



Democratic and Popular Republic of Algeria
Ministry of Higher Education and Scientific Research



Amar Telidji University-Laghouat

FACULTY: TECHNOLOGY

DEPARTMENT: PROCESS ENGINEERING

MASTER THESIS

Presented by: **Slimi Khira chahinaz & Ben Chettouh Djahida**

DOMAIN: Science and Technology

FIELD: Process Engineering

OPTION: Materials Process Engineering

Theme:

**Bio agricultural waste for the efficient removal
of cationic dye from aqueous system**

JURY MEMBER:

Name and Surname	Grade	Title/Position
Pr. DJEDID Mebrouk	Professor	President
Dr. ALAOUNIA Nadjette	MCB	Examiner
Dr. BOUDAUD Asma	MCA	Supervisor
Ms. BEN YAHIA Fatma	PhD student	Co-Supervisor

Promotion : JUNE 2025

Dedication

To those who, after God, played a vital role in helping me reach this stage...

To my dear parents, the guiding light and source of compassion in my life—thank you for instilling in me values that shaped my path, and for your limitless support throughout every step of my academic and personal journey.

To my beloved siblings, who have always been a pillar of strength and support—I deeply appreciate your love and constant encouragement.

To my sister, Fatima Zahra, whose positive spirit gave me strength and hope through every difficult moment—your words and your smile were an invaluable source of support.

To my dear grandmother, whose sincere prayers have always accompanied me, lighting my path and bringing peace to my heart—may you remain my endless blessing.

To all my respected family members, I send you my deep gratitude and love for your constant support and encouragement.

To my loyal friends, who walked alongside me in this journey filled with both challenges and achievements, my heartfelt thanks for your presence and friendship.

To everyone who left a mark on my heart... I dedicate this humble work to you, as a token of appreciation and loyalty.

Shahinaz

Dedication

*In the name of **Allah**, the Most Gracious, the Most Merciful
All praise is due to **God**, first and last, who granted me strength, patience, and
inspiration to complete this work*

*I dedicate this work to all those who have influenced my journey, whether near or
far, through their love, support, and kind presence...*

*To my dear **mother** and beloved **father**,
Thank you for your sacrifices, prayers, patience, and infinite love.
This work is first and foremost the fruit of your devotion — may it reflect the trust you
placed in me.*

*To my siblings: **Hamza, Brahim, Safouane, and Siham**,
Thank you for always being there, for your constant encouragement, and your
unwavering support.*

*To my dear friends: **Iman, Fatiha ..**
And to all those who shared this path with me...
Your friendship has been a source of strength and light along the way.*

Djahida

Acknowledgments

*First and foremost, we sincerely thank **God** for granting us faith, courage, determination, and a supportive environment, enabling us to complete this modest work under the best conditions.*

*We would like to express our deep gratitude to our supervisor, **Ms. BOUDAUD Asma** and **Ms. BENYAHIA Fatma**, for the trust she placed in us by accepting to guide our work and for her valuable advice throughout the completion of this research.*

*Our sincere thanks also go to **the members of the Process Engineering laboratory**, for their invaluable assistance, expert guidance, and for providing us with the necessary equipment to conduct our experiments.*

*We extend our gratitude to all **the members and professors of the Process Engineering Departement** for the knowledge they have imparted to us throughout our academic journey.*

*Finally, we express our heartfelt appreciation to **our families and friends** for their unwavering support, encouragement, and patience throughout this period of hard work and research.*

Table of Content

Table of Contents

Dedication	
Acknowledgements	
List of Abbreviations	
List of Figures	
List of Tables	
General introduction	1
Chapter 1 : Bibliographic Summary	
1. Introduction	4
2. Wastewaters	4
2.1. Generalities	4
2.2. Types of waste waters	4
3. Waters Pollution by dyes	5
3.1. Generalities on dyes	5
3.2. Classification of dyes	6
3.3. Toxicity of dyes	9
3.4. Current treatment methods for dye removal	9
3.5. Methylene blue dye	11
4. Adsorption	12
4.1. Definition of adsorption	12
4.2. Types of adsorptions	12
4.3. Factors affecting adsorption of dye	14
4.3.1. Effect of solution pH	14
4.3.2. Effect of amount of adsorbent	14
4.3.3. Effect of initial dye concentration and contact time	15
4.3.4. Effect of temperature	15
4.3.5. Effect of ionic strength	15
4.4. Dye adsorption kinetic-study	16
4.5. Adsorption isotherm models	16
4.6. Thermodynamic parameters	16
5. Adsorbents	17
5.1. Generalities on Adsorbents	17
5.2. Low-cost adsorbents for dye removal	17

Chapter 2: Experimental Protocol

1. Introduction	19
2. Materials and reagents	19
2.1. Materials	19
2.2. Reagents	19
3. Preparation of Reagents	19
3.1. Preparation of methylene blue dye	19
3.2. Preparation of NaOH Solution (0.1 M)	20
3.3. Preparation of H ₂ SO ₄ Solution (0.1 M)	20
4. Preparation of biosorbent	20
5. Adsorption experiments	20
5.1. Effect of adsorbent mass	21
5.2. Effect of pH	22
5.3. Effect of initial concentration and contact time	22
5.4. Effect of temperature	23
5.5. Effect of ionic strength	23

Chapter 3: Results and Discussion

1. Introduction	25
2. Calibration curve	25
3. Effect of physico-chemical parameters	26
3.1. Effect of mass	26
3.2. Effect of pH	27
3.3. Effect of contact time and concentration	28
3.4. Effect of temperature	29
3.5. Effect of ionic strength	30
4. Kinetic study	31
4.1. Pseudo first order PFO	31
4.2. Pseudo second order PSO	32
5. Isotherm study	34
5.1. Langmuir Isotherm	34
5.2. Freundlich Isotherm	36
6. Thermodynamic study	38
6.1. ΔH° (Enthalpy Change)	39

Table of Contents

6.2. ΔS° (Entropy Change)	39
6.3. ΔG° (Gibbs Free Energy)	39
7. Comparison Study	40
General Conclusion	42
Bibliographic References	43
Appendix	
Abstract	

List of Abbreviations

Abbreviations	Designation
PS	Peanut Shells
MB	Methylene Blue
C ₀	Initial concentration of adsorbate
C _e	Equilibrium concentrations
V	Volume of solution
M	Mass of adsorbent
M	Molarity
Q	Adsorption capacity
R	Removal efficiency
Min	Minute
Mg	Milligram
H	Hour
λ max	Maximum wavelength
pH	Hydrogen potential
T	Time
T	Temperature
UV-vis	Ultraviolet-visible
Q _e	Quantity adsorbed at equilibrium
K	Kelvin

List of figures

N°	Title	Page
Figure 1.1	Molecular structure of Methylene blue	11
Figure 1.2	Physical and chemical adsorption	13
Figure 2.1	Peanuts Shell preparation steps	20
Figure 3.1	Calibration curve of methylene blue at $\lambda_{\max} = 664 \text{ nm}$ Effect of	25
Figure 3.2	Adsorbent mass (PS) on adsorption (T=25 °C, 150 rpm, C= 100 mg/L, 50 mL, t= 120 min)	26
Figure 3.3	Effect of pH on the adsorption of methylene blue MB (25°C, 100 mg/L, 150 rpm, 0,6 g, 120 min, 50 mL)	27
Figure 3.4	Effect of time and concentration on the adsorption of MB dye (25°C, 100 mg/L, 150 rpm, 1,2 g, 100 mL)	28
Figure 3.5	Effect of the temperature on the adsorption of MB (150 rpm, 0,6 g, 50 mL, 20 min)	29
Figure 3.6	Effect of salts masses on the adsorption removal of MB dye.	30
Figure 3.7	Graphical presentation of PFO for MB adsorption	31
Figure 3.8	Graphical presentation of PSO for MB adsorption	33
Figure 3.9	Modeling of the experimental results of the MB dye using the Langmuir model	35
Figure 3.10	Modeling of the experimental results of the MB dye using the Freundlich model	37
Figure 3.11	Van't Hoff plots of Ln Kd against 1/T	38

List of Tables

N°	Title	Page
Table 1.1	Classification of dyes according to the chemical structure adapted from	07
Table 1.2	Classification of dye based on their chemical nature adapted from	07
Table 1.3	Advantages and disadvantages of dye removal methods	10
Table 1.4	Some physico-chemical properties of MB	12
Table 1.5	Differences between physical and chemical adsorption	13
Table 1.6	Thermodynamic expressions for an adsorption system	16
Table 3.1	parameters for modeling adsorption kinetics using PFO model for MB dye	33
Table 3.2	parameters for modeling adsorption kinetics using PSO model for MB dye	34
Table 3.3	Langmuir constants for MB dye adsorption	37
Table 3.4	Freundlich constants for MB dye adsorption	38
Table 3.5	Thermodynamic parameters of MB dye adsorption	40
Table 3.6	Comparison of peanut shells with other adsorbents for methylene blue dye removal in batch adsorption process	41

GENERAL INTRODUCTION

Protecting water is vital for life on Earth and environmental sustainability . Industrial and metallurgical effluent pollutants are a major source of water pollution each year [1].

Among the most problematic pollutants found in industrial effluents are synthetic dyes, which are widely used across various sectors. Throughout the world, many industries, such as the cosmetic, food, and paper industries, use dyes in large quantities. Most of these dyes are used in the textile industry for their chemical stability and ease of synthesis. The global coloring production is more than 7×10^5 tons per year, with Azo coloration accounting for 60 to 70% of the total [2]. However, there are serious environmental problems with the use of these synthetic dyes .These industrial aqueous effluents may include tinctorial effluents, which may contain chemicals that are toxic to microbial populations as well as toxic or carcinogenic to humans or animals . Therefore, it is important to look for efficient methods and materials for their removal. Many methods have been suggested for wastewater treatment and dyes removal, like adsorption , biodegradation , oxidation , or photocatalytic degradation . Adsorption belongs to the simplest, noncomplicated, and low-cost method for removing various types of pollution, including dyes. Various types of adsorbents such as carbon-based materials [3].

this research aims to find an alternative method for the usage of activated carbon, which was costly to be used commercially for the organic compounds . Therefore, the more cost-effective and widely abundant agricultural waste was investigated for its potentials such as banana peels , sugarcane bagasse, coconut husks, paddy husks and , lime shells, Neem leaves , barley, rice husk and wood dust . The adsorbent material must have high adsorbent characteristics, potentially capable in ion exchange, cheap and easily available [4].

Our study focuses on the adsorption of methylene blue dye from wastewater using a low-cost natural material: peanut shells. The objective is to evaluate the efficiency of this biosorbent in dye removal and study the effects of various factors on the adsorption process.

The study is divided into three chapters:

The first chapter presents the theoretical background related to wastewater, dyes, and adsorption mechanisms.

The second chapter describes the experimental procedures and the preparation of the adsorbent.

The third chapter presents and analyzes the results using kinetic and isotherm models to better understand the adsorption behavior.

Finally ,this study concludes with a general conclusion that summarizes the main results.

Chapter 1.
Bibliographic Summary

1. Introduction

Water pollution by industrial dyes is one of the most significant environmental challenges facing the world today due to its negative impact on ecosystems and human health. Dyes are widely used in various industries, leading to the discharge of large quantities into wastewater, where they are difficult to degrade naturally. Among the effective techniques for removing these pollutants, adsorption stands out as a promising solution due to its high efficiency and low cost. This study aims to explore this technique and its role in improving water quality while highlighting the effects of dyes and different treatment methods.

2. Wastewaters

2.1. Generalities

Wastewater is used water that has been affected by domestic, industrial and commercial use. The composition of all wastewaters is thus constantly changing and highly variable, which is why it is so difficult to pinpoint a singular definition of the word itself.

The composition of wastewater is 99.9% water and the remaining 0.1% is what is removed. This 0.1% contains organic matter, microorganisms and inorganic compounds. Wastewater effluents are released to a variety of environments, such as lakes, ponds, streams, rivers, estuaries and oceans. Wastewater also includes storm runoff, as harmful substances wash off roads, parking lots and rooftops [5]

2.2. Types of waste waters

Often used interchangeably with the term sewage, "sewage" technically denotes any wastewaters which pass through a sewer. Prior to entering a wastewater treatment plant, wastewater is sometimes called raw wastewater or raw sewage.

