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COMPARATIVE STUDY ON THE REMOVAL OF METHYLENE BLUE DYE USING NATURAL CLAYS FROM TWO DEPOSITS

By

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A Thesis submitted to the school of chemical and Bio engineering as part of partial fulfillment of the requirements for the degree of master’s science (chemical and Bio engineering in the environmental engineering stream)

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Approval Page

This is to certify that the thesis prepared by Simegn Getu, titled “Comparative Study on the Removal of Methylene Blue Dye Using Natural Clays from Two Deposits,” and submitted in partial fulfillment of the requirements for the Master of Science degree in Chemical Engineering, adheres to the university’s regulations and meets the accepted standards of originality and academic quality.

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Abstract

Synthetic dyes, particularly methylene blue (MB), are widely used in the textile industry and often discharged into water bodies, where they create serious ecological and health risks due to their Chemical stability, toxicity, and resistance to conventional treatment methods. Adsorption has emerged as one of the most efficient and economical techniques for dye removal, and natural clays are gaining attention as promising low-cost adsorbents. This study investigates the comparative adsorption performance of natural clays obtained from two different deposits named as Belesa and Homecho. the comparative performance of clays from different deposits in Ethiopia, in terms of their efficiency for dye removal, has not been systematically explored. This study aims to conduct a comparative analysis on the removal of methylene blue dye using natural clays from two distinct deposits in Ethiopia. By examining factors such as mineral composition, surface area and pore structure, the research seeks to identify the most effective clay material for dye removal. Both Belesa and Homecho clays were systematically characterized using X-ray diffraction (XRD) to determine mineral composition, Brunauer–Emmett–Teller (BET) analysis for surface area measurement, X-ray Fluorescent (XRF) to know the elemental composition and Thermogravimetric–differential thermal analysis (TG–DTA) to evaluate thermal behavior. Batch adsorption experiments were carried out at an initial MB concentration of 20 mg/L, with adsorbent dosages of 0.2–0.6 g and contact times of 20–100 minutes. Results showed that both clays exhibited high adsorption efficiency, with removal percentages exceeding 95% and maximum adsorption capacity reaching 10 mg/g with Belesa clay demonstrating slightly superior performance due to its favorable mineralogical composition, reactive surface functional groups, and well-developed mesoporous structure. Equilibrium was achieved within 60 minutes for both clays. However, this study suggest that adsorption performance is influenced not only by surface area but also by pore size, pore volume, crystallinity, and mineral composition indicating that both clays possess high and comparable surface areas suitable for adsorption applications. These findings highlight the potential of naturally available clays as sustainable adsorbents for textile wastewater remediation and provide insights into the influence of mineralogy and surface properties on adsorption performance.

Key Words: Methylene blue, Adsorption, Natural clay, Batch adsorption, Wastewater treatment

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Contents

List of Abbreviation and Acronyms

Abbreviation and Acronyms	Meaning
BC	Belesa clay
HC	Homecho clay
TG-DTA	Thermogravimetric Differential Thermal Analysis
MB	Methylene Blue Dye
BET	Brunauer Emmett and Teller
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
AC	Activated Carbon
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
AOP	Advanced Oxidation process
SSA	Specific Surface Area
CEC	Cation Exchange Capacity

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1. INTRODUCTION

1.1 Background of the study

The rapid expansion of industries such as textiles, leather, paper, and printing has resulted in significant amounts of dye-laden wastewater being discharged into the environment. Methylene blue is one of the most commonly used synthetic dyes for coloring materials like cotton, wool, and silk. While it is not highly dangerous in small amounts, higher concentrations of methylene blue can pose serious threats to aquatic life and human health. Long-term exposure may lead to respiratory issues, nausea, and damage to the central nervous system. Additionally, its strong coloration decreases light penetration in water, which can disrupt photosynthesis and negatively impact aquatic ecosystems (Al-Tohamy et al., 2022).

Various approaches have been explored for removing dyes from wastewater, such as coagulation-flocculation, membrane filtration, advanced oxidation processes, electrochemical treatment, and biological degradation. Nonetheless, many of these methods can be expensive, generate secondary pollutants, or fail to achieve complete dye removal. Among these, adsorption has become one of the most efficient, adaptable, and cost-effective techniques because of its straightforwardness, high effectiveness at low dye concentrations, and the potential to regenerate the adsorbent materials (Khan et al., 2025; Subhi et al., 2022).

Although activated carbon is still considered the most efficient adsorbent, its high manufacturing costs restrict widespread use. As a result, researchers have turned to more affordable and locally accessible options like agricultural waste, industrial by-products, and natural minerals. Natural clays, in particular, have garnered significant attention due to their availability, low price, large surface area, cation exchange abilities, and favorable structural features for adsorption. Numerous studies have shown that clays such as bentonite, kaolinite, and montmorillonite can effectively remove organic dyes like methylene blue from water (Gu et al., 2019; Subhi et al., 2022).

Importantly, the adsorption performance of clay is strongly influenced by its mineralogical composition and physicochemical properties, which can vary significantly depending on the geological origin of the deposit. Clays obtained from different sites may therefore exhibit different dye removal efficiencies. Despite numerous studies on clays as adsorbents, comparative investigations of clays from distinct deposits within the same region are still limited (Aziz et al., 2022; Lafo et al., 2023).

This study aims to address this gap by evaluating and comparing the methylene blue dye removal performances of two natural clay samples collected from different deposit sites. Through characterization, adsorption experiments, and comparative analysis, the study seeks to identify the more efficient clay material and contribute to the development of low-cost, sustainable adsorbents for wastewater treatment applications.

1.2 Statements of the problem

Following the government's initiative to transition towards a manufacturing-based economy, several industries, especially labor-intensive textile and leather sectors, have been established in Ethiopia in the past few decades. By their nature, these textile and leather industries produce large volumes of effluent streams rich in various pollutants, including synthetic dyes like methylene blue, which are used extensively in the production processes. The discharge of untreated or inadequately treated wastewater from these industries into water bodies poses significant environmental risks, as methylene blue is toxic, non-biodegradable, and can disrupt aquatic ecosystems and harm human health (Abbas, 2022; Al-Tohamy et al., 2022; Khan et al., 2022).

Currently, Traditional wastewater treatment techniques like chemical coagulation, membrane filtration, and synthetic adsorbents encounter issues including high operational expenses, limited effectiveness, and environmental concerns (Zinicovscaia, 2016). As a result, there is an increasing demand for low-cost, sustainable, and effective alternatives to address the issue of dye contamination in water (Crini et al., 2019).

Natural clays have emerged as a promising solution due to their abundance, cost-effectiveness, and high adsorption capacity (Alshameri et al., 2019). These clays, being available locally, could provide an environmentally friendly and economically viable option for removing contaminants like methylene blue from wastewater. However, the comparative performance of clays from different deposits in Ethiopia, in terms of their efficiency for dye removal, has not been systematically explored.

This study aims to conduct a comparative analysis on the removal of methylene blue dye using natural clays from two distinct deposits in Ethiopia. By examining factors such as mineral composition, surface area and pore structure, the research seeks to identify the most effective clay material for dye removal. The goal is to provide a sustainable, locally available solution that aligns with Ethiopia's manufacturing growth while addressing the environmental challenges posed by wastewater effluents from the textile and leather industries.

The findings of this study could have important implications for the development of cost-effective, sustainable water treatment solutions that contribute to both the local economy and environmental protection.

1.3. Objectives

1.3.1 General Objective

To evaluate and compare the adsorption performance of natural clay samples obtained from two different deposits for the removal of methylene blue dye from aqueous solutions.

1.3.2 Specific Objectives

- To analyze the physicochemical properties of the clay samples
- To determine the adsorption capacity of each clay for methylene blue removal under varying conditions.
- To compare the adsorption performances of the two clay samples and identify which deposit provides the most efficient adsorbent.

1.4. Significance of the study

Releasing colored wastewater from factories into the environment can lead to serious environmental issues. Therefore, completing this study is crucial for stakeholders such as dye and cloth manufacturing factories. Utilizing natural adsorbents, which are special materials, can effectively remove color from contaminated water. These natural solutions often outperform other methods because they are more efficient, affordable, produce less sludge, and minimize secondary pollution.

1.5. Scope of the study

This research investigates and compares the ability of natural clays from two different sources to remove methylene blue dye from wastewater. It examines the physical and chemical characteristics of the clays such as surface area, particle size, and mineral composition to determine how factors like contact time and amount of clay used affect their adsorption performance. The experiments are conducted in the lab using synthetic methylene blue solutions, which are common in the textile industry and tend to persist in wastewater. Importantly, the study focuses solely on unaltered, natural clays without any chemical modifications or activation methods. The results offer a comparison of how clays from different geological origins perform but do not explore large-scale application, clay regeneration, reuse, or the removal of other pollutants.

2. Literature Review

2.1. Introduction to Dye pollution

Industrial wastewater refers to water contaminated with both dissolved substances and suspended particles, generated by activities such as manufacturing, processing, cleaning, and cooling, and released as waste. It typically contains various pollutants depending on the industry, including organic compounds like oils, greases, and solvents; inorganic chemicals such as heavy metals, acids, alkalis, and salts; nutrients like nitrogen and phosphorus; toxic substances like dyes, phenols, and pesticides; along with suspended solids and heat from cooling processes, which can lead to thermal pollution (Ahmed et al., 2021).

Discharging untreated wastewater into the environment can cause serious environmental damage. It pollutes water bodies such as rivers, lakes, and oceans, reducing oxygen levels necessary for aquatic life and potentially releasing toxic substances that can be fatal to fish, shellfish, and other organisms. Excess nutrients like nitrogen and phosphorus can lead to algae blooms, causing eutrophication, which further depletes oxygen and harms aquatic ecosystems.

Using contaminated water for irrigation can harm soil health by adding salts, heavy metals, and toxic substances, leading to decreased fertility. It also poses risks to human health, as consuming contaminated water or seafood may result in illnesses, neurological issues, or cancer. Additionally, exposure to certain chemicals can cause skin, eye, or respiratory problems (Younas et al., 2021).

Industrial thermal pollution can raise water temperatures, negatively impacting aquatic species that are sensitive to temperature changes (Ilyas et al., 2019). These impacts not only damage ecosystem but also reduce the availability of clean water, fisheries, and recreational opportunities, ultimately affecting communities and economies.

Industrial dyes are chemicals used in manufacturing that can contaminate water, making it unsafe for drinking. One such dye, methylene blue (MB), is particularly hazardous because it can cause health issues, lead to cancer, and is not biodegradable. As a result, it poses significant risks to both human health and the environment (Khan et al., 2022). Methylene blue is a positively charged dye commonly used in textiles, paper, leather, and printing because of its vibrant color, affordability, and durability. However, when released into water, it can hinder sunlight penetration, affecting aquatic plant photosynthesis and posing toxicity to aquatic life even at low levels. In humans, exposure can lead to eye irritation, vomiting, breathing problems, and in severe cases, methemoglobinemia, which impairs the blood's capacity to transport oxygen (Sudarshan et al., 2023). In many industries, it is used in nearby bodies of water in concentrations of 10 to 20 mg/L (Radoor et al., 2021).

To avoid these problems, industries should carry out pre-treatment procedures, set up effective effluent treatment facilities, recycle and reuse wastewater whenever feasible, adhere to strict environmental standards, and adopt cleaner production methods to minimize waste production from the outset (Okereke et al., 2016)

Due to stricter regulations on the organic pollutants in industrial wastewater, it has become crucial to eliminate dyes before discharge. The Environmental Protection Agency permits a maximum concentration of 0.2 mg/L for methylene blue dye in wastewater (Thabede et al., 2020).

Discharge rules require that the acceptable color level not surpass 10 milligrams of platinum-cobalt units per liter. Furthermore, Ethiopia's provisional environmental standard, suggested by the Environmental Protection Authority (EPA), establishes a maximum limit of 5 mg/l for adsorbable organic halogenated compounds (Haimanot Mabtamu, 2007).

International rules regarding dye concentrations in industrial wastewater vary by country, but all generally stress the importance of reducing color and organic content before discharge. In Ethiopia, the Environmental Protection Authority's provisional standards specify a maximum allowable color of 10 mg pt-co/L and restrict adsorbable organic halogenated compounds to 5 mg/L (Authority, 2012).

Similarly, India sets a permissible limit of 400 Hazen units for the effluents discharged from dye and dye-intermediate manufacturing industries (Baranwal & Agrawal, 2022), Canada has established specific standards for azo disperse dyes like Disperse Yellow 3, allowing concentrations of up to 146,520 µg/L in formulation effluents and 240,000 µg/L during textile dyeing processes (de Borst, 2023).

Regional frameworks like those under ESCAP in Asia set standards for effluents discharged into inland waters, estuaries, or marine environments, requiring the color to be “not objectionable” and BOD_5 limits between 20 and 50 mg/L, along with specified COD levels. International textile wastewater standards generally permit color concentrations from 50 to 550 Pt-Co (Hazen) units, with COD limits ranging from 80 to 250 mg/L, and pH values maintained between 6 and 9 (Khandegar & Saroha, 2013). In the European Union, direct numerical limits for dyes are infrequent; instead, wastewater discharges are managed under the Urban Wastewater Treatment Directive, which regulates organic pollutants such as BOD, COD, and suspended solids. Additionally, ecolabel programs set restrictions on hazardous impurities present in textile dyes (Directive, 1991). Overall, these standards reflect an international move toward more stringent restrictions on effluent color, organic pollutants, and toxic dye residues, emphasizing the increasing environmental awareness related to wastewater contaminated with dyes.

Table 2.1. some international and local standards regarding to dye level in the effluents

Country/region	Colour/dye limit	Equivalent in mg pt-Co/L	Notes
Ethiopia (EPA-provisional standards)	<u><</u>1o mg pt-Co/L	10	Also limits to 5 mg/L
Keneya (water quality regulations,2024)	< 40 Hazen units	~40 mg pt-Co/L	Applies to effluent into sewers or environment
Bangladesh (ECR standards-Textile effluent)	<u><</u> 150 Hazen units	~150 mg pt-Co/L	Specific to textile waste water into inland surface waters
India (Dye &dye intermediate industry standards)	<u><</u> 400 Hazen units	~400 mg pt-Co/L	For discharge into surface water , also regulates PH,TSS,metals
European union (EU)	No fixed colour limit	-	Controlled indireactly via COD,BOD,TSS permits
WHO guidelines	No direct colour limit	-	Focuses on health risks, not aesthetic colour

Table 2.2. international standard regarding discharge of dye effluent into the environment *(Roy & Saha, 2021b).*

Factor	Standard allowed
Temperature	< 42°c
COD	< 50 mg/L
PH	Between 6&9
BOD	< 30 mg/L
Noxious pollutants	Totally unacceptable
Color	< 1 ppm
Suspended particulates	< 20 mg/L

2.2. Dye Removal Technologies

Wastewater pollutants are primarily divided into two groups: organic and inorganic substances. Organic pollutants consist of items such as pesticides, phenols, herbicides, petroleum products, dyes, oils, biphenyls, fats, proteins, starches, and pharmaceuticals. Inorganic pollutants include chemical fertilizers, potentially toxic elements (PTEs), and excess nutrients. These contaminants degrade water quality and pose serious environmental challenges. To mitigate these problems, various treatment methods are employed, including chemical reactions, membrane filtration, reverse osmosis, chemical precipitation, solvent extraction, oxidation, and adsorption. Of these, adsorption is particularly favored due to its simplicity, cost-effectiveness, and the fact that it does not produce secondary pollution through byproducts (Younas et al., 2021).

The efficient elimination of dyes is essential in wastewater treatment before discharge because these substances are very resistant to natural breakdown and are usually not removed by standard treatment methods.

