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Je soussigne : Boucharab Imane

Certifier que l'étudiant (e) :
Lina Euchi

Spécialité : Master 02 Chimie des Materiaux

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I. Boucharab

Visa de L'encadrant

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Lyna Euchi

THESIS TITLE

Adsorption Behavior of Synthetic Dyes onto Algerian Marrubium vulgare

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The Examination Committee:

Chair:	BOUAOUD Yasmina	MCA	University of Skikda
Examiner:	OUILIA Souhila	MCB	University of Skikda
Supervisor:	Bouchareb Imane	MCB	University of Skikda

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Résumé

Cette étude évalue l'efficacité d'une biomasse naturelle (MV biomass) comme biosorbant à faible coût pour l'élimination du Crystal Violet (CV) à partir de solutions aqueuses. Les essais d'adsorption en mode batch ont permis de déterminer les conditions optimales : un temps d'équilibre de 60 min, une masse de biosorbant de 0,5 g et un pH de 7, avec un rendement d'élimination supérieur à 94 %.

Les résultats ont montré que le modèle de Langmuir (R^2 = 0,9973) décrit le mieux les isothermes d'adsorption, tandis que le modèle cinétique du pseudo-second ordre (R^2 = 0,99997) représente le mieux les données expérimentales, indiquant que la chimisorption est le mécanisme prédominant. Ainsi, la biomasse MV apparaît comme un biosorbant efficace, économique et écologique, offrant un fort potentiel pour le traitement des eaux usées contaminées par les colorants.

Mots-clés : **Biomasse MV ; Crystal Violet ; Biosorption ; Adsorption ; Langmuir ; Pseudo-second ordre**.

الملخص

تقيمّ هذه الدراسة فعالية كتلة حيوية طبيعية) MV(كمادة امتزاز حيوي منخفضة التكلفة لإزالة صبغة Crystal Violet (CV)من المحاليل المائية. وقد مكّنت تجارب الامتزاز الدفعي Batch( )adsorptionمن تحديد الظروف المثلى للعملية، والتي تمثلت في زمن توازن قدره 60 دقيقة، وكتلة مادة ممتزة مقدارها 5.0 غ، ودرجة حموضة) pH(تساوي 7، مع تحقيق كفاءة إزالة تجاوزت 94. % أظهرت النتائج أن نموذج **لانغموير) 3799. 0 =R^2) **(Langmuir) هو الأكثر ملاءمة لوصف متساويات الامتزاز، في حين أن النموذج الحركي من **الرتبة الثانية الكاذب ة-Pseudo-second ( )order(قدمّ أفضل توافق مع البيانات التجريبية، مما يشير إلى أن الامتزاز الكيميائي Chemisorption( )هو الآلية السائدة في العملية.

وبناءً على ذلك، تبرز الكتلة الحيوية **MV** كمادة امتزاز حيوي فعالة، اقتصادية، وصديقة للبيئة ، وتمتلك إمكانات واعدة في معالجة المياه العادمة الملوثة بالأصباغ.

الكلمات المفتاحية: **الكتلة الحيوية MV؛ الكريستال البنفسجي (Crystal Violet)؛ الامتزاز الحيوي؛ الامتزاز؛ نموذج لانغمويز؛ النموذج الحركي من الرتبة الثانية الكاذبة.

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Dedication

Praise be to Allah the Almighty, who has allowed me to see this long-awaited day.

I dedicate this modest work to:

To my dearest mother:

To the one who sacrificed her nights for my comfort, and whose daily prayers illuminated my path toward success. No words can express my gratitude for your unconditional love. **To my dearest father:**

My role model, my guide, and my greatest support. To the one who worked tirelessly to provide me with the opportunity to succeed, and who taught me the values of patience and perseverance. It is thanks to your sacrifices that I am here today.

To my dear brothers and sisters :Nidal, Retaj, and Sajed.
To my dear friends: Boudjemaa Yasmine, Geudmani Aya, and Rebouch Ikram.

May our bond last forever, and may success follow you in every step you take.

To myself:

I dedicate this work to myself, in recognition of your patience, and in celebration of your victory.

To my entire family:

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Table of Contents

List of Tables

List of figures

Introduction ……1

Chapter I

I.1. Water Pollution 6

I.2. Sources of Water Pollution 6

I.2.1 Industrial Pollution 6

I.3. Types of Water Pollution 8

I.3.1. Chemical Pollution 8

I.3.2. Organic Pollution 8

I.3.3. Thermal Pollution 9

I.4. Definition of a Dye 9

I.5. Dye structure and color..... 10

I.6 Nature of Dyes 11

I.6.1. Natural Dyes 11

I.5.2. Synthetic dyes 12

I.6. Use and Application of Dyes 12

I.7. Overview of Crystal Violet 13

I.7. 1. Definition 13

I.7.2. Properties of CV 13

I.7.3. Toxicity 14

I.8. Dye Removal Techniques 15

I.8.1. Adsorption 15

I.8.2. Coagulation - Electrocoagulation 17

I.8.3. (Advanced) Oxidation Processes (AOP) 18

I.8.4. Biological treatment 19

I.8.6. Main issues with conventional methods 21

Chapter II

II.1.1. Definition 23

II.1.2. Principle 24

II.2. Types of Adsorptions 24

II.2.1. Physical Adsorption 25
II.2.2. Chemical Adsorption 25
II.3. Adsorption Isotherm Models 25
II.3.1. Langmuir Model 26
II.3.2. Freundlich Model 26
II.4. Adsorption Kinetics 27
II.5. Adsorption Kinétique Modeling 28
II.5.1. Pseudo-First-Order Kinetic Model (Lagergren Model) 29
II.6. Main factors influencing adsorption 29
II.7. Biomass as an Adsorbent 30
II.7.1.Defintion of Biomass 31
II.7.2. Types of Biomass 31
II.7.3. Criteria for Selecting Adsorbents 32
II.7.4. Parameters for Evaluating the Effectiveness of Adsorbents……..33
II.7.4.1. Adsorption Capacity 33
II.7.4.2. Adsorption Kinetics 33
II.7.5. Transport Mechanism 34
II.8. Presentation of the Ferfour study localization 34
II.9. Botanical description 35
II.9.1. Chemical Composition 35
II.10. Adsorptive Properties of Biomass 36

Chapter III

III.1. Apparel and products used 40
III.1.1 Apparel UV-visible spectrophotometer (Cary 60 UV-Vis) 40
III.2. Preparation of the Adsorbent, Adsorbate, and Reagent Solutions……..43
III.2.1. Biomass preparation (the Adsorbent) 43
III.2.3. Preparation a 0.1 M sodium chloride solution 44
III.2.3. Preparation a 0.1 M Magnesium Chloride Solution……44
III.2.4. Preparation of a 0.1 M Sodium Sulfate Solution 44
III.3. Determination of the pH of MV 45
III.4. Batch Adsorption of Crystal Violet onto Marrubium vulga……..45
III.4.1. Preparation of the Stock Solution 45

III.4.2. Preparation of Standard Solutions for the Calibration Curve……45
III.4. pH of Zero Charge (pH zpc) 46
III.4. Batch optimization studies 47
III.4.1. Contact Time Effect..... 47
III.4.2. Effect of adsorbent mass 47
III.4. 3.pH effect of the solution 47
III.5. Isothermal Adsorption of Crystal Violet 48
III.6. Experimental Protocol: Adsorption Kinetics Study……49

Chapter IV

IV.1. The Calibration Curve of Crystal Violet 52
Figure IV.1: The Calibration Curve of Crystal Violet 52
IV.2. Determination of the pH of MV 53
IV.3. pH of Zero Charge (pH zpc) 53
IV.4. Batch optimization studies 54
IV.4 1. Effect of Contact Time 54
IV.4.2 Effect of biosorbent mass 55
IV.2.2. Effect of the initial concentration of the adsorbate 56
IV.2. 3Effect of pH 57
IV.3. Isothermal Adsorption of Crystal Violet 59
IV.4. Adsorption kinetics study 61
IV.4. 1. Pseudo-first-order kinetic model 61
IV.4.2. Pseudo-Second-order kinetic model 62
Conclusion……65
References bibliographies
Resum

List of Tables

Chapter I :Water pollution & Synthetic Dyes

TableI.1: the main types of these two groups……11

Table I.2: shows some of the physicochemical properties of this dye……....12

Table I.3: Methods for removal of pollutants……22

TableIII.1: Physicochemical characteristics of the reagents used……42

Chapter IV : Results & Discussion

Table IV.1: The values of Absorption and Concentration……...52

TableIV.2: pH measurement during the time ……53

TableIV.3: Results of equilibrium time on the adsorption of Crystal Violet by Biomass……..….54

Table IV.4: The results of effect of Biosorbent mass ……...55

Table IV.5: Effect of the Initial Dye Concentration on the Adsorption Capacity and Removal Efficiency of Crystal Violet …….....56

Table IV.6: The effect of pH on the adsorption of Crystal Violet …….58

Table IV.4: The Freundlich model calculation ……...59

Table IV.4: The Freundlich model calculation …….60

Table IV.7: Pseudo-second-order model Calculations……62

List of figures

Figure II.1: Adsorption at the solute/solid interface……24

Figure II.2: Types of adsorptions……26

Figure II.3: The adsorption isotherms in the liquid phase ……..…..27

Figure II.4: Biomass-to-power supply system…….32

Chapter III : Materials &Methods

Figure III.1: Apparel UV-visible spectrophotometer (Cary 60 UV-Vis)……..…40

FigureIII.1: Steps for preparing the adsorbent……43

Figure III.2 : A stock solution of crystal violet (CV)…….…….45

Figure III.3: a series of standard solutions……..…45

Figure III.4: Monitor pH before and after adding the adsorbent……48

Chapter IV :Results & Discussion

Figure IV.1: The Calibration Curve of Crystal Violet……..52

Figure IV.2: Determination of the Zero Point of Charge (PZC)…….....53

FigureIV.3: Effect of contact time on the adsorption capacity at an initial Crystal Violet concentration of 30 mg/L…….54

Figure IV.4: Influence of biosorbent mass on crystal violet adsorption……...56

Figure IV.5: Effect of the Initial Dye Concentration on the Adsorption Capacity and Removal Efficiency of Crystal Violet……57

Figure IV.5: Effect of the Initial Dye Concentration on the Adsorption Capacity and Removal Efficiency of Crystal Violet……...58

FigureIV.7: Linearized Freundlich isotherm for crystal violet adsorption……..59

FigureIV.7: Linearized Langmuir isotherm for the adsorption of crystal violet……60

Figure IV.7: The linear form of the pseudo-first-order model……61

Figure IV.8: The linear form of the pseudo-second-order model……62

Introduction

In recent years, the issue of sustainable water supply has gained considerable importance worldwide. Beyond the quantitative demands of agricultural and industrial activities, water quality remains a critical factor for both human health and ecosystem integrity. Among the most persistent environmental challenges related to water is pollution control, particularly in the context of wastewater treatment. Biological treatment methods remain the most widely employed approaches in industrialized countries; however, the removal of specific recalcitrant pollutants, such as synthetic dyes, continues to pose significant technical and economic challenges.

Synthetic dyes are among the most hazardous pollutants due to their extensive use in various industries, especially the textile sector. Cationic dyes, including Crystal Violet, are commonly used in commercial applications; however, their environmental persistence and tendency to accumulate in aquatic ecosystems have raised serious ecological concerns. Their presence in water bodies can harm aquatic organisms and disrupt entire food chains, necessitating the development of efficient and sustainable remediation strategies.

In response to these environmental threats, numerous treatment technologies have been explored for dye removal from wastewater. These include biological treatment, membrane filtration, chemical and electrochemical oxidation, reverse osmosis, ion exchange, electrolysis, and adsorption [1]. Despite their effectiveness, many of these methods suffer from significant drawbacks, such as high capital and operational costs, the generation of hazardous sludge, and complex process requirements. Among these technologies, adsorption has emerged as one of the most promising and widely adopted techniques, owing to its operational simplicity, high removal efficiency, and economic viability. Nevertheless, conventional adsorption processes may generate secondary waste in the form of spent adsorbents, which require proper disposal or regeneration [2].

Activated carbon is universally recognized as an effective adsorbent for the removal of a wide range of aqueous pollutants [3]. However, its large-scale application is often constrained by its relatively high production and regeneration costs. This limitation has motivated growing research interest in the development of low-cost, sustainable, and environmentally friendly alternative adsorbents. A variety of non-conventional materials have been investigated for their pollutant removal capabilities [4]. Although some low-cost adsorbents exhibit lower adsorption

capacities than commercial activated carbon [5], recent studies have demonstrated that certain biomass-derived carbonaceous materials and their composites can achieve comparable or even superior dye adsorption performance [6]. Consequently, the search for inexpensive and ecofriendly adsorbents remains a highly active and evolving research field.

In this context, biosorbents derived from natural and agricultural wastes have attracted considerable attention due to their abundance, biodegradability, low cost, and the presence of diverse functional groups that facilitate pollutant binding. Materials such as charcoal, peat, chitin, microbial biomass (fungi, bacteria, and yeast), and wood-based products have been extensively studied [7]. The utilization of locally available natural resources not only reduces treatment costs but also promotes a circular economy approach, aligning with the principles of green chemistry and sustainable development.

Among the various cationic dyes, Crystal Violet was selected as the target pollutant in this study due to its widespread industrial use, high stability in aqueous environments, and known toxicological effects. Its removal serves as a relevant model for evaluating the performance of novel biosorbent materials under controlled laboratory conditions.

Against this background, the present study is centered on evaluating the effectiveness of adsorption technology for the removal of organic dyes from aqueous solutions using a locally derived biosorbent material. Special attention is given to the influence of key physicochemical parameters—such as contact time, initial dye concentration, adsorbent dosage, pH, and temperature—on the adsorption process [8]. The ultimate goal is to gain deeper insight into the adsorption behavior, optimize removal efficiency, and contribute to the development of practical and sustainable wastewater treatment solutions.

In this master's thesis is organized into four main chapters, structured as follows:

Chapter 1: Theoretical Background – Provides a comprehensive overview of water pollution, the classification and environmental impacts of synthetic dyes, and an evaluation of commonly used wastewater treatment techniques.