- a. **Domestic wastewater** originates from activities such as restroom usage, bathing, food preparation and laundry.
- b. **Commercial wastewater** from non-domestic sources, such as beauty salons or auto body repair shops, for example. This wastewater may contain hazardous materials and requires special treatment or disposal.

- c. **Industrial wastewater** originates from industrial or commercial manufacturing processes, such as agriculture, and are usually more difficult to treat than domestic wastes. Industrial wastewater's composition varies on an industry-by-industry basis [5].

3. Waters pollution by dyes

Water is the source of life on the planet's surface. Water safety has become a crucial requirement for safe drinking water as a result of the increase in activities that can pollute water supplies. Every year, thousands of tons of dyes used in industry are discharged into water [6]

3.1. Generalities on dyes

Dyestuffs are hydro or oil-soluble, colored organic chemical compounds that are usually dissolved in water and bound to surfaces or fabrics to impart color to textiles. The majority of dyes are complex organic molecules that are designed to bind strongly to the polymer molecules that make up the textile fiber, and must be able to withstand a wide range of external effects [7].

Dyes as colored organic compounds or mixtures used to color paper, cloth, plastics and leather. The dye substrate must be resistant to washing and stable to light. It is important to note that not all colored materials are dyes, as a dye must be fixed to the material to give it a permanent color [8]

Dyes are usually large aromatic molecules, often with many rings linked together. An aromatic ring structure linked to a side chain in the dye molecule structure is necessary for resonance and hence for the transfer of color [9].

The resonance structures responsible for color are those that cause the shifting or appearance of absorption bands in the visible spectrum of light. In the synthesis of a dye, the correlation of chemical structure and color is achieved by a chromogen-chromophore-auxochrome combination.

Three essential groups can be found in a dye molecule: the chromophore, auxochrome and matrix [10]. Thus, dyes are organic colorants that contain at least one unsaturated compound (chromophores) and one functional group (auxochromes). The chromophore present in the

structure may be an aromatic structure containing benzene, naphthalene, or anthracene rings. The chromophore group responsible for the color formation is represented by the following radicals: azo ($-N=N-$); carbonyl ($=C=O$); carbon ($=C=C=C=$); carbon-nitrogen ($>C=NH$ or $-CH=N-$); nitroso ($-NO$ or $N-OH$); nitro ($-NO$ or $=NO-OH$); and sulfur ($>C=S$, and other carbonsulfur groups).

These, in combination with a chromogen, form the basis for the chemical classification of dyes. Since the chromogen-chromophore structure is often insufficient to provide adequate solubility and thus the dye cannot adhere to the fiber of the material, auxochromes are required. Auxochromes enhance the color of the dye.

Auxochromes, also known as binding affinity groups, can be amine ($-NHX_2$), hydroxyl ($-OH$), carboxyl groups ($-COOH$), aldehydes ($-CHO$), sulfonic acid ($-SO_3H$) or their derivatives [7].

3.2. Classification of dyes

There are several ways for classification of commercial dyes. It can be classified in terms of structure, colour and application methods [11]. However, due to the complexities of the colour nomenclature from the chemical structure system, the classification based on application is often favourable [12].

The classification based on chemical structure for the common class of the dyes is presented in Table 1.1. Table 1.2 represents the different applications based on classification. Other than the above, dyes are also usually classified based on their particle charge upon dissolution in aqueous application medium such as cationic (all basic dyes), anionic (direct, acid, and reactive dyes), and non-ionic (dispersed dyes) [11].

Table 1.1 : Classification of dyes according to the chemical structure adapted from [13].


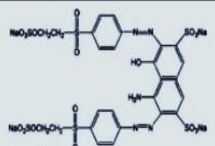
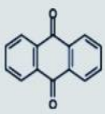
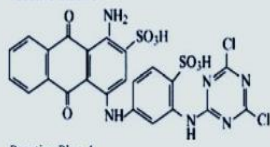
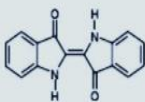
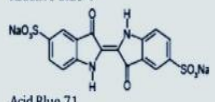

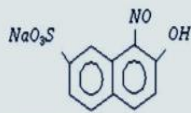

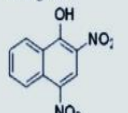
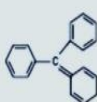
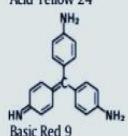
Class	Chromophores	Example
Azo dyes		 Reactive Black 5
Antraquinone dyes		 Reactive Blue 4
Indigoid dyes		 Acid Blue 71
Nitroso dyes		 Acid green 1
Nitro dyes		 Acid Yellow 24
Triarylmethane dyes		 Basic Red 9

Table 1.2 (A) : Classification of dye based on their chemical nature adapted from [14].

Class	Substrate	Method of application	Chemical types
Acid.	Wool, nylon, silk, inks, leather and paper.	Generally from neutral to acidic bath	Antraquinone, xanthene, azo (including, nitroso, premetallised), nitro, and triphenylmethane.
Basic	Basic Inks, paper, polyacrylonitrile, treated nylon, and polyester	Applied from acidic dye baths	Hemicyanine, azo, cyanine, diazahemicyanine, azine diphenylmethane, xanthene, triarylmethane

Table 1.2 (B) : Classification of dye based on their chemical nature adapted from [14].

Direct	Nylon, rayon, paper, leather and cotton	Applied from neutral or a little alkaline bath containing additional electrolyte	Phthalocyanine, azo, oxazine, and stilbene
Disperse	Polyamide, acrylic polyester, acetate, and plastics	Fine aqueous dispersions often applied by high temperature/ pressure or lower temperature carrier methods; dye may be padded on cloth and thermo fixed	Benzodifuranone, azo, anthraquinone, nitro, and styryl
Reactive	Wool, cotton, silk and nylon.	Reactive site on dye reacts with functional group on fibre to bind dye covalently under influence of heat and pH.	Anthraquinone, formazan, phthalocyanine, azo, oxazine and basic
Sulphur	Rayon and cotton	Aromatic substrate vatted with sodium sulphide and reoxidised to insoluble sulphur-containing products on fibre	Indeterminate structure
Vat	Wool and cotton	Water-insoluble dyes solubilised by dropping in sodium hydrogen sulphite, then exhausted on reoxidised and fibre.	Indigoids and anthraquinon

3.3. Toxicity of dyes

Basic dyes have high intensity of colours and are greatly visible even in very little concentration. The complex dyes are generally chromium based, which is carcinogenic. Dyes may affect the photosynthetic activity in aquatic life due to decreased light penetration and may also be toxic to some aquatic life due to the presence of metals, aromatics, etc. . Furthermore, dyes are also carcinogenic, mutagenic, or teratogenic in various microbiological, fish species. Additionally it can also cause severe damage to human beings such as dysfunction of the kidney, reproductive system, liver, brain and central nervous system .

Azo dyes are toxic because of the presence of toxic amines in the effluent . Similarly anthraquinonebased dyes are most resistant to degradation and remains colour for a large time in effluents . Reactive dyes are water soluble and 5–10% of the dyes go in the dye bath giving highly coloured effluent causing serious troubles in the environment . Additionally, reactive dyes that are chemically stable and having little biodegradability are likely to pass through conventional treatment plants untreated, so their elimination is of great importance. Due to their toxic effects, dyes have generated much concern regarding its use. It has been informed to cause mutagenesis, chromosomal fractures, carcinogenesis, and respiratory toxicity. Therefore focuses on specific methods and technologies to remove dyes from different kinds of wastewater streams are desired [11]

3.4. Current treatment methods for dye removal

There are numerous methods to treat dye bearing effluents. In spite of the availability of many techniques to remove dye contaminants from wastewaters, such as coagulation, chemical oxidation, membrane separation process, electrochemical and aerobic and anaerobic microbial degradation, each of these methods have inherent limitations. The technologies can be divided into three categories: physical, chemical and biological [15]. All of these methods have their own advantages and disadvantages. Table 1.3 shows the advantages and disadvantages of different dye removal methods.

Table 1.3 : Advantages and disadvantages of dye removal methods [16]

Methods	Advantages	Disadvantages
Chemical Methods		
Oxidative process	Simplicity of application	(H ₂ O ₂) agent needs to activate by some Means
Ozonation	Ozone can be applied in its gaseous state and does not increase the volume of wastewater and sludge	Short half-life [20 min]
Fenton's reagent	Fenton's reagent is a suitable chemical means	Sludge generation
Sodium hypochloride [NaOCl]	Initiates and accelerates azo-bond cleavage	Release of aromatic amines
Electrochemical destruction	No consumption of chemicals and no sludge build up	Relatively high flow rates cause a direct decrease in dye removal
Biological Methods		
Decolorization by white-rot fungi	White-rot fungi are able to degrade dyes using enzymes	Enzyme production has also been shown to be unreliable
Adsorption by living/dead microbial biomass	Certain dyes have a particular affinity for binding with microbial species	Not effective for all dyes
Anaerobic textile dye bioremediation systems	Allows azo and other water-soluble dyes to be decolorized	Anaerobic breakdown yields methane and hydrogen sulphide
Other microbial	Decolorized in 24–30 h	Under aerobic conditions cationic

cultures [Mixed bacterial]		dyes are not readily metabolized
Physical Methods		
Adsorption by activated carbon	Good removal of wide variety of Dyes	Cost of activated carbon
Membrane filtration	Removes all dye types	Concentrated sludge production
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Irradiation	Adsorbent loss, effective oxidation at lab scale	Requires a lot of dissolved O ₂
Electro-kinetic coagulation	Economically feasible	High sludge production

3.5. Methylene blue dye

Methylene blue dye is a heterocyclic aromatic chemical compound with a planar structure .It has a molceular weight and chemical formula of 319.85 g/mol and C₁₆H₁₈N₃Sl (Fig. 1), respectively . MB dye is a prevalent blue, cationic, and thiazine type of dye that has been widely applied in the textile industry as a fiber coloring agent , and also in the field of medicine as staining agents, and for prophylactic and therapeutic purposes.Table1 presents the extensive details of the other physicochemical properties of MB dye are presented . [17]

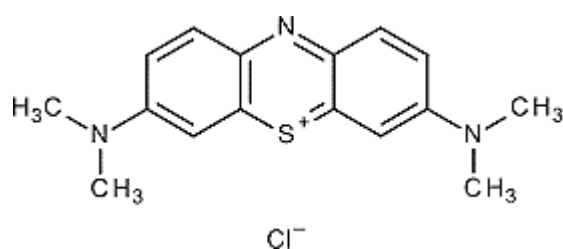


Figure 1.1: Molecular structure of Methylene blue [18]

Table 1.4: Some physico-chemical properties of MB [17].

Parameters	Values/names
Maximum wavelength of absorption (λ_{max})	664 nm
Another name	Swiss blue
Ionization	Basic
Degree of solubility	3.55%
Color index name	Basic blue 9
Color index number	52015
Aqueous pH	Strongly acidic between pH 2.0–3.5

4. Adsorption

4.1. Definition of adsorption

Adsorption is a phenomenon that describes the interaction between two different phases that forms an interface layer by transfer of a molecule from a fluid bulk (liquid or gas) to a solid surface [19]. the process of adsorption can be physical or chemical.

Adsorption is a process in which pollutants are adsorbed on the solid surface. Basically, it is a surface phenomenon and adsorption takes place by physical forces but, sometimes, weak chemical bondings also participate in adsorption process. A molecule (pollutant) adhered to the solid surface is called an adsorbate, and the solid surface as an adsorbent. Adsorption is controlled by various parameters such as temperature, nature of the adsorbate and adsorbent, and the presence of other pollutants along with the experimental conditions (pH, concentration of pollutants, contact time, particle size, and temperature) [20].