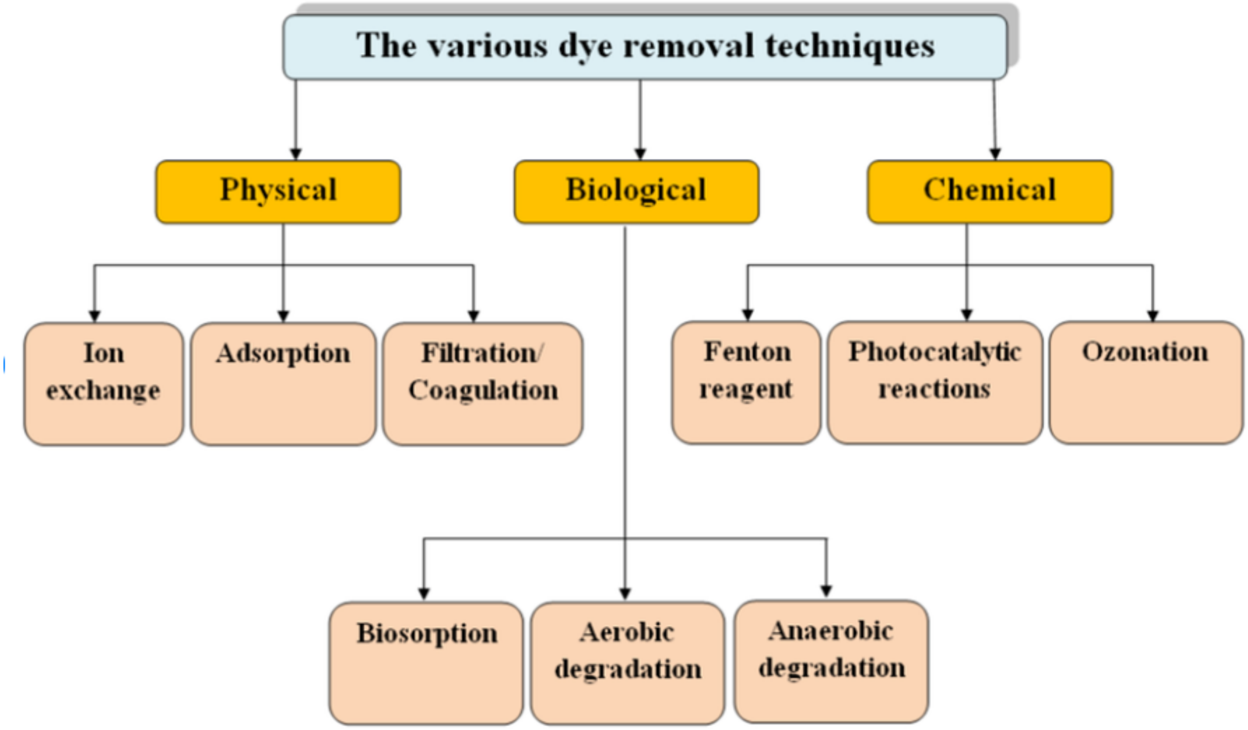

Figure 2.1. Different possible Dye removal technologies (Kumari et al., 2023).

2.2.1. Physicochemical Methods

These rely on separating dyes from water with out altering their chemical structure and best for quick and effective dye removal.

2.2.1.1 Adsorption

Adsorption is commonly used in industrial processes to purify wastewater. It involves a mass transfer mechanism where a solid material selectively removes dissolved contaminants from a liquid by attracting and binding them to its surface (Adeyemo et al., 2017).

Adsorption is a process in which molecules of a substance (the adsorbate) from a liquid or gas adhere to the surface of a solid material (the adsorbent) via physical forces or chemical bonds. This technique is widely used in water and wastewater treatment to remove different organic and inorganic contaminants. In this process, the pollutant molecules are attracted to and remain on the surface of the adsorbent, like clay (Khan et al., 2025).

When attempting to remove dye from colored water using a special substance that can absorb the dye, several factors influence its effectiveness. These factors include the duration of contact between the dye and the material, the water's pH level (its acidity or alkalinity), the amount of cleaning material used, and the initial concentration of dye in the water. Recently, researchers have become highly interested in this cleaning technique because it proves to be more effective than other water purification methods (Mashkoor & Nasar, 2020) and is regarded as the most effective method because it offers high removal efficiency, simple operation, affordability, and the ability to reuse the adsorbents. (Dutta et al., 2021).

The U.S. Environmental Protection Agency (EPA) states that adsorption provides several benefits, including low operating costs, effective removal of pollutants, quick reaction times, and straightforward design and operation. In many cases, the adsorbent can also be regenerated for reuse (Karthik & Meenakshi, 2015).

Adsorption is a very efficient technique for separation and is considered better than other wastewater treatment methods because it is inexpensive initially, has a straightforward design, is easy to operate, and can withstand toxic contaminants (Sen & Dawood, 2014). It employs adsorbents such as activated carbon, natural clays, zeolites, agricultural byproducts, or biosorbent, which are highly efficient for removing various dyes, particularly methylene blue. This method is simple, effective even at low dye concentrations, and is especially suitable for cationic dyes like methylene blue, which can be easily extracted through adsorption (Ahmad et al., 2015).

The effectiveness of adsorption relies on the physical and chemical characteristics of both the adsorbent material and the substance being captured. An adsorbent's selectivity is influenced by factors like its capacity to adsorb, surface area, availability, and overall affordability (Sen & Dawood, 2014).

Physical Adsorption

This occurs when the interactions between the adsorbate and adsorbent are weak, like van der Waals forces, hydrogen bonds, or dipole-dipole interactions. Typically, physical adsorption is easy to undo (Allen & Koumanova, 2005). Under appropriate pressure and temperature conditions, this type of adsorption can lead to multiple layers of adsorbate molecules building up on the surface of the adsorbent. The energy required for this process is relatively low, generally less than 40 kJ/mol. As a result, it does not require high temperatures or significant activation energy and usually takes place at lower temperatures, similar to how vapors condense on liquid surfaces (Aljamali et al., 2021).

Chemical Adsorption

Chemisorption occurs when the adsorbate and adsorbent create strong bonds, like covalent or ionic bonds, through electron transfer. Typically, this form of adsorption is viewed as irreversible in most cases (Allen & Koumanova, 2005). The initial phase of a chemical reaction between an adsorbent surface and an adsorbate requires a significant amount of energy and usually occurs at elevated temperatures. This stage is marked by adsorption energies greater than 40 kJ/mol. Unlike physical adsorption, this process is highly selective, irreversible, and results in the formation of just one molecular layer. Typical examples include oxygen binding to coal surfaces and hydrogen chloride adhering to iron surfaces (Aljamali et al., 2021).

Advantages of Adsorption

The adsorption technique is widely preferred because of its simplicity and versatility. It is easy to carry out, typically involving the straightforward addition of adsorbents to water or mixing tanks. Moreover, this method is safe, economical, and effective at removing various contaminants such as organic, inorganic, and biological pollutants (Ali et al., 2023).

Adsorption is a well-established method for separating contaminants and is highly effective for cleaning water. Its widespread use is due to its affordability, adaptable design, straightforward operation, and ability to handle toxic substances. Moreover, adsorption does not generate dangerous by-products, produces high-quality purified water, and is cost-effective (Crini, 2006).

2.2.1.2 Memberane Filtration

It utilizes the micropores and selective permeability of membranes to filter wastewater and isolate particular substances. This approach offers multiple advantages, including excellent separation performance, reduced energy usage, simple operation, and minimal generation of secondary pollution. However, its widespread use is still constrained by factors like the requirement for specialized equipment, significant upfront costs, and issues like membrane fouling. It effectively removes dyes through size and charge exclusion, yielding high-quality treated water, but it remains costly, energy-intensive, and prone to membrane fouling (Ghaly et al., 2014).

2.2.1.3 Coagulation-Flocculation

Coagulation involves using coagulants such as alum, ferric salts, and polyaluminum chloride, along with flocculants like polymers, to destabilize dye molecules and form larger particles that settle out of the water. This method is effective for removing insoluble or colloidal dyes but produces sludge as a byproduct. It is commonly used to remove color from textile wastewater and can partially reduce chemical oxygen demand (COD), depending on the coagulant chosen. The process works by lowering the zeta potential on particle surfaces, encouraging them to clump together into larger flocs. Different types of polymers cationic, anionic, and nonionic are used as coagulants in this process.

The coagulation process has several significant drawbacks. Firstly, the chemicals employed are expensive and cannot be recovered or reused, leading to their disposal after use. Secondly, dyes that are highly water-soluble tend to resist coagulation, necessitating higher amounts of coagulants and thus raising treatment expenses. Thirdly, the process produces colored sludge that requires proper management and legal disposal. Lastly, and most importantly, this sludge is often toxic and can elevate the total dissolved solids (TDS) in the treated water (Singh & Arora, 2011).

2.2.1.4 Ion Exchange

Ion exchange is a widely used technique for removing dyes from water, relying on the strong attraction between charged dye molecules and the functional groups on ion exchange resins. During the process, ions are swapped, forming stable bonds that help separate the dyes efficiently. However, the performance of these resins can be hindered by interfering substances or may deteriorate quickly if exposed to unexpectedly high concentrations of contaminants (Sharma et al., 2014).

Various cationic and anionic resins are utilized to eliminate ionic dyes such as methylene blue, methyl orange, and malachite green from water. The efficiency of these ion exchangers is influenced by factors including the dye concentration in the solution and the quantity of resin used. Generally, dye removal is more effective at lower dye concentrations and with larger resin doses. Recently, anionic exchangers have become increasingly popular for treating wastewater contaminated with azo dyes.

Ion exchange techniques are successful in eliminating different contaminants; however, they are costly and generate highly toxic sludge that requires careful disposal. Furthermore, although the adsorbent remains intact during the process, its effectiveness decreases when targeting a wide range of dyes (Gu et al., 2019; Khan et al., 2025). Additionally, the process is lengthy and costly to operate. To overcome these limitations and improve overall removal effectiveness, ion exchange is frequently integrated with adsorption and membrane filtration methods (Ali et al., 2023).

2.2.2 Chemical Methods

These methods involve breaking down or oxidizing dyes to achieve complete degradation; however, they generate sludge due to the chemicals used, and disposing of this sludge is costly.

2.2.2.1 Advanced Oxidation Processes (AOPs)

Advanced Oxidation Processes (AOPs) are treatment methods designed to remove organic contaminants from water and wastewater. They work by generating highly reactive hydroxyl radicals (•OH) that can non-selectively degrade and completely mineralize a wide range of pollutants, including dyes (Deng & Zhao, 2015).

This approach employs strong oxidants like ozone, hydrogen peroxide, Fenton's reagent, and titanium dioxide photocatalysis to decompose dyes into smaller, less harmful substances. It is especially effective for resistant dyes such as methylene blue, though it entails high costs and necessitates careful handling of chemicals.

- Ozonation is an effective and quick technique for removing color from wastewater by breaking the double bonds in many dyes, using ozone as an oxidizing agent. It also helps decrease or eliminate foaming caused by residual surfactants and can significantly reduce chemical oxygen demand (COD). Moreover, it improves the biodegradability of effluents containing toxic and non-biodegradable substances by partially oxidizing these stubborn pollutants into simpler, more biodegradable forms (Ayeche, 2012). A major benefit of ozonation is that it does not lead to an increase in wastewater volume or sludge production. Its use in large-scale applications is growing, mainly as a final polishing step after treatments like filtration that reduce suspended solids and enhance decolorization.
- Fenton's process uses Fenton’s reagent a mixture of hydrogen peroxide (H_2O_2) and ferrous iron (Fe^{2+}) to effectively treat wastewater containing dyes. This method is capable of breaking down both soluble and insoluble dyes that are difficult to degrade using traditional biological methods.

  Although this method is effective, it faces significant drawbacks, such as producing large amounts of sludge that are difficult to dispose of, requiring extended treatment durations, and being less effective for specific dye types like disperse and vat dyes (Roy & Saha, 2021a).

- Sodium hypochlorite is widely utilized as an oxidizing agent, particularly in treating textile wastewater, where it helps break down azo bonds more quickly. However, its primary disadvantages include the production of carcinogenic aromatic amines and other harmful by-products, along with high operational costs, which make its application less favorable (Karthik et al., 2014).

Sodium hypochlorite (NaOCl) interacts with the amino groups in dye molecules via chlorine radicals (Cl•), promoting the breakdown of azo bonds and leading to decolorization. However, it is not effective for disperse dyes. Typically, increasing chlorine concentrations enhances decolorization efficiency. However, the application of chlorine in dye removal has declined due to its harmful environmental impact, particularly the production of aromatic amines that are carcinogenic or toxic (Robinson et al., 2001).

- Photochemical treatment uses UV light and hydrogen peroxide (H_2O_2) to decompose dye molecules into carbon dioxide (CO_2) and water (H_2O). This method depends on generating hydroxyl radicals that aid in breaking down the dyes. When exposed to UV radiation, substances like H_2O_2 become activated, and the efficiency of dye removal is influenced by factors such as UV intensity, pH, the chemical makeup of the dye, and the composition of the dye solution (Robinson et al., 2001).

The by-products produced during photochemical treatment vary based on the starting materials and the extent of decolorization, potentially including halides, metals, inorganic acids, organic aldehydes, and organic acids. This treatment method for dye-laden wastewater has several benefits, such as not generating sludge and greatly reducing bad odors. It produces high-quality treated water and is regarded as a cost-effective approach (Robinson et al., 2001).

2.2.3 Biological Methods

Biological treatment is frequently the most cost-effective and efficient method for cleaning pollution compared to using machinery or chemicals. It involves tiny living organisms such as bacteria, yeast, algae, and fungi to eliminate contaminants from industrial waste. These microorganisms can consume, decompose, or trap pollutants, resulting in cleaner water. Common approaches include employing fungi to alter color, microbes to degrade waste, and allowing microorganisms to adhere to pollutants for removal. However, implementing these methods in practice faces several challenges: biological systems often require large amounts of land, are vulnerable to changes in wastewater composition and toxic substances, and are difficult to modify or relocate. Additionally, traditional biodegradation techniques often struggle to fully remove color, as some complex or synthetic organic compounds resist breakdown despite the efforts of microorganisms (Crini, 2006).

Utilizing microorganisms to degrade synthetic dyes offers a straightforward and appealing treatment method. Nonetheless, the biological mechanisms can be complex, and this approach might be less efficient for highly toxic dyes, potentially demanding considerable time to achieve results (Forgacs et al., 2004; Khan et al., 2025).

2.2.3.1 Aerobic and Anaerobic Degradation

Bacteria and fungi are the most thoroughly researched microorganisms used for treating wastewater contaminated with dyes. In aerobic environments, bacteria produce enzymes that decompose organic substances. For more than twenty years, efforts have been directed toward discovering and isolating aerobic bacteria that can degrade various dyes. Although some dyes can be effectively treated, many are resistant to biological breakdown or cannot be broken down under aerobic conditions (Gupta & Suhas, 2009).

Certain bacteria, fungi (such as white-rot fungi), and algae have the ability to decompose dyes. White-rot fungi are microorganisms that can degrade lignin, the complex polymer found in the cell walls of woody plants (Robinson et al., 2001).

Anaerobic degradation occurs in environments without oxygen. Through anaerobic digestion, complex organic substances can be broken down, enabling further treatment either aerobically or via other dye removal methods. This biodegradation process involves an initial decolorization phase, where microorganisms break the azo nitrogen double bond in dyes, followed by a second phase that decomposes aromatic amines. Typically, decolorization happens under anaerobic conditions. This approach has certain drawbacks, such as requiring additional aerobic treatment and generating harmful by-products. Therefore, it is advisable to use a combination of anaerobic and aerobic processes for more efficient breakdown of textile dyes (Sen & Dawood, 2014). An important advantage of this anaerobic system, besides its capacity to decolorize soluble dyes, is its ability to produce biogas. This biogas can be harnessed for generating heat and electricity, helping to reduce energy expenses (Robinson et al., 2001).

