is considerably lower than that of divalent ions. As a result, the variation in m_v under the influence of 1000 mg/L of Cr(VI) was less prominent than that observed under the presence of 1000 mg/L of Pb^{2+} and Zn^{2+} .

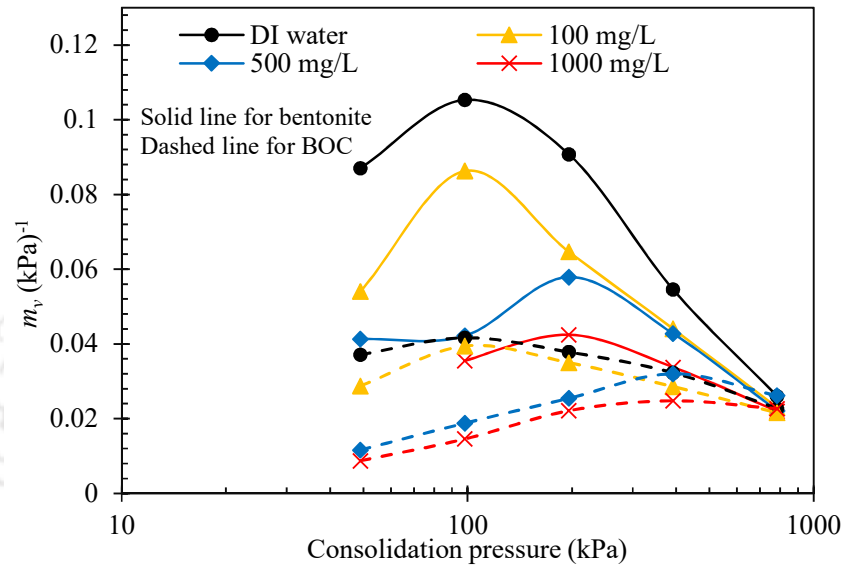


Fig. 6.22 Variations in m_v for bentonite and BOC with change in consolidation pressure and Pb^{2+} concentrations

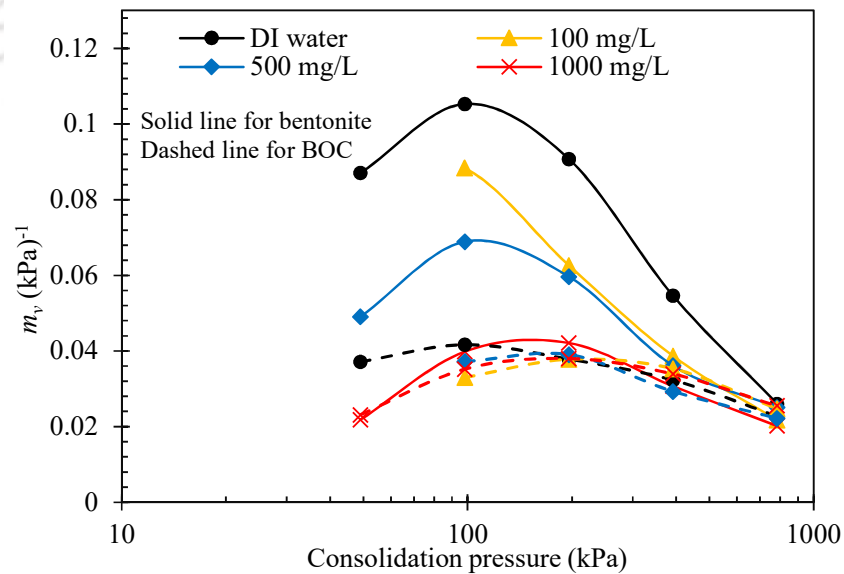


Fig. 6.23 Variations in m_v for bentonite and BOC with change in consolidation pressure and Zn^{2+} concentrations

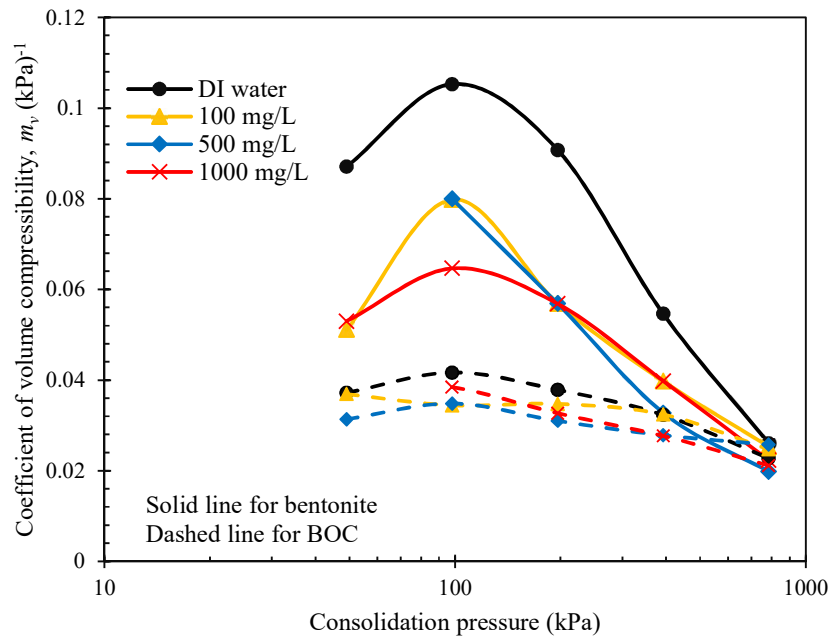


Fig. 6.24 Variations in m_v for bentonite and BOC with change in consolidation pressure and Cr(VI) concentrations

6.2.7 Effect of heavy metals addition on the microstructural behaviour of the compacted bentonite and BOC

(a) Scanning Electron Microscopic Analysis

In conjunction with the aforementioned analyses, a series of microstructural investigations were conducted, employing FESEM, EDS, and FTIR. These investigations were carried out to provide additional support for the underlying mechanisms described in the previous sections.

The FESEM images depicted in Fig. 6.25 revealed distinctive surface morphological features of bentonite and BOC permeated with different heavy metals. Bentonite and BOC displayed flaky, uniform layers and well-defined edges in DI water. The presence of montmorillonite minerals imparted a flaky dispersed structure for both bentonite and organoclay (Mitchell and Soga, 2005). The FESEM images of bentonite and BOC samples in DI water showed the presence of a more dispersed structure. Unlike bentonite, the presence of organic groups within the interlayers of organoclay reduced the repulsive forces in BOC and resulted in the formation of microcracks within the microstructure. The presence of the microcracks in BOC increased the hydraulic conductivity compared to the bentonite samples in DI water.

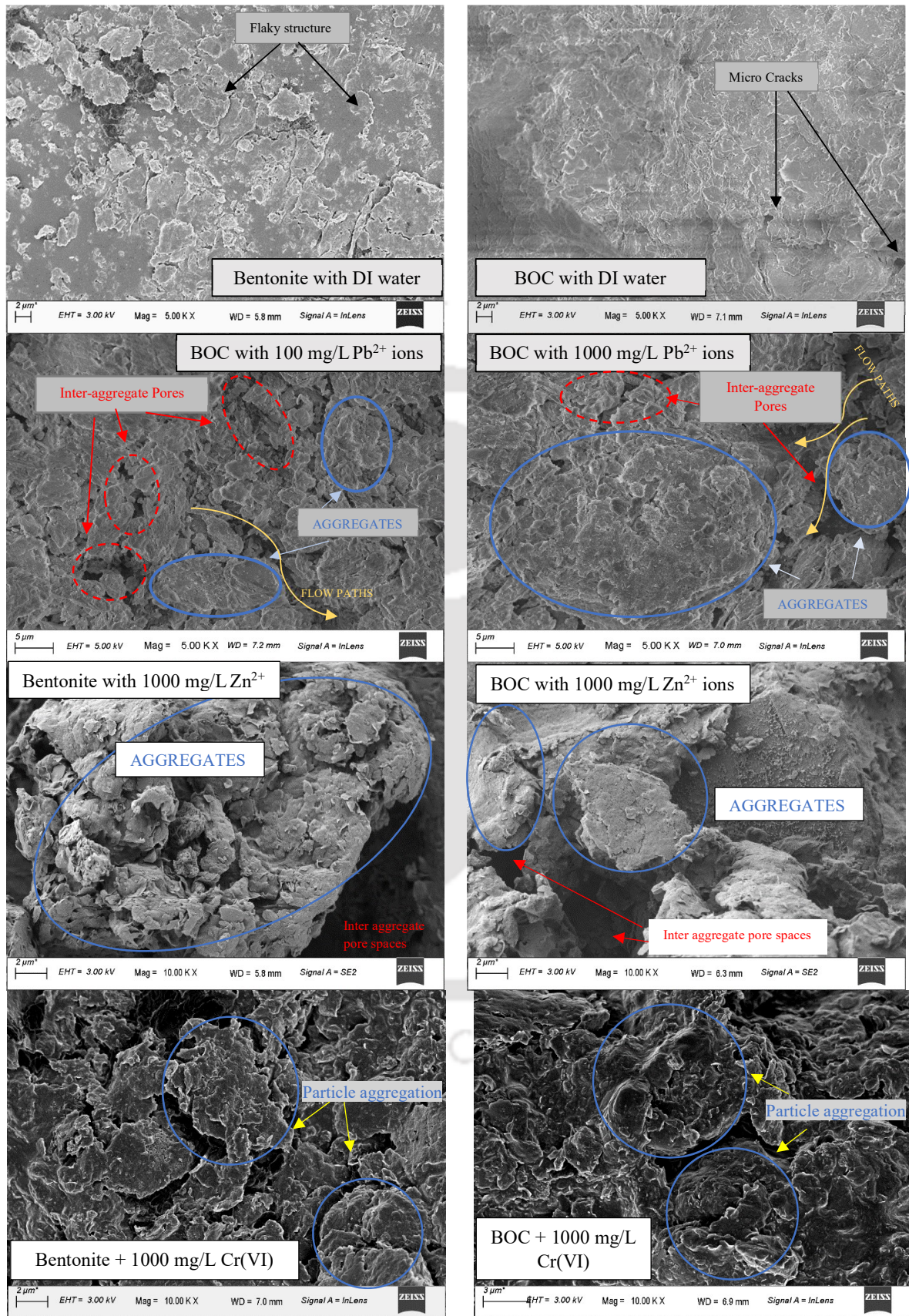


Fig. 6.25 FESEM images for bentonite and BOC permeated with different permeants

The introduction of heavy metal ions into the soil system had a notable impact on the soil fabric of both bentonite and BOC. In dry conditions, the exchangeable Na^+ ions balance the negative charges on the surface of bentonite. Upon the addition of Pb^{2+} or Zn^{2+} or K^+ ions, a cation exchange occurs by replacing Na^+ ions with Pb^{2+} or Zn^{2+} or K^+ ions, resulting in reduced surface negative charges and particle agglomeration, which leads to alterations in the soil fabric. At lower metal ion concentrations, small aggregated particles began to form, changing the particle orientation from a dispersed fabric to an edge-to-edge flocculated soil structure. However, the permeation of higher concentrations of heavy metal ions clearly induced the formation of larger aggregated particles, transforming the soil structure into a face-to-face aggregated configuration and thereby creating wider flow paths. As a result, the inter-particle pore volume increases, thereby increasing the hydraulic conductivity of the samples permeated with heavy metal ions. This observed variation in soil structure is consistent with the findings of Fan et al. (2013), who observed similar alterations in the soil structure of a kaolinite-bentonite mixture when subjected to Pb^{2+} permeation.

In the case of BOC samples, a similar variation in soil structure was evident. Notably, particle flocculation was observed at higher heavy metal ion concentrations, resulting in the formation of larger aggregated particles. However, it's important to note that the extent of flocculation due to the permeant fluids may vary depending on the proportion of liner constituents and may account for the alterations observed in the geotechnical properties of bentonite and BOC.

(b) Energy Dispersive X-ray Spectroscopy

Figure 6.26 depicts the elemental composition of bentonite and BOC permeated with different permeant fluids. The higher percentage of Na^+ in bentonite and BOC indicated that the bentonite used could be basically sodium bentonite. The EDS data shown in these figures indicates a quantitative increase in Pb^{2+} or Zn^{2+} in both bentonite and BOC permeated with lead nitrate and zinc nitrate solutions compared to that with DI water. Additionally, there was a reduction in Na^+ concentrations. These results confirm the probable ion exchange mechanism occurred between Na^+ from bentonite and BOC and Pb^{2+} or Zn^{2+} from permeant solutions. Also, the weight percentage of cationic heavy metal ions was lower in BOC than in bentonite. Therefore, the data affirms the limited ion exchange between organic cations in organoclay and Pb^{2+} ions from the solution. The results from adsorption studies also indicated better Pb^{2+} retention ability of bentonite compared to organoclay.

