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EDUARDO
MONDLANE

FACULTY OF ENGINEERING
Department of Chemical Engineering
Master in Hydrocarbon Processing Engineering

SYNTHESIS OF VERMICULITE BIO-ORGANOCLAYS WITH DIMER FATTY ACID-BASED POLYAMIDE CHAINS FOR OIL AND GAS FIELD PRODUCED WATER TREATMENT

A dissertation submitted to the faculty of Engineering in partial fulfilment of the requirements for the Degree of Master of Science in Hydrocarbon Processing Engineering

Student: Theoneste Kananira

Maputo
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Supervisor: Prof. Afonso Daniel Macheca

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AUTHENTICITY STATEMENT

Statement of originality

I, Theoneste Kananira, hereby declare that the undersigned dissertation submitted to the faculty of Engineering for the award of Master of Science in Hydrocarbon Processing Engineering is my own work and has not been submitted by me or another person for the award of any other degree at the University.

(Theoneste Kananira)

DEDICATION

I dedicate my dissertation project to: Almighty, and I would also like to sincerely thank my beloved parents, brothers and sisters for their encouragements and their supports; since the beginning of my studies; their material assistance; their love; as well as their moral support and encouragements.

AKNOWLEDGEMENT

I would like to thank all those who helped me in this dissertation particularly my supervisor Prof. Afonso Daniel Macheca, he freely devoted part of his time to the supervision of this work from the beginning to the end. May his remarks and his pieces of advice find the reward in this work.

I would like to express my special thanks to the Center of Studies in Oil and Gas Engineering Technology (CS-OGET) for funding my studies to pursue this master’s degree.

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Finally, my thanks are also addressed to my university colleagues; their unforgotten moral supports and friendship to help me throughout my studies. I considerably thank all comrades who prayed for me during the studying journey in Eduardo Mondlane University.

PREFACE

The global oil and natural gas sector constitutes a vital component of contemporary society and provides the energy needed to drive economies and foster technological development. However, the large amounts of produced water that are produced as a result of its activities present serious environmental problems and also not easy to manage. The produced water from the oil and natural gas sector is frequently characterised by excessive salinity, heavy metals, hydrocarbons, microorganisms and other organic chemicals as contaminants.

Innovative materials and techniques for handling produced water have become critical in the pursuit of sustainable industrial operations. One intriguing remedy among these is organovermiculite which is a modified clay mineral with special adsorption and ion-exchange capabilities. The organovermiculite has the hydrophobic and organophilic characteristics enable the efficient removal of organic pollutants and heavy metals from complex aqueous systems, making it a valuable material in the treatment of produced water from oil and gas operations.

The present study puts into application in the concerns of produced water handling by exploring the synthesis of the modified vermiculite, functional properties and its performance in petroleum and natural gas real world scenario, this work highlights the organovermiculite potential to revolutionize simulated produced water treatment in the oil and natural gas industries. While natural gas and oil industries progress promise economic benefits, must ensure development does not come at the cost of environmental degradation. New technologies like organovermiculite offer innovative solutions to traditional natural gas and oil industries pollutants. With prudent regulation and concerted private-public efforts, businesses can incorporate modern compounds into responsible management strategies. In forging ahead, let the ambitions be tempered by safeguarding fragile ecosystems for generations to come. With care and compromise, prosperity can coexist with pristine natural habitats for the best future and sustainability of oil and natural gas industries.

This work is undertaken as a pre-requirement for the completion of Master’s degree in Hydrocarbon Processing Engineering at the Faculty of Engineering of the Eduardo Mondlane University. The first phase of this work comprises the preparation and characterisation of vermiculite (neat vermiculite and modified vermiculite) with SEM, XRD, XRF, BET analytical techniques and particle distribution as discussed in chapter 3. The second phase comprises with the evaluation of the adsorbent’s performance in the removal of copper as inorganic substance and phenol as organic substance. The produced water treatment in copper and phenol removal is simulated on laboratory scale and follows the process of adsorption filtration mechanism. The Uv-visible spectroscopy is used as analytical technique for measurement and excel as tool of data analysis.

Dissertation outline

This dissertation comprises of five chapters and references. The background of and the problem statement are detailed in chapter 1. The literature review on oil and natural gas industry, clay mainly vermiculite and application as adsorbent for produced water treatment are detailed in chapter 2. The chapter 3 describes the materials and the methods used on laboratory scale to carry out this study. Results and discussion are presented in chapter 4. The "Reference" provides consulted and cited related materials relevant to the present work. Additional data is presented in the last pages referred to as appendix.

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RESUMO

A extração de petróleo e gás natural tem sido setores dominantes na economia global desde o início do século XIX. Embora essenciais para a sociedade, a extração e o processamento desses recursos têm impactos ambientais significativos, sendo a água de produção (AP) o aspecto mais preocupante. O estudo investigou o potencial da vermiculita modificada (VMT) como adsorvente para a remoção de contaminantes da AP. Entretanto, foi dada ênfase especial ao cobre e ao fenol. A microscopia eletrônica de varredura (MEV) revelou uma estrutura natural da VMT composta por pilhas imperfeitas com lamelas em escala micrométrica, significativamente mais espessas do que folhas individuais. A VMT natural apresentou uma área superficial BET de 1,49 m²/g, com um d_{50} de 890 µm. Após a exfoliação térmica, a área superficial aumentou para 12,4 m²/g, com um valor de d_{50} correspondente de 12,4 µm. Após a organomodificação com 7,5% em peso de polímero, a área superficial BET diminuiu para 8,78 m²/g, enquanto o tamanho das partículas (d_{50}) aumentou para 139 µm, confirmando a incorporação do polímero. A análise de fluorescência de raios X (FRX) indicou um teor de vermiculita inferior a 50%, consistente com a vermiculita de Palabora. A análise de difração de raios X (DRX) da VMT não modificada exibiu múltiplos reflexos, indicativos de uma mistura mineral. Após a modificação, a argila apresentou intensidades de pico menores, atribuídas à delaminação das folhas e à redução do tamanho das partículas devido à expansão térmica e à integração do polímero. A análise termogravimétrica (TGA) revelou perda de massa em toda a faixa de temperatura tanto para a VMT natural quanto para a modificada, com maior perda de massa nesta última devido às moléculas orgânicas do polímero. Experimentos de adsorção em batelada demonstraram baixa eficiência de remoção para fenol (≈23%) e cobre (≈54%) da água de produção para a VMT natural. Após a organomodificação, a eficiência de remoção de fenol melhorou significativamente (≈74%), enquanto a eficiência de remoção de cobre reduziu drasticamente para 13%. Esses achados sugerem que modificações específicas da VMT podem otimizar suas capacidades de adsorção para contaminantes específicos, embora trade-offs devam ser considerados ao direcionar múltiplos poluentes. Recomenda-se mais pesquisas sobre técnicas de modificação e condições de aplicação para maximizar seu potencial no tratamento de água de produção.

Palavras-chave: Adsorção, organovermiculita, água de produção

ABSTRACT

Oil and natural gas extraction have been dominant sectors in the global economy since the early 19th century. Although essential to society, the extraction and processing of these resources have significant environmental impacts with produced water (PW) being the most concern. The study investigated the potential of modified vermiculite (VMT) as an adsorbent for removing contaminants from PW. Special emphasis, however, was given to copper and phenol. Scanning electronic microscopy (SEM) revealed a natural VMT structure consisting of imperfect stacks with flake lamellae in the micrometer range, significantly thicker than individual sheets. Neat VMT had a BET surface area of 1.49 m^2/g with a d_{50} of 890 µm. After thermal exfoliation, the surface area increased to 12.4 m^2/g, with a corresponding d_{50} value of 12.4 µm. Following organomodification with 7.5 wt.% polymer, the BET surface area decreased to 8.78 m^2/g, while the particle size (d_{50}) increased to 139 µm, confirming polymer incorporation. X-ray fluorescence (XRF) analysis indicated a vermiculite content below 50%, consistent with Palabora vermiculite. X-ray diffraction (XRD) analysis of the unmodified VMT displayed multiple reflections, indicative of a mineral mixture. After modification, the clay exhibited lower peak intensities, attributed to sheet delamination and particle size reduction due to thermal expansion and polymer integration. Thermogravimetric analysis (TGA) revealed mass loss across the entire temperature range for both natural and modified VMT, with greater mass loss in the latter due to organic molecules from the polymer. Batch adsorption experiments demonstrated low removal efficiency for phenol (≈23%) and copper (≈54%) from produced water for neat VMT. After organomodification, phenol removal efficiency significantly improved (≈74%), whereas copper removal efficiency reduced drastically to 13%. These findings suggest that tailored modifications of VMT can optimize its adsorption capabilities for specific contaminants, though trade-offs must be considered when targeting multiple pollutants. Further research into modification techniques and application conditions is recommended to maximize its potential in produced water treatment.

Keywords: Adsorption, organovermiculite, produced water

LIST OF ABBREVIATIONS AND ACRONYMS

CEC: Cation Exchange Capacity
MBTBu: Million British Thermal Units
PW: produced water
SEM: Scanning Electron microscopy
USD: United State Dollar
VMT: vermiculite
XRD: X-ray diffraction

CHAP 1

1. INTRODUCTION

1.1. Background

The natural gas and petroleum sectors encircle the main global energy sector and drive the world economy since centuries, oil use is still highest in the transportation sector, followed by petrochemicals and industrial use. Energy is consumed whenever you consume anything (Bullard & Herendeen, 1975). An integral element of the globalized economy is played by the oil and gas sectors, and globalization has stimulated ever-increasing indirect energy flows in international trade (Kan et al., 2019). By 2035, global energy consumption is anticipated to increase by 30% and the world will still continue the investment in oil and gas sectors (IEA, 2023), which put a burden to higher energy supply to the global economy that can induce world- wide concern about energy security, costs, climate change and environment degradation. Current and upcoming trends may be influenced by the sections on energy demand, technology use, and technological advancement (Mattick et al., 2010; Scheffran et al., 2020). These days, a country's energy consumption is a key measure of its richness or poverty. The world consumes 400 quads/yr of total energy which is equivalent to 200 million B/D of this, 40% is oil, 22% is gas, 24% is coal, 6% is nuclear and 8% comprises all other energy forms, mostly hydroelectric to the other side wind and solar combined make up less than 0.5% of the total mix (Economides et al., 2001).

The main by-product of extracting natural gas and oil is produced water which is the main waste liquid in the natural gas and petroleum industry. The produced water which rises as a reservoir ages as a result of reservoir depletion and its accompanying water intrusion or encroachment (Al Battashi et al., 2019; Dandekar, 2013; Hussain et al., 2014). A complex mixture of organic and inorganic compounds, both dissolved and particulate, makes up produced water, which can range from intense saltwater brine to practically freshwater and also vary greatly from location to location and even over time in the same well. The metal species that are contained in produced water may include iron, copper, manganese, potassium, calcium, aluminium, antimony, etc. and produced water bears organic components like benzene, phenols, polyaromatic hydrocarbons, etc. (Jacobs et al., 1992; Neff et al., 2011a).

Common practices in the oil and natural gas industry for handling produced water is to treat it by using physical or chemical method. The treated water might be a useful and safe commodity for even other sectors like agriculture.

Physical methods such as adsorption uses activated carbon, zeolites, resins, etc. or chemical treatment like coagulation and flocculation in the removal of suspended solids and colloid particles though it is not effective while dealing with dissolved constituents. Activated carbon can remove soluble benzene, toluene, ethylbenzene and xylene (BTEX) but organoclay can remove insoluble free hydrocarbons that contribute to total petroleum hydrocarbons. The organovermiculite can be synthesized by combining the neat prepared natural vermiculite with a quaternary ammonium salt or surfactant (polymer) to induce it with a property of making it compatible with organic substances (Fakhru'l-Razi et al., 2009).

The preparation of the clay material (natural vermiculite) is by thermal expansion under higher temperature in muffler furnace or chemical expansion using hydrogen peroxide. The fresh surface of VMT nanosheet exposed after exfoliation has a large number of reactivity reaction sites, which leads it to have outstanding reactivity compared to expanded VMT (M. Li et al., 2021).

The neat and organomodified clay can be characterized through analytic technique in the studies of its behavioral performance. XRD (X-ray Diffraction), XRF (X-ray Fluorescence), SEM (Scanning Electron Microscopy), BET (Brunauer-Emmett-Teller), and TGA (Thermogravimetric Analysis) are analytical techniques used to characterize vermiculite and organovermiculite. XRD identifies the crystalline structure and interlayer spacing changes after modification. XRF determines the elemental composition, highlighting any chemical changes during organophilization. SEM provides high-resolution images of surface morphology and layer structure. BET measures the specific surface area and porosity, which are crucial for understanding adsorption properties. TGA assesses thermal stability and decomposition behaviour, indicating the effectiveness of organic modification. Together, these techniques provide comprehensive insights into the structural, chemical, and thermal properties of vermiculite and organovermiculite (Malai et al., 2020; Muiambo et al., 2015). The adsorbent performance explained by the adsorption capacity, cation exchange capacity(CEC), rate constant of pseudo first or second order kinetics and its behaviour to adopt Freundlich or Langmuir.

1.1.1. Produced water

Produced water is a by-product generated during the extraction of oil and natural gas from underground reservoirs (Clark & Veil, 2009). Produced water from a hydrocarbon well including flow back water, formation water, injected fluids, water condensing from the gas phase and mixtures (Zemlick et al., 2018)

When a fluid combination is created, hydrocarbons rise to the top of the mixture. This produced fluid typically consists of a mixture of produced water and hydrocarbons, either gaseous or liquid. In addition to generated solids (sand or silt), injected fluids, and additives that might have been added to the formation during exploration and production, the produced water also contains dissolved or suspended solids (Onwuachi-Iheagwara, 2012). The produced water can be found contaminated with fats, lubricants, cutting liquids, heavy hydrocarbons such as tars, greases, crude oils, diesels oil and even light hydrocarbons such as kerosene, jet fuel and gasoline (Mysore et al., 2005). Because of its composition and potential environmental impact, the treatment is essential before disposal or use. Among the techniques for water disposal include treatment and discharge, reinjection into subsurface formations, and reuse for additional industrial applications (Nasiri et al., 2017; Sowder et al., 2010).

The general practice in use for produced water treatment is gravity-based separation and discharge into the environment, which can pollute soil, surface water and underground water in contrast other management and treating technologies like de-oiling (removal of dispersed oil and grease), desalination, removal of suspended particles and sand, removal of soluble organics, removal of dissolved gases, removal of naturally occurring radioactive materials, disinfection and softening (to remove excess water hardness). The removal of inorganics and organics compounds using clay material and organoclay via adsorption process (Arthur et al., 2005; Fakhru'l-Razi et al., 2009).

1.1.2. Clay modification

The clay modification must be aware of the characteristics of both the interacting compound (water, polymer, organic/inorganic molecule) and the clay mineral in question. Different states of matter (solid, melting solid, liquid, gas, and plasma) can interact with clay minerals and other substances in the environment (Bergaya & Lagaly, 2006).

The fact that vermiculite expands considerably when heated suggests that intercalation or other chemical processes may enhance the material qualities (Adewuyi & Oderinde, 2019). Natural clay minerals like vermiculite or montmorillonite are chemically modified to become organophilic and compatible with organic solvents or polymers. This process is known as clay modification or organomodification.

Usually, ion exchange is used to do organomodification (refer to figure 8 in chapter 2) by substituting organic cations like quaternary ammonium salts for the naturally existing inorganic cations (such Na^+ and Ca^{2+}) in the clay interlayer gaps. Initially, the clay is dissolved in water to form a slurry, and then the organic modifier is added. To guarantee full ion exchange, the mixture is heated, homogenized and stirred then left to react. The final organoclay product is then obtained by filtering, washing, and drying the modified clay to get rid of extra reagents. The clay's capacity to interact with organic matrices is improved by this change, which qualifies it for use in adsorption of inorganic and organic produced water components (de Araújo Medeiros et al., 2009; Tabana et al., 2019). Organomodification bridges the gap between inorganic clay minerals and organic materials; the use of organic polymer like polyamide in the modification of clay vermiculite enhances the functionality and performance of clay-based materials (Tjong et al., 2002).

