



**DEVELOPMENT AND PERFORMANCE OF MODIFIED ADSORBENTS
FOR METHYLENE BLUE REMOVAL**

By

HAMAD NOORI HAMAD HAMAD

**Thesis Submitted to the School of Graduate Studies, Universiti Putra
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Degree of Doctor of Philosophy**

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in
fulfilment of the requirement for the degree of Doctor of Philosophy

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March 2024

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This study addresses the urgent need for effective Methylene Blue (MB) removal from aqueous solutions due to its environmental and health hazards. Current treatment methods are often inefficient or costly, necessitating the development of superior adsorbents. The research focuses on the preparation and optimization of Activated Carbon (AC) derived from oil palm empty fruit bunches (EFB) and Activated Bentonite Clay (ABC) for MB adsorption. AC was produced using a multi-stage activation involving zinc chloride (ZnCl_2) at 700°C , sulfuric acid (H_2SO_4) at 210°C , and ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) at 260°C , while ABC was synthesized via sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) treatments at 110°C . Comprehensive characterization was conducted using Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Brunauer-Emmett-Teller (BET) analysis, X-ray Fluorescence (XRF), Thermogravimetric Analysis (TGA), and X-ray Diffraction (XRD). The results revealed that AC achieved a remarkable MB removal efficiency of 99.91% with an adsorption capacity of 90.827 mg/g and a surface

area of 939.63 m²/g, while BABC demonstrated a removal efficiency of 99.593% and an adsorption capacity of 22.131 mg/g with a surface area of 74.15 m²/g. Both adsorbents conformed to Langmuir and Freundlich isotherm models and exhibited second-order kinetics. AC showed successful regeneration for up to 4 cycles and BABC for up to 3 cycles. The findings highlight the superior performance of AC and BABC compared to commercial activated carbon, underscoring their potential as cost-effective solutions for efficient water purification and contributing to advancements in environmental remediation technologies.

Keywords: Adsorption, Methylene Blue Removal, Bentonite Clay, Empty Fruit Bunch, Low-Cost Adsorbents.

SDG: GOAL 6: Clean Water and Sanitation

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PEMBANGUNAN DAN PRESTASI PENJERAP TERUBAHSUAI UNTUK PENYINGKIRAN METHYLENE BLUE

Oleh

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Kajian ini menangani keperluan mendesak untuk penyingkiran berkesan Metilena Biru (MB) daripada larutan akueus disebabkan oleh bahaya terhadap alam sekitar dan kesihatan. Kaedah rawatan semasa sering kali tidak berkesan atau mahal, yang memerlukan pembangunan penjerap yang lebih baik. Penyelidikan ini memfokuskan pada penyediaan dan pengoptimuman Karbon Teraktif (AC) yang diperoleh daripada tandan buah kosong kelapa sawit (EFB) dan Tanah Liat Bentonit Teraktif (ABC) untuk penjerapan MB. AC dihasilkan menggunakan proses pengaktifan pelbagai peringkat yang melibatkan zink klorida (ZnCl_2) pada suhu 700°C , asid sulfurik (H_2SO_4) pada suhu 210°C , dan ammonium sulfat ($(\text{NH}_4)_2\text{SO}_4$) pada suhu 260°C , manakala ABC disintesis melalui rawatan natrium hidroksida (NaOH) dan asid sulfurik (H_2SO_4) pada suhu 110°C . Pencirian menyeluruh dilakukan menggunakan Mikroskop Elektron Imbasan (SEM), Spektroskopi Inframerah Transformasi Fourier (FTIR), analisis Brunauer-Emmett-Teller (BET), Pendarfluor Sinar-X (XRF), Analisis Termogravimetrik (TGA), dan Pembelauan Sinar-X (XRD).

Hasil kajian menunjukkan bahawa AC mencapai kecekapan penyingkiran MB yang cemerlang sebanyak 99.91% dengan kapasiti penjerapan sebanyak 90.827 mg/g dan luas permukaan sebanyak 939.63 m²/g, manakala BABC menunjukkan kecekapan penyingkiran sebanyak 99.593% dan kapasiti penjerapan sebanyak 22.131 mg/g dengan luas permukaan sebanyak 74.15 m²/g. Kedua dua penjerap mematuhi model isoterma Langmuir dan Freundlich serta mempamerkan kinetik susunan kedua. AC menunjukkan kejayaan regenerasi sehingga 4 kitaran dan BABC sehingga 3 kitaran. Penemuan ini menekankan prestasi unggul AC dan BABC berbanding karbon teraktif komersial, menekankan potensi mereka sebagai penyelesaian kos efektif untuk pembersihan air yang cekap dan menyumbang kepada kemajuan dalam teknologi pemulihan alam sekitar.

Kata Kunci: Penjerapan, Penyingkiran Methylene Blue, Tanah Liat Bentonite, Tandan Kosong Kelapa Sawit, Penjerapan Kos Rendah.

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LIST OF ABBREVIATIONS

AABC	Acid Activated Bentonite Clay
ABC	Activated Bentonite Clay
AC	Activated Carbon
$(\text{NH}_4)_2\text{SO}_4$	Ammonium Sulphate
BABC	Base Activated Bentonite Clay
BC	Bentonite Clay
BET	Brunauer-Emmett-Teller
CHNOS	Carbon, Hydrogen, Nitrogen, Oxygen, Sulfur
CAC	Commercial Activated Carbon
C_e	Equilibrium Concentration
CEC	Cation Exchange Capacity
C_i	Initial Concentration
DW	Distilled Water
D-R	Dubinin-Radushkevich Constant
FC	Fixed Carbon Content
FTIR	Fourier Transform Infrared Spectroscopy
K_F	Freundlich Constant
R	Gas Constant 8.314
ΔG°	Gibbs Free Energy
HCL	Hydrochloric Acid
K_L	Langmuir Constant
q_{max}	Maximum Adsorption Capacity
MB	Methylene Blue
MC	Moisture Content
OPEFB	Oil Palm Empty Fruit Bunch

PPM	Parts Per Million
Ph	Potential Of Hydrogen
PFO	Pseudo First Order
K_1	Pseudo First Order Rate Constant
PSO	Pseudo Second Oeder
K_2	Pseudo Second Order Rate Constant
R.F	Regeneration By Furnace Treatment
R.S	Regeneration By Stirring Treatment
SAC	Spent Activated Carbon
SEM	Scanning Electron Microscopy
NaOH	Sodium Hydroxide
ΔH°	Standard Enthalpy Change
ΔS°	Standard Entropy Change
H_2SO_4	Sulphuric Acid
K_T	Temkin Constant
B_T	Temkin Equilibrium Binding Rate
TGA	Thermogravimetric Analysis
VC	Volatile Content
WHO	World Health Organization
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
$ZnCl_2$	Zinc Chloride

CHAPTER

INTRODUCTION

1.1 Background

Access to clean water is a critical global issue with far-reaching implications. Only 3.5% of the Earth's water is suitable for human consumption without treatment. The majority, approximately 96.5%, requires further purification before humans can safely use it (Hausmann et al., 2021).

Water scarcity compounds the problem, with projections indicating that by 2050, a significant percentage of the global population will face freshwater shortages (Kang et al., 2022). Inadequate wastewater treatment practices pose risks to human health and the environment, as untreated effluent is discharged into water bodies (Wilkinson et al., 2022). Acknowledging the urgency of the situation, the United Nations aims to reduce untreated wastewater by 50% by 2030 (Kang et al., 2022).

By 2030, global industrial water demand is expected to rise from 800 billion cubic meters to 1500 billion cubic meters, with industrial water withdrawals projected to increase by 22%. This challenges sustainable water resource management, particularly in regions already affected by water scarcity (Vajnhandl & Valh, 2014).

The textile industry generates significant volumes of wastewater containing pollutants like dyes and heavy metal ions (Affat, 2021). Among these

pollutants, methylene blue (MB) has gained particular attention due to its widespread use and potential environmental and health risks. MB is an aniline dye with a chemical formula of $C_{16}H_{18}N_3SCl$ extensively employed for various applications, including paper coloring, cotton and wool dyeing, temporary hair coloring, and staining. The presence of MB in e.g. wastewater creates one serious problem because lower concentrations may seriously affect certain organisms causing an increase in heart rate, cyanosis up to jaundice and vomiting then shock together with Heinz body formation followed by tissue necrosis as well (Arias-Ortiz & Vincent, 2024; Dimbo et al., 2024; Yang et al., 2024).

Most traditional wastewater treatment ways have a lower removal percentage for MB because of the complex molecular structure (Bhattacharjee et al., 2022). Therefore, other means of MB removal have been investigated by researchers. In recent years, adsorption has been regarded as a reliable method due to its cost-effectiveness, simplicity, and applicability. The application of activated carbon to remove the MB is commonly carried out, however, it has a high cost which limits its wide use (Al-Ghouti & Da'ana, 2020; Y. Wang et al., 2024).

In light of this constraint, scientists have turned attention to the development of low-cost adsorbents by making use of agro-industrial waste and residues such as palm kernel shells (PKS), coconut shell wastes on an empty fruit bunch (EFB) (Singer et al., 2021). Activated carbon derived from oil palm empty fruit bunches (EFB), has surfaced as a promising adsorbent. EFB

constitutes a significant by-product of the palm oil industry, generating substantial quantities of biomass waste. The conversion of EFB into activated carbon not only addresses waste management concerns but also yields a high-surface-area material suitable for adsorption processes. These new adsorbents could have broader applications for MB removal than traditional activated carbon and perform better in terms of sustainability, efficiency and cost (Singer et al., 2021; Somsiripan et al., 2023).

Bentonite, which belongs to the family of clay minerals is also found effective in the adsorption process for MB removal. Bentonite is characterized by its ionic exchanger, high surface area, and charged surface edges (Li et al., 2019). This is because of its interlayer space which offers a high capability to adsorb large amounts of water contaminants also known as the swelling capacity. Due to their high surface area, interlayer spacing, and exchangeable ions, these rigidify when they are hydrated; this results in exceptional adsorption capacities allowing them to remove cationic and anionic water contaminants including MB from the solutions (Busch et al., 2020).

The study seeks to leverage these innovations to improve wastewater treatment strategies and reduce environmental pollution by MB, helping access to clean water.

1.2 Problem statement

Methylene blue (MB) accounts for a significant part of the overwhelming annual along with other dyes production of around 7 million tons has a

considerable share in the textile, leather, and paper industries. However, almost 10% of this amount about 700.000 tons is dumped into the ambient after dyeing and preparing. The MB has a high level of toxicity as well as environmental impact that makes it very pollute and hazardous for health (Dihom et al., 2022; Sudarshan et al., 2023).

MB is toxic due to its ability to form carcinogenic by-products when it undergoes chemical transformations. In particular, there are conditions in which MB can be reduced to benzidine, a known carcinogen. Benzidine derivatives are capable of intercalation into cellular DNA and can therefore lead to mutations with a resulting increase in the likelihood that they would be associated with cancer. MB is a non-degradable dye, as it shows chemical stability due to its complex molecular configuration and hence stays in an environment for a long period accumulating into soil and water reservoirs. Such persistence raises both health and environmental concerns due to the contribution of MB to permanent carcinogenic effects (Eldeeb et al., 2022; Sorekine et al., 2022).

Despite its harmful impacts MB is still used since it works very well in industrial processes where replacing MB with an alternative may not provide the same-quality and profitable solution. Nevertheless, the conventional wastewater treatment processes are inefficient for removing MB out of water due to cost, difficulty of operation, and side effects. Moreover, there have been concerns about environmental pollution and health impacts due to their presence in wastewater. Thus, there exists a critical need for more effective treatment

methods to mitigate this ongoing challenge (Din et al., 2021).

New findings show that other types of adsorbents like bentonite clay and activated carbon from EFB are compelling alternatives. EFB conversion into activated carbon is one of the methods to solve waste management problems and has a high surface area which is suitable for adsorption with sustainability & low cost compared to commercial activated carbon. Bentonite clay and other adsorbent materials are used as effective sensors because bentonite is natural, abundant, and inexpensive with a remarkably high cation exchange capacity (CEC) and a large surface area. Adsorption is one of the simple and amenable methods to remove pollutants MB from wastewater. This study will take advantage of the above-mentioned low-cost adsorbents and benefits from this method to improve the removal efficiency of MB (Othmani et al., 2021).

Most of the previous investigations on MB adsorption onto activated carbon were focused on a single-stage activation process using ZnCl_2 and oil palm empty fruit bunches (EFB). However, all cited studies have stopped short of demonstrating the full activation process with $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 as a second step for increased mechanical properties in addition to added functional groups. This is an area that remains unexplored but provides great potential to improve the performance of activated carbon from oil palm waste (ALAM et al., 2007; Wirasnita et al., 2015).

Likewise, studies describing the activation of bentonite clay have mainly examined H_2SO_4 utilization at 70% (Gandhi et al., 2022; Noyan et al., 2007; Önal & Sarikaya, 2007; Tebeje et al., 2022). However, the activation of bentonite clay with NaOH has not been extensively studied. One of these underexplored strategies is to change surface adsorption properties and introduce more reactive sites. This work aims to fill this knowledge gap and provide solutions through the investigation of these new activation methods that may give better insights for enhancement in MB adsorption using activated carbon AC and bentonite clay BC.

1.3 Research question

The research questions concentrate on optimizing the synthesis and performance of adsorbents for methylene blue removal. Key areas include activation methods, adsorption efficiency, and regeneration potential.

- How does chemical activation (ZnCl_2 , H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, NaOH) affect the quality of activated carbon from oil palm empty fruit bunches (EFB)?
- What are the optimal conditions for synthesizing bentonite clay for methylene blue removal?
- Which physico-chemical properties of the synthesized adsorbents influence their adsorption performance, and which samples exhibit the best performance based on these properties?
- What are the adsorption capacities, kinetics, isotherms, and thermodynamics of the selected adsorbents?
- How effective are the synthesized adsorbents in regeneration and reusability over multiple cycles?

- How do the synthesized adsorbents compare to commercial activated carbon in adsorption efficiency and cost-effectiveness for methylene blue removal?

1.4 Objectives

The objectives of this thesis are twofold. The first part involves the preparation of adsorbents, specifically activated carbon derived from oil palm empty fruit bunches (EFB) and bentonite clay. These materials are investigated for their potential as cost-effective, high-performance adsorbents for methylene blue (MB) removal from aqueous solutions. The second part focuses on studying the adsorption behavior, including optimization during adsorption, kinetics, isotherms, thermodynamics, and the regeneration and reusability of the adsorbents.

Thus, the following specific objectives were pursued:

1. **Synthesis of Adsorbents:** To synthesize high-quality activated carbon from oil palm empty fruit bunches (EFB) and bentonite clay through a controlled chemical activation process involving ZnCl_2 , H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, and NaOH , ensuring optimal MB removal performance.
2. **Characterization and Optimization:** To characterize the physico-chemical properties of the synthesized activated carbon and bentonite clay, and to select the best-performing samples based on these characterizations for further adsorption studies.
3. **Adsorption Studies and Comparison:** To investigate the adsorption properties, regeneration, and reusability of the selected adsorbents for MB removal, and compare their effectiveness with commercial activated carbon.

1.5 Scope and limitation of study

The study focuses on the preparation, characterization, and performance evaluation of modified adsorbents, specifically activated carbon derived from oil palm empty fruit bunches (EFB) and bentonite clay (BC), for Methylene Blue (MB) removal from aqueous solutions:

- i. The production of activated carbon involves a two-step activation process using ZnCl_2 and either H_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$, while bentonite clays are treated with H_2SO_4 or NaOH , both are used to enhance adsorption properties, making use of their natural abundance, cost-effectiveness, cation exchange capacity, and substantial surface area.
- ii. Characterization of the synthesized adsorbents was done using spectroscopic, analytical, and thermal techniques to analyze surface morphology, structure characterization, chemical composition structural information from FTIR analysis of heat treatment effects on weight losses and Anson stability. The techniques including Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), X-ray fluorescence spectrometer (XRF), Brunauer Emmett Teller (BET) analysis, Thermogravimetric Analysis (TGA).
- iii. The study attempted to optimize the dye adsorption process at different key experimental factors such as pH (4-10), adsorbent dosage (0.4-0.65g for AC and 0.5-0.95g for BC), initial dye concentration (50-500 ppm for AC and 50-200 ppm for BC), contact time (30-180 minutes for AC and 45-315 minutes for BC), temperature (ranging from 25-55°C), and agitation speed (maintained at a constant 135 rpm). Batch adsorption experiments were carried out at these conditions to find the optimal dose using World Health Organization (WHO) standards for drinking water quality as a guideline.

- iv. The adsorption capacity and mechanism of samples were determined by Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich models to understand adsorption capacity and mechanism. Adsorption kinetics was described by the pseudo-first-order and pseudo-second-order models to determine the adsorption rate and efficiency of MB. The adsorption process feasibility and spontaneous nature were evaluated by using thermodynamic parameters (Gibbs free energy, ΔG°); enthalpy change (ΔH°), and entropy change (ΔS°).
- v. The study also evaluated the regeneration and reusability abilities of the prepared adsorbents in batch adsorption systems. The regeneration study aimed to determine the number of cycles the adsorbents could undergo while maintaining high adsorption efficiency.
- vi. The obtained results allow for comparing the modified adsorbents (AC and BC) with commercial activated carbon for decolorizing MB from an aqueous solution, using low-cost sustainable adsorbents derived from agricultural and natural sources.
- vii. Lastly, a stirring speed of 135 rpm was employed in all adsorption processes to provide sufficient agitation and mass transfer that would obviate kinetic limitations for easy comparison. This allowed consistent experimental design and a more focused understanding of the adsorbents' performance under different influential factors upon adsorption.

1.6 Significance of the study

This research delves into the utilization of activated carbon (AC) derived from oil palm empty fruit bunches (EFB) and bentonite clay (BC) as potential adsorbents for the removal of methylene blue (MB) dye from wastewater. With a focus on addressing the imperative demand for effective treatment of dyeing

effluents, this study is directed toward mitigating the environmental and health risks stemming from the toxicity and persistence of MB.

The use of methylene blue (MB) as a model compound in research and treatment studies helps to understand how organic dyes behave in wastewater. Utilizing the endeared features of its structural similarity, it offers us information that can be harnessed to help provide possible new approaches in preventing unwanted by-products during the treatment processes of effluents containing MB and similar dyes (Hameed et al., 2007).

The findings of this study are important in terms of waste management in the oil palm industry sector in Malaysia. Utilizing industry by-products (EFB) as material to convert into activated carbon transformed the waste dumping problem and at the same time fulfilled a high-surface-area material for adsorption. The method provides a green and inexpensive option in the development of commercial activated carbon. Furthermore, bentonite clay is naturally widespread, and its low-cost availability makes it an interesting adsorbent material for MB removal.

The adsorption method has been chosen due to its easy implementation, efficiency, and ability to remove contaminants such as MB from wastewater. It is conducted to investigate the adsorption equilibrium of MB onto AC derived from EFB and BC which are affected by some parameters such as pH, temperature, initial dye concentration, dosage of adsorbent used, and contact time. The study aims to develop efficient and low-cost adsorbents for dye

wastewater treatment by optimizing these parameters.

In conclusion, this study feeds into an overarching effort towards one of the UN SDGs — Goal 6: Clean Water and Sanitation. Consequently, the study is in line with what can be considered water-oriented strategies that seek to ensure the availability and sustainable management of water for all by developing efficient treatment processes for wastewater and promoting safe recycling of waste: saline industrial effluents from source-to-discharge. Water efficient processing methods and sustainable industrial practices are in line with global efforts of water efficiency across all sectors, including initiatives focused on ensuring access to sustainably managed drinking water for everyone.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Water pollution, especially those caused due to organic and also inorganic pollutants such as heavy metal ions and dyes represents hazardous both for the environment as well as human health. It has led to the exploration of a variety of techniques including physiochemical, chemical, and biological methods (Periyasamy, 2024; Sudarshan et al., 2023). Of all these, adsorptive treatment as a physiochemical method has been proven to be efficient in treating pharmaceutical effluent. Activated carbon, various biomasses waste, and inorganic materials viz supplementary clay have been utilized as adsorbents for these benefits of a focus on efficiency, easy availability, simplicity and low cost (Varsha et al., 2022).

The effectiveness of an adsorbent depends on several factors such as the time exposure, adsorbate initial concentration, temperature, and pH solution for guar gum nanoparticles as well as amounts of dechlorophylizer agent. Therefore, kinetic as well as isotherm studies are necessary to reveal the behaviors of adsorbent and its feasibility for pollutant removal. However, wastewater treatment is strategic and it has always been deemed an essential intervention to alleviate environmental contamination of heavy metal ions and organic spills. Thus, the selection of tactics and optimization of appropriate adsorption techniques are necessary to enhance removal effectiveness (Bhat et al., 2023; Periyasamy, 2024).

2.2 Textile wastewater characteristics

Around 280,000 tons of textile dyestuff are discharged into the global environment yearly by (N. Kumar et al., 2023; Sudarshan et al., 2023). The pollution of surface water is also exacerbated by the fact that dyeing operations are highly energy-intensive and inefficient, while a large number of hazardous chemicals are used to form wet processes such as dyeing, scouring bleaching, or finishing. Wastewater from textile plants differs in composition according to the types of processes it passes through which are classified into different categories; e.g. dyeing, finishing, printing washing, and others (Tomar et al., 2023). These categories display different quantities of flow and pollutants, including dyes, inorganic substance classes as well as organic compounds, heavy metals, and pH-adjusting chemicals with problems. Some textile dyeing and printing processes generate specific contaminants illustrated in Table 1, like pulp, alkali, cotton gum, hemicellulose, and cellulose pollutants; chemicals were dyes and additives (Mia et al., 2019; Periyasamy, 2024).

Table 1 : Pollutants from textile and dyeing processes

Process	Compounds
Printing	Color, solvents, urea, metals
Finishing	Waxes resins, stearate, softeners, spent, acetate, chlorinated compounds, solvents
Mercerizing	NaOH, high of pH
Dyeing	Acidity/alkalinity, color, metals, salts, sulphide, surfactants, assistants of organic processing, formaldehyde
Desizing	Waxes, ammonia, starch, sizes, enzymes
Scouring	Insecticides and disinfectants residues, waxes, sizes, soaps, enzymes, fats, pectin, oils, spent solvents, surfactants, antistatic agents, NaOH
Bleaching	sodium silicate / organic stabilizer, AOX, H ₂ O ₂ , high pH

(Mia et al., 2019)

2.2.1 Composition and sources

Textile wastewater has the most important properties at high levels of chemical oxygen demand (COD), color, pH flow variations, temperature rise or waste sludge, and low biodegradability (Periyasamy, 2024). Those contaminants include toxic substances, colored and chlorinated compounds, recalcitrant organic chemicals, surfactants, and salts. In an integrated textile mill, composite wastewater comprises various chemicals such as dyes, pigments, starches, soaps, detergents, fatty acids, and carbonates. Table 2 presents the characteristics of typical textile industry effluent indicating the various pollutants present in a given sample of wastewater (Panagopoulos, 2021; Periyasamy, 2024).

Table 2 : Effluent characteristics of textile industry

Parameters	Values
pH	7.0 - 9.0
Temp (°C)	35 – 45
COD (mg/l)	150 - 12,000
BOD (mg/l)	80 - 6,000
TDS (mg/l)	2,900 -3,100
TSS (mg/l)	15 - 8,000
TKN (mg/l)	70 – 80
Color (Pt-Co)	50 – 2500
Cl (mg/l)	1000 – 1600
Na (mg/l)	6,000

(Panagopoulos, 2021)

2.2.2 Toxicological and environmental impacts

Wastewater produced from textile mills adds a significant amount of pollution to the environment. Textile effluent is characterized by high color and other organic matter which are highly toxic to aquatic life and disturb the food chain (Kishor et al., 2021; N. Kumar et al., 2023). Its blue effluent is hazardous and

unsightly, creating health risks for humans as well as the environment. These MWW are polluted by different pollutants, such as sediments, oil and fats, BOD₅ and COD, grease, and particulate materials which will contribute to the occurrence of DO depletion that affects aquatic ecosystems. Another example of a toxic heavy metal, chromium frequently occurs in textile wastewater and can build up over time throughout the food chain. Textile mills use dyes and chemicals in excess which has made effluent dark which increases water turbidity and harms photosynthesis and wildlife. Low pigment levels are also sufficient to destabilize marine life as well as a food web (Kishor et al., 2021; Saxena et al., 2020). It has been proven that the accumulation of dyes causes instability in aquatic systems and soil leaching, resulting in groundwater contamination. Exposure over an extended period to dye effluents has been associated with several health complications, namely immune suppression, and for instance could cause kidney damage, central nervous system disorders as well as reproductive issues. This event leads to anaerobic or smelly compounds and causes a decrease in the organic material, and biological activity of bioremediation (Gayathiri et al., 2022).

2.2.2.1 Direct and indirect effects

The environmental impact of textile wastewater is divided into direct and indirect effects. The direct effects are the disliking of colored effluents, which cause interference with sunlight penetration and inflict undue damage to aquatic life. The re-oxygenation capacity of water bodies can be lessened by the presence of dyes and other pollutants, that may alter marine organisms. Another direct consequence is groundwater pollution causing the death of

marine life forms (Tariq & Mushtaq, 2023; X. Wang et al., 2022).

The indirect effects of nutrient enrichment can cause eutrophication in waterways, leading to oxygen depletion and a loss of aquatic fauna. Additionally, colored allergens in wastewater can increase genotoxicity and microtoxicity, posing threats to human health. Inhaling waste emissions from industrial and vehicular sources can harm the human immune system, making individuals more susceptible to diseases. Table 3 provides a summary of these direct and indirect impacts (Tariq & Mushtaq, 2023; X. Wang et al., 2022).

Table 3 : Environmental impacts of colored wastewater

Direct effects	Indirect effects
Aesthetically displeasing The obstruction of sunlight penetration can cause harm to aquatic life Certain factors can hinder the re-oxygenation capacity of the system. Groundwater's pollution	Eutrophication The presence of colored allergens can enhance genotoxicity and microtoxicity Exposure to certain factors can diminish the immune defense capability of human beings can result in the death of aquatic organisms

(X. Wang et al., 2022)

2.2.2.2 Eutrophication

Methylene blue is an important dye used to color wood, fibers, and textiles as well its presence in textile wastewater leads to serious environmental effects like eutrophication. Because these dyes are high in nutrients like nitrogen and phosphorous, they can lead to harmful algal blooms (HABs) which hurt water bodies. However, when these algae die in the surface layer and are decomposed under darkness by aerobic bacteria that cannot respire with nitrate hypoxia occurs downstream micropollutant concentrations escalate

due to dynamic internal loads (Khan et al., 2023). Furthermore, when large colonies of algae form sunlight can be blocked to the point that plants living in coastal waters and other aquatic locations are not able to get enough energy from photosynthesis thus collapsing the ecosystem further. Certain algal blooms are also capable of producing toxins that contaminate water supplies with potentially toxic impacts on human and wildlife health. Textile wastewater also contributes to the eutrophication process through dyes and other chemicals present in it which degrade water quality, fisheries, and tourism and raise treatment costs (N. Kumar et al., 2023; Tariq & Mushtaq, 2023).

2.3 Methylene blue in textile industry

Methylene blue (MB) is a synthetic dye, well-known in the textile Industry because of its intense blue color as much as for stability. It is very common in the dyeing of all natural fabrics, especially cotton wool and silk because it gives a deep color that lasts long. In general, the large consumption of MB causes serious environmental and health problems influencing wastewater treatment (Abdul Sattar et al., 2024; Choi, 2022). The growth of the dye sector is closely connected with the expansion of the textile market. Dyes are extensively used in Malaysia such as in the batik industry (Izwan Anthonysamy et al., 2023).

2.3.1 Properties and utilizes of methylene blue

Methylene blue (MB) stands for 3,7-bis (Dimethylamino) phenothiazin-5-ium chloride), it is a thiazine dye with a chemical name having a molecular formula of $C_{16}H_{18}N_3SCl$ and this compound has a weight imprint of approximately 319.85 g/mol (Abdul Sattar et al., 2024; Choi, 2022). MB is oxidized (it has a

deep blue color) and reduced to its leuco form, leukomethylene blue (LMB), which is colorless. The water solubility of the dye enables it to be in solution forming a methylene blue cation ($C_{16}H_{18}N_3S^+$) and one chloride anion (Cl^-), which makes this organic compound useful for different industries (Choi, 2022).

Textile industry applications: MB is used to dye natural fibers such as cotton, wool, and silk in textiles. Its robust colorfastness and high visibility make it a preferred choice for producing vibrant blue shades (Abdul Sattar et al., 2024; Choi, 2022). MB's applications extend to dyeing paper, creating temporary hair colors, and even in particular medical and scientific contexts.

Medical Uses: MB serves several critical functions in medicine. It is employed to treat methemoglobinemia, a condition where hemoglobin is impaired, reducing the blood's oxygen-carrying capacity (Anand et al., 2023; Fossen Johnson, 2019). MB acts as a reducing agent, restoring the normal function of hemoglobin. Additionally, it is used as a bacteriological stain and indicator due to its ability to bind to various biological tissues and cell structures (Choi, 2022; Morozova et al., 2023).

Chemical Structure: The structure of MB is characterized by a central phenothiazine ring with two dimethylamino groups attached. The molecular structure is depicted in Figure 1, illustrating the dye's complex arrangement that contributes to its distinctive color and functionality (Cragan, 1999).

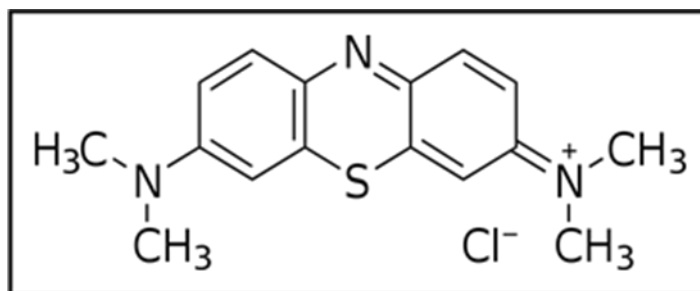


Figure 1 : Chemical Structure of MB
(Cragan, 1999)

Despite its utility, MB's environmental persistence and resistance to biodegradation pose significant challenges in wastewater management (Arias-Ortiz & Vincent, 2024; Dimbo et al., 2024; Yang et al., 2024).

2.3.2 Environmental and health effects of methylene blue

Methylene blue's environmental and health impacts are of considerable concern due to its persistence and toxicity.

2.3.2.1 Environmental impact

Methylene blue contamination in aquatic systems can lead to severe ecological disturbances. The dye imparts a strong color to water, reducing light penetration and inhibiting photosynthesis in aquatic plants. This reduction in photosynthesis adversely affects the oxygen levels in the water, potentially killing aquatic organisms and disrupting the entire aquatic food chain (Dutta et al., 2024).

MB is also known to accumulate in sediments, persisting for long periods. This accumulation can disturb benthic ecosystems, affecting organisms that reside

in or rely on the sediment environment. The dyes affinity for binding with organic and inorganic particles enhances its mobility and persistence in aquatic environments, posing long-term risks to ecological health (Arias-Ortiz & Vincent, 2024; Dimbo et al., 2024; Yang et al., 2024).

2.3.2.2 Health impact

Human exposure to MB can occur through contaminated water, occupational contact, or medical applications. Acute exposure to high concentrations can cause adverse symptoms such as nausea, vomiting, abdominal pain, and skin irritation. Chronic exposure, even at lower concentrations, can have more severe health implications (Arias-Ortiz & Vincent, 2024; Dimbo et al., 2024; Yang et al., 2024).

One primary health concern associated with MB is its potential to induce methemoglobinemia. By interfering with the normal function of hemoglobin, MB can reduce the blood's ability to transport oxygen, leading to symptoms such as cyanosis, headache, fatigue, and, in severe cases, life-threatening conditions (Arias-Ortiz & Vincent, 2024; Dimbo et al., 2024; Yang et al., 2024).

MB can also impact the central nervous system, potentially causing confusion, dizziness, and, at higher doses, convulsions and coma. Long-term exposure has been linked to liver and kidney damage, further complicating its health impacts. Additionally, there is a concern about MB's potential to cause genetic mutations and cancer, although more research is required to understand these risks entirely.

Given these significant environmental and health effects, effectively removing MB from wastewater are crucial to mitigate its adverse impacts.

2.3.2.3 Traditional methods for MB removal

The removal of MB from wastewater is beneficial in reducing its environmental and health risks. There are different classical methods each of which has some advantages and limitations (Din et al., 2021).

The biological ways degrade MB through metabolic processes that use microorganisms for instance bacteria and fungi (Deng et al., 2020). The techniques presented are eco-friendly and cost-effective, which evinces an ecologically sound method for decolorization of the dye. Nevertheless, they are not very useful for high-density dye solutions because of the toxicity effect on micro-organisms metabolic skills by MB that contributes to reduced activity and limits the potential application (Goli et al., 2019).

This is followed by coagulation and flocculation with the addition of chemical substances (e.g., alum, ferric chloride, polyaluminum chloride) to wastewater. These chemicals cause dyes to then degrade and aggregate to form bigger flocs that can be settled or floated out. This process proved successful in removing suspended particles and colloidal dyes; however, the resultant sludge requires further treatment before disposal which carries a high overall economic burden (Nnaji et al., 2022).

Ozone treatment works on a solid oxidation basis with MB degrading to other less toxic substances following O₃ utilization. While this process is very good in breaking the complexity of dyestuff molecules, at the industrial level it would have a substantial cost due to the high energy for its production. In addition, ozone treatment can produce secondary by-products that need further remediation leading to increased complexity in the whole process (Hussain et al., 2022).

The electrochemical methodologies utilize electrical currents to induce redox reactions for degrading MB. While these methods are very effective in removing dyes, they can be energy-intensive and require sophisticated equipment. Regarding this, the expensive of operating cost and maintenance for heavy machinery may be led to a major disadvantage in using the equipment (Al-Gheethi et al., 2022).

Ion exchange resins, which exchange ions between the resin and untreated water. This method can be costly as resins are expensive and need to be regenerated periodically. However, it may be useful when considering operational cost, resin replacement frequency, and their role in supporting gene therapy process viability (Deivayanai et al., 2024).

Membrane filtration methods, such as ultrafiltration (UF), reverse osmosis (RO), nanofiltration (NF), and microfiltration (MF), utilize selectively permeable membranes to separate dye molecules from aqueous solutions based on size exclusion or charge interaction. While they offer high removal efficiency, the

operational cost is high due to membrane fouling, necessitating frequent cleaning and replacement (Fernández-Medrano et al., 2022).

Fenton's reagent, or hydrogen peroxide and ferrous iron mix ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), develops hydroxyl radicals that can efficiently degrade MB. Though such a method is effective in its decontamination of the water; it yields iron sludge which needs to be correctly and cleanly disposed of, bringing more waste management issues in this way too.

The photochemical treatment consists of the reaction of hydrogen peroxide (H_2O_2) with ultraviolet radiation to induce the generation of reactive species that can be strong oxidants for destroying MB [45]. Though an efficient process it would require a well light source which consumes energy and in turn causes higher operating costs (M. I. Ahmad & Bensalah, 2022).

Photocatalytic treatment using titanium dioxide (TiO_2) with UV radiation produces some reactive species that assist in degrading MB. The method has very high efficiency in removing dyes, but is UV light-dependent and needs expensive and precious catalysts that have great demands on controlling the reaction conditions (Koe et al., 2020).

Adsorption is a very used method, because of its simple strategy and efficiency. The most commonly used adsorbents are activated carbons for their high surface area and capacity. Similarly, however, other cheap adsorbents have been investigated such as clay minerals and agricultural by-products (e.g. rice husk and coconut shell) along with industrial waste

materials including fly ash or bottom ashes, etc. Adsorption is a highly efficient method of removing MB even in small amounts however the adsorbent requires extensive regeneration or replacement which will ultimately affect its feasibility as well as cost (Wang et al., 2023).

Different methods for methylene blue removal have varied mechanisms, and the selection of the appropriate method or combination depends on wastewater characteristics and effluent standards. For a comprehensive review of traditional removal methods, refer to Table 4 for a comparison of their advantages and disadvantages.

Table 4 : MB removal technologies in textile wastewater

Method	Advantages	Disadvantages
Biological methods (fungi, algae, bacteria, microbial fuel cell)	Environmentally friendly, low cost, effective in removing organic pollutants	Slow process, requires a large area, may not be effective in removing inorganic pollutants
Coagulation/Flocculation	Effective in removing suspended solids, can be used as a pretreatment step	May not be effective in removing dissolved pollutants, requires a large area
Ozone treatment	Effective in removing color and odor, can be used as a disinfectant	High energy consumption, expensive equipment
Electrochemical methods	Effective in removing organic pollutants, can be used for disinfection	High energy consumption, expensive equipment
Ion-exchange resins	Effective in removing heavy metals and other inorganic pollutants	Expensive, requires frequent replacement
Separation techniques (membrane filtration techniques, ultrafiltration, reverse osmosis, nanofiltration, microfiltration)	Effective in removing dissolved pollutants, can be used as a pretreatment step	Expensive equipment, requires frequent maintenance
Fenton's reagent (H_2O_2 - Fe^{2+} salts) for treatment	Effective in removing organic pollutants, can be used for disinfection	High chemical consumption, may generate sludge
Photochemical (H_2O_2 -UV radiation)	Effective in removing organic pollutants, can be used for disinfection	High energy consumption, expensive equipment
Photo catalytical (TiO_2 -UV radiation)	Effective in removing organic pollutants, can be used for disinfection	High energy consumption, expensive equipment
Adsorption	Effective in removing organic pollutants, can be used as a pretreatment step	Requires frequent replacement of adsorbent material

(Hamad & Idrus, 2022)

2.4 Adsorption technique for MB removal

Adsorption was introduced in the 18th century as one of the aspects of the removal of contaminants from liquids or gases and is an important process in environmental engineering. The process of adsorption is one in which molecules or ions are removed from a liquid or gaseous phase onto the surface of a solid substance, called sorbent, and the substances being

accumulated on its surface are referred to as an adsorbate (Q. Ibrahim et al., 2022). This process occurs when the adsorbate concentration at the surface of an adsorbing solid is more than its bulk phase, then it happens and gets adhered to the solid site. Different active sites on the surface of the adsorbent have different energies and therefore interact differently with the particular adsorbate. These interactions may be physical or chemical, depending on the strength of the bond between adsorbate and adsorbent (Pellenz et al., 2023).

The internal type has two main types physisorption & chemisorption which are based on interaction strength. Physisorption is mostly asymptotic and involves weak van der Waals forces or hydrogen bonding, electrostatic interactions, etc. generally at low temperatures with minimal enthalpy change. Whereas, chemisorption involves covalent solid bonds and is undertaken under high temperatures that generally only lead to monolayer coverage of the surface (X. Wang et al., 2023; Y. Wang et al., 2024). As shown in Figure 2, adsorbates are linked to the surface of the absorption as illustrated by swapping liquid phase properties comprising concentration, pH, or temperature which can influence and may result from desorption when transferred all through the solution once more Collected again on section (El-Baz et al., 2020).

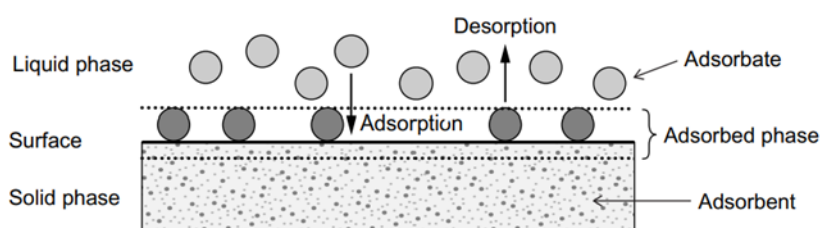


Figure 2 : Concept of Adsorption
(El-Baz et al., 2020)

The efficiency of adsorption used for methylene blue (MB) removal from wastewater depends on the type of absorbents, surface area, and interactions between MB dye with each variation commonly. Adsorption also has the advantage of being a simple and efficient method of dealing with several types of pollutants (Y. Wang et al., 2024). However, it is not perfect and has its corresponding limitations mostly revolving around the necessity to often replace or regenerate adsorbent material. In contrast, other methods (such as biological treatment, coagulation/flocculation, and separation techniques) are effective only concerning specific types of pollutants. Ozone and electrochemical methods effectively remove organics but may not specifically target MB, while ion exchange resins are more suited to heavy metals than MB. The treatment method choice should align with the specific characteristics of the wastewater and practical considerations, including cost and environmental impact (Arias-Ortiz & Vincent, 2024; Dimbo et al., 2024; Yang et al., 2024).

2.4.1 Adsorption mechanisms

Adsorption mechanisms involve a range of physical and chemical interactions that facilitate the adherence of adsorbates (molecules or ions) to adsorbent surfaces. These interactions include Van der Waals forces, electrostatic attractions, hydrogen bonding, and hydrophobic effects (Al-Ghouti & Da'ana, 2020). The adsorption process occurs in three main stages: first, the diffusion of adsorbates into the boundary fluid film surrounding the adsorbent; second, surface diffusion within the adsorbent's pores; and third, the actual adsorption at active sites on the adsorbent surface. Factors such as pH, which influences

the charge and ionization states of both adsorbates and adsorbents, chemical composition, which determines the type of interactions possible, and salt concentration, which can alter electrostatic interactions or solubility, all affect the efficiency of adsorption. Reactive dyes are capable of binding covalently with adsorbents and others which interact only through non-covalent forces. The reverse process, desorption whereby adsorbates are released into the liquid phase controlled by changes in environmental conditions such as pH may also take place (Arias-Ortiz & Vincent, 2024; Dimbo et al., 2024; Yang et al., 2024). Mechanisms such as these, depicted in Figure 3 are fundamental when optimizing adsorption processes.