4.2. Types of adsorption

4.2.1. Physic-Adsorption

As result of the bonds that those atoms have with the neighboring atoms of the same substance. Adsorption is carried out on such surfaces through natural attractive forces or the so-called vander waals forces (3). This type of adsorption can be in the form of multiple layers of the adsorbent material on the surface of the adsorbent material when suitable conditions of

pressure and temperature are available. The adsorbent and the adsorbent, which is estimated at less than (40 kJ/mol), therefore, this type of adsorption does not need high temperatures and does not require activation energy and occurs at low temperatures similar to the process of condensation of vapors on the surfaces of liquid materials [21].

4.2.2. Chemical Adsorption

This type of adsorption occurs on surfaces that are not electronically unsaturated, as such surfaces tend to form chemical bonds with the atoms or molecules that have been adsorbed. As a first step in the chemical reaction that occurs between the adsorbent surface and the adsorbent material, this type of adsorption needs a high activation energy, as well as the accompanying temperatures are high and estimated in a quantity greater than ((40 kJ/mol), and this type of adsorption is specific and is not reversed and limited by its layer Oxygen adsorption on coal surface, hydrogen chloride adsorption on iron surface. The Factors affecting on Adsorption [21].

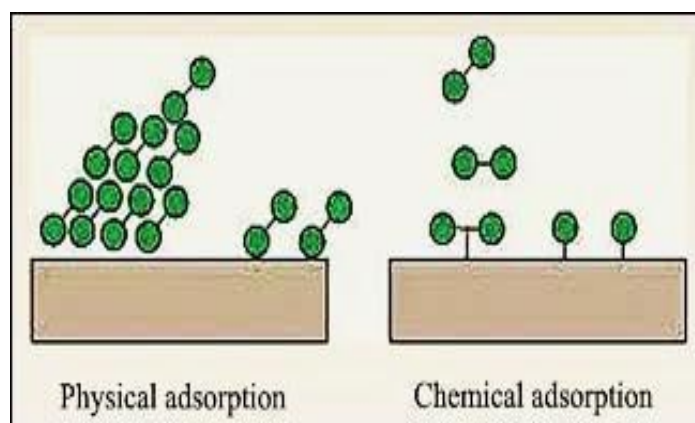


Figure 1.2: Physical and chemical adsorption [21].

Table 1.5: Differences between physical and chemical adsorption [19].

Criteria	Physical Adsorption	Chemical Adsorption
Specificity	Non-specific.	Highly-specific
Nature of adsorption	Depend on nature of adsorbent.	Depend on nature of adsorbent.
Reversibility	Reversible process.	Mainly irreversible
Enthalpy	Low (20-40 kJ/mol).	Higher than physical adsorption

		(40-300 kJ/mol).
Activation energy	Does not require high activation energy.	Require high activation energy.
Layer of adsorption of interfacial region (saturation)	Multi layers.	Mono layer.
Bonding	Weak Van der Waals, London forces, and dipole-dipole attraction This attraction has longer range than chemical type, and there is no chemical composition change for substrate.	Strong ionic bond, or covalent bond formed between substrate and adsorbent, there is a chemical composition change. This attraction has shorter range than the physical type.

4.3. Factors affecting adsorption of dye

4.3.1. Effect of solution pH

According to several papers, the key parameter in almost all adsorption processes is the pH of the dye solution. This factor affects the capacity of the adsorbent and the efficiency of the process. The pH affects the solution chemistry of contaminants, the activity of functional groups in the adsorbent, the competition with coexisting ions in the solution, and the surface charge of the adsorbent. The pH of the aqueous medium can also influence the properties of the adsorbent, the adsorption mechanism, and the dissociation of dye molecules. Not only the adsorbent but also the chemical structure of the dye can be altered by the pH of the solution. The pH changes the surface charge and the degree of ionization of the adsorbed ion [7].

4.3.2. Effect of Amount of adsorbent

The amount of adsorbent is an important parameter for determining the adsorbent capacity for a given amount of adsorbent under operating conditions. In general, the percentage of dye removal increases with increasing the amount of adsorbent with increasing the number of adsorption sites on the adsorbent surface. The effect of the amount of adsorbent material presents

an idea for the adsorption process, which is economically viable [16].

4.3.3. Effect of Initial Dye Concentration and contact time

The initial dye concentration is perhaps one of the most important factors influencing the adsorption process, as it indirectly affects the efficiency of dye removal by reducing or increasing the availability of binding sites on the adsorbent surface [7].

Generally, dye removal rate increase with an increase in contact time to a certain extent. Due to deposition of dyes on the available adsorption site on adsorbent material, any further increase in contact time will not increase the uptake [22]. At this point, the amount of dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of dye being adsorbed onto the adsorbent. The time required to attain this state of equilibrium is termed the equilibrium time and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions [23].

4.3.4. Effect of temperature

Temperature is another important parameter in the physico-chemical adsorption process due to the fact that the amount of adsorbent capacity can be related to the process temperature. If the amount of adsorption sites increases with increasing temperature, this indicates that the adsorption process is endothermic. This may be due to the increment of the mobility of dye molecules, as the number of active sites for adsorption increases with increasing the process temperature. On the other hand, there are several adsorption processes in which increases in temperature adsorption capacity have declined, indicating the exothermic adsorption process. In this kind of adsorption, the adsorption forces between the dye species and the active sites on the adsorbent surface decreased, resulting in a decrease in the adsorption process [24]

4.3.5. Effect of ionic strength (IS)

A recent studies have shows that ionic strength has a significant impact on the adsorption process, especially in systems involving electrstatic interactions between the adsorbent surface and the adsorbate. an increase in IS compresses the electrical double layer, which can either weaken or enhance adsorption depending on the charge characteristics of the interacting species

[25, 26]; additionally coexisting ions may compete with target molecules for active sites, leading to reduced adsorption efficiency in some cases [27, 28]

4.4. Dye adsorption Kinetic-study

The controlling mechanisms of adsorption process such as chemical reaction, diffusion control or mass transfer coefficient are used to determine kinetic models. The kinetics of dye adsorption onto adsorbent materials is prerequisite for choosing the best operating conditions for the full-scale batch process. The study of adsorption kinetics illustrates how the solute uptake rate and obviously this rate control the residence time of the adsorbate at the solution interface. This rate is most importance when designing the adsorption system and this rate can be calculated from kinetic study.

4.5. Adsorption isotherm models

The adsorption isotherms describe the pathway of the interaction of a substrate from the bulk solution to the surface of adsorbate. It represents a relation between the amount of substrate adsorbed per unit mass of adsorbent and the substrate concentration or pressure in the bulk solution at a fixed temperature, for this study both Langmuir and Freundlich modesls areinvestigated [30]

4.6. Thermodynamic parametres

Thermodynamic parameters such as ΔG (Gibbs free energy change), ΔH (enthalpy change) and ΔS (entropy change) are among the most important features involved in establishing an adsorption system. Its original concepts assume that energy cannot be gained or lost, which entropy change is the driving force in an isolated system. ΔG (Gibbs free energy change), ΔH (enthalpy change) and ΔS (entropy change) for a particular system can be computed according to the thermodynamic equations in Table 1.6[29].

Table 1.6: Thermodynamic expressions for an adsorption system [29]

Expression	Equation	Parameters
Arrhenius	$\ln K = \ln A - \frac{E}{RT}$	Apparent activation energy
Gibbs	$\Delta G = -RT \ln K$	Free energy change Enthalpy change

Van't Hoff	$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$ <p>With</p> $K_d = \frac{q_e}{C_e}$	
-------------------	--	--

5. Adsorbents

5.1. Generalities on Adsorbents

An adsorbent is a solid material that allows liquid or gaseous molecules to bind to its surface. Adsorbent's performance depends on the chemical and physical properties of the adsorbent surface, as well as that of the soluble substances. Characteristics of a suitable adsorbent material should include a large surface area and a minimum volume. Other features must consist of high mechanical strength, chemical and thermal stability, high porosity and small pore diameter resulting into more exposed surface area and hence suitable surface chemistry giving rise to high adsorption capacity. Adsorbents can be modelled as pellets, rods, mouldings, or monoliths to fit the required application. Many materials have been used for adsorbents for various applications such as treatment of water, separation, catalysis, indicators, and desiccants. Some commonly used adsorbents include agriculture and industrial wastes, activated carbon, clays, biopolymers and nanomaterials [34].

5.2. Low cost adsorbents for dye removal

Selection of the precursor for the development of low cost adsorbents depends on many factors. The precursor should be freely available, in-expensive and non-hazardous in nature. In recent times, attention has been focused on different natural solids, which are able to remove pollutants from contaminated water at low cost. Cost is an important parameter for comparing the sorbent materials. In general, a sorbent can be assumed to be "low cost" if it requires little processing and is abundant in nature, or waste material from another industry, which has lost its economic or is a by-product or further processing values. There are many low cost adsorbents that have been used for the removal of dyes. Also certain waste products from industrial and agricultural operations, natural materials and biosorbents represent potentially economical alternative sorbents. Many of them have been tested and proposed for dye removal. Waste treatment by adsorption using low cost adsorbent is a demanding area as it has double benefits i.e. water treatment and waste management [11].

Chapter 2.

Experimental Protocol

1. Introduction

In order to perform standard batch adsorption experiments of methylene blue on the adsorbent, we first prepared the peanut shells. The purpose of this study was to illustrate the practicality, efficiency, speed, behaviour at high temperature of this adsorbent.

2. Instruments and reagents

2.1. Instruments

- ✓ pH meter
- ✓ stirred batch (ST 30)
- ✓ Drying Oven (MEMMERT)
- ✓ Analytical Precision Balance (SCALTEC)
- ✓ UV-Visible Spectrophotometer (SECOMEM)
- ✓ Magnetic Stirrer

2.2. Reagents

- Methylene blue
- Sulfuric acid (95%).
- Sodium hydroxide (98%).

3. Preparation of reagents

3.1. Preparation of methylene blue dye

To prepare a methylene blue solution, with a concentration of 1000 ppm, weigh 1 g of methylene blue powder using an analytical balance, then transfer the dye to a 1L volumetric flask. Add a small amount of distilled water and stir the solution until the methylene blue dissolves completely. Then, gradually add distilled water until the volume reaches the calibration mark, and thoroughly mix the solution to ensure uniform distribution of the dye.

3.2. Preparation of NaOH solution (0.1 M)

To prepare a **0.1 M** sodium hydroxide solution, 0,4 grams of sodium hydroxide ($M = 40$ g/mol, 98% purity) were weighed and dissolved in 100 mL of distilled water.

3.3. Preparation of H₂SO₄ solution (0.1M)

To prepare a 0.1 M sulfuric acid solution, 0.2805 mL of concentrated sulfuric acid ($M = 98$ g/mol, 95% purity, density = 1.84 g/mL) was taken and diluted in 100 mL of distilled water.

4. Preparation of biosorbent

To prepare biosorbent, several essential steps are carried out to enhance their physical and chemical properties, aiming to improve their efficiency in removing pollutants from water.

Specifically, the dirt particles on the surfaces of the materials were removed by washing with distilled water, and the materials were then dried at 105°C for 1 day until the water evaporated. and grounded to obtain uniform size particles.