1.2. Motivation

The sector of energy, transport, services, business cover more than 70% with the bases of activities related to oil, gas and water (Tong et al., 2018). Oil and gas will continue to be in high demand because they are anticipated to be the primary energy sources for some time to come. As more regions are made accessible for exploration and as our technologies advance, we also hope to witness a steady rise in the success and output of exploration (Chambers, 1996). The availability of clay material as earth contents is huge. For modern living, clay has also become essential and a vital component of plastics, paints, paper, rubber, and cosmetics. Clay is also the material used to create a variety of ceramic products, including porcelain, bricks, tiles, and sanitary ware. The distinct structural and chemical characteristics of organovermiculite which make it an efficient adsorbent for both heavy metals and organic contaminants provide an incentive for its use in the removal of copper and phenol from produced water. Vermiculite is a clay mineral that occurs naturally and has a high surface area, layered structure, and cation exchange capacity. Its affinity for organic molecules like phenol is increased when it undergoes organomodification, which results in an increase in interlayer spacing and a hydrophobic surface. Through electrostatic interactions, the negatively charged layers of vermiculite can simultaneously draw in and hold onto positively charged copper ions. Organovermiculite is a versatile and effective material for produced water treatment because of its dual activity, which enables it to manage complicated produced water pollutants.

As a depolluting agent, clay has no harmful effects on the environment (Bergaya & Lagaly, 2006). Traditional treatment methods may struggle to simultaneously remove both inorganic and organic pollutants efficiently in produced water and wastewater while organovermiculite offers a sustainable and cost-effective solution due to its high adsorption capacity, stability, and reusability. The adsorption process is a cheap technique that makes use of easily accessible adsorbents (Kennedy et al., 2018) . Due to its simplicity, adaptability in design, high efficiency, and affordability, adsorption has been the most widely used technique for treating produced water and wastewater (España et al., 2019).

Adsorption materials are easily prepared and thermally stable, and the adsorption process is straightforward to design and run. Furthermore, the procedure generates no unnecessary by-products, and thermal desorption allows for the regeneration of the solid components (Kőnig-Péter et al., 2014).

1.3. Problem statement

The water produced from a reservoir along with hydrocarbons is a complex mixture of organic molecules (like phenols and benzene), salts, heavy metals (including copper, lead, and zinc), dissolved and scattered hydrocarbons, and occasionally naturally occurring radioactive materials. The geological formation, extraction techniques, and well age all have a significant impact on the produced water composition. If produced water is not adequately managed, it poses significant dangers to the environment and human health because of its high toxicity and ability to contaminate soil, groundwater, and surface water. For the oil and natural gas sector, treating and disposing of produced water are major obstacles, especially in areas with strict environmental laws and scarce water supplies.

Depending on the extraction methods and reservoir geology, produced water might have a very different composition. The produced water from natural gas platforms has ten times more toxicity than the petroleum well discharge henceforth treating this water for reuse is crucial (Al-Ghouti et al., 2019). Conventional treatment methods, such as filtration, chemical precipitation, and biological treatment, often fail to address the complex and variable nature of produced water contaminants, particularly when both heavy metals and organic pollutants are present.

The problem statement revolves around the need for efficient, cost-effective, and sustainable technologies to treat produced water before its discharge or reuse.

Because of the interchange of interlamellar cations, primarily Na^+ and Ca^{2+} which imparts a hydrophilic property to the clay mineral surface, clay vermiculites can therefore interact with a wide range of produced water contaminants particularly heavy metal ions. To the other view clay will be unable to adapt as adsorbent for organic contaminants due the strong competition with the polar water molecules (Abate & Masini, 2005). On mineral surfaces, metal ions exchange for organic cations through intercalation of a polyamide (modifier), releasing the metal cations into solution. The surfaces of the clay can be significantly altered to become highly organophilic when swapped with specific organic cations that include substantial organophilic moieties. Consequently, the organoclay combination is enhanced as adsorbent of organic species that are weakly soluble in water (Boyd et al., 1988). Without treating, handling, and disposing of produced water can be expensive and can impact the overall economics of petroleum and natural gas production.

1.4. Research objectives

Organically modified clays or organophilic clays; are clay minerals that have been chemically modified with organic compounds to enhance their performance in organic and inorganic pollutants removal in produced water. The objectives of modified bio-organoclays revolve around the synthesis and study of the performance, functionality and sustainability in produced water treatment application. However, the emphasis is the organomodified vermiculite in the removal of phenol and copper in the produced water.

1.4.1. General objective

- ✓ The general objective of this study is to synthesize vermiculite bio-organoclays with dimer fatty acid-based polyamide chains for produced water treatment from oil field reservoir.

1.6.2. Specific objectives

- ✓ To prepare the neat vermiculite by thermal expansion
- ✓ To characterize the clay (vermiculite) material (data provided from appropriate analytical techniques for material characterization)
- ✓ To modify (functionalize) the vermiculite to organovermiculite and increase its chemical functionality
- ✓ To characterize the bio-organovermiculite and evaluate its performance and efficiency in the removal of copper and phenol contaminants

1.7. Methodology

The synthesis of organovermiculite begins with the purification of natural vermiculite, which involves washing and sieving to remove impurities. Heating for thermal expansion and milling and sizing.

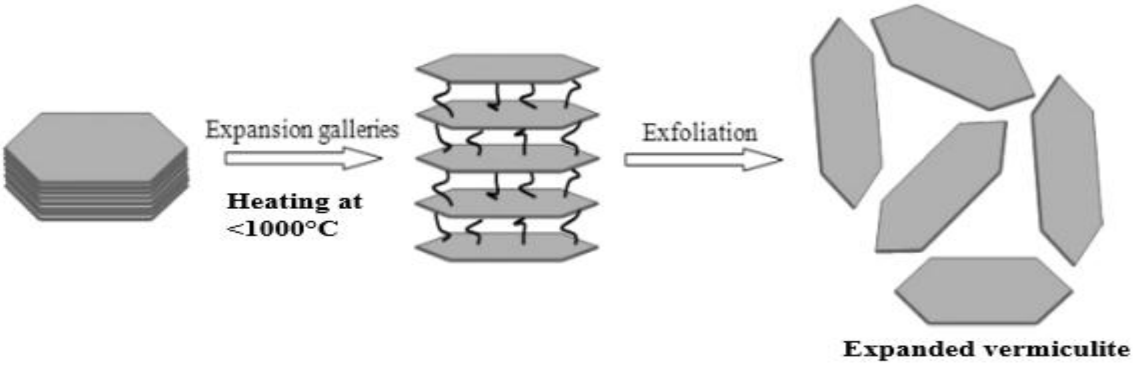

Figure 1: Schematic of thermal expansion of clay

The purified and sized vermiculite is then dispersed in glacial acetic acid to form a slurry. An organic modifier, fatty acid polyamide salt is added to the slurry under constant stirring rate. The reaction is allowed to proceed for several minutes to ensure complete replacement of interlayer inorganic cations (e.g., Na^+, Ca^{2+}) with organic cations. Figure 2 shows complete intercalation of polymer in a typical clay.

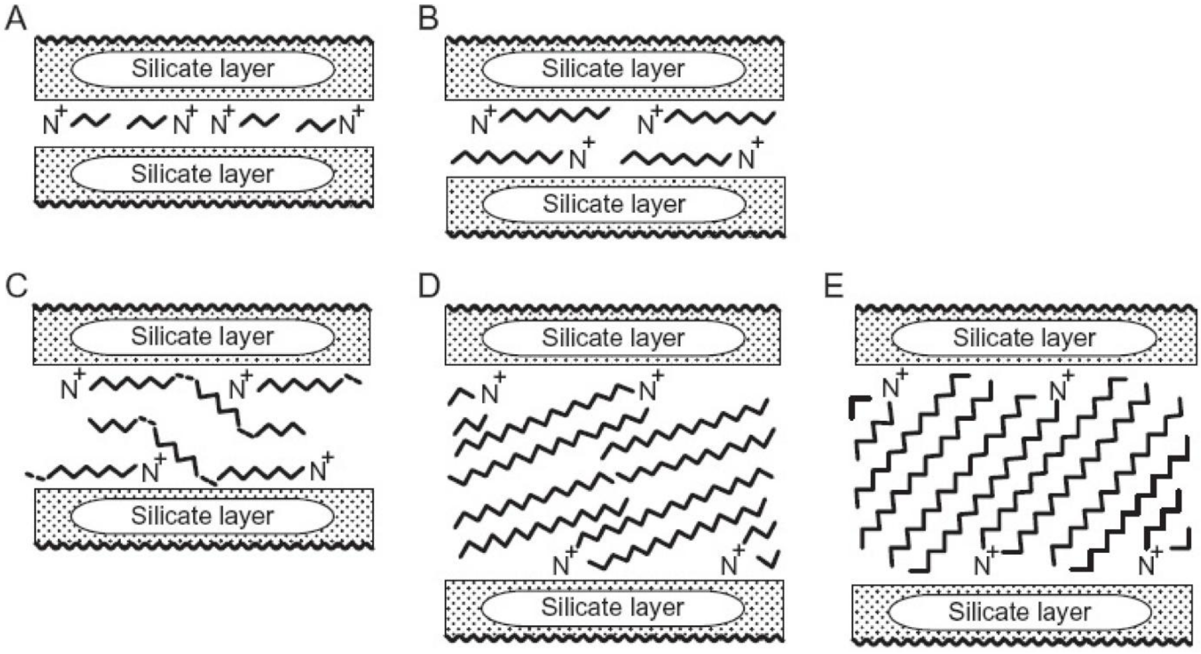

Figure 2: Arrangement of alkylammonium ions in the interlayer space of clay (Adapted from Perelomov et al., 2021)

The organovermiculite is then filtered, washed repeatedly to remove excess modifier, and dried at moderate temperatures (60–100°C) to obtain the organically modified vermiculite. There are four different main phases followed in the project which are discussed below.

1.7.1. Selection of clay material and clay pre-processing

Because of its phyllosilicate structure, which is layered, and its capacity to expand thermally, vermiculite displays a number of distinct physical and chemical characteristics. Hydrated magnesium-aluminium-iron silicate is one of the chemical constituent make-up and appears brown, golden or bronze. It can withstand the higher temperature from 700°C to 1000°C and above. The higher temperature contributes to the evaporation all the water that makes up all the layers which causes the vermiculite to expand.

1.7.2. Clay modification

Structural and surface alterations of the prepared clay mineral are performed to strengthen the affinity of the vermiculite mineral to a particular type of pollutant, or to boost its adsorption capacity or contaminant removal efficacy. To enhance the properties of natural clay minerals, such as vermiculite by replacing inorganic cations in the clay interlayer spaces with organic cations the clay becomes organophilic which increases its compatibility with organic pollutants and solvents. This modification expands the interlayer spacing, improves dispersion in organic matrices, and enhances adsorption capacity for organic pollutants and heavy metals. Organomodification also introduces functional groups that can interact with specific contaminants, making it a versatile and efficient for adsorption process. Reaction 1 shows the typical organomodification process.

$$\text{Vermiculite–M}^+ + \text{R–NH}_3^+\text{X}^- \rightarrow \text{Vermiculite–R–NH}_3^+ + \text{M}^+\text{X}^- \qquad (1)$$

Where Vermiculite–M^+ is the natural vermiculite with exchangeable cations ($M^+ = Na^+$, Ca^{2+}, Mg^{2+}). R–$NH_3^+X^-$ is the quaternary ammonium salt (e.g., alkylammonium, such as cetyltrimethylammonium bromide, Cetyltrimethylammonium bromide, etc.). Vermiculite–R–NH_3^+ is the organomodified vermiculite and M^+X^- is the exchanged inorganic salt (e.g., NaCl, $CaCl_2$).

1.7.3. Mineralogical and chemical characterisation

A variety of analytical approaches are needed to characterize vermiculite and organovermiculite, a mineral that is part of the phyllosilicate group, in order to comprehend its composition, structure, thermal behaviour, and other physical and chemical properties. Several analytical techniques are used to understand the vermiculite clay type and its organomodified form. X-Ray Diffraction (XRD) to study its mineral structural composition of the crystalline phase. Scanning Electron Microscopy (SEM) to identify particle shape and surface morphology of vermiculite. Thermogravimetric Analysis (TGA) to study the thermal stability and decomposition patterns of vermiculite. To quantify the major and trace elements (such as Si, Mg, Fe, and Al) in vermiculite, which aids in the mineral classification and purity evaluation via X-ray Fluorescence (XRF) technique. Capacity (CEC) to study the behaviour and potentiality of vermiculite in exchanging cations (Campos et al., 2009; Jlassi et al., 2017).

1.7.4. Treatment of produced water and clay performance evaluation

The clay and organoclay in the treatment of produced water emerge multiple procedures, the produced water that emerges from petroleum and natural gas wells along with hydrocarbons and different components. The treatment of the produced water simulated on the laboratory scale at the University of Eduardo Mondlane, Chemical Engineering laboratory, University of Eduardo Mondlane is used and the analytical laboratory methods using adsorption filtration method. The clay performance evaluation in the copper and phenol removal is measured using Uv-visible spectroscopy at respective ranges of the wave length.

CHAP 2

2. LITERATURE REVIEW

Despite increased efforts to switch to renewable energy, the petroleum and natural gas industry continues to play a crucial role in the global economy. Recent years have shown that the sector remains a key contributor to the world energy supply, making up a sizeable portion of global energy consumption. The geopolitical investment in energy sector of the natural gas and petroleum continues increasing which consequently sustain the economic trophic level worldwide. As global energy demand rises, natural gas is playing an important strategic role in energy supply where the petroleum and natural gas industry encompasses various institutions, including petroleum and natural gas companies responsible for the extraction, processing, manufacturing and refineries that contribute significantly to state revenue through the management of these resources. Petroleum and natural gas serve as both a source of income for the state budget and a crucial energy source (Khatib, 2014; Maharani & Akbar, 2023).

According to IEA (2023), the figure 3 shows the prices on the global market in the oil and natural gas sectors in the first half of 2023 fossil fuel prices decreased but market equilibrium is still precarious. In September 2023, the price of crude oil rose again above USD 90 per barrel. In Europe natural gas frequently trades for more than USD 50 per MBtu which is more than USD 250 per barrel of oil. Around USD 10 per MBtu was the new pricing in Europe, however it was still excessive when compared to the past decade.

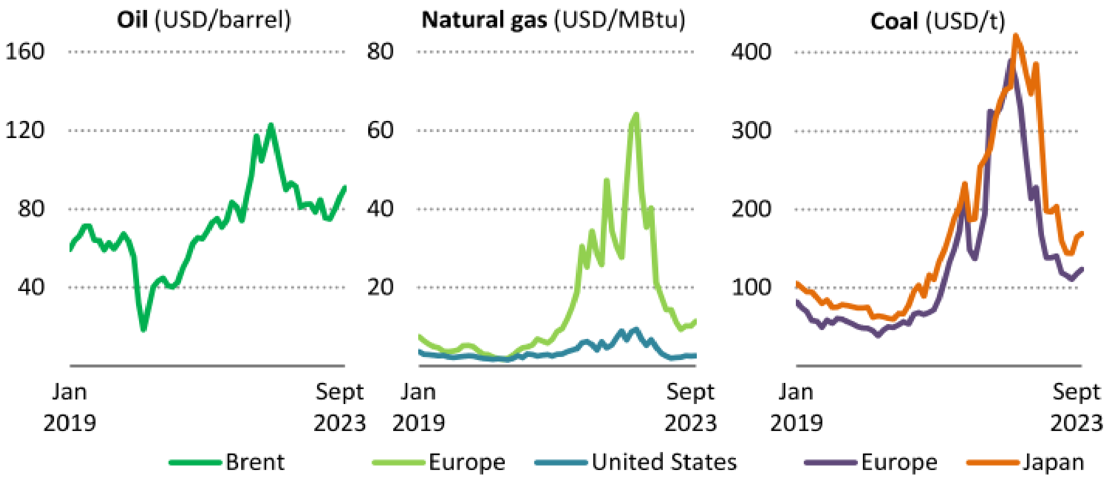

Figure 3: Prices for oil, natural gas and coal, January 2019 to September 2023

Source: US EIA (2023); Argus (2023); McCloskey (2023)

When hydrocarbons are extracted from wells, a mixture of oil, gas, and water are brought to the surface. This produced water differ in volume, from one to another depending on the geological formation. Produced water makes up 80% of the residuals and wastes generated during natural gas production and accounts for the majority of the waste stream in oil and natural gas production activities on offshore platforms (Al-Ghouti et al., 2019).

Produced water is gathered and treated for reuse, reinjected into the reservoir, or disposed of in accordance with environmental standards after being separated from hydrocarbons at the surface. Because of its complicated makeup which includes hydrocarbons, salts, heavy metals, and other contaminants where its management is essential to petroleum and natural gas operations.

