



**A Comparative Study on the Efficacy of Modified Clay Soil for the Decolouration of
Acidic and Basic Textile Dyes: A Case Study**

BY

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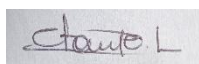
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**A DISSERTATION SUBMITTED TO THE DEPARTMENT OF EARTH SCIENCES,
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF EARTH SCIENCE IN HYDROLOGY AND WATER RESOURCES AT
THE FACULTY OF SCIENCE, ENGINEERING, AND AGRICULTURE,
UNIVERSITY OF VENDA**

FEBRUARY 2025

DECLARATION

I Chauke Livingstone (Student number 16000798) declare that this dissertation “**A Comparative Study on the Efficacy of Modified Clay Soil for the Decolouration of Acidic and Basic Textile Dyes: A Case Study**” for the award of the degree of Masters of Earth Sciences in Hydrology and Water Resources (ESMMES) at the University of Venda, has not previously been submitted by me for a degree or any other institution and that all the reference materials contained therein have been duly acknowledged.



Signature:.....

Date:.....06/02/2025.....

DEDICATION

I dedicate this study to my mother Chauke Girly, my sister Chauke Tinyiko Njakeni, my brother Chauke Hleko, and my friend Muntsu Mufunwa Evidence. For their inspiration, support, motivation, and encouragement throughout my research project period.

ACKNOWLEDGEMENT

I am grateful to the **Almighty God** for giving me the strength and wisdom to complete my dissertation.

My special thanks go to my supervisor **Prof J.R Gumbo** and my co-supervisor **Dr T Ngulube** for your support and for guiding me on the proper route of my studies. Additionally, throughout the conception and implementation of this research project, they offered helpful critiques and recommendations.

I sincerely thank all the Department of Earth Sciences staff members who helped me with this research. I want to acknowledge and appreciate all my friends' support.

I am appreciative of the unwavering support I have received from my friend **Muntsu Evidence Mufunwa**, my mother **Chauke Girly**, my sister **Chauke Tinyiko**, my brother **Chauke Hleko**, and my entire family.

ABSTRACT

Dyes play a crucial role in the production of various products, including paper, plastics, and leather. However, their release into the environment leads to pollution and poses health risks to both humans and animals. Therefore, it is essential to treat dye-containing effluents before they are discharged into the environment. This study employed a cost-effective method to remove dyes from wastewater by utilizing natural clay as an adsorbent. The efficacy of $\text{Mn}^{2+}/\text{Al}^{3+}$ oxide-modified Mukondeni black clay soil (smectite) in removing acidic (Methyl Orange, MO) and basic (Crystal Violet, CV) textile dyes was evaluated. A 1:3 modified smectite ratio was identified as the most effective adsorbent. Characterization using X-ray Fluorescence (XRF), Brunauer-Emmet-Teller (BET), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Fourier Transform Infrared (FTIR), and Point of Zero Charge (PZC) revealed that Modified-SMT contained 18.42% Al_2O_3 and 61.08% SiO_2 , had a surface area of 35.30 m^2/g , and featured functional groups such as C–O, C–O–C, and O–H, with a PZC at pH 4.30. Maximum dye removal efficiencies were recorded at 91.95% for MO after 90 min under the conditions (initial dye concentration = 20 mg/L, temperature = 30 °C, contact time = 90 minutes, shaking speed = 250 rpm, solution volume = 30 mL, and an adsorbent mass = 2 g). For CV, an efficiency of 96.35% was achieved after 30 minutes under conditions (initial dye concentration = 20 mg/L, temperature = 30 °C, contact time = 30 minutes, shaking speed = 250 rpm, solution volume = 30 mL, and an adsorbent mass = 0.1 g). Adsorption isotherm analysis indicated that MO followed a multilayer mechanism on heterogeneous surfaces (Freundlich model), while CV exhibited monolayer adsorption on homogeneous surfaces (Langmuir model). Kinetic studies confirmed pseudo-second-order behaviour. Thermodynamic parameters $\Delta H = -47.72$ KJ/mol and $\Delta S = -0.17$ J/mol/K showed that MO adsorption was non-spontaneous and exothermic ($\Delta G = 12.64$ KJ/mol for 80 °C), whereas $\Delta H = 22.64$ KJ/mol and $\Delta S = 0.09$ J/mol/K for CV adsorption was spontaneous and endothermic ($\Delta G = -9.55$ KJ/mol for 80 °C). The adsorbent retained its efficiency over four regeneration cycles, demonstrating its suitability as a sustainable and effective solution for dye removal in wastewater treatment. It can be concluded that $\text{Mn}^{2+}/\text{Al}^{3+}$ oxide-modified Mukondeni black clay soil (smectite) can remove both MO and CV dye from aqueous solution.

Keywords: Adsorption, Dyes, Equilibrium, Isotherm, Kinetics, Smectite, Thermodynamic

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LIST OF ABBREVIATIONS AND ACRONYMS

BET	Brunauer-Emmet-Teller analysis
CEC	Cation Exchange Capacity
CV	Crystal Violet dye
CV-MSMT	Crystal Violet loaded $\text{Mn}^{2+}/\text{Al}^{3+}$ oxide-modified smectite
EDS	Energy Dispersive Spectroscopy analysis
FTIR	Fourier Transform Infrared analysis
MO	Methyl Orange dye
Modified-SMT	$\text{Mn}^{2+}/\text{Al}^{3+}$ oxide-modified smectite
MO-MSMT	Methyl Orange loaded $\text{Mn}^{2+}/\text{Al}^{3+}$ oxide-modified smectite
NA	Not applicable
pH	Potential of hydrogen
PZC	Point of Zero Charge
RAW-SMT	Smectite Black Mukondeni Clay Soil
rpm	revolutions per minute
SEM	Scanning Electron Microscopy analysis
UV-Vis	Ultraviolet-Visible Spectrometer
XRD	X-ray Diffraction analysis
XRF	X-ray Fluorescence analysis
SMT	Smectite clay

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CHAPTER ONE: INTRODUCTION

1.1 Background

Water is one of the most vital natural resources on planet Earth. However, it is continuously contaminated by various contaminants (Shabir *et al.*, 2022), and dyes are one of the primary contributors to water contamination in aquatic bodies. Dyes are toxic pollutants that cause environmental, ecosystem, and human problems. They are widely used in various fields and discharged into drinking water sources (Islam *et al.*, 2023). Multiple industries, such as plastics, rubber, textile, leather, cosmetics, food, and papermaking, use various dyes, which occur in the effluents discharged from some industries (Pandey *et al.*, 2020).

Colour is the most visible indicator of water contamination because it affects the transmission of sunlight into streams (Ardila-Leal *et al.*, 2021). Dyes in water are toxic and unwanted even at small concentrations (1 mg/L) (Velusamy *et al.*, 2021) and need to be eliminated before the wastewater is discharged into the environment (water bodies). The existence of dye in water results in the disruption of the photosynthetic process of aquatic organisms and diminish light penetration (Wang *et al.*, 2024). It also reduces oxygen levels in water bodies, which harms the flora (Sharma *et al.*, 2021), and fauna (Mehra *et al.*, 2021).

Crystal Violet (CV) is a cationic dye often utilized in various manufacturing sectors such as pharmaceuticals, biological stains, and leather. It is extremely harmful when inhaled or swallowed and can lead to serious health risks such as permanent blindness, cyanosis, increased heartbeat skin, and eye irritation (Abbasi *et al.*, 2020). Methyl Orange (MO) is a regularly utilized anionic azo dye discharged from various manufacturing sectors, including plastics, paper, textile, and cosmetics, into aquatic environments (Wu *et al.*, 2021). It is carcinogenic and mutagenic (Hanafi and Sapawe, 2020); hence, it is necessary to remove these dyes from waste streams before their release into aquatic bodies (Hynes *et al.*, 2020).

Dye treatment from wastewater is costly and demands higher energy consumption (Al-Tohamy *et al.*, 2022). Several effective techniques of elimination of dye molecules are adsorption, biological process, membrane process, ozonation, ion-exchange, photo-electrochemical, reverse osmosis, coagulation, and degradation (Slusarski-Santana *et al.*, 2022; Nishat *et al.*, 2023; Date and Jaspal, 2024).

The adsorption method is considered to be the common treatment technique for removing dyes from aqueous effluents due to its ease of maintenance, low cost, ease of design, flexibility, ease of operation, and resilience to toxic pollutants (Sirajudheen *et al.*, 2021).

Some of the materials used for adsorption studies to remove textile dyes include agricultural wastes such as *Vitellaria paradoxa* leaves (Shehu and Ibrahim, 2024), wheat waste, groundnut shell, and cotton waste (Varsani *et al.*, 2024), and clay minerals such as bentonite (Mutahir *et al.*, 2022), montmorillonite (Boudjemaa, 2020), vermiculite (Cao *et al.*, 2020), Moroccan natural clay (Loukili *et al.*, 2021), and kaolinite (Ighnih *et al.*, 2023).

Activated carbon is a common and effective dye sorbent, but its large-scale application is hindered by its relatively high price, high operating cost, and problems with regeneration. Therefore, there is an increasing demand for affordable, renewable, commonly accessible materials to be used as adsorbents for removing dye colours. In adsorption studies evaluating activated carbon and clay minerals to remove textile dye from the wastewater, it was concluded that clay minerals have greater potential for adsorption capabilities than activated carbon at the same temperature and pH conditions (Sadiku *et al.*, 2022).

Clays are cheap minerals that are abundantly available naturally. They are used in adsorption studies due to their mineral composition and properties, such as high porosity, high ion exchange capacity, large specific surface areas, layered structure, mechanical and chemical stability (Mudzielwana *et al.*, 2016; Sadiku *et al.*, 2022). Smectites are the most well-known and widely used industrial clay minerals. The smectite group consists of clay minerals of various origins and chemical composition. It is a non-metallic clay family that mainly consists of hydrated sodium calcium aluminium silicate, a group of monoclinic clay-like minerals with a general formula $(Ca, Na, H)(Al, Mg, Fe, Zn)_2(Si, Al)_4O_{10}(OH)_2 \cdot nH_2O$. Chemically, they are hydrated sodium calcium aluminium magnesium silicate hydroxides $(Na, Ca)_x(Al, Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$ (Kausar *et al.*, 2018; Pajak, 2021).

The structure of this type of clay is 2:1, consisting of a central octahedral sheet of alumina lying between two tetrahedral sheets of silica and enabling multiple substitutions in each sheet. Most of the technical applications of smectite focused on its high cation exchange capacity (CEC) (Moraes *et al.*, 2017). Generally, the modification reaction used to prepare the modified smectite involves replacing the interlayer cations (e.g. Na^+ , K^+ , Ca^{2+}) with specific species (metal oxides species such as Al^{3+} and Mn^{2+}) to change the surface and structural properties of

clay (Ma and Zhu, 2006). In this comparative study, the efficacy of modified clay soil for the decolouration of acidic and basic textile dye was investigated.

1.2 Problem statement

The increase of global population has resulted in the higher production of textile products, leading to a correspondence rise in textile mills and their effluents causing a big problem of pollution in the environment. The textile sectors are the biggest consumers of dyes (Dutta *et al.*, 2022). Dyes harm the terrestrial and aquatic ecosystems, as well as human well-being. The discharge of dye effluents from industrialization into the aqueous streams affects water quality and pollutes the water bodies (Kapanga *et al.*, 2024).

The health of terrestrial animals and human beings that depend on such water bodies is at high risk. Water that is contaminated by textile dyes poses serious diseases (asthma, allergies, nausea, skin, and eye irritation, tuberculosis, and cancer) if consumed internally and used externally. It harms various important organs (liver, heart, brain, and kidney) and systems (immune, reproductive, and respiratory) of human organisms (Slama *et al.*, 2021).

Textile dye effluents discharged into the environment also affect aquatic life. The availability of even a very small amount of dye concentration in natural water bodies decreases photosynthetic activity by blocking light penetration and disrupting the biological metabolism processes in aquatic life (Ghosh *et al.*, 2020). Therefore, aquatic plants, aquatic animals, and other living organisms in the rivers will be affected (AbdEllatif *et al.*, 2019).

These lead to the extinction of some of the indigenous flora and fauna found in the water bodies, it also alters the aquatic ecosystems, and result in the growth of alien flora because of the toxic chemicals that are contained in the textile dye effluents. Fishing industries were affected, potentially leading to job scarcity and poverty in developing countries, especially in the local regions (rural areas). The release of wastewater contaminated by textile dye into the aquatic environment pollutes potable water sources and leads to water scarcity (Solayman *et al.*, 2023).

1.3 Rationale of the study

Various industries throughout the world use textile dyes to manufacture their products. They discharge dye effluent into the rivers, negatively affecting the ecosystem and the aquatic environment. Numerous research studies have been conducted on techniques to remove dyes from wastewater. However, low-cost methods that small-scale industries can use to treat wastewater are hardly available. Therefore, there is a need to look at the naturally occurring

local materials that are abundantly available and can be used as adsorbents to remove dye from wastewater.

Natural clay mineral is regarded as an important adsorbent material because of its low cost, abundance in nature, small size (less than 2 μm), high cations exchange capacity, chemical stability, and large specific area (Zhang *et al.*, 2021). It is recommended to be used in the adsorption studies. It can remove contaminants from wastewater. This comparative study seeks to investigate the efficacy of modified clay soil for the removal of acidic and basic textile dyes.

1.4 Research objectives

1.4.1 Main objectives

- To compare the efficacy of $\text{Mn}^{2+}/\text{Al}^{3+}$ oxide-modified smectite for the decolouration of acidic (Methyl Orange) and basic (Crystal Violet) dye.

1.4.2 Specific objectives

- To apply $\text{Mn}^{2+}/\text{Al}^{3+}$ oxide-modified smectite to determine the best ratio for removing both MO and CV dye
- To optimize conditions suitable for removing acidic (Methyl Orange) and basic (Crystal Violet) dye from the aqueous solution.
- Employing various characterization techniques to determine the physicochemical properties of raw smectite (Mukondeni black) clay soil, and $\text{Mn}^{2+}/\text{Al}^{3+}$ oxide-modified smectite before and after the adsorption of Methyl Orange and Crystal Violet dye.
- To assess the equilibrium model that best describes the adsorption process and kinetic studies
- To evaluate desorption and regeneration studies

1.5 Research questions

- Which ratio of $\text{Mn}^{2+}/\text{Al}^{3+}$ oxide-modified smectite has the highest percentage removal for both acidic and basic dye?
- Which optimum conditions best describe the removal of acidic (Methyl Orange) and basic (Crystal Violet) dye from the aqueous solution using $\text{Mn}^{2+}/\text{Al}^{3+}$ oxide-modified smectite?
- What are the physicochemical characterizations of raw smectite (Mukondeni black) clay soil, and $\text{Mn}^{2+}/\text{Al}^{3+}$ oxide-modified smectite before and after use in the batch experiments?

- Which equilibrium model best describes the adsorption process and kinetic process in this study?
- Does the regeneration assessment determine that the dye-loaded $\text{Mn}^{2+}/\text{Al}^{3+}$ oxide-modified smectite is suitable for reuse?

1.6 Hypothesis

Modified smectite-rich black clay soil can effectively remove textile dyes from aqueous solutions.

1.7 Outline of the dissertation

Chapter 1 outlined the background of the study together with the problem statement, rationale of the study, research objectives (main and specific objectives), research questions, and hypothesis. **Chapter 2** covered the literature reviews of textile dyes, classification of textile dyes, physicochemical characteristics of crystal violet (CV) and methyl orange (MO) textile dyes, impact of dyes on the environment, methods of textile dye removal from wastewater, other studies that used adsorbent materials to remove dyes from aqueous solution, and decolourization of textile dyes with clay materials. **Chapter 3** comprises of the methodology. **Chapter 4** includes results and discussion. **Chapter 5** consists of a conclusion and recommendations. **References** include all the references utilized in the research. **The appendix** consists of the raw data from the study.

CHAPTER TWO: LITERATURE REVIEW

2.1 Textile dyes

Gita *et al.* (2017) defined a textile dye as a synthetic chemical compound with an aromatic structure recalcitrant to biodegradation due to its xenobiotic nature. Dyes are organic compounds that produce colours and provide colours to different materials such as cosmetics, papers, drugs, fur, greases, hairs, waxes, plastics, and textile materials (Ngulube *et al.*, 2017).

2.2 Acidic and Basic dyes

Acidic and basic dyes have been widely used in various industrializations to manufacture different materials. Different dyes have various descriptions, main applications, chemical types, groups, and examples. Table 2.1 shows the differences between acidic and basic textile dyes.

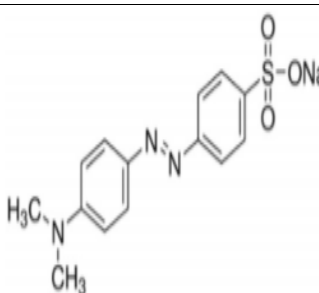
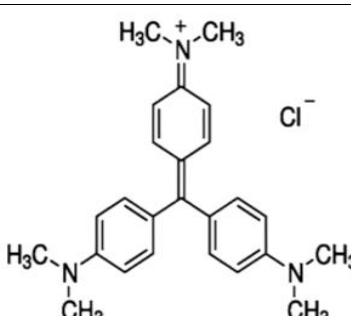
Table 2.1: Comparison between acidic and basic textile dyes (Sahu and Singh, 2019; Younas *et al.*, 2021; Benkhaya *et al.*, 2020).

Textile dyes	Acidic	Basic
Definition	Is an anionic dye and it has a negative charge	Is a cationic dye and it has a positive charge
Description	Simple to apply with a poor fastness.	Demands careful application to avoid uneven dyeing.
Main application	Includes polyester fibres, modified rayon, and nylon	Composed of cellulosic and protein fabric
Chemical type	Nitroso, nitro, and xanthene	Anthraquinone, anthraquinone oxazine, cyanine, acridine, and hemicyanine
Auxochromic Groups	COOH, SO ₃ and OH	NH ₂ , NHR, and NR ₂
Examples	Methyl Orange, Congo Red, Acid Red 27, and Direct Red 81	Crystal Violet, Rhodamine B, Malachite Green, and Methylene Blue

2.3 Physicochemical characteristics of Methyl Orange (MO) and Crystal Violet textile dye (CV).

The physicochemical characteristics of MO and CV are classified according to the parameters as indicated below in Table 2.2. MO is a typical anionic azo dye (Zayed *et al.*, 2018), while CV is a synthetic cationic dye (Menkiti *et al.*, 2018).

Table 2.2: Physicochemical characteristics of Methyl Orange (MO) (Munagapati *et al.*, 2017) and Crystal Violet (CV) textile dye (Loqman *et al.*, 2017).

Parameters	MO dye	CV dye
Suggested name	Methyl Orange	Crystal Violet
λ_{max} (nm)	464	590
Molecular formula	$C_{14}H_{14}N_3NaO_3S$	$C_{25}H_{30}N_3Cl$
Molecular weight (g/mol)	327.3	407.98
Chemical structure		

2.4 Environmental effects of textile dyes

Textile industries discharge effluents that cause pollution to the environment. Textile dye effluents released from various industries result in severe surface and groundwater pollution. Additionally, excessive dye concentrations in water bodies reduce photosynthetic activity and light penetration, resulting in oxygen shortages and disrupting the biological cycles of aquatic biota. (Dutta *et al.*, 2022). Contamination of water affects downstream human activities such as recreation, irrigation, fishing, and drinking (Sahu and Singh, 2019).

Discharged effluents from textile industries cause an indirect impact on the earth's surface by causing soil erosion. Toxic chemicals released from textile effluent affect bacteria and fungi

that make the soil fertile (Mohan and Shukla, 2022). Textile wastewater released from industry has a lasting effect on people, livestock, and vegetation health. In humans, it causes skin cancer and allergies. Human functioning cells are harmed by toxic chemical pollutants when synthetic dyes are processed (Sahu and Singh, 2019).

2.5 Methods of textile dyes removal from wastewater

There are three types of wastewater treatment processes such as biological, physical, and chemical techniques. The biological processes include the use of aerobic processes, anaerobic processes, and single-cell (fungal, algal, and bacterial) (Ikram *et al.*, 2021). Physicochemical methods include the use of ozonation, coagulation-flocculation, oxidation with NaOCl (Sodium hypochlorite), precipitation, Fenton processes, and electrokinetic coagulation (Mwashighadi, 2020). Table 2.3 and Table 2.4 show the different physicochemical methods and biological methods of dye removal from wastewater respectively. (Sahu and Singh, 2019).

Table 2.3: Different physicochemical methods of dye removal from wastewater (Sahu and Singh, 2019; Piaskowski *et al.*, 2018).

Techniques	Stage of treatment	Benefits	Disadvantages
Membrane separation	Main treatment	high efficacy of removal for all dye types.	Costly and demand more pressure.
Electrokinetic coagulation	Pre/Main treatment	Cost-effective	Large production of sludge
Ozonation	Main treatment	Effective for azo dye removal applied in gaseous state: no alteration of volume	Inappropriate for dispersed dyes that produce aromatic.
Precipitation, Coagulation-flocculation	Pre/Main treatment	Inexpensive	Agglomerates undergo treatment and separation. selected state of operation

Table 2.4: Different biological methods of dye removal from wastewater (Sahu and Sigh, 2019; Azam *et al.*, 2022).

Techniques	Stage of treatment	Benefits	Disadvantages
Single-cell (fungal, algal, and bacterial)	Post-treatment	Excellent removal effectiveness at low concentrations and volumes.	Maintenance is expensive
Aerobic process	Post-treatment	Partial or complete	High costly
Anaerobic process	Main treatment	Resistant to wide range of complex coloured compounds Biogas released is used for steam generation	Prolonged adjustment period

2.6 Mukondeni clay as an adsorbent to treat wastewater.

Clay minerals are regarded as effective adsorbents for removing pollutants, such as textile dyes from wastewater. Clay is used in adsorption studies because its lamellar structure provides large specific areas (Elmoubarki *et al.*, 2015). Mukondeni clay has been known to have good potential for treating wastewater. It has been used to remove toxic chemicals from aqueous solution (Gitari *et al.*, 2019). However, modifying makes it work excellent as an effective adsorbent to remove pollutants from aqueous solution.

Modification enhances the adsorption capacity by altering the surface areas of the adsorbent and introducing suitable ions (positive ions) to remove pollutants from wastewater (Ngulube *et al.*, 2017). Due to its strong abilities (to allow it to be put under a high fire temperature), it has traditionally been used to make ceramic filters that improve water quality. It is also used to make cooking and structural arts pots because it does not break easily. These pots and structural arts are painted with paintings representing Venda and Tsonga culture and sold to local people, business people, and tourists (Kawale, 2014).

2.7 Decolourization of MO and CV using clay minerals

Different clay materials have been used to remove Methyl Orange and Crystal Violet dye from the aqueous solution (Ahamad *et al.*, 2024; Ike *et al.*, 2024). It was found that most of the clay removes textile dyes with a greater percentage of removal. Each clay material has a different optimum time depending on the mechanisms of the aqueous solution that happens when the adsorbent interacts with the dye molecules (George *et al.*, 2024). Different clay materials work differently towards the dye molecules, even if the dye is the same (Adeyemo *et al.*, 2017). Table 2.5 shows the decolourization of Methyl Orange and Crystal Violet textile dye using clay minerals.

Table 2.5: Decolourization of Methyl Orange (MO) and Crystal Violet (CV) textile dye using clay minerals.

Clay Mineral	Dye Type	Optimum conditions	Highest Removal (%)	Authors
Chitosan/diatomite composite	Methyl Orange (MO)	Time 40 min, pH 5.0, Conc. 50mg/L	88.37%	Zhao <i>et al.</i> (2017).
Chitosan/Saponin-bentonite	Methyl Orange (MO)	pH 4.80, Temp. 60°	70.4%	Laysandra <i>et al.</i> (2019).
Green-coloured local clay (North eastern Morocco)	Crystal Violet (CV)	Initial dye conc. 125 mg/L, Adsorbent dose 2.5 g/L, Time 40 min	95.3%	Loqman <i>et al.</i> (2017).
Awka Clay	Crystal Violet (CV)	pH 6, Temp. 45°C, Conc 300 mg/L, Time 66.2 min	NA	Collins and Elijah (2019).
Natural zeolite	Crystal Violet (CV)	pH 10, Temp 25°C, adsorbate-to-adsorbent ratio (a/A) 0.1 g/g	NA	Sarabadan <i>et al.</i> (2019).

2.8 Factors Influencing the Dye Adsorption Process

Adsorption is a process where molecules (adsorbates) adhere to the surface of solid materials (adsorbents). The effectiveness of the adsorption process is influenced by various important factors that control the interaction between the adsorbent (clay material) and the adsorbate (dyes). Knowledge of these factors is crucial for the effective optimization of adsorption mechanisms used in dye removal.

2.8.1 pH of Solution

pH (potential of hydrogen) is the measure of hydrogen ion (H^+) concentration in a solution. The pH of the solution plays a vital role in the adsorption process as it influences the surface charge of the adsorbent as well as the ionization state of the adsorbate (Lamrani *et al.*, 2025). The adsorption capacity of an adsorbent is significantly influenced by the pH of the solution. At lower pH levels, the removal of anionic dye increases due to electrostatic attraction between the negatively charged dye molecules and the positively charged surface of the adsorbent. At higher pH, most adsorbent surfaces become negatively charged, leading to electrostatic repulsion with anionic dyes and reduced adsorption.

To support the general trends observed in various studies, the effect of pH on dye removal efficiency was reviewed. Marubini *et al.* (2025) investigated the adsorptive removal of Crystal Violet dye from aqueous solution using a Vermiculite-Based Geopolymer (VBG). The findings showed that the removal of CV by VBG was less effective in acidic conditions and slightly higher under basic conditions. At higher pH levels, there was more electrostatic contact between the dye molecules and the adsorbent. Optimum CV removal conditions were attained at 15 min. Khan *et al.* (2025) evaluated the toxic anionic Azo dye removal from artificial wastewater by using Polyaniline/Clay Nanocomposite adsorbent: isotherm, kinetics and thermodynamic study. The study showed that the percentage removal of anionic dyes from aqueous solutions is typically higher under acidic conditions (low pH), primarily because of the electrostatic attraction between the negatively charged dye molecules and the positively charged adsorbent surfaces. Additionally, Van der Waals forces, especially in adsorbents with very small pore sizes, contribute to this effect, which commonly occurs when the pH is below 5.

2.8.2 Contact Time

Contact time defines as the amount of time the adsorbent is allowed to interact with the dye-containing solution during the adsorption process. It affects the time required to reach adsorption equilibrium. The duration of interaction between the dye and adsorbent influences the adsorption efficiency. Typically, the adsorption capacity and elimination efficiency of dyes increases with the extension of contact time. Initially, the dye adsorption onto the adsorbent surface occurs rapidly due to the availability of abundant active sites; however, as these sites become occupied, the rate of adsorption gradually decreases until it reaches equilibrium, where no further significant uptake occurs (Lamrani *et al.*, 2025).

Alorabi *et al.* (2021), used the Natural Clay as a Low-cost adsorbent for Crystal Violet dye removal and antimicrobial activity. The adsorption of crystal violet (CV) dye was studied under batch conditions, with all influencing parameters optimized. The optimal operating conditions were determined to be an equilibrium contact time of 120 minutes, an adsorbent dosage of 30 mg, a temperature of 25 °C, and an initial dye concentration of 400 mg/L. The highest adsorption capacities recorded for the NCQ1 and NCQ3 adsorbents were 206.73 mg/g and 203.66 mg/g, respectively.

2.8.3 Initial Dye Concentration

Initial concentration is a key factor in minimizing mass transfer resistance of dye molecules from the liquid phase to the solid phase. The dye removal efficiency is strongly influenced by the initial dye concentration (Lamrani *et al.*, 2025). It also Influences the kinetics and equilibrium adsorption capacity.

Gomaa *et al.* (2022), studied the effects of CV dye concentration from 5 to 200 ppm. It was found that CV uptake grew as the dye concentration increased, until it reached equilibrium and a peak saturation capacity of 118 mg/g. At higher dye concentrations, the dye adsorption showed a slight increase due to competition of a huge quantity of CV molecules at the active sites of the MMT-mAmCs adsorbent.

2.8.4 Adsorption Dosage

Lamrani et al. (2025), reported that more of research demonstrated that the percent of the adsorbed substance at equilibrium increased with increasing adsorbent dosage. An increase in adsorbent dosage typically enhances removal efficiency by providing more active binding sites. However, an excessively high dosage can result in particle aggregation or overlapping of sites, which may reduce the effective surface area and hinder adsorption performance.

El Kassim et al. (2023), state that the dye removal efficiency increases with increasing adsorbent dose, decreases with increasing initial dye concentration when using Natural Safiot Clay (NSC) obtained from Safi city (Morocco) to remove cationic dyes. Jawad et al. (2023) reported that an increase in NIBC dosage from 0.02 g to 0.06 g resulted in a rise in MB decolourization from 5.6% to 99.5%, primarily due to the increased number of active adsorption sites provided by the higher adsorbent amount.

2.8.5 Temperature

Temperature significantly affects the adsorption process by influencing both its kinetics and thermodynamics. In endothermic adsorption systems, an increase in temperature generally enhances the adsorption capacity, as the added thermal energy promotes greater interaction between the dye molecules and the adsorbent surface. Conversely, in exothermic processes, higher temperatures tend to reduce adsorption efficiency, likely due to the weakening of adsorptive forces and a shift in equilibrium away from adsorption (Lamrani *et al.*, 2025).

According to Aragaw and Alene (2022), the influence of temperature on dye adsorption was investigated at 30 °C, 50 °C, and 70 °C, using an initial dye concentration of 20 mg/L, an adsorbent dosage of 1 g/100 mL, a contact time of 60 minutes, and pH values of 9 for BY 28, and 3 for CR and RR 120. The study revealed that the removal efficiency for all dyes declined as the temperature increased from 30 °C to 70 °C. These findings indicate that the adsorption process was more effective at lower temperatures, suggesting an exothermic nature of dye adsorption onto the prepared adsorbent.

2.9 Advantages and Disadvantages of Common Adsorbents Used in Dye Removal

Understanding the advantages and disadvantages of common adsorbents aids in selecting effective and sustainable materials for dye removal. It supports optimizing treatment processes by balancing performance, cost, and environmental impact. This knowledge also guides future improvements and practical applications in wastewater treatment. Table 2.6 describes the advantages and disadvantages of a common adsorbent for the removal of dyes.

Table 2.6: Advantages and Disadvantages of Common Adsorbents used in Dye Removal.

Adsorbents	Advantages	Disadvantages
1. Activated carbon (Dutta <i>et al.</i> , 2021)	Its large surface area and porous nature contribute to its strong adsorption capabilities.	Relatively high cost, particularly in bulk treatment processes.
2. Biochar and Agricultural Waste-based Adsorbents (Such as sawdust, rice husks, banana peels, and nuts shells) (Pandey <i>et al.</i> , 2023)	Widely available, low-cost, and environmentally safe	Frequently exhibit low adsorption efficiency for specific dye types
3. Clay-based Adsorbents (Such as Bentonite, Montmorillonite, and Smectite) (Dhar <i>et al.</i> , 2023)	Cost effective, easily accessible and modifiable to increase its adsorption potential	If not managed correctly, the spent material can lead to disposal problems.
4. Magnetic Nanoparticles (Such as Fe ₃ O ₄ -based adsorbents) (Younas <i>et al.</i> , 2021)	Allows for simple recovery through magnetic separation techniques.	Expensive preparation and surface treatment procedures.

CHAPTER THREE: METHODOLOGY

3.1 Materials and Methods

3.1.1 Materials

Smectite Mukondeni Black Clay Soil was obtained from Mukondeni Village, Vhembe District Municipality, Limpopo, South Africa. All chemicals and reagents are of analytical grades and were purchased from Rochelle Chemicals in Johannesburg, South Africa. These include CV, MO, HCl, NaOH, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, MnCl_2 , NaCl, and KCl. Methyl Orange ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$) and Crystal Violet ($\text{C}_{25}\text{H}_{30}\text{N}_3\text{Cl}$) have maximum absorbency at the wavelength of 505 nm and 616 nm, respectively.

3.1.2 Modification of Smectite Mukondeni Black Clay Soil

The raw smectite (Mukondeni black) clay soil sample was milled for 4 min using a grinding machine (Retsch RS 200, South Africa). It was sieved using a mechanical sieve (King-Test VB 200/300 sieve shaker, South Africa) into small fragments ($\leq 250 \mu\text{m}$) and dried in the air for 8 h. After drying the sample, 60 g of raw clay was weighed (in grams) into a weighing boat and placed in the analytical balance (Radwag AS 220.R2, Poland).

Raw clay was mixed with 1 L of Milli-Q water to make an S/L ratio of 12 g: 1 L and stirred constantly. The supernatant was removed from the clay, and the remaining residue clay was dried in a drying oven (LASEC IBLPDHG-9240A, South Africa) for 12 h at 110°C . The dried clay was removed from the drying oven and milled to pass through $\leq 250 \mu\text{m}$ pore sieve. The obtained clay was stored inside a tightly labelled polyethylene container. The same procedure was repeated to get a sufficient amount of the clay.

Manganese and Aluminium oxide were derived from MnCl_2 and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, respectively. Aliquots of 0.1 M MnCl_2 and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ solutions were added together at different proportions in 250 mL polyethylene bottles, with a final volume of each resulting solution being 20 mL. The volume of molar ratio of Mn^{2+} to Al^{3+} that were considered were 1:1, 1:2, 1:3, 1:4, 1:5, 2:1, 3:1, 3:2, and 5:1 consecutively. 2 g of raw clay was weighed into each of the 250 mL polyethylene bottles and shaken at 250 rpm using an Eco Bath (LABOTEC WATER BATH 207, South Africa) for 20 min to ensure proper soaking of the clay. 30 mL of 0.1 M NaOH was transferred into polyethylene bottles to precipitate $\text{Al}(\text{OH})_3$ and $\text{Mn}(\text{OH})_2$. The mixtures were continuously shaken at 250 rpm speed for 30 min. The mixtures were air dried in open air for two hours to ensure complete precipitation of the metals.