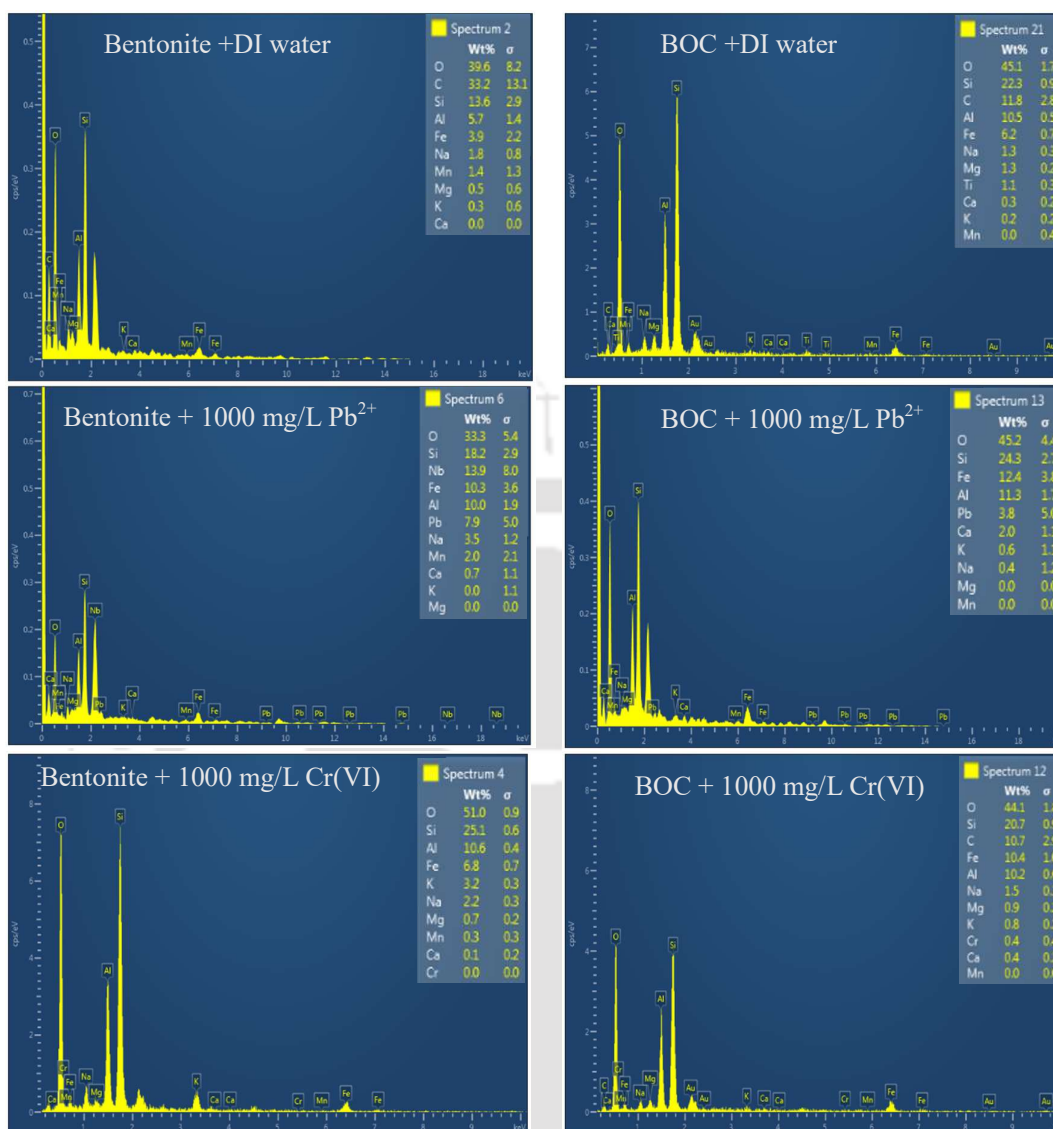


Fig. 6.26 EDS data for bentonite and BOC permeated with different permeants

Contrary to cationic heavy metals, in the case of potassium dichromate solutions, bentonite displayed a negligible amount of chromium, while BOC showed a slight quantitative increase in chromium fraction. Furthermore, for the same permeant fluid, there was a quantitative increase in K⁺ observed in both bentonite and BOC, with a higher fraction seen in the former one. The significant quantitative rise of potassium element in 1000 mg/L Cr(VI) affirms the probable cation exchange between K⁺ from the potassium dichromate solutions with Na⁺ in both bentonite and BOC samples. Thus, the data confirms the reduction in swelling and increase in hydraulic conductivity at higher concentrations of Cr(VI) solutions due to the ion exchange process and the subsequent drop in diffuse double-layer thickness. The weight

percentage of chromium in both bentonite and BOC samples at 1000 mg/L Cr(VI) exhibited only a slight variation. This assures the predominant effect of K^+ ions from potassium dichromate solution in altering the geotechnical properties such as hydraulic conductivity, swelling and compressibility of bentonite and BOC samples. The slightly higher amount of chromium in BOC could be due to the adsorption of anionic Cr(VI) onto the organoclay surface. Hence, the variation in geotechnical properties in BOC could be a combined effect of K^+ ions and Cr(VI) ions. Furthermore, the EDS data also confirms the lesser effectiveness of bentonite in adsorbing Cr(VI) ions (as discussed in Chapter 4) due to the high negative charge density at the particle surface.

(c) Fourier Transform Infrared Spectroscopy

The structural bonds present in the consolidated bentonite and BOC samples under various cationic heavy metal solutions are illustrated in Figs. 6.27 to 6.28. The presence of organic cations in organoclay was confirmed by the appearance of bonds at wavenumber 1469, 2851 and 2922 cm^{-1} . BOC samples permeated with DI water and 1000 mg/L $\text{Pb}^{2+}/\text{Zn}^{2+}$ also showed peaks at 2851 and 2922 cm^{-1} , but the magnitude was very low due to the smaller proportion of organoclay in BOC. The presence of these peaks at high cationic metal ion concentrations recommends that ion exchange between organic cations and $\text{Pb}^{2+}/\text{Zn}^{2+}$ ions was not prevalent in the BOC samples under investigation.

The permeation of lead or zinc ions did not yield significant alterations in the FTIR spectra of bentonite and BOC. However, a slight difference in OH vibrational peak intensities (at 1634 and 3621 cm^{-1}) was observed, and it can be ascribed to the varying binding affinities of metal cations toward the interlayer water. Water molecules tend to coordinate with interlayer cations, and any remaining water is held within the interlayer holes. Consequently, water molecules that are coordinated to the cations may migrate to the bi-trigonal cornered holes on the siloxane surface. This migration affects the OH groups and subsequently alters the intensities of the associated vibrational peaks (Tabak et al., 2011).

Figure 6.29 displays the FTIR spectra of compacted bentonite and BOC samples permeated with different concentrations of Cr(VI) ions. The main deviation was observed in the position and intensity of the various bands due to the possible interaction between the clay surface and the permeant solution. The alteration in the swelling and water adsorption capacity of the samples can be identified with the help of symmetric ($\sim 3600 \text{ cm}^{-1}$), asymmetric stretching ($\sim 3460 \text{ cm}^{-1}$), and bending ($\sim 1630 \text{ cm}^{-1}$) bands of water. Since the type of exchangeable cation

and the strength of hydrogen bonds affect the intensity and positions of these bands, the process of cation exchange in the bentonite and BOC samples must be reflected in the FTIR spectra (Madejova et al., 2002). Higher concentrations (1000 mg/L) of Cr(VI) ions shifted the asymmetric stretching band position from 3621cm^{-1} to 3623cm^{-1} and also drastically declined the intensity of the peak. However, the presence of the symmetric stretching vibration at 3405cm^{-1} disappeared for bentonite and BOC samples permeated with 1000 mg/L Cr(VI) solution. High concentrations of K^+ and heavy metal ions expelled bound water from the interlayer space of bentonite and formed isolated clusters by cation exchange with water molecules. The water of these clusters was unable to form hydrogen bonds and cause interlayer collapse, thus considerably reducing swelling (Madejova et al., 2002). Similarly, the bending vibration of bentonite shifted to a higher wavenumber from 1634 cm^{-1} to 1636 cm^{-1} . These variations in the -OH stretching and bending bands represent the strength reduction of hydrogen bonds and a lower quantity of adsorbed water at higher levels of heavy metal solutions. Hence, the considerable reduction in swelling and increased hydraulic conductivity of the bentonite and BOC samples permeated with Cr(VI) ions can be reaffirmed with the help of these spectra.

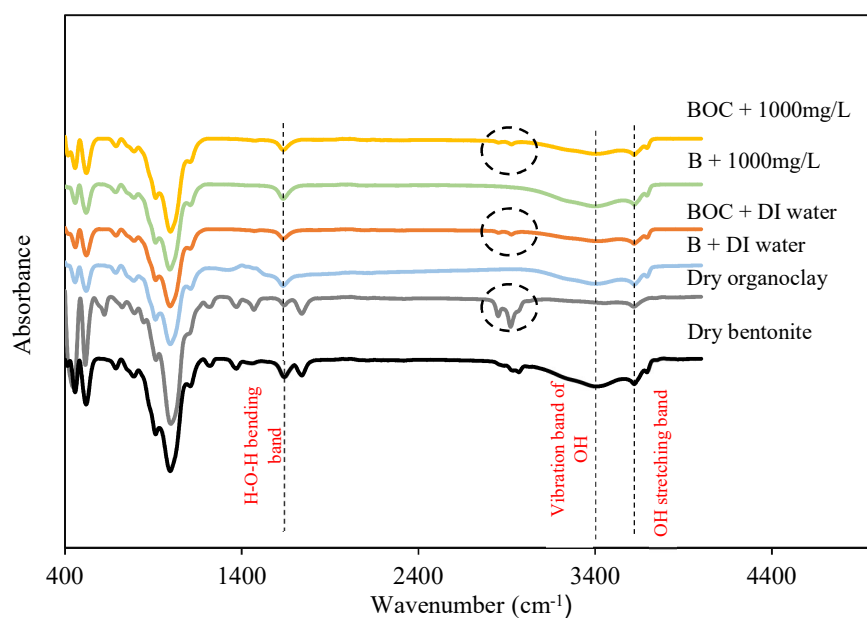


Fig. 6.27 FTIR spectra for bentonite (B) and BOC permeated with DI water and 1000 mg/L Pb^{2+} concentrations

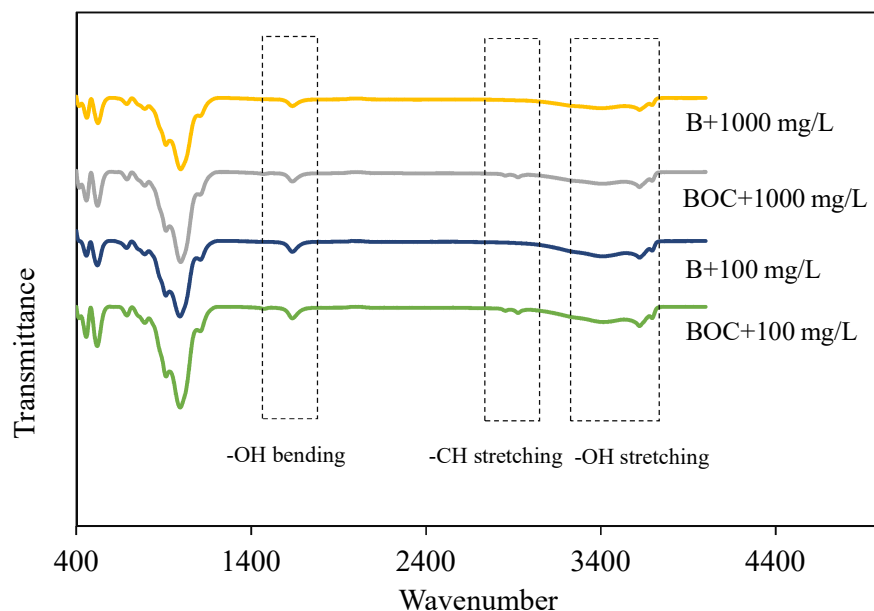


Fig. 6.28 FTIR spectra for bentonite (B) and BOC permeated with 100 and 1000 mg/L Zn^{2+} concentrations

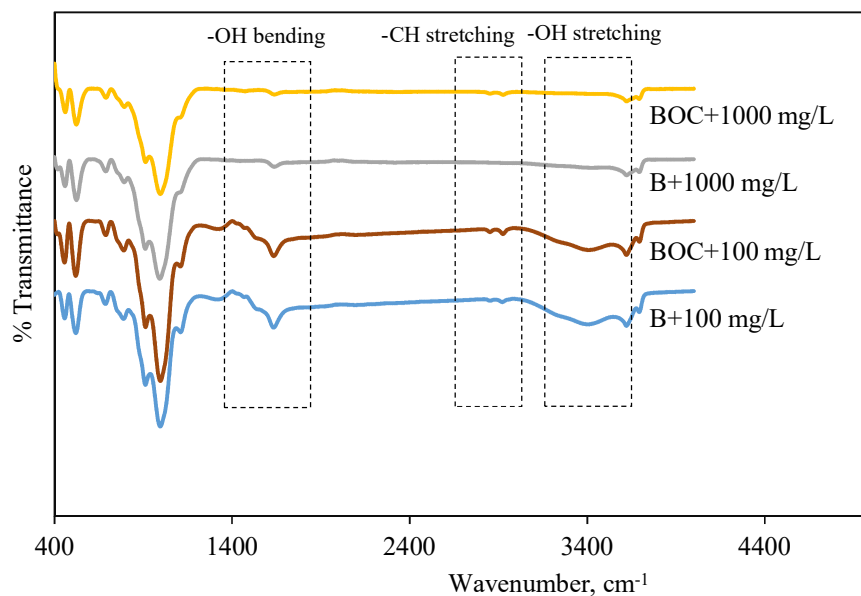


Fig. 6.29 FTIR spectra for bentonite (B) and BOC permeated with DI water and 1000 mg/L Cr(VI) concentrations

Furthermore, the alteration in the Si environment of bentonite and BOC under the effect of potassium dichromate solutions can be understood from the variation in the intensity and position of Si-O-Si stretching ($\sim 995\text{cm}^{-1}$), -OH stretching of Al-Al-OH or Al-OH-Al ($\sim 912\text{cm}^{-1}$), bending of Al-O-Si ($\sim 519\text{cm}^{-1}$), and Si-O-Si ($\sim 456\text{cm}^{-1}$). There was a slight shift in the

position and reduction in these intensities, but the variations were not significant, which might be due to less or no sorption of Cr(VI) ions onto the bentonite. Furthermore, the larger radius of K^+ ions restricts its ability to sink into the hexagonal holes of tetrahedral sheets in the bentonite sample and reduces the effect on structural modification (Madejova et al., 2002; Eren and Afsin, 2008).

6.3 Summary

This study investigates the impact of different concentrations (0 to 1000 mg/L) of cationic (Pb^{2+} and Zn^{2+}) and anionic (Cr(VI)) heavy metals on the physical, chemical and mechanical behaviour of bentonite and BOC. The chemical compatibility of both liner materials under different pore fluids was assessed using liquid limit, pH analysis, free swell index, swell potential, swell pressure, compression index, consolidation parameters and hydraulic conductivity. Additionally, the microstructural properties of consolidated samples after permeation with different heavy metal ions were investigated using FESEM, EDS and FTIR to investigate the plausible mechanisms. The following conclusions were summarised based on the outcomes of the study:

- The rise in both cationic and anionic heavy metal concentrations reduced the liquid limit, free swell index, swell pressure and swell potential of both bentonite and BOC. This reduction was notably more significant in bentonite due to the considerable compression in the diffused double-layer thickness. In BOC, the presence of 10% hydrophobic organoclay fraction was not much affected by the heavy metal ions and thus displayed relatively lesser variation in liquid limit and swelling properties.
- Among the cationic heavy metals, Pb^{2+} ions resulted in higher liquid limit and swelling values for bentonite compared to Zn^{2+} ions. This is attributed to the insufficient interaction between lead ions and the bentonite surface due to precipitation at higher pH levels. In contrast, BOC exhibited similar variations for both metal ions, with zinc ions exhibiting slightly higher liquid limit and swelling values due to significantly lower zinc adsorption by the organoclay fraction, resulting in a comparatively lower reduction in DDL thickness.
- Increasing metal ion concentrations resulted in a significant increase in the hydraulic conductivity and reduced pH and compressibility for bentonite. BOC also followed a similar trend but with minimal impact of permeant fluid characteristics on these properties. For instance, at a void ratio of 1.0, the hydraulic conductivity of bentonite

increased 11.3 times when the permeant fluid changed from DI water to 1000 mg/L Pb^{2+} ions, compared to the 3.9 times increase noted for BOC.

