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Dedication

First and foremost, ***Alhamdulillah.*** *All praise and thanks are due to* ***Allah (SWT),*** *the Almighty, whose boundless mercy, guidance, and blessings have been a constant source of strength throughout my academic journey. By His grace alone, I was endowed with the determination, patience, and resilience necessary to accomplish this work. To Him belongs all praise for granting me the opportunity, ability, and perseverance to bring this endeavor to completion.*

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"The roots of education are bitter, but the fruit is sweet."

Khalil

Dedication

*First **Alhamdulillah.** All praise and gratitude are due to **Allah (SWT)**, the Almighty, for His endless blessings, mercy, and guidance. It is only through His grace that I found the strength and perseverance to complete this work*

I dedicate this work to my beloved parents.

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Abstract

List of Abbreviations

A *: Absorbance*

AFM *: Atomic Force Microscopy*

BET *: Brunauer–Emmett–Teller (surface area measurement)*

BM *: Methylene Blue*

C *: Concentration*

C_0 *: Initial concentration of the adsorbate*

CCE *: Cuminum cyminum Extract.*

Ce *: Equilibrium concentration of the adsorbate*

d *: Density*

DCF *: Diclofenac (pharmaceutical pollutant)*

FTIR *: Fourier Transform Infrared Spectroscopy*

h *: Hour*

IR *: Infrared*

I *: Transmitted intensity of the beam passing through the sample*

I0 *: Intensity of the reference beam*

ICP-OES *: Inductively Coupled Plasma – Optical Emission Spectrometry*

IUPAC *: International Union of Pure and Applied Chemistry*

K1 *: First-order rate constant*

K2 *: Second-order rate constant*

Kd *: Equilibrium distribution constant*

KF *: Freundlich constant*

KL *: Langmuir constant*

m *: Mass of adsorbent*

M *: Molarity*

MB : Methylene Blue

min *: Minute*

n *: Freundlich coefficient*

NICUS *: Nutraceutical Industrial Cumin Seed*

nm *: Nanometer*

P *: Purity*

pH *: Hydrogen potential*

List of abbreviations, figures, tables

PFO *: Pseudo-First Order*

ppm *: Parts per million*

PSO *: Pseudo-Second Order*

qt *: Amount of solute adsorbed at time t*

qe *: Amount of solute adsorbed at equilibrium*

qe,exp *: Experimental adsorption capacity*

Qads *: Adsorption capacity*

Qm *: Maximum adsorption capacity*

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

R^2 *: Coefficient of determination*

R(%) *: Removal efficiency*

rpm *: Revolutions per minute*

SEM *: Scanning Electron Microscopy*

t *: Time*

T° *: Temperature*

TC *: Treated Cumin*

TTAB *: Tetradecyltrimethylammonium Bromide (cationic surfactant)*

UV : Ultraviolet

V *: Volume of solution*

XPS *: X-Ray Photoelectron Spectroscopy*

XRD *: X-Ray Diffraction*

$\Delta H°$ *: Enthalpy change*

$\Delta S°$ *: Entropy change*

$\Delta G°$ *: Gibbs free energy change*

ε *: Molar absorption coefficient*

λmax *: Maximum absorption wavelength*

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General Introduction

General introduction

Water is an important natural resource and is essential for the survival of all living organisms. It is used in domestic, agricultural, and many industrial activities. However, the rapid growths of industries and urban areas have significantly contributed to the contamination of water resources through the discharge of untreated or poorly treated wastewater into the environment. Among the different types of pollutants found in wastewater, synthetic dyes are considered a major environmental problem because of their strong color, complex chemical structure, persistence, and possible toxic effects. Many industries, including textile, paper, plastic, leather, cosmetic, and printing industries, release colored effluents containing organic dyes that are difficult to remove by conventional treatment methods **[1]**. Methylene blue (MB) is one of the most widely used cationic dyes in industrial applications. It is commonly applied in textile dyeing, medical uses, and laboratory analysis. Although it has several useful applications, its release into water bodies can cause serious environmental and health problems. The presence of methylene blue in aquatic systems reduces light penetration, disturbs photosynthetic activity, decreases dissolved oxygen levels, and negatively affects aquatic organisms. In addition, prolonged exposure to methylene blue may lead to adverse effects on human health, including irritation, respiratory problems, and other toxicological impacts **[2]**. Therefore, removing methylene blue from contaminated water is an important environmental issue.

Several methods have been used for the removal of dyes from wastewater, including coagulation–flocculation, membrane filtration, ion exchange, oxidation, biodegradation, and electrochemical treatment. However, many of these methods have limitations such as high cost, sludge production, incomplete removal, and complicated operation. Among these methods, adsorption is considered one of the most effective and practical techniques because it is simple, efficient, low-cost, and easy to operate **[3]**. Adsorption is a surface phenomenon in which dye molecules are transferred from the liquid phase and attached to the surface of a solid material called an adsorbent. The efficiency of adsorption depends mainly on the properties of the adsorbent, such as surface area, porosity, chemical composition, and available functional groups. Activated carbon is widely used as an adsorbent because of its high adsorption capacity and porous structure. However, its high production and regeneration costs limit its use on a large scale, especially in developing countries. For this reason, researchers have focused on finding low-cost, natural, renewable,

and environmentally friendly adsorbents. Agricultural materials and plant-based wastes are especially attractive because they are cheap, available, biodegradable, and can be used for pollutant removal from water **[4]**.

In this study, cumin is proposed as a natural and low-cost adsorbent for the removal of methylene blue from aqueous solutions. Cumin contains organic components such as cellulose, hemicellulose, lignin, proteins, and other surface functional groups. These groups may help in the adsorption of dye molecules through electrostatic attraction, hydrogen bonding, and surface interactions. The use of cumin as an adsorbent may provide a simple and sustainable approach for dye removal, while also supporting the use of natural agricultural materials for environmental applications.

The main objective of this study is to investigate the adsorption of methylene blue from aqueous solutions using cumin as a biosorbent. The effect of different experimental parameters, including contact time, pH, adsorbent dose, initial dye concentration, ionic strength, and temperature, will be studied. In addition, adsorption kinetic and isotherm models will be applied to better understand the adsorption behavior and evaluate the efficiency of cumin for methylene blue removal.

This dissertation is organized into four main chapters:

- **The first chapter** presents a general overview of dye pollution in water, wastewater treatment methods, and the adsorption process.
- **The second chapter** reviews previous studies related to the adsorption of dyes using natural and agricultural adsorbents, with particular focus on methylene blue removal.
- **The third chapter** describes the materials, chemicals, and experimental procedures used in this study, including adsorbent preparation, adsorption experiments, and analytical methods.
- **The fourth chapter** presents and discusses the experimental results of methylene blue adsorption onto cumin, including the effects of operating parameters, adsorption kinetics, and isotherm studies.

Finally, the general conclusion summarizes the main findings of the research and provides recommendations for future studies on the use of natural adsorbents in wastewater treatment.

Chapter I:
General Overview

I.1. Introduction

Water quality is threatened by various pollutants, among which industrial dyes represent a major concern. These dyes originate from several sectors, including the textile, food, pharmaceutical, cosmetic, leather, and printing industries. Their discharge into water bodies can contaminate aquatic environments and endanger aquatic ecosystems.

Industrial dyes are often persistent, toxic, and difficult to degrade. They can alter water quality, disturb biodiversity, and pose risks to human health. In response to these environmental challenges, governments, regulatory authorities, and industries have made increasing efforts to monitor, treat, and regulate contaminated wastewater before its discharge into the environment.

I.2. Water pollution

Water pollution is considered one of the most serious environmental problems because water is closely connected to air, soil, and living organisms. Due to its physicochemical properties, water is often used as a medium for the disposal of domestic, agricultural, and industrial waste. When these wastes are discharged without proper treatment, water becomes not only polluted but also a carrier of pollutants **[5]**.

Water pollution can occur at different levels including **[6]**:

- Groundwater or water sources, mainly due to the infiltration of contaminated wastewater.
- Surface water such as rivers, lakes, and streams, which may be polluted by the discharge of untreated or poorly treated effluents.
- Water supply networks, where contamination may occur through damaged pipes, poor sanitation, or inadequate treatment.

I.3. Different types of pollution

Water pollution can be classified into several types according to the nature of the pollutant.

I.3.1. Physical pollution

Physical pollution is characterized by changes in the physical properties of water, such as turbidity, color, temperature, and the presence of suspended or floating materials. This type of pollution may result from soil erosion, industrial discharges, solid wastes, or thermal

releases. It also includes thermal pollution, caused by an abnormal increase or decrease in water temperature, and radioactive pollution, which may originate from natural or artificial sources **[6]**.

I.3.2. Chemical pollution

Chemical pollution results from the release of toxic substances such as nitrates, phosphates, heavy metals, acids, bases, pesticides, detergents, dyes, and other toxic compounds. Their presence can change the chemical composition of water and make it unsafe for aquatic life, agriculture, industry, and human consumption.

Chemical pollutants are commonly classified into several categories, including undesirable chemical substances, pesticides and related products, detergents, dyes, and other toxic elements **[7]**.

I.3.3. Biological pollution

Biological pollution is caused by the proliferation of microorganisms in water, influenced by hygiene conditions, populations and ecological characteristics. The main pathogenic organisms include bacteria, viruses, parasites and fungi, contributing to bacterial, viral or parasitic pollution **[6]**.

I.4. Sources of water pollution

Water pollution may originate from natural or human activities. The major sources include natural, industrial, domestic, and agricultural sources.

I.4.1. Natural pollution

The presence of undesirable substances in water is not always caused by human activity. Some natural phenomena can also contribute to water pollution. For example, the contact of water with mineral deposits may lead, through erosion or dissolution, to increased concentrations of heavy metals, arsenic, and other minerals. Volcanic eruptions, natural oil seepage, and underwater hydrocarbon discharges may also contribute to water contamination **[8]**.

I.4.2. Industrial pollution

Industrial pollution is one of the major sources of water contamination. Unlike domestic pollution, which is generally more constant in composition, industrial wastewater is highly variable because it depends on the type of industry and the processes in which water is used **[8]**.

According to industrial activity, various types of pollution can be found, including **[8]**:

- Metals such as lead, zinc, arsenic, copper, mercury and cadmium in industrial wastewater harm humans and other animals.
- Dyes and additives used by textile industries may constitute a serious threat to the environment.
- Hydrocarbons from petroleum industries, transport activities, ships, oil platforms, and pipelines.
- Organic matter and fats from slaughterhouses, and food processing industries.
- Acids, bases and various chemical products from chemical industries, and tanneries.
- Hot water discharges, which cause thermal pollution by changing the normal temperature of aquatic environments.
- Radioactive materials from nuclear power plants, and radioactive waste treatment activities.
- Pesticides such as DDT (Dichloro-diphenyl-trichloroethane; $C_{14}H_9Cl_5$), including insecticides, rodenticides, fungicides and herbicides, which are chemical compounds with toxicological properties widely used in agriculture and may contaminate surface and groundwater.

I.5. Dyes

I.5.1. Generalities

A dye is a colored substance that has the ability to impart color to a material. In addition to having its own color, a dye must show affinity toward the substrate on which it is applied, such as textile fibers. This affinity between the dye and the fiber is one of the main reasons why dyes are difficult to remove from wastewater.

Synthetic dyes are designed to meet several performance requirements, including resistance to washing, abrasion, light exposure, chemical oxidation, detergents, and microbial degradation. These properties improve the durability of dyed products but also increase the persistence of dyes in the environment. Dyes with strong acidic or basic characteristics usually show high affinity toward fibers, which further enhances their stability and reduces their biodegradability [**9]**.

I.5.2. Definitions

Coloring substances are characterized by their ability to absorb light radiation in the visible spectrum (from 380 to 750 nm). The transformation of white light into colored light by reflection on a body, or by transmission or diffusion, results from the selective absorption of energy by certain groups of atoms called chromophores.

The molecule containing the chromophore is called a chromogen. The intensity of color depends mainly on the nature of the chromophore and its ability to participate in electronic transitions. Other groups, known as auxochromes, can intensify the color or modify the shade by changing the electronic environment of the chromophore. Common auxochrome groups include amino, hydroxyl, alkoxy, and other electron-donating groups **[9]**.

Table I.1: Main chromophore and auxochrome groups, classified by increasing intensity **[9]**

Chromophore groups	**Auxochrome groups**
Azo (-N=N-)	Amino ($-NH_2$)
Nitroso (-NO or -N-OH)	Methyl-amino ($-NHCH_3$)
Carbonyl (=C=O)	Dimethyl-amino
Vinyl (-C=C-)	$N(CH_3)_2$)
Nitro ($-NO_2$ or =NO-OH)	Hydroxyl (-HO)
Sulphide (C=S)	Alkoxyl (-OR)
	Electron-donor groups

I.5.3. Classification of dyes

Dyes can be classified mainly according to their chemical structure or according to their method of application. These two classification systems are commonly known as chemical classification and tinctorial classification **[10, 11]**.

a. Chemical classification

The classification of dyes according to their chemical structure is based on the nature of the chromophore group, which constitutes the skeleton necessary for the coloration of the molecule **[10, 12]**.

b. Tinctorial classification

Tinctorial classification is based on the practical application of dyes to different substrates. This classification is more useful for dyeing processes because it provides information about dye solubility, affinity toward specific fibers, and the type of bonding involved in dye fixation.The interaction between the dye and the substrate may occur through ionic bonds, hydrogen bonding, Van der Waals forces, or covalent bonds. Based on application properties, dyes can be classified into several groups, including acid dyes, basic dyes, direct dyes, reactive dyes, disperse dyes, vat dyes, sulfur dyes, and mordant or metal-complex dyes **[12]**.

I.5.4. Toxicity of dyes

The toxicity of dyes depends mainly on their chemical structure, concentration, degradation products, and exposure conditions. Some dyes and their by-products may be harmful to aquatic organisms and humans. In particular, many studies have reported the toxic, mutagenic, and carcinogenic effects of certain azo dyes, indicating that wastewater containing these dyes should be treated before being discharged into the environment **[13]**. Their toxicity is due to the presence of carcinogenic groups such as aromatic groups, phthalogenic groups, cyanuric groups and salts of barium and lead. These carcinogenic groups attack the pyrimidine bases of DNA and RNA and consequently cause alteration of the genetic code with mutation and risk of cancer **[14]**.