After equilibration, the excess NaOH solution was removed by centrifuging the mixtures at 5000 rpm for 10 min using a centrifuge (Laboratory Centrifuge LMC-3000, England). The solid residuals were removed from centrifuging tubes and emptied into a 250 mL beaker, and the supernatant was discarded. The co-precipitated metal hydroxide clay soil was placed in an oven and dried at 110° for 13 h. After drying, samples were milled and passed through a ≤ 250 μm pore sieve to obtain homogeneous particle size. The obtained clay samples were used for the decolouration of MO and CV dyes.

3.2 Characterizations of the samples

3.2.1 Point of Zero Charge

The point of zero charge was evaluated using 0.1 M KCl solution. 0.1 M HCl and 0.1 M NaOH solutions were utilized to adjust the initial pH of the solution from 2 to 12. A mass of 1.5 g of $\text{Mn}^{2+}/\text{Al}^{3+}$ Oxide modified Smectite-rich black clay was added to 50 mL of the solution. The mixture was poured into 250 mL polyethylene bottles and placed into the incubator shaker at a speed of 250 rpm. After 24 hours, the samples were taken from the shaker, poured into 50 mL centrifuge bottles, and centrifuged at 5000 rpm for 10 minutes using a Laboratory Centrifuge (LMC-3000, England). The final pH (pH_{final}) was recorded. Change in pH was calculated as the difference in initial pH (pH_{i}) and final pH (pH_{f}). The difference between initial and final pH values ($\Delta\text{pH} = \text{pH}_{\text{i}} - \text{pH}_{\text{f}}$) was plotted against pH_{i} . The point of intersection of the resulting curve abscissa, at which $\Delta\text{pH} = 0$, was taken as a point of zero charge.

3.2.2 X-ray fluorescence (XRF) analysis

The XRF was used for the determination of the elemental composition (chemical composition) of the adsorbent. XRF (Miniflex II, Rigaku, Japan) was used to determine the chemical composition and chemical compounds of the adsorbent. The samples (Raw-SMT, Modified-SMT, MO-MSMT, and CV-MSMT) were dried for 8 hours in an oven set at a temperature of 110° C. This was done to remove the moisture that could affect the accuracy of the analysis. The dried samples were milled for 4 hours using a grinding machine into a uniform fine powder. This ensures smoothness and consistency for accurate XRF analysis. The powdered samples were sieved using a mechanical sieve to pass through the ≤ 250 μm to achieve uniform particle size for accurate results.

A binding agent (boric acid) was added in small amounts to the powdered sample to assist in forming a pellet. The mixture was pressed into a solid, compact pellet using a hydraulic press under high pressure, preparing it for XRF analysis. Calibration of the XRF instrument was

performed using standard reference materials with known elemental compositions to ensure precise measurements. The prepared pellet was then carefully placed on the sample holder of the XRF instrument. Device parameters such as voltage, current, and scan duration were set according to the manufacturer's specifications for the adsorbent material. These emitted X-rays were detected and recorded by the instrument's detector, resulting in a spectrum representing the sample's elemental composition.

3.2.3 Brunauer-Emmett-Teller (BET) analysis

BET evaluates the specific area of an adsorbent based on the gas adsorption measurements. BET (Horiba SA -9600, England) was utilized to measure the specific area of an adsorbent. The samples (Raw-SMT, Modified-SMT, MO-MSMT, and CV-MSMT) were dried for 8 hours in an oven set at a temperature of 110° C to remove all the moisture that could affect the adsorption measurements. The dried samples were stored in airtight plastic containers. Samples were milled into a fine powder to ensure uniformity and maximize surface area exposure. The powdered samples were sieved to achieve a consistent particle size ($\leq 250 \mu\text{m}$) for accurate measurements.

The instrument was calibrated with certified reference materials that had known surface areas to ensure precise and reliable results. Nitrogen gas (N_2) was selected as the adsorbate due to its inert properties and well-documented adsorption behaviour. Approximately 0.2 g of each powdered sample was weighed and placed in the degassing unit. The samples were degassed under vacuum at 200°C for 3 hours to remove adsorbed impurities such as water and organic residues. Following degassing, the samples were cooled to room temperature in a dry, inert atmosphere to prevent any contamination.

The degassed samples were transferred to the analysis chamber of the BET instrument, where nitrogen gas was introduced at controlled pressures, and the adsorption-desorption isotherm was recorded. Data were gathered over a relative pressure range (P/P_0) from 0.05 to 1.0 to create the adsorption isotherm. The single-point surface area was determined from nitrogen adsorption at a specific relative pressure, typically around $P/P_0 \approx 0.3$. The BET surface area was calculated using the Brunauer-Emmett-Teller equation applied to the linear section of the adsorption isotherm within the P/P_0 range of 0.05–0.35.

The Langmuir surface area was determined by fitting the data to the Langmuir adsorption model, which assumes adsorption occurs in a monolayer. The specific surface areas (single-

point, BET, and Langmuir) were automatically calculated by the instrument's software. Isotherm plots were created to illustrate the adsorption-desorption behaviour of the samples.

3.2.4 X-ray diffraction (XRD) analysis

XRD determines the crystal structure of the adsorbent. XRD (XRDynamic 500, Austria) was used to analyse the physical properties of the crystal structure of the adsorbent. The X-Ray Diffractometer used a Cu-K α radiation source with a wavelength of 1.5406 Å. Prior to use, it was calibrated following the manufacturer's instructions to guarantee precise and reliable results. The samples (Raw-SMT, Modified-SMT, MO-MSMT, and CV-MSMT) were dried and finely milled to ensure uniformity and enhance the accuracy of the diffraction measurements. An amount of 1 g for each powdered sample was transferred into a sample holder, with the surface carefully smoothed to ensure consistency in results. The sample holder containing the powdered sample was then precisely placed in the XRD chamber for analysis.

The X-ray tube was operated at a voltage of 40 kV and a current of 30 mA, parameters well-suited for clay materials to produce high-intensity X-rays. The diffraction angle (2θ) was scanned from 5° to 80°. The recorded XRD pattern revealed diffraction peaks corresponding to the crystalline planes within the samples. The resulting diffraction data were analysed using the software provided with the XRDynamic 500 to determine the phase composition and crystallinity of the adsorbent.

3.2.5 Scanning Electron Microscopy (SEM) analysis

SEM was used to analyze the surface morphology of the adsorbent, with a JEOL JSM-6610LV (Japan) producing images to reveal various characteristics of the material. The instrument operated in high vacuum mode to achieve high-resolution imaging. SEM images were captured at a resolution of 10 μm and a magnification of 5000 $\times$. Samples, including Raw-SMT, Modified-SMT, MO-MSMT, and CV-MSMT, were dried and finely ground into a powder to ensure a representative surface analysis. A small amount of the powdered sample was evenly distributed onto a double-sided carbon tape affixed to a metallic stub. The stub was securely placed in the SEM chamber, which was evacuated to create a high-vacuum environment.

Surface images were then captured at 5000 $\times$ magnification to examine key morphological features, such as particle size, shape, porosity, and texture. Specific areas of interest were further analysed to identify unique material properties.

3.2.6 Energy Dispersive Spectroscopy (EDS) analysis

EDS was used to perform the elemental analysis and chemical characterization of the adsorbent. The analysis was carried out using a JEOL JSM-6610LV (Japan) equipped with an integrated EDS detector, which facilitates simultaneous imaging and elemental analysis. To prepare the samples (Raw-SMT, Modified-SMT, MO-MSMT, and CV-MSMT), they were dried to eliminate any moisture that could affect the results. The dried samples were finely ground into a uniform powder to ensure consistency. A small portion of the powder was evenly spread onto a double-sided carbon tape attached to a metallic sample stub. The electron beam was directed and focused on the sample surface to obtain detailed imaging and generate X-rays.

These produced spectra representing the elemental composition. Spectra were collected from multiple regions of the sample to ensure a comprehensive analysis. Techniques such as point analysis, line scans, and elemental mapping were employed to examine the elemental distribution. The resulting spectra were processed using specialized software to identify peaks corresponding to different elements. Quantitative data, including the elements' number, element name and atomic concentration of the detected elements, were extracted. Elemental mapping and line scan data provided additional insights into the spatial distribution of elements on the sample surface.

3.2.7 Fourier Transform Infrared (FTIR) analysis

FTIR analysis was used to identify the functional groups present in the adsorbent, utilizing a Nicolet IS50 spectrometer (Thermo Fisher Scientific, Japan). The FTIR spectrometer was set to scan within the range of 500 to 4000 cm^{-1} . To prepare the samples (Raw-SMT, Modified-SMT, MO-MSMT, and CV-MSMT), they were thoroughly dried to remove any moisture that might interfere with the analysis. Each dried sample was finely milled to achieve uniformity. A small amount of the sample (0.003 g) was mixed with 0.1 g of potassium bromide (KBr), a transparent matrix material, in a 1:100 ratio.

The mixture was compressed under high pressure using a hydraulic press to form a thin, transparent pellet suitable for FTIR analysis. The FTIR spectrometer was set to record spectra within the range of 500 to 4000 cm^{-1} to detect the vibrational frequencies of functional groups commonly associated with adsorbent materials. During analysis, the intensity of infrared light

transmitted through the sample was measured, and the spectrum was recorded. The collected data were stored for further interpretation and analysis.

3.3 Batch Experiments

3.3.1 Preparation of MO and CV textile dyes

CV and MO stock solutions of 1000 mg/L were prepared by dissolving 1 g of dye into 1 L of de-ionized water in a volumetric flask (preparation was done in two different flasks). Various working concentrations were prepared from the stock solution using equation (3.1).

$$C_1 V_1 = C_2 V_2 \dots \dots \dots (3.1)$$

Where C_1 is the initial concentration, C_2 is the final concentration, V_1 is the initial volume and V_2 is the final volume.

Solutions were analysed at the maximum wavelength of 505 nm for MO and 616 nm for CV using a UV-Vis spectrometer (Thermo Fisher Scientific, ORION AQUAMATE VIS 7000, China). After calibration, a standard calibration curve was obtained. Equations (3.2) and (3.3) were used to calculate the percentage of dye removal and the quantity of dye adsorbed respectively.

$$\% \text{ dye removal} = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \dots \dots \dots (3.2)$$

$$q_e = \frac{C_i - C_f}{w} V \dots \dots \dots (3.3)$$

Where C_i and C_f (mg/L) are the initial MO/CV concentration and the concentration at equilibrium, q_e is the quantity of MO/CV adsorbed, V is the volume of the solution (L) and w is the mass of adsorbent (g).

3.3.2 Testing various ratios of the adsorbent to determine an effective ratio that can remove MO and CV dyes from the aqueous solution.

Different ratios (1:1, 1:2, 1:3, 1:4, 1:5, 2:1, 3:1, 3:2, 5:1) of $\text{Mn}^{2+}/\text{Al}^{3+}$ modified Smectite were used to find the ratio with the best percentage removal of dyes. Various masses (0.1, 0.5, 1, and 1.5 g) were used to remove MO dye from the aqueous solution, while 0.01, 0.03, 0.05, and 0.1 g were used for the removal of CV dye. The variation in mass selection was influenced by the adsorbent's higher efficiency in removing CV dye, which prompted the use of different quantities for comparative analysis. Each adsorbent was poured into separate 250 mL polyethylene bottles and mixed with the volume of 30 mL of the initial concentration of 20

mg/L of MO and CV. It was shaken at 250 rpm for 30 minutes and the temperature was set at 30 °C. Then it was centrifuged at 5000 rpm for 10 minutes. The results were then measured using a UV-Vis Spectrometer.

3.3.3 To determine the effect of contact time, concentration, dosage, temperature and pH in the removal of MO and CV textile dyes using Mn²⁺/Al³⁺ Oxide modified Smectite (Mukondeni black) clay soil

3.3.3.1 Effect of Contact Time

In this experiment, various clay masses of Mn²⁺/Al³⁺ Oxide modified Smectite (Mukondeni black) clay soil were employed. The masses of 0.1, 0.5, 1, and 2 g of the adsorbent were used to remove MO dye from the aqueous solution, while 0.01, 0.03, 0.05, and 0.1 g of the adsorbent were used to remove CV dye. Each mass of the adsorbent was placed into the separated 250 mL polyethylene bottles and agitated with 30 mL containing a dye concentration of 20 mg/L of CV and MO, respectively. The mixtures were shaken at 250 rpm speed for 5-240 minutes in a water bath kept at a constant temperature of 30 °C. After 5 minutes, the first set of the mixture was taken out of the incubator shaker and transferred into 50 mL centrifuge tubes.

The samples were centrifuged at 5000 rpm for 10 minutes. The supernatant was poured into a cuvette and analysed in a UV-Vis spectrometer. After the intervals of 5, 20, 30, 45, 60, 75, 90, 120, 150, 210, and 240 minutes, the process of taking out 250 mL of polyethylene bottles from the water bath (shaker) was carried out again. To avoid confusion, all polyethylene bottles were marked based on their various time intervals. Finally, all the samples of different time intervals were studied and compared to the control (dye solution without an adsorbent) to calculate the percentage removal of CV and MO dyes at different times. The percentage removal of CV and MO was determined from equation (3.2) and the quantity adsorbed was determined from equation (3.3).

3.3.3.2 Effect of adsorbent dosage and initial dye concentration

Various concentrations of 20 mg/L, 50 mg/L, 80 mg/L, 100 mg/L, and 150 mg/L for MO and CV were prepared and used. Various weights (0.5, 1, 1.5, and 2 g) of Mn²⁺/Al³⁺ Oxide modified Smectite-rich black clay were measured and used to remove MO dye whereas 0.1, 0.5, 1, and 1.5 g were utilized to remove CV dye from the aqueous solution. The mixture was placed into a shaker with a speed of 250 rpm and a temperature of 30 °C. The reaction of equilibrium time was applied in the experiment (30 minutes for CV dye and 90 minutes for MO dye). The mixture was poured into centrifuge tubes. The samples were centrifuged for 10 minutes at 5000

rpm. The supernatant was poured into the cuvette and run in the UV-Vis spectrometer. The same procedure applied in section (3.2.2.1) was repeated to calculate the percentage removal at various concentrations.

3.3.3.3 Effect of Temperature

For the effect of temperature, 30 mL of 20 mg/L of MO and CV were poured into 250 mL polyethylene bottles. The masses of 1.5 g and 0.1 g of $\text{Mn}^{2+}/\text{Al}^{3+}$ oxide-modified Smectite-rich black clay were utilized for MO and CV dye removal, respectively. The mixtures were placed into a shaker with a speed of 250 rpm for the equilibrium time (30 minutes for CV dye and 90 minutes for MO dye) at different temperatures of 30, 40, 50, 60, 70, and 80 °C respectively. The mixture was taken out from the incubator shaker after the equilibrium time was reached and placed into the centrifuge tubes. The samples were centrifuged for 10 minutes at 5000 rpm and then analysed by UV-spectrometer.

3.3.3.4 Effect of pH

A pH range from 2 to 12 was examined to evaluate its effect on the adsorption process. 20 mg/L of MO and CV dye concentration was placed into the different 250 ml polyethylene bottles. 0.5 g, 1 g, and 1.5 g of $\text{Mn}^{2+}/\text{Al}^{3+}$ Oxide modified Smectite-rich black clay were used to remove MO dye, while 0.01 g, 0.05g, and 0.1 g were utilized for CV dye removal. 0.1 M HCl and 0.1 M NaOH were used to adjust the pH solution. The pH was determined using an ORION STAR A214 pH/ISE Meter, Germany. The mixture was placed in the shaker at a speed of 250 rpm and a temperature of 30 °C. After the time interval of equilibrium was reached, the samples were removed, centrifuged at 5000 rpm for 10 minutes, and run in the UV-Vis spectrometer.

3.4 Adsorption Isotherm Modelling

Adsorption isotherms define an adsorbent's equilibrium performance at constant temperature. It relies on the adsorbed species, adsorbate, adsorbent, and various physical properties of the solution, such as pH, ionic strength, and temperature (Yan *et al.*, 2017; Al-Ghouti and Da'ana, 2020). In this research, the adsorption behaviour of the adsorbent was evaluated using the isotherm models, including Langmuir adsorption isotherms, Freundlich adsorption isotherm, Dubinin- Radushkevich (DR) isotherm and Temkin isotherm.

3.4.1 Langmuir adsorption Isotherm

The Langmuir isotherm is an empirical model that considers the adsorbed layer to be one molecule thick, representing monolayer adsorption. It assumes that the adsorption process

occurs at identical and equivalent localized sites and that the adsorption is homogeneous, with each molecule possessing a constant enthalpy and adsorption activation energy. Furthermore, all sites are assumed to have an equal affinity towards the adsorbate, and there is no transmigration of adsorbates within the surface plane (Kundu and Gupta, 2006; Al-Ghouti and Da'ana, 2020). It is expressed in equation (3.4).

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{K_L q_{max}} \right) \frac{1}{C_e} \dots \dots \dots (3.4)$$

Where C_e is the equilibrium concentration of MO and CV (mg/L), q_e is the quantity of MO and CV adsorbed at equilibrium (mg/g), q_{max} is the maximum amount adsorbed (mg/g) and K_L is the adsorption constant (L/mg). The values of K_L and q_{max} were obtained from the slope and the intercept of the plots of $1/C_e$ versus $1/q_e$

3.4.2 Freundlich adsorption Isotherm

Freundlich adsorption isotherm is an empirical adsorption model that describes the adsorption on heterogeneous surfaces. The isotherm does not predict any saturation on the adsorbent by the adsorbate, implying multilayer adsorption (Thakur and Kaur, 2017). The linearized form of the Freundlich equation is given by equation (3.5).

$$\log q_e = \log K_f + \left(\frac{1}{n} \right) \log C_e \dots \dots \dots (3.5)$$

Where K_f is the Freundlich constant, and $1/n$ is the heterogeneity factor. q_e (mg/g) is the adsorption density and C_e is the concentration of MO and CV in solution at equilibrium (mg/L).

3.4.3 Dubinin- Radushkevich (DR) Isotherm

This isotherm assumes that the adsorption curve is related to the porosity of the adsorbent. It is useful for identifying whether the process involves chemisorption or physisorption and determining the apparent energy of adsorption. The D-R model does not assume that the adsorbent surface is homogeneous (Sampranpiboon *et al.*, 2014; Musah *et al.*, 2022; Mahanty *et al.*, 2023). It is expressed by equations (3.6), (3.7), and (3.8).

$$q_e = q_m \exp(-K\varepsilon^2) \dots \dots \dots (3.6)$$

$$\text{Where } \varepsilon = RT \ln \left(\frac{C_s}{C_e} \right) \dots \dots \dots (3.7)$$

Where q_e (mg/g) represents the amount of adsorbate adsorbed per unit mass of adsorbent and q_{max} (mg/g) is the maximum adsorption capacity, $K \left(\frac{\text{mol}^2}{\text{kJ}^2} \right)$ is a constant associated with the sorption energy (mol/kJ), ϵ is the Polanyi potential, T is the absolute temperature in Kelvin, R is the universal gas constant (8.314 J/mol/K), C_s is the saturation solubility and C_e is the equilibrium concentration of adsorbate.

E , representing the free energy of the adsorption for each molecule of the adsorbate, is expressed by equation (3.8)

$$E = \frac{1}{\sqrt{2K}} \dots \dots \dots (3.8)$$

E (kJ/ mol) is the mean adsorption energy indicating the heat of adsorption, which can signify whether the process is physical or chemical.

3.4.4 Temkin Isotherm

In the Temkin isotherm, the heat of sorption decreases linearly with increasing sorption coverage on the adsorbent due to interactions between the adsorbent and the adsorbate (Sampranpiboon *et al.*, 2014; Musah *et al.*, 2022). The linear form is given by equations (3.9) and (3.10).

$$q_e = \beta \ln \alpha + \beta \ln C_e \dots \dots \dots (3.9)$$

$$\text{Where } \beta = \frac{RT}{b} \dots \dots \dots (3.10)$$

R is the ideal gas constant (8.314 J/mol/K), T is the absolute temperature in Kelvin, b is the Temkin constant associated with the heat of adsorption (J/mol), β is the Temkin constant related to maximum binding energy (J/mol) and α is the equilibrium binding constant (L/mg).

3.5 Kinetic Studies

Adsorption kinetics describe the rate at which an adsorbate is retained or released from an aqueous solution at the solid-phase interface (Musah *et al.*, 2022). In this study, kinetic modelling, including the Pseudo-first-order model, Pseudo-second-order model, Elovich model, and intraparticle diffusion model, were used to evaluate the adsorption process.

3.5.1 Pseudo-first-order model

The model assumes that the rate of change in adsorbate uptake at a specific reaction time is directly proportional to the difference in concentration and the rate at which the adsorbate is

removed over time (Edet and Ifelebuegu, 2020; Musah *et al.*, 2022). It is expressed by equation (3.11) and (3.12).

$$\frac{dq_t}{dt} = k_t (q_e - q_t) \dots \dots \dots (3.11)$$

Where q_e represents the adsorption capacity of the adsorbent at equilibrium (mg/g), q_t represents the adsorption capacity of the adsorbent at time t (mg/g), k_t represents the rate constant for pseudo-first-order adsorption (min^{-1}).

After equation (3.11) is integrated and boundary conditions are applied

$t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$, the integrated form of equation (3.11) becomes:

$$\log (q_e - q_t) = \log (q_e) - \frac{K_1}{2.303} t \dots \dots \dots (3.12)$$

When the values of $\log(q_e - q_t)$ are plotted linearly against t , the resulting graph of $\log(q_e - q_t)$ versus t yields a linear relationship. From this plot, the values of k_t and q_e can be determined from the slope and intercept, respectively.

3.5.2 Pseudo-second-order model

The pseudo-second-order rate equation has been utilized to study chemical adsorption kinetics in liquid solutions based on solid-phase adsorption (Taiwo and Chinyere, 2016; Musah *et al.*, 2022). It can be expressed in the form of equation (3.13)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots \dots \dots (3.13)$$

Where k_2 is the constant speed of the adsorption model of pseudo-second-order (g/mg min^{-1}); if this equation is checked by tracing t/q_t according to t , we must obtain a line of slope $1/q_e$ and ordinate in the beginning equal to $1/(k_2 q_e^2)$.

3.5.3 Elovich model

This model further explains pseudo-second-order kinetics, assuming the adsorbent surface has energetic heterogeneity. The Elovich model was applied to the chemisorption of dyes onto heterogeneous adsorbent surfaces (Oguanobi *et al.*, 2024). The linear form of Elovich is expressed by equation (3.14).

$$qt = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \dots \dots \dots (3.14)$$

Where α (mg/g/min) represents the initial adsorption rate and β (g/mg) is the desorption constant related to the extent of the surface coverage and activation energy for chemisorption.

3.5.4 Intraparticle diffusion model

The adsorption mechanism by an adsorbent is explained by the diffusion or transport of the adsorbate from the solution onto the solid phase. The intraparticle diffusion model suggests that the plot of qt against $t^{\frac{1}{2}}$ should be linear (Toor and Jin, 2012). The intraparticle diffusion rate constant, K_{ip} (mg/g min^{0.5}), can be obtained from the slope of the plot of qt (mg/g) versus $t^{0.5}$ according to the equation (3.15).

$$k_{ip} = \frac{qt}{t^{0.5}} + C_{ip} \dots \dots \dots (3.15)$$

Where C_{ip} (mg/g) is a constant, the thickness of the boundary layer, and can be calculated from the intercept of the plot. The larger the C_{ip} , the greater the surface adsorption contribution to the rate-limiting step.

3.5.5 Thermodynamic Studies

Thermodynamic studies are crucial for understanding heat changes, spontaneity, the feasibility of adsorption on the surface of an adsorbent, and the adsorption mechanism. If there is an increase in a property known as enthalpy (ΔH°), it indicates that the process requires additional heat to occur and raising the temperature can accelerate it. On the other hand, a negative value of Gibbs free energy (ΔG°) indicates that the process is spontaneous, and the spontaneity typically increases with rising temperature. (Singh *et al.*, 2024). Thermodynamic parameters like change in enthalpy (ΔH°), change in entropy (ΔS°), and Gibbs free energy (ΔG°) can be calculated using the following equations.

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \text{ (Van, t Hoff equation)} \dots \dots \dots (3.16)$$

$$\Delta G = -RT \ln K_d \dots \dots \dots (3.17)$$

$$\text{Where } K_d = \frac{q_e}{C_e} \dots \dots \dots (3.18)$$

$$\Delta G = \Delta H - T\Delta S \dots \dots \dots (3.19)$$

Where K_d is the adsorption equilibrium constant, R is the universal gas constant $=8.314$ J/mol/K, C_e (mg/L) is the equilibrium concentration, q_e (mg/g) is the equilibrium adsorption capacity, ΔG° is the Gibbs free energy, ΔH° is the change in enthalpy, ΔS° is the change in entropy, and T (K) is the temperature in Kelvin.

3.6 Regeneration Studies

Different reagents, including de-ionized water, ultra water, 0.1M NaOH, 0.1M NaCl, 0.1M HCl, and 0.1M KCl, were used to determine an effective reagent for regeneration and desorption processes. 2 g of Mn^{2+}/Al^{3+} Oxide modified Smectite-rich black clay was poured into 250 mL polyethylene bottles containing 30 mL of 20 mg/L of MO dye. In contrast, 0.15 g of Mn^{2+}/Al^{3+} Oxide modified Smectite-rich black clay was poured into 250 mL polyethylene bottles containing 30 mL of 20 mg/L of CV dye.

The solutions containing the MO dye were shaken for an optimum time of 90 minutes at a temperature of 30°C using an incubator shaker. The solutions containing CV dye were shaken for an optimum time of 30 minutes. Both solutions (MO/CV dyes) were centrifuged at 5000 rpm for 10 min. The supernatants were discharged, and the residues were poured inside the 250 mL polyethylene bottles containing 50 mL of each reagent and washed. The reagents mixed with the residues were placed in an incubator shaker and shaken for the optimum time at the temperature of 30°C .

The residues from the CV bottles were shaken for 30 minutes, whereas the residues from the MO bottles were shaken for 90 minutes. After the washing process was done. The samples were centrifuged again, and the supernatants were discharged. The residues were dried for 5 hours at 90° . The dried residues were tested in batch experiments to select the residue with the best percentage of dye removal. After being selected, it was utilised to continue with the regeneration processes to obtain the number of cycles. The UV-Vis Spectrometer was used to determine the concentration of MO and CV dyes before and after the adsorption processes. The same procedure was repeated until the dried solid residues (dye-loaded adsorbents) were unable to continue removing the dyes in an aqueous solution.

CHAPTER 4: RESULTS AND DISCUSSION

4.0 Introduction

This chapter explores the adsorption of methylene orange (MO) and crystal violet (CV) dyes onto modified SMT. It outlines the modification process and the characterization of the clay using various techniques, including PZC, XRF, BET, XRD, SEM, EDS, and FTIR, to assess its properties. Batch experiments were conducted to investigate the impact of factors such as contact time, adsorbent dosage, dye concentration, temperature, and pH on adsorption efficiency. It also includes the analysis of adsorption isotherms, kinetic and thermodynamic studies, and desorption/regeneration tests. The adsorption mechanisms, including electrostatic interactions and ion exchange, are discussed, and the performance of modified SMT is compared with other clays for dye removal.

4.1 Modification of the Clay Soil

Various ratios and masses play a crucial role in adsorption studies (Aljeboree *et al.*, 2024). Different ratios (1:1, 1:2, 1:3, 1:4, 1:5, 2:1, 3:1, 3:2, 5:1) of Mn^{2+}/Al^{3+} modified Smectite were tested to determine the ratio with the best percentage removal of MO and CV dyes. Table 4.1 below shows the percentage (%) removal of Methyl Orange (MO) dye using various ratios and Masses of Mn^{2+}/Al^{3+} modified Smectite Black Mukondeni Clay.

Table 4.1: The percentage (%) removal of Methyl Orange (MO) dye using various ratios and masses of Mn^{2+}/Al^{3+} modified Smectite Black Mukondeni Clay. (Conditions: Initial Concentration = 20 mg/L, temperature = 30 °C, time = 30 minutes, shaking speed = 250 rpm, Volume = 30 mL).

Mass (g)	Ratio (%)								
	1:1	1:2	1:3	1:4	1:5	2:1	3:1	3:2	5:1
0.1	12.07	12.93	17.66	11.77	19.72	12.17	11.66	14.17	13.33
0.5	36.5	40.8	55.8	39.2	25.43	28.64	26.74	41.06	39.83
1.0	62.64	61.41	76.54	58.33	44.83	42.5	35.54	61.57	61.53
1.5	72.44	74.57	82.46	73.35	73.36	52.54	43.9	73.5	74.36

Table 4.2 shows the percentage (%) removal of Crystal Violet (CV) dye using various ratios and masses of $\text{Mn}^{2+}/\text{Al}^{3+}$ modified Smectite Black Mukondeni Clay.

Table 4.2: The percentage (%) removal of Crystal Violet (CV) dye using various ratios and masses of $\text{Mn}^{2+}/\text{Al}^{3+}$ modified Smectite Black Mukondeni Clay. (Conditions: Initial Concentration = 20 mg/L, temperature = 30 °C, time = 30 minutes, shaking speed = 250 rpm, Volume = 30 mL).

Mass (g)	Ratio (%)								
	1:1	1:2	1:3	1:4	1:5	2:1	3:1	3:2	5:1
0.01	55.76	61.53	65.64	58.84	52.68	62.18	55.38	64.47	58.11
0.03	63.17	66.38	77.49	64.67	59.20	65.46	60.43	69.27	65.83
0.05	68.27	72.30	90.21	68.25	63.61	72.83	65.49	76.52	73.66
0.1	74.78	77.94	96.43	75.42	68.25	76.28	78.99	83.97	81.47

The results show that ratio 1:3 of $\text{Mn}^{2+}/\text{Al}^{3+}$ modified Smectite has the best percentage removal for both dyes (MO and CV) compared to other ratios due to the presence of high porosity and fractures, large specific surface areas, surface charges, and surface function groups (Sadiku *et al.*, 2022). These properties enabled the modified clay to remove acidic and basic textile dyes from the aqueous solution. The modification significantly improved the clay's ability to remove both acidic and basic textile dyes by strengthening the attraction between the dyes and the clay. However, it was observed that the adsorbent was more effective in removing CV dye compared to MO dye. After testing all the ratios for removing MO and CV dyes from the aqueous solution, the 1:3 ratio showed the highest percentage of removal compared to the other ratios. As a result, the 1:3 ratio of $\text{Mn}^{2+}/\text{Al}^{3+}$ modified Smectite was chosen for the continuation of the batch experiments.

4.2 Characterization Studies

4.2.1 Point of Zero Charge

The point of zero charge can be explained as the point at which the charge of the positive sites on the adsorbent surface is equal to the negative ones, and the value of the net charge of the sorbent is at zero (İlktaç, 2023). Figure 4.1 shows the line graph of the change in pH versus initial pH, whereby the point of change in pH is zero.

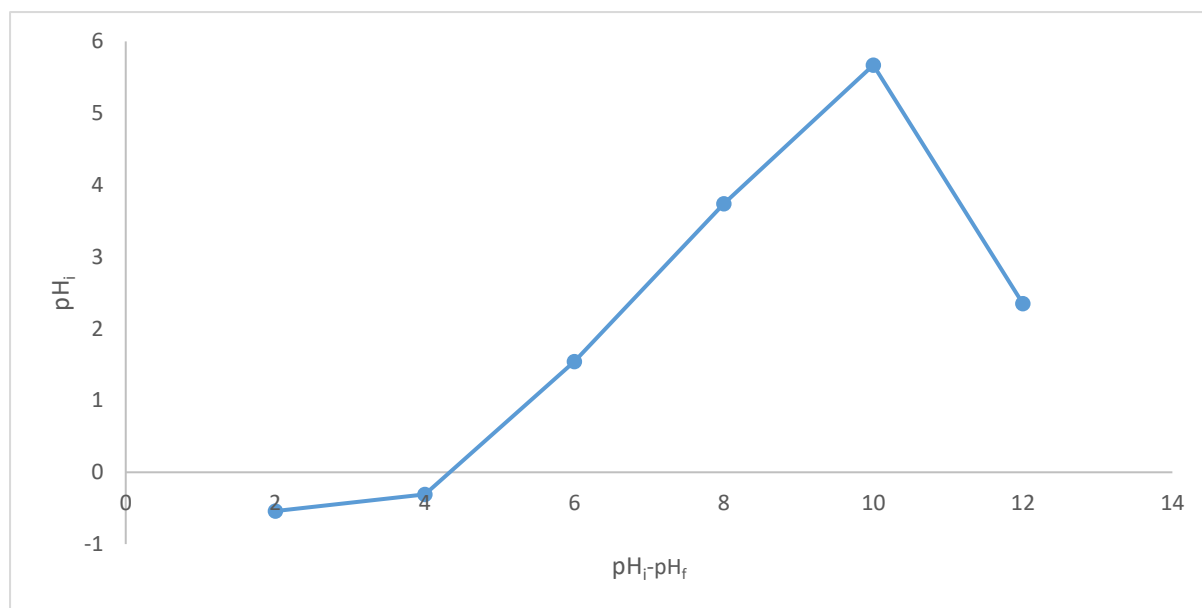


Figure 4.1: Point of Zero Charge. (Conditions: 0.1 M KCl, mass = 1.5 g, time = 24 hours, volume = 50 mL, shaking speed = 250 rpm, temperature = 30 °C, pH values = 2 to 12).

In this study, the pH at the point of zero charge of modified SMT was 4.30. This point was identified as pH at the point of zero charge. The surface charge of an adsorbent is negative when the pH is higher than the pH_{PZC} and the adsorbent becomes positively charged when the pH is lower than the pH_{PZC} (İlktaç, 2023). This is corroborated by the results recorded in 4.3.4 because when pH is lower than the pH_{PZC} , the surface of modified SMT becomes positively charged, which makes it easy to attract MO dye (anionic dye) because of its electrostatic attraction. If pH is greater than the pH_{PZC} , the surface of modified SMT becomes negatively charged and makes it easier for the adsorption of CV because it is a cationic dye. The surface of modified SMT becomes neutral when pH is equal to the pH_{PZC} causing the rate of adsorption to decrease due to the weak electrostatic force between the dye and the adsorbent.

4.2.2 X-ray fluorescence (XRF) analysis

The X-ray fluorescence (XRF) method was used to determine the chemical composition and chemical compounds available in the Raw-SMT, Modified-SMT, MO-MSMT, and CV-MSMT. The chemical parameters and their composition percentage are presented in Table 4.3.