- Unlike bentonite, the variations in heavy metal ion concentrations had less impact on the consolidation parameters (t_{90} , c_v and m_v) and the compression behaviour of BOC. Additionally, the impact of potassium dichromate solution on the consolidation parameters of bentonite was comparatively less significant than that of lead nitrate and zinc nitrate solutions. This difference is attributed to the greater influence of divalent cations, such as Pb^{2+} and Zn^{2+} , compared to monovalent K^+ ions on the DDL thickness of bentonite.
- When the permeant fluid was replaced from DI water to 1000 mg/L Cr(VI) concentration, the compression index of bentonite and BOC decreased by 31.6% and 15.4%, respectively. Similarly, 1000 mg/L Pb^{2+} ion concentration resulted in a percentage reduction of 31.6% and 15.4%, respectively.
- Potassium dichromate solutions exhibited a similar trend in geotechnical properties for both bentonite and BOC as cationic heavy metal solutions. However, the mechanisms differ: in cationic heavy metal solutions, the primary mechanism is the interaction between exchangeable Na^+ cations in bentonite and Pb^{2+} or Zn^{2+} ions from the permeant solution, leading to DDL thickness collapse. In potassium dichromate solutions, the interaction between Cr(VI) and bentonite is limited, with the major mechanism likely being ion exchange between K^+ from the solution and exchangeable Na^+ ions, compressing DDL thickness and altering the macrostructural and microstructural properties.
- The relatively lower variation in geotechnical properties of BOC indicates that incorporating 10% organoclay into bentonite significantly enhanced mechanical strength and reduced chemical sensitivity, particularly at high metal ion concentrations. The absence of ion exchange reactions between covalently bonded interlayer organic cations and permeant Pb^{2+} or Zn^{2+} or K^+ ions, along with suppression of DDL expansion in the remaining 90% bentonite, contributed to the comparatively nominal variations in the geochemical properties of BOC.
- FESEM and EDS analyses reconfirmed the limited ion exchange reaction in the organoclay fraction and underscored the low chemical reactivity of BOC. The results from FTIR data indicated limited alterations in the structural bonds of bentonite and BOC under the influence of heavy metals.

The impact of organic solutions on the hydraulic barrier performance of organoclay-amended bentonite

7.1 General

During the service period of a waste containment facility, there may be a chance of the liner being in contact with various organic contaminants. The performance of the commonly adopted bentonite barriers is superior when in contact with water or other low-strength aqueous solutions. However, similar to inorganic salts and heavy metals, the long-term barrier efficiency of bentonite may deteriorate when exposed to organic solutions, especially in its concentrated form (Acar and Oliveri, 1989; Goodarzi et al., 2016). Upon contact with organic solvents, natural clays or bentonite may tend to flocculate and shrink instead of swelling. Therefore, bentonite, which was considered a promising material for waste disposal engineering systems due to its low permeability, might be less effective in engineered disposal systems containing high concentrations of multiple contaminants. Previous research showed that the above-mentioned drawback of bentonite barriers in organic fluids can be minimised by using organic surfactant-modified clays or organoclays. The organic cations (i.e. QAC) present in the interlayer of organoclays facilitate the sorption of organic contaminants and improve the organophilicity of clays (Gates, 2004; de Paiva, 2006; Zhao et al., 2017). The organophilic clays display a hydrophobic environment or a hydrophobic partitioning phase generated by the intercalation of long alkyl chain surfactants, enlarging their interlayer space and resulting in the enhancement of adsorption/removal of organic compounds. Additionally, the organoclay displays better sealing ability when permeated with organic solutions due to the increased swelling. However, this geotechnical performance depends upon several factors such as type and concentration of permeant and characteristics of organoclay.

The majority of the prior research focused on the geochemical characteristics of organoclays and their application as hydraulic barriers (Lo and Young, 2001; Lee et al., 2012; Akbulut et al., 2013; Benson et al., 2015). The research outcomes indicated that organoclay enhanced physical and physicochemical properties, including hydraulic conductivity, sorptive capacity, swelling index, suspension stability, strength, and stiffness, when compared to unmodified clays (Lo et al., 1997; Bate et al., 2004; de Paiva and Morales, 2012; Zhao et al., 2017). The superior sorption ability of organoclay in various organic contaminants, including hydrophobic non-polar organics, was extensively examined. When in contact with organic

liquids, organoclays exhibit low hydraulic conductivity, high swelling tendency and high plasticity. However, from a practical point of view and economic considerations, researchers have suggested the use of organoclays as an amendment to conventional barriers to improve the efficiency of the barrier when permeated with organic contaminants or petroleum products. A few studies explored the potential use of organoclays as an amendment for compacted clay liners (CCLs) in waste containment and pollutant attenuation. Lo (2001) and Lo et al. (2003) investigated the potential of organoclays to be used as an amendment to the local soil-bentonite barrier. The sorption tests, compaction tests and hydraulic conductivity test results performed with real leachate indicated that organoclay addition improved the organic removal efficiency by maintaining the hydraulic conductivity in the permissible range. The study's findings indicated that the optimal combination of soil materials to be utilised as a compacted liner to resist the flow of leachate and chemical flux was 20% bentonite, 20% organoclay, and 60% local soil. As a result, the barrier thickness can be significantly reduced.

Lee et al. (2012) studied the performance of PRBs consisting of organoclay and organoclay-sand mixture for restricting the hydraulic conductivity of multiple polynuclear aromatic hydrocarbons (PAHs). The organoclays were found to have very high hydraulic conductivity in water and low conductivity in non-aqueous phase liquid (NAPL), which consists of PAHs. The study recommended a minimum of 25% organoclay for attaining sufficiently low hydraulic conductivities (10^{-10} m/s) for organoclay-sand mixtures. The outcomes suggested the effective utilisation of organoclays for variably permeable reactive barriers since they block NAPL advection, permitting water flow with dissolved PAHs and better adsorption of dissolved PAHs from flowing water. The barrier performance of organoclay and organoclay-sand mixture permeated with four pure organic fluids and five different types of fuels was investigated by Benson et al. (2015). The results showed that the hydrophobicity of the organic solution and highly refined fuels was directly related to the swelling and sorption capacity of organoclay while inversely related to its hydraulic conductivity. The authors suggested the use of at least 50% organoclay in a sand-organoclay mixture to impede the permeability of gasoline and jet fuel, while at least 75% organoclay for diesel and fuel oil. Javadi et al. (2017) studied the swelling, permeability and contaminant retention of compacted silty clay amended organoclay against gasoline and naphthalene. The study concluded that the addition of 10% organoclay slightly increased the hydraulic conductivity to water but improved the swelling and hydraulic behaviour in gasoline. The results also suggested that a minimal proportion of organoclay should be utilised for optimal hydraulic performance and improved confinement of organic

fluids. It is important to note that an increased amount of organoclay can result in surpassing the hydraulic conductivity criteria for hydraulic barriers. Most geotechnical studies focused on sand-organoclay mixtures or local soil-organoclay mixtures to restrict the percolation of low-polarity organic fluids or fuels. As far as the author's knowledge, no studies have been carried out to examine the effect of organoclay amendment on Indian bentonite when exposed to phenol and acetone, which are commonly found in various industrial effluents and leachates (Acar and Olivieri, 1987; Estabragh et al., 2021).

The objective of this chapter is to understand the impact of two organic solutions (acetone and phenol) on the swelling behaviour, compressibility, consolidation parameters and hydraulic performance of bentonite and organoclay-amended bentonite. The diluted solutions of acetone and phenol (0, 5, 10 and 20%) were used in the current research because the landfill leachates and industrial leachates may not contain pure organic contaminants (Liu et al., 2008; Ahmadinejad et al., 2020). The chemical properties of both permeant solutions are given in Table 7.1. The presence of acetone and phenol in the natural environment has been of great concern owing to its toxicity and reactivity. Moreover, most of the previous research focused on organic fluids in their pure form. Limited studies were performed on the influence of diluted organic fluids on organoclay-based barriers. Therefore, this study targeted the hydraulic barrier performance of bentonite and BOC when subjected to dilute organic contaminants. By considering the volatile nature of the organic fluids, proper care was taken during the experimental analysis to avoid evaporation.

Table 7.1 Properties of permeant liquids (Acar and Olivieri, 1987; Erdogan et al., 2023; Goudarzi and Goodarzi, 2010)

Solvent Properties	Water	Acetone	Phenol
Chemical Formula	H ₂ O	C ₃ H ₆ O	C ₆ H ₆ OH
Solubility at 25 °C (g/L)	N/A	infinity	86.34
Viscosity at 20 °C (centipoise)	0.890	0.33	12.7
Dipole moment (debyes)	1.87	2.9	1.45
Density at 20 °C (g/cc)	0.98	0.79	1.07
Surface tension (mN/m)	72.8	23.3	38.20
Octanol-water partition coefficient	N/A	-0.24	1.46
Class	N/A	T	H, T, S, P

Note: T = Toxic, H = Hazardous, S = Section 311 compound, P = Priority pollutant, N/A = not applicable

7.2 Impact of organic solutions (acetone and phenol) on the hydraulic barrier performance of compacted bentonite and BOC

7.2.1 Influence of organic solutions on the swelling properties of bentonite and BOC

The swelling characteristics of liner materials are directly linked to their low permeability, making them a crucial parameter in designing landfill liners. Tables 7.2, 7.3 and 7.4 present the free swell index, swell potential and swell pressure of both bentonite and BOC mixed with varying concentrations of acetone and phenol, respectively. For bentonite, the variation in these swelling properties under organic solutions was similar to that observed with inorganic salts and heavy metals, as explained in previous chapters. The change in organic concentration and fluid characteristics significantly altered the swell properties of bentonite and BOC.

Replacing DI water with 20% phenol and 20% acetone decreased the free swell index of bentonite from 36 mL/2g to 18 and 24 mL/2g, respectively. Similarly, for a similar change in pore fluids, a percentage decline in swell pressure of 37.8% for 20% phenol and 13.3% for 20% acetone was noted. The magnitude of swell potential was also reduced in a similar way, from 37.2% in DI water to 12.9% for 20% phenol and 19.5% for 20% acetone. This indicates a persistent decline in the swelling behaviour of bentonite as organic fluid concentrations increase, with phenol exhibiting a more noticeable influence than acetone.

The rising concentration of organic fluids is believed to cause a decrease in the dielectric constant of the pore fluid, which could potentially account for bentonite's decline in swell tendency. The literature also postulated that the clay-pore fluid interactions highly depend on the dielectric constant (ϵ) of pore fluid. The ϵ of the organic fluids considered in this study is significantly less than that of water. At 20 °C, the ϵ of water, pure acetone and pure phenol are 80.2, 20.7 and 13.1, respectively (Acar and Olivieri, 1989; Goodarzi et al., 2016). Consequently, the ϵ of diluted acetone and phenol solution decreases as the organic liquid/water ratio increases, leading to a decline in the swell behaviour of bentonite. Similar to swelling properties, a reduction in plasticity was also observed for montmorillonite soils with rising organic concentrations (Kaya and Fang, 2000; Olgun and Yildiz, 2010; Goodarzi et al., 2016). These trends were attributed to the variations in interparticle forces and DDL behaviour. The reduction in dielectric constant and increase in concentrations led to a decrease in double-layer repulsive forces, causing DDL shrinkage, flocculation, and closer packing of clay particles. As a result of these changes, the hydration of clay particles decreased significantly, reducing their swelling ability.

Table 7.2 Free Swell Index of bentonite and BOC under various concentrations of acetone and phenol

Concentrations of organic liquids (%)	Bentonite		BOC	
	Acetone	Phenol	Acetone	Phenol
0 (DI water)	36	36	18	18
5	30	24	16	20
10	28	21	22	21
20	24	18	24	23

Table 7.3 Swell Potential of bentonite and BOC under various concentrations of acetone and phenol

Concentrations of organic liquids (%)	Bentonite		BOC	
	Acetone	Phenol	Acetone	Phenol
0 (DI water)	36.78	36.78	17.36	17.36
5	28.13	23.92	14.38	9.61
10	24.57	20.13	15.53	20.42
20	19.49	12.87	20.87	22.92

Table 7.4 Swell Pressure of bentonite and BOC under various concentrations of acetone and phenol

Concentrations of organic liquids (%)	Bentonite		BOC	
	Acetone	Phenol	Acetone	Phenol
0 (DI water)	450	450	350	350
5	460	410	395	395
10	405	380	450	440
20	390	280	440	425

Goodarzi et al. (2016) suggested that bentonite's swelling properties are more influenced when the dielectric constant of pore fluid is greater than 50. This implies that dilute organic solutions may result in a significant reduction in swelling tendency compared to pure solutions. This statement is also supported by the results of Spagnoli et al. (2012), which concluded that electrical repulsive forces among clay particles remain almost unchanged below a dielectric constant of 50 but decrease substantially when the dielectric constant is between 80 and 50.

Thus, more diluted organic solutions have a greater effect on DDL contraction, resulting in less water uptake when the dielectric constant is more than 50. The results from this study also yielded similar findings.

Additionally, it was also noted that the expansion ability of bentonite was influenced by the type of organic fluids. Phenol had a more pronounced influence on the swelling behaviour of bentonite than acetone. This can be partially attributed to the order of the dielectric constant (ϵ) of organic solutions ($\epsilon_{\text{phenol}} < \epsilon_{\text{acetone}}$) and the subsequent impact on the bentonite fabric due to the interaction between bentonite and phenol. The bentonite mixtures inundated with phenol, which has the lowest ϵ values, exhibited the highest reduction in swelling properties. According to Goodarzi et al. (2016), the ϵ of water and 20% acetone solution are 80.4 and 68.46, respectively. From Gouy Chapman's theory, if all other parameters remain constant, then the DDL thickness of bentonite mixed with 20% acetone solution in comparison to DI water could be approximately $(68.46/80.4)^{0.5} = 0.92$. However, their geotechnical properties don't vary proportionally to this calculation. This implies that the decrease in DDL thickness due to decreasing dielectric constant alone doesn't fully explain the observed differences in engineering properties. In addition to the dielectric constant, other organic fluid characteristics, such as pH, surface potential, polarity and viscosity, may also contribute to the clay particle rearrangement affecting geochemical properties (Goodarzi et al., 2016). The pH values for the acetone solutions of 5%, 10%, and 20% concentrations were measured to be 5.83, 5.62, and 5.32, respectively. Similarly, the phenol concentrations of 5%, 10%, and 20% were found to have pH values of 4.28, 4.00, and 3.92, respectively.

