ADSORPTION OF METHYL ORANGE DYE FROM AQUEOUS SOLUTION USING CLAY OBTAINED FROM UTEH UZALLA BENIN CITY, EDO STATE

BY

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UNIVERSITY OF BENIN,

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FEBRUARY, 2025.

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A PROJECT REPORT SUBMITTED TO THE DPARTMENT OF CHEMISTRY, FACULTY OF PHYSICAL SCIENCES IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE UNIVERSITY OF BENIN, BENIN CITY.AWARD OF BACHELOR OF SCIENCE (BSc. HONS). DEGREE.

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CERTIFICATION

This is to certify that this research project was carried out by AGATHA CHIDIOGO OBIAJULU with the matriculation number PSC2007993 under the supervision of PROF. MRS. S.I. OMONMHENLE in the Department of Chemistry, Faculty of Physical sciences, University of Benin, Benin City, Edo State.

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DEDICATION

This project research is dedicated to the Almighty God who in His infinite mercy saw me through my journey in the University of Benin, And to my loving Mum, Mrs Leticia Obiajulu

ACKNOWLEGEMENT

I am filled with immense joy as I express gratitude to everyone who played a part in making this endeavour a success. First and foremost, profound gratitude is directed towards God Almighty for His guidance and providence throughout this journey.

A heartfelt acknowledgment is owed to Prof Mrs S.I Omonmhenle for her patience, support, and invaluable guidance throughout this research. I also extend my gratitude to the Head of Department, Prof. Emmanuel E. I. Irabor, my lecturers, the entire staff of the department, for their dedication to imparting knowledge and shaping my academic path.

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To my beloved Mum and siblings, who have been my constant source of love, encouragement, whose prayers, sacrifices, and unwavering support have been my greatest source of strength, thank you for always believing in me in every step of my academic journey. I am forever grateful.

Lastly, I acknowledge my own efforts, dedication, and perseverance throughout this project. The challenges faced and overcomed have been a valuable learning experience, and I am grateful for the opportunity to grow both personally and academically through this work.

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ABSTRACT

The contamination of water bodies by synthetic dyes such as methyl orange from industrial effluents poses a significant environmental challenge due to their toxicity, persistence, and resistance to biodegradation. This study investigates the adsorption capacity of Uteh-Uzalla clay for the removal of Methy orange from aqueous solutions. . The clay was characterized using SEM, BET, XRD, TGA, and FTIR to determine its surface morphology, elemental composition, crystalline phases, thermal stability, and functional groups. BET analysis revealed a surface area of 170.571 m^2/g, a pore volume of 0.109cm^3/g, and an average pore size of 2.411nm, indicating a mesoporous structure suitable for adsorption. Thermogravimetric analysis (TGA) showed significant weight loss between 200°C and 600°C, attributed to the dehydroxylation of clay minerals, confirming its thermal stability.FTIR analysis indicated the presence of kaolinite with functional groups such as O–H stretching at 3693.8 cm^{-1}, Si–H stretching at 2117.1 cm^{-1}, and H–O–H bending at 1636.3 cm^{-1}. SEM imaging revealed a porous, agglomerated structure that could facilitate adsorption. Elemental analysis revealed that silicon (64.23%) and aluminum (29.98%) were the dominant elements, consistent with kaolinite's composition. XRD analysis showed moderate crystallinity, with peaks corresponding to kaolinite and quartz. The raw clay was then modified into sodium clay using sodium chloride, and further treated with humic acid to enhance its adsorption properties. Adsorption studies were conducted to evaluate the effects of key parameters such as pH, contact time, and temperature, on dye removal efficiency was quantified using UV-visible spectrophotometry at 464nm. Adsorption experiments showed that the optimal adsorption condictions are temperature of 70°C, pH of 10 and Contact time of 120 mins. The study concludes that modified Uteh-Uzalla clay is an effective and low-cost adsorbent for methyl orange removal and offers potential for wastewater treatment applications.

CHAPTER ONE

1.0 INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

The contamination of water bodies by synthetic dyes from industrial effluents, particularly from textile, leather, and pharmaceutical industries, has become a major environmental concern (Forgacs *et al.*, 2004). Methyl orange, an anionic azo dye, is widely used as a pH indicator and in textile dyeing, and its presence in wastewater is problematic due to its toxicity, stability, and resistance to biodegradation (Ahmad *et al.,* 2022). The removal of Methyl orange from aqueous solutions is essential to prevent environmental pollution and associated health risks.

Adsorption is considered one of the most efficient and cost-effective techniques for dye removal from wastewater due to its simplicity, high efficiency, and reusability of adsorbents (Crini & Badot, 2008). Among various adsorbents, natural clays have gained attention because of their high surface area, cation exchange capacity, and low cost (Moussout *et al.,* 2018). Clay minerals such as kaolinite, montmorillonite, and bentonite have been extensively studied for their ability to adsorb dyes from aqueous solutions (Ghrab *et al.,* 2020).

The adsorption efficiency of clays depends on several parameters, including pH, initial dye concentration, contact time, adsorbent dosage, and temperature (Wang & Wang, 2018). The interaction between Methyl orange molecules and clay surfaces is influenced by electrostatic attraction, hydrogen bonding, and van der Waals forces (Mittal *et al.,* 2021). Studies have shown that the adsorption of Methyl orange onto natural clay often follows pseudo-second-order kinetics, suggesting chemisorption as the rate-limiting step (El-Katori *et al.,* 2020).

In Nigeria, clay deposits are abundant and have been explored for various applications, including adsorption and wastewater treatment (Okoya *et al.*, 2014). The Uteh-Uzalla clay in Benin City is rich in kaolinite, quartz, and smectite, which enhances its adsorptive properties (Ekezie *et al.,* 2023). However, there is limited research on its effectiveness for Methy orange removal. This study aims to investigate the adsorption performance of Uteh-Uzalla clay for the removal of Methyl orange from aqueous solutions by evaluating key process parameters such as pH, contact time, and adsorption isotherms.

1.1.2 Background of the Study

Water pollution is a global concern, particularly due to the discharge of synthetic dyes from industries such as textiles, leather, and pharmaceuticals. These dyes, including methyl orange, are not only visually unappealing in water bodies but also pose significant environmental and health risks due to their toxicity, non-biodegradability, and potential carcinogenic effects (Forgacs *et al.,* 2004). The presence of such pollutants in aquatic ecosystems can disrupt photosynthesis in aquatic plants, reduce dissolved oxygen levels, and threaten aquatic life.

Various methods have been developed to remove synthetic dyes from wastewater, including chemical coagulation, oxidation, membrane filtration, and biological treatments (Ahmad *et al.*, 2022). However, these techniques often suffer from high operational costs, inefficiency at low dye concentrations, and the generation of secondary pollutants. Among these, adsorption has emerged as one of the most efficient and economically viable methods for dye removal due to its simplicity, cost-effectiveness, and high removal efficiency (Crini & Badot, 2008).

The choice of adsorbent plays a crucial role in adsorption efficiency. While activated carbon is the most commonly used commercial adsorbent, its high production cost limits its large-scale application. As a result, research has shifted toward naturally available and low-cost materials, such as clay minerals, which possess high surface area, cation exchange capacity, and chemical stability (Ghrab *et al.,* 2020). Clays such as kaolinite, montmorillonite, and bentonite have been extensively investigated for their adsorption capabilities, with promising results in removing various organic pollutants, including dyes, from wastewater (Mittal *et al.,* 2021).

Nigeria is endowed with vast clay deposits that have been used for various industrial applications, but their potential for wastewater treatment remains underexplored. The Uteh-Uzalla clay deposit in Benin City is rich in kaolinite, quartz, and smectite, minerals known for their adsorption capacity (Ekezie *et al.,* 2023). Despite its availability, there is limited research on its efficiency in removing Methyl orange and other dyes from aqueous solutions. Investigating the adsorption potential of Uteh-Uzalla clay could provide a cost-effective, sustainable alternative to commercial adsorbents for dye removal in wastewater treatment.

1.1.3 Statement of the Problems

The increasing contamination of water bodies by synthetic dyes like methyl orange (MO) poses serious environmental and health risks due to their toxicity, persistence, and resistance to biodegradation. While adsorption is recognized as an effective dye removal technique, the efficiency of natural adsorbents such as clay depends on several key factors, including mineral composition, contact time,temperature,and pH (Ahmad *et al.,* 2022).

Despite the abundance of clay deposits in Nigeria, there is limited research on the physicochemical properties and adsorption performance of Uteh-Uzalla clay for Methyl orange removal. Characterizing its structure, composition, and surface properties is essential to understanding its adsorption potential. Without this knowledge, its suitability as a low-cost, sustainable alternative to commercial adsorbents remains uncertain (Ekezie *et al.*, 2023).

1.1.4 Justification / Relevance of the Research Work

Water pollution caused by synthetic dyes, particularly methyl orange , poses significant environmental and health hazards due to its toxicity, persistence, and resistance to conventional wastewater treatment methods (Ahmad *et al.*, 2022). The need for cost-effective, sustainable, and locally available adsorbents has driven research into natural materials like clay, which are abundant and possess excellent adsorption properties. However, the adsorption potential of Uteh-Uzalla clay for Methyl orange removal has not been thoroughly investigated, necessitating this study.