Table 4.3: XRF data of chemical compositions of Raw-SMT, Modified-SMT, MO-MSMT, and CV-MSMT

Oxide Composition (%)	Raw-SMT	Modified-SMT	MO-MSMT	CV-MSMT
MgO	3.86	2.46	2.50	2.88
Al ₂ O ₃	16.95	18.42	19.36	17.12
SiO ₂	64.42	61.08	62.17	68.02
P ₂ O ₅	0.04	0.04	0.08	0.04
K ₂ O	1.06	0.98	1.12	0.98
CaO	2.40	1.86	1.86	2.45
TiO ₂	1.12	1.04	1.15	0.91
MnO	0.10	1.32	0.16	0.08
Fe ₂ O ₃	10.03	11.52	11.56	7.02
Total	99.98	99.72	99.96	99.5

The analysis shows that the highest weight percentages (wt. %) of oxides available in Raw-SMT, Modified-SMT, MO-MSMT, and CV-MSMT were found in SiO₂ (64.42 %, 61.08 %, 62.17 %, and 68.02 %) respectively. Al₂O₃ represented an oxide with the second highest weight (%). Raw-SMT recorded 16.95 %, Modified-SMT recorded 18.42 %, MO-MSMT recorded 19.36% and CV-MSMT recorded 17.12 %. The higher weight percentage (wt. %) of SiO₂ and Al₂O₃ detected by XRF in all samples shows that all the samples belong to the group of aluminosilicates (Alorabi *et al.*, 2021). Other oxides present in small amounts were P₂O₅, K₂O, and TiO₂.

Modified-SMT has the highest weight percentage (wt. %) of Al₂O₃ and MnO compared to Raw-SMT. This is due to the smectite (Mukondeni) clay modification by Mn²⁺/Al³⁺. Modified-SMT and Raw-SMT recorded 1.32 % and 0.10 % for MnO, respectively. After the batch experiments, MO-MSMT had a higher content of Al₂O₃ and MnO than CV-MSMT due to the interaction of the elements and compounds between the dyes and the adsorbent in an aqueous

solution. The increased MnO and Al₂O₃ content in the MO-MSMT indicates stronger interactions between the sulfonic and azo groups in MO and the metal ions (Mn²⁺ and Al³⁺) on the smectite surface. On the other hand, the interactions between the amine group of CV dye and the metal ions are less intense, leading to a low content in the CV-MSMT as observed in Table 4.3 (Dutta *et al.*, 2021).

4.2.3 Brunauer-Emmett-Teller (BET) analysis

The surface area of an adsorbent is one of the most crucial physical properties that restricts its quality and efficacy (Brunauer *et al.*, 1938; Ngulube *et al.*, 2018; Cigeroglu *et al.*, 2024). Table 4.4 shows the surface areas of Raw-SMT, Modified-SMT, MO-MSMT and CV-MSMT.

Table 4.4: Surface areas of Raw-SMT, Modified-SMT, MO-MSMT and CV-MSMT

Samples	Single point surface area (m ² /g)	BET surface area (m ² /g)	Langmuir surface area (m ² /g)
Raw-SMT	29.5874	30.0321	211.7171
Modified-SMT	35.1066	35.2951	251.4065
MO-MSMT	3.5412	3.5481	-80.9932
CV-MSMT	13.9737	14.1147	119.2320

The Raw-SMT has a BET surface area of 30.0321 m²/g. After the modification, the BET surface area increased by 5.263 m²/g. The high surface area of an adsorbent implies high adsorption capacity (Khan *et al.*, 2023). After CV and MO textile dye adsorption, the BET surface area decreases. MO-MSMT and CV-MSMT recorded the BET surface area of 3.5481 m²/g and 14.1147 m²/g respectively. This happened because the results show that the adsorbent is saturated with dyes, leaving only a few active sites available (Sulistyaningsih *et al.*, 2024).

Raw-SMT and Modified-SMT displayed almost the same values of single-point surface area (m²/g) and BET surface area (m²/g). The values of Langmuir surface area (m²/g) are very high compared to the values of single-point surface area and BET surface area. This suggests that Raw-SMT and Modified-SMT have a high adsorption capacity due to the presence of active sites in the adsorbent. After adsorption, MO-MSMT and CV-MSMT recorded low values of Single point and BET surface area, suggesting that the adsorption sites are limited (Sulistyaningsih *et al.*, 2024).

4.2.4 X-ray diffraction (XRD) analysis

The crystal structures of Raw-SMT, Modified-SMT, MO-MSMT, and CV-MSMT were characterized by X-ray diffraction. Figure 4.2 shows the change observed in the trends of the samples.

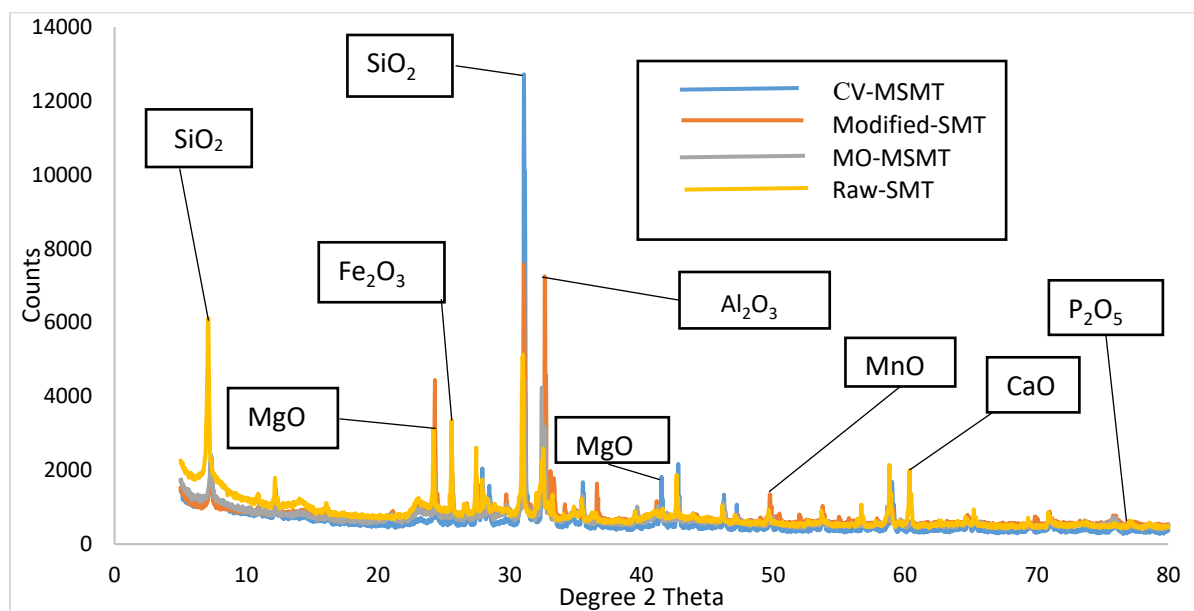


Figure 4.2: XRD data analysis of CV-SMT, Modified-SMT, MO-MSMT, and Raw-SMT

The sharp peaks observed at $7.10^\circ 2\theta$ and $31.09^\circ 2\theta$ are characteristic of quartz (SiO₂) (Darwis et al., 2020). Peaks at $24.19^\circ 2\theta$ and $41.50^\circ 2\theta$ suggest the presence of magnesium, likely originating from the smectite structure. The peak at $25.60^\circ 2\theta$ corresponds to iron oxides, indicating the presence of Fe within the clay matrix. Iron oxides play a role in influencing the structural and chemical properties of the clay (Yu et al., 2024). Peaks at $32.69^\circ 2\theta$ are attributed to aluminium oxides (Al₂O₃), which are critical components of smectite's layered structure, reflecting the presence of alumina (Prins, 2020). The peak at $49.75^\circ 2\theta$ represents manganese oxide, which may have been incorporated during the modification process. A peak at $60.48^\circ 2\theta$ indicates calcium oxide, likely associated with interlayer cations within the smectite structure. Lastly, the small peak at $77.53^\circ 2\theta$ suggests the presence of phosphate, naturally occurring as part of the mineralogical composition of the structure.

Raw-SMT exhibits the most intense peaks, signifying a higher degree of crystallinity. The prominent peaks of SiO₂ and Al₂O₃ indicate that the raw material largely retains its natural structure with minimal alterations. Following modification, the peak intensities show slight

shifts due to structural changes induced by the incorporation of $\text{Mn}^{2+}/\text{Al}^{3+}$ into Raw-SMT. After methyl orange (MO) dye adsorption, the peaks become slightly less intense, reflecting changes in crystallinity caused by the adsorption process. In contrast, the adsorption of crystal violet (CV) dye results in an increase in the peak intensity of SiO_2 .

4.2.5 Scanning Electron Microscopy (SEM) analysis

The morphology and surface texture of Raw-SMT, Modified-SMT, MO-MSMT, and CV-MSMT were analysed using scanning electron microscopy. The SEM images were obtained in the resolution of $10\ \mu\text{m}$ and magnification of 5000 are displayed in Figure 4.3 below.

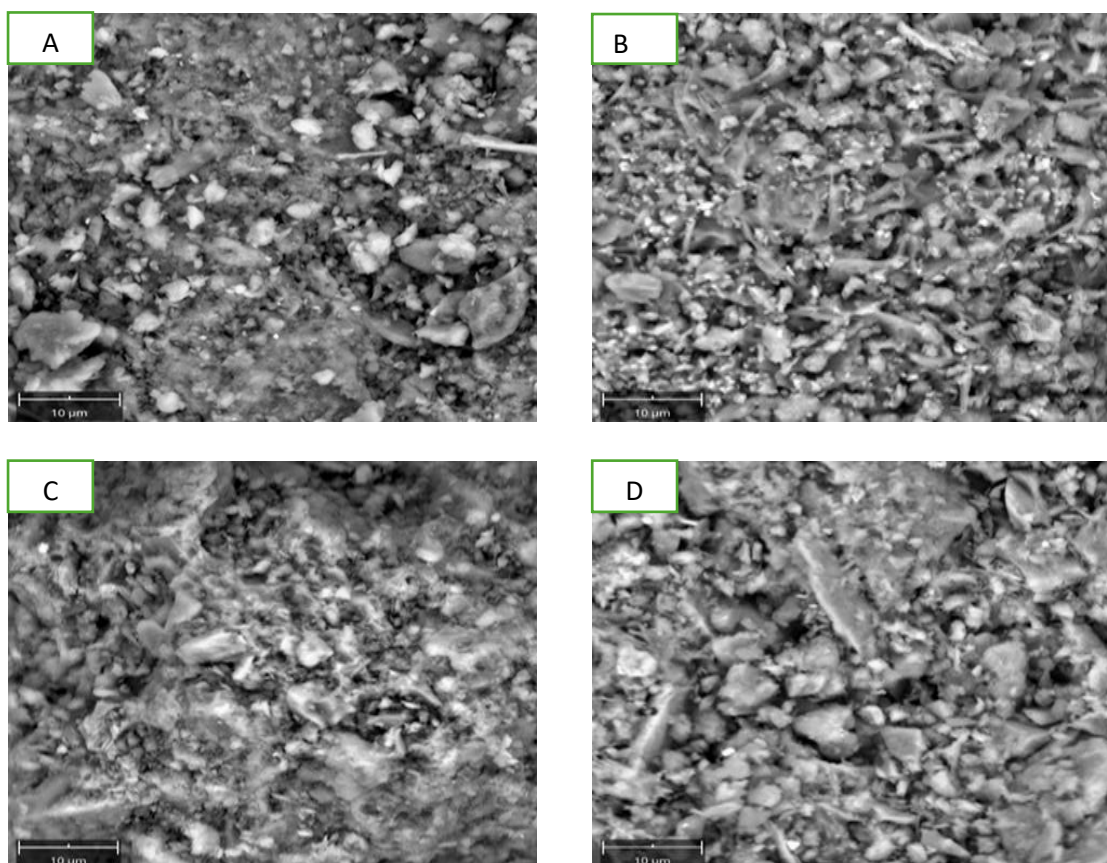


Figure 4.3: SEM analysis of (A) Raw-SMT, (B) Modified-SMT, (C) MO-MSMT, (D) CV-MSMT

It can be observed or seen from the results obtained that the Raw-SMT image appeared to have rough aggregates, gravel surfaces, and irregular shapes. The modification greatly impacted the adsorbent by changing the surface of the adsorbent.

The Modified-SMT is very porous because aggregates have visible openings. This means that the adsorbent has a large surface area which can enable it to adsorb the textile dyes. MO-MSMT and CV-MSMT show that the aggregates have closed due to the saturation of an adsorbent by MO and CV textile dyes (Mogharbel *et al.*, 2024). The results obtained by SEM show the heterogeneous and irregular morphology for all samples.

4.2.6 Energy Dispersive Spectroscopy (EDS) analysis

Energy dispersive spectroscopy analysis was used to determine the chemical elements found in Raw-SMT, Modified-MSMT, MO-MSMT, and CV-MSMT and the results are shown in Table 4.5.

Table 4.5: EDS analysis of Raw-SMT, Modified SMT, MO-MSMT, and CV-MSMT

Samples	Element Number	Symbol	Atomic Concentration
Raw-SMT	14	Si	19.1
	13	Al	13.1
	8	O	52.1
Modified-SMT	14	Si	13.9
	8	O	72.6
	25	Mn	0.4
MO-MSMT	8	O	66.9
	13	Al	6.6
	38	Sr	3.8
CV-MSMT	8	O	71.7
	14	Si	13.1
	26	Fe	3.7

Different clays have different chemical elements. The major elements observed in Raw-SMT were Si, Al, and O as indicated in Table 4.5. The minor elements were K and Ba as shown in Figure 4.4.

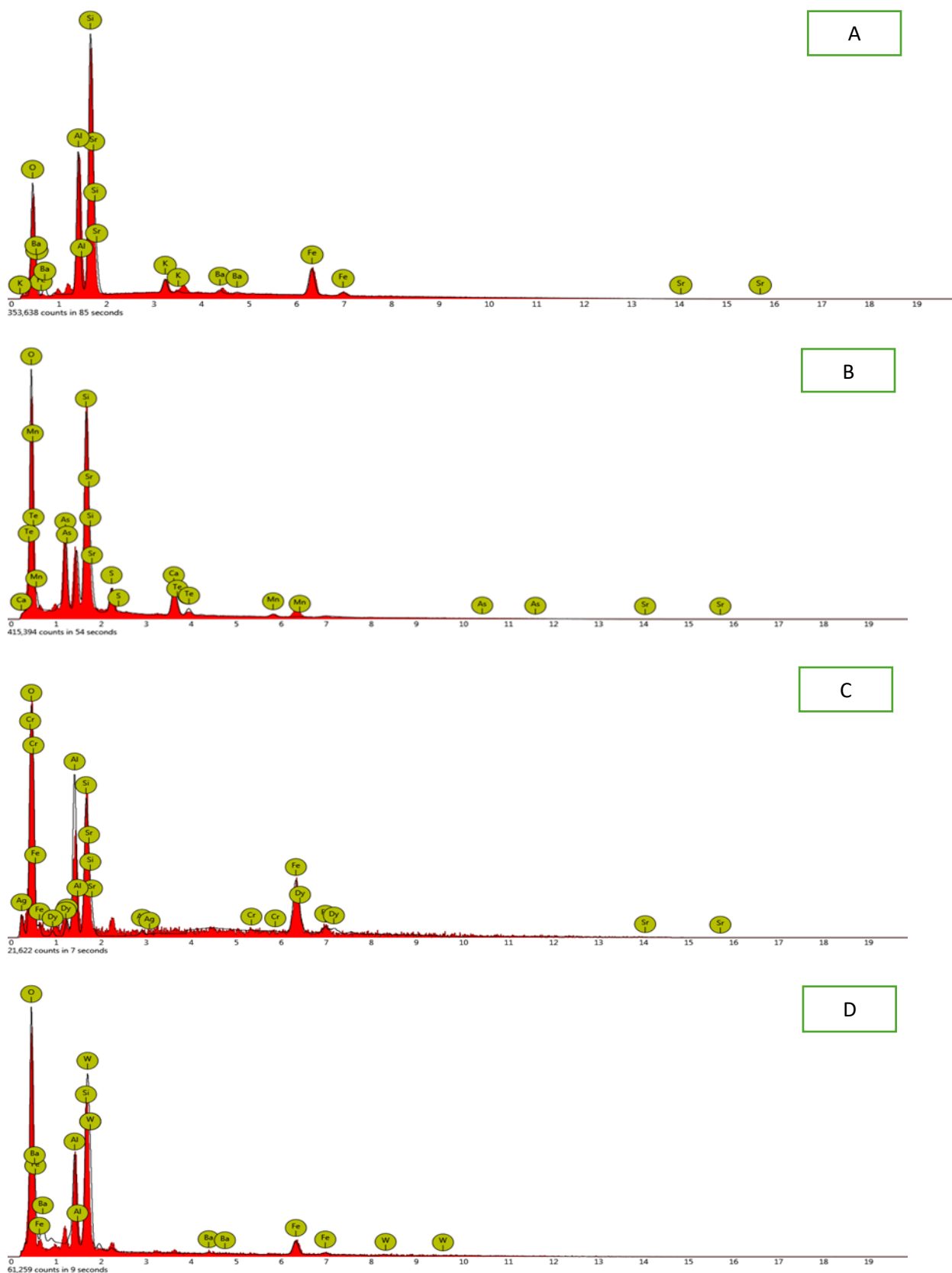


Figure 4.4: EDS data analysis for (A) Raw-SMT, (B) Modified-SMT, (C) MO-MSMT, and (D) CV-MSMT

Modified-SMT shows the presence of elements of Manganese (Mn) and Sulfur (S) in the adsorbent due to modification of the adsorbent (Smectite) by MnCl_2 and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. After the adsorption of MO dye, elements such as (Dysprosium) Dy and (Chromium) Cr appeared, while after adsorption of CV dye, the element of (Tungsten) W appeared. The adsorption of dyes altered the surface characteristics and composition of the clay, increasing its ability to interact with certain elements. This may result in the detection of elements such as Dy, Cr, or W during post-adsorption analysis, which were previously undetectable or present in negligible amounts.

4.2.7 Fourier Transform Infrared (FTIR) analysis

The Figure 4.5 illustrates the Fourier transform infrared (FTIR) analysis of Raw-SMT, Modified-SMT, MO-MSMT, and CV-MSMT at the wavelength range of 500 to 4000 cm^{-1} .

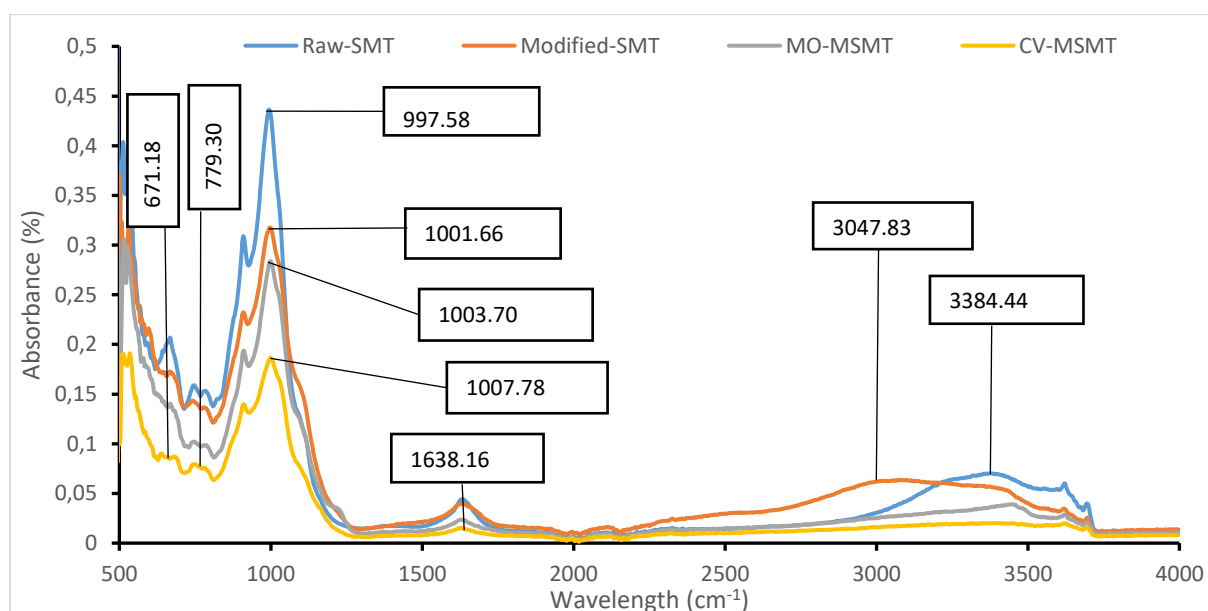


Figure 4.5: FT-IR analysis of Raw-SMT, Modified-SMT, MO-MSMT, and CV-MSMT at the absorbance spectra of the wavelength range of 500 to 4000 cm^{-1} .

FT-IR results in Figure 4.5 show wavelengths of 671.18 cm^{-1} and 779.30 cm^{-1} , revealing the bending vibration of Si-O or Al-O bonds in the structures of the Raw-SMT (Yusuf, 2023). The spectrum of modified SMT shows the shift and formation of a new peak due to the modification, which alters the surface of the adsorbent. The spectrum after the adsorption of MO and CV dye reveals the change in the properties of the adsorbent surface due to the interaction with dye molecules. This interaction involves the electrostatic force of attraction (Salahshoori *et al.*, 2024). The broad peak observed at wavelengths of 997.58 cm^{-1} for Raw-

SMT, 1001.66 cm^{-1} for Modified-SMT, 1003.70 cm^{-1} for MO-MSMT, and 1007.78 cm^{-1} for CV-MSMT attributes to the presence of C-O stretching in C-O-C group (Zhuang *et al.*, 2020).

The wavelength of 1638.16 cm^{-1} observed in all samples is due to the bending vibration of water (O-H bending) (Largo *et al.*, 2020). The peak wavelength of 3047.83 cm^{-1} for Modified-SMT and 3384.44 cm^{-1} for Raw-SMT shows the presence of O-H (hydroxyl group) stretching vibration (Ullah *et al.*, 2021).

4.3 Batch experiments

4.3.1 Effect of Contact Time

Time plays a vital role in adsorption studies. Modified SMT was used to examine the percentage removal of MO and CV textile dyes, and the results are shown in Figures 4.6 and 4.7. Figure 4.6 shows the effect of contact time on the removal of MO textile dye.

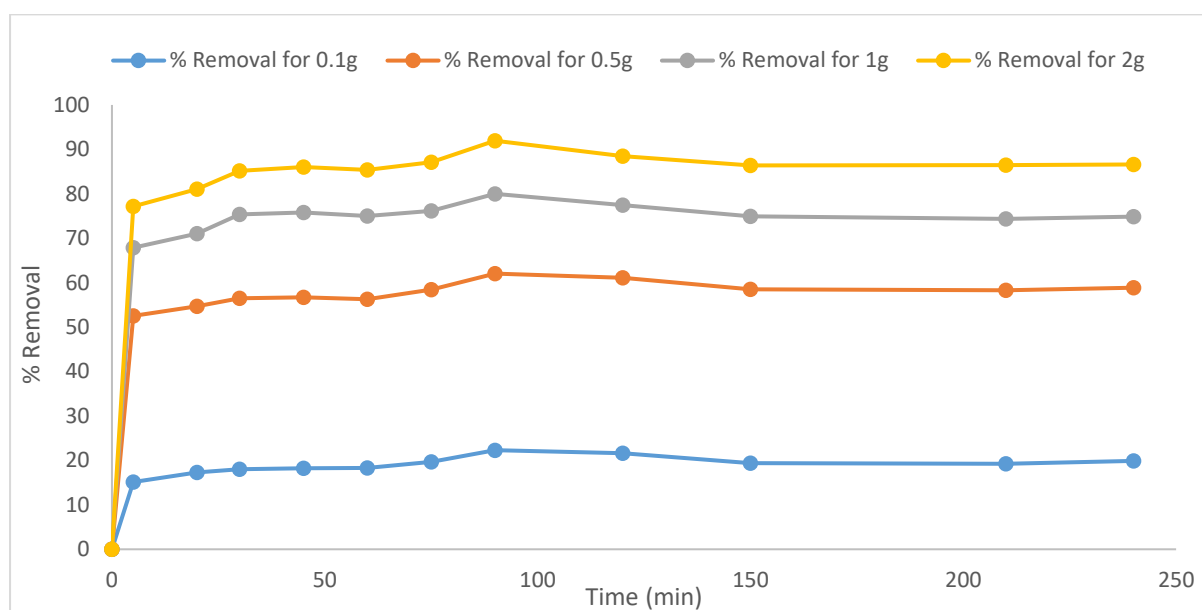


Figure 4.6: Effect of contact time on MO textile dye removal. (Conditions: initial concentration = 20 mg/L, temperature = 30 °C, time = 5 to 250 minutes, shaking speed = 250 rpm, volume = 30 mL, masses = 0.1 g to 2 g).

For MO textile dye, the removal of dye increased with increasing contact time of up to 90 minutes. This implies that the adsorbent active site was unoccupied with enough dye concentration in the solution. At 90 minutes 0.1 g recorded 22.3 %, 0.5 g recorded 62.05 %, 1 g recorded 79.99 %, and 2 g recorded 91.95 %. However, after 90 minutes of contact time

(optimum time), a reduction in the adsorption capacity of the MO dye was observed. The removal almost remained constant from 150 minutes to 240 minutes, as shown in Figure 4.6. This suggests that there was a lack in the availability of active surface areas to adsorb more dye concentration (Aragaw and Alene, 2022).

Figure 4.7 shows the effect of contact time on the removal of CV textile dye.

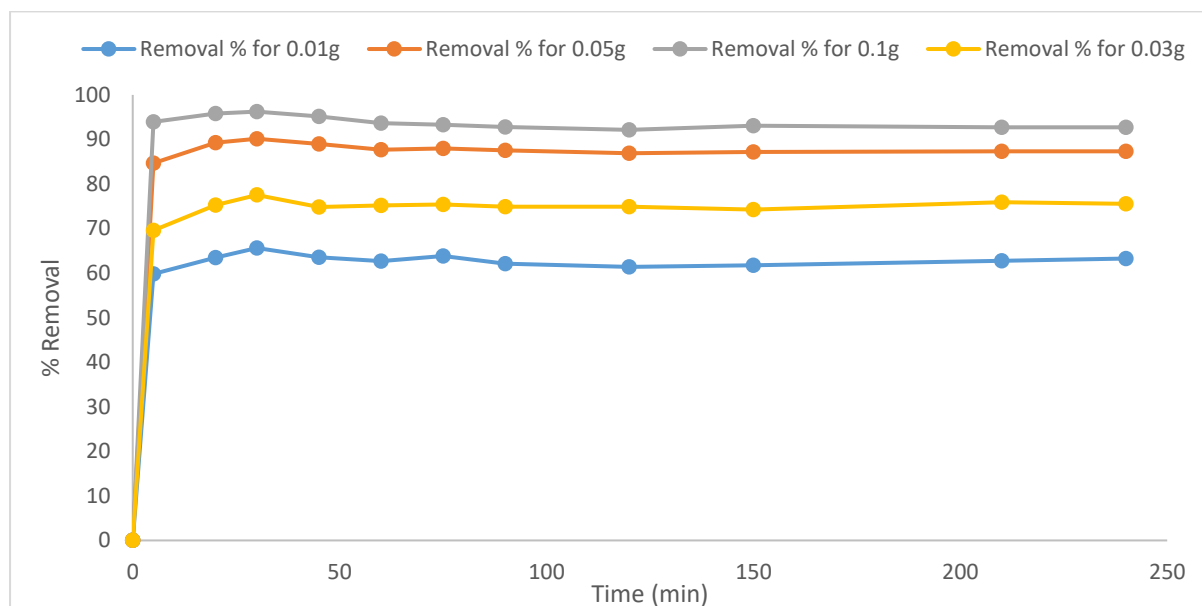


Figure 4.7 Effect of contact time on CV textile dye. (Conditions: initial concentration = 20 mg/L, temperature = 30 °C, time = 5 to 250 minutes, shaking speed = 250 rpm, volume = 30 mL, masses = 0.01 g to 0.1 g).

For CV textile dye, a rapid adsorption rate of adsorption of CV dye in the solution was observed because free sites were available in the adsorbent particle's surface. 30 minutes was recorded as an optimum shaking time because of higher adsorption percentage removals of CV dye. At 30 minutes 0.01g recorded 65.63%, 0.03g recorded 77.53%, 0.05g recorded 90.16%, and 0.1g recorded 96.25%. After 30 minutes, there was a decrease in adsorption capacity. This is due to the reduction in the availability of free sites in the adsorbent to adsorb CV dye or because some of the available active sites were already occupied. After 90 minutes the stability of adsorption capacity was observed, as shown in Figure 4.7. This is because all the active sites were almost occupied, or the adsorbent was fully saturated with the concentration of CV dye (Miyah *et al.*, 2017; Debnath and Das, 2023).

It was found that the adsorbent is more effective in removing CV textile dye (basic) compared to MO textile dye (acidic). The percentage removal efficiency of MO and CV textile dyes onto modified SMT is influenced by the molecular structure, molecular size, and the nature of the dye (basic or acidic) (Aragaw and Alene, 2022). Most of the clay materials are permanently negatively charged. Smectite is a type of clay that is composed of negatively charged silica, however, modifying it by Mn^{2+}/Al^{3+} caused it to change the charges from negative to positive. The presence of positively charged ions on the surface of an adsorbent causes the repulsion forces to be active between the acidic (MO) textile dye and the adsorbent. On the other hand, it causes the forces of attraction to be active between the basic (CV) textile dye and the adsorbent (Ngulube *et al.*, 2017). Therefore, the adsorption process revealed to be more effective in removing CV dye compared to MO dye, with a higher percentage of dye observed for the CV dye.

4.3.2 Effect of adsorbent dosage and initial dye concentration

Figure 4.8 shows the effect of adsorbent dosage and initial dye concentration for MO textile dye and Figure 4.9 shows the effect of adsorbent dosage and initial dye concentration for CV textile dye.

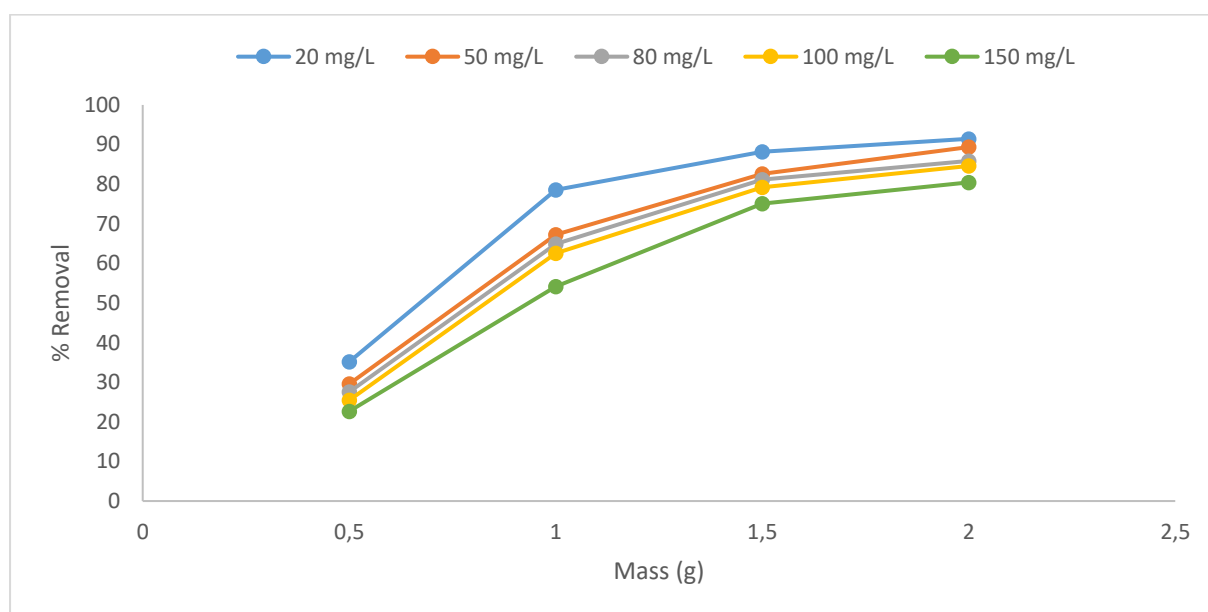


Figure 4.8: Effect of dosage and initial dye concentration for MO textile dye. (Conditions: initial dye concentration = 20 mg/L to 150 mg/L, masses = 0.5 g to 2 g, volume = 30 mL, time = 90 minutes, temperature = 30 °C, Shaking speed = 250 rpm).

Figure 4.8 shows that a direct correlation exists between the weight of the adsorbent utilized and the percentage removal of MO dye. When the adsorbent dosage increases, the percentage removal of dye also increases due to the availability of a large surface area of the adsorbent to adsorb more dye concentration (Abdallah and Alprol, 2024). The trend in Figure 4.9 below shows the increase in percentage removal as the masses of the adsorbent increase. The adsorption capacity of CV increases with increased adsorbent dosage because more surface area implies a higher number of adsorbent sites attained by an increase in the mass of the adsorbent (Aljeboree *et al.*, 2024).