As a result of the oxidation reaction, acetone might be able to produce two molecules of acid, according to the following equation:



The decrease in the pH may be a consequence of this acid production, which can further contribute to the reduction in DDL thickness and changes in swelling properties (Estabragh et al., 2018). Similarly, the acidic nature of phenol (Al Bsoul et al., 2021) may be responsible for the variations in the geochemical behaviour of bentonite. Additionally, the bond in phenol is less polar due to the electron-withdrawing effect of the benzene ring. Low polarity fluids lack the ability to form strong non-bonded interactions with the interlayer water or the clay particles, which leads to a decrease in the potential of the clay interlayer to expand.

In the case of BOC, a similar declining trend in swelling was observed at low organic concentrations (5%), followed by an increase in swelling properties at higher organic concentrations (>5%) compared to bentonite. Therefore, an increase in the organic fluid/water ratio may enhance the swelling properties of BOC. The 10% organoclay fraction in BOC might not have significant interactions with the organic solution initially, leading to limited organic molecules interacting with the organoclay fraction. Furthermore, the effect of the dielectric constant and contraction of DDL of the remaining 90% bentonite will be pronounced at 5% organic solutions, thereby reducing its swelling properties. As the concentration of organic fluid increases, the organoclay fraction begins to interact with the organic molecules along with the bentonite particles. The 10% organoclay content in BOC might be sufficient to improve swelling behaviour in organic fluids, as organoclay tends to swell better in organic solutions. Consequently, at 20% concentrations of acetone and phenol, BOC exhibited higher free swell, swell pressure, and swell potential compared to DI water and exhibited enhanced swelling characteristics than bentonite.

Compared to acetone, phenol had a greater influence on the swell characteristics of BOC, which is attributed to its fluid characteristics. The lower polarity and solubility of phenol might result in greater interaction with organoclay fraction. The phenol can penetrate the organoclay interlayer through a partition mechanism, forming bonds with the quaternary alkyl ammonium cations. This interaction leads to an expansion of the interlayer space, as confirmed by the increased swelling observed at higher phenol concentrations. A prior study by Nafees and Waseem (2014) also demonstrates that phenol adsorbs and penetrates the interlayer space of surfactant-modified montmorillonite, resulting in interlayer expansion. The longer alkyl chains of surfactant molecules in the organoclay interlayer provide a higher affinity for organic compounds, particularly for less polar phenol, and phenol sorption primarily occurs primarily through a partitioning mechanism.

(b) Time – swelling variations

The temporal variation of swelling for bentonite and BOC inundated with different concentrations of acetone and phenol are depicted in Figs. 7.1 and 7.2. In all cases, the swell curve followed an S-shaped curve, indicating an initial slow increase in swelling with time, followed by a rapid rise, and finally reaching an asymptomatic value. The initial slow rate portion is considered initial swelling, followed by primary swelling, and the final asymptotic region is termed secondary swelling. The majority of swelling occurred in the primary swell

region, with less than 12% constituting the initial swell region. Upon adding water to the soil, the hydration of dry clay occurs when water is drawn into the interlayers of clay sheets. When the permeant solution was very diluted organic fluid, double-layer swelling occurred considerably, and a large amount of water was drawn in the double-layer region. As the concentration of organic solution further increases, more water molecules are replaced by organic molecules from bentonite particles, leading to decreased swelling. The extent of the swelling depends on the type and concentration of the permeant fluid.

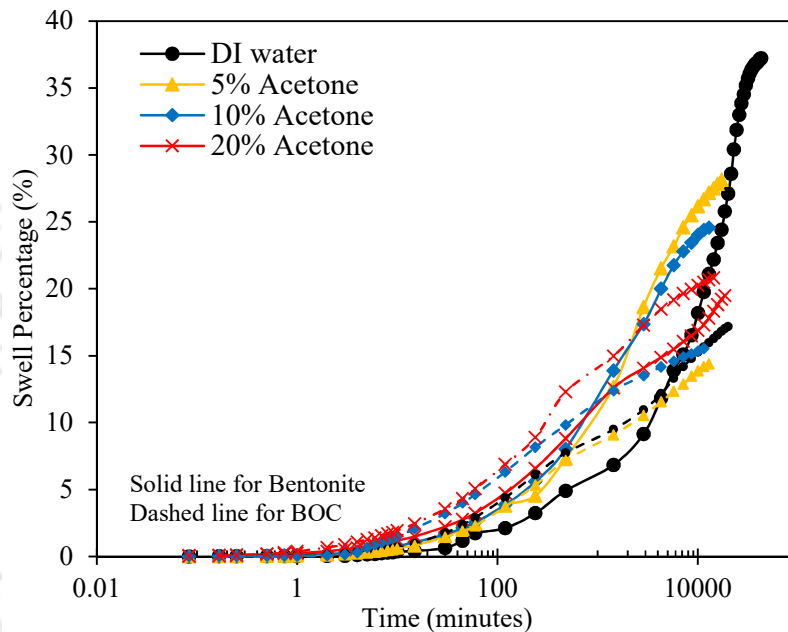


Fig. 7.1 Time-swelling plot for bentonite and BOC inundated with acetone

When the inundating fluid was water, BOC exhibited lower swelling percentages in all swell stages, especially in the primary swell region, compared to bentonite due to its hydrophobic behaviour. As the organic concentration increases, the swelling fraction in each stage slightly reduces due to the higher proportion of water and the significant impact of hydrophobicity in the mixture. Organoclays, being both hydrophobic and organophilic, exhibit more affinity towards organic molecules. Therefore, as the concentration of organic fluid increases, the organoclay fraction tends to swell more, resulting in increased swelling in all stages. The primary swelling region showed the most significant amount of swelling, indicating higher microstructure swelling (Rao et al., 2006). It should also be noted that BOC showed more swelling at 20% organic fluid than bentonite. This indicates that BOC could show better barrier performance in high organic contaminants than bentonite since the higher swelling tendency can be directly linked to lower hydraulic conductivity.

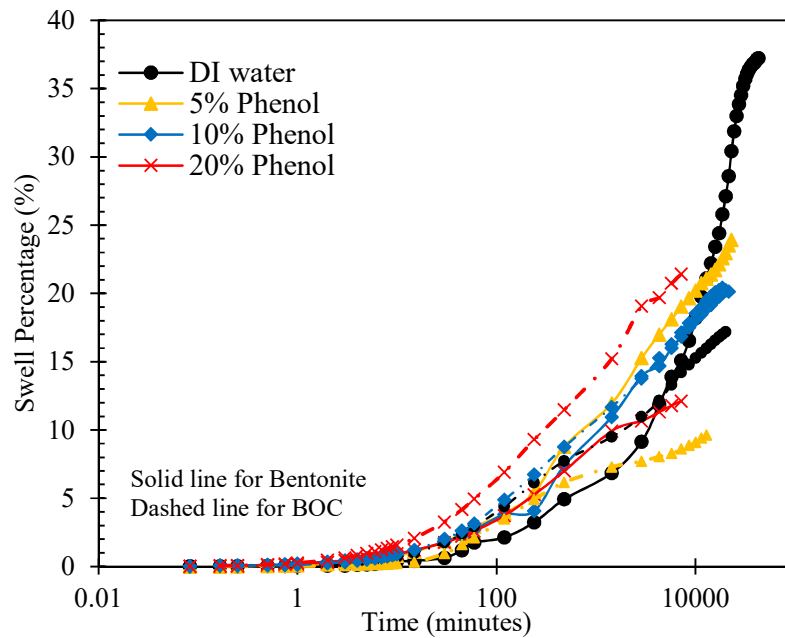


Fig. 7.2 Time-swelling plot for bentonite and BOC inundated with phenol

7.2.2 Variation of hydraulic conductivity with void ratio for samples permeated with different concentrations of organic solutions

The permeability coefficient (k) or hydraulic conductivity of bentonite and BOC samples, inundated with varying concentrations of acetone and phenol, were calculated from oedometer test results and are presented in Figs. 7.3 and 7.4. The results indicated that the concentration and properties of organic fluid play a vital role in determining the permeability of bentonite and BOC. The permeability of BOC varies based on the organoclay fraction, with higher organoclay fractions potentially leading to a rise in the hydraulic conductivity in DI water.

For bentonite, the k value consistently increases with an increase in the acetone and phenol concentrations. The bentonite permeated with 20% phenol displayed the highest k value, irrespective of the applied consolidation pressure. As the concentration of organic fluid increases, the interparticle repulsive forces decline, resulting in the collapse of DDL thickness. The clay particles tend to come closer to each other and form flocs, which create channels and increase the inter-particle void spaces or macropores, facilitating contaminant flow. Similar results were noted for bentonite permeated with inorganic salts and heavy metals. Prior studies conducted by Goodarzi et al. (2016), Olgun and Yildiz (2010), and Mosavat and Nalbantoglu (2013) also concluded that adding organic fluid can result in increased hydraulic conductivity of bentonite.

As more acetone or phenol penetrated the soil pores, water layers were progressively displaced from the clay surfaces, thereby creating gaps not completely filled by adsorbed organic molecules, resulting in an increase in pore space for liquid flow. While acetone can displace water from clay surfaces due to its higher dipole moment, it may not form as many adsorbed layers as water due to its lower dielectric constant and higher molecular weight. The substantial upsurge in k for bentonite in phenol is attributable to the low dielectric constant and acidic pH of phenol. The reduction in pH can further diminish the surface potential of clays, resulting in DDL compression. The acidic pH can also disintegrate bentonite particles, leading to several macro voids and microvoids, which increase k . Thus, the combined impact of dielectric constant, type and concentration of organic fluid, and pH on the DDL compression likely contribute to the rise in k . However, the variation in k due to the increase in acetone/water ratio does not significantly alter the k of bentonite as much as observed with phenol.

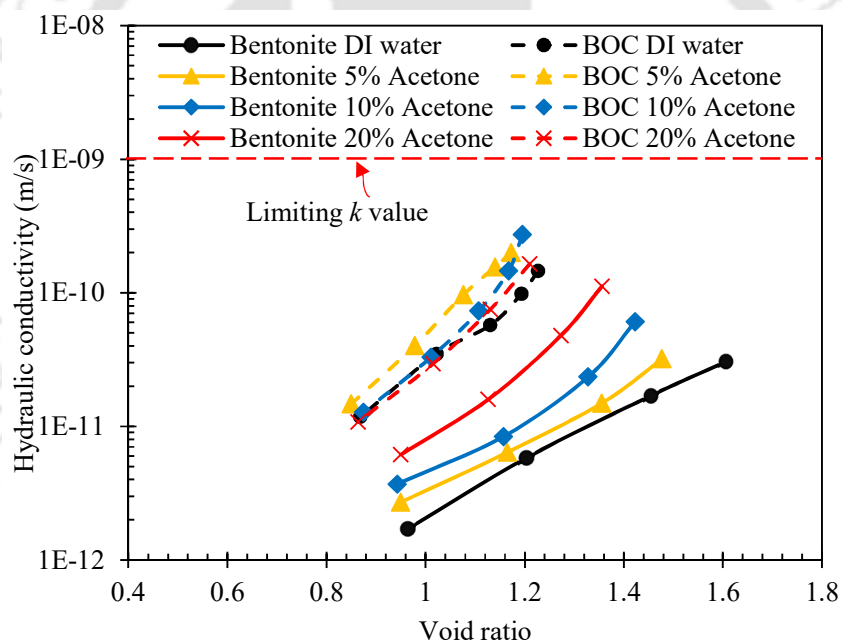


Fig. 7.3 Hydraulic conductivity variations of bentonite and BOC at varied concentrations of acetone

The presence of surfactants on the organoclay interlayer resulted in a decrease in their dielectric constant, repulsive forces and an increase in van der Waals attractive forces, leading to a suppressed DDL around clay particles (Sadrekarimi, 2022). This is the reason for the higher hydraulic conductivity of BOC in DI water. Introducing organic solutions increased the k value of BOC at 5% organic fluid concentration. However, a further rise in organic concentration led to a decline in the k value of BOC.

As shown in Fig. 7.3, acetone permeation did not significantly impact the k value of BOC, whereas the k of bentonite was relatively more influenced by acetone addition. The permeation of phenol solutions also initially increased the k of BOC, particularly at low applied stresses. However, a further rise in phenol concentrations reduced the k of BOC substantially. At 20% phenol solution, the k of BOC was lower than that of bentonite. It can be postulated that increasing phenol concentration beyond 20% may further increase k for bentonite while maintaining a lower k for BOC. Thus, the addition of 10% organoclay to bentonite exhibited superior barrier performance in high organic concentrated leachates. The amine chains of organoclay fraction cause them to swell due to the chemical hydrophobic interactions when permeated with phenol. Since the organoclay fraction swells in the presence of organic fluids, it can effectively fill the cracks formed due to the shrinkage of the remaining 90% bentonite as a result of its lower dielectric constant. The probable flow paths created by the shrinkage of DDL of bentonite fractions get sealed up by the swelling of organoclay fraction in organic solutions. The higher concentrations of organic fluids result in a more effective reduction in hydraulic conductivity. However, very high proportions of phenol or acetone might not be encountered in waste containment facilities such as landfills; hence, this study's organic fluid proportion was limited to 20%.

Prior literature suggested that the sorption of organic compounds onto organoclay increased with a decrease in water solubility (Benson et al., 2015). The solubility of phenol in water is comparatively lower, 82.8 g/L or approximately 8%, while acetone is completely miscible in water (i.e. solubility in water is 1000 g/L) (Benson et al., 2015). Therefore, as concentration increases, the solubility of phenol could be considerably less than that of acetone. In addition to solubility, the low hydraulic conductivity of BOC at higher phenol concentrations can also be attributed to the high viscosity of phenol compared to acetone. This may explain the increased interaction of phenol molecules with BOC, leading to a significant decrease in the hydraulic conductivity of BOC at higher proportions of phenol. Benson et al. (2015) also found an inverse relationship between the hydraulic conductivity and viscosity of permeant fluid in organoclay contaminated with organic fluids. Although organic fluids such as acetone and phenol induce shrinkage and flocculation of the bentonite fraction in BOC samples, the simultaneous swelling and dispersion of the organoclay fraction compensated for this effect, maintaining a low hydraulic conductivity on the order of 10^{-10} m/s or less (Lo and Yang, 2001).