Chapter 2: Biosorbent Preparation and Characterization – Describes the preparation process of the biosorbent material, and the theoretical principles governing the adsorption phenomenon.

Chapter 3: Materials and Experimental Methods – Presents the chemicals, equipment, and experimental procedures employed throughout the study, including adsorption batch experiments.

Chapter 4: Results and Discussion – Presents and interprets the experimental data obtained from the adsorption studies of Crystal Violet, including the effect of various parameters, isotherm modeling, and kinetic analysis.

Chapter I

Water Pollution & Synthetic dyes

I.1. Water Pollution

Water pollution is any physical, chemical, or biological change to water quality induced by the introduction of pollutants into aquatic environments. These contaminants might come from natural processes or, more typically, human activities like industrial production, agriculture, and urbanization. Water pollution contaminates rivers, lakes, groundwater, and seas, rendering them unsuitable for drinking, irrigation, industrial usage, and aquatic life. It is also a significant environmental and public health concern worldwide [9].

Toxic compounds, pathogenic microbes, organic waste, suspended particles, and an excess of nutrients can all be found in polluted water. These toxins can destabilize aquatic ecosystems, diminish biodiversity, and accumulate in live animals via the food chain.

According to the World Health Organization, contaminated water is responsible for millions of deaths each year due to waterborne diseases such as cholera, dysentery, and typhoid fever. Therefore, protecting water resources has become essential for sustainable development and environmental preservation [10].

I.2. Sources of Water Pollution

Water pollution originates from several anthropogenic and natural sources. The principal sources include industrial, agricultural, and domestic activities.

I.2.1 Industrial Pollution

Industrial pollution is considered one of the most dangerous forms of water contamination because industries release large quantities of toxic chemicals into aquatic environments. Industrial effluents often contain hazardous substances such as heavy metals (lead, mercury, cadmium, chromium), dyes, acids, solvents, hydrocarbons, and radioactive materials [11].

Industries such as textile manufacturing, petroleum refining, mining, metallurgy, pharmaceutical production, and chemical processing are major contributors to water

pollution. In the textile industry, for example, large amounts of synthetic dyes are discharged into water bodies during dyeing and finishing processes. Many of these dyes are toxic, non-biodegradable, and resistant to conventional wastewater treatment methods [12]. Heavy metals released from industrial discharges can accumulate in sediments and aquatic organisms, causing bioaccumulation and biomagnification through the food chain. These pollutants may lead to severe health problems in humans, including neurological disorders, kidney damage, and cancer [13]. Moreover, industrial wastewater can alter the pH, temperature, turbidity, and dissolved oxygen content of water, thereby affecting aquatic ecosystems and reducing biodiversity.

***b*) Agricultural Pollution**

Agricultural activities are another major source of water pollution, especially due to the intensive use of fertilizers, pesticides, herbicides, and animal manure. Rainfall and irrigation water transport these pollutants from agricultural lands into nearby rivers, lakes, and groundwater systems [14].

Nitrogen- and phosphorus-based fertilizers are widely used to improve crop productivity. However, excessive application of these nutrients causes nutrient enrichment in aquatic ecosystems, a phenomenon known as eutrophication. Eutrophication stimulates excessive growth of algae and aquatic plants, leading to algal blooms that reduce light penetration and dissolved oxygen levels in water [15]. Pesticides and herbicides used in agriculture may persist in the environment for long periods and contaminate groundwater resources. Chronic exposure to these chemicals can have toxic effects on aquatic organisms and may pose risks to human health through drinking water contamination [16].

c) Domestic Pollution

Domestic or municipal pollution results mainly from household wastewater generated by kitchens, bathrooms, laundries, and toilets. Domestic wastewater contains organic matter, detergents, oils, nutrients, plastics, pharmaceuticals, and pathogenic microorganisms such as bacteria, viruses, and parasites [17]. In many developing countries, untreated or partially treated sewage is directly discharged into rivers and coastal waters because of insufficient sanitation infrastructure. This practice severely affects water quality and contributes to the spread of waterborne diseases [18].

Detergents used in households often contain phosphates and surfactants that contribute to eutrophication and toxicity in aquatic ecosystems. In addition, pharmaceutical residues and personal care products are emerging contaminants that may affect aquatic organisms even at very low concentrations [19]. Plastic waste from domestic activities also represents a growing environmental concern. Microplastics can persist in aquatic environments for decades and may be ingested by marine organisms, eventually entering the human food chain.

I.3. Types of Water Pollution

I.3.1. Chemical Pollution

Chemical pollution refers to the contamination of water by toxic chemical substances originating from industrial, agricultural, and domestic sources. Common chemical pollutants include heavy metals, pesticides, fertilizers, detergents, petroleum hydrocarbons, dyes, and pharmaceutical compounds [20].

Heavy metals such as mercury, lead, cadmium, and arsenic are particularly dangerous because they are non-biodegradable and can accumulate in living organisms. Longterm exposure to these substances may cause severe health disorders, including nervous system damage, liver dysfunction, and cancer.

Synthetic dyes used in textile industries are another important category of chemical pollutants. Many dyes are stable, resistant to biodegradation, and aesthetically undesirable even at low concentrations. Some azo dyes may degrade into carcinogenic aromatic amines under certain environmental conditions [21].

Chemical pollutants can alter the physicochemical properties of water, reduce water quality, and negatively affect aquatic biodiversity. Therefore, effective treatment methods are required to remove these contaminants before wastewater discharge.

I.3.2. Organic Pollution

Organic pollution is caused by the presence of biodegradable organic substances in water, including domestic sewage, food residues, agricultural waste, plant debris, and animal manure [22].

The decomposition of organic matter by microorganisms consumes dissolved oxygen present in water. As oxygen levels decrease, aquatic organisms such as fish and invertebrates may suffer from stress or death. Severe oxygen depletion can create anaerobic conditions associated with foul odors and the production of toxic gases such as methane and hydrogen sulfide.

The degree of organic pollution is commonly evaluated using parameters such as Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). High BOD and COD values indicate significant organic contamination and poor water quality. Organic pollution may also stimulate microbial growth and increase the presence of pathogenic microorganisms, making water unsafe for human consumption and recreational activities.

I.3.3. Thermal Pollution

Thermal pollution occurs when human activities increase the temperature of natural water bodies. This type of pollution is mainly associated with industrial cooling systems, thermal power plants, and nuclear power stations that discharge heated water into rivers or lakes [23].

An increase in water temperature reduces the solubility of dissolved oxygen, thereby affecting aquatic organisms that depend on adequate oxygen concentrations for survival. Higher temperatures can also accelerate the metabolic rates of aquatic species, increasing their oxygen demand while less oxygen is available [24].

Thermal pollution may disturb reproductive cycles, migration patterns, and species diversity within aquatic ecosystems. Sensitive species may disappear and be replaced by more temperature-tolerant organisms, leading to ecological imbalance. Additionally, elevated temperatures can enhance the growth of algae and microorganisms, further deteriorating water quality.

I.4. Definition of a Dye

Dye, substance used to impart color to textiles, paper, leather, and other materials such that the coloring is not readily altered by washing, heat, light, or other factors to which the material is likely to be exposed. Dyes differ from pigments, which are finely ground

solids dispersed in a liquid, such as paint or ink, or blended with other materials. Most dyes are organic compounds (i.e., they contain carbon), whereas pigments may be inorganic compounds (i.e., they do not contain carbon) or organic compounds. Pigments generally give brighter colours and maybe dyes that are insoluble in the medium employed.

Color has always fascinated humankind, for both aesthetic and social reasons. Throughout history dyes and pigments have been major articles of commerce. Manufacture of virtually all commercial products involves color at some stage, and today some 9,000 colorants with more than 50,000 trade names are used. The large number is a consequence of the range of tints and hues desired, the chemical nature of the materials to be colored, and the fact that color is directly related to the molecular structure of the dye.

I.5. Dye structure and color

Advances in structural theory led to investigations of correlations between chemical constitution and color. In 1868 German chemists Carl Graebe and Carl Liebermann recognized that dyes contain sequences of conjugated double bonds: X=C—C=C—C=C—…, where X is carbon, oxygen, or nitrogen.

The electromagnetic spectrum spans a wavelength range of 10^{12} metres, from long radio waves (about 10 km) to short X-rays (about 1 nm), but human eyes detect radiation over only the small visible range of 400–700 nm. Organic compounds absorb electromagnetic energy, but only those with several conjugated double bonds appear coloured by the absorption of visible light (*see* spectroscopy: Molecular spectroscopy). Without substituents, chromophores do not absorb visible light, but the auxochromes shift the absorption of these chromogens into the visible region. In effect, the auxochromes extend the conjugated system. Absorption spectra (plots of absorption intensity versus wavelength) are used to characterize specific compounds.

In visible spectra, the absorption patterns tend to be broad bands with maxima at longer wavelengths corresponding to more extended conjugation. The position and shape of the absorption band affect the appearance of the observed Colour. Many compounds absorb in the ultraviolet region, with some absorptions extending into the violet (400–430 nm) region. Thus, these compounds appear yellowish to the eye—i.e., the perceived

Colour is complementary to the absorbed Colour. Progressive absorption into the visible region gives orange (430–480 nm), red (480–550 nm), violet (550–600 nm), and blue (600–700 nm); absorption at 400–450 and 580–700 nm gives green. Black objects absorb all visible light; white objects reflect all visible light. The brilliance of a Colour increases with decreasing bandwidth. Synthetic dyes tend to give brilliant colours. This undoubtedly led to their rapid rise in popularity because, by comparison, natural dyes give rather drab, diffuse colorations.

They contain functional groups responsible for their color, called chromophores, as well as groups that facilitate their binding, known as auxochromes [25]. Table **I.1** below presents the main types of these two groups. Dyeing's are characterized by their ability to absorb light radiation in the visible spectrum (from 380 to 750 nm).

TableI.1: the main types of these two groups.

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

I.6 Nature of Dyes

Dyes are colorful chemical compounds, either natural or synthetic, that are typically organic in nature and have the potential to permanently color the substrate to which they are applied under specific conditions. A dye is defined in modern industrial terms as a product made up of pure organic coloring materials mixed with various additives and coupling agents that make it easier to apply. There are two major categories of dyes:

I.6.1. Natural Dyes

There are fewer natural dyes than there are synthetic dyes. Natural dyes are derived from plants, trees, lichens, insects, and mollusks; yellow colors are the most common. Natural dyes fall into two categories: mordant dyes and vat dyes. Only the former is poorly soluble in water.

Mordant dyes

Many natural dyes cannot bind directly to textile fibers without prior treatment. This treatment, called mordanting, involves the precipitation of metal oxides such as aluminum (Al), iron (Fe), cobalt (Co), and chromium (Cr) within the fibers. These metal oxides then form an insoluble lake with the dye, firmly fixing it to the textile material.

Vat dyes

Among natural dyes, indigo is characterized by its specific application method, which requires the preparation of a vat, a solution obtained through alkaline reduction. The term “vat” has been retained to describe a group of dyes that are insoluble in water but become soluble through reduction into a leucon form that has affinity for fibers.

I.6.2. Synthetic dyes

The raw materials of synthetic dyes are compounds such as benzene, derived from the distillation of coal tar. For this reason, synthetic dyes are commonly referred to as coal tar dyes. From these raw materials, intermediates are produced through a series of chemical processes, which generally involve the substitution of one or more hydrogen atoms in the original compound by specific elements or functional groups.

I.7. Use and Application of Dyes

Dyes are widely used in various industrial sectors, particularly in the food industry for coloring food and beverages, as well as in the production of paints, inks, and plastics [26]. Textile dyes are mainly divided into two categories: natural dyes derived from plant or animal sources, such as indigo, purple dye, turmeric, and safflower, and synthetic dyes produced in laboratories. Synthetic dyes offer a wide range of bright colors at lower cost; however, they may present toxicological risks [27].

I.8. Overview of Crystal Violet

I.8. 1. Definition

Crystal violet (CV) is a synthetic cationic dye belonging to the Triarylmethane class and is also known as Basic Violet 3, Gentian Violet, or Methyl Violet 10B. It is widely used in several fields, including microbiology and histology as a biological stain, in veterinary medicine, and in the poultry industry as a feed additive to control intestinal parasites and fungal infections. In addition, it is extensively applied in textile dyeing and paper printing industries [28].

Crystal violet is recognized as a hazardous compound due to its toxicological effects. It can be absorbed through the skin, causing irritation, and is also harmful when inhaled or ingested. Prolonged or high-level exposure has been associated with serious health risks, including organ toxicity, eye irritation, and potential carcinogenic effects. For this reason, its presence in wastewater is considered a major environmental concern, and its effective removal from aqueous systems is essential [29].

I.8.2. Properties of CV

Crystal Violet is a synthetic cationic dye belonging to the triarylmethane class. It is characterized by a deep violet color and high molar absorptivity in the visible region of the spectrum, which makes it easily detectable by spectrophotometric methods.

From a physicochemical point of view, crystal violet is readily soluble in water and polar solvents due to its ionic nature. In aqueous solution, it exists mainly as a positively charged species, which allows strong electrostatic interactions with negatively charged surfaces such as cell walls, fibers, and various adsorbent materials.

CV is chemically stable under normal conditions; however, it can undergo degradation under light exposure or in the presence of strong oxidizing agents. It shows strong affinity for organic materials and is widely used as a biological stain due to its ability to bind to cellular components.

Table I.2: shows some of the physicochemical properties of this dye

I.8.3. Toxicity

Name	Crystal violet

Symbol	CV
Chloride - Basic	Violet 3
Family	Basic Dye
Essential Formula	$C_{25}H_{30}ClN_3$
Molar Mass (g/mol)	407.979 ± 0.025 g/mol (C 73.6%, H 7.41%, Cl 8.69%, N 10.3%)
Solubility	4 $g \cdot L^{-1}$ (water, 25 °C)
Purity (%)	>90
λ_{max}	590 nm
pH	5.9
pKa	0.8
Color	Acid form (yellow); transition range (pH = 0.0 to pH = 1.8); pH 1.8 basic form (blue violet), pH 9 (transparent)

The discharge of dye-containing effluents into aquatic environments represents a major environmental problem. The toxicity of dyes is often related to the lack of knowledge of their chemical structures, which vary from one class to another, as well as to improper handling and usage conditions.