Table 2.3. The Advantages and Disadvantages of various Dye removal technologies *(Sen & Dawood, 2014).*

Separation Technique	Advantages	Disadvantages
Physicochemical		
Adsorption	High capacity for removing various dyes	Adsorbents can be costly, require disposal, and some have low surface area
Ion exchange	Sorbents are not lost during treatment	Less effective for disperse dyes
Membrane filtration	Effective for a wide range of dyes and produces high-quality effluent	Best suited for low-volume treatment; generates sludge
Electro kinetic coagulation	Cost-effective method	Requires additional flocculation and filtration steps; produces sludge
Chemical		
Fenton reagent	Effective and inexpensive	Produces sludge that requires proper disposal
Ozonation	Does not generate sludge	Very short half-life (~20 min) and high operational costs
Photocatalyst	Cost-effective with low operational expenses	Some photocatalysts may degrade into toxic by-products
Biological		
Aerobic degradation	Efficient for azo dye removal and low operational cost	Slow process and requires conditions suitable for microbial growth
Anaerobic degradation	By-products can be used as energy sources	Requires subsequent aerobic treatment; produces methane and hydrogen sulfide

2.3. Different Adsorbents used for dye removal

Adsorbents are solid substances characterized by extensive surface areas, enabling them to attract and trap molecules (adsorbates) from liquids or gases on their surfaces. In wastewater treatment, their primary role is to remove dyes and other pollutants that are difficult to degrade biologically or through standard methods. Various types of adsorbents exhibit different capacities for effectively removing particular contaminants from wastewater (Younas et al., 2021).

2.3.1 Activated carbon

Most solid materials can attract and hold substances on their surfaces, but their efficiency in treating wastewater depends on characteristics like their structure, polarity, porosity, and surface area. The target substances are usually organic compounds that can lead to problems like discoloration and bad smells. Common materials used for adsorption in wastewater treatment include activated carbon, organic polymers, and silica-based substances (Mohammed, 2011).

Activated carbon, also called activated charcoal, is a type of carbon characterized by a highly porous surface. Although it belongs to the graphite family, it has an amorphous structure. Its distinct properties such as a vast network of pores, a large surface area, and chemical polarity are influenced by the raw materials and manufacturing methods employed. In recent times, activated carbon has found extensive applications in multiple industries. However, its production and regeneration can be expensive, and its disposal presents environmental concerns because it is typically derived from non-renewable resources like coal and petroleum (Adeyemo et al., 2017).

There has been increasing interest in developing eco-friendly, renewable, and cost-effective raw materials for producing activated carbon. Biomass, especially agricultural waste, has become a popular alternative for creating new types of activated carbon. Examples of waste materials used for activated carbon production include palm kernel shells, used coffee beans, cassava peels, rice husks, sugarcane bagasse, olive husks, hazelnut shells, almond shells, and walnut shells. The selection of raw material significantly affects the characteristics of the resulting activated carbon, including its surface area, porosity, and particle size. Activated carbon is typically classified based on particle size into three categories: Powdered Activated Carbon (PAC), Granular Activated Carbon (GAC), and Activated Carbon Fibers (ACF) (Ali et al., 2023).

Due to its widespread accessibility and low cost, coal is the main raw material used to produce activated carbon. However, activated carbon has notable drawbacks: it can be expensive and is not particularly efficient or practical for eliminating disperse and vat dyes (Crini, 2006). Commercial activated carbon is commonly employed as an adsorbent for dye removal.

Researchers have explored cost-effective and unconventional adsorbents for dye removal from wastewater because of the high costs linked to production and regeneration. Different materials, including commercial activated carbon, minerals, clays, agricultural waste, and activated carbon derived from agricultural by-products, have been utilized for this purpose (Sen & Dawood, 2014).

Activated carbon needs to be either reactivated or safely disposed of after use. Reconditioning it usually causes a 10–15% reduction in its effectiveness (Robinson et al., 2001). This prompting many researchers to explore and develop alternative low-cost adsorbents.

2.3.2 Low cost Adsorbent

Due to the previously mentioned challenges, there has been a growing interest in identifying alternative sorbents to replace expensive activated carbon. Recently, attention has shifted toward using various natural solid materials that can effectively eliminate pollutants from contaminated water at a lower cost. Cost plays a vital role when evaluating and comparing different adsorbents. Bailey et al. note that a low-cost sorbent is one that is naturally abundant, requires minimal processing, or is available as a by-product or waste from other industries. A variety of industrial and agricultural wastes, natural materials, and biosorbent are viewed as promising and economical alternatives to traditional adsorbents (Crini, 2006). Low-cost adsorbents are primarily categorized into two groups. The first group is based on their availability and includes (a) natural materials like wood, peat, coal, and lignite; (b) industrial, agricultural, or household waste and by-products such as slag, sludge, fly ash, bagasse fly ash, and red mud; and (c) synthetic materials, classified by their composition as inorganic or organic. The second group is determined by their inherent properties, dividing them into (a) organic and (b) inorganic types (Gupta et al., 2009).

2.3.2.1 Waste materials from Agriculture and Industry

Agricultural and industrial by-products are considered cost-effective adsorbents because they are readily available, inexpensive, require minimal processing, and are effective for adsorption. Many types of agricultural and wood waste can be transformed into activated carbon (AC), providing a renewable and affordable resource. Since these waste materials generally have low economic value and can cause disposal problems, repurposing them offers a practical solution. Converting such by-products into AC not only yields economic advantages and reduces waste disposal costs but also provides a cheaper alternative to commercial activated carbons. Furthermore, industrial solid wastes like metal hydroxide sludge, fly ash, and red mud are inexpensive and locally accessible, making them suitable for use as adsorbents in dye removal processes (Crini, 2006).

2.3.2.2 Natural materials

This category includes natural materials that are used directly or with minimal processing and usually have limited or no other uses. Examples of such materials include:

- Wood

Poots et al. investigated using wood as a cost-effective alternative to activated carbon for removing telon blue. They proposed that, because of its low expense, wood doesn't need to be regenerated after adsorption; instead, it can be burned to recover heat for steam production. However, the study noted some limitations, such as the lengthy contact time of 8 hours and the relatively low capacity of wood to adsorb telon blue (Gupta et al., 2009).

- Coal

Coal consists of substances rich in carbon and mineral material, formed from the breakdown of plant matter. Its ability to adsorb substances varies based on the type of vegetation it originated from and the extent of physical and chemical changes it has experienced after deposition (Crini, 2006).

Coal is both affordable and widely accessible in many areas, and its notable characteristics make it highly effective at adsorbing various organic and inorganic pollutants (Simate et al., 2016).

- Peat

Peat is one of the most thoroughly researched natural materials utilized as an alternative adsorbent. Poots et al. examined its effectiveness without any prior treatment for removing telon blue and found that peat performed significantly better than wood (Gupta et al., 2009).

Peat is a complex, porous soil composed of organic material at various stages of decomposition. It is categorized into four types moss peat, herbaceous peat, woody peat, and sedimentary peat based on its original material. As an abundant, inexpensive, and easily accessible biosorbent, peat can absorb a wide range of pollutants. Its main components include lignin, cellulose, fulvic acid, and humic acid. Lignin and humic acid contain polar functional groups such as alcohols, aldehydes, ketones, carboxylic acids, phenolic hydroxyls, and ethers, which facilitate chemical bonding. This polarity makes peat particularly effective for removing dyes from water solutions (Crini, 2006).

- Clay

Clay is a naturally occurring, fine-grained substance found on Earth's surface, composed of particles smaller than 2 micrometers. It primarily contains water, alumina, silica, and minerals produced through the weathering of rocks. Its structure consists of interconnected polyhedral units formed by oxygen anions and silicon, often incorporating aluminum cations (Gu et al., 2019; Velde, 1995).

Humans have historically utilized clays because they are inexpensive, readily accessible, and possess excellent adsorption and ion-exchange capabilities. Different kinds of clay, including ball clay, bentonite, common clay, fire clay, and kaolin, fall under this category (Gupta et al., 2009).

Natural clays are commonly used as adsorbents for dye removal from water because they are readily accessible, inexpensive, highly porous, possess excellent ion-exchange properties, and are non-toxic (Dutta et al., 2021).

Clay is capable of eliminating about 70% of the waste from a water purification system, while the other 30% can be eliminated with activated carbon (Adeyemo et al., 2017). Native and processed clays have demonstrated effective performance as adsorbents for eliminating different metals, organic substances, and dyes (Singh & Arora, 2011).

2.4. Clays as Natural Adsorbents

Natural clays are effective at absorbing certain colored dyes, particularly those with a positive charge, due to their negative charge. Researchers can modify the surface of clays to enhance their ability to remove other types of dyes. They have experimented with various clay types to extract dyes from fabrics and to eliminate metal ions like zinc from water (Sen & Dawood, 2014).

Clays' capacity to adsorb substances primarily stems from the overall negative charge in their mineral structure, allowing them to attract and hold positively charged particles. Additionally, their extensive surface area and porosity play a crucial role in enhancing their sorption capabilities (Crini, 2006).

Activated carbon and clay are frequently utilized as adsorbents in adsorption processes. Activated carbon, in particular, is extensively used for eliminating colored organic compounds due to its high capacity to adsorb organic materials, making it one of the most popular and versatile adsorbents available.

Despite its effectiveness, the use of certain natural adsorbents faces challenges including limited natural availability, slow adsorption rates, low capacity for large molecules due to their microporous structure, disposal issues, and the high cost and complexity of regeneration. These limitations have driven the search for alternative, affordable, and efficient adsorbents such as clay-based materials. In recent years, soil clay materials have become increasingly popular as substitutes for commercial adsorbents because they are inexpensive, readily available, possess a large surface area, are non-toxic, and have ion-exchange capabilities (Adeyemo et al., 2017).

Clays possess a diverse range of physical properties, including their tiny particle size, hardness, high plasticity, cohesiveness, suitable shrinkage, and resistance to heat, along with their surface-decorating capability. Their minuscule particles and large specific surface area, due to a complex porous structure, enhance their physical and chemical interactions with dissolved materials. These interactions are primarily affected by factors such as crystallinity, electrostatic forces, adsorption, and cation exchange. Furthermore, the extensive porous surface area suggests a strong bonding potential on clay surfaces (Gu et al., 2019).

2.4.1 Types of clay

Some of the common types of clays used as adsorbents are

- **Kaolinite Clay**

Kaolinite is a type of soft, chalky clay that we often call china clay or kaolin with chemical formula $Si_4Al_4O_{10}(OH)_8$. Its special structure is like stacked layers that stick together tightly because of tiny hydrogen bonds, so the layers don’t spread apart or get much bigger when they get wet. This means it doesn’t swell up like some other clays do when water is added. Kaolinite does not swell in water and have lower surface areas of 10 to 20 m^2/g (Maček et al., 2013) and cation exchange capacity (<1 centimole/kg). Also, because of its simple structure and low surface area, kaolinite doesn't hold onto many extra tiny particles or ions (which are like tiny charged pieces). This makes it less good at trapping or exchanging these particles compared to other types of clay (Kumari & Mohan, 2021).

Kaolin clay, or china clay, is a gentle, pale-colored material that can absorb and hold harmful contaminants, much like a sponge absorbs water. Because of this property, it is commonly utilized to cleanse polluted water by extracting pollutants like heavy metals, dyes, and oils (Khan et al., 2025).

- **Bentonite Clay**

Bentonite is a special type of clay made mostly of a mineral called montmorillonite. It has many tiny surfaces that help it grab onto dirt, bad metals, and other unwanted stuff. Because of this, it's often used to clean dirty water and to make oils and wines purer and better (Khan et al., 2025).

- **Montmorillonite Clay**

Montmorillonite is a unique type of clay that expands when it absorbs water and possesses a large surface area, typically ranging from 50 to 840 square meters per gram (Maček et al., 2013) and highest adsorption capacity to work with. People utilize clay to purify water and soil by trapping and holding onto harmful substances such as heavy metals, chemicals, and radioactive materials, preventing them from causing damage. There are various types of clay, each suited for specific cleaning tasks. To enhance their effectiveness, clays often require particular preparation methods. Since different clays have varying capacities to capture contaminants, scientists select the appropriate type based on the specific pollutants they aim to remove (Khan et al., 2025). This compound, with the chemical formula (Na,Ca)0.33, (Al,Mg)2Si4O10(OH)2·nH2O, serves as a specialized adsorbent material for eliminating different pollutants, including positively charged heavy metals and brightly colored dyes (Subhi et al., 2022).

- ❖ Important characteristics that enable natural clays to effectively adsorb contaminants in wastewater treatment and pollutant elimination (Jemai et al., 2024).
- Clay minerals possess a large surface area because of their tiny particles and layered configuration, providing many external and internal sites for capturing pollutants.
- Cation exchange capacity (CEC) is the ability of clay minerals to exchange positively charged ions between their surfaces and the surrounding liquid. This property enables them to adsorb heavy metals, dyes, and other positively charged pollutants..
- Many natural clays have tiny and medium-sized pores that enhance the flow and retention of pollutants within the clay.
- Mineral composition including minerals like kaolinite, montmorillonite, and illite affects the efficiency of adsorption processes. Variations in chemical elements such as aluminum,

silicon, iron, and magnesium influence surface charge, reactivity, and the ability to attract different pollutants.

- Clay surfaces can acquire negative charges depending on the pH level and mineral content, which enables them to attract positively charged dyes and heavy metals through electrostatic interactions.
- Swelling capacity in specific clays like bentonite or montmorillonite causes their layers to expand, which helps them absorb and trap pollutants.

Several research studies have investigated the removal of methylene blue dye from wastewater through adsorption using clay as the adsorbent, focusing on optimizing various operational parameters of the adsorption process. (El-Habacha et al., 2024) investigated the use of natural clay to eliminate methylene blue dye from water. They examined how factors such as adsorbent dosage, contact time, pH, and initial dye concentration influence the process. The highest adsorption capacity recorded was 81.185 mg/g for a methylene blue concentration of 100 mg/L at an initial pH of 6.43, temperature of 293K, and an adsorbent dose of 1 g/L. (Bingül, 2022) investigated the use of natural clay to eliminate methylene blue (MB) from water. The highest removal efficiency achieved was 94.69%, using an adsorbent dose of 0.3 g L^-1 and a dye concentration of 20 mg L^-1. Kinetic analysis revealed that at lower adsorbent doses, MB adsorption followed pseudo-first-order kinetics, while at higher doses, it aligned with pseudo-second-order kinetics. A recent study by (Loutfi et al., 2023) investigated the adsorption of methylene blue (MB) using Moroccan clay. The researchers varied several independent parameters, including adsorbent dose (from 0.05 to 5 g/L), dye concentration (100 to 1000 mg/L), contact time (10 to 120 minutes), temperature (20-60°C), and solution pH (3-12). They achieved an optimal adsorption capacity of 456.62 mg/g. The adsorption kinetics aligned well with a pseudo-second-order model, showing a high correlation coefficient of $R^2 = 0.99$. In addition to this, (Sarma et al., 2011) investigated the removal of methylene blue dye from water using natural and modified clay. They examined how factors such as pH, initial dye concentration, clay amount, contact time, and temperature influenced the process. The data fitted best with second-order kinetics. Across a temperature range of 303 to 333 K, the Langmuir monolayer capacity increased for three kaolinite types from approximately 45.5–56.5 mg/g to 45.9–57.8 mg/g and 46.3–58.8 mg/g, respectively. Similarly, for three montmorillonite types, capacity rose from about 163.9–181.8 mg/g to 166.7–188.8 mg/g and 172.4–192.3 mg/g.

(Amrhar et al., 2023) investigated the use of natural muscovite clay for removing methylene blue (MB) from water. Their study examined how various factors such as adsorbent amount (5-40 mg), contact duration (1-60 minutes), solution pH (3.7-11.78), stirring speed (100-900 rpm), initial MB concentration (15-80 mg/L), and temperature (293.15-333.15 K) influence the adsorption process. The optimum adsorption capacity was 59.828 mg/g at the initial concentration of 80 mg/L, 293.15K and adsorbent mass of 20mg.

According to the reviewed literature, the primary factors influencing the adsorption process are the initial pH of the solution, contact time, adsorbent dosage, and the initial concentration of methylene blue dye. However, in this study, the focus is not on optimization but rather on comparing the removal efficiencies of two different natural clays from different regions. Therefore, the main factors considered in this research are contact time and adsorbent dosage.