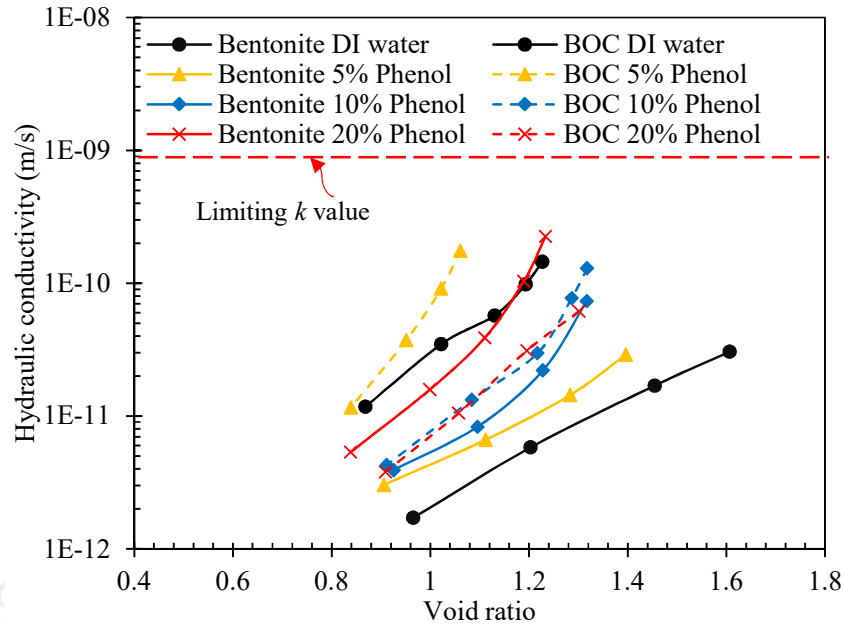


Fig. 7.4 Hydraulic conductivity variations of bentonite and BOC at varied concentrations of phenol

7.2.3 Impact of organic solutions on the compressibility characteristics of bentonite and BOC

(a) Compression curves (e -log σ' curves)

The compression behaviour in terms of final void ratios after the interaction of bentonite and BOC samples with different concentrations of acetone and phenol are depicted in Figs. 7.5 and 7.6. The compression of bentonite specimens inundated with higher concentrations of organic solutions was significantly lower than their counterparts that were inundated with water. As applied stress increased, bentonite specimens displaying the lowest swelling underwent the lowest compression (or lowest change in void ratio), similar to the observations with inorganic salts and heavy metals. At lower organic concentrations (5%), BOC exhibited a decline in swell behaviour and hence displayed a lower magnitude of compressibility than the respective bentonite samples. When the concentration of acetone and phenol exceeded 5%, swelling increased, and hence, an upward shift in the compressibility curve was observed for BOC samples. Therefore, the organic fluid type and applied vertical stress significantly influence the compressibility behaviour of bentonite and BOC.

In bentonite, increased concentrations of organic fluids can cause a reduction in DDL thickness, an increase in modified effective stress, an increase in shearing resistance, and a

consequent decline in compressibility and hydraulic conductivity. The decline in dielectric constant due to the addition of organic solutions increases the attractive forces and decreases the repulsive forces in the system. Since the magnitude of interparticle repulsive forces is comparatively lesser in organic solutions than in water, the effect of applied stresses on the reduction in void ratio or compressibility is also less. This occurs because the applied stress acts as a restraint against the expansion of the DDL, resulting in a reduction in the deformation (Schanz et al., 2018). The relatively flatter consolidation curve (beyond 20 kPa) obtained at higher organic concentrations can be attributed to the stiffer performance achieved after the interaction of bentonite with organic solutions with lower dielectric constants. This interaction results in the compression of DDL and the formation of flocculated clay clusters. These clusters become larger, and particles tend to settle even before the application of external loading, which is termed osmotic consolidation (Goodarzi et al., 2016).

When compared to acetone, more impact of organic fluid concentration on the compressibility of bentonite was observed in phenol. At lower concentrations, the difference in dielectric constant between the solutions and their subsequent influence on the DDL thickness might not be significant, making other factors, such as pH and pore fluid characteristics, more influential. According to Goodarzi et al. (2016), the pH of soil suspensions showed no significant variations when the acetone/liquid ratio was increased from 0 to 80%. On the other hand, phenol solution, being an acid, can affect the pH of bentonite and BOC suspensions, resulting in a more pronounced decrease in void ratio for phenol-permeated samples. The presence of phenol solutions also lowers the dielectric constant of the pore fluid and reduces the extension of long-range double-layer repulsive forces. Consequently, attractive forces dominate, causing particles to flocculate or agglomerate. The resulting changes in soil fabric led to increased hydraulic conductivity of bentonite with increased phenol concentrations.

When compared to bentonite, BOC initially showed a downward shift in the e -log σ' curve when the permeant was changed from DI water to 5% acetone or phenol solutions. With a further rise in organic concentrations from 5% to 20%, there was an upward shift in the curve, representing more volume change at higher concentrations. However, the influence of acetone on the compressibility behaviour of BOC was minimal as compared to phenol. Additionally, compared to bentonite, the impact of organic solutions on the compressibility characteristics of BOC was relatively low.

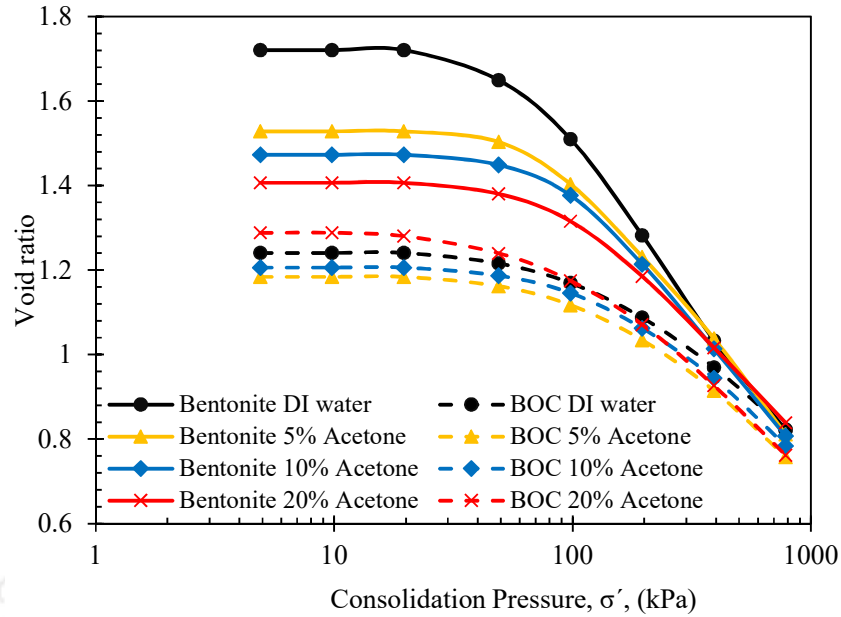


Fig. 7.5 The e -log σ' curves for bentonite and BOC permeated with acetone solutions

At low concentrations of organic solution (particularly for phenol), there was a competitive interaction between water and phenol in bentonite-organoclay mixes. As a result, the interaction of organic molecules with organoclay particles gets restricted by the hydrophobic behaviour of organoclay, leading to a decrease in the compressibility of BOC initially. As the concentrations of organic liquids increase further, more organic molecules tend to interact with organoclays, resulting in an improved swelling of BOC samples and increased compressibility. In the BOC samples permeated with DI water and diluted organic fluids, the organic surfactants in the organoclay interlayer might reduce the interparticle repulsive forces, and the hydrophobicity of the organoclay fraction suppresses the influence of the dielectric constant on the DDL contraction of the remaining 90% bentonite. This explains why BOC had lower compressibility than bentonite at all organic concentrations except 20%. Additionally, the organoclay fraction swells and compresses more in low dielectric constant fluids. At 20% organic concentration, organophilicity or organic affinity of organoclay fraction dominates, which leads to the increase in the swelling and compressibility of BOC. Since the variation in the dielectric constant of acetone-water solutions doesn't significantly vary, its influence on the compressibility of BOC is also less pronounced. But, in the case of less polar phenol, more interaction occurs with organoclay fraction compared to more polar acetone solutions. Thus, the influence of phenol on the compressibility of BOC was higher.

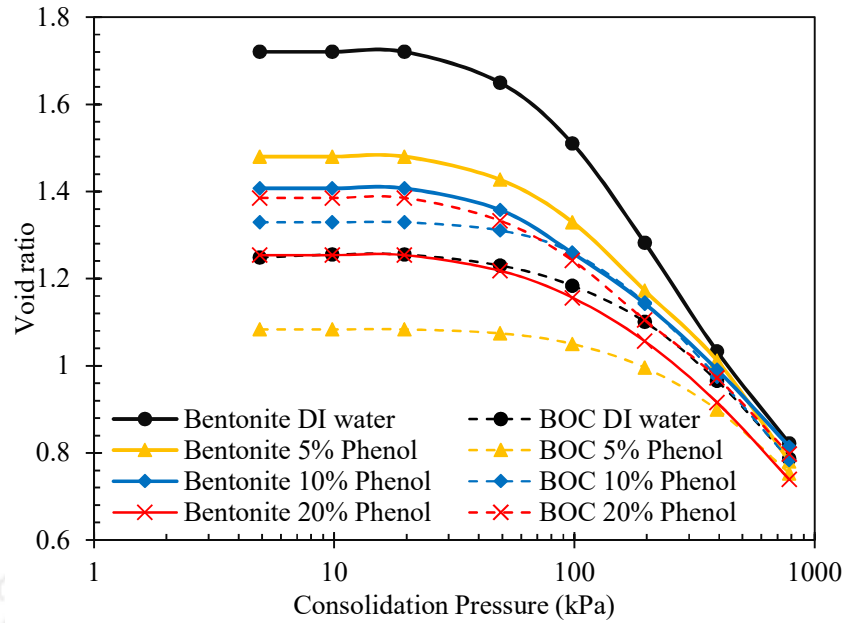


Fig. 7.6 The e -log σ' curves for bentonite and BOC permeated with phenol solutions

(b) Compression index, C_c

The variation in the compression index of bentonite and BOC in the presence of various concentrations of acetone and phenol is displayed in Figs. 7.7 and 7.8. When the organic/water ratio was increased from 0 to 20%, the C_c of bentonite decreased by 23.7% for acetone and 30.3% for phenol. A considerable reduction in the C_c of bentonite was observed even with the addition of smaller percentages of organic fluids. In the findings of Goordazi et al. (2016), a substantial reduction in bentonite's compressibility characteristics was noted when the organic fluid/water ratio was less than 60%. However, the magnitude of this varies depending on the fluid characteristics and the organic chemical-clay interactions.

Irrespective of the percentage organic concentration, phenol had more impact on the C_c of bentonite than acetone. The results were consistent with the values of swelling parameters and compression curves discussed earlier. The trend was in accordance with the decreasing order of its dielectric constant. Therefore, the variation in the compression index of bentonite can be correlated with the variation in its interparticle repulsive forces and DDL thickness. In another aspect, bentonite's lower compressibility in phenol-soil mixtures can be correlated with the fluid characteristics such as the pH of the solution. Phenol is considered a weak acid. Hence, the reduction in pH due to the phenol addition led to a decrease in volume change and an increase in the H^+ concentration in the system. The rising H^+ ions in the pore fluid make the

surface charge density of the clay surface less negative, and exchangeable Na^+ cations in the interlayer may get desorbed (Goodarzi et al., 2016). Additionally, the reduction in pH promotes a positive edge to the negative surface of clay particles and forms edge-to-face card houses, which leads to particle flocculation and reduced compressibility.

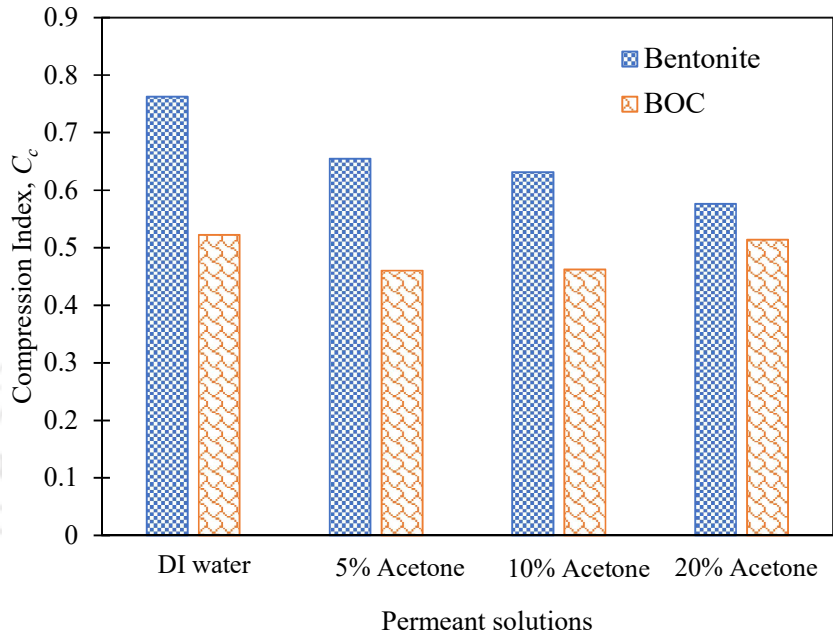


Fig. 7.7 C_c values for bentonite and BOC permeated with different acetone concentrations

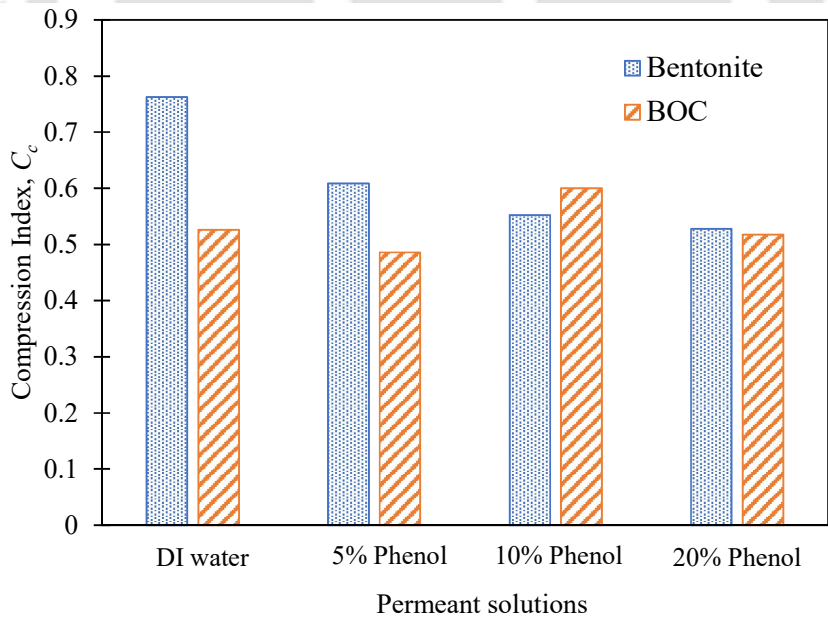


Fig. 7.8 C_c values for bentonite and BOC permeated with different phenol concentrations

The C_c value of BOC exhibited similar values within the range of organic fluid concentrations assessed. However, when compared to DI water, a slight reduction in C_c was observed at 5% organic solution, and a further rise in concentration increased the C_c of BOC. As the organic/water ratio was increased from 0 to 10%, the C_c of BOC decreased by 13.2% for acetone and increased by 13.2% for phenol. It is noteworthy that phenol permeation had a relatively greater impact on the C_c of BOC than acetone permeation. Nevertheless, at 20% phenol, the C_c value of BOC showed a slight declining trend. However, it should be noted that the impact of the organic solution on the compression index of BOC was relatively minimal compared to bentonite. Of all the BOC samples, the samples inundated with 8% phenol displayed then highest C_c value of 0.60.