This research is justified based on the following key factors:

1. Sustainable and Cost-Effective Alternative to Commercial Adsorbents;

Commercial adsorbents like activated carbon are highly effective but are expensive and difficult to regenerate for large-scale wastewater treatment (Crini & Badot, 2008). Uteh-Uzalla clay, being naturally abundant and locally available, provides a low-cost alternative that could be widely adopted for dye removal, particularly in developing regions.

2. Bridging Knowledge Gaps in Clay Characterization;

Despite the availability of Uteh-Uzalla clay, its physicochemical properties and adsorption mechanisms remain underexplored. Comprehensive characterization of its mineral composition, surface structure, and chemical properties is essential to determine its suitability for adsorption applications *(Ekezie et al., 2023).*

3. Understanding Key Adsorption Parameters for Process Optimization;

The effectiveness of adsorption depends on factors such as temperature, pH, and stirring rate. However, there is limited data on how these factors influence the adsorption of Methyl orange onto Uteh-Uzalla clay. Optimizing these conditions can enhance adsorption efficiency, making it a more viable option for wastewater treatment.

4. Contribution to Environmental Protection and Wastewater Management;

Uncontrolled discharge of dye-laden wastewater threatens aquatic ecosystems, drinking water sources, and public health. By developing an efficient, low-cost adsorption system using natural clay, this study contributes to environmentally friendly wastewater treatment solutions. The findings could support local industries and regulatory bodies in adopting sustainable pollution control measures *(Mittal et al., 2021).*

5. Potential for Industrial and Academic Applications;

The results of this study could benefit industries seeking affordable wastewater treatment solutions, as well as researchers working on adsorption science, materials engineering, and environmental remediation. The study will also provide baseline data for further investigations into clay-based adsorbents for pollutant removal.

1.1.5 Scope of the Study

The scope of this study involves the collection, characterization and Modification of clay from Uteh-Uzalla village, Benin city, Edo State, for its application in dye adsorption. The clay was initially analyzed using FTIR, SEM-EDX, TGA, BET and XRD to determine its structural and elemental composition. To enhance its adsorption capacity, the clay was modified into sodium clay using sodium chloride, followed by acid activation with humic acid. The modified clay was then utilized as an adsorbent for methyl orange dye removal. Adsorption studies were conducted to evaluate the effects of pH, Temperature, and contact time on dye removal efficiency. Spectrophotometric analysis was performed at 465nm using a UV-visible spectrophotometer to quantify adsorption performance and determine optimal conditions for effective dye removal.

1.1.6 Aims and Objectives

The aim of this study is to use a clay obtained from a geographical location in benin city (uteh uzalla community) to adsorb Methyl orange from aqueous solution

The following objectives were set to achieve the aim above;

- collect the clay from Uteh-Uzalla Benin city, Edo State.
- converting it into sodium clay and further activating it with humic acid.
- characterize the raw using XRD, SEM-EDX,TGA,FTIR and BET surface area
- prepare standard solutions of methyl orange dye and generate a calibration curve using a UV-visible spectrophotometer.

- investigate the effects of Time, pH, and Temperature on the adsorption efficiency of the modified clay.
- determine the optimal conditions for maximum dye removal efficiency using spectrophotometric analysis.
- Subject the data to thermodynamics study

1.2 LITERATURE REVIEW

1.2.1 Introduction to Adsorption Technology

Adsorption is a fundamental separation and purification process in which molecules from a liquid or gas adhere to the surface of a solid material, known as the adsorbent. This process is widely used in various industrial and environmental applications, including water treatment, air purification, and chemical processing (Foo & Hameed, 2010). Adsorption is preferred over other removal techniques due to its simplicity, cost-effectiveness, and high efficiency in removing pollutants such as dyes, heavy metals, and organic contaminants from aqueous solutions (Crini & Badot, 2008).

1.2.2 Types of Adsorption

Adsorption can be classified into two main types based on the nature of the interactions between the adsorbate (the substance being adsorbed) and the adsorbent (Singh & Mishra, 2019):

1.Physical Adsorption

This type of adsorption is also known as physisorption. It is due to weak Van Der Waals forces between adsorbate and adsorbent that binds them together. There is no transfer or sharing of electron through new equilibrium adjustment takes place without losing the original association of electron with their respective interactive species. Presence of these weak bond is characterised by low heat of adsorption usually less than 10kcal/mol(63-84kj/mol). Their adsorption is appreciated only at temperature below the boiling point of adsorbate. It is reversible in nature and nonspecific with respect to the adsorbent.

Characteristics

- This type of adsorption is caused by physical forces.
- Physisorption is a weak phenomenon.
- This adsorption is a multi-layered process.
- Physical adsorption is not specific and takes place all over the adsorbant.
- Surface area, temperature, pressure, nature of adsorbate effects physisorption.
- Energy for activation is low (20-40kg/mol)

2.Chemical Adsorption

This type of adsorption is also known as chemisorption. It is due to strong chemical forces of bonding type between adsorbate and adsorbent. In many cases, the adsorption of a substance at a surface involves the formation of chemical bonds between the adsorbate and adsorbent due to the transfer of sharing or electron. It is generally characterised by high degree of heat adsorption i.e. more than 20-50kcal/mol and can occur at high temperature. It usually irreversible in nature and no specific with both adsorbate and absorbent.

Characteristics

- This type of adsorption is caused by chemical forces.
- It is a very strong process.
- This type of adsorption is almost a single-layered phenomenon.
- Chemisorption is highly specific and takes place at reaction centres on the adsorbant.

● Surface area, temperature, nature of adsorbate effects chemisorption.

● Energy of activation is very high 40-400Kj/mol.

1.2.3 Adsorption Mechanism

The adsorption process occurs in several steps (Wang & Guo, 2020):

1. Transport of the adsorbate molecules from the bulk solution to the adsorbent surface.
2. Diffusion of the adsorbate into the pores or active sites of the adsorbent.
3. Attachment of the adsorbate molecules onto the adsorbent surface through physical or chemical interactions.
4. Establishment of equilibrium, where the adsorption rate equals the desorption rate.

The efficiency of adsorption is influenced by factors such as the surface area of the adsorbent, pore size distribution, temperature, pH, and the nature of the adsorbate.

1.2.4 Applications of Adsorption Technology

Adsorption is extensively used in various fields, including:

- ★ Water and Wastewater Treatment: Removal of dyes, heavy metals, and organic pollutants (Crini, 2006).
- ★ Gas Separation and Purification: Used in air purification, removal of volatile organic compounds (VOCs), and carbon dioxide capture.
- ★ Catalysis: Adsorption plays a critical role in catalytic reactions by providing active sites for reactants.
- ★ Biomedical Applications: Drug delivery systems and toxin removal from biological fluids.

1.2.5 Methyl Orange and Its Environmental Impact

1.2.5.1 Introduction to Methyl Orange

Methyl Orange is a synthetic azo dye commonly used as a pH indicator in laboratories and as a dye in textile, paper, and pharmaceutical industries (Gupta & Suhas, 2009). It belongs to the class of azo dyes, which contain the characteristic –N=N– azo bond, responsible for their vibrant colors and chemical stability. Due to its widespread industrial applications, large amounts of Methyl orange and similar dyes are discharged into aquatic ecosystems, posing significant environmental and health concerns (Saratale *et al.*, 2011).

1.2.5.2 Chemical Structure and Properties of Methyl Orange

1. Chemical Structure of Methyl Orange;

Methyl Orange is an azo dye with the molecular formula $C_{14}H_{14}N_3NaO_3S$. It contains an azo (-N=N-) functional group that connects two aromatic rings, giving it a highly conjugated system responsible for its vibrant color and chemical stability.

2. Molecular Structure Details:

- IUPAC Name: Sodium 4-{[4-(dimethylamino)phenyl]azo}benzenesulfonate
- Molecular Weight: 327.33 g/mol
- Functional Groups:
- Azo (-N=N-) group: Responsible for the dye's chromophoric properties.
- Dimethylamino ($-N(CH_3)_2$) group: Influences the pH-sensitive behavior.
- Sulfonate ($-SO_3^-$) group: Enhances solubility in water.

3. Structural Formula:

The structural representation of Methyl Orange is:

CH3

|

N=N—C6H4—N(CH3)2

|

$SO3^{-}Na^{+}$

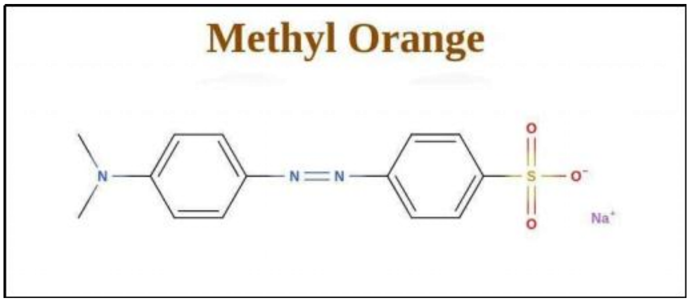


Fig 1; *Structure of Methyl Orange.*

1. 2.5.3 Properties of Methyl Orange

1.Physical Properties;

- Appearance: Orange-red crystalline powder
- Solubility: Highly soluble in water; slightly soluble in ethanol
- Melting Point: Decomposes before melting

2. pH Sensitivity: Changes color depending on pH:

- ➢ pH < 3.1: Red
- ➢ pH 3.1 - 4.4: Orange

- pH > 4.4: Yellow

3. Chemical Properties

- Azo Bond Stability: The (-N=N-) bond provides high chemical stability, making it resistant to photodegradation.
- Acid-Base Indicator: Methyl orange is widely used as a pH indicator due to its distinct color change in acidic and basic conditions.
- Oxidation Sensitivity: Can undergo oxidative degradation, producing aromatic amines, which may be toxic.
- Resistance to Biodegradation: Due to its complex structure, Methyl orange persists in the environment and is difficult to break down naturally.