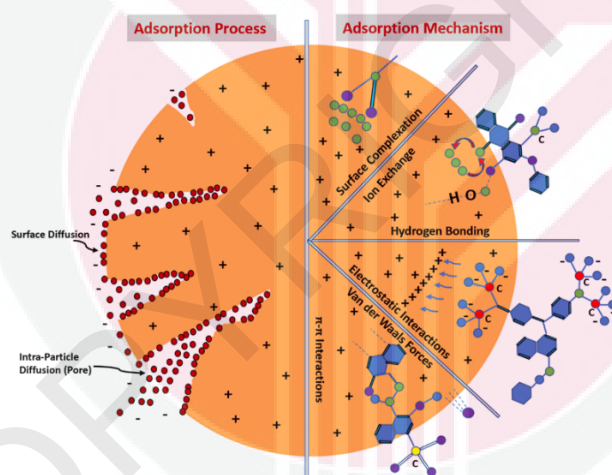


Figure 3 : Mechanisms of MB Removal
(Hamad & Idrus, 2022)

2.4.1.1 Physisorption

The adsorbing process in physisorption or physical adsorption is a reversible solid-to-reactant interaction driven by weak intermolecular forces including van der Waals, hydrogen bonding, and electrostatic interactions (El-Baz et al., 2020). There is no new chemical bond that can form these events usually

happen at low temperatures, with small enthalpy changes, and favor the formation of multilayer adsorbate at the surface of the adsorbent. It is a versatile, easy-to-operate method with a wide range of applications and is thus widely used for the elimination of organic contaminants from water in wastewater treatment facilities. However, it is not as selective as chemisorption but with less activation energy in general (Al-Ghouti & Da'ana, 2020).

2.4.1.2 Chemisorption

Chemisorption (chemical adsorption) is defined as having strong chemical bonds usually covalent formed between the adsorbate and the surface. This method is carried out at higher temperatures which also require drastic changes in enthalpy and high activation energy (Al-Ghouti & Da'ana, 2020). Chemisorption usually causes a monolayer of adsorbate molecules, maybe due to the strong binding forces. This adsorption is specific and the maximum selectivity shown can be useful in the removal of particular contaminants like some metals and reactive dyes etc. showing far more stable attachment compared to physisorption (Agboola & Benson, 2021; El-Baz et al., 2020). Table 5 differentiates physical and chemical adsorption trends.

Table 5 : Comparison of physical vs. chemical adsorption

Chemical adsorption	Physical adsorption
Discriminative surface adherence	Non-discriminatory surface adhesion
Irreversible	Reversible, allowing for desorption
Through chemical bonding	Absence of chemical bonding
Monomolecular layer on the surface	Molecular condensation in the capillaries

(Agboola & Benson, 2021)

2.4.2 Adsorption isotherms

Adsorption isotherms are of great importance when it comes to the design and optimization of adsorption processes. They give a quantified representation of the way adsorbates interact with adsorbent conditions (Al-Ghouti & Da'ana, 2020). and aid in evaluating sorption capacity and efficiency. This adsorption equilibrium model helps us to know the interaction between how many amounts of various components are in a solution and on solid partition light sensibly anyway not completely (Al-Ghouti & Da'ana, 2020; Y. Wang et al., 2024).

The Langmuir isotherm model describes adsorption on a surface with a fixed number of identical sites and each site can accommodate only one molecule. Such a model assumes adsorption to occur either in a uniform monolayer, i.e. once all the sites are full no more adsorption can take place. It is well-suited for systems in which an adsorbate forms a monolayer on the surface and no attar active interactions between adsorbate molecules occur (Kinniburgh, 1986).

However, the Freundlich isotherm model suits heterogeneous surfaces with non-similar energies support for adsorption. It hypothesizes that adsorption sites vary in their affinity for the adsorbate, suggesting an uneven distribution of such sites. This model has applications for systems where the adsorbent surface is not homogeneous and can capture a large range of concentrations (Weber & Chakravorti, 1974).

The Temkin isotherm model embodies the interactions of adsorbate–adsorbent in its structure. It makes the simplifying assumption that the heat of adsorption decreases linearly with increasing coverage and assumes a flat distribution for adsorption energy across the surface. The model is appropriate for cases where interactions between the adsorbate and adsorbent are nonnegligible, which influences all over the process of such physisorption (Johnson & Arnold, 1995).

The Dubinin–Radushkevich (D-R) isotherm model: is used for the adsorption of gases on solid surfaces. It applies most accurately to adsorption on microporous adsorbents and has special utility for the analysis of gas-phase sorption at pressures in low ranges. The D-R model could give us some kind of knowledge on the adsorption power and behavior importantly in cases in which materials have various porosity structures as well (Rand, 1976).

These models give different perspectives on the adsorption process to reveal how various types of adsorbates interact with adsorbents as a function of temperature or pressure. The use of the proper model depends on what

adsorbate that is being subjected to analysis.

2.4.3 Adsorption kinetics

The adsorption kinetics is of utmost importance in understanding how fast a pollutant can be removed from an aqueous solution. This field is concerned with the rate, at which adsorbates are extracted from the liquid phase and transferred onto the surface of an adsorbent. The design of efficient treatment systems is important, and fast capture & efficiency for the effective adsorption processes are specialized (Al-Ghouti & Da'ana, 2020; Tan & Hameed, 2017; Y. Wang et al., 2024).

Adsorption kinetics encompasses several steps, the adsorbate molecules transport from the bulk solution to the surface of a solid known as external mass transfer, which is followed by penetration into the porous structure through intra-particle or pore diffusion stage back-diffusion involved, and lastly binding of this molecule with specific sites at the outermost layer on this complex composite. This process is controlled by different factors, related to the adsorbent, the concentration of the adsorptive, or features of the solution such as room temperature and pH value (Bețianu et al., 2020; Y. Wang et al., 2024).

The pseudo-first-order (PFO) and the more general pseudo-second-order models (PSO) are commonly used to describe adsorption kinetics. Pseudo-first order model This is based on the assumption that the rate of adsorption at any instant will be directly proportional to the concentration remaining up to

equilibrium which can. It performs reasonably well in predictable adsorption where the rate-limiting step is primarily the mass transportability to the surface of the base material (Al Ashik et al., 2023).

In contrast, the pseudo-second-order model assumes that adsorption velocity is proportional to the square concentration difference between equilibrium and at time t . This model is frequently used when the rate-limiting step of the adsorption process is the chemical interaction between the adsorbate and the surface. It is useful for predicting adsorption processes on systems with identical active sites (Al-Ghouti & Da'ana, 2020; Y. Wang et al., 2024).

2.4.4 Thermodynamics of adsorption

The thermodynamic properties are very important for the characteristics, nature, and the feasibility of adsorption process. These parameters include free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°). The equilibrium sorption constant with ΔG° , enables us to obtain some idea about the spontaneity of a process. A negative ΔG° value signifies adsorption is spontaneous, whereas a positive value denotes non-spontaneity. The value of ΔG° indicates the spontaneity values for adsorption (Al-Ghouti & Da'ana, 2020; Y. Wang et al., 2024).

Enthalpy change (ΔH°) reveals information about heat exchange during adsorption. A positive ΔH° means that the process is endothermic (it absorbs heat from its surroundings), and a negative one indicates an exothermic process, consequently releasing heat. The entropy change (ΔS°) settles the

order or disorderliness in a solid-liquid interface for adsorption. Positive ΔS° , for example, results in greater disorder whilst negative ΔS° means less entropy.

The Van't Hoff plot, $\ln(K)$ vs. $1/T$, is used to calculate thermodynamic parameters. By analyzing $\ln K$ as a function of $1/T$, we can determine how temperature influences the adsorption process. For example, a positive ΔH° (endothermic) favors higher temperature for greater adsorption, while an exothermic process favors lower temperatures.

Thermodynamic insights are fundamental to the optimization of adsorption processes and efficient elimination of contaminants from different media, such as water (Al-Ghouti & Da'ana, 2020; Ichou et al., 2020; Y. Wang et al., 2024).

2.4.5 Factors affecting adsorption

Knowledge of the multiple factors affecting adsorption is important to optimize methylene blue (MB) removal from wastewater. These are the factors such as initial dye concentration, adsorbent dose-response, contact time, pH study and agitation speed, textile effluent temperature, surface area, solutes solubility characteristics molecule size on pore sizes. All of those determinants have a key role in the efficiency and effectiveness of adsorption.

- i. **Initial dye concentration effect:** The level of the dye in wastewater significantly affects the adsorption process. As the dye concentration in an aqueous solution increase, removal efficiency generally decreases due to the rapid saturation of the fixed adsorption capacity of the adsorbent. With the increase in initial concentration, the active

sites on the surface of the adsorbent available become insufficient to bind all dye molecules which reduces the removal percentage. On the opposite, low initial concentration allows fuller utilization of active sites on adsorbent per mol dye resulting in higher removal efficiency (Albayati et al., 2024; Hassan et al., 2024; Holliday et al., 2024).

- ii. **Adsorbent dosage effect:** The adsorption of dye is strongly contingent upon the quantity of used adsorbents; Increasing the adsorbent dose increases the number of available active sites for dye removal efficiency. The degree of dye adsorption usually increases linearly with the higher dosage of an adsorbent until it saturates and no additional changes are recorded (Albayati et al., 2024; Hassan et al., 2024; Holliday et al., 2024).
- iii. **Contact time effect:** Contact time is most important for the adsorption phenomenon. In general, the higher contact time leads to a faster dye removal rate before reaching equilibrium. A lot of crystal nuclei provide plenty of adsorbing sites for dye molecules, so the capability is quick at this stage. Once these sites are filled, the adsorption rate decreases visibly, and more increases in contact time hardly affect further increment of AC (Albayati et al., 2024; Hassan et al., 2024; Holliday et al., 2024).
- iv. **pH effect:** The pH affects one as it will ionize or non-ionize adsorbate, surface charge adsorption. pH changes can modify shifts in functional groups on the adsorbent surface, thereby leading to alterations of maximum adsorption capacity. For example, during adsorption: under acidic or basic conditions, the dye molecules may be bound to and inhibited by near-surface interaction with an adsorbent so that whenever they are released into the water phase (Albayati et al., 2024; Gao et al., 2021; Hassan et al., 2024; Holliday et al., 2024; Kamran et al., 2022).
- v. **Agitation speed effect:** The effect of initial adsorption on the exchange significantly depends on the velocity at which stirring is

attended to, as it influences the dispersion in solute within the solution and boundary layer thickness around surrounding particles. The higher the agitation speed, is better the contact between the adsorbent and adsorbate which leads to an increase in the rate of dye removal (Albayati et al., 2024; Hassan et al., 2024; Holliday et al., 2024).

vi. **Temperature effect:** The temperature is a vital parameter that influences the adsorption phenomenon. In endothermic processes the mobility of dye molecules is facilitated at higher temperatures and more active sites are available for adsorption. On the other hand, with an exothermic process, a higher temperature might reduce adsorption efficiency. The viscosity of the solution, along with changing the temperature also changes and impacts on diffusion rate between adsorbate molecules (Albayati et al., 2024; Gao et al., 2021; Hassan et al., 2024; Holliday et al., 2024; Kamran et al., 2022).

vii. **Surface area effect:** Adsorbents presenting a more extensive surface region will often show greater adsorption capacities as an outcome of active sites available. The dye adsorption also might be improved due to the existence of certain chemical groups on the surface of an adsorbent. For instance, primary surface groups would be suitable for anionic dye adsorption and the presence of acidic oxygen-containing functional motifs enhances cationic dyes removal. Surface modification, like thermal treatment, greatly enhances the adsorption capability (Albayati et al., 2024; Hassan et al., 2024; Holliday et al., 2024; Kamran et al., 2022).

viii. **Solute (adsorbate) solubility in liquid (wastewater):** The ability of the adsorptive to bring its aroma into drinking does a pivotal split-up over deodorization skill. Less soluble compounds can be more adsorbable when compared to highly soluble. This is because the nonpolar substances have less attraction for water which makes them easier and be removed. Adsorption is influenced by factors such as molecular size, soluble nature, and the presence of functional groups

with less soluble compounds more readily adsorbed (Mansour et al., 2018).

- ix. **Numbers of carbon atoms:** Larger hydrocarbons are generally less polar and adsorbed easily mainly in the homologous series. This increase in adsorption levels occurs eg. for the acids formic acetic propionic butyric acid. Indeed, the larger the carbon chains are less polar and thus have more of an anhydrophobic surface which may explain their greater adsorption (Moreira et al., 2023).
- x. **Molecular size vs. pore sizes:** The molecular size of the adsorbate compared with pore sizes in an Adsorbent is important for good absorption. The adsorption capacity decreases due to the inability of larger molecules to penetrate smaller pores. The use of smaller particles is supposed to increase mass transfer and make it easier to approach the adsorbent achieving equilibrium. The adsorption efficiency depends on the surface area, pore size distribution and surface chemistry (Liu et al., 2022).

2.4.6 Desorption

Adsorption mechanisms studies and the possibility of regeneration of adsorbents require desorption study. By studying desorption, we can learn about the nature and strength of adsorbate-adsorbent bonds. Weakly bound dyes appear physisorption is the main mechanism and neutral water can effectively desorb them. In comparison, the desorption process with acidic or alkaline water demonstrates ion exchange mechanisms that likely involve stronger chemical bonds and/or electrostatic interactions (Y. Wang et al., 2024).

Several studies have even shown different dyes to behave in a significantly altered desorption manner. Desorption tests with pinecone material showed different desorption rates for the dye numbers acid black 26, green 25, and blue seven. The desorption of Acid black 26 and acid blue seven was high, which indicated a rapid rate but weaker adsorptive forces leading to lower interaction strength by acid green 25 with a clay surface. For acetic acid in another study, it was effective to some extent as a dissolving agent while NaOH and H₂O did not decouple significant desorption effect or diluted animal-plant interaction affinity during ginger plant dye projection (Al-Ghouti & Da'ana, 2020; Rápó & Tonk, 2021).

2.5 Low-cost adsorbents for MB removal

Using a low-cost adsorbent derived from natural and waste materials offers an effective and economical solution for removing MB from wastewater.

2.5.1 Agricultural waste: oil palm biomass

The efficiency of removal was found to be higher in the case of industrial wastewater and low-cost adsorbents are economically effective for treatment. These adsorbents are prepared through inexpensive agricultural wastes which act as a better alternative to industrial or solid waste by-products with very little processing. Furthermore, owing to the excellent physico-chemical characteristics and low cost arguably of minimum disposal impact agriculture-based sorbents effectively lessened dyehouse effluent (Chong et al., 2023; May et al., 2019).

Palm oil is an important agricultural crop, one of the invaluable cash crops to many nations (Malaysia ranks second among all countries in exporting palm), and contributes significantly to its Gross National Income. Each year, the oil palm production process turns out large amounts of biomass from by-products created during activities and processing on an oil... These by-products are Oil Palm Trunks (OPT), Oil Palm Fronds (OPF), Empty Fruit Bunches (EFB), Mesocarp Fibers (MF), Palm kernel Shells (PKS), and the final reject of the palm oil converting process that is Processing unit treatment effluent can be directly utilized for bioenergetic. The waste and residue biomass is usually either landfilled or burned, causing significant environmental problems (May et al., 2019; Pulingam et al., 2022; Somsiripan et al., 2023).

Many research studies have been conducted to convert oil palm biomass into value-added products and solve this problem. The reuse of POME and OPF is used in biogas fermentation results that have been made gains for both resources, while bagasse plate useful to study the frequency parameters, EFB, MF with PKS typically found on mills respectively were planted together about 75% percent was able modestly processed. Table 6 shows the produced biomass per year in Malaysia (2019). The ultimate and proximate concern of these biomasses shows that they are potential candidates for acting in activated carbon (AC) production. The oil palm biomass has a carbon content similar to wood, which is one of the most common precursors for AC production. Moreover, the low ash content of oil palm biomass is also helpful in the acceptance of AC with a high surface area (Ilyas et al., 2022; May et al., 2019).

By converting oil palm biomass to adsorbents, can economically benefit from wastewater treatment and reduce waste discharge into the environment. The recycled biochar from these studies has great reuse potential and is produced using sustainable practices and agricultural waste (May et al., 2019; Mohd Azmi et al., 2022; Somsiripan et al., 2023).

Table 6 : Annual oil palm biomass in Malaysia

Types of oil palm biomass	Yield (Mt)
Oil palm trunk	3.6
Oil palm frond	21.7
Palm kernel shell	4.46
Empty fruit bunch	7.34
Mesocarp fibre	7.72

(Onoja et al., 2019)

2.5.1.1 Oil palm empty fruit bunch (EFB)

Agricultural waste such as empty fruit bunch is an abundant resource from oil palm processes in Malaysia (see Figure 4). It comprises cellulose, hemicellulose, and lignin as major constituents with extractives and ash in trace amounts. EFB seems to have potential for adsorbent and AC as it was a dye treatment process. EFB with a respective content of 45–50% cellulose and 25–35% lignin should be an auspicious source for preparing AC. Virgin ACs from EFB are highly effective in dye adsorption from wastewater, due to their high surface area and large number of available sites (Kasim et al., 2018; May et al., 2019; Somsiripan et al., 2023).

EFB can also be applied in bioenergy production, animal feed, and organic fertilizer, as well growing of mushrooms or molds, etc. Due to high moisture

content, low bulk density and heterogeneity are difficult in many applications, pre-treatment methods such as drying, palletization, or torrefaction have been carried out before use (Singer et al., 2021; Somsiripan et al., 2023).

AC by adsorption using EFB is presented as a sustainable solution for dye removal. This composition (including the percentages of cellulose and lignin) is what forms the basis for creating efficient adsorbents. Additionally, EFB's versatility of applications across different sectors further indicates its high recovery potential for waste and renewable energy generation (Kasim et al., 2019; Somsiripan et al., 2023).



Figure 4 : Oil Palm Tree

2.5.2 Clay minerals

Clay minerals are phyllosilicates, with an atomic structure consisting of silica tetrahedra and alumina-based octahedral sheets that form layers. Such minerals have three kinds of external properties: outer-sphere, edge, and interlayer space disks that can exchange ions as well as adsorb. Clay

minerals, including montmorillonite, kaolinite, bentonite, and illite are favorable adsorbents because of their highly achievable levels of adsorption capacity. Bentonite is specifically good for removing water organic pollutants owing to its three-layered structure and the negative surface charge that gets further increased with the substitution of aluminum atoms at lower valence elements sites, or by replacement of silica atom sites. Another reason is that the negative charge produced by its dissociation stacking method makes it easier to absorb. In general, phyllosilicates and clay minerals are potential adsorbents for water treatment applications based on investigations by (Ewis et al., 2022; Kelechukwu & Akaranta, 2021; Sanavada et al., 2023; Zhang et al., 2024).

Kaolin or china clay is a naturally occurring non-expansive phyllosilicate Kaolinite mineral that evolves with a geological process having allotropic growth. It is composed of numerous trace materials, including anatase and rutile, feldspar, iron oxide (two-thirds ferrous), mica; montmorillonite which binds the flint-like chert grains together. While kaolin has less surface area and cation adsorption capacity than other clays such as montmorillonite, its adsorptive properties can be increased by modification. In another case, sodium tetraborate modified-kaolinite provides a better surface for the adsorption of molecules like Aniline Blue (Chai et al., 2020).

Because of its tunability, as well as its wide surface area and high pore volume; zeolites have become potential adsorbents for different types of pollutants such as heavy metals also organic compounds, or radioactive elements.

However, to a certain extent, they are available for functionalization depending on the nature of the contaminant, pH or temperature, and the presence of competitive ions. However, zeolites have limitations including selectivity and renewability problems (Kordala & Wyszowski, 2024).

Diatomite is a light-coloured, soft, and lightweight sedimentary rock that is mostly composed of diatom remains. Jordanian diatomite can efficiently remove MB dye at very low concentrations however, the adsorption capacity of un-modified this material is not sufficient to be used for these purposes (Zuluaga-Astudillo et al., 2023).

Table 7 shows the pros and cons of various adsorbents such as activated carbon, agricultural/industrial by-products, bentonite, and zeolites (Zhou et al., 2019).

Table 7 : Adsorbent pros and cons

Adsorbent	Advantages	Disadvantages
Activated Carbon	High surface area	High cost
Biosorbents	High adsorption capacity	High market cost
Agricultural and industrial by-products	Available in abundance	Sorption propertied depends on origin
Bentonite	High surface area, high cation exchange capacity and low cost	Need modification for adsorption of anionic dyes
Zeolite	High ion exchange capacity and surface area	Complex sorption mechanism

(Zhou et al., 2019)

2.5.2.1 Bentonite clay

Bentonite is a natural silicate clay that predominantly contains montmorillonite with great adsorbing properties. Its characteristic layer is formed by a silicon

tetrahedral sheet and aluminum octahedral separated from them, which permits a partial replacement of one by another to give rise to an overall negative charge. The exchangeable cations from the compound, such as sodium (Na), calcium (Ca^{2+}), or magnesium (Mg^{2+}) etc., counterbalance this negative charge. Due to these exchangeable cations, bentonite has a high ion-exchanging capacity that increases its adsorption performance (Ewis et al., 2022; Kelechukwu & Akaranta, 2021; Sanavada et al., 2023; Zhang et al., 2024).

Some of the unique characteristics of bentonite are its small particle size, high porosity and surface area, and extensive cation exchange capacity. Together these properties make it a superior adsorbent. The enhanced BET surface area and porosity offer abundant adsorption active sites, the improved CEC brings strong cation exchange capability for the comprehensive removal of organic pollutants (dyes) and heavy metals. Montmorillonites have a three-layered structure and negative surface charge which makes them more efficient in the adsorption of water pollutants (Kelechukwu & Akaranta, 2021; Zhang et al., 2024).

Due to its vastly diverse range of functions, bentonite has several applications in various industries. It is also utilized as a binder and purifying agent in the pharmaceutical, and cosmetic industries. For example, in the drilling industry, bentonite is of vital importance as it can stabilize boreholes and prevent leakages from drill fluid. Bentonite is used in the ceramics industry to provide strength to ceramic bodies and are binder for molds into which moderately

plastic moist mud is packed. Besides, bentonite is utilized in the refining of oils and fats as well as paints for modification of viscosity and stability (Sanavada et al., 2023; Zhang et al., 2024).

A significant advantage of bentonite is its worldwide availability which makes it a cheap and efficient adsorbent. Furthermore; these natural mesopores and their modifiable behavior makes them ideal properties for one of many applications. One example is treating bentonite with acids or under high-temperature conditions so that the surface properties are modified, and as a result, its capability of adsorbing different contaminants varies greatly depending on what kind you use. These changes also produced properties of bentonite that are essential for water treatment and industrial applications (The structure of the bentonite is shown in Figure 5 (Al-Risheq et al., 2021; Sanavada et al., 2023).

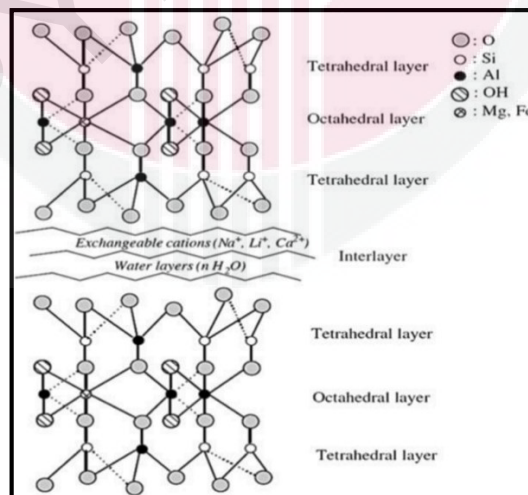


Figure 5 : Bentonite Structure
(Al-Risheq et al., 2021)

2.5.3 Modification of adsorbents

Modifying adsorbents significantly improves their properties, including surface area, porosity, and functional groups, thereby improving their adsorption efficiency for removing contaminants from wastewater. This section delves into the various modification techniques applied to clay minerals and activated carbon (AC).

2.5.3.1 Modification of biomass-derived activated carbon

As a versatile material that can be widely used in many aspects such as sewage treatment, air purification, and some industrial processes, activated carbon (AC) is obtained from high-carbon precursors with an activation method. This mechanism called activation undergoes either a physical or chemical process that intensifies the surface area and porosity of carbon material leading to a high adsorption capacity (Danish & Ahmad, 2018).

Physical Activation: Physical activation of biomass-derived granule-activated carbon is typically divided into two stages namely, carbonization and activation. This is at temperatures between 300 and 600°C, where a two-stage process takes place: first the precursor material thermally decomposes releasing volatile species (degassing) followed by conversion into carbon-rich char. This is in turn followed by an activation phase at higher temperatures (700 to 1300°C) where oxidizing gases such as steam, CO₂, or N₂ may be used. It results in the formation of voids that end up increasing surface area into char, causing a porous structure. Protects the precursor from combusting during activation by using an inert gas (e.g. nitrogen). Parameters like

carbonization time, activation temperature, and gas flow rate can be tuned to enhance the efficacy of physical activation which further enhances yield as well as surface area (Reza et al., 2020; Rodríguez-Reinoso & Molina-Sabio, 1992).

Chemical Activation: Chemical activation consists of the impregnation by a chemical agent before heat treatment. This method is performed at milder temperatures (400 to 600 °C) than the physical activation process and gives activated carbon with high surface area and porosity. Some of the common chemical agents used in this process include ZnCl_2 , H_2SO_4 , and $(\text{NH}_4)_2\text{SO}_4$ each having its advantages ZnCl_2 creates mesoporosity and high surface area activated carbon (Hongxia Zhao et al., 2022; Uğurlu et al., 2008; Yağmur & Kaya, 2021). The H_2SO_4 can promote the generation of micropores, increase its acid sites, and improve anions adsorption such as basic dyes (Q. Chen et al., 2020; May et al., 2019; Sultana et al., 2022; Yadavalli et al., 2017). During activation, $(\text{NH}_4)_2\text{SO}_4$ promotes the formation of pores and functional groups but restrains tar and residue generation (Ennaciri et al., 2020; Linh et al., 2019). KOH and H_3PO_4 would be used as other chemical agents depending on activation requirements altering the structural/chemical characteristics of activated carbon. Despite the benefits, chemical activation is not without fault; it must be rinsed properly to avoid chemicals left over and cleanup can get exorbitant as well sometimes targeting other harmful materials in the process (Calero & Ligeró, 2023).

As observed in Table 8, it has shown the better adsorption capacity of methylene blue on EFB-derived activated carbon due to these modification techniques.

Table 8 : MB adsorption efficiency of EFB-derived AC

EFB adsorbents	pH	Efficiency	Isotherm/kinetic	Analysis	Ref.
Activated carbon	7	41.98 mg/g	Langmuir/2	FTIR, BET, SEM	(Wirasnita & Hadibarata, 2014)
Magnetic Biochar	2, 10	31.25 mg/g	Langmuir/2	FTIR, SEM	(Mubarak et al., 2015)
Activated carbon	2	24.00 mg/g	Freundlich/2	BET, SEM	(Baloo et al., 2021)
Activated carbon	7, 3	103.1 mg/g	Langmuir/2	FTIR	(Sajab et al., 2013)
Activated carbon	-	50.76 mg/g	Langmuir/2	SEM	(Sajab et al., 2013)
Activated carbon	7.8	32.3 mg/g	Langmuir/ -	BET	(Nasir et al., 2015)
Activated carbon	11	50.07 mg/g	Sips/ 1	EDX, FTIR, XRD, SEM, BET	(Ab Aziz et al., 2023)
Biochar	6-7	62.52 ± 0.48 mg/g	Langmuir/2	FTIR, BET, SEM, EDX	(I. Ibrahim et al., 2021)

2.5.3.2 Modification of clay minerals

A few of the techniques to improve adsorbing efficiency in Clays, specifically Bentonite include modifications that change its structure as well as chemical properties. The modifications were done to improve surface area, cation exchange capacity, and adsorption efficiencies. Key methods include:

Acid Activation: In this method, clay is treated with inorganic acids e.g. sulfuric acid (H₂SO₄) (Gandhi et al., 2022; Noyan et al., 2007; Önal & Sarikaya, 2007;

Tebeje et al., 2022) or hydrochloric acid (HCl) (Info, 2013; Yener et al., 2012), at high temperatures. Acid activation results in the increase of surface area and pore volume, as well as alteration in the cation exchange capacity (CEC) and coordination/parent metal distribution on those external solid acid sites. The treatment process managed to remove impurities and altered the chemical properties of clay corresponding enhancement in its adsorptive capacity (Rouhani et al., 2021; Wan et al., 2015).

Base Activation: Activating with strong bases such as KOH and NaOH during the activation process changes all cation exchangeable elements to enable higher negative charges in clay (Amran & Zaini, 2021; Jais et al., 2021; A. Kumar & Lingfa, 2022). Therefore, the adsorption performance of different pollutants is improved. Base activation is less harmful to the environment as compared to acid activation and possesses cogency for water treatment and soil remediation applications (Amran & Zaini, 2021; Jais et al., 2021).

High-temperature thermal activation also enhances the properties of modified clays. Firing the clay at high temperatures increases surface area and as a result adsorption sites. However, overheating can reduce pore area and destroy the structure. The overall performance of the clay was optimized by combining thermal activation along with chemical means i.e. acid or base activation (Liew et al., 2016).

Other methods like polymer modification, pillaring, and organoclay preparation are additional techniques that serve to improve the adsorption properties of

clay. Grafting involves the polymer modification onto clay surfaces (Anirudhan et al., 2009), while pillaring introduces polycations that stabilize the structure of clays (Auer & Hofmann, 1993). Cationic surfactants are employed during the organoclay preparation to render an organic pollutant affinity surface of clay which is necessary for efficient adsorption (Li et al., 2018).

Table 9 illustrates these modification techniques using the adsorption capacities and efficiencies of different activated clays for MB elimination.

Table 9 : MB adsorption capacity of activated clays

Clay (adsorbents)	pH	Efficiency	Isotherm/kinetic	Analysis	Ref.
Montmorillonite	7.3	99.47%	Langmuir/2	FTIR, XRD	(Chang et al., 2016)
Montmorillonite	5	95.95%	Toth/ 2	FTIR, XRD	(P. Sharma et al., 2016)
Moroccan Illitic	3	13.698 mg/g	Langmuir/2	XRD	(Amrhar et al., 2015)
Natural Illitic clay mineral	9.6	24.87 mg g ⁻¹	Langmuir/2	XRD, FTIR	(Ozdes et al., 2014)
Montmorillonite	5	150.2 mg/g	Langmuir/2	XRD, FTIR, TGA	(Fan et al., 2014)
Palygorskite clay	7	78.11mg/g	Langmuir/-	XRD, BET	(H. Chen et al., 2011)
Montmorillonite	9	97.75 mg g ⁻¹	Langmuir/2	XRD, SEM, VSM	(Ai et al., 2011)

2.5.4 Regeneration of adsorbents

Reuse and regeneration of adsorbents, cheaply prepared from both activated carbon (AC) or clay minerals are a key criterion for sustainability. Adsorbents are typically decommissioned when they become loaded with contaminants, resulting in higher operational costs and more waste. This source of adsorbents can be regenerated instead, so the demand for new materials is

reduced and waste minimized. Different techniques are used for the regeneration of adsorbents, steam method, heat method, chemical methods electrochemical supercritical CO₂ microwave usage, etc. The selection of the method varies from nature contamination, costings, and process conditions (Akeremale et al., 2023; Faheem et al., 2024; Huang et al., 2024; Velempini et al., 2023; Yasri & Roberts, 2024).

Thermal Regeneration consists of heating the spent adsorbent, usually at high temperatures in an inert or oxidizing environment. These adsorbates are removed by thermally decomposing them in a process known as pyrolysis. It will also generate CO₂ emissions and reduce the mechanical strength. Temperature and conditions need to be optimized accurately to balance efficiency with sustainability, however achieving 100% recovery of adsorption capacity is still problematic due to possible carbon loss and regeneration mass (Faheem et al., 2024; Sithole, 2024).

Chemical Regeneration: Chemical Reagents are used to desorb contaminants. Depending on the adsorbates and sorbents, acidic and alkaline reagents are most commonly used. The process is based on the treatment of saturated adsorbents with liquid chemicals that either dissolve or react chemically against contaminants after which desorbed compounds and residual reagents are removed. It is efficient to regenerate chemically, but finding reagents can be difficult so as not to damage adsorbents and completely remove contaminants. When the reagents are not abated it is an additional point of complexity and cost (Faheem et al., 2024).

Steam Regeneration: In this technique, the contaminated air can be released due to higher temperatures in the absorbent material by passing steam through the adsorbent bed. The thermal decomposition, steam oasis oxidation polymerization, and adsorbent vapor decomposing heat carbonation. However, which of the adsorbents to be used depends on the types of contaminant and their characteristics because they separately vary from each other determining only absorbance value (Djamila et al., 2024; El Gamal et al., 2018).

The electrochemical regeneration is affected by applying an electric current across the saturated adsorbent, thereby promoting the desorption of contaminants captured therein. This method has the benefit of its selectivity over relevant adsorbates and moderate energy requirements. Nevertheless, it is often constrained by the conductance of the adsorbent material and from nature's providing of distinct kinds of them (Yasri & Roberts, 2024).

Supercritical CO₂ Regeneration employs supercritical carbon dioxide to desorb contaminants. The method is clean and green, as it does not use any dangerous chemicals and leaves behind minimal waste. However, the actual cost of supercritical maintenance and a requirement for pricey machinery may reduce its utility (Azzouz & Roy, 2023).

Microwave regeneration heats the saturated adsorbent by microwave radiation to desorb contaminants. It provides fast and even heating throughout, cutting down on recharging time. However, efficiency is influence

by the moisture content of the adsorbent and the nature of the contaminant. However, the high initial costs of microwave systems could limit full adoption (Huang et al., 2024).

2.5.5 Characterization methods for adsorbents

The importance of characterizing adsorbents lies in giving a prospect regarding their structural and functional properties which very well dictate the possible knock within the adsorption capacity limiting process. Activated carbon and bentonite clay were characterized by numerous analytical techniques to determine its impurities such as AC which is derived from EFB or agricultural waste, and BC which is obtained from the family of clay minerals. To characterize the adsorbents, several analytical techniques have been employed such as Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller (BET) Analysis, Fourier Transform Infrared Spectroscopy FTIR, X-ray Diffraction (XRD), proximate and ultimate analyses for AC and X-ray Fluorescence (XRF) for BC (Acharya et al., 2018; Cheblaoui et al., 2023; Haghjoo et al., 2023; Pellenz et al., 2023; Thue et al., 2023).

Thermogravimetric Analysis (TGA): TG is used to determine the thermal stability and composition of adsorbents by measuring weight loss against changing temperatures in a controlled environment. This method is informative on the decomposition temperatures and thermal degradation trends, key in assessing the suitability of adsorbents for high-temperature applications (Annane et al., 2023).

Scanning Electron Microscopy (SEM) is used to probe the surface morphology and microstructure of adsorbents. Surface texture, porosity, and particle size distribution showing the characteristics that are ultimately responsible during the adsorption process were determined by SEM images. Basic high-resolution SEM analysis provides information but the method is too limited to identify even surface modifications and any changes in the integrity of both AC as well BC (Pellenz et al., 2023).

The specific surface area, pore volume, and pore size distribution of the adsorbents were determined by Brunauer-Emmett-Teller (BET) Analysis. BET analysis is important to determine the adsorption capacity, as a broader surface area correlates closely with more sites for absorption. BET analysis shows the amount of surface area available for adsorption and correspondingly also a prediction on how efficient such adsorbents might be (Annane et al., 2023; Pellenz et al., 2023).

FTIR (Fourier Transform Infrared Spectroscopy) is done for the identification of functional groups on adsorbent surfaces. Functional groups responsible for the adsorption mechanism were determined by FTIR spectra to obtain a better understanding of chemical bonds and molecular interaction in these adsorbents. This enabled to study of the chemical modification and surface functionalization of AC and BC (Annane et al., 2023; Pellenz et al., 2023).

For all the adsorbents, their crystalline structure and phase composition were determined by X-ray Diffraction (XRD). The mineralogical composition and

structural changes after modification were identified from XRD patterns. It is suggested to be useful for the identification of crystalline phases especially in BC, and also can detect any structural changes resulting from the activation process of AC (Annane et al., 2023; Pellenz et al., 2023).

The purpose of the proximate and ultimate analyses is to help in determining AC composition, covering, fixed carbon, moisture content, volatile matter, and ash are performed specifically for evaluation. The analysis yielded extensive elemental and combustion property data in support of understanding AC performance for adsorption applications (Rubi et al., 2023).

Elemental Composition Analysis: X-ray Fluorescence (XRF) analysis, used for BC. On the other hand, XRF gave quantitatively accurate information on both major and minor constituents of BC which is important for purity tests and examination of suitability as an adsorbent (Cheblaoui et al., 2023).

2.6 Summary

This chapter provides a systematic summary of the chemical structure of dyes in industrial effluent from dyeing industries. This chapter describes various methods of dye removal explaining its advantages and disadvantages. this chapter discusses adsorption as a water and wastewater treatment strategy extolling its simplicity, eco-friendliness, and energy effectiveness.

This review concentrates on economical and effective adsorbents for dye removal primarily clays. Although they have potential, clays are limited to

simple dyes as a result of the negatively charged surfaces. Therefore, clay modification methods are elaborated for improved clay surface and adsorptive properties. Conversely, porous materials such as AC derived from EFB contain high porosity and surface area making it a suitable choice for water treatment. The pollutant removal potential of both AC and BC has been reported for heavy metals, dyes pesticides, phenols, etc. but the high cost as compared to commercial activated carbon (CAC) is a limitation. This review highlights the cost-effective biomass and natural clay precursors of AC and BC for fabricating them. Textural characteristics of AC or BC depend on the precursor and activation conditions. Advanced adsorption performance of the prepared AC and BC, can be achieved by physical method or chemical approach in adjusting synthesis parameters.

This corresponds to the development of isotherm, kinetics, and thermodynamics models which are important in characterizing adsorbate distribution at equilibrium. The data required for basic dye abatement purification terminative normalization as well as improving reusability effective designing.

CHAPTER 3

METHODOLOGY

3.1 General overview

The chapter describes the methodology utilized while investigating the adsorption of methylene blue (MB) from an aqueous solution. The main highlight is in the utilization of low-cost adsorbents; particularly activated carbon (AC) derived from oil palm empty fruit bunch (OPEFB) and also alternative ones which as bentonite clay (BC). This chapter presents a comprehensive description of the materials used as well as processing steps undertaken for adsorbent preparation and characterization to determine their chemical composition and physical properties. The adsorption performances of the modified adsorbents are studied focusing on their MB uptakes, along with a particular interest in the regeneration and reusability capabilities in batch adsorption systems. This chapter is the basis of our forthcoming analysis and interpretation helping us to understand, in greater detail, all underlying complex interactions between adsorbents-MB into aqueous solutions. The experimental observations are also detailed here in Figure 6.

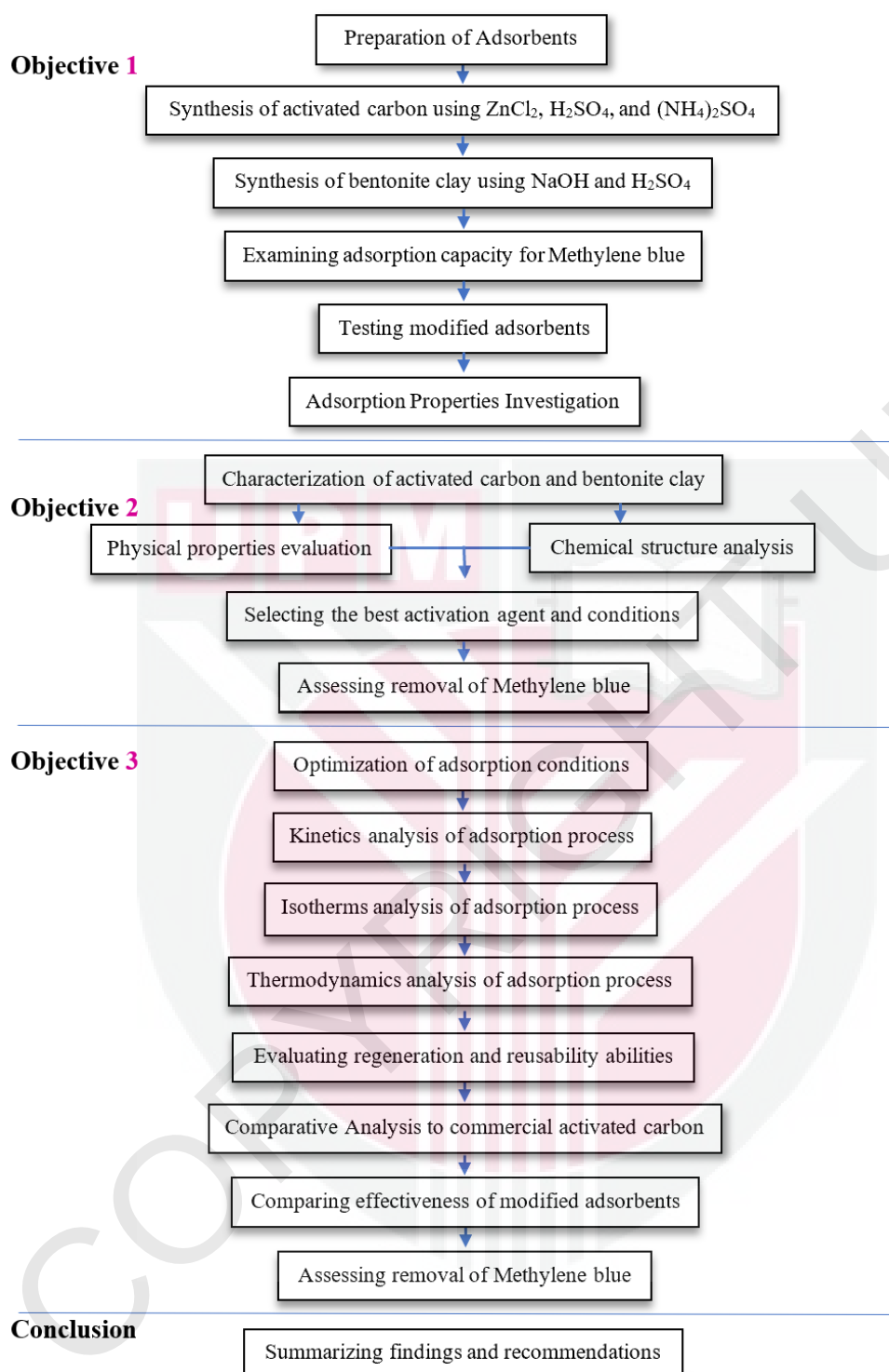


Figure 6 : Research Methodology and Experimental Process Flowchart

3.2 Sample and chemical materials collection

Methylene blue (MB) as a powder was purchased from Chemiz Malaysia Sdn. Bhd, shown in Figure 7, was used as this study's target pollutant.