At higher applied loads, the effect of pore fluid characteristics will be less, and the void ratio of all the samples converges to a similar value. When the applied consolidation pressure exceeds almost 300 kPa, the void ratio for bentonite and BOC with DI water and various organic fluid/water mixes were found to be almost identical. This implies that the compression index of bentonite and BOC highly depends on the physicochemical factors up to an overburden consolidation stress of 300 kPa, beyond which it is insignificant. A similar result was obtained by Olgun and Yildiz (2010), who suggested an consolidation stress of 200 kPa as the threshold above which mechanical factors begin to affect geotechnical behaviour rather than physicochemical factors. Goodarzi et al. (2016) noted a compressive pressure of 400 kPa as the threshold value for sodium bentonite subjected to various concentrations of organic contaminants. The decrease of the double layer as a consequence of breaking interparticle bonding by high pressures due to external stress can be the reason for the convergence. Thus, the effect of organic fluid characteristics on the DDL thickness and its consequence on soil compressibility declines at higher organic concentrations and higher external consolidation stresses.

7.2.4 Impact of organic solutions on the consolidation parameters of bentonite and BOC.

(a) Time for 90% consolidation (t_{90})

The plot in Figs. 7.9 and 7.11 illustrate the t_{90} of bentonite and BOC inundated with varying acetone/water and phenol/water ratios, respectively. For better representation, the t_{90} of BOC permeated with various acetone and phenol concentrations are further represented in Figs. 7.10 and 7.12, respectively. The concentration of organic solutions ranged from 0% (DI water) to 20%, and the corresponding variation of t_{90} under different applied consolidation stresses was

noted. As shown in the figures, irrespective of the soil type and pore fluid, the t_{90} value increased with the rise in applied vertical consolidation stresses.

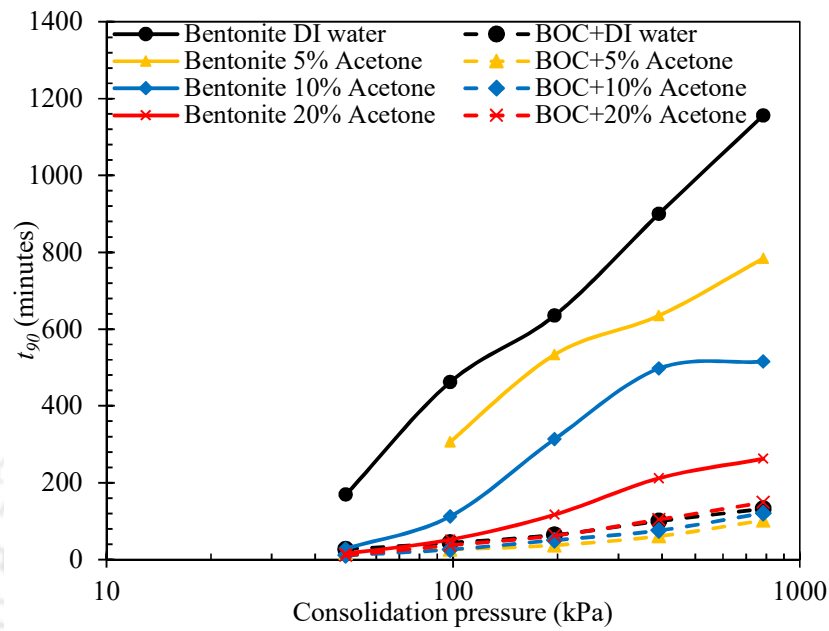


Fig. 7.9 Relationship between t_{90} and consolidation pressures of bentonite and BOC permeated with various concentrations of acetone

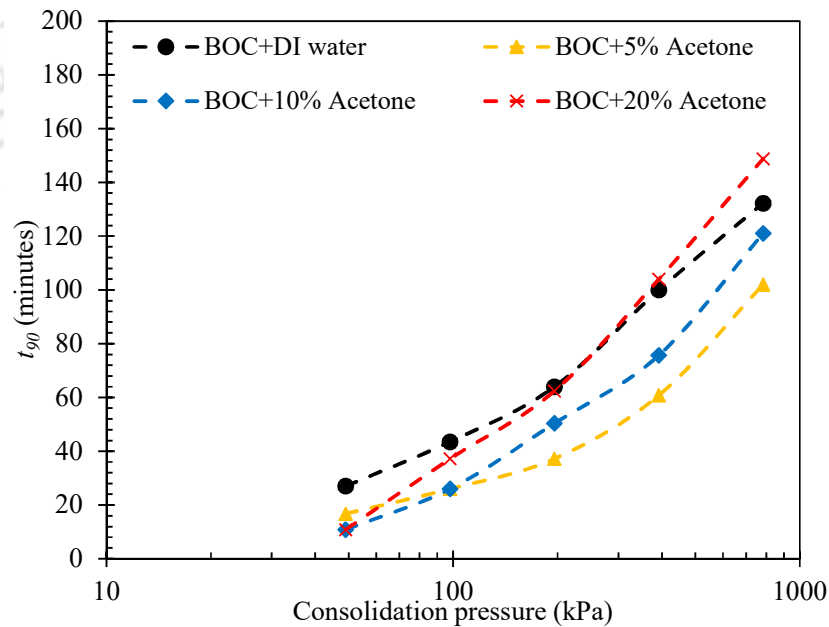


Fig. 7.10 t_{90} versus consolidation pressure plot for BOC permeated with acetone solutions

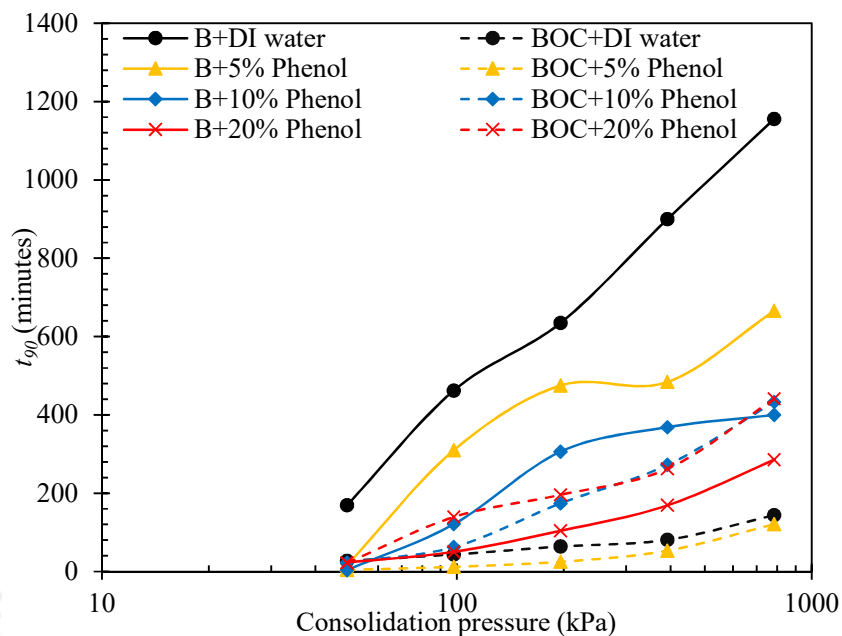


Fig. 7.11 Relationship between t_{90} and consolidation pressures of bentonite and BOC permeated with various concentrations of phenol

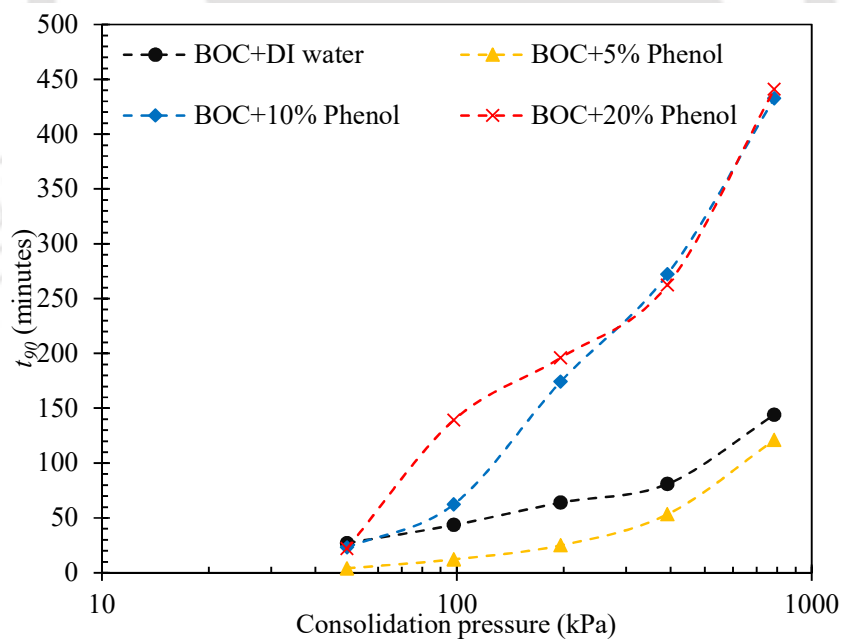


Fig. 7.12 t_{90} versus consolidation pressure plot for BOC permeated with phenol solutions

Furthermore, the addition of acetone and phenol solutions significantly reduced the t_{90} value of bentonite. In contrast, the impact of acetone and phenol on the t_{90} of BOC initially resulted in a slight decrease, followed by a subsequent increase. Compared to the acetone, a significant rise was observed in the presence of phenol as the concentration increase. For

instance, at 784 kPa, the replacement of permeant fluid from DI water to 20% acetone and 20% phenol solution decreased the t_{90} of bentonite from 1156 to 262.44 minutes and to 285.61 minutes, respectively. Under the same conditions, BOC exhibited an increase in t_{90} from 132.25 to 148.8 minutes and to 441 minutes, respectively.

(b) Coefficient of consolidation (c_v)

Figures 7.13 and 7.14 show c_v values versus effective consolidation stress plots for bentonite and BOC permeated with various concentrations of acetone and phenol. As shown from the data, c_v decreases with an increase in effective consolidation stress for all samples. As the concentration of the organic solution increases, the c_v of bentonite increases significantly. At low consolidation stresses and high organic concentrations, a rapid consolidation rate was noted for bentonite. This implies that when the bentonite liner is in contact with a leachate having high concentrations of organic fluid, more rapid settlement may occur at any consolidation stresses. This impact will be much more severe for phenol than acetone contamination.

From the Fig. 7.13, it was noted that the rise in vertical consolidation pressure from 98 kPa to 784 kPa decreased the c_v value of bentonite permeated with DI water from $2.95 \times 10^{-5} \text{ cm}^2/\text{s}$ to $6.71 \times 10^{-6} \text{ cm}^2/\text{s}$. However, for the same change in applied consolidation stresses, bentonite permeated with 20% of acetone and phenol decreased the c_v value from $2.1 \times 10^{-4} \text{ m}^2/\text{s}$ to $2.8 \times 10^{-5} \text{ cm}^2/\text{s}$ and $1.9 \times 10^{-4} \text{ cm}^2/\text{s}$ to $2.4 \times 10^{-5} \text{ cm}^2/\text{s}$, respectively. At higher vertical stresses, particles come closer to each other and increase the interparticle repulsion, further preventing the consolidation and decreasing the c_v value. However, the increase in organic concentration decreases the dielectric constant and contracts the DDL thickness, resulting in the reduction of repulsive forces. As a result, rapid consolidation of bentonite samples occurs, and hence, a higher c_v value was noted. Prior research also showed similar c_v trends for bentonite-based liners in the presence of various organic solutions (Amarasinghe et al., 2012).

In BOC samples permeated with acetone, the c_v values were least influenced by the concentration and type of pore fluid, while phenol-permeated BOC showed much disparity in c_v value. Unlike bentonite, which showed a consistent increase with organic fluid concentration, the c_v of BOC initially increased when the pore fluid changed from DI water to 5% of the organic solution and then decreased with a further rise in concentration. For instance, at fixed consolidation stress of 196.1 kPa, when the pore fluid was changed from DI water to 20% acetone, c_v of BOC remained almost the same from $1.5 \times 10^{-4} \text{ cm}^2/\text{s}$ to $1.6 \times 10^{-4} \text{ cm}^2/\text{s}$.

However, for the same stress, when the pore fluid was changed from DI water to 20% phenol, the c_v of BOC decreased from $1.5 \times 10^{-4} \text{ cm}^2/\text{s}$ to $5.19 \times 10^{-5} \text{ cm}^2/\text{s}$.