1.2.5.4 Behavior of Methyl Orange in Aqueous Solution

MO behaves differently under various pH conditions:

- In Acidic Medium (pH < 3.1): The dye exists in its protonated form, appearing red.
- In Neutral or Basic Medium (pH > 4.4): The dye loses a proton, transitioning to its anionic form, which is yellow.
- At Intermediate pH (3.1 - 4.4): A color transition occurs, showing an orange hue.

This property makes Methyl orange valuable as a pH indicator in titrations, especially for strong acid–weak base reactions.

1.2.5.5 Environmental Impact of Methyl Orange

1. Water Pollution

The discharge of Methyl orange into water bodies leads to severe contamination due to its resistance to biodegradation. Azo dyes, including Methyl orange, are highly stable under environmental conditions, making natural degradation processes inefficient (Crini, 2006). The presence of Methyl orange in water reduces light penetration, which disrupts aquatic photosynthesis and negatively affects the ecosystem (Kansal *et al.*, 2007).

2. Toxicity to Aquatic Life

Methyl orange and its degradation products have been reported to be toxic to aquatic organisms. Studies show that azo dyes can break down into aromatic amines, which are carcinogenic and mutagenic (Pandey *et al.*, 2007). Exposure to Methy orange-contaminated water can lead to:

- Disruption of aquatic food chains.
- Bioaccumulation of toxic compounds in fish and other aquatic species.
- Changes in reproductive and growth patterns of aquatic organisms (*Kumar et al.,* 2019).

3. Health Hazards to Humans

Human exposure to Methyl orange can occur through contaminated drinking water, industrial exposure, or food adulteration. Several health risks are associated with MO and its derivatives:

Carcinogenicity: Azo dyes can degrade into toxic aromatic amines, which are known carcinogens. Long-term exposure has been linked to bladder cancer and other malignancies (Saratale *et al.*, 2011).

- ★ Allergic Reactions: Contact with MO may cause skin irritation and allergic reactions in sensitive individuals.
- ★ Neurotoxicity: Some studies suggest that synthetic dyes, including Methyl orange, may have neurotoxic effects, affecting brain function and development (*Katheresan et al., 2018).*

4. Persistence and Challenges in Removal

Methyl orange is highly resistant to conventional wastewater treatment methods due to its complex molecular structure and stability. Traditional treatment techniques, such as biological degradation, are often ineffective. Consequently, alternative removal methods such as adsorption, advanced oxidation processes, and membrane filtration are being explored for Methyl orange removal (Garg *et al.*, 2004).

1. 2.5.6 Mitigation Strategies

To minimize the environmental impact of Methyl orange several approaches have been proposed:

- ➢ Adoption of Eco-Friendly Dyes: Industries are encouraged to switch to biodegradable and less toxic alternatives.
- ➢ Advanced Wastewater Treatment: Techniques like adsorption using natural adsorbents (e.g., clays, activated carbon) and photocatalytic degradation are promising solutions *(Gupta et al., 2009).*
- ➢ Strict Environmental Regulations: Governments and regulatory bodies enforce strict discharge limits on industrial dye effluents to reduce environmental *pollution (Kansal et al., 2007).*

1.2.6 Clay as an Adsorbent for Dye Removal

Dye pollution from industries such as textiles, leather, and paper manufacturing is a major environmental concern due to the toxic, non-biodegradable, and highly stable nature of synthetic dyes (Crini, 2006). Among various treatment methods, adsorption has gained significant attention due to its cost-effectiveness, efficiency, and ease of operation (Gupta & Suhas, 2009). Natural clay materials have been extensively studied as low-cost, eco-friendly adsorbents for dye removal from wastewater due to their high surface area, ion exchange capacity, and chemical stability *(Mittal et al., 2010).*

1.2.6.1 Chemical Structure of Clay;

Clay minerals consist of silicon-oxygen tetrahedral sheets and aluminum (or magnesium)-oxygen octahedral sheets, which form layered structures. The fundamental unit is either:

- 1:1 structure (Kaolinite) – One tetrahedral and one octahedral sheet.

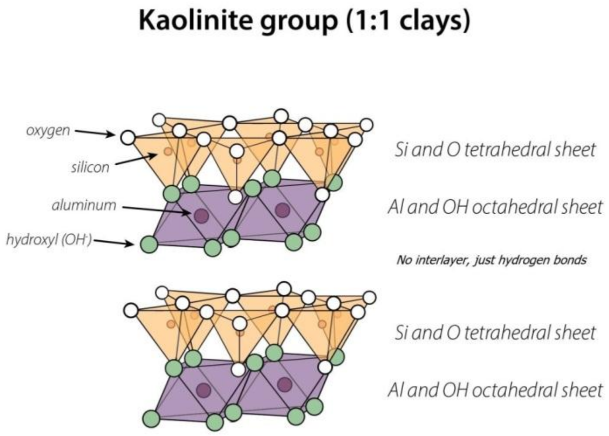


Fig 2; *structure of kaolinite*

- 2:1 structure (Montmorillonite, Bentonite) – Two tetrahedral sheets sandwiching one octahedral sheet.

These layers are negatively charged, allowing clay to attract cations or dye molecules for adsorption *(Bergaya et al., 2006).*

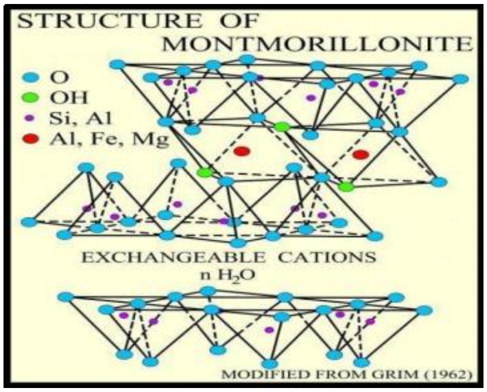


Fig 3; *Structure of montmorillonite*

1.2.6.2 General Chemical Formula of Clay;

$(Al, Mg, Fe)_X (Si, Al)_4 O_{10}(OH)_2 . nH_2O$

Where:

- Si and Al are found in tetrahedral sheets.
- Al, Mg, and Fe are present in octahedral sheets.
- OH and H_2O contribute to hydration and adsorption properties.

1.2.6.3 Chemical Composition of Clay

Clay contains various oxides that determine its adsorption efficiency. Typical compositions include (Brindley & Brown, 1980):

Table 1: Chemical composition of clay

Compound	Role in adsorption	Typical percentage (%)
SiO (silica)	Provides structural framework	40-60%
Al_2O_3 (alumina)	Influence cation exchange	15-30%
Fe_2O_3 (iron oxide)	Enhances electrostatic interaction	1-10%
MgO (Magnesia)	Affects layer charge and expansion	1-10%
CaO (lime)	Improves on exchange capacity	0-5%
Na_2O, K_2O (Alkali oxides)	Swelling and intercalation	0-5%
H_2O (water)	Essential for interlayer expansion	Variable

- The presence of exchangeable cations (Na^+, Ca^{2+}, Mg^{2+}, K^+) in the interlayer spaces plays a key role in adsorption mechanisms (Gupta & Suhas, 2009).

1.2.6.4 Properties of Clay as an Adsorbent

- ❖ Clay minerals, primarily composed of aluminosilicates, exhibit excellent adsorption properties due to their:
- ❖ High Surface Area: Provides more active sites for adsorption.
- ❖ Layered Structure: Allows intercalation and trapping of dye molecules.
- ❖ Negative Surface Charge: Facilitates electrostatic attraction with cationic dyes.
- ❖ Cation Exchange Capacity (CEC): Enables ion exchange interactions with dyes.
- ❖ Hydrophilicity: Enhances interaction with aqueous dye solutions (Bergaya et al., 2006).

1.2.6.5 Types of Clays Used for Dye Adsorption

All clay minerals have a similar chemical composition, a layered structure, at a great affinity for water. Some swell easily and may double in thickness when Wet.They reversibly bind tons, particularly metal cations. These properties results from the structure of clay minerals. There are four main classes of clay minerals.

i The Kaolinite group

ii The Illite group

iii The chlorite group

iv The montmorillonite group

The Kaolinite

Kaolinite is a clay mineral with the chemical composition $Al_2Si_2O_5(OH)_4$

It is an important industrial mineral. It is a layered silicate mineral, with one tetrahedral sheet of silica (SiO_4) linked through oxygen atoms to one octahedral sheet of alumina (AlO_6) octahedra. This clay mineral is the weathering product of feldspars. It has a white powdery appearance. Kaolinite is named after a locality in china called kaolin, which invented porcelain (known as China) using the local clay mineral. The ceramics industry uses it extensively. Because kaolinite is electrically balanced, its ability of adsorb ions is less than that of other clay minerals. Still, kaolinite was used as the main ingredient for the original formulation of the diarrhoea remedy, kaopectate.