These compounds are known for their toxicity, mainly due to their complex structures and high molecular weights, which make them resistant to biodegradation and promote their accumulation in the environment. Azo dyes are considered among the most toxic classes. Numerous studies have shown that azo compounds exhibit carcinogenic effects in humans [30]. This carcinogenicity is mainly attributed to the formation of aromatic amines resulting from the chemical or enzymatic cleavage of azo bonds [31]. The risk of exposure to these compounds is increased because they are generally lipophilic. These aromatic amines can be absorbed through the skin, inhalation of dust particles, and possibly ingestion.

The toxicity of azo dyes is further enhanced by the presence of substituent groups on the aromatic ring, particularly methyl ($-CH_3$), nitro ($-NO_2$), and halogen groups (especially chlorine) [32]. In contrast, the presence of other substituents such as sulfonate groups ($-SO_3H$) tends to reduce their toxicity.

Indigoid dyes are also considered highly toxic. Contact with these substances may cause skin, eye, and respiratory irritation, as well as permanent damage to the cornea and conjunctiva, particularly during handling of dye powders. Allergic skin reactions, asthma, and occupational rhinitis are frequently observed.

Triphenylmethane derivatives also present significant health risks similar to other dye classes. They may cause eczema and gastric disorders, and repeated exposure or injection can even lead to carcinogenic effects [33].

I.9. Dye Removal Techniques

In the search for efficient methods to remove dyes from aqueous solutions, several treatment techniques have been developed and extensively investigated.

I.9.1. Adsorption

The mechanism of adsorption is based on physical and/or chemical interactions between the adsorbent and the substance to be removed from a usually aqueous solution.

Adsorption has been shown as a preference over other methods of water treatment with respect to dye removal, as it offers lower initial cost, easy operation and flexibility compared to other methods. The important parameters for an efficient adsorbent are its capacity (amount of sorbed dye per mass of adsorbent), the equilibrium rate (how fast adsorption occurs) and the regeneration (how easy is to regenerate and reuse the adsorbent) [34].

The capacity of an adsorbent is judged by its porosity and available surface area. The bigger is not always the better, as there is a need for the optimum combination of pore size, porosity and surface area, alongside the chemistry of the adsorbent (functionalisation or available adsorption sites). The available surface area, porosity and chemistry can also affect the equilibrium rate, the time needed for capacity to be reached.

Also, these factors affect regeneration, based on the binding strength of the pollutant on the adsorbent and the porosity. It should be mentioned that biosorption is another type of adsorption, where pollutants are being adsorbed on dead (or inactive) biomass,

through physical or chemical interactions, not related to metabolism. Bio-sorption is affected by the same factors as non-bio adsorbents (pH, T, ions among others), follows similar kinetic mechanisms and is subjected to the same techniques for characterization [35].

Major differences between adsorption and biosorption are the delicate nature of some bio-sorbents (for example dead cells), the natural abundance of some biosorbents (for example agricultural biomass), and the valorisation of materials which are regarded as waste (for example dead cells that were used in other processes, agricultural biomass).

Amongst many adsorbents explored such as activated carbon, peat, silica-based adsorbents, zeolites or other naturally derived substances, activated carbon is widely studied for dye adsorption. It is also the dominant adsorbent in industry, based on its great adsorption ability, high surface area, stability and homogeneity [36]. Main issues with respect to use of activated carbon as a dye adsorbent, are the high cost of production and regeneration and the possibility of decreased efficiency due to material loss during regeneration, [37] [38], [39]. When activated carbon from leaves was used for adsorption of Acid Green 25, adsorption was more effective in acidic solutions and that past the initial, external uptake, diffusional limitations due to pore structure delayed equilibrium, regardless of the over 900m^2/g surface area [40].

In this case, despite the lower surface area (about 60m^2/g), adsorption capacity was high due to a mesoporous structure that prevented strong diffusional limitations [41]. Chu et al. studied the adsorption of an anthraquinone dye (X-BR) on activated carbon derived from aquatic biomass debris [42]. Decolorisation capacity (555mg dye/g adsorbent) of that type of activated carbon was found higher than commercial carbon products, potentially due to much higher surface area (around 1400m^2/g). Further, they revealed that acidic conditions favoured adsorption and the amount of adsorbent used was important as at higher adsorbent concentrations, aggregation of the adsorbent caused partial clogging of the adsorptive active sites. Another frequently discussed option in the area of adsorption, is the family of zeolites, materials abundant in nature, but with substantially lower adsorption capacity and again facing the issue of high regeneration costs [43], [44].

Besides activating carbon and zeolites, silicon-based materials have been studied extensively for pollutants adsorption [45], [46]. Their interesting properties such as

ability for a wide range of pore size and surface areas, durability, ease of functionalization and relatively cheaper regeneration compared to activated carbon (lower temperature required), have made them excellent candidates for water treatment with many examples on dye adsorption [47], [48].

However, issues such as manufacturing cost and diffusional limitations arising from high throughput in industrial scale applications combined with larger sized organic pollutants, have prevented them from being widely implemented in water treatment. Despite those difficulties, research is showing positive signs on their industrial implementation [49].

I.9.2. Coagulation - Electrocoagulation

Chemical coagulation or flocculation, although quite popular in the past, has been replaced by newer methods or is being used in combination with other methods, in order to reduce the effect of some major drawbacks such as sludge production and need for further treatment of the effluent [50]. The principle of coagulation and flocculation methods is the opposite charge between the soluble pollutant (e.g. dye) and coagulant, that makes the pollutant become insoluble.

Coagulants used are mostly based on Aluminium and iron, sometimes assisted by polymeric coagulants. The factors of importance during coagulation are the type and dose of coagulant needed and the size and "sturdiness" of the coagulated pollutants (also known as floccs) which dominates their ease of removal [51]. Sludge production is a direct implication of coagulation, which poses one of the main concerns around the use of this method, as there is further treatment required, on a potentially more toxic waste stream than the original one. Recently, the process of coagulation was coupled with electrochemistry and electrochemical coagulation gained interest with respect to textile effluent decolorisation.

Towards that direction, electrochemical coagulation producing in-situ coagulants based on Aluminium or iron, showed great dye removal (RB19 as a representative anthraquinone dye, but other dyes were studied as well) and associated time [52].

I.9.3. (Advanced) Oxidation Processes (AOP)

Oxidation Processes belong to chemical methods that can be used for water treatment. The most widely known oxidation processes include Fenton's process, Ozonation and use of hydrogen peroxide, and more recently, photocatalysis. The operating principle is the generation of free hydroxyl radicals that are able to oxidise organic molecules in a non-selective way and lead to their mineralisation [53]. In the case of Fenton process, the presence of ferric ions can lead to promotion of pollutants coagulation [54], combining aspects of both oxidation and coagulation processes.

Photocatalysis is a relatively modern technique, where hydroxyl radicals are produced by the interaction of Ultra Violet light with a semiconductor photo-catalyst [55]. In every case, there are several factors of importance to the oxidation process used, such as the amount of oxidant produced and conditions of production, current, pH of solution, type and intensity of light source, mode of addition of the oxidant/semiconductor, structure of reactor and stability of the process.

All these factors are crucial for the time needed for mineralisation (or adequate results) and the cost effectiveness of the process.

What is worth highlighting with respect to **AOP** is the very short reaction times required, usually minutes, leading usually to very good efficiencies in reduction not only of color, but also of COD/BOD levels. Main disadvantages of these methods are the cost of oxidative agents (ozone, peroxide) and radiation sources that can pose difficulties on their consideration of scale-up and also the production of sludge in the case of Fenton's reaction [56], [57].

Also, upon examining simulated effluents instead of isolated dyes, the efficiency of the treatments dropped about 10%, fact expected yet indicating that efficiency is still high. Similarly, Lovato [58] examined degradation of RB19 using Ozonation and UV radiation. They found that UV radiation alone was not very effective, but ozonation or ozonation assisted by UV radiation were highly efficient, both removing almost 100% of the colour within 5mins. However, it was noticed that compared to ozonation, the combination with UV radiation lead to much higher mineralisation percentage (40% and more than 90% respectively). Two different studies also showed that ozonation can be quite effective for degradation of RB19 (both 100% in a matter of minutes),

promoting its biodegradability based on reduction of the toxicity of the fragments [59] and showing the importance of the electrolytes to the decolorisation and identification of fragments [60].

Using a slightly different anthraquinone dye, Reactive Blue 4, Gozmen [61] examined its decolorisation using different AOP, wet air and peroxide oxidation, photocatalysis using various oxides and Fenton's reagent. They found that although all treatments showed high effectiveness (100% color removal in less than 60min) and relatively high removal of TOC, wet peroxide worked faster. However, this treatment required 35% w/w peroxide solution and a temperature of at least 100C^{o}, factors that might be limiting for industrial application.

I.9.4. Biological treatment

Biological methods have been used for water treatment for many years, especially in sewage water treatment, in the form of activated sludge. They can offer distinct advantages compared to physicochemical methods but also challenges regarding their efficiency 48. The most common categorisation is based on aerobic and anaerobic operation of the microorganisms involved, however, based on the ability to use isolated enzymes, there should have been a proposed categorisation to include them. Based on the latest argument, one could say that the available biological methods can be divided on whether they are performed inside a cell (bacteria, fungi, yeasts or algae) or using isolated enzymes. Others have proposed that use of enzymes falls in between chemical and biological treatment, as we are "taking advantage" of chemical reactions performed by isolated biological compounds [62].

Some of the clear differences between biological and non-biological methods include the lower starting concentration of dyes examined and the longer time needed for decolorisation in biological methods, leading to the conclusion that biological methods might not be as effective as physical and chemical methods. From the studies examined on biological treatment of anthraquinone dyes, the highest starting concentration was 300 mg/L of various anthraquinone dyes of acid and basic structure, using an e-coli culture [62].

I.9.5. Emerging Methods for color removal

A relatively new category of water treatment processing for pollutants' removal, including dyes, is use of advanced nanomaterials (or nanoparticles) with a size range of up to 100nm. Their action falls somewhere within chemical and physical methods, comprising aspects of both. Some examples of explored nanomaterials are metal oxides (zinc and titanium among others), carbon nanotubes, and nanochitosan. [63]. The application of nanomaterials for dye degradation from effluents is not yet thoroughly researched, but their advantages (such as durability, much higher surface area than conventional materials, unique confined spaces and conditionally easy scale up and low cost) lead to potential interest for their industrial application [64].

Nanomaterials can be used as adsorbents of dyes with very promising results, especially when coupled with AOP usually based on photocatalysis. Using zinc oxide nanoparticles to remove Reactive Blue 19 dye showed very good results, indicating high capacity, up to 167mg dye per g adsorbent and short contact time (max 20 minutes) [65].

Research coupling use of zinc and titanium oxides with photocatalysis by irradiation showed that nanoparticles can be quite effective in assisting degradation of a model anthraquinone dye, but their efficiency depends on the structure of the dye [66]. A similar experiment looked at the optimisation of the degradation of Acid Green 25 using immobilised TiO_2 nanoparticles coupled with UV light photocatalysis [67] and further examined the importance of the chemical structure of dyes in degradation [68].

While research shows is that nanoparticles can be a good approach for further investment into water treatment, there are some specific drawbacks to their use. Their toxicity is not thoroughly researched yet, however, there are strong indications that nanomaterials can be toxic to both humans and the aquatic environment [69]. Another disadvantage to their use as adsorbents is the need for regeneration (same as with conventional adsorbents).

I.9.6. Main issues with conventional methods

There are many research papers reviewing the industrially available methods and proposing new ones. Every category and method has advantages and disadvantages

related to the following criteria: efficiency under various conditions, practicability, requirements of pre- and post- treatment and environmental impact; all the aforementioned ultimately relate to cost (see Table1-1 for a general comparison between physical, chemical and biological methods). Based on available literature, a method which could be universally applied and satisfy all demands simultaneously does not exist [70]. and majority of methods cannot be used as a holistic approach [71].

As many researchers have proposed, the best dye removal approach should be a combination of available and under-development methods, combining their strong points and mitigating their disadvantages [72], [73].

It also shows that while AOPs are a quite promising category of methods, they still need refinement, whereas biological methods, past the traditional digestion, offer a novel approach to tackling the problem of dye presence in water. However, although enzymes work effectively towards dye degradation, there are issues about their industrial implementation that need to be addressed.

Table I.3: Methods for removal of pollutants [74].

Physical methods (adsorption, filtration)	Chemical methods (coagulation / flocculation, (AOP, photocatalysis)	Biological methods (using microorganisms or isolated enzymes, or via bio-sorption)
Advantages	**Advantages**	**Advantages**
Industrially mature methods	Some industrially mature methods (e.g. coagulation, flocculation)	Some industrially mature methods (e.g. activated sludge, aerobic digestion)
Highly efficient (conditional on combination of adsorbent / pollutant)	Highly efficient, but not highly selective	Environmentally friendly, of lower cost, with lower water input required
Good knowledge of the processes and the physical chemistry required	AOPs are quite fast (minutes – hours) and can lead to complete mineralisation	Dye structure is broken down to less toxic by-products, colour is removed or subdued
	Easily combined with other methods	Immobilisation can increase reusability, operational stability
Disadvantages	**Disadvantages**	**Disadvantages**
Dye is removed but not degraded, so further treatment is required	Some methods are not industrially mature yet (AOPs)	Some methods are not industrially mature yet (isolated enzymes)
Difficulty in regenerating absorbents and filters/membranes	Can lead to sludge production that is toxic and requires further treatment	Limited knowledge and control of exact action and/or degradation pathway
Depend on the structure of the dye and the adsorbent	Costly due to energy requirements	Many factors to be taken under consideration (T, pH, agitation, inhibitors, activators, chemistry of degradation, nutrients)
Adsorbents might be of high cost	Unsustainable (use of harsh chemicals, production of secondary pollution)	Use of cultures requires high residence time (days) due to diffusion phenomena or the period of culture development
Require long residence time (hours – days)	Coagulation/flocculation do not degrade dye structure	

Chapter II

Adsorption and Biomass

II.1. General Information on Adsorption

II.1.1. Definition

Adsorption at the solute/solid interface is a physical or chemical phenomenon in which molecules present in a liquid or gaseous effluent become attached to the surface of a solid material. This process depends both on the nature of the interface and on the physicochemical properties of the adsorbate. It occurs spontaneously due to the presence of unbalanced forces at the surface of the solid, which may be of physical or chemical nature. These interactions lead to two main types of adsorptions: chemisorption and physisorption [75,76].