Among industrial dyes, particular interest is given to the toxicity of azo dyes, characterized by the presence of the azo group (–N=N–).

The breaking of azo bonds leads to the formation of primary amines which cause methemoglobinemia, characterized by an obstruction of oxygen transport in the blood. Respiratory allergy to reactive dyes was reported for the first time by Alanko in subjects employed in weighing and mixing these dyes in powder form for two years and presenting asthma and/or occupational rhinitis **[15]**.

I.5.5. Dye removal processes

Significant quantities of dyes can be released into wastewater during industrial dyeing processes. This is mainly related to the incomplete fixation of dyes onto fibers. The degree of dye fixation depends on the dye class, fiber type, dyeing conditions, and the nature of the dye–fiber interaction. Table I-2 summarizes the estimation of the fixation degrees of different dyes on textile fibers. Showing that, dyes with low fixation rates may lead to higher dye losses in effluents.

Table I-2: Estimation of the fixation degrees of different dyes on textile fibers **[16]**

Dye class	Fiber used	Fixation degree (%)	Losses in effuent (%)
Acid	Polyamide	80 - 95	5 - 20
Basic	Acrylic	95 - 100	0 - 5
Vat	Cellulose	80 - 95	5 - 20
Direct	Cellulose	70 - 95	5 - 30
Dispersed	Synthetic	90 - 100	0 - 10
Reactive	Cellulose	50 - 90	10 - 50
Sulfur	Cellulose	60 - 90	10 - 40
Metalliferous	Wool	90 - 98	2 - 10

Azo dyes represent one of the largest classes of synthetic dyes and account for a major proportion of dyes listed in the color Index. Many azo dyes are used as acid, reactive, and direct dyes. Due to their wide use, high water solubility, and incomplete fixation in some dyeing processes, they are among the most frequently discharged dyes in textile wastewater.

Several treatment methods have been developed for the removal of dyes and other organic pollutants from wastewater. These methods can be generally classified into physical, chemical, and biological treatments. Physical methods include adsorption, membrane filtration, precipitation, coagulation, flocculation, and sedimentation. Chemical methods include oxidation using ozone, hydrogen peroxide, sodium hypochlorite, or other oxidants, as well as reduction and ion exchange. Biological methods include aerobic and anaerobic degradation processes **[16].**

Although many of these techniques can be effective, their efficiency depends on the dye structure, wastewater composition, operating conditions, and treatment cost. Among these methods, adsorption is widely considered a simple and efficient technique for dye removal, especially when low-cost and natural adsorbents are used. Therefore, adsorption will be discussed in more detail in the following sections.

I.6. Adsorption

Adsorption phenomena were first observed in liquids by Lowitz in 1785. A few years later, one of the earliest industrial applications of adsorption was reported in sugar refining, where charcoal was used to decolorize syrups. In 1860, charcoal was also used to remove unpleasant taste and odor from water. At the beginning of the twentieth century, adsorption techniques developed further with the progress of scientific understanding. During the First World War, the purification ability of activated carbon was demonstrated in several practical applications **[17]**.

I.6.1. Definition of adsorption

Several definitions have been given by various authors; we report in these paragraphs the most common ones **(Figure I.1)**:

Adsorption is a physico-chemical phenomenon resulting in a modification of concentration at the interface between two immiscible phases: (liquid/solid) or (gas/solid); we therefore identify the pair (adsorbate/adsorbent).

Adsorption by a solid is defined as the phenomenon of fixation of molecules of a gaseous or liquid phase on the surface of this solid.

Adsorption can also be defined as a physical operation of separation of mixtures, and the process in which a substance is removed by another in which it becomes concentrated at the interface **[18]**.

Adsorption is a surface phenomenon by which atoms or molecules of a fluid (adsorbates) are fixed on a solid surface (adsorbent) according to various processes of more or less intensity thanks to physical and/or chemical interactions **[19]**.

In general, adsorption is defined as a process resulting in a net accumulation of a substance at the interface between two phases **[20]**.

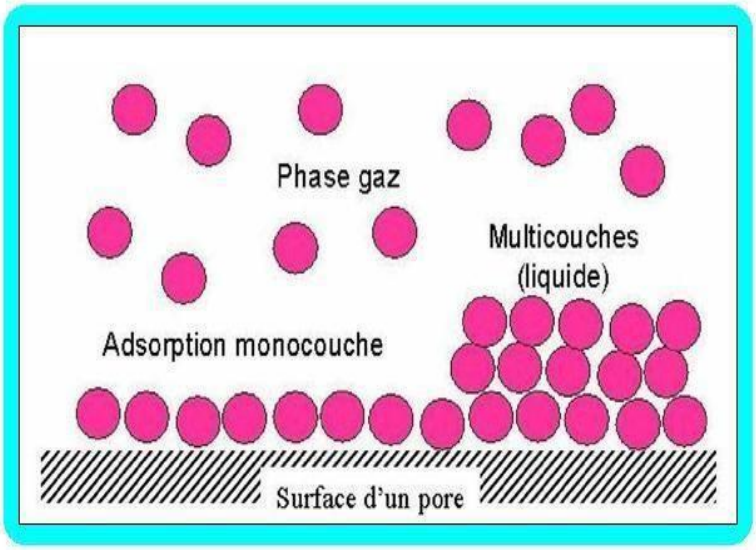


Figure I.1: Simplified diagram representing the adsorption phenomenon.

I.6.2. Nature of adsorption

Adsorption is generally divided into two main types: physical adsorption and chemical adsorption (Table I.3). Physical adsorption, or physisorption, is governed by weak intermolecular forces, whereas chemical adsorption, or chemisorption, involves stronger chemical interactions between the adsorbate and the adsorbent surface **[21]**.

.

Table I.3: Comparison between physical adsorption and chemical adsorption **[21]**

Properties	**Physical adsorption**	**Chemical adsorption**
Type of bond	Van der Waals bond	Chemical bond
Process temperature	Relatively low compared to the boiling temperature of the adsorbate	Higher than the boiling temperature of the adsorbate
Molecular individuality	Molecular individuality is preserved	Destruction of molecular individuality
Desorption	Easy	Difficult
Kinetics	Rapid, independent of temperature	Very slow
Heat of adsorption	Less than 10 kcal/mole	Greater than 10 kcal/mole
Energy involved	Low	High
Type of formation	Multilayer and monolayer formation	Monolayer formation

I.6.3. Adsorption mechanisms

During the adsorption of a species on a solid, the mass transfer of molecules occurs from the fluid phase toward the center of the adsorbent **[22]**.

1. External mass transfer (external diffusion) which corresponds to the transfer of the solute from the bulk of the solution to the external surface of the particles.

2. Internal mass transfer in the pores (internal diffusion) which takes place in the fluid filling the pores. The molecules propagate from the surface of the grains toward their center through the pores.

3. Surface diffusion: for certain adsorbents, there may also exist a contribution from the diffusion of adsorbed molecules along the surfaces of the pores at the scale of an adsorbent grain.

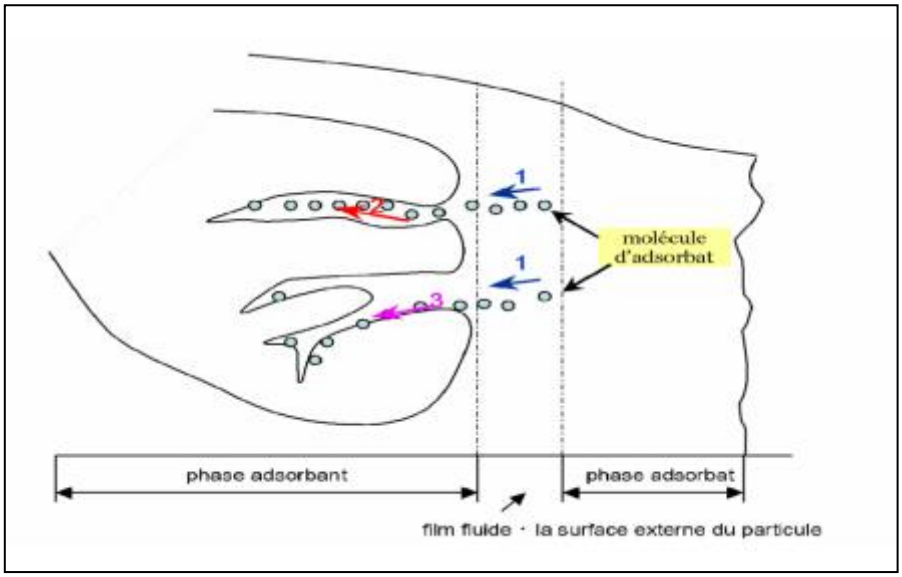


Figure I.2: Diagram of the transport mechanism of an adsorbate within a grain **[22]**.

I.6.4. Factors influencing adsorption

The efficiency of adsorption depends on several factors related to the adsorbent, the adsorbate, and the operating conditions. When a solid is brought into contact with a solution, both the solute and the solvent may compete for adsorption sites. In wastewater treatment, the desired case is when the pollutant molecules are adsorbed more strongly than the solvent molecules. The main factors affecting adsorption are discussed below **[23]**:

a. Temperature

Temperature can significantly affect the adsorption process. In many cases, adsorption is exothermic; therefore, increasing temperature may decrease adsorption capacity. However, in some systems, higher temperature can improve adsorption by increasing molecular mobility and pore diffusion. Therefore, the effect of temperature should be evaluated experimentally for each adsorbent–adsorbate system.

b. Nature of the adsorbent

The properties of the adsorbent strongly influence adsorption efficiency. Important adsorbent characteristics include particle size, porosity, specific surface area, pore size distribution, and surface functional groups. Smaller particle size generally increases the available surface area and improves contact between the adsorbent and the pollutant.

However, if the pores are smaller than the adsorbate molecules, adsorption inside the pores may be limited even when the surface has strong affinity for the pollutant.

c. Nature of the adsorbate

Adsorption also depends on the properties of the adsorbate, such as molecular size, molecular weight, polarity, solubility, charge, and chemical structure. Good adsorption usually requires affinity between the adsorbent surface and the adsorbate molecules. In general, polar adsorbents tend to adsorb polar molecules, whereas non-polar adsorbents show greater affinity toward non-polar molecules. For organic compounds, adsorption may increase with molecular size and hydrophobicity.

d. Molecular orientation

The orientation of adsorbate molecules on the adsorbent surface depends on the type of interaction between the molecule and the surface. Molecules may attach flat or vertically depending on their structure, functional groups, and the nature of the adsorbent. This orientation can influence the surface coverage and the adsorption capacity.

For example, the adsorption of fatty acids of general formula CH_3-(CH_2)n-COOH in an organic solvent adsorbed on certain metals such as platinum shows vertical orientation and the molecular area of the acid is 20.5 Å. On carbon black the fatty acid molecule lies flat 114 Å.

e. Specific surface area

Specific surface area is one of the most important parameters in adsorption. It represents the accessible surface area per unit mass of adsorbent. In general, adsorbents with higher specific surface area provide more available adsorption sites and therefore may show higher adsorption capacity. However, adsorption also depends on pore accessibility and the chemical nature of the surface, not only on surface area.

I.6.5. Modeling of isotherms

The parameters obtained from isotherm modeling provide important information on the adsorption mechanism, surface properties and adsorbent–adsorbate affinities.

The two most commonly used three parameter models are the models of Langmuir and Freundlich.

- **Langmuir model**

This model is very useful for the monomolecular adsorption of a solute forming a monolayer on the surface of an adsorbent; this model is used when the following conditions are satisfied **[24]**:

The adsorbed species is fixed on a single well-defined site, each site is capable of fixing only one adsorbed species, the adsorption energy of all sites is identical and independent of other species already adsorbed on neighboring sites.

It is described by the following expression:

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{k_1 \times Q_m} \times \frac{1}{c_e} \qquad \textbf{(I.1)}$$

With:

q: quantity of substance adsorbed at equilibrium per unit weight of the adsorbent (adsorption capacity) (mg/g).

$\mathbf{q_m}$: adsorption capacity at saturation (mg/g).

$\mathbf{C_e}$: concentration of the substrate in adsorbate at equilibrium (mg/l).

$\mathbf{K_L}$: Langmuir constant.

- **Freundlich model**

The empirical Freundlich model is based on adsorption on heterogeneous surfaces **[25]**.

$$lnQ_e = lnk_f \times \frac{1}{n} lnc_e \qquad \textbf{(I.2)}$$

With:

$\mathbf{q_e}$: quantity adsorbed per gram of the solid.

$\mathbf{C_e}$: concentration of the adsorbate at adsorption equilibrium.

$\mathbf{k_f}$ and **1/n**: Freundlich constants characteristic of the efficiency of a given adsorbent with respect to a given solute.

I.6.6. Kinetic modeling

Adsorption kinetics is used to study the rate of adsorption and to understand the time required for the adsorption process to reach equilibrium. Kinetic studies are important because they provide information about the possible rate-controlling steps involved in adsorption. **[26]**:

Kinetic models are used to analyze experimental adsorption data and to identify the adsorption rate mechanism. The most commonly used kinetic models are the pseudo-first-order and pseudo-second-order models.

- Pseudo-first-order model (PFO)

The expression is given by Lagergren **[27]**:

$$\frac{dqt}{dt} = K1(qe - qt) \qquad \textbf{(I.3)}$$

Where:

K_1: rate constant of first-order adsorption reaction.

q_e: quantity adsorbed at equilibrium (mg/g).

qt: quantity adsorbed at time t (mg/g).

t: contact time (min).

After integration with the initial conditions qt = 0 at t = 0, the equation becomes:

$$Qt = qe(1 - e^{-k1t}) \qquad \textbf{(I.4)}$$

The linearization of the previous equation gives:

$$Ln\ (qe - qt) = lnqe - k1t \qquad \textbf{(I.5)}$$

By plotting ln (qe − qt) = f(t), a straight line is obtained which gives k_1 and qe.