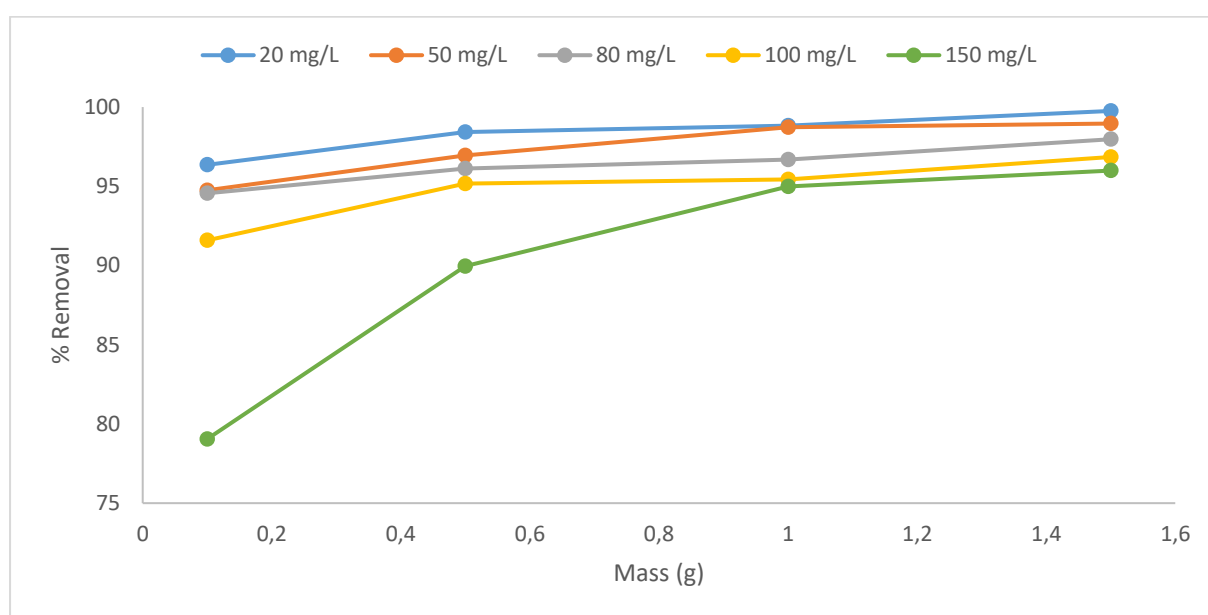


Figure 4.9: The effect of dosage and initial dye concentration for CV textile dye. (Conditions: initial dye concentration = 20 mg/L to 150 mg/L, masses = 0.1 g to 1.5 g, volume = 30 mL, time = 30 minutes, temperature = 30 °C, Shaking speed = 250 rpm).

4.3.3 Effect of Temperature

Temperature is important in adsorption experiments as it affects the mobility and solubility of dye molecules in an adsorbent's aqueous solution and surface properties (Cheruiyot *et al.*, 2019; Akter *et al* 2024). The effect of temperature was investigated on MO and CV textile dye adsorption on modified SMT at 30, 40, 50, 60, 70, and 80 °C. Figure 4.10 shows the percentage removal of MO with variation in temperature.

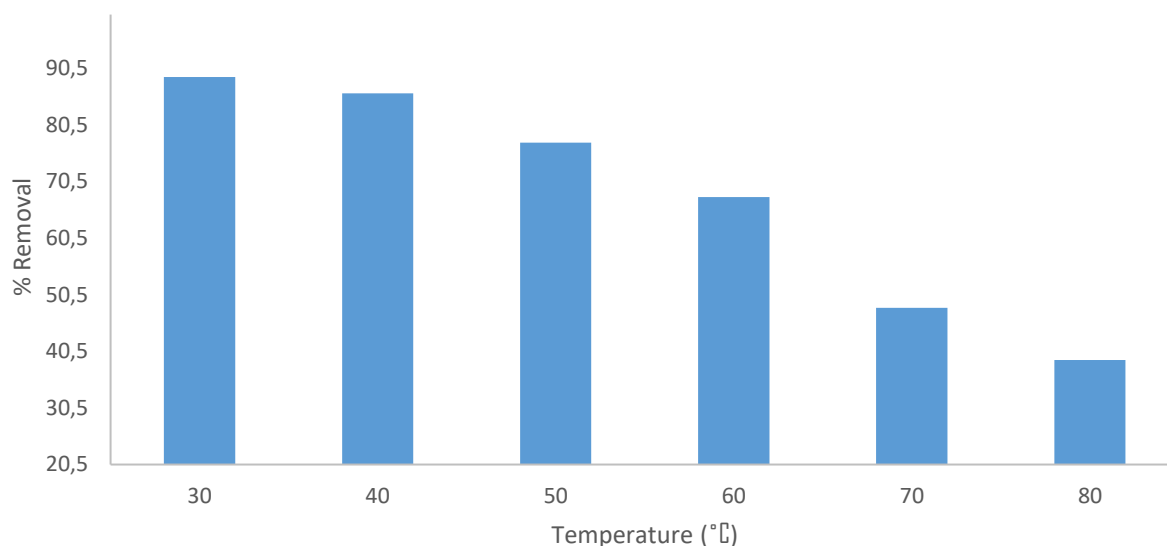


Figure 4.10: Effect of temperature for MO textile dye. (Conditions: initial dye concentration = 20 mg/L, temperature = 30 °C to 80 °C, time = 90 minutes, mass = 1.5 g, volume = 30 mL, shaking speed = 250 rpm).

The observed trends in Figure 4.10 shows a decrease in adsorption efficiency, dropping from 88.95% at 30°C to 38.95% at 80°C. This indicates that the adsorption process is exothermic (Faleh and Radhy, 2021). It is noted that the decrease in the percentage removal of MO dye with an increase in temperature is mostly caused by the weakening of adsorptive forces between the active sites of the adsorbent and the MO (Van der Waals forces and the dye molecule forces) (El Gamala *et al.*, 2020). Figure 4.11 shows the percentage removal of CV with variation in temperature.

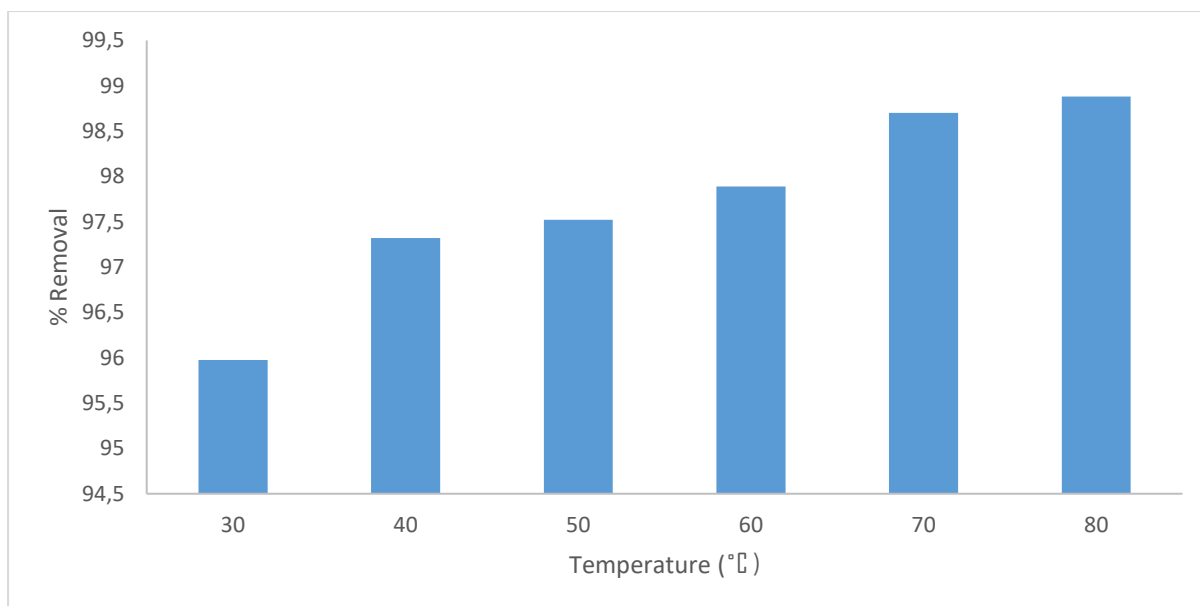


Figure 4.11: Effect of temperature for CV textile dye. (Conditions: initial dye concentration = 20 mg/L, temperature = 30 °C to 80 °C, time = 30 minutes, mass = 0.1 g, volume = 30 mL, shaking speed = 250 rpm).

The trends shown in Figure 4.11 indicate an increase in adsorption efficiency as the temperature rises, from 95.98% at 30°C to 98.88% at 80°C. This suggests that the adsorption process is endothermic (Rajoriya *et al.*, 2021). The mobility of the CV dye molecule increases with the increase in temperature. Similar trends have been reported by Patel *et al.* (2021).

4.3.4 Effect of solution pH on the adsorption of MO and CV textile dyes.

The effect of solution pH plays a great role in adsorption efficiency. It influences the removal process by controlling the modified SMT surface properties and the ionization of MO and CV textile dyes (Badawy *et al.*, 2023). The influence of solution pH on MO textile dye was studied and the results are shown in Figure 4.12.

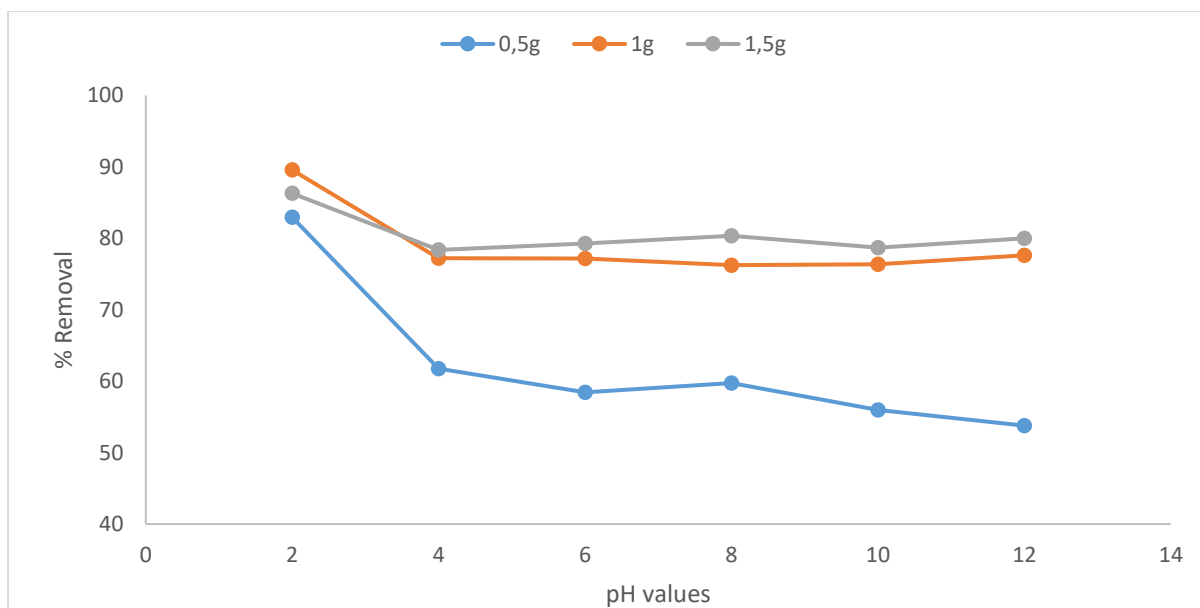


Figure 4.12 Effect of solution pH for MO textile dye. (Conditions: initial concentration = 20 mg/L, pH values = 2 to 12, temperature = 30 °C, time = 90 minutes, mass = 0.5 g to 1.5 g, volume = 30 mL, shaking speed = 250 rpm).

The outcomes revealed that the percentage removal of MO textile dye by modified SMT peaked at pH 2. At pH 2, 0.5 g recorded 82.95 %, 1 g recorded 98.75 %, and 1.5 g recorded 96.30 % dye removal. The optimum percentage removal of MO textile dye was obtained at pH 2. The findings show that the efficiency percentage removal of MO textile dye by modified SMT was at maximum in an acidic medium and minimum in a basic medium. At low pH values (acidic condition) there was an increase in the percentage removal of anionic dye in an aqueous solution. Methyl orange textile dye is an anionic dye (negatively charged) and the modified SMT is positively charged. Therefore, there is an attraction of electrostatic force between the MO textile dye and the adsorbent. Increasing the pH medium caused a gradual decrease of the positive charge on the adsorbent surface due to deprotonation of the functional groups (Najafi *et al.*, 2021). Hence the percentage removal of CV by modified SMT was observed to be low at the basic medium compared to the acidic medium. The influence of solution pH on CV dye adsorption was studied and the results are shown in Figure 4.13.

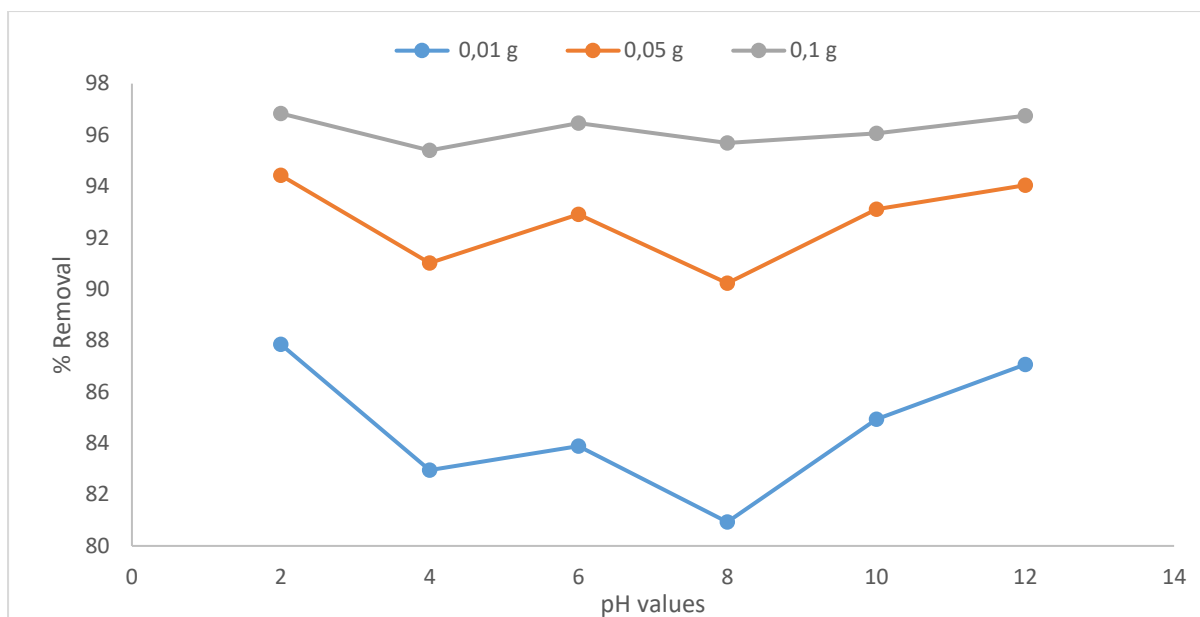


Figure 4.13: Effect of a solution pH for CV textile dye. (Conditions: initial concentration = 20 mg/L, pH values = 2 to 12, temperature = 30 °C, time = 30 minutes, mass = 0.01 g to 0.1 g, volume = 30 mL, shaking speed = 250 rpm).

At pH 2, the best removal of CV textile dye from the aqueous solution was accomplished. At pH 2, 0.01 g recorded 87.85 %, 0.05 g recorded 94.43 %, and 0.1 g recorded 96.84 %. After that, the percentage removal of CV textile dye slightly reduced and form a zig zag shape as the pH value increased to 8 which caused a decrease in the amount of CV dye concentration absorbed by modified SMT. This trend was achieved due to an increase in the negative charge density on the surface of an adsorbent in low pH (acidic medium) (Cheruiyot *et al.*, 2019). After pH 8, there was an increase in the percentage removal of dye due to the electrostatic attraction of the CV textile dye and the adsorbent.

4.4 Adsorption Isotherm Modelling

Adsorption isotherms are typically utilized to design and comprehend the interaction mechanism between the adsorbate and adsorbent at equilibrium (Majd *et al.*, 2022). This study examined the adsorption isotherm of MO and CV dye onto Modified SMT using five concentrations (20 mg/L, 50 mg/L, 80 mg/L, 100 mg/L, and 150 mg/L). Linear regressions were employed to estimate the parameters, and R^2 values were calculated for each case.

4.4.1 Langmuir Adsorption Isotherm

Table 4.6 shows the Langmuir parameters for the adsorption of MO dye using various masses of Modified-SMT.

Table 4.6: Langmuir parameters for the adsorption of MO dye using different masses (0.5 g, 1 g, 1.5 g, and 2 g) of Modified-SMT.

Masses (g)	$q_{\max}$ (mg/g)	KL (L/mg)	R^2
0.5	3.404835	0.010811	0.9975
1	2.675227	0.049006	0.9839
1.5	2.639219	0.064394	0.9909
2	2.325581	0.077968	0.9988

For MO dye, the maximum amount adsorbed ($q_{\max}$) was obtained at 3.404835 mg/g for 0.5 g, 2.675227 mg/g for 1 g, 2.639219 mg/g for 1.5 g, and 2.325581 mg/g for 2 g. The adsorption constant (KL) recorded 0.010811 L/mg for 0.5g, 0.049006 L/mg for 1 g, 0.064394 L/mg for 1.5 g, and 0.077968 L/mg for 2 g as shown in Table 4.6.

As the mass of the adsorbent increases, the maximum amount absorbed ($q_{\max}$) decreases, indicating that the adsorption sites are not being fully utilized. When the adsorbent mass is lower, the surface area of the adsorbent is more efficiently used, resulting in a higher $q_{\max}$. Meanwhile, the Langmuir constant (KL) increases with the adsorbent mass, suggesting that the adsorption process becomes more effective as the mass of the adsorbent increases. The separation factor (RL) values differ according to the initial concentrations. For all adsorbent masses, the RL values decrease with an increase in the initial concentration. All the RL values are between 0 and 1, as indicated in Table 4.7, implying that the adsorption process is favorable (Rajabzadeh *et al.*, 2020). Table 4.7 shows the separation factor (RL) values for MO dye.

Table 4.7: The separation factor (RL) values for MO dye

	RL Values				
Masses (g)	20 mg/L	50 mg/L	80 mg/L	100 mg/L	150 mg/L
0.5	0.877019	0.724239	0.614714	0.553625	0.443598
1	0.826253	0.554946	0.420688	0.35264	0.228814
1.5	0.86788	0.64133	0.50746	0.42746	0.29334
2	0.88242	0.706858	0.531534	0.4544	0.304284

The R^2 values for Langmuir Adsorption Isotherm were 0.9975 for 0.5 g, 0.9839 for 1 g, 0.9909 for 1.5 g, and 0.9988 for 2 g as indicated in Figure 4.14. Figure 4.14 shows the Langmuir Adsorption Isotherm for MO dye at the different masses of modified-SMT.

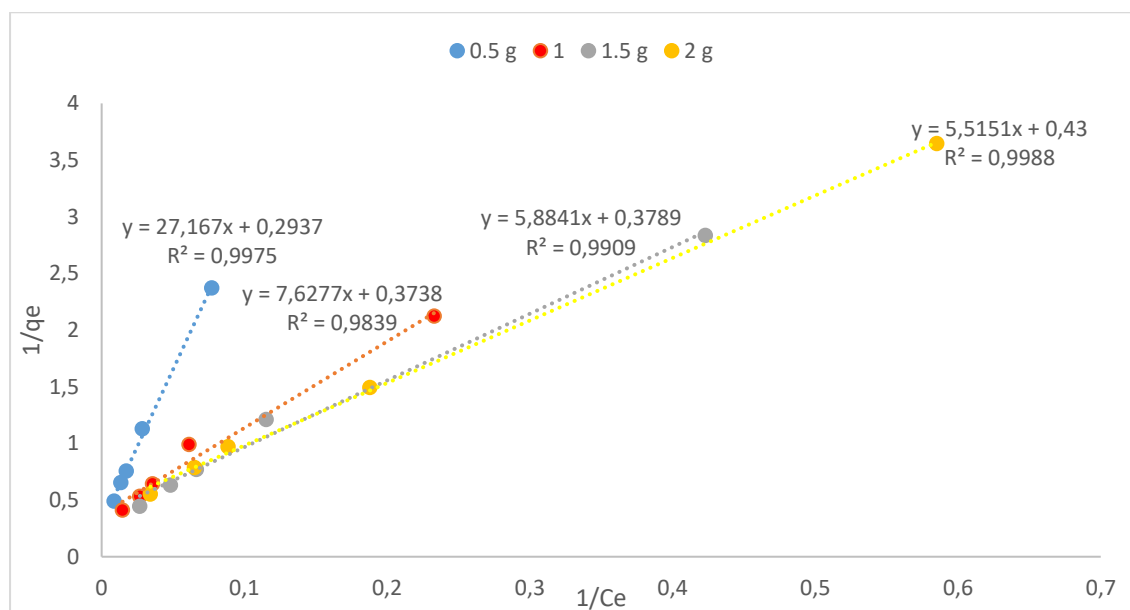


Figure 4.14: Langmuir Adsorption Isotherm for MO dye at the masses of 0.5 g, 1 g, 1.5 g and 2 g

The data was observed to align more closely with the Langmuir adsorption isotherm, suggesting that the adsorption occurs more effectively at homogeneous sites on the Modified-SMT surface and forms a monolayer (Chauke *et al.*, 2024). The high R^2 values validate the suitability of the Langmuir model, emphasizing the monolayer adsorption process.

Table 4.8 shows the Langmuir parameters for the adsorption of CV dye using different masses (0.1 g, 0.5 g, 1 g, and 1.5 g) of Modified-SMT.

Table 4.8: Langmuir parameters for the adsorption of CV dye using different masses (0.1 g, 0.5 g, 1 g, and 1.5 g) of Modified-SMT.

Masses (g)	$q_{\max}$ (mg/g)	KL (L/mg)	R^2
0.1	42.0168	0.21795	0.9965
0.5	7.02247	0.63628	0.9871
1	4.23908	0.7046	0.9878
1.5	1.82183	5.67632	0.9579

For CV dye, the maximum amount adsorbed ($q_{\max}$) was recorded as 42.0168 mg/g for 0.1 g, 7.02247 mg/g for 0.5 g, 4.23908 mg/g for 1 g, and 1.82183 mg/g for 1.5 g. The adsorption constant (KL) was 0.21795 L/mg for 0.1 g, 0.63628 L/mg for 0.5 g, 0.7046 L/mg for 1 g, and 5.67632 L/mg for 1.5 g as presented in Table 4.8. With an increase in adsorbent mass, $q_{\max}$ decreases, showing that adsorption sites are less efficiently utilized. Meanwhile, KL rises, indicating that adsorption becomes stronger with more adsorbent. The RL values fall between 0 and 1, as shown in Table 4.9, indicating that the adsorption process is favourable. As the initial concentration of CV dye rises, the RL values tend to decrease for all adsorbent masses. Table 4.9 shows the separation factor (RL) values for CV dye.

Table 4.9: The separation factor (RL) values for CV dye

	RL Values				
Masses (g)	20 mg/L	50 mg/L	80 mg/L	100 mg/L	150 mg/L
0.1	0.86287	0.63609	0.51321	0.35299	0.1274
0.5	0.83374	0.50671	0.33613	0.2455	0.0945
1	0.85794	0.69088	0.34895	0.23697	0.15885
1.5	0.7830	0.25306	0.09786	0.05296	0.02846

The R^2 values for Langmuir Adsorption Isotherm were 0.9965 for 0.1g, 0.9871 for 0.5 g, 0.9878 for 1 g, and 0.9579 for 1.5 g, as shown in Figures 4.15 and Figure 4.16. High R^2 values suggest monolayer adsorption mechanisms. The data fits better on Langmuir adsorption isotherms, which take place on homogenous sites on modified-SMT. Figure 4.15 shows the Langmuir Adsorption Isotherm for CV dye at the various masses of modified-SMT (0.1 g, 0.5 g and 1 g).

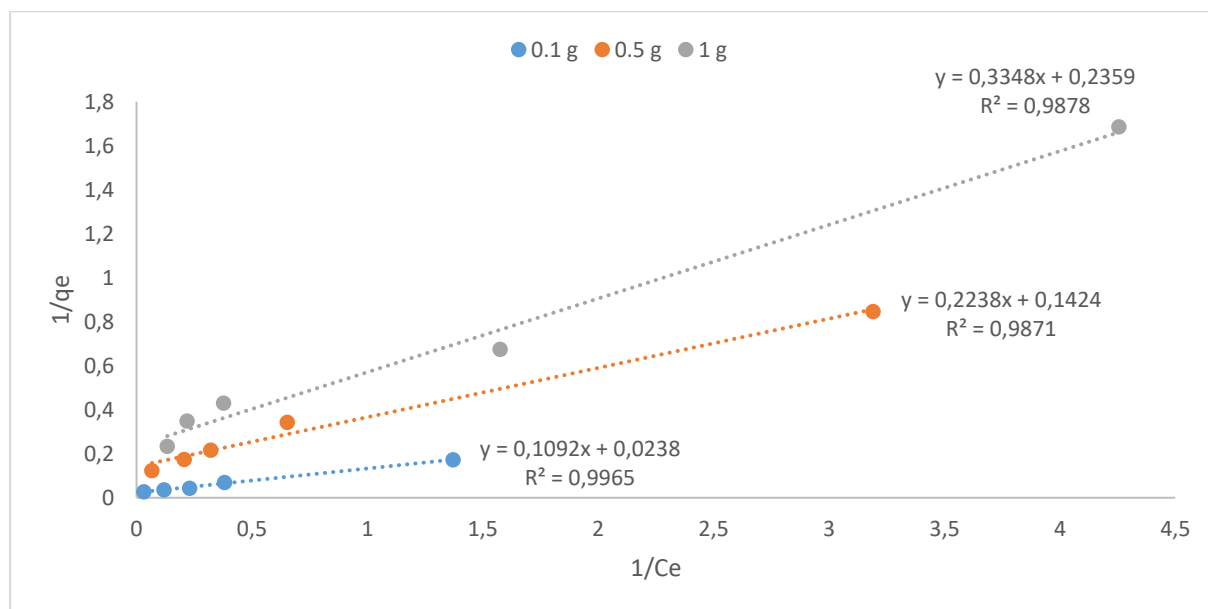


Figure 4.15: Langmuir Adsorption Isotherm for CV dye at the masses of 0.1 g, 0.5 g and 1 g

Figure 4.16 shows the Langmuir Adsorption Isotherm for CV dye at the mass of 1.5 g for modified SMT.

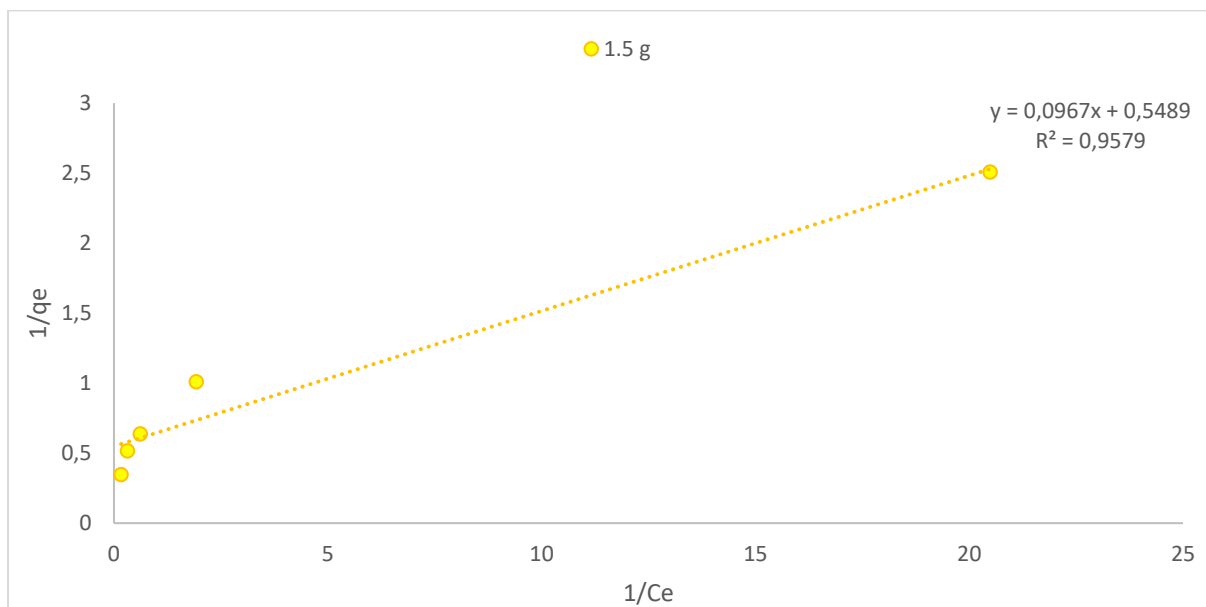


Figure 4.16: Langmuir Adsorption Isotherm for CV dye at the masses of 1.5 g

4.4.2 Freundlich Adsorption Isotherm

Table 4.10 shows the Freundlich parameters for the adsorption of MO dye using different masses (0.5 g, 1 g, 1.5 g, and 2 g) of Modified-SMT.

Table 4.10: Freundlich parameters for the adsorption of MO dye using different masses (0.5 g, 1 g, 1.5 g, and 2 g) of Modified-SMT.

Masses (g)	n	K _f	R ²
0.5	1.37741	0.0666	0.9982
1	1.6369	0.1934	0.9931
1.5	1.4675	0.1961	0.998
2	1.5092	0.2038	0.9935

For MO dye, the Freundlich constant (n) was 1.37741 for 0.5 g, 1.6369 for 1 g, 1.4675 for 1.5 g, and 1.5092 for 2 g. The value of n is higher than one ($n > 1$), as shown in Table 4.10, implying that the adsorption process is favourable and that more additional sites were available for

adsorption. The Freundlich constant (K_f) recorded 0.0666 mg/g for 0.5 g, 0.1934 mg/g for 1 g, 0.1961 mg/g for 1.5 g, and 0.2038 mg/g for 2 g. The R^2 values were 0.9982 for 0.5 g, 0.9931 for 1 g, 0.998 for 1.5 g, and 0.9935 for 2 g as indicated in Figure 4.17. Figure 4.17 shows the Freundlich Adsorption Isotherm for MO dye at the various masses of 0.5 g, 1 g, 1.5 g and 2 g for modified SMT.

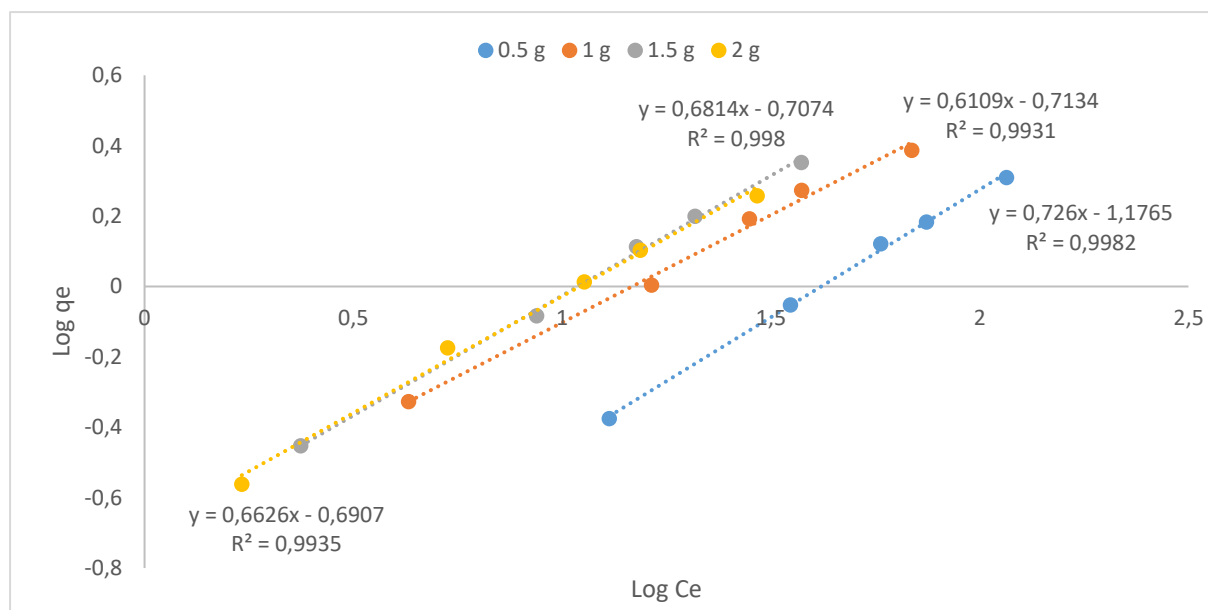


Figure 4:17: Freundlich Adsorption Isotherm for MO dye at the mass of 0.5 g, 1 g, 1.5 g and 2 g

It was concluded that the data fits well into the Freundlich model. Therefore, this shows that the adsorption of MO dye is more effective on a heterogeneous surface, following a multilayer adsorption mechanism. Table 4.11 shows the Freundlich parameters for the adsorption of CV dye using different masses (0.1 g, 0.5 g, 1 g, and 1.5 g) of Modified-SMT.

Table 4.11 Freundlich parameters for the adsorption of CV dye using different masses (0.1 g, 0.5 g, 1 g, and 1.5 g) of Modified-SMT

Masses (g)	n	K_f	R^2
0.1	2.0563	8.4528	0.8899
0.5	1.952744	2.3153	0.9791
1	1.9459	1.45546	0.9561
1.5	2.5025	1.30677	0.9955

For CV dye, the Freundlich constant (n) was 2.05636 for 0.1 g, 1.92744 for 0.5 g, 1.9459 for 1 g, and 2.5025 for 1.5 g. The adsorption process is favourable, and the Freundlich constant (n) is higher than one. The Freundlich constant (K_f) was 8.4528 mg/g for 0.1 g, 2.3153 mg/g for 0.5 g, 1.45546 mg/g for 1 g, 1.30677 mg/g for 1.5 g. The highest K_f at the lowest mass (0.1 g) indicates that adsorption capacity per unit mass diminishes as the adsorbent mass increases. This is probably caused by overlapping active sites or saturation effects at higher masses. The R^2 was 0.8992 for 0.1 g, 0.9791 for 0.5 g, 0.9561 for 1 g, and 0.9955 for 1.5 g as shown in Table 4.11 and Figure 4.18. Figure 4.18 shows the Freundlich adsorption isotherms for CV dye at the various masses of modified SMT.