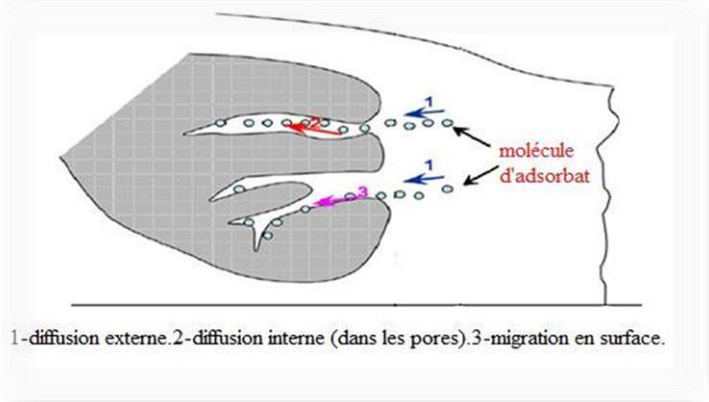


Figure II.1: Adsorption at the solute/solid interface

II.1.2. Principle

Adsorption is a surface phenomenon by which atoms or molecules are retained on the surface of a solid substrate through various interaction mechanisms. Certain materials such as clays, zeolites, and activated carbon are considered excellent adsorbents due to their high specific surface areas. The reverse process of adsorption is called desorption, in which the adsorbed molecules or atoms are released from the surface of the substrate.

The adsorption process is based on the ability of solid surfaces to retain molecules through weak interactions, such as Van der Waals forces. This property is related to the structure of the solid, where surface atoms are not fully balanced due to structural asymmetry. The adsorption of molecules helps to reduce this surface energy imbalance by forming a layer of adsorbed species on the solid surface.

II.2. Types of Adsorptions

Depending on the amount of energy involved between the adsorbent and the adsorbate, the forces. responsible for the surface adsorption can be physical or chemical in nature, thus, leading to two types of adsorptions:

- Physical adsorption “physisorption”
- Chemical adsorption “chemisorption"

II.2.1. Physical Adsorption

This phenomenon of adsorption by solids is due to physical interaction forces between the atoms constituting the surface layer of the solid and the molecules of the gaseous or liquid phase in contact with the solid. These interaction forces involve Van der Waals forces as well as hydrogen

bonds. They exist regardless of the nature of the solid and the adsorbate molecules. Electrostatic (Coulombic) forces also exist if the solid or gas is polar in nature (attraction between two dipoles of two molecules). Dispersive forces, of the London dispersion type, can come into play due to the rapid fluctuation of the electron density in each molecule. In this case, the energies involved are low and less than 20 kcal/mol; the adsorption is then reversible. The adsorption sites do not lead to specific adsorption [77].

II.2.2. Chemical Adsorption

In this case, adsorption involves chemical interactions between the surface atoms of the solid and the adsorbate molecules. It consists of a transfer of charges and a redistribution of these charges between the adsorbed species and the adsorbent. This leads to the formation of strong bonds with a covalent or ionic character.

In this case, the energy involved is higher and the distance between the surface and the adsorbed molecules is shorter than in the case of physisorption. Chemical adsorption occurs at specific functional groups or particular sites on the surface of the substrate. The energies involved generally range between 20 and 100 kcal/mol, and the adsorption is irreversible [78]

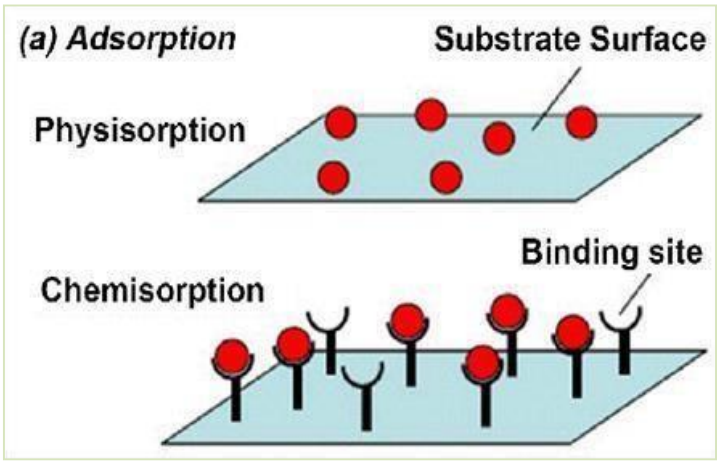


Figure II.2: Types of adsorptions

II.3. Adsorption Isotherm Models

An adsorption process can be described using an adsorption isotherm, such an isotherm is a curve that represents the relationship between the amount of solute adsorbed per unit mass of adsorbent q_e (mg/g) and the concentration of solute in solution C_e (mg/L).

II.3.1. Langmuir Model

The equation (1) is known as the Langmuir equation, which was proposed by Langmuir in 1915 [79] and later confirmed in 1916 [80]. It describes type **I** isotherms. Once the values of Q_e and C_e are determined experimentally, this equation allows the determination of K_L and B, which are characteristic parameters of the Langmuir model. The Langmuir equation represents monolayer adsorption without interaction between adsorbed molecules, occurring on a surface with a finite number of adsorption sites having identical energy.

$$Q_e = (_____ (1k+l\times klccee)) \quad \text{..... (Eq. II.1)}$$

Where:

- Q_e: amount of substance adsorbed at equilibrium per unit mass of adsorbent (adsorption capacity) (mg/g);
- C_e: equilibrium concentration of the adsorbate in solution (mg/L).

Some authors have compiled numerous Langmuir isotherms and found that they exhibited 4 types (Figure **II.3**), which have been quite precisely linked to various modes of attachment [81].

- **Type S**: Indicates a vertical adsorption of polar mono functional molecules on a polar adsorbent and in a polar solvent (example: phenol on alumina).
- **Type L**: Normal Langmuir, indicates the flat adsorption of bi functional molecules.
- **Type H:** Starts with a positive value but not zero, indicates high affinity, meaning that adsorption is complete at low concentrations.
- **Type C:** The straight line means there is competition between the solute and the solvent to occupy the sites with the same distribution, concerning flexible molecules that can penetrate deep into the pores to displace the solvent.

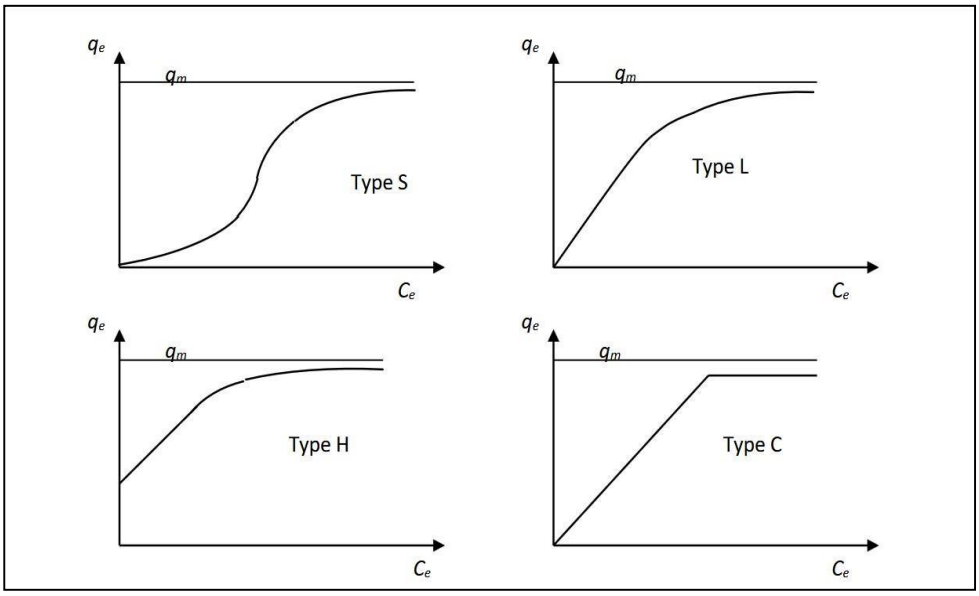


Figure II.3: The adsorption isotherms in the liquid phase [82].

II.3.2. Freundlich Model

In contrast to the Langmuir model, the Freundlich equation (Eq. 2) is often used to describe adsorption isotherms of different types (I, II, or III). It was proposed empirically to represent the behavior of various adsorption systems without assuming a uniform surface or a monolayer formation.

Its expression is given as follows:

1

$$Q_e = K_f \times C_{En} \quad \text{..... (Eq. II.2)}$$

Where:

✓ Q_e and C_e represent the adsorption capacity at equilibrium (mg/g) and the equilibrium concentration of the adsorbate in solution (mg/L), respectively; ✓

K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity.

The value of n provides important information about the adsorption process. When n > 1 (generally between 2 and 10), it indicates a favorable adsorption process. On the other hand, values of n < 1 suggest weak or less favorable adsorption.

II.4. Adsorption Kinetics

The knowledge of adsorption equilibrium parameters makes it possible to determine the adsorption capacities of a given support. In addition, determination of kinetic parameters is necessary to predict the shape of adsorption curves.

The transfer of an adsorbate from the liquid phase to an adsorption site, as illustrated in Figure (III.2), involves the following steps [83]:

➤ **First step:** Transfer of the adsorbate from the liquid phase to the boundary layer of the liquid film surrounding the solid particle (by convection or diffusion). This is a very fast step.

➤ **Second step:** Transfer of the adsorbate through the liquid film toward the external surface of the adsorbent. This is a fast step.

➤ **Third step:** Diffusion inside the adsorbent particle under the influence of the concentration gradient. This is a slow step and can occur through two mechanisms:

- **3a:** In the adsorbed state, by surface diffusion.
- **3b:** In the free state, by pore diffusion.

➤**Fourth step:** Adsorption within the micropores of the adsorbent. This is a very fast step.

II.5. Adsorption Kinétique Modeling

To evaluate the mass transfer mechanism and determine the rate-controlling steps of the adsorption process, the experimental data are systematically analyzed using two fundamental kinetic models: the pseudo-first-order and the pseudo-second-order models.

II.5.1. Pseudo-First-Order Kinetic Model (Lagergren Model)

To evaluate the mass transfer mechanism and determine the rate-controlling steps of the adsorption process, the experimental data are systematically analyzed using two fundamental kinetic models: the pseudo-first-order and the pseudo-second-order models.

1. Pseudo-First-Order Kinetic Model (Lagergren Model)

The pseudo-first-order kinetic model, initially introduced by Lagergren [104], is historically the first-rate equation formulated to describe liquid-solid phase adsorption based on solid capacity. This macroscopic model assumes that the rate of adsorption at any given time is directly proportional to the difference between the equilibrium adsorption capacity (q_e)and the amount of solute adsorbed at that specific time (q_t). It is generally associated with a physisorption (physical adsorption) mechanism governing the initial stages of the process, as reviewed in recent literature [105].

The differential form of this kinetic law is expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

After integrating this equation using the boundary conditions (q_t= 0 at t = 0 and $q_t = q_t$) at t = t), the standard linear form is obtained:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 \times t$$ Where:

q_e: represent the adsorption capacities at equilibrium ($mg \cdot g^{-1}$). q_t: denotes the amount of pollutant adsorbed at time ($mg \cdot g^{-1}$). k_1:is the pseudo-first-order rate constant (min^{-1}).

2. Pseudo-Second-Order Kinetic Model (Ho & McKay Model)

The pseudo-second-order kinetic model, widely popularized and validated by Ho and McKay [106], relies on a different mechanistic approach. It postulates that the ratelimiting step of the process is not mass transfer, but rather chemisorption (chemical adsorption).

This mechanism involves valence forces through the sharing or exchange of electrons between the active functional sites of the adsorbent and the adsorbate molecules [107].

The fundamental differential expression is defined by the following relationship:

$$\frac{d}{dt}q_t = k_2(q_e - q_t)^2$$

By integrating this equation under the same initial conditions, it is transformed into its most rigorous and graphically exploited linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{1}{q_e} \times t$$

Where:

k_2: represents the pseudo-second-order specific rate constant ($g.mg^{-1}.min^{-1}$).

q_2:is the adsorption capacity at time t (mg/g) k_2: pseudo-second-orde rate constant ($g.mg^{-1}.min^{-1}$) t: time (min)

II.6. Main factors influencing adsorption

The adsorption equilibrium between an adsorbent and an adsorbate depends on numerous factors, the main ones of which are described below:

- ***Specific surface area***: Adsorption is proportional to it.
- ***Nature of the adsorbate :*** LUNDELIUS Rule "The less soluble a substance is in the solvent, the better it is adsorbed."
- ***Hydrogen potential (pH):*** Adsorption strongly depends on the pH of the solution and consequently will influence the charge of the adsorbent surface, the degree of ionization, and thespeciation of the adsorbate. The acid-base characteristics of the functional groups on the surface change with pH. They become basic for pH < pHPZC by adsorption of H+ ions (PZC: point of zero charge) (hence the adsorption of anions is favored at pH < pHPZC), and they become acidic for pH > pHPZC by adsorption of OH- ions (hence the adsorption of cations is favored at pH > pHPZC).
- ***Polarity:*** A polar solute will have a greater affinity for the solvent or the adsorbent [87,88].
- ***Temperature***: For economic reasons, adsorption is carried out at room temperature, that is, the temperature of the water to be treated. Temperature influences both the adsorption rate and the equilibrium concentration.

- ***Case of mixtures***: They can promote or hinder adsorption (example: ionic strength). They constitute the matrix of the solution, which retains or expels the adsorbate. It is one of the least well-known aspects of adsorption theory.