Kaolinite has a low shrink-swell capacity and a low cation-exchange capacity (1-15 meq/100g). In many parts of the world it is coloured pink-orange-red by iron oxide, giving it a distinct rust hue. Lighter concentrations yield white, yellow or light orange colour. Commercial grades of kaolin are supplied and transported as dry powder, semi-dry noodle or liquid slurry.

Uses

The main use of the mineral kaolinite (about 50% of the time) is the production of paper, its use ensures the gloss on some grades of coated paper. Kaolin is also known for its capabilities to induce and accelerate blood clotting. Kaolin is used (or was used in the past):

. in toothpaste

. in cosmetics

. as a light-diffusing material in white incandescent light bulbs

. for facial masks or soap (known as white clay)

. as adsorbents in water and waste water treatment.

The Illite

Illite is a group of closely related non-expanding clay minerals. Illite is a secondary mineral precipitate, and an example of a phyllosilicate, or layered aluminosilicate. Illite resembles muscovite in mineral composition, only finer -grained. It is named after the state of Illinois, and is the dominant clay mineral in mid western soils. The chemical formula is given as $(k,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2.(H_2O)]$,but there is considerable in (isomorphic)substitution. It occurs as aggregates of small monoclinic grey to white crystals. Due to the small size, positive identification usually requires x-ray diffraction or SEM-EDS(automated mineralogy)analysis.

The crystallinity of illite has been used as an indicator of metamorphic grade in clay-bearing rocks metamorphosed under conditions between diagnesis and low grade metamorphism with increasing temperature, illite is thought to undergo a transformation into muscovite (Warr and Cox, 2016).

The Chlorite

The Chlorite are a group of phyllosilicate minerals. Chlorites can be described by the following four endmembers based on their chemistry via substation of the following four elements in the silicate lattice; Mg, Fe, Ni and Mn. In addition, zinc, lithium, and calcium species are known. The great range in composition results in considerate variation in physical, optical, and x-ray properties. Similarly, the range of chemical composition allows chlorite group minerals to exist over a wide range of temperature and pressure conditions. For this reason, Chlorite minerals are ubiquitous minerals within low and medium temperature metamorphic rocks, some igneous rocks, hydro thermal rocks and deeply buried sediments.

This clay mineral is the weathering product of mafic silicates and is stable in cool, dry or temperate climates. It occurs along with illite in Midwestern soils. It is also found in some metamorphic rocks, such as Chlorite schist. Various types of chlorite stone have been used as raw material for carving into sculptures and vessels since prehistoric times.

The Montmorillonite

Montmorillonite is a very soft phyllosilicate group of minerals that form when they precipitate from water solution as microscopic crystals, known as clay. It is named after Montmorillon in France. Montmorillonite, a member of the smectite group, is a 2:1 clay, meaning host it has two tetrahedral sheets of silica sandwiching a central octahedral sheet of alumina. The particles are plate-shaped with an average diameter around 1μm and a thickness of 0.96nm; magnification of about 25,000 times, using an electron microscope, is required to see individual clay particles. Members of this group include, amongst others saponite, nontronite, beidellite, and hectorite.

Montmorillonite is a subclass of smectite, a 2:1 phyllosilicate mineral characterized as having greater than 50% octahedral charge, its cation exchange capacity is due to isomorphous substitution of Mg for Al in the central alumina plane. The substitution of lower valence cations in such instances leaves the nearby oxygen atoms with a negative charge that can attract cations. In contrast, beidellite is smectite with greater than 50% tetrahedral charge originating from ismorphous substitution of Al for Si in the silica sheet.

The individual crystals of montmorillonite clay are not tight bound hence, water can intervene, causing the clay to swell. The water content of montmorillonite is variable and it increases greatly in volume when it absorbs water. Chemically, it is hydrated sodium calcium aluminium magnesium silicate hydroxide $(Na,Ca)0.33(Al,Mg)_2(Si_4O_{10})\ (OH)_{2.}nHO$. Potassium, iron and other cations are common substitutes, and the exact ratio of cations varies with source. It often occurs intermixed with chlorite, muscovite, illite, cookeite, and kaolinite.

Uses

Montmorillonite is used in the oil drilling industry as a component of drilling mud, making the mud slurry viscous, which helps in keeping the drill bit cool and removing drilled solids. It is also used as a soil additive to hold soil water in drought-prone soils, used in the construction of earthen dams and leaves, and to prevent the leakage of fluids. It is also used as a component of foundry sand and as a desiccant to remove moisture from air and gases. The swelling property makes montmorillonite containing bentonite useful also as an annular seal or plug for water wells and as a protective liner for landfills. Other uses include as an anticaking agent in animal feed, in papermaking to minimize deposit formation, and as a retention and drainage aid component. Montmorillonite has also been used in cosmetics.

1.2.7 Characterization of Clay as an Adsorbent

To assess its effectiveness for dye removal, clay is characterized using various analytical techniques:

1.Mineralogical Composition (X-ray Diffraction - XRD)

The crystalline structure of the clay was analyzed using X-ray diffraction (XRD) to identify the mineral phases present. This technique enabled the detection of key clay minerals such as kaolinite, illite, and montmorillonite, along with other associated minerals. Understanding the mineral composition is essential for assessing the clay's suitability for industrial applications, including ceramics and construction materials.

2.Surface Morphology and Elemental Composition (Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy - SEM-EDX)

The physical structure and chemical composition of the clay particles were examined using SEM-EDX. This analysis provided high-resolution images to observe particle size, shape, and surface texture while also determining the elemental composition. The data obtained from SEM-EDX offered insights into the porosity and reactivity of the clay, which are crucial factors for applications such as water filtration and soil enhancement.

3.Specific Surface Area and Porosity (Brunauer-Emmett-Teller - BET Analysis)

The adsorption capacity of the clay was assessed using the BET method, which measured its specific surface area, pore volume, and pore size distribution. These parameters are key indicators of the clay's effectiveness as an adsorbent in environmental applications such as pollutant removal and industrial filtration. The results from this analysis provided valuable information on the clay’s potential use in processes requiring high surface area materials, such as catalysis and adsorption.

4.Thermal Stability and Decomposition Characteristics (Thermogravimetric Analysis - TGA)

The thermal behavior of the clay was evaluated using thermogravimetric analysis (TGA), which monitored weight loss during heating. This analysis provided insights into the moisture content, decomposition temperatures, and overall thermal stability of the clay. The results are particularly relevant for applications in ceramics, where high-temperature processing is required, and for assessing the material's stability under different conditions.

5.Chemical Functional Groups and Bonding (Fourier-Transform Infrared Spectroscopy - FTIR)

The chemical structure of the clay was further analyzed using FTIR spectroscopy to identify functional groups such as hydroxyl (-OH) and silicate (Si–O) groups. This technique helped in understanding the clay’s chemical bonding and interaction potential with other materials, which is essential for predicting its behavior in various industrial processes.

1.2.8 Mechanisms of Dye Adsorption by Clay

The adsorption of dyes onto clay materials occurs through various mechanisms, including:

1. Electrostatic Interactions:

Cationic dyes bind to negatively charged clay surfaces.

Anionic dyes require surface modification to enhance adsorption (Gupta et *al*., 2011).

2. Ion Exchange:

Clays with high CEC can exchange their interlayer cations (e.g., Na^+, Ca^{2+}) with dye molecules.

3. Hydrogen Bonding and π-π Interactions:

Common for dyes with aromatic structures interacting with clay surfaces (Sarmah & Pillai, 2020).

4. Pore Filling and Surface Adsorption:

Dye molecules physically adsorb on the clay surface or penetrate interlayer spaces (García-Mendieta *et al.*, 2022).

1.2.9 Modification of Clay for Enhanced Adsorption

While natural clays exhibit good adsorption capacity, modifications can further enhance their efficiency:

- Acid Activation: Increases surface area and porosity.
- Organic Modification: Functionalization with surfactants improves hydrophobic interactions with dyes.
- Thermal Treatment: Alters the clay structure to improve dye adsorption.
- Polymer-Clay Composites: Improve adsorption efficiency through hybrid material properties (Gupta & Saleh, 2013).

1.2.10 Advantages and Limitations of Clay Adsorbents

Table 2: Advantages and Limitations of Clay Adsorbents

Advantages	**Limitations**
Low cost and abundant	Limited adsorption for certain dyes
High stability and reusability	Requires modification for optimal performance
Biodegradable and eco friendly	Possible leaching of ions into water
Simple regeneration methods	Swelling properties can affect adsorption

1.2.11 Effect of Adsorption Parameters on Dye Removal

The efficiency of dye removal via adsorption depends on several key parameters. Understanding how these parameters influence adsorption helps optimize conditions for maximum dye removal.