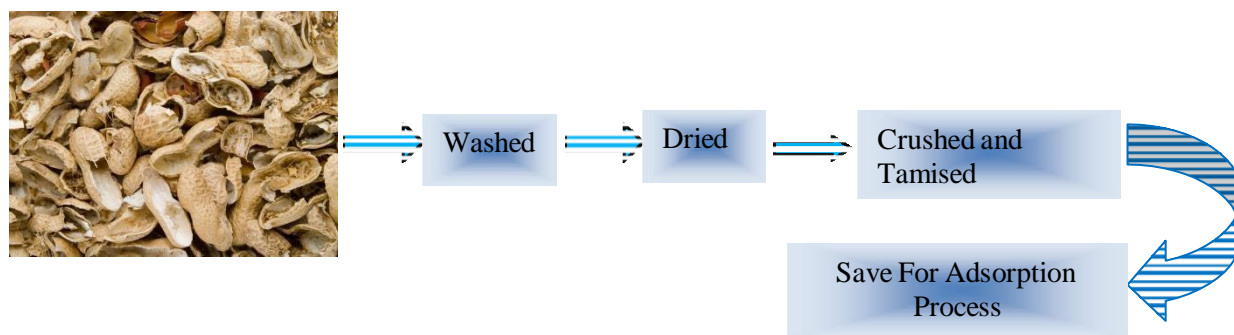


Figure 2.1: Biosorbent preparation steps

5. Adsorption experiments

Solutions of various concentrations were prepared from a stock solution with an initial concentration of 1000 ppm. These solutions were then subjected to the adsorption process using a biosorbent under varying experimental conditions. The parameters studied included the mass of the adsorbent, temperature, agitation speed, pH, initial concentration of the adsorbate, and different contact times [29]

Additionally, the effect of possible ionic interactions between the adsorbent and the adsorbate was investigated. After the contact between the solution and the biosorbent, absorbance measurements were carried out using a UV-Visible spectrophotometer (UV-Vis), which allowed for the calculation of the removal efficiency (%) using the following equation:

$$R(\%) = (C_a / C_0) \times 100 \quad (1)$$

Where:

C_0 : Initial concentration of the adsorbate (mg/L),

C_a : Concentration at a specific time (mg/L)

The amount of adsorbate adsorbed per unit mass of biosorbent was also calculated using the following equation:

$$Q \text{ (mg/g)} = (C_a/m) \times V \quad (2)$$

Where:

Q : Amount of adsorbed substance at time (mg/g),

V : Volume of the solution (L)

m : Mass of the biosorbent (g)

5.1. Effect of adsorbent mass

In this study, the focus was on evaluating the effect of the amount of biosorbent used on the efficiency of methylene blue dye removal from the solution. The experiment was carried out using different biosorbent masses (0.05:1gram). The experimental conditions included an initial dye concentration of 100 ppm, a temperature of 25°C, a neutral pH (pH = 7), a

constant stirring speed of 150 rpm, a contact time of two hours, and a solution volume of 50 milliliters. The aim of this part of the study was to determine the optimal biosorbent mass that achieves the highest adsorption efficiency under the specified conditions.

5.2. Effect of pH

pH is considered one of the key factors influencing the adsorption behavior. Therefore, a series of experiments was conducted to investigate the effect of pH on the removal of methylene blue dye using a biosorbent. The experiments were carried out using a fixed solution volume of 50 mL, containing 0.6 grams of the adsorbent and an initial dye concentration of 100 ppm. The temperature (25°C), contact time (2 hours), and stirring speed (150 rpm) were also maintained constant. The pH values (2,4,5.25,7.46,8.2,10.3,11.04,12.23) were adjusted using 0.1 M solutions of NaOH and H₂SO₄ in order to evaluate the adsorption performance across a wide range of acidic and alkaline conditions, and to determine the optimal pH level for achieving maximum adsorption efficiency.

5.3. Effect of initial concentration and time contact

In this part of the study, the effects of both contact time and initial concentration of methylene blue dye on the performance of the adsorption process using a biosorbent were evaluated. The experiments were conducted using a fixed biosorbent mass of 1.2 grams in a solution volume of 150 mL, while maintaining a neutral pH (pH = 7) and a constant stirring speed of 150 rpm. Dye solutions with different initial concentrations (20,60,100 ppm) were prepared, and instant samples were collected at specific time intervals (1,2,3,5,10,15,20,25,30,45,60,90,120,150,180 min) by withdrawing 5 mL of the solution using a syringe, followed by filtration to analyze the remaining dye concentration. All experiments were performed at a constant temperature of 25°C. This part of the experiment aimed to study the evolution of the adsorption process over time and to determine the impact of initial concentrations on removal efficiency, in order to identify the optimal operating conditions.

5.4. Effect of temperature

The effect of temperature on the adsorption of methylene blue dye using a biosorbent was studied in order to evaluate how thermal variations influence adsorption efficiency. The experiments were carried out using a fixed biosorbent mass of 0.6 grams in a solution volume of 50 mL, with a pH of 7.46. A constant contact time of 20 minutes was maintained, and different initial dye concentrations (20, 60, and 100 ppm) were used. The experiments were conducted at three different temperatures: 25, 40, and 50°C.

5.5. Effect of ionic strength

This part of the study focused on evaluating the effect of ionic strength on the adsorption of methylene blue dye using a biosorbent, through the addition of varying amounts of two different salts: sodium chloride (NaCl) and sodium sulfate (Na₂SO₄). The experiments were conducted under fixed conditions, using a biosorbent mass of 0.6 grams in a 50 mL solution, with a pH of 7.46, an initial dye concentration of 100 ppm, and a contact time of 20 minutes. Solutions were prepared with different salt quantities (1, 3, and 5 grams) to investigate the influence of ionic strength resulting from differences in ion type and charge.

The choice of NaCl and Na₂SO₄ aimed to compare the effects of monovalent ions (Na⁺ and Cl⁻) versus divalent ions (SO₄²⁻), and to determine how these ions affect the surface charge balance of the biosorbent, and consequently, the efficiency of the adsorption process

Chapter 3.

Results And Discussion

1. Introduction

The removal of dyes from wastewater is a critical process in environmental engineering. This chapter investigates the factors influencing the adsorption of Methylene Blue (MB) dye, focusing on variables such as adsorbent dosage, pH, temperature, contact time, and ionic strength. It also explores the kinetics, isotherms, and thermodynamics of the adsorption process, providing valuable insights into its efficiency and practical applications.

2. Calibration curve

The calibration curve method is considered a precise and reliable approach, especially in dye adsorption applications;

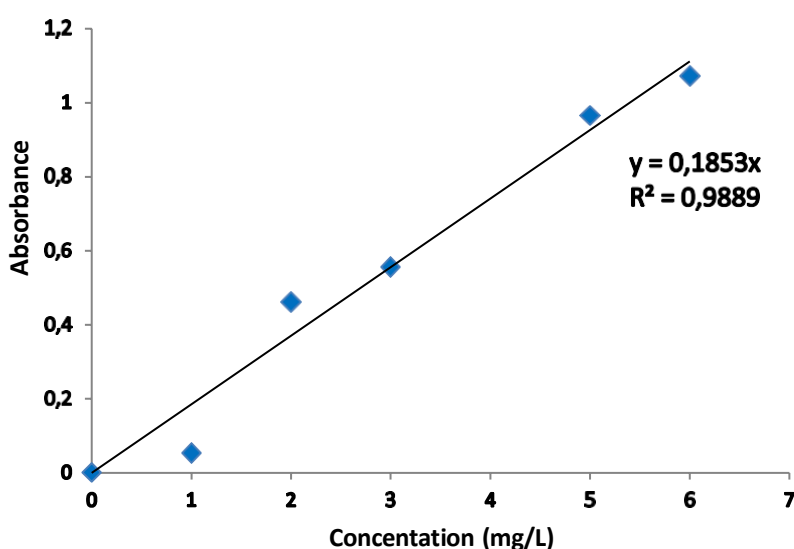


Figure 3.1: Calibration curve of methylene blue at $\lambda_{\max} = 664 \text{ nm}$

Standard solutions of Methylene Blue (MB) dye with concentrations ranging from 1 to 6 ppm were prepared, and their absorbance was measured using a UV-Visible spectrophotometer at a wavelength of **664 nm**. The resulting calibration curve showed a linear relationship between absorbance and concentration, confirming the applicability of Beer–Lambert's law [35, 36].

The resulting equation in **Figure 3.1** is:

$$y = 0.1853x \quad (1)$$

where

y is the absorbance measured,

x is the dye concentration in mg/L,

$R^2 = 0.9889$, indicating a strong fit of the data to the linear model. A straight-line equation with a high correlation R^2 was derived and used to determine unknown concentrations. The high R^2 value shows that the calibration curve is reliable and accurate.

3. Effect of physico-chemical parameters

3.1. Effect of mass

In adsorption experiments, the effect of mass is one of the key factors influencing dye removal efficiency. The amount of adsorbent dosage was varied in the given range from 0.05 to 1 g.

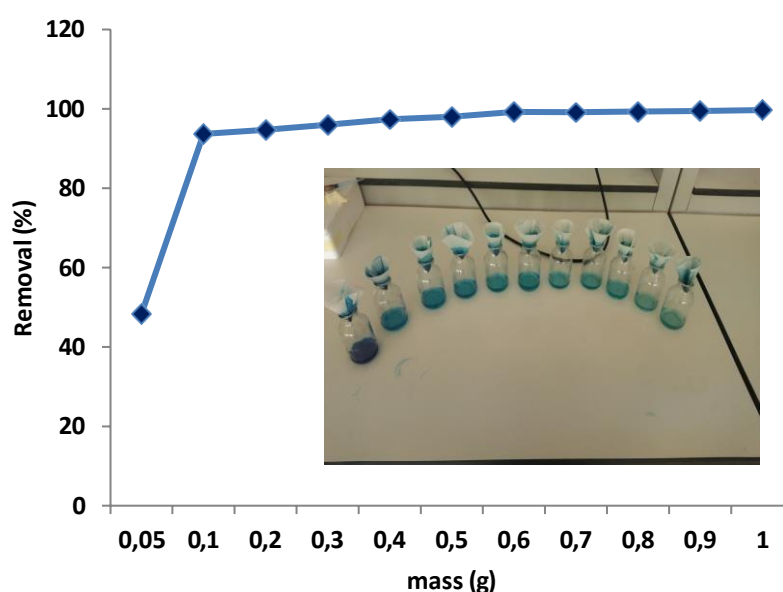


Figure 3.2: Effect of adsorbent mass (PS) on adsorption ($T=25\text{ }^{\circ}\text{C}$, 150 rpm, $C=100\text{ mg/L}$, 50 mL, $t=120\text{ min}$)

It was observed from the graphs **Figure 3.2** that increasing the dosage increases the % **removal of methylene blue**. As there was no drastic increase in the adsorption rate on increasing the dosage of adsorbent beyond 0.6 g of biosorbent, hence, from economic point of view, **0.6 g** was taken as optimum dosage for removal of methylene blue. It can be attributed to the increase in adsorbent sites for more adsorption of the dye [37].

This stabilization can be explained by the adsorption system reaching saturation, where all dye molecules present in the medium have already been adsorbed. Consequently, any further increase in adsorbent mass does not significantly affect the amount adsorbed due to the fixed dye concentration.

Additionally, excessive accumulation of adsorbent may lead to particle agglomeration, which hinders access to some of the active adsorption sites. Similar findings have been reported in previous studies on dye adsorption using various adsorbents, where an increase in adsorbent dosage initially enhances removal efficiency until a certain threshold, beyond which no noticeable improvement is observed. [16]

3.2. Effect of pH

The pH of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity [38], The effect of variation of pH on adsorption rates were studied from the data and the graph obtained between % removal of methylene blue(y) vs. pH(x) [3] , The effect of pH was studied in the range of 2 to 12 (Figure 3.3)

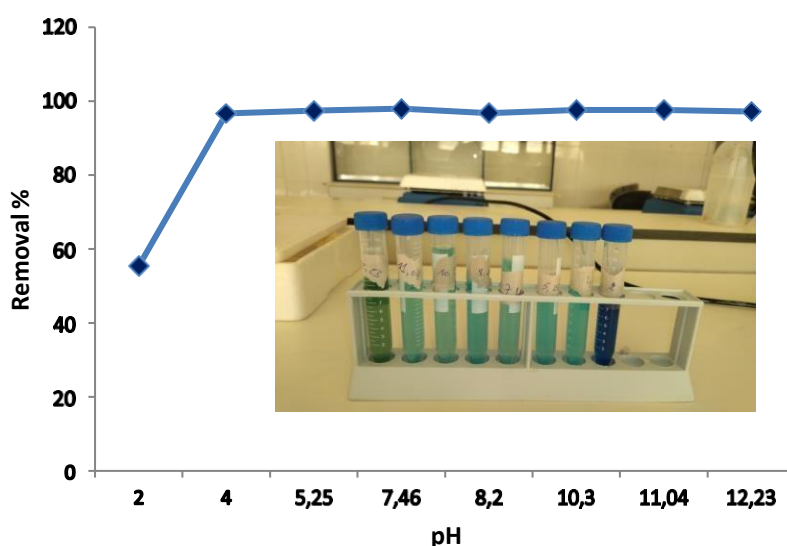


Figure 3.3: Effect of pH on the adsorption of methylene blue MB (25°C, 100 mg/L, 150 rpm, 0.6 g, 120 min, 50 mL)

A significant increase in dye removal efficiency was observed as the pH increased from 2 to 7, with the maximum removal recorded at pH = 7.46, making it the optimal value in this system.