This model makes it possible to describe the phenomena occurring during the first minutes of the adsorption process **[28]**.

- Pseudo-second-order model (PSO)

The pseudo-second-order model (PSO) is given by the following expression **[29]**:

$$\frac{dQt}{dt} = K_2(Qe - Qt)^2 \qquad \textbf{(I.6)}$$

Where:

K_2: rate constant of second-order adsorption reaction (mg/g.min).

Q_e: quantity adsorbed at equilibrium (mg/g).

Q_t: quantity adsorbed at time t (mg/g).

t: contact time (min).

After integration we obtain:

$$\frac{1}{Qt} = (1/(K_2.Qe)^2 + \left(\frac{1}{Qe}\right).t \qquad \textbf{(I.7)}$$

By plotting t/qt = f(t), a straight line is obtained which gives k_2 and qe.

Compared with the pseudo-first-order model, the pseudo-second-order model is often applicable over a wider range of adsorption time.

I.6.7. Thermodynamic study

The adsorption of a solute from an aqueous solution onto the surface of a solid adsorbent can be considered a thermodynamic equilibrium between the solute remaining in solution and the solute adsorbed on the adsorbent surface **[30]**:

This equilibrium is characterized by an equilibrium constant K_d, given by the law of mass action:

$$K_d = \frac{q_e}{C_e} \quad \textbf{(I.8)}$$

Knowing that:

$$q_e = \frac{(C_0 - C_e)\cdot V}{m} \quad \textbf{(I.9)}$$

Therefore:

$$q_e = \frac{(C_0 - C_e)\, V}{m\ C_e} \quad \textbf{(I.10)}$$

Where:

q_e: amount adsorbed at equilibrium;

C_0: initial solute concentration;

C_e: equilibrium residual concentration.

The thermodynamic parameters, including Gibbs free energy change ΔG^0, enthalpy change ΔH^0, and entropy change $\Delta S^0$are used to evaluate the nature and feasibility of the adsorption process It is expressed as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \textbf{(I.11)}$$

Where:

ΔH: enthalpy change (J/mol);

ΔS: entropy change (J/mol·K).

The variation in energy can also be expressed in terms of the equilibrium constant:

$$\Delta G = \Delta G^\circ + RT\ln K_d \quad \textbf{(I.12)}$$

At equilibrium:

$$\Delta G = 0 \quad \textbf{(I.13)}$$

Therefore:

$$\Delta G^\circ = -RT\ln K_d \qquad \textbf{(I.14)}$$

The Gibbs free energy ΔG° is also related to the standard enthalpy of adsorption and standard entropy by the following relation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Thus:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad \textbf{(I.15)}$$

I.6.8. Adsorbents

Adsorbents are solid materials capable of retaining molecules, ions, or atoms on their surface through physical or chemical interactions. Although almost all solids can show adsorption to some extent, only materials with suitable surface area, porosity, and surface chemistry are practically useful as adsorbents.

Industrial adsorbents generally possess high specific surface area and developed pore structures. According to the IUPAC classification, pores are classified as micropores when their diameter is less than 2 nm, mesopores when their diameter is between 2 and 50 nm, and macropores when their diameter is greater than 50 nm.

The most common industrial adsorbents include activated carbon, zeolites, silica gel, activated alumina, and activated clays. However, due to the relatively high cost of some commercial adsorbents, increasing attention has been given to low-cost natural and agricultural materials for wastewater treatment applications **[31]**.

I.6.9. Field of application of adsorption

Adsorption is widely used in several industrial and environmental applications because of its simplicity, efficiency, and versatility. The main applications of adsorption include **[26]**:

- Drying of gases and liquids.
- Purification of gases.
- Treatment of oils.
- Decolorization of liquids.
- Removal of taste and odor from water.
- Treatment of textile wastewater.
- Removal of dyes and other organic pollutants from wastewater.

Chapter II:
Literature Review

II.1. Introduction

Methylene blue (MB) is a widely used cationic dye and a common model pollutant in adsorption studies due to its strong color, stability, and environmental impact. Its presence in wastewater can harm aquatic life, making its removal an important treatment objective.

Recently, agricultural wastes and natural materials have gained attention as low-cost adsorbents for dye removal. Materials such as rice husk, coconut shell, lemon leaves, green pea residues, and fruit peels are abundant, biodegradable, and rich in functional groups, allowing them to interact with dye molecules through electrostatic attraction, hydrogen bonding, pore filling, and surface interactions.

This chapter reviews recent studies, particularly from 2016 to 2024, on the use of agricultural and natural adsorbents for methylene blue removal from water. Special attention is also given to cumin-based materials, including cumin seed powder, cumin residues, and modified cumin waste, as potential biosorbents for the removal of dyes, pharmaceuticals, and heavy metals. This review provides the scientific basis for using cumin as a sustainable, low-cost, and environmentally friendly adsorbent for wastewater treatment.

II.2. Bibliographic review of MB as an adsorbate

Methylene blue (MB) is a cationic dye belonging to the phenothiazine family. It is commonly found as a dark green crystalline powder and may exist in different hydrated forms, among which the trihydrate form is the most common. Because of its strong color, stable molecular structure, and environmental relevance, MB is widely used as a model organic pollutant in adsorption studies. Its presence in water can negatively affect aquatic ecosystems and may cause harmful effects on living organisms. Therefore, the reduction or removal of MB from wastewater before discharge is an important environmental requirement **[32]**.

Several recent studies have investigated the removal of MB using agricultural wastes and natural adsorbents.

- **MC Holiday et al. (2024) s**tudied the adsorption of methylene blue using green peas as a low-cost adsorbent. Their results showed that the Freundlich isotherm provided the best fit for the equilibrium data, indicating heterogeneous adsorption behavior. The adsorption kinetics followed the pseudo-second-order model, and the maximum adsorption capacity reached 167 mg/g at low temperature **[33]**.
- **Rahmaiana Zein et al. (2022)** performed a series of experiments on the adsorption of methylene blue using lemon leaves as adsorbents. The optimal conditions were pH 9, an initial concentration of 600 mg/L, a contact time of 45 min at room temperature, and desorption at 25 °C. The equilibrium data fitted both Langmuir and Freundlich isotherms. Kinetic studies indicated that the pseudo-second-order model best describes the adsorption process. Thermodynamic analysis showed that the process is exothermic, with adsorption capacity increasing from 43.1556 mg/g to 122.1211 mg/g under optimized conditions **[34]**.
- **Jawad et al. (2021)** investigated the adsorption of methylene blue onto activated carbon derived from Lantana camara wood. The study demonstrated that the Langmuir isotherm model provided the best fit for the equilibrium data, with a maximum monolayer adsorption capacity of 277.78 mg/g. The adsorption kinetics followed the pseudo-second-order model, and thermodynamic analysis confirmed the process to be spontaneous and endothermic in nature **[35]**.
- **Alvear et al. (2020)** investigated the removal of methylene blue from aqueous solutions using rice husk under different conditions and obtained a maximum experimental adsorption capacity of 240 mg/g for bio-composite beads. They also found that pH had no significant effect on dye removal efficiency, while temperature and ionic strength led to a decrease. The removal process was analyzed using isotherm models to determine the adsorption mechanism, and the Freundlich isotherm along with the pseudo-second-order kinetic model showed the best agreement with the experimental data **[36]**.
- **Kahului et al. (2019)** investigated activated carbon derived from coconut shells for MB removal from aqueous solutions. The prepared adsorbent showed high removal efficiencies of 99.42% and 98.64% at pH 8. The adsorption process was best described by the Freundlich isotherm and pseudo-second-order kinetic model,

suggesting that surface heterogeneity and strong adsorbent–adsorbate interactions contributed to the removal process **[37]**.

II.3. Bibliographic review of cumin as an adsorbent

Cumin (Cuminum cyminum L.) and cumin-derived materials have recently received attention as low-cost and natural adsorbents for the removal of pollutants from aqueous solutions. Different forms of cumin-based materials, such as raw seed powder, biomass residues, spent cumin, modified cumin waste, and plant extracts, have been investigated for the adsorption of dyes, pharmaceutical pollutants, and heavy metals. The adsorption ability of cumin is mainly related to its organic composition, which may include cellulose, hemicellulose, lignin, proteins, phenolic compounds, and different surface functional groups. These components can interact with pollutants through electrostatic attraction, hydrogen bonding, surface complexation, and pore-filling mechanisms.

- **Dhaif-Allah, M. A. H. et al. (2024)** has also been studied for the removal of Acid Blue 113, an azo dye, from water onto cumin seed spent, obtained as a nutraceutical industrial by-product,The study evaluated the effects of pH, adsorbent dosage, temperature, particle size, and initial dye concentration on adsorption performance. The maximum experimental adsorption capacity was reported to be 96 mg/g. The adsorption kinetics were best described by the pseudo-second-order model, while thermodynamic analysis indicated that the process was endothermic and non-spontaneous under the studied conditions. FTIR and SEM analyses confirmed surface changes after dye adsorption **[38]**.
- **Rajeshkumar et al. (2023)** investigated the use of biosynthesized nanoparticles derived from Cuminum cyminum for the adsorption of the cationic dye Red 95 from aqueous solution. Batch adsorption experiments showed that the removal efficiency depended on operating parameters such as pH, contact time, and adsorbent dosage. Under optimized conditions, dye removal efficiencies higher than 85% were reported **[39]**.
- **Abadian, S., et al. (2022)** investigated the use of Cuminum cyminum agricultural waste modified with tetradecyltrimethylammonium bromide (TTAB) for the removal of diclofenac sodium from aqueous solution. The prepared adsorbent was characterized

using field emission scanning electron microscopy, Fourier-transform infrared spectroscopy, nitrogen adsorption–desorption analysis, and point of zero charge measurements. The effects of adsorbent dosage, contact time, initial diclofenac concentration, and solution pH were examined. The kinetic data fitted well with the pseudo-second-order model, while the Langmuir isotherm gave a maximum adsorption capacity of 93.65 mg/g **[40]**.

- **Fouda, A. S. et al. (2021) s**tudied the adsorption behavior of Cuminum cyminum extract on aluminum in hydrochloric acid medium. Although this work focused on corrosion inhibition rather than wastewater treatment, it is still relevant because it demonstrates the ability of cumin extract components to adsorb onto a solid surface. The adsorption behavior followed the Langmuir isotherm, and the maximum inhibition efficiency reached 93.1% at 25 °C using 300 ppm of cumin extract. Surface characterization using XPS, AFM, and FTIR confirmed the formation of an adsorbed protective layer on the aluminum surface [38]. This study supports the presence of active functional groups in cumin extract that can participate in surface interactions **[41]**.
- **Mohseni, M. et al. (2020)** examined the possibility of using adsorbents derived from the solid biomass residues of cumin varieties as the available biomass to decontaminate heavy metals from pharmaceutical effluents. The initial concentrations of Nickel, Zinc, Copper, Cobalt, and Lead in untreated effluents, and those treated with Cuminum cyminum and Bunium persicum residues, were analyzed by ICP-OES. The findings revealed that the cumin herbal extraction residues can significantly decrease ($P \leq 0.05$) the concentration of these heavy metals in pharmaceutical effluents and wastewater, with scientific evidence yielding impressive outcomes for removing total Lead by more than 88% efficacy **[42].**

Chapter III:
Experimental studies

III.1. Introduction

The aim of this study is to evaluate the efficiency of cumin powder as a low-cost natural adsorbent for the removal of methylene blue from aqueous solutions. This chapter presents the experimental methodology used to investigate the adsorption of methylene blue onto cumin. The adsorption experiments were carried out under different operating conditions, including adsorbent mass, solution pH, contact time, initial dye concentration, ionic strength, and temperature.

This chapter also describes the apparatus, materials, chemical reagents, preparation methods, UV–Visible spectrophotometric analysis, and calculation procedures used to determine the adsorption performance. The experimental work was conducted at the Process Engineering Research Laboratory, Department of Process Engineering, University of Laghouat.

III.2. Apparatus, materials and reagents used

III.2.1. Apparatus

- Analytical balance ;
- Magnetic stirrer ;
- Water bath shaker ;
- pH meter ;
- UV-visible spectrophotometer ;
- Laboratory Oven ;
- Variable-volume micropipette 100 – 1000 µL.

III.2.2. Materials used

- Graduated cylinder, capacity of 10, 50, 100 mL ;
- Volumetric flasks, capacity of 100, 250, 500 and 1000 mL ;
- Beakers, 50, 100, 250 mL ;
- Test tube of 5 mL ;
- Magnetic stir bars ;
- Cuvettes ;
- Glass funnel ;

- Spatula ;
- Watch glass ;
- Filter paper ;
- Test tube rack ;
- Funnels ;
- Wash bottle ;
- Crystallizing dishes

III.2.3. Chemical reagents used

The chemical reagents used in this study and their properties are grouped in Table III.1.

Table III.1: Characteristics of the reagents used.

Chemical reagent	Chemical formula	Molar mass g/mol	Density	Purity	Physical state
Sodium hydroxide	NaOH	39.99	–	98%	Crystalline solid
Sulfuric acid	H2SO4	98,08	1,84	98%	Liquid
Sodium chloride	NaCl	58,44	2,16	99,9%	Powder
Methylene blue	C16H18N3SCI	319.852	–	–	Powder

In our study, the dye Methylene Blue, designated by the acronym MB, was selected as the pollutant and acting as the adsorbate.

III.3. Determination of MB by UV-Visible spectroscopy

It is a quantitative analysis technique that makes it possible to determine the concentration of a solute in a solution by exploiting the interaction of the electrons of the solute molecules with light. The concentrations of the different solutions used as well as the equilibrium concentrations were determined by analysis using a UV-Visible spectrophotometer (Appendix 1) at the maximum wavelength (λ max). This method is based on the Beer-Lambert law **[30]**.

The absorbance A of the solution is then calculated using Equation III.1.

$$A = -\log\left(\frac{I}{I_0}\right) \qquad \textbf{(III.1)}$$

Where:

A: absorbance of the solution at a wavelength λ;

I_0: intensity of the reference beam;

I: transmitted intensity of the beam passing through the sample.