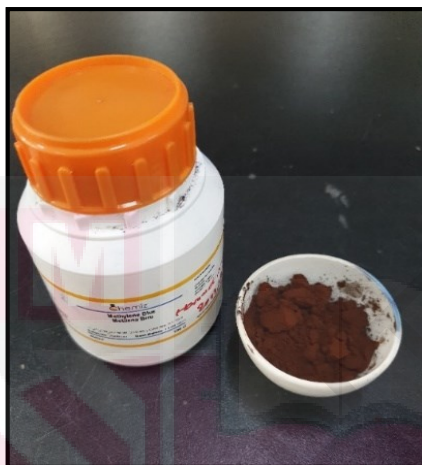


Figure 7 : Methylene Blue Powder (MB)

The experimental work involved the use of certain chemicals, including zinc chloride (ZnCl_2), sodium hydroxide (NaOH), sulphuric acid (H_2SO_4), hydrochloric acid (HCl), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and Sodium persulphate ($\text{Na}_2\text{S}_2\text{O}_8$). All of these chemicals were purchased from R&M Chemicals company, a quality provider for most essential lab-grade chemicals. They are widely employed for the synthesis and modification of a wide range of materials such as activated carbon and bentonite clay, used in numerous applications.

3.2.1 Preparation and characteristic of methylene blue

Methylene blue (MB) solution was prepared with high-purity distilled water, and all other reagents were estimated to be of analytical grade. For a gram of

MB to be measured, it was weighed with adequate precision and dissolved into 1 L distilled water for making the stock solution at a concentration of 1000 ppm as per (Equation 3.1) below. The solution was stirred well using a magnetic stirrer until complete dissolution. In (Equation 3.2), the stock solution was diluted into various lower concentrations.

The stock solution was diluted further to attain different concentrations carefully representing real-world conditions used in the experiment, with a typical 200 ppm concentration being most employed. This concentration was selected according to known values of dyes MB in industries reported by other previous studies, mainly from textile, leather, and paper industries.

The purity of the MB used in this experiment was confirmed by using a UV spectrophotometer (Shimadzu UV-1800). The purity was confirmed by the presence of characteristic absorption peaks at 663 nm and 609 nm in the UV-visible spectrum for the MB solution. These peaks are the usual standard benchmarks for a pure MB, and their presence without additional peaks indicates minimal impurities (Bhuyan et al., 2016; Khairnar & Shrivastava, 2019; Khosa et al., 2011).

The following adsorption studies were carried out using this solution, which was verified as the MB solution that relies on standard methods. These experiments are described in detail and with their corresponding methodology segments below.

MB is a powder,

Each 1g of MB gives 1000 ppm/L by applying this formula:

$$\text{PPM} = \frac{\text{MASS OF SOLUTE (g)}}{\text{MASS OF SOLVENT (g)}} \times 10^6 \quad \text{equation (3.1)}$$

1 PPM = 1 mg/L, So 1000 PPM = 1000 mg/L

1 L = 1000 g = 1000000 mg

The volumetric flask (1000ml) was filled with 1000 ml of DW, and 1 g of MB was weighed, added to the flask, and subsequently shaken,

Another formula can be employed to dilute the initial high concentration of 1000 ppm to achieve a lower concentration (Nandiyanto et al., 2023):

$$C_1V_1 = C_0V_0 \quad \text{equation (3.2)}$$

Where; C_0 : concentration of MB, 1000 mg/L = 1 g of MB in 1 L of DW, V_0 : volume of each dosage from stock solution to be added, C_1 : concentration of each MB dosage, V_1 : volume of sample.

3.2.2 Sample preservation

Methylene blue (MB) is a commonly used dye in various industries and research laboratories. Proper handling and storage of MB samples are essential to maintain the integrity and stability of the paint and the quality and reliability of the data obtained from the experiments.

MB solutions are stored by volumetric flasks in a cool, dark, and dry place, away from direct sunlight and heat sources. The samples are labelled and tightly sealed to prevent evaporation and contamination.

3.3 Adsorbent selection

Adsorption is a process where an adsorbent material is used to remove impurities from liquids or gases. Activated carbon is commonly used as an adsorbent due to its high surface area and ability to adsorb various compounds. Empty fruit bunch (EFB) and bentonite clay (BC) are low-cost, renewable, and eco-friendly adsorbents successfully used to remove MB from aqueous solutions. These materials have high adsorption capacities and can be optimized for maximum efficiency. BC is a volcanic ash-derived material with a high adsorption capacity, while EFB is produced from agricultural waste.

3.3.1 Oil palm empty fruit bunch (OPEFB)

A natural oil palm empty fruit bunch (EFB) was collected from Oil Palm Mill Sdn. Bhd, in seri Seri Ulu Langat, Banting, Selangor, Malaysia, as shown in Figure 8. Cut to small pieces, washed with distilled water, dried at 100°C, and kept at room temperature 25°C until it is used for further activations as an adsorbent to eliminate MB from aqueous solutions.



Figure 8 : Empty Fruit Bunch (EFB)

3.3.1.1 Prepare empty fruit bunch-based activated carbon

The two-stage activation process to produce AC from EFB. During the first stage of production zinc chloride (ZnCl_2), which is a very common dehydrating agent, is added to create and develop mainly pre-dominant pores in carbon structure, which is crucial in the applications of adsorption capacity (Hongxia Zhao et al., 2022; Uğurlu et al., 2008; Yağmur & Kaya, 2021). The second stage uses either H_2SO_4 which further enhances the pore structure and other characteristics (Q. Chen et al., 2020; May et al., 2019; Sultana et al., 2022; Yadavalli et al., 2017) or ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) which improves pore formation and introduce functional groups in activation (Ennaciri et al., 2020; Linh et al., 2019). The accompanying flowchart illustrates the activation process for EFB-based activated carbon production, as shown in Figure 9.

First Stage

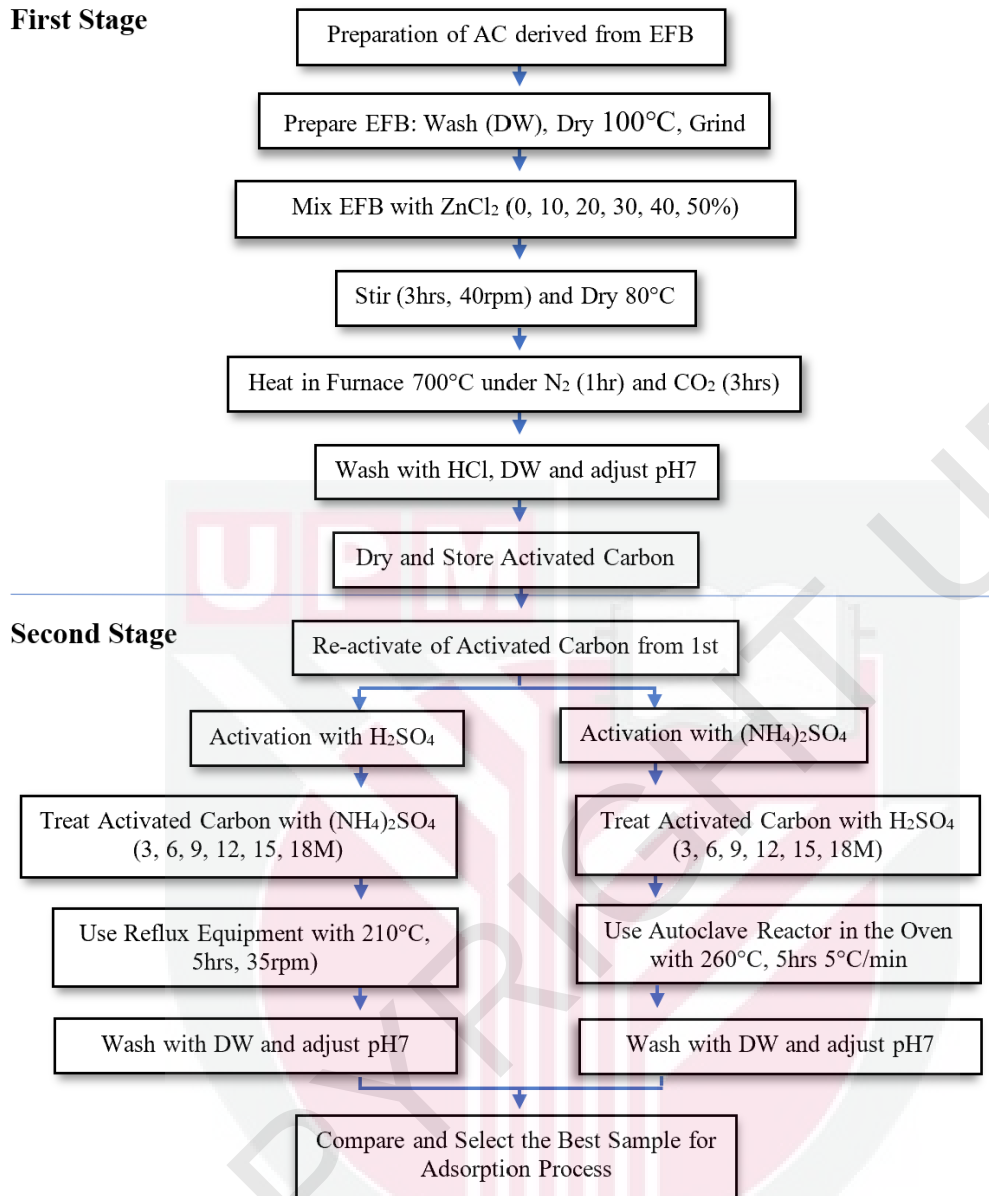


Figure 9 : Activation Process Flow for OPEFB-Based AC

First stage: EFB was washed with distilled water (DW) for removing impurities, then dried in a 100°C oven. After grinding to a powder with a size less than 1mm, it was mixed with zinc chloride (ZnCl₂) at different dosages (0%, 10%, 20%, 30%, 40%, and 50%) using a 10g to 38ml ratio. The mixture was stirred at room temperature (40rpm) for 3 hours, followed by drying at 80°C in an oven for another 3 hours. It underwent a 4-hour treatment at 700°C

in a horizontal tube furnace (carbolite: 12/65/550-TZF) (see in Figure 10), with 1 hour under nitrogen gas (N_2) and 3 hours under carbon dioxide (CO_2) at a flow rate of 20 ml/min and a heating rate of $20^\circ C$ per minute. Subsequently, it was washed with 1M hydrochloric acid (HCl) and then with DW until a pH of 7 was achieved. Finally, it was dried in a $100^\circ C$ oven for 2 hours before being stored.



Figure 10 : Horizontal Tube Furnace

Second stage: there are two activations:

- i. **Sulfuric acid:** The produced AC from furnace (1st) was treated with sulfuric acid (H_2SO_4 98%) with different concentrations 3M, 6M, 9M, 12M, 15M, and 18M using reflux method (DMS series- MTOPS, digital heating mantle with stirring) with $210^\circ C$, 5hrs, 35rpm, and portion 2g: 20ml shown in Figure 11.

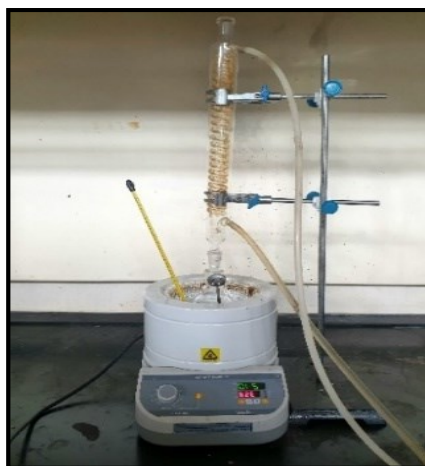


Figure 11 : Stirring Mantle (Reflux Method)

- ii. **Ammonium Sulfate:** The produced AC from furnace (1st) was treated with ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) with different concentrations 3M, 6M, 9M, 12M, 15M, and 18M using hydrothermal autoclave reactor (nonmagnetic 316 stain steel-TECHINSTRO, PPL LINED) (3MPa) as shown in Figure 12, in the oven with 260°C, 5hrs, 5°C per minute, and with portion 2g: 20ml.



Figure 12 : Thermal Autoclave Reactor

3.3.2 Bentonite clay

In this study, pure bentonite clay (CAS: 1302-78-9) as shown in Figure 13 was bought from R&M Sdn. Bhd, chemicals Malaysia and kept in room temperature 25°C to be utilized as an adsorbent for removing MB from aqueous solutions.

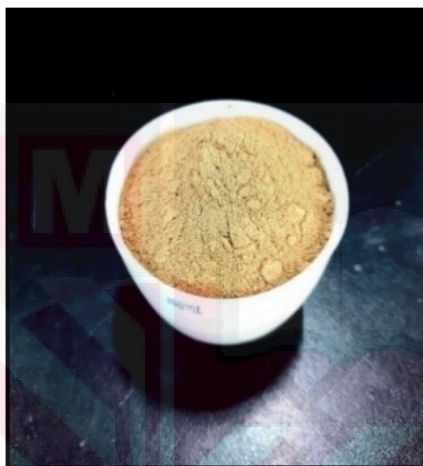


Figure 13 : Pure Chemically Bentonite Clay

3.3.2.1 Prepare activated bentonite clay (ABC)

The activation of bentonite clay (BC) involves acid activation with sulfuric acid (H_2SO_4) and base activation with sodium hydroxide (NaOH), enhancing its adsorption properties, illustrated in Figure 14. Acid activation with H_2SO_4 significantly increases the clay's surface area and porosity, as existing literature supports (Gandhi et al., 2022; Noyan et al., 2007; Önal & Sarikaya, 2007; Tebeje et al., 2022). On the other hand, NaOH activation, a relatively novel approach, improves adsorption efficiency and surface reactivity and is more environmentally friendly and cost-effective. This method's potential for enhancing MB removal in wastewater treatment underscores its efficacy and sustainability (Amran & Zaini, 2021; Jais et al., 2021; A. Kumar & Lingfa, 2022)

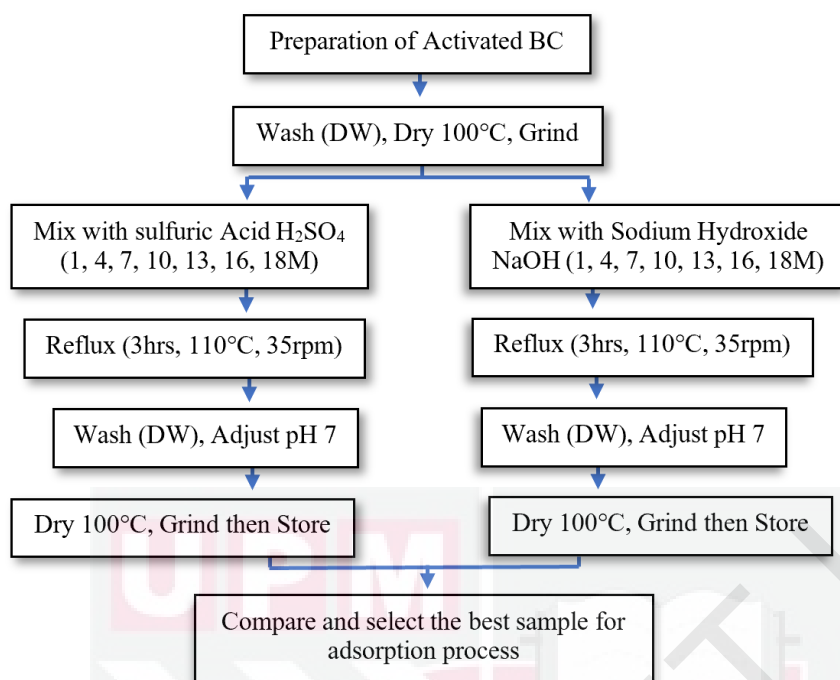


Figure 14 : Activation Process Flowchart for BC (Acid and Base)

- i. **Acid-activated bentonite clay (AABC):** BC as an adsorbent was washed with DW for removing impurities, followed by drying at 100°C in an oven, and subsequently ground. Chemically pure BC was mixed with sulfuric acid (H₂SO₄ 98%) at different concentrations (1M, 4M, 7M, 10M, 13M, 16M, and 18M) using the reflux method (DMS series-MTOPS, digital heating mantle with stirring) for 3 hours at 110°C and 35rpm, with a ratio of 8g to 70ml. It was then washed with DW until reaching a pH of 7, dried in a furnace for 3 hours at 100°C, ground, and stored for later use.
- ii. **Base-activated bentonite clay (BABC):** BC was washed with DW for removing impurities, then dried at 100°C in an oven and subsequently ground. Chemically pure bentonite clay (BC) was mixed with sodium hydroxide (NaOH) at different concentrations (1M, 4M, 7M, 10M, 13M, 16M, and 18M) using the reflux method shown in Figure 14 via equipment (DMS series- MTOPS, digital heating mantle with stirring) for 3 hours, as demonstrated in Figure 18, at 110°C and 35rpm, with a ratio of 8g to 70ml. It was then washed with DW until reaching a pH

of 7, dried in a furnace for 3 hours at 100°C, ground, and stored for later use.

3.4 Adsorption method

Adsorption is a commonly used method for removing dyes from wastewater, with MB being a frequently studied dye. The process involves optimizing parameters such as contact time, MB initial concentration, temperature, pH, and adsorbent dosage to achieve efficient dye removal. Adsorption isotherm models (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich) help understand the equilibrium behavior, while kinetic models (pseudo-first order, pseudo-second order) determine the adsorption rate. Thermodynamic studies provide insights into system energetics and feasibility. Regeneration and reusability of adsorbents, like AC and ABC, contribute to cost reduction and environmental sustainability as shown in Figure 15. The formula for adsorption and removal can be written as equation (3.3 and 3.4) (Hashem et al., 2024; Shi et al., 2023; J. Wang & Guo, 2020; Y. Wang et al., 2024):

$$q = \frac{(C_i - C_e)}{v} * m \quad \text{equation (3.3)}$$

$$\text{Removal (\%)} = \left(\frac{C_i - C_e}{C_i} \right) * 100\% \quad \text{equation (3.4)}$$

The equation links solute adsorption (q) per unit adsorbent mass (mg/g) to initial (C_i) and equilibrium (C_e) solute concentrations (mg/L), solution volume (V) in liters, and adsorbent mass (m) in grams.

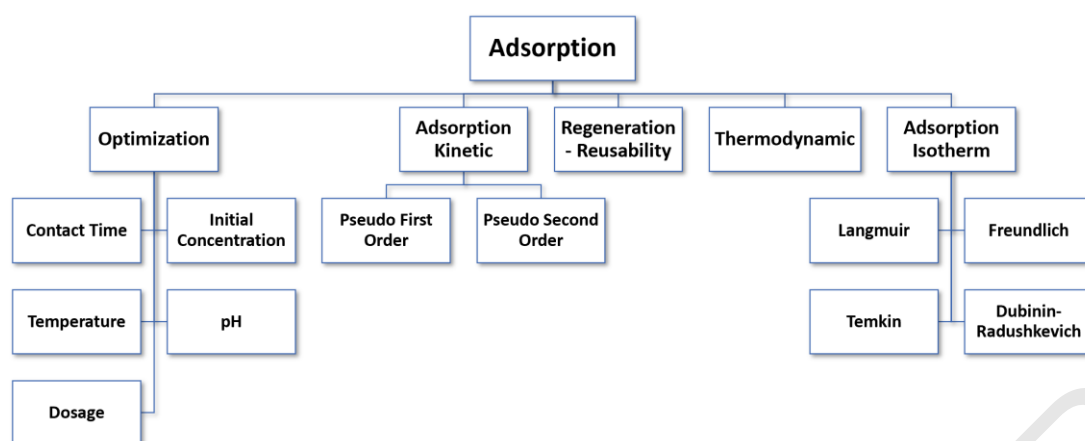


Figure 15 : Adsorption Method Process Flowchart

3.4.1 Optimization parameters

The adsorption experiments were optimized using EFB-activated carbon and bentonite clay as an adsorbent under a constant agitation shaking system at 135 rpm (KS 4000 I control-IKA). The optimization was performed in five principal parameters contact time, initial concentrations, temperature, pH, and dosage. These parameters were selected based on their critical influence on the adsorption efficiency, as supported by previous studies. For this purpose, the UV-Vis spectrophotometric method was employed and the adsorption study was determined through calibration of multi-concentration MB solutions with a standard curve to find out residual dye concentrations. Several parameters have been systematically changed to optimize the adsorption processing step.

Contact time was also changed to find out the optimum period for the highest adsorption. For AC, contact times ranged from 30 to 180 min with intervals of 30 min, while for BC, the range of contact times was set between 45 and 360 minutes with intervals of 45 min. Earlier studies have shown a great deal of

influence on the sorption process during the same periods (Alardhi et al., 2023; Aljar et al., 2021).

This work investigated different initial MB concentrations to find the maximum adsorption capacity. The concentration of AC ranges from 50 to 500 ppm, while the concentration range of BC is from 50 to 200 ppm. These different concentrations are important for knowing the adsorption capability of various levels of pollutants of these concentrations by adsorbents (Aljar et al., 2021; Mousavi, 2022).

Temperature was also altered (25 to 55°C) to investigate its impact on adsorption dynamics with both adsorbents. Temperature fluctuates in the range from 25°C to 55 °C for AC and BC. The temperature fluctuations indicate thermodynamic concerns performed in the adsorption process (Aljar et al., 2021; Dhevi et al., 2023).

The reaction pH values were adjusted for the adsorbents used by 0.1 M HCl and NaOH from (4 to 10) for the adsorption of MB solution. In this pH range, the effect of acidity and alkalinity on adsorption efficiency was examined since PH significantly plays a role in changes in surface charge by agglomeration or ionization behavior of dye (Eleraky et al., 2022; Wu et al., 2022).

A systematic investigation determined the optimal adsorbent dosage for effective MB elimination while adhering to WHO drinking water standards. For AC, adsorbent dosages ranged from 0.4 to 0.65 g; for BC, adsorbent dosages ranged from 0.5 to 0.95 g. Determining the optimal dosage ensures maximum

adsorption capacity and compliance with stringent water quality guidelines (Alardhi et al., 2023; Gupta et al., 2024; Hassaan et al., 2023; Ravi & Pandey, 2019).

3.4.2 Adsorption isotherm models

The adsorption isotherm models such as Langmuir Isotherms, Freundlich, Temkin, and Dubinin-Radushkevich were applied to demonstrate the interaction process of MB concentration as an adsorbate on strong affinity toward BC and AC in potential stages of conventional water treatment. The valuable information from the models is about adsorption mechanisms and molecular interactions of MB molecules with faces for given types of surfaces. These models like Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich were shown by the equations in (Equation 3.5 to 3.8) Such equations do investigate the adsorption process under experimental conditions (Hashem et al., 2024; Shi et al., 2023; J. Wang & Guo, 2020; Y. Wang et al., 2024):

$$q = \frac{Q_m * b * c}{1 + b * c} \quad \text{equation (3.5)}$$

$$q = K_F * C^{1/n} \quad \text{equation (3.6)}$$

$$q = \frac{R_T}{b_T} * \ln(A * C) \quad \text{equation (3.7)}$$

$$q = q_o * \exp(-\beta * \varepsilon^2) \quad \text{equation (3.8)}$$

Where Q_m is Maximum adsorption capacity, b is Langmuir constant, C is Equilibrium concentration of the adsorbate, K_F is Freundlich constant, n is Freundlich exponent, b_T is Temkin constant, A is Temkin isotherm constant, q is Maximum adsorption capacity in D-R model, β is D-R constant, ε is Polanyi

potential.

3.4.3 Adsorption kinetics modeling

The adsorption kinetic study used pseudo-first-order PFO kinetics and pseudo-second-order PSO models to investigate the rate of adsorption with time. The models provide a comprehending of the mechanisms and kinetics in the adsorption process under a certain experimental system. The pseudo-first-order (PFO) and the pseudo-second-order (PSO) models are shown in Equations 3.9 to 3.12, respectively (Ezzati, 2020; Hashem et al., 2024; Hu et al., 2014; Shi et al., 2023).

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} * t \quad \text{equation (3.9)}$$

$$\ln\left(\frac{c_i}{c_e}\right) = -K_1 * t \quad \text{equation (3.10)}$$

$$\frac{t}{q_t} = \frac{1}{K_2 * q_e^2} + \frac{t}{q_e} \quad \text{equation (3.11)}$$

$$tq = \frac{1}{K_2 * q_e^2} * (q_e^2 - q^2) + q_e * t \quad \text{equation (3.12)}$$

Where q_e is the amount of adsorption at equilibrium q_t is the amount of adsorbed species in time t , and K_1 and k_2 are the first and second rate constants.

3.4.4 Thermodynamic study

The thermodynamics such as Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were carried out to determine the feasibility, spontaneity, and nature of the adsorption process of MB on AC and ABC are presented of the

experimental data achieved as follows (R. Ahmad & Ansari, 2021; Ichou et al., 2020; Shi et al., 2023; Y. Wang et al., 2024):

The Gibbs energy change of a reaction is ΔG° which shows the maximum work that can be obtained in constant temperature and pressure from a thermodynamical system, respectively. This equation (3.13) can be used to calculate ΔG° (Ichou et al., 2020):

$$\Delta G^\circ = -RT \ln K \quad \text{equation (3.13)}$$

where R is the gas constant (8.314 J/mol*K), T is the absolute temperature (K), and K is the equilibrium constant obtained from the Langmuir isotherm model.

The negative value of ΔG° indicates that the adsorption process is spontaneous and feasible.

The enthalpy change (ΔH°) represents the heat exchanged between the system and the surroundings during the adsorption process, while the entropy change (ΔS°) represents the degree of disorder or randomness of the system.

The ΔH° and ΔS° can be calculated using the following equations (Ichou et al., 2020; Y. Wang et al., 2024):

$$\Delta H^\circ = (RT^2/K) * d(\ln K)/dT \quad \text{equation (3.14)}$$

$$\Delta S^\circ = -R(d(\ln K)/dT) \quad \text{equation (3.15)}$$

where $d(\ln K)/dT$ is the slope of the $\ln K$ vs. $1/T$ plot obtained from the Langmuir

isotherm model.

3.4.5 Regeneration and reusability

From an economical and practical standpoint, successful regeneration of the adsorbents is vital for mass application in technology. The present study examined OPEFB-based AC and BC regeneration for MB in batch adsorption setup.

Regeneration of AC, two procedures were applied:

First: Wash the spent adsorbents with distilled water to take off any unabsorbed MB molecules on the surface. Then, the adsorbents were dried in a furnace for 3 hours at 135°C.

Second: the spent adsorbents were added to 250 ml for stirring with 15rpm for 3 hours at 80°C, then dried in the oven for 3 hours at 100°C.

The regenerated adsorbents were then used for another adsorption experiment using the same initial concentration of MB and the same experimental conditions as the initial experiment.

There are four techniques in one method for the regeneration study of base-activated bentonite clay (BABC).

Stirred at 80°C and 15rpm for 1 and 2 hours with 0.1:0.2 portion through sodium persulphate.

- i. Sample 1: 1 hour by using 70 ml
- ii. Sample 2: 2 hours by using 70 ml
- iii. Sample 3: 1 hour by using 250 ml
- iv. Sample 4: 2 hours by using 250 ml

The reusability study utilized the same adsorbents for multiple adsorption cycles by applying the same optimization conditions. After each adsorption cycle, the spent adsorbents were regenerated using the procedure mentioned above and used for the next cycle.

The regeneration and reusability efficiency of the adsorbents were assessed based on the percentage of the initial adsorption capacity of the fresh adsorbents.

3.4.6 Characterization analyses

To study the properties and behavior of AC derived from OPEFB and BC, characterization analysis is of utmost importance. This section describes the approach used to characterize these adsorbents.

- i. **X-ray diffraction (XRD):** Xpert Highscore software was used to analyze the results obtained by SHIMADZU XRD6000 and the crystal structure of BC and AC were verified by some literature. Sample preparation and scanning were conducted to determine the mineralogical composition of the samples, as well as their crystallinity.
- ii. **Scanning Electron Microscopy (SEM):** The surface morphology of BC and AC were visualized using HITACHI S3400-N. Thin sections were mounted on stubs and analyzed to establish particle size, shape,

and surface features.

- iii. **Brunauer-Emmett-Teller (BET):** analysis of the specific surface area and pore size distributions were performed at a degassing temperature of 250°C for AC and 100°C for BC using a MICROMERITICS 3FLEX instrument under N₂ gas, as reported in previous works to calculate the BET parameters of BC and AC. The adsorption capacity and surface attributes of these samples were measured after being degassed.
- iv. **Fourier Transform Infrared Spectroscopy (FTIR):** FT-IR spectrums were acquired on a PERKIN ELMER SPECTRUM 100 with comparison to previous works for the identification of functional groups present in BC and AC. The functional groups and chemical bonds were characterized over the 650–4000 cm⁻¹ range for the samples.
- v. **Thermogravimetric Analysis (TGA):** This analysis was carried out by a TGA/DSC3+ METTLER TOLEDO spectrometer to assess the thermal stability and decomposition modes of BC and AC, as tabled along with literature review findings. Weight loss was monitored as a function of temperature for samples heated under a controlled atmosphere.
- vi. **X-ray fluorescence Analysis (XRF):** Measured by SHIMADZU EDX-720, the analysis results were compared with the literature to decide what is doped into BC.
- vii. **Proximate and ultimate analyses:** AC physical-chemical properties were evaluated by proximate and ultimate analyses; Primarily, these methods furnish key information on the elemental composition and physical properties of AC. Standard procedures were used to measure: the moisture content, volatile matter, fixed carbon, and ash content of AC by proximate analysis. The procedures followed were.

Moisture Content (MC): was determined by heating samples in an oven to a certain temperature and then keeping them there until they reached a constant weight. MC was determined using the formula (Gani et al., 2023):

$$MC(\%) = \left(\frac{\text{wet weight} - \text{dry weight}}{\text{wet weight}} \right) \times 100 \quad \text{equation (3.16)}$$

Volatile Matter (VM): Samples were heated to a specified temperature under controlled conditions to measure the volatile matter. VM was calculated as (Gani et al., 2023):

$$VM(\%) = \left(\frac{\text{weight before heating} - \text{weight after heating}}{\text{dry weight}} \right) \times 100 \quad \text{equation (3.17)}$$

Fixed Carbon (FC): FC was determined by subtracting the moisture and volatile matter from the dry weight (Gani et al., 2023):

$$FC(\%) = \left(\frac{\text{dry weight} - MC - VM}{\text{dry weight}} \right) \times 100 \quad \text{equation (3.18)}$$

Ash Content: Samples were combusted in a muffle furnace to determine the ash content (Gani et al., 2023):

$$Ash(\%) = \left(\frac{\text{weight of residue after combustion}}{\text{dry weight of sample}} \right) \times 100 \quad \text{equation (3.19)}$$

$$\text{Proximate Analysis} = 100\% - (MC + VM + FC + Ash) \quad \text{equation (3.20)}$$

Ultimate analysis: Performed by LECO CHN628S and analyzed based on previous research which confirmed AC's C, H, N & S & O contents. The elemental composition was calculated as (Gani et al., 2023):

$$\text{Ultimate Analysis} = 100\% - (C + H + N + S + O) \quad \text{equation (3.21)}$$

3.4.7 Statistical Analysis and Data Handling

The experimental results were validated through statistical analysis. Precision and goodness-of-fit of the adsorption models were analyzed by calculation of standard deviation (SD), and coefficient of determination (R^2). Experiments were analyzed with analysis of variance to determine the significance between different experimental parameters. Data analysis and graph plotting were performed using the Excel and Origin programs.

- i. Excel: Used for data preprocessing, basic statistics analysis, and initial plotting.
- ii. Origin: Employed for advanced data analysis, detailed statistical evaluation, and high-quality graphical representation.
- iii. Xpert Highscore Software: For the known mineralogical identification through references and extended for advanced XRD data analysis,
- iv. corresponding with previous studies.
- v. UV-Vis spectrophotometer: It was applied for the adsorption study and used to calibrate MB concentrations to determine residual dye concentration, accurately.
- vi. Commercial activated carbon (CAC), an air purifier, mega cell enterprise (M) Sdn Bhd, and used as a commercial adsorbent was purchased with the performance data compared to the modified adsorbents.

CHAPTER 4

RESULTS AND DISCUSSION OF EMPTY FRUIT BUNCH

4.1 Introduction

Chapter 4 concentrates on the results and discussion of the research findings related to activated carbon (AC). The results address the research questions that formed the basis of the study. This part of the research utilized the adsorption process to reduce the concentration of methylene blue (MB) by treating it with activated carbon sourced from empty fruit bunches (EFB) of oil palm. AC was activated, by a dual-step activation method with ZnCl_2 for the first step and then followed up with H_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$ to enhance its adsorptive properties. The current study investigates the potential of this modified AC for removing MB from aqueous solutions, and compares its abilities with commercial activated carbon (CAC).

4.2 Synthesis of activated carbon

This study effectively synthesized high-quality of AC from EFB to serve as efficient adsorbents for eliminating MB from aqueous solutions. The synthesis required a precisely controlled two-stage chemical activation method. Initially, ZnCl_2 was employed in a furnace at 700°C under N_2 and CO_2 atmospheres, followed by a second-stage activation with either H_2SO_4 at 210°C via a reflux technique or $(\text{NH}_4)_2\text{SO}_4$ at 260°C in a hydrothermal autoclave reactor. Dual-stage activation with 50% (ZnCl_2) and 6M $(\text{NH}_4)_2\text{SO}_4$ greatly increased AC adsorption capabilities, as proven by detailed characterization analysis and stringent lab measurements.

In the first stage, various ZnCl_2 dosages (0% to 50%) were examined to determine the optimal dosage for MB removal. The activation was conducted over 24 hours at a temperature of 25°C , a natural pH of 6, and an initial concentration of 50-100 ppm, using a shaker at 135 rpm in a 100mL sample volume. The best activation dosage for MB elimination was found to be 50%, achieving a 100% removal rate at 50 ppm and a 97.774% removal rate at 100 ppm. This was demonstrated in Tables 10, and Figure 16. The 50% ZnCl_2 dosage was optimal because it provided the highest surface area and optimal pore development necessary for efficient adsorption. Lower dosages did not fully activate the carbon, resulting in fewer adsorption sites, while higher dosages may have led to excessive pore widening, reducing the overall surface area and thereby the adsorption efficiency. ZnCl_2 acts as a dehydrating agent, promoting the development of a porous structure. The 50% dosage achieved a balance where sufficient ZnCl_2 was present to facilitate the creation of micro and mesopores without causing structural collapse or excessive ash content that would impede adsorption.

Table 10 : ZnCl_2 activation results for AC (50ppm)

C_i (mg/l)	Abs (nm)	C_e (mg/l)	Removal %	Activation (ZnCl_2 %)
50	1.177	8.622	82.754	0%
50	2.612	19.174	61.311	10%
50	2.609	19.152	61.355	20%
50	0.268	1.938	96.114	30%
50	0.049	0.328	99.365	40%
50	0.000	0.00	100	50%
100	0.307	2.225	97.774	50%

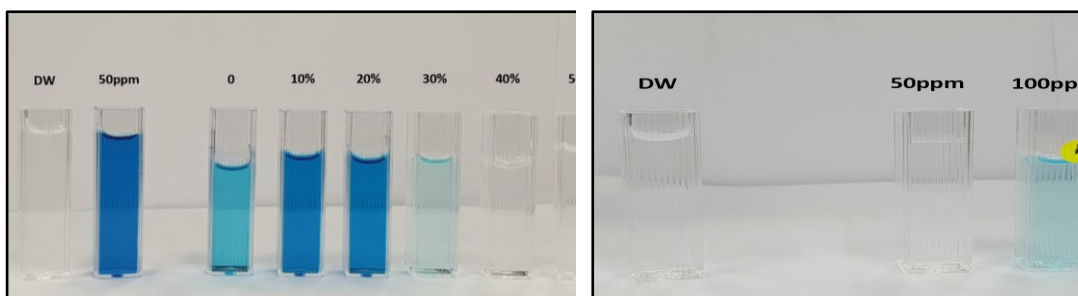


Figure 16 : ZnCl_2 Activation of AC: (a) 50 ppm, (b) 50-100 ppm Results

In the second stage, the AC was further activated using varying dosages of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ (3M to 18M). This activation was also performed over 24 hours under specific conditions (pH 6, 25°C , initial concentration 200 ppm, 0.6g dosage, 135 rpm shaker). The results showed that H_2SO_4 activation achieved a maximum removal percentage of 99.96% at 12M, while $(\text{NH}_4)_2\text{SO}_4$ activation achieved an even higher and faster removal percentage of 99.99% at 6M. These findings demonstrate the significantly improved adsorption capacity of the reactivated AC, indicating its potential for efficient removal of MB from aqueous solutions. This was shown in Tables 11 and 12 and Figures 17 and 18. The second-stage activation with 6M $(\text{NH}_4)_2\text{SO}_4$ was optimal due to its ability to introduce nitrogen-containing functional groups onto the AC surface. Such functional groups could enhance the electrostatic interactions between AC and high content anionic dye (MB) molecules, which in turn improved adsorption capacity. At 6M, this was the high enough concentration that could react favorably with the carbon surface and caused higher hydrophilicity as well which led to more MB-active sites on C-H columns for cationic dye (MB) adsorption. At low concentrations, this may not introduce enough functional groups, while at high concentrations there will be possible over-functionalization which could block adsorption sites or degrade the

material.

Table 11 : H₂SO₄ activation results for AC (200ppm)

C _i (mg/l)	Abs (nm)	C _e (mg/l)	Removal %	Activation (H ₂ SO ₄)
200	0.127	0.902	99.548	3M
200	0.02	0.115	99.942	6M
200	0.043	0.284	99.857	9M
200	0.013	0.063	99.968	12M
200	0.022	0.130	99.934	15M
200	0.022	0.130	99.934	18M



Figure 17 : H₂SO₄ Activation Results for AC (200ppm)

Table 12 : (NH₄)₂SO₄ activation results for AC (200ppm)

C _i (mg/l)	Abs (nm)	C _e (mg/l)	Removal %	Activation (NH ₄) ₂ SO ₄
200	0.011	0.049	99.975	3M
200	0.006	0.012	99.993	6M
200	0.146	1.041	99.479	9M
200	0.022	0.130	99.934	12M
200	0.113	0.799	99.600	15M
200	0.012	0.056	99.971	18M

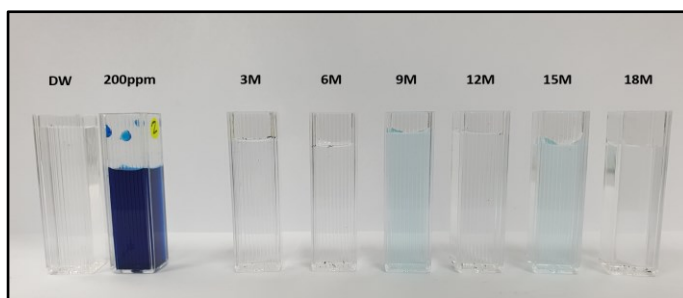


Figure 18 : $(\text{NH}_4)_2\text{SO}_4$ Activation Results for AC (200ppm)

The concentration of MB in the samples was done using a UV-spectrophotometer (UV-1800 SHIMADZU) to absorb light at different wavelengths. The standard wavelength of selected dyes for MB was 663 nm as presented in Figure-19 echoed by previous studies (Bhuyan et al., 2016; Khairnar & Shrivastava, 2019; Khosa et al., 2011). The calibration curve was made with different known MB concentrations, see Appendix C; the absorbance of 663 nm at these standard concentration values was plotted to graph a line as calibrate and it allowed calculation of the other samples' concentrations. Therefore, such a method guarantees accurate and repeatable MB concentration measurement in the analyzed samples.

As the results show, for MB removal from aqueous solution using this adsorbent, a dual-stage activation process by 6M $(\text{NH}_4)_2\text{SO}_4$ after activating 50% ZnCl_2 not only enhances the efficiency of simultaneous chemical and physical activation inducing but also improves high-performance capability. These results satisfy our first goal to synthesize the best AC with the highest MB elimination efficiency.

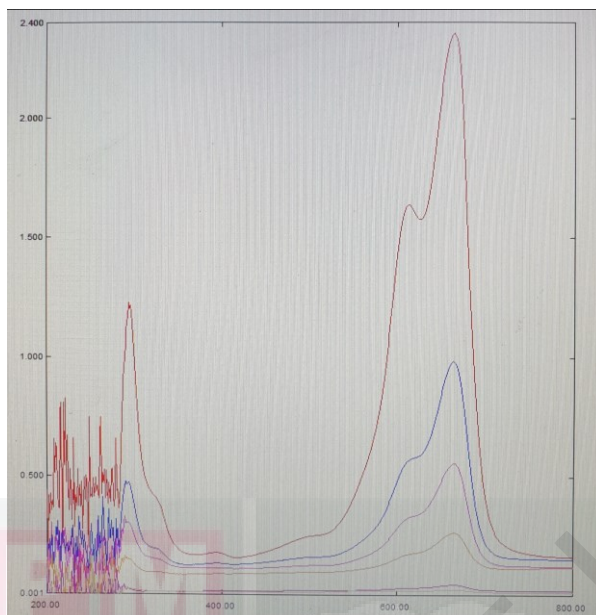


Figure 19 : UV-Spectrophotometer Results of MB (663 nm)

4.3 Characterization of activated carbon

Characterizing of AC is an important element of this study since it provides for a better knowledge of the adsorbents' physical and chemical characteristics. To achieve this, different analytical techniques have been applied, including CHNOS analysis, scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) analysis, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). These techniques are important for information adsorbent surface area, pore dimensions, chemical composition, and also crystalline framework. This characterization of the AC will help in determining a suitable activating agent and optimum conditions for removing MB from aqueous solutions.

4.3.1 Proximate and ultimate analysis

A proximate approach was conducted to the AC sample such as ash content, volatile matter determination, moisture, and fixed carbon analysis. Also, ultimate CHONS analysis was performed over the untreated and AC samples to monitor their chemical compositions (before/after activation) through the CHN628S-LECO instrument. The summary of these findings is in Table 13.