2.1. Oil and natural gas field byproducts

Byproducts alongside primary hydrocarbon production including produced water, natural gas liquids, associated gas (often flared or processed) and condensates which are recovered during extraction and others like drilling cuttings, scale deposits from pipelines and waste gases such as carbon dioxide and hydrogen sulfide. Some of these byproducts like natural gas liquids and sulphur have commercial value while others such as produced water and drilling waste require treatment or disposal to mitigate environmental impacts (Abbas et al., 2021).

Water is frequently produced when natural gas and oil are extracted from onshore and offshore wells. Formation water is freshwater or saltwater that has been trapped alongside natural gas and oil for millions of years in a geologic reservoir made up of layers of impermeable rock in the earth crust and a porous sedimentary rock formation. The global production of produced water is still as much as 39.5Mm^3 day^{-1}. By 2025, it is anticipated that the water to oil ratio for crude oil resources will average 12 (v/v) due to well ageing (Al-Ghouti et al., 2019; Dickhout et al., 2017; Jiménez et al., 2018).

The composition of produced water might differ significantly based on the geological formation and the unique features of the oil or gas field. Salts, minerals, hydrocarbons, and occasionally minute amounts of naturally occurring radioactive elements are dissolved in it. Figure 4 shows the idealized petroleum reservoir where the produced water can be generated during the extraction, this produced water is separated from gas during the production process (Veil et al., 2004).

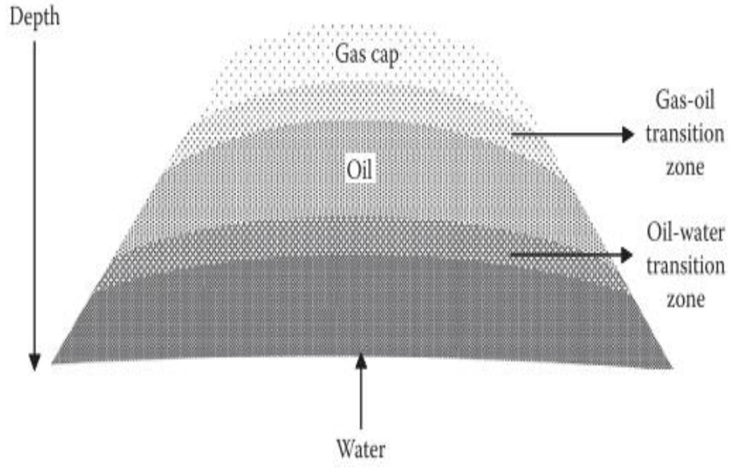

Figure 4: Schematic of an idealized petroleum reservoir showing gas, oil, and water distribution. Adapted from (Dandekar, 2013)

Note that due to capillary forces, which resist complete gravity segregation, water is also found (in small amounts) in all zones of the reservoir, including the gas cap.

Because it varies depending on the location and extraction process, produced water from oil or natural gas production does not have a set and consistent volume. Table 1 shows the case study of reported produced water volume across different countries. An estimated 667 million metric tons of produced water were discharged offshore throughout the world including 21.1 million tons to offshore water mostly in the U.S. Gulf of Mexico and 358 to 419 million tons to offshore waters of Europe mostly in the North Sea (Neff et al., 2011b).

Table 1: Volumes of produced water associated with gas production in different countries.

Country	Produced water bbl/year
USA	21,000,000
Australia	207,570,000
China	45,917,000
Colorado	92,274,300
Iraq	105,853,190
Oman	1.84×10^9
Qatar	50,508,816.54

Adapted from (Al-Ghouti et al., 2019; Clark & Veil, 2009)

More than 95% of produced water from hydrocarbon resource is disposed by reinjecting in the hydrocarbon well which may be associated with oil and natural gas production into a special underground injection control wells or into petroleum wells to enhance recovery or to sustain reservoir pressure (Clark & Veil, 2009).

Production water currently is handled through recycling, treatment, spreading, discharge, infiltration deep well injection depending on the geological profile and survey. The produced water after treatment and recycle can serve in different areas. The most fundamental and necessary needs for human beings is water which is used for different industrial and household purposes, food production, washing, sanitation, energy recovery, stages of water cycles, agricultural livestock mostly in regions with water scarcity (Plappally & Lienhard, 2012). Water can also serve in enhancing the production of hydrocarbons, hydraulic fracturing in the development of unconventional reservoir (Li et al., 2015).

2.1.1. Composition of produced water

Produced water, a complex mixture of organic (hydrocarbons and non-hydrocarbons), inorganic (metals, salts,...) and chemicals (Igunnu & Chen, 2014). These compounds appeared in the produced water as dissolved and dispersed oil compounds, dissolved formation minerals, production chemical compounds, production solids (including formation solids, corrosion and scale products, bacteria, waxes, and asphaltenes) and dissolved gases (Arthur et al., 2005; Igunnu & Chen, 2014).

The produced water-soluble organic compounds are polar constituents and found distributed in low and medium carbon ranges. Produced waters from gas reservoir are comparatively more harmful than oil production produced waters because they include larger levels of low molecular weight aromatic hydrocarbons including benzene, toluene, ethylbenzene, and xylene (BTEX) than oil operations produced waters do. Table 3 shows the heavy metals composition of PW and table 2 shows a summarized oilfield produced water components and other parameters. Table 4 shows in separate the organic composition of gas and oil field produced water components. According to studies, the produced water released from natural gas and condensate platforms are roughly ten times more hazardous than those released from oil platforms (Jacobs et al., 1992).

Table 2: Summary of oilfield-produced water parameters (Al-Ghouti et al., 2019; Al-Kindi et al., 2022; Fakhru'l-Razi et al., 2009; Jiménez et al., 2018; Nasiri et al., 2017)

Parameter	Values (mg/L)	Metals/Heavy metals	Values (mg/L)
Density (kg/m^3)	1014 – 1140	Calcium	13 -25800
Surface tension (dynes/cm)	43 – 78	Sodium	132 – 97000
TOC (mg/L)	0 – 1500	Potassium	24 – 4300
COD (mg/L)	1220	Magnesium	8 – 6000
TSS (mg/L)	1.2 – 1000	Iron	< 0.1-100
pH	4.3 – 10	Aluminium	310 – 410
Total oil (IR; mg/L)	2 – 565	Boron	5 – 95
Volatile (BTX, mg/L)	0.39 – 35	Barium	1.3 – 650
Base/neutrals (mg/L)	< 140	Cadmium	< 0.005–0.2
Total non-volatile oil and grease by GLC/MS base (µg/L)	275	Chromium	0.02 – 1.1
Chloride (mg/L)	80 – 200000	Copper	< 0.002-1.5
Bicarbonate (mg/L)	77 – 3990	Lithium	3 – 50
Sulfate (mg/L)	< 2 – 1650	Manganese	< 0.004-175
Ammoniacal nitrogen (mg/L)	10 – 300	Lead	0.002 – 8.8
Sulfite (mg/L)	10	Strontium	0.02 – 1000
Total polar (mg/L)	9.7 – 600	Titanium	< 0.01-0.7
Higher acids (mg/L)	< 1 – 63	Zinc	0.01 – 35
Phenols (mg/L)	0.009 – 23	Arsenic	< 0.005-0.3
VFA's (volatile fatty acids) (mg/L)	2 – 4900	Mercury	< 0.001-0.002
		Silver	< 0.001-0.15
		Beryllium	< 0.001 – 0.004

Table 3: Heavy metals in produced water (Stephenson, 1992b)

Metal	Average (µg/L)	Standard deviation (µg/L)	Maximum (µg/L)	Minimum (µg/L)
Cd	27	12	98	0
Cr	186	68	390	0
Cu	104	180	1455	0
Pb	315	670	5700	2
Ni	192	307	1674	0
Ag	63	17	152	12
Zn	170	253	1600	17

The organic components of produced water differ from platform to another depending on the nature of reservoir and oil or natural gas pre-treatment (Tibbetts et al., 1992).

Table 4: Phenols and volatile organic compounds in produced water (Stephenson, 1992b)

	Phenols (µg/L)	Benzene (µg/L)	Toluene (µg/L)	C_2 benzene (µg/L)
Gas production				
Average	4743	5771	5190	700
Standard deviation	5986	4694	4850	1133
Maximum	21522	12150	19800	3700
Minimum	150	683	1010	51
Oil production				
Average	1049	1318	1065	221
Standard deviation	889	1468	896	754
Maximum	3660	8722	4902	6010
Minimum	0	2	60	6

The organic constituents may be dispersed or dissolved. According to Dyke & Bartels (1990) & Stephenson (1992) the dispersed oil consists of small droplets suspended in the aqueous phase. Dispersed oil can rise on the surface and can cause a higher biological oxygen demand in the produced water handling process. Deep-water crude has a large polar constituent, which increases the number of dissolved hydrocarbons in produced water. The natural occurring hydrocarbons in produced water include organic acids, polycyclic aromatic hydrocarbons, phenols and volatiles. These components are largely responsible for the toxicity of produced water entering the environment. According to Azetsu-Scott et al. (2007) when produced water is combined with ambient seawater, it experiences physico-chemical changes, such as the precipitation of heavy metals.

2.4. Clay and vermiculite

2.4.1. Clay

Clay is a naturally occurring, fine-grained material composed primarily of hydrous aluminium silicates and other minerals like kaolinite, illite and montmorillonite, naturally mostly clay structure is of the phyllosilicate setting (Velde, 1992).Clay minerals, such as kaolinite, montmorillonite, and illite, are very reactive and versatile due to their layered structure, high surface area, and cation exchange capacity. Clays can be distinguished by their capacity to solidify when burnt, their hardness when dry, and their flexibility when wet. The study of clay mineralogy plays a significant role in understanding the geological processes related to the formation and migration of hydrocarbons in sedimentary rocks (Huggett, 2005; Jiang, 2012).

The clay can exhibit the following properties (Bergaya & Lagaly, 2006)

- ✓ One dimensional layer in the range of nanometres
- ✓ Anisotropy of the layers of particles
- ✓ Different types of surfaces, basal planar, interlayer surfaces, surface edges
- ✓ The probability of modifying external and even internal surfaces (by adsorption, ion exchange, grafting, etc.)
- ✓ Hardening on drying or firing.
- ✓ Colloidal sized particles
- ✓ Moderate layer charge
- ✓ Small pH dependent anion exchange capacity
- ✓ Tendency to intercalate foreign materials, such as macromolecules and organic compounds

- ✓ Presence of cations such as Li^+ to - and Na^+ to - exchanged forms to exhibit significant interlayer swelling in water. In ideal circumstances, the layers can fully delaminate
- ✓ The phyllosilicates, also known as the sheet silicate family which minerals are characterised by layered structures made up of polymeric sheets of SiO_4 tetrahedral connected to sheets of (Al, Mg, Fe)$(O,OH)_6$ octahedral.

According to Valkov & Simha (2012) one or more atoms can combine to form a plane (e.g., a plane of Si and Al atoms, a plane of basal oxygen atoms). Figure 5 shows how the structure of an "octahedral sheet" is made up of edge-sharing octahedral and "tetrahedral sheet" is made up of continuous corner-sharing tetrahedral. The interlayer material that keeps the layers apart can be organic compounds, hydroxide octahedral sheets, cations or hydrated cations.

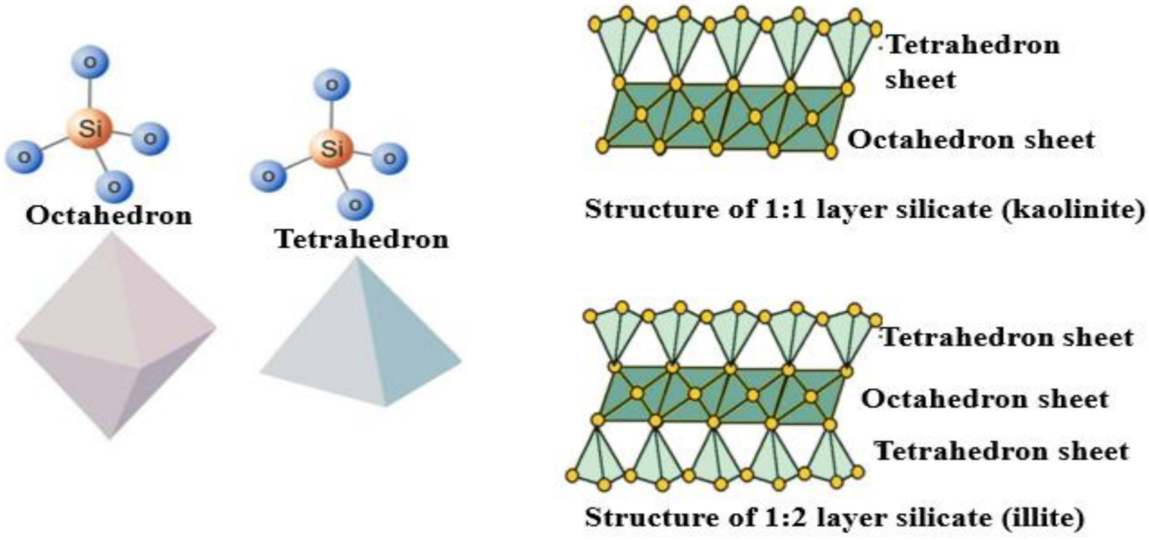

Figure 5: Octahedron and tetrahedron structure form of clay (Al-Ani & Sarapää, 2008)

2.4.1.2. Vermiculite

Vermiculite is a mica-type trioctahedral silicate clay mineral with 2:1 layered structure like the well-known montmorillonite. From figure 6 the model structure of vermiculite shows that each layer is composed of octahedrally coordinated cations that are Mg^{2+}, $Al^{3+}$and Fe^{3+} sandwiched by tetrahedrally coordinated cations that are Si^{4+} and Al^{3+} (W. Wang & Wang, 2019). The interlayer cations balance the negative charge generated by isomorphic substitutions (e.g., Al^{3+} replacing Si^{4+} in tetrahedral sheets or Mg^{2+} replacing Al^{3+} in octahedral sheets).

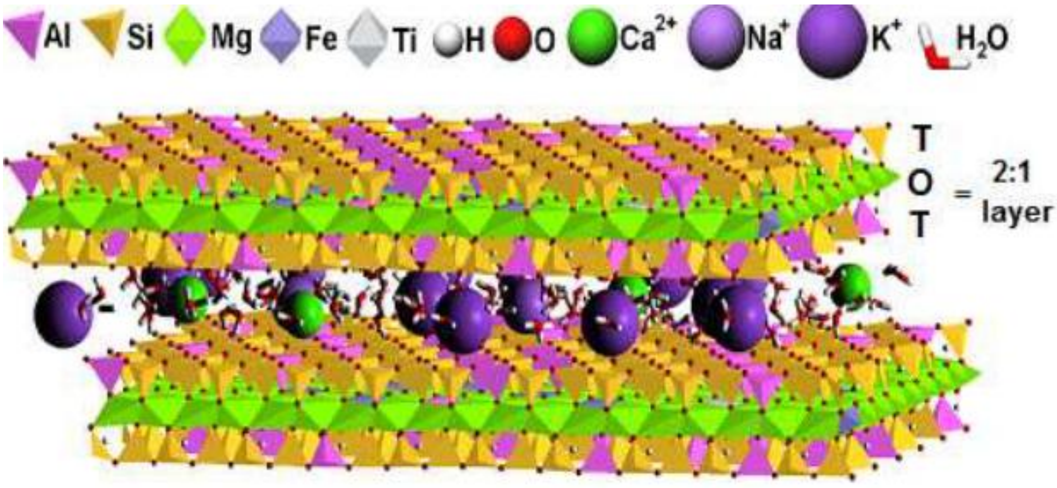

Figure 6: Model of the structure of vermiculite (Adapted from Valkov & Simha, 2012)

Vermiculite has a talc-like structure in which some Fe^{3+} has been substituted for Mg^{2+} and some Al^{3+} for Si^{4+} with the resulting charge balanced by hydrated interlayer cations, most commonly Mg^{2+} (Huggett, 2005). Figure 7 and figure 8 show the vermiculite that is a 2:1 phyllosilicate clay mineral with a layered structure consisting of two tetrahedral silica sheets sandwiching an octahedral alumina sheet and the interlayer space containing exchangeable cations (e.g., Mg^{2+}, Ca^{2+}) and water molecules which allows significant expansion or even exfoliation upon heating. This structure grants vermiculite high cation exchange capacity, adsorption properties and thermal stability.