2.5 Factors affecting adsorption on clays

Different factors such as the pH of the solution, temperature, starting dye concentration, and the quantity of adsorbent employed can affect how effectively dye is adsorbed.

2.5.1 Effect of PH of Solution

The adsorption process is significantly influenced by pH, as it affects both the chemical nature of the dye and the functional groups on the adsorbent. At low pH levels, anionic dyes tend to be more readily adsorbed onto negatively charged adsorbents. Conversely, higher pH values favor the adsorption of cationic dyes onto negatively charged surfaces and reduce the adsorption of anionic dyes. To optimize adsorption efficiency, pH must be carefully adjusted according to factors such as the type and modifications of the clay and the specific dye. Additionally, pH impacts how dye molecules interact with the adsorbent; for example, the adsorption of cationic dyes decreases at lower pH because the carboxylic groups on the adsorbent become protonated (Khan et al., 2025). The effectiveness of cationic dyes being removed declines when the pH level decreases (Subhi et al., 2022).

2.5.2 Effect of Temperature

Dye adsorption can either absorb heat (endothermic) or release heat (exothermic). In endothermic reactions, higher temperatures boost the amount of dye adsorbed, whereas in exothermic reactions, increasing temperature reduces adsorption. For instance, increasing the temperature improves Congo red dye adsorption on modified hectorite clay, whereas it reduces methylene blue dye adsorption on montmorillonite clay (Khan et al., 2025).

2.5.3 Effect of initial dye concentration and Contact time

The amount of dye adsorbed per gram and the percentage of dye removed are significantly influenced by the initial dye concentration. Higher starting concentrations lead to saturation of all adsorption sites, decreasing overall removal efficiency. As both contact time and initial dye concentration increase, the amount of dye adsorbed (mg/g) also rises. The initial dye concentration acts as a driving force, facilitating the transfer of dye from the solution to the adsorbent by overcoming resistance (Khan et al., 2025).

2.5.4 Effect of Adsorbent dosage

Increasing the amount of the mixture enhances the color removal efficiency because a higher dosage provides a greater surface area and more active sites for adsorption. (Khan et al., 2025). Generally, adding more adsorbent improves removal efficiency since a greater amount offers additional sorption sites (Subhi et al., 2022).

2.5.5 Effect of clay composition and origin

Studies indicate that the specific makeup and geological source of clays significantly influence their effectiveness in removing methylene blue (MB). For instance, a natural Moroccan clay rich in montmorillonite demonstrated a remarkable ability to absorb or attract substances of 315.05 mg/g. This high efficiency is due to the smectite minerals' strong cation exchange abilities and their swelling characteristics (Azizi et al., 2025). Likewise, altering local clays can significantly improve their effectiveness; For instance, clay alginate beads impregnated with sodium dodecyl sulfate (SDS) achieved an impressive highest adsorption capacity of 1468.5 mg/g, vastly surpassing that of unmodified native clay (Almas et al., 2023).Conversely, base-activated bentonite clays demonstrated moderate capacities, around 22.13 mg/g, but still achieved high removal efficiencies when optimized. This indicates that straightforward treatments can enhance the cost-effectiveness of using clays for wastewater cleanup (Hamad et al., 2024). Raw clays, even without any treatment, can exhibit valuable properties; for example, a natural clay from South-East Morocco (TMG) was able to adsorb 81.19 mg/g of MB, highlighting that the performance of untreated clays can differ significantly based on their mineral composition and purity (El-Habacha et al., 2024). Overall, the research indicates that smectite-rich clays tend to have the highest adsorption capacity. In contrast, kaolinite-rich clays typically exhibit lower uptake unless they are activated. Additionally, factors such as impurities, exchangeable cations, and the clay's structural characteristics shaped by its source also it plays a crucial role in the decision-making process of how effectively the clay can adsorb substances.

Several research studies have been carried out on the removal of methylene blue dye from wastewater through adsorption using clay and other adsorbent materials. (Mulushewa et al., 2021) investigated the use of zeolite-x and kaolin as effective adsorbents for removing methylene blue from textile wastewater. They reported particle sizes of 40.77 nm for zeolite-x and 0.45 nm for kaolin. Zeolite-x demonstrated the best performance at an optimal pH of 4, achieving a removal efficiency of 97.77%, while kaolin was most effective at pH 6 with a removal efficiency of 86.86%. The optimal contact times were 60 minutes for zeolite-x and 80 minutes for kaolin. The ideal adsorbent dosages were 0.4 grams for zeolite-x and 0.6 grams for kaolin, resulting in removal efficiencies of 97.12% and 87.75%, respectively. The confirmed square sum errors were 1.0×10^-4 for zeolite-x and 1.0×10^-3 for kaolin. Adsorption isotherm data fitted better to the Freundlich model than the Langmuir model, and the kinetics aligned most closely with a pseudo-second-order model. Overall, zeolite-x exhibited higher removal efficiency than kaolin under the same conditions.

3. MATERIALS AND METHODS

3.1. Materials

The following apparatus and equipment's were used in this study such as :Drying oven, mortar and rubber-tipped pestle, Standard sieve, Mechanical sieve shaker, Analytical Balance, Jar test machine, UV visible spectrophotometer (X-ma 1200 spectrophotometer), filter paper, beaker, pipette, Measuring cylinder**,** Thermometer, Hydrometer, XRD, XRF, Distilled water and MB dye.

3.1.1. Collection and pretreatment of adsorbent (natural clay)

The Belessa clay deposit is located in the Central Ethiopian Regional State, approximately 240 to 285 kilometers south of Addis Ababa. It lies northeast of the town of Hosanna and is accessible via the Addis Ababa–Hosanna highway, followed by a secondary road leading directly to the site. The area benefits from good logistical connectivity, which supports both field investigations and potential future industrial development

The Homicho clay deposit is situated in the Central Ethiopian Regional State, approximately 250 to 290 kilometers south of Addis Ababa. It is located northwest of the town of Hosanna and can be accessed via the Addis Ababa–Hosanna highway. To reach Hommecho from Hosanna, turn right onto a connecting road that leads to the site. Hommecho is about 55 kilometers northwest of Hosanna, and the drive from Hosanna to Hommecho takes approximately 2 to 3 hours by car.

The raw samples which have been collected from the two sites, Homicho and Belesa, were highly moist, especially those brought from Homicho, thus, open air drying of the samples was pertinent prior to the size reduction. After the homogenizing the samples manually, portions were taken from each sample and sun dried in an open air for several days by placing each sample on a canvas and spreading it. The sun dried samples were then placed in a jaw crusher which reduces the gangue in to a reasonable size. The out puts of the jaw crusher were directly taken to the milling machine to further reduces the particle size of each sample significantly. The outputs from the miller were then sieved using 63µm size sieve with the help of vibratory shaker. The powders which pass through the 63µm size sieve were collected in plastic containers and stored after being labelled. The over sizes were returned back to the milling machine for second round milling.

Figure 3.1. Homecho clay

Figure 3.2. Belesa clay

3.1.2 preparation of constituted wastewater

Methylene blue dye served as a representative contaminant to assess the adsorption abilities of two natural clays sourced from different deposits. The chemical formula of methylene blue dye is $C_{16}H_{18}ClN_3S$ with color Index(CI) 52015 and molecular weight of 319.85gmol^{-1}(Khan et al., 2022). The IUPAC name of methylene blue dye is [3,7-bis(dimethylamino) phenothiazine chloride tetera methylthionine chloride]. The molecular structure of methylene blue is illustrated in the diagram below.

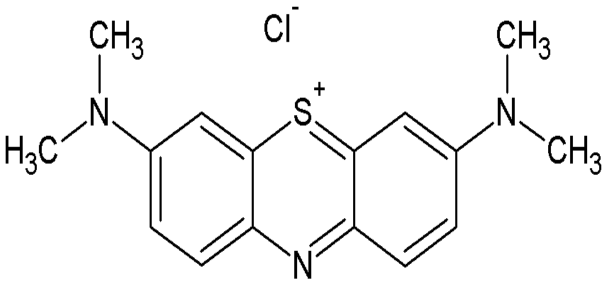

Figure 3.3. molecular structure of methylene blue

Methylene blue was sourced from the Chemical and Bioengineering Laboratory at Addis Ababa Institute of Technology and was used without any additional purification. It appears as a solid, odorless, dark green powder at room temperature, producing a blue solution when dissolved in water. In its oxidized form, methylene blue has a distinctive deep blue color, while it becomes colorless when reduced (Khan et al., 2022). A dye stock solution was made by dissolving 1 gram of methylene blue in 1000 milliliters of distilled water. The experimental solutions were then prepared by diluting this stock solution with distilled water to the desired concentrations. The highest absorbance of methylene blue was measured at 663 nm using a UV-vis spectrophotometer (Khan et al., 2022).

3.2. Physicochemical Characterization of Raw Adsorbent

Physicochenical characterization of the two natural clays (BC and HC) were investigated using the following technigues. The arrangement of atoms within the crystal and phase composition of the adsorbent was analyzed using X-ray diffraction. In addition to this, the specific surfacce area was investigated by using Brunauer, Emmett, and Teller method (BET) based on adsorption and desorption isotherms of nitrogen gas at room temperature and perssure of 760mmHg.

3.2.1 Particle size analysis of the clay deposits

Particle size analysis is conducted to assess the distribution of particle sizes in clay samples, which is crucial for their adsorption capabilities. Generally, smaller particles offer a greater surface area relative to their volume and reveal more active sites, thereby potentially improving the effectiveness of dye removal. By analyzing particle size distribution, it becomes possible to compare different clays, optimize their preparation, and better explain variations in adsorption capacity and removal efficiency.

Since the clay samples are mixed type, composed of fine and cores particle, a combination of sieving and sedimentation tests were used to analyze the particle size distributions of each sample. The analysis were made following the standard procedures from ASTM D6913 / ISO 17892-4

Since the samples are not highly cohesive dry sieving procedures were followed. ASTM/ISO standard sieves were used for analysis. Mechanical sieve shaker was used for consistent agitation of the sample on the stacked sieves. Analytical balance (accurate to 0.01 g) was used to measure the fractions retained on each sieve. Drying oven and mortar and rubber-tipped pestle were used for drying and gentle disaggregation of the samples respectively.

First some amount of each sample was dried in the oven at 110°C for 24 hours to remove moisture. Then each dry mass was recorded (M_t = total mass of the sample). After recording the dry mass, each sample underwent gentle crushing to break down aggregates using a rubber-tipped pestle. The crushing was done carefully to avoid breaking individual particles. 200g of each sample were then measured and placed on top of the stacked sieves which were arranged in descending orders. The sample loaded sieve stack was then fixed in the mechanical sieve shaker and a vibration of 150 oscillations/min was applied for 15 Minutes. Then the sieve stacks were carefully disassembled and the retained clay factions on each sieve (M_i) were carefully collected and weighed. The mass of clay samples on each sieve were recorded in a data table and then percept retained and cumulative passing were calculated using the following formula:

% Retained on each sieve = $(M_i / M_t) \times 100$ %, Where, Mi= mass of sample retained on a given sieve (g) and Mt= total mass of the original sample (g)

Cumulative Passing = 100% – Sum of % retained on all coarser sieves.

The silt and clay fractions (<75 µm) of the samples were determined using standard sedimentation tests following ASTM D7928 standard procedure.

For the standard sedimentation tests a 1000 mL glass made sedimentation cylinder were used. Sodium hexametaphosphate, $(NaPO_3)_6$ was used as a dispersing agent. High-speed mixer was used for mechanical stirring the clay suspension. Thermometer was used to measure suspension temperature. Analytical balance (accuracy 0.01 g) was used to measure the mass of clay samples. Electric oven was used for drying samples. Stopwatch was used to measure sedimentation time. ASTM 152H hydrometer (range: 0.995–1.038 g/mL). Hydrometer jar (~1000 mL).

Before conducting the sedimentation analysis, the samples were oven-dried at 110°C for 24 hours. Then, 50 grams of each dry sample were mixed with 125 mL of a 4% sodium hexametaphosphate aqueous solution, which acts as a dispersing agent. The mixture was vigorously stirred for 5–10 minutes using a mechanical mixer. Afterward, it was left undisturbed for 16 hours to allow for better dispersion. The resulting suspension was then passed through a No. 200 sieve (75 µm) to remove particles larger than 75 µm. The dispersed and wet-sieved sample was transferred to a 1000 mL sedimentation cylinder, and distilled water was added until the suspension reached the 1000 mL mark. The cylinder was caped and inverted 15 times to mix the suspension well and then placed in a vibration-free area. Hydrometer was then inserted and initial reading was recorded (R_o) at 0 min. Several readings were recorded at 0.25, 0.5, 1, 2, 4, 8, 15, 30, 60, 120, and 1440 min. During each reading, the hydrometer was inserted 10 sec before the readings were taken to minimize disturbance. Temperature was also recorded at each interval since it affects viscosity of the suspension. The top of the meniscus was read not the liquid level. Temperature correction was applied as per ASTM D422. The particle size and % finer were calculated using the equations below:

$$D = \sqrt{\frac{18\mu.h}{(\rho_s - \rho_w).g.t}} \quad \text{…………………………………………………………………… (eq.1)}$$

Where: D = Particle diameter (mm), μ = Dynamic viscosity (from temperature table), h = effective depth (from ASTM D422), ρ_s= Soil density (~2.65 g/cm^3), ρ_w= Water density (~1 g/cm^3), t = Time.

$$N = \frac{R - R_0}{M_s} \times 100 \quad \text{…………………………………………………………………… (eq.2)}$$

Where: N= % finer, R= Corrected hydrometer reading, R_0 = Zero correction, M_s= Mass of dry soil (g)

3.2.2. Specific surface area characterization

Determining the specific surface area of clay samples is important because it directly affects their ability to adsorb substances and their overall effectiveness. Clays with larger surface areas offer more active sites for dye molecules, enhancing their removal efficiency. Measuring surface area also enables comparisons between various clay types and helps understand how factors like mineral content, particle size, and porosity impact their adsorption properties.

The specific surface areas of the two clays were measured using the Brunauer-Emmett-Teller (BET) method, which relies on nitrogen gas adsorption and desorption at room temperature and atmospheric pressure (760 mmHg) in Bahirdar University's laboratory. Additionally, the surface area was also assessed through the adsorption and desorption isotherms of natural gas at 77.3K and 760 mmHg.

3.2.3 Mineralogical analysis (XRD)

X-ray diffraction (XRD) is a non-destructive method that effectively examines the crystalline arrangement within materials. In this study, XRD was employed to determine whether the clay samples were crystalline or amorphous. Each type of mineral exhibits a distinct X-ray diffraction pattern. The diffraction angle 2θ was measured across the range from 2° to 70° (Chaddha et al., 2021).

The mineralogical analyses were made using XRD analysis at Adama Science and Technology University, Material Science and Engineering department lab. Powder samples < 63µm were prepared and sent to the specified lab. The samples were prepared on a sample holder and were placed in a spatter coater where it is coated by gold particles for good imaging. The spatter coated samples were then placed in an X-ray diffractometer (Shimadzu, XRD7000, Japan). The XRD analyses were made using CuKα radiation at 40 kV and 30 mA. The samples were scanned in the 2θ range of $2°–70^{o}$ with a scan rate of $0.02° s^{-1}$. The purpose of collecting this data was to analyze the crystalline structure of the clays.

3.2.4 Chemical analysis (XRF)

X-ray fluorescence (XRF) analysis was important to examine the elemental makeup of the clay samples. This method offers both qualitative and quantitative data on major, minor, and trace elements within the material. Determining the availability of oxides such as Si, Al, Fe, Ca, and Mg is essential for assessing the mineralogical composition and overall purity of the clays. The chemical information obtained through XRF helps clarify variations in adsorption behavior, as differences in silica, alumina, iron oxides, or carbonates strongly influence surface charge, available active sites, and reactivity. Hence, XRF serves as an important tool in linking the chemical characteristics of the clays to their efficiency in dye removal.