The literature report that at lower pH, the surface charge may get positively charged, thus making (H^+) ions compete effectively with dye cations causing a decrease in the amount of dye adsorbed. At higher pH, the material biopolymers, mainly lignin and cellulose chains, may get negatively charged, which enhances the positively charged dye cationic through electrostatic forces of attraction [39].

In neutral medium (pH = 7):

This condition represents an ideal electrostatic balance, where neither H^+ nor OH^- dominates the system, making adsorption sites optimally available.

Therefore, the adsorption efficiency reaches its peak and remains stable beyond this point.

3.3. Effect of contact time and concentration

Figure 3.4 The results showed that the removal efficiency increased progressively with the rise in both concentration and contact time, until reaching a plateau at a concentration of 100 ppm and a contact time of 20 minutes, beyond which no significant increase was observed.

This behaviour can be explained by the saturation of active adsorption sites on the surface of the biosorbent. The initial increase in dye concentration provides more methylene blue molecules available for interaction with the available adsorption sites, enhancing the adsorption process until equilibrium is reached. As for the contact time, adsorption occurs rapidly at the beginning due to the abundance of vacant sites, then gradually slows down until reaching equilibrium, where most sites are occupied and the adsorption rate levels off. [16, 40].

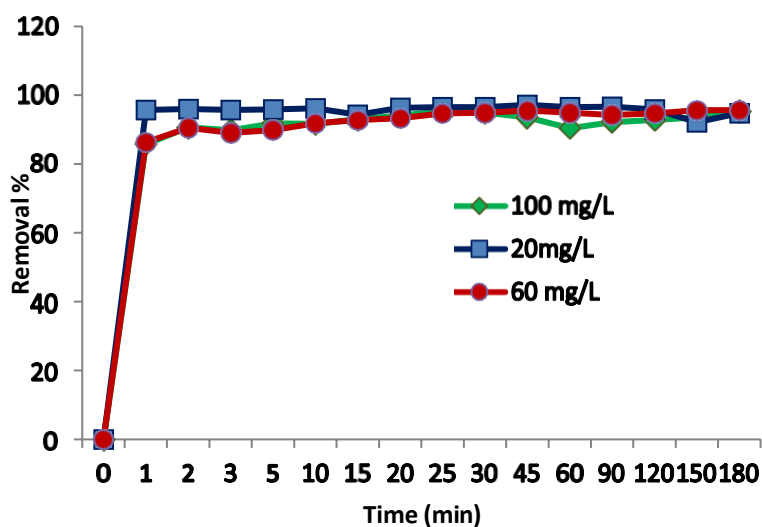


Figure 3.4: Effect of time and concentration on the adsorption of MB dye (25°C, 100 mg/L, 150 rpm, 1.2 g, 100 mL)

3.4. Effect of temperature

The temperature is usually an important factor which affects many adsorption processes, and it is an indicator of the adsorption nature [41].

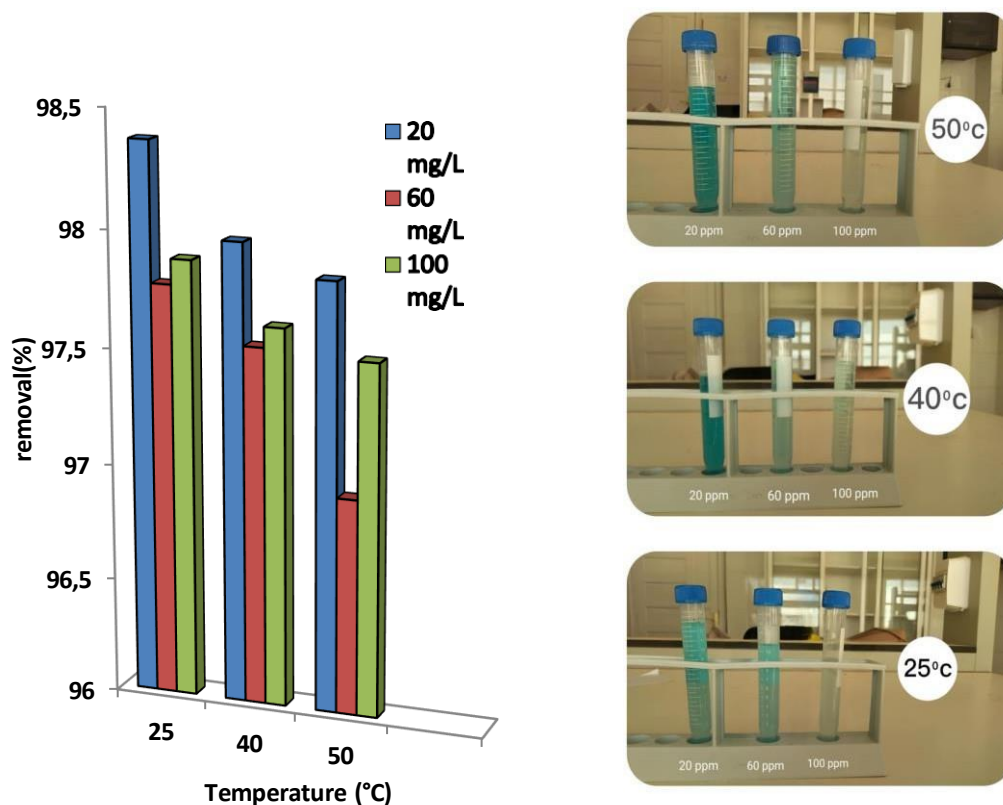


Figure 3.5: Effect of the temperature on the adsorption of MB (150 rpm, 0.6 g, 50 mL, 20 min)

Figure 3.5 shows that the highest removal efficiency of methylene blue dye is achieved at a temperature of 25°C, which is therefore identified as the optimal temperature for adsorption in this system. Beyond this point, a slight decrease in removal is observed at 40°C and 50°C, This suggests that the reaction is **exothermic** and the temperature increase is having a **negative effect on the adsorption mechanism** [42].

As temperature increases, the kinetic energy of dye molecules also increases, which may lead to desorption from the adsorbent surface due to weakened interactions between the dye and the active sites.

3.5. Effect of ionic strength

Extensive investigations carried out on adsorption of dyes revealed that the extent of dye uptake was strongly influenced by the concentration and nature of the electrolyte ionic species added to the dye-bath [39].

It is evident from the figure 10 that the salt mass has a varying effect on the removal of methylene blue (MB) depending on the type of salt used. The increase in NaCl mass from 1g to 5g leads to a gradual rise in the removal percentage, indicating that NaCl enhances the adsorption efficiency. In contrast, the removal percentage in the presence of Na₂SO₄ remains almost constant with increasing mass, suggesting a limited effect of this salt on the adsorption process. This difference can be attributed to the ability of Na⁺ ions in NaCl to reduce the electrostatic repulsion between the positively charged dye molecules and the surface of the adsorbent, thereby facilitating better adsorption. On the other hand, SO₄²⁻ ions in Na₂SO₄ may have a weaker influence on surface interactions or may compete with dye molecules for active sites, which explains the nearly unchanged removal efficiency.

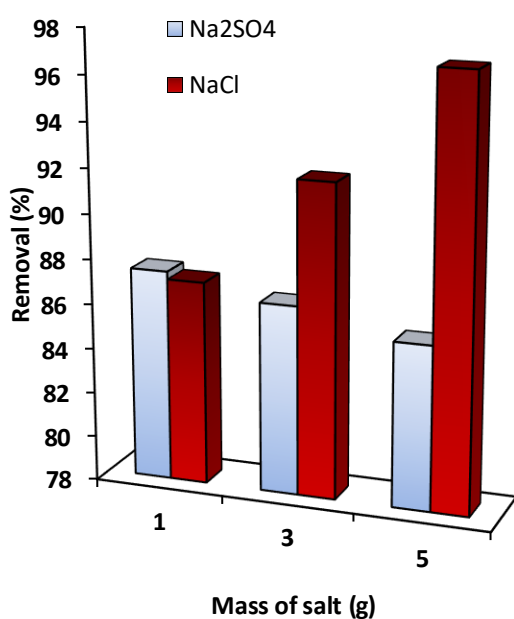


Figure 3.6: Effect of salts masses on the adsorption removal of MB dye.

4. Kinetic study

Kinetics study is essential in understanding the adsorption process as it provides information on the rate of adsorption and the mechanism that controls it. In this study, the kinetic data was analyzed using the pseudo-first order (PFO), the pseudo second order (PSO) [43]

4.1. Langergren pseudo –first order model

When adsorption is preceded by diffusion through a boundary, the kinetics in most systems follow the pseudo-first-order rate equation [29]

The linearised integral form of the pseudo-first-order model generally expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

Where; q_t and q_e are the adsorption capacities at time t and at equilibrium, respectively (mg/g), k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}) and t is the contact time (min). To plot $\log (q_e - q_t)$ versus t gives a linear relationship from which k_1 and predicted q_e can be determined from the slope and intercept of the plot respectively. [11]

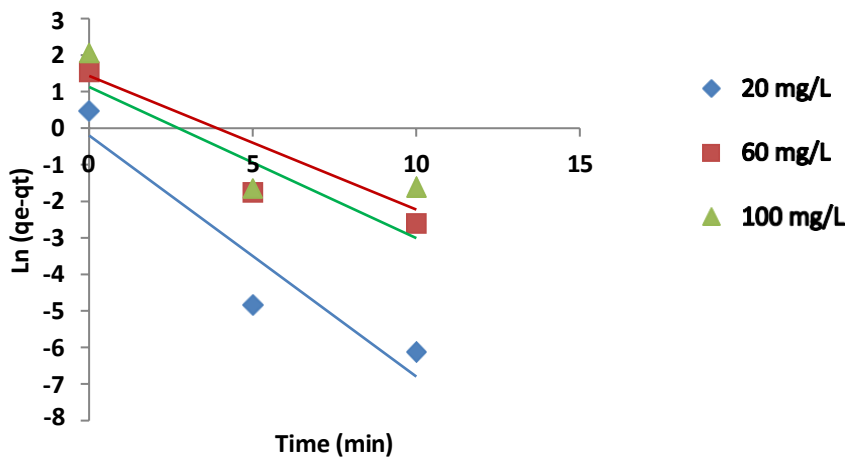


Figure 3.7: Graphical presentation of PFO for MB adsorption

Figure 3.7 shows the relationship between $\ln (q_e - q_t)$ and time at different initial concentrations (20, 60, and 100 mg/L). It can be observed from the plots that the PFO model did not fit the

experimental data well, particularly at higher concentrations, indicating a deviation from the ideal linear behavior.

According to the parameters presented in **Table 3.1**, the correlation coefficient (R^2) did not exceed 0.90, ranging from 0.7409 to 0.8953. This suggests that the model fails to adequately describe the adsorption process. Moreover, the calculated values of q_e differed significantly from the experimental ones, further highlighting the limitations of this model in representing the adsorption mechanism.

Table 3.1: parameters for modeling adsorption kinetics using PFO model for MB dye

Concentration (mg/L)	20	60	100
q_e	0,82	3,1	4,2
K_1	1,52	0,95	0,84
R^2	0,8892	0,8953	0,7409

4.2. Lagergren pseudo-second-order model on dye adsorption

Contrary to the other model, the pseudo-second-order equation predicts the behavior over the whole time of adsorption, with the adsorption (chemisorption) mechanism being the rate controlling step, which involves valency forces through electrons sharing or exchange (between adsorbate and adsorbent) [29].