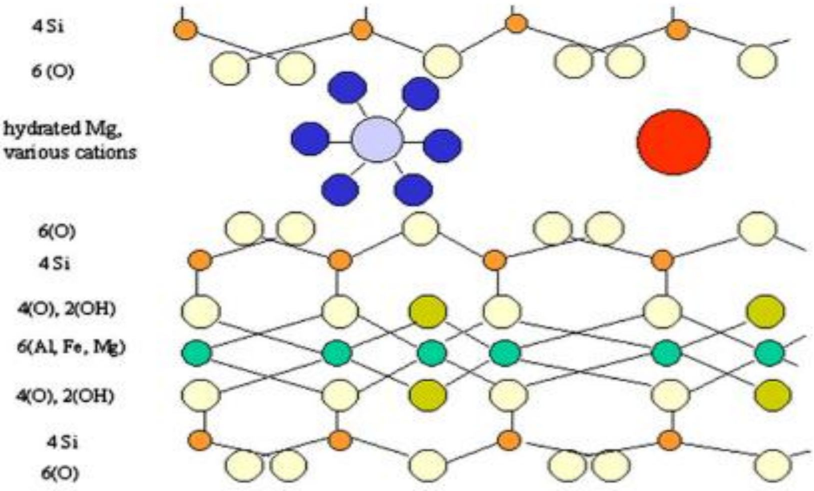

Figure 7: Diagrammatic representation of vermiculite (Zhang et al., 2009)

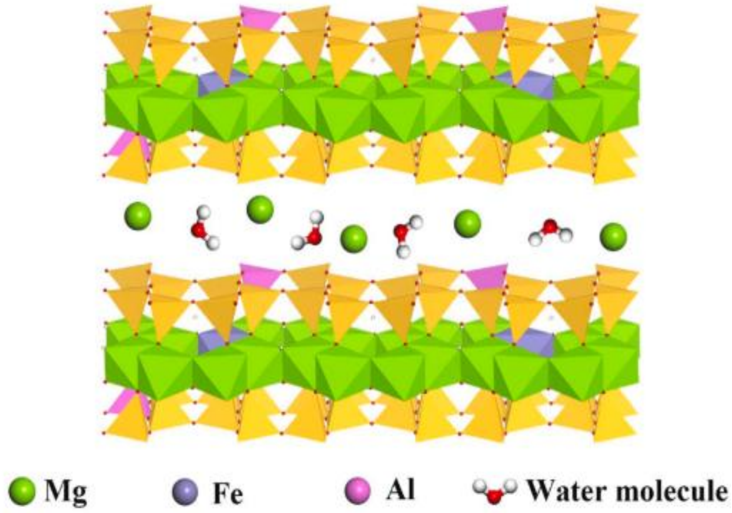

Figure 8: Schematic diagram of VMT structure.

According to Li et al. (2021) the single layer of VMT has a typical 2:1 structure, which consist of two layers of silicon oxygen tetrahedron sandwiched by a layer of magnesium oxygen octahedron. There are many cations, such as $K^{+,}$ Mg^{2+}, Ca^{2+} and so on, in the interlayer of VMT to maintain electrical balance. The chemical formula of vermiculite can be generally expressed as $(Mg, Ca)_{0.3-0.45}(H_2O)_n \{(Mg, Fe, Al)_3(Al, Si)_4O_{10}(OH)_2\}$ (Salih et al., 2022).

2.4. Cation exchange capacity

The measure of the power of clay to swap its interlayer cations is measured by cation exchange capacity. The CEC which is the quantity of basic filler material carried by the interlayer cations that can be exchanged out to equalize the electrical charge of 100 grams of calcined clay (Jlassi et al., 2017).

According to Huggett (2005), because of their huge surface area and small particle size, clay minerals have a comparatively high CEC. The surfaces of the particles in the structure of clay minerals have negative charges, which draw and retain cations. Depending on the particular type of clay, the strength of this attraction and the total ability to store these cations vary. Table 5 shows the CEC which the essential characteristic of clay and other soil types signifying the capacity to retain and swap cations such calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^{+}) and sodium (Na^{+}).

Table 5: Typical values for cation exchange capacities of some clays

	meq/100g
Kaolinite	3-18
Halloysite	5-40
Chlorite	10-40
Illite	10-40
Montmorillonite	60-150
Vermiculite	100-215

Cation exchange capacity in milliequivalent per gram

2.5. Swelling capacity

Due of its layered structure and water-absorbing capacity, vermiculite has a high swelling capacity. Vermiculite expands dramatically when exposed to heat; this process is called exfoliation. Water trapped in its layers evaporates quickly, causing the material to inflate up to eight or thirty times its initial size. Table 6 illustrates the characteristics of clay types including surface area and swelling potential.

Table 6: Summary of clay mineral properties (J. Xu et al., 2005)

		interlayer condition/bonding	CEC [cmol/kg]	swelling potential	Specific Surface area(m^2/g)	Basal spacing
Vermiculite	2:1(expanding)	Weak bond, great expansion	100-150	High	500-700	1.0-1.5+
Kaolinite	2:1(non-expanding)	Lack of interlayer surface, strong bonding	3-15	Almost none	5-20	0.72
Montmorillonite	2:1 (expanding)	Very weak bonding, great expansion	80-150	High	700-800	0.98-18+
Hydrous mica	2:1(non-expanding)	Partial loss of K, strong bonding	10-40	Low	50-200	1.0
Chlorite	2:1:1 (expanding)	Moderate to strong bonding, non-expanding	10-40	None	-	1.4

See also: The data cited from the work of Sabine Grunwald, University of Florida, USA. http://grunwald.ifas.ufl.edu

2.5. Clay vermiculite modification

From a statistical perspective, geologists employ accurate terminology to classify clay minerals, which exhibit a uniform structure. These minerals generally originate from chemical alterations or thermal fluctuations in proximity to the Earth's surface.

2.5.1. Thermal expansion of vermiculite

Clay minerals typically form within a temperature range of 4 to 250°C. When temperatures exceed this range, sheet silicate minerals are categorized as metamorphic and often display larger grain sizes compared to those characteristic of clay minerals (Velde, 1992). The properties of the clay surface can be markedly changed when clay minerals are subjected to mild to moderate heat treatment. Figure 9 shows the expansion and exfoliation mechanism of clay where vermiculite flakes expand and exfoliate in response to high-temperature heat ranges from 700°C to 1000°C for few minutes in a muffle furnace. The substantial expansion of vermiculite upon heating implies that the material properties could be improved by intercalation or other chemical procedures (Adewuyi and Oderinde, 2019; Marcos and Rodríguez, 2010).

As a result, the mechanisms behind VMT expansion and exfoliation are closely related. The degree of VMT interlayer interaction force weakening is the primary factor separating exfoliation from expansion where exfoliation of VMT happens when the rapid heating of vermiculite causing trapped water to vaporize and separate the layers (the interlayer interaction force weakens to a certain level) of the mineral into accordion-like flakes, significantly increasing vermiculite volume (Li et al., 2021).

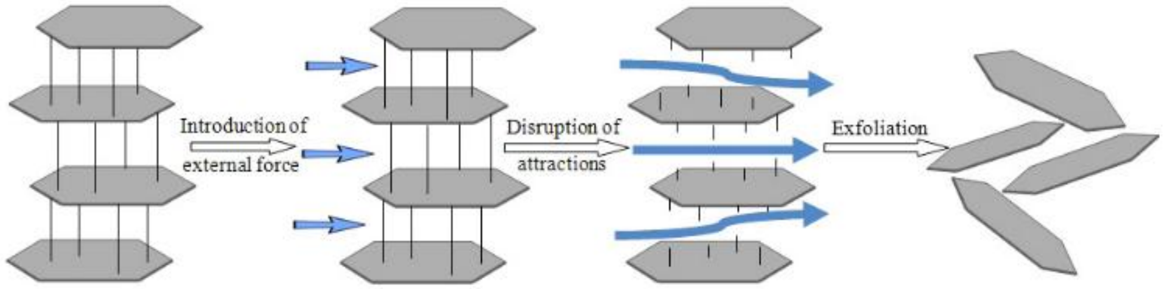

Figure 9: Schematic representation of the mechanisms for the exfoliation of silicate minerals (Jia & Song, 2014)

Because exfoliation exposes the surfaces between VMT layers, the exfoliated VMT nanosheets have a greater specific surface area than expanded VMT. The freshly exposed VMT nanosheet surface following exfoliation contains a high number of reactivity reaction sites, making it more reactive than expanded VMT (M. Li et al., 2021). The shift in surface characteristics happens mainly because of the redistribution of hydrated cationic species in the clay interlayers and dehydroxylation of the clay silanol and aluminol groups. As a result, the clay surface's electronegativity may alter, which could have an impact on how the substance interacts with pollutants in the environment. The pore size distribution and surface area of clay minerals can also be altered by heat treatment (España et al., 2019; Toor et al., 2015).

2.6. Organomodification

Vermiculite flakes have numerous industrial uses because of their capacity to expand and exfoliate when exposed to high temperatures (Malla, 2018). The exfoliation induces the required surface area and spaces where an organic cation such as quaternary ammonium ions replace the hydrophilic interlayer cations such as Na^+ and Mg^{2+} which results in the surface to become organophilic. Organomodification transforms naturally hydrophilic vermiculite into an organophilic material. Figure 10 shows the process of preparing organoclays which involves the incorporation of organic molecules in vermiculite. In organomodification the most and commonly used organic molecules for clay modification are cationic ammonium (quaternary) surfactant (Wang et al., 2011; Zhang et al., 2009). Organomodification of vermiculite involves chemically altering its surface to enhance compatibility with organic polymers which improves its dispersion and performance in composite materials.

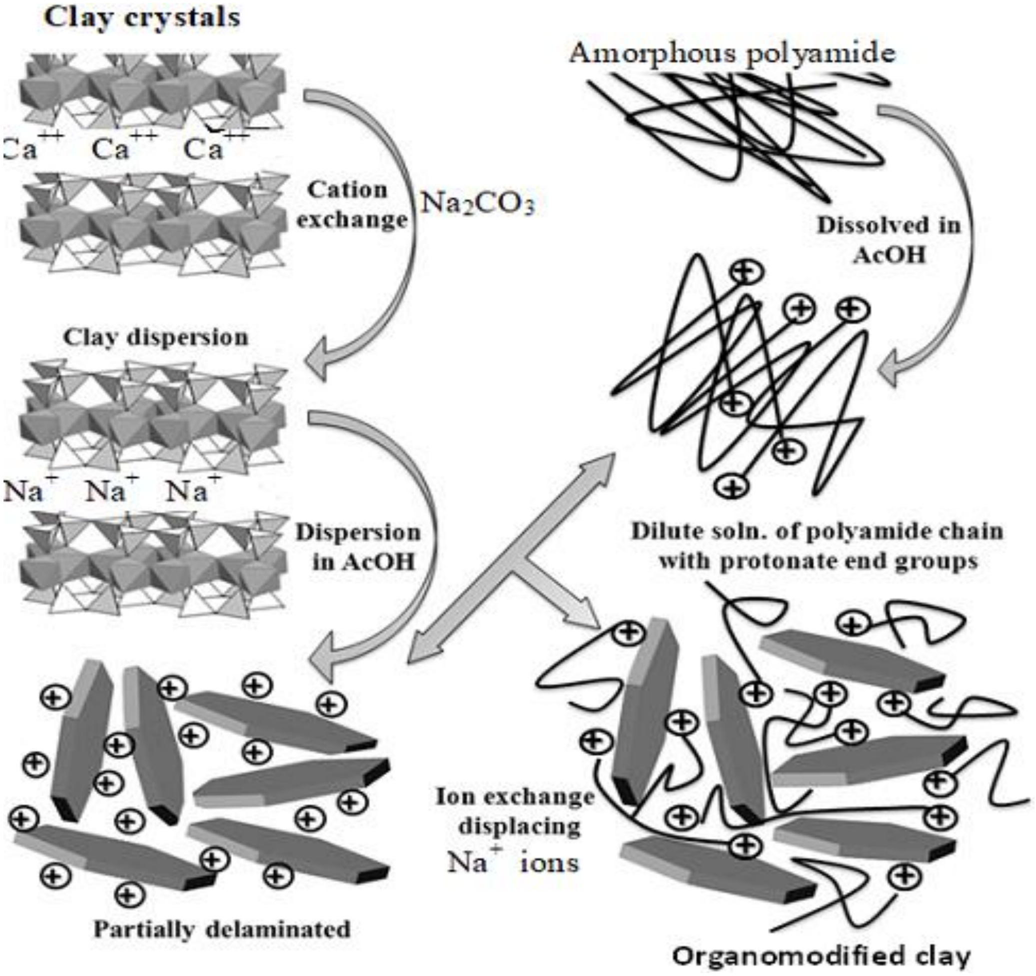

Figure 10: Schematic representation of the route to clay organo-modification via solution intercalation of the polymer chains. Adapted from (Macheca et al., 2014a)

2.7. Adsorbent characterisation

In the study and understanding the vermiculite adsorption behavior, pore structure, and surface characteristics, porosity, thermal stability and composition using different analytic methods.

BET (Brunauer-Emmett-Teller) is the common method used for the surface area measurements. The process involves nitrogen gas adsorption at cryogenic temperatures to determine surface characteristics with exfoliated vermiculite typically showing increased surface area due to layer separation. Meanwhile, particle distribution of vermiculite often analysed via laser diffraction or dynamic light scattering which evaluates the size range and uniformity of its flakes or granules.

Scanning Electron Microscopy (SEM) for images of the surface morphology. The characterisation that involves coating the sample with a conductive material (e.g., gold or carbon) to prevent charging and then exposing it to a focused electron beam in a high-vacuum chamber. The emitted secondary electrons generate high-resolution images revealing surface morphology, layer separation and exfoliation characteristics at micro to nanoscale resolutions (Batista et al., 2021).

X-ray diffraction (XRD) of vermiculite involves directing a monochromatic X-ray beam at the sample and measuring the angles and intensities of the diffracted rays to determine the crystal structure, phase composition, and interlayer spacing. The characteristic basal spacing shifts upon heating or organomodification revealing dehydration, exfoliation or intercalation effects. XRD identifies impurities and quantifies crystallinity or amorphous.

Thermogravimetric analysis (TGA) involves heating the vermiculite sample at a controlled rate in a specified atmosphere (e.g., air or nitrogen) while continuously measuring its weight loss. This process reveals key thermal behaviors such as dehydration (loss of interlayer water at ~100–200°C), dehydroxylation (structural OH loss at ~500–900°C) and organic modifier decomposition.

X-ray Fluorescence (XRF) analysis of vermiculite involves irradiating the sample with high-energy X-rays causing its atoms to emit secondary (fluorescent) X-rays with element specific wavelengths. By measuring these emitted wavelengths and their intensities the XRF determines the elemental composition (e.g., Mg, Al, Si, Fe, K) and quantifies oxides (e.g., SiO_2, MgO, Al_2O_3) present in vermiculite.

2.8. Waste water handling

Produced water is most often considered a waste (Arthur et al., 2005). Waste water from the oil sector is one of the major causes of water contamination. Water pollution is caused by the presence of oil, oil derivatives and other organic materials in it (Magar & Jadhav, 2020).

Industrial operation such as metal-cutting, forming, rolling, and finishing processes, manufacturing and machining facilities typically use machining coolants. Oil-in-water emulsions with a 2 to 5% oil concentration stabilized chemically are commonly used as coolants. About 30,000 mg/Litre free floating oil content and an emulsified oil concentration of 300–7,000 mg/Litre can be found the wastewater that is discharged from the industrial washers used to clean the produced parts. Reusing the water requires the removal or significant reduction of these oils (Weintraub et al.1983).

The storage, transportation, treatment, and disposal of water are all important aspects of unconventional oil and gas extraction (Smith et al., 2017). Numerous oil firms may nearly be considered water corporations considering that every 75 million barrels (11.9 million m^3) of oil produced globally each day results in around 210 million barrels (33.4 million m^3) of water being produced. The expense of handling water is high; estimates for each barrel of water vary from 5 to over 50 cents. The cost of treating water in an oil producing well with an 80% water cut might reach $4 for every barrel of oil produced (Bray, 2023).