The pollutant concentration in the sample is determined from the absorbance using the Beer–Lambert law (Equation III.2).

III.3.1. Beer-Lambert law

The principle of analysis by UV-visible spectrophotometry is based on the Beer-Lambert law. The latter is used to establish a relationship between absorbance, sample thickness and the concentration of absorbing species. The Beer-Lambert law is only valid if the following conditions are respected **[43]**:

- Monochromatic light
- Very dilute solutions
- No reflection, diffusion or fluorescence of the incident beam.

The Beer-Lambert law is expressed in the following form:

$$A = \varepsilon \cdot L \cdot C \qquad \textbf{(III.2)}$$

With:

A: Absorbance of the solution (unitless);

Ɛ: Molar extinction (absorption) coefficient ($L.mole^{-1}.cm^{-1}$).

L: Path length or cuvette length (cm);

C: Molar concentration of the adsorbing species ($mol.L^{-1}$).

III.3.2. Determination of λ max

The maximum absorption wavelength λ max was determined by recording the absorption spectrum of a sample solution at a concentration of 100 mg/L of MB, after scanning wavelengths in the visible range from 400 to 800 nm. After identifying the maximum absorption wavelength of methylene blue, a standard MB solution was prepared from the

stock dye solution (1 g/L) to measure the absorbance and plot the appropriate calibration curves. Thus, the analysis revealed a λ max value equal to 664 nm **[43]**.

III.3.3. Establishment of the calibration curve

- To establish the calibration curve, the following steps must be followed:
- Preparation of the stock solution of 1000 ppm and the blank standard
- Preparation of standard solutions with concentrations ranging from 15 ppm to 10 ppm from the stock solution;
- Set the wavelength at λ = 664 nm for MB determination,
- Perform the different readings for the prepared standards,
- Plot the calibration curve of absorbance as a function of concentrations.

III.3.4. Determination of the residual concentration of the sample

After the equilibrium time, the samples are filtered then analyzed by UV-Visible spectroscopy.

The residual dye concentration is determined from the linear equation of the calibration curve obtained previously.

III.4. Methylene Blue

Methylene blue (MB) is a basic cationic dye derived from phenothiazine (Appendix 2), it plays a predominant role in various fields, such as biology where it is used as an antimicrobial and photodynamic agent, as well as in solar cells as a photosensitizer.

It is also used in photocatalysis and mainly in the textile industries. However, it is important to note that generally about 10 to 15% of the dyes used are lost in basic dyes such as MB are reported to cause dermatitis, skin irritation and cancer. In case of inhalation, it can cause rapid or difficult breathing in the short term, while ingestion by mouth produces a burning sensation and can cause nausea, vomiting and mental confusion.

Therefore, MB poses harmful effects on aquatic ecosystems and its removal from water is thus essential **[44]**.

III.4.1. Physicochemical properties of Methylene Blue

The main physico-chemical characteristics of methylene blue are presented in Table III.2.

Table III.2: Main physico-chemical characteristics of MB **[45].**

Name	Methylene blue (MB)
Chemical name	**3,7-bis(dimethylamino) phenazathionium chloride**
Synonyms	**Methylthioninium chloride, C.I. 52015, C.I. Basic Blue 9 (hydrate)**
Family	Basic dyes
Semi-developed formula	$C_{16}H_{18}ClN_3S$
Chemical name	3,7-bis-(dimethylamino) phenazathionium
Molar mass (g/mol)	319.85 g mol^{-1}
Solubility	40 $g{\cdot}L^{-1}$ at 20 °C
Nature	Cationic
Ionization	Basic
Melting temperature	Decomposes upon heating above 190 °C
Dimensions (A°)	15 (diameter)
λ max	664 nm
C.I. number	52015
C.I. name	Basic Blue 9
Chemical structure	

III.4.2. Toxicity of Methylene Blue

Toxicological data related to the use of methylene blue in humans over many years have so far indicated the absence of danger associated with the use of this product as a medication, provided that the total administered dose does not exceed 7 mg/kg. It may cause chest pain,

dyspnea, anxiety, tremors, hypertension, and even skin discoloration if the dose is high. Methylene blue is not highly dangerous, but it has a harmful effect on living organisms and water bodies **[46]**.

III.4.3. Fields of application of Methylene Blue

The main fields of application of methylene blue are **[47]**:

- Dyeing of silk and wool (approximately 0.3 to 2%), and cellulosic fibers.
- Leather and hides (shade adjustment).
- Coloring of paper in bulk, by dipping (crepe paper), or by spraying.
- Alcohol-based dyes.
- Coloring of chemical products: sulfuric acid (up to 20 g/L), acetic acid (pure or diluted), phosphoric acid, formic acid, etc.
- Marking of cationic or non-ionic chemical products (10 to 100 g/m³).
- Laboratory and medical analysis reagent.
- Temporary coloring of powders intended for cooking (the dye disappears when heated).
- Phytosanitary products.
- Aquariums: treatment of white spot disease in fish (ichthyophthiriasis), at a maximum rate of 0.5 to 2 mg/L of water.

III.5. Cumin

Cuminum cyminum L., commonly known as cumin, is an annual herb belonging to the Apiaceae family. It is widely cultivated in Mediterranean regions, North Africa, and parts of Asia. Cumin seeds are commonly used as a culinary spice and in traditional medicine because of their aromatic and bioactive compounds.

Cumin seeds contain essential oils, mainly cuminaldehyde, as well as carbohydrates, proteins, lipids, dietary fibers, flavonoids, and phenolic compounds. From an adsorption point of view, cumin powder can be considered a lignocellulosic biomass containing cellulose, hemicellulose, lignin, and different surface functional groups such as hydroxyl, carboxyl, and carbonyl groups. These functional groups may interact with pollutant

molecules through hydrogen bonding, electrostatic attraction, surface complexation, and pore-filling mechanisms.

Because of its availability, low cost, natural origin, and functional chemical composition, cumin may be considered a promising biosorbent for the removal of organic pollutants, including methylene blue, from aqueous solutions **[48]**.

II.6. Experimental methodology

III.6.1. Preparation of reagent solutions

• Preparation of NaOH (0.1 M):

To prepare the NaOH solution (0.1 M), 0.4 g of NaOH is weighed (m = 39.99 g/mol, p = 98%). This quantity is dissolved in distilled water in a 100 ml volumetric flask and distilled water is added up to the calibration mark. This solution is used to adjust the pH.

• Preparation of H_2SO_4 (0.1 M):

To prepare a solution of H_2SO_4 (0.1 M), 0.30 ml of H_2SO_4 is taken (M = 98.08 g/mol, P = 95%, d = 1.84). This quantity is dissolved in distilled water in a 100 ml volumetric flask and distilled water is added up to the calibration mark. This solution is also used to adjust the pH.

• Preparation of the stock dye solution:

We prepared the stock solution of methylene blue, with a concentration of 1 g/L, by weighing 1 g of powder using a precision electronic balance. This quantity was added to a glass volumetric flask with a capacity of 1,000 ml, followed by the addition of distilled water up to the calibration mark. Then, the flask was covered with aluminum to avoid degradation due to light during subsequent experiments.

• Preparation of the daughter solution:

From the stock solution, we prepared several solutions of different concentrations (15, 30, 50, 100, 150 ppm). To obtain a diluted solution according to the following dilution law:

$$C_1 . V_1 = C_2 . V_2 \qquad \textbf{(III.3)}$$

C_1: concentration of the stock solution (mol/l);

C_2: concentration of the daughter solution;

V_1: volume of the stock solution to be taken;

V_2: volume of the daughter solution.

III.6.2. Preparation of the adsorbent "Cumin"

In this study, cumin was used as the adsorbent. This adsorbent was collected from the local market of Laghouat, Algeria. The adsorbent preparation protocol is presented in the diagram of Figure III.1, which includes the following four steps: washing, drying, grinding, and sieving.

✓ **Washing:** The collected cumin was cut into small pieces and then washed several times with boiling distilled water for 30 minutes to remove impurities such as sand and dust.

✓ **Drying:** After washing the sample, drying was carried out in an oven at a temperature of 105°C for 24 hours in order to eliminate all traces of moisture.

✓ **Grinding:** Grinding was performed using an electric grinder to obtain a homogeneous material suitable for laboratory studies, producing small-sized particles. To obtain particles with well-defined dimensions, sieving is necessary.

✓ **Sieving:** The particles used for the adsorption tests were mechanically separated using a sieve with a particle size corresponding to a diameter less than or equal to 0.325 mm, before being stored in airtight containers for later use.

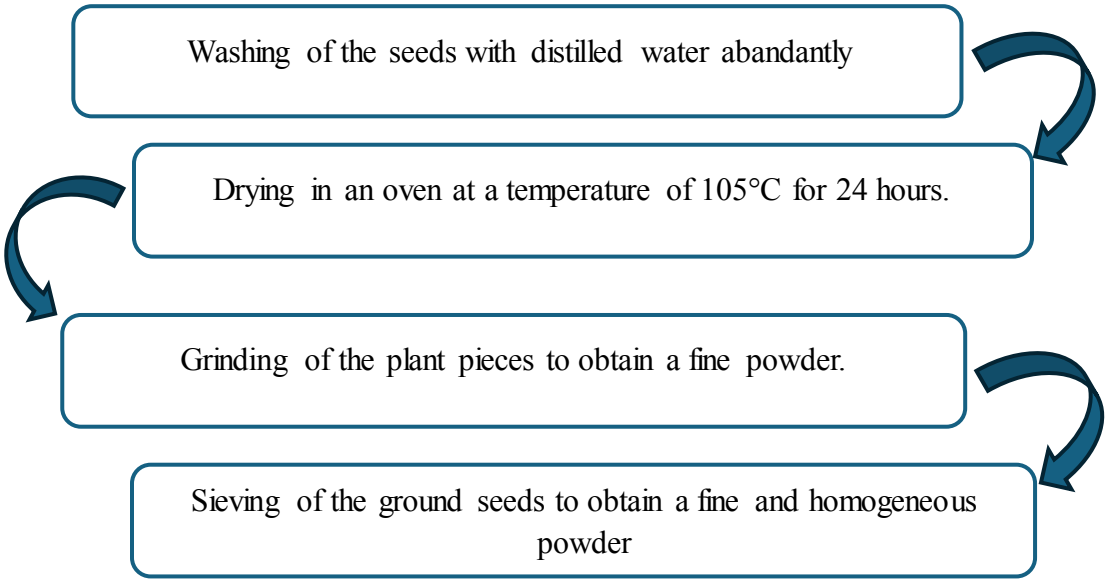


Figure III.1: Protocol for cumin adsorbent preparation.

III.7. Adsorption test protocol

Adsorption experiments are carried out in a batch system with a series of flasks that were used to study certain effects such as the effect of mass, temperature, time, concentration, ionic strength and pH, then diluted to measure the concentration using the UV-visible spectrophotometer.

III.7.1. Effect of adsorbent mass

The effect of the mass of treated cumin (TC) on adsorption was studied. To do this, we followed the following steps: we weighed the adsorbent material with different masses (0.05 - 0.1 - 0.2 - 0.3 - 0.4 - 0.5 - 0.6 - 0.8 - 1 g), added a volume of 50 ml of aqueous methylene blue dye solution (concentration of 50 ppm) into flasks, then placed the flasks in a water bath under agitation for two hours at a temperature of 25°C and a stirring speed of 150 rpm. After the elapsed time, the solutions were filtered, then diluted if necessary before being analyzed using a UV-visible spectrophotometer at a wavelength of 664 nm.

III.7.2. Effect of pH

The initial pH value of the solution plays a crucial role in the adsorption process. We prepared eight flasks, by adding the optimal mass of cumin weighed using a balance. Then, we added 50 ml of methylene blue solution with a concentration of 50 ppm into each flask. The pH was adjusted by adding a few drops of a sulfuric acid solution (0.1 M) or sodium hydroxide (0.1) to obtain the desired pH values (2–10). The flasks were placed in a stirred bath at a temperature of 25°C and at a speed of 150 rpm.

for 2 hours. Then, the samples were filtered and diluted. Finally, the analysis was carried out using a UV spectrophotometer at a wavelength of λ max = 664 nm.

III.7.3. Effect of contact time and initial concentration

To evaluate the impact of the initial concentration of the adsorbate on the efficiency of cumin in adsorption, as well as to estimate the equilibrium time of the interaction between a solution and the adsorbent material, several experiments were conducted.

The initial concentrations of methylene blue dye were varied from 15 to 150 mg/l, the samples were prepared by weighing cumin into four separate beakers, to which aqueous

methylene blue dye solutions at different concentrations were added. These mixtures were stirred at room temperature for 2 hours, with sampling carried out at specific time intervals. After sampling, the samples were diluted and analyzed using an ultraviolet-visible spectrophotometer, using a wavelength of 664 nm.

III.7.4. Effect of concentration

The tests were carried out by stirring 50 ml of dye solutions (MB) at different concentrations (15, 50, 100 and 150 ppm), with the optimal amount of adsorbent, at a temperature of 25°C. The obtained solutions were then filtered and directly analyzed using a UV-visible spectrophotometer at the appropriate wavelength for MB (λ max = 664 nm).

III.7.5. Effect of temperature

In order to study the effect of temperature on the adsorption process of methylene blue, experiments were carried out according to the following steps: a solution with a concentration of 50 ppm was prepared and heated to different temperatures (25, 35, 45, 55°C). Then, the optimal mass of adsorbent material was weighed and placed in four separate flasks, to which 50 ml of methylene blue dye solution were added. These mixtures were maintained under continuous stirring at 150 rpm during the equilibrium time.

III.7.6. Effect of Ionic Strength

Industrial and natural waters contain many salts that can affect dye adsorption; therefore, it is very important to evaluate the effect of ionic strength on the adsorption process.

- To solutions containing 50 ppm of MB, different amounts of NaCl (1, 3, and 6 g) were added and brought into contact with the optimal adsorbent mass (0.8 g). The mixtures were maintained under constant stirring at 150 rpm for 2 hours at room temperature.