Table 13 : Characterize the proximate and ultimate for raw EFB and AC

Proximate	substance	Ash (%)	Volatile matter (%)	Moisture (%)	Fixed carbon (%)	
	AC	13.546	18.486	3.713	64.255	
Ultimate	substance	C (%)	H (%)	N (%)	S (%)	O (%)
	Raw EFB	71.77	2.957	2.032	0.569	22.672
	AC	44.55	6.282	0.7278	0.158	48.2822

The proximate analysis of EFB-derived AC found significant changes compared to raw EFB. Ash content decreased to 13.546%, the volatile matter was 18.486% and moisture dropped down to the value of 3.713%; however, fixed carbon increased up till it reached around %64. This is consistent with the results of previous research, which proves that the activation process significantly improves the carbonaceous structure and eliminates volatile components (Ge et al., 2020; Sayin et al., 2016; R. Zakaria et al., 2021). These data indicate that the produced AC was able to convert EFB efficiently with convenient for MB adsorption.

Moreover, the final analysis revealed significant changes in elemental composition. The carbon content decreased from 71.77% in raw EFB to

44.55% in AC and its hydrogen content increased from originally 2.957% at the beginning of the process, up to the final value equaling dry basis 6.282%. The shifts indicated the formation of hydroxyl (O-H) and carbonyl (C=O) surface functional groups, which contribute to adsorption by offering more binding sites for different physicochemical species in an aqueous solution because of their low band gap. This increment in hydrogen contents denotes increasing reactive sites onto the surface of AC making better interaction with MB molecules, aligning with previous studies (Altıntig et al., 2017; R. Zakaria et al., 2021).

Additionally, lower nitrogen and sulfur contents minimize the signal overlap related to adsorption processes. This indicated the formation or an improvement in oxygen comprising functional groups after activation. These groups are known to improve adsorption as they provide more binding sites. Therefore, an increase in oxygen content of (48.2822%) means that the development of surface characteristics is achieved which helps to ameliorate effective adsorption (Altıntig et al., 2017; Ravichandran et al., 2018).

These compositional enhancements highlight the potential of AC as a capable MB absorbent. The relatively low carbon content and high hydrogen contents in the adsorbents are beneficial to produce AC with sufficient surface reactivity that allows for a rich capacity through MB removal.

4.3.2 Thermogravimetric analysis (TGA)

The raw EFB sample was analyzed for thermal stability and composition via thermogravimetric analysis (METTLER TOLEDO TGA/DSC3+). TGA analysis thus shows the weight transformations of a sample during controlled heating. The temperature range of 25-800°C was used to give a better understanding of the thermal behavior exhibited by the sample as demonstrated in Figure 20.

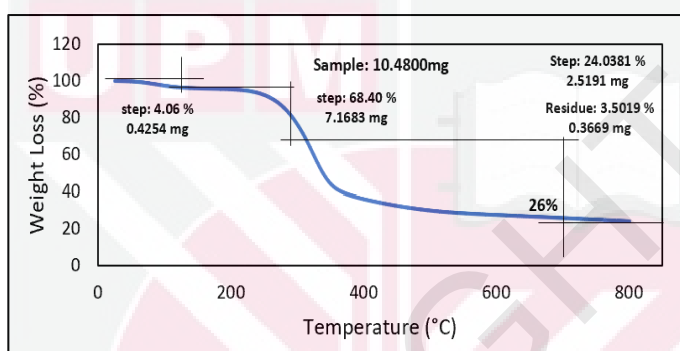


Figure 20 : TGA: Raw Empty Fruit Bunch

During the TGA analysis, two stages of weight loss could be identified. The first stage was -4.06% because of the evaporation of volatile components and volatilization losses from low-molecular-weight gases, moisture, and volatile organic compounds. The second stage was marked by a loss of weight equal to -68.40% probably related to the thermal decomposition of organic content. A percentage of the residue retained after decomposition was quantified as 26% at 700°C and remained relatively steady through to a heating temperature beyond this peak, (24.038%) at 800°C which confirmed that some components showed instability towards decomposition under certain heat conditions consistent with previous work showing percentages in the line up to similar qualities; around 29% (Chala et al., 2018).

The TGA test on the EFB sample showed a dual-step degradation approximately at 200°C and 400 °C, which is in line with previous work that reported an enthalpy for water evaporation within this temperature range (Nur Afifah, 2020; Sefadi & Luyt, 2012). Moreover, the persistence of stable residuals from this second phase refers to more resistant materials with higher melting points.

4.3.3 Scanning electron microscopy (SEM)

In this work, a study of the two-stage activation process has been carried out for the synthesis of AC with high quality by applying HITACHI S3400-N. First, the activation was performed at different concentrations of ZnCl₂ (0%, 10%, 20%, 30%, 40%, and 50%) to find out which concentration increase has positive effects on results: the highest increase in performance. The SEM analysis of AC activated with 50% of ZnCl₂ presented a highly developed surface morphology that was involved in extended area porosity, these results were similar to previous investigations (Osman et al., 2016; Wirasnita et al., 2014, 2015; R. Zakaria et al., 2021; S. Zakaria et al., 2014). The 50% of ZnCl₂ was chosen for optimal activation which showed it could activate freeze-popped cells efficiently while allowing some structural preservation. Dosages under 50% were inactive, which does not provide enough activation and results in poor surface macroporosity and adsorption capacity, or conversely, the concentrations caused hyper-activation accompanied by surface wear and pore shrinkage that reduced both the structural stability and adsorptive capacity of AC. As a result, 50% ZnCl₂ was chosen as a compromise between effective activation and the preservation of the AC structure.

In the following stage, activation was carried out using $(\text{NH}_4)_2\text{SO}_4$ at various concentrations: 3M, 9M, 12M, 15M, and 18M. Figure 22 shows SEM images of various phases (a-d for 3M, e-h for 9M, i-l for 12M, m-p for 15M, and q-t for 18M) at scales of 0.2k, 1k, 4k, and 6k, respectively. The best activation was 6M $(\text{NH}_4)_2\text{SO}_4$. SEM analysis at this concentration with the prior 50% ZnCl_2 activation resulted in notable improvements in surface morphology which included increasing porosity and pore dimensions as shown in Figure 21 (e-h). The selection of 6M $(\text{NH}_4)_2\text{SO}_4$ provided no effects such over-activated or structural damage while contributing further increase by raising surface porosity and pore volume. Concentrations less than 6M were insufficient for significant morphological augmentation, whilst concentrations more than 6M resulted in declining advantages and increased risk of structural degeneration. 6M $(\text{NH}_4)_2\text{SO}_4$ was the best concentration for attaining the necessary activation without sacrificing structural integrity (Ennaciri et al., 2020; Linh et al., 2019). The efficiency of the two-stage activation method is demonstrated by the considerable increase in surface area and pore volume with 6M $(\text{NH}_4)_2\text{SO}_4$ over 50% ZnCl_2 . Previous investigations have shown that this morphological improvement is critical for the AC's increased MB adsorption capability (Dong et al., 2021).

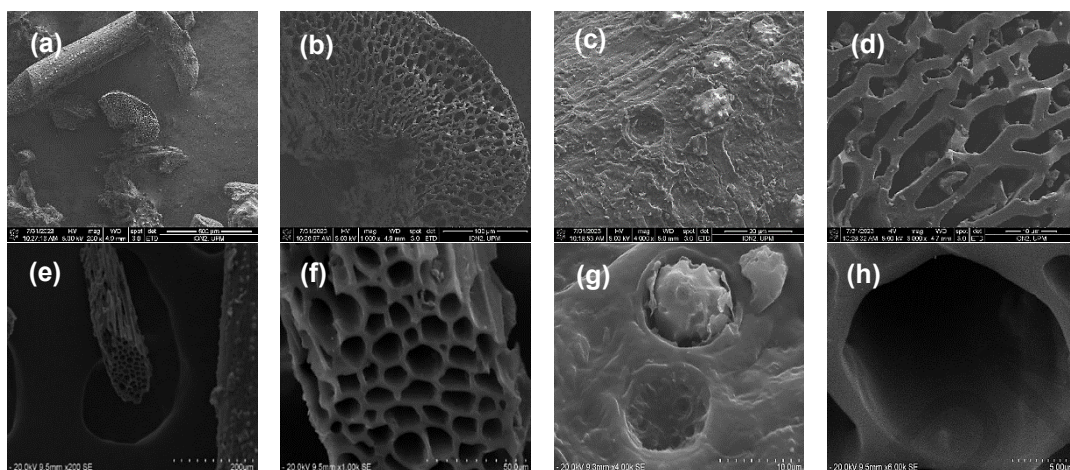


Figure 21 : SEM Images of AC Morphology: (a-d) ZnCl_2 Activation at 50% and (e-h) $(\text{NH}_4)_2\text{SO}_4$ at 6M, Scales 0.2k–6k

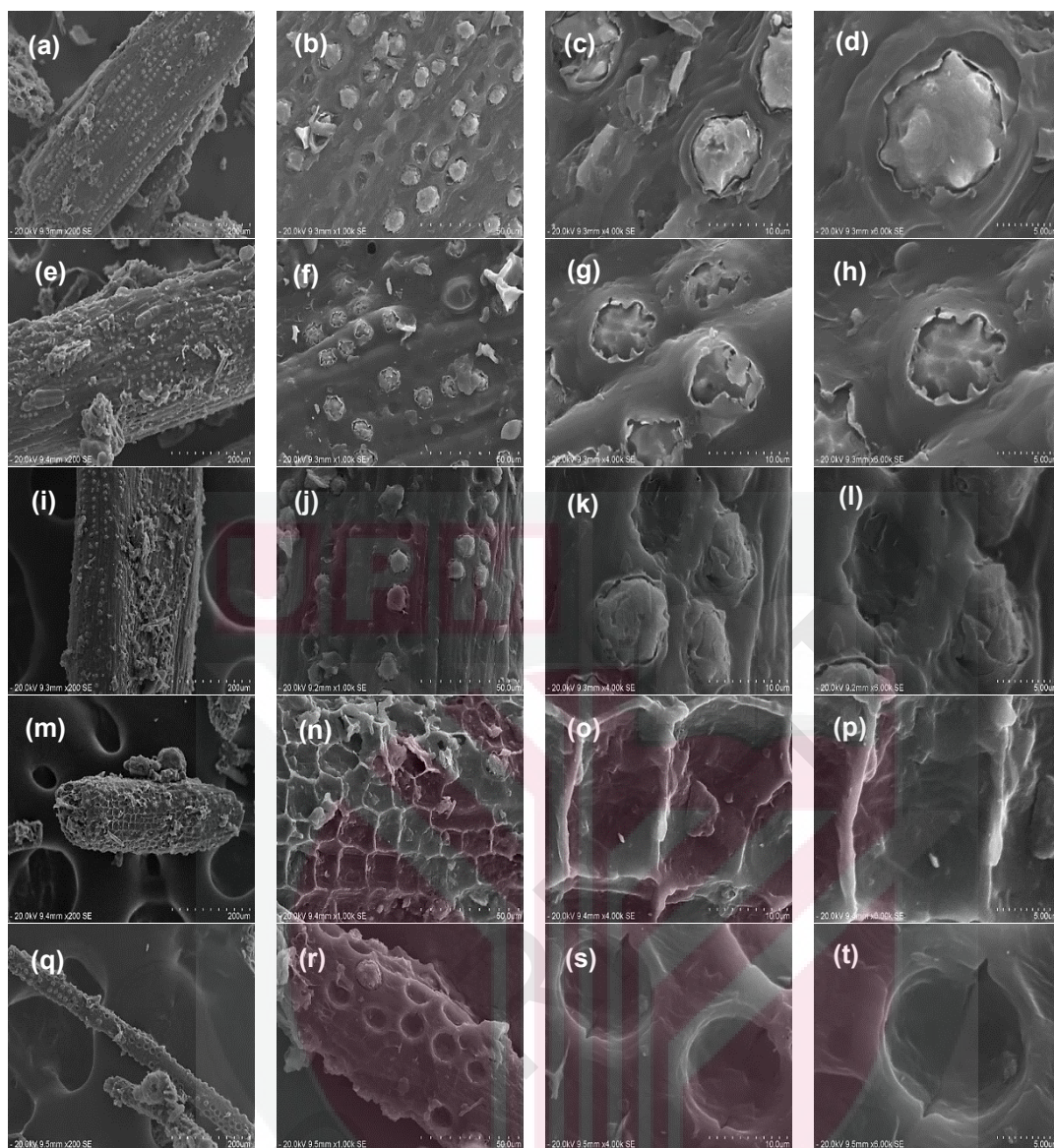


Figure 22 : SEM Images of AC Morphology with $(\text{NH}_4)_2\text{SO}_4$: (a-d) 3M, (e-h) 9M, (i-l) 12M, (m-p) 15M, (q-t) 18M, Scales 0.2k–6k

4.3.4 Brunauer-emmett-teller (BET)

BET analysis was performed on AC samples set with varying activation dosages for the first step (50%) of ZnCl_2 , along with the second step (3M, 6M, 9M, 12M, 15M, and 18M) of $(\text{NH}_4)_2\text{SO}_4$ to assess their surface area, pore volume, and pore size using machines (MICROMERITICS 3FLEX) at degassing temperature N_2 (250°C), as demonstrated in Table 14.

Table 14 : Surface area and pore volume of AC

BET	ZnCl ₂ activation	(NH ₄) ₂ SO ₄ activation					
Activated carbon	50%	3M	6M	9M	12M	15M	18M
Surface area (m ² /g)	936.43	904.91	939.63	884.20	826.4	742.03	925.72
Pore volume (cm ³ /g)	0.31	0.53	0.65	0.53	0.38	0.60	0.65
Pore size (Å)	1.34	11.83	13.90	11.97	9.20	16.29	14.22

The BET analysis findings of AC for the two phases of activation show considerable enhancements in surface area, pore volume, and pore size. In the first stage, activation with 50% ZnCl₂ produced a surface area of 936.43 m²/g, a pore volume of 0.31 cm³/g, and a pore size of 1.34 nm, which is roughly in line with previous investigations (940.132 m²/g) by (Altıntig et al., 2017), 1040 m²/g by B. Li et al., (2020) and 0.65 to 1.4 nm by (Phothong et al., 2021). This first activation provided the groundwork for further advances.

In the second step, activation with (NH₄)₂SO₄ at various doses had variable results. At 3M activation, the surface area fell to 904.91 m²/g. However, the pore volume grew to 0.53 cm³/g and the pore size extended to 11.83 nm. This indicates that the 3M dose caused the creation of bigger pores, leading to a greater pore volume with a modest loss in surface area.

At the ideal 6M activation dose, the surface area rose significantly to 939.63 m²/g, suggesting a successful augmentation. The pore volume grew to 0.65 cm³/g, while the pore size extended to 13.90 nm. The 6M activation had the largest surface area and pore volume of the four doses, demonstrating an

efficient strategy for increasing the AC's adsorption capability.

Nevertheless, once the activation dose exceeded 6M, the surface area, pore volume, and pore size declined. At 9M activation, the surface area fell to 884.20 m²/g. This might be due to the over-activated of the carbon, causing the breakdown or blocking of certain pores. With 12M activation, the surface area dropped to 826.40 m²/g, most likely due to severe activation that caused carbon structural disruption.

At 15M activation, the surface area declined slightly to 742.03 m²/g, suggesting the formation of new pores. Nevertheless, this pattern also exhibited a greater pore volume of 0.60 cm³/g and a bigger pore size of 16.29 nm, indicating that the carbon structure may not be as maintained properly as during the 6M activation.

The 18M activation produced in a considerable improvement in surface area to 925.72 m²/g, suggesting restoration in the carbon structure. Pore volume continued high at 0.65 cm³/g, with a pore size of 14.22 nm, demonstrating the effective creation of bigger pores.

The increased surface area, pore volume, and pore size noticed in the 6M activation of (NH₄)₂SO₄ are most likely due to most effective activation conditions that effectively open up new pore structures while avoiding excessive harm to the carbon matrix, as demonstrated by SEM analysis on pages 83-85 and in line with previous investigations by (Yadavalli et al., 2017). As shown in laboratory trials, the optimal balance of pore creation and

structural preservation at this dose resulted in the maximum adsorption capacity and effectiveness for MB elimination. The effective improvement in the second stage, notably at 6M $(\text{NH}_4)_2\text{SO}_4$ activation, demonstrates the two-stage activation process's ability to produce highly efficient AC adsorbents for a variety of water treatment uses (Ennaciri et al., 2020; Linh et al., 2019).

4.3.5 Fourier-transform infrared (FTIR)

FTIR analysis was performed on AC samples to explore modifications to functional groups caused by various activation doses. The first step used 50% ZnCl_2 , and different doses of $(\text{NH}_4)_2\text{SO}_4$: 3M, 6M, 9M, 12M, 15M, and 18M. This investigation attempted to investigate the influence of different activation doses on the characteristics of AC, using SPECTRUM 100 PERKIN ELMER equipment spanning a spectrum ranging from $650\text{-}4000\text{ cm}^{-1}$, as indicated in the full FTIR spectrum figure (Figure 23) and specified in Table 15.

i. First stage activation of AC (50% ZnCl_2):

The FTIR spectrum for AC treated with 50% ZnCl_2 shows substantial peaks, referring the presence of numerous functional groups. A signal at 1559.36 cm^{-1} reveals carbonyl groups via C=O stretching, whereas peaks between 857.90 and 423.68 cm^{-1} relate to bending vibrations in C-H bonds, suggesting aliphatic hydrocarbons. These results are consistent with published FTIR spectra for AC, notably reported by Devi et al., (2020) and Gore et al., (2020). The presence of various functional groups, notably oxygen and acidic groups, increases the carbon's hydrophilicity and adsorption capacity for MB. The carbonyl and hydroxyl groups, in particular, can form hydrogen bonds and

interact electrostatically with the amine groups in MB, enhancing sorption.

ii. Second stage activation of AC (NH₄)₂SO₄ dosages:

The FTIR spectra of AC activated with 3M reveal peaks at 2338.45 cm⁻¹ (C=O stretching), 1741.60 cm⁻¹ (C-O stretching), 1545.90 cm⁻¹ (asymmetric C-H stretching of methylene groups), and 1095.99 cm⁻¹. These functional groups, particularly carbonyl (C=O) and ether/alcohol (C-O), are essential for MB adsorption via dipole-dipole interactions and hydrogen bonding. These groups react with the aromatic rings and sulfonic groups of MB, increasing its adsorption ability (Abdullah et al., 2023; Al Ashik et al., 2023; Ali et al., 2020; Cuhadaroglu & Uygun, 2008; Gore et al., 2020).

The FTIR spectrum of AC activated with 6M shows peaks at 3746.25 cm⁻¹ (O-H stretching), 3012.96 cm⁻¹ (C-H stretching), 2338.57 cm⁻¹ (C=O stretching), 1740.39 cm⁻¹ (carbonyl groups), 1545.92 cm⁻¹ (asymmetric C-H stretching), 1365.32 cm⁻¹ (bending vibrations in CH₂ or CH₃ groups), 1219.97 cm⁻¹ (C-N stretching), and 944.38 cm⁻¹ (bending). These functional groups promote adsorption via hydrogen bonding, dipole-dipole interactions, and π - π interactions with the aromatic rings of MB (Abdullah et al., 2023; Al Ashik et al., 2023; Ali et al., 2020; Cuhadaroglu & Uygun, 2008; Gore et al., 2020).

Activated with 9M exhibits peaks at 3384.53 cm⁻¹ (O-H stretching), 2325.36 cm⁻¹ (C $\equiv$ N stretching), 1636.11 cm⁻¹ (C=C stretching), 1365.14 cm⁻¹ (C-H bending), 1217.00 cm⁻¹ (C-O stretching), and 721.67 cm⁻¹ (C-H bending). These groups help with MB adsorption via hydrogen bonding, dipole-dipole

interactions, and non-specific van der Waals interactions with the polar groups of MB (Abdullah et al., 2023; Al Ashik et al., 2023; Ali et al., 2020; Cuhadaroglu & Uygun, 2008; Gore et al., 2020).

The FTIR spectrum of AC activated with 12M shows peaks at 3746.16 cm^{-1} (O-H stretching), 3013.65 cm^{-1} (C-H stretching), 2327.18 cm^{-1} ($\text{C}\equiv\text{N}$ stretching), 1740.66 cm^{-1} (C=O stretching), 1545.44 cm^{-1} (C=C stretching), 1366.09 cm^{-1} (C-H bending), 1219.12 cm^{-1} (C-O stretching), and 953.73 cm^{-1} (C-H bending). These groups improve MB adsorption via hydrogen bonding, dipole-dipole interactions, and non-specific interactions with van der Waals (Abdullah et al., 2023; Al Ashik et al., 2023; Ali et al., 2020; Cuhadaroglu & Uygun, 2008; Gore et al., 2020).

The FTIR spectra of AC activated with 15M reveals peaks at 3381.95 cm^{-1} (O-H stretching), 1637.09 cm^{-1} (C=C stretching), 1214.60 cm^{-1} (C-O stretching), and 713.84 cm^{-1} (C-H bending). These functional groups help in MB adsorption via dipole-dipole interactions, hydrogen bonding, and van der Waals forces (Abdullah et al., 2023; Al Ashik et al., 2023; Ali et al., 2020; Cuhadaroglu & Uygun, 2008; Gore et al., 2020).

While activation at 18M shows peaks at 3747.85 cm^{-1} (O-H stretching), 3372.45 cm^{-1} (N-H stretching), 2344.98 cm^{-1} ($\text{C}\equiv\text{N}$ stretching), 1739.03 cm^{-1} (C=O stretching), 1548.25 cm^{-1} (C=C stretching), 1366.02 cm^{-1} (C-H bending), 1214.82 cm^{-1} (C-O stretching), and 705.60 cm^{-1} (C-H bending). These functional groups promote MB adsorption via hydrogen bonding, dipole-

dipole interactions, π - π interactions, and non-specific van der Waals interactions (Abdullah et al., 2023; Al Ashik et al., 2023; Ali et al., 2020; Cuhadaroglu & Uygun, 2008; Gore et al., 2020).

Ultimately, the two-stage activation method, which includes a 50% ZnCl_2 dose followed by different concentrations of $(\text{NH}_4)_2\text{SO}_4$, greatly improves the surface area, porosity, and functional groups of AC. The first stage with ZnCl_2 establishes necessary functional groups, but the second stage with $(\text{NH}_4)_2\text{SO}_4$, especially at 6M, introduces new functional groups such as O-H stretching and aromatic structures. These functional groups increase adsorption capacity and efficiency, enabling AC extremely efficient in eliminating MB from aqueous solutions. Carbonyl, hydroxyl, and aromatic groups use hydrogen bonding, π - π interactions, dipole-dipole interactions, and non-specific van der Waals forces to enhance MB adsorption and improve adsorbent performance. The 6M $(\text{NH}_4)_2\text{SO}_4$ activation yields the most encouraging findings, demonstrating the ability to function as an effective adsorbent for water treatment uses.

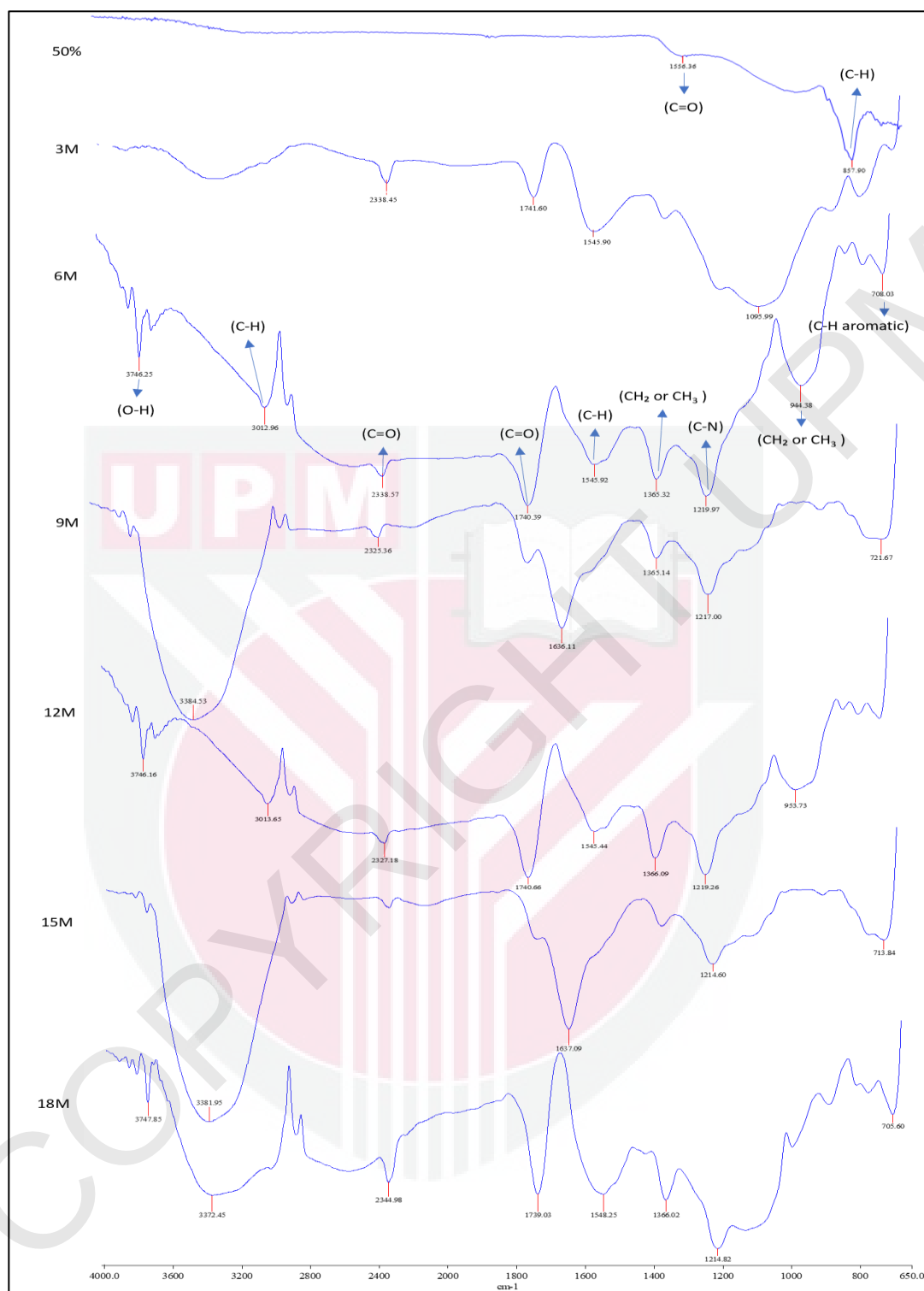


Figure 23 : Combined FTIR Spectra of AC Samples at Different Dosages

Table 15 : FTIR peaks and functional groups for AC at various dosages

Stage/activation	Peak wavelength (cm ⁻¹)	Functional groups	Interaction	Reference
1 th (ZnCl ₂) 50%	1559.36, 857.90	(C=O), (C-H)	Hydrophilicity, Enhanced adsorptive behavior	(Devi et al., 2020; Gore et al., 2020; Mousavi, 2022; R. Zakaria et al., 2021)
2 th ((NH ₄) ₂ SO ₄) 3M	2338.45, 1741.60, 1545.90, 1095.99	C=O, C-O, C-H, C-O	Hydrogen bonding, dipole- dipole, electrostatic	(Ali et al., 2020; Cuhadaroglu & Uygun, 2008;
2 th ((NH ₄) ₂ SO ₄) 6M	3746.25, 3012.96, 2338.57, 1740.39, 1545.92, 1365.32, 1219.97, 944.38, 708.03	O-H, C-H, C=O, C=O, C-H, CH ₂ or CH ₃ , C-N, CH ₂ or CH ₃ , C-H aromatic	Hydrogen bonding, dipole- dipole, van der Waals forces, π-π, chemical	da Silva Alves et al., 2021; George et al., 2024; Hidayu et al., 2013; Liou, 2004; Misra et al., 2006;
2 th ((NH ₄) ₂ SO ₄) 9M	3384.53, 2325.36, 1636.11, 1365.14, 1217.00, 721.67	O-H, C≡N, C=C, C-H bending, C-O, C-H bending	Hydrogen bonding, dipole- dipole, van der Waals, π-π interactions	Mousavi, 2022; Sari et al., 2014; R. Zakaria et al., 2021; S. Zakaria et al., 2014)
2 th ((NH ₄) ₂ SO ₄) 12M	3746.16, 3013.65, 2327.18, 1740.66, 1545.44, 1366.09, 1219.12, 953.73	O-H, C-H, C≡N, C=O, C=C, C-H bending, C-O, C-H bending	Hydrogen bonding, dipole- dipole, van der Waals, π-π interactions	
2 th ((NH ₄) ₂ SO ₄) 15M	3381.95, 1637.09, 1214.60, 713.84	O-H, C=C, C-O, C-H	Hydrogen bonding, dipole- dipole interactions, and van der Waals forces	
2 th ((NH ₄) ₂ SO ₄) 18M	3747.85, 3372.45, 2344.98, 1739.03, 1548.25, 1366.02, 1214.82, 705.60	O-H, N-H, C≡N, C=O, C=C, C-H bending, C-O, C-H bending	Hydrogen bonding, dipole- dipole, van der Waals forces, π-π	

4.3.6 X-ray diffraction (XRD)

XRD has been applied in beneficially characterizing the structural changes resulting from different activation doses when it comes to activated carbons. In the present study, two sets of samples (Raw EFB and EFB impregnated 50% ZnCl_2), as well as activated with $(\text{NH}_4)_2\text{SO}_4$ concentration in the range between 3M to 18 M were studied. The data were represented using a SHIMADZU XRD-6000 instrument, and the diffraction patterns were recorded over 2θ ranges.

XRD studies of raw EFB depicted two high-intensity peaks around 44° , and it was also observed at 64.38° (2θ) with the corresponding maximum intensities of 310 and 350 respectively which indicated crystalline nature. These peaks represent the presence of different carbon-linked crystalline phases which is in agreement with previous studies (Bakti & Gareso, 2018; Riyanto et al., 2020; Xie et al., 2014).

i. First stage activation of AC (50% ZnCl_2):

In the case of EFB treated with 50% ZnCl_2 -induced XRD, values were observed at 44° and 64.36° peaked with an intensity fluctuating between 510 and peak value 412 respectively. These peaks can be assigned to the retention of carbonaceous crystalline phases, in good agreement with what is observed by other authors during activation using ZnCl_2 (Bakti & Gareso, 2018; Riyanto et al., 2020; Xie et al., 2014).

ii. Second stage activation of AC (NH₄)₂SO₄ dosages:

For the 3M activation, strong peaks were observed at 44° (668) and a second less intense peak appeared mildly above the statistical background level at ~64.32° (332). These peaks had significant intensity indicating considerable structural ordering along the carbon planes of crystals (002) and (004). These results are parallel with recent studies, regarding the similar activation pathway (Bakti & Gareso, 2018; Riyanto et al., 2020; Xie et al., 2014).

XRD analysis performed on the 6M activated sample showed peaks at approximately 44 and 64.34 with respective intensities of 630 and 262, these results imply the persistence of certain crystalline stages indicating alterations in crystallographic nature induced by the activation mechanism of carbon species. In line with the previous findings on AC (Bakti & Gareso, 2018; Riyanto et al., 2020; Xie et al., 2014).

The 9M activation exhibited strong peaks at 44° and 64.3° with intensities of 490 and 246 respectively. The peaks indicate the crystalline structures conservation inside AC that is suitable with findings in some AC studies (Bakti & Gareso, 2018; Riyanto et al., 2020; Xie et al., 2014).

The XRD diagnostics of 12M AC showed the two prominent peaks at 44.5° and 64.34° with intensity values of 580 and 266. This result indicates the crystalline stages are preserved and there is no structural deformation, which agrees with previous reports on AC (Bakti & Gareso, 2018; Riyanto et al., 2020; Xie et al., 2014).

XRD examination of the activated sample 15M showed peaks around 44° , and at $\sim 64.34^\circ$ with intensities of approximately 240 and intensity values was only about 154 respectively. These peaks proved the maintenance of crystallinity in AC that was similar to previous findings (Bakti & Gareso, 2018; Riyanto et al., 2020; Xie et al., 2014).

XRD structure of 18M AC appeared with two peaks at $\sim 44^\circ$ and $\sim 64.3^\circ$ with intensities were 332 and 202 respectively. These peaks confirmed the presence of crystal phases of carbon and their conservation after activation as previously recorded (Bakti & Gareso, 2018; Riyanto et al., 2020; Xie et al., 2014).

The XRD analysis of AC samples, in the end, confirmed that there are unique crystalline phases that appeared peaks which exhibited regularly around 44° and also 64.34° . Variations in peak intensity over the activation phases are due to differences in precursor concentrations and crystallization, which are corroborated by previous works on carbonaceous substance activation (Bakti & Gareso, 2018; Riyanto et al., 2020; Xie et al., 2014). The AC developed by the 6M activation dose exhibited a wide range and intense peaks related to functional groups as anticipated that can contribute excellent sorption capacity towards MB. An exhaustive compilation of these results can be found in Figure 24 which summarizes the entire XRD data for a vast sample set in Figures.

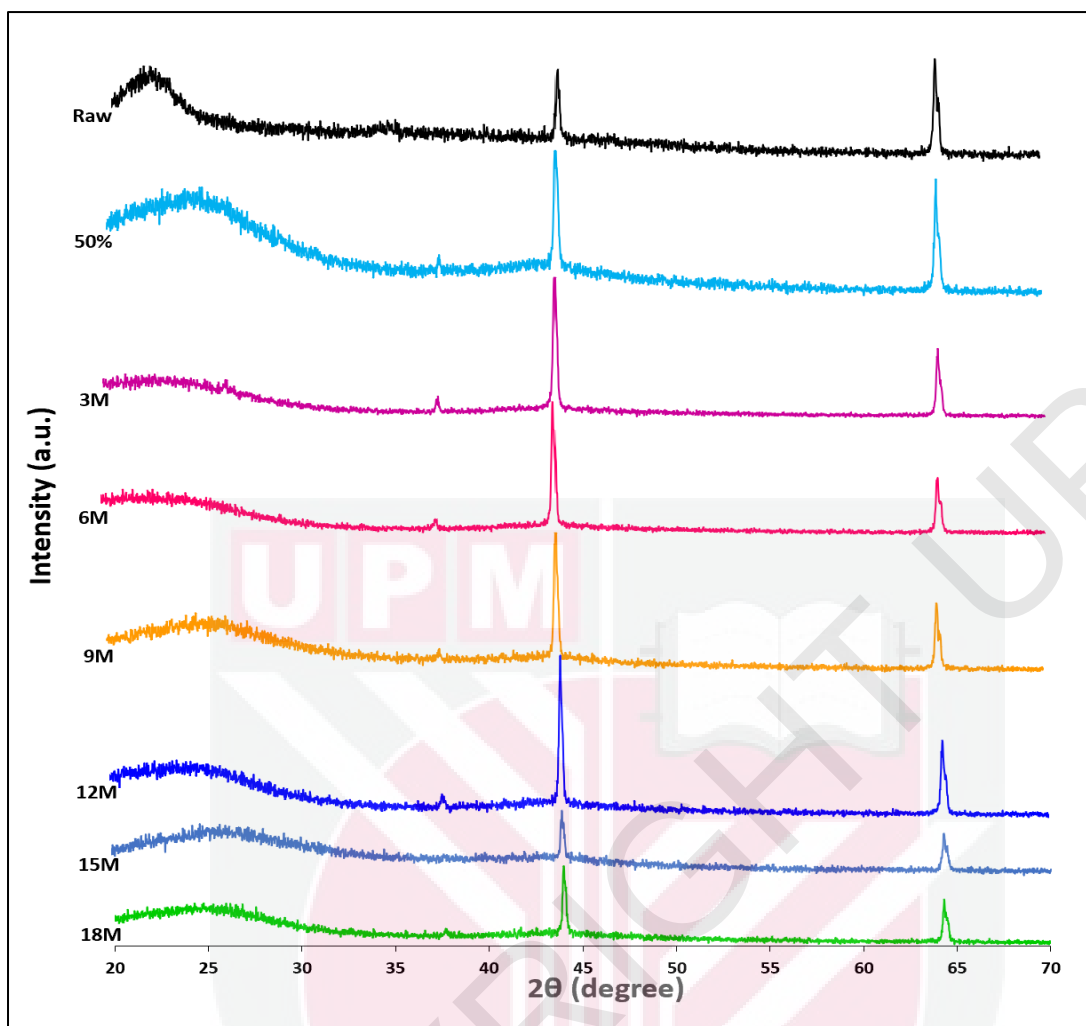


Figure 24 : XRD Peaks and Intensities for AC Samples

4.4 Adsorption investigations of activated carbon

AC was widely used as an adsorbent to remove MB from aqueous solutions due to its high adsorption efficiency and capacity. In the study, AC adsorption for amounts of MB uptake was investigated. The implementations of optimization methodologies, adsorption isotherm models, kinetic studies, and thermodynamic investigations provided in-depth information on AC-based adsorbents as well. The study helps understand well the adsorption process and offers valuable data for designing efficient removal systems for MB using AC.

4.4.1 Optimization of adsorption conditions

This study examined the effects of five parameters on MB adsorption capacities with AC for the optimization process. The parameters were the contact time (30 to 180 minutes), initially concentration (50-500 ppm), pH (4-10), temperature (25-55°C), and adsorbent dose (0.4-0.65 g). The aim was to determine the optimal conditions for achieving the highest adsorption capacity by varying these parameters. The results obtained from this investigation contribute to the development of efficient and cost-effective adsorption processes for MB removal and water treatment applications.

- i. **Contact time:** The adsorption process spanned 180 minutes to attain equilibrium, with an optimal point observed at 90 minutes duration offered significant removal with a shorter processing time than 120 to 180 minutes. Employing 0.6g of adsorbent, a 200 ppm (mg/L) MB concentration, 25°C temperature, and pH 6 in 100 mL, intervals of 30 minutes were used for agitation at 135 rpm. Results detailing contact time effects are presented in Table 16, visually depicted in Figure 25.

Table 16 : Contact time results for AC (200ppm)

C_i (mg/l)	Abs (nm)	C_e (mg/l)	Removal %	q_t (mg/g)	Time (min)
200	0.167	1.196	99.401	33.133	30 min
200	0.063	0.431	99.784	33.261	30 min
200	0.041	0.269	99.865	33.288	30 min
200	0.032	0.203	99.898	33.299	30 min
200	0.025	0.152	99.923	33.307	30 min
200	0.025	0.152	99.923	33.307	30 min

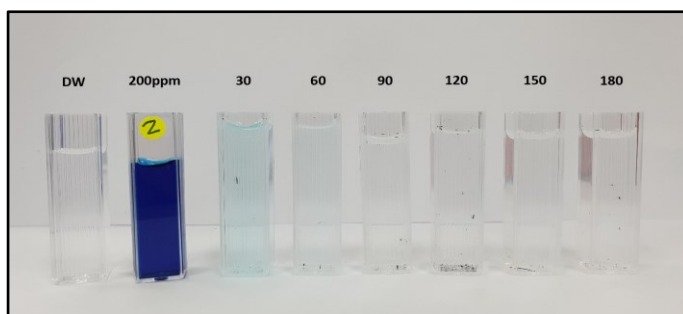


Figure 25 : Contact Time Results for AC (200ppm)

Through an exploration of diverse contact durations (30, 60, 90, 120, 150, 180 minutes) at 25°C and pH 6, employing an adsorbent dosage of 0.6g and initial concentration of 200 ppm, the optimal point emerged at 90 minutes, aligning with precedent research (P. S. Kumar et al., 2011). During this period, MB concentration significantly diminished to 0.269 ppm, yielding a remarkable 99.865% elimination efficiency and 33.288 mg/g adsorption capacity. These outcomes underscore AC's swift and effective adsorption attributes in a concise timeframe. Kumar et al., (2011) noted that within the range of 50-250 ppm, 30°C, pH 6.5, 2g, and 0-120 min in 100 mL, dye adsorption increased with extended contact times, peaking around 90 minutes at 23 mg/g. Prolonging the interval to 120 minutes saw a marginal 0.8% improvement in MB removal. Furthermore, as indicated by Dhevi et al., (2020) , at 120 ppm, 25°C, and 60 min in 25 mL, 94% MB removal was achieved. Figure 26 visually delineates C_e and q_e fluctuations with changing times.

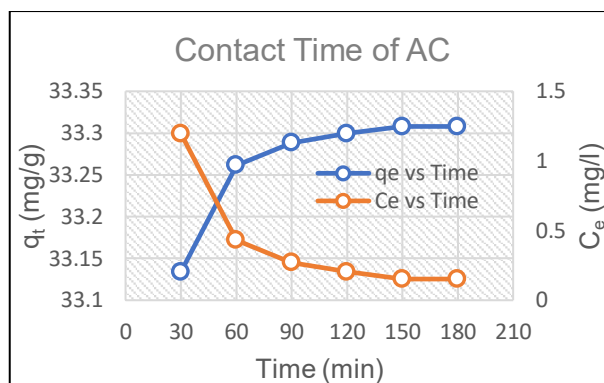


Figure 26 : Optimization Graph for Contact Time of AC

- ii. **MB Initial concentration:** The optimal adsorption process duration was calculated to be 90 minutes, encompassing initial concentrations spanning 200 to 500 ppm. Conducted at 25°C, pH 6, 0.6g in 100mL, employing shaker equipment operating at 135 rpm within 100mL, outcomes are succinctly summarized in Table 17 and visually depicted through Figure 27.