The chemical compositional analyses were made using XRF at Arbaminch University central lab. Powder samples < 63µm were prepared and sent to the specified lab. The samples were oven-dried at 110°C for 24 hours and were homogenized to make them representative. Glass fusion beads were prepared by heating a mixture of 0.5 g of each clay sample and 5 g lithium borate flux ($Li_2B_4O_7$ or 50:50 $LiBO_2$-$Li_2B_4O_7$) in a platinum crucible at 1100°C for 15 min and then pouring it into a mold to form a homogeneous glass bead. The samples were loaded in to the spectrometer and the measurement program was run for 10 min. with the help of data analysis and acquisition software the X-ray spectra from the spectrophotometer were translated to an understandable oxide and trace element composition.

3.2.5 Thermal analysis (Thermogravimetry analysis) (TGA)

Thermogravimetric–differential thermal analysis (TG–DTA) was employed to investigate the thermal stability and decomposition behavior of the clay samples. This method provides insight into the sequential weight loss steps and the associated thermal effects as the temperature increases. The TG profile illustrates different stages of mass reduction linked to the evaporation of adsorbed moisture, the dehydroxylation of lattice-bound hydroxyl groups, the combustion of organic matter, and the decomposition of carbonates. At the same time, the DTA curve distinguishes whether these transitions are endothermic or exothermic, reflecting structural modifications or oxidation reactions. Thus, TG–DTA is a valuable tool for characterizing the mineral composition, monitoring phase transformations, and assessing the stability of clays, while also clarifying changes in surface hydroxyl groups and adsorption sites that govern their efficiency in dye removal.

The thermogrvimetric analyses were performed at Bahir Dar University central lab. Powder samples < 63µm were prepared and sent to the specified lab. The instrument was calibrated using standard samples prior to the measurement. 20g sample was loaded in to the instrument using alumina crucible. The instrument was operated in an air atmosphere, heating at a rate of 10°C per minute from 25°C up to 1000°C. The mass loss occurring during this process was measured using a highly precise microbalance integrated into the instrument. The data was then collected using the integrated data acquisition system.

3.3 Methods

3.3.1 Batch adsorption experimental procedure

A standard methylene blue dye stock solution with a concentration of 1000 mg/L was created by dissolving 1 gram of methylene blue dye in 1 liter of distilled water. A 20 mg/L solution was then prepared by diluting this stock solution. The study involved examining the adsorption of methylene blue dye onto natural clays, conducted in ten beakers with stirring using a Jar test machine, using 100 mL of solution in each beaker for specified durations. After each batch adsorption experiment, a portion of the sample was collected from the reactor and filtered through filter paper. The absorbance of each filtrate was measured at 663 nm using an X-ma 1200 spectrophotometer. Standard solutions with concentrations ranging from 0 to 30 mg/l were prepared, and a calibration curve passing through the origin was plotted by correlating these concentrations with their respective absorbance values. The calibration curve exhibits an R^2 value of 0.99, confirming adherence to Beer-Lambert law and ensuring the statistical reliability of the measurements. Subsequently, the concentrations of each filtrate were calculated by recording their absorbance values and applying these to the standard curve equation. Finally, the perecentage of methylene blue dye removal and adsorption capacity was calculated using the equation:-

$$\%\ \text{Removal Efficiency} = \frac{(C_i - C_f)}{C_i} \times 100\% \quad \text{(eq.3)}$$

Where Ci and cf are the initial and final methyl blue dye concentration in (mg/L) respectively.

$$q_e = \frac{(C_0\text{-}C_e)v}{m} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (eq.4)$$

Where Co and Ce are the initial and equilibrium methyl blue dye concentration in (mg/L) respectively and m is adsorbent mass

Table 3.1. Absorbance value of methylene blue dye concentration at 663 nm wavelength

concentration (mg/l)	Absorbance (UV)
0	0.0000
5	0.2943
10	0.5894
15	0.8458
20	1.2342
25	1.5534
30	1.8896

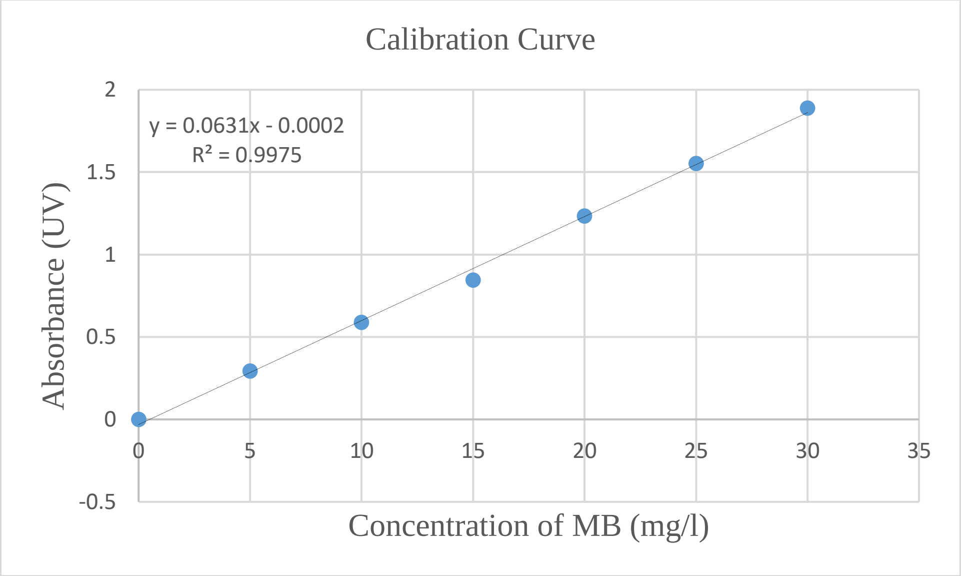

Figure 3.4. calibration curve for methylene blue dye

The calibration curve of Methylene Blue (MB) dye, illustrated in Figure 3.4, exhibits a distinct linear correlation between absorbance and concentration across the range of 0–30 mg/L. The regression equation obtained was $y = 0.063x-0.0002$, with a correlation coefficient (R^2) = 0.9975, signifying an excellent degree of linearity. This result confirms adherence to the Beer–Lambert law within the examined concentration range, implying that the absorbance of the MB solution increases proportionally with dye concentration (Gürses et al., 2016).

The high coefficient of determination (R^2) reflects the accuracy and reproducibility of the spectrophotometric readings, indicating that the established calibration curve is reliable for estimating unknown MB concentrations in subsequent adsorption studies. Comparable linear calibration behaviors have been reported in previous investigations employing natural and modified clays as (Loutfi et al., 2023), thereby reinforcing the dependability of the present analytical approach.

3.3.2 Individual effect of parameters on the adsorption process

The individual effect of each variable on the methylene blue dye adsorption efficiency of the two different natural clays were studied based on one variable at a time experiment. The effect of each operating parameter was investigated with a batch adsorption experiment. Primarily a factor time experiment was conducted by varying time (20 60 100) min and keeping the other parameter like initial concentration(20mg/l) and adsorbent dosage at constant value (0.4g). Then a factor adsorbent dosage experiment was conducted by varying adsorbent dosage (0.2 0.4 0.6) g and keeping time constant (60min). In this preliminary test the effect of one variable was investigated by keeping the other parameters at constant value.

Multiple research studies have examined the extraction of dyes from water solutions starting with an initial concentration of 20 mg/L. For instance, a study on the removal of Acid Red G dye using bio-carbon demonstrated effective treatment at this concentration reach 96.17% (Wu et al., 2022). (Carhuarupay-Molleda et al., 2025) reported that natural clay could remove 94.69% of MB dye when used at an adsorbent dose of 0.3 g/L and with an initial dye concentration of 20 mg/L. This high removal rate underscores the effectiveness of natural clays in dye adsorption processes

4. Result and Discussion

4.1 physicochemical Characterization of the two natural clay adsorbents

4.1.1 Specific surface area analysis

Table 4.1 displays the BET surface area analysis results of Belesa and Homecho clays. As can be observed form the result, Belesa and Homecho clays have almost identical specific surface areas (SSA) (331.743 and 333.740 m²/g, respectively), indicating a similar number of available adsorption sites. However, their pore properties differ considerably. Belesa clay possesses a much larger average pore size (16.93 nm) than Homecho clay (2.261 nm), implying that BC has wider and more accessible pores that promote easier diffusion of dye molecules and improve adsorption efficiency. In contrast, although HC exhibits a slightly higher pore volume, the difference is very minimal. Considering the accessibility of the pores for the large dye molecules, adsorption efficiency is likely influenced more strongly by surface area, pore size distribution, and surface chemistry than by pore volume alone. Hence, the higher dye removal performance of Belesa clay is mainly associated with its larger pore structure rather than differences in surface area.

Table 4.1. Specific surface area of BC and HC

Sample name	BET surface area (m2/g)	Pore size (nm)	Pore volume (cm^3/g)
BC	331.743	16.93	0.06388
HC	333.740	2.261	0.06886

The specific surface area analysis (SSA) results shown in Table 4.1 are significantly higher than the typical range reported for unmodified natural clays, which commonly lie between 10–150 m²/g, depending on their mineral composition and texture (David et al., 2020). Many researchers reported a relative low surface area for natural clays and have employed several modifications to enhance the surface area of natural clays. For instance, A study by (El-Geundi et al., 2014) reported that the natural clay had a specific surface area of 78.4 m²/g. According to the study conducted (Panda et al., 2010), acid treatment significantly enhanced the surface area of kaolin clay. Specifically, treatment with 1 M acid resulted in a threefold increase in surface area, while treatment with 10 M acid further enhance the surface area from 23 m²/g to 143 m²/g. A research conducted by (David et al., 2020) indicates that the BET surface area of the raw (natural) kaolin was first measured to be 19.17 m²/g. Following modification, the surface area increased substantially, reaching values in the range of approximately 208.7 to 247.9 m²/g, depending on the specific treatment method employed. (Shattar et al., 2020) used nitric acid (acid activation) to modify the bentonite clay and reported that the surface area maximize from 120.35 m²/g to 464.92 m²/g. (Osmić et al., 2024) also reported that activating bentonite with 15 % sulfuric acid reportedly increased its surface area from 95.519 m²/g to 346.467 m²/g (i.e. almost triple) under specific activation conditions. A research conducted by (Ouaddari et al., 2024) indicates that BET analysis showed that the purified clays PSC (67.81 m²/g), PRC (68.54 m²/g), and PBC (92.98 m²/g) had notably greater specific surface areas compared to their raw counterparts, SC (39.52 m²/g), RC (41.93 m²/g), and BC (66.93 m²/g). The SSA analysis results of Belesa and Homecho clays are even comparable to or exceeding those of acid-activated or thermally treated clays reported in literature (e.g., 200–350 m²/g after modification) (Al-Degs et al., 2000; Eren & Afsin, 2008). The elevated surface areas obtained in this study suggest that both clays possess a highly porous structure and a large number of accessible active sites, which highlights the potential of these Ethiopian natural clays as low-cost and efficient adsorbents for dye. Such high SSA values could be attributed to the presence of montmorillonite minerals, known for their expansive layer structures and interlayer surface exposure. Moreover, the close similarity in the surface area values of the two samples indicates that the Belesa and Homecho deposits share comparable montmorillonite mineral.

This finding is remarkable because the Belesa and Homecho natural clays, without any acid or thermal activation, exhibited surface areas (331.743 and 333.740 m²/g, respectively) that are comparable to or even higher than those reported for chemically or thermally modified clays in previous studies (200–350 m²/g). This suggests that both clays possess an inherently porous structure and high internal surface accessibility, likely due to their smectitic mineral composition. Therefore, they represent promising natural adsorbents that do not require additional modification to achieve efficient pollutant removal.

4.1.2 X-Ray Diffraction (XRD) Analysis

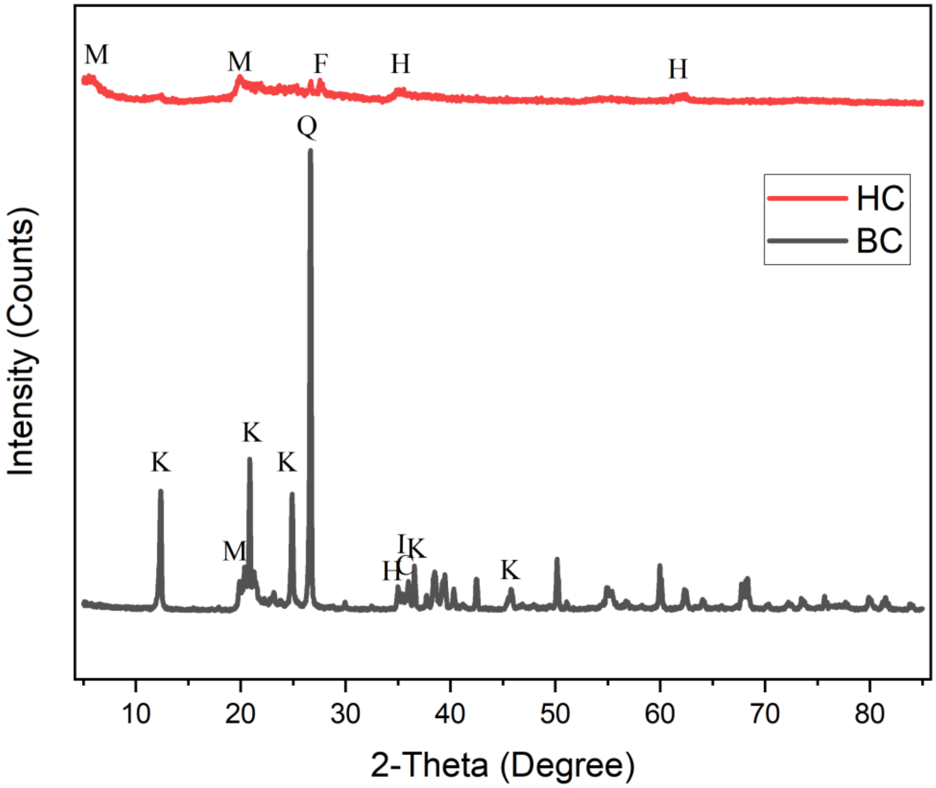

Figure 4.1. The mineralogical composition of BC and HC

X-ray diffraction analysis of the samples identified their mineral compositions. The characterization indicates that both the Belesa and Homecho clays are mixtures of various clay minerals. As shown in Figure 4.1, the Belesa clay sample contains a higher proportion of quartz (Q), which is composed of silicon dioxide (SiO_2). Quartz is a non-clay mineral commonly found as an impurity in natural deposits. The presence of a significant amount of quartz in the clay can improve its surface reactivity and its ability to adsorb cationic dyes (Celoria, 2024). while quartz itself is not a highly active adsorbent, its presence can enhance the overall adsorption performance of natural clays by improving structural stability, porosity, and durability (Eloussaief & Benzina, 2010).

Small amounts of additional minerals like kaolinite (K), montmorillonite (M), calcite (C), and illite (I) were detected through XRD analysis. The Belesa clay (BC) shows numerous sharp and strong diffraction peaks, indicating a highly crystalline structure. Notably, peaks corresponding to kaolinite (K) are observed around 12° and 25° (2θ) (Badr et al., 2021; Shaban et al., 2018), montmorillonite (M) at lower angles around 6–7° and ~20°(Fil et al., 2014), and illite (I) at ~8–9° and ~17–18° (Pataracha0 et al., 2019). (Eloussaief and Benzina (2010)) reported that kaolinite-rich clays exhibited higher dye removal due to the abundance of surface hydroxyl groups that can attract cationic dye molecules. (Dahdouh et al., 2020) observed that kaolinite-rich Algerian clays achieved efficient removal of methylene blue at near-neutral pH due to surface charge effects.

A strong and distinct peak observed at ~26.6° corresponds to quartz (Q) which is commonly present as an impurity in natural clays (Asadi et al.), the dominant non-clay phase. Hematite (H), an iron oxide impurity, is identified from peaks at ~33°, 35°, 54°, and 63° 2θ (Powell et al., 2021), matching the standard pattern of hematite. Hematite, an iron oxide mineral, provides additional surface hydroxyl groups (Fe–OH) that enhance dye adsorption through electrostatic attraction. These observations indicate that the Belesa clay is a heterogeneous material consisting of a combination of clay minerals (kaolinite, montmorillonite, illite, hematite and calcite).