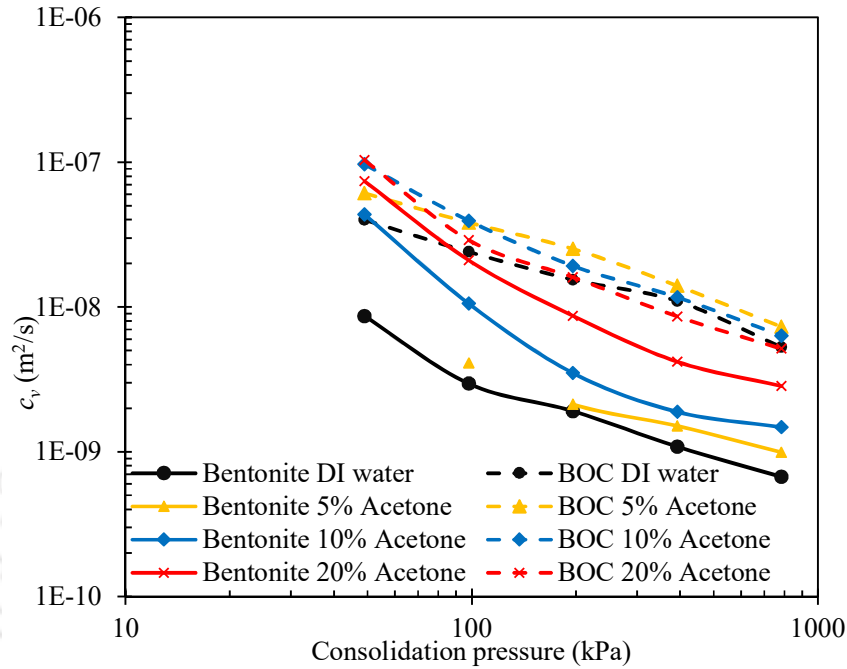


Fig. 7.13 Plot of coefficient of consolidation versus effective consolidation stress for bentonite and BOC sample saturated with various concentrations of acetone

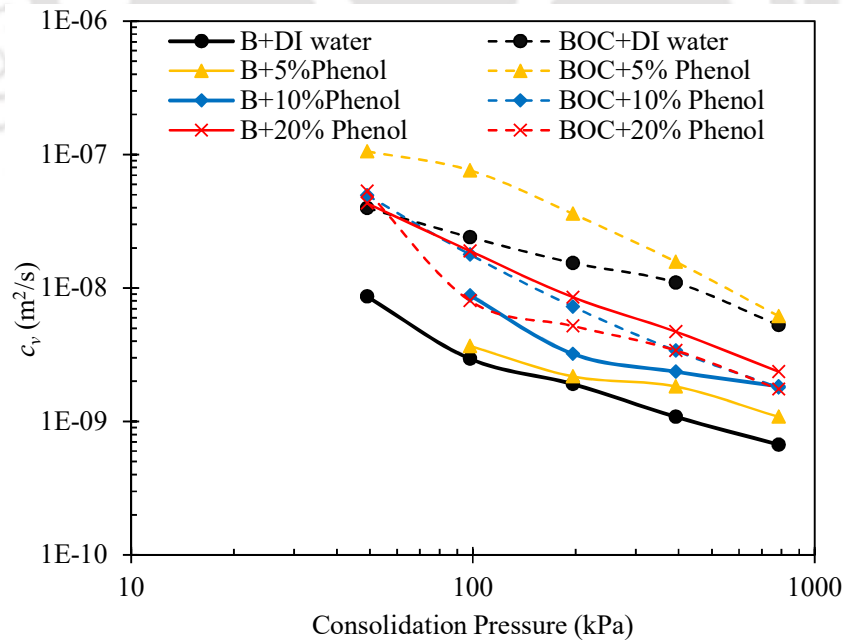


Fig. 7.14 Plot of coefficient of consolidation versus effective consolidation stress for bentonite (B) and BOC sample saturated with various concentrations of phenol

(c) Coefficient of volume compressibility (m_v)

The relationship between the coefficient of volume change and the consolidation pressure for bentonite and BOC saturated with different concentrations of acetone and phenol are illustrated in Figs. 7.15 and 7.16. For any organic permeant concentration, the m_v value of bentonite initially increased, reached a peak value and then decreased with a rise in consolidation pressure. The m_v behaviour of bentonite with increased consolidation stress was similar in organic solutions as well as inorganic solutions. For bentonite samples saturated with dilute acetone and phenol solutions, the rise in concentration reduced the m_v value irrespective of the applied stresses. The lower dielectric constant of organic pore fluids compressed the DDL thickness, reduced the compressibility, and consequently reduced the m_v value of bentonite. For example, at a consolidation pressure of 98.1 kPa, the m_v value of bentonite reduced from 0.105 kPa⁻¹ in DI water to 0.054 kPa⁻¹ in 20% acetone and to 0.056 kPa⁻¹ for 20% phenol solutions. At the same pressure, BOC exhibited a m_v value of 0.042 kPa⁻¹ in DI water to 0.058 kPa⁻¹ in 20% acetone and 0.078 kPa⁻¹ in 20% phenol.

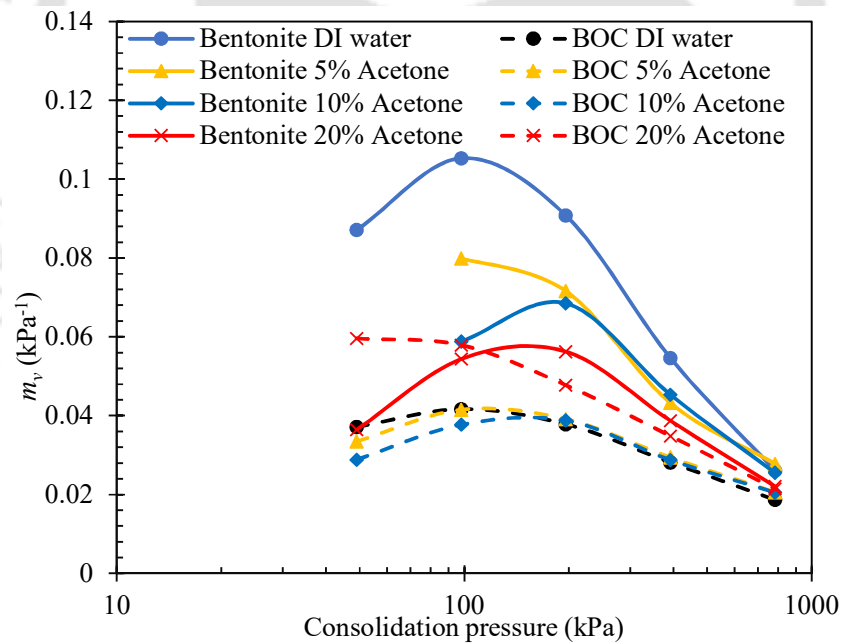


Fig. 7.15 Plot of coefficient of volume compressibility versus effective consolidation stress for bentonite and BOC sample saturated with various concentrations of acetone

The m_v of BOC also displayed similar variation with an increase in applied stresses. However, the influence of organic fluid concentration on m_v value was not similar to that with bentonite. The addition of a very dilute concentration of phenol and acetone decreased the m_v

values of BOC. However, as the phenol and acetone concentration increased to 20%, the m_v exhibited a significant rise, particularly at lower applied consolidation stresses. The phenol permeation showed a substantial increase in BOC's m_v value compared to acetone. At lower concentrations, the interactions of organic fluid might be hindered by the competitive action between organic molecules and water.

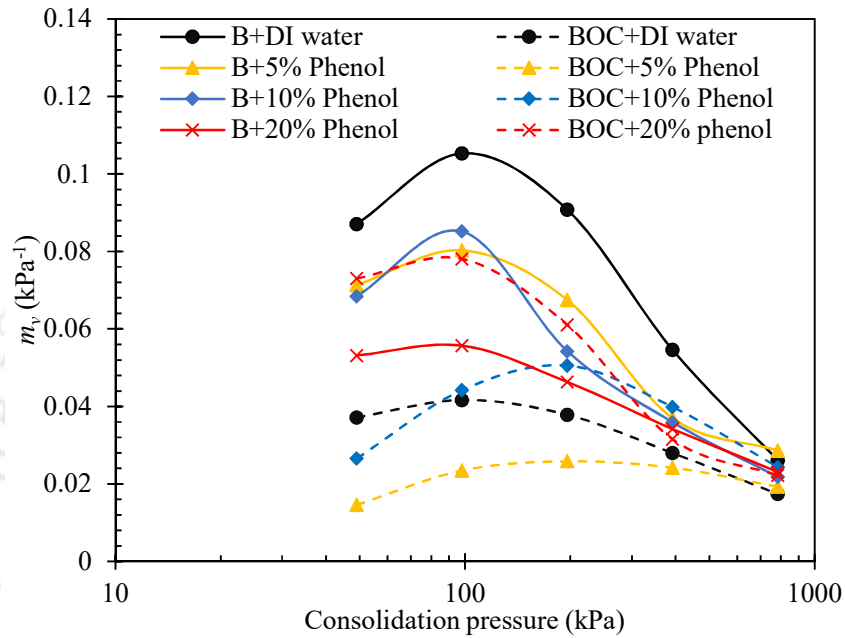


Fig. 7.16 Plot of coefficient of volume compressibility versus effective consolidation stress for bentonite (B) and BOC sample saturated with various concentrations of phenol

7.2.5 Effect of organic fluids on the microstructural behaviour of the compacted bentonite and BOC

(a) FESEM Images

The FESEM images shown in Fig. 7.17 present visual evidence of a flocculated structure in bentonite and BOC samples when the pore fluid was replaced from water to 10% phenol. The fabric of organic-permeated bentonite samples transforms from a dispersed particle-based form (in DI water) to a more agglomerated composition. This transformation correlates with the observed decrease in free swelling, compressibility, and swelling potential of the bentonite due to organic permeation. At a 10% organic concentration, a clustered structure with large macro-pores becomes evident, leading to a significant increase in soil permeability, as shown in Fig. 7.17. The addition of organic solutions gradually increases the face-to-face aggregation and flocculation of clay particles, resulting from the collapse of the diffuse double layer and a

substantial reduction in surface charge density, thereby decreasing the swelling parameters. Comparatively, the microstructural changes are more pronounced in phenol-permeated samples than in acetone-permeated samples. These findings highlight phenol's greater impact on soil performance, as confirmed by the macro-level test results in this study. Additionally, the degradation of the bentonite structure occurs when phenol solutions are permeated through bentonite, which can form numerous micropores and macro-pores in the structure, as seen in the FESEM images. However, in the case of BOC, even though flocculation might occur, the extent of alumina and silica sheet disintegration might be limited due to the presence of organoclay fraction. As a result, hydraulic conductivity decreases with increased concentrations of phenol.

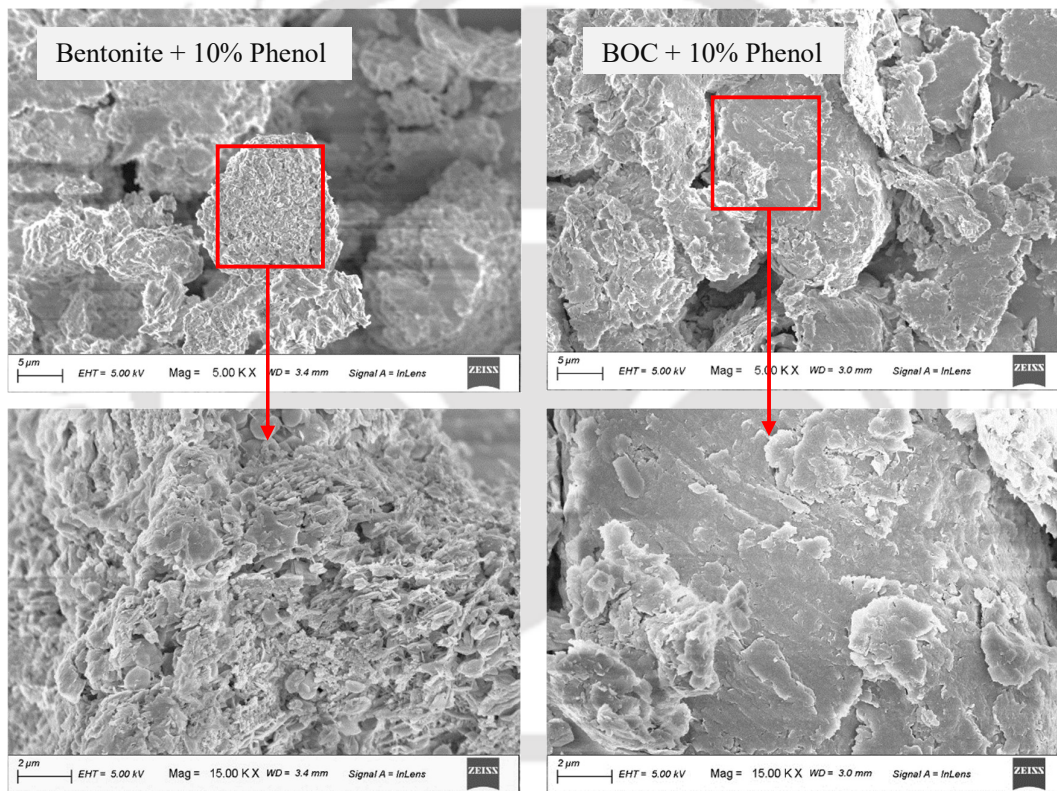
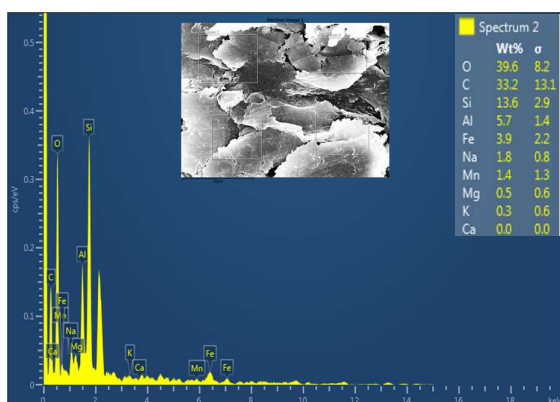
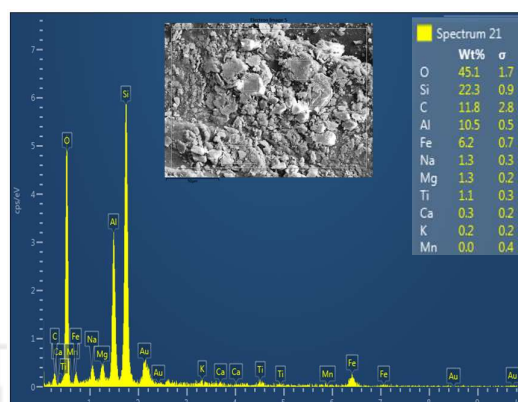