1. Effect of pH

- pH significantly affects the surface charge of the adsorbent and the ionization state of the dye. For anionic dyes like methyl orange:
- At low pH (acidic conditions), clay surfaces become positively charged, enhancing electrostatic attraction with negatively charged dye molecules (Akar et al., 2010).
- At high pH (alkaline conditions), excess hydroxyl ions compete with anionic dye molecules, reducing adsorption efficiency (Gupta & Suhas, 2009).

2. Effect of Temperature

- Temperature influences adsorption by affecting:
- Dye solubility – Higher temperatures increase dye solubility, affecting mass transfer rates.

- Adsorbent surface activity – Some adsorption processes are endothermic, improving dye uptake at higher temperatures, while others are exothermic, where higher temperatures decrease adsorption *(Karthikeyan et al., 2005*).
- Activation energy – Higher temperatures can enhance diffusion of dye molecules into clay pores.

3. Effect of Contact Time

The adsorption process occurs in three phases:

- Rapid initial adsorption due to availability of active sites.
- Gradual equilibrium phase as sites become occupied.
- Plateau phase where no significant adsorption occurs.
- Longer contact time generally improves adsorption but reaches equilibrium after a certain period (Ho & McKay, 1999).

4. Effect of Initial Dye Concentration

- Higher dye concentrations provide a greater driving force for mass transfer, increasing adsorption. However, at very high concentrations:
- Adsorption sites become saturated.
- Competition for available sites reduces adsorption efficiency (*Garg et al., 2004).*

5. Effect of Adsorbent Dosage

Increasing the amount of clay provides more active sites for adsorption. However:

- Beyond a certain dosage, adsorption plateaus as all dye molecules are removed from the solution.
- Excess adsorbent may lead to particle aggregation, reducing available surface area *(Vijayaraghavan et al., 2008).*

1.2.12: ADSORPTION THERMODYNAMICS

Thermodynamic parameters determine whether the adsorption process is spontaneous and feasible by evaluating Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) changes.

$\Delta G° = -RT\ln K_c$

$\ln K_c = (\Delta S°/R) - \Delta H°/RT$

Where:

$\Delta G°$ = Gibbs free energy change (kJ/mol)

$\Delta H°$ = Enthalpy change (kJ/mol)

$\Delta S°$ = Entropy change (J/mol·K)

R = Universal gas constant (8.314 J/mol·K)

T = Absolute temperature (K)

Kc = Adsorption equilibrium constant

Interpretation of Thermodynamic Parameters:

$\Delta G° < 0$ ‘n → Spontaneous adsorption

$\Delta G° > 0$ ‘n → Non-spontaneous adsorption

$\Delta H° > 0$ ‘n → Exothermic (favorable at lower temperatures)

$\Delta H° > 0$ ‘n → Endothermic (favorable at higher temperatures)

$\Delta S^\circ > 0$ ‘n → Increased randomness at solid-liquid interface

If lnKc against 1/T gives a straight line, the slope and intercept yield ΔH° and ΔS°, confirming the feasibility of the adsorption process.

Thermodynamics: A negative confirms that adsorption is spontaneous, while indicates whether the process is endothermic or exothermic.

1.2.13: Research Gaps

Despite extensive research on adsorption for dye removal, several gaps remain in the understanding and optimization of methyl orange adsorption using clay, particularly Uteh-Uzalla clay. These gaps include:

- **Limited Studies on Uteh-Uzalla Clay for Dye Adsorption**

Most adsorption studies focus on commercially available clays like kaolinite, bentonite, and montmorillonite (Gupta & Suhas, 2009). However, the adsorption potential of locally available Uteh-Uzalla clay remains largely unexplored. There is limited data on its chemical composition, thermal stability, and surface characteristics for effective dye adsorption.

- **Incomplete Understanding of Adsorption Mechanisms**

Although adsorption isotherms and kinetic models have been widely applied, there is still a need for deeper insights into the adsorption mechanisms involved in methyl orange removal using Uteh-Uzalla clay.

- **Optimization of Adsorption Parameters**

Many studies do not comprehensively explore the effect of adsorption conditions (pH, temperature, stirring rate, contact time) on dye remova*l (Akar et al., 2010*). A systematic investigation of these parameters is crucial to determine the optimal conditions for maximum dye removal efficiency.

- **Lack of Thermodynamic Insights**

Few studies analyze the thermodynamics of adsorption on natural clay. Understanding whether the adsorption process is spontaneous (negative ΔG°), endothermic or exothermic (ΔS°), and the randomness of adsorption (ΔH°) is important for industrial applications *(Karthikeyan et al., 2005*).

- **Need for Clay Modification to Enhance Adsorption Capacity**

Natural clays may have limited adsorption capacity due to small pore sizes or weak electrostatic interactions. Surface modifications (acid activation, thermal treatment, or surfactant modification) could significantly improve adsorption performance *(Vijayaraghavan et al., 2008).* However, research on the modification of Uteh-Uzalla clay is scarce.

CHAPTER TWO

MATERIALS AND METHODS

2.1 MATERIALS

2.1.1 Apparatus

- Magnetic stirrer
- Mechanical shaker
- Centrifuge
- UV-visible spectrophotometer
- Fourier Transform Infrared Spectrometer (FTIR)
- Scanning electron microscope (SEM) equipped with an EDX detector. (SEM-EDX)
- X-ray Diffractometer (XRD)
- Thermogravimetric Analyzer (TGA)
- Surface Area Analyzer (BET)
- Volumetric flasks (100 mL)
- Glassware (beakers, measuring cylinders, pipettes)
- Gas cylinder
- Thermometer
- pH meter
- Mortal
- Pestle
- 125µm mesh sieve
- Sample containers

2.1.2 Reagents

- Clay sample (collected from uteh uzalla benin city, Edo State)
- Sodium chloride ($NaCl$)
- Deionized water
- Distilled water
- Silver nitrate ($AgNO_3$)
- Humic acid (1 M solution)
- Dye sample
- pH adjusters (for alkalinity adjustments)

2.2 METHODOLOGY

2.2.1 Site selection and sample collection

The clay used in this study was collected from Uteh-Uzalla, Benin City, Edo State, Nigeria. A known clay deposit region. The selection of the site was based on visible clay exposure and minimal contamination. Samples were obtained from a depth of 40-50 meters below the surface to avoid organic matter interference. A shovel and hand auger were used for excavation, and approximately 20 kg of clay was collected in airtight plastic bags to preserve its natural properties.

Plate 2.2.1: Field sampling location for clay collection at uteh Uzalla benin city

2.2.2 Characterization of Uteh-Uzalla Clay

The characterization of the raw Uteh-Uzalla clay was performed before modification to determine its structural, textural, and chemical properties. The process began with sample collection from Uteh-Uzalla, Benin City, followed by sun-drying for 48 hours to remove moisture. The dried clay was then ground using a mortar and pestle to achieve a finer particle size and subsequently sieved through a 125µm mesh to obtain uniform particles suitable for characterization.

Deionized water was used throughout the process to prevent contamination, and the prepared clay samples were packaged in 10g of 6 portions in separate containers for different analytical techniques. Scanning Electron Microscopy (SEM) was used to examine the surface morphology and particle distribution, while Brunauer-Emmett-Teller (BET) analysis determined the specific surface area, pore volume, and pore size distribution.whereas X-ray Diffraction (XRD) identified the crystalline phases and mineralogical composition. Additionally, Thermogravimetric Analysis (TGA) was conducted to assess thermal stability and decomposition behavior by monitoring weight loss as a function of temperature.

2.2.3 Preparation of Clay Sample

50g of clay sample were mixed with 1.0M sodium chloride solution and stirred for 24 hours at room temperature and atmospheric pressure. It was washed thoroughly with distilled water until tested negative to silver nitrate solution. The sodium clay was acidified with 1.0 M humic acid and stirred for 24 hours, then filtered, and washed thoroughly with 0.01M NaCl solution. Thereafter, dried.

The dried prepared clay was stored in airtight container from where portions were used for dye adsorption studies.

2.2.4 Preparation of Dye Solutions

A stock solution of the dye was prepared by dissolving 1 g of the dye in a 100 mL volumetric flask with distilled water to obtain a concentration of 1 g/L. From this stock solution, serial dilution varying concentrations (0.00 mg/L, 10mg/L, 100mg/L, 200mg/L, and 500mg/L) were prepared from the stock.

2.2.5 Adsorption Experiment

Batch adsorption of 500 mg/L methyl orange (MO) was studied under varying temperature (25 – 70°C), contact time (15 – 150 min), and pH (6–10). Solutions were agitated at 150 rpm in a Mechanical shaker, except for temperature studies using a magnetic stirrer. pH was adjusted with 0.1M HCl or NaOH. After adsorption, samples were Centrifuged and residual Methyl orange were analyzed using UV - Vis Spectrophotometer at wavelength 464nm.

The amount adsorbed was calculated using Equation 1.

$$Qe\,(mg/g) = \frac{(Co - Ce)V}{m}$$

Where;

Q_e is the amount of Methyl orange adsorb by adsorbent in mg/g, C_o is the initial concentration, C_e is the final concentration, m is the mass of the Adsorbent used in g, V is the volume of the Methyl orange solution in litres.