Unlike the Belesa-clay, the XRD patterns of Homecho clay (HC) displayed a markedly different profile. The patterns mainly consisted of broad humps with significantly weaker peak intensities, indicating a partial loss of crystallinity and suggesting that the samples are predominantly amorphous. However, Homecho clay exhibited distinct peaks characteristic of Montmorillonite at approximately 19.8° and 5.5°, a clay mineral known for its high water absorption, plasticity, and numerous active sites for adsorbing cationic pollutants like methylene blue (MB). Additionally, notable peaks corresponding to Hematite appeared around 41°, 50°, and 62.4° 2-theta angles. Hematite, often considered an impurity in clay samples, contributes to the coloration when the clay is fired (Wei et al., 2016).

Overall, the transformation from a highly crystalline Belesa clay to a predominantly amorphous Homecho clay indicates that the modification enhanced surface properties like porosity and surface area while decreasing crystallinity. These structural alterations are beneficial for adsorption purposes, as amorphous materials generally offer more accessible active sites for pollutant capture and exhibit higher adsorption capacity due to their increased specific surface area (Su et al., 2017; Yan et al., 2016).

4.1.3 Particle size distributions of the two clay deposits

Table 4.2. particle size distributions of BC and HC

Sample ID	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	Key Observations
BC	8.0	53.4	16.9	21.7	Balanced clay/silt
HC	7.6	50.2	21.7	20.5	Sand-dominated, moderate gravel

The particles size analysis results were summarized in Table 4.2. above. Sand is the major portion of the Belesa samples followed by clay. In similar case, the major constituent of Homecho sample were sand followed by silt.

The particle size analysis of the Belesa and Homecho samples reveals distinct depositional environments and potential industrial applications. The Belesa sample (BC) is predominantly composed of sand, with a secondary clay fraction (i.e. it is clayey sand) and traces of gravel in the sample, suggesting deposition in high-energy fluvial or alluvial systems near active sediment sources like rivers.

The balanced distribution of sand, silt, and clay in Belesa clay enhances its porosity and creates better pathways for dye molecule diffusion, leading to quicker adsorption. Additionally, the higher clay content provides numerous fine particles having an extensive surface area and numerous active sites for adsorption. In contrast, the higher silt content in Homecho clay may decrease pore connectivity and slow down the movement of dye molecules within the material. Overall, the ideal mix of moderate sand and ample clay in Belesa clay offers a texture that improves both the accessibility and availability of adsorption sites, resulting in higher dye removal efficiency compared to Homecho clay.

4.1.4. Mineral composition of the two clay deposits (XRF)

Table 4.3Mineral composition of BC and HC

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	TiO_2	LOI	Total Fluxes
BC	59.00	28.29	0.98	0.12	0.72	0.54	0.75	7.63	1.38
HC	51.97	23.27	6.07	1.75	1.88	1.98	0.95	9.91	5.61

The chemical make up of clay samples significantly influences their ability to adsorb dyes. The chemical composition analysis results presented on Table 4.3. revealed that the most abundant oxides in the the clay samples are SiO_2 and Al_2O_3 which are mainly associated with clay minerals. Belesa clay (BC) has a higher content of SiO_2 (59%) and Al_2O_3 (28.29%), indicating substantial quartz and kaolinite presence. Quartz though inert chemically,enhances mechanical strength and porosity, aiding dye difussion,while kaolinite offers surface OH groups and cation exchange sites crucial for adsorbing positively charged dyes like MB.

Conversely , Homecho clay (HC) contains lower SiO_2 (51.97%) and Al_2O_3 (23.27%) but higher amount of Fe_2O_3 (6.07%), CaO (1.75%), MgO (1.88%). The increased Fe_2O_3 , can improve adsorption through surface complexation with dyes , and the presence of ca^{2+} and Mg^{2+} ions supports cation exchange processes. However, the higher levels of Fe_2O_3 and flux oxides may block clay pores, limiting access to hydroxyl groups. HC has high LOI than BC . Moderately high LOI is beneficial for adsorption because it can create additional porosity and diffusion pathways**,** enhancing dye removal. However, if LOI is too high, it may reduce structural integrity or block active sites, leading to uneven adsorption (Saad et al., 2024). Therefore, while HC favor specific adsorption mechanisms involving iron and cationexchange , BC is likely to offer more uniform and active adsorption owing to its higher kaolinite content and stable porous structure. Overall, an optimal mineral composition combines adequate kaolinite with balanced quartz and Fe_2O_3 levels,, providing structural support, active sites, and multiple adsorption pathways for effective dye removal.

4.1.5. Thermogravimetric differential thermal analysis (TG-DTA)

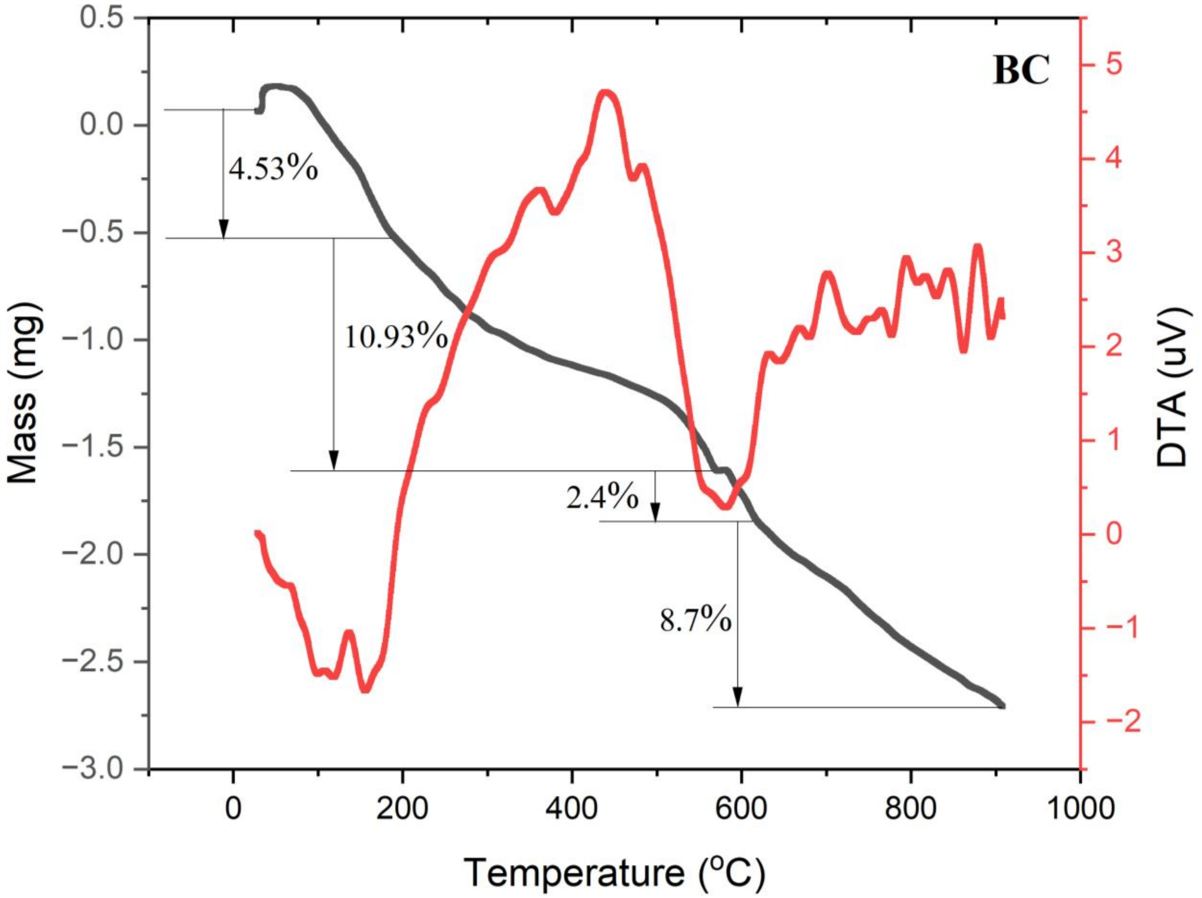

Figure 4.2. Thermogravimetric and Differential Thermal Analysis for BC

The TG–DTA graph of the BC clay sample illustrates how its weight and thermal behavior change as the temperature rises. The thermogravimetric (TG) curve (shown in black) indicates the sample's mass decreases, while the differential thermal analysis (DTA) curve (shown in red) reveals whether thermal events are endothermic or exothermic. At temperatures below 150 °C, there is a minor weight loss of 4.53%, due to the evaporation of physically adsorbed water and surface moisture, which is associated with a small endothermic peak. From approximately 150 °C to 400 °C, a more substantial mass reduction of 10.93% occurs, corresponding to dehydroxylation of clay minerals, degradation of organic matter, or release of structural water, accompanied by a prominent endothermic signal. Between 400 °C and 600 °C, an additional 2.4% mass loss is observed, likely from further dehydroxylation or minor organic decomposition, with a modest

DTA response. Above 600 °C, there is a significant loss of 8.7%, linked to the breakdown of carbonates or unstable mineral phases, along with a slight exothermic reaction. Overall, the thermal analysis indicates that BC clay undergoes several decomposition stages initial moisture removal, dehydroxylation, and mineral degradation at specific temperature ranges. Heating reduces surface OH groups, potentially decreasing adsorption sites, and promotes the formation of Fe_2O_3 at higher temperatures, which may create new active sites for adsorption. In conclusion, thermal treatment modifies the clay's surface chemistry and mineral structure, thereby influencing its adsorption capabilities.

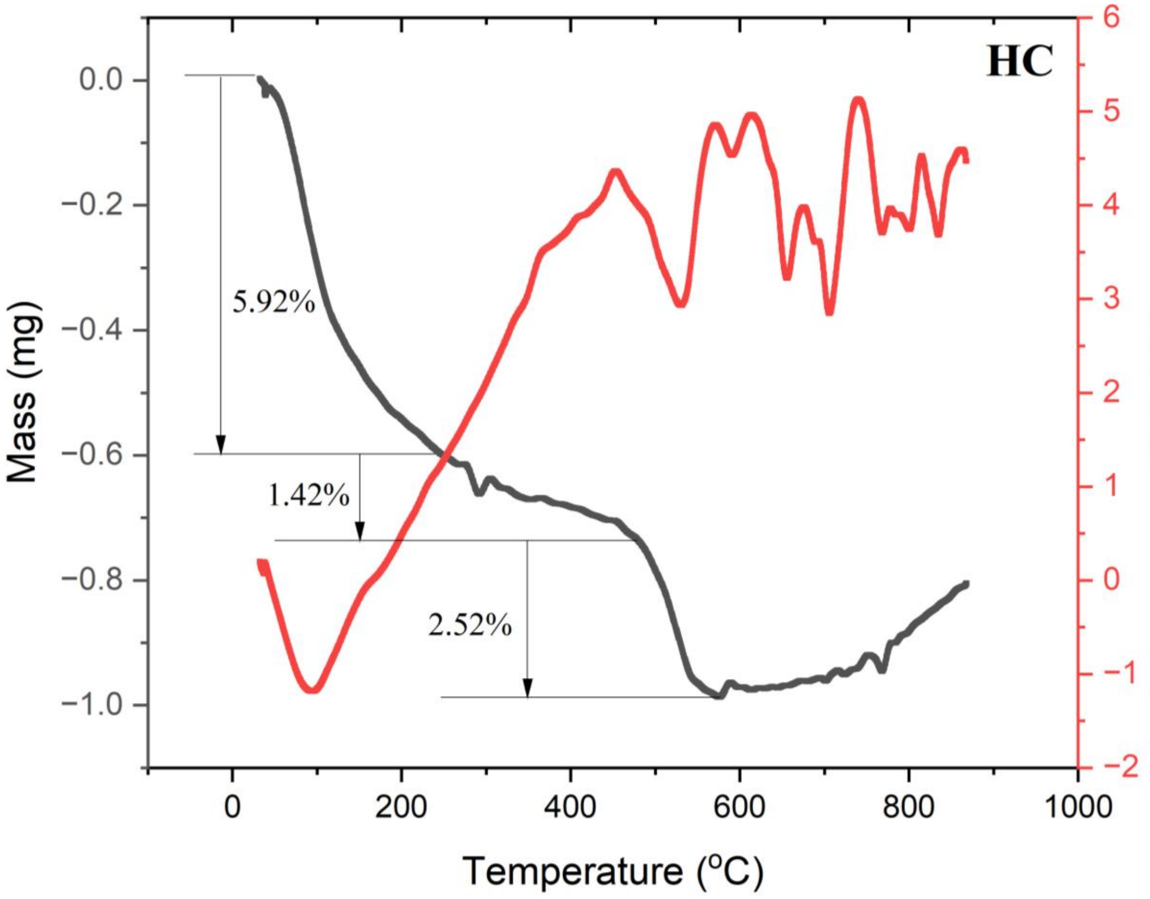

Figure 4.3. Thermogravimetric and Differential Thermal Analysis for HC

The TG–DTA analysis of the Homecho clay sample (HC) identifies distinct thermal events associated with mass loss and thermal effects. The thermogravimetric (TG) curve indicates three main stages of weight reduction: an initial 5.92% loss below 150 °C caused by physically adsorbed water; a smaller 1.42% loss between approximately 150 °C and 400 °C likely due to interlayer water or dehydration of hydroxyl groups; and a larger 2.52% loss from 400 °C to 600 °C Produced by dehydroxylation of structural hydroxyl groups in clay minerals. After 600 °C, the mass stabilizes. The DTA curve displays peaks indicating endothermic reactions linked to water removal and dehydroxylation, with minor fluctuations above 400 °C indicating overlapping thermal processes or minor phase changes. Overall, HC clay undergoes stepwise dehydration and dehydroxylation, losing about 9–10% of its mass, but remains thermally stable beyond 600 °C. This indicates that the clay retains most of its hydroxyl groups and porous structure under moderate heating (up to 350 °C), making it suitable for adsorbing polar and cationic dyes via hydrogen bonding and cation exchange. High-temperature treatments are unnecessary and could alter its surface chemistry; thus, minimal activation suffices to enhance dye removal while maintaining its inherent adsorption capabilities.

The negative mass values in the TG curve indicate progressive mass loss relative to the initial sample mass. The initial mass is taken as the baseline (zero), so downward/negative shift simply reflects the amount of weight lost due to moisture evaporation, organic matter removal, dehydroxylation, and structural decomposition.