The adsorption kinetic may be described by the pseudo-second order model. The differential equation is generally known and described as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

Where; K_2 ($g \text{ (mg min)}^{-1}$) is the second-order rate constant of adsorption. Integrating Eq. (2) for the boundary conditions $q_t = 0 - q_t$ at $t = 0 - t$ is simplified and linearised to get

$$\frac{t}{q_t} = 1 / (k_2 q_e^2) + \frac{1}{q_e} t \quad (4)$$

The second-order rate constants were used to calculate the initial sorption rate, given by the following equation:

$$h = K_2 q_e^2 \quad (5)$$

The plot of t/q_t versus t shows a linear relationship. Values of K_2 and equilibrium adsorption capacity q_e were calculated from the intercept and slope of the plot of t/q_t versus t according to Eq. (3) [11].

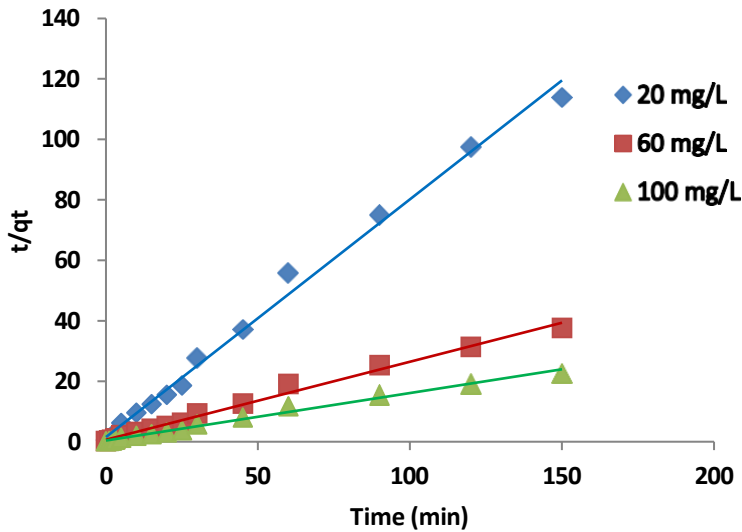


Figure 3.8: Graphical presentation of PSO for MB adsorption

In contrast, **Figure 3.8** presents the relationship between t/q_t and time, and a strong linearity is observed across all studied concentrations. The parameters in **Table 3.2** reveal very high correlation coefficients ($R^2 > 0.99$), indicating an excellent fit of the PSO model to the experimental data.

Additionally, the q_e values calculated from the PSO model closely matched the experimental data, reinforcing the model's validity. The observed decrease in the rate constant (K_2) with increasing initial dye concentration is attributed to competition among dye molecules for active adsorption sites.

Table 3.2: parameters for modeling adsorption kinetics using PSO model for MB dye.

Concentration (mg/L)	20	60	100
q_e	1,27	3,88	6,37
K_2	0,39	0,094	0,056
R^2	0,994	0,9918	0,99

The comparison between the two kinetic models showed that the pseudo-second-order (PSO) model was more suitable for describing the adsorption behavior of methylene blue onto the adsorbent. This is supported by the high correlation coefficient ($R^2 > 0.99$) and better agreement between the calculated and experimental values of adsorption capacity at equilibrium. The PFO model showed poor fit at higher concentrations. These results suggest that the adsorption process is likely governed by chemisorption, and the PSO model is the most appropriate.

5. Isotherm study

To better understand the interaction between methylene blue (MB) dye molecules and the surface of adsorbent, the experimental data were fitted using two commonly applied isotherm models: **Langmuir and Freundlich**. The modeling was performed at three different temperatures (25°C, 40°C, and 50°C), and the results are presented in **Figures 3.7 and 3.8**, along with the corresponding isotherm constants in **Tables 3.3 and 3.4**.

5.1. Langmuir Isotherm

Langmuir isotherm is the simplest isotherm model obtained in 1916, which was originally derived from studying of the adsorption of gases by solids. It describes the single adhesion layer on the homogenous surface [31], where the attraction between molecules adsorbed on the adsorbate and non-adsorbed analyte in the bulk solution decreases as they are getting away from the adsorbate surface.

There is a limitation of Langmuir equation because it assumes that adsorption is monolayer with no attraction between molecules on the surface of adsorbate. Therefore, this model is for low concentration or low pressure for the gas system. Langmuir isotherm is defined according to the following mathematical equations:

$$q_e = q_m K_L \frac{C_e}{(1 + K_L C_e)} \quad (6)$$

Where q_e is the equilibrium amount of solute adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of solute (mg/L), q_m is the adsorption capacity of the monolayer (mg/g), and K_L is the Langmuir constant related to the energy and affinity of binding sites of adsorption (L/mg), eq (9) can be written in the following linear form (I)

$$K_d = \frac{C_e}{q_e} \quad (7)$$

$$\frac{q_e}{C_e} = q_m K_L - K_L q_e \quad (8)$$

Other linear forms of Langmuir results from taking the inverse of Eq. (9), to get linear form (II)

$$\frac{1}{q_e} = \left(\frac{1}{q_m K_L}\right) \left(\frac{1}{C_e}\right) + \frac{1}{q_m} \quad (9)$$

or by multiplying equation (11) by C_e , to get linear form

$$C_e \frac{q_e}{q_e} = \left(\frac{1}{q_m K_L}\right) C_e + \left(\frac{1}{q_m}\right) C_e \quad (10)$$

The values of q_m and K_L can be evaluated from the slope and the intercept of the plot of the linear forms of Langmuir equation. [32]

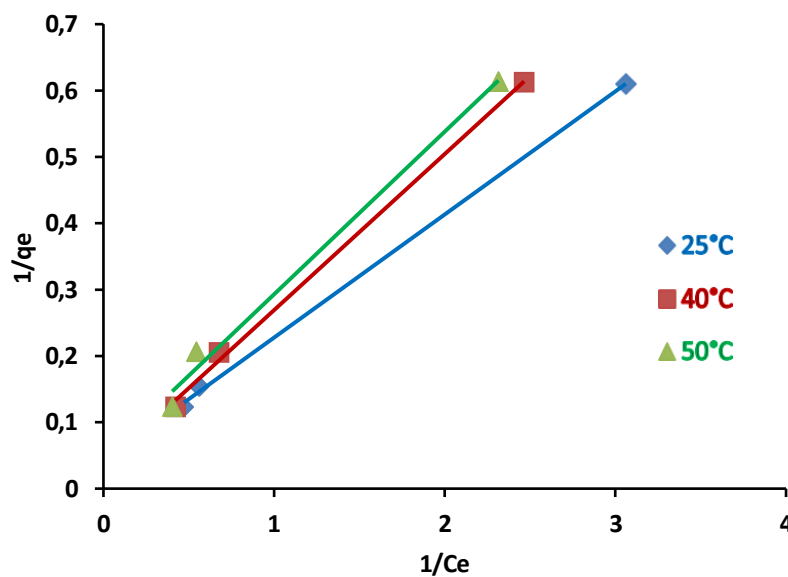


Figure 3.9: Modeling of the experimental results of the MB dye using the Langmuir model

According to the Langmuir isotherm, the monolayer adsorption of a homogeneous surface is used to determine the finite number of sites without interaction between the adsorbed molecules [44]. As shown in **Figure 3.9**, the plots of $1/q_e$ versus $1/C_e$ exhibit good linearity at all tested temperatures, indicating that the model fits the experimental data well. This is further supported by the high correlation coefficients ($R^2 > 0.99$) listed in **Table 3.3**.

Notably, the maximum adsorption capacity (q_m) increased from 29,5 mg/g at 25°C to 23.87 mg/g at 40°C, before slightly decreasing to 20.96 mg/g at 50°C. This suggests an optimal adsorption performance at ambiante temperature, potentially due to enhanced molecular mobility and favorable energetic interactions. The values of K_L , the Langmuir equilibrium constant, also reflect a relatively strong affinity between MB molecules and the adsorbent surface.

Table 3.3: Langmuir constants for MB dye adsorption

	25°C	40°C	50°C
q_m	29,5	23,87	20,96
K_L	0,23	0,14	0,19
R^2	0,9993	0,9982	0,9913

5.2. Freundlich Isotherm

Freundlich isotherm is a special case of Langmuir, used for modeling the multi-layer adsorbed on heterogeneous surfaces; it can be explained by the following equations

$$q_e = K_F C_e^\beta = K C_e^{1/n} \quad (11)$$

Where q_e is the equilibrium amount adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of the adsorbate in solution (mg/L); K_F is the Freundlich isotherm constant, and n is the adsorption intensity. [32]The logarithmic linear form of the Freundlich equation is given as:

$$\log q_e = \log(K_F) + \left(\frac{1}{n}\right) (\log C_e) \quad (12)$$

- If $n = 1$; the partition between the two phases is independent of the concentration.
- If $1/n < 1$; normal adsorption.
- If $1/n > 1$; cooperative adsorption.

The constants k_F and n change with temperature to reflect the fact that the adsorbed sum builds more gradually as temperature rises, and more pressing components are required to saturate the surface [33].

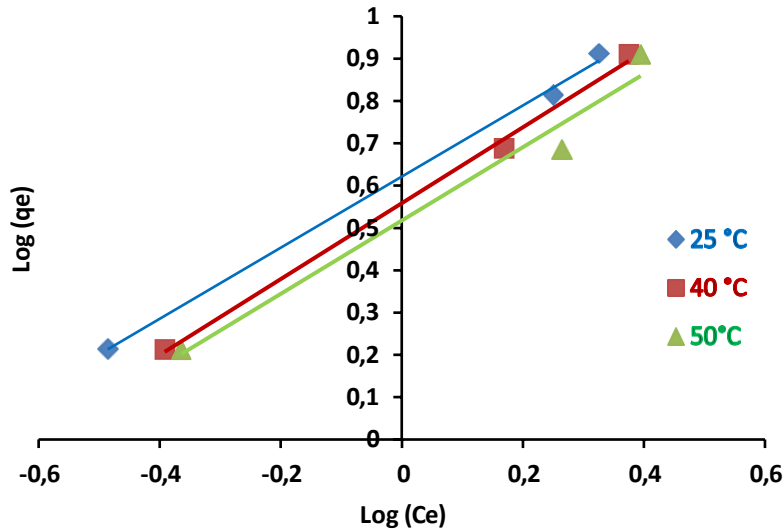


Figure 3.10: Modeling of the experimental results of the MB dye using the Freundlich model

The adsorption process was analysed by using the Freundlich isotherm model which consists of a multilayer distribution process of the adsorbed molecules [44]. showed acceptable linearity **Figure 3.10**, with correlation coefficients ranging from 0.9747 to 0.9979 (**Table 3.4**). However, the R^2 values were consistently lower than those obtained with the Langmuir model.

Additionally, the Freundlich constants (K_F and $1/n$) confirm a favorable adsorption process ($1/n < 1$). However, the variation of K_F with temperature showed less consistency than q_m in the Langmuir model, indicating a less precise fit. The highest K_F (4.18 mg/g·(L/mg) $^{1/n}$) was observed at 25°C, with a slight decrease at higher temperatures.

Table 3.4: Freundlich constants for MB dye adsorption

	25°C	40°C	50°C
K_F	4,18	3,62	3,29
$1/n$	0,8404	0,8966	0,8659
R^2	0,9979	0,997	0,9747

The Langmuir model demonstrated a better overall correlation and more consistent trends in adsorption capacity. This suggests that the adsorption of MB dye primarily occurs via monolayer coverage on a relatively homogenous surface, supporting the assumption of the Langmuir mechanism.

6. Thermodynamic study

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. Gibb’s free energy change, ΔG° , is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG° is a negative value. The thermodynamic parameters of Gibb’s free energy change, ΔG° , enthalpy change, ΔH° , and entropy change, ΔS° , for the adsorption processes are calculated using the following equation [45]

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

To better understand the nature of the adsorption process, the thermodynamic parameters ΔH° , ΔS° , and ΔG° were determined at different temperatures (25°C, 40°C, and 50°C) using the Van’t Hoff equation, as illustrated in **Figure 3.11**, the linear relationship between $\ln K_d$ and $1/T$ confirms that the adsorption process follows predictable thermodynamic behavior.