CHAPTER THREE

3.0 RESULTS AND DISCUSSION

3.1: X- ray DIFFRACTION (XRD)

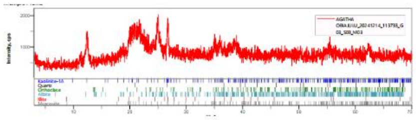


Fig 3.1: XRD pattern

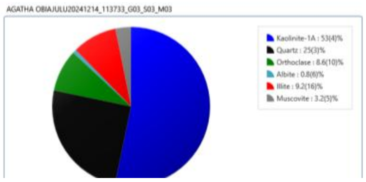


Fig 3.2: Different phases of the clay sample

DISCUSSION

The sample is composed of a mixture of clay minerals (kaolinite, illite), feldspars (orthoclase, albite), quartz, and mica (muscovite). This combination is typical of many sedimentary and metamorphic rocks. The crystallite sizes vary significantly, with kaolinite showing larger crystallite sizes (around 200 Å) compared to other phases like quartz and orthoclase, which have smaller crystallite sizes (around 30-50 Å).The presence of multiple phases suggests a complex mineralogical composition. The high figure of merit values for quartz, orthoclase, and albite indicate a good match with the reference patterns, confirming their presence in the sample.

3.2: SCANNING ELECTRON MICROSCOPY(SEM)/ ENERGY DISPERSIVE X-ray SPECTROSCOPY (EDX)

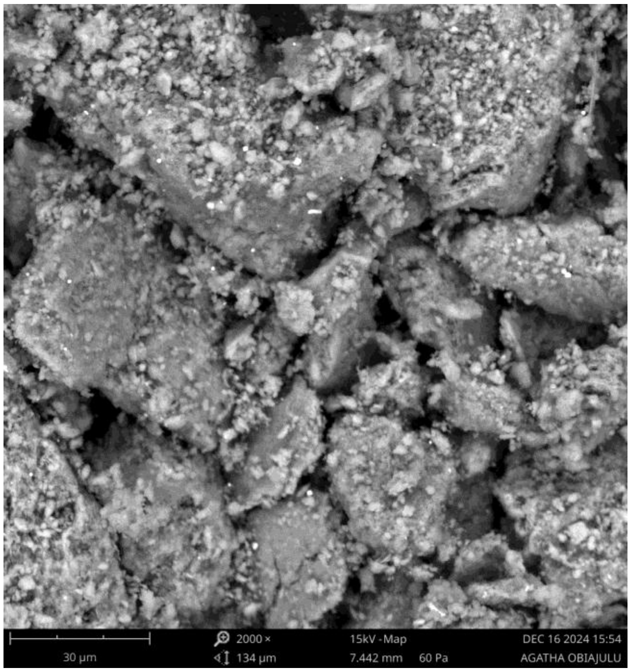


Fig 3.3: SEM image of the sample

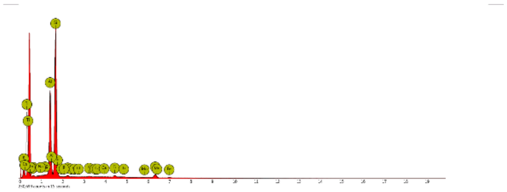
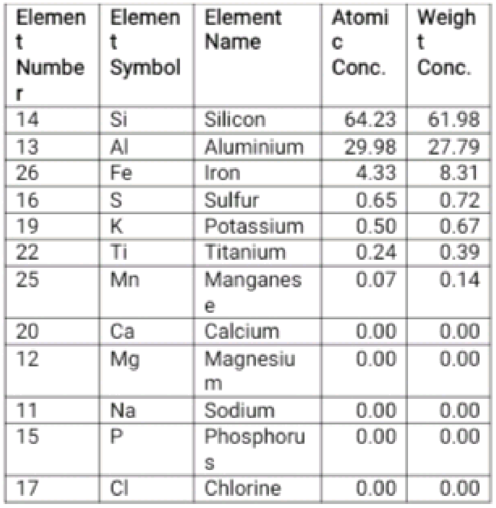


Fig 3.4: EDX result of the clay sample

Table 3.1: Elemental Composition of the clay



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
14	Si	Silicon	64.23	61.98
13	Al	Aluminium	29.98	27.79
26	Fe	Iron	4.33	8.31
16	S	Sulfur	0.65	0.72
19	K	Potassium	0.50	0.67
22	Ti	Titanium	0.24	0.39
25	Mn	Manganese	0.07	0.14
20	Ca	Calcium	0.00	0.00
12	Mg	Magnesium	0.00	0.00
11	Na	Sodium	0.00	0.00
15	P	Phosphorus	0.00	0.00
17	Cl	Chlorine	0.00	0.00

DISCUSSION:

The SEM image of the clay sample reveals an irregular, agglomerated structure with varying particle sizes, indicating a heterogeneous morphology typical of natural clays. The presence of both fine and coarse particles suggests poor crystallinity, which is common in kaolinite-rich clays. The rough surface texture and dispersed granules may be attributed to the presence of silica and alumina, as confirmed by the elemental analysis. Additionally, the porous nature observed could enhance the sample's adsorption capacity, making it suitable for industrial applications such as catalysis and pollutant removal.

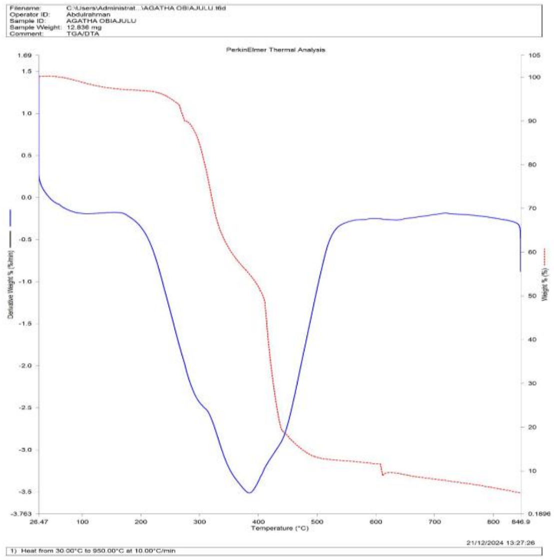
The elemental composition of the clay sample (table 3.1) indicates that silicon (Si) and aluminum (Al) are the dominant elements, with atomic concentrations of 64.23% and 29.98%, respectively, confirming the presence of aluminosilicate minerals like kaolinite. Iron (Fe) is present at 4.33%, suggesting iron oxide impurities, while sulfur (S), potassium (K), titanium (Ti), and manganese (Mn) appear in minor amounts, possibly from accessory minerals. The absence of calcium (Ca), magnesium (Mg), sodium (Na), phosphorus (P), and chlorine (Cl) suggests that the sample lacks carbonate or saline components. This composition aligns with typical clay minerals used in industrial and environmental applications.

3.3: BRUNAUER EMMET TELLER(BET)

Table 2: BET surface area of the clay sample

PARAMETERS	VALUES
BET Surface Area (m^2/g)	170.571
Pore Volume (cm^3/g)	0.109
Pore size (nm)	2.411

3.4: THERMOGRAVIMETRIC ANALYSIS (TGA)



Filename: C:\Users\Administrat...\AGATHA OBIAJULU.t6d
Operator ID: Abdulrahman
Sample ID: AGATHA OBIAJULU
Sample Weight: 12.836 mg
Comment: TGA/DTA

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1) Heat from 30.00°C to 950.00°C at 10.00°C/min

Fig 3.5:TGA of clay sample

Discussion

The provided thermogravimetric analysis (TGA) and differential thermal analysis (DTA) graphs correspond to a clay sample analyzed using PerkinElmer Thermal Analysis equipment. TGA measures the weight loss of a sample as a function of temperature, while DTA records the heat flow associated with phase transitions or decomposition reactions.

From the TGA curve, the clay sample exhibits a multi-stage weight loss pattern. The initial mass loss at lower temperatures (typically below 200°C) is likely due to the removal of adsorbed water or loosely bound surface moisture. This step is characteristic of clay minerals, which have hygroscopic properties. The second major weight loss, occurring between 200°C and 600°C, can be attributed to the dehydroxylation of structural water from clay minerals such as kaolinite or montmorillonite. During this stage, the breakdown of hydroxyl (-OH) groups leads to the formation of metakaolinite in kaolinite-based clays, with a significant mass reduction observed.

Beyond 600°C, the weight loss slows down, indicating the transformation of the clay into an amorphous or partially crystalline phase. In some clays, particularly those containing carbonates, decomposition of minerals like calcite or dolomite may contribute to additional weight loss in the range of 600°C to 800°C. The remaining residue after 800°C is likely composed of thermally stable oxides, such as silica and alumina, which do not decompose further under the applied heating conditions.

The DTA curve in the TGA-DTA plot provides additional insights into the thermal behavior of the clay. Endothermic peaks correspond to dehydration and dehydroxylation processes, while exothermic peaks may be associated with crystallization or phase transitions. The presence of a prominent endothermic peak around 400°C–600°C aligns with the dehydroxylation of clay minerals, while minor peaks at higher temperatures may indicate structural rearrangements or phase transformations.