- ***Nature of the adsorbent:*** Any solid is a potential adsorbent.

II.7. Biomass as an Adsorbent

II.7.1.Defintion of Biomass

Organic materials originating from living matter or complexes of organic and inorganic materials are collectively referred to as biomass. Biomass includes but not limited to only living organisms, such as plants and animals, but also the excrement of animals, sludge, and waste wood [89]. Sometimes, it is referred to as stored energy, a renewable organic material derived from plants and animals that can serve as sources of energy. Biomass is made up of carbohydrate and has less energy storage problems when compared with other renewable sources such as solar and wind [90]. Wastes such as agricultural/agro-industries wastes and municipal wastes and purposely grown energy crops such as sugarcane, corn, wheat, etc. are the main sources of biomass [91].

Biomass can be converted into several useful forms of energy using different processes briquette and biochar. There are several factors which could affect the choice of conversion process; these can include [92]: the type of usage, quantity, and characteristics of biomass feedstock, the desired form

of the energy environment. In addition to being a food source to animals, and renewable raw material, it can be used for energy production, carbon sequestration and, as an essential element to produce hydrochars and activated carbons [93]. Figure II.3 shows a biomass-to-power supply system.

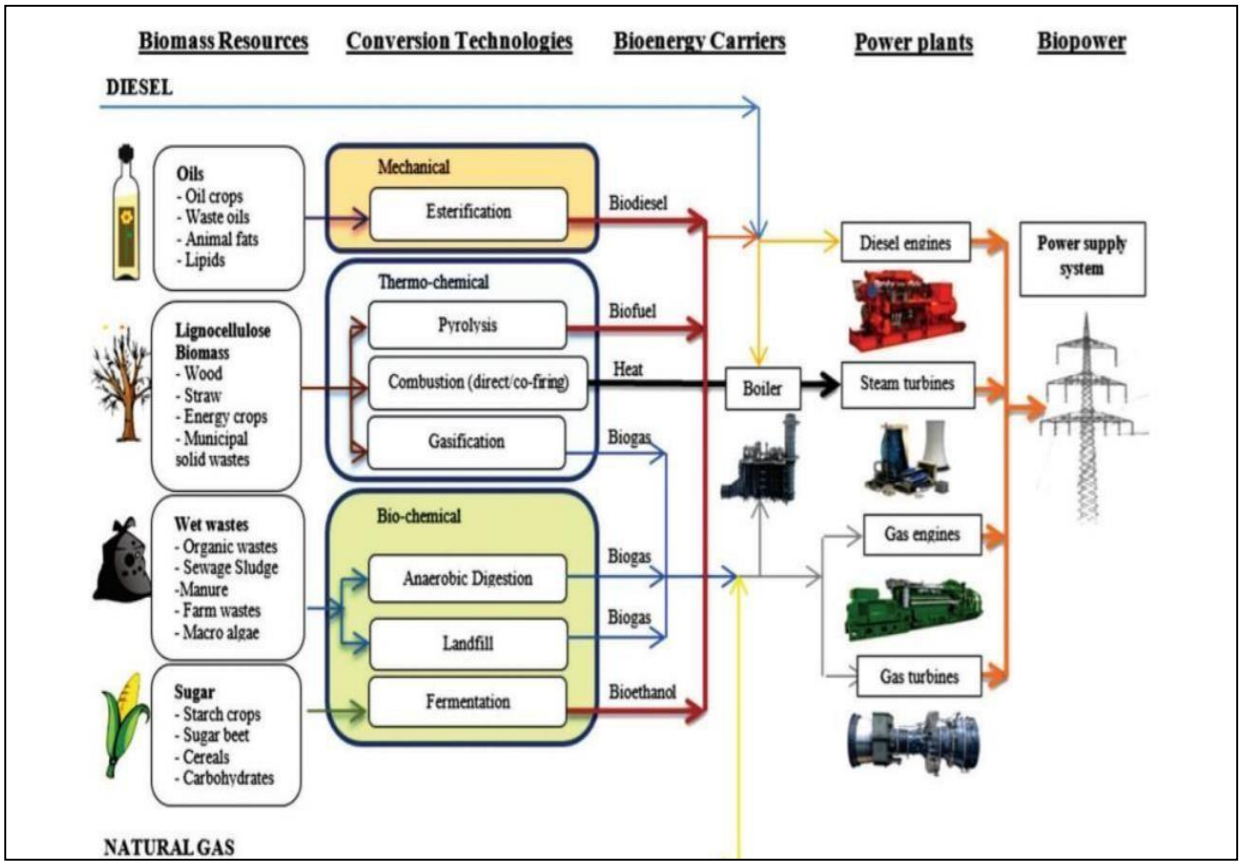


Figure II.4: Biomass-to-power supply system

II.7.2. Types of Biomass

- ***Woody biomass:*** includes components whose major constituents are carbohydrates and lignin including live trees, forest and manufacturing residues, or consumer waste materials [94].
- ***Herbaceous biomass*** : which is obtained from plants with a non-woody stem which dies at the end of the growing season [95]. It includes grain and seed crops from the food processing industry and their by-products. Herbaceous crops can be sub-divided into agricultural residues and energy crops [94].

Aquatic biomass : includes algae and emerging plants. These include marine or freshwater algae, macroalgae or micro algae, seaweed, kelp, lake weed, and water hyacinth [96]. Aquatic weeds have exceptionally high reproduction rates and are rich in cellulose and hemicellulose with a very low lignin content, which makes them efficient as biofuel crops.

II.7.3. Criteria for Selecting Adsorbents

The choice of adsorbents is closely dependent on the intended applications.
Generally, the evaluation of the qualities of an adsorbent can be based on several criteria [97,98,99,100].

- Capacity: It concerns the quantities of constituents to be removed that are adsorbed.
- Selectivity: Selectivity are relative capacities of adsorption of constituents in relation to other constituents.
- Regenerability : For processes with situ regeneration, the adsorbents must be easy to regenerate.
- Kinetics: The search for the best costs for adsorption processes leads to the use of increasingly faster adsorption cycles in order to increase hourly productivity and reduce investments.

II.7.4. Parameters for Evaluating the Effectiveness of Adsorbents

II.7.4.1. Adsorption Capacity

The adsorption capacity is the amount of pollutants that the material can adsorb under determined operating conditions. It is the main parameter used to estimate the sorption capacity of an adsorbent.
It is expressed in milligrams (mg) or mill moles (mmole) of pollutants adsorbed per gram (g) of dry material.

The evaluation of a material's adsorption capacity involves the description of the equilibrium reactions produced between the adsorbent and the adsorbate, after a contact time.
This description is carried out using adsorption isotherms. Thanks to the tests conducted at constant temperature, the calculation of the maximum adsorption capacity is carried out using mathematical models [101].

II.7.4.2. Adsorption Kinetics

The adsorption kinetics is the second parameter indicating the purification performance of an adsorbent. It allows estimating the amount of pollutants adsorbed as a function of time. Kinetics provides information related to the adsorption mechanism and the mode of transfer of solutes from the liquid phase to the solid phase [102].

II.7.5. Transport Mechanism

1) Migration in solution

The solute must be transported to the surface of the adsorbent. This movement depends on the size of the particle as much as on the agitation present in the solution, but it is generally rapid. [103]

2) Diffusion in the film

The solute must still diffuse thru the water film that envelops the adsorbing particle. The rate of mass transfer thru the water film is directly proportional to the surface area developed by all the adsorbing particles and thus proportional to the size of each of them.

3) Internal diffusion or diffusion in the pores

The substance adsorbed on the surface of a particle can also be within the pores of the particle itself. There is, indeed, diffusion thru the film toward the surface of the particle but also within its pores.

II.8. Presentation of the Ferfour study localization

The mountainous region of Ferfour is in the Daïra of Azzaba, in the wilaya of Skikda; It is bordered by a set of hilly and forested formations characteristic of northeastern Algeria. The area is marked by a succession of hills and small mountains with a general spatial continuity. It is characterized by moderate altitudes ranging between foothill zones and surrounding highlands. The landscape shows a rugged morphology with sometimes steep slopes, intensified by significant water erosion.

Indeed, these slopes are dissected by a network of temporary streams (oueds) and their tributaries, which transport materials toward lower areas.

The climate is of the humid Mediterranean type, with hot and dry summers and relatively cool and rainy winters, promoting the development of abundant and diverse natural vegetation.

Within the framework of this study, the species *Marrubium vulgare* was selected for the preparation of a bioadsorbent, due to its local availability and its potential physicochemical properties in biosorption applications.

II.9. Botanical description

Marrubium vulgare is a perennial herbaceous plant with a grayish appearance, reaching a height of 25 to 60 cm, and showing some resemblance to mint.

Its stems are square in cross-section and may be simple or branched, erect or slightly prostrate at the base, and covered with a white cottony down.

Its leaves are opposite and petiolate, oval to rounded shape, downy, irregularly toothed, wrinkled, and of a whitish-green color. The reproduction of this plant is ensured by pollinating insects. Marrubium vulgare flowers from April to October. The flowers are small (1.2 to 1.5 cm in length), white, and grouped in compact whorls spaced along the stem. The corolla is bilabiate, with a three-lobed lower lip and a twolobed upper lip.

The calyx has ten short teeth. The plant has four stamens hidden within the corolla tube.

II.9.1. Chemical Composition

The chemical composition of lignocellulosic biomass is mainly based on three fundamental structural components, namely cellulose, hemicellulose, and lignin, which together form a complex and organized matrix responsible for the physical and chemical characteristics of the plant material.

Cellulose is a linear polysaccharide composed of glucose units linked by β (1→4) glycosidic bonds. It represents the main structural component of plant cell walls and is responsible for the mechanical strength of the biomass. The presence of numerous hydroxyl groups in its structure allows the formation of hydrogen bonds, which

contributes to the stability of the material and its potential interaction with adsorbate molecules.

Hemicellulose is an amorphous heteropolymer composed of different sugar units such as xylose, mannose, and glucose. It has a branched and less ordered structure compared to cellulose, which makes it more accessible and reactive. This characteristic provides additional functional sites capable of interacting with various pollutants, particularly metal ions and polar molecules.

Lignin is a complex aromatic polymer formed by the polymerization of phenylpropanoid units. It acts as a binding material between cellulose and hemicellulose, ensuring rigidity and structural cohesion of the biomass. Its structure contains several functional groups such as hydroxyl, methoxyl, and carbonyl groups, which allow it to participate in different adsorption interactions, especially with organic compounds.

The association of these three components gives lignocellulosic biomass some heterogeneous structure rich in functional groups, which plays an important role in its behavior as a potential adsorbent material.

II.10. Adsorptive Properties of Biomass

Biomass derived from plant materials is widely considered as an efficient and lowcost adsorbent due to its natural abundance, biodegradability, and physicochemical properties. Its adsorption behavior is mainly attributed to the presence of various functional groups such as hydroxyl, carboxyl, phenolic, and carbonyl groups distributed within the lignocellulosic structure.

The surface of biomass is generally porous, which provides a relatively high specific surface area and facilitates the diffusion and retention of different adsorbate molecules. In addition, the heterogeneous nature of biomass allows the occurrence of several interaction mechanisms, including electrostatic attraction, hydrogen bonding, ion exchange, and Van der Waals forces.

The adsorption capacity of biomass is influenced by several operational parameters such as pH, temperature, contact time, particle size, and initial concentration of the

pollutant. Moreover, different physical or chemical treatments can be applied in order to improve its adsorption performance by increasing surface area and exposing additional active sites.

Overall, lignocellulosic biomass represents a promising alternative to conventional adsorbents such as activated carbon, particularly in wastewater treatment applications, due to its efficiency, availability, and environmental compatibility.

Chapter III

Materials & Methods

III.1. Apparel and products used

III.1.1 Apparel UV-visible spectrophotometer (Cary 60 UV-Vis)

1) Principle

Spectrophotometric analysis is based on studying the change in light absorption by a medium as a function of the concentration of a constituent. The concentration of the absorbing substance is deduced from the proportion of light intensity absorbed by the solution. Spectrophotometric analysis uses essentially monochromatic light. The absorptiometer has become more important than volumetric analysis and is now the most widely used method.



Figure III.1: Apparel UV-visible spectrophotometer (Cary 60 UV-Vis)

Beer-Lambert's law allows for a direct relationship between the absorbance of a solution and the concentration of a species. The total absorbance at a given wavelength is the sum of the absorbances of the different species present in the solution. Therefore, to measure the concentration of a given species using this method, one must either have a pure solution or know the concentrations of the other species present. The molar extinction coefficient of a molecule depends on the wavelength considered; the wavelength chosen for the measurement is generally the one for which the coefficient is highest, thus maximizing the sensitivity of the method. The advantages of this method are its ease and speed of use.

$$A = \varepsilon . L . C$$ **(Eq III.1)** Where

:

- **A :** Absorbance (without unit)
- $\boldsymbol{\varepsilon}$ **:** the coefficient of adsorption of extinction mole (L.mole^{-1}.cm^{-1})
- $\boldsymbol{L}$**:** the length of the cup or the length of the lumineux (cm)
- $\boldsymbol{C}$**:** the concentration of mole of space adsorbent (mol.L^{-1})

2) Determination of λ_{max}

The maximum absorption wavelength λ_{max} was determined by establishing the absorption spectrum of a sample of a 100 mg/L dye solution after scanning the visible range (200–800 nm). After determining the maximum absorption wavelength for Crystal Violet, a standard dye solution was prepared from the stock dye solution (1 g/L) to measure absorbance and plot appropriate calibration curves. The analysis yielded a value of λmax = 588 nm.

3) Determination of the calibration curve

To establish the calibration curve of a dye using Beer-Lambert's law, the following steps are generally followed :

Prepare a series of standard solutions of the dye at different known concentrations and within the desired concentration range.

Measure the absorbance (A) of each standard solution at the maximum absorption wavelength (**λmax = 588 nm**) determined previously, using a UV-visible spectrophotometer and a cuvette of known optical path length (l) (usually 1 cm).

Plot the curve A = f(c).

According to Beer-Lambert's law (A = ε.l.c), this curve must be a straight line passing through the origin.