Table 17 : MB Initial concentration results for AC (200-500ppm)

C_i (mg/l)	Abs (nm)	C_e (mg/l)	Removal %	q_e (mg/g)	Time (min)
200	0.041±0.002	0.269	99.865	33.288± 33.290	90
250	0.058	0.394	99.802	41.600	90
300	0.086	0.600	99.699	49.899	90
350	0.133	0.946	99.526	58.175	90
400	0.433	3.152	98.423	66.141	90
450	0.831	6.078	96.960	73.986	90
500	1.239	9.078	95.460	81.820	90

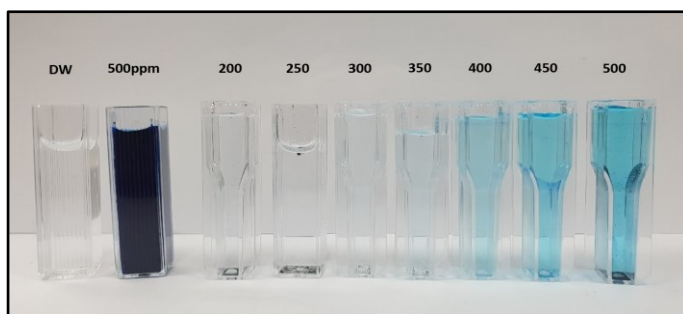


Figure 27 : MB Initial Concentration Results for AC (200-500ppm)

By systematically altering MB's initial concentration (ranging from 200, 250, 300, 350, 400, 450, to 500 ppm) under specific conditions (25°C, 0.6g adsorbent dosage, 90-minute contact time, pH of 6. MB of 500 ppm emerged as the optimal concentration. Within this range, AC achieved a final concentration of 9.078 ppm, signifying a notable 95.460% removal efficiency and 81.820 mg/g adsorption capacity. These findings underscore AC's efficacy in adsorbing MB, even at elevated concentrations, rendering it suitable for wastewater treatment involving higher dye levels. Zakaria et al., (2021) reported an 80% MB elimination at an initial concentration of 500 ppm, pH 6, 24 hours, 1 g, and 30°C in 100 mL. Similarly, Mousavi (2022) attained 52% MB elimination using 12.5g, pH 11, 90 minutes, 25°C, and 500 ppm in 100mL through applied RSM. Figure 28 visually presents C_e and q_e fluctuations during variations in initial concentration.

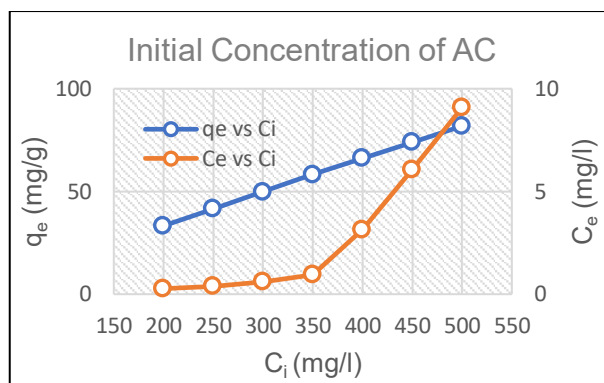


Figure 28 : Optimization Graph for MB Initial Concentration of AC

iii. **Temperature:** The temperature parameter within the adsorption process was meticulously explored across the range of 25 to 55°C. The initial solution concentration stood at a constant 500 ppm. Conducted under controlled conditions of a fixed 90-minute contact time, pH 6, 0.6g dosage, and utilizing shaker equipment with an agitation speed of 135 rpm in 100 mL, the extensive ramifications of these experimental endeavors are succinctly synthesized in Table 18 and visually portrayed through Figure 29.

Table 18 : Temperature results for AC (500ppm)

C_i (mg/l)	Abs (nm)	C_e (mg/l)	Removal %	q_e (mg/g)	Temp °C
500	1.239±0.001	9.078	95.460	81.820	25
500	1.216	8.909	95.545	81.848	30
500	0.830	6.071	96.964	82.321	35
500	0.472	3.438	98.280	82.760	40
500	0.350	2.541	98.729	82.909	45
500	0.277	2.005	98.997	82.999	50
500	0.282	2.041	98.979	82.993	55

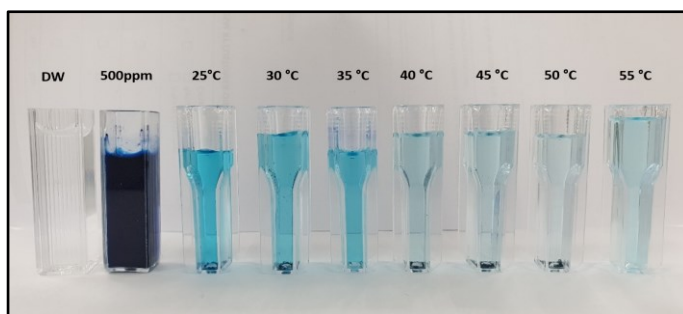


Figure 29 : Temperature Results for AC (500ppm)

By systematically altering the temperature variable (ranging from 25, 30, 35, 40, 45, 50, to 55°C) while maintaining uniformity in dosage, pH, initial concentration, and contact time (0.6g, pH 6, 500 ppm, 90-minute), the optimum temperature of 50°C was ascertained. At this specific temperature, AC exhibited an ultimate concentration of 2.005 ppm, marking an impressive 98.997% elimination efficiency and 82.999 mg/g adsorption capacity. These outcomes accentuate the thermodynamically favorable essence of the adsorption process, where elevated temperatures amplify kinetics and overall AC efficiency, congruous with prior investigations (Dhevi et al., 2023; Sharma & Uma, 2010). Sharma & Uma (2010) explored temperatures within the range of 30-50°C, noting that MB removal escalated from 93.20-99.16% as temperature increased. Similarly, Dhevi et al., (2023) witnessed the percentage of MB removal rising from 77.3-84.6% within a 30-50°C span, achieving a notable adsorption capacity of 28.8 mg/g at 50°C compared to 22.6 mg/g at 20°C. The deduced conclusion underscores the direct correlation between elevated temperatures and augmented adsorption capacity. This interplay is elegantly illustrated in Figure 30, graphically encapsulating fluctuations in C_e and q_e during temperature variations.

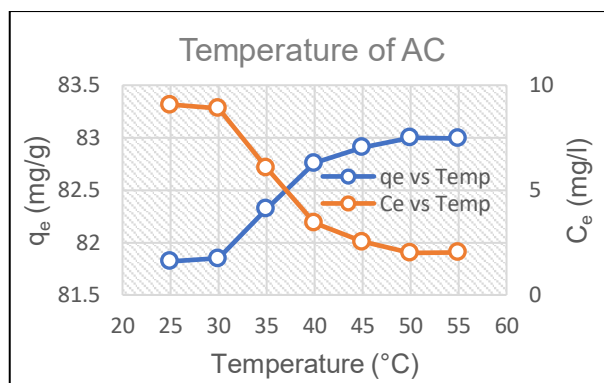


Figure 30 : Optimization Graph for Temperature of AC

iv. pH: The adsorption investigations encompassed a pH spectrum spanning 4 to 10, all the while maintaining the temperature at a constant 50°C. The initial solution concentration remained fixed at 500 ppm, with an unvarying contact time of 90 minutes and a dosage of 0.6g. The experimental protocol employed a shaker mechanism operating within a 100 mL volume at 135 rpm, the experimental details are presented in Table 19 and visually depicted in Figure 31.

Table 19 : pH results for AC (500ppm)

C_i (mg/l)	Abs (nm)	C_e (mg/l)	Removal %	q_e (mg/g)	pH
500	0.319	2.313	98.843	82.947	4
500	0.163	1.166	99.416	83.138	5
500	0.282 ±0.005	2.041	98.979	82.993	6
500	0.070	0.483	99.758	83.252	7
500	0.104	0.733	99.633	83.211	8
500	0.041	0.269	99.865	83.288	9
500	0.066	0.453	99.773	83.257	10

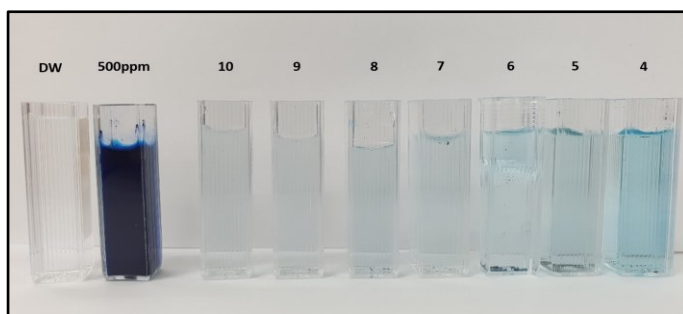


Figure 31 : pH Results for AC (500ppm)

The meticulous analysis of pH's influence on the adsorption process (pH values: 4, 5, 6, 7, 8, 9, 10) was undertaken while diligently preserving consistency in dosage, contact time, temperature, and initial concentration (0.6g, 90 minutes, 50°C, 500 ppm). Significantly, pH 9 emerged as the optimal condition, aligning with precedent findings (P. S. Kumar et al., 2011). At this pH level, the terminal MB concentration precipitously diminished to 0.269 ppm, attaining an exceptional 99.865% removal efficiency and an adsorption capacity of 83.288 mg/g. These findings underscore the role of electrostatic interactions, as pH impacts the surface charge of the AC, influencing its affinity for MB. Kumar et al., (2011) explored the pH range of 2-10 and identified the optimal pH as 9 and 10, with the adsorption capacity rising from 7.72-24.51 mg/g. Furthermore, Thabede et al., (2020) scrutinized pH levels within the (1-9) range, producing surface deprotonation at pH 9, corresponding to maximal adsorption capacity for both lead ions (Pb^{2+}) and the MB dye. Figure 32 vividly encapsulates the dynamic interplay of C_e (equilibrium concentration) and q_e (adsorption capacity) throughout pH variations.

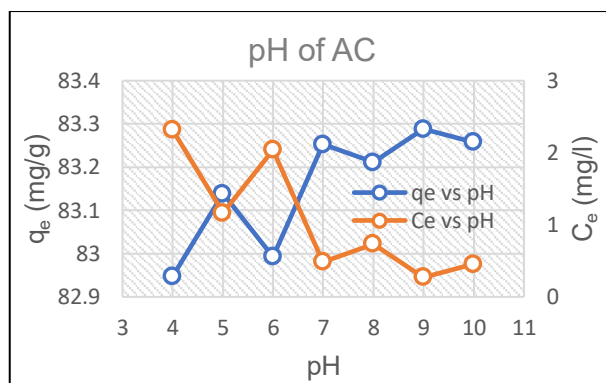


Figure 32 : Optimization Graph for pH of AC

v. Adsorbent Dosage: Adsorption experiments were performed with various adsorbent dosages ranging from 0.4 to 0.65 g under the pH of 9 and temperature at 50°C respectively whereas the initial concentration of the solution was at level 500 ppm and contact time for time 90-minute, using a shaker at an agitation speed of 135 rpm, and volume 100 mL. Furthermore, an overview of the experiment details is included in Table 20 with a pictorial representation shown as Figure 33.

Table 20 : Dosage results for AC (500ppm)

C_i (mg/l)	Abs (nm)	C_e (mg/l)	Removal %	q_e (mg/g)	Dosage (g)
500	0.323	2.343	99.5314	124.414	0.4
500	0.221	1.593	99.6814	110.757	0.45
500	0.178	1.277	99.7446	99.744	0.5
500	0.065	0.446	99.9108	90.827	0.55
500	0.041±0.002	0.269	99.9462	83.288	0.6
500	0.002	0.00	100	76.923	0.65

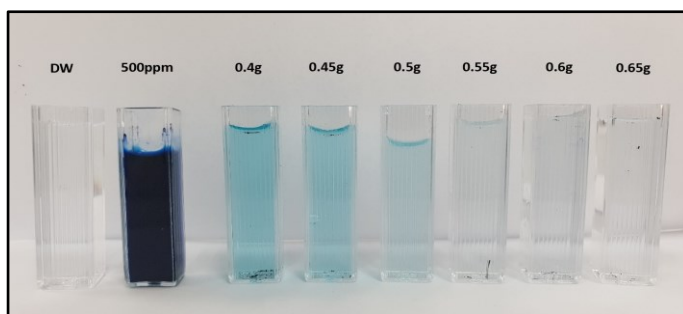


Figure 33 : Dosage Results for AC (500ppm)

Through meticulous manipulation of the adsorbent dosage (0.4, 0.45, 0.5, 0.55, 0.6, 0.65 g), while upholding pH 9, a temperature of 50°C, contact time of 90 minutes, and an initial concentration of 500 ppm, an optimal dosage of 0.55 g emerged, harmonizing with the stipulations of WHO drinking water guidelines. At this dosage, MB's ultimate concentration experienced a marked reduction to 0.446 ppm, culminating in a remarkable elimination efficiency of 99.91% and an adsorption capacity of 90.827 mg/g. These findings underscore the efficiency and economic viability of the designated dosage for proficient MB elimination, rendering it amenable to diverse industrial applications. In their exploration of dosage variations (0.4-0.6 g) in 50 mL, Sharma & Uma (2010) observed that escalating the adsorbent dose from 0.40 to 0.60 g led to an escalation in MB removal from 86.75% to 99.83%. Enhanced adsorbent quantities were anticipated to yield more pronounced MB removal. Figure 34 graphically elucidates alterations in C_e and q_e throughout the dosage adjustments.

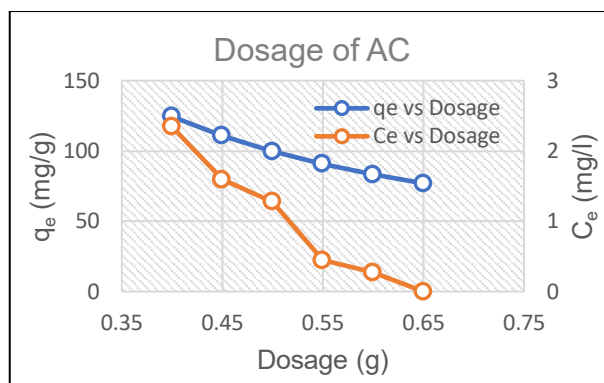


Figure 34 : Optimization Graph for Dosage of AC

The optimization study has yielded highly positive outcomes, providing strong evidence of the efficacy and economic viability of AC derived from EFB for the adsorption of MB. Through meticulous parameter adjustments, including a dosage of 0.55g, optimal contact time of 90 minutes, initial concentration of 500ppm, the temperature of 50°C, and pH of 9, this study has successfully achieved the optimal conditions for efficient adsorption. Significantly, the resulting adsorption capacity of (8 Pt-Co), equivalent to (8 UTC), falls well below the maximum value of 15 UTC as stipulated by WHO standards for drinking water. Table 21 illustrates the optimized dosage according to WHO.

Table 21 : Optimization of MB adsorption using AC vs. WHO standard

Dosage (g)	Abs (nm)	C _e (mg/l)	Color (Pt-Co)	WHO standard
0.4	0.323	2.343	30	15 UTC
0.45	0.221	1.593	21	
0.5	0.178	1.277	17	
0.55	0.065	0.446	8	
0.6	0.041	0.269	3	
0.65	0.002	0.00	0	

The results of this investigation significantly contribute to the advancement of knowledge in the field, particularly regarding the use of AC derived from EFB for MB adsorption. Moreover, these findings hold great promise for developing efficient wastewater treatment methods, further emphasizing the rest of this research's importance and practical implications.

4.4.2 Adsorption isotherms

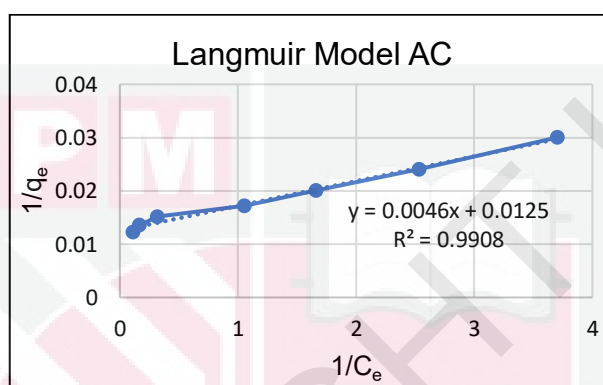
The adsorption isotherm models were applied to analyze the adsorption of MB onto the AC. Four commonly used models, namely Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich, were employed to assess the equilibrium behavior of the adsorption process.

i. Langmuir model:

The Langmuir model postulates monolayer adsorption on a homogenous surface, where adsorption transpires at distinct sites sans intermolecular interaction. The elevated R-squared value of 0.9908 underscores a robust correlation between the Langmuir model and empirical data. This infers that MB's adsorption onto the AC surface ensues via a monolayer adsorption mechanism. The Langmuir model's commendable congruence, showcasing a $q_{\max}$ of 80, intercept of 0.0125, slope of 0.0046, and K_L (Langmuir constant) of 0.368, suggests the constraint of specific adsorption sites on the AC surface dictating the adsorption capacity, as depicted in Table 22 and graphically in Figure 35.

Table 22 : Langmuir isotherm results for AC

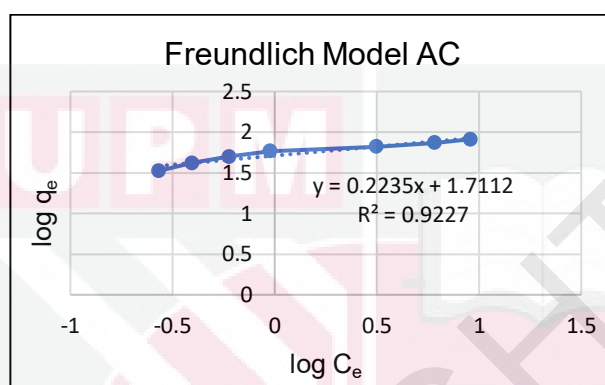
C_i	C_e	$1/C_e$	$\log C_e$	$\ln C_e$	q_e	$1/q_e$	$\log q_e$
200	0.269	3.705	-0.568	-1.309	33.288	0.030	1.522
250	0.394	2.532	-0.403	-0.929	41.600	0.024	1.619
300	0.600	1.664	-0.221	-0.509	49.899	0.020	1.698
350	0.946	1.056	-0.023	-0.055	58.175	0.017	1.764
400	3.152	0.317	0.498	1.148	66.141	0.015	1.820
450	6.078	0.164	0.783	1.804	73.986	0.013	1.869
500	9.078	0.110	0.958	2.205	81.820	0.012	1.912

**Figure 35 : Langmuir Isotherm Results Graph for AC****ii. Freundlich model:**

The widely employed Freundlich model encompasses adsorption on heterogeneous surfaces, assuming multilayer adsorption. It accounts for adsorbate-adsorbent interactions, incorporating both specific and non-specific bonding. Empirical data from this investigation demonstrates a reasonably apt adherence to the Freundlich model, as indicated by the R-squared value of 0.9227. This implies that MB's adsorption onto the AC surface is governed by a blend of specific and non-specific interactions, signifying heterogeneous site presence. The Freundlich constant (K_F) is computed as 51.42804, with an intercept of 1.7112 and slope 0.2235 reinforcing the model's relevance in characterizing adsorption behavior, outlined in Table 23 and visibly in Figure 36.

Table 23 : Freundlich isotherm results for AC

C_i	C_e	$1/C_e$	$\log C_e$	$\ln C_e$	q_e	$1/q_e$	$\log q_e$
200	0.269	3.705	-0.568	-1.309	33.288	0.030	1.522
250	0.394	2.532	-0.403	-0.929	41.600	0.024	1.619
300	0.600	1.664	-0.221	-0.509	49.899	0.020	1.698
350	0.946	1.056	-0.023	-0.055	58.175	0.017	1.764
400	3.152	0.317	0.498	1.148	66.141	0.015	1.820
450	6.078	0.164	0.783	1.804	73.986	0.013	1.869
500	9.078	0.110	0.958	2.205	81.820	0.012	1.912

**Figure 36 : Freundlich Isotherm Results Graph for AC****iii. Temkin model:**

The Temkin model, accounting for adsorbate-adsorbent interactions and uniform heat of adsorption distribution, incorporates coverage-related capacity diminishment due to such interactions. The commendable R-squared value of 0.9679, intercept of 53.663, and slope of 12.43 obtained for the Temkin model underscores its remarkable congruence with the empirical data. This implies the substantial contributions of both adsorbate-adsorbent interactions and adsorption heat in the adsorption mechanism. The observed capacity decrease, concurrent with increasing coverage, concurs with the assumptions intrinsic to the Temkin model. Moreover, derived constants B_T and K_T quantified as 12.43 and 74.97963 respectively, provide further substantiation of the model's aptness in delineating adsorption dynamics, as depicted in

Table 24, and visually in Figure 37.

Table 24 : Temkin isotherm results for AC

C_i	C_e	$1/C_e$	$\log C_e$	$\ln C_e$	q_e	$1/q_e$	$\log q_e$
200	0.269	3.705	-0.568	-1.309	33.288	0.030	1.522
250	0.394	2.532	-0.403	-0.929	41.600	0.024	1.619
300	0.600	1.664	-0.221	-0.509	49.899	0.020	1.698
350	0.946	1.056	-0.023	-0.055	58.175	0.017	1.764
400	3.152	0.317	0.498	1.148	66.141	0.015	1.820
450	6.078	0.164	0.783	1.804	73.986	0.013	1.869
500	9.078	0.110	0.958	2.205	81.820	0.012	1.912

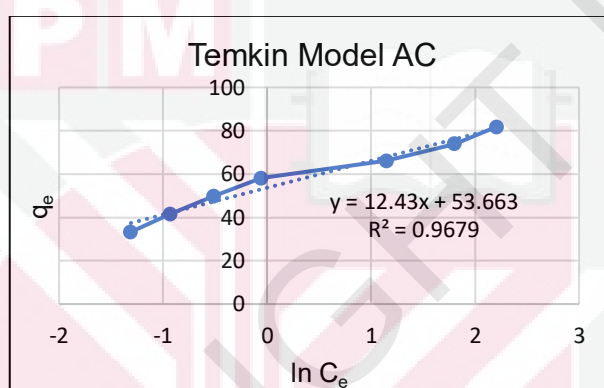


Figure 37 : Temkin Isotherm Results Graph for AC

iv. Dubinin-Radushkevich model:

The Dubinin-Radushkevich model is founded on the premise of heterogeneous surface-associated physical adsorption. It factors in the potential energy of the adsorbate and assumes diffusion-mediated adsorption into micropores. The observed R-squared value of 0.9579, intercept of 4.2895, slope of $-6.00E-08$, and adsorption capacity q_m of 72.929 mg/g for the Dubinin-Radushkevich model substantiates its satisfactory alignment with the empirical data, as displayed in Table 25 and graphically in Figure 38. This underscores the implication of physical interactions in the adsorption of MB on the AC surface, primarily taking place within micropores with energy of 16666666.67

KJ/mol.

Table 25 : Dubinin-Radushkevich isotherm results for AC

$\ln(q_e)$	$1/C_e$	$1+1/C_e$	$\ln(1+1/C_e)$	e	e^2	β^2	β
3.505	3.705	4.705	1.548	3837.212	14724196	3.60E-15	6.00E-08
3.728	2.532	3.532	1.262	3126.772	9776705		
3.910	1.664	2.664	0.980	2428.179	5896053		
4.063	1.056	2.056	0.721	1786.609	3191973		
4.191	0.317	1.317	0.275	682.663	466029.3		
4.303	0.164	1.164	0.152	377.334	142381		
4.404	0.110	1.110	0.104	258.890	67024.16		

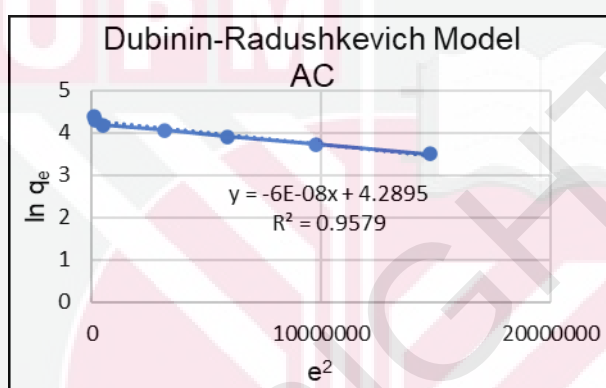


Figure 38 : Dubinin-Radushkevich Isotherm Results Graph for AC

This study analyzed adsorption isotherm utilizing four models: Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich. The determination coefficient (R squared) values obtained for each model were as follows: Langmuir (0.9908), Freundlich (0.9227), Temkin (0.9779), and Dubinin-Radushkevich (0.9579). the Langmuir model exhibited the best fit (R squared = 0.9908) for the adsorption of MB on AC derived from EFB consistent with previous studies (Baloo et al., 2021; I. Ibrahim et al., 2021; Wirasnita et al., 2014). This suggests that the adsorption process follows monolayer adsorption on a homogeneous surface with no interaction between adsorbed molecules. The Langmuir model's high R squared value and the calculated parameters ($q_{\max} = 80$, $K_L =$

0.368) support its effectiveness in describing the adsorption behavior.

4.4.3 Adsorption kinetics

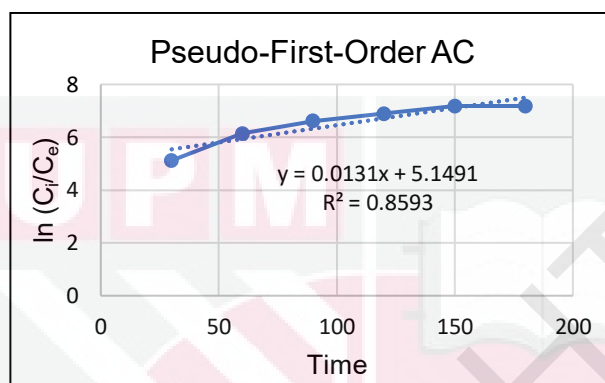
Kinetic adsorption refers to the study of the rate at which adsorption occurs and the mechanism behind it. In the case of MB adsorption using AC, two popularly utilized kinetic models are the pseudo-first-order (PFO) and pseudo-second-order models. The pseudo-first-order (PSO) model assumes that the adsorption rate is directly proportional to the variance between the initial and equilibrium concentrations. It provides information about the initial adsorption rate and predicts the adsorption capacity. On the other hand, PSO suggests that the interaction between the adsorbate and adsorbent surface controls the adsorption rate.

i. Pseudo-first-order model (PFO):

The pseudo-first-order (PFO) model postulates proportionality between the adsorption rate and the disparity between equilibrium and instantaneous adsorbate concentrations with intercept of 5.1491, slope of 0.0131, and adsorption capacity of 172.2764 mg/g. It signifies adherence to first-order kinetics, entailing an exponential decrease in the adsorption rate over time. The attained R^2 value of 0.8593 validates a satisfactory fit for the pseudo-first-order model, yet the computed rate constant (K_1) $7.28E-05$ is notably modest, as presented in Table 26 and visibly in Figure 39.

Table 26 : Pseudo-first-order kinetics for AC

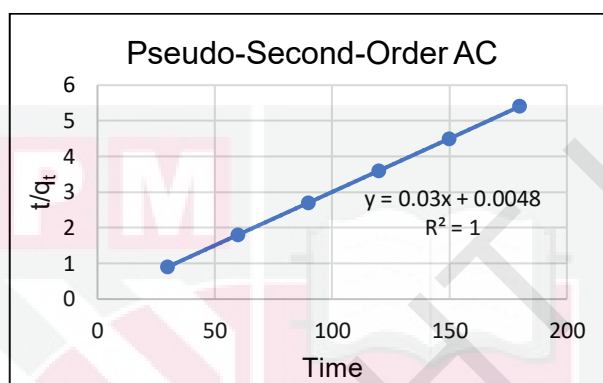
C_i	C_t	q_t	$\ln (C_i/C_t)$	Time
200	1.196	33.133	5.119335	30
200	0.431	33.261	6.139965	60
200	0.269	33.288	6.611361	90
200	0.203	33.299	6.892867	120
200	0.152	33.307	7.182192	150
200	0.152	33.307	7.182192	180

**Figure 39 : Pseudo-First-Order Kinetics Graph for AC****ii. Pseudo-second-order model (PSO):**

The pseudo-second-order (PSO) model posits that the adsorption rate is directly proportionate to the square of the adsorbate concentration adhered to the adsorbent surface. This framework implies second-order kinetics and entails chemisorption or robust interactions between adsorbate and adsorbent. The PSO model is exceptionally fitting ($R^2 = 1$), corroborating its precision in characterizing the adsorption process. The computed rate constant (K_2) of 0.1875 signifies a comparatively elevated adsorption rate with adsorption capacity of 33.333 mg/g, intercept of 0.0048 and slope of 0.03, as detailed in Table 27 and visually in Figure 40.

Table 27 : Pseudo-second-order kinetics for AC

C_i	C_e	q_t	Time	t/q_t
200	1.196	33.133	30	0.905442
200	0.431	33.261	60	1.803914
200	0.269	33.288	90	2.703677
200	0.203	33.299	120	3.603712
200	0.152	33.307	150	4.503558
200	0.152	33.307	180	5.404269

**Figure 40 : Pseudo-Second-Order Kinetics Graph for AC**

In the adsorption kinetics study, two models, namely the pseudo-first-order and pseudo-second-order models, were employed to analyze the adsorption of MB on AC derived from EFB. The results obtained for the R squared values and rate constants are pseudo-first-order (R squared = 0.8593, $K_1 = 7.28E-05$) and pseudo-second-order (R squared = 1, $K_2 = 0.1875$).

Based on these findings, the pseudo-second-order model is preferred over the pseudo-first-order model. The pseudo-second-order model demonstrates a perfect fit (R squared = 1) and suggests a chemisorption mechanism, which aligns with the strong interaction between MB and the AC surface consistent with previous studies (Baloo et al., 2021; I. Ibrahim et al., 2021; Wirasnita et al., 2014). This model provides a more comprehensive understanding of the

adsorption kinetics and can be considered for further investigations and practical applications.

4.4.4 Thermodynamic study of adsorption

Thermodynamic investigations offer profound insights into the energetics and feasibility of adsorption processes. This study explored the impact of temperature variation (25-55°C) on MB adsorption utilizing AC. ΔG (Gibbs free energy), ΔH (enthalpy), and ΔS (entropy) were computed to evaluate the spontaneity, heat of adsorption, and randomness of the process. By optimizing adsorption across diverse temperatures, a comprehensive understanding of thermodynamic behavior was gained, enhancing insights into MB-activated carbon interactions. The acquired thermodynamic data, presented in Table 28 and graphically in Figure 41, hold the potential for refining the adsorption process design, offering substantial contributions to the field's advancement with R^2 of 0.9413, intercept of 21.838, and slope of -5884.9.

Table 28 : Thermodynamic results for AC

Temp	T	K_L	$\ln K_L$	Temp	ΔH° (KJ/mol)	ΔS° (KJ/mol)	ΔG° (KJ/mol)
25	298	9.012998	2.198668	25	48.92706	181.5611	-5.44736
30	303	9.187114	2.217802	30			-5.58696
35	308	13.55971	2.607103	35			-6.67604
40	313	24.07213	3.181055	40			-8.278
45	318	32.62849	3.485186	45			-9.21432
50	323	41.39601	3.723184	50			-9.99832
55	328	40.66291	3.705316	55			-10.1044

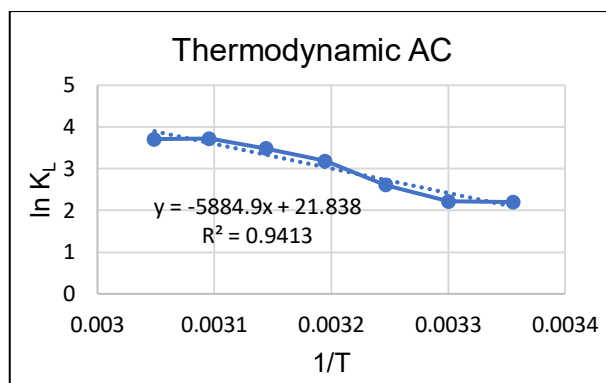


Figure 41 : Thermodynamic Results Graph for AC

The thermodynamic analysis conducted in this study aimed to investigate the effect of temperature on the adsorption process of MB using AC derived from EFB. The temperatures examined ranged from 25°C to 55°C, and the initial concentration of MB was maintained at 500 ppm.

The positive value of ΔH° indicates that the adsorption process is endothermic, requiring an input of energy. This suggests that the adsorption of MB onto the AC is favoured at higher temperatures, where the increased thermal energy promotes the adsorption process.

A positive sign for ΔS° indicates that randomness or disorder of the system increases upon adsorption. It can be ascribed to the breaking of solute-solvent interactions and the formation of new adsorbate-adsorbent interplay. The positive ΔS° value indicates the entropy of disorder increased, which makes it consistent with this adsorption process accompanied by a calm state.

The thermodynamic analysis indicated that the process is spontaneous and favorable, which confirms earlier studies on the adsorption of MB over AC

(Egbosiuba et al., 2020; Ghasemi & Asadpour, 2007; Üner et al., 2016). Besides, the negative values of ΔG° at all temperatures demonstrate that adsorption is a reasonable process and with increasing temperature generally works in favor of higher loads or concentrations. The positive values of ΔH° and ΔS° indicate that the adsorption is a feasible endothermic process governed by entropy, which is in agreement with earlier reports (Egbosiuba et al., 2020; Sharma & Uma, 2010).

4.4.5 Regeneration and reusability of activated carbon

In this research, two types of regeneration methods were used for the restoration of AC for MB adsorption. The first method involved washing spent adsorbents with DW and drying for 3 hours at 135°C (R.F). The second method comprised stirring spent adsorbents in a 250 ml solution at 80°C for 3 hours (R.S), followed by oven drying at 100°C for 3 hours. These techniques effectively rejuvenated the adsorbents for subsequent experiments. Regenerated adsorbents were then employed in another adsorption study under identical optimization conditions (0.55g, 50°C, 500 ppm, 90-minute, and pH of 9), as depicted in Table 29 and Figure 42. This approach yielded insights into the efficacy of regeneration methods in restoring adsorption capacity.

Table 29 : Regeneration and reusability of AC

Sample	C_i (mg/l)	Abs (nm)	C_e (mg/l)	q_t (mg/g)	Removal %	Cycle
R.F	500	0.13	0.924	90.741	99.815	1
R.S	500	0.59	4.306	90.126	99.138	
R.F	500	0.471	3.431	90.285	99.313	2
R.F	500	0.605	4.416	90.106	99.116	3
R.F	500	2.441	23.199	86.690	95.360	4

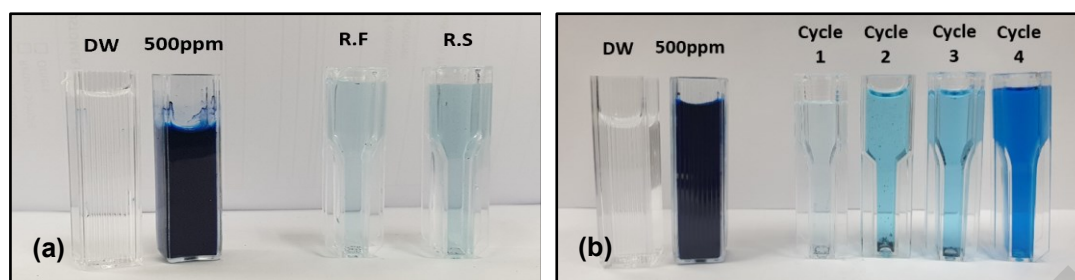


Figure 42 : Regeneration and Reusability of AC: (a) Cycle 1 Results, (b) Cycle 1-4

The regeneration and reusability of adsorbents are crucial for their practical application. This study tested two regeneration methods: furnace treatment (R.F) and stirring in a solution (R.S). The adsorbent was then reused under optimized conditions.

At the first cycle, R.F. showed an ultimate MB concentration of 0.924 ppm, an adsorption capacity of 90.741 mg/g, and an elimination efficiency of 99.815%. R.S had slightly higher values: ultimate concentration of 4.306 ppm, adsorption capacity of 90.126 mg/g, and elimination efficiency of 99.138%. Both methods were effective, but R.F. was more efficient.

However, efficiency gradually decreased in subsequent cycles. In the second cycle, R.F. had a final concentration of 3.431 ppm, an adsorption capacity of 90.285 mg/g, and an elimination efficiency of 99.313%. By the fourth cycle, the ultimate MB concentration increased to 23.199 ppm, with an adsorption capacity of 86.690 mg/g and an elimination efficiency of 95.360%. This decrease is due to accumulated impurities and changes in the adsorbent's structure.

R.F. was superior because the high temperature of the furnace treatment facilitated the desorption and removal of impurities. The decline in cycle efficiency is attributed to pore blockage and changes in the adsorbent's surface consistent with previous studies (W. H. Li et al., 2011; Shende & Mahajani, 2002). Shende & Mahajani, (2002) used heating (150-200°C) and lasted 4 cycles, while W. H. Li et al., (2011) used 300°C and lasted for 3 cycles, the ability of adsorption decreased significantly (95-85%).

In summary, furnace treatment (R.F) effectively regenerated the adsorbent, but efficiency decreased with cycles due to impurities and structural changes. These findings emphasize the importance of regeneration strategies and consider limitations when utilizing AC for MB elimination.

4.4.5.1 FTIR and BET analysis before and after adsorption

FTIR and BET analyses were used to examine the changes in surface chemistry and porosity of the AC following MB adsorption, revealing key factors in its adsorption efficiency.

- i. **BET analysis:** The BET analysis was used to compare the surface area of the AC product before and following the MB adsorption procedure, as shown in Table 30.

Table 30 : BET analysis of AC before and after adsorption

Activated carbon	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (Å)
Before Adsorption	939.63	0.65	13.90
After Adsorption	778.823	0.503	12.921
After 4 Cycle	741.267	0.471	12.283

Before adsorption, the AC had an initial surface area of 939.63 m²/g, a pore volume of 0.65 cm³/g, and a pore size of 13.90 Å, representing its initial properties.

The AC surface area after MB adsorption, regeneration, and reuse was 778.823 m²/g. During this process, the pore volume decreased to 0.503 cm³/g and the pore size was reduced to 12.921 Å.

The specific surface area was estimated to be 741.267 m²/g with a pore volume of 0.471 cm³/g and an average pore size of 12.283 Å for the AC after cycle four adsorption. Several reasons can be provided for the loss of surface area, pore volume, and smaller pores after the regeneration process and reusability cycle-4 adsorption employing them as a sorbent material. The adsorption of MB produced a reduction in the surface area and pore volume due to the dye molecules occupying active sites on ACs surfaces accessible as well as porosity, but Fagbohun et al., (2022) obtained low specific surface areas for heat-regenerated activated carbons prepared.

In addition, the reconstruction process that included some cases as temperature treatment may lead to the reshaping of pore structure on a nano-scale during reactivation. This might lead to some pore closure or partial blockage, causing a reduction in pore size corroborating the findings of earlier research conducted by Hwang et al., (2020), they noted that it is possible for surface area and regenerated spent activated carbon (SAC) via a thermal process can be recovered only about 60%, indicating part of the surface was

lost during regeneration.

Furthermore, both the expected and explained modifications in surface area, pore volume, and pore size take place during regeneration and reuse whilst around cycle four adsorption is observed. During the regeneration step, adsorbed species are presumably desorbed from AC and this might be cause for additional structural alterations.

ii. **FTIR analysis:** The FTIR analysis is also useful for examining the adsorption interaction between MB molecules and AC surface, by a device (SPECTRUM 100 PERKIN ELMER) at a spectrum range of 650-4000 cm^{-1} as depicted in Figure 43.

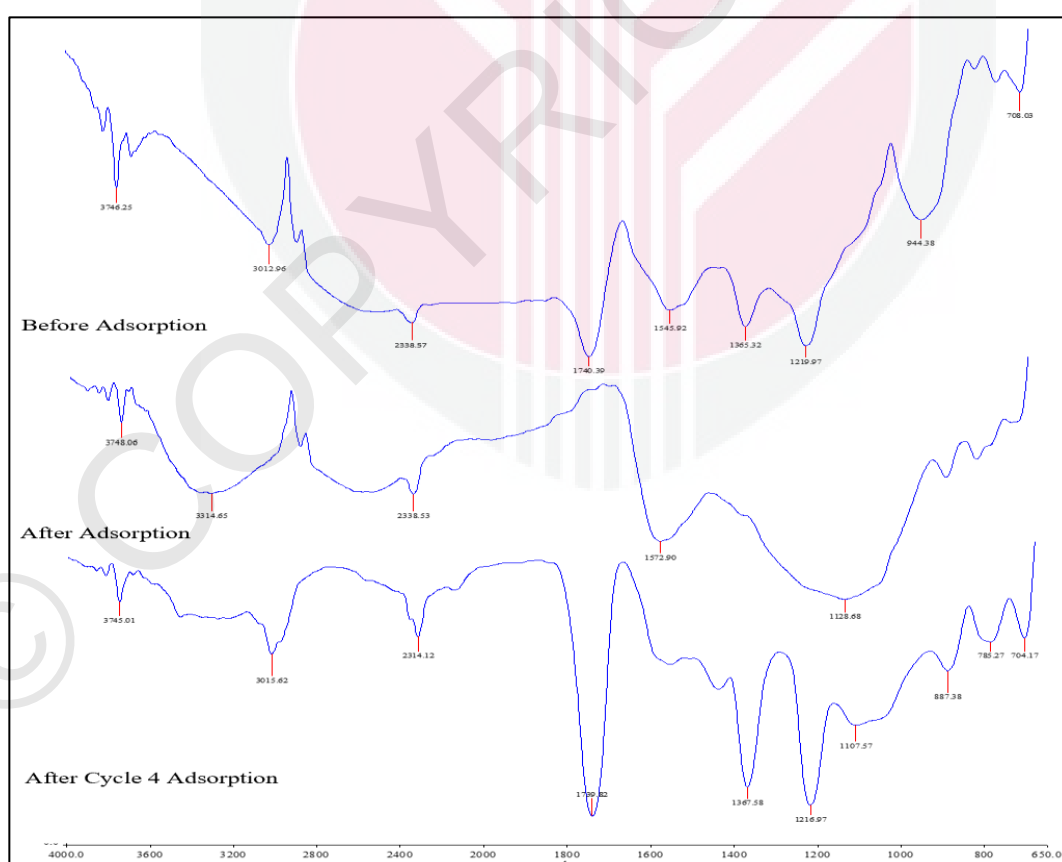


Figure 43 : FTIR of AC (6M $(\text{NH}_4)_2\text{SO}_4$) Before and After Adsorption

The initial adsorption procedure began with the FTIR measurement of the AC surface which showed 9 different distinct peaks around 3746.25, 3012.96, 2338.57, 1740.39, 1545.92, 1365.32, 1216.97, 944.38, and 708.03 cm^{-1} . These peaks are well related to functional groups present on the AC surface of hydroxyl ($-\text{OH}$), carbonyl ($\text{C}=\text{O}$), and vibrations of aromatic rings (Gore et al., 2020). These functional groups play an important role in MB adsorption because of their propensity for interacting with MB molecules.