The curves **Figure 3.11** show a gradual increase in $\ln K_d$ with rising temperature for all studied concentrations (20, 60, and 100 mg/L), suggesting a slight improvement in adsorption capacity as temperature increases. This behavior indicates that the adsorption process may be thermally activated and possibly involves mild chemical interactions.

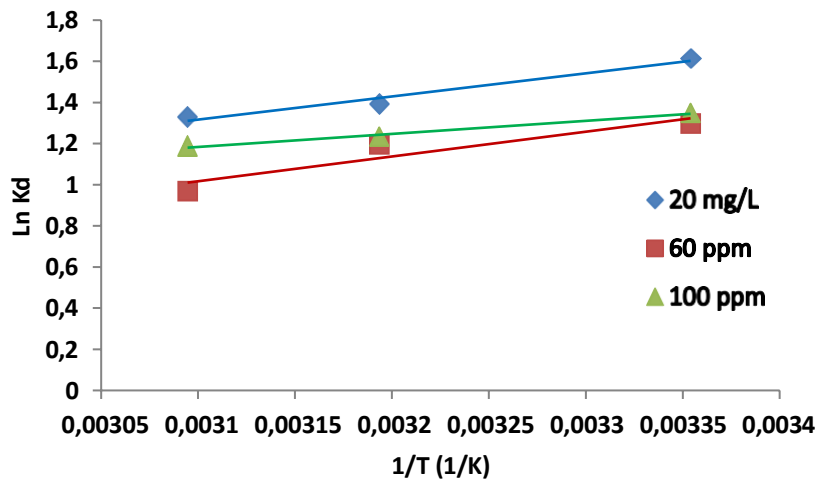


Figure 3.11: Van’t Hoff plots of $\ln K_d$ against $1/T$ (k^{-1}) ($\ln K_d = (-\Delta H^\circ / R) 1/T + \Delta S^\circ / R$)

6.1. ΔH° (Enthalpy Change)

The negative values of ΔH° at all concentrations (-9.35, -10.013, -5.27 kJ/mol) indicate that the adsorption **process is exothermic**. This implies that increasing the temperature does not significantly favor the adsorption, which is typical of **physical adsorption** or weak chemisorption.

6.2. ΔS° (Entropy Change)

The negative values of ΔS° (-18.04, -22.58, -6.49 J/mol K) suggest a **decrease in randomness at the solid-liquid interface during adsorption**. This may be due to the structured arrangement of dye molecules on the adsorbent surface.

6.3. ΔG° (Gibbs Free Energy)

All ΔG° values were found to be negative under the studied conditions, indicating that the adsorption is spontaneous.

Table 3.5: Thermodynamic parameters of MB dye adsorption

Concentration (mg/ L)	ΔH° (kJ/ mol)	ΔS° J/(mol.K)	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (KJ/mol)		
			$T_1 = 298K$	$T_2 = 313K$	$T_3 = 323K$
20	-9,352	-18,04	-3, 97	-3,7	-3,5
60	-10,013	-22,58	-3,25	-2,92	-2,69
100	-5,2697	-6,49	-3,33	-3,23	-3,17

The thermodynamic results reveal that the adsorption of methylene blue is an exothermic, ordered process, and spontaneous under the experimental conditions. The relatively low ΔH° values suggest the involvement of physical or weak chemical interactions, and the limited enhancement with increasing temperature supports previous findings from the kinetic study.

7. Comparison Study

A comparison of several biosorbents utilized in batch adsorption process to remove MB dye is shown in Table 3.6. According to the finding, the biosorbent derived from peanut shells utilized in this study had the best removal efficiency 99,2 % and adsorption capacity 29,5%. Compared to other biosorbents,

These results show that the biosorbent examined in this work achieves the highest dye removal efficiency while matching and even surpassing the adsorption capacity of the best-performing materials previously reported ‘‘that chemically or physically treated’’. This demonstrates the developed biosorbent’s potential usefulness and efficacy for wastewater treatment.

Table 3.6: Comparison of peanut shells with other adsorbents for methylene blue dye removal in batch adsorption process

Biosorbent	Removal %	Adsorption Capacity(mg/g)	Reference
Lagenaria vulgaris	95,9	11,37	[46]
Activated coconut Shells		30,3	[47]
Biochar from sunflower husk	99	29	[48]
Leaves and flowers of Solanum incanum	98		[49]
Pomegranate peel	92	13,54	[50]
Peanut shells	99,2	29,5	This study

CONCLUSION

In conclusion, this study aimed to evaluate the effectiveness of using an unconventional and low-cost adsorbent material ‘‘peanut shells’’ for the removal of methylene blue dye from aqueous medium. The research yielded promising results, confirming the potential use of this biosorbent in a raw form. The main results are:

- ✓ The optimal mass of the adsorbent material was determined to be **0.6 g for 100 mg/L**, which provided the highest dye removal efficiency.
- ✓ It was observed that the optimal pH for the adsorption process is **7 for ~ 97%**, indicating that a neutral environment enhances adsorption efficiency.
- ✓ The initial dye concentration showed an optimal value at **100 mg/L**, where adsorption occurred effectively, and the optimal contact time was found to be **20 min**, which is sufficient to reach equilibrium between the dye and the adsorbent.
- ✓ Experiments were conducted at a temperature of **25°C**, which corresponds to room temperature, showing that the process does not require additional thermal energy.
- ✓ Through kinetic data analysis, it was found that the Pseudo-second order model best represents the adsorption mechanism with $R^2 = 0,99$, indicating that the interaction is chemical in nature.
- ✓ Regarding equilibrium models, the Langmuir model showed the best fit with the experimental data $R^2 = 0,9993$, suggesting that adsorption occurs on a monolayer surface of the adsorbent.
- ✓ It was found that salts with monovalent ionic strength were more favorable for the adsorption process than divalent ones, highlighting the importance of the nature of coexisting ions in the aqueous medium and their influence on adsorption efficiency.
- ✓ A comparative study showed that the peanut shells used in this work and various other biosorbent reveal a close similarity in adsorption capacity (mg/g) of Langmuir isotherm. Notably, several of the referenced materials underwent chemical or thermal modifications, whereas untreated, raw peanut shells were employed in the present study.

Based on these results, it can be concluded that the use of agricultural waste is an effective and sustainable option for treating water contaminated with cationic dyes, opening new opportunities for environmental and economic applications in industrial wastewater treatment.

REFERENCES

- [1] Hamri, N., Imessaoudene, A., Hadadi, A., Cheikh, S., Boukerroui, A., Bollinger, J.-C., Amrane, A., Tahraoui, H., Tran, N., Ezzat, A. O., Al-Lohedan, H. A., & Mouni, L. (2024). Enhanced adsorption capacity of methylene blue dye onto kaolin through acid treatment: Batch adsorption and machine learning studies. *Water*, 16(2), 243. <https://doi.org/10.3390/w16020243>
- [2] Djama, C., Bouguettoucha, A., Chebli, D., Amrane, A., Tahraoui, H., Zhang, J., & Mouni, L. (2023). Experimental and Theoretical Study of Methylene Blue Adsorption on a New Raw Material, *Cynara scolymus*—A Statistical Physics Assessment, *Sustainability*, 15(10364). <https://doi.org/10.3390/su151310364>
- [3] Ederer, J., Orchard, P., Šrámová, M., Klušná, J., Toblasz, J., Smržová, D., Lupínková, S., & Janoš, P. (2022). A Study of Methylene Blue Dye Interaction and Adsorption by Monolayer Graphene Oxide. *Hindawi Adsorption Science & Technology*, 2022, Article ID 7385541, 16 pages. <https://doi.org/10.1155/2022/7385541>
- [4] Hurairah, S. N., Lajis, N. M., & Halim, A. A. (2020). Methylene Blue Removal from Aqueous Solution by Adsorption on Archidendr on jiringa Seed Shells. *Journal of Geoscience and Environment Protection*, 8, 128-143. <https://doi.org/10.4236/gep.2020.82009>
- [5] Tuser, C , What is wastewater, *Water & Wastes Digest*. Retrieved from, <https://www.wwdmag.com>
- [6] Hosny, N. M., Gomaa, I., & Elmahgary, M. G. (2023). Adsorption of polluted dyes from water by transition metal oxides: A review. *Applied Surface Science Advances*, 15, 100395. <https://doi.org/10.1016/j.apsadv.2023.100395>
- [7] Rápo, E., & Tonk, S. (2021). Factors affecting synthetic dye adsorption; desorption studies: A review of results from the last five years (2017–2021). *Molecules*, 26(5419). <https://doi.org/10.3390/molecules26175419>
- [8] Chatwal, G.R. *Synthetic Dyes*; Himalaya Publishing House: Mumbai, India, 2009; ISBN 978-81-8488-220-9
- [9] IARC Working Group on the Evaluation of Carcinogenic Risk to Humans. *General Introduction to the Chemistry of Dyes*; International Agency for Research on Cancer: Lyon, France, 2010; ISBN 978-92-832-1299-7
- [10] Benkhaya, S.; M'rabet, S.; El Harfi, A. A Review on Classifications, Recent Synthesis and Applications of Textile Dyes. *Inorg.Chem. Commun.* 2020, 115, 107891.

- [11] Yagub, M. T., Sen, T. K., Afroze, S., & Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption: A review. *Advances in Colloid and Interface Science*, 209, 172-184. <https://doi.org/10.1016/j.cis.2014.04.002>
- [12] Gupta V. Application of low-cost adsorbents for dye removal—a review. *J Environ Manage* 2009;90(8):2313–42
- [13] Ali H. Biodegradation of synthetic dyes—a review. *Water Air Soil Pollution* 2010;213(1):251–73
- [14] Hunger K. *Industrial dyes*. Germany: Wiley-VCH; 2007.
- [15] Ghoreishi S, Haghghi R. Chemical catalytic reaction and biological oxidation for treatment of non-biodegradable textile effluent. *Chem Eng J* 2003;95(1):163–9
- [16] Salleh MAM, et al. Cationic and anionic dye adsorption by agricultural solid wastes: a comprehensive review. *Desalination* 2011;280(1):1–13.
- [17] Oladoye, P. O., Ajiboye, T. O., Omotola, E. O., & Oyewola, O. J. (2022). Methylene blue dye: Toxicity and potential elimination technology from wastewater. *Results in Engineering*, 16, 100678. <https://doi.org/10.1016/j.rineng.2022.100678>
- [18] Akrou, H., Jellali, S., & Bousselmi, L. (2015). Enhancement of methylene blue removal by anodic oxidation using BDD electrode combined with adsorption onto sawdust. *Comptes Rendus Chimie*, 18(2), 110-120. <https://doi.org/10.1016/j.crci.2014.09.006>
- [19] Alaqarbeh, M. (2021). Adsorption phenomena: Definition, mechanisms, and adsorption types: Short review. *RHAZES: Green and Applied Chemistry*, 13, 43–51. ISSN: 2605-6895.
- [20] Ali, I. (2012). New generation adsorbents for water treatment. *Chemical Reviews*, 112(10), 5073–5091. <https://doi.org/10.1021/cr300133d>
- [21] Aljamali, N. M., Aldujaili, R. A. B., & Alfatlawi, I. O. (2021). Physical and Chemical Adsorption and its Applications. *International Journal of Thermodynamics and Chemical Kinetics*, 7(2), 1–8. Retrieved from <http://chemical.journalspub.info/index.php?journal=JTCK&page=article&op=view&path%5B%5D=SD-1168>
- [22] Razi, M. A. M., Mohd H. M. A., & Hamdan, R. (2017). Factor Affecting Textile Dye Removal Using Adsorbent From Activated Carbon: A Review. *MATEC Web of Conferences*, 103, 06015. <https://doi.org/10.1051/matecconf/201710306015>
- [23] M.A. Mohd Salleh, D. K. Mahmoud, N.A. Awang Abu, W.A. Wan Abdul Karim and A. Idris, Methylene blue adsorption from aqueous solution by langsung (lansium domesticum) peel, *J. Purity, Utility Reaction Environ.*, 1, 472-495 (2012)