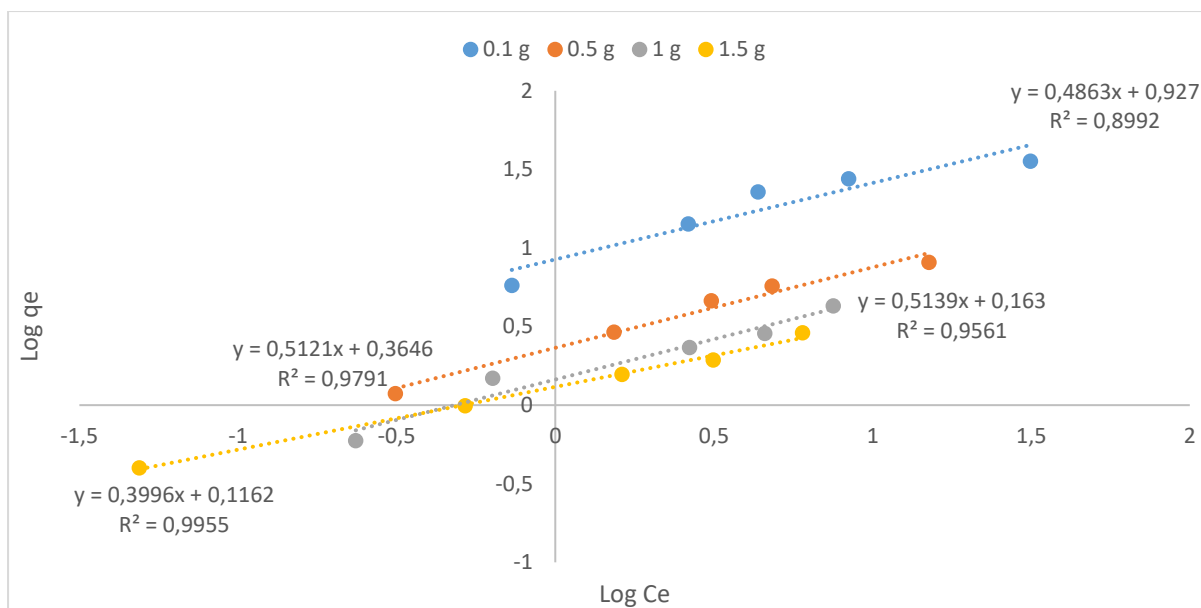


Figure 4.18: Freundlich Adsorption Isotherm for CV dye at the masses of 0.1 g, 0.5 g, 1 g and 1.5 g of modified SMT.

It is revealed that the data does not fit well into the Freundlich model. The Freundlich parameters show that the adsorption of CV dye onto modified SMT does not follow multilayer adsorption on heterogeneous surfaces.

4.4.3 Dubinin- Radushkevich (DR) Isotherm

Table 4.12 shows the Dubinin- Radushkevich (DR) Isotherm parameters for MO dye removal using 0.5 g, 1 g, 1.5 g, and 2 g of modified SMT.

Table 4.12: Dubinin- Radushkevich (DR) Isotherm parameters for MO dye removal using 0.5 g, 1 g, 1.5 g, and 2 g of modified SMT.

Mass (g)	T (k)	K (mol/K/J)	Q (mg/g)	Energy (KJ/mol)	R ²
0.5	303.15	6×10^{-9}	7.76×10^{-5}	9128.709	0.9996
1	303.15	3×10^{-9}	1.15×10^{-5}	12909.94	0.8108
1.5	303.15	4×10^{-9}	4.53×10^{-5}	11180.34	0.9767
2	303.15	5×10^{-9}	8.18×10^{-5}	10000	0.9979

For MO dye, the adsorption capacity (q) recorded 7.76×10^{-5} mg/g for 0.5 g, 1.15×10^{-5} mg/g for 1 g, 4.53×10^{-5} mg/g for 1.5 g and 8.18×10^{-5} mg/g for 2 g. The constant (K) values which

are associated with the sorption energy recorded 6×10^{-9} mol/k/J for 0.5 g, 3×10^{-9} mol/k/J for 1 g, 4×10^{-9} mol/k/J for 1.5 g and 5×10^{-9} mol/k/J for 2 g. The absolute temperature of 303.15 K was used. The adsorption energy (E) recorded 9128.709 KJ/mol for 0.5 g and 12909.94 KJ/mol for 1 g, 11180.34 KJ/mol for 1.5 g, and 10000 KJ/mol for 2 g. The R^2 values were 0.9996 for 0.5 g, 0.8108 for 1 g, 0.9767 for 1.5 g, and 0.9979 for 2 g, as shown in Table 4.12.

The Dubinin-Radushkevich (DR) Isotherm analysis for MO dye removal shows that the Langmuir constant (K) remains low across all tested masses, implying that the adsorption sites on Modified-SMT are fully saturated. Adsorption capacity (q) increases with the adsorbent mass, indicating that a higher mass provides more adsorption sites. The energy values suggest that chemisorption is the dominant mechanism. Chemisorption occurs when a covalent bond is formed between the adsorbate and the substrate through the sharing or transfer of electrons (Al-Ghouti and Da'ana, 2020). The model's fit (R^2) is highest at 0.5 g, indicating the best agreement with the DR isotherm, while it slightly declines at higher masses, particularly at 1 g. In conclusion, MO dye removal is most effective at 0.5 g of Modified-SMT, with chemical adsorption being the primary mechanism. Figure 4.19 shows the Dubinin- Radushkevich (DR) Isotherm for MO dye at the various masses of modified SMT.

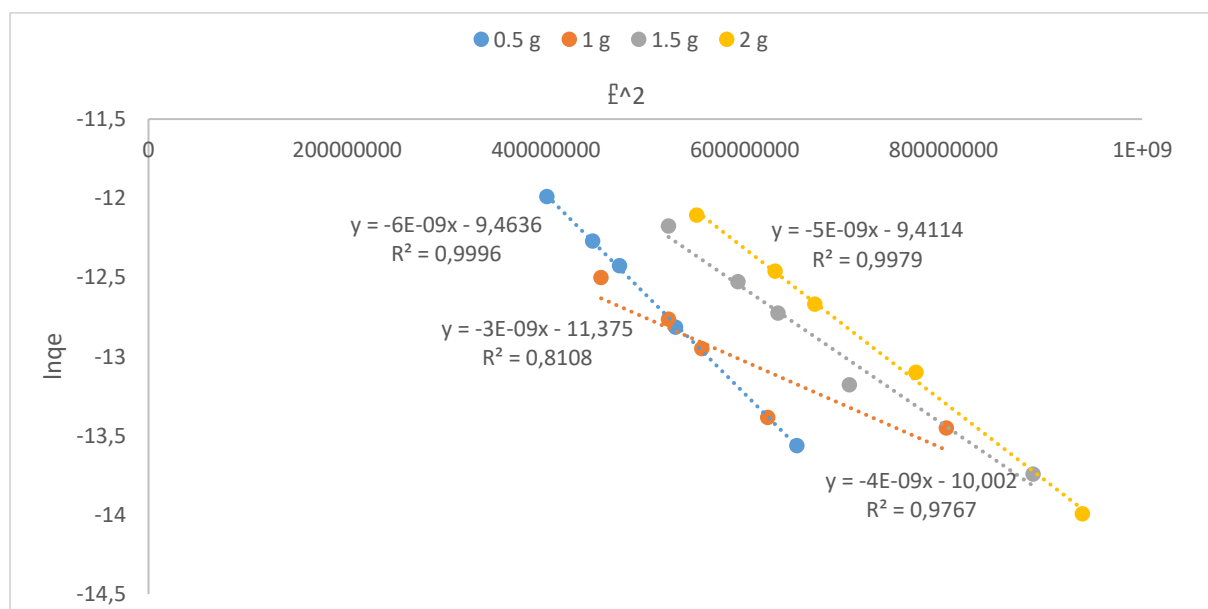


Figure 4.19: Dubinin- Radushkevich (DR) Isotherm for MO dye adsorption at the masses of 0.5 g, 1 g, 1.5g and 2 g of modified SMT

Table 4.13 shows the Dubinin- Radushkevich (DR) Isotherm parameters for CV dye removal using 0.1 g, 0.5 g, 1 g, and 1.5 g of modified SMT.

Table 4.13: Dubinin- Radushkevich (DR) Isotherm parameters for CV dye removal using 0.1 g, 0.5 g, 1 g, and 1.5 g of modified SMT.

Mass (g)	T (k)	K (mol/K/J)	Q (mg/g)	Energy (KJ/mol)	R ²
0.1	303.15	3×10^{-9}	7.5855×10^{-4}	12909.94	0.9297
0.5	303.15	3×10^{-9}	1.959×10^{-4}	12909.94	0.9901
1	303.15	3×10^{-9}	1.103×10^{-4}	12909.94	0.9617
1.5	303.15	2×10^{-9}	3.823×10^{-5}	15811.39	0.9887

For CV dye, the adsorption capacity (q) recorded 7.5855×10^{-4} mg/g for 0.1 g, 1.959×10^{-4} mg/g for 0.5 g, 1.103×10^{-4} mg/g for 1 g, and 3.823×10^{-5} mg/g for 1.5 g. The constant (K) values were 3×10^{-9} mol/k/J for 0.1 g, 0.5 g and 1 g, and 2×10^{-9} mol/k/J for 1.5 g. The 303.15 K was used as an absolute temperature. The adsorption energy (E) recorded 12909.94 KJ/mol for 0.1 g, 0.5 g, and 1 g and 15811.39 KJ/mol for 1.5 g. The R^2 values were 0.9297 for 0.1 g, 0.9901 for 0.5 g, 0.9617 for 1 g, and 0.9887 for 1.5 g, as shown in Table 4.13.

The Langmuir constant (K) values are consistently low, implying that the adsorption sites are not highly concentrated. The adsorption capacity (q) increases with higher adsorbent masses, suggesting that more adsorption sites become available as the mass increases. The energy values (E) are high, indicating that chemisorption is the primary mechanism, with the energy being higher at 1.5 g, pointing to stronger chemical interactions at this mass. The R^2 values are highest at 0.5 g (0.9901), reflecting a good fit to the DR isotherm model. While the fit slightly decreases at 1 g, it remains high at 1.5 g, showing a consistent and reliable adsorption process.

Figure 4.20 shows the Dubinin- Radushkevich (DR) Isotherm for CV dye adsorption at the masses of 0.1 g, 0.5 g, 1 g, and 1.5g of modified SMT.

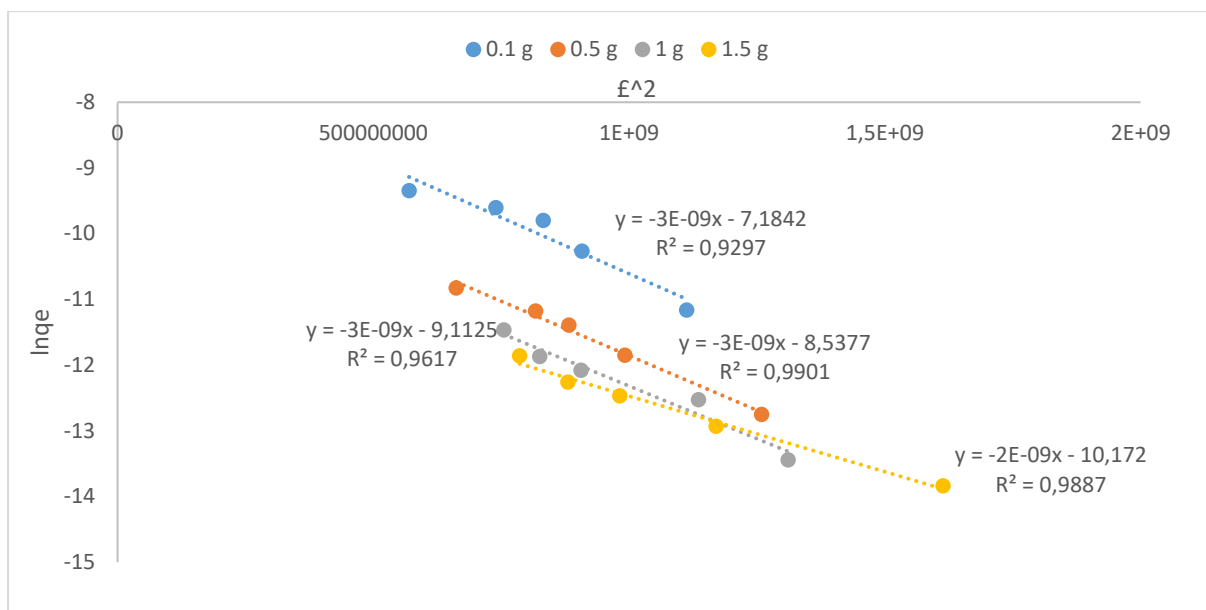


Figure 4.20: Dubinin- Radushkevich (DR) Isotherm for CV dye adsorption at the masses of 0.1 g, 0.5 g, 1 g, and 1.5 g of modified SMT.

4.4.4 Temkin Adsorption Isotherm

Table 4.14 shows the parameters of Temkin adsorption Isotherm for MO dye removal using various masses (0.5 g, 1 g, 1.5 g and 2 g) of the modified SMT

Table 4.14: Parameters of Temkin adsorption Isotherm for MO dye removal using various masses (0.5 g, 1 g, 1.5 g and 2 g) of the modified SMT

Mass (g)	β (J/mol)	b (J/mol)	α (L/mg)	R^2
0.5	0.7198	3501.513	0.118965	0.9592
1	0.7062	3568.945	0.365491	0.9473
1.5	0.6671	3778.128	0.5569	0.9298
2	0.523	4819.1	0.805532	0.9545

For MO dye, the heat of the adsorption (β) recorded 0.7198 J/mol for 0.5 g, 0.7062 J/mol for 1 g, 0.6671 J/mol for 1.5 g and 0.523 J/mol for 2 g. The Temkin constant (b) recorded 3501.513 J/mol for 0.5 g, 3568.945 J/mol for 1 g, 3778.128 J/mol for 1.5 g, and 4819.1 J/mol for 2 g. It was noted the adsorption was chemisorption. These results are corroborated by the findings on Dubinin- Radushkevich (DR) Isotherm. The equilibrium binding constant (α) recorded

0.118965 L/mg for 0.5 g, 0.365491 L/mg for 1 g, 0.5569 L/mg for 1.5 g, and 0.805532 L/mg for 2 g as shown in Table 4.14. The Temkin adsorption isotherm plot of MO dye removal onto modified SMT was linear with R^2 of 0.9592 for 0.5 g, 0.9473 for 1 g, 0.9298 for 1.5 g, and 0.9545 for 2 g as shown in Table 4.14 and Figure 4.21. Figure 4.21 shows the Temkin Adsorption Isotherm for MO dye removal using 0.5 g, 1 g, 1.5 g, and 2 g of modified SMT.

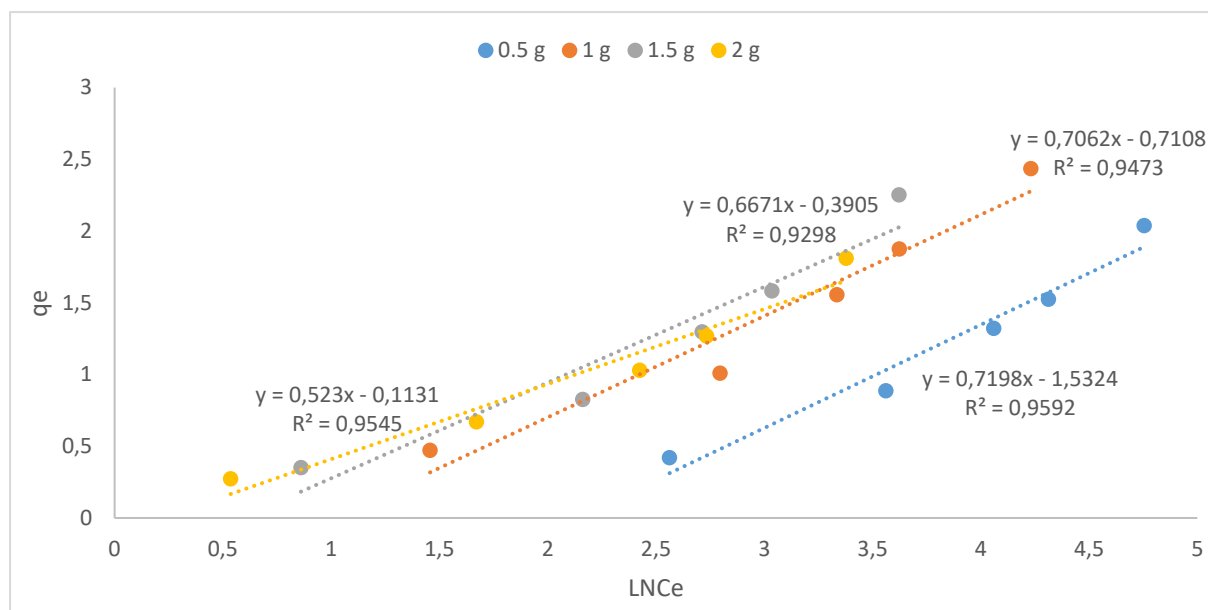


Figure 4.21: Temkin Adsorption Isotherm for MO dye removal using 0.5 g, 1 g, 1.5 g, and 2 g of modified SMT.

Table 4.15 shows the parameters of Temkin adsorption Isotherm for CV dye removal using various masses (0.1 g, 0.5 g, 1 g and 1.5 g) of the modified SMT.

Table 4.15: Parameters of Temkin adsorption Isotherm for CV dye removal using various masses (0.1 g, 0.5 g, 1 g and 1.5 g) of the modified SMT

Mass (g)	β (J/mol)	b (J/mol)	α (L/mg)	R^2
0.1	8.195	307.5521	2.832637	0.9754
0.5	1.8104	1392.173	4.711678	0.9685
1	0.9295	2711.554	7.097647	0.9157
1.5	0.4261	5915.018	44.2856	0.8289

For CV dye, the heat of the adsorption (β) was 8.195 J/mol for 0.1 g, 1.8104 J/mol for 0.5 g, 0.9295 J/mol for 1 g, 0.4261 J/mol for 1.5 g. The Temkin constant (b) recorded 307.5521 J/mol for 0.1 g, 1392.173 J/mol for 0.5 g, 2711.554 J/mol for 1 g, 5915.018 J/mol for 1.5 g. Therefore, the adsorption was chemisorption. The equilibrium binding constant (α) was found to be at 2.832637 L/mg for 0.1 g, 4.711678 L/mg for 0.5 g, 7.097647 L/mg for 1 g, and 44.2856 for 1.5 g, as presented in Table 4.15. The Temkin adsorption isotherm plot of CV dye removal onto modified SMT was linear with R^2 of 0.9754 for 0.1 g, 0.9685 for 0.5 g, 0.9157 for 1 g, and 0.8289 for 1.5 g, as shown in Table 4.15. The results corroborated with the findings in DR adsorption Isotherms. Figure 4.22 shows the Temkin adsorption isotherms for CV dye removal using masses of 0.1 g, 0.5 g, 1 g, and 1.5 g of modified SMT.

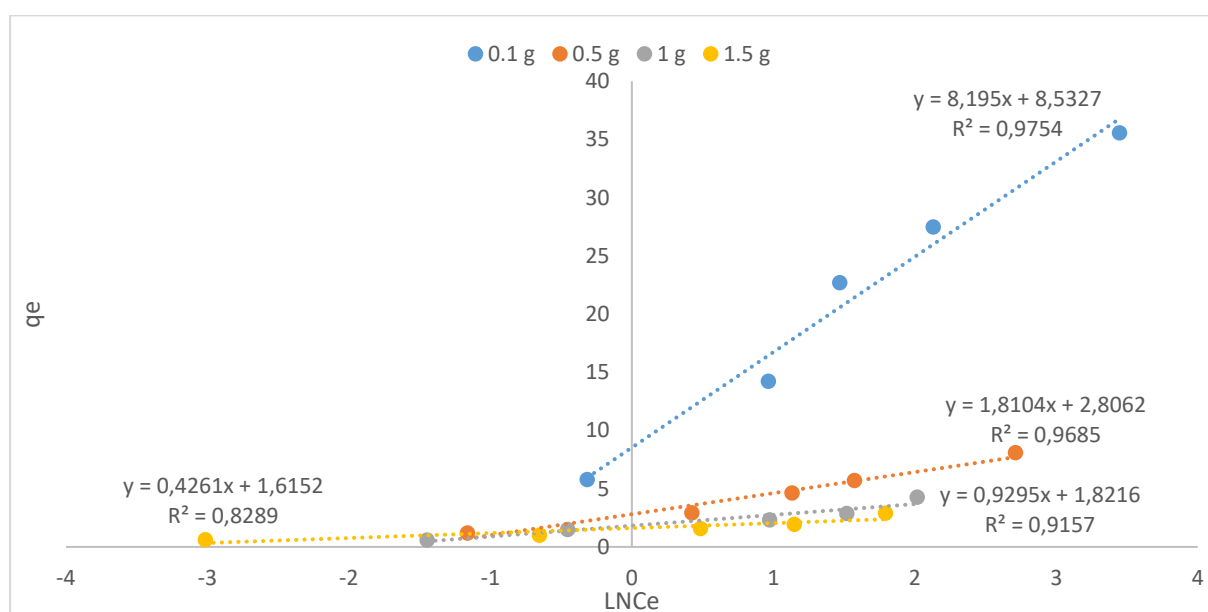


Figure 4.22: Temkin Adsorption Isotherm for CV dye removal using 0.1 g, 0.5 g, 1 g and 1.5 g of modified SMT

4.5 Kinetic Studies

Pseudo-first-order, Pseudo-second-order, Elovich, and intra-particle diffusion models were evaluated to show the dynamics and mechanisms of the adsorption process of MO and CV dye onto a modified SMT surface.

4.5.1 Pseudo-first-order model

Table 4.16 shows the parameters of Pseudo-first order for MO dye removal at various masses of modified SMT.

Table 4.16: Parameters of Psuedo-first order for MO dye removal using various masses (0.5 g, 1 g, and 2 g) of modified SMT.

Mass (g)	q_e (mg/g)	K_1 (min^{-1})	R^2
0.5	0.0655	0.0016	0.1068
1	0.0388	0.0011	0.0229
2	0.0355	0.0015	0.0444

For MO dye, the adsorption capacity of the adsorbent at equilibrium (q_e) was at 0.0655 mg/g for 0.5 g, 0.0388 mg/g for 1 g, and 0.0355 mg/g for 2 g. The first-order sorption rate constant (K_1) was at 0.0016 min^{-1} for 0.5 g, 0.0011 min^{-1} for 1 g, and 0.0015 min^{-1} g for 2 g. The pseudo-first-order kinetic model gave a linearized coefficient (R^2) of 0.1068 for 0.5 g, 0.0229 for 1 g, and 0.0444 for 2 g as shown in Table 4.16. It was noticed that the MO dye removal onto modified SMT does not obey the pseudo-first-order model. Figure 4.23 shows the Pseudo-first order for MO dye removal onto modified SMT.

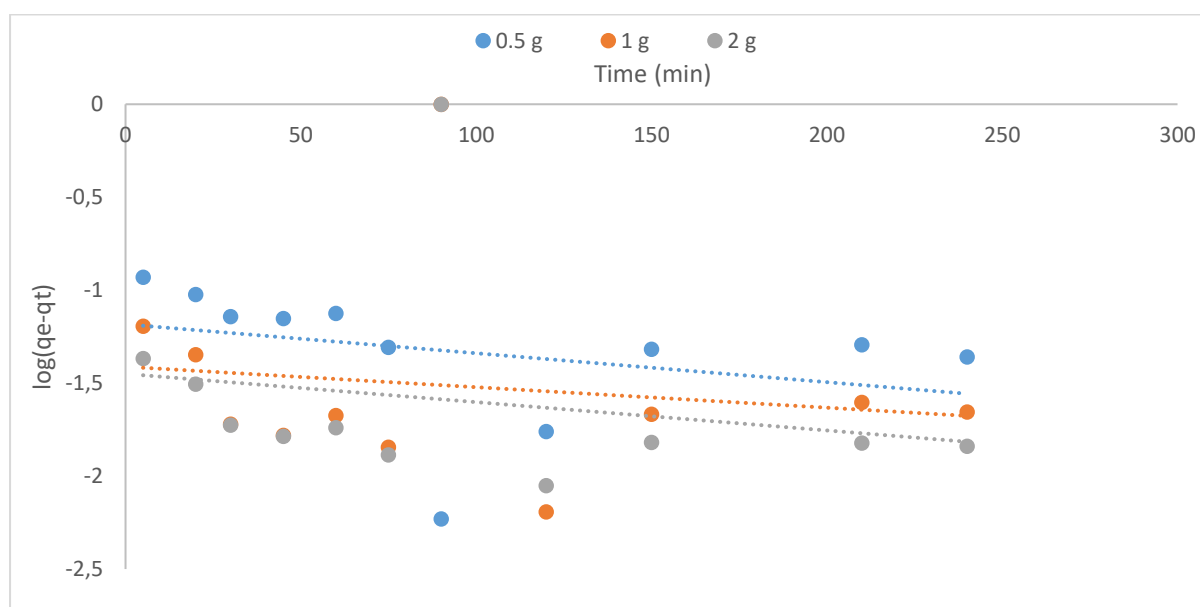


Figure 4.23: Pseudo-first order of MO dye removal onto modified SMT.

Table 4.17 shows the parameters of Pseudo first order for CV dye removal onto modified SMT.

Table 4.17: Parameters of Pseudo-first order for CV dye removal using 0.1 g of modified SMT

Mass (g)	q_e (mg/g)	K_1 (min^{-1})	R^2
0.1	0.0518	-0.0035	0.3024

For CV dye, the adsorption capacity of the adsorbent at equilibrium (q_e) was 0.0518 mg/g for 0.1g. The first-order sorption rate constant (K_1) was at -0.0035 min^{-1} as shown in Table 4.17. The linearized coefficient (R^2) value ($R^2 = 0.3024$) was lower as shown in Figure 4.24. This means the CV dye removal onto modified SMT does not obey the pseudo-first-order model. Figure 4.24 shows the pseudo-first-order model for CV dye removal onto modified SMT.

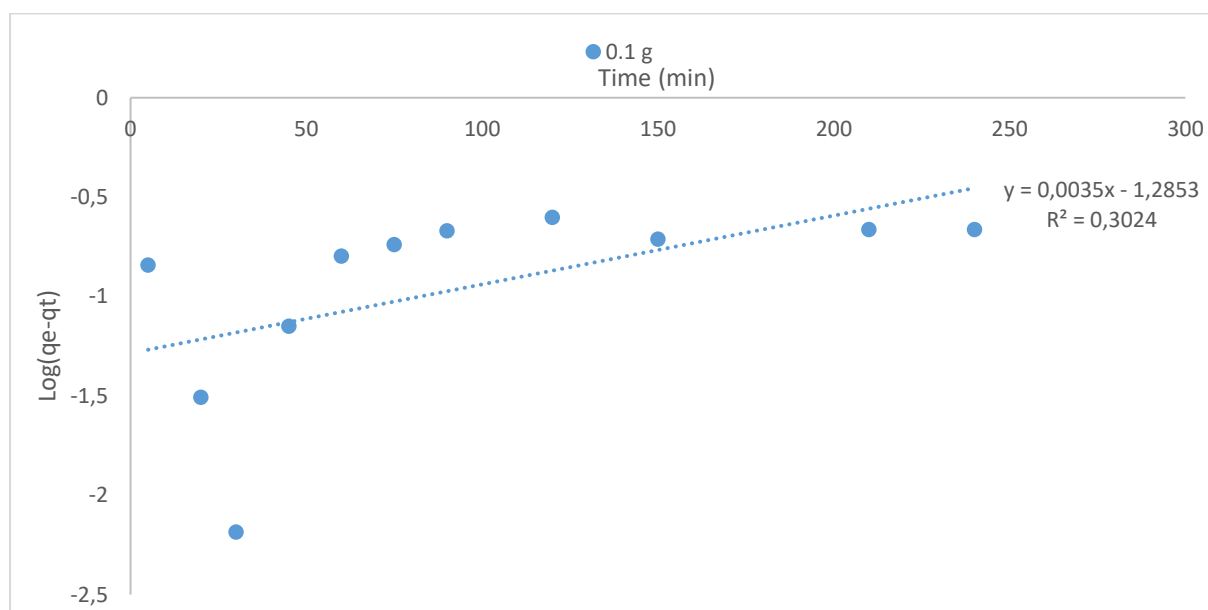


Figure 4.24: Pseudo-first order of CV dye removal onto modified SMT

4.5.2 Pseudo-second order model

Table 4.18 shows the parameters of Pseudo-second order for MO dye removal onto modified SMT.

Table 4.18: Parameters of Pseudo-second-order for MO dye removal onto modified SMT

Mass (g)	Calculated q_e (mg/g)	K_2 (g/mg min ⁻¹)	R^2
0.5	0.7095	2.2647	0.999
1	0.4506	-3.3341	0.9987
2	0.2607	-156.684	0.9994

For MO dye, the calculated q_e was 0.7095 mg/g for 0.5 g, 0.4506 mg/g for 1 g, and 0.2607 mg/g for 2 g. The experimental data agrees very well with this. The correlation between the calculated and experimental q_e values for MO dye adsorption confirms that the process adheres to the pseudo-second-order kinetic model, which is based on chemisorption as the controlling mechanism. The observed decline in q_e with increasing adsorbent dosage follows the expected adsorption pattern, where a greater number of available adsorption sites result in a lower adsorption capacity per unit mass. This consistency supports the applicability of the pseudo-second-order model in describing the adsorption kinetics, suggesting that the process is governed by strong chemical interactions, including electron transfer, ion exchange, or surface complexation (Abara *et al.*, 2021).

The constant speed of the adsorption model of pseudo-second order (k_2) recorded 2.2647 g/mg min⁻¹ for 0.5 g, -3.3341 g/mg min⁻¹ for 1 g, -156.684 g/mg min⁻¹ for 2 g as indicated in Table 4.18. The linearized coefficient (R^2) values were 0.999 for 0.5 g, 0.9987 for 1g, and 0.9994 for 2 g, as shown in Figure 4.25. Therefore, MO dye removal onto modified SMT obeys the pseudo-second-order-model. Figure 4.25 shows the pseudo-second-order for MO dye removal onto modified SMT.

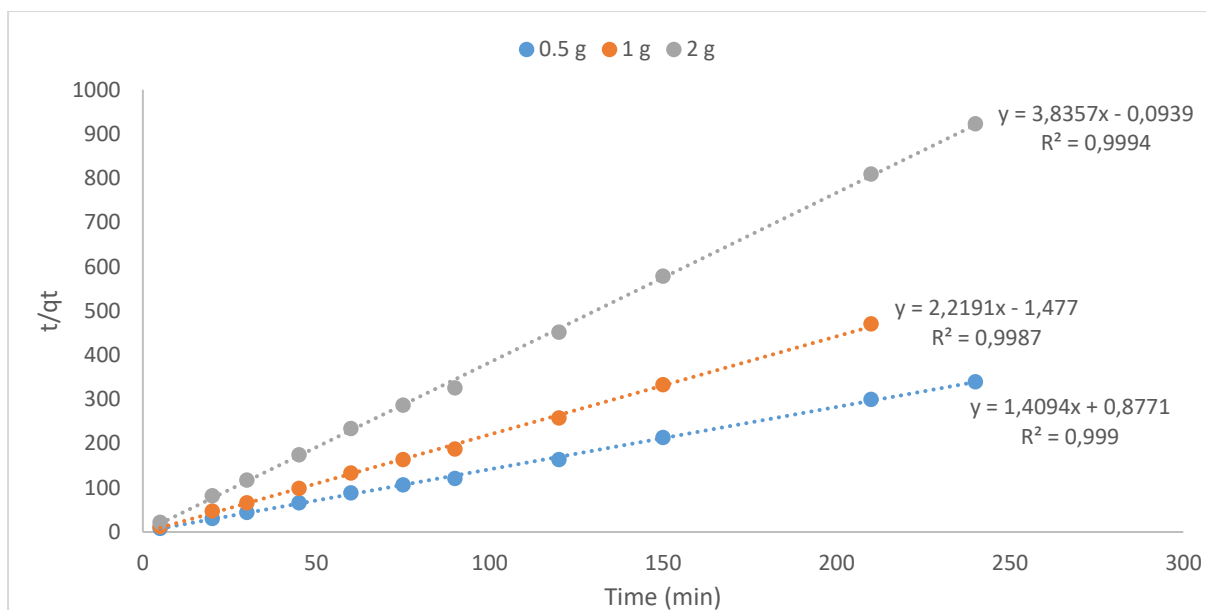


Figure 4.25: Pseudo-second-order for MO dye removal onto modified SMT

Table 4.19 shows the parameters of Pseudo second order for CV dye removal onto modified SMT.

Table 4:19: Parameters of Pseudo-second-order for CV dye removal onto modified SMT

Mass (g)	Calculated q_e (mg/g)	K_2 (g/mg min ⁻¹)	R^2
0.1	5.5463	-0.2671	1

The calculated q_e was at 5.5463 mg/g for 0.1 g of modified SMT for the removal of CV dye from the aqueous solution. It agrees very well with the experimental data. The constant speed of the adsorption model of pseudo-second-order (k_2) was at -0.2671 g/mg min⁻¹, as indicated in Table 4.19. The linearized coefficient (R^2) was at 1, as shown in Figure 4.26. This means CV dye removal onto modified SMT fits very well in the pseudo-second-order model. Figure 4.26 shows the pseudo-second-order for CV dye removal onto modified SMT. This indicates that electron transfer, ion exchange, or surface interactions are fundamental to the dye removal process, confirming that adsorption follows pseudo-second-order kinetics rather than being governed by physical diffusion (Ahmad and Ejaz, 2023).