4.2 Adsorption Experiment and Effect of Individual Parameters

4.2.1 Effect of Adsorbent Dosage

Table 4.4 The effect of Adsorbent dosage on removal efficiency and adsorption capacity of Belesa clay

Adsorbent Dose(g)	Final Concentration (mg/l)	Removal efficiency(%)	Adsorption capacity(mg/g)
0.2	0.622	96.8	9.9
0.4	0.244	98.8	4.9
0.6	0.178	99.1	3.2

Table 4.5 The effect of Adsorbent dosage on the Removal efficiency and Adsorption capacity of Homecho clay

Adsorbent Dose(g)	Final Concentration (mg/l)	Removal efficiency(%)	Adsorption capacity(mg/g)
0.2	0.6968	96.5	9.9
0.4	0.5206	97.4	4.9
0.6	0.1317	99.3	3.2

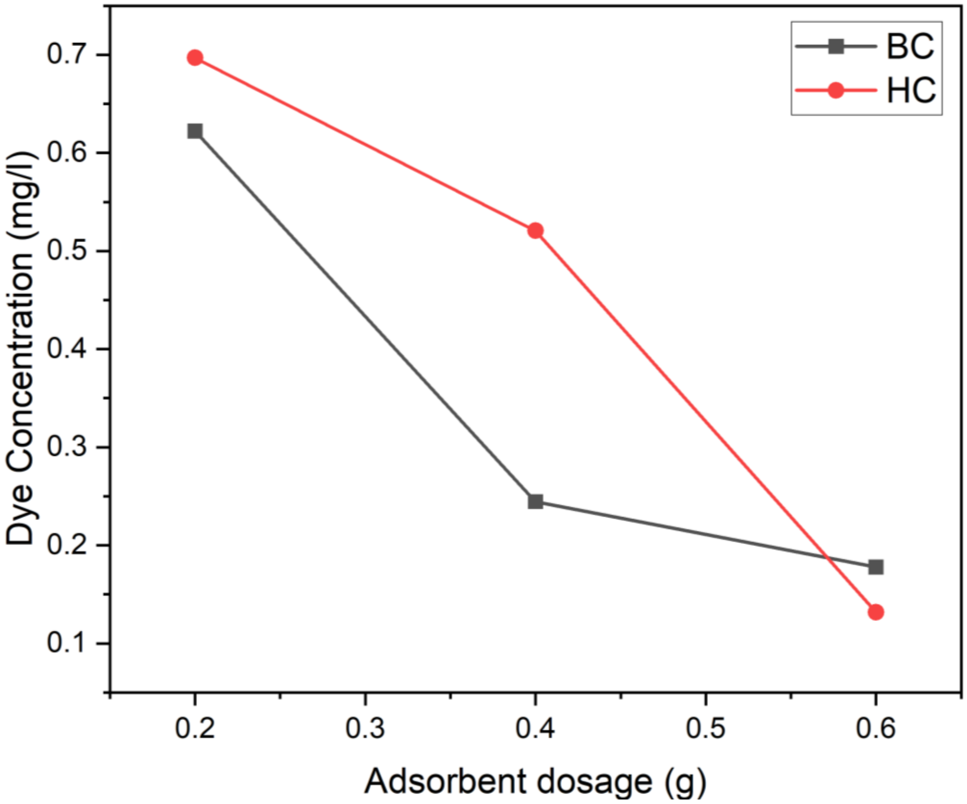

Figure 4.4. The concentration of dye in the adsorbent treated waste water

Figure 4.4 demonstrates how changing the amount of adsorbent affects the residual dye levels of methylene blue when using Belesa (BC) and Homecho (HC) clays. The findings indicate that increasing the clay amount results in a consistent reduction in dye concentration for both types, indicating better removal performance. This effect is attributed to the larger number of active sites and increased surface area at higher clay quantities, which promote stronger interactions between the dye molecules and the adsorbent. At the lowest dose of 0.2 g, BC had a slightly lower residual dye concentration (0.62 mg/L) compared to HC (0.70 mg/L), indicating better adsorption performance. When the dosage was raised to 0.4 g, residual concentrations dropped to 0.24 mg/L for BC and 0.52 mg/L for HC, with BC showing better efficiency at this level. At the maximum dose of 0.6 g, both clays nearly completely removed the dye, with residual concentrations of 0.18 mg/L for BC and 0.13 mg/L for HC, suggesting that adsorption sites had become saturated and equilibrium was reached.

The slightly greater efficiency of Belesa clay at lower doses may be due to its mineral composition, especially its higher quartz content, which boosts surface reactivity and enhances its ability to adsorb cationic dyes. Other studies have also observed that increasing the dosage of the adsorbents improves dye removal, as more binding sites become available for adsorption (e.g., (Hamri et al., 2024; Mulushewa et al., 2021; Ouaddari et al., 2024)). Overall, both natural clays demonstrated strong adsorption capacities and high potential as low-cost, eco-friendly materials for textile dye wastewater treatment.

As the amount of adsorbent increases, its adsorption capacity declines, potentially due to the formation of clay mineral clusters that reduce the available surface area and obstruct specific adsorption sites. With higher clay content, the equilibrium concentration of the dye decreases, resulting in a lower amount of dye being adsorbed (Sibhat et al., 2025).

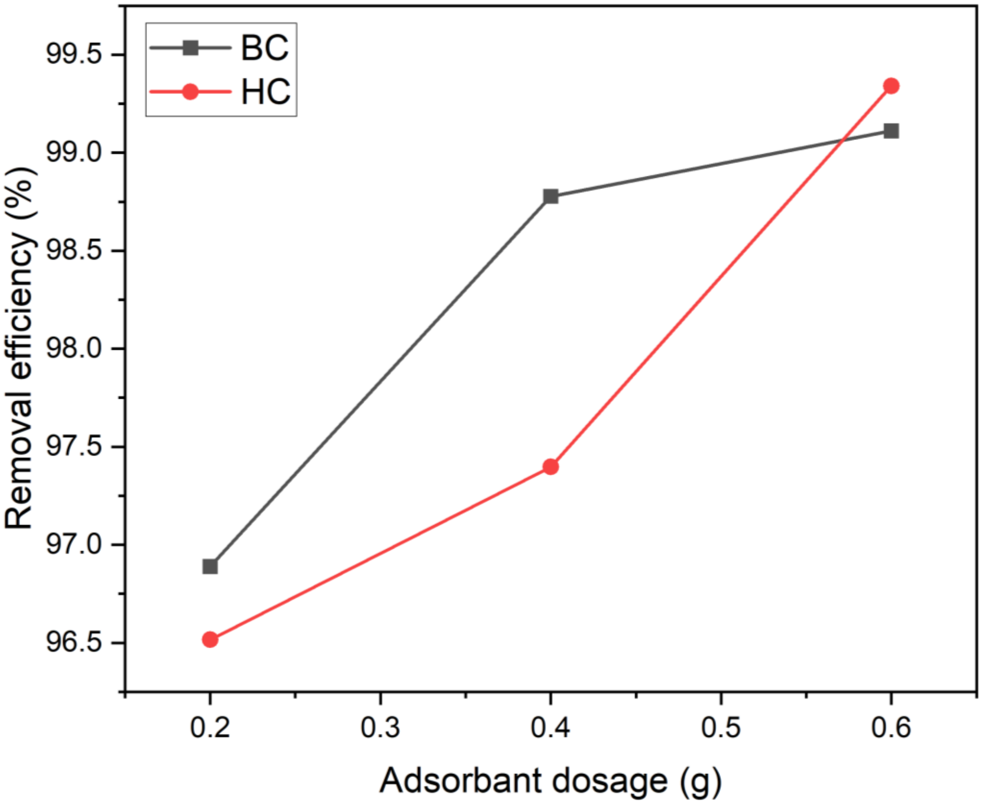

Figure 4.5. Adsorption efficiency as a function of adsorbent dosage

Figure 4.5 shows how the amount of adsorbent affects the removal of methylene blue using Belesa (BC) and Homecho (HC) clays. As the adsorbent amount increased, the removal efficiency improved for both clays. Starting from a low dose of 0.2 g, BC achieved about 97% removal, while HC reached approximately 96.5%. Increasing the dosage to 0.4 g raised the efficiencies to around 99% for BC and 97.4% for HC. At the highest tested dose of 0.6 g, both clays nearly completely eliminated the dye, with removal efficiencies over 99%.

This pattern suggests that increasing the amount of adsorbent improves the adsorption process by offering more active sites and a larger surface area, leading to more effective interactions between dye molecules and the adsorbent. Similar results have been observed in earlier research, where adding more clay or natural adsorbents enhanced dye removal efficiency because of the greater number of binding sites and decreased competition among dye molecules (e.g.,(Ouaddari et al., 2024) (Ibrahim et al., 2023)).

Both clays exhibited excellent adsorption capabilities, but Belesa clay generally achieved slightly higher removal efficiency than Homecho clay at lower dosages. This advantage may be due to Belesa clay's mineral makeup and surface properties, especially its higher quartz content, which likely improves surface reactivity and affinity for cationic dyes. At higher dosages, however, both clays reached equilibrium with nearly complete dye removal, highlighting their effectiveness as affordable, eco-friendly options for treating textile dye wastewater.

The adsorption study of methylene blue using the natural Belesa and Homecho clay revealed an adsorption capacity of 10 mg/g, indicating that even unmodified clays possess inherent dye removal capabilities. This result is consistent with previous studies on natural clays; for instance, raw kaolinite has been reported to exhibit adsorption capacities ranging from 13.99 mg/g (He et al., 2018) to 44.48 mg/g (Hamri et al., 2024) , while raw bentonite showed capacities between 2.2 mg/g (Hajjaji & El Arfaoui, 2009) and 24.29 mg/g (Hamad et al., 2024) . Although the adsorption capacity of the present clay is lower than that of some treated or activated clays reported in the literature, it demonstrates that natural clays are effective, low-cost, and environmentally friendly adsorbents for dye removal. The moderate adsorption capacity observed in this study can be attributed to the lower surface area and cation exchange capacity of unmodified clay. These findings highlight the potential of natural Belesa/Homecho clay for sustainable wastewater treatment, and suggest that further modification or optimization could enhance its adsorption performance.

Both Belesa and Homecho clays show a decrease in their ability to adsorb Methylene Blue as the amount of clay used increases, although the overall percentage of dye removed actually improves. Specifically, the adsorption capacity declines from 9.9 mg/g with 0.2 g of clay to 4.9 mg/g at 0.4 g, and further to 3.2 mg/g at 0.6 g, all starting with an initial dye concentration of 20 mg/L. This decrease in capacity is likely due to the saturation of available adsorption sites; adding more clay results in more active sites than dye molecules, so fewer dye molecules are adsorbed per gram of clay. Moreover, higher clay dosages may lead to particle aggregation and overlapping, which can reduce the effective surface area and limit dye molecules from reaching active sites.

At higher doses, adsorbent particles tend to aggregate, decreasing their effective surface area for adsorption. Consequently, the adsorption capacity per unit mass drops (Foo & Hameed, 2010; Ma et al., 2020). Additionally, when the number of available adsorption sites exceeds the amount of dye molecules, many sites remain unoccupied, leading to a lower adsorption capacity per gram of the adsorbent (Gholizadeh et al., 2013; Hashem et al., 2024; Nwabanne & Igbokwe, 2012). Additionally, increasing the amount of adsorbent can cause overlapping of adsorption sites or pore blockage, which reduces the efficiency per unit mass (Ezeh et al., 2017; Gholizadeh et al., 2013)

4.2.2 Effect of Time

Table 4.6. The effect of time on the Removal efficiency and adsorption capacity of Belesa clay

Time (min)	Concentration (mg/l)	Removal efficiency(%)	Adsorption capacity(mg/g)
20	2.467	87.66	4.3
60	0.244	98.78	4.9
100	0.376	98.12	4.9

Table 4.7. The effect of time on the removal efficiency and Adsorption capacity of Homecho clay

Time (min)	concentration	Removal efficiency(%)	Adsorption capacity(mg/g)
20	4.2984	78.5	3.9
60	0.5206	97.4	4.9
100	0.8825	95.6	4.9

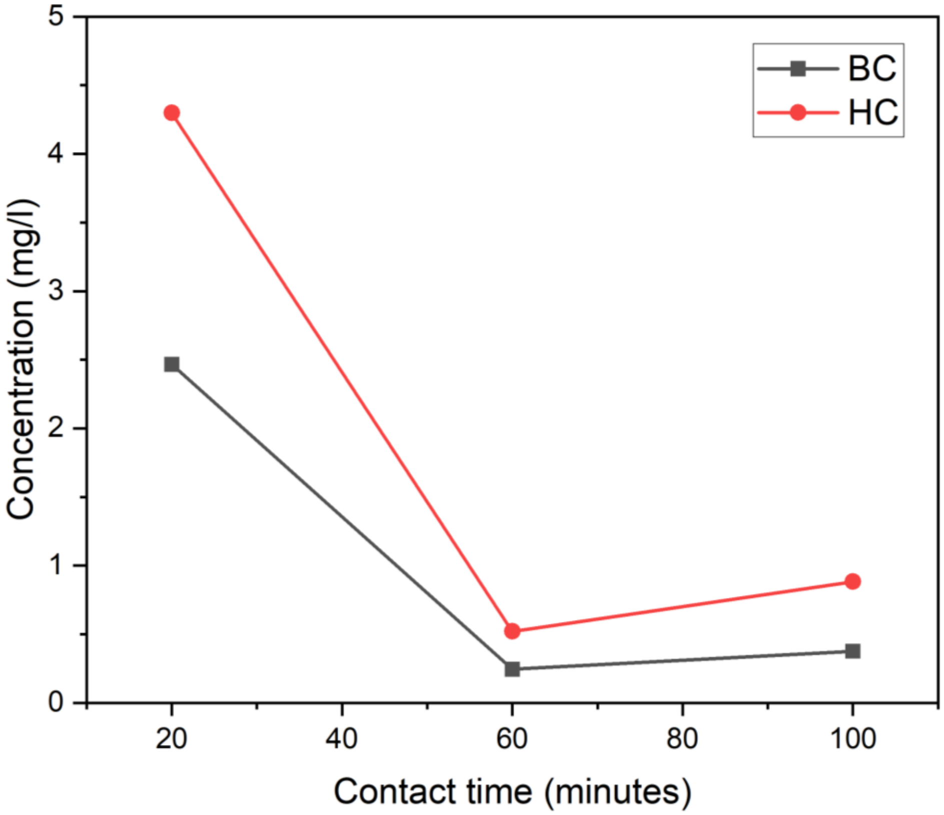

Figure 4.6. Dye concentrations of the treated waste at different contact time with the adsorbent

Figure 4.6 illustrates how methylene blue concentration changes over contact time for Belesa (BC) and Homecho (HC) clays. As the contact time extended from 20 to 100 minutes, the methylene blue concentration in the solution decreased rapidly during the first 60 minutes for both types of clay. Following this initial phase, the concentration remained steady, indicating that adsorption equilibrium had been achieved. In the case of Belesa clay, the dye concentration dropped from 2.467 mg/L at 20 minutes to 0.244 mg/L at 60 minutes, resulting in a removal efficiency of 98.78%. Similarly, Homecho clay saw its concentration decrease from 4.298 mg/L at 20 minutes to 0.521 mg/L at 60 minutes, with a removal efficiency of 97.4%. After 60 minutes, the concentrations slightly increased to 0.376 mg/L for Belesa clay and 0.883 mg/L for Homecho clay at 100 minutes, indicating that equilibrium had been reached and additional contact time did not improve dye adsorption.

The early stage of adsorption occurs rapidly because there are many available active sites on the clay surfaces that readily bind with methylene blue molecules. As these sites become occupied, the rate of adsorption decreases and gradually stabilizes at equilibrium. This pattern is consistent with previous studies involving dye removal using natural clays and other low-cost adsorbents. (e.g., (El Kerdoudi et al., 2023)

Compared to Homecho clay, Belesa clay consistently demonstrated greater dye removal efficiency and lower residual dye levels across all time points. This suggests that Belesa clay has a higher adsorption capacity and more accessible active sites for dye binding.

The findings indicate that both Belesa and Homecho natural clays are effective in adsorbing methylene blue, reaching equilibrium in about 60 minutes. However, Belesa clay shows a marginally better performance.