Naturally existing in the subsurface formations, produced water is a by-product of the extraction of oil and gas and frequently contains a variety of pollutants. Reservoir water contains differing concentrations of inorganic contaminants than seawater, including minerals and heavy metals from the geological formations (Strømgren et al., 1995). Environmentally friendly produced water management procedures are also required, or the operator risked regulatory action. The process for handling produced water is determined by the type of water, its location, its volume, and the resources that are available (Arthur et al., 2005).

The results and effects of releasing produced water into the environment have recently grown to be a serious environmental problem due to the increasing volume of trash created worldwide. Therefore various physical, chemical and biological techniques are used in the conventional treatment of produced water. Because of the limited area on offshore platforms, small physical and chemical systems are utilized to handle the management of produced water (Fakhru'l-Razi et al., 2009).

In order to satisfy beneficial use requirements or pre-disposal regulation limits, generated water may need to be treated. Oilfield water treatment can enable producers have more alternatives for managing their water resources, including advantageous uses that may eventually bring about financial and social benefits. The waste water management and handling must environmentally viable and eco-friendly.

The technologies of produced water treatment as centrifuge, gas floatation, hydro cyclone, lime softening, reverse osmosis, constructed wetland, others may be used. The adsorption technique of produced water treatment using different adsorbents demonstrated the lower energy demand and straightforward process can lead to reduced operational costs compared to other treatment technologies and also economic and flexible produced handling and management (Mao et al., 2021; P. Xu et al., 2008).

Groundwater and various process waters are frequently contaminated with oil and grease. Fats, lubricants, cutting fluids, heavy hydrocarbons like tars, grease, crude oil, and diesel oils, and light hydrocarbons like kerosene, jet fuel, and gasoline can all be found in produced water. When clay is modified becomes organophilic and its affinity with organic molecules increases. Oil, grease, and other organic materials that are soluble only partially can be eliminated with the application of modified clay (Alther, 1995; Rodrigues et al., 2010). Adsorption is a kind of simple and effective method for pollute water treatment to remove the contaminant in pollute, such as oil (de Araújo Medeiros et al., 2009; Ugarte et al., 2005). Nevertheless, the hydrophilic nature of the vermiculite surface leads a low oil removal. Several methods to produce more hydrophobic vermiculite with higher oil adsorption are based on polymer coating

Because of their small particle sizes, high specific surface area, and high cation exchange capacity, clays have the ability to extract heavy metal contaminants from aqueous solutions. The substitution of Mg^{2+} and Fe^{2+} in place of Al^{3+} in the octahedral positions and, to a greater extent, Al^{3+} in place of Si^{4+} in the tetrahedral positions is known to cause vermiculites to have extremely high cation exchange capacities ranges from 120 to150 meq/100 g (Malandrino et al., 2006).

Due to the large CEC and the existence of localized charge sites vermiculite serve as an extremely effective agent for eliminating hazardous cations from aqueous solutions, including Cu^{2+}, Pb^{2+}, Cd^{2+}, $Zn^{2+,}$ and Ni^{2+} (J.Ugarte & Monte, 2005) and as a negative side brought by industrialization, heavy metals disposals are not biodegradable and damage the environment. Adsorption is being popular to be an economically viable alternative technique for removing metal ions from wastewater and water supplies (Badawy et al., 2010).

2.9. Equilibrium and kinetic studies

The study of adsorption isotherms deals with how adsorbate molecules disperse between the liquid/gas phase and the solid phase (adsorbent) at equilibrium. Any adsorbate/adsorbent system the most popular method too obtain isotherm parameters is to do equilibrium studies at various solution volumes, adsorbent masses or starting pollutants concentrations which is a crucial consideration in adsorbent design. Also studies the impact of solution volume to the adsorbent mass ratio (V/M) on the equilibrium uptake of pollutant solution at various starting concentrations (Periasamy & Namasivayam, 1994). Freundlich and Langmuir isotherm describe if the adsorbate/adsorbent interaction is homogeneous/heterogeneous and even give the characteristic of the monolayer or multilayer adsorption process.

The kinetics study which merely describe the rate mechanism of interaction between adsorbent and adsorbate (pollutants) which arise the understanding adsorption rate dependence on the difference between equilibrium and current adsorption (first order) or adsorption rate dependence on the square of available adsorption sites (Second order), which all both equilibrium and kinetic studies improve the optimization of industries applications (Nandi et al., 2008).

CHAP 3.

3. MATERIALS AND METHODS

3.1. Materials

Vermiculite is a natural mineral that is created when biotite or phlogopite, which are both members of the mica group of minerals weather or alter (Muiambo et al., 2015; Valkov & Simha, 2012). Vermiculite is a clay type of magnesium-aluminium-iron silicate that is hydrated and laminar. Mg-VMT grade superfine (1 mm size) from Palabora Complex Mining (South Africa) was obtained from Mandoval Vermiculite. Chemically, Palabora VMT is a trioctahedral VMT intermediate between mica and VMT. The polyamide of choice is dimer fatty acid-based polyamide (co-polyamide - Euremelt 2140 grade) which is supplied by Huntsman Advanced Materials and all the chemicals are obtained from UEM chemical engineering department laboratory and used the way they are.

3.2. Methods

3.2.1. Clay preparation and characterization

3.2.1.1. Raw vermiculite preparation

Thermal expansion of vermiculite is a process that involves heating the mineral to cause exfoliation or expansion, which results in its characteristic lightweight structure. Vermiculite (VMT) has a unique characteristic of volume expansion after heating, forming highly porous material called expanded VMT, which can be further exfoliated into two-dimensional nanosheets (M. Li et al., 2021). The raw vermiculite was washed with distilled water to remove impurities and dried at 70$^{℃}$ in a period of 6 hours to evaporate the water. Thermal treatment involves heating up the raw clay minerals to the desired temperature (200 °C–1000 °C) for a given period of time (mostly 2–4 h) (España et al., 2019).

3.2.1.2. Exfoliation and delamination of vermiculite using thermal shock

Most of vermiculite when heated quickly to above about 230 °C will lose their interlayer water which induces to flakes exfoliating to form concertina shaped granules (Addison, 1995). The vermiculite was heated at 700°C in a 12min time in a muffler. The expanded flakes of vermiculite after cooling are brought to mill for size conditioning, milled vermiculite can then be sieved with a 200-mesh sieve to obtain particles of the desired size, such as 75 micrometres (µm). The 75 µm vermiculite powder can be ready to the next step of organomodification (see figure 8 in chapter 2).

Figure 11: Raw vermiculite and high temperature muffle furnace

Figure 12: Mill, 200 mesh sieve and ultraturax rotator

Figure 13: Mortar and pestle

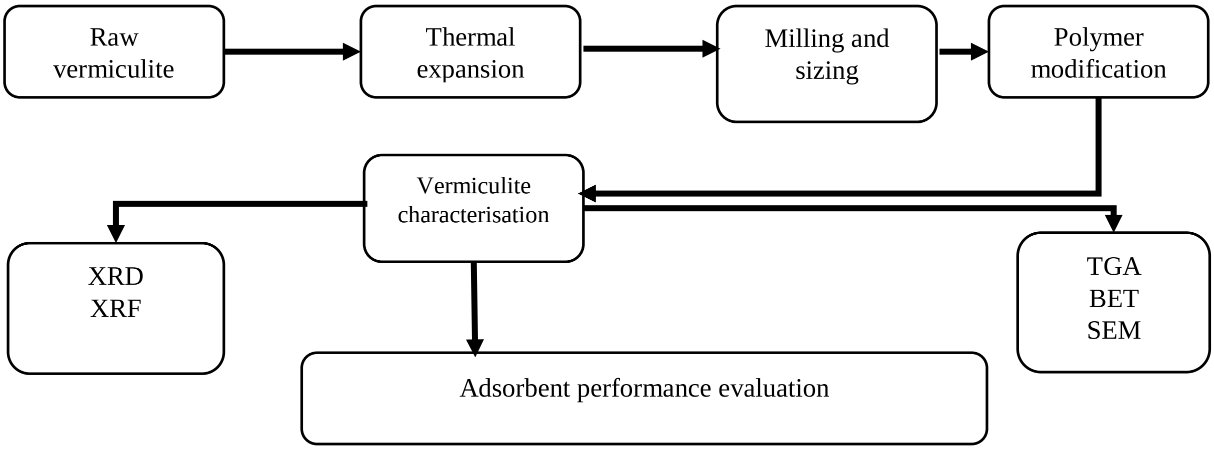

Figure 14: Workflow diagram

3.2.1.3. Vermiculite modification with polymer

- ✓ The 10% fatty acid polyamide was prepared by weighing 100g sample of the polyamide (polymer)and dissolved in a well measured volume of glacial 99% acetic acid in 1000ml stainless container (Macheca et al., 2014b).
- ✓ The mixture was then stirred at a 100rpm to make homogenous solution and heated to 40°C to enhance a proper dissolution of polyamide in acetic acid.
- ✓ Three samples of 150g of 75 µm vermiculite were weighed and put in a 2L glass, the glacial 99% acetic acid was added to the VMT to make a slurry. Using the ultraturax the solution were mixed at 2000rpm for 10 minutes to form a homogenous
- ✓ A well measured volume of polymer solution was poured to the slurry VMT and a stirr the mixture period of 30 minutes at 2000rpm. The corresponding volumes of polyamide to make the concentration 2.5%w/w, 5.0 %w/w and 7.5% w/w were used respectively.
- ✓ Then the organomodified vermiculite was kept for 3 days. The organomodified was washed three times per day to remove excess solvent.
- ✓ After the removal of excess solvent, the organovermiculite was dried in an over at a temperature of 70°C.
- ✓ After drying, the organomodified cake was remilled using mortar and pestle and resized using the same mesh to reach 75 µm prepared sample

3.2.1.4. Cation exchange capacity measurement

The cation exchange capacity is calculated by saturating the vermiculite sample with ammonium cation (ammonium acetate method) and then measuring and displacing the adsorbed cations (Campos et al., 2009; Lutenegger, 2022).

- ✓ The well ground vermiculite sample with a size less than 2mm is prepared
- ✓ Sample the 2g of well dried vermiculite
- ✓ Wash the sample with distilled water to remove soluble salts and dry the sample in oven at 105°C for 24 hours

a) Vermiculite saturation with ammonium ions

- ✓ Place the sample in an Erlenmeyer flask followed by the addition of 50mL of 1M ammonium acetate solution
- ✓ Using a magnetic stirrer, stir for 30min at moderate rate and at room temperature
- ✓ Decant the solution and repeat 3 times to ensure that exchange sites are saturated with ammonium ions.
- ✓ Wash the sample with enough distilled water to remove the excess ammonium ions from the solution

b) Cation displacement with exchangeable cations

- ✓ Add 50mL of 1M potassium chloride to the saturated vermiculite and stir the mixture for 30min.
- ✓ Repeat for three times

c) Quantification of the cation

- ✓ Analyse the concentration of ammonium ions using Uv-visible spectrophotometer

$$\mathrm{CEC} = \frac{\mathrm{NH_4^+\ released\ in\ meq.}}{\mathrm{mass\ of\ the\ sample\ in\ grams}} \times 100 \qquad (1)$$

Where, NH_4^+ is the concentration of ammonium ions in meq/L, reading from UV-visible spectrophotometer and 100 is the conversion factor to meq/100g.

3.2.1.5. Clay samples characterizations

Elemental composition was determined using X-ray fluorescence (XRF) spectroscopy. Major elemental analysis was executed on fused beads using an ARL9400XP+X-ray fluorescence

(XRF) spectrometer. The samples were milled in a tungsten carbide milling pot to achieve particle sizes <75 µm and dried at 100°C and roasted at 1000°C to determine the loss on ignition (LOI) values. Then 1 g sample was mixed with 6 g of lithium tetraborate flux and fused at 1050°C to make a stable fused glass bead. The Thermo Fisher ARL Perform'X Sequential XRF with OXSAS software was used for analyses.

X-ray diffraction was conducted on a PANalytical X'Pert Pro powder diffractometer with an X'Celerator detector and variable divergence and receiving slits with Fe-filtered CoK α radiation (λ= 0.17901 nm) in the 2θ range of 2–60° at a scan rate of $1.0^{\circ}\text{min}^{-1}$.

Thermogravimetric analysis (TGA) was performed on a Perkin Elmer Pyris 4000TGA instrument using the dynamic method. About 15 mg of the sample (vermiculite or polymer) was placed in open 150µL alumina pans. Temperature was scanned from 25 to 950°C at a rate of 10°C min^{-1} with air flowing at a rate of 50 mL min^{-1}.

Particle size distribution, in the range 0.01µm to 10 mm, was determined using the low angle laser light scattering (LALLS) method on a Malvern Mastersizer 3000 instrument. The refractive indices used were 1.520 (for vermiculite) and 1.330 (for water).

Specific surface area was determined using nitrogen and the BET method at liquid nitrogen temperatures with a MicrometricsTristar II BET instrument. Prior to measurements, samples were degassed under vacuum (10^{-3} mbar) at100°C for 24 h.

A Zeiss Ultra 55 FESEM Field emission scanning electron microscope (FESEM) was used to study the morphology of the vermiculite samples and the fracture surface morphology of the composites at 1 kV. The vermiculite samples were coated with carbon prior to analysis.

3.2.2. Adsorption studies of prepared samples

Vermiculite's adsorption capacity is crucial to assess its potential as an environmental remediation agent. Both the complexity and diversity of pollutants (organics and heavy metals) found in oil and natural gas produced water challenge vermiculite's ability to securely fasten harmful substances to its layered particles (Brião et al., 2021).

Making stock solutions with established quantities of each targeted pollutants is the first step in simulated water with phenol or copper produced water for calibration standards. Figure 15, for phenol make a high-concentration stock solution of 1000ppm by dissolving well measured quantity of pure phenol in distilled water. To obtain a comparable high-concentration stock solution for copper, dissolve a known quantity of copper sulphate ($CuSO_4 \cdot 5H_2O$) in distilled water. Use serial dilution techniques to create a set of five diluted standards that are 50 ppm, 100 ppm, 150 ppm, 200 ppm, 250 ppm. Utilize analytical technique UV-Visible spectrophotometry for phenol (which measures absorbance at 270 nm) and 610 nm for copper to confirm the amount of the substances.

Note that the copper standards, put two drops of 20% ammonia to make colored complexes before measuring the absorbance. From the figure below the absorbance against concentration are best fitted with a correlation coefficient greater than 0.9. The copper and phenol are targeted as one of the components (refer to table 2, table 3 and table 4 in chapter 2) of produced water that can be simulated for the study of bio-organoclay performance and characterization as adsorbent.

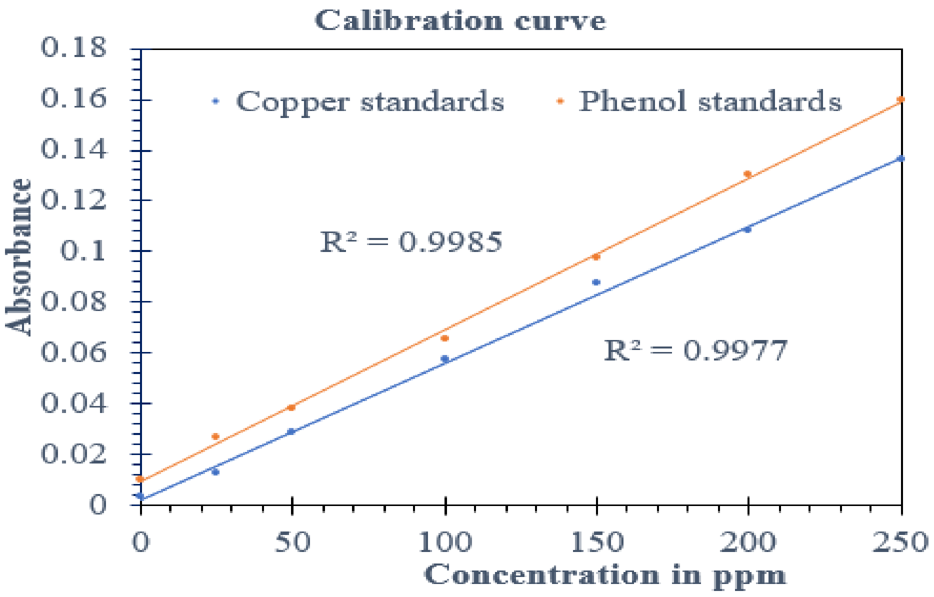

Figure 15: Calibration curve of Copper and Phenol standards

3.2.2.1. Equilibrium study

To determine when adsorption reaches equilibrium and vermiculite's ability to adsorb a copper or phenol components at a set temperature (room temperature of 30$^{\circ C}$). This entails calculating the correlation between the adsorbate(phenol or copper) concentration in the solution C_e and the amount adsorbed onto vermiculite q_e (Das & Bandyopadhyay, 1992). The equation 2 is used to calculate adsorption efficiency.

$$q_e = \frac{(C_o - C_e)\,V}{m} \qquad (2)$$

Where:

q_e: adsorption efficiency in mg/g

C_0: Initial copper/phenol concentration (mg/L)

C_e: Equilibrium copper/phenol concentration (mg/L)

V: Volume of the solution (L)

m: Mass of the vermiculite(adsorbent) in grams.