Determine the equation of the calibration line using linear regression:

A = a.c Where a is the slope, which is simply the product ε.l

This calibration curve then allows the unknown concentration of a dye solution to be determined by measuring its absorbance at λmax and using the equation: c = A/a, (good linearity (R^2 close to 1) is required for this method to be accurate).

4) Determination of the Residual Concentration of the Sample

To determine the residual concentration of a compound in a sample using BeerLambert's Law, follow these steps:

- Measure the absorbance (A) of the sample at the maximum absorption wavelength (λ_{max}) of the compound being analyzed, using a UV-Visible spectrophotometer and a cuvette with a known optical path length (l).
- Have the previously established calibration curve available, which relates absorbance to concentration according to A = a.c + b, where a = ε.l and b is a constant.
- By modifying the Beer-Lambert law equation, we obtain: c = (A - b)/a.
- Substitute A with the absorbance value measured for the sample, and a and b with the values from the calibration curve.
- Calculate the concentration c of the absorbing species present in the sample.

This calibration method allows for reliable quantitative analysis provided that BeerLambert's law is strictly followed.

III.1.2. Products used

Chemical Reagent	***Chemical Formula***	***Molar mass g/mol***	***Density***	***Physical state***
Crystal violet	$C_{25}H_{30}ClN_3$	407.99 g/mol	1.19 g/cm^3	Poudre
Hydrochloricacid	HCl	36.46 g/mol^{-1}	1.18 g/cm^3	Liquid
Sodium hydroxid	NaOH	40g/mol^{-1}	2.13 g/cm^3	Solid crystalline
Sodium chloride	NaCl	58,44 g/mol^{-1}	2.160g/cm^3	Solid crystalline

Magnesium chloride	$MgCl_2.6H_2o$	203.3 g/mol^{-1}	1.56 g/cm^3	Solid crystalline
Sodium sulfate	Na_2SO_4	142.04 g/mol^{-1}	2.66 g/cm^3	Solid crystalline

III.2. Preparation of the Adsorbent, Adsorbate, and Reagent Solutions

III.2.1. Biomass preparation (the Adsorbent)

Marrubium vulgare was used as an adsorbent, and several steps were followed before its use:

Step 1: Marrubium vulgare was washed with regular water, then rinsed with distilled water to remove impurities such as sand and dust. After washing, the samples were air-dried to ensure no moisture remained.

Step 2: The samples were placed in an oven for five days, four hours each day, at a temperature of 80°C.

Step 3: The samples were ground using an electric mill to obtain homogeneous material suitable for laboratory studies, which produced small granules. To obtain granules of fine dimensions, the material was saved to obtain a fine, homogeneous powder.



FigureIII.1: Steps for preparing the adsorbent.

III.2.3. Preparation a 0.1 M sodium chloride solution

To prepare a 0.1 M sodium chloride solution, weigh 0.5844 g of sodium chloride (molar mass = 58.44 g/mol, density = 2.160 g/cm³). Dissolve this amount in distilled water in a 100 mL volumetric flask, then add distilled water and titrate 15 mL of the solution to the titration mark while shaking.

III.2.3. Preparation a 0.1 M Magnesium Chloride Solution

To prepare a 0.1 M magnesium chloride solution, weigh 2.033 g of magnesium chloride (molar mass = 203.30 g/mol, density = 1.56 g/cm³). Dissolve this amount in distilled water, then add 15 mL of the solution to a 100 mL volumetric flask. Next, add distilled water up to the titration line while shaking.

III.2.4. Preparation of a 0.1 M Sodium Sulfate Solution

To prepare a 0.1 M Sodium Sulfate solution, weigh 2.033 g of sodium sulfate (molar mass = 142.04 g/mol, density = 2.66 g/cm³). Dissolve this amount in distilled water, then add 15 mL of the solution to a 100 mL volumetric flask. Next, add distilled water up to the titration line while shaking.

III.3. Determination of the pH of MV

The evolution of the pH of the suspension was monitored to evaluate the influence of the biomass on the aqueous medium. The experiment was carried out according to the following procedure:

1. Measure exactly **50 mL** of distilled water and pour it into the Erlenmeyer flask.
2. Measure and record the initial pH of the distilled water before adding the biomass.
3. Immediately start the timer and gently stir the suspension to ensure uniform mixing (if using a stirrer, keep speed low and constant).
4. Immerse the pH electrode fully into the suspension.
5. Record the pH values at the following time intervals (in minutes):
   1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 15, 25, 35, 45, 55, 65, 75, 85, and 95.

1. Between readings (if the electrode is removed), rinse it with distilled water and gently dry it before re-immersing.

III.4. Batch Adsorption of Crystal Violet onto Marrubium vulgar

III.4.1. Preparation of the Stock Solution

A stock solution of crystal violet (CV) was prepared by dissolving **2.0 g** of the dye in **1 L** of freshly distilled water under continuous stirring until complete dissolution. This yielded a stock solution with a concentration of **2000 mg/L**. Working solutions of the desired concentrations were subsequently prepared by appropriate dilution of the stock solution with distilled water prior to the adsorption experiments.



Figure III.2 : A stock solution of crystal violet (CV)

III.4.2. Preparation of Standard Solutions for the Calibration Curve

From the stock solution, a series of standard solutions with concentrations ranging from 10 to 50 mg/L were prepared by appropriate dilution with distilled water. These standards were used to construct the calibration curve by plotting **absorbance versus concentration**, in accordance with the **Beer–Lambert law**.



Figure III.3: a series of standard solutions

III.4. pH of Zero Charge (pH zpc)

Determining this property allows us to better understand the nature of the charges existing on the surface of the adsorbent as a function of the pH_i of the solution and consequently to better understand the effect of the pH_i on the CV removal rate.

Procedure

1. Prepare **10 Erlenmeyer flasks** (or plastic bottles with lids), each containing **50 mL** of **0.1 M NaCl** solution.
2. Adjust the initial pH of each solution to the following values using dilute **0.1 M HCl** or **0.1 M NaOH**:
   2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 (include pH 9 for a complete series).
   Measure and record the exact initial pH (pH_i) of each solution after adjustment.
3. Add exactly **0.1 g** of the adsorbent to each flask.
4. Cap or cover the flasks and stir continuously at **150 rpm** at room temperature for **24 hours**.
5. After 24 h, measure the **final pH (pHf)** of each suspension.
6. Calculate the pH change: **$\Delta pH = pH_f - pH_i$** for each point.
7. Plot **ΔpH (y-axis) vs. pHi (x-axis)**.
8. The **pH_{pzc}** is the value of pHi where **ΔpH = 0** (i.e., the curve crosses the x-axis).

III.4. Batch optimization studies

III.4.1. Contact Time Effect

To Determine the equilibrium time (t_{eq}) required for the adsorption process.

1. Prepare **8 beakers**, each containing:
   - 100 mL of CV solution (30 mg/L) ○ 0.5 g of *Marrubium vulgare* biomass ○ Natural pH (unadjusted)
2. Stir at **150 rpm** at room temperature for the following time intervals:
   - 10, 15, 30, 45, 60, 90, 120, and 180 minutes.
3. After each interval, immediately separate the adsorbent by centrifugation at **3000 rpm** for 15 minutes.
4. Measure the residual CV concentration using a UV-Vis spectrophotometer at **589 nm**.

5. Plot adsorption capacity (qt) vs. time. Identify the **equilibrium time (t_{eq})** where qt stabilizes.

III.4.2. Effect of adsorbent mass

To Determine the optimum adsorbent dosage at equilibrium.

1. Prepare **7 beakers**, each containing:
   - 100 mL of CV solution (30 mg/L)
   - Different masses of MV biomass: **0.1, 0.2, 0.4, 0.5, 0.6, 0.8, and 1.0 g**
   - Natural pH
2. Stir at **150 rpm** at room temperature for t_{eq} (60min) .
3. Centrifuge at **3000 rpm** for 15 minutes.
4. Measure the residual concentration at **589 nm**.
5. Calculate q_e (mg/g) or removal percentage for each mass. Select the **optimum mass** (typically where the removal curve begins to plateau).

III.4. 3.pH effect of the solution

The pH of an aqueous solution influence on the surface properties of the adsorbent and ionization/ dissociation of functional groups on the adsorbate molecule, which play important role in the whole adsorption process. In this work , we Investigate how pH affects CV adsorption.

1. Prepare **7 beakers**, each containing:
   - 100 mL of CV solution (30 mg/L)
   - The **optimum adsorbent mass** (as determined above)
   - Adjust the initial pH to exactly: **4, 5, 6, 7, 8, 9, and 10** using dilute HCl or NaOH.
2. Monitor pH before and after adding the adsorbent. Preferably use buffered solutions or check that pH drift is minimal.
3. Stir at **150 rpm** at room temperature for t_{eq}.
4. Centrifuge at **3000 rpm** for 15 minutes.
5. m easure the residual concentration at **589 nm**.



Figure III.4: Monitor pH before and after adding the adsorbent

III.5. Isothermal Adsorption of Crystal Violet

The adsorption isotherm models generally used to design and to understand the mechanism of interaction existing between adsorbate and the adsorbent at equilibrium. In this work, two isotherm models (Langmuir and Freundlich) were applied to describe the distribution of dye ions between the liquid phase and the solid phase at constant temperature.

Adsorption isotherm experiments were carried out to describe the distribution of Crystal Violet (CV) dye ions between the liquid phase and the solid phase (biomass) at equilibrium.

1. The experiments were conducted at room temperature (**20°C**) using initial CV concentrations of **10, 20, 30, 40, and 50 mg/L**.
2. For each experiment, 100 mL of dye solution was mixed with **0.5 g** of dried biomass in 250 mL Erlenmeyer flasks.
3. The initial pH of each solution was measured and adjusted to a constant value of 6.0 ;
4. The flasks were agitated in an orbital shaker at 150 rpm for **60** minutes, which was previously determined to be the equilibrium time.
5. After agitation, the solid phase was separated from the liquid phase by centrifugation at 3000 rpm for 15 minutes.

6. The supernatant was analyzed using a UV-Vis spectrophotometer, and the residual dye concentration was determined using a calibration curve at the maximum wavelength of 588 nm.

III.6. Experimental Protocol: Adsorption Kinetics Study

The objective of this study is to investigate the rate of adsorption of Crystal Violet (CV) dye onto the biomass and to determine the kinetic parameters governing the process. The experimental data will be fitted to pseudo-first-order and pseudo-second-order kinetic models.

A batch adsorption technique was employed to study the kinetics of CV adsorption onto the biomass.

1. **Preparation:** A series of identical 250 mL Erlenmeyer flasks were prepared. Each flask was filled with exactly **100 mL** of the CV solution at a concentration of **30 mg/L**.
2. **Addition of Adsorbent:** A precisely weighed amount of **0.5 g** of the biomass was added to each flask.
3. **Agitation:** All flasks were placed in an orbital shaker and agitated at a constant speed of **150 rpm** at room temperature (20 °C) for a total contact time of **180 minutes**.
4. **Sampling at Time Intervals:** To monitor the adsorption progress over time, individual flasks were removed from the shaker at predetermined time intervals: **5, 10, 15, 20, 30, 40, 50, 60 …..until 180 minutes**.
5. **Separation:** Immediately after removal, the contents of each flask were transferred to centrifuge tubes and centrifuged at **3000 rpm** for **15 minutes** to separate the solid biomass from the liquid supernatant.
6. **Analysis:** The supernatant (clear liquid) from each time interval was carefully collected. The residual concentration of CV dye in each supernatant was determined using a UV-Vis spectrophotometer. The absorbance of the samples was measured at the maximum wavelength of **588 nm**.

Chapter IV Results & Discussion

IV.1. The Calibration Curve of Crystal Violet

The calibration curve of Crystal Violet (CV) was established by measuring the absorbance of standard solutions at the maximum absorption wavelength (**λmax = 589 nm**), previously determined by wavelength scanning. Standard solutions with concentrations ranging from **0 to 8 mg/L** were prepared, and their absorbance values were recorded using a UV–Visible spectrophotometer. A calibration curve was then constructed by plotting absorbance versus concentration. The best-fit linear regression line was obtained using the least-squares method.

The excellent linearity of the calibration curve (R^2 = **0.99975**) confirms that Crystal Violet obeys the Beer–Lambert law within the investigated concentration range. The obtained results are presented in **Table IV.1**, while the corresponding calibration curve is shown in **Figure IV.1**

Table IV.1: The values of Absorption and Concentration

C (mg/L)	0	0.5	1	2	3	5	8
Absorbance	0	0.053	0.1096	0.2123	0.3356	0.4696	0.9117

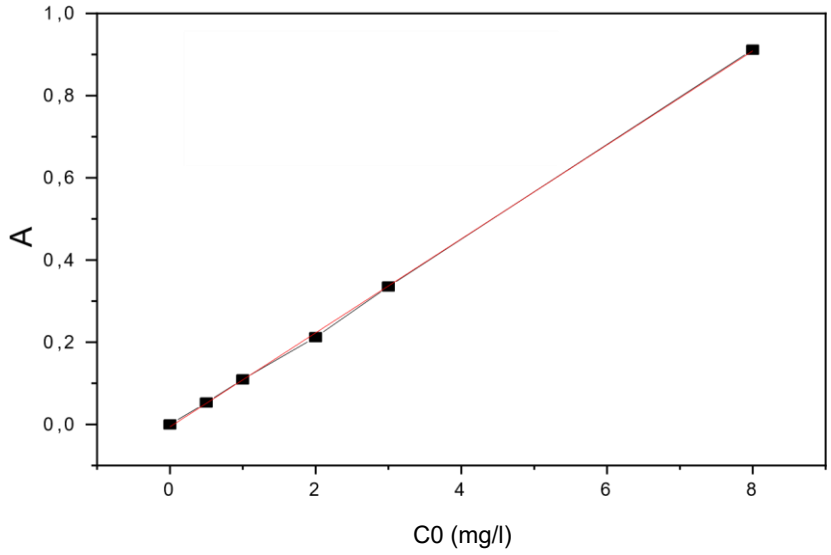


Figure IV.1: The Calibration Curve of Crystal Violet

IV.2. Determination of the pH of MV

The following table presents the pH measurements recorded at different time intervals during the experiment

TableIV.2: pH measurement during the time

Time (min)	1	1.5	2	2.5	3	3.5	4	4.5	5	15	25	35	45
pH	6.72	6.72	6.78	6.77	6.79	6.79	6.78	6.79	6.97	6.78	6.77	6.77	6.76
Time	55	65	75	85	95								
pH	6.76	6.75	6.75	6.75	6.74								

According to the pH values presented in Table IV.2, The pH measurements showed excellent stability throughout the experiment, remaining within the narrow range of 6**.72–6.97.** This negligible variation confirms that the biomass **is chemically stable in** an aqueous medium and does not release significant amounts of acidic or alkaline species. Therefore, the biomass can be considered inert with respect to pH under the investigated conditions, making it a suitable material for adsorption processes without causing undesirable changes in the water chemistry.