Following the adsorption procedure, the FTIR analysis revealed modifications to peak locations and intensities relative to the original spectrum. New peaks at 3314.65, 2338.53, 1572.90, and 1128.68 cm^{-1} emerged, indicating that new functional groups were formed or existing ones altered in response to MB adsorption. The FTIR peak changes suggest that there are meaningful chemical processes or adsorption. The reasons were various interactions like electrostatic attractions, hydrogen bonding, and π - π interaction facilitation by the AC surface for adsorption of dyestuffs onto it. After regenerating and reusing the adsorbent, the measured FTIR analysis of the frequency spectrum obtained was similar to that of the first spectrum after the adsorption process. The peaks at 3015.62 cm^{-1} , 2314.12 cm^{-1} , 1739.82 cm^{-1} , 1367.58 cm^{-1} , 1216.97 cm^{-1} , 1107.57 cm^{-1} , 887.38 cm^{-1} , 785.27 cm^{-1} , and 704.17 cm^{-1} indicate that the functional groups were restored to or preserved on the surface during the regeneration of AC. This suggests that thermal treatment in the furnace was used as part of the regeneration process. The original functional groups on the surface of the adsorbent were maintained, and it could continue to be used for MB adsorption, as was previously reported by (Ali et al., 2020;

Cuhadaroglu & Uygun, 2008).

The data provided in this study are vital evidence of how MB adsorption on AC reacts. The differences in the FTIR spectra's appearance before and after the adsorption process, as well as after regeneration, as well as the apparent possibility of reuses of adsorbent, engender the manner that some functional groups on the AC surface interact with the MB material during the adsorption. Moreover, the good retention of a few functional groups after the regeneration procedure demonstrates the efficacy of the applied regeneration method.

4.4.6 Comparative study with commercial activated carbon

This work aimed to investigate and compare the performances of modified MB adsorbent with commercial activated carbon (CAC) for extracting MB from an aqueous solution. Some parameters were analyzed in this comparison, removal efficiency, adsorption capacity, BET (Brunauer-Emmett-Teller) surface area analysis, and FTIR Fourier Transform Infrared spectroscopy. The useful information on the adapted adsorbents for comparison to CAC adsorbent was obtained as comparative results of this study. These observations help to further elucidate their removal capabilities for MB and may contribute to the design of more practical and eco-friendly adsorption technologies.

- i. **Comparison of BET analysis:** Results of the conducted BET analysis (MICROMERITICS 3FLEX) on the surface, pore volume, and size for AC with CAC are shown in Table 31. The porosity features of the biochars indicated in this study helped to understand different

adsorption potentials and potential utilizations for MB removal.

Table 31 : BET comparison of AC vs. CAC

Adsorbent	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (Å)
AC	939.63	0.65	13.90
CAC	1000	1	15

The pore size of an adsorbent is a significant criterion that has a great influence on the selectivity and capacity of different species. The pore sizes of the AC and CAC are 13.90 Å, and 15 Å consecutively.

The adsorption behavior of the AC with only 939.63 m²/g, as shown from this study was superior to that of CAC at a higher surface area value (1000 m²/g). This implies pore volume; pore size and unique properties of AC contribute to a better MB uptake compared with CAC in addition to the optimized conditions and functional groups.

- ii. **Comparison of FTIR analysis:** A comparison of FTIR spectra (Figure 44) for vitreous AC and CAC in the range from 650–4000 cm⁻¹ was employed throughout a spectrum region by using SPECTRUM 100 PERKIN ELMER slew turning point investigations. Reflected through the parallel spectrum variations, these dynamics reveal large-scale modifications in chemical structure and surface activity on configurations leading to crucial information concerning their MB adsorption potential.



Figure 44 : FTIR Spectra Comparison: AC vs. CAC

The FTIR spectrum of AC, peaks at 3746.25 cm^{-1} , 3012.96 cm^{-1} , 2338.57 cm^{-1} and 1740.39 cm^{-1} showed the existence of functional groups such as hydroxyl (-OH) and carbonyl (C=O) aromatic compounds. The groups are highly adsorbent and can interact with organic pollutants, such as MB (Gore et al., 2020). The distinctive peak pattern of AC indicates the high adsorption capacity for wastewater treatment applications (Ali et al., 2020; Cuhadaroglu & Uygun, 2008).

Figure 44 shows the difference in peak positions and intensities from AC FTIR spectra concerning CAC, showing a comparison of both. The CAC shows numerous relationships with lower wavenumbers such as 1557.17 cm^{-1} which correspond to many different kinds of functional groups in the precursor materials (Kristianto et al., 2016). These variations underscore the different

compositions of AC, in terms of chemicals and their varying adsorptive property thus qualifying it as a better sorbent.

Developing these novel adsorbents, AC and BABC, has various benefits. For starters, their characteristic peak patterns in FTIR analysis show the existence of functional groups that are ideal for adsorption operations. This shows that the adsorption capacity and efficiency are higher than those of CAC.

In summary, FTIR analysis indicates that AC is formed whose structural units possess potential functional groups for adsorption processes. The adsorption capacity of AC was much higher and more energy-efficient compared to CAC in the removal of MB. These strides in adsorbent preparation reflect hope for wastewater treatment and environmental applications by augmenting the effectiveness combined with cost-competence.

- iii. **Comparison of Adsorption Efficiency and Effectiveness:** In comparing AC and CAC, optimized AC (90 min, 500 ppm, 50C, pH 9, 0.55 g) consistently outperforms CAC regarding adsorption efficiency and effectiveness. AC achieves significantly lower final concentrations of the MB dye, indicating a higher adsorption capacity than CAC. Furthermore, AC demonstrates higher removal percentages, showing its ability to effectively remove the dye from the solution within the specified time intervals as shown in Tables 32, 33 and Figures 45, 46.

Table 32 : Optimized AC for MB removal (500ppm)

C_i (mg/l)	Abs (nm)	C_e (mg/l)	q_t (mg/g)	Removal %	Time (min)
500	0.321	2.328	90.485	99.534	30
500	0.137	0.975	90.731	99.804	60
500	0.062	0.424	90.831	99.915	90
500	0.036	0.233	90.866	99.953	120
500	0.022	0.130	90.885	99.973	150
500	0.022	0.130	90.885	99.973	180

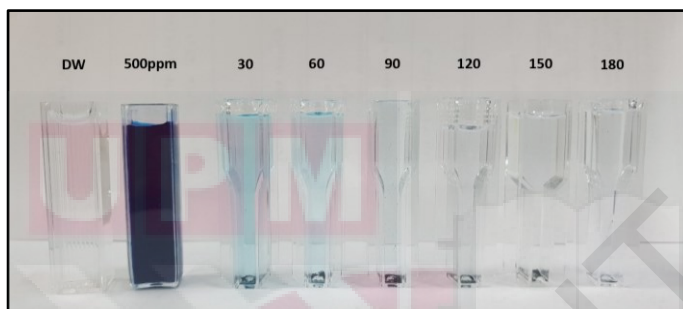


Figure 45 : Optimized AC Results for 500ppm

Table 33 : CAC vs. AC for MB removal (500ppm)

C_i (mg/l)	Abs (nm)	C_e (mg/l)	q_t (mg/g)	Removal %	Time (min)
500	2.224	20.908	87.107	95.818	30
500	1.976	18.289	87.583	96.342	60
500	1.56	13.896	88.382	97.220	90
500	1.226	8.983	89.275	98.203	120
500	0.959	7.019	89.632	98.596	150
500	0.829	6.063	89.806	98.787	180

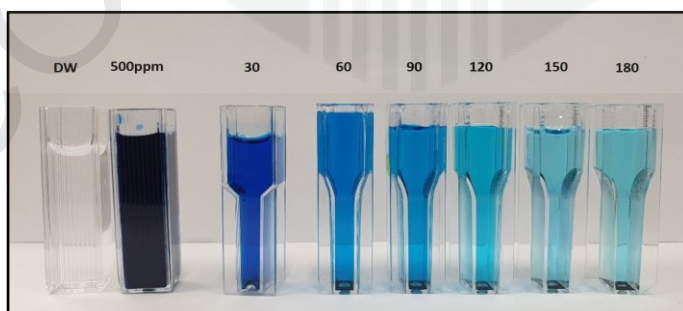


Figure 46 : CAC vs. AC Results for 500ppm

Several reasons contribute to AC outperforming the current CAC Although the specific surface area of AC was slightly lower than CAC (939.63 m²/g for AC Vs 1000 m²/g for CAC), it is because their functional groups make them more amenable to MB adsorption on different activation levels. AC may improve its adsorption properties by including functional groups (OH, C=O) and aromatic structures. These functional groups operate as the site of action for dye molecules to engage and bind, resulting in increased adsorption capacity and removal efficiency (Abdullah et al., 2023; Al Ashik et al., 2023; Ali et al., 2020; Cuhadaroglu & Uygun, 2008; Gore et al., 2020).

CHAPTER 5

RESULTS AND DISCUSSION OF BENTONITE CLAY

5.1 Introduction

The work related to BC has been conducted and the findings are highlighted in Chapter 5. It explains various steps in general for the adsorption-based process to remove color from methylene blue (MB) dye by using bentonite clay. BC were activated by alkali (NaOH) or mineral acid (H_2SO_4) to improve adsorption abilities. In the present study, we examine the potential utilize of this functionalized BC for the elimination of MB from aqueous solutions and the extent to which it is a cost-effective substitute for available commercial adsorbents.

5.2 Synthesis of bentonite clay

The present study aimed at an appropriate preparation of high-quality bentonite clay (BC) and its chemical activation using a controlled process with sulfuric acid (H_2SO_4) and sodium hydroxide NaOH for efficient removal of MB. The principal purpose was to increase the adsorption power of BC and also enable it to work effectively in the heavy concentration MB removal process.

Light absorbance at a specific wavelength was used to determine the MB content of samples as assessed by a UV-spectrophotometer (UV-1800 SHIMADZU). MB showed a characteristic peak at 663 nm, in alignment with earlier reported literature (Bhuyan et al., 2016; Khairnar & Shrivastava, 2019; Khosa et al., 2011). The calibration curve is prepared in the usual way by

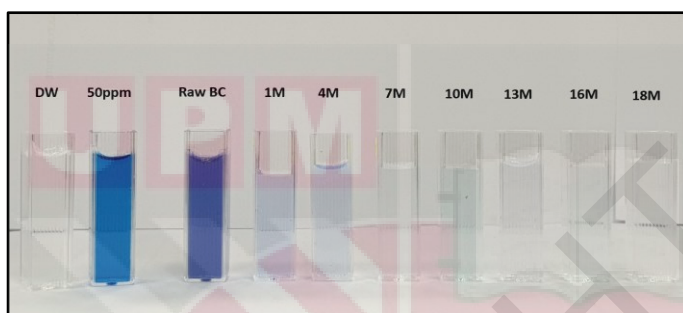
taking some known MB concentrations and plotting their absorbance readings at 663 nm against these quantities (details are mentioned in Appendix C) depicted in Figure 19. The plot of this process was performed for the calculation of the concentration of unknown samples. The variance in results among the samples studied ensures that the MB concentration levels of the investigated samples are analyzed accurately and reliably.

The study then activated BC using both acid (H_2SO_4) and base (NaOH). Various activation doses vis, 1M to 18M were utilized to examine the effect on MB adsorption capacity respectively. The adsorption experiments were conducted under specific conditions: shaker equipment at 135 rpm, adsorbent dosage of 0.8g, pH 7, initial MB concentration of 50 ppm, contact time of 24 hours, and a temperature of 25°C in a sample volume of 100 mL.

The results indicated that the optimal activation dosage for efficient MB elimination was 16M NaOH , as shown in Tables 34 and 35, and visually represented in Figures 47 and 48. For acid activation with H_2SO_4 , the removal percentage reached a peak of 99.783% at a 7M dosage. For base activation with NaOH , the removal percentage peaked at 99.842% with a 16M dosage. The greater elimination % with base activation indicates a more comprehensive and efficient adsorption process than acid activation.

Table 34 : H₂SO₄ activation results for BC (50ppm)

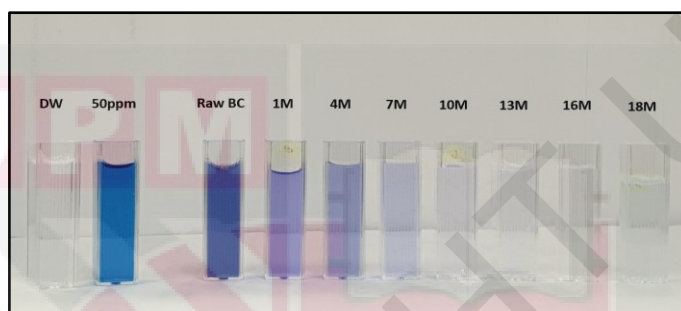
C _i (mg/l)	Abs (nm)	C _e (mg/l)	Removal %	Activation (H ₂ SO ₄)
50	2.639	47.380	5.238	0
50	0.096	0.674	98.651	1 M
50	0.06	0.409	99.180	4 M
50	0.019	0.108	99.783	7 M
50	0.127	0.902	98.195	10 M
50	0.027	0.166	99.666	13 M
50	0.061	0.416	99.166	16 M
50	0.02	0.115	99.769	18 M

**Figure 47 : H₂SO₄ Activation Results for BC (50ppm)**

In comparison to raw bentonite, acid-activated bentonite clay (AABC) performed better in terms of adsorption. Increasing the activation dosage lowered the ultimate MB concentration, suggesting improved adsorption efficiency. The maximal removal % obtained at 7M activation dose showed that AABC has a higher adsorption capacity.

Table 35 : NaOH activation results for BC (50ppm)

C_i (mg/l)	Abs (nm)	C_e (mg/l)	Removal %	Activation (NaOH)
50	2.639	47.380	0.052	0
50	0.188	1.350	97.298	1 M
50	0.191	1.372	97.254	4 M
50	0.075	0.519	98.960	7 M
50	0.029	0.181	99.636	10 M
50	0.018	0.100	99.798	13 M
50	0.015	0.078	99.842	16 M
50	0.032	0.203	99.592	18 M

**Figure 48 : NaOH Activation Results for BC (50ppm)**

The adsorption capacity of base-activated bentonite clay (BABC) was also higher than raw BC. As the activation dosage rose, the decrease in MB final concentration demonstrated enhanced adsorption capacity. The elimination % reached the maximum of 16M, which was the ideal dose for base activation.

This selection of 16M BABC was based on its greater adsorption capacity and efficiency when compared with different activation doses. The base activation process probably left more active groups on the surface of the BC and showed a higher adsorption load for MB molecules. A significant concern and the robust validation of experimental results as a complex set provide explanatory insight into why the chemical activation process seems demonstrably effective, enabling modified bentonite clay to become an economically viable alternative in MB elimination for adsorbents commercially.

Activating BC with H_2SO_4 and NaOH increased its adsorption capabilities for MB removal. The ideal doses of 7M for acid activation and 16M for base activation produced elimination efficiencies greater than 99.7%. This study reveals that BABC is a better and more cost-effective adsorbent for wastewater treatment applications.

5.3 Characterization of bentonite clay

The bentonite clay was characterized by the method of TGA (thermal stability), XRF (elemental composition), SEM (surface morphology) BET (surface area), and FTIR (functional group) which is confirmed by selected elemental composition with (crystallography studies) using XRD. These analyses were essential for the optimization of clay removal efficiency in MB.

5.3.1 Thermogravimetric analysis (TGA)

TGA of raw BC was carried out to determine its thermal stability and composition by employing a METTLER TOLEDO TGA/DSC3+ instrument. The content of TGA analysis is useful in understanding the sample weight during heating under controlled conditions. The temperature range (25–150°C) was chosen and the thermal behavior of the sample was more precise as given in Figure 49.

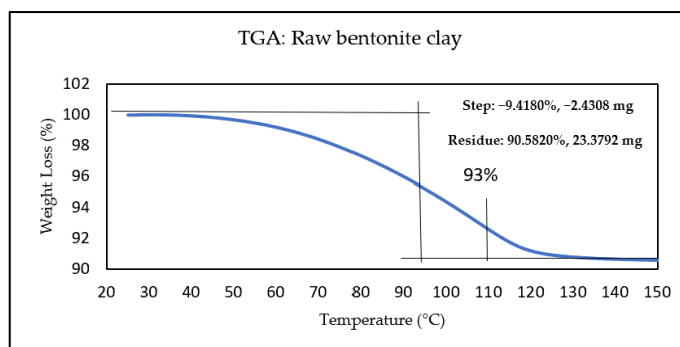


Figure 49 : TGA: Raw Bentonite Clay

TGA analysis was used to study the thermal behavior of raw bentonite clay at temperatures ranging from 0 to 150°C. The step sizes of -9.4180% and -2.4308mg allowed for exact weight loss tracking throughout the investigation. The initial stage exhibited a weight reduction of -9.4180%, suggesting the elimination of volatile components. A large residue (90.5820%; 23.3792 mg) indicated that the fundamental BC structure was stable over the time, the same results were observed by Elnaggar et al., (2022) and SARIKAYA, (2000). Noticeably, the BC demonstrated excellent stability at 110°C with a ~93% residue corresponding to key adsorption properties in line with earlier studies of approximately 93% by Elnaggar et al., (2022), and about 96% by SARIKAYA, (2000), and about 94.5% by (Hebbar et al., 2018). This method constantly kept fine control over temperatures to save precious clay layers like silica (SiO_2) and alumina (Al_2O_3) from damage which are considered responsible for the adsorption processes.

5.3.2 X-ray fluorescence (XRF)

XRF analysis was used to investigate raw bentonite clay and alkaline activated clay with a weight proportion of NaOH 16M, and Table 36 shows their

compositional alterations using (EDX-720 SHIMADZU). This knowledge is critical for assessing activated clay's effectiveness as an adsorbent for removing MB from aqueous solutions.

Table 36 : Chemical composition of raw BC and BABC (16M NaOH)

Compound	Raw BC	BABC (16M)
SiO ₂	52.39	47.353
Al ₂ O ₃	18.69	31.294
Na ₂ O	2.147	12.001
MgO	2.357	3.182
MnO	0.526	0.568
ZnO	0.080	0.095
K ₂ O	0.278	0.183
CaO	0.968	1.732
TiO ₂	1.291	1.471

The XRF analysis findings show considerable compositional differences between raw bentonite clay and BABC (16M NaOH). Upon activation, numerous components in the clay showed substantial changes. The SiO₂ concentration dropped from 52.39% in raw clay to 47.353% in activated clay. This reduction can be attributed to the dissolution of silica in the alkaline environment during activation. Conversely, the Al₂O₃ content increased from 18.69% in the raw clay to 31.294% in the activated clay. The higher Al₂O₃ percentage suggests enhanced adsorption properties since Al₂O₃ is recognized for its adsorptive capabilities.

Furthermore, the Na₂O content significantly increased from 2.147% in the raw clay to 12.001% in the activated clay. The presence of Na₂O facilitates ion exchange processes, which can positively influence the adsorption of cationic dyes such as MB. The stable MgO content at 3.182% indicates that

magnesium does not undergo significant changes during activation.

Additional elements like MnO, ZnO, K₂O, CaO, and TiO₂ were also present in both raw and activated clays. However, their concentrations remained relatively low compared to SiO₂, Al₂O₃, and Na₂O.

The chemical changes in BABC indicate that it may be suitable for MB adsorption. The greater Al₂O₃ percentage indicates better adsorption capabilities with SiO₂, whilst the higher Na₂O content improves ion exchange processes, both of which lead to effective dye removal. XRF analysis also gives a bit more knowledge on the chemical change during the activation process and further proves its application for water treatment as an efficient adsorption which is in good agreement with the performance of BABC (Elnaggar et al., 2022; Gandhi et al., 2022).

5.3.3 Scanning electron microscopy (SEM)

The surface morphology and microstructural properties of BC samples activated with H₂SO₄ (AABC) and NaOH (BABC), by a high Scanning Electron Microscopy S3400-N HITACHI were examined. The investigation has identified some notable differences between the two modes of activation.

Figure 50 (e-h) showed an expanded morphology with considerable particle join and homogeneity of BABC showed a fine and clear outline with improved particle connectivity and uniformity. Such improved structure is likely attributable to the specific binding of NaOH with a clay network that facilitates

reliable and uniform particle packings. In contrast, the acid-activated clay (AABC) showed a less ordered structure with an agglomeration of particles, as may be seen in Appendix B: Figure 1.

Studies of particle aggregation showed that BABC was more uniformly accumulated, suggesting better dispersion and higher availability to reactive sites. The enhanced dispersion is very important for adsorption operations as it results in more surface area available for MB molecules to interact eventually increasing the overall effectiveness of the process, in line with previous studies of activated clays (Gandhi et al., 2022; Kelechukwu & Akaranta, 2021).

The porosities of activated clays were observed by SEM examination to show the details of pore architectures. The base activation process produced more pervasive and regular pores enhancing the clay's adsorption potential in addition to its reactivity. These holes make it possible to pass molecules of MB through the density into itself and react with the chemical state of clay particles at a larger adsorption rate.

When SEM images were taken, the base activation method could provide a uniform size and morphology of particles, which showed effective control over the preparation process. This consistency is important to ensure predictable adsorption performance and thus reliability in real applications. The reduction of the homogeneity observed in BABC is due to positive activity by NaOH, which causes degradation and leaves some fresh active surfaces on it (Gandhi et al., 2022; Kelechukwu & Akaranta, 2021).

SEM characterization at different scales (200 μm , 50 μm , 10 μm , and 3 μm), revealed the better structural features of BABC over acid-activated clay, which indicates that the BABC had much better structural properties than AABC. It can be summarized that the detailed morphological features were the successful base activation process on bentonite clay, in improving adsorption capabilities to remove MB.

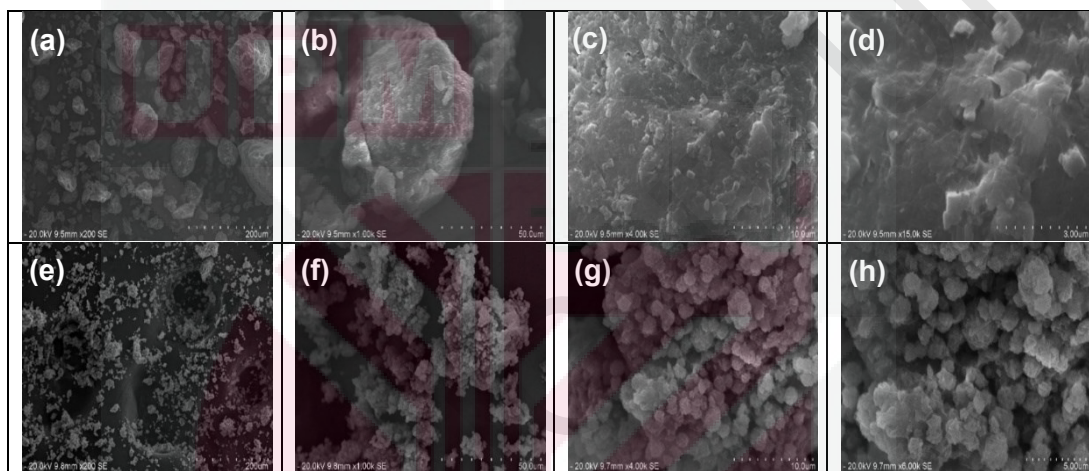


Figure 50 : Images of BC Morphology: (a-d) Raw BC, (e-h) 16M BABC

5.3.4 Brunauer-emmett-teller (BET)

BET analysis was conducted on raw and BABC samples prepared with different activation dosages (1M, 4M, 7M, 10M, 13M, 16M, and 18M) of NaOH and best activation dosage (7M) of H_2SO_4 as shown in appendix B to assess their surface area and pore volume and size using equipment (MICROMERITICS 3FLEX) at degassing temperature N_2 (77K) illustrated in Table 37.

Table 37 : Surface area and pore volume and size of raw BC and BABC

BET	BC	BABC						
Activation	Raw	1M	4M	7M	10M	13M	16M	18M
Surface Area (m ² /g)	9.86	30.90	55.71	70.72	65.20	60.28	74.15	51.97
Pore Volume (cm ³ /g)	0.22	0.38	0.72	1.01	0.73	0.80	1.11	0.69
Pore Size (Å)	162.4	246.01	259.23	288.37	225.69	266.75	300.2	266.78

The raw bentonite clay initially exhibited surface area and pore volume and size values of 8.86 m²/g, 0.22 cm³/g, and 162.6 Å, respectively (Gumede & Musonge, 2022). As the NaOH activation dosage increased from 1M to 4M, there was a gradual enhancement in surface area (30.90 to 55.71 m²/g) and pore volume (0.38 to 0.72 cm³/g), indicating the creation of more porous structures. The trend continued, and at 7M NaOH activation, a significant increase of (70.72 m²/g) in surface area and (1.01 cm³/g) in pore volume was observed, demonstrating the successful development of porous sites. Surprisingly, at higher dosages of 10M and 13M, a slight reduction in surface area (65.20 and 60.28 m²/g) and pore volume (0.73 and 0.80 cm³/g) occurred, which may be attributed to possible aggregation or the formation of larger pores due to excessive NaOH concentration.

However, 16M NaOH activation showed a substantial increase in surface area (74.15 m²/g) and pore volume (1.11 cm³/g), reaffirming its potential to enhance porosity and adsorption capacity. Even at 18M NaOH activation, the surface area (51.97 m²/g) was still higher than the raw clay, signifying the importance of NaOH activation in increasing porosity. Comparing the best activation with 7M H₂SO₄ (surface area 72.76 m²/g, pore volume 0.106 cm³/g, pore size 121.23 Å) Elnaggar et al., (2022), 16M NaOH activation exhibited higher

surface area and pore volume (74.15 m²/g and 1.11 cm³/g, respectively), suggesting its superiority as an adsorbent, offering promising potential for environmental applications in MB and other pollutant removal from aqueous solutions consistent with previous studies (Elnaggar et al., 2022; Gumede & Musonge, 2022).

5.3.5 Fourier transform infrared (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was employed to analyze the structural modifications of bentonite clay activated with various NaOH concentrations (1M, 4M, 7M, 10M, 13M, 16M, and 18M). The FTIR spectra were recorded using a SPECTRUM 100 PERKIN ELMER spectrometer over the 650-4000 cm⁻¹ range.

Raw Bentonite Clay (Figure 51): The raw BC spectrum shows significant peaks at 3623.71 cm⁻¹ and 3408.81 cm⁻¹, indicative of hydroxyl (OH) stretching vibrations, reflecting the existence of surface hydroxyl groups. The peak at 2324.67 cm⁻¹ suggests CO₂ presence, while the peaks at 1738.71 cm⁻¹ and 1638.06 cm⁻¹ correspond to carbonyl (C=O) stretching, revealing organic groups. Peaks at 1472.56 cm⁻¹, 1009.97 cm⁻¹, 917.12 cm⁻¹, 789.89 cm⁻¹, and 692.84 cm⁻¹ are associated with the clay's silicate and aluminum silicate framework (Gandhi et al., 2022; Tabak et al., 2011).

1M NaOH Activation (Figure 51): The FTIR spectrum for 1M NaOH activation reveals enhanced peaks for hydroxyl groups at 3812.36 cm⁻¹ and 3745.25 cm⁻¹, and a prominent hydroxyl stretching peak at 3620.04 cm⁻¹. The carbonyl

group peak at 1742.45 cm^{-1} suggests interaction with organic molecules. Notably, the spectrum indicates changes in the clay structure due to NaOH activation, which affects the interaction sites available for MB (Reddy T et al., 2017; Tabak et al., 2011; Verma & Riaz, 2018).

4M NaOH Activation (Figure 51): For 4M activation, the FTIR spectrum shows peaks at 3811.78 cm^{-1} and 3746.45 cm^{-1} corresponding to hydroxyl groups. The carbonyl peak at 1740.32 cm^{-1} and changes in the Si-O and Al-O bonds (peaks at 1216.32 cm^{-1} , 1007.77 cm^{-1} , and 695.44 cm^{-1}) suggest modifications in the clay's surface chemistry, potentially enhancing MB adsorption sites (Reddy T et al., 2017; Tabak et al., 2011; Verma & Riaz, 2018).

7M NaOH Activation (Figure 51): The spectrum for 7M activation displays peaks similar to the 4M activation, with enhanced hydroxyl stretching at 3401.66 cm^{-1} and increased intensity of the carbonyl group peak at 1740.32 cm^{-1} . The modification in functional groups, including CH_2/CH_3 bending (1455.86 cm^{-1}) and Si-O bending (1369.04 cm^{-1}), indicates further changes in the clay's surface chemistry (Reddy T et al., 2017; Tabak et al., 2011; Verma & Riaz, 2018).

10M NaOH Activation (Figure 51): In the 10M activation spectrum, peaks at 3811.81 cm^{-1} and 3746.08 cm^{-1} highlight the presence of hydroxyl groups. The carbonyl group peaks at 1740.28 cm^{-1} and changes in CH_2/CH_3 bending (1457.16 cm^{-1}) and Si-O stretching (1216.60 cm^{-1}) reveal structural alterations

that may influence the adsorption efficiency of MB (Reddy T et al., 2017; Tabak et al., 2011; Verma & Riaz, 2018).

13M NaOH Activation (Figure 52): The 13M activation spectrum shows prominent peaks at 3811.75 cm^{-1} and 3746.49 cm^{-1} for hydroxyl groups, with a carbonyl peak at 1739.54 cm^{-1} . The modifications in Si-O and Al-O bonds (peaks at 1215.25 cm^{-1} and 703.45 cm^{-1}) suggest significant surface changes, enhancing interaction with MB (Reddy T et al., 2017; Tabak et al., 2011; Verma & Riaz, 2018).

16M NaOH Activation (Figure 52): For 16M activation, the spectrum reveals peaks at 3811.26 cm^{-1} and 3746.45 cm^{-1} for hydroxyl groups and a strong carbonyl peak at 1740.38 cm^{-1} . Changes in CH_2/CH_3 bending (1466.53 cm^{-1}) and Si-O stretching (1215.40 cm^{-1}) reflect modifications that likely increase MB binding sites (Reddy T et al., 2017; Tabak et al., 2011; Verma & Riaz, 2018).

18M NaOH Activation (Figure 52): The FTIR spectrum for 18M activation shows peaks at 3811.81 cm^{-1} and 3746.21 cm^{-1} , indicative of hydroxyl groups. The carbonyl peak at 1740.77 cm^{-1} and alterations in CH_2/CH_3 bending (1457.32 cm^{-1}) and Si-O stretching (1217.57 cm^{-1}) suggest extensive surface modifications that enhance MB adsorption (Reddy T et al., 2017; Tabak et al., 2011; Verma & Riaz, 2018).

Interaction Mechanisms with MB: The interactions between these functional groups and MB include various types of reactions:

Hydrogen Bonding: Hydroxyl groups (-OH) on the activated clay surface can form hydrogen bonds with the nitrogen atoms in the MB molecule. This interaction is particularly strong because hydrogen bonds are directional and contribute to the stability of the adsorbed species.

Electrostatic Interactions: The carbonyl groups (C=O) and silicate groups (Si-O) on the clay surface can interact electrostatically with the positively charged amine groups in MB. This interaction is significant because the electrostatic forces can enhance the adsorption capacity, especially under conditions where the pH favors the ionization of the functional groups.

Van der Waals Forces: These are non-specific interactions that occur between the clay surface and MB molecules. Van der Waals forces are weaker compared to hydrogen bonding and electrostatic interactions, but they still play a crucial role in the overall adsorption process, especially at lower concentrations of the adsorbate (Reddy T et al., 2017; Tabak et al., 2011; Verma & Riaz, 2018).

Conclusion: The FTIR research shows that NaOH activation dramatically changes the functional groups on the bentonite clay surface. Enhanced hydroxyl groups, as well as alterations in carbonyl and Si-O linkages, imply that MB has more interaction sites. Among them, 16M NaOH activation has the most prominent peaks, suggesting the greatest level of functional group

exposure. Many more hydroxyl, carbonyl, and silicate groups present upon FTIR peak temperature enhance its ability to bond with MB through hydrogen bonding, electrostatic interactions as well as van der Waal Force. The adsorption capacity of bentonite clay is enhanced by 16M NaOH activation, resulting in superior functional group accessibility, making it a suitable treatment for improving removal characteristics.

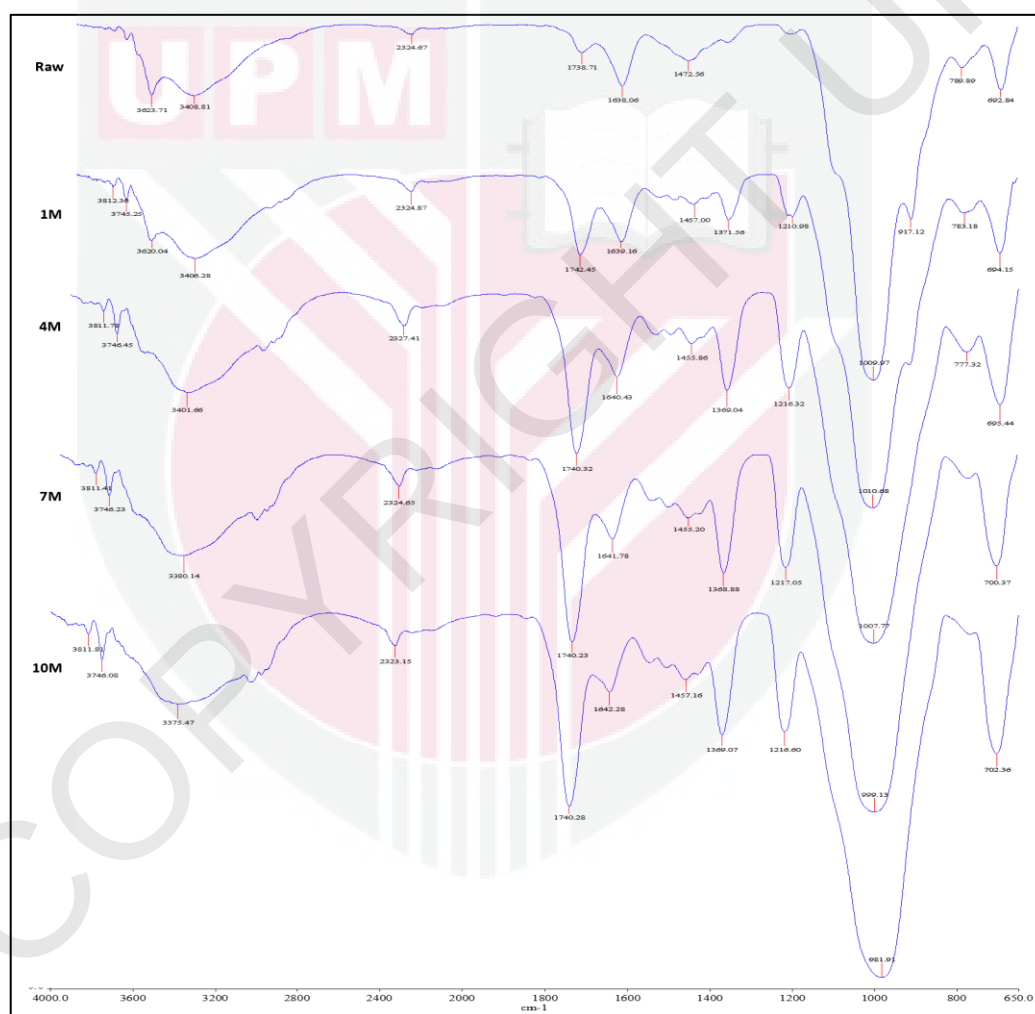


Figure 51 : FTIR Spectra of Raw and BABC (1, 4, 7, 10M)

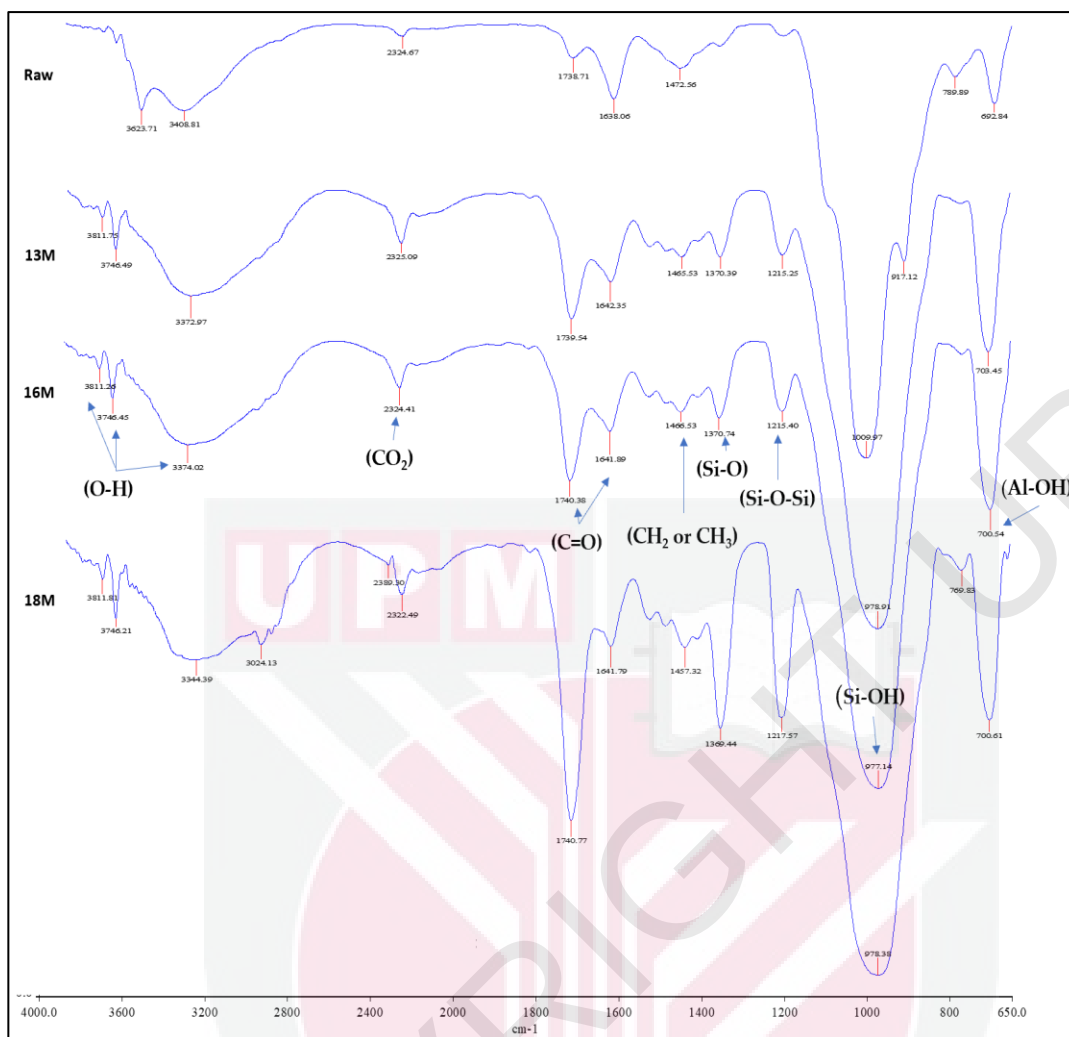


Figure 52 : FTIR Spectra of Raw and BABC (13, 16, 18M)

5.3.6 X-ray diffraction (XRD)

X-ray diffraction (XRD) method It is an essential method to determine the crystal structure and phase composition of material. The structural changes of BC by activation with different doses of NaOH were studied. XRD patterns of raw BC and NaOH-activated BABC samples at concentrations 1M, 4M, 7M, 10 M, 13 M, 16 M and 18 M were recorded using XRD6000 SHIMADZU instrument equipped over the range of angles (2θ) shown in Figure 53, (Na_2O ($\otimes$), SiO_2 ($\triangle$), Al_2O_3 (∇), and MgO ($\square$)).

Raw Bentonite Clay: The XRD pattern of the Raw BC was portrayed with several significant peaks explaining its mineral makeup it. Using Xpert Highscore Software, the peaks at 29.48° and 61.86° (intensities of 134 and 66) were indexed to silicon dioxide (SiO_2). Further, the peak at 33.14° (intensity of 58) was indexed to sodium oxide (Na_2O). The peaks at 35.72° and 48.62° (intensity of 112 and 40) have been assigned to aluminum oxide (Al_2O_3), while a peak at 54.12° (62 intensity range) is related to magnesium oxide (MgO), these results in line with previous studies (Hebbar et al., 2018; Reddy T et al., 2017). These values are close to the mineral stages that Durowaye et al., (2017) reported and used as a basis for understanding the NaOH activation effect.

1M NaOH activation: BC was significantly increased in structure due to the peaks appearing as major differentiation. Peaks corresponding to Na_2O were 24.38° and 33.42° (intensities 38 and 32 respectively), while Al_2O_3 was 49.58° (intensity 18). Peaks of MgO were at 54.2° (intensity 24), while SiO_2 was at 62.24° (intensity 36). This modification indicated a partially degraded clay matrix and new phases, which might have resulted from developing porosity potential up to adsorption capacity (Hebbar et al., 2018; Reddy T et al., 2017).

4M NaOH activation: The increase of the NaOH concentration to a value higher than 1 M led to an even more drastic change of structure. Na_2O peaks were observed at 24.5° , 25.48° , and 33.24° with intensities of (42, 48, and 62 respectively), while Al_2O_3 was at 28.06° , 43.18° , and 49.48° with intensities of (48, 44, and 24 respectively). SiO_2 appeared at peaks 35.64° , 61.66° , and 64°

with intensities of (66, 32, and 26 respectively), while MgO was at 54.1° (intensity 36), indicating higher levels of Na₂O and Al₂O₃, compared to 1M NaOH sample suggests a greater extent of structural alteration enabling enhanced accessibility for ion exchange, adsorption (Hebbar et al., 2018; Reddy T et al., 2017).

7M NaOH activation: The XRD pattern for BC activated with 7 M NaOH gave a peak at 24.3°, 26.46°, and 33.14° with intensities of (82, 44, and 50 respectively) referred to Na₂O, while peaks of SiO₂ were at 29.78°, 31.56°, 61.72°, and 64.02° with intensities of (106, 42, 34, and 26 respectively). Moreover, Al₂O₃ was observed at peaks 34.84°, 42.68°, and 49.52° with intensities of (70, 40, and 24 respectively), while MgO was noted at 53.98° (intensity 32). The enhanced intensity of SiO₂ and Na₂O peaks along with new peaks arise due to the formation of Al₂O₃ and MgO during the activation process indicating a substantial structural modification due to 7M NaOH activation (Hebbar et al., 2018; Reddy T et al., 2017).