Fig. 7.17 FESEM images of bentonite and BOC permeated with 10% phenol solutions

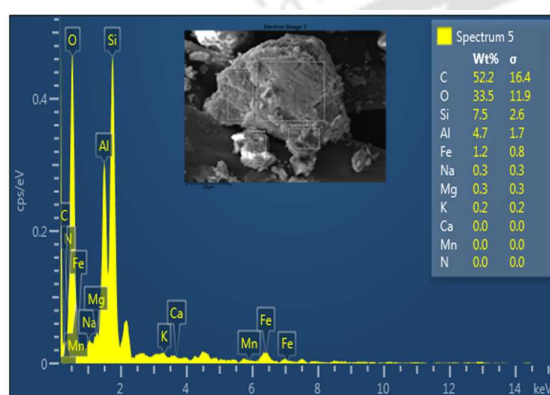
Bentonite + DI water



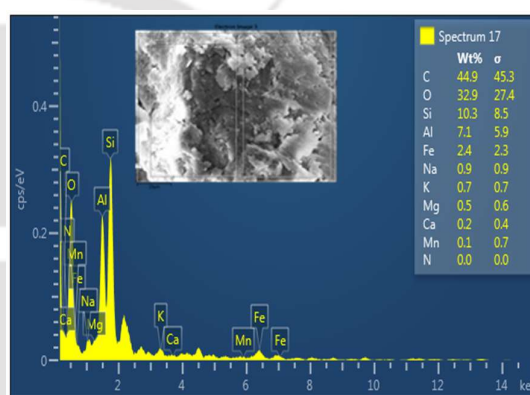
BOC + DI water



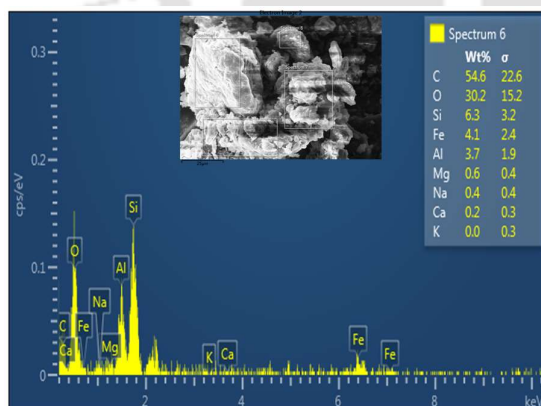
Bentonite + 10% Phenol



BOC + 10% Phenol



Bentonite + 20% Phenol



BOC + 20% Phenol

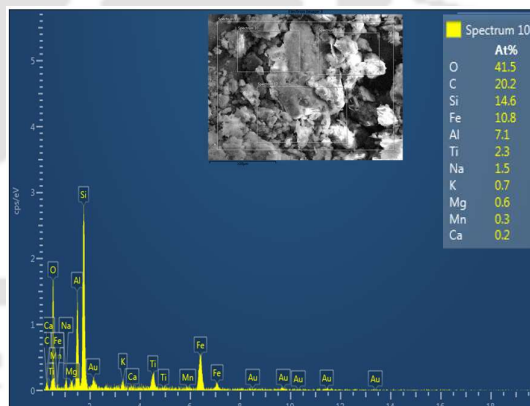


Fig. 7.18 EDS spectra for bentonite and BOC permeated with phenol solutions

(b) EDS spectra

The EDS spectra and elemental composition for consolidated bentonite and BOC samples subjected to phenol solution permeation are presented in Fig. 7.18. The weight percentages indicate that the proportions of silicon, aluminium, and iron decrease upon exposure to phenol solutions. The reduction in weight percentages of these elements might be attributed to the dissolution of these elements in organic fluids. Compared to BOC, bentonite exhibited even lower elemental weight percentages. Desjardins (1996) suggested that the low pH (<4-4.5) and high pH (>9) conditions can dissolve structural Al^{3+} , Si^{4+} and Fe^{3+} available in the montmorillonite. Therefore, the pH variations and pore fluid characteristics considered in the present study might have induced structural changes in the bentonite specimens, as reflected in the EDS data. These structural changes can further alter the geotechnical properties of bentonite and BOC.

7.3 Summary

This chapter examines the swelling, hydraulic conductivity, compressibility, and consolidation behaviour of organoclay-amended bentonite under the influence of organic contaminants, specifically acetone and phenol, at concentrations ranging from 0 to 20%. The results indicated that even the addition of 10% organoclay could significantly improve the hydraulic barrier performance of BOC when permeated with organic solutions, even in its dilute form. The key findings are summarised as follows:

- The free swell index, swell pressure, and swell potential of BOC initially decreased at low organic fluid concentrations (5%) and then increased with higher concentrations (10 and 20%). In contrast, bentonite showed a persistent decline in swell behaviour with the rise in organic contaminant concentrations.
- The impermeable performance of BOC significantly improved with increasing organic fluid concentrations, whereas the hydraulic conductivity of bentonite exhibited a rise, indicating poor hydraulic performance. At 20% phenol, BOC exhibited lower hydraulic conductivity than bentonite.
- The compressibility of bentonite significantly declined at high organic fluid/water ratios and at higher applied consolidation stresses. In BOC, compressibility initially reduced slightly and then increased with higher organic fluid concentrations. However,

compared to bentonite, BOC exhibited minimal variation in compressibility characteristics under the influence of organic fluids.

- The t_{90} and m_v of bentonite decreased substantially with rising organic fluid concentration, while the c_v consistently increased. BOC displayed a similar trend initially, followed by a reverse trend at higher organic concentrations.
- The deterioration of bentonite's barrier performance is primarily due to the collapse of DDL thickness, influenced by changes in the dielectric constant, pH, viscosity, polarity and solubility of the permeant fluid. Increasing organic concentrations may decrease the dielectric constant, pH, polarity and solubility while increasing the viscosity. The difference in these permeant fluid characteristics contributed to the changes in clay's DDL thickness and altered the interaction between permeant organic molecules and clay particles.
- In BOC, the organophilic properties of the organoclay fraction enhanced the interaction between organic molecules from permeants and organic moieties in the organoclay interlayer. This interaction is more effective when the pore fluid's solubility, polarity and hydrophilicity are lower. Effective interaction occurs between permeants and the organoclay fraction in BOC at higher organic fluid concentrations, enhancing the hydraulic barrier performance. At low concentrations (5%), the presence of more water subsides this interaction, and the hydrophobic behaviour of organoclay dominates.
- Phenol had a more significant impact on the geotechnical properties of bentonite and BOC than acetone due to its greater impact on DDL thickness as a consequence of its fluid characteristics.

Conclusions and Recommendations for future studies

This chapter provides a comprehensive summary of the key findings of the research work, as well as the limitations of the study and recommendations for future research in the field.

8.1 Major conclusions from this study

The primary objective of the study was to investigate the feasibility of incorporating 10% organoclay into conventional bentonite as a hydraulic barrier for multiple-contaminant environments. The physical properties of commercially procured organoclay and bentonite were characterised, and their adsorption performance for phenol and various heavy metals was assessed. A comprehensive evaluation of swelling behaviour, hydraulic conductivity, consolidation parameters, and compressibility of the bentonite-organoclay composite (BOC) and bentonite was conducted in the presence of inorganic salts, heavy metals, and organic solutions. The study included contaminants commonly found in waste containment facilities, such as NaCl, CaCl₂, Pb²⁺, Zn²⁺, Cr(VI), acetone, and phenol, at various concentrations. The specific conclusions are enlisted below:

- Bentonite exhibited effective adsorption for cationic heavy metals (Pb²⁺ and Zn²⁺) but showed limited adsorption for hexavalent chromium and phenol. On the other hand, organoclay demonstrated superior adsorption for hexavalent chromium and phenol, along with good removal efficiencies for cationic heavy metals. The removal efficiencies of heavy metals and phenol by both bentonite and organoclay were influenced by the initial pH and adsorbate concentrations.
- The incorporation of 10% organoclay significantly altered the geotechnical properties of bentonite in DI water. The liquid limit, free swell, swell potential, swell pressure, and compression index decreased, while the hydraulic conductivity and the coefficient of consolidation increased. However, the hydraulic conductivity of BOC remained within the suggested range for hydraulic barriers by the USEPA (1988) guidelines.
- An increase in inorganic salts and heavy metals concentration resulted in a decrease in the liquid limit, free swell index, swell pressure, swell potential, compression index, time for 90% consolidation, and coefficient of volume change for both bentonite and BOC. At the same time, the coefficient of permeability and coefficient of consolidation increased. Nevertheless, BOC demonstrated less chemical sensitivity and more stable

behaviour compared to bentonite, which showed significant variations in response to inorganic contaminants.

- The efficiency of bentonite's hydraulic barrier performance was compromised in the presence of organic fluids. However, the swelling properties and hydraulic behaviour of BOC improved with increasing organic fluid concentrations, especially at high concentrations (>10%) of phenol solution.

In conclusion, incorporating 10% organoclay into conventional bentonite liners could effectively prevent the migration of organic and inorganic contaminants while maintaining hydraulic conductivity within acceptable limits.

8.2 Scientific contributions and practical implications of the research

- The study elucidates the adsorption mechanisms of commercially procured bentonite and organoclay for removing heavy metals and phenol under varying pH and adsorbate concentrations. Therefore, the outcomes help in understanding the contaminant interactions with the bentonite and organoclay liners. This will help the engineers and researchers to effectively utilise and tailor these materials for the application of waste containment.
- The research systematically evaluated the impact of different contaminants on the physical and hydraulic behaviour of bentonite and organoclay-amended bentonite. The findings support the utilisation of BOC in the design of more effective hydraulic barriers for waste containment facilities, which are capable of handling a wider range of contaminants. The detailed assessment of geotechnical properties provides valuable guidelines for selecting and optimising materials for hydraulic barriers in different contamination scenarios, ensuring long-term performance and stability.
- The study's findings can guide policymakers and regulatory bodies to update standards and guidelines for the construction and maintenance of hydraulic barriers in waste containment systems, ensuring environmental protection and public safety.
- Although organoclay is typically more expensive than natural clayey soil, this cost is justified if the material can provide adequate protection to soils and groundwater. If the landfill barrier fails, the remediation of landfill site soil contaminated with leachate is often challenging and costly, whereas preventing contamination is more feasible and economical. Thus, to ensure reliable soil and aquifer protection in a cost-effective manner, using organoclay as an amendment to bentonite liners may be a preferable

option. Furthermore, the superior contaminant adsorption capabilities of organoclays can enhance the effectiveness and longevity of hydraulic barriers, leading to long-term cost savings and reduced environmental impact.

8.3 Scope for the future research

1. A comprehensive investigation can be made on the influence of microbial activity, including microbial interactions and external atmospheric conditions, on the engineering behaviour of organoclay-amended bentonite liners.
2. The research can be extended by studying the utilisation of BOC as a component in geosynthetic clay liners.
3. The volume change behaviour and strength characteristics of the proposed liner material under the influence of various leachate constituents may be further explored.
4. The individual and competitive sorption performance of other leachate constituents on organoclay-amended bentonite can be further analysed.
5. The current study mainly focuses on the use of commercially procured cationic surfactant-modified organoclay as an amendment to bentonite liners. The study can further be extended by synthesising organoclays using more environmentally sustainable and cost-effective surfactants and analysing their effectiveness as hydraulic barriers.
6. The sorption performance and hydraulic barrier performance of the proposed liner material under the influence of real landfill leachates (mixed contaminant environment) can be further investigated. The impact of other crucial factors can also be considered.

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PUBLICATIONS

International Journals (Published)

- ❖ **Roy, R., & Mishra, A. K. (2024).** Hydrophobic nanoclay amended bentonite for improved barrier performance under hazardous leachate permeation, *Environmental Processes*, 11(3), 50.
- ❖ **Roy, R., & Mishra, A. K. (2023).** Utilization of organoclay amended bentonite for hydraulic barrier applications under adverse electrolyte environment. *Journal of Environmental Chemical Engineering*, 11(5), 110829.
- ❖ **Roy, R., & Mishra, A. K. (2023).** Consolidation and Compressibility Behavior of Compacted Nanoclay-Amended Bentonite Liners Inundated with Inorganic Salt Solutions. *Journal of Hazardous, Toxic, and Radioactive Waste*, 27(4), 04023023.

International Journals (Under Review)

- ❖ **Roy, R., & Mishra, A. K.** Engineering and microstructural evaluation of hydrophobic nanoclay amended bentonite under the influence of Cr(VI) contaminant: A focus on hydraulic barrier application, *Journal of Geotechnical and Geoenvironmental Engineering*. ASCE (**Review comments Submitted**).

Book Chapters

- ❖ **Roy, R., and Mishra, A.K. (2024).** Effect of Lead and Zinc on Hydraulic Conductivity and Swelling Characteristics of Nanoclay-Amended Bentonite. In: Hazarika, H., Haigh, S.K., Chaudhary, B., Murai, M., Manandhar, S. (eds) Sustainable Construction Resources in Geotechnical Engineering. IC-CREST 2023. Lecture Notes in Civil Engineering, vol 448. Springer, Singapore. https://doi.org/10.1007/978-981-99-9227-0_46
- ❖ **Roy, R., & Mishra, A. K. (2022, December).** Effect of Sodium Chloride on Plasticity, Swelling, and Compressibility Characteristics of Organo-Nanoclay Amended Bentonite. In Indian Geotechnical Conference (pp. 229-238). Singapore: Springer Nature Singapore.

International conferences

- ❖ **Roy, R., and Mishra, A.K.** Impact of municipal solid waste leachate and fly ash leachate on the geotechnical behaviour of bentonite and organoclay amended bentonite liners, 7th EurAsia Waste Management Symposium, Istanbul, Turkey, 21st to 23rd October, 2024.
- ❖ **Roy, R., and Mishra, A.K.** Effect of Lead and Zinc on Hydraulic Conductivity and Swelling Characteristics of Nanoclay Amended Bentonite, 2nd International Conference on construction resources for environmentally sustainable technologies, Fukuoka, Japan, 20th to 22nd November, 2023. (Poster Presentation)
- ❖ **Roy, R., and Mishra, A.K.** Geotechnical properties of acetone-contaminated bentonite and kaolinite-bentonite mixture, 21st Southeast Asian Geotechnical Conference and 4th AGSSEA Conference, Bangkok, Thailand, 25th to 27th October, 2023.

- ❖ **Roy, R.,** and Mishra, A.K. Impact of cationic and anionic heavy metals on the geotechnical characteristics of the bentonite-based liner, *9th International Conference on Environmental Geotechnology, Recycled Waste Material and Sustainable Engineering*, Crete, Greece, 25th to 28th June, 2023.
- ❖ **Roy, R.,** Sarma, S., and Mishra, A.K. Effect of anionic biopolymer on the geotechnical properties of bentonite-based barriers. *4th International Conference on Waste Management*, IIT Guwahati, India, 18th to 19th May, 2023.

National Conferences:

- ❖ **Roy, R.,** and Mishra, A.K. Effect of Sodium Chloride on Plasticity, Swelling and Compressibility Characteristics of Organo-Nanoclay Amended Bentonite, *Indian Geotechnical Conference 2022*, Kochi, India, 15th to 17th December, 2022.

Achievements

- ❖ Received **BEST PAPER AWARD** for oral presentation titled “Effect of anionic biopolymer on the geotechnical properties of bentonite-based barriers” in *4th International Conference on Waste Management* held at IIT Guwahati, India from 18th to 19th May, 2023.
- ❖ Received **CSIR (Council of Scientific & Industrial Research) TRAVEL GRANT** for attending *21st Southeast Asian Geotechnical Conference and 4th AGSSEA Conference* held in Bangkok, Thailand during 25th to 27th October, 2023.
- ❖ Received **ISSMGE (International Society for Soil Mechanics and Geotechnical Engineering) TRAVEL GRANT** for attending *the 21st Southeast Asian Geotechnical Conference and 4th AGSSEA Conference held in Bangkok, Thailand, from 25th to 27th October, 2023.*