IV.3. pH of Zero Charge (pH zpc)

The point of zero charge, pHpzc, is an important parameter that characterizes the surface of an adsorbent material. It indicates the pH value at which the net charge of the adsorbent surface is zero. The graph below illustrates the determination of the pH of zero charge ($pH_{(zpc)}$).

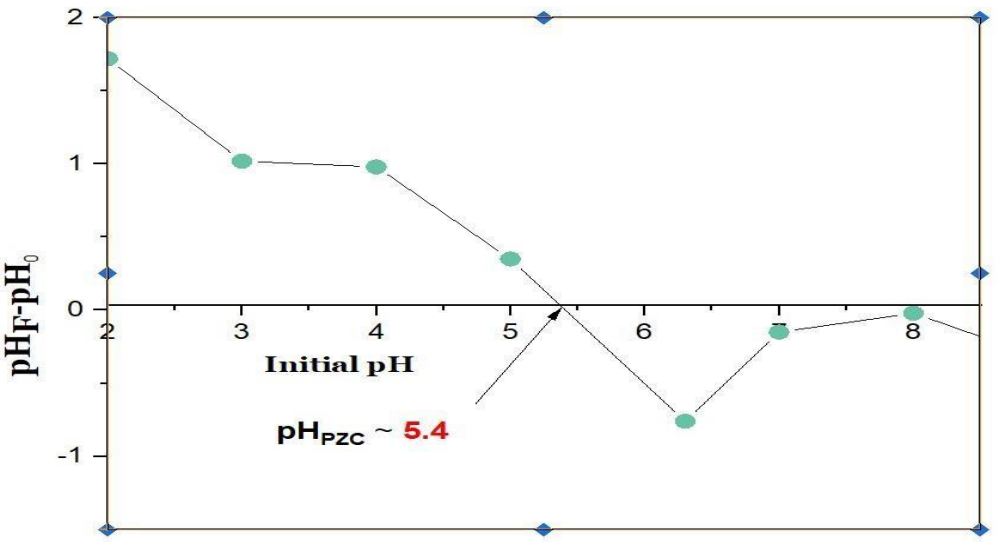


Figure IV.2: Determination of the Zero Point of Charge (PZC)

According to graph, We find the value of pHPZC = 5.4 . At pH values under pHPZC, the adsorbent surface is positively charged and at pH values over pHPZC, the adsorbent is negatively charged.

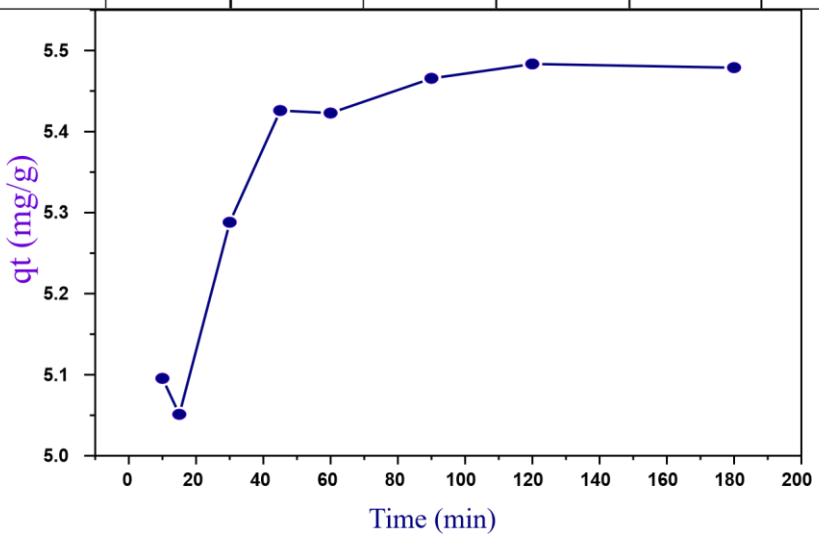
IV.4. Batch optimization studies

IV.4 1. Effect of Contact Time

The following table presents the results of equilibrium time on the adsorption of Crystal Violet by Biomass.

TableIV.3: Results of equilibrium time on the adsorption of Crystal Violet by Biomass.

Temps(min)	**10**	**15**	**30**	**45**	**60**	**90**	**120**	**180**
Absorbance	0.5131	0.5631	0.4030	0.3249	0.3267	0.3024	0.2926	0.2949
C_e(mg/L)	4.5227	4.9744	3.5601	2.8701	2.8860	2.6714	2.5849	2.6051
R%	84.92	83.42	88.13	90.43	90.38	91.08	91.38	90.32
q_t (mg/g)	5.0955	5.0051	5.2880	5.4260	5.4228	5.4657	5.4833	5.4789



FigureIV.3: Effect of contact time on the adsorption capacity at an initial Crystal Violet concentration of 30 mg/L

FigureIV.3 illustrates the effect of contact time on the adsorption capacity of Crystal Violet. The adsorption capacity increased during the first 45 min owing to the availability of a large number of vacant active sites on the adsorbent surface. As the contact time increased, the adsorption rate gradually decreased due to the progressive occupation of these active sites and the reduction in the concentration gradient between the solution and the adsorbent.

At **60 min**, the adsorption capacity reached **5.423 mg/g**, corresponding to a removal efficiency of **90.38%**. Beyond this contact time, only slight variations in both the adsorption capacity and removal efficiency were observed, indicating that the adsorption process had nearly reached equilibrium. Therefore, a contact time of **60 min** was selected as the optimum

operating time for all subsequent adsorption experiments, since it provided high removal efficiency while minimizing the overall treatment time.

IV.4.2 Effect of biosorbent mass

The following table presents the results The results of effect of Biosorbent mass

Table IV.4: The results of effect of Biosorbent mass

C_i (mg/l)	30	30	30	30	30	30	30
The mass (g)	0.1	0.2	0.3	0.5	0.6	0.8	1
Concentration (mg/L)	4.2	2.7	2.2	1.8	2.2	2.3	2.2
Adsorption	0.479	0.3007	0.2527	0.2527	0.2510	0.2577	0.2535
q_e (mg/g)	25.8	13.65	6.95	5.64	4.63	3.46	2.78
R%	86	91	92.66	94	92.66	92.3	92.66

As shown in Figure IV.4, the removal efficiency (R%) increased progressively with increasing adsorbent mass until reaching an optimum value at 0.5g, where a maximum removal efficiency of approximately 94% was achieved. Beyond this optimum mass, a further increase in the adsorbent dosage resulted in a slight decrease in the removal efficiency. This behavior may be attributed to particle aggregation and the overlapping of adsorption sites at higher adsorbent dosages, which reduce the effective surface area available for adsorption.

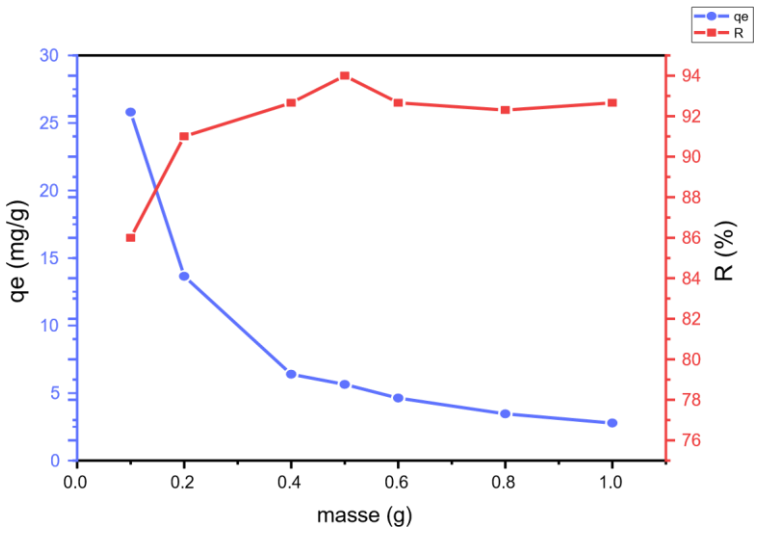


Figure IV.4: Influence of biosorbent mass on crystal violet adsorption

IV.2.2. Effect of the initial concentration of the adsorbate

The effect of the initial Crystal Violet concentration on the adsorption performance was investigated by varying the dye concentration from **10 to 50 mg/L** while keeping all other operating parameters constant. The results are summarized in Table IV.5.

Table IV.5: Effect of the Initial Dye Concentration on the Adsorption Capacity and Removal Efficiency of Crystal Violet

C_0(mg/L)	10	20	30	40	50
Absorbance	0.1263	0.2204	0.2962	0.3581	0.5316
C_e(mg/L)	1.1157	1.9470	2.6166	3.1634	4.6961
R%	88.843	90.26	91.28	92.09	90.61
q_e(mg/g)	1.7769	3.6106	5.4767	**7.3673**	9.0678

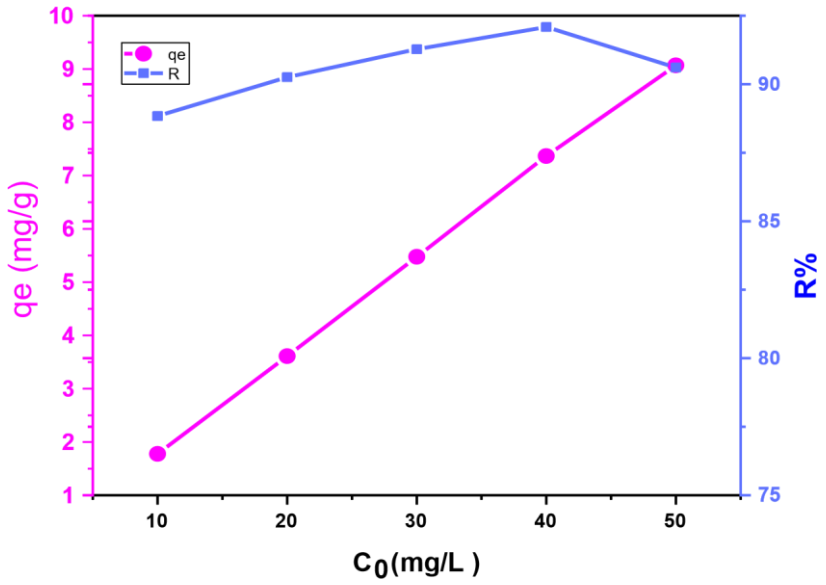


Figure IV.5: Effect of the Initial Dye Concentration on the Adsorption Capacity and Removal Efficiency of Crystal Violet.

As shown in Figure IV.4, We observed tht the initial Crystal Violet concentration increased from **10 to 40 mg/L**, the removal efficiency increased from **88.84%** to **92.09%**, owing to the greater availability of dye molecules for adsorption onto the active sites of the adsorbent. At **50 mg/L**, the removal efficiency slightly decreased to **90.61%**, which may be attributed to the gradual saturation of the available adsorption sites.

In contrast, the adsorption capacity (q_e) increased with increasing initial dye concentration, reaching its highest value at **50 mg/L**. This behavior indicates that higher initial concentrations provide a greater driving force for mass transfer, resulting in increased dye uptake by the adsorbent.

IV.2. 3Effect of pH

The effect of solution pH was studied for adsorption of Crystal violet on MV at Room Temperature, initial concentration (30 mg/L) and 0.5g amount of adsorbent, for an hour the effect of pH on the adsorption of Crystal Violet is presented in Table IV.6.

Table IV.6: The effect of pH on the adsorption of Crystal Violet

pH	4	5	6	7	8	9	10

Absorbance	0.6743	1.0125	0.4241	0.3592	0.3531	0.3279	0.3279
C_e	5.9567	8.9443	3.7465	3.1731	3.1193	2.8966	2.8966
R%	80.14	70.19	87.51	86.54	89.60	90.34	90.34
q_e	4.81	4.21	5.25	5.37	5.38	5.42	5.42

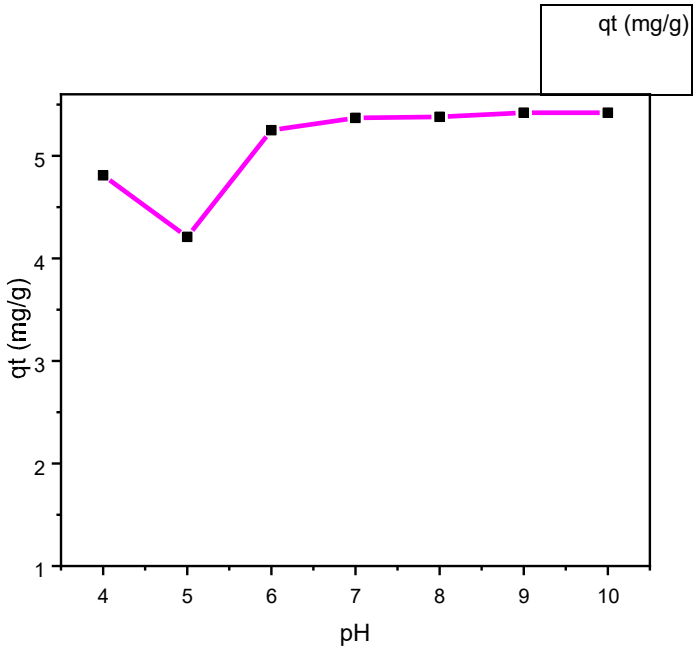


Figure IV.6: The effect of pH on the adsorption of C V

The results show that the removal efficiency was strongly influenced by the solution pH. At acidic pH values (pH 4–5), the adsorption efficiency was relatively low, with removal efficiencies of 80.14% and 70.19%, respectively. This behavior may be attributed to the competition between H^+ ions and Crystal Violet molecules for the active sites on the adsorbent surface. As the pH increased from 6 to 9, the removal efficiency increased significantly, reaching a maximum value of 90.34% at pH 9. The adsorption capacity (q_e) also increased from 4.81 to 5.42 mg/g. This improvement can be explained by the fact that, at pH values above the $pH_{(zpc)}$ =5.4, the adsorbent surface becomes negatively charged because of deprotonation. This promotes electrostatic attraction between the negatively charged surface and the cationic Crystal Violet molecules, thereby enhancing the adsorption process.