III.8. Measurement of adsorption capacity

The adsorption capacity is expressed by the following relation **[49]**:

$$Q_{ads} = \frac{(C_0 - C_e) \times V}{m} \qquad \textbf{(III.4)}$$

Q_{ads} : Amount adsorbed (mg/g);

V : Volume of the solution (L); m: Mass of adsorbent (g);

C_0 : Initial concentration of the adsorbate at t = 0 (mg/l);

C_e : Equilibrium concentration of the adsorbate (mg/l).

III.9. Determination of dye removal efficiency

The removal rate R (%), is expressed by the following relation **[49]**:

$$R\ \% = \frac{(C_0 - C_e) * 100}{C_0} \qquad \textbf{(III.5)}$$

With:

c: Initial concentration of the adsorbate (mg/l).

Ce: Equilibrium concentration of the adsorbate (mg/l).

III.10. Kinetic Study

This study allowed us to determine the kinetic order, the model that best describes the adsorption kinetics of MB by TC, the time required to reach equilibrium, and to determine the adsorption rate constants of MB. Therefore, two models were studied: the pseudo-first-order model and the pseudo-second-order model **[30]**.

III.10.1. Pseudo-first-order model

In the case of apparent first-order kinetics, plotting log(qt − qe) versus time t allows the equilibrium adsorption capacity (qe) and the rate constant K_1 to be calculated from the intercept and slope of the straight line.

III.10.2. Pseudo-second-order model

The equilibrium adsorption capacity (qe) and the rate constant K_2 can be determined experimentally from the slope and intercept of the linear function t/qt = f(t).

III.11. Isotherm study

This study is carried out at four different temperatures. Previously, the solution of the adsorbate MB is introduced at concentrations varying from 15, 50 and 100 ppm, to which the same optimized mass of adsorbent is added. The tests are carried out under a stirring

speed of 150 rpm during the equilibrium time. To study the isotherms, two isotherm models were applied: Langmuir and Freundlich according to equations (I.1) and (I.2).

III.11.1. Langmuir model

Plotting (1/qe) versus (1/Ce) allows the graphical determination of qm and KL using the linearized Langmuir equation.

III.11.2. Freundlich isotherm

Plotting ln(qe) versus ln(Ce) makes it possible to determine KF and 1/n. The intercept represents ln(KF), while the slope corresponds to (1/n) of the linear Freundlich model.

III.12. Thermodynamic study

The thermodynamic parameters, including Gibbs free energy change ΔG^0, enthalpy change ΔH^0, and entropy change ΔS^0 (I.11), (I.14) and (I.15) are used to evaluate the nature and feasibility of the adsorption process by **[30]**: $\ln K_d = f(\frac{1}{T})$.

Chapter IV: Results and discussion

IV.1. Introduction

This chapter presents and discusses the experimental results obtained for the adsorption of methylene blue (MB) onto cumin (*Cuminum cyminum*) powder used as a natural biosorbent. The effect of several operating parameters was examined, including adsorbent mass, contact time, initial dye concentration, solution pH, temperature, and ionic strength.

The adsorption kinetics were evaluated using the pseudo-first-order and pseudo-second-order models in order to describe the rate of MB adsorption onto cumin powder. In addition, the equilibrium data were analyzed using the Langmuir and Freundlich isotherm models to understand the adsorption behavior and estimate the adsorption capacity. A thermodynamic study was also carried out to evaluate the feasibility and nature of the adsorption process.

IV.2. Establishment of the dye calibration curve

To determine the maximum wavelength absorbed by methylene blue, a UV–Vis spectroscopic analysis was carried out over a wavelength range of 400 to 800 nm. The obtained results revealed that the maximum absorption wavelength of methylene blue is **664 nm**. Different concentrations were prepared and analyzed using UV–Vis spectroscopy, and a linear calibration graph was established by correlating methylene blue concentration with its absorbance. The following curve illustrates this relationship (Figure IV.1).

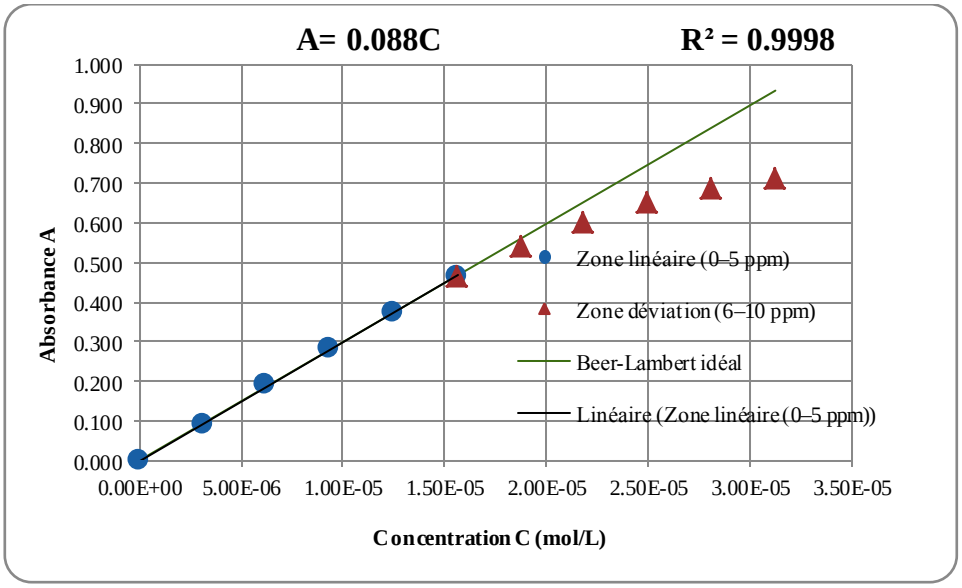


Figure IV.1: Calibration curve of MB at λmax = 664 nm.

The analysis of the data allowed us to establish the calibration curve of methylene blue (MB), presented in Figure IV.1.

The curve shows a linear relationship between absorbance (A) and concentration (C), passing through the origin. This relationship is mathematically expressed by the equation **A = 0.088 C**, with a regression coefficient of **R^2 = 0.9998**. This equation was subsequently used to determine the residual MB concentration after adsorption experiments

IV.3. Optimization of Operating Conditions

IV.3.1. Effect of Adsorbent Mass

The adsorbent dosage is considered one of the most important parameters affecting the adsorption efficiency of methylene blue (MB) onto cumin-based adsorbent. In order to determine the optimal adsorbent mass, a series of experiments was carried out using 50 mL of methylene blue solution while varying the amount of adsorbent from 0.05 to 1 g under constant experimental conditions. The obtained results were used to evaluate the influence of adsorbent dosage on the removal efficiency of MB, as illustrated in Figure IV.2.

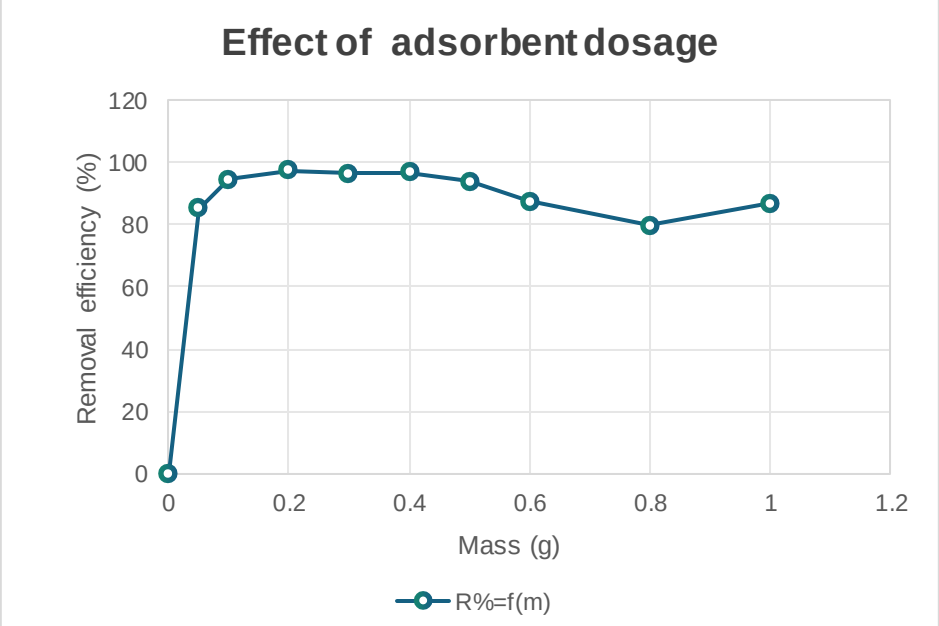


Figure IV.2: Effect of Adsorbent Mass.

[MB] = 50 ppm, V = 50 mL, contact time = 120 min, agitation speed = 150 rpm (3 to 4), T = 298K.

The results presented in Figure IV.2 show that the removal efficiency of methylene blue increased rapidly with increasing cumin powder mass, reaching a maximum value of approximately 97% at 0.4 g. This improvement can be explained by the greater number of available adsorption sites and the larger contact surface provided by the increased adsorbent dose.

Beyond 0.4 g, the removal efficiency became nearly constant, with slight fluctuations between 90% and 97%. This plateau indicates that, after the optimum adsorbent mass is reached, the remaining dye concentration in solution becomes low and the addition of more adsorbent does not significantly improve MB removal. Therefore, 0.4 g was selected as the optimum adsorbent mass for the following adsorption experiments.

IV.3.2. Effect of pH

The pH of the solution is one of the most critical parameters in adsorption processes, as it directly affects both the surface charge of the adsorbent and the ionization state of the adsorbate. The effect of pH was studied over a range of 8 to 8.5, using 0.1 M NaOH and 0.1 M H_2SO_4 to adjust the pH. Experiments were conducted with V = 50 mL, C_0 = 50 ppm, T = 298 K, and t = 120 min. Results are shown in Figure IV.3.

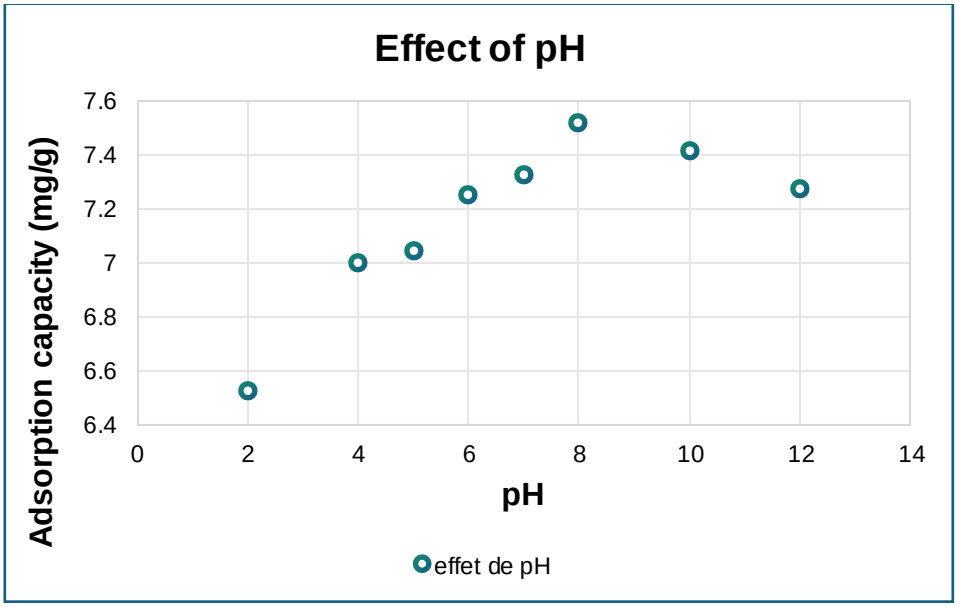


Figure IV.3: Effect of pH

C_0 = 50 ppm, m = 0.4 g, V = 50 mL, agitation speed = 150 rpm.

The adsorption capacity of methylene blue onto cumin powder was strongly affected by solution pH. As the pH increased from 2 to 8, the adsorption capacity gradually improved, reaching a maximum of about 7.52 mg/g at pH 8. This improvement may be due to the reduced protonation of cumin surface groups, which favors attraction with the cationic MB molecules. At higher pH values, a slight decrease was observed, possibly because of changes in the surface environment under strongly alkaline conditions. Therefore, pH 8 was selected as the optimum pH for further experiments.

IV.3.3. Effect of contact time and initial concentration

The study of the contact time effect is essential for determining the time required to reach adsorption equilibrium, which is a key criterion for evaluating the kinetic performance of the biosorbent. Experiments were conducted for five initial MB concentrations (15, 30, 50, 100, and 150 ppm). Samples were withdrawn at regular time intervals (1, 5, 10, 15, 20, 30, 3, 60, 90, and 120 min) and analyzed by UV-Visible spectrophotometry. The results are presented in Figure IV.4.

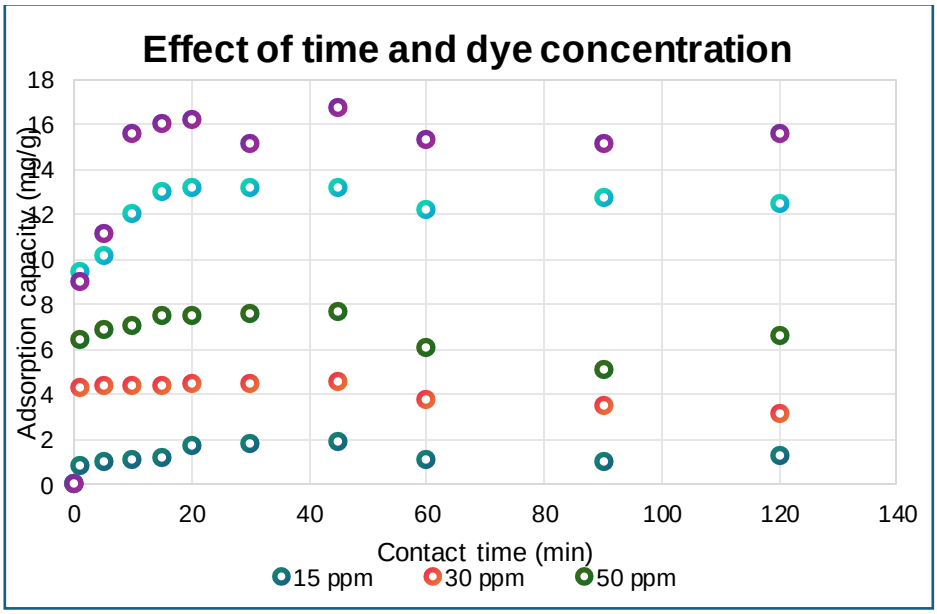


Figure IV.4: Effect of Contact Time

Experimental conditions: V = 100 mL, m = 0.8 g, N = 150 rpm, T = 298 K. Initial concentrations: 15, 30, 50, 100, and 150 ppm.