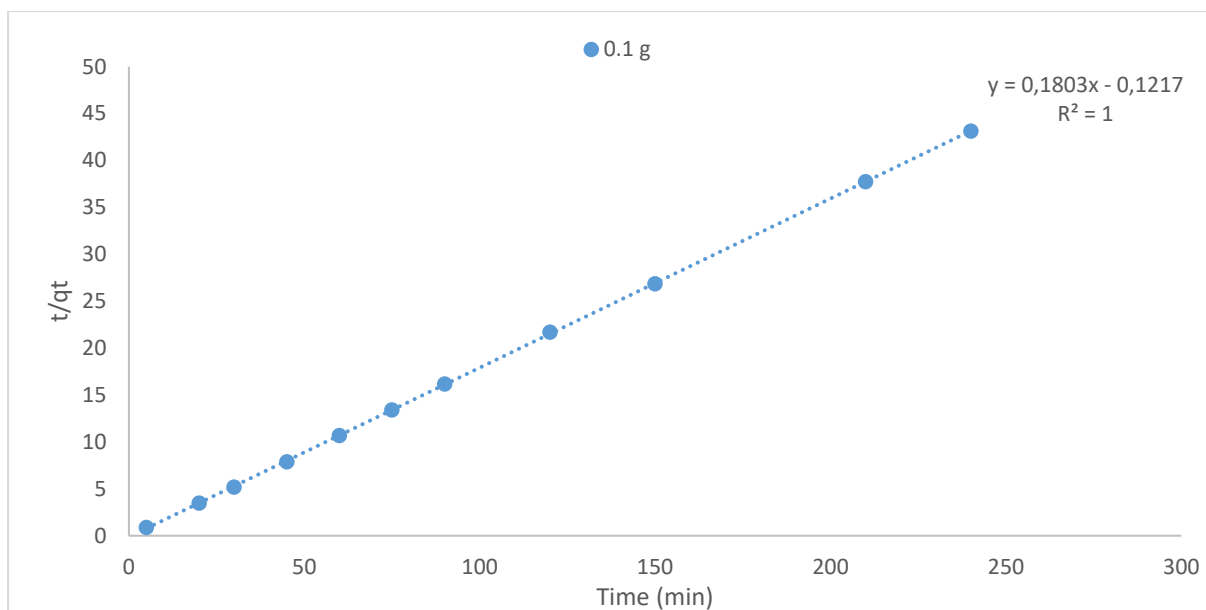


Figure 4.26: Pseudo-second-order for CV dye removal onto modified SMT

4.5.3 Elovich model

Table 4.20 shows the parameters of Elovich model for MO dye removal onto modified SMT.

Table 4.20: Parameters of Elovich Model of MO dye adsorption onto modified SMT.

Mass (g)	β (g/mg)	α (mg/g/min)	R^2
0.5	44.6428	9.41×10^9	0.6318
1	87.7193	2.33×10^{13}	0.4702
2	126.5823	1.67×10^{10}	0.6204

For MO dye, the initial adsorption rate (α) was 9.41×10^9 mg/g/min for 0.5 g, 2.33×10^{13} mg/g/min for 1 g, and 1.67×10^{10} mg/g/min for 2 g. The desorption constant (β) was 44.6428 g/mg for 0.5 g, 87.7193 g/mg for 1 g, and 126.5823 g/mg for 2 g, as shown in Table 4.20. The coefficient of determination (R^2) was 0.6318 for 0.5 g, 0.4702 for 1 g, and 0.6204 for 2g, as shown in Figure 4.27. The data does not follow the Elovich kinetic model. Figure 4.27 shows the Elovich plot for the adsorption of MO dye onto modified SMT.

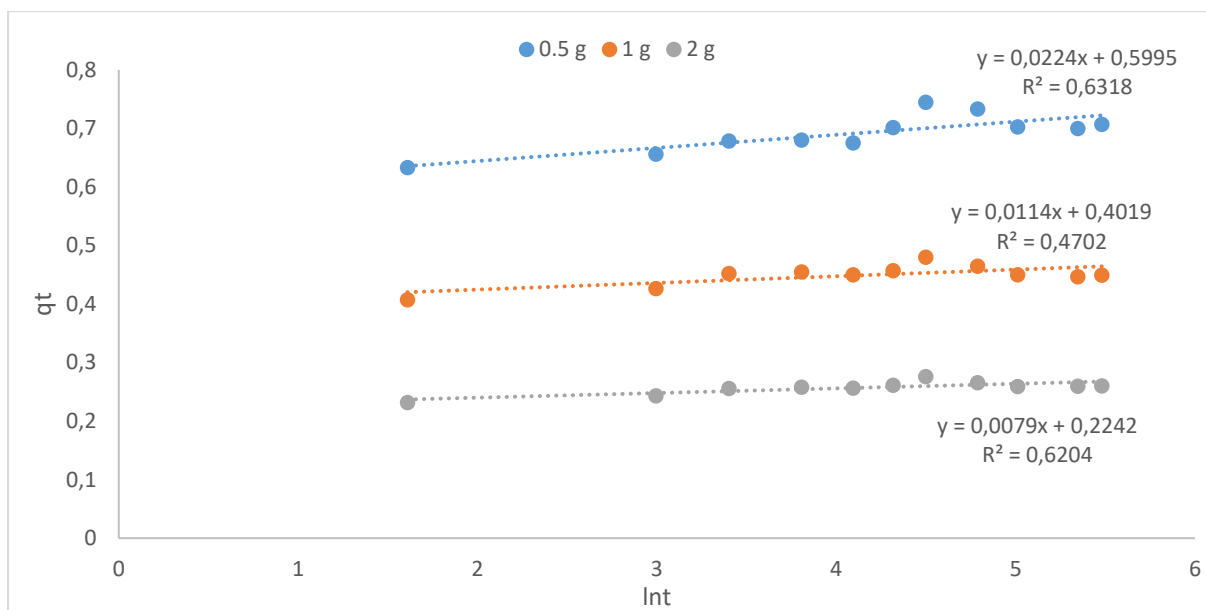


Figure 4.27: Elovich plot for MO dye onto modified SMT

Table 4.21 shows the parameters of Elovich model for CV dye adsorption onto modified SMT.

Table 4.21: Parameters of Elovich Model of CV dye adsorption onto modified SMT

Mass (g)	β (g/mg)	α (mg/g/min)	R^2
0.1	-22.0751	N/A	0.3958

For CV dye, the desorption constant (β) was -22.0751 g/mg for 0.1 g, as shown in Table 4.21. The R^2 was very low ($R^2 = 0.3958$), as shown in Figure 4.28. The data of CV dye adsorption onto modified SMT does not obey the Elovich kinetic model. Figure 4.28 Elovich plot for CV dye onto modified SMT.

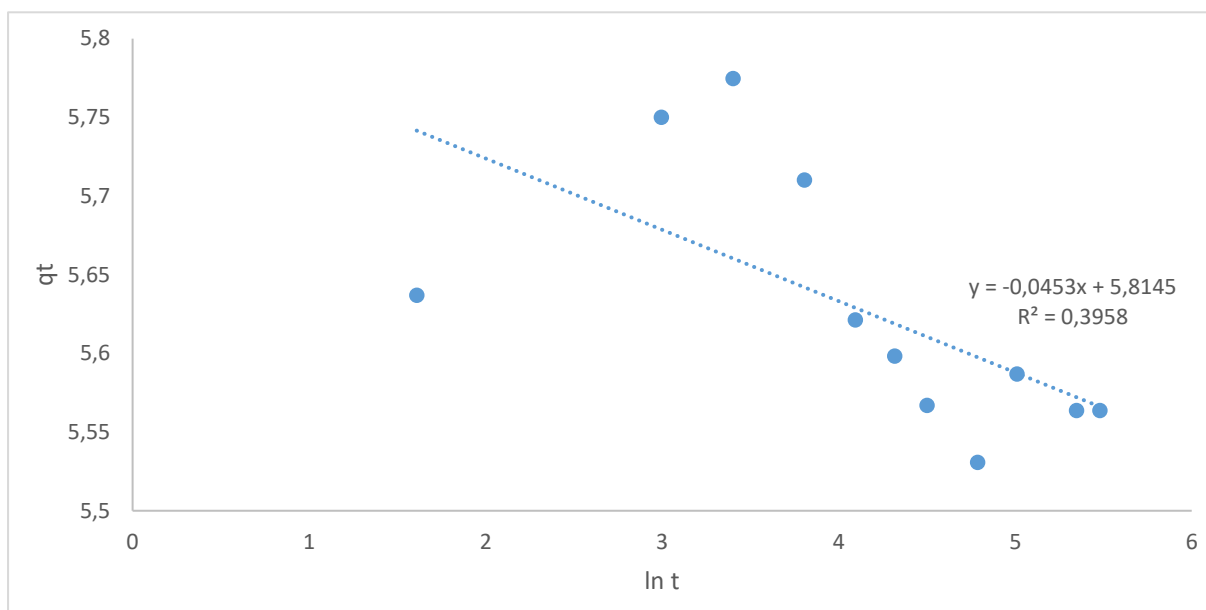


Figure 4.28: Elovich plot for CV dye onto modified SMT

4.5.4 Intra-particle diffusion model

Table 4.22 shows the parameters of intra-particle diffusion for MO dye adsorption onto the modified SMT.

Table 4.22: Parameters of intra-particle diffusion for MO dye onto modified SMT

Mass (g)	K_{ip} (mg/g. min ^{0.5})	C_{ip} (mg/g)	R^2
0.5 g	0.0054	0.6437	0.4897
1 g	0.0023	0.4287	0.248
2 g	0.0022	0.2381	0.4818

For MO dye, the intra-particle diffusion rate constant (K_{ip}) was 0.0054 mg/g.min^{0.5} for 0.5 g, 0.0023 mg/g.min^{0.5} for 1 g, and 0.0022 mg/g.min^{0.5} for 2 g. The constant (C_{ip}) was 0.6437 mg/g for 0.5 g, 0.4287 mg/g for 1 g, and 0.2381. The coefficients of determination (R^2) were 0.4897 for 0.5g, 0.248 for 1 g, and 0.4818 for 2 g, as shown in Table 4.22.

The intra-particle diffusion model for MO dye adsorption onto modified SMT suggests that the process is not mainly governed by diffusion within the particles, as shown by the relatively low R^2 values. The reduction in K_{ip} and C_{ip} with increasing adsorbent mass indicates that diffusion plays a less important role as the adsorbent quantity rises. This implies that other mechanisms, such as external mass transfer or surface adsorption, might be affecting the overall adsorption

process. Figure 4.29 shows the intra-particle diffusion plot for MO dye adsorption onto the modified SMT.

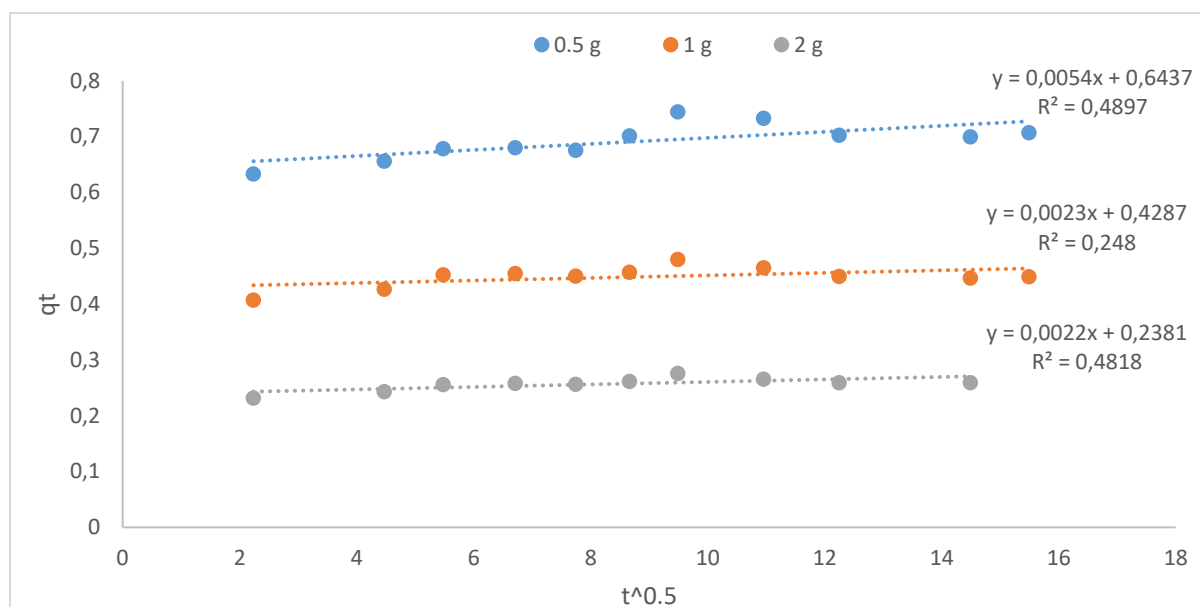


Figure 4.29: The intra-particle diffusion plot of MO dye removal onto modified SMT

Table 4.23 shows the parameters of intra-particle diffusion for CV dye removal onto modified SMT.

Table 4.23: Parameters of intra-particle diffusion for CV dye removal onto modified SMT

Mass (g)	K_{ip} (mg/g. min ^{0.5})	C_{ip} (mg/g)	R^2
0.1	-0.0141	5.7528	0.5063

For CV dye, the intra-particle diffusion rate constant (K_{ip}) was -0.0141 mg/g.min^{0.5} for 0.1 g. The constant (C_{ip}) was 5.7528 mg/g. The R^2 was 0.5063 as shown in Table 4.23. The negative K_{ip} value and the low R^2 indicate that the intra-particle diffusion model does not fit on CV dye removal process on modified SMT. This suggests that the adsorption may not be primarily driven by intra-particle diffusion, and other factors, such as surface adsorption or external mass transfer, could be more influential in the process. Figure 4.30 shows the intra-particle diffusion plot for CV dye removal onto the modified SMT.

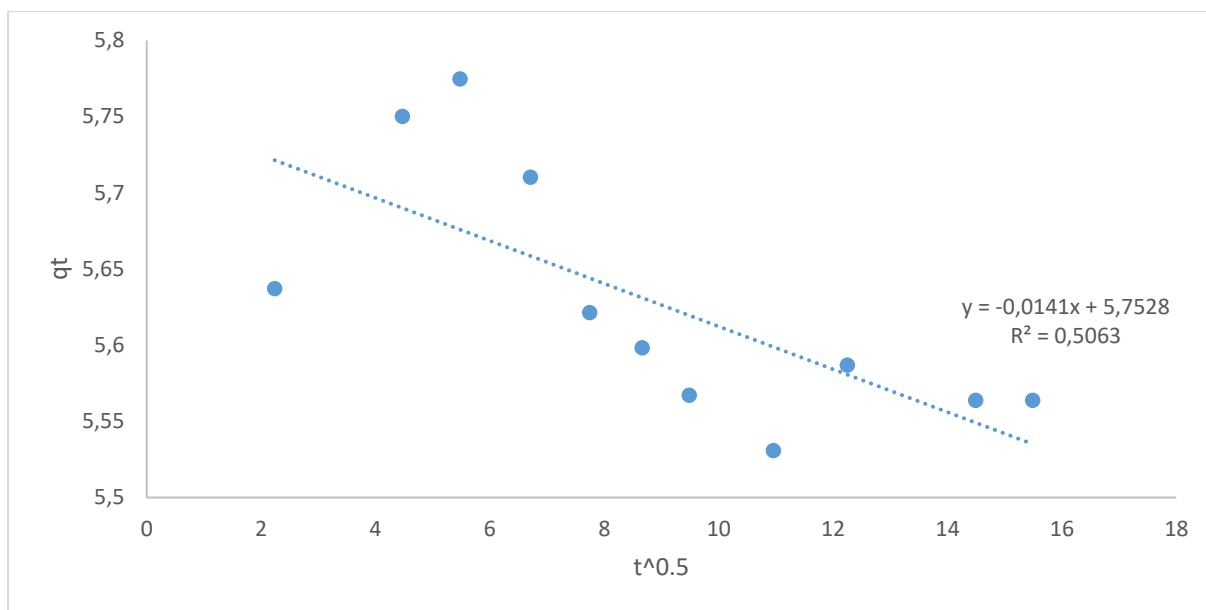


Figure 4.30: The intra-particle diffusion plot of CV dye removal onto modified SMT

4.6 Thermodynamics Studies

Table 4.24 shows the parameters of thermodynamics for MO dye removal onto modified SMT.

Table 4.24: Parameters of thermodynamics for MO dye removal onto modified SMT

Mass (g)	Temperature (°C)	Temperature (K)	ΔH (kJ/mol)	ΔS (J/mol/K)	ΔG (kJ/mol)
1.5	30	303.15	-47.7157	-0.1709	4.09341
	40	313.15			5.802435
	50	323.15			7.511461
	60	333.15			9.220487
	70	343.15			10.92951
	80	353.15			12.63854

For MO dye, the approximate thermodynamics values are shown in Table 4.24. The study includes the temperatures from 303.15 K to 353.15 K. The change in enthalpy (ΔH) value was -47.7157 kJ/mol, and the change in entropy (ΔS) value was -0.1709 J/mol/K. The Gibbs free energy (ΔG) recorded positive values at all working temperatures. This means that the adsorption was non-spontaneous, and it needs to be provided with energy (Badran *et al.*, 2024). The negative value of ΔH reveals that the adsorption process was exothermic (Khan *et al.*, 2024). If ΔS is negative, the reaction decreases entropy and is favoured in the direction that reduces disorder. The Van't Hoff plot of $\ln K_d$ against $1/T$ (K) gives a linear graph with a coefficient (R^2) of 0.9758, as shown in Figure 4.31.

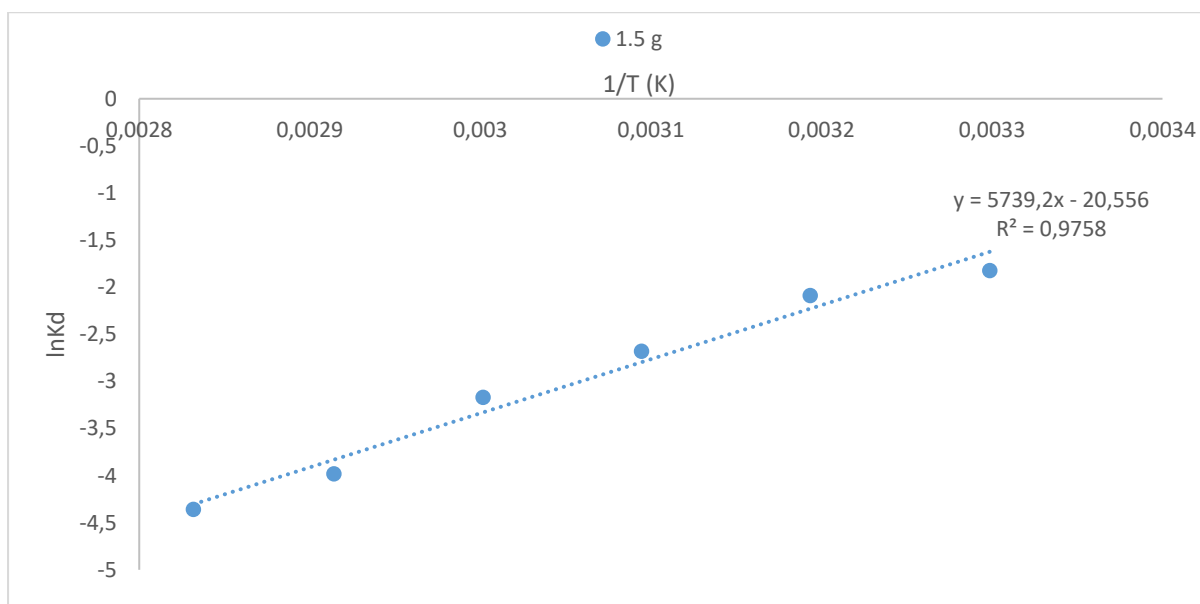


Figure 4.31: The thermodynamics plot of MO dye removal onto modified SMT

Table 4.25 shows the parameters of thermodynamics for CV dye removal onto modified SMT.

Table 4.25: Parameters of thermodynamics for CV dye removal onto modified SMT

Mass (g)	Temperature (°C)	Temperature (K)	ΔH (kJ/mol)	ΔS (J/mol/K)	ΔG (kJ/mol)
0.1	30	303.15	22.64318	0.091163	-4.99289
	40	313.15			-5.90452
	50	323.15			-6.81615
	60	333.15			-7.72778
	70	343.15			-8.63941
	80	353.15			-9.55104

For CV dye, the thermodynamic parameters are presented in Table 4.25. The change in enthalpy (ΔH) value was 22.64318 KJ/mol, and the change in entropy (ΔS) value was 0.091163 J/mol/K. The Gibbs free energy (ΔG) recorded negative values at all working temperatures (303.15 K to 353.15 K). This means that the adsorption was spontaneous and feasible (Huerta-Ángeles *et al.*, 2024). The positive value of ΔH reveals that the adsorption process was endothermic (Arshad *et al.*, 2024). If ΔS is positive, the reaction increases entropy and is favoured in the direction that increases disorder. The Van't Hoff plot of $\ln k_d$ against $1/T$ (K) gives a linear graph with a coefficient (R^2) of 0.9544, as shown in Figure 4.32.

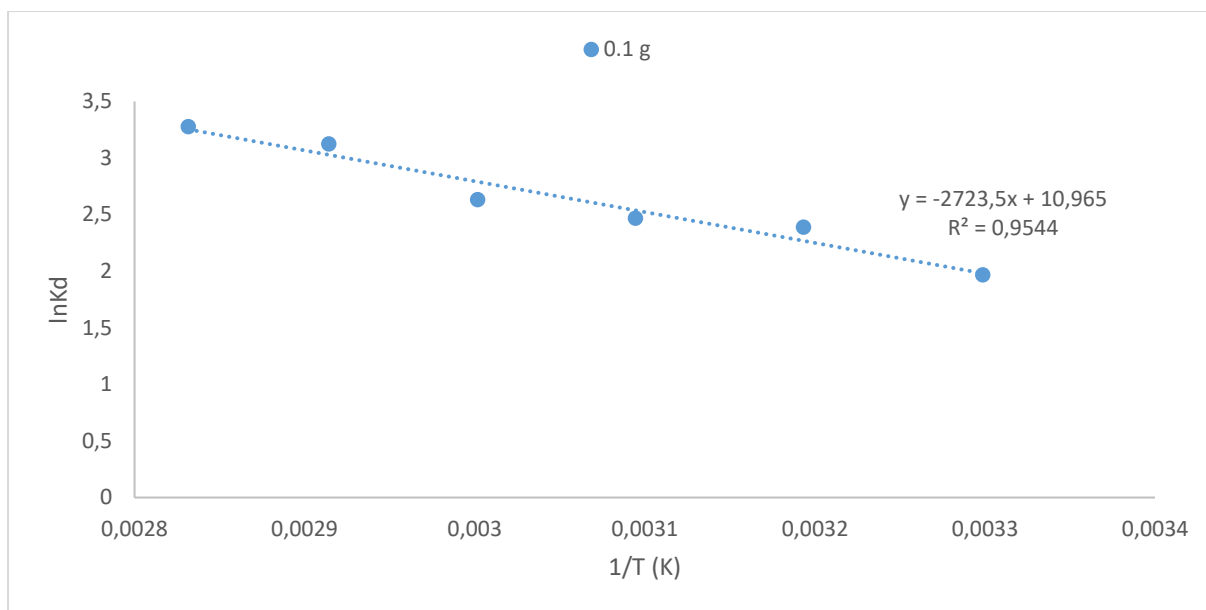


Figure 4.32: The thermodynamics plot of CV dye removal onto modified SMT

4.7 Desorption and Regeneration

Desorption cycles were examined to assess the regeneration potential of the adsorbent. Figures 4.33 and 4.34 show different reagents/ chemical solvents used to test the desorption process on MO-loaded modified SMT and CV-loaded modified SMT respectively.

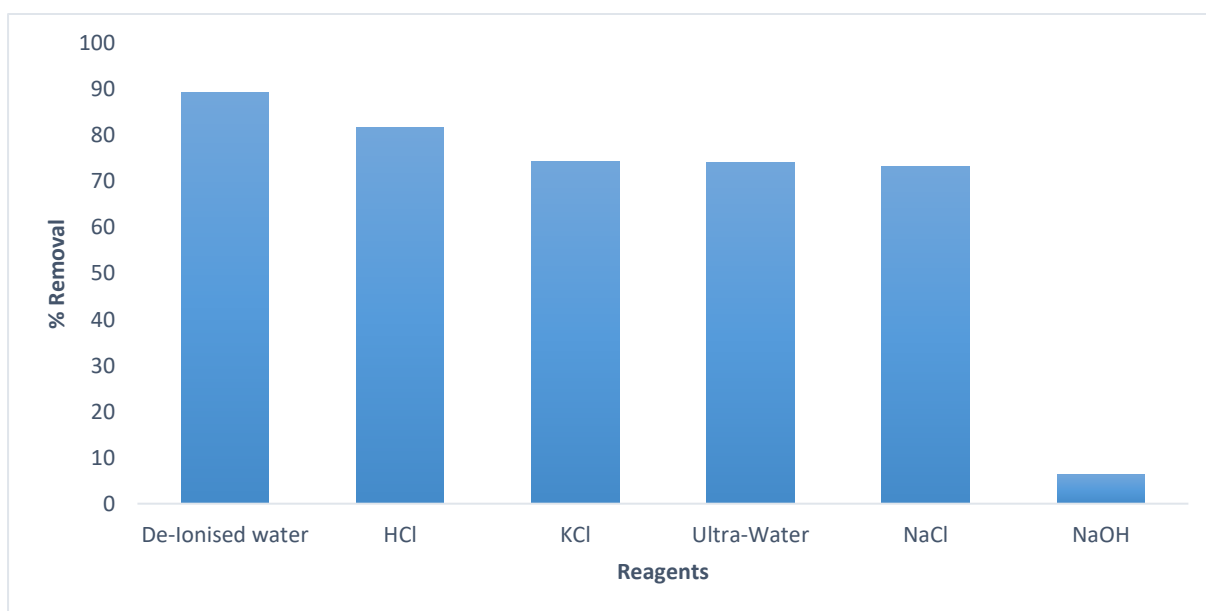


Figure 4.33: Desorption and testing reagent for MO textile dye (initial dye concentration = 20 mg/L, time = 90 min, mass = 2 g, volume = 30 mL, shaking speed = 250 rpm, temperature = 30 °C).

The percentage removal for MO dye was recorded as follows: 89.225 % for de-ionized water, 81.8 % for HCl, 74.265 % for KCl, 74.11 % for Ultra-water, 73.35 % for NaCl, and 6.25 % for NaOH as indicated in Figure 4.33. The descending order trend of reagents goes this way: de-ionized water > HCl > KCl > Ultra-pure water > NaCl > NaOH. The second solvent that follows De-ionized water is hydrochloric acid (HCl). Anionic dye molecules are attracted towards positively charged particles on the surface of the adsorbent. HCl and KCl are effective in desorbing anionic dye molecules by competing for the adsorbent's binding sites. H^+ ions from HCl neutralizes the surface's positive charge, while K^+ ions from KCl displace the dye molecules. Conversely, NaOH is less effective as OH^- ions increase the surface's negative charge, strengthening dye retention. Thus, the desorption efficiency depends on the reagent used. Figure 4.34 shows the desorption and the testing reagents for CV textile dye.

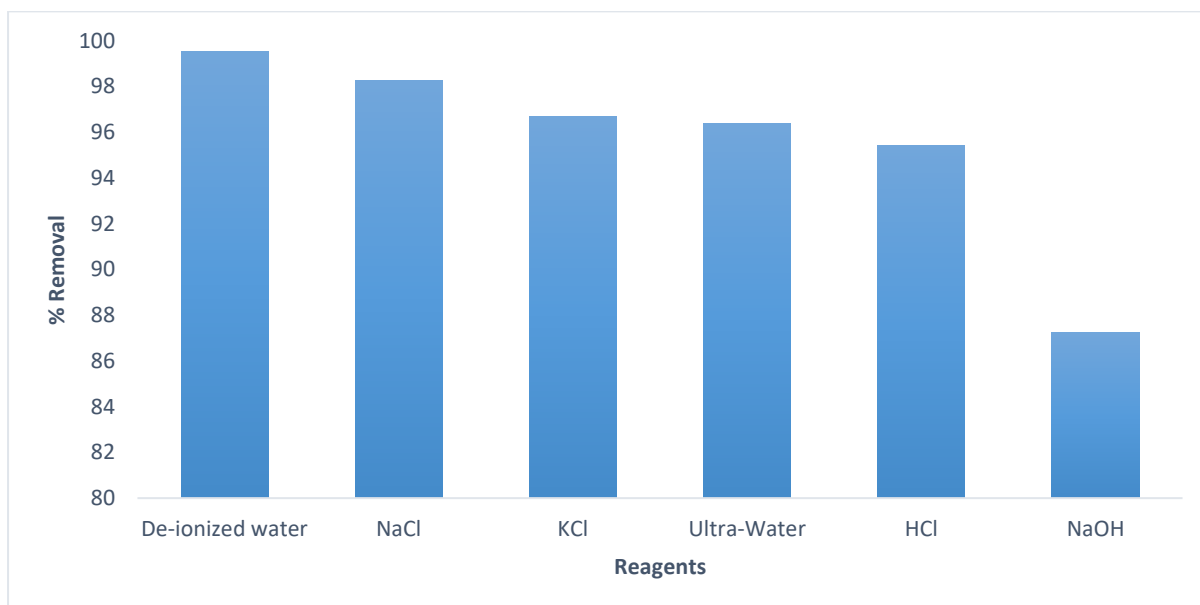


Figure 4.34: Desorption and testing reagent for CV textile dye (initial dye concentration = 20 mg/L, time = 30 min, mass = 0.15 g, volume = 30 mL, shaking speed = 250 rpm, temperature = 30 °C).

The percentage removal of CV dye was recorded as follows: 99.54 % for de-ionized water, 98.275 % for NaCl, 96.67 % for KCl, 96.36 % for Ultra-pure water, 95.4 % for HCl, and 87.26 % for NaOH as indicated in Figure 4.34. The descending order trend of reagents goes this way: De-ionized water > NaCl > KCl > Ultra-pure water > HCl > NaOH. Desorption of CV dye may take place due to the electrostatic repulsion and the surface of an adsorbent. Cationic dye (CV)

molecules are attracted toward the negatively charged surface of the adsorbent (Mohammad and Suzylawati, 2020). The de-ionized water recorded the highest percentage of removal for both MO and CV dyes. This happens because de-ionized water does not have ions that will compete with dye molecules when it interacts with the adsorbent. The pH of de-ionized water is neutral, making it easy to interact with acidic and basic dyes and suitable for continuing the process of regeneration.

The process of regeneration is important in adsorption studies because it allows an adsorbent to be regenerated and used again. De-ionized water was used as a reagent to wash the adsorbent after every cycle. Each cycle was triplicated to validate the results. It was noted that as the adsorbent was continuously used, the percentage removal of textile dyes decreased. Figure 4.35 shows the regeneration of Modified-SMT on MO textile dye with 4 cycles, and the experiment was done using an initial mass of 2 g of Modified-SMT loaded with MO dye. However, as the cycle continues, the mass of an adsorbent keeps on reducing.

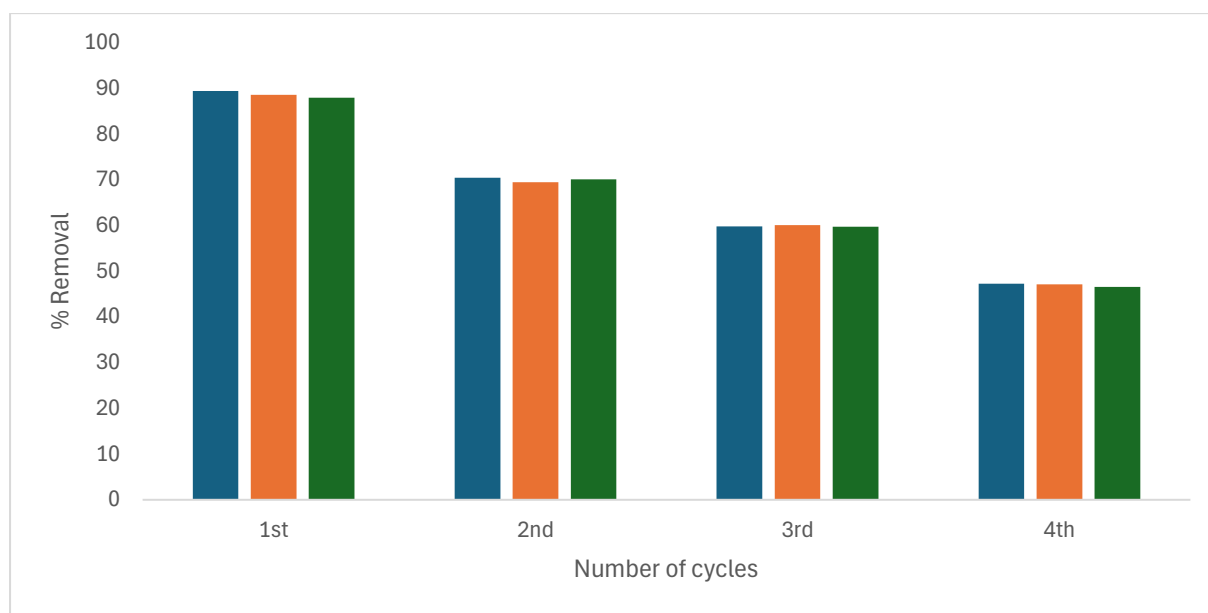


Figure 4.35: Regeneration of Modified-SMT on MO textile dye (Conditions: Initial dye concentration = 20 mg/L, initial mass of modified SMT = 2 g, time = 90 minutes, volume = 30 mL, shaking speed = 250 rpm, temperature = 30 °C).

After every cycle, the adsorbent was washed with de-ionized water and dried in an oven at 90 °C for 8 hours. Figure 4.36 shows the regeneration trend of Modified-SMT on CV textile dye with 4 cycles. The experiment was done using the initial mass of 0.15 g of Modified SMT loaded with CV dye. However, as the cycle continues the mass of an adsorbent keeps on reducing.