3.5 : FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

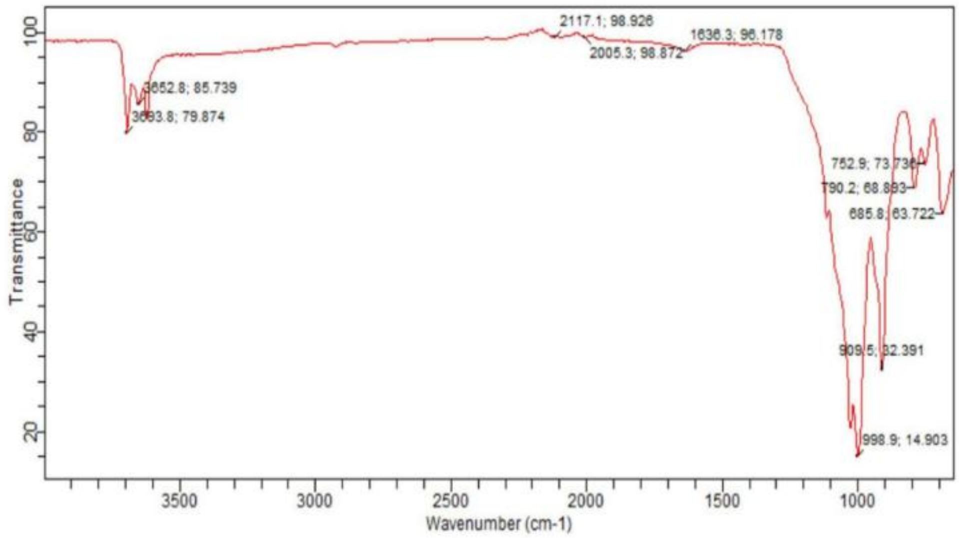

Fig 3.6: FTIR profile for clay sample

Table 3.3: Relevant peaks and functional group

Wavenumber (cm^{-1})	Transmittance (%)	Functional group
3693.8	79.874	O-H stretching
2117.1	98.926	Si-H stretching
1636.3	96.178	H-O-H bending
909.5	32.391	Al-O-H bending
752.9	73.734	Si-O stretching

Discussion;

The FTIR spectrum of the clay sample reveals key functional groups characteristic of its mineral composition. The strong peak at 3693.8 cm^{-1} corresponds to O–H stretching, indicating the presence of kaolinite, while the intense band at 2117.1 cm^{-1} suggests Si–H stretching, likely from silane species. The 1636.3 cm^{-1} peak is attributed to H–O–H bending, confirming adsorbed water, which is common in clay minerals. Additionally, the 909.5 cm^{-1} band corresponds to Al–O–H bending, further supporting the presence of kaolinite, while the 752.9 cm^{-1} peak represents Si–O stretching, indicative of quartz impurities. These findings confirm that the sample primarily consists of kaolinite with traces of quartz and silane species, with notable water retention due to its hydrophilic nature.

3.6 ADSORPTION

3.6.1: CALIBRATION CURVE

Table 3.4: Standard curve point for calibration

Concentration (mg/L)	Absorbance
0	0
10	0.07
100	0.701
200	1.652
500	2.938

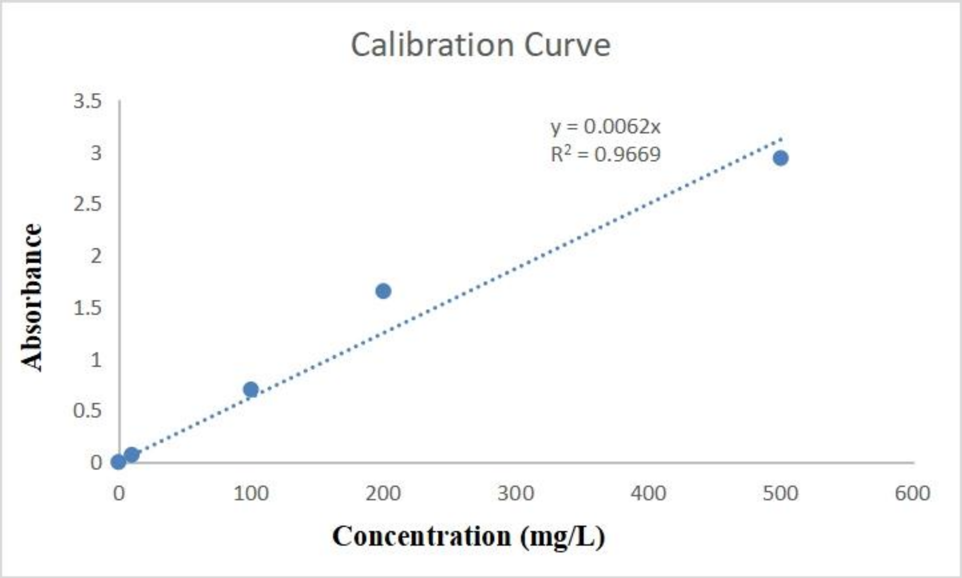

Fig 3.7:Standard calibration curve for methyl orange at 465nm

3.6.2: EFFECT OF CONTACT TIME

Table 3.5: Effect of Contact time

EFFECT OF TIME

TIME (MINS)	INITIAL CONC. (C_0) (mg/L)	FINAL CONC. (C_e)	VOLUME of SOLUTION (ml)	TEMP. (^oC)	ADSORBENT DOSAGE (g)	AMOUNT ADSORBED (Q_e) (mg/g)
15	500	441.1	20	25	0.1	11.78
30	500	392.5	20	25	0.1	21.5
60	500	362.3	20	25	0.1	27.54
90	500	323.8	20	25	0.1	35.24
120	500	316.7	20	25	0.1	36.66
150	500	321.6	20	25	0.1	35.68

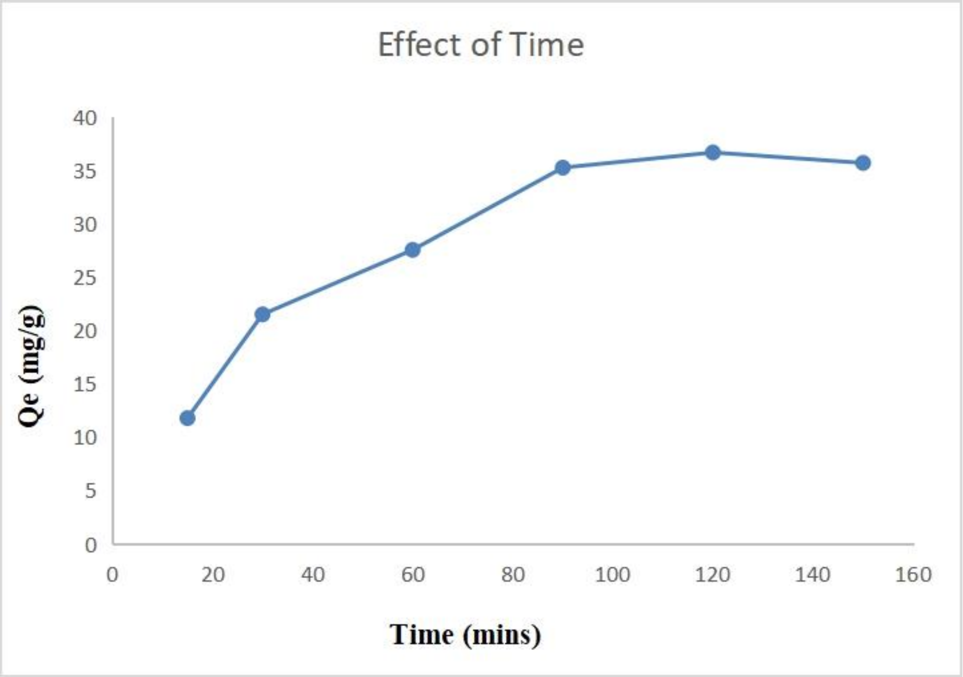

Fig 3.8: Graph of Q_e against contact time

Discussion

The effect of time on the amount adsorbed of methyl orange dye at adsorbent dose of 0.1g, concentration of 500mg/L and at temperature of 25^oC is shown in Figure 3.8 The adsorption plot indicates a time-dependent increase in the amount adsorbed (Qe), with a rapid initial adsorption phase followed by slow uptake phase approaching toward equilibrium. It was observed that within the first 90 mins, amount adsorbed increased significantly from 11.78 mg/g to 35.24 mg/g, suggesting a high availability of active sites. A slight further increase was observed, with Qe reaching 36.66 mg/g at 120 mins, suggesting near-equilibrium conditions. However, beyond this point, a gradual decrease in adsorption capacity was noted, with Qe decreasing to 35.68 mg/g at 150 mins, possibly due to desorption or rearrangement of adsorbed molecules on the adsorbent surface. This trend indicate that 120 mins had the highest contact time.