The Figure IV.4 shows that MB adsorption onto cumin powder increased with contact time for all initial dye concentrations. A rapid uptake was observed during the first 20 min, mainly due to the availability of free active sites on the adsorbent surface. After this period, the adsorption capacity changed only slightly, indicating that equilibrium was nearly reached. Therefore, 20 min was selected as the equilibrium contact time.

The equilibrium adsorption capacity also increased with the initial MB concentration, from about 1.74 mg/g at 15 ppm to 16.2 mg/g at 150 ppm. This increase can be explained by the higher concentration gradient, which enhances mass transfer of MB molecules from the solution to the cumin surface.

IV.3.4. Effect of initial concentration

To further investigate the effect of initial MB concentration on adsorption, experiments were performed with concentrations of 15, 30, 50, 100, and 150 ppm, using m = 0.8 g, V = 100 mL, t = 60 min, and T = 298 K. Results are illustrated in Figure IV.5.

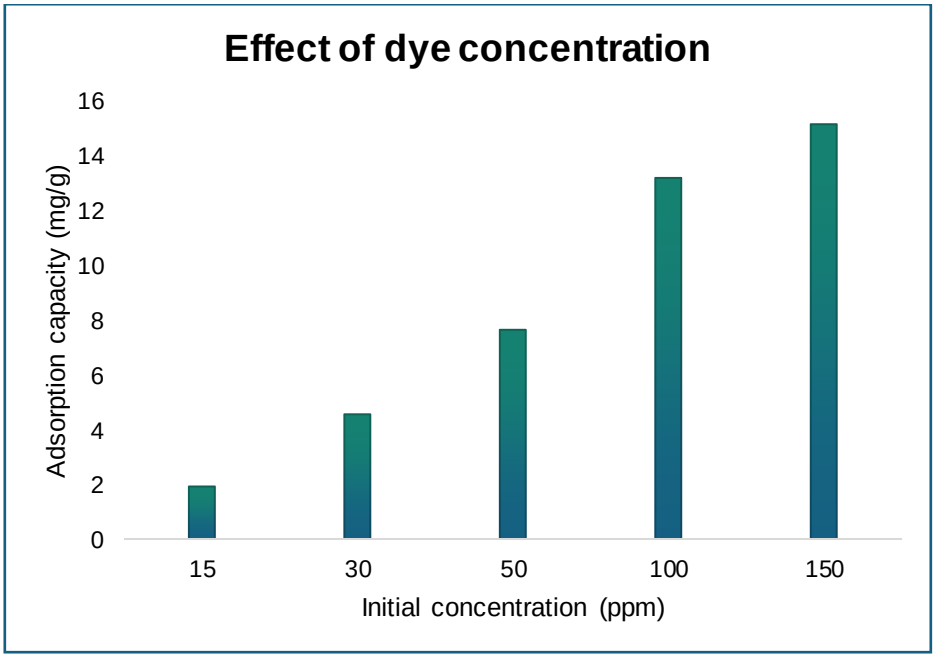


Figure IV.5: Effect of Initial Concentration: Qads (mg/g) = f(C_0)
Experimental conditions **:** V = 100 mL, m = 0.8 g, t = 60 min, T = 298 K.

The Figure IV.5 shows that the adsorption capacity increased as the initial MB concentration increased, rising from about 2 mg/g at 15 mg/L to nearly 14 mg/g at 150 mg/L. This trend is mainly due to the higher concentration gradient, which improves the transfer of MB molecules from the solution to the cumin surface. At low dye concentration, many adsorption sites remain unoccupied, whereas at higher concentration, more MB molecules are available to occupy these sites. This confirms that the adsorption capacity of cumin powder depends strongly on the initial dye concentration.

IV.3.5. Effect of Temperature

The effect of temperature on MB adsorption onto cumin was examined at, 308, 318, and 328 K, with m = 0.4 g, V = 50 mL, t = 30 min, and pH = 7. Multiple initial concentrations (15, 30, 50, 100, and 150 ppm) were used to construct isotherm data at each temperature. The variation of adsorption capacity with temperature is presented in Figure IV.6.

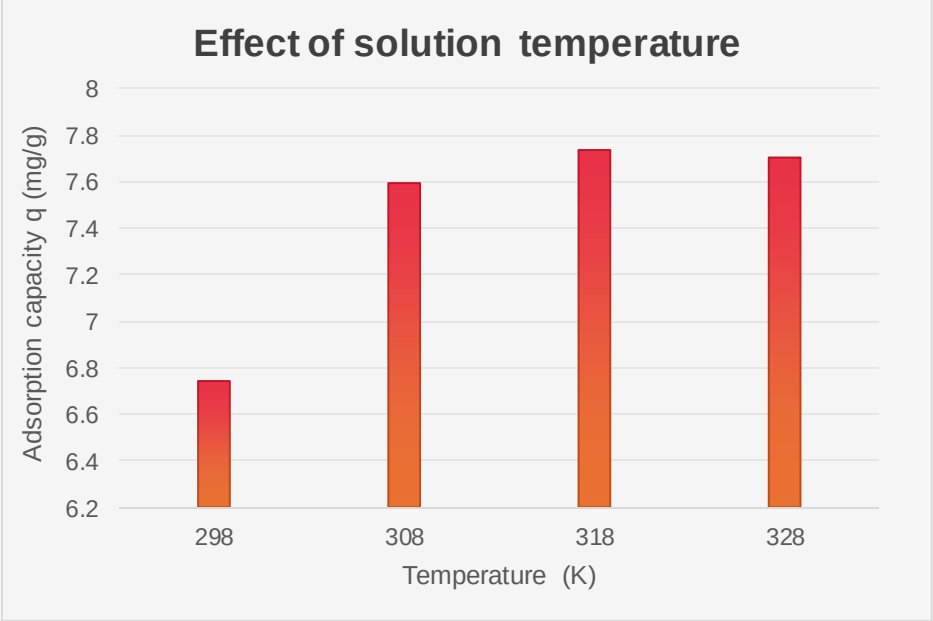


Figure IV.6: Effect of Temperature: Qads = f(T).

The effect of temperature was studied at four temperature levels (298, 308, 318, and 328 K) to assess the thermodynamic nature of the adsorption process. The results indicate that the adsorption capacity $Q_a$ds (mg/g) increases progressively from 298 K to 318 K, suggesting an endothermic adsorption process: the supply of thermal energy to the system promotes

the mobility of MB molecules in solution, facilitating their diffusion toward and fixation onto the active sites of the cumin biosorbent.

However, a notable decrease in adsorption capacity is observed at 328 K. This inflection point indicates that beyond 318 K, the thermal energy supplied to the system exceeds the binding energy of the adsorbate-adsorbent interactions. Therefore, the optimal removal capacity of 7.73 mg/g is achieved at a temperature of 318 K.

The temperature range of 298 – 318 K was thus retained for thermodynamic analysis.

IV.3.6. Effect of Ionic Strength

Natural and industrial wastewaters typically contain dissolved inorganic salts that can influence the adsorption of organic pollutants. The effect of ionic strength was investigated by adding sodium chloride (NaCl) at varying concentrations to MB solutions.

Results are shown in Figure IV.7.

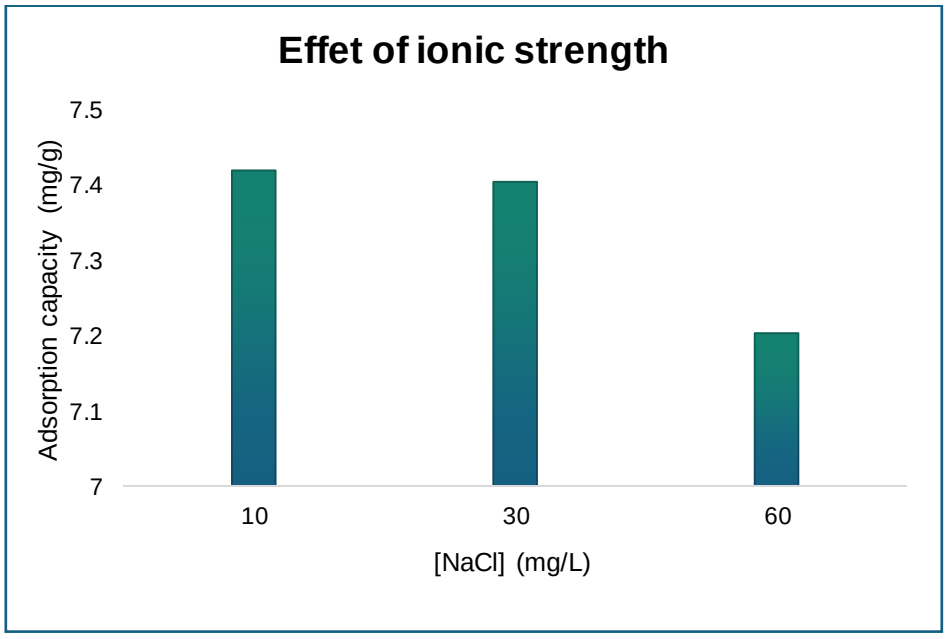


Figure IV.7: Effect of Ionic Strength: Qads (mg/g) = f([NaCl]).
Experimental conditions: C_0 = 50 ppm, V = 100 mL, m = 0.8 g, t = 90 min, T = 298 K.
NaCl masses tested: 1, 3, and 6 g.

The Figure IV.7 indicates that the adsorption capacity decreases slightly as the NaCl concentration increases from 10 to 60 g/L, with Qads declining from approximately 7.5 mg/g at 10 g/L to 7.1 mg/g at 60 g/L. This modest reduction can be attributed to

competition between Na^+ cations and the cationic MB molecules for the negatively charged active sites on the cumin surface. Nevertheless, the effect remains limited, demonstrating that cumin maintains satisfactory adsorption performance even in saline conditions, which is an important practical advantage for treating real industrial effluents containing dissolved salts.

IV.4. Kinetic Study

Kinetic modeling of the adsorption process is essential to understand the rate-controlling mechanism and to predict the time required to reach equilibrium. Two widely used kinetic models were fitted to the experimental data: the pseudo-first-order (PFO) model and the pseudo-second-order (PSO) model. The kinetic experiments were conducted for five initial MB concentrations (15, 30, 50, 100, and 150 ppm) using m = 0.4 g in 100 mL solution, at N = 150 rpm and T = 298K.

IV.4.1. Pseudo-First-Order Model (PFO)

The pseudo-first-order model, originally proposed by Lagergren, assumes that the rate of adsorption is proportional to the number of unoccupied sites on the adsorbent surface. Its linearized form is given by:

$$\mathbf{Ln(qe - qt) = ln(qe) - K_1 .t}$$

The plot of ln(qe − qt) versus time t yields a straight line from which K_1 and qe,cal are extracted from the slope and intercept, respectively. The linearized plots for all studied concentrations are shown in Figure IV.8.

IV.4.2. Pseudo-Second-Order Model (PSO)

The pseudo-second-order model assumes that the rate-controlling step involves chemisorption through sharing or exchange of electrons between the adsorbate and the adsorbent. Its linearized form is:

$$\mathbf{t/qt = 1/(K_2 \cdot qe^2) + (1/qe) \cdot t}$$

A plot of t/qt versus t provides K_2 from the intercept and qe from the slope. The linearized PSO plots are presented in Figure IV.9.

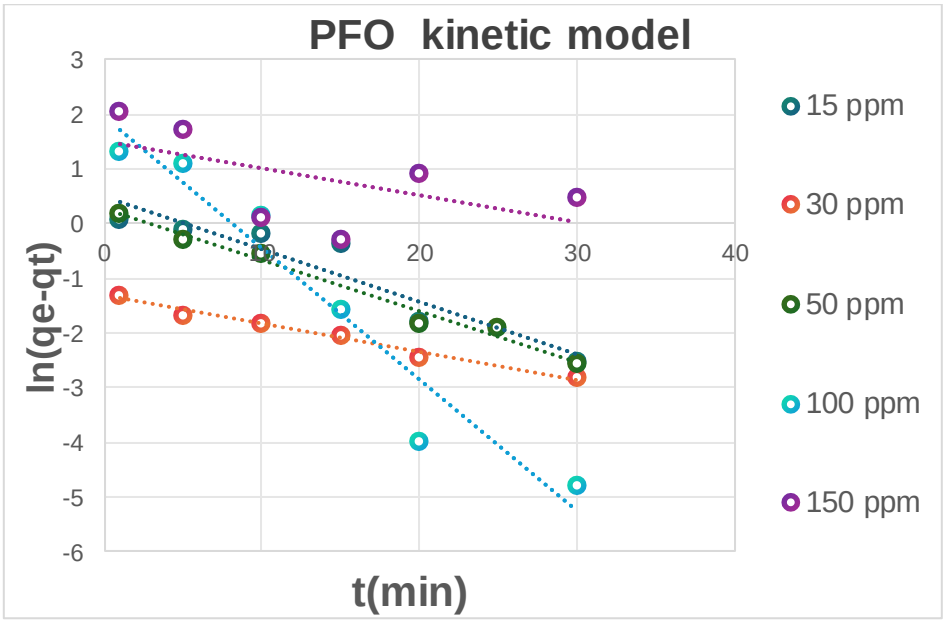


Figure IV.8: Linearized pseudo-first-order kinetic plots for MB adsorption onto cumin at different initial concentrations: ln(qe−qt) = f(t).