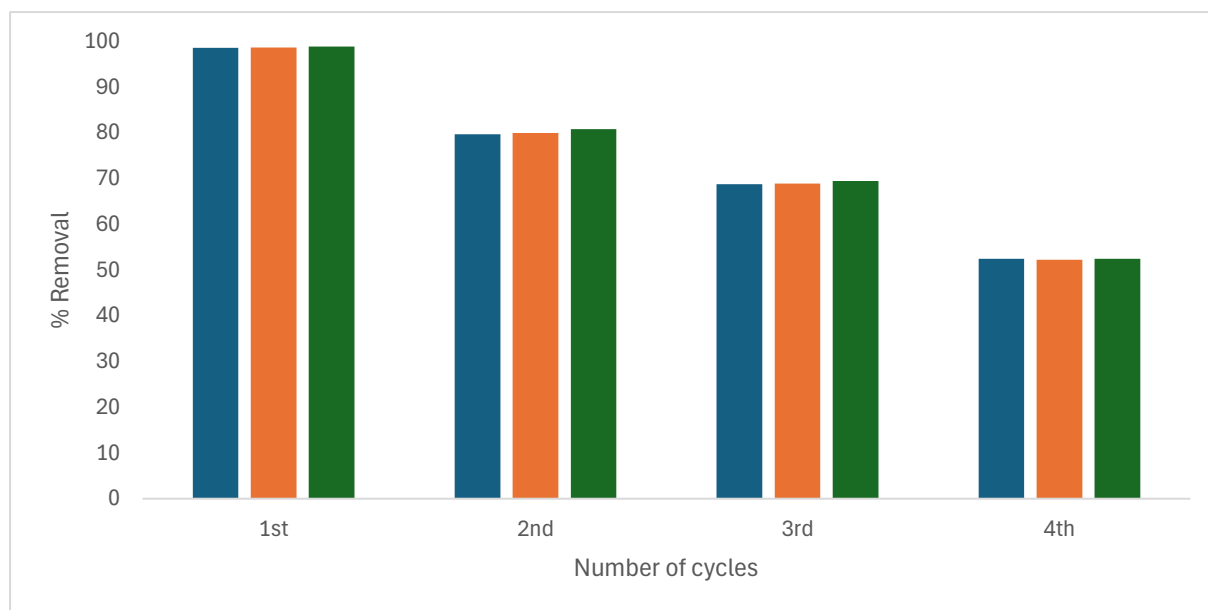


Figure 4.36: Regeneration of Modified-SMT on CV textile dye (Conditions: Initial dye concentration = 20 mg/L, initial mass of SMT = 0.15 g, time = 30 minutes, volume = 30 mL, shaking speed = 250 rpm, temperature = 30 °C).

After every cycle, an adsorbent was washed with de-ionized water and dried in an oven at 90 °C for 8 hours. The regenerated adsorbent maintained high-adsorption retention effectiveness after 4 cycles toward the MO and CV textile dye.

4.8 Proposed mechanisms of MO and CV dye adsorption onto modified SMT

The introduction of Mn^{2+}/Al^{3+} onto the surface of smectite (Mukondeni clay soil) lead to these possible mechanisms of MO and CV dye adsorption onto modified SMT. The adsorption of methylene orange (MO) and crystal violet (CV) dyes onto modified SMT (smectite clay) is driven by a variety of physical and chemical interactions (Alorabi *et al.*, 202; Al Kausor *et al.*, 2022). Electrostatic attraction is a major factor, with MO, being negatively charged, attracted to the positively charged surface of modified SMT, while CV, which is positively charged, is

drawn to the negatively charged surface of the clay (Al Kausor *et al.*, 2022; Ouachtak *et al.*, 2023). In addition, van der Waals forces contribute to the adsorption process, as weak interactions between the dye molecules and the clay's surface help secure the dyes, particularly when the clay has a large surface area and plenty of available adsorption sites (Zhang *et al.*, 2021). Ion exchange also plays a significant role, particularly for MO, as the clay exchanges its cations for the anionic dye molecules, which increases the adsorption (Avila *et al.*, 2021). Surface complexation occurs when the active sites on modified SMT, such as hydroxyl or metal ions, form complexes with the dye molecules, further enhancing the adsorption (Wang *et al.*, 2024)

Other mechanisms, such as hydrogen bonding, also help the process, especially with dyes like MO, which contain functional groups that can form bonds with the hydroxyl groups on the clay surface (Mokhtar *et al.*, 2024). Additionally, surface adsorption allows dyes to be adsorbed not only on the outer surface of the clay particles but also within the internal mesopores or micropores (Paredes-Quevedo *et al.*, 2021). These mechanisms work together to improve the overall adsorption capacity of modified SMT for both MO and CV dyes. The effectiveness of each mechanism depends on factors like the specific modifications made to the clay, the properties of the dye, and environmental conditions such as pH and temperature (George *et al.*, 2024).

4.9 Comparison of modified SMT with other clays on MO and CV dye adsorption.

Conducting a comparison of various clay-based adsorbents for the removal of Crystal Violet (CV) and Methyl Orange (MO) dyes is important to assess their performance and suitability under batch experimental conditions. This type of analysis not only evaluates how well each material removes dyes but also provides insight into their regeneration potential, which is vital for long-term and practical use. Comparing these adsorbents helps determine their feasibility for large-scale application, particularly in industrial wastewater treatment. Materials that show both high adsorption efficiency and strong regenerative capacity over multiple cycles are more likely to be recommended for industrial implementation (El Messaoudi *et al.*, 2024). Table 4.26 shows the comparison of modified SMT with other clay materials for MO and CV dye adsorption.

Table 4.26: Comparison of modified SMT with other clay on MO and CV dye adsorption

Parameters	CV dye - Modified SMT	CV - Magnetized Bentonite (Ahmed & Nasar, 2024)	MO - Modified SMT	MO - Modified Moroccan Clay (Abbou <i>et al.</i> , 2023)
Max Adsorption Efficiency (%)	96.25	93.97	91.95	99
Adsorbent Dose (g)	0.1	Not provided	2	0.5
Contact Time (min)	30	80	90	60
Temperature (°C)	30	30	30	Not provided
Best Desorbing Agent	Deionized water	0.1 M HCl	Deionized water	0.1 M HCl
Best Desorption Efficiency (%)	99.54	84.2	89.26	98
Desorption After 4th Cycle (%)	52.29 to 52.50	58.3	44.25 to 47.1	82
Number of Regeneration Cycles	4 cycles (triplicated)	4 cycles	4 cycles (triplicated)	5 cycles
Regeneration Validated by Repeats	Yes	Not provided	Yes	Not provided
Industrial Application Potential	Recommended	Recommended	Recommended	Recommended

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The research showed that acidic (Methyl Orange, MO) and basic (Crystal Violet, CV) dyes could be removed by Modified-SMT from an aqueous solution. Ratio 1:3 of Modified-SMT was found to have the highest percentage removal of MO and CV dyes than other ratios. It was selected to continue with the batch experiments because of its effectiveness towards the decolouration of both MO and CV dyes. The increased porosity and surface area of Modified-SMT is essential for its role as an adsorbent, with modifications creating more active sites for dye molecules to bond. Its layered structure forms small pores that capture dye molecules, aiding in the adsorption process. When these layers expand through modification, it further boosts the surface area, enhancing the material's ability to remove dyes. At a contact time of 90 minutes, the Modified-SMT achieved the highest percentage of MO dye removal from the aqueous solution. Conversely, at a contact time of 30 minutes, the Modified-SMT showed the highest percentage of CV dye removal from the aqueous solution. The adsorbent (Modified-SMT) was found to be effective at pH 2 when removing both MO and CV dyes. BET characterization recorded the BET surface area of 30.0321 m²/g for Raw-SMT and 35.2951 m²/g for Modified-SMT. This suggests that the modification process expanded the surface area of the clay, improving its ability to adsorb dyes. The XRF analysis reveals that the Raw-SMT had the highest oxide compositions of Al₂O₃ (16.95%) and SiO₂ (64.42%) while Modified-SMT had highest oxide compositions of Al₂O₃ (18.42%) and SiO₂ (61.08%) respectively. This implies that the modification process changed the chemical composition of the clay, which could enhance its ability to adsorb. The increased Al₂O₃ content in the modified clay may facilitate better interactions with dye molecules, thereby improving the adsorption efficiency of Modified-SMT. For both MO and CV dyes the pseudo-second order kinetic model best described the kinetic data, while the Langmuir model accurately represented the equilibrium data. Thermodynamic studies reveal that the adsorption process of MO dye is non-spontaneous and exothermic, while the adsorption of CV dye is spontaneous and endothermic. The regeneration process proved effective over four cycles, showing that Modified-SMT can be reused several times with a significant decrease in its adsorption capacity. This suggests it could be a sustainable and cost-efficient option for dye removal applications. The Mn²⁺/Al³⁺ oxide-modified smectite performed well in removing dyes under controlled settings. However, in actual wastewater, the presence of competing ions like Ca²⁺, Mg²⁺, and Cl⁻ could interfere with adsorption by affecting active sites or surface charge. Since the material operates through ion

exchange and electrostatic forces, its efficiency should be further tested in complex, real-world systems.

5.2 Recommendations

1. **Adopt Modified-SMT as an effective adsorbent:** Given its ability to effectively remove Methyl Orange (MO) and Crystal Violet (CV) dyes, Modified-SMT should be considered for wastewater treatment.
2. **Investigate other contaminants:** Exploring the ability of Modified-SMT to adsorb other pollutants could increase its applicability in environmental remediation.
3. **Evaluate in real-world settings:** Testing Modified-SMT in practical wastewater treatment environments will help assess its real-world performance and efficiency.

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APPENDIX

A1: The percentage (%) removal of Methyl Orange (MO) dye using various ratios and masses of Mn^{2+}/Al^{3+} modified Smectite Black Mukondeni Clay. (Conditions: Initial Concentration = 20 mg/L, temperature = 30 °C, time = 30 minutes, shaking speed = 250 rpm, Volume = 30 mL).

Ratio 1:1

Mass (g)	Ci (mg/L)	Cf (mg/L)	Removal (%)
0	0	0	0
0.1	20	17.586	12.07
0.5	20	12.7	36.5
1	20	7.473	62.635
1.5	20	5.512	72.44

Ratio 1:2

Mass (g)	Ci (mg/L)	Cf (mg/L)	Removal (%)
0	0	0	0
0.1	20	17.413	12.933
0.5	20	11.84	40.8
1	20	7.717	61.413
1.5	20	5.086	74.566

Ratio 1:3

Mass (g)	Ci (mg/L)	Cf (mg/L)	Removal (%)
0	0	0	0
0.1	20	16.468	17.66
0.5	20	8.84	55.8
1	20	4.692	76.54
1.5	20	3.508	82.46

Ratio 1:4

Mass (g)	Ci (mg/L)	Cf (mg/L)	Removal (%)
0	0	0	0
0.1	20	17.646	11.77
0.5	20	12.16	39.2
1	20	8.334	58.33
1.5	20	5.33	73.35

Ratio 1:5

Mass (g)	Ci (mg/L)	Cf (mg/L)	Removal (%)
0	0	0	0
0.1	20	16.056	19.72
0.5	20	14.914	25.43
1	20	11.034	44.83
1.5	20	5.328	73.36

Ratio 2:1

Mass (g)	Ci (mg/L)	Cf (mg/L)	Removal (%)
0	0	0	0
0.1	20	17.566	12.17
0.5	20	14.273	28.635
1	20	11.5	42.5
1.5	20	9.493	52.535

Ratio 3:1

Mass (g)	Ci (mg/L)	Cf (mg/L)	Removal (%)
0	0	0	0
0.1	20	17.668	11.66
0.5	20	14.653	26.735
1	20	12.893	35.535
1.5	20	11.22	43.9

Ratio 3:2

Mass (g)	Ci (mg/L)	Cf (mg/L)	Removal (%)
0	0	0	0
0.1	20	17.166	14.17
0.5	20	11.786	41.066
1	20	7.686	61.566
1.5	20	5.3	73.5

Ratio 5:1

Mass (g)	Ci (mg/L)	Cf (mg/L)	Removal (%)
0	0	0	0
0.1	20	17.334	13.33
0.5	20	12.033	39.83
1	20	7.693	61.533
1.5	20	5.127	74.363

Mass (g)	Ratio 1:1	Ratio 1:2	Ratio 1:3	Ratio 1:4	Ratio 1:5	Ratio 2:1	Ratio 3:1	Ratio 3:2	Ratio 5:1
0.1	12.07	12.933	17.66	11.77	19.72	12.17	11.66	14.17	13.33
0.5	36.5	40.8	55.8	39.2	25.43	28.635	26.735	41.066	39.83
1	62.635	61.413	76.54	58.33	44.83	42.5	35.535	61.566	61.533
1.5	72.44	74.566	82.46	73.35	73.36	52.535	43.9	73.5	74.363

A2: The percentage (%) removal of Crystal Violet (CV) dye using various ratios and masses of Mn²⁺/Al³⁺ modified Smectite Black Mukondeni Clay. (Conditions: Initial Concentration = 20 mg/L, temperature = 30 °C, time = 30 minutes, shaking speed = 250 rpm, Volume = 30 mL).

Ratio 1:1

Mass (g)	Ci (mg/L)	Cf (mg/L)	Removal (%)
0.01	20	8.848	55.76
0.03	20	7.366	63.17
0.05	20	6.346	68.27
0.1	20	5.044	74.78

Ratio 1:2

Mass (g)	Ci (mg/L)	Cf (mg/L)	Removal (%)
0.01	20	7.694	61.53
0.03	20	6.724	66.38
0.05	20	5.54	72.3
0.1	20	4.412	77.94

Ratio 1:3

Mass (g)	Ci (mg/L)	Cf (mg/L)	Removal (%)
0.01	20	6.872	65.64
0.03	20	4.502	77.49
0.05	20	1.958	90.21
0.1	20	0.714	96.43

Ratio 1:4

Mass (g)	Ci (mg/L)	Cf (mg/L)	Removal (%)
0.01	20	8.232	58.84
0.03	20	7.066	64.67
0.05	20	6.35	68.25
0.1	20	4.916	75.42

Ratio 1:5

Mass (g)	Ci (mg/L)	Cf (mg/L)	Removal (%)
0.01	20	9.464	52.68
0.03	20	8.16	59.20
0.05	20	7.278	63.61
0.1	20	6.35	68.25

Ratio 2:1

Mass (g)	Ci (mg/L)	Cf (mg/L)	Removal (%)
0.01	20	7.564	62.18
0.03	20	6.908	65.46
0.05	20	5.434	72.83
0.1	20	4.744	76.28

Ratio 3:1

Mass (g)	Ci (mg/L)	Cf (mg/L)	Removal (%)
0.01	20	8.924	55.38
0.03	20	7.914	60.43
0.05	20	6.902	65.49
0.1	20	4.202	78.99

Ration 3:2

Mass	Ci	Cf	Removal
(g)	(mg/L)	(mg/L)	(%)
0.01	20	7.106	64.47
0.03	20	6.146	69.27
0.05	20	4.696	76.52
0.1	20	3.206	83.97

Ratio 5:1

Mass	Ci	Cf	Removal
(g)	(mg/L)	(mg/L)	(%)
0.01	20	8.378	58.11
0.03	20	6.834	65.83
0.05	20	5.268	73.66
0.1	20	3.706	81.47

Mass	Ratio	Ratio	Ratio	Ratio	Ratio	Ratio	Ratio	Ratio	Ratio
(g)	1:1	1:2	1:3	1:4	1:5	2:1	3:1	3:2	5:1
0.01	55.76	61.53	65.64	58.84	52.68	62.18	55.38	64.47	58.11
0.03	63.17	66.38	77.49	64.67	59.2	65.46	60.43	69.27	65.83
0.05	68.27	72.3	90.21	68.25	63.61	72.83	65.49	76.52	73.66
0.1	74.78	77.94	96.43	75.42	68.25	76.28	78.99	83.97	81.47

B1: Effect of contact time on MO textile dye removal. (Conditions: initial concentration = 20 mg/L, temperature = 30 °C, time = 5 to 250 minutes, shaking speed = 250 rpm, volume = 30 ML, masses = 0.1 g to 2 g).

Time (Min)	Mass (g)	Ci (mg/l)	Cf (mg/l)	% Removal
0	0	0	0	0
5	0.1	20	16.98	15.1
20	0.1	20	16.54	17.3
30	0.1	20	16.39	18.05
45	0.1	20	16.36	18.2
60	0.1	20	16.34	18.3
75	0.1	20	16.06	19.7
90	0.1	20	15.54	22.3
120	0.1	20	15.68	21.6
150	0.1	20	16.13	19.35
210	0.1	20	16.15	19.25
240	0.1	20	16.02	19.9

Time (min)	Mass (g)	Ci (mg/l)	Cf (mg/l)	% Removal
0	0	0	0	0
5	0.5	20	9.448	52.56
20	0.5	20	9.069	54.655
30	0.5	20	8.696	56.52
45	0.5	20	8.665	56.675
60	0.5	20	8.743	56.285
75	0.5	20	8.313	58.435
90	0.5	20	7.591	62.045
120	0.5	20	7.782	61.09
150	0.5	20	8.293	58.533
210	0.5	20	8.34	58.3
240	0.5	20	8.221	58.895

Time (min)	Mass (g)	Ci (mg/l)	Cf (mg/l)	% Removal
0	0	0	0	0
5	1	20	6.427	67.865
20	1	20	5.787	71.065
30	1	20	4.926	75.37
45	1	20	4.843	75.785
60	1	20	4.997	75.015
75	1	20	4.767	76.165
90	1	20	4.001	79.995
120	1	20	4.505	77.475
150	1	20	5.008	74.956
210	1	20	5.122	74.387
240	1	20	5.028	74.86

Time (min)	Mass (g)	Ci (mg/l)	Cf (mg/l)	% Removal
0	0	0	0	0
5	2	20	4.562	77.19
20	2	20	3.793	81.035
30	2	20	2.962	85.19
45	2	20	2.801	85.995
60	2	20	2.921	85.391
75	2	20	2.577	87.111
90	2	20	1.609	91.952
120	2	20	2.302	88.486
150	2	20	2.722	86.39
210	2	20	2.714	86.43
240	2	20	2.674	86.627

B2: Effect of contact time on CV textile dye. (Conditions: initial concentration = 20 mg/L, temperature = 30 °C, time = 5 to 250 minutes, shaking speed = 250 rpm, volume = 30 mL, masses = 0.01 g to 0.1 g).

Time (Min)	Mass (g)	C_i (mg/l)	C_f (mg/l)	% Removal
0	0	0	0	0
5	0.01	20	8.03	59.85
20	0.01	20	7.297	63.515
30	0.01	20	6.874	65.63
45	0.01	20	7.285	63.575
60	0.01	20	7.462	62.69
75	0.01	20	7.226	63.87
90	0.01	20	7.583	62.085
120	0.01	20	7.725	61.375
150	0.01	20	7.645	61.775
210	0.01	20	7.454	62.73
240	0.01	20	7.343	63.285

Time (Min)	Mass (g)	C_i (mg/l)	C_f (mg/l)	% Removal
0	0	0	0	0
5	0.03	20	6.088	69.56
20	0.03	20	4.954	75.23
30	0.03	20	4.494	77.53
45	0.03	20	5.032	74.84
60	0.03	20	4.958	75.21
75	0.03	20	4.92	75.4
90	0.03	20	5.025	74.875
120	0.03	20	5.022	74.89
150	0.03	20	5.155	74.225
210	0.03	20	4.813	75.935
240	0.03	20	4.894	75.53

Time (Min)	Mass (g)	Ci (mg/l)	Cf (mg/l)	% Removal
0	0	0	0	0
5	0.05	20	3.069	84.655
20	0.05	20	2.15	89.25
30	0.05	20	1.969	90.155
45	0.05	20	2.209	88.955
60	0.05	20	2.457	87.715
75	0.05	20	2.399	88.005
90	0.05	20	2.494	87.53
120	0.05	20	2.618	86.91
150	0.05	20	2.56	87.2
210	0.05	20	2.533	87.335
240	0.05	20	2.533	87.335

Time (Min)	Mass (g)	Ci (mg/l)	Cf (mg/l)	% Removal
0	0	0	0	0
5	0.1	20	1.21	93.975
20	0.1	20	0.833	95.835
30	0.1	20	0.751	96.245
45	0.1	20	0.966	95.17
60	0.1	20	1.262	93.69
75	0.1	20	1.339	93.305
90	0.1	20	1.443	92.785
120	0.1	20	1.564	92.18
150	0.1	20	1.377	93.115
210	0.1	20	1.454	92.73
240	0.1	20	1.454	92.73

C1: Effect of dosage and initial dye concentration for MO textile dye. (Conditions: initial dye concentration = 20 mg/L to 150 mg/L, masses = 0.5 g to 2 g, volume = 30 mL, time = 90 minutes, temperature = 30 °C, Shaking speed = 250 rpm).

20 mg/L

Mass (g)	Ci (mg/L)	Cf (mg/L)	% Removal
0.5	20	12.9716	35.142
1	20	4.291	78.545
1.5	20	2.364	88.18
2	20	1.709	91.455

50 mg/L

Mass (g)	Ci (mg/L)	Cf (mg/L)	% removal
0.5	50	35.22	29.56
1	50	16.365	67.27
1.5	50	8.685	82.63
2	50	5.319	89.362

80 mg/L

Mass (g)	Ci (mg/L)	Cf (mg/L)	% removal
0.5	80	57.976	27.53
1	80	28.1	64.875
1.5	80	15.073	81.159
2	80	11.304	85.87

100 mg/L

Mass (g)	Ci (mg/L)	Cf (mg/L)	% removal
0.5	100	74.58	25.45
1	100	37.46	62.54
1.5	100	20.8	79.2
2	100	15.4	84.6

150 mg/L

Mass (g)	Ci (mg/L)	Cf (mg/L)	% removal
0.5	150	116.021	22.653
1	150	68.775	54.15
1.5	150	37.41	75.06
2	150	29.325	80.45

C2: The effect of dosage and initial dye concentration for CV textile dye. (Conditions: initial dye concentration = 20 mg/L to 150 mg/L. masses = 0.1 g to 1.5 g, volume = 30 mL. time = 30 minutes, temperature = 30 °C, Shaking speed = 250 rpm).

20 mg/L

Mass (g)	Ci (mg/L)	Cf (mg/L)	% removal
0.1	20	0.7292	96.354
0.5	20	0.3134	98.433
1	20	0.235	98.825
1.5	20	0.0488	99.756

50 mg/L

Mass (g)	Ci (mg/L)	Cf (mg/L)	% removal
0.1	50	2.625	94.75
0.5	50	1.53	96.94
1	50	0.635	98.73
1.5	50	0.52	98.96

80 mg/L

Mass (g)	Ci (mg/L)	Cf (mg/L)	% removal
0.1	80	4.352	94.56
0.5	80	3.104	96.12
1	80	2.648	96.69
1.5	80	1.624	97.97

100 mg/L

Mass (g)	Ci (mg/L)	Cf (mg/L)	% removal
0.1	100	8.41	91.59
0.5	100	4.83	95.17
1	100	4.57	95.43
1.5	100	3.15	96.85

150 mg/L

Mass (g)	Ci (mg/L)	Cf (mg/L)	% removal
0.1	150	31.425	79.05
0.5	150	15.06	89.96
1	150	7.515	94.99
1.5	150	6.015	95.99

D1: Effect of temperature for MO textile dye. (Conditions: initial dye concentration = 20 mg/L, temperature = 30 °C to 80 °C, time = 90 minutes. mass = 1.5 g, volume = 30 mL, shaking speed = 250 rpm).

Temp (°C)	C _i (mg/L)	C _f (mg/L)	% Removal
0	0	0	0
30	20	2.21	88.95
40	20	2.787	86.065
50	20	4.523	77.385
60	20	6.45	67.75
70	20	10.36	48.2
80	20	12.21	38.95

D2: Effect of temperature for CV textile dye. (Conditions: initial dye concentration = 20 mg/L. temperature = 30 °C to 80 °C, time = 30 minutes, mass = 0.1 g, volume = 30 mL, shaking speed = 250 rpm).

Temp (°C)	C _i (mg/L)	C _f (mg/L)	% Removal
0	0	0	0
30	20	0.805	95.975
40	20	0.536	97.32
50	20	0.496	97.52
60	20	0.422	97.89
70	20	0.26	98.7
80	20	0.224	98.88

E1: Effect of solution pH for MO textile dye. (Conditions: initial concentration = 20 mg/L, pH values = 2 to 12, temperature = 30 °C, time = 90 minutes, mass = 0.5 g to 1.5 g, volume = 30 mL. shaking speed = 250 rpm).

pH	Mass (g)	Initial Conc	Final Conc	% Removal
0	0	0	0	0
2	0.5	20	3.411	82.945
4	0.5	20	7.645	61.775
6	0.5	20	8.315	58.425
8	0.5	20	8.056	59.72
10	0.5	20	8.802	55.99
12	0.5	20	9.244	53.78

pH	Mass (g)	Initial Conc	Final Conc	% Removal
0	0	0	0	0
2	1	20	2.086	89.57
4	1	20	4.559	77.205
6	1	20	4.569	77.155
8	1	20	4.751	76.245
10	1	20	4.731	76.345
12	1	20	4.478	77.61

pH	Mass (g)	Initial Conc	Final Conc	% Removal
0	0	0	0	0
2	1.5	20	2.741	86.295
4	1.5	20	4.325	78.375
6	1.5	20	4.142	79.29
8	1.5	20	3.929	80.355
10	1.5	20	4.264	78.68
12	1.5	20	4.005	79.975

E2: Effect of a solution pH for CV textile dye. (Conditions: initial concentration = 20 mg/L, pH values = 2 to 12, temperature = 30 °C, time = 30 minutes, mass = 0.01 g to 0.1 g, volume = 30 mL, shaking speed = 250 rpm).

pH	Mass (g)	Initial Conc	Final Conc	% Removal
0	0	0	0	0
2	0.01	20	2.43	87.85
4	0.01	20	3.41	82.95
6	0.01	20	3.222	83.89
8	0.01	20	3.814	80.93
10	0.01	20	3.014	84.93
12	0.01	20	2.587	87.065

pH	Mass (g)	Initial Conc	Final Conc	% Removal
0	0	0	0	0
2	0.05	20	1.114	94.43
4	0.05	20	1.798	91.01
6	0.05	20	1.418	92.91
8	0.05	20	1.954	90.23
10	0.05	20	1.379	93.105
12	0.05	20	1.19	94.05

pH	Mass (g)	Initial Conc	Final Conc	% Removal
0	0	0	0	0
2	0.1	20	0.632	96.84
4	0.1	20	0.92	95.4
6	0.1	20	0.708	96.46
8	0.1	20	0.862	95.69
10	0.1	20	0.786	96.07
12	0.1	20	0.65	96.75

F1: Point of Zero Charge. (Conditions: 0.1 M KCl. mass = 1.5 g, time = 24 hours, volume = 50 mL, shaking speed = 250 rpm, temperature = 30 °C, pH values = 2 to 12).

Initial pH	Final pH	Initial pH – final pH
2	2.54	-0.54
4	4.31	-0.31
6	4.46	1.54
8	4.26	3.74
10	4.33	5.67
12	9.65	2.35

G1: Langmuir Adsorption Isotherm for MO dye at the masses of 0.5 g, 1 g, 1.5 g and 2 g

C0 mg/L	Ce mg/L	1/Ce	log Ce	LN Ce	qe	1/qe	log qe	Intercept	qmax	Slope	KL	RL	W(g)	V(L)	R2
20	12.9708	0.077096	1.112967	2.562701	0.421752	2.371062	-0.37494	0.2159	4.63177	32.025	0.00674	0.877	0.5	0.03	0.9989
50	35.22	0.028393	1.546789	3.561614	0.8868	1.12765	0.8868	0.2159	4.631774	32.025	0.00674	0.747	0.5	0.03	0.9989
80	57.976	0.017249	1.763248	4.060029	1.32144	0.75675	0.121047	0.2159	4.63177	32.025	0.00674	0.649	0.5	0.03	0.9989
100	74.58	0.013408	1.872622	4.311872	1.5252	0.655652	0.183327	0.2159	4.63177	32.025	0.00674	0.597	0.5	0.03	0.9989
150	116.021	0.008619	2.064537	4.753771	2.03874	0.490499	0.309362	0.2159	4.63177	32.025	0.00674	0.497	0.5	0.03	0.9989
20	4.291	0.233046	0.632559	-0.45798	0.47127	2.121926	-0.32673	0.2085	4.796163	4.796163	0.016504	0.826253	1	0.03	0.9954
50	16.365	0.061106	1.213916	2.795145	1.00905	0.991031	0.003913	0.2085	4.796163	12.633	0.016504	0.547885	1	0.03	0.9954
80	28.1	0.035587	1.448706	3.33577	1.557	0.642261	0.192289	0.2085	4.796163	12.633	0.016504	0.430975	1	0.03	0.9954
100	37.46	0.026695	1.573568	3.623274	1.8762	0.532992	0.273279	0.2085	4.796163	12.633	0.016504	0.33773	1	0.03	0.9954
150	68.775	0.01454	1.837431	4.23084	2.43675	0.410383	0.386811	0.2085	4.796163	12.633	0.016504	0.28772	1	0.03	0.9954
20	2.364	0.423012	0.373647	0.860355	0.35272	2.83511	-0.45257	0.2102	4.757374	8.6443	0.024317	0.86788	1.5	0.03	0.9993
50	8.685	0.115181	0.93877	2.161597	0.8263	1.210214	-0.08286	0.2102	4.757374	8.6443	0.024317	0.451294	1.5	0.03	0.9993
80	15.073	0.066344	1.1782	2.712905	1.29854	0.770956	0.113455	0.2102	4.757374	8.6443	0.024317	0.339517	1.5	0.03	0.9993
100	20.8	0.048077	1.318063	3.034953	1.584	0.631313	0.199755	0.2102	4.757374	8.6443	0.024317	0.291401	1.5	0.03	0.9993
150	37.41	0.026731	1.572988	3.621938	2.2518	0.444089	0.35253	0.2102	4.757374	8.6443	0.024317	0.215167	1.5	0.03	0.9993
20	1.709	0.585138	0.232742	0.535908	0.274365	3.64478	-0.56167	0.3906	2.560164	5.9671	0.065459	0.88242	2	0.03	0.9897
50	5.319	0.188005	0.72583	1.671285	0.670215	1.492059	-0.17379	0.3906	2.560164	5.9671	0.065459	0.23403	2	0.03	0.9897
80	11.304	0.088464	1.053232	2.425157	1.03044	0.970459	0.013023	0.3906	2.560164	5.9671	0.065459	0.160341	2	0.03	0.9897
100	15.4	0.064935	1.187521	2.734368	1.269	0.788022	0.103462	0.3906	2.560164	5.9671	0.065459	0.132522	2	0.03	0.9897
150	29.325	0.034101	1.467238	3.37844	1.810125	0.552448	0.257709	0.3906	2.560164	5.9671	0.065459	0.092431	2	0.03	0.9897

G2: Langmuir Adsorption Isotherm for CV dye at the masses of 0.1 g, 0.5g, 1 g, and 1.5g

C0 mg/L	Ce mg/L	1/Ce	log Ce	LN Ce	qe	1/qe	log qe	Intercept	qmax	Slope	KL	RL	W(g)	V(L)	R2
20	0,7292	1,37137	-0,1372	-0,3158	5,78124	0,17297	0,76202	0,0238	42.0168	0,1092	0.21795	0.86287	0,1	0,03	0.9965
50	2,625	0,38095	0,41913	0,96508	14,2125	0,07036	1,15267	0,0238	42.0168	0,1092	0.21795	0.63609	0,1	0,03	0.9965
80	4,352	0,22978	0,63869	1,47064	22,6944	0,04406	1,35592	0,0238	42.0168	0,1092	0.21795	0.51321	0,1	0,03	0.9965
100	8,41	0,11891	0,9248	2,12942	27,477	0,03639	1,43897	0,0238	42.0168	0,1092	0.21795	0.35299	0,1	0,03	0.9965
150	31,425	0,03182	1,49728	3,4476	35,5725	0,02811	1,55111	0,0238	42.0168	0,1092	0.21795	0.1274	0,1	0,03	0.9965
20	0,3134	3,19081	-0,5039	-1,1603	1,1812	0,8466	0,07232	0,1424	7.02247	0,2238	0.63628	0.83374	0,5	0,03	0.9871
50	1,53	0,65359	0,18469	0,42527	2,9082	0,34386	0,46362	0,1424	7.02247	0,2238	0.63628	0.50671	0,5	0,03	0.9871
80	3,104	0,32216	0,49192	1,13269	4,61376	0,21674	0,66405	0,1424	7.02247	0,2238	0.63628	0.33613	0,5	0,03	0.9871
100	4,83	0,20704	0,68395	1,57485	5,7102	0,17513	0,75665	0,1424	7.02247	0,2238	0.63628	0.2455	0,5	0,03	0.9871
150	15,06	0,0664	1,17782	2,71204	8,0964	0,12351	0,90829	0,1424	7.02247	0,2238	0.63628	0.0945	0,5	0,03	0.9871
20	0,235	4,25532	-0,6289	-1,4482	0,59295	1,68648	-0,227	0,2359	4.23908	0,3348	0.7046	0.85794	1	0,03	0.9878
50	0,635	1,5748	-0,1972	-0,4541	1,48095	0,67524	0,17054	0,2359	4.23908	0,3348	0.7046	0.69088	1	0,03	0.9878
80	2,648	0,37764	0,42292	0,9738	2,32056	0,43093	0,36559	0,2359	4.23908	0,3348	0.7046	0.34895	1	0,03	0.9878
100	4,57	0,21882	0,65992	1,51951	2,8629	0,3493	0,45681	0,2359	4.23908	0,3348	0.7046	0.23697	1	0,03	0.9878
150	7,515	0,13307	0,87593	2,0169	4,27455	0,23394	0,63089	0,2359	4.23908	0,3348	0.7046	0.15885	1	0,03	0.9878
20	0,0488	20,4918	-1,3116	-3,02	0,39902	2,50611	-0,399	0,5489	1.82183	0,0967	5.67632	0.7830	1,5	0,03	0.9579
50	0,52	1,92308	-0,284	-0,6539	0,9896	1,01051	-0,0045	0,5489	1.82183	0,0967	5.67632	0.25306	1,5	0,03	0.9579
80	1,624	0,61576	0,21059	0,48489	1,56752	0,63795	0,19521	0,5489	1.82183	0,0967	5.67632	0.09786	1,5	0,03	0.9579
100	3,15	0,31746	0,49831	1,1474	1,937	0,51626	0,28713	0,5489	1.82183	0,0967	5.67632	0.05296	1,5	0,03	0.9579
150	6,015	0,16625	0,77924	1,79426	2,8797	0,34726	0,45935	0,5489	1.82183	0,0967	5.67632	0.02846	1,5	0,03	0.9579

H1: Freundlich Adsorption Isotherm for MO dye at the mass of 0.5 g, 1 g, 1.5 g and 2 g

C0 (mg/L)	Ce (mg/L)	Log ce	qe	Log qe	V(L)	W(g)	slope	Intercept	n	Kf	R2
20	12.9708	1.112967	0.421752	-0.37494	0.03	0.5	0.726	-1.1765	1.37741	0.0666	0.9982
50	35.22	1.546789	0.8868	-0.05217	0.03	0.5					
80	57.976	1.763248	1.32144	0.121047	0.03	0.5					
100	74.58	1.872622	1.5252	0.183327	0.03	0.5					
150	116.021	2.064537	2.03874	0.309362	0.03	0.5					
20	4.291	0.632559	0.47127	-0.32673	0.03	1	0.6109	-0.7134	1.6369	0.1934	0.9931
50	16.365	1.213916	1.00905	0.003913	0.03	1					
80	28.1	1.448706	1.557	0.192289	0.03	1					
100	37.46	1.573568	1.8762	0.273279	0.03	1					
150	68.775	1.837431	2.43675	0.386811	0.03	1					
20	2.364	0.373647	0.35272	-0.45257	0.03	1.5	0.6814	-0.7074	1.4675	0.1961	0.998
50	8.685	0.93877	0.8263	-0.08286	0.03	1.5					
80	15.073	1.1782	1.29854	0.113455	0.03	1.5					
100	20.8	1.318063	1.584	0.199755	0.03	1.5					
150	37.41	1.572988	2.2518	0.35253	0.03	1.5					
20	1.709	0.232742	0.274365	-0.56167	0.03	2	0.6626	-0.6907	1.5092	0.2038	0.9935
50	5.319	0.72583	0.670215	-0.17379	0.03	2					
80	11.304	1.053232	1.03044	0.013023	0.03	2					
100	15.4	1.187521	1.269	0.103462	0.03	2					
150	29.325	1.467238	1.810125	0.257709	0.03	2					

H2: Freundlich Adsorption Isotherm for CV dye at the mass of 0.1 g, 0.5 g, 1 g and 1.5 g of modified SMT.