Although initial batch tests have found that vermiculite can reliably retain moderate amounts of heavy metals and organic chemicals per gram, further exploration of its adsorption capacity in a wide range of real-world mixtures is still required. The development of vermiculite as an efficient clean-up tool depends on clarifying its adsorptive behaviour under different conditions to guarantee any recruited vermiculite will thoroughly extract all imminent toxins from a given medium (Salih et al., 2022).

3.2.2.2. Equilibrium isotherms

a. Langmuir isotherm

Such a monolayer adsorption on a homogenous surface of the adsorbent

$$\mathrm{q_e} = \frac{\mathrm{q_{max}\,K_L\,C_e}}{\mathrm{1+K_L C_e}} \qquad (3)$$

Where q_{max} is the maximum capacity in mg/g and K_L is the Langmuir constant in L/mg

Linearizing Langmuir equation, we have:

$$\frac{\mathrm{C_e}}{\mathrm{q_e}} = \frac{1}{\mathrm{q_{max}\,K_L}} + \frac{\mathrm{C_e}}{\mathrm{q_{max}}} \qquad (4)$$

b. Freundlich isotherm

Such a multilayer adsorption on a heterogeneous surface of the adsorbent

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (5)$$

Where K_F is the Freundlich constant in (mg/g) (L/mg) $^{1/n}$ and n is the heterogeneity factor.

Linearizing Freundlich equation we have:

$$ln\ q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (6)$$

3.2.2.3. Kinetic studies

The goal of a vermiculite adsorption kinetic study is to assess how quickly an adsorbate such as copper ions, phenol, or other contaminants are eliminated from a solution over time. It offers information on process efficiency and design and aids in identifying the adsorption mechanism, including whether it adheres to physical or chemical adsorption (Długosz & Banach, 2018).

a) Pseudo-first order model:

$$\frac{dq_t}{dt} = k_{1(}q_e - q_t) \text{ o r } q_t = q_e(1 - e^{k_1 t}) \quad (7)$$

Linearizing the equation 7 we have:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

Where q_t is adsorption capacity at time t in (mg/g), q_e is the equilibrium adsorption capacity (mg/g), k_1 is pseudo-first-order rate constant in min^{-1} and t is time in minute.

b) Pseudo-second order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

Where k_2 is the pseudo-second-order rate constant (g/mg.min)

CHAP 4.

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4. RESULTS AND DISCUSSION

4.1. Scanning Electron microscope (SEM)

When heated, the hydrous phyllosilicate mineral vermiculite expands (exfoliates) because interlayer water quickly turns into steam. The morphology of thermal exfoliated vermiculite is investigated using a local chemical analysis sample scanning electron microscope. The micrograph generated at an accelerating voltage of 1.0Kv enhances the vermiculite surface details for both neat vermiculite (figure 16a and b) and thermal exfoliated (figure 16c and d).

SEM images (figure 16a and b) neat vermiculite exhibit a highly porous, accordion-like structure. The layers of vermiculite are separated showing voids and gaps between the flakes. The flakes appear thin and irregular, with curled edges, indicating successful exfoliation; wavy edges are characteristics of exfoliated vermiculite (see figure 16c and d). At a working distance of 3.5mm and accelerating voltage of 1.0Kv with a scale of $20\mu m$ the micrograph figure 16.b displays the voids between the layers of vermiculite, which are visible as dark areas in the SEM image.

Figure 16c and d, display the concertina-like expansion caused by 700°C temperature shock during thermal expansion. At a working distance of 2.4mm and accelerating voltage of 1.0Kv with a scale of $100\mu m$ the micrograph shows accordion vermiculite flakes surface as a success of thermal shock.

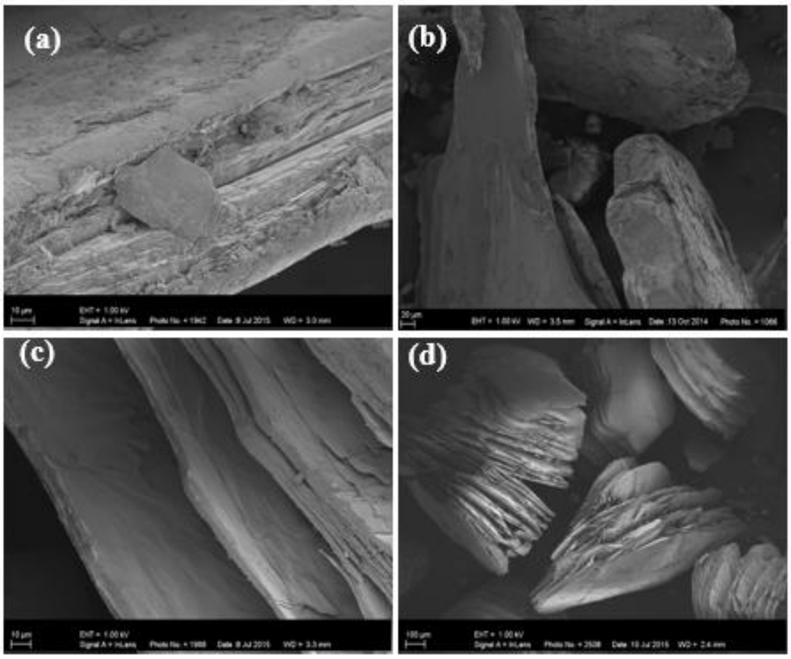

Figure 16: SEM micrograph of raw vermiculite

4.1.2. Thermogravimetric analysis

Figure 17 and 18 of thermally exfoliated vermiculite and organovermiculite 7.5% VMT show the weight loss as a function of temperature. Figure 17 shows the vermiculite that has been heated to high temperatures, causing it to expand and exfoliate. And then subjected to gradual temperature change; the weight loss below 100°C is often caused by the evaporation of moisture and adsorbed water. The relative weight loss between 100°C and 700°C is due the dehydroxylation structure of vermiculite and the destruction of Van der Waals forces in the molecular structure. Thermally exfoliated vermiculite has a relative mass loss of up to 93% at a temperature of over 400°C. This is attributed to vermiculite natural structural bonds which are strong ionic bonds between magnesium and aluminium that contribute to the stability of vermiculite crystal lattice. The organomodified 7.5% VMT shows a stable relative mass at 65% above 400°C due to either the dehydroxylation of the vermiculite structure itself or the breakdown of any residual organic material (Song et al., 2021; Su et al., 2016; Tuchowska et al., 2019).

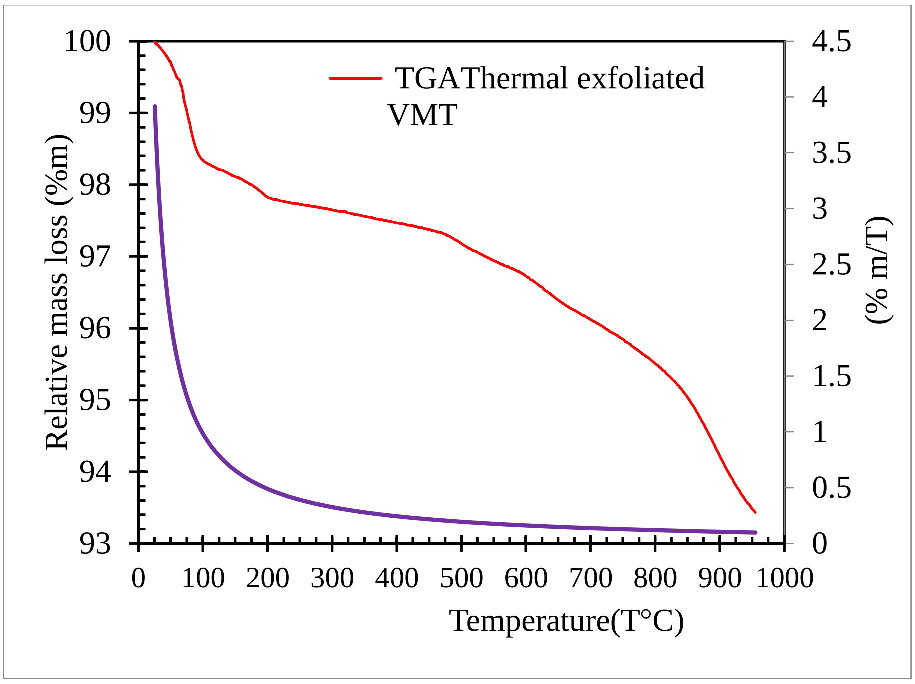

Figure 17: TGA of thermal exfoliated VMT thermograph

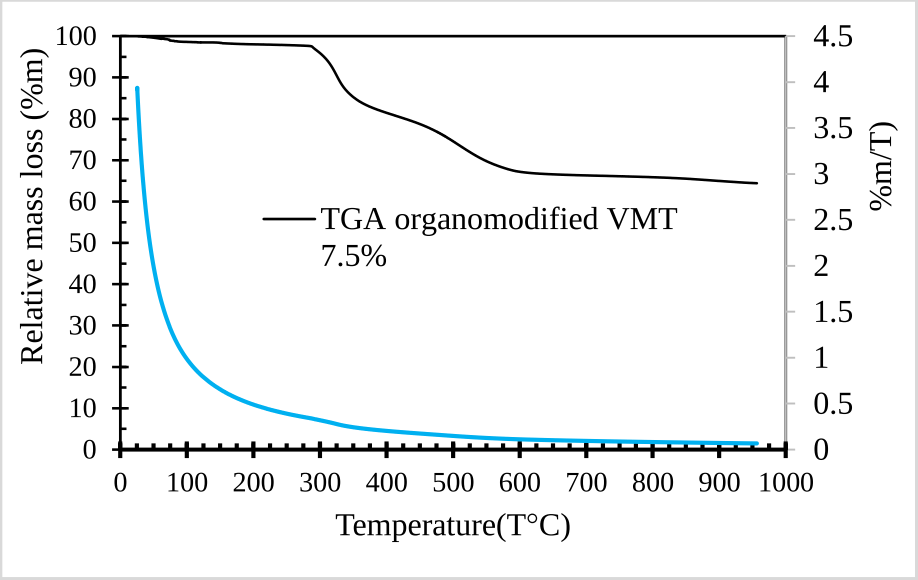

Figure 18: TGA of organomodified VMT 7.5% thermograph

4.1.3. X-ray diffraction (XRD)

In the study of vermiculite, X-ray diffraction (XRD) is crucial because it offers comprehensive details about the material's mineral makeup, degree of expansion, and crystal structure. The typical XRD pattern of thermal exfoliated VMT and organovermiculite VMT 7.5% is presented on figure 19. The higher intense peaks are observed at the angle 2θ =2 and 2θ=8. In general, a sample's crystallinity is closely correlated with the peak strength and width in its XRD pattern. The sharp and broad peak in thermal exfoliated vermiculite lies between the 2θ =8 and 2θ=12 which is the characteristic of crystalline structure of thermal exfoliated and with a decrease in intensity at the same 2θ =8 and 2θ=12 with organovermiculite VMT 7.5%, there it indicates that after modification with polymer the vermiculite becomes less crystalline (Salih et al., 2022).

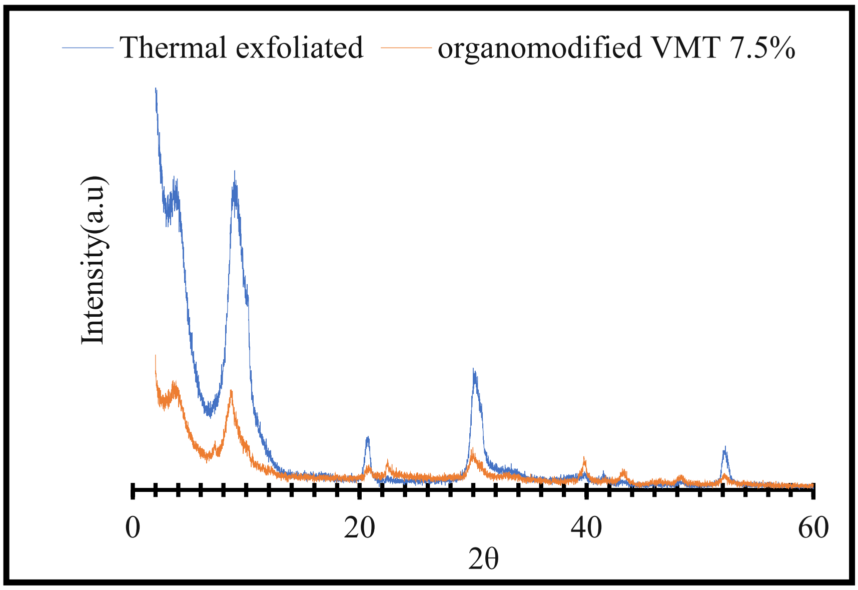

Figure 19: X-ray diffractogram of thermal exfoliated and organomodified VMT 7.5%

4.1.4. Brunauer–Emmett–Teller (BET) and particle distribution

The BET is essential for describing the surface area of materials, such as vermiculite and organomodified VMT, a layered silicate mineral that is frequently employed in organic and heavy metal adsorption and removal in produced water. These excellent properties are the basis of VMT nanosheet as an excellent adsorption material (M. Li et al., 2021).

Table 7: Brunauer–Emmett–Teller (BET) of neat, thermal exfoliated and organomodified vermiculite samples

Sample	**d_{10}**	**d_{50}**	**d_{90}**	**BET, m^2/g**	**Key observations**
Neat VMT	423	890	1760	1.49	Large particle size, low surface area
Thermally exfoliated	2.91	12.4	39.2	12.4	Fine particle size, high surface area due to exfoliation
Organomodified VMT (7.5% polymer)	46.8	139	481	8.78	Moderate particle size and surface area; polymer modification adds functionality

The BET of 1.49 m^2/g presents the low surface area is consistent with the large particle size and limited porosity of neat VMT. The particle sizes are large, with a median (d_{50}) of 890 µm. This indicates that the raw vermiculite (neat vermiculite) is relatively coarse. In the case of thermal exfoliation has the BET of 12.4 m^2/g where surface area increases significantly due to the exfoliation process. The thermal shock which creates more surface area by breaking down the layers and reducing particle size which are significantly smaller, with a median (d_{50}) of 12.4 µm which therefore shows that thermal exfoliation breaks down the large particles into much finer ones.

The organomodification with polymer 7.5 %, the particle sizes are intermediate, with a median (d_{50}) of 139 µm. The modification process (likely involving polymer intercalation) results in particles larger than the thermally exfoliated sample but smaller than the neat VMT which presents the BET of 8.78 m^2/g.

4.1.5. X-ray fluorometry (XRF)

The chemical formula of vermiculite can be generally expressed as $(Mg, Ca)_{0.3–0.45}(H_2O)_n\{(Mg, Fe, Al)_3(Al, Si)_4O_{10}(OH)_2\}$(Salih et al., 2022). Here the XRF data displays the neat vermiculite composition, thermal exfoliated and organomodified 7.5% VMT (see table 10 in Appendix). The XRF measurements present the vermiculite composition as 42.55wt% SiO_2, 24.39wt% MgO, 10.06wt% Al_2O_3, 9.49wt% Fe_2O_3 , 6.21wt% K_2O, 4.61wt%CaO, 1.13wt% P_2O_5 and 1.16wt% TiO_2. Slight changes of SiO_2, MgO, and Fe_2O_3 content in the three samples suggest minor structural changes during exfoliation.

The Loss of Ignition (LOI) of 19.8% in thermally exfoliated vermiculite which is higher than neat VMT, reflecting the loss of interlayer water and hydroxyl groups due to heating. The LOI of 36.2% in organomodified 7.5% VMT which is very high, due to polymer composition as an indication of the presence interlayer water and the organic polymer during intercalation.