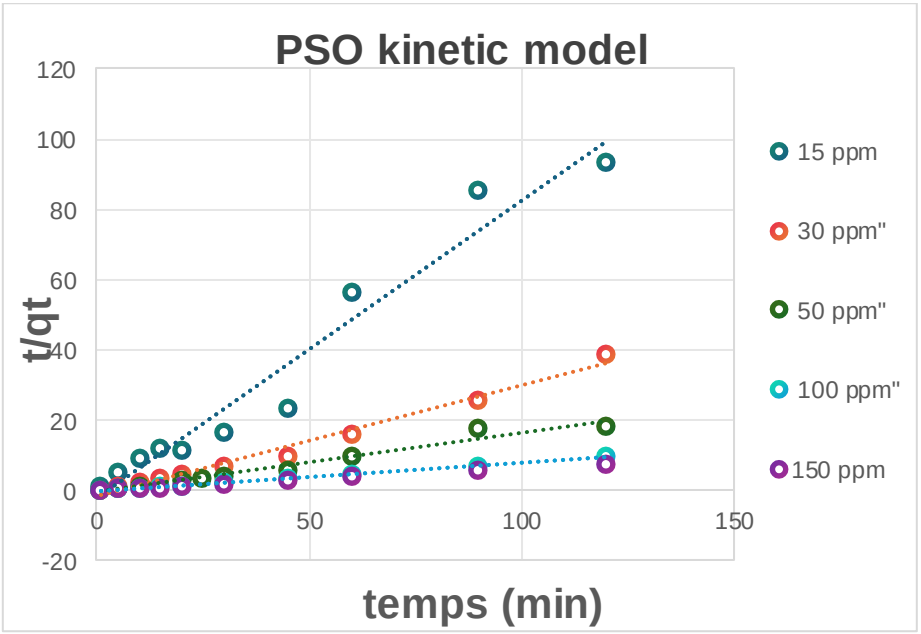


Figure IV.9: Linearized pseudo-second-order kinetic plots for MB adsorption onto cumin at different initial concentrations: t/qt = f(t).

The kinetic parameters derived from both models are summarized in Table IV.1, along with the experimental equilibrium adsorption capacities (qe,exp).

Table IV.1: PFO and PSO kinetic parameters for MB adsorption onto cumin.

Kinetic model		**Pseudo-first-order**			**Pseudo-second-order**		
C (ppm)	**$q_e$exp (mg/g)**	**PFO $q_e$cal (mg/g)**	**K_1 (min^{-1})**	**R^2 (PFO)**	**PSO $q_e$cal (mg/g)**	**K_2 (g/mg.min)**	**R^2 (PSO)**
15	1.913	1.614	0.0958	0.880	1.180	0.406	0.956
30	4.547	0.265	0.0506	0.980	3.189	0.198	0.985
50	7.631	1.286	0.0923	0.983	5.914	0.363	0.965
100	13.172	1.286	0.2396	0.938	12.547	5.775	0.999
150	16.742	4.470	0.0488	0.314	15.723	1.472	0.999

The analysis of Table IV.1 clearly demonstrates that the pseudo-second-order (PSO) model provides a significantly better fit to the experimental data compared to the pseudo-first-order (PFO) model across all studied concentrations. The PSO correlation coefficients R^2 range from 0.965 to 0.999, consistently higher than those of the PFO model, which showed particularly poor fitting at 150 ppm (R^2 = 0.314). Furthermore, the calculated equilibrium adsorption capacities qe,cal derived from the PSO model are in excellent agreement with the experimentally measured values qe,exp for concentrations of 100 and 150 ppm. In contrast, the PFO model significantly underestimates qe at most concentrations.

These results confirm that the adsorption of MB onto cumin follows pseudo-second-order kinetics.

IV.5. Isotherm Study

Adsorption isotherms describe the equilibrium relationship between the adsorbent surface and the adsorbate at a constant temperature. Two classical isotherm models, Langmuir and Freundlich were applied to the experimental equilibrium data collected at four temperatures (298, 308, 318, and 328 K).

IV.5.1. Langmuir Isotherm Model

The Langmuir model assumes monolayer adsorption onto a homogeneous surface with a finite number of identical sites and no lateral interaction between adsorbed molecules. Its linearized form is:

$$1/qe = 1/(KL.qm.Ce) + 1/qmMB$$

A plot of 1/qe versus 1/Ce gives a straight line with slope 1/(KL·qm) and intercept 1/qm, from which qm and KL are determined. The Langmuir linearized plots at all temperatures are shown in Figure IV.10.

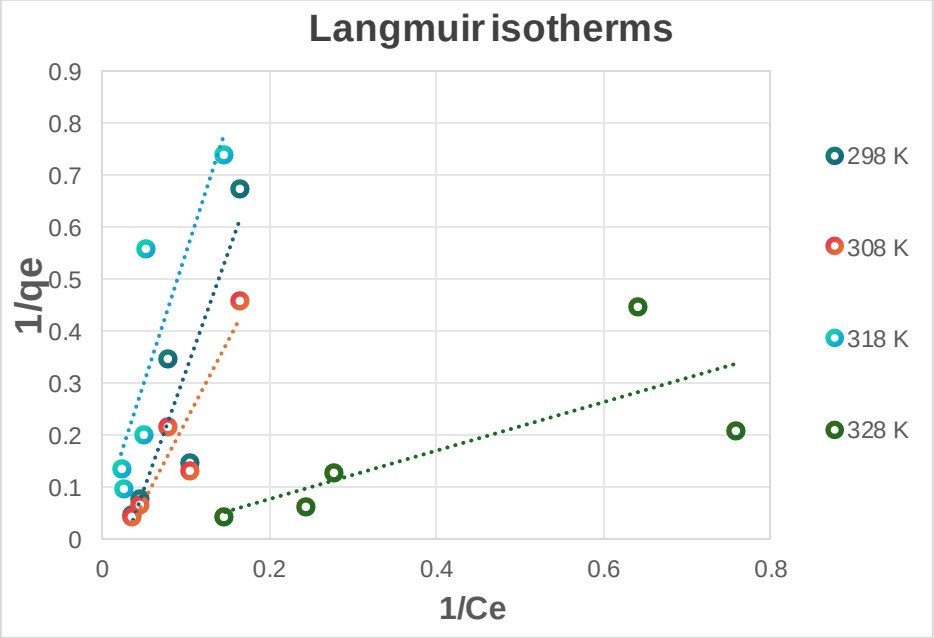


Figure IV.10: Linearized Langmuir isotherm plots for MB adsorption onto cumin: 1/qe = f(1/Ce).

IV.5.2. Freundlich Isotherm Model

The Freundlich model describes non-ideal adsorption on heterogeneous surfaces and allows for multilayer adsorption. Its linearized form is:

$$\ln(qe) = \ln(KF) + (1/n) \cdot \ln(Ce)$$

The plot of ln(qe) versus ln(Ce) provides KF from the intercept and 1/n from the slope. Linearized Freundlich plots are presented in Figure IV.11.

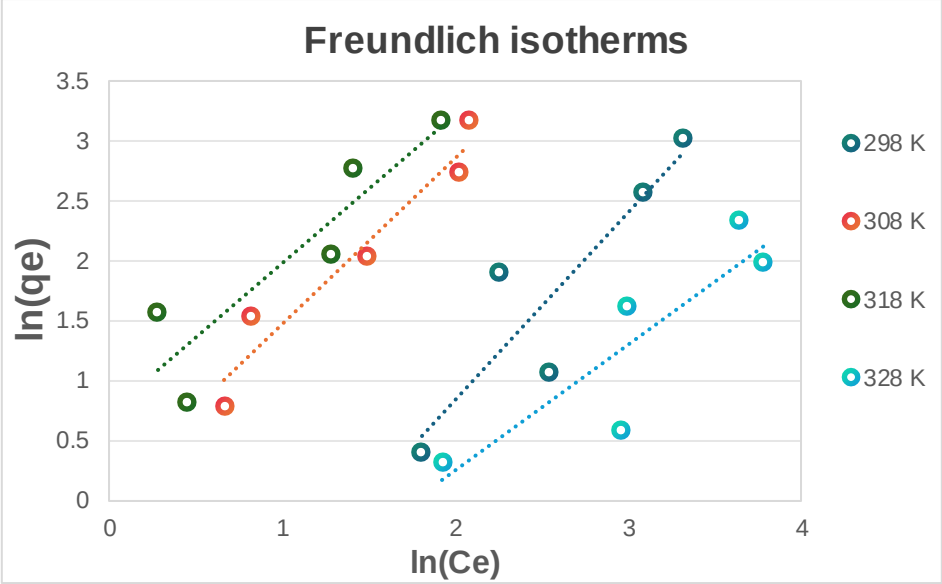


Figure IV.11: Linearized Freundlich isotherm plots for MB adsorption onto cumin

Table IV.2: Langmuir and Freundlich isotherm parameters for MB adsorption onto cumin at different temperatures.

Model	Langmuir			Freundlich		
T (K)	K_L (L/mg)	Q□ (mg/g)	R^2 Langmuir	1/n	K_F (mg/g)	R^2 Freundlich
298	0.0281	7.98	0.791	0.635	0.100	0.811
308	0.0402	33.78	0.640	0.715	1.071	0.937
318	0.0314	68.49	0.584	0.806	2.118	0.824
328	0.0107	18.90	0.750	0.947	0.155	0.770

According to the obtained results (Table IV.2), it is observed that the Freundlich model exhibits higher coefficients of determination (R^2), ranging from 0.770 to 0.937, compared to those of the Langmuir isotherm. This suggests that the adsorption data of methylene blue (MB) onto TC are better described by the Freundlich adsorption model, indicating a multilayer adsorption process. Furthermore, the value of the Freundlich constant provides useful information for evaluating the feasibility and favorability of the adsorption process.

In addition, the highest coefficient of determination (R^2) was recorded at a temperature of 318 K, reaching 0.937, compared to 328 K where the R^2 value did not exceed 0.824. Accordingly, 318 K is considered the optimal temperature for achieving the best performance of the studied system.

IV.6. Thermodynamic Study

A thermodynamic study was conducted to determine the spontaneity, nature, and energy changes associated with MB adsorption onto cumin. The thermodynamic parameters, Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°), were calculated from the distribution coefficient Kd using:

$$\mathbf{Kd = qe / Ce}$$

$$\mathbf{\ln Kd = \Delta S°/R - \Delta H°/(R \cdot T) \quad \rightarrow \quad \Delta G° = -R \cdot T \cdot \ln Kd}$$

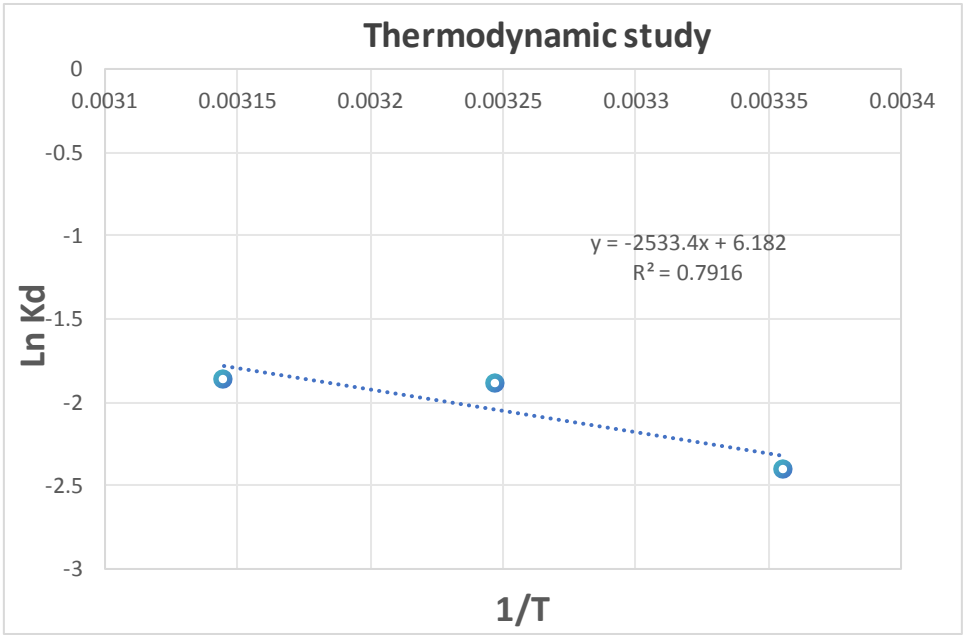


Figure IV.12: Van't Hoff linear plot for MB adsorption onto cumin: ln Kd = f(1/T)

The values of ΔH° and ΔS° were obtained from the slope (−ΔH°/R) and intercept (ΔS°/R) of the van't Hoff plot ln Kd = f(1/T). The data at 328 K was excluded from the linear regression, as explained in Section IV.3.5, since the adsorption mechanism changes at that temperature due to dominant desorption phenomena. The thermodynamic plot is presented in Figure IV.12.

Table IV.3: Thermodynamic parameters for MB adsorption onto cumin (data at 328 K excluded from regression).

T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol·K)	Nature
298	-14.96			
308	-16.17	21.05	120.86	**Spontaneous, endothermic**
318	-17.38			

The thermodynamic parameters for MB adsorption onto cumin powder are presented in Table IV.3 for the temperature range of 298–318 K. The standard Gibbs free energy values were negative at all studied temperatures, with ΔG^0 values of −14.96, −16.17, and −17.38 kJ/mol at 298, 308, and 318 K, respectively. These negative values indicate that the adsorption process is spontaneous and thermodynamically favorable. The increase in the negative magnitude of ΔG^0 with temperature suggests that adsorption becomes more favorable at higher temperatures within this range.

The positive enthalpy change, ΔH^0 = +21.05 kJ/mol, indicates that the adsorption process is endothermic. This means that moderate heating favors MB adsorption, probably by increasing the mobility of dye molecules and improving their diffusion toward the active sites of the cumin surface. Since the ΔH^0 value is lower than 40 kJ/mol, the adsorption is mainly associated with physical interactions such as electrostatic attraction, hydrogen bonding, and Van der Waals forces. However, the good fitting of the pseudo-second-order

kinetic model suggests that surface interactions may also contribute to the adsorption process.