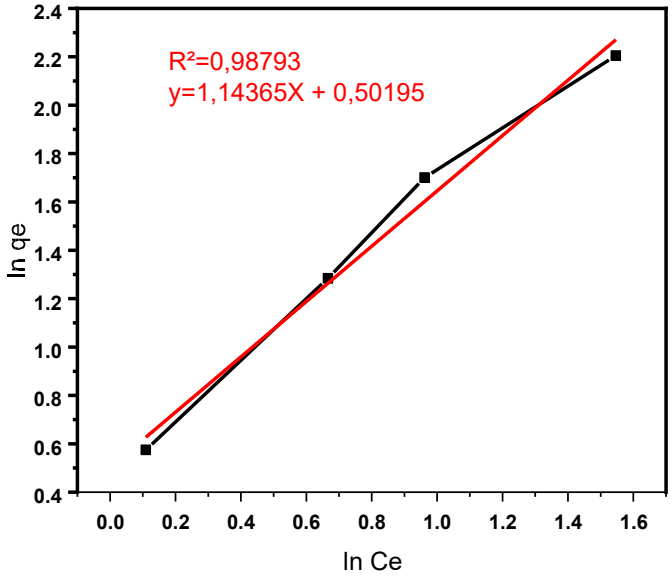
IV.3. Isothermal Adsorption of Crystal Violet

The adsorption isotherm models generally used to design and to understand the mechanism of interaction existing between adsorbate and the adsorbent at equilibrium. In this work, two

isotherm models (Langmuir and Freundlich) were applied to describe the distribution of dye ions between the liquid phase and the solid phase at constant temperature.

Table IV.4: The Freundlich model calculation

C_0(mg/l)	10	20	30	40	50
Absorbance	0.1263	0.2204	0.2962	0.3581	0.5316
C_e(mg/l)	1.1157	1.9470	2.6166	3.1634	4.6961
q_e(mg/g)	1.7769	3.6106	5.4767	7.3673	9.0678
Ln C_e	0.1095	0.6663	0.9619	1.1516	1.5467
Ln qe	0.5749	1.2839	1.7005	1.9970	2.2047

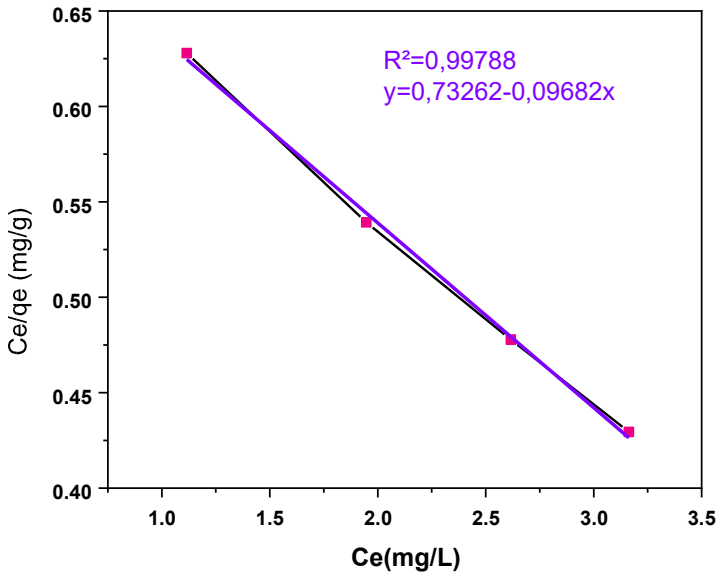


FigureIV.7: Freundlich crystal violet

Linearized isotherm for adsorption

Table IV.5: Langumir model Calculations

C_0(mg/l)	10	20	30	40	50
Absorbance	0.1263	0.2204	0.2962	0.3581	0.5316
C_e(mg/l)	1.1157	1.9470	2.6166	3.1634	4.6961
C_e/q_e (mg/g)	0.6279	0.5392	0.4778	0.4294	0.5189



FigureIV.7: Linearized Langmuir isotherm for the adsorption of crystal violet

Regarding the results of fitting linear forms, we find that the coefficients of determination (R^2) show that the Langmuir model achieves the highest value of $R^2 = 0.9973$, indicating that it better describes the experimental data than the Freundlich model with $R^2 = 0.9897$.

This result suggests that adsorption occurs on a homogeneous surface with active sites of equal energy. Therefore, the Langmuir model is considered the most suitable model for explaining the adsorption behavior in this study.

IV.4. Adsorption kinetics study

In this study, the adsorption kinetics were analyzed using three widely applied kinetic models: The Pseudo-first-order model and the Pseudo-second-order model. These models were employed to fit the experimental data and determine the kinetic behavior of the adsorption process.

IV.4. 1. Pseudo-first-order kinetic model

The pseudo-first-order kinetic model, also known as the Lagergren model, is one of the earliest and most widely used models for describing adsorption kinetics. The linear form of the pseudo-first-order model is:

$$Ln\ (q_e - q_t) = \ln(q_e) - k_1 t$$

Table IV.6: Pseudo-first-order model Calculations

Time (min)	10	15	30	45	60	90	120	180

Absorbance	0.5131	0.5631	0.4030	0.3249	0.3267	0.3024	0.2926	0.2949
C_e(mg/L)	4.523	4.974	3.560	2.870	2.886	2.672	2.585	2.605
R%	84.89	83.42	88.13	90.43	90.38	91.09	91.38	91.31
q_t (mg /g)	5.093	5.005	5.288	5.426	5.423	5.466	5.483 qe	5.479
q_e -q_t	-0.39	0.478	0.195	0.057	0.006	0.017	0	0.004
Ln (q_e -q_t)	-0.942	-0.738	-1.635	-2.865	-2.813	-4.075		-5.521

Slope	-0.02988
K_1	0.02988 min^{-1}
R^2	0.91307
q_e	0.422mg/g

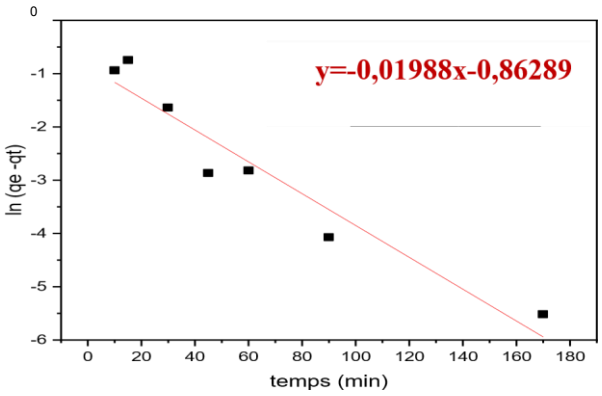


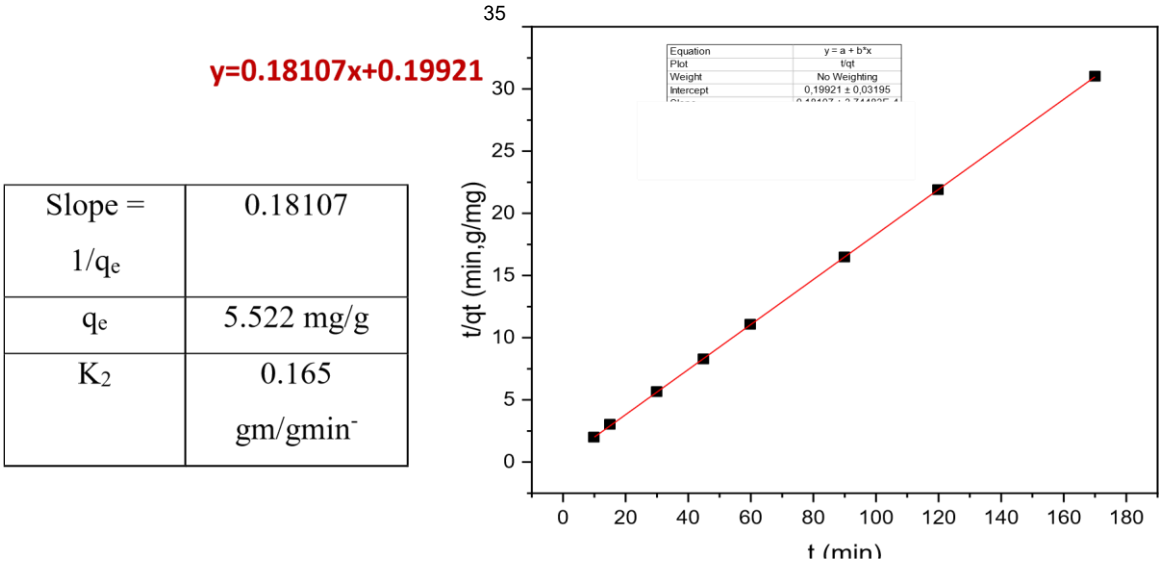
Figure IV.7: The linear form of the pseudo-first-order model

IV.4.2. Pseudo-Second-order kinetic model

The pseudo-second-order kinetic model is widely used to describe adsorption processes in which chemisorption is considered the rate-controlling step. This model assumes that the adsorption rate depends on the square of the number of unoccupied adsorption sites and is related to the adsorption capacity of the adsorbent. The linear form of the pseudo-secod order model is: $\frac{t}{q_t} = \frac{1}{k_2 q_{2e}} + \frac{t}{q_e}$

Table IV.7: Pseudo-second-order model Calculations

Time (min)	10	15	30	45	60	90	120	180
q_t (mg /g)	5.093	5.005	5.288	5.426	5.423	5.466	5.483	5.479
t/ q_t (min. g/mg)	1.964	2.997	5.673	8.293	11.064	16.465	21.886	31.30



Slope = $1/q_e$	0.18107
q_e	5.522 mg/g
K_2	0.165 gm/gmin

Figure IV.8: The linear form of the pseudo-second-order model

The adsorption kinetics of the studied system were analyzed using both the pseudo-firstorder and pseudo-second-order models in order to identify the most appropriate model describing the experimental data.

The results obtained from the pseudo-first-order model showed a relatively low correlation coefficient ($R^2 \approx 0.91–0.92$), and a significant deviation between the calculated equilibrium adsorption capacity ($q_e = 0.422$ mg g^{-1}) and the experimental value ($q_e \approx 5.48$ mg g^{-1}). This discrepancy indicates that the pseudo-first-order model does not adequately represent the adsorption mechanism of the studied system, suggesting that it is not the controlling model for the process.

In contrast, the pseudo-second-order model exhibited an excellent fit to the experimental data, with a correlation coefficient of $R^2 = 0.99997$. Moreover, the calculated equilibrium adsorption capacity ($q_e = 5.522$ mg g^{-1}) was very close to the experimental value (q_e =

5.479 mg g^{-1}), confirming the reliability of this model in describing the adsorption kinetics.

The agreement between experimental and calculated values suggests that the adsorption process is more likely governed by **chemisorption** involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate. This indicates that the adsorption rate is controlled by the availability of active sites on the adsorbent surface rather than simple physical diffusion.

Overall, the pseudo-second-order model provides the most accurate description of the adsorption kinetics of the studied system, highlighting its suitability for representing the mechanism and behavior of the adsorption process.

General Conclusion

General Conclusion

The present study was undertaken to evaluate the feasibility and efficiency of utilizing a natural, low-cost biosorbent, designated as MV biomass, for the removal of Crystal Violet (CV), a cationic dye widely used in textile and industrial applications, from aqueous solutions.

To achieve this objective, a series of batch adsorption experiments was conducted to optimize the main operating parameters. The results showed that the optimum conditions corresponded to an equilibrium time of 60 min, an adsorbent dosage of 0.5 g, and a solution pH of 7, under which a maximum removal efficiency exceeding 94% was obtained.

To better understand the adsorption mechanism, the point of zero charge (pHpzc) of the biosorbent was determined and found to be 5.4. This result indicated that the biomass surface becomes negatively charged at pH values above 5.4, thereby promoting the electrostatic attraction of the positively charged CV molecules. Consequently, the increase in adsorption efficiency observed at alkaline pH values is in good agreement with the surface charge characteristics of the biosorbent.

Furthermore, the equilibrium adsorption data were best described by the Langmuir isotherm model (R^2 = 0.9973), suggesting monolayer adsorption on a homogeneous surface with energetically equivalent active sites. Likewise, kinetic analysis revealed that the pseudosecondorder model (R^2 = 0.99997) provided an excellent fit to the experimental data, with the calculated adsorption capacity (qe = 5.522 mg/g) being very close to the experimental value (qe = 5.479 mg/g). These findings indicate that chemisorption, involving strong electrostatic and chemical interactions, is the predominant mechanism controlling the adsorption process.

In addition, the stable pH values recorded throughout the experiments confirmed the good chemical stability of the biomass in aqueous media, further supporting its potential application in wastewater treatment. Taken together, these findings demonstrate that MV biomass represents a promising alternative to conventional adsorbents such as activated carbon because of its high adsorption efficiency, low cost, wide availability, and environmental sustainability.

In conclusion, this study provides a solid scientific basis for the valorization of MV biomass as a sustainable biosorbent for the removal of Crystal Violet from aqueous solutions. The

General Conclusion

excellent adsorption performance, favorable kinetics, and eco-friendly nature of this material highlight its potential for future large-scale wastewater treatment applications.

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