- [24] Soltani, A., Faramarzi, M., & Mousavi Parsa, S. A. (2021). A review on adsorbent parameters for removal of dye products from industrial wastewater. *Water Quality Research Journal*, 56(4), 181. <https://doi.org/10.2166/wqrj.2021.023>
- [25] Y. Zhang, C. Zhu, A. Li, effect of ionic strength on removal of toxic pollutants from aqueous media with multifarious adsorbents, A review, *The Science of The Total Environment*, 2018. <https://doi.org/10.1016/j.scitotenv.2018.07.279>
- [26] Pereira, R.C., Anizelli, P.R., Di Mauro, E., Valezi, D.F., da Costa, A.C.S., Zaia, C.T.B.V., Zaia, D.A.M. The effect of pH and ionic strength on the adsorption of glyphosate onto ferrihydrite. *Geochemical Transactions*, 2019. <https://doi.org/10.1186/s12932-019-0063-1>
- [27] Gonçalves, R.G.L., Lopes, P.A., Pochapski, D.J., de Oliveira, L.C.A., Pinto, F.G., Neto, J.L., Tronto, J. Effect of pH, ionic strength, and temperature on the adsorption behavior of Acid Blue 113 onto mesoporous carbon. *Environmental Science and Pollution Research*, 2022. <https://doi.org/10.1007/s11356-022-21193-y>
- [28] Zhang, Y., Zhu, C., Li, A. Effects of ionic strength on removal of toxic pollutants from aqueous media with multifarious adsorbents: A review. *The Science of The Total Environment*, 2018. <https://doi.org/10.1016/j.scitotenv.2018.07.279>
- [29] Foo, K. Y., & Hameed, B. H. (2010). An overview of dye removal via activated carbon adsorption process. *Desalination and Water Treatment*, 19(1-3), 255-274. <https://doi.org/10.5004/dwt.2010.1214>
- [30] V. Bolis, *Fundamentals in Adsorption at the Solid-Gas Interface. Concepts and Thermodynamics. Calorimetry and Thermal Methods in Catalysis*. Springer-Verlag, Auroux, A. (Author) *springer series in materials science*, Berlin-Heidelberg, 154; chapter 1, 1-50, (2013). Electronic ISBN: 978-3-642-11954-5
- [31] E. Covelo, F. Vega, M. Andrade, Heavy Metal Sorption and Desorption Capacity of Soils Containing Endogenous Contaminants, *J. Hazard. Mater*, 143, 419-430, (2007). <https://doi.org/10.1016/j.jhazmat.2006.09.047>
- [32] Alaqarbeh, M., Adsorption phenomena: Definition, mechanisms, and adsorption types: Short review. *RHAZES: Green and Applied Chemistry*, (2021). 13, 43–51. ISSN: 2605-6895
- [33] Agarwala, R., & Mulky, L. (2023). Adsorption of dyes from wastewater: A comprehensive review. *ChemBioEng Reviews*, 10(3), 326–335. <https://doi.org/10.1002/cben.202200011>
- [34] Abegunde, S. M., Idowu, K. S., Adejuwon, O. M., & Adeyemi-Adejolu, T. (2020). A review on the influence of chemical modification on the performance of adsorbents.

Resources, Environment and Sustainability, 1, 100001.
<https://doi.org/10.1016/j.resenv.2020.100001>

[35] Skoog, D. A., West, D. M., Holler, F. J., & Crouch, S. R. *Fundamentals of Analytical Chemistry* (9th ed.). (2013). Cengage Learning

[36] Christian, G. D. *Analytical Chemistry* (6th ed.). John Wiley & Sons. (2004).

[37] Samal, D. P. Characterization and study of adsorption of methylene blue dye using activated carbon [Bachelor's thesis, National Institute of Technology Rourkela. (2014).

[38] Amuda, O. S., Olayiwola, A. O., Alade, A. O., Farombi, A. G., & Adebisi, S. A. Adsorption of methylene blue from aqueous solution using steam-activated carbon produced from *Lantana camara* stem, *Journal of Environmental Protection*, (2014). 5, 1352-1363.
<https://doi.org/10.4236/jep.2014.513129>

[39] Boumediene, M., Benaïssa, H., George, B., Molina, S., & Merlin, A. (2018). Effects of pH and ionic strength on methylene blue removal from synthetic aqueous solutions by sorption onto orange peel and desorption study. *Journal of Materials and Environmental Sciences*, 9(6), 1700–1711. <https://doi.org/10.26577/jmes.2018.9.6.190>

[40] Kyzas, G. Z., & Deliyanni, E. A. Modified activated carbons from potato peels as green adsorbents for the removal of cationic dyes. *Chemical Engineering Research and Design*, (2014). 92(9), 1653–1663.

[41] Amrhar, O., Nassai, H., & Elyoubi, M. S. Adsorption of a cationic dye, Methylene Blue, onto Moroccan Illitic Clay. *Journal of Materials and Environmental Sciences*, (2015). 6(11), 3054–3065

[42] Ifguis, O., Ziat, Y., Belkhanchi, H., Ammou, F., Moutcine, A., & Laghlimi, C. Adsorption mechanism of Methylene Blue from polluted water by *Opuntia ficus indica* of Beni Mellal and Sidi Bou Othmane areas: A comparative study. *Chemical Physics Impact*, (2023). 6, 100235. <https://doi.org/10.1016/j.chphi.2023.100235>

[43] De Castro, M. L. F. A., Abad, M. L. B., Abarca, R. R. M., Paoprasert, P., Divine, M. J., Sumalinog, A. G., & de Luna, M. G. Adsorption of Methylene Blue dye and Cu(II) ions on EDTA-modified bentonite: Isotherm, kinetic and thermodynamic studies. *Sustainable Environment Research*, (2018). 28, 197–205. <https://doi.org/10.1016/j.serj.2018.04.001>

[44] Lussa, M. O., Wijayanti, A., Kusumadewi, R. A., & Hadisubroto, R. (2020). The Mixing Speed Effect and Mass of Adsorbent On Copper (Cu) Removal from Wastewater by Water Hyacinth Leaves. *E3S Web of Conferences*, 148, 05006.
<https://www.google.com/search?q=https://doi.org/10.1051/e3sconf/202014805006>

- [45] He, J., Hong, S., Zhang, L., Fu, F., Gao, G., & Ho, Y.-S. Equilibrium and thermodynamic parameters of adsorption of methylene blue onto rectorite. *Fresenius Environmental Bulletin*, (2010). 19(11a), 2635-2640.
- [46] S. Franceschini, C. Sendeski, K. Lima, K. Nicolini, and J. Nicolini, Agreeen adsorbent : effect of chemical modification of biosorbents on the adsorption of methylene blue and malachite green, *Anais da Academia Brasileira de Ciências*, 2023
- [47] Abbas, M. Trari, M. Adsorption Behaviour of methylene blue onto activated coconut shells: kinetic, thermodynamic, mechanism, and regeneration of the adsorbent, *Dose-Response*, 2024.
- [48] Sawalha, H. Bader, A. Sarsour, J. AlJabari, M. and Elldon, R. Removal of methylene blue from wastewater using Bio-char derived from Agricultural residues in Palestine: Performance and Isotherm Analysis, *Processes*, 2022.
- [49] Hamza, S. Al Shehri, S. H. Alanazi, W.S. Alnafaei, A. Alorabi, A. Alkorbi, and F. AlHarthi, Adsorption of methylene blue by biosorption on Alkali-treated *Solanum incanum*: isotherm, equilibrium, and mechanism, *Sustainability*, 2022
- [50] Waghmare, S. Ghodmare, A. Khalid, F. Alfaisal, S. Alam, M.Khan, and Y. Ezaier, Adsorption of methylene blue dye onto phosphoric acid-treated pomegranate peel adsorbent: Kinetic and thermodynamic studies, *Desalination and water treatment*, 2024.



Appendix.1: UV-Visible Spectrophotometer



Appendix.2: Different masses of the adsorbent



Appendix.3: Temperature variation in the Stirred Bath (ST 30)

عنوان المذكرة: النفايات الزراعية الحيوية لإزالة فعالة لصبغة كاتيونية من نظام مائي

اللقب: سليمي وبن شتوح الاسم: خيرة شهيناز و جهيدة
المؤطر: بوداود أسماء و بن يحي فاطمة

ملخص: تستكشف هذه الأطروحة فعالية الامتزاز كطريقة بسيطة وفعالة لمعالجة المياه الملوثة بأزرق الميثيلين ونظرًا لارتفاع تكلفة طرق المعالجة التقليدية، تم اعتماد قشور الفول السوداني كمادة مازة طبيعية منخفضة التكلفة وصديقة للبيئة، تم إجراء تجارب معملية لتقييم كفاءة الامتصاص في ظل الظروف المثالية، وأظهرت النتائج أن مادة PS لها كفاءة عالية في إزالة الصبغة MB بنسبة 98% عند 0.6 غ ودرجة حموضة 7 ودرجة حرارة 25 درجة مئوية، وقد أكدت الدراسة الحركية حركية الدرجة الثانية الزائفة ، أفضل وصف للامتصاص هو نموذج لانغموير المتساوي الحرارة، مع سعة أحادية الطبقة تبلغ 29.5 ملغ/غ. أشارت الدراسات الديناميكية الحرارية إلى أن العملية كانت عفوية، وطاردة للحرارة، وانخفاض في العشوائية عند واجهة السائل الصلب أثناء الامتزاز
كلمات مفتاحية: الامتزاز، نفايات زراعية، أزرق الميثيلين، المياه العادمة، تيرموديناميك.

Memory title: Bio agricultural waste for the efficient removal of cationic dye from aqueous system

Name: Slimi & Ben Chettouh First name: Khira chahinaz & Djahida
Supervised by: Dr. Boudaoud Asma & Ms. Ben yahia Fatma

Abstract:

This thesis explores the effectiveness of adsorption as a simple and efficient method for treating water contaminated with methylene blue MB. Due to the high cost of conventional treatment methods, peanut shells PS were adopted as a low-cost, environmentally friendly natural adsorbent. Laboratory experiments were conducted to evaluate the adsorption efficiency at optimized conditions, the results showed that PS have a high efficiency for MB dye removal 98% at 0,6 g, pH 7, and 25°C. Kinetic study confirmed pseudo-second-order kinetics. The Langmuir isotherm model best described adsorption, with a monolayer capacity of 29,5 mg/g. Thermodynamic studies indicated the process was spontaneous, exothermic, and decrease in randomness at the solid-liquid interface during adsorption.

Key words: Adsorption, Agricultural waste, Methylene Blue, Wastewater, Thermodynamic.

Titre du mémoire : Déchets agricole biosourcés pour l'élimination efficace de colorant cationique dans les systèmes aqueux

Nom: Slimi & Ben Chettouh Prénom : Khira chahinaz & Djahida
Encadreur: Dr. Boudaoud Asma & Mme. Ben yahia Fatma

Résumé: Cette thèse explore l'efficacité de l'adsorption comme méthode simple et efficace pour traiter l'eau contaminée par le bleu de méthylène MB. En raison du coût élevé des méthodes de traitement conventionnelles, les coques d'arachide PS ont été adoptées comme adsorbant naturel peu coûteux et respectueux de l'environnement. Des expériences en laboratoire ont été menées pour évaluer l'efficacité de l'adsorption dans des conditions optimisées. Les résultats ont montré que les PS ont une efficacité élevée pour l'élimination du colorant MB de 98 % à 0,6 g, pH 7 et 25 °C. L'étude cinétique a confirmé la cinétique du pseudo-second ordre. Le modèle d'isotherme de Langmuir décrit le mieux l'adsorption, avec une capacité monocouche de 29,5 mg/g. Les études thermodynamiques ont indiqué que le processus était spontané, exothermique et qu'une diminution du caractère aléatoire à l'interface solide-liquide pendant l'adsorption.

Mots clés : Adsorption, les déchets agricole, Bleu de Méthylène, Eaux usées, Thermodynamiques.