10M NaOH activation: 10M NaOH Activation: activation of 10M NaOH showed peaks for Na₂O at 24.5°, 31.9°, and 33.4° with intensities of 119, 54, and 38, respectively. Al₂O₃ showed peaks at 34.84°, 43°, and 58.46° with intensities of 66, 48, and 32, respectively, while SiO₂ showed peaks at 35.84° and 64.32° with intensities of 56 and 28, respectively. MgO was measured at 52.1° and 54.14° with intensities of 38 and 26, respectively, in line with (Hebbar et al., 2018; Reddy T et al., 2017). High Na₂O concentration and consistent SiO₂ and Al₂O₃ levels for the 10M NaOH activation reflect that the NaOH

concentration increases the clay's adsorption behavior by structurally optimizing the clay.

13M NaOH activation: For 13M NaOH, the XRD pattern revealed peaks of Na_2O 24.42° (intensity 166) and 24.54° (intensity 70), Al_2O_3 of 28.28° (intensity 36), 34.72° (intensity 94), 42.82° (intensity 60), and 58.34° (intensity 32), while SiO_2 was 31.7° (intensity 62), 35.66° (intensity 54), 36.8° (intensity 32), 62.26° (intensity 24), and 64.1° (intensity 52), and MgO was 52.18° (intensity 30) and 54.14° (intensity 26), in line with (Hebbar et al., 2018; Reddy T et al., 2017). The outcomes illustrated a significant increase in the amount of Na_2O and different regions for SiO_2 , Al_2O_3 , and MgO. Enhanced peak intensities mean the activation is performed under stricter conditions at which accessible structural modifications are favorable to adsorption.

16M NaOH activation: XRD peaks for 16M NaOH were measured for Na_2O at 24.44°, 25.52°, 26.56°, and 33.24° with intensities 170, 36, 80, and 62, respectively. Al_2O_3 was measured at 28.3°, 34.7°, 37.7°, 41.04°, 42.8°, 49.48°, and 58.36° with 36, 92, 32, 24, 60, 26, and 38, respectively. SiO_2 was indicated at 29.48°, 31.64°, 35.62°, 62.3°, 63.98°, and 69.42° with 58, 56, 58, 28, 34, and 28 intensities. MgO was measured at 51.98°, 52°, and 54.2° with 28, 24, and 28 intensities. Marked structural changes observed at this NaOH concentration demonstrated that the 16M NaOH activated the clay by hugely increasing the porosity and surface area of the clay hence adsorption capacity (Hebbar et al., 2018; Reddy T et al., 2017).

18M NaOH activation: At 18M NaOH Activation: At 18M NaOH, the Na_2O peaks noted in the XRD pattern were 24.48° , 26.82° , and 33.28° with intensities 158, 76, and 58, respectively. SiO_2 peaks were 31.84° , 35.76° , 62.02° , 64.1° , and 69.4° , with intensities of 50, 64, 26, 24, and 28, respectively. Al_2O_3 peaks in the aforementioned were 34.72° , 42.94° , and 58.32° , with intensities of 78, 58, and 34, respectively. MgO peaks were 54.16° , with an intensity of 22 (Hebbar et al., 2018; Reddy T et al., 2017). The peaks in this pattern were highly pronounced, with the exceptions of the others being less strong and marked. These results indicate structural modifications, with the production of peaks for Na_2O , SiO_2 , and Al_2O_3 . However, decreases in the intensity of the others and the potential for over-activation suggest that 18M NaOH, though still altering the structure of the clay, is less effective at enhancing adsorption characteristics.

In summary, The XRD analysis of BABC showed that the structure underwent significant alterations after NaOH activation which finally resulted in a higher adsorption capacity. Testing multiple concentrations, a solution with 16M NaOH was observed to be the best with better development in high surface area and microporosity required for adsorption performance. Concentrations above 16M, e.g., 18 M show diminished returns and hence imply that up to this concentration (16M NaOH) offers the best compromise for accountability modification with adsorption performance.

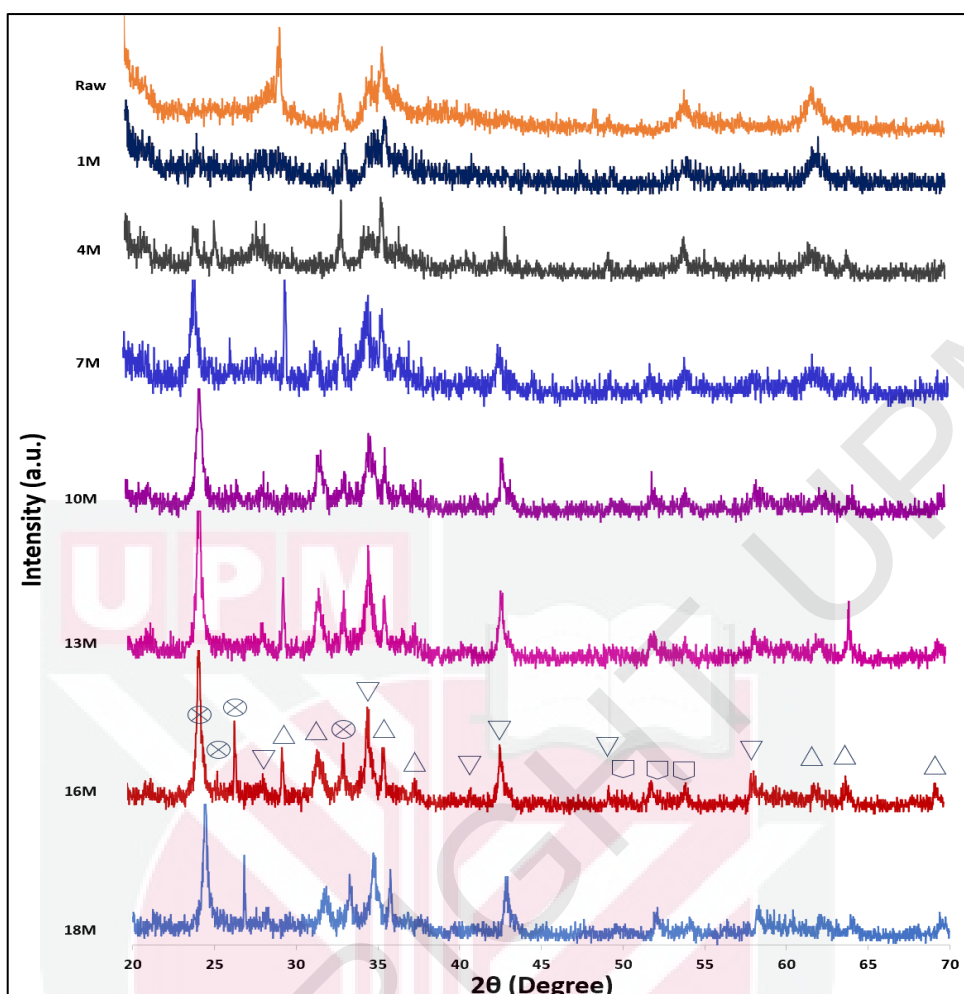


Figure 53 : XRD Analysis of Various BABC's Samples

5.4 Adsorption studies of bentonite clay

This study looks at the adsorption capacity of BABC to absorb MB, a dye that is widely utilized in numerous sectors. The adsorption process was tuned utilizing several factors such as contact duration, starting concentration, temperature, pH, and dose. Adsorption isotherm models, kinetic models, and thermodynamic studies were used to better understand the adsorption behavior and causes. The BABC's regeneration and reusability characteristics were also studied, to develop a more sustainable and cost-effective adsorption technique.

5.4.1 Optimization of adsorption conditions

In this optimization examination, the influences of five factors on MB adsorption capacity using BABC were examined. These unique and natural conditions were contact duration (45-315 minutes), starting MB-concentration (50-200 ppm), pH (4-10), temperature (25-50°C), and adsorbent dose (0.5-0.95 g) in 100 mL. The goal was to find the best conditions for maximum adsorption capacity by altering these factors. The findings of this work lead to the enhancement of efficient and cost-effective adsorption techniques for MB removal and water treatment applications.

- i. **Contact time:** The adsorption process lasted 315 mins to reach equilibrium, while ideal circumstances at 270 mins provided considerable elimination in a faster operation period than 315 mins. The investigation was carried out at 25°C, pH 7, an adsorbent dosage of 0.8g, and an initial MB-concentration of 50 ppm in 100 mL. Periodic intervals of 45 minutes using a shaker with agitation speed at 135 rpm were employed, as depicted in Table 38 and visually represented in Figure 54.

Table 38 : Contact time results for BABC (50ppm)

C_i (mg/l)	Abs (nm)	C_e (mg/l)	Removal %	q_t (mg/g)	Time (min)
50	2.162	20.253	59.493	3.718	45
50	1.745	15.850	68.299	4.268	90
50	0.459	3.343	93.313	5.832	135
50	0.217	1.563	96.872	6.054	180
50	0.171	1.225	97.548	6.096	225
50	0.067	0.461	99.077	6.192	270
50	0.046	0.306	99.386	6.211	315

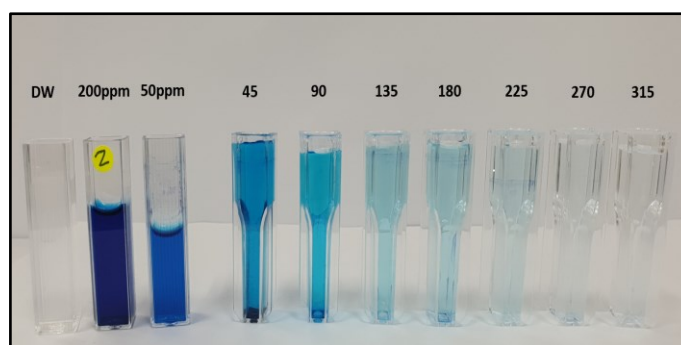


Figure 54 : Contact Time Results for BABC (50ppm)

By differing the contact time (45, 90, 135, 180, 225, 270, 315 minutes), while maintaining temperature, pH, dosage, and MB initial concentration, the most favorable outcome emerged at 270 minutes in volume of 100 mL. During this period, the final concentration of MB reached 0.461 ppm, demonstrating an impressive elimination efficiency of 99.077%. The adsorption capacity achieved was 6.192 mg/g, emphasizing the BC's pronounced affinity for MB. Aljar et al., (2021) achieved equilibrium at 300 minutes (20-320 minutes) with 95% MB removal using 200 ppm, 1.5g, pH of 8, 150 rpm, and 30°C in 50 mL. Similarly, El-latif et al., (2010) reached equilibrium at 360 minutes, obtaining approximately 90% removal with 8g, pH of 9, 22°C, 500 rpm, and 20 ppm in 800 mL. Al-asheh & Banat, (2003) completed the process within the first 5 hours (300 minutes) at pH 9, 25°C, and MB concentrations up to 80 ppm in 50 mL. Figure 55 illustrates variations in C_e and q_e during changes in contact time.

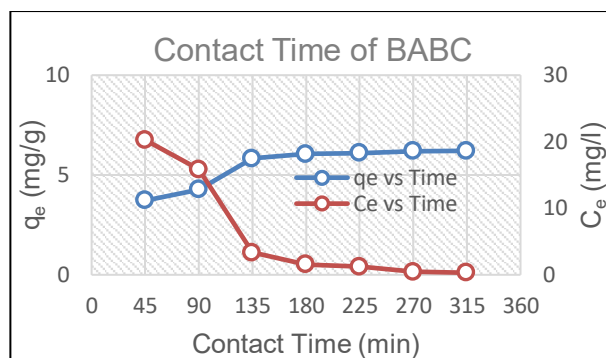


Figure 55 : Optimization Graph for Contact Time of BABC

- ii. **MB Initial concentration:** Maintaining a constant time of 270 minutes, the MB initial concentration of the solution was systematically varied from 50 to 200 ppm. The experimental parameters remained unaltered, encompassing an adsorbent dosage of 0.8g, and a pH of 7, a temperature of 25°C. The adsorption process was monitored at intervals of 45 minutes, employing a shaker at 135 rpm, as depicted in Table 39 and visibly in Figure 56.

Table 39 : MB Initial concentration results for BABC (75-200ppm)

C_i (mg/l)	Abs (nm)	C_e (mg/l)	Removal %	q_t (mg/g)	Time (min)
75	0.16	1.144	98.473	9.231	270
100	0.182	1.306	98.693	12.336	270
125	0.291	2.108	98.313	15.361	270
150	0.439	3.196	97.869	18.350	270
175	0.595	4.343	97.518	21.332	270
200	0.773	5.652	97.173	24.293	270

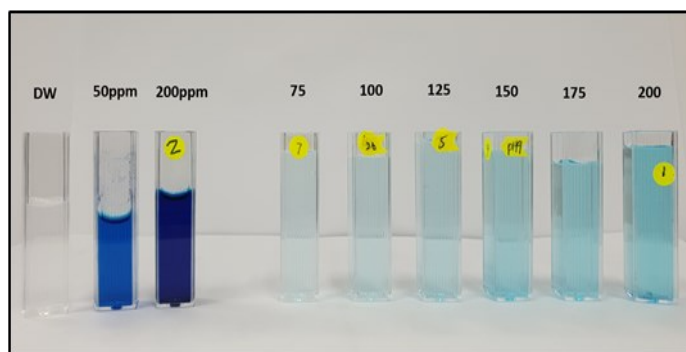


Figure 56 : MB Initial Concentration Results for BABC (75-200ppm)

The influence of MB initial concentration (75 to 200 ppm) on adsorption was examined within the framework of 25°C, a dosage of 0.8g, a contact time of 270 minutes, and a pH of 7. The most suitable score stands out among the assessed concentrations at 200 ppm. The resulting MB concentration was notably diminished to 5.652 ppm, leading to a remarkable elimination efficiency of 97.173%. Notably, the adsorption capacity attained an impressive value of 24.293 mg/g. Aljar et al., (2021) achieved a 95% MB elimination rate within 300 minutes (5 hours), employing 200 ppm, 1.5g, pH 8, and 30°C in 50 mL.

Furthermore, the research by Miz et al., (2014) delved into the adsorption of MB onto Na-bentonite clay. The study revealed the significant impact of initial concentration on the adsorption process, observing a direct relationship between the adsorption capacity and increasing MB initial concentration. Figure 57 supplies a graphical representation of the alterations in C_e and q_e throughout the changes in MB initial concentration.

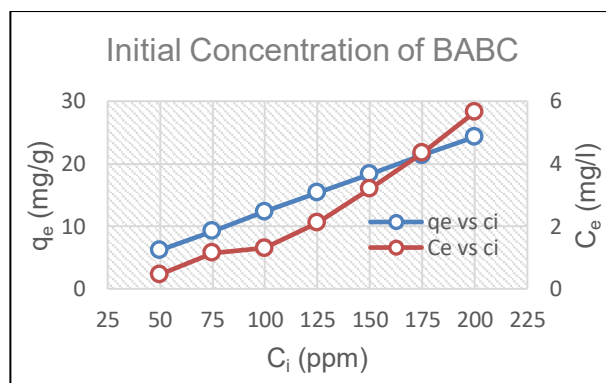


Figure 57 : Optimization Graph for MB Initial Concentration of BABC

iii. **Temperature:** While holding the MB initial concentration fixed at 200 ppm, temperature fluctuations spanned from 25-50°C. The time remained at 270 minutes, with other unaltered variables: a pH of 7 and a 0.8g dosage. Monitoring of the adsorption process was performed through shaker equipment, operating at 135 rpm, and measurements were carried at 45-minute intervals, as presented in Table 40 and visually in Figure 58.

Table 40 : Temperature results for BABC (200ppm)

C_i (mg/l)	Abs (nm)	C_e (mg/l)	Removal %	q_t (mg/g)	Temp °C
200	0.773±002	5.652	97.173	24.293	25
200	0.815	5.961	97.019	24.254	30
200	1.108	8.115	95.942	23.985	35
200	1.37	10.041	94.979	23.744	40
200	1.57	11.512	94.243	23.560	45
200	1.621	11.887	94.056	23.514	50

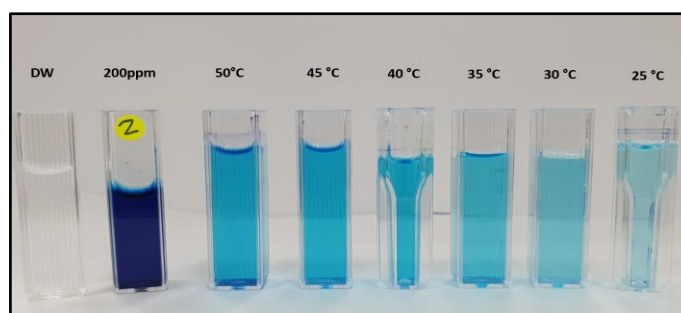


Figure 58 : Temperature Results for BABC (200ppm)

The impact of temperature (25, 30, 35, 40, 45, 50, 55°C) on process was investigated under specific conditions, including an adsorbent 0.8g dosage, pH of 7, MB-200ppm initial concentration, and a time of 270 minutes. Noticeably, optimal results emerged at the lowest temperature, 25°C, in line with prior investigation (S. Ibrahim & Ali, 2020; Ravi & Pandey, 2019). This temperature yielded a final MB concentration of 5.652 ppm, accompanied by an impressive elimination efficiency of 97.173% and an adsorption capacity of 24.293 mg/g. Additionally, Aljar et al., (2021) explored a temperature range (20, 30, 40, 50°C), revealing a rise in removal efficiency from 20-30°C. At 30°C, a 95% removal rate was achieved after 200 minutes, whereas 90% removal necessitated 300 minutes at 20°C. However, MB's removal rate displayed limited enhancement at 40°C and 50°C compared to 30°C. Likewise, Al-asheh & Banat, (2003) found optimal outcomes at 25°C while investigating temperatures (25, 35, 45°C). Figure 59 visually represents variations in C_e and q_e during temperature changes.

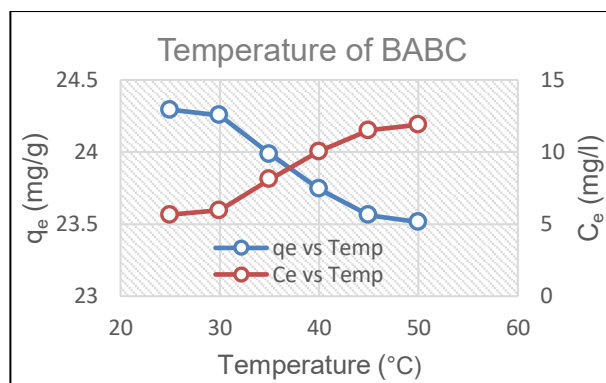


Figure 59 : Optimization Graph for Temperature of BABC

iv. pH: Maintaining a temperature of 25°C, the pH range of 4-10 was systematically explored while maintaining all other parameters constant. The contact time remained fixed at 270 minutes, with MB concentration of 200 ppm and an adsorbent dosage of 0.8g. The adsorption process was continuously monitored utilizing shaker equipment at 135 rpm, and outcomes were recorded at 45-minute intervals, as depicted in Table 41 and Figure 60.

Table 41 : pH results for BABC (200ppm)

C_i (mg/l)	Abs (nm)	C_e (mg/l)	Removal %	q_t (mg/g)	pH
200	2.367	22.418	88.790	22.197	4
200	1.241	9.093	95.453	23.863	5
200	0.904	6.615	96.692	24.173	6
200	0.773±001	5.652	97.173	24.293	7
200	0.975	7.137	96.431	24.107	8
200	1.999	14.666	92.666	23.166	9
200	2.462	18.071	90.964	22.741	10

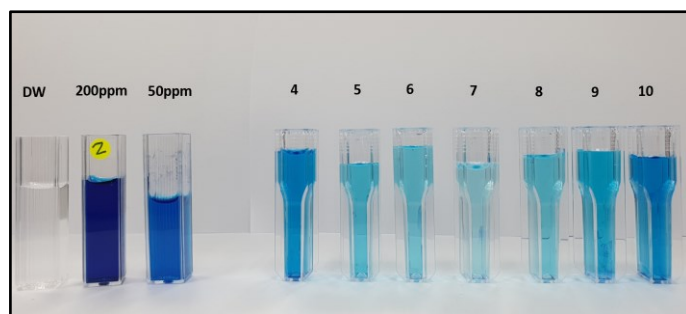


Figure 60 : pH Results for BABC (200ppm)

To comprehensively assess the influence of pH (4, 5, 6, 7, 8, 9, 10) on the adsorption process, meticulous experiments were conducted under consistent conditions: 200 ppm of MB concentration, 270-minute time, 25°C temperature, and an adsorbent 0.8g dosage. The optimal pH was determined to be 7, yielding an ultimate MB-concentration of 5.652 ppm, in alignment with previous research (Duwal, 2013; Eleraky et al., 2022; Ravi & Pandey, 2019). Notably, this pH level achieved an elimination efficiency of 97.173%, coupled with an adsorption capacity of 24.293 mg/g. The interplay of C_e and q_e during pH variations is visually elucidated in Figure 61.

The strong ability to absorb and remove dye at pH 7 stems from the perfect surface charge helpful surface chemistry that boosts working groups, and the best solution makeup for MB to interact. These conditions lead to strong electrical pull and hydrogen bonds between the clay surface and MB molecules resulting in good absorption. pH 7 shows the best mix of surface charge, solution makeup, and how clay and minerals work together, which is key to boosting how well MB is removed.

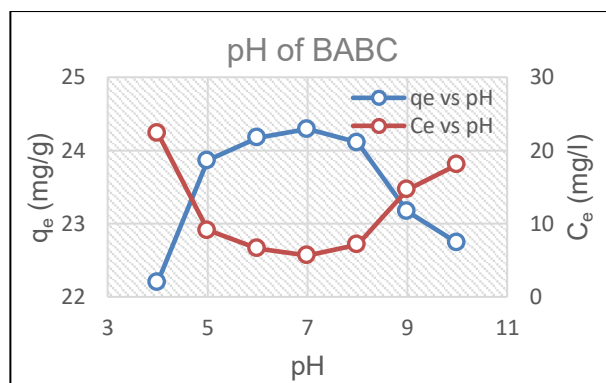


Figure 61 : Optimization Graph for pH of BABC

v. **Adsorbent Dosage:** Maintaining the pH at 7, an investigation was conducted into the dosage range of 0.5 to 0.95g, while keeping all other parameters unaltered. The adsorption process occurred at a fixed temperature of 25°C, with a time of 270 minutes and a MB initial concentration of 200 ppm. Measurements were systematically taken at 45-minute intervals, facilitated by shaker equipment operating at 135 rpm. The outcomes of these analyses are presented in Table 42 and visually depicted in Figure 62.

Table 42 : Dosage results for BABC (200ppm)

C_i (mg/l)	Abs (nm)	C_e (mg/l)	Removal %	q_t (mg/g)	Dosage (g)
200	1.484	13.093	93.453	37.381	0.5
200	1.079	7.902	96.048	32.016	0.6
200	0.874	6.394	96.802	27.657	0.7
200	0.773±002	5.652	97.173	24.293	0.8
200	0.376	2.733	98.633	23.207	0.85
200	0.115	0.813	99.593	22.131	0.9
200	0.022	0.130	99.934	21.038	0.95

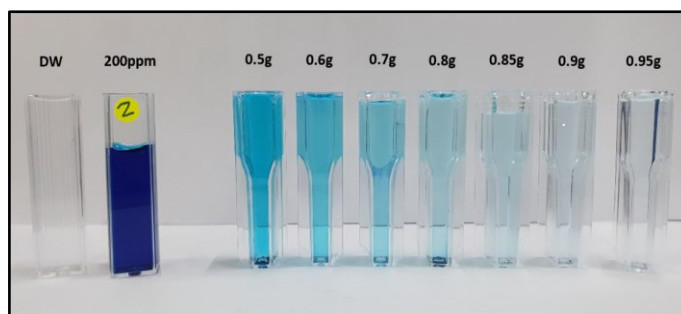


Figure 62 : Dosage Results of BABC for 200ppm

Exploring the influence of dosage (0.5, 0.6, 0.7, 0.8, 0.85, 0.9, 0.95g) on adsorption under conditions of 200 ppm initial concentration, 25°C temperature, pH7, and 270 minutes contact time revealed optimal performance at a dosage of 0.9g. This specific dosage resulted in a remarkable reduction of the final MB concentration to 0.130 ppm, thus achieving a noticeable elimination effectiveness of 99.593%. The corresponding adsorption capacity was recorded as 21.131 mg/g, eloquently showcasing the elevated adsorption capability of the BC. This aligns with earlier research by Taher et al., (2018), and Ravi & Pandey, (2019) , which underscored the potency of BABC as a robust adsorbent for MB, its adsorption capacity increasing proportionally with dosage. Figure 63 depicts the oscillations in C_e and q_e as dose changes.

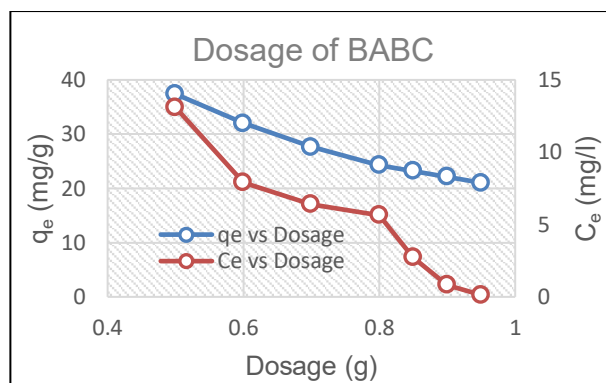


Figure 63 : Optimization Graph for Dosage of BABC

This research aimed to optimize the adsorption of MB using BABC with a 16M NaOH activation dosage while meeting WHO drinking water standards. Through rigorous experiments, the optimal conditions were determined to be a contact time of 270 minutes, a MB initial concentration of 200 ppm, a temperature of 25°C, a pH of 7, and an adsorbent dosage of 0.9g. Under the same conditions, BABC showed a high adsorption capacity of 12 pt-co (which represented an equivalent to 12 UTC), which is below its admissible maximum value proposed by WHO agencies of up to 15 UCT for drinking water. Table 43 shows the optimized dosage of BABC according to WHO.

Table 43 : Optimization of MB adsorption using BABC vs. WHO standard

Dosage (g)	Abs (nm)	C_e (mg/l)	Color (pt-co)	WHO standard
0.5	1.484	13.093	69	15 UTC
0.6	1.079	7.902	61	
0.7	0.874	6.394	49	
0.8	0.773	5.652	47	
0.85	0.376	2.733	33	
0.9	0.115	0.813	12	
0.95	0.022	0.130	1	

The findings of this study highlight the effectiveness of BABC as an adsorbent for MB elimination in water treatment applications. The optimal conditions offer

a practical and economically viable solution for efficient MB elimination while adhering to stringent water quality requirements. These results contribute to advancing knowledge in the field and underscore the potential of the BABC as a promising adsorbent for pollutant elimination in water treatment processes.

5.4.2 Adsorption isotherms

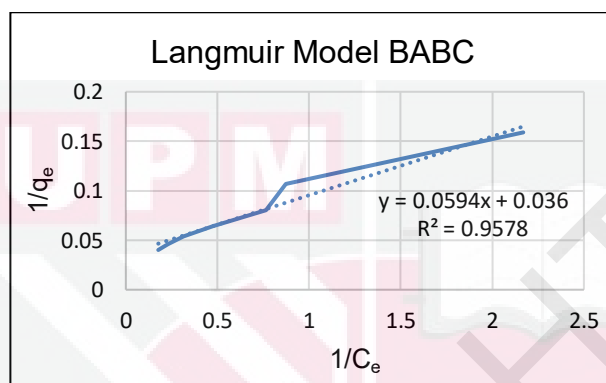
This study investigated MB adsorption using BABC and analyzed it with four isotherm models. The Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich models determined adsorption capacities and provided insights into surface properties and interactions. Evaluating the models' fitting results helps understand adsorption mechanisms and optimize BABC for efficient MB removal.

i. Langmuir model:

The Langmuir model postulates monolayer adsorption on a uniform surface. The obtained R-squared value of 0.9578 substantiates the suitability of the Langmuir model for the experimental data with intercept of 0.036, slope of 0.0594. The calculated K_L value of 0.002 denotes a low adsorption rate constant, while the maximum adsorption capacity (q_{max}) of 27.778 underscores the surface's potential. These outcomes are concisely summarized in Tables 44 and visually depicted in Figure 64. The elevated R-squared value indicates the Langmuir model's robust representation of adsorption behavior, while its alignment suggests that the formation of a monolayer of adsorbate molecules on the surface aptly elucidates the adsorption of MB on the BC adsorbent.

Table 44 : Langmuir isotherm results for BABC

C_i	C_e	$1/C_e$	$\log C_e$	$\ln C_e$	q_e	$1/q_e$	$\log q_e$
50	0.461	2.169	-0.336	-0.774	6.292	0.158	0.798
75	1.144	0.873	0.058	0.135	9.367	0.106	0.971
100	1.306	0.765	0.116	0.267	12.485	0.080	1.096
125	2.108	0.474	0.323	0.745	15.584	0.064	1.192
150	3.196	0.312	0.504	1.162	18.686	0.053	1.271
175	4.343	0.230	0.637	1.468	21.795	0.045	1.338
200	5.652	0.176	0.752	1.732	24.905	0.040	1.396

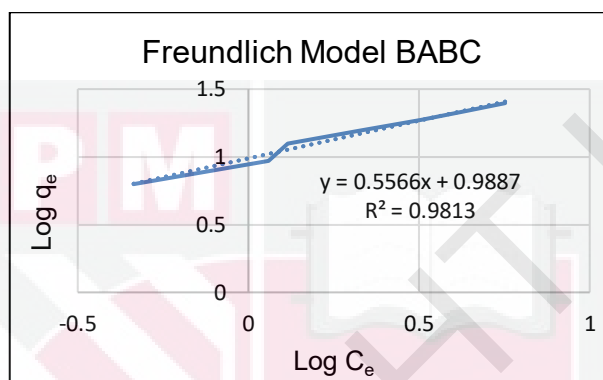
**Figure 64 : Langmuir Isotherm Results Graph for BABC**

ii. Freundlich model:

The Freundlich model postulates multilayer adsorption on a non-uniform surface. It exhibits a notable fit to the experimental data, evident by the R^2 value of 0.9813, intercept of 0.9887, slope of 0.5566, and the computed K_F value of 9.743. This high R-squared value indicates the aptness of the Freundlich model in accurately representing the adsorption of MB onto BABC, as succinctly displayed in Table 45 and graphically in Figure 65. The K_F value reflects the adsorption capacity, with its higher value indicating an augmented adsorption potential. The Freundlich model is favoured due to its superior fit and its ability to elucidate the multilayer adsorption process on an assorted surface, rendering it well-suited for this particular system.

Table 45 : Freundlich Isotherm Results for BABC

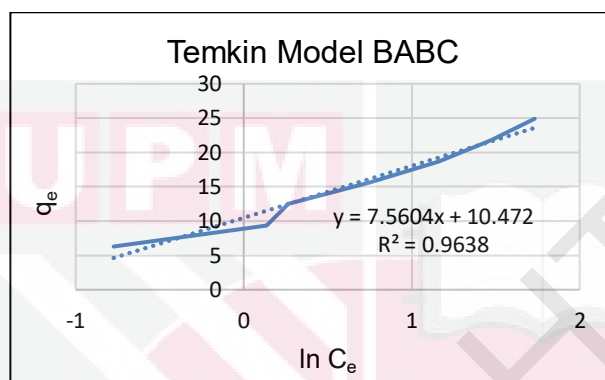
C_i	C_e	$1/C_e$	$\log C_e$	$\ln C_e$	q_e	$1/q_e$	$\log q_e$
50	0.461	2.169	-0.336	-0.774	6.292	0.158	0.798
75	1.144	0.873	0.058	0.135	9.367	0.106	0.971
100	1.306	0.765	0.116	0.267	12.485	0.080	1.096
125	2.108	0.474	0.323	0.745	15.584	0.064	1.192
150	3.196	0.312	0.504	1.162	18.686	0.053	1.271
175	4.343	0.230	0.637	1.468	21.795	0.045	1.338
200	5.652	0.176	0.752	1.732	24.905	0.040	1.396

**Figure 65 : Freundlich Isotherm Results Graph for BABC****iii. Temkin model:**

The Temkin model postulates a non-linear decline in adsorption energy as surface coverage increases. The derived R^2 value of 0.9431 signifies a reasonably good fit of the Temkin model to the empirical data with intercept of 10.472, and slope of 7.5604. The computed K_T value of 3.995 and B_T of 7.5604 correspond to the equilibrium binding constant for adsorption, as exemplified in Table 46 and visually in Figure 66. The moderate R-squared value implies the Temkin model's reasonable ability to depict the adsorption behavior. Nevertheless, the comparatively lower R-squared value in comparison to the Freundlich model underscores the latter's superior representation of the MB adsorption process onto BABC.

Table 46 : Temkin isotherm results for BABC

C_i	C_e	$1/C_e$	$\log C_e$	$\ln C_e$	q_e	$1/q_e$	$\log q_e$
50	0.461	2.169	-0.336	-0.774	6.292	0.158	0.798
75	1.144	0.873	0.058	0.135	9.367	0.106	0.971
100	1.306	0.765	0.116	0.267	12.485	0.080	1.096
125	2.108	0.474	0.323	0.745	15.584	0.064	1.192
150	3.196	0.312	0.504	1.162	18.686	0.053	1.271
175	4.343	0.230	0.637	1.468	21.795	0.045	1.338
200	5.652	0.176	0.752	1.732	24.905	0.040	1.396

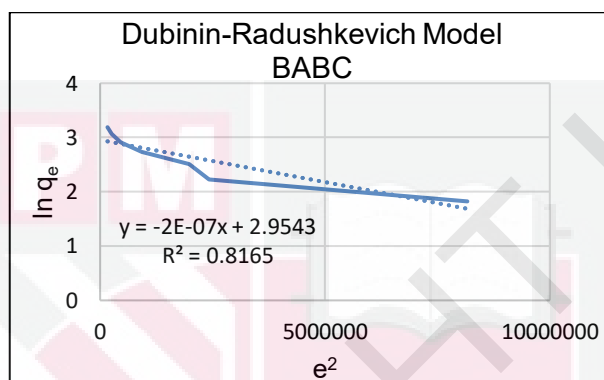
**Figure 66 : Temkin Isotherm Results Graph for BABC**

iv. Dubinin-Radushkevich model:

The Dubinin-Radushkevich model is commonly used to explore the adsorption mechanism and the nature of interactions between the adsorbent and adsorbate. The obtained R^2 value of 0.8165 indicates a good fit of the Dubinin-Radushkevich model to the experimental data. The q_m value of 19.188 signifies the maximum adsorption capacity as illustrated in Table 47 and visually in Figure 67. Although the R-squared value (0.8165) is lower than the other models, the Dubinin-Radushkevich model still provides insights into adsorption with intercept of 2.9543, slope of $-2.00E-07$, adsorption capacity of 19.188 mg/g, and energy of 5000000 KJ/mol. However, it may not fully capture the complexity of the adsorption behavior for MB on the BABC, suggesting potential limitations in its application.

Table 47 : Dubinin-Radushkevich isotherm results for BABC

$\ln(q_e)$	$1/C_e$	$1+1/C_e$	$\ln(1+1/C_e)$	e	e^2	β^2	β
1.823	2.169	3.169	1.153	2857.718	8166549	4E-14	2.00E-07
2.222	0.873	1.873	0.627	1555.407	2419290		
2.512	0.765	1.765	0.568	1408.104	1982757		
2.731	0.474	1.474	0.388	961.8587	925172.2		
2.909	0.312	1.312	0.272	674.4138	454833.9		
3.060	0.230	1.230	0.207	513.3665	263545.1		
3.190	0.176	1.176	0.162	403.603	162895.4		

**Figure 67 : Dubinin-Radushkevich Isotherm Results Graph for BABC**

In this study, the adsorption behavior of MB on BABC was analyzed utilizing four adsorption isotherm models: Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich. Each model was evaluated based on its fitting to the experimental data and its suitability for describing the adsorption process. Among the models, the Freundlich model demonstrated the best fit with the highest R-squared value of 0.9813 corresponded to previous studies by (Banat et al., 2003; Benhouria et al., 2015) . These features, especially the higher KF value, and capacity to represent multilayer adsorption on heterogeneous surfaces make it a better model than others of this adsorbent. Thus, the Freundlich model appropriately described MB adsorption on BABC.

5.4.3 Adsorption Kinetics

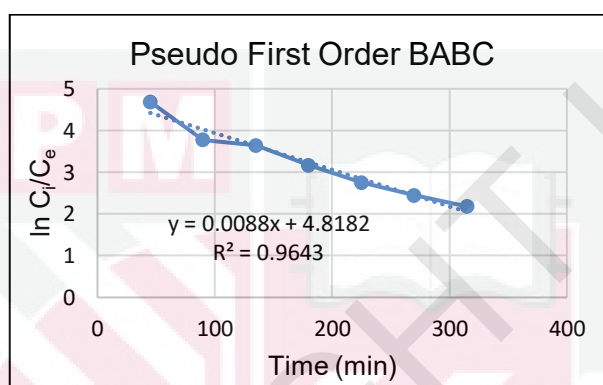
This study investigated the kinetic adsorption of MB on BABC. Followed by an analysis of adsorption kinetics via the well-used pseudo-first-order (PFO) and pseudo-second-order (PSO) models. These models help us to understand the mechanism and rate of adsorption. The experimental results were reviewed in terms of a model-theoretical approach for calculating kinetic parameters, as well as the models' adequacy for modeling adsorption. It is used to optimize adsorption conditions and forecast how MB would react when inhibited by BABC.

i. Pseudo-first-order model (PFO):

The PFO resulted in an R-squared value of 0.9643, intercept of 4.8182, slope of 0.0088, and adsorption capacity of 123.7422 mg/g, signifying a satisfactory alignment between the model and the empirical data. The PFO model's premise is that the adsorption rate is directly symmetrical to the disparity between the equilibrium adsorption capacity and the adsorbate's quantity adsorbed at a particular moment. The calculated positive rate constant ($K_1 = 0.0000279$) enhances the model's credibility by offering a meaningful interpretation. The outcomes of the PFO model are presented in Table 48 alongside the graphical representation in Figure 68.

Table 48 : Pseudo-first-order kinetics for BABC

C_i (mg/l)	C_e (mg/l)	q_t (mg/g)	$\ln C_i/C_e$	Time (min)
50	0.461	6.192	4.686	45
50	1.144	6.106	3.776	90
50	1.306	6.086	3.644	135
50	2.108	5.986	3.166	180
50	3.196	5.850	2.750	225
50	4.343	5.707	2.443	270
50	5.652	5.543	2.179	315

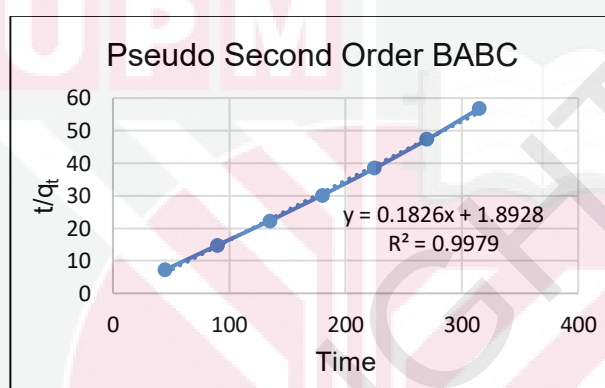
**Figure 68 : Pseudo-First-Order Kinetics Graph for BABC**

ii. Pseudo-second-order model (PSO):

Conversely, the (PSO) model displayed a heightened R-squared value of 0.9979, intercept of 1.8928, slope of 0.1826, and adsorption capacity of 5.476 mg/g, denoting an exceptional concordance between the empirical data and model predictions. This model posits that the adsorption rate is contingent on the square of the residual adsorbate concentration, a characteristic often attributed to chemisorption mechanisms encompassing robust chemical interactions. The calculated positive rate constant ($K_2 = 0.01762$) adds to the model's credibility, substantiating its pertinence in elucidating the kinetic dynamics of the adsorption process. The outcomes of the PSO model are delineated in Table 49 complemented by the visual representation in Figure

Table 49 : Pseudo-second-order kinetics for BABC

C_i (mg/l)	C_e (mg/l)	q_t (mg/g)	Time (min)	t/q_t (min/mg/g)
50	0.461	6.192	45	7.267
50	1.144	6.106	90	14.737
50	1.306	6.086	135	22.179
50	2.108	5.986	180	30.067
50	3.196	5.850	225	38.458
50	4.343	5.707	270	47.309
50	5.652	5.543	315	56.823

**Figure 69 : Pseudo-Second-Order Kinetics Graph for BABC**

In the adsorption kinetic study, two models, the pseudo-first-order and pseudo-second-order, were used to analyze the data. The fitting quality was evaluated using R-squared values. PSO model has a higher R-squared value of 0.9979, showing more accuracy in predicting the adsorption kinetics, which is consistent with prior research (Amrhar et al., 2015; Benhouria et al., 2015; Chang et al., 2016). This model also sheds light on the chemisorption process, which requires strong interactions between the adsorbate and adsorbent surfaces.

5.4.4 Thermodynamic Study of Adsorption

To enhance MB adsorption onto BABC, thermodynamic concerns were addressed, including a thorough analysis of temperature's effect on adsorption kinetics. The empirical experiments ranged in temperature from 25-50°C. Thermodynamic variables including ΔG° , ΔH° , and ΔS° helped understand the adsorption process's spontaneity, heat fluctuations, and unpredictability (R^2 of 0.951, intercept of -9.922, and slope of 3399.3. This temperature-centric work contributes to a better understanding of the thermodynamic parameters that govern the interaction of MB with BABC. These findings are crucial for enhancing and establishing effective methods. Table 50 completely summarizes the major findings. While Figure 70 depicts the obtained thermodynamic results.