C ₀ (mg/L)	C _e (mg/L)	Log c _e	q _e	Log q _e	V(L)	W(g)	slope	Intercept	n	K _f	R ²
20	0.7292	-0.1372	5.78124	0.76202	0.03	0.1	0.4863	0.927	2.0563	8.4528	0.8899
50	2.625	0.41913	14.2125	1.15267	0.03	0.1					
80	4.352	0.63869	22.6944	1.35592	0.03	0.1					
100	8.41	0.9248	27.477	1.43897	0.03	0.1					
150	31.425	1.49728	35.5725	1.55111	0.03	0.1					
20	0.3134	-0.5039	1.1812	0.07232	0.03	0.5	0.5121	0.3646	1.952744	2.3153	0.9791
50	1.53	0.18469	2.9082	0.46362	0.03	0.5					
80	3.104	0.49192	4.61376	0.66405	0.03	0.5					
100	4.83	0.68395	5.7102	0.75665	0.03	0.5					
150	15.06	1.17782	8.0964	0.90829	0.03	0.5					
20	0.235	-0.6289	0.59295	-0.227	0.03	1	0.5139	0.163	1.9459	1.45546	0.9561
50	0.635	-0.1972	1.48095	0.17054	0.03	1					
80	2.648	0.42292	2.32056	0.36559	0.03	1					
100	4.57	0.65992	2.8629	0.45681	0.03	1					
150	7.515	0.87593	4.27455	0.63089	0.03	1					
20	0.0488	-1.3116	0.39902	-0.399	0.03	1.5	0.3996	0.1162	2.5025	1.30677	0.9955
50	0.52	-0.284	0.9896	-0.0045	0.03	1.5					
80	1.624	0.21059	1.56752	0.19521	0.03	1.5					
100	3.15	0.49831	1.937	0.28713	0.03	1.5					
150	6.015	0.77924	2.8797	0.45935	0.03	1.5					

I1: Dubinin- Radushkevich (DR) Isotherm for MO dye adsorption at the masses of 0.5 g, 1 g, 1.5g and 2 g of modified SMT

C0 (mg/L)	Ce (mg/L)	C0 (mol/L)	Ce (mol/L)	qe (mol/g)	lnqe	R (J/mol/K)	T(K)	1/Ce	ln (1/Ce)	E= R*T*ln(1/Ce)	E2	Mass(g)
20	12.9708	6.11004E-05	3.96261E-05	1.28846E-06	-13.5621	8.314	303.15	25235.91	10.13602	25546.72	652635040.7	0.5
50	35.22	0.000152751	0.000107598	2.72412E-06	-12.8134	8.314	303.15	9293.867	9.13711	23029.07	530338176.1	0.5
80	57.976	0.000244402	0.000177118	4.01292E-06	-12.426	8.314	303.15	5645.957	8.638695	21772.87	474057986.5	0.5
100	74.58	0.000305502	0.000227843	4.68942E-06	-12.2702	8.314	303.15	4388.978	8.386852	21138.13	446820528	0.5
150	116.021	0.000458253	0.000354447	6.2118E-06	-11.9891	8.314	303.15	2821.3	7.944953	20024.37	400975503.1	0.5
20	4.291	6.11004E-05	1.31091E-05	1.43974E-06	-13.451	8.314	303.15	76282.92	11.2422	28334.73	802856878.9	1
50	16.365	0.000152751	4.99954E-05	1.54133E-06	-13.3829	8.314	303.15	20001.83	9.903579	24960.87	623045178.8	1
80	28.1	0.000244402	8.58461E-05	2.37833E-06	-12.9491	8.314	303.15	11648.75	9.362955	23598.29	556879220.4	1
100	37.46	0.000305502	0.000114441	2.86592E-06	-12.7626	8.314	303.15	8738.121	9.07545	22873.67	523204614.5	1
150	68.775	0.000458253	0.000210109	3.72216E-06	-12.5012	8.314	303.15	4759.433	8.467884	21342.36	455496420.1	1
20	2.364	6.11004E-05	7.22207E-06	1.07757E-06	-13.7408	8.314	303.15	138464.5	11.83837	29837.3	890264246.3	1.5
50	8.685	0.000152751	2.65329E-05	1.89327E-06	-13.1772	8.314	303.15	37689.11	10.53713	26557.66	705309252.1	1.5
80	15.073	0.000244402	4.60483E-05	2.9753E-06	-12.7252	8.314	303.15	21716.31	9.985819	25168.15	633435750	1.5
100	20.8	0.000305502	6.35444E-05	3.62936E-06	-12.5265	8.314	303.15	15737.02	9.663771	24356.46	593237301.1	1.5
150	37.41	0.000458253	0.000114288	5.15947E-06	-12.1747	8.314	303.15	8749.8	9.076786	22877.03	523358626.5	1.5
20	1.709	6.11004E-05	5.22103E-06	8.38191E-07	-13.992	8.314	303.15	191533.1	12.16282	30655.03	939730750.5	2
50	5.319	0.000152751	1.62497E-05	2.04752E-06	-13.0989	8.314	303.15	61539.75	11.02744	27793.44	772475083.5	2
80	11.304	0.000244402	3.4534E-05	3.14802E-06	-12.6687	8.314	303.15	28957	10.27357	25893.39	670467501.6	2
100	15.4	0.000305502	4.70473E-05	3.87682E-06	-12.4605	8.314	303.15	21255.2	9.964357	25114.06	630715803.7	2
150	29.325	0.000458253	8.95885E-05	5.52997E-06	-12.1053	8.314	303.15	11162.15	9.320284	23490.74	551814934.4	2

I2: Dubinin- Radushkevich (DR) Isotherm for CV dye adsorption at the masses of 0.1 g, 0.5 g, 1 g, and 1.5g of modified SMT.

C ₀ (mg/L)	C _e (mg/L)	C ₀ (mol/L)	C _e (mol/L)	q _e (mol/g)	lnq _e	R (J/mol/K)	T(K)	1/C _e	ln(1/C _e)	E= R*T*ln(1/C _e)	E2	Mass(g)
20	0.7292	4.9E-05	1.79E-06	1.42E-05	-11.1644	8.314	303.15	559489.9	13.23478	33356.8	1112675902	0.1
50	2.625	0.000123	6.43E-06	3.48E-05	-10.2649	8.314	303.15	155421	11.95389	30128.46	907724129.2	0.1
80	4.352	0.000196	1.07E-05	5.56E-05	-9.79686	8.314	303.15	93745.4	11.44834	28854.27	832568673	0.1
100	8.41	0.000245	2.06E-05	6.73E-05	-9.60562	8.314	303.15	48511.3	10.78955	27193.87	739506519.4	0.1
150	31.425	0.000368	7.7E-05	8.72E-05	-9.3474	8.314	303.15	12982.66	9.47137	23871.54	569850273.9	0.1
20	0.3134	4.9E-05	7.68E-07	2.9E-06	-12.7524	8.314	303.15	1301787	14.07925	35485.18	1259198295	0.5
50	1.53	0.000123	3.75E-06	7.13E-06	-11.8514	8.314	303.15	266653.6	12.49371	31489	991557099.4	0.5
80	3.104	0.000196	7.61E-06	1.13E-05	-11.3899	8.314	303.15	131436.9	11.78628	29706.02	882447401.7	0.5
100	4.83	0.000245	1.18E-05	1.4E-05	-11.1767	8.314	303.15	84467.91	11.34413	28591.61	817480388.3	0.5
150	15.06	0.000368	3.69E-05	1.98E-05	-10.8276	8.314	303.15	27090.31	10.20693	25725.44	661798168.9	0.5
20	0.235	4.9E-05	5.76E-07	1.45E-06	-13.4416	8.314	303.15	1736085	14.36714	36210.79	1311221393	1
50	0.635	0.000123	1.56E-06	3.63E-06	-12.5263	8.314	303.15	642488.2	13.3731	33705.42	1136055663	1
80	2.648	0.000196	6.49E-06	5.69E-06	-12.0772	8.314	303.15	154071	11.94517	30106.47	906399730.2	1
100	4.57	0.000245	1.12E-05	7.02E-06	-11.8671	8.314	303.15	89273.52	11.39946	28731.08	825474688.1	1
150	7.515	0.000368	1.84E-05	1.05E-05	-11.4663	8.314	303.15	54288.76	10.90207	27477.46	755011053.6	1
20	0.0488	4.9E-05	1.2E-07	9.78E-07	-13.8377	8.314	303.15	8360246	15.939	40172.48	1613827975	1.5
50	0.52	0.000123	1.27E-06	2.43E-06	-12.9294	8.314	303.15	784576.9	13.5729	34208.99	1170254926	1.5
80	1.624	0.000196	3.98E-06	3.84E-06	-12.4695	8.314	303.15	251219.2	12.43408	31338.72	982115540.6	1.5
100	3.15	0.000245	7.72E-06	4.75E-06	-12.2578	8.314	303.15	129517.5	11.77157	29668.94	880245952.5	1.5
150	6.015	0.000368	1.47E-05	7.06E-06	-11.8613	8.314	303.15	67827.1	11.12472	28038.62	786163969.1	1.5

J1: Temkin Adsorption Isotherm for MO dye removal using 0.5 g, 1 g, 1.5 g, and 2 g of modified SMT.

Mass (g)	C ₀ (mg/L)	C _e (mg/L)	LN C _e	q _e	R	T	Slope=β (J/mol)	Intercept	b (J/mol)	α (L/mg)	R ²
0.5	20	12.9708	2.562701	0.421752	8.314	303.15	0.7198	-1.5324	3501.513	0.118965	0.9592
0.5	50	35.22	3.561614	0.8868	8.314	303.15					
0.5	80	57.976	4.060029	1.32144	8.314	303.15					
0.5	100	74.58	4.311872	1.5252	8.314	303.15					
0.5	150	116.021	4.753771	2.03874	8.314	303.15					
1	20	4.291	1.45652	0.47127	8.314	303.15	0.7062	-0.7108	3568.945	0.365491	0.9473
1	50	16.365	2.795145	1.00905	8.314	303.15					
1	80	28.1	3.33577	1.557	8.314	303.15					
1	100	37.46	3.623274	1.8762	8.314	303.15					
1	150	68.775	4.23084	2.43675	8.314	303.15					
1.5	20	2.364	0.860355	0.35272	8.314	303.15	0.6671	-0.3905	3778.128	0.5569	0.9298
1.5	50	8.685	2.161597	0.8263	8.314	303.15					
1.5	80	15.073	2.712905	1.29854	8.314	303.15					
1.5	100	20.8	3.034953	1.584	8.314	303.15					
1.5	150	37.41	3.621938	2.2518	8.314	303.15					
2	20	1.709	0.535908	0.274365	8.314	303.15	0.523	-0.1131	4819.1	0.805532	0.9545
2	50	5.319	1.671285	0.670215	8.314	303.15					
2	80	11.304	2.425157	1.03044	8.314	303.15					
2	100	15.4	2.734368	1.269	8.314	303.15					
2	150	29.325	3.37844	1.810125	8.314	303.15					

J2: Temkin Adsorption Isotherm for CV dye removal using 0.1 g, 0.5 g, 1 g and 1.5 g of modified SMT

Mass (g)	C ₀ (mg/L)	C _e (mg/L)	LN C _e	q _e	R	T	Slope=β (J/mol)	Intercept	b (J/mol)	a(L/mg)	R ²
0.1	20	0.729	-0.31608	5.7813	8.314	303.15	8.195	8.5327	307.5521	2.832637	0.9754
0.1	50	2.625	0.965081	14.2125	8.314	303.15					
0.1	80	4.352	1.470636	22.6944	8.314	303.15					
0.1	100	8.41	2.129421	27.477	8.314	303.15					
0.1	150	31.425	3.447604	35.5725	8.314	303.15					
0.5	20	0.313	-1.16155	1.18122	8.314	303.15	1.8104	2.8062	1392.173	4.711678	0.9685
0.5	50	1.53	0.425268	2.9082	8.314	303.15					
0.5	80	3.104	1.132692	4.61376	8.314	303.15					
0.5	100	4.83	1.574846	5.7102	8.314	303.15					
0.5	150	15.06	2.712042	8.0964	8.314	303.15					
1	20	0.235	-1.44817	0.59295	8.314	303.15	0.9295	1.8216	2711.554	7.097647	0.9157
1	50	0.635	-0.45413	1.48095	8.314	303.15					
1	80	2.648	0.973805	2.32056	8.314	303.15					
1	100	4.57	1.519513	2.8629	8.314	303.15					
1	150	7.515	2.016901	4.27455	8.314	303.15					
1.5	20	0.049	-3.01593	0.59853	8.314	303.15	0.4261	1.6152	5915.018	44.2856	0.8289
1.5	50	0.52	-0.65393	0.9896	8.314	303.15					
1.5	80	1.624	0.484892	1.56752	8.314	303.15					
1.5	100	3.15	1.147402	1.937	8.314	303.15					
1.5	150	6.015	1.794256	2.8797	8.314	303.15					

K1: Pseudo-first-order of MO dye removal onto modified SMT.

Time (min)	Mass (g)	C0 (mg/l)	Ct (mg/l)	% Removal for 0.5 g	qt	qe	qe-qt	log(qe-qt)	qe (mg/g)	K1 (min-1)	R2
0	0	0	0	0	0	0	0	0	0	0	0
5	0.5	20	9.448	52.56	0.63312	0.75042	0.1173	-0.9307	0.0655	0.0016	0.1068
20	0.5	20	9.069	54.655	0.65586	0.75042	0.09456	-1.02429			
30	0.5	20	8.696	56.52	0.67824	0.75042	0.07218	-1.14158			
45	0.5	20	8.665	56.675	0.6801	0.75042	0.07032	-1.15292			
60	0.5	20	8.743	56.285	0.67542	0.75042	0.075	-1.12494			
75	0.5	20	8.313	58.435	0.70122	0.75042	0.0492	-1.30803			
90	0.5	20	7.591	62.045	0.74454	0.75042	0.00588	-2.23062			
120	0.5	20	7.782	61.09	0.73308	0.75042	0.01734	-1.76095			
150	0.5	20	8.293	58.53	0.70242	0.75042	0.048	-1.31876			
210	0.5	20	8.34	58.3	0.6996	0.75042	0.05082	-1.29397			
240	0.5	20	8.221	58.895	0.70674	0.75042	0.04368	-1.35972			

Time (min)	Mass (g)	C0 (mg/l)	Ct(mg/l)	% Removal for 1 g	qt	qe	qe-qt	log (qe-qt)	qe (mg/g)	K1 (min-1)	R2
0	0	0	0	0	0	0	0	0	0	0	0
5	1	20	6.427	67.865	0.40719	0.47127	0.06408	-1.19328	0.0388	0.0011	0.0229
20	1	20	5.787	71.065	0.42639	0.47127	0.04488	-1.34795			
30	1	20	4.926	75.37	0.45222	0.47127	0.01905	-1.72011			
45	1	20	4.843	75.785	0.45471	0.47127	0.01656	-1.78094			
60	1	20	4.997	75.015	0.45009	0.47127	0.02118	-1.67407			
75	1	20	4.767	76.165	0.45699	0.47127	0.01428	-1.84527			
90	1	20	4.001	79.995	0.47997	0.47127	-0.0087	#NUM!			
120	1	20	4.505	77.475	0.46485	0.47127	0.00642	-2.19246			
150	1	20	5.008	74.956	0.44976	0.47127	0.02151	-1.66736			
210	1	20	5.122	74.387	0.44634	0.47127	0.02493	-1.60328			
240	1	20	5.028	74.86	0.44916	0.47127	0.02211	-1.65541			

Time (min)	Mass (g)	C0 (mg/l)	Ct (mg/l)	% Removal for 2 g	qt	qe	qe-qt	log(qe-qt)	qe (mg/g)	K1 (min ⁻¹)	R2
0	0	0	0	0	0	0	0	0	0	0	0
5	2	20	4.562	77.19	0.23157	0.274365	0.042795	-1.36861	0.0355	0.0015	0.0444
20	2	20	3.793	81.035	0.243105	0.274365	0.03126	-1.50501			
30	2	20	2.962	85.19	0.25557	0.274365	0.018795	-1.72596			
45	2	20	2.801	85.995	0.257985	0.274365	0.01638	-1.78569			
60	2	20	2.921	85.39	0.256185	0.274365	0.01818	-1.74041			
75	2	20	2.577	87.11	0.261345	0.274365	0.01302	-1.88539			
90	2	20	1.609	91.95	0.275865	0.274365	-0.0015	#NUM!			
120	2	20	2.302	88.486	0.26547	0.274365	0.008895	-2.05085			
150	2	20	2.722	86.39	0.25917	0.274365	0.015195	-1.8183			
210	2	20	2.714	86.43	0.25929	0.274365	0.015075	-1.82174			
240	2	20	2.674	86.627	0.25989	0.274365	0.014475	-1.83938			

K2: Pseudo-first-order of CV dye removal onto modified SMT

Time (Min)	Mass (g)	C0(mg/l)	Ct (mg/l)	% Removal	qt	qe	qe-qt	Log(qe-qt)	qe (mg/g)	K1 (min ⁻¹)	R2
0	0	0	0	0	0	0	0	0	0	0	0
5	0.1	20	1.21	93.975	5.637	5.78124	0.14424	-0.84091	0.0518	-0.0035	0.3024
20	0.1	20	0.833	95.835	5.7501	5.78124	0.03114	-1.50668			
30	0.1	20	0.751	96.245	5.7747	5.78124	0.00654	-2.18442			
45	0.1	20	0.966	95.17	5.7102	5.78124	0.07104	-1.1485			
60	0.1	20	1.262	93.69	5.6214	5.78124	0.15984	-0.79631			
75	0.1	20	1.339	93.305	5.5983	5.78124	0.18294	-0.73769			
90	0.1	20	1.443	92.785	5.5671	5.78124	0.21414	-0.6693			
120	0.1	20	1.564	92.18	5.5308	5.78124	0.25044	-0.6013			
150	0.1	20	1.377	93.115	5.5869	5.78124	0.19434	-0.71144			
210	0.1	20	1.454	92.73	5.5638	5.78124	0.21744	-0.66266			
240	0.1	20	1.454	92.73	5.5638	5.78124	0.21744	-0.66266			

L1: Pseudo-second-order for MO dye removal onto modified SMT

Time (min)	t/qt (mg.g- 1.min-1)	Mass (g)	Slope	Intercept	qe (mg/g)	qe^2	K2	R2
0	0	0	0	0	0	0	0	0
5	7.897397	0.5	1.4094	0.8771	0.709522	0.503421	2.264746	0.999
20	30.49431							
30	44.23213							
45	66.16674							
60	88.83361							
75	106.9564							
90	120.88							
120	163.6929							
150	213.5475							
210	300.1715							
240	339.5874							

Time (min)	t/qt (mg.g- 1.min-1)	Mass (g)	Slope	Intercept	qe (mg/g)	qe^2	K2	R2
0	0	0	0	0	0	0	0	0
5	7.897397	0.5	1.4094	0.8771	0.709522	0.503421	2.264746	0.999
20	30.49431							
30	44.23213							
45	66.16674							
60	88.83361							
75	106.9564							
90	120.88							
120	163.6929							
150	213.5475							
210	300.1715							
240	339.5874							

Time (min)	t/qt (mg.g-1.min-1)	Mass (g)	Slope	Intercept	qe (mg/g)	qe^2	K2	R2
0	0	0	0	0	0	0	0	0
5	21.59174	2	3.8357	-0.0939	0.260709	0.067969	-156.684	0.9994
20	82.26898							
30	117.3847							
45	174.4287							
60	234.2057							
75	286.977							
90	326.2465							
120	452.0285							
150	578.7707							
210	809.904							
240	923.4676							

L2: Pseudo-second-order for CV dye removal onto modified SMT

Time (Min)	t/qt (mg.g-1.min-1)	Mass (g)	Slope	Intercept	qe (mg/g)	qe^2	K2	R2
0	0	0	0	0	0	0	0	0
5	0.886997	0.1	0.1803	-0.1217	5.546312	30.76157	-0.26712	1
20	3.4782							
30	5.195075							
45	7.880635							
60	10.6735							
75	13.39692							
90	16.16641							
120	21.69668							
150	26.84852							
210	37.74399							
240	43.13599							

M1: Elovich plot for MO dye onto modified SMT

Time (min)	ln t	Mass (g)	C0 (mg/l)	Ct (mg/l)	qt (mg/g)	R2	Slope	Intercept	β	ln β	Intercept * β	ln α	α (mg.g-1.min-1)
0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	1.609438	0.5	20	9.448	0.63312	0.6318	0.0224	0.5995	44.64286	3.798694	26.76339286	22.9647	9.41E+09
20	2.995732	0.5	20	9.069	0.65586								
30	3.401197	0.5	20	8.696	0.67824								
45	3.806662	0.5	20	8.665	0.6801								
60	4.094345	0.5	20	8.743	0.67542								
75	4.317488	0.5	20	8.313	0.70122								
90	4.49981	0.5	20	7.591	0.74454								
120	4.787492	0.5	20	7.782	0.73308								
150	5.010635	0.5	20	8.293	0.70242								
210	5.347108	0.5	20	8.34	0.6996								
240	5.480639	0.5	20	8.221	0.70674								

Time (min)	ln t	Mass (g)	C0 (mg/l)	Ct(mg/l)	qt (mg/g)	R2	Slope	Intercept	β	ln β	Intercept * β	ln α	α (mg.g-1.min-1)
0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	1.609438	1	20	6.427	0.40719	0.4702	0.0114	0.4019	87.7193	4.474142	35.25438596	30.78024	2.33E+13
20	2.995732	1	20	5.787	0.42639								
30	3.401197	1	20	4.926	0.45222								
45	3.806662	1	20	4.843	0.45471								
60	4.094345	1	20	4.997	0.45009								
75	4.317488	1	20	4.767	0.45699								
90	4.49981	1	20	4.001	0.47997								
120	4.787492	1	20	4.505	0.46485								
150	5.010635	1	20	5.008	0.44976								
210	5.347108	1	20	5.122	0.44634								
240	5.480639	1	20	5.028	0.44916								

Time (min)	ln t	Mass (g)	C0 (mg/l)	Ct (mg/l)	qt (mg/g)	R2	Slope	Intercept	β	ln β	Intercept * β	ln α	α (mg.g-1.min-1)
0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	1.609438	2	20	4.562	0.23157	0.6204	0.0079	0.2242	126.5823	4.840893	28.37974684	23.53885	1.67E+10
20	2.995732	2	20	3.793	0.243105								
30	3.401197	2	20	2.962	0.25557								
45	3.806662	2	20	2.801	0.257985								
60	4.094345	2	20	2.921	0.256185								
75	4.317488	2	20	2.577	0.261345								
90	4.49981	2	20	1.609	0.275865								
120	4.787492	2	20	2.302	0.26547								
150	5.010635	2	20	2.722	0.25917								
210	5.347108	2	20	2.714	0.25929								
240	5.480639	2	20	2.674	0.25989								

M2: Elovich plot for CV dye onto modified SMT

Time (Min)	ln t	Mass (g)	C0(mg/l)	Ct (mg/l)	qt (mg/g)	R2	Slope	Intercept	β	ln β	Intercept * β	ln α	α (mg.g-1.min-1)
0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	1.609438	0.1	20	1.21	5.637	0.3958	-0.0453	5.8145	-22.0751	#NUM!	-128.355	#NUM!	#NUM!
20	2.995732	0.1	20	0.833	5.7501								
30	3.401197	0.1	20	0.751	5.7747								
45	3.806662	0.1	20	0.966	5.7102								
60	4.094345	0.1	20	1.262	5.6214								
75	4.317488	0.1	20	1.339	5.5983								
90	4.49981	0.1	20	1.443	5.5671								
120	4.787492	0.1	20	1.564	5.5308								
150	5.010635	0.1	20	1.377	5.5869								
210	5.347108	0.1	20	1.454	5.5638								
240	5.480639	0.1	20	1.454	5.5638								

N1: The intra-particle diffusion plot of MO dye removal onto modified SMT

Time (min)	Mass (g)	C0 (mg/l)	Ct (mg/l)	qt (mg/g)	$t^{0.5}$	Slope	Intercept	K_{ip} (mg/g. $min^{0.5}$)	Cip (mg/g)	R2
0	0	0	0	0	0	0	0	0	0	0
5	0.5	20	9.448	0.63312	2.236068	0.0054	0.6437	0.0054	0.6437	0.4897
20	0.5	20	9.069	0.65586	4.472136					
30	0.5	20	8.696	0.67824	5.477226					
45	0.5	20	8.665	0.6801	6.708204					
60	0.5	20	8.743	0.67542	7.745967					
75	0.5	20	8.313	0.70122	8.660254					
90	0.5	20	7.591	0.74454	9.486833					
120	0.5	20	7.782	0.73308	10.95445					
150	0.5	20	8.293	0.70242	12.24745					
210	0.5	20	8.34	0.6996	14.49138					
240	0.5	20	8.221	0.70674	15.49193					

Time (min)	Mass (g)	C0 (mg/l)	Ct(mg/l)	qt (mg/g)	$t^{0.5}$	Slope	Intercept	K_{ip} (mg/g. $min^{0.5}$)	Cip (mg/g)	R2
0	0	0	0	0	0	0	0	0	0	0
5	1	20	6.427	0.40719	2.236068	0.0023	0.4287	0.0023	0.4287	0.248
20	1	20	5.787	0.42639	4.472136					
30	1	20	4.926	0.45222	5.477226					
45	1	20	4.843	0.45471	6.708204					
60	1	20	4.997	0.45009	7.745967					
75	1	20	4.767	0.45699	8.660254					
90	1	20	4.001	0.47997	9.486833					
120	1	20	4.505	0.46485	10.95445					
150	1	20	5.008	0.44976	12.24745					
210	1	20	5.122	0.44634	14.49138					
240	1	20	5.028	0.44916	15.49193					

Time (min)	Mass (g)	C ₀ (mg/l)	C _t (mg/l)	q _t (mg/g)	t ^{0.5}	Slope	Intercept	K _{ip} (mg/g. min ^{0.5})	C _{ip} (mg/g)	R ²
0	0	0	0	0	0	0	0	0	0	0
5	2	20	4.562	0.23157	2.236068	0.0022	0.2381	0.0022	0.2381	0.4818
20	2	20	3.793	0.243105	4.472136					
30	2	20	2.962	0.25557	5.477226					
45	2	20	2.801	0.257985	6.708204					
60	2	20	2.921	0.256185	7.745967					
75	2	20	2.577	0.261345	8.660254					
90	2	20	1.609	0.275865	9.486833					
120	2	20	2.302	0.26547	10.95445					
150	2	20	2.722	0.25917	12.24745					
210	2	20	2.714	0.25929	14.49138					
240	2	20	2.674	0.25989	15.49193					

N2: The intra-particle diffusion plot of CV dye removal onto modified SMT

Time (Min)	Mass (g)	C ₀ (mg/l)	C _t (mg/l)	q _t (mg/g)	t ^{0.5}	Slope	Intercept	K _{ip} (mg/g. min ^{0.5})	C _{ip} (mg/g)	R ²
0	0	0	0	0	0	0	0	0	0	0
5	0.1	20	1.21	5.637	2.236068	-0.0141	5.7528	-0.0141	5.7528	0.5063
20	0.1	20	0.833	5.7501	4.472136					
30	0.1	20	0.751	5.7747	5.477226					
45	0.1	20	0.966	5.7102	6.708204					
60	0.1	20	1.262	5.6214	7.745967					
75	0.1	20	1.339	5.5983	8.660254					
90	0.1	20	1.443	5.5671	9.486833					
120	0.1	20	1.564	5.5308	10.95445					
150	0.1	20	1.377	5.5869	12.24745					
210	0.1	20	1.454	5.5638	14.49138					
240	0.1	20	1.454	5.5638	15.49193					

O1: The thermodynamics plot of MO dye removal onto modified SMT (mass of 1.5 g)

Temperature (°C)	T (K)	1/T (K)	C _i (mg/L)	C _i (mol/L)	C _e (mg/L)	C _e (mol/L)	q _e	q _e /C _e	lnK _d	Slope	Intercept	delta H	delta S	delta G(KJ/mol)
30	303.15	0.003299	20	6.11E-05	2.21	6.75E-06	1.09E-06	0.160995	-1.82638	5739.2	-20.556	-47.7157	-0.1709	4.09341
40	313.15	0.003193	20	6.11E-05	2.787	8.51E-06	1.05E-06	0.123524	-2.09132					5.802435
50	323.15	0.003095	20	6.11E-05	4.523	1.38E-05	9.46E-07	0.068437	-2.68184					7.511461
60	333.15	0.003002	20	6.11E-05	6.45	1.97E-05	8.28E-07	0.042016	-3.16972					9.220487
70	343.15	0.002914	20	6.11E-05	10.36	3.17E-05	5.89E-07	0.01861	-3.98405					10.92951
80	353.15	0.002832	20	6.11E-05	12.21	3.73E-05	4.76E-07	0.01276	-4.36144					12.63854

O2: The thermodynamics plot of CV dye removal onto modified SMT (mass of 0.1 g)

Temperature (°C)	T (K)	1/T (K)	C _i (mg/L)	C _i (mol/L)	C _e (mg/L)	C _e (mol/L)	q _e	q _e /C _e	lnK _d	Slope	Intercept	delta H	delta S	delta G(KJ/mol)
30	303.15	0.003299	20	4.9E-05	0.805	1.97E-06	1.41E-05	7.153416	1.96759	-2723.5	10.965	22.64318	0.091163	-4.99289
40	313.15	0.003193	20	4.9E-05	0.536	1.31E-06	1.43E-05	10.89403	2.388215					-5.90452
50	323.15	0.003095	20	4.9E-05	0.496	1.22E-06	1.43E-05	11.79677	2.467826					-6.81615
60	333.15	0.003002	20	4.9E-05	0.422	1.03E-06	1.44E-05	13.91801	2.633184					-7.72778
70	343.15	0.002914	20	4.9E-05	0.26	6.37E-07	1.45E-05	22.77692	3.125748					-8.63941
80	353.15	0.002832	20	4.9E-05	0.224	5.49E-07	1.45E-05	26.48571	3.276606					-9.55104

P1: Desorption and testing reagent for MO textile dye (initial dye concentration = 20 mg/L, time = 90 min, mass = 2 g, volume = 30 mL, shaking speed = 250 rpm, temperature = 30 °C).

Reagent Solutions	Final Conc (mg/l)	Removal (%)
De-Ionised water	2.149	89.255
0.1 M HCl	3.64	81.8
0.1 M KCl	5.147	74.265
Ultra-Water	5.178	74.11
0.1 M NaCl	5.33	73.35
0.1 M NaOH	18.75	6.25

P2: Desorption and testing reagent for CV textile dye (initial dye concentration = 20 mg/L, time = 30 min, mass = 0.15 g, volume = 30 mL, shaking speed = 250 rpm, temperature = 30 °C).

Reagent Solutions	Final Conc (mg/l)	Removal (%)
De-Ionised water	0.092	99.54
0.1 M NaCl	0.345	98.275
0.1 M KCl	0.666	96.67
Ultra-Water	0.728	96.36
0.1 M HCl	0.92	95.4
0.1 M NaOH	2.548	87.26

Q1: Regeneration of Modified-SMT on MO textile dye (Conditions: Initial dye concentration = 20 mg/L, mass = 2 g, time = 90 minutes, volume = 30 mL, shaking speed = 250 rpm, temperature = 30 °C).

1st Cycle

Final Conc (mg/L)	Removal (%)
2.124	89.38
2.291	88.545
2.42	87.9

2nd Cycle

Final Conc (mg/L)	Removal (%)
5.911	70.445
6.105	69.475
5.98	70.1

3rd Cycle

Final Conc (mg/L)	Removal (%)
8.041	59.795
7.984	60.08
8.064	59.68

4th Cycle

Final Conc (mg/L)	Removal (%)
10.55	47.25
10.58	47.1
10.69	46.55

Q2: Regeneration of Modified-SMT on CV textile dye (Conditions: Initial dye concentration = 20 mg/L, mass = 0.15 g, time = 30 minutes, volume = 30 mL, shaking speed = 250 rpm, temperature = 30 °C).

1st Cycle

Final Conc (mg/L)	Removal (%)
0.281	98.595
0.268	98.66
0.224	98.88

2nd Cycle

Final Conc (mg/L)	Removal (%)
4.063	79.685
4.004	79.98
3.832	80.84

3rd Cycle

Final Conc (mg/L)

6.246
6.214
6.112

Removal (%)

68.77
68.93
69.44

4th Cycle

Final Conc (mg/L)

9.503
9.543
9.501

Removal (%)

52.485
52.285
52.495