4.1.6. Cation exchange capacity

Vermiculite's capacity to store and exchange cations, or positively charged ions, is measured by its CEC (Alexiades & Jackson, 1965). Vermiculite has a large surface area and a layered structure with negatively charged sites that attract and hold cations like Ca^{2+}, Mg^{2+}, K^+, Na^+. The obtained value of 157 meq/100mg of the CEC vermiculite indicates that it is higher and exhibit a lot of exchange sites. In addition, according to Sarkar et al. (2019) the negative surface charge and water-loving properties, high (CEC) and surface area of vermiculite minerals facilitate the adsorption of inorganic and organic contaminant cations through cation exchange mechanisms.

4.2. Adsorption studies

4.2.1. Copper and phenol removal performance

The figure 20 displays the study of a 50ppm Cu^{2+} and phenol samples treatment carried at room temperature and at 150 rpm.The replication of three essays was done and the mean absorbance was used to calculate the corresponding concentration.

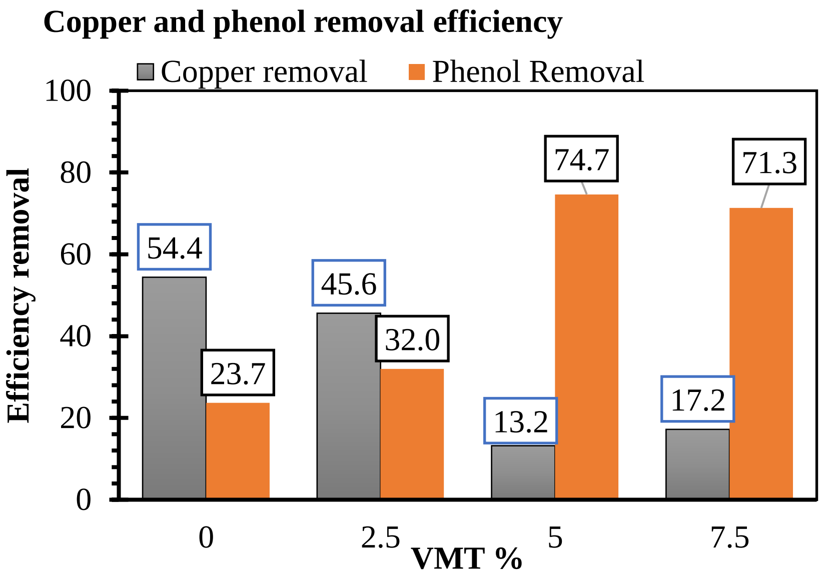

Figure 20: Copper and phenol removal efficiency

The Cu^{2+} removal efficiency is calculated using the equation below

$$\%RE = \frac{C_0 - C_e}{C_0} \times 100 \qquad (9)$$

Where C_0 is the initial aliquot concentration in ppm and C_e is the final equilibrium concentration in ppm.

The four clay samples which of them 2.5%w/w VMT, 5.0% w/w VMT and 7.5% w/w VMT are organically modified with the polymer. The copper solution prepared at 50 ppm to be treated showed a solubility behaviour dependent on the amount of organic part present in the clay. In a solution of 7.5%w/w VMT which showed the least efficiency removal for copper 17.2% the solution presented an almost heterogeneous phase as long as it presented the higher amount of organic part than other samples. In a non-modified clay shows the maximum copper efficiency removal of 54.4. The efficiency further increases to 74.7% in a VMT 5%w/w showing that doubling the VMT concentration significantly improves phenol removal. The VMT 5%w/w exhibits a moderate particle size and higher surface area than neat and 2.5%w/w VMT. Therefore, the good interaction between polymer components and organic phenol, phenol forms hydrogen bonds or other interactions with organovermiculite surface functional groups. The phenol contaminant removal efficiency increases with VMT concentration, but the rate of increase slows down at higher concentrations.

a. Effect of time on pollutant adsorption

The data plotted on figure 21 represent the adsorption percentage of phenol and copper onto 5%w/w VMT adsorbent over time in a produced water sample. Initially, at 5 minutes, the adsorption percentages for both phenol and copper are low (1.37% and 1.37%), indicating that the adsorption process is in its early stages. As time progresses, the adsorption percentages increase, with copper showing a slightly faster adsorption rate compared to phenol (refer also to table 13 in Appendix where the copper shows the higher adsorption rate, adsorption equilibrium and higher correlation coefficient). On the other side, at 15 minutes, the adsorption of phenol reaches 7.83%, while copper reaches 4.08%. This difference may be attributed to the stronger affinity of 5%w/w VMT for phenol due organic functionality.

By 60 minutes, the adsorption percentages for both contaminants increase significantly, with phenol reaching 10.9% and copper reaching 10.87%. This suggests that the adsorption process is approaching equilibrium, where the available active sites on the organovermiculite surface are becoming saturated.

At 120 minutes, the adsorption percentages climax, with phenol at 11% and copper at 13.7%, indicating that equilibrium has likely been achieved. Concluding this, the slightly higher adsorption percentage for copper compared to phenol at equilibrium may be due to the inherent properties of vermiculite, which has a higher affinity for metal ions like copper. The data also highlights the importance of contact time in adsorption processes, as longer exposure times allow for greater interaction between the contaminants and the adsorbent. Overall, the results demonstrate that vermiculite is effective in removing both phenol and copper from oil and natural gas produced water, with copper being slightly more efficiently adsorbed due to its ionic nature and stronger interactions with the adsorbent.

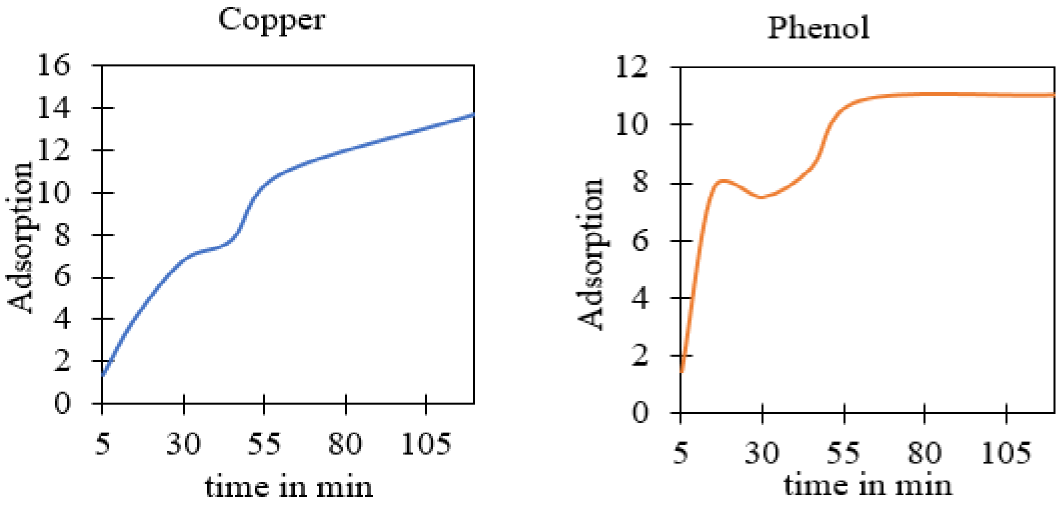

Figure 21: Curve of effect of time on pollutant removal

b. Effect of initial concentration

The figure below shows that as the initial concentration increases, the copper ion adsorption capacity gradually increases, from 1.0044 mg/g at 20 mg/L to 6.1714 mg/g at 140 mg/L. This pattern suggests that even at the greatest concentration measured, the organovermiculite adsorption capacity is not yet saturated and that it has a greater affinity for copper ions.

The rising qe values imply that copper ions engage in more dynamic interactions with the adsorbent, maybe occupying more binding sites or building multilayers as their concentration in the solution increases. The Freundlich isotherm model, which explains adsorption on heterogeneous surfaces with different affinities, is more in line with this behaviour. The distinct adsorption patterns of copper and phenol highlight organovermiculite's selectivity and potential for targeted pollutants removal.

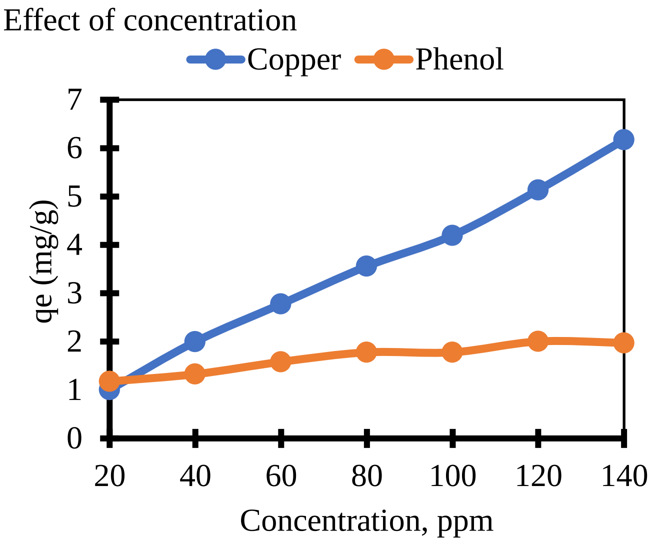

Figure 22: Effect of concentration on adsorbent

4.2.2. Equilibrium study

4.2.2.1. Equilibrium curve

Figure 23 illustrates ploted data of the equilibrium concentration (Ce) of phenol and copper in the solution and the corresponding adsorption capacity (qe) of 5%w/w VMT for both contaminants.

For phenol, the equilibrium concentration increases from 14.1 mg/L to 130.1 mg/L, while the adsorption capacity (qe) remains relatively low, ranging from 1.17 mg/g to 2 mg/g. This suggests that vermiculite has a limited capacity for adsorbing phenol, likely due to the weak interactions between the organic phenol molecules and the adsorbent surface. This may be due to phenol adsorption typically relies on van der Waals forces, hydrophobic interactions, or hydrogen bonding, which are less effective compared to the stronger interactions involved in metal ion adsorption. As a result, even at higher equilibrium concentrations, the adsorption capacity for phenol does not increase significantly, indicating that the active sites on the adsorbent surface are quickly saturated.

In contrast, the adsorption capacity for copper shows a more pronounced increase with rising equilibrium concentrations. The Ce values for copper range from 14.9 mg/L to 109.1 mg/L, while the qe values increase from 1.004 mg/g to 6.1 mg/g. This indicates that adsorbent has a higher affinity for copper ions, likely due to ion exchange mechanisms or electrostatic interactions between the positively charged copper ions and the negatively charged sites on the adsorbent s surface. The layered structure of vermiculite, with its high cation exchange capacity, allows for more efficient uptake of metal ions like copper. The increasing qe values with higher Ce suggest that the adsorption process for copper is not yet saturated within the tested concentration range, aligning with the Freundlich isotherm model, which describe multilayer adsorption on heterogeneous surfaces.

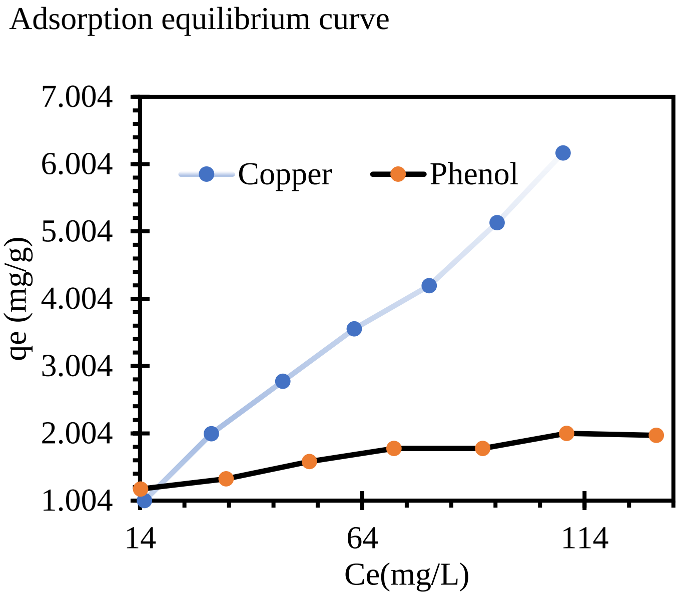

Figure 23: Adsorption capacity vs adsorption equilibrium of Copper and Phenol

4.2.2.2. Freundlich and Langmuir isotherms

The study of adsorption of copper as heavy metal and phenol as organic pollutant in oil and gas produced water can indicate whether the process of adsorption is homogenous or heterogeneous, both copper and phenol show the favourability of being adsorbed onto vermiculite (Salih et al., 2022). Table 8 data shows that both adsorbates have the heterogeneity factor greater than one which implies multilayer adsorption. A higher K_F value compared to copper indicates better adsorption capacity for phenol with 0.58. Theoretical maximum adsorption capacity for copper, indicating the adsorbent can hold up to 25.51 mg of copper per gram under ideal conditions. Figure 24, the Freundlich model (R^2=0.996) fits the data better than the Langmuir model (R^2= 0.75) that suggests that copper adsorption process likely occurs on a heterogeneous surface and may involve multilayer adsorption. Both models Langmuir and Freundlich fit the data well for copper with the correlation coefficients (R^2=0.988) and (R^2=0.962) respectively which also suggests that phenol adsorption likely occurs as a monolayer on a homogeneous surface.

Table 8: Data of Freundlich and Langmuir isotherm for copper and Phenol

	Freundlich isotherm	
Parameter	Copper	Phenol
n	1.14	3.93
K_F	0.095	0.58
R^2	0.996	0.962
	Langmuir isotherm	
Parameter	Copper	Phenol
Qmax(mg/g)	25.51	2.256
K_L(L/mg)	0.00269	0.0521
R^2	0.75	0.988

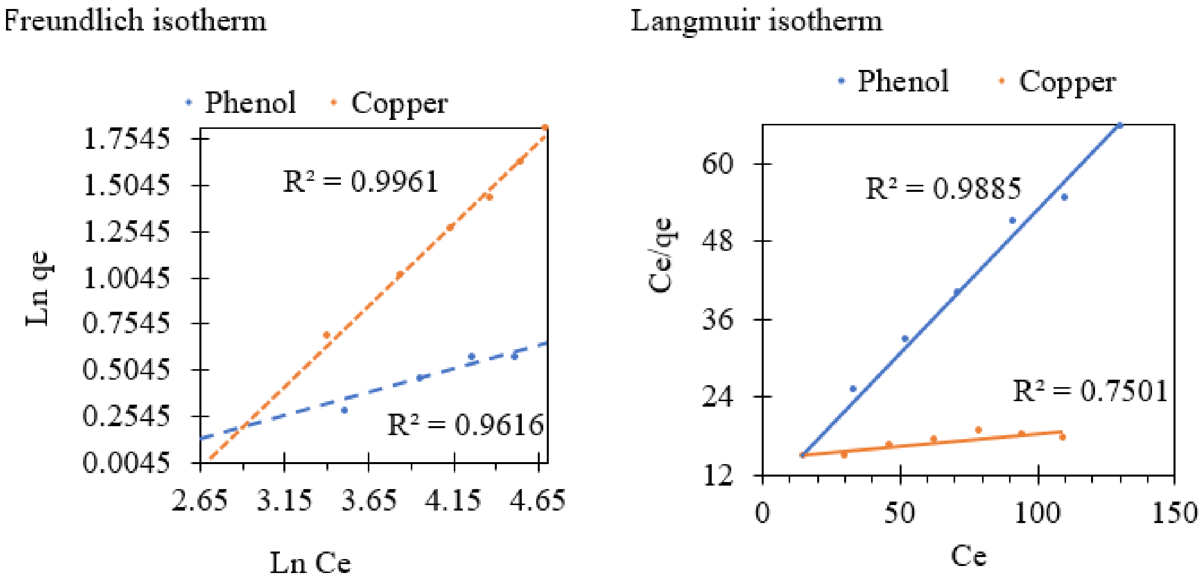

Figure 24: Freundlich and Langmuir isotherms

4.2.3. Kinetic study

This study demonstrated that both first order and second order kinetics can describe the adsorption process of vermiculite adsorbent over copper and phenol pollutants. However, the model is best fit for second for both pollutants. The chemical behaviour of copper and phenol are different and mainly phenol exhibits a complex mechanism during the removal. The data calculated demonstrated that the kinetic model that can describe the adsorption process is the second order equation.