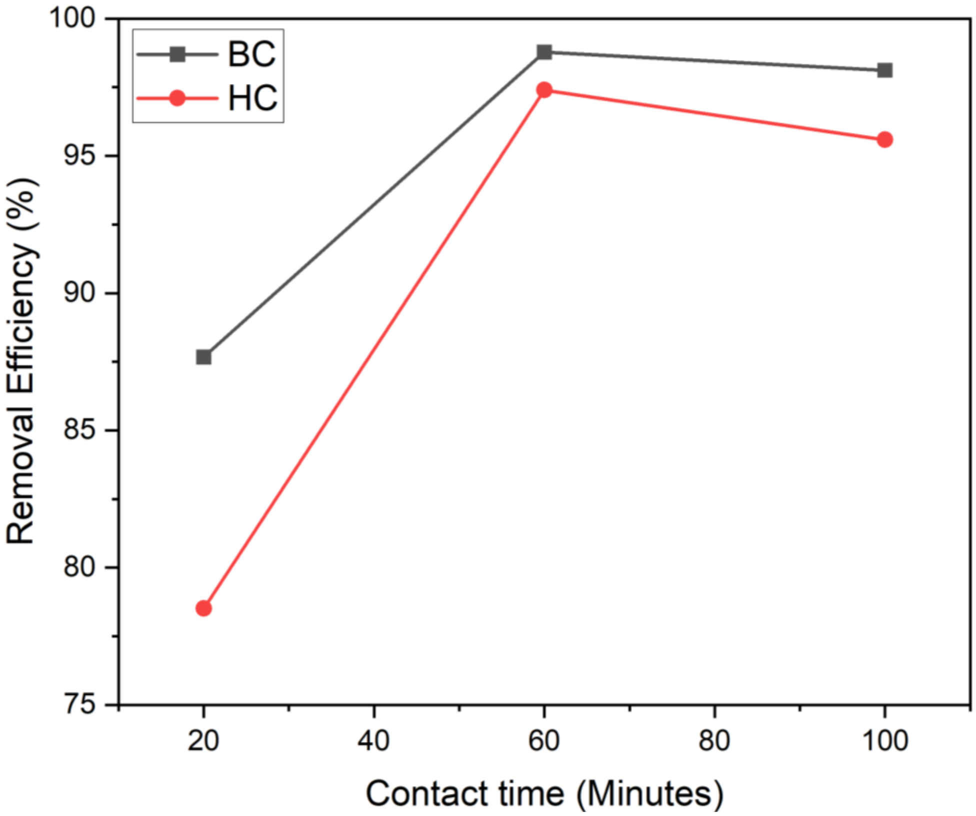

Figure 4.7. Removal efficiencies as a function of contact time

Effect of contact time on methylene blue removal efficiency using Belesa (BC) and Homecho (HC) clays is shown in Figure 4.7. The data indicates that removal efficiency increases rapidly with contact time up to 60 minutes for both types of clay, after which it levels off, implying that equilibrium is nearly achieved. At 20 minutes, BC attains around 88% removal efficiency, while HC reaches approximately 78.5%, showing that a significant amount of dye is quickly adsorbed early on. This rapid adsorption is probably caused by the high concentration difference between the dye solution and the clay's active sites, which facilitates faster dye molecule transfer.

As the contact time increases to 60 minutes, the removal efficiency reaches around 99% for BC and 97% for HC, showing that most adsorption occurs within this period. Beyond 60 minutes, the efficiency slightly decreases or stabilizes about 98% for BC and 95% for HC at 100 minutes indicating that the active sites on the clay surfaces become saturated and the system reaches equilibrium. The minor decline may be caused by desorption or rearrangement of dye molecules on the adsorbent surfaces.

The observed pattern aligns with earlier research on the adsorption of methylene blue and other positively charged dyes onto natural clays, showing a quick initial uptake that gradually slows down as the system nears equilibrium. For instance, (Ouaddari et al., 2024) reported that natural bentonite and kaolinite clays achieve maximum dye removal within 60–90 minutes due to the quick occupation of surface sites and gradual interparticle diffusion control at later stages. Similar behavior has also been noted by Ibrahima et al. (2024), who observed equilibrium after one hour in methylene blue adsorption on clay minerals, with removal efficiencies exceeding 95%.

The findings demonstrate that both Belesa and Homecho clays have quick adsorption rates and high dye removal abilities, with Belesa clay performing marginally better throughout the study. This enhanced effectiveness may be due to its higher quartz content, which offers more accessible sites for dye molecule adsorption. The rapid attainment of equilibrium and the high removal rates indicate that these natural Ethiopian clays are promising, cost-effective adsorbents for the treatment of textile dye wastewater.

The BET surface area and porosity analyses help explain the adsorption behaviors of Belesa (BC) and Homecho (HC) clays. Although both adsorbents have nearly identical specific surface areas (around 332 m^2/g), their pore structures differ significantly. Belesa clay features a much larger average pore size (16.93 nm) compared to Homecho clay (2.261 nm), indicating that BC has a predominantly mesoporous structure that facilitates the diffusion and retention of larger dye molecules like methylene blue. In contrast, Homecho's narrower pores suggest a more microporous nature, which may limit dye diffusion and restrict access to internal adsorption sites, leading to lower adsorption efficiency. Despite similar pore volumes, Belesa's broader pore channels improve access and utilization of active sites. Overall, Belesa clay’s enhanced removal capacity is mainly due to its well-developed, more open pore network, which allows for quicker molecular diffusion and stronger interactions with dye molecules, even though its surface area is slightly lower.

Although BET analysis indicated that Homecho clay has a slightly higher specific surface area than Belesa clay, Belesa clay demonstrated better removal efficiency for methylene blue. This is likely due to its mineralogical and structural features. XRD analysis revealed that Belesa clay has higher amounts of quartz and kaolinite, both of which provide abundant surface hydroxyl and silanol (Si–OH) groups. These functional groups improve electrostatic attraction and hydrogen bonding with cationic dyes. Additionally, Belesa clay may have a more negatively charged surface, strengthening electrostatic interactions with methylene blue. Its pore structure probably includes more accessible mesopores, improving the penetration of dye molecules into internal adsorption sites. The crystalline structure of Belesa clay promotes the development of organized adsorption layers, enhancing the availability of active sites and their attraction to the dye.

The chemical analysis data further confirm that Belesa clay has superior adsorption capacity compared to Homecho clay. Belesa clay contains a higher percentage of SiO_2 (59%) and Al_2O_3 (28.29%), suggesting the presence of quartz and kaolinite phases. These minerals offer numerous surface silanol (Si-OH) and alumino (Al-OH) groups, which enhance dye adsorption via hydrogen bonding and electrostatic interactions (Greathouse et al., 2015; Sagita et al., 2021) . Unlike other clays, Homecho clay has lower levels of SiO_2 and Al_2O_3, indicating a reduced presence of these reactive mineral components. Additionally, it has a significantly higher Fe_2O_3 content (6.07%), which may hinder adsorption processes. Iron oxides can bind organic compounds or occupy surface sites, potentially obstructing dye molecules from interacting effectively with the clay surface (Sun et al., 2023; Talbot et al., 2021) .

Belesa clay exhibits better removal efficiency due to its higher silica–alumina content, lower levels of flux oxides (5.61%) which cause less structural distortion, and fewer impurities such as iron and flux oxides that can hinder surface activity. In contrast, Homecho clay has a higher loss on ignition (9.91%), indicating more volatile or organic impurities that can block active sites and reduce adsorption capacity. Additionally, lower overall fluxes in BC contribute to a more stable structure, enhancing its adsorption performance for methylene blue.

The adsorption of Methylene Blue on both Belesa and Homecho clays improved with increasing contact time up to 60 minutes, after which it stabilized. Homecho clay's capacity rose from 3.9 mg/g at 20 minutes to 4.9 mg/g at 60 minutes, remaining constant at 4.9 mg/g up to 100 minutes. Likewise, Belesa clay's capacity increased from 4.3 mg/g at 20 minutes to 4.9 mg/g at 60 minutes, with no notable changes afterward.

The initial quick increase in adsorption capacity occurs because there are many unoccupied active sites on the clay surface at the beginning. Over time, these sites become gradually filled with dye molecules. After about 60 minutes, equilibrium is reached, indicating that most active sites are occupied and extending the contact time further does not significantly enhance adsorption.

Overall, Belesa clay exhibited better adsorption performance than Homecho clay, thanks to its advantageous mineral makeup, reactive surface groups, and highly developed mesoporous structure. These features position Belesa clay as a more efficient and promising natural adsorbent for removing methylene blue and possibly other cationic dyes from water.

5. Conclusion and Recommendations

5.1 Conclusion

The investigation into methylene blue adsorption using Belesa (BC) and Homecho (HC) clays revealed that both natural Ethiopian clays are highly efficient and eco-friendly materials for removing dye from water. The research indicated that adsorption occurred rapidly during the initial 60 minutes and then stabilized, reaching equilibrium. The quick increase in adsorption initially is due to the abundance of active sites and the significant concentration gradient between the dye solution and the adsorbent.

The Belesa (BC) and Homecho (HC) clays have almost similar specific surface areas (SSA), measuring 331.743 m^2/g and 333.740 m^2/g respectively. BC features larger pores (16.93 nm) and greater quartz content, making it more crystalline, whereas HC is amorphous with smaller pores (2.261 nm) and a slightly higher pore volume (0.06886 cm^3/g). These differences suggest that adsorption capacity is influenced not just by surface area, but also by factors such as pore size, pore volume, mineral makeup, and crystallinity. Both clays demonstrate high and comparable surface areas suitable for adsorption, with HC being slightly more amorphous and having a marginally higher SSA, while BC's structure is more crystalline with more quartz content.

Generally, Both Belesa and Homecho clays demonstrated highly effective removal rates exceeding 95%, indicating their excellent adsorption properties, quick action, and high efficiency. These qualities make them promising, affordable, and sustainable options for treating dye-polluted textile wastewater.

But, the findings indicate that Belesa clay consistently achieved marginally better removal efficiency than Homecho clay. This is likely due to its mineral composition, which enhances the availability of adsorption sites and strengthens surface interactions with cationic dye molecules, as well as its larger pore size.

5.2. Recommendation

In this study Belesa clay and Homecho clay were evaluated for their ability to reject methylene blue dye from synthetic wastewater in batch experiments. From this point of view for further studies, the following points must be taken into account.

- For future work, it is recommended to investigate regeneration and reuse studies would provide valuable insights into their long-term applicability in wastewater treatment.

- The adsorption of methylene blue dye was conducted using synthetic water batch-wise, but the synthesis wastewater doesn't contain other pollutants that can affect the adsorption process such as other dye staff and heavy metals. Therefore, it is recommended to use real industrial methylene blue dye-loaded wastewater effluent for more real and effective investigation.

- Future research should examine the adsorption capabilities of Belesa and Homecho clays for various dyes and industrial wastewater to assess their broader applicability.

- It is better to try to modify or activate the clay , for example through acid or heat treatments, to improve their adsorption capacity and selectivity.

APPENDICES

Appendix A: Physiochemical analysis

Table A-1 Specific surface area , pore size and pore volume of Belesa and Homecho clays

Quantachrome NovaWin - Data Acquisition and Reduction
for NOVA instruments
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version 11.0

Analysis Report
Operator:bdu Date:2007/01/01 Operator:bdu Date:8/27/2025
Sample ID: Simegn 2 Filename: C:\QCdata\Physisorb\Simegn 2 samp.qps
Sample Desc: Comment:
Sample weight: 0.1 g Sample Volume: 0.02564 cc Sample Density:3.9 g/cc
Outgas Time: 8.0 hrs OutgasTemp: 300.0 C
Analysis gas: Nitrogen Bath Temp: 77.3 K
Press. Tolerance:0.100/0.100 (ads/des)Equil time: 60/60 sec (ads/des) Equil timeout: 240/240 sec (ads/des)
Analysis Time: 45.0 min End of run: 2007/01/01 3:09:31 Instrument: Nova Station B
Cell ID: 2 F/W version: 0.00
Adsorbate Nitrogen Temperature 77.350K
Molec. Wt.: 28.013 g Cross Section: 16.200 Å² Liquid Density: 0.808 g/cc

Surface Area Data

MultiPoint BET 3.337e+02 m²/g

Pore Volume Data

HK method cumulative pore volume 6.373e-02 cc/g
SF method cumulative pore volume 6.886e-02 cc/g

Pore Size Data

HK method pore Radius (Mode) 1.838e+00 Å
SF method pore Radius (Mode) 2.261e+00 Å

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Analysis Report
Operator:bdu Date:2007/01/01 Operator:bdu Date:8/27/2025
Sample ID: Simegn 2 Filename: C:\QCdata\Physisorb\Simegn 2 samp.qps
Sample Desc: Comment:
Sample weight: 0.1 g Sample Volume: 0.02564 cc Sample Density:3.9 g/cc
Outgas Time: 8.0 hrs OutgasTemp: 300.0 C
Analysis gas: Nitrogen Bath Temp: 77.3 K
Press. Tolerance:0.100/0.100 (ads/des)Equil time: 60/60 sec (ads/des) Equil timeout: 240/240 sec (ads/des)
Analysis Time: 45.0 min End of run: 2007/01/01 3:09:31 Instrument: Nova Station B
Cell ID: 2 F/W version: 0.00
Adsorbate Nitrogen Temperature 77.350K
Molec. Wt.: 28.013 g Cross Section: 16.200 Å² Liquid Density: 0.808 g/cc

Relative Volume @ STP 1 / [W((Po/P) - 1)]

```
    Pressure
     P/Po                  cc/g

      5.67970e-02            19.5389              2.4659e+00
      1.21961e-01            34.3220              3.2381e+00
      2.08053e-01            53.7897              3.9078e+00
      2.73382e-01            68.7513              4.3786e+00
      3.58549e-01            88.6581              5.0445e+00

                          BET summary
                        Slope =      8.324
                      Intercept =      2.111e+00
              Correlation coefficient, r =      0.995819
                      C constant=      4.943

                     Surface Area =     333.740 m²/g



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                          for NOVA instruments
                    ©1994-2010, Quantachrome Instruments
                            version 11.0

Analysis                            Report
Operator:bdu             Date:2007/01/01    Operator:bdu             Date:8/27/2025
Sample ID:  Simegn            Filename:     C:\QCdata\Physisorb\Simegn BS 1.qps
Sample Desc:               Comment:
Sample weight: 0.1 g          Sample Volume: 0.02564 cc        Sample Density:3.9 g/cc
Outgas Time:   8.0 hrs         OutgasTemp:    300.0 C
Analysis gas:  Nitrogen        Bath Temp:     77.3 K
```

```
Press. Tolerance:0.100/0.100 (ads/des)Equil time: 60/60 sec (ads/des) Equil timeout: 240/240 sec
(ads/des)
Analysis Time: 41.7 min          End of run:    2007/01/01 1:09:58  Instrument:    Nova Station B
Cell ID:       2                                  F/W version:   0.00
Adsorbate      Nitrogen               Temperature    77.350K
           Molec. Wt.: 28.013  g    Cross Section: 16.200  Å²     Liquid Density: 0.808  g/cc

         Relative                 Volume @ STP              1 / [ W((Po/P) - 1) ]
         Pressure
          P/Po                      cc/g

           4.83310e-02              14.8859                  2.7297e+00
           1.34531e-01              34.1125                  3.6459e+00
           1.97599e-01              48.0496                  4.1007e+00
           2.81238e-01              66.8186                  4.6853e+00
           3.48095e-01              82.0573                  5.2065e+00

                                    BET summary
                                 Slope =        8.050
                              Intercept =        2.448e+00
                   Correlation coefficient, r =        0.995714
                              C constant=        4.288

                            Surface Area =       331.743 m²/g


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                              for NOVA instruments
                        ©1994-2010, Quantachrome Instruments
                                  version 11.0
```

Analysis Report

Operator:bdu Date:2007/01/01 Operator:bdu Date:8/27/2025
Sample ID: Simegn Filename: C:\QCdata\Physisorb\Simegn BS 1.qps
Sample Desc: Comment:
Sample weight: 0.1 g Sample Volume: 0.02564 cc Sample Density:3.9 g/cc
Outgas Time: 8.0 hrs OutgasTemp: 300.0 C
Analysis gas: Nitrogen Bath Temp: 77.3 K
Press. Tolerance:0.100/0.100 (ads/des)Equil time: 60/60 sec (ads/des) Equil timeout: 240/240 sec (ads/des)
Analysis Time: 41.7 min End of run: 2007/01/01 1:09:58 Instrument: Nova Station B
Cell ID: 2 F/W version: 0.00
Adsorbate Nitrogen Temperature 77.350K
Molec. Wt.: 28.013 g Cross Section: 16.200 Å^2 Liquid Density: 0.808 g/cc

Surface Area Data

MultiPoint BET	3.317e+02 m^2/g

Pore Volume Data

HK method cumulative pore volume	5.887e-02 cc/g
SF method cumulative pore volume	6.388e-02 cc/g

Pore Size Data

HK method pore Radius (Mode)	8.837e+00 Å
SF method pore Radius (Mode)	1.693e+01 Å

Appendix B: experimental work pictures

UV

Belesa clay

Vial filled with sample

Homecho clay

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