3.6.3 EFFECT OF pH

Table 3.6: Effect of pH

pH	INITIAL CONCENTRATION (C_0) (mg/L)	FINAL CONCENTRATION (C_e)	VOLUME of SOLUTION (ml)	TIME (min)	TEMP. (^oC)	ADSORBENT DOSAGE (g)	AMOUNT ADSORBED (Q_e) (mg/g)
6	500	373.4	20	30	25	0.1	25.32
7	500	358.1	20	30	25	0.1	28.38
8	500	364.7	20	30	25	0.1	27.06
9	500	347.3	20	30	25	0.1	30.54
10	500	336.8	20	30	25	0.1	32.64

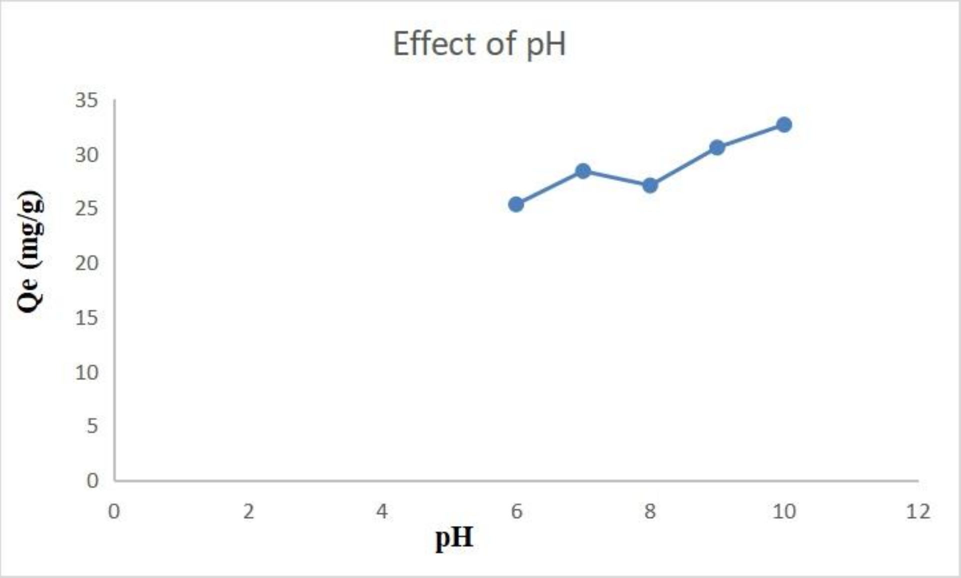

Fig 3.9: Graph of Qe against pH

Discussion

Figure 3.9 and Table 3.6 present the effect of pH on the adsorption of methyl orange dye on 0.1g of the adsorbent, concentration of 500mg/L and at temperature of 25^{o}C. It was observed that as the pH increased from 6 to 10, the amount adsorbed of the dye also increased, ranging from 25.32 mg/g at pH 6 to 32.64 mg/g at pH 10. This indicate that adsorption was more favorable under alkaline conditions, possibly due to enhanced electrostatic interactions between the methyl orange dye and the adsorbent surface.

3.6.4 EFFECT OF TEMPERATURE

Table 3.7: Effect of Temperature

TEMP (^{0}C)	INITIAL CONCENTRATION (C_0) (mg/L)	FINAL CONCENTRATION (C_e)	VOLUME OF SOLUTION (ml)	TIME (min)	ADSORBENT DOSAGE (g)	AMOUNT ADSORBED (Q_e) (mg/g)
25	500	395.22	20	30	0.1	20.956
40	500	292.65	20	30	0.1	41.47
50	500	245.32	20	30	0.1	50.936
60	500	239.24	20	30	0.1	52.152
70	500	194.02	20	30	0.1	61.196

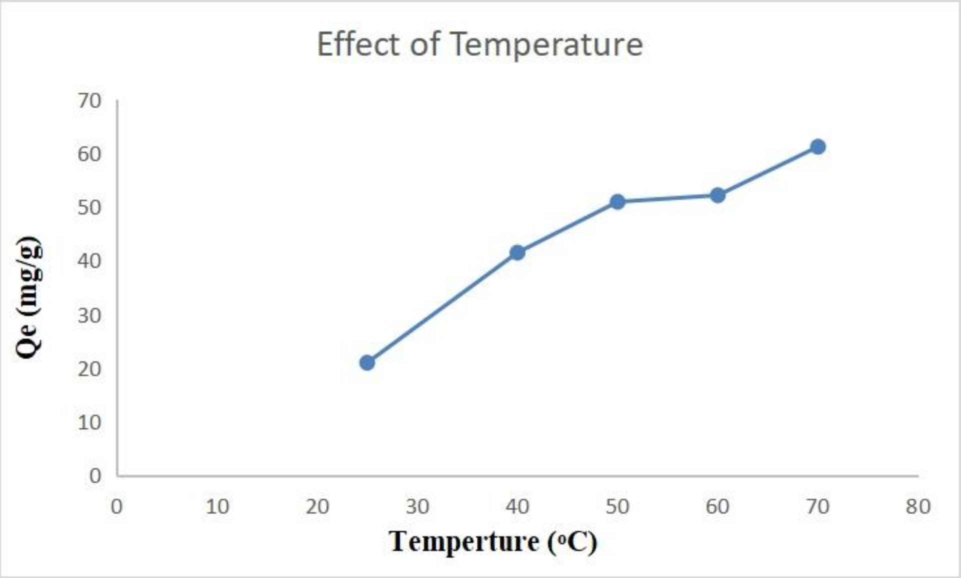

Fig 3.10: Graph of Qe against temperature

Discussion

The effect of temperature on the amount adsorbed of methyl orange dye using 0.1g of adsorbent, concentration of 500mg/L and at time of 30mins is shown in Figure 3.10 and Table 3.7 It was observed that as the temperature increased from 25°C to 70°C, amount adsorbed also increased, from 20.956 mg/g at 25°C to 61.196 mg/g at 70°C. The results suggested that the adsorption process was endothermic, meaning that higher temperatures enhanced the interaction between the methyl orange and adsorbent.

3.7: THERMODYNAMICS STUDY

Table 3.8:Thermodynamic parameters

Temperature (°c)	Temperature (k)	1/T (K^{-1})	K_c	$\ln K_c$	ΔG°(kj/mol)
25	**298.15**	**0.0033**	**0.0530**	**-2.9375**	**7821.53**
40	**313.15**	**0.0032**	**0.1417**	**-1.9540**	**5087.30**
50	**323.15**	**0.0031**	**0.2076**	**-1.5721**	**4223.71**
60	**333.15**	**0.0030**	**0.2180**	**-1.5233**	**4219.25**
70	**343.15**	**0.0029**	**0.3154**	**-1.1530**	**3292.02**

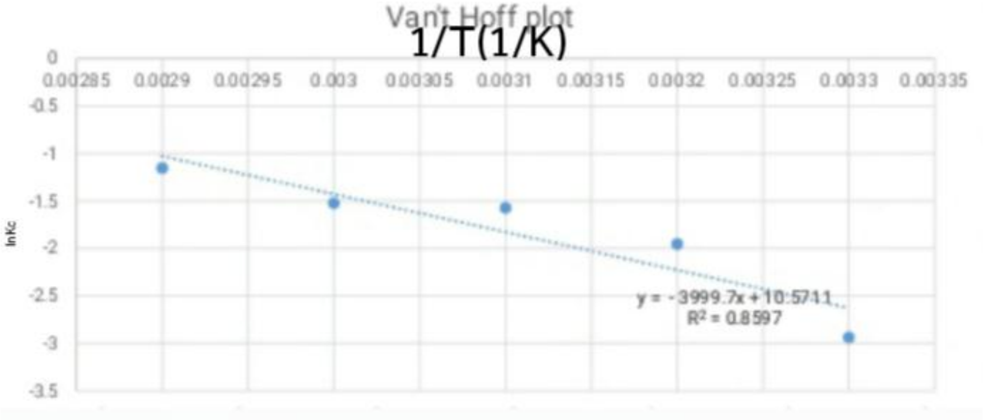

Fig 3.11: graph of $\ln k_c$ against 1/T

Discussion

The Van't Hoff plot in Figure (3.11)illustrates the relationship between the equilibrium constant (lnK) and the reciprocal of temperature (1/T). The linear equation obtained, $y = -3999.7x + 10.571$ with an R^2 value of 0.8897, indicates a strong correlation. From the slope, the enthalpy change ($\Delta H°$) was calculated as 33.24 kJ/mol, confirming that the adsorption process is endothermic. The positive entropy change ($\Delta S°$=87.9J/mol•K) suggests increased disorder at the solid-liquid interface. These results indicate that higher temperatures favor adsorption, enhancing the interaction between methyl orange and the adsorbent.

3.8: CONCLUSION

This study successfully demonstrated the potential of modified Uteh-Uzalla clay as an efficient adsorbent for the removal of methyl orange from aqueous solutions. The clay was characterized using SEM, BET, XRD, TGA, and FTIR. The results showed that the dorminant phase of the clay is kaolinite though contaminated with other phases. The surface area was 170.571m^2/g with pore size of 2.411 nm. The elemental composition is showing high concentration of Si and Al. The optimal adsorption condictions are temperature of 70°C, pH of 10 and Contact time of 120 mins. These results suggest that Uteh-Uzalla clay is a cost-effective, eco-friendly alternative to commercial adsorbents for wastewater treatment applications.

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