4.2.3.1. Pseudo-first order kinetics

Despite the phenol correlation coefficient 0.91 lower than of copper 0.95, the value still shows a strong match to the pseudo-first-order model. This implies that, although other processes (like chemisorption) might potentially be involved, physisorption or diffusion may also be a part of the phenol adsorption process. Figure 25, the pseudo-first-order model was well-fitted by both systems having both the correlation coefficient great than 0.9, indicating that the predominant mechanism for the adsorption of both copper and phenol is either physisorption or diffusion.

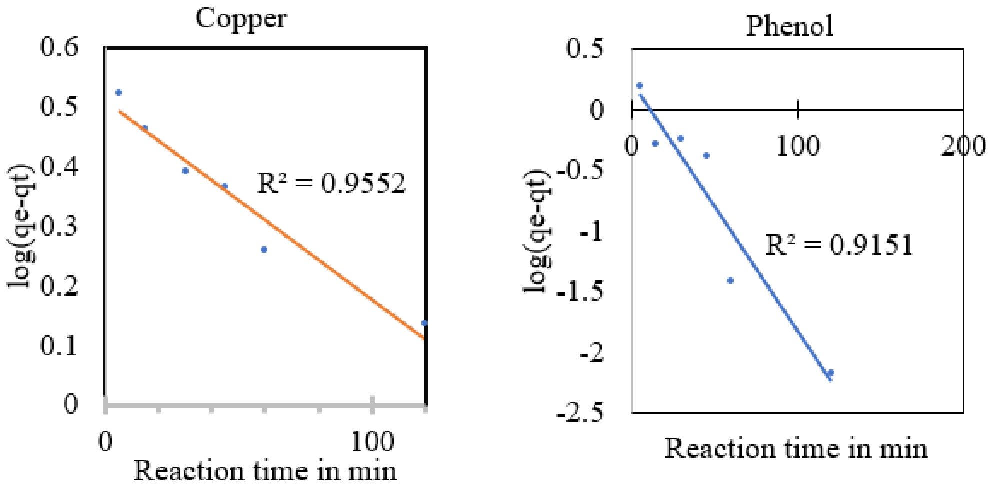

Figure 25: Pseudo first order of copper and phenol

4.2.3.2. Pseudo second order

The maximum amount of copper that can be adsorbed per gram of the adsorbent at equilibrium is 3.503 mg/g as calculated (see table 13 in the appendix). Copper has a higher rate constant (K_2 =0.613*)* compared to the rate constant of phenol (K_2=0.419*)*, that indicates copper pollutants are adsorbed faster than phenol pollutants. The vermiculite adsorbent can hold more copper than phenol at equilibrium as the adsorption capacity for Copper is (qe=3.503 mg/g) compared to phenol. Both systems fit the pseudo-second-order model well (R^2=0.9), suggesting that chemisorption is the dominant mechanism for both copper and phenol adsorption. However, the slightly lower correlation coefficient for phenol suggests that other mechanisms (e.g., intra-particle diffusion) may also contribute to phenol adsorption**.** The interaction of the adsorbate and the adsorbent occurred by either physical weak forces (Kennedy et al., 2018).

Figure 26 shows that the vermiculite adsorbent demonstrates to be less effective for phenol removal compared to copper with a slower rate and lower capacity. However, it still shows potential for phenol removal, especially in low-concentration scenarios.

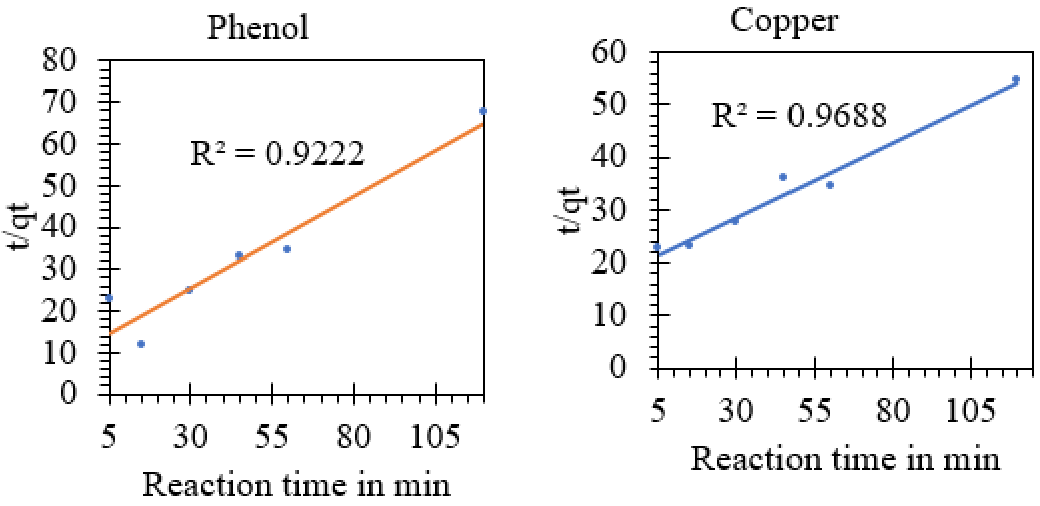

Figure 26: Pseudo second order curve of copper and phenol

CHAP 5.

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5. CONCLUSION AND RECOMMENDATION

5.1. CONCLUSION

The experimental results of this study lead to the following conclusion:

- ✓ The vermiculite activation (exfoliation) has gone to success through the SEM image displaying the soft edges surface (see figure 16 c and d)
- ✓ The cation exchange capacity of the vermiculite found to be 157 meq/100gram which is a good indication of the ion-ion exchange during adsorption
- ✓ The organomodified vermiculite show a thermal resistant capacity therefore in case harsh condition the adsorbent cannot be altered (see figure 18)
- ✓ Organomodified VMT 7.5%w/w shows surface area of 8.78 m^2/g improved surface properties with enhanced functionality due to polymer incorporation.
- ✓ Organovermiculite is highly effective at adsorbing copper ions due to its high K_F and K_L values
- ✓ Organovermiculite has a lower adsorption capacity and affinity for phenol compared to copper, as indicated by the lower K_F and K_L values
- ✓ The poor fit of the Langmuir model suggests that phenol adsorption may involve more complex mechanisms, such as multilayer adsorption or interactions with surface functional groups.
- ✓ The adsorption mechanisms of organomodified vermiculite with fatty acid polyamide polymer follows a pseudo second order kinetics for the removal of copper as heavy metal and phenol as organics in the produced water.

5.2. RECOMMENDATIONS

- ✓ For analytical techniques

Use other analytical techniques in the analysis (inductive coupled plasma-Atomic absorption spectroscopy, FT-IR or even HPLC to compare the results with Uv-visible spectrophotometry

- ✓ For Copper removal

Vermiculite adsorbent is an excellent adsorbent for copper ions, and its high adsorption capacity and affinity make it suitable for water treatment applications targeting heavy metals. Use vermiculite as a primary adsorbent for copper removal.

- ✓ For phenol removal

Organovermiculite may not be the most effective adsorbent for phenol removal. Consider using alternative adsorbents (e.g., activated carbon) or modifying vermiculite with another polymer than fatty acid polyamide to enhance its adsorption capacity for organic compounds. Use organovermiculite as a supplementary adsorbent for phenol removal and optimize pH (neutral to slightly acidic) for phenol removal.

- ✓ For optimization

Copper adsorption is highly pH-dependent. Perform experiments to determine the optimal pH range for maximum copper removal efficiency and study the load effect on the performance

- ✓ For fixed-bed or batch Systems

Vermiculite can be used in fixed-bed columns or batch adsorption systems for copper removal. Its high affinity ensures efficient removal even at low copper concentrations

- ✓ For green industry

Recycling and reuse of organovermiculite adsorbent is a crucial aspect for the sustainability of the adsorption process on both pilot and industrial scale.

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APPENDIX

Table 9: BET and particle distribution data of vermiculite

Particle sizes (μm) and BET surface areas of vermiculite (VMT) samples.

Sample	d_{10}	d_{50}	d_{90}	BET, m^2/g
Neat VMT	423	890	1760	1.49
Thermally exfoliated	2.91	12.4	39.2	12.4
Organomodified VMT (7.5% polymer)	46.8	139	481	8.78

Table 10: XRF – Vermiculite (VMT)

Sample	SiO_2	MgO	Al_2O_3	Fe_2O_3	K_2O	CaO	P_2O_5	TiO_2	LOI
Neat VMT	42.55	24.39	10.06	9.49	6.21	4.61	1.13	1.16	8.70
Thermally-exfoliated VMT	43.22	23.96	9.86	9.27	5.97	4.79	1.57	1.13	19.8
Organomodified VMT (7.5% polymer)	43.33	27.63	11.26	8.71	7.33	0.51	0.02	1.22	36.2

Neat VMT – Before thermal exfoliation

LOI – Los of ignition

Table 11: Freundlich isotherm calculation

FREUNDLICH										
COPPER										
Co	Abs$_1$	Abs$_2$	Abs$_3$	Mean Abs	Ce	Vol.	mass	qe	ln Ce	ln qe
mg/L					mg/L	L	g	mg/g		
20	0.0096	0.0097	0.0098	0.0097	14.978	0.1	0.5	1.0044	2.70658	0.00439
40	0.0172	0.0175	0.0170	0.0172	30.006	0.1	0.5	1.9988	3.4014	0.69255
60	0.0249	0.0257	0.0252	0.0253	46.114	0.1	0.5	2.7772	3.83112	1.02144
80	0.0331	0.0330	0.0339	0.0333	62.213	0.1	0.5	3.5574	4.13056	1.26903
100	0.0413	0.0419	0.0420	0.0417	79.021	0.1	0.5	4.1958	4.36971	1.43408
120	0.0496	0.0490	0.0495	0.0494	94.321	0.1	0.5	5.1358	4.5467	1.63624
140	0.0573	0.0585	0.0547	0.0568	109.143	0.1	0.5	6.1714	4.69266	1.81993
K_F	0.095007447									
n	1.144557628									
R^2	0.9961									
PHENOL										
Co	Abs$_1$	Abs$_2$	Abs$_3$	Mean Abs	Ce	V	m	qe	ln Ce	ln qe
mg/L					mg/L	L	g	mg/g		
20	0.0091	0.0093	0.0094	0.0093	14.116	0.1	0.5	1.1768	2.64731	0.1628
40	0.0188	0.0189	0.0189	0.0189	33.361	0.1	0.5	1.3278	3.50739	0.28352
60	0.0282	0.0283	0.0282	0.0282	52.087	0.1	0.5	1.5826	3.95292	0.45907
80	0.0379	0.0378	0.0378	0.0378	71.106	0.1	0.5	1.7788	4.26417	0.57594
100	0.0478	0.0478	0.0478	0.0478	91.104	0.1	0.5	1.7792	4.512	0.57616
120	0.0572	0.0572	0.0572	0.0572	109.981	0.1	0.5	2.0038	4.70031	0.69505
140	0.0673	0.067	0.0673	0.0673	130.122	0.1	0.5	1.9756	4.86847	0.68087
K_F	0.58047996									
n	3.929273084									
R^2	0.9616									

Table 12: Langmuir isotherm calculation

LANGMUIR ISOTHERM							
COPPER							
Co	Abs$_1$	Abs$_2$	Abs$_3$	Mean abs	Ce	qe	Ce/qe
mg/L					mg/L	mg/g	L/g
20	0.0096	0.0097	0.0098	0.0097	14.978	1.0044	14.91
40	0.0172	0.0175	0.0170	0.0172	30.006	1.9988	15.01
60	0.0249	0.0257	0.0252	0.0253	46.114	2.7772	16.6
80	0.0331	0.0330	0.0339	0.0333	62.213	3.5574	17.49
100	0.0413	0.0419	0.0420	0.0417	79.021	4.1958	18.83
120	0.0496	0.0490	0.0495	0.0494	94.321	5.1358	18.37
140	0.0573	0.0585	0.0547	0.0568	109.143	6.1714	17.69
K_L	0.002694528						
qmax	25.51020408						
R^2	0.7501						
Phenol							
Co	Abs$_1$	Abs$_2$	Abs$_3$	Mean abs	Ce	qe	Ce/qe
mg/L					mg/L	mg/g	L/g
20	0.0091	0.0092	0.0094	0.0093	14.116	1.1768	12
40	0.0188	0.019	0.0189	0.0189	33.361	1.3278	25.13
60	0.0282	0.028	0.0282	0.0282	52.087	1.5826	32.91
80	0.0379	0.038	0.0378	0.0378	71.106	1.7788	39.97
100	0.0478	0.048	0.0478	0.0478	91.104	1.7792	51.21
120	0.0572	0.057	0.05719	0.0572	109.981	2.0038	54.89
140	0.0673	0.067	0.0673	0.0673	130.122	1.9756	65.86
K_L	0.052094598						
qmax	2.25631769						
R^2	0.9885						

Table 13: Pseudo first order data calculation

Kinetic study									
PSEUDO-FIRST ORDER									
	COPPER								
time(min)	Vol	mass	Co	Ct	qt	qe	log(qe-qt)	qe-qt	Removal
	L	g	mg/L	mg/L	mg/g	3.5574		mg/g	%
5	0.1	0.5	80	78.9	0.22		0.52341	3.3374	1.375
15	0.1	0.5	80	76.734	0.6532		0.46303	2.9042	4.0825
30	0.1	0.5	80	74.552	1.0896		0.39231	2.4678	6.81
45	0.1	0.5	80	73.772	1.2456		0.36395	2.3118	7.785
60	0.1	0.5	80	71.3	1.74		0.25945	1.8174	10.875
120	0.1	0.5	80	69.041	2.1918		0.13532	1.3656	13.69875
Rate constant		(-0.0033min^{-1})							
Calculated qe		1.662628859							
R^2		0.95							
	PHENOL								
time(min)	Vol	mass	Co	Ct	qt	qe	log(qe-qt)	qe-qt	Removal
	L	g	mg/L	mg/L	mg/g	1.779		mg/g	%
5	0.1	0.5	80	78.9	0.22		0.19279	1.5588	1.375
15	0.1	0.5	80	73.731	1.2538		-0.2798	0.525	7.83625
30	0.1	0.5	80	74.002	1.1996		-0.2372	0.5792	7.4975
45	0.1	0.5	80	73.172	1.3656		-0.3838	0.4132	8.535
60	0.1	0.5	80	71.3	1.74		-1.4112	0.0388	10.875
120	0.1	0.5	80	71.14	1.772		-2.1675	0.0068	11.075
Rate constant		(-0.0205min^{-1})							
Calculated qe		1.253							
R^2		0.91							

Table 14: Pseudo second order data calculation

Pseudo Second order					
Copper				Phenol	
time	qt	t/qt		qt	t/qt
min	mg/g			mg/g	
5	0.22	22.7273		0.22	22.73
15	0.6532	22.9639		1.2538	11.96
30	1.0896	27.533		1.1996	25.01
45	1.2456	36.1272		1.3656	32.95
60	1.74	34.4828		1.74	34.48
120	2.1918	54.7495		1.772	67.72
Rate constant(g/g.min)	0.613			0.418	
qe(mg/g)	3.50262697			2.260908885	
R^2	0.96			0.92	

CURRICULUM VITAE

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Gender: Male
Residence: Maputo

Nationality: Rwanda

2. PROFILE

I am competent and committed candidate with great performance aligned with skills, knowledge and Good attitudes at workplace. Here are some of my moral values & social skills

- Effective and patient communication skills
- Team work spirit
- Hard worker with a time management spirit

Ability to perform as expected with appreciated performance and results

3. EDUCATION BACKGROUND

Date	**Name**	**Degree**
2012-2016:	UNIVERSITY OF RWANDA/College of Science and Technology	A_0 Bachelors of Science in Environmental Chemistry
2009-2011:	Ecole de Science de MUSANZE	A_2 Secondary school certificate in Mathematics, Chemistry and Biology

4. WORKING EXPERIENCE

2021-2022: Data manager Mudende Health Centre

2020-2021: Enumerator in surveys (Research Hub, Real group, ACER RSS…)

2019-2020: Nature and Environment Conservation ITP Company

2018-2019: Greenhouse Agronomist at Mudende seed production Ltd

5. Additional skills

Skills in water treatment and waste water treatment and solid waste management

Skills in brewery process

Leadership skills

6. LANGUAGES

	WRITING	SPEAKING	LISTENING	READING
ENGLISH	Excellent	Excellent	Excellent	Excellent
KINYARWANDA	Excellent	Excellent	Excellent	Excellent
FRENCH	Excellent	Good	excellent	Excellent
PORTUGUESE	Good	Good	Good	Good
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I declare that from the best of my knowledge that all provided information is sincere and correct

KANANIRA Theoneste