Table 50 : Thermodynamic results for BABC

T	1/T	K_L	$\ln K_L$	ΔH° (KJ/mol)	ΔS° (KJ/mol)	ΔG° (KJ/mol)
298	0.00335	4.298	1.458	-28.261	-82.491	-3.612
303	0.0033	4.068	1.403			-3.535
308	0.00324	2.955	1.083			-2.775
313	0.00319	2.364	0.860			-2.239
318	0.00314	2.046	0.716			-1.893
323	0.00309	1.978	0.682			-1.831

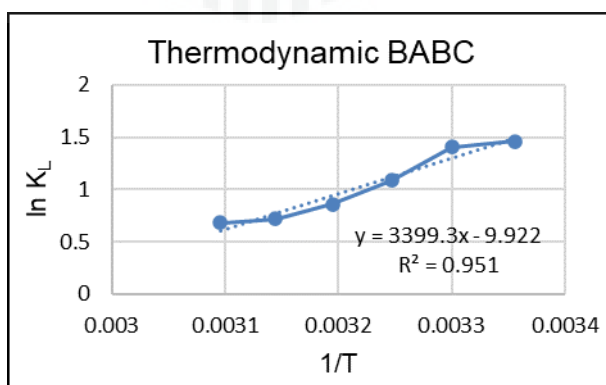


Figure 70 : Thermodynamic Results Graph for BABC

The influence of temperature on the adsorption process was explored in the thermodynamic study, with temperatures ranging from 25-50°C. The final concentrations and adsorption capacities were calculated at each temperature to better understand the system's thermodynamic behavior.

From 25-50 °C the final concentrations of adsorbate decreased and it could be seen that at higher temperatures the degree of adsorption is little. These results suggest that adsorption has a greater efficiency in the cooler temperature range and hence an increased capacity.

This gave negative values for ΔG° at all temperatures. The result indicates that the adsorption is spontaneous and thermodynamically feasible under-investigated conditions. The increase in temperature results in the decrease of ΔG° (ΔG° turns positive), indicating that the adsorption process becomes more feasible at high temperatures than at low temperatures.

A ΔH° indicating a negative value for this parameter means that adsorption is an exothermic process (Table 3). This indicates some kind of heat is released after the adsorption, which corresponds to physisorptions or lack of chemical interactions between both.

The negative entropy change (ΔS°) implies decreased randomness or uncertainty during the adsorption process. This is in full agreement with the observed decreased mobility of adsorbed molecules on an adsorbent surface.

In conclusion, thermodynamic study evidenced the spontaneous and

exothermic nature of sorption that takes place with a loss in entropy which is in accord with early investigations (De Castro et al., 2018; Ravi & Pandey, 2019). If ΔG° becomes negative, the expected adsorption conditions are to be favorable. An exothermic nature of the process means that chemical interactions do participate in this phase, while reduced entropy shows an ordering of molecules on the adsorbent surface.

5.4.5 Regeneration and reusability of bentonite clay

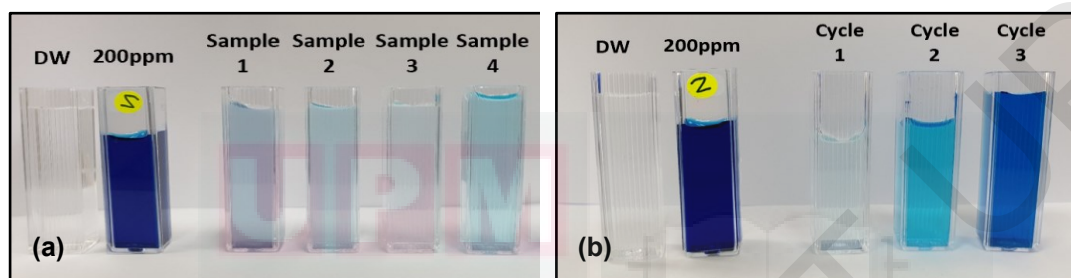
BABC was treated with four different regeneration strategies for the restoration of adsorption ability. The regenerator process consists of clay stirring at 80 °C and 15 rpm for different periods (1, 2 hours) according to the volume ratio ranging from sodium persulfate.

- i. By using 70 ml for 1 hour as sample 1
- ii. By using 70 ml for 2 hours as sample 2
- iii. By using 250 ml for 1 hour as sample 3
- iv. By using 250 ml for 2 hours as sample 4

The regenerated adsorbents were then utilized in another adsorption investigation, employing the same experimental optimization conditions as the initial experiment 0.9g, 25C, 200ppm, 270min, and pH7. The results produce insights into the regenerative capacity and reusability of the BABC for sustained MB elimination. Table 51, and Figure 71 show results of regeneration and reusability.

Table 51 : Regeneration and reusability of BABC

Sample	C_i (mg/l)	Abs (nm)	C_e (mg/l)	q_t (mg/g)	Removal %	Cycle
Sample 1	200	0.997	7.299	35.036	96.350	1
Sample 2	200	0.435	3.166	35.787	98.416	
Sample 3	200	0.15	1.071	36.168	99.464	
Sample 4	200	0.394	2.865	35.842	98.567	
Sample 3	200	1.668	15.036	33.629	92.481	2
Sample 3	200	58.333	25.757	19.360	70.833	3

**Figure 71 : Regeneration and Reusability of BABC: (a) Cycle 1, (b) Cycle 1-3**

In the regeneration and reusability study, a method involving stirring at 80°C and 15 rpm, along with a sodium persulphate mixture, was developed for regenerating the adsorbent. Four techniques were tested and evaluated for their effectiveness in subsequent reusability cycles. Among them, sample 3, involving a larger volume of the regeneration solution and a longer modification duration, demonstrated the best interpretation in terms of ultimate MB concentration, adsorption capacity, and elimination efficiency.

However, it should be noted that the efficiency of the regenerated adsorbent gradually decreased with each successive cycle convenient to previous investigation by Azha et al., (2021), and Taylor et al., (2014), they showed that MB's percentage removal has decreased by numbering of cycles . In the second and third cycles, there was a remarkable reduction in adsorption

capacity and removal effectiveness corresponded to study by Azha et al., (2021), which achieved removal about 95% in 3 cycles with 100ppm, pH7, and 70°C. This reduce can be assigned to factors such as incomplete restoration of the adsorbent's properties during regeneration and surface saturation or fouling caused by repeated use.

5.4.5.1 FTIR and BET analysis before and after adsorption

FTIR and BET analyses for bentonite clay concentrate on identifying alterations in functional groups and surface area pre- and post-adsorption, shedding light on its adsorption mechanisms.

- i. **BET analysis:** The BET examination was performed to assess the modifications to the surface area of the BABC material before and following MB adsorption utilizing equipment (MICROMERITICS 3FLEX), as indicated in Table 52.

Table 52 : BET analysis of BABC before and after adsorption

BABC	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (Å)
Before Adsorption	74.14	1.11	300.20
After Adsorption	73.1430	0.668	182.726
After Cycle 3	53.86	0.479	136.543

Before adsorption, the BABC had 74.15 m²/g surface area, 1.11 cm³/g pore volume, and 300.20 Å pore size. After MB adsorption, the surface area of the BABC declined slightly to 73.1430 m²/g from the starting value. The pore capacity fell to 0.668 cm³/g, resulting in less accessible space. The pore size was reduced to 182.726 Å, indicating an alteration in the clay's pore structure.

After the third regeneration cycle and reusability, BABC had a surface area of 53.86 m²/g, pore volume of 0.479 cm³/g, and pore size of 136.543 Å.

A comparison to the original properties shows that both adsorption and regeneration cycles have a decreased surface area, pore volume, and pore size. The surface area decreased from 74.15 m²/g to 53.86 m²/g, and the adsorption sites became less than before. The pore volume declined from 1.11 cm³/g to 0.479 cm³/g, indicating that fewer pores were accessible for adsorbate molecules, and the specific surface area also fell accordingly. The results of the work BABC pore size decreased from 300.20 Å to 136.543 Å, implying that different properties were altered by adsorption and desorption.

The reduced level of surface region, pore volume, and size might be associated with the adsorption of a certain quantity of MB occupied the floor websites as nicely because it crammed dyes into pores. In such cases, the interaction of MB with the clay surface can cause structural changes that could have reduced pore sizes as dye led to some occupation and alteration in the functional groups on the expanded layer surfaces.

Additionally, surface area, pore volume, and size after MB adsorption in BABC have changed as expected due to some projected results from previous works (Azha et al., 2021; Shahadat, 2018; Taylor et al., 2014). Adsorption of MB on clay material results in changes in its porosity and surface characteristics.

ii. FTIR analysis: The FTIR analysis (SPECTRUM 100 PERKIN ELMER) (650-4000 cm⁻¹) results reveal distinct peak patterns for BABC as

shown in Figure 72. These distinctions offer valuable insights into the chemical composition and surface functionality of the materials, presenting substantial proof for the effective development of novel adsorbents with increased efficacy along with economic efficiency.

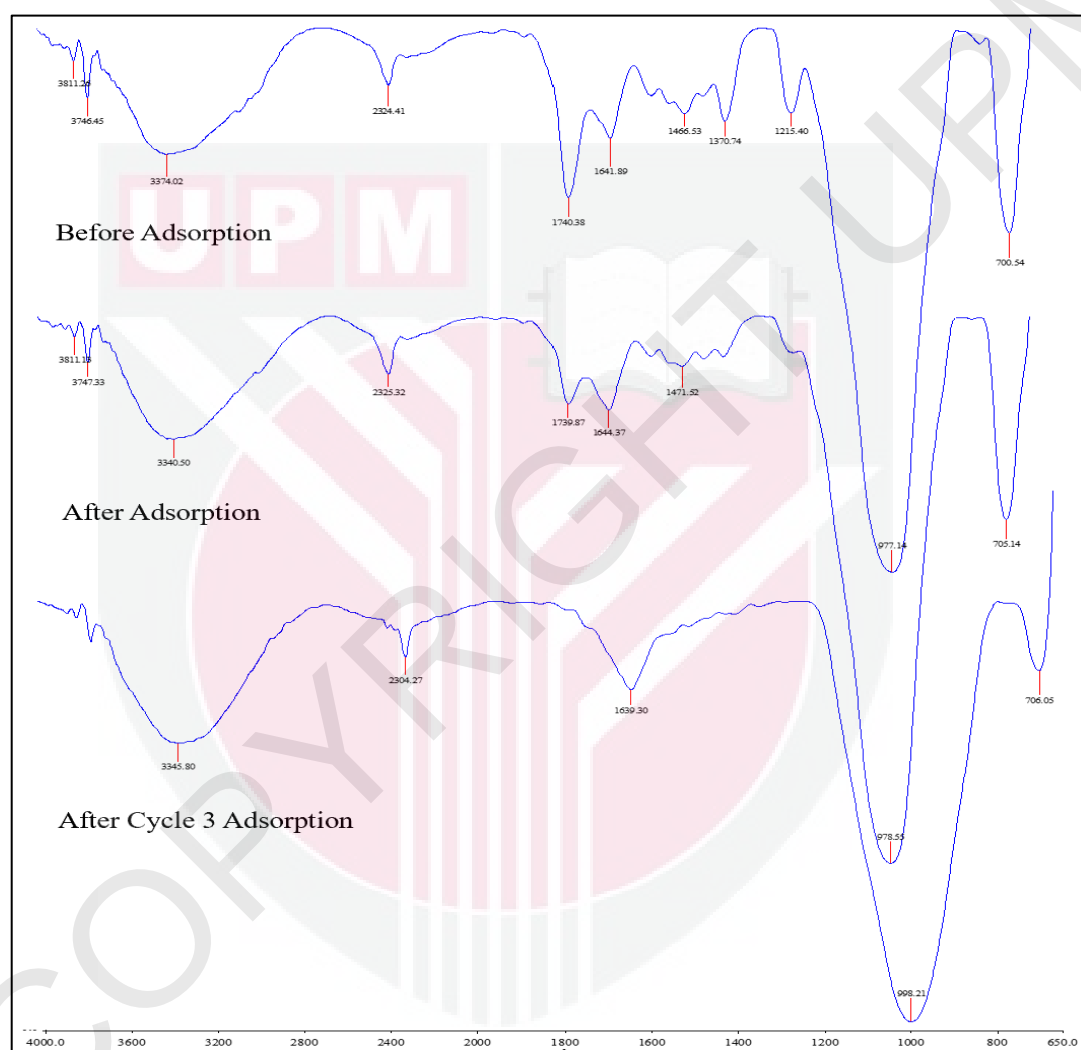


Figure 72 : FTIR of (16M BABC) Before and After Adsorption

The FTIR spectrum of BABC before the adsorption process demonstrated various characteristic peaks because it contains numerous functional groups. The peak at 3811.26 cm^{-1} represents the stretching vibrations of hydroxyl groups that are within the clay structure. The peaks at 3746.45 cm^{-1} , 3374.02

cm^{-1} , and 2324.41 cm^{-1} represent the stretching vibrations of free silanol, hydrogen-bonded hydroxyl, and bonded water on the clay surface. The peaks observed at 1740.38 cm^{-1} , 1641.89 cm^{-1} and 1466.53 cm^{-1} represent carbonyl stretching, Si-O bending of water and C-H bending respectively in line with (Reddy T et al., 2017).

The FTIR spectrum showed that some changes in the IR peaks of a BABC were carried out after adsorption, indicating interactions between the BABC and MB. These shifts and peaks' variations showed changes in the peaks, demonstrating different functional groups' involvement in the adsorption process. The peaks at 3811.13 cm^{-1} , 3747.33 cm^{-1} , and 3340.50 cm^{-1} demonstrated slight changes, showing possible involvement in the hydrogen and silanol interactions with MB.

After the regeneration and reusability using sodium persulfate at high temperatures and stirring, additional changes in the FTIR spectrum were noticed. These shifts and peak variation showed that the adsorbed MB is removed, and the functional groups on the clay are restored. The new peaks at 3345.80 cm^{-1} , 2304.27 cm^{-1} , 1639.30 cm^{-1} , 998.21 cm^{-1} , and 706.05 cm^{-1} infinitesimal indicated reformation of the functional groups, including O-H, Si-OH group, among others, on the clay surface, consistent with (Reddy T et al., 2017; Tabak et al., 2011; Verma & Riaz, 2018).

The structural changes during the adsorption of MB on BABC are reflected in its FTIR spectra, which suggest that not only does MB readily adsorb upon

BABC but certain functional groups play a relatively critical role participating in this process. The forms and intensity of the peaks reveal chemical activities between MB molecules and the clay surface mounts adsorption involved.

The results of the FTIR study give the necessary information to confirm the efficiency of the adsorption process and regeneration as well as reusing basic bentonite clay. Different functional groups play an important role in the adsorption process; therefore, understanding function-specific mechanisms can increase knowledge of this technique and additionally facilitate further improvement.

5.4.6 Comparative study with commercial activated carbon

The present research aimed to study and compare the operation of physically modified BABC adsorbents with that of commercial activated carbon (CAC) for removing MB from water solutions. Several criteria such as removal efficiency, adsorption capacity, BET surface area analysis, and FTIR spectroscopy were employed to compare. The comparison results indicate the feasibility and performances of the functionalized adsorbents compared to CAC. The results help in an improved understanding of MB removal and allow further the application of new, more suitable green adsorption technology.

- i. **BET analysis comparison:** BET result (MICROMERITICS 3FLEX) comparison of specific surface area, pore volume, and size between BABC vs CAC is provided in Table 53 This comparison gives meaningful insights into the porous nature of these materials, as porosity is a very important measurement to evaluate their performance

for elimination of MB and adsorption capacities.

Table 53 : BET comparison of BABC vs. CAC

Adsorbent	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (Å)
BABC	74.14	1.11	300.20
CAC	1000	1	15

Pore size influences the selectivity and adsorption capacity of an adsorbent. For the model CAC, relative to that of BABC (300.20 Å), its pore size is smaller (15 Å), therefore it cannot adsorb as many MB molecules as BABC, and therefore worse adsorption performance than its counterpart was shown.

The large-sized pores of BABC could accommodate larger dye molecules more efficiently, and the diffusion limitation is also minimized without skirmish to available surface area in that regard to improved adsorption kinetics. This is especially crucial for practical applications where it is desirable to quickly eliminate molecular impurities. In other words, the BABC can attract more MB to adhere on its surface which is suggested by a larger pore volume of 1.11 cm³/g compared to CAC of 1 cm³/g indicating that more adsorption sites are available, increasing the overall capacity for MB absorption. As previously stated, the surface of BABC is also altered by introduction to the base, and its chemical structure may incorporate functional groups that can be used to interact more effectively with MB molecules. It is safe to assume that because of these aspects of advantageous pore size, shape, or makeup, BABC is potentially a cheaper, environmentally friendlier alternative to CAC.

ii. **FTIR analysis comparison:** An FTIR study using a SPECTRUM 100 PERKIN ELMER, within the region of cm^{-1} was conducted on both BABC and CAC as illustrated in Figure 73. These spectrum modifications offer important new insights on the potential adsorption capacity of both compounds, by exposing intrinsic differences in terms of molecular structure and surface activity between BABC and CAC.

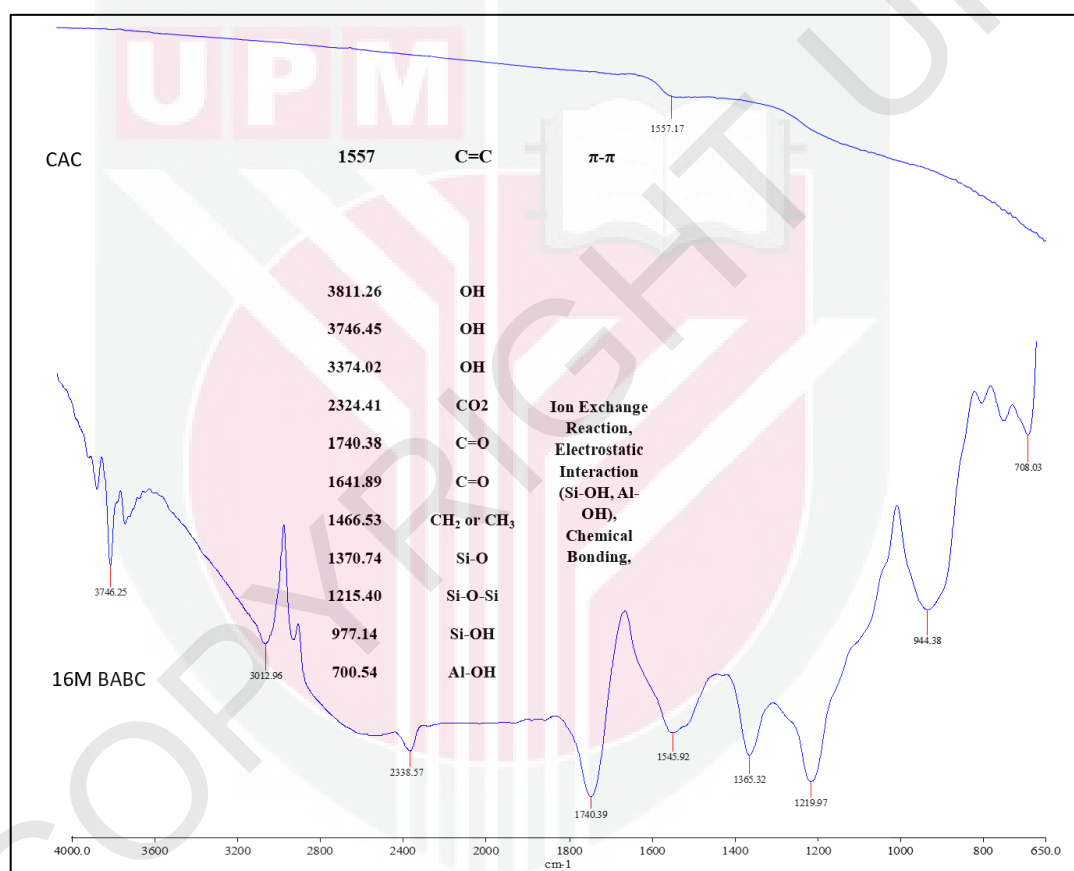


Figure 73 : FTIR Analysis of BABC (16M) vs. CAC

Three main peaks from the FTIR spectra for BABC are observed, at 3811.26 cm^{-1} , 3746.45 cm^{-1} , and 3374.02 cm^{-1} . These spectra show some of the peaks present in silicates, aluminosilicate compounds and may be due to hydroxyl (OH) groups as well, in line with (Reddy T et al., 2017; Tabak et al., 2011;

Verma & Riaz, 2018). These functional groups have been previously reported to improve the adsorptive properties of BABC towards MB and other pollutants. The distinctive peak pattern of the BABC indicates that it could be an economic and alternative adsorbent material.

The positions and intensities of the peaks from FTIR spectra for BABC are different compared to CAC. CAC also had the same peak of a functional group, which indicated that maybe there was more precursor material and several valuable groups in addition (1557.17 cm^{-1}) (Kristianto et al., 2016). The difference in peak patterns of BABC confirms its chemical composition and adsorption characteristics, which is indicative that it has been successfully developed as a potentially improved adsorbent.

In summary, the FTIR analysis confirmed that BABC was successfully synthesized and it possesses surface functional groups favorable for adsorbate-adsorbent interactions. Though the adsorption effectiveness of BABC and CAC components for MB removal is compared; it has been found reasonably good compared to CAC. The larger pore diameters and the more desirable functional groups facilitate that the adsorbent interacts with MB dye, thereby BABC has better potential for competitive removal to some extent than CAC. The rise in efficacy and cost-effectiveness of adsorbent design have made these interesting developments from the perspective of environmental applications, such as wastewater treatment.

iii. Comparison of Adsorption Efficiency and Effectiveness: Optimized

BABC (270-minute, 200 ppm, 25°C, pH of 7, 0.9g) exhibits better adsorption efficiency and efficacy as compared to CAC. As MB final concentrations are lower with BABC than with CAC, this suggests that BABC has a better adsorption capability. As seen in Tables 54 and 55 as well as Figures 74 and 75, BABC also shows greater clearance percentages at each time interval, indicating its improved capacity to remove the dye. The distinct qualities of BABC are responsible for its enhanced performance. In contrast to CAC (1000 m²/g), BABC has a substantially greater pore size of 300.20 Å though has a lesser surface area of 74.14 m²/g. This bigger pore size makes MB molecules easier to access and diffuse inside BABC's porous structure, which boosts the material's ability for adsorption and elimination effectiveness.

Table 54 : Optimized BABC for MB removal (200ppm)

C _i (mg/l)	Abs (nm)	C _e (mg/l)	q _t (mg/g)	Removal %	Time (min)
200	1.416	12.375	20.847	93.812	45
200	1.111	8.137	21.318	95.931	90
200	0.879	6.431	21.507	96.784	135
200	0.463	3.372	21.847	98.313	180
200	0.208	1.497	22.055	99.251	225
200	0.113	0.799	22.133	99.600	270

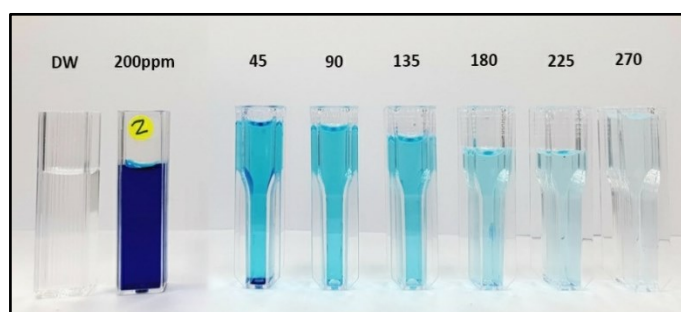
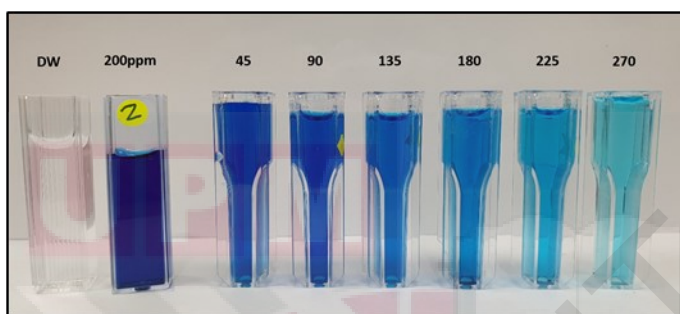


Figure 74 : Optimized BABC Results for 200ppm

Table 55 : CAC vs. BABC for MB removal (200ppm)

C_i (mg/l)	Abs (nm)	C_e (mg/l)	q_t (mg/g)	Removal %	Time (min)
200	2.593	40.079	17.768	79.960	45
200	2.263	21.319	19.853	89.340	90
200	1.918	17.676	20.258	91.161	135
200	1.624	11.909	20.898	94.045	180
200	1.306	9.571	21.158	95.214	225
200	1.058	7.747	21.361	96.126	270

**Figure 75 : CAC vs. BABC Results for 200ppm**

The better performance of BABC is a result of several variables. First of all, the improved adsorption kinetics and decreased mass transfer resistance of BABC are attributed to the expanded pore size distribution that facilitates the easier penetration and diffusion of MB molecules. Larger dye molecules, like MB, whose adsorption would be hampered by CAC's smaller pores, would benefit greatly from this property. Moreover, Hydroxyl ($-OH$) and Aluminosilicates which are rich within the surface of BABC also advocate for bonding strength with MB molecules. Such interactions are hydrogen bonding, electrostatic attraction, and π - π interaction between the benzene ring in MB molecule to BABC molecules which increase the adsorption process for elimination from aqueous solutions. The third pro of BABC is that it is derived from a cheap widely available element as Bentonite clay, ultimately to be an economic method replacement for CAC. In addition, the activation process of

BABC consumes less energy and is more eco-friendly compared with CAC processes that usually adopt high-temperature treatment followed by a chemical activator using harsh chemicals.

Finally, the developed BABC was found to be highly stable and could be easily regenerated after multiple cycles without significant loss of adsorption capacity. The latter property enhances its practicable applicability for consecutive and long-term wastewater treatment operations in which adsorbent reusability and sustainability are of paramount importance. Thus, BABC is an effective and efficient alternative adsorbent to remove MB from the aqueous solution because of its larger pore size, and good surface chemistry cost-effective than CAC. The reported properties act as an added advantage for the application of BABC in wastewater treatment processes, especially for MB dye elimination.

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

In this research, high-quality adsorbents were synthesized by chemical activation in the implementation of methylene blue (MB) dye elimination from aqueous solutions. The ZnCl_2 and $(\text{NH}_4)_2\text{SO}_4$ treated AC was prepared by a two-step method to enhance the surface area in turn increased adsorption properties. Bentonite clay was activated with NaOH to produce active sites for adsorption. Results from the study also suggest promising potentials for these designed adsorbents in MB removal methods and can be utilized as a high-performing yet cost-effective solution for water treatment facilities.

SEM, FTIR, BET, XRF, XRD, CHNOS, and TGA tests were done on activated carbon (AC) and base activated bentonite clay (BABC). The results showed that the AC has a porous structure with interconnected pore networks, which is advantageous for adsorption. The surface area of AC reached $939.63 \text{ m}^2/\text{g}$ with optimal activation dosage $6\text{M } (\text{NH}_4)_2\text{SO}_4$, while BABC has a layered structure and its interlayer spaces favor adsorption; and 16M NaOH was found to be the optimum activation dosage for BABC with a surface area of $74.15 \text{ m}^2/\text{g}$.

AC obtained a high elimination efficiency of 99.91% and an adsorption capacity of 90.827 mg/g with an adsorption duration of 90 minutes, a MB initial concentration of 500 ppm, a temperature of 50°C , a pH of 9, and an adsorbent

dose of 0.55 g chosen based on WHO recommendations for drinking water. The experimental findings were consistent with the Langmuir isotherm and the second-order kinetic model. The adsorption process was found to be endothermic, and the AC adsorbent showed good regeneration capabilities after four cycles.

BABC had a removal effectiveness of 99.593% and an adsorption capacity of 22.131 mg/g after 270 minutes of adsorption at a starting MB concentration of 200 ppm, a temperature of 25°C, a pH of 7, and an adsorbent dosage of 0.9 g determined based on WHO drinking water standards. The Freundlich isotherm and second-order kinetic modes are proper with the experimental information. It is concluded that the adsorption is a spontaneous and exothermic process, with efficient performance of the regeneration of the BABC adsorbent after three consecutive cycles.

The new modified MB adsorbents are contrasted with commercial activated carbon (CAC) adsorbents for the removal effectiveness of MB from aqueous solutions. The removal efficiency is 90 and 50°C temperature, 500 ppm initial concentration, 9 pH, and a 0.55-g adsorbent dose, after adsorbed for 90 minutes gave the greatest removal efficiency and adsorption capacity was 99.715 % and 90.831 mg/g AC. Under the same experimental conditions, CAC had removal efficiency and capacity discharged are 97.220 % and 88.382 mg/g is somewhat less than the AC. By incorporating essential functional groups like hydroxyl O-H and carbonyl C=O functional groups that are structured, this method allows high development of H bond, and raising

the surface reactivity significantly increases MB adsorption.

For BABC under an adsorption cycle of 270 minutes and 7 Pm PH and 25°C 200 ppm initial concentration and 0.9 g of adsorbate what gives pH of the removal efficiency and adsorption capacity of the BACB is 99.600 % and the adsorption capacity was 22.133 mg/g, while CAC recorded an evacuation rate and adsorption capacity under similar conditions of removal effectiveness and capacity for 96.126 % and 21.361 mg/g. The FTIR examination of 16M NaOH-activated BABC revealed peaks representing hydroxyl groups, water molecules, carbon dioxide, carbonyl groups, CH₂ or CH₃ bending, Si-O bending, Si-O-Si bonding, Si-OH stretching, and Al-OH bending, which indicate functional groups required for MB adsorption, with the crucial functional groups including the hydroxyl groups, water molecules, carbonyl groups, CH₂ or CH₃ bending, Si-O bending, Si-O-Si bonding, Si-OH stretching, and Al-OH bending, resulting high improvement and increase significantly in surface reactivity of the MB adsorption.

6.2 Recommendations

Optimize Adsorbents: Enhance activated carbon (AC) and base-activated bentonite clay (BABC) adsorbents for better MB removal by investigating various activation agents, concentrations, and conditions.

Agitation Speed Variation: Investigate the impact of different agitation speeds (more than 135 rpm) on the adsorption efficiency of AC and BABC adsorbents for MB removal. Determine the optimal agitation speed that enhances

adsorption kinetics and overall performance.

Regeneration and Reuse: Study ways to regenerate and reuse adsorbents, exploring desorption methods and assessing their potential for multiple cycles.

Real Wastewater Application: Evaluate AC and BABC adsorbents in treating actual MB-containing wastewater, considering necessary adjustments for effective performance.

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APPENDICES

Appendix A

Table 1 : WHO guidelines for drinking water

Parameter	Group	RECOMMENDED RAW WATER QUALITY	DRINKING WATER QUALITY STANDARDS
		Acceptable Value (mg/litre (unless otherwise stated))	Maximum Acceptable Value (mg/litre (unless otherwise stated))
Total Coliform	1	5000 MPN / 100 ml	0 in 100 ml
<i>E. coli</i>	1	5000 MPN / 100 m	0 in 100 m
Turbidity	1	1000 NTU	5 NTU
Color	1	300 TCU	15 TCU
pH	1	5.5 - 9.0	6.5 - 9.0
Free Residual Chlorine	1	-	0.2 - 5.0
Combined Chlorine	1	-	Not Less Than 1.0
Temperature	1	-	-
<i>Clostridium perfringens</i> (including spores)	1	-	Absent
Coliform bacteria	1	-	-
Colony count 22°	1	-	-
Conductivity	1	-	-
Enterococci	1	-	-
Odour	1	-	-
Taste	1	-	-
Oxidisability	1	-	-
Total Dissolved Solids	2	1500	1000
Chloride	2	250	250
Ammonia	2	1.5	1.5
Nitrat	2	10	10
Ferum/Iron	2	1.0	0.3
Fluoride	2	1.5	0.4 - 0.6
Hardness	2	500	500
Aluminium	2	-	0.2
Manganese	2	0.2	0.1
Chemical Oxygen Demand	2	10	-

Appendix B

i. XRF analysis

Table 2 : XRF Chemical composition of raw and AABC (16M NaOH, 7M H₂SO₄)

Compound	AABC (7M)
SiO ₂	79.121
Al ₂ O ₃	11.920
Na ₂ O	0.089
MgO	0.644
MnO	0.013
ZnO	0.014
K ₂ O	0.121
CaO	0.342
TiO ₂	2.245

ii. BET analysis

Table 3 : Surface area and porosity of optimal AABC sample

Activation	7M
Surface Area (m ² /g)	42.76
Pore Volume (cm ³ /g)	0.106
Pore Size (Å)	121.23

iii. SEM analysis

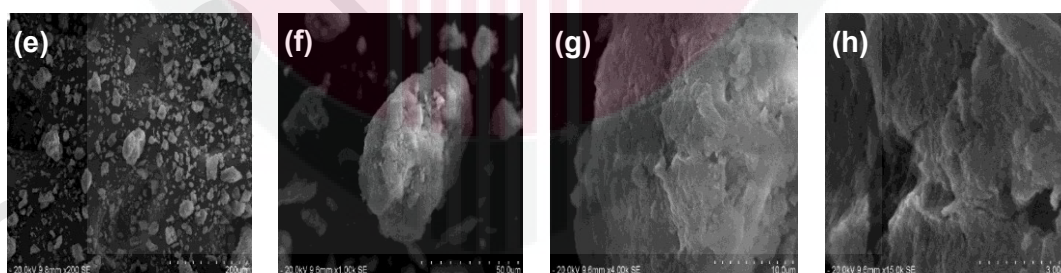


Figure 1 : SEM of AABC (7M) at Different Scales (200µm, 50µm, 10µm, 3µm)

iv. FTIR analysis

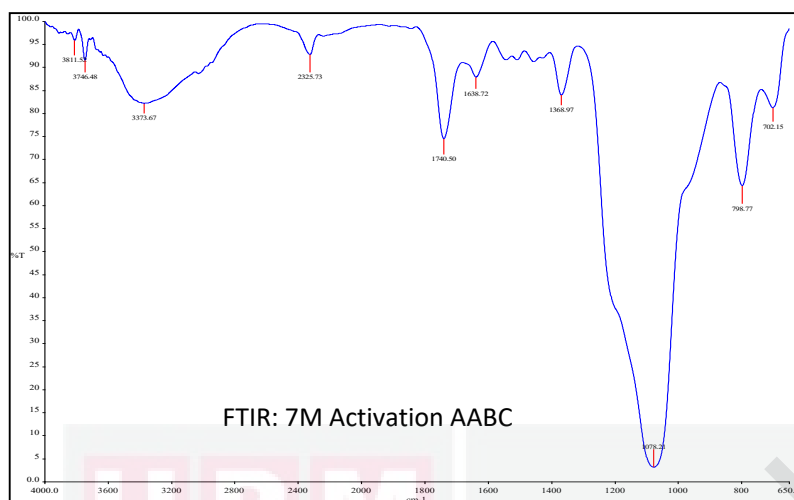


Figure 2 : FTIR of AABC (7M)

The infrared spectrum analysis of the sample revealed several characteristic peaks: 3811.52 cm^{-1} and 3746.48 cm^{-1} , indicating potential presence of hydroxyl groups (O-H) or moisture absorption; 3373.67 cm^{-1} , associated with stretching vibrations of hydroxyl groups (O-H) or water molecules; 2325.73 cm^{-1} , possibly attributed to carbon dioxide (CO_2) or instrumental noise/artifact; 1740.50 cm^{-1} , suggesting the presence of carbonyl groups (C=O) or other functional groups related to organic compounds; 1638.72 cm^{-1} , potentially associated with water bending vibrations or C=O stretching vibrations; 1368.97 cm^{-1} , corresponding to Si-O bending vibrations; 1078.21 cm^{-1} , indicating stretching vibrations of Si-O bonds; 798.77 cm^{-1} , potentially corresponding to Si-O-Si stretching vibrations; and 702.15 cm^{-1} , suggesting Al-OH bending vibrations (Elnaggar et al., 2022; Gandhi et al., 2022).

v. XRD analysis

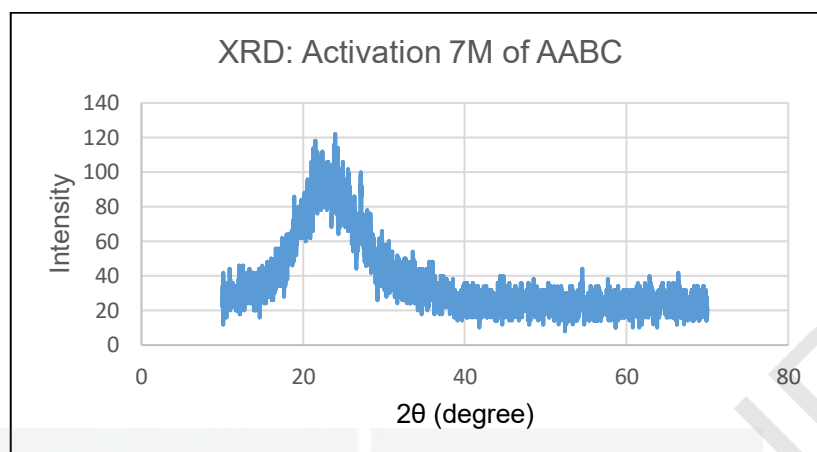


Figure 3 : XRD of AABC (7M)

The X-ray diffraction (XRD) analysis of acid-activated bentonite clay (AABC) activated with a 7M revealed prominent peaks at approximately 23° and 27.1° with intensities of 122 and 100, respectively. These peaks are attributed to SiO₂ (silicon dioxide) and Al₂O₃ (aluminum oxide). The XRD patterns were obtained using XRD6000 SHIMADZU equipment, measuring the diffraction angles at 2θ (degrees). These results are consistent with previous studies by (Tabak et al., 2011).

Appendix C

Calibration

Table 4 : Calibration of MB (0-10ppm)

λ	Absorbance	Concentration
663	0.001	0.01
663	0.003	0.02
663	0.006	0.04
663	0.017	0.08
663	0.025	0.16
663	0.047	0.32
663	0.098	0.64
663	0.192	1.28
663	0.35	2.56
663	0.68	5
663	1.018	7.5
663	1.37	10

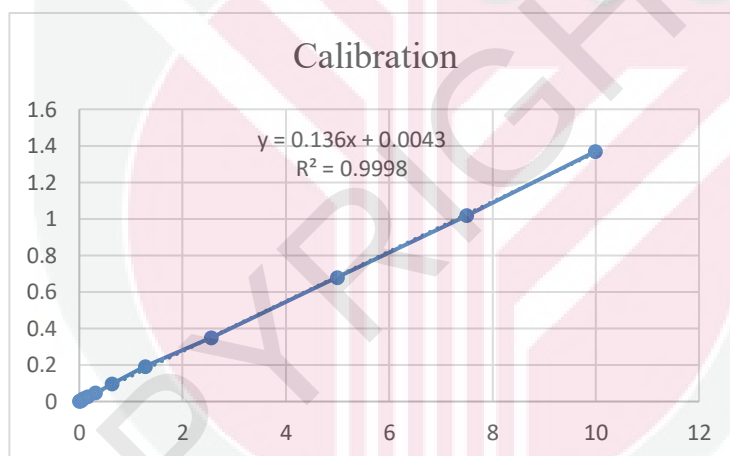


Figure 4 : Calibration graph of MB (0-10ppm)

Table 5 : Calibration of MB (4-20ppm)

λ	Absorbance	Concentration
663	4	0.599
663	8	1.021
663	12	1.4
663	16	1.757
663	20	2.125

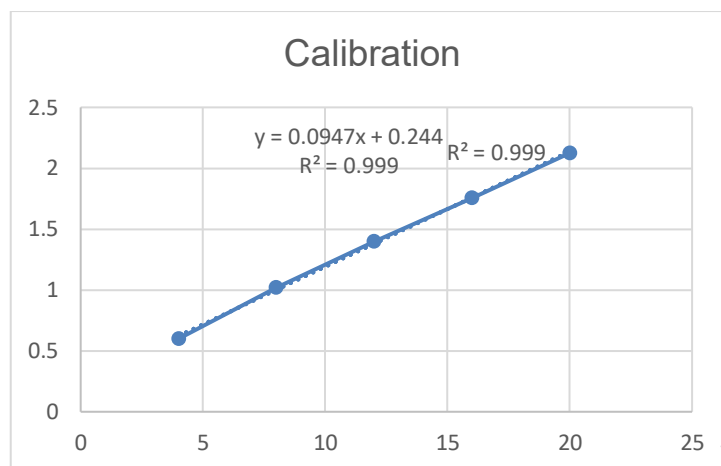


Figure 5 : Calibration Graph of MB (4-20ppm)

Table 6 : Calibration of MB (25-50ppm)

λ	Absorbance	Concentration
663	25	2.498
663	30	2.531
663	35	2.564
663	40	2.594
663	45	2.626
663	50	2.657

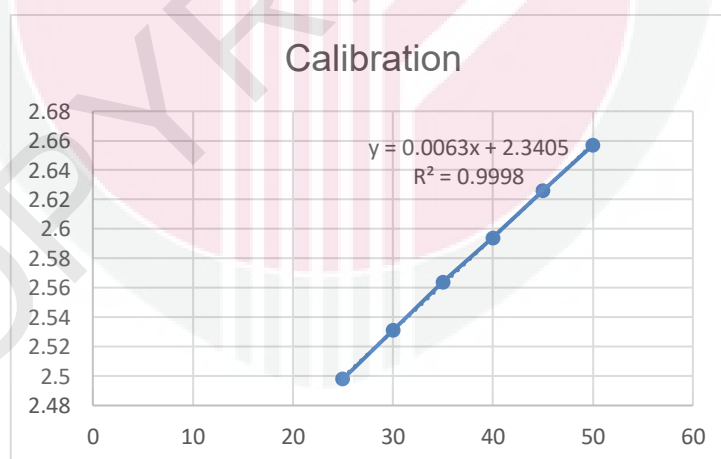


Figure 6 : Calibration graph of MB (25-50ppm)

LIST OF PUBLICATIONS

- Hamad, H. N., Idrus, S., Yusuf, B., & Jamali, N. S. (2024). Enhancing methylene blue removal: synthesis, characterization, and performance evaluation of chemically activated carbon adsorbents. *Process Biochemistry*. **(Published)**
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<https://doi.org/10.3390/pr12040738>
- Hamad, H. N., & Idrus, S. (2022). Recent developments in the application of bio-waste-derived adsorbents for the removal of methylene blue from wastewater: a review. *Polymers*, 14(4), 783. **(Published)**
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