The positive entropy change, ΔS^0 = +120.86 J/mol·K, reflects an increase in randomness at the solid–liquid interface during adsorption. This may be related to the release of water molecules from the hydration shell of MB ions and from the cumin surface during the adsorption process. Overall, the thermodynamic results show that MB adsorption onto cumin powder is spontaneous, endothermic, and mainly entropy-driven under the studied conditions.

The data obtained at 328 K were not included in the thermodynamic regression because this temperature showed a decrease in adsorption capacity and did not follow the same trend observed between 298 and 318 K. This suggests that 328 K may represent a transition region where higher thermal energy weakens the interaction between MB molecules and the adsorbent surface, making desorption more significant.

IV.7. Comparative Study

The following tables compare the adsorption performance reported in the present study with findings from related graduation theses and published scientific literature. Table IV.4 focuses on Methylene Blue (MB) as an adsorbate across different biosorbents, while Table IV.5 specifically evaluates studies using *Cuminum cyminum* (cumin) as an adsorbent for various pollutants. Rows highlighted in green correspond to the results obtained in the present work.

Table IV.4: Comparative Study of MB dye as adsorbate

Adsorbent Used	Optimal pH	Equilibrium Time (min)	Kinetic Model	Best Isotherm	qmax (mg/g)	Source
Green pea waste (biosorbent)	7 - 12	240	PSO	Freundlich	167 (theoretical)	**[33]**
Lemon leaves (biosorbent)	9	45	PSO	Langmuir	122.12	**[34]**
Activated carbon (Lantana camara wood)	/	60	PSO	Langmuir	277.78	**[35]**
Rice husk bio-composite beads	/	/	PSO	Freundlich	274.9	**[36]**
Activated carbon (coconut shell)	6	45 - 60	PSO	Langmuir	320	**[37]**
Vegetable waste biosorbent	7	30	PSO	Freundlich	370.4	**[43]**
Cumin seeds (*Cuminum cyminum*)	8	20	PSO	Freundlich	68.49	This work, 2026

The Table IV.4 confirms that MB is widely used as a model pollutant across diverse biosorbents, with reported qmax values ranging from 37.31 mg/g (pea shells) to 277.78 mg/g (activated carbon from Lantana camara). The maximum adsorption capacity obtained in the present study for raw cumin seeds 68.49 mg/g is comparatively modest, which is expected given that no chemical or thermal activation was applied. However, cumin achieves equilibrium in only 20 minutes, which is significantly faster than most reported materials. The pseudo-second-order kinetic model was consistently the best-fitting model across all studies, confirming chemisorption as the dominant rate-controlling mechanism.

Table IV.5: Comparative Study — Cumin *(Cuminum cyminum)* as Adsorbent

Pollutant Removed	Optimal pH	Equil. Time	Kinetic Model	Best Isotherm	qmax / Efficiency	Cumin Form / Modification	Source
Cationic Red 95 dye	5	40 min	/	/	143.64 mg/L	Biosynthesized nanoparticles (CcNPs)	**[38]**
Al^{3+} dissolution inhibition (corrosion)	/	/	/	Langmuir	93.1% efficiency at 300 ppm	Cuminum cyminum extract (CCE)	**[39]**
Diclofenac sodium (pharmaceutical)	2	300 min	PSO	Langmuir	93.65 mg/g	TTAB cationic surfactant-modified	**[40]**
Acid Blue 113 (azo dye)	2	N/A	PSO	Freundlich	96 mg/g	Raw nutraceutical cumin seed spent (NICUS)	**[41]**
Heavy metals: Ni, Zn, Cu, Co, Pb	/	/	/	/	88%	Raw biomass residues of cumin	**[42]**
Methylene Blue (MB) cationic dye	8	20 min	PSO	Freundlich	68.49 mg/g	Raw ground cumin seed powder (no modification)	This work, 2026

The Table IV.5 demonstrates that *Cuminum cyminum* has been successfully applied as an adsorbent for a wide spectrum of pollutants, including synthetic dyes, pharmaceutical compounds, and heavy metals. The adsorption capacity of modified or activated cumin materials such as TTAB-functionalized cumin waste (93.65 mg/g) and nutraceutical cumin spent (96 mg/g) far exceeds that of the raw powder used in the present work. This highlights the significant potential for improvement through chemical or thermal modification of raw cumin seeds. Notwithstanding, the present study demonstrates that even unmodified raw cumin powder is an effective, cost-free**,** and readily available biosorbent for MB removal, with the key advantages of rapid equilibrium, no pre-treatment requirement, and satisfactory performance under variable ionic strength conditions.

General conclusion

The present study was carried out with the primary objective of evaluating the potential of cumin powder *(Cuminum cyminum)* as a low-cost, natural biosorbent for the removal of methylene blue (MB), a cationic dye widely used in textile industries, from aqueous solutions via the adsorption process.
This work contributes to the development of economically viable and environmentally sustainable alternatives to conventional water treatment methods, through the valorization of locally available agro-industrial materials in Algeria.

The adsorbent was prepared by washing, drying at 105°C for 24 hours, grinding, and sieving to a particle size below 0.325 mm. Batch adsorption experiments were conducted to systematically investigate the influence of adsorbent dosage, solution pH, contact time, initial dye concentration, temperature, and ionic strength. Kinetic, isotherm, and thermodynamic studies were subsequently performed.

The results obtained allow the following conclusions to be drawn:

- The removal efficiency increased with adsorbent mass, reaching a maximum of 97.5% at an optimal dosage of 0.4 g, beyond which no significant improvement was observed due to active site saturation.
- The pH study revealed that adsorption is maximized at pH 8, attributed to the deprotonation of surface functional groups on cumin, which enhances electrostatic attraction with the cationic MB molecules.
- Adsorption equilibrium was reached within approximately 20 minutes for all concentrations studied, with an initial rapid phase driven by high active site availability, followed by a slower phase associated with progressive surface saturation.
- The adsorption capacity increased proportionally with the initial MB concentration, ranging from 1.91 mg/g at 15 ppm to 16.74 mg/g at 150 ppm, driven by the greater concentration gradient promoting mass transfer.
- Temperature had a positive effect on adsorption between 25°C and 45°C, confirming the endothermic nature of the process. A decrease in adsorption capacity

was observed at 55°C, indicating that excessive thermal energy promotes desorption.

- The ionic strength study showed a slight decrease in adsorption capacity with increasing NaCl concentration, attributed to competition between Na^+ cations and MB molecules for negatively charged surface sites. Cumin nonetheless maintained satisfactory performance under saline conditions.
- Kinetic modeling confirmed that the pseudo-second-order (PSO) model best described the adsorption process (R^2 = 0.965–0.999), indicating that chemisorption involving electron exchange between cumin's functional groups (hydroxyl, carboxyl, carbonyl) and MB cations is the rate-controlling mechanism.
- Isotherm analysis showed that the Langmuir model provided the best fit at 25°C (qmax = 7.98 mg/g), while the Freundlich model was more appropriate at 35°C and 45°C, reflecting the emergence of surface heterogeneity at higher temperatures. The Freundlich exponent $n > 1$ confirmed favorable adsorption at all temperatures.
- Thermodynamic analysis confirmed the spontaneous ($\Delta G° = -14.96$ to -17.38 kJ/mol), endothermic ($\Delta H° = +21.05$ kJ/mol), and entropy-driven ($\Delta S° = +120.86$ J/mol·K) nature of the adsorption process, consistent with physisorption with some contribution of chemical interactions.

Overall, these results confirm that cumin powder constitutes an effective, eco-friendly, and economically attractive biosorbent for MB removal. Although its maximum adsorption capacity is lower than that of chemically activated materials, cumin presents key practical advantages: fast equilibrium (15–20 min), no chemical pre-treatment required, and wide local availability.

Its use promotes the valorization of natural agricultural resources and supports the development of accessible water treatment solutions adapted to developing countries.

To further enrich this work, the following perspectives are recommended for future studies:

- ✓ Conduct a more complete characterization of cumin using SEM, XRD, and BET surface area analysis to better understand its structural and surface properties.
- ✓ Explore the improvement of adsorption performance through chemical or thermal activation of cumin, aiming to increase its specific surface area and adsorption capacity.
- ✓ Extend the study to the removal of anionic dyes, heavy metals, and pharmaceutical micropollutants to evaluate the broader applicability of this biosorbent.
- ✓ Investigate the regeneration and reusability of cumin adsorbent through desorption studies to assess its long-term economic viability for industrial-scale applications.
- ✓ Test the biosorbent on real industrial effluents under complex operating conditions to validate its practical performance and confirm its feasibility for large-scale wastewater treatment.

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Appendix

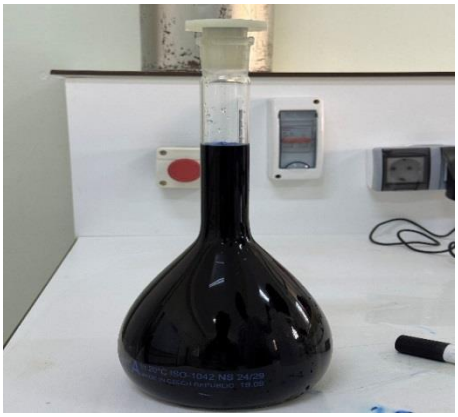
Appendix 1: UV-Visible Spectrophotometer.



Appendix 2: Appearance of the methylene blue dye.



Appendix 3: Stock solution of methylene blue (1000 ppm)



Appendix 4: The pH meter.



Appendix 5: Shaking water bath



Appendix 6: Mass Effect Experimental Setup



عنوان المذكرة: تقييم فعالية المخلفات الزراعية كممتزّات حيوية مستدامة في إزالة الأصباغ الاصطناعية من المياه.

اللقب و الإسم : وذناني خليل عبد الحق و مشيكل يوسف
المؤطر: أ.د. جديد مبروك و د. سعد الله كلثوم

ملخص: يركز هذا العمل على دراسة إزالة صبغة أزرق الميثيلين من المحاليل المائية بواسطة الامتزاز باستخدام مادة ماصة حيوية محلية قائمة على الكمون كمادة ممتزة. وقد أُجريت دراسة تجريبية لتقييم كفاءة هذه المادة في الامتزاز، حيث أظهرت نتائج واعدة تجعلها خيارًا اقتصاديًا وفعالًا لمعالجة المياه. تمت دراسة تأثير عدة عوامل تشغيلية، منها زمن التلامس، وكتلة المادة الممتزة، والتركيز الابتدائي للصبغة، ودرجة الحرارة، والأس الهيدروجيني، والقوة الأيونية. أظهرت النتائج أن توازن الامتزاز تحقق بعد 20 دقيقة من زمن التلامس. كما أدى ارتفاع التركيز الابتدائي للصبغة إلى زيادة سعة الامتزاز، في حين تم تسجيل أعلى كمية ممتزة من أزرق الميثيلين عند درجة حموضة تساوي 8. وقد وُجد أن نموذج الحركية من الرتبة الثانية هو الأكثر ملاءمة لوصف حركية الامتزاز في الظروف التشغيلية المثلى. بالإضافة إلى ذلك، أظهر نموذج فريندلش أفضل توافق مع بيانات متساويات الامتزاز، مع سعة امتزاز قصوى بلغت 68.49 ملغ/غ.

كلمات مفتاحية: الامتزاز ؛ الميثيلين الأزرق ؛ صبغة (ملون) ؛ الكمون ؛ مادة ماصة حيوية ؛ معالجة مياه.

Memory title: Evaluation of agro-waste as sustainable biosorbents for the removal of synthetic dyes from water.

Name and First name: OUDENANI Khalil Abdelhak & MECHIKEL Youcef
Supervised by: Pr. Dr. DJEDID Mebrouk & Dr. SAADALAH Kelthoum

Abstract:
This work focuses on the adsorption-based removal of methylene blue from aqueous solutions using a local cumin-based biomaterial as an adsorbent. An experimental study was conducted to evaluate its adsorption performance, demonstrating its potential as a promising low-cost material for water treatment. The influence of several operating parameters, including contact time, adsorbent dosage, initial dye concentration, temperature, pH, and ionic strength, was investigated. The results showed that adsorption equilibrium was reached within 20 minutes of contact time. An increase in the initial dye concentration enhanced the adsorption capacity, while the highest methylene blue uptake was achieved at pH 8. The adsorption kinetics were best described by the pseudo-second-order model under optimal operating conditions. Furthermore, the Freundlich isotherm model provided the best fit to the experimental adsorption data, with a maximum adsorption capacity of 68.49 mg/g.
Key words : Adsorption ; Methylene Blue ; Dye ; Cumin ; Biosorbent ; Water Treatment.

Titre du mémoire : Évaluation des déchets agro-industriels en tant que biosorbants durables pour l'élimination des colorants synthétiques des eaux.

Nom et Prénom: OUDENANI Khalil Abdelhak & MECHIKEL Youcef
Encadreur: Pr. Dr. DJEDID Mebrouk & Dr. SAADALAH Kelthoum

Résumé: Ce travail porte sur l'étude de l'adsorption du bleu de méthylène en solution aqueuse à l'aide d'un biomatériau local à base de cumin utilisé comme adsorbant. Une étude expérimentale a été réalisée afin d'évaluer ses performances d'adsorption, mettant en évidence son potentiel comme matériau prometteur et économique pour le traitement des eaux. L'influence de plusieurs paramètres opératoires, notamment le temps de contact, la masse d'adsorbant, la concentration initiale du colorant, la température, le pH et la force ionique, ont été examiné. Les résultats obtenus ont montré que l'équilibre d'adsorption est atteint après 20 minutes de contact. L'augmentation de la concentration initiale du colorant favorise la capacité d'adsorption, tandis que la quantité maximale de bleu de méthylène adsorbée est obtenue à un pH de 8. Les données cinétiques sont mieux décrites par le modèle cinétique du pseudo-second ordre dans les conditions optimales de fonctionnement. Par ailleurs, le modèle d'isotherme de Freundlich présente le meilleur ajustement aux données expérimentales, avec une capacité maximale d'adsorption de 68,49 mg/g.

Mots clés : Adsorption ; Bleu de méthylène ; Dye ; Cumin ; Biosorbant ; Traitement des eaux.