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DEDICATION

I dedicate this work:

*To my **dear father**, my first and last hero, whose strength and sacrifices have always inspired me.*

*To my **dear mother**, a source of endless tenderness, love, and encouragement.*

*To my beloved brother, **Montasser Bellah**, and my dear sisters, **Hadjer** and **Khawla**, as well as their husbands, **Billel** and **Sabri**, for their constant support and affection.*

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With love and gratitude.

Résumé

Ce travail porte sur l'étude de l'élimination du violet de cristal (CV), un colorant cationique synthétique largement utilisé dans l'industrie textile et la microbiologie, par adsorption sur des biomatériaux dérivés d'écorces de grenade. Trois adsorbants ont été synthétisés et comparés : le biocharbon brut (BC), le biocharbon modifié par du MnO_2 (BC/MnO_2), et le biocharbon modifié par du MnO_2 et du zinc (BC/MnO_2/Zn), ce dernier préparé par une approche inspirée de la chimie verte. L'influence des principaux paramètres opératoires a été étudiée, notamment la masse d'adsorbant, le pH, la concentration initiale en colorant et la température. Les résultats ont montré que la modification de surface améliore considérablement les performances d'adsorption. Le composite BC/MnO_2/Zn s'est révélé le plus efficace, atteignant un taux d'élimination supérieur à 90 % dès une dose de 0,05 g, grâce à l'effet synergique du MnO_2 et du zinc qui multiplient les sites actifs et renforcent les interactions électrostatiques avec le colorant cationique. L'adsorption est favorisée en milieu légèrement basique (pH 8–9) et augmente avec la température, suggérant un processus endothermique. La modélisation des isothermes a montré que le modèle de Langmuir décrit le mieux les données expérimentales, indiquant une adsorption en monocouche sur des sites homogènes. L'analyse cinétique a révélé que le modèle pseudo-second ordre est le plus adapté, confirmant la prédominance d'un mécanisme de chimisorption impliquant des liaisons chimiques entre les groupements fonctionnels de surface et les molécules de colorant.

Mots clés : Adsorption ; Violet de cristal ; Biocharbon ; MnO_2 ; Zinc ; Écorces de grenade.

Abstract

This work focuses on the removal of crystal violet (CV), a synthetic cationic dye widely used in the textile industry and microbiology, by adsorption onto biomaterials derived from pomegranate peels. Three adsorbents were synthesized and compared: pristine biochar (BC), MnO_2-modified biochar (BC/MnO_2), and MnO_2- and zinc-modified biochar (BC/MnO_2/Zn), the latter prepared using a green chemistry-inspired approach. The influence of key operating parameters was investigated, including adsorbent mass, pH, initial dye concentration, and temperature. The results showed that surface modification significantly enhances adsorption performance. The BC/MnO_2/Zn composite proved to be the most efficient, achieving removal rates exceeding 90% at a dose as low as 0.05 g, owing to the synergistic effect of MnO_2 and zinc, which increase active sites and strengthen electrostatic interactions with the cationic dye. Adsorption was favored under slightly basic conditions (pH 8–9) and increased with temperature, suggesting an endothermic process. Isotherm modeling showed that the Langmuir model best described the experimental data, indicating monolayer adsorption onto homogeneous sites. Kinetic analysis revealed that the pseudo-second-order model provided the best fit, confirming a predominant chemisorption mechanism involving chemical bonding between surface functional groups and dye molecules.

Keywords: Adsorption; Crystal violet; Biochar; MnO_2; Zinc; Pomegranate peels.

الملخص

يتمحور هذا العمل حول دراسة إزالة صبغة البنفسجي البلوري (CV)، وهي صبغة كاتيونية اصطناعية تُستخدم على نطاق واسع في صناعة النسيج والميكروبيولوجيا، باستخدام عملية الامدصاص على مواد حيوية مشتقة من قشور الرمان. تم تحضير ثلاثة مواد ماصة ومقارنتها: الفحم الحيوي الخام (BC)، والفحم الحيوي المعدّل بـ $_2$MnO و($BC/_2MnO$)، والفحم الحيوي المعدّل بـ $_2$MnO والزنك ($BC/_2MnO/Zn$)، وهذا الأخير تم تحضيره باستخدام مقاربة الكيمياء الخضراء. دُرِس تأثير المعاملات التشغيلية الرئيسية كجرعة المادة الماصة ودرجة الحموضة والتركيز الابتدائي للصبغة ودرجة الحرارة. أظهرت النتائج أن تعديل السطح يحسّن أداء الامدصاص بشكل كبير، إذ حقق المركّب $BC/_2MnO/Zn$ أعلى كفاءة، بلغت نسبة إزالة تتجاوز 90% بجرعة تصل إلى 0.05 غ فقط، بفضل التأثير التكاملي بين $_2$MnO والزنك. يتحسّن الامدصاص في الوسط القاعدي الخفيف (pH 8–9) ويزداد مع ارتفاع درجة الحرارة، مما يشير إلى طبيعة ماصة للحرارة. بيّن نمذجة الأيزوثرمات أن نموذج لانغمويير يصف البيانات بشكل أفضل، مما يدل على امدصاص أحادي الطبقة. وكشف التحليل الحركي أن نموذج الرتبة الثانية الزائفة هو الأنسب، مما يؤكد تغلب آلية الكيميسوربشن التي تتضمّن تكوين روابط كيميائية بين مجموعات سطح المادة الماصة وجزيئات الصبغة.

الكلمات المفتاحية: الامدصاص؛ البنفسجي البلوري؛ الفحم الحيوي؛$_2$ MnO؛ الزنك؛ قشور الرمان.

List of abbreviations

BC : Biochar

BC/MnO_2 : Manganese oxide-doped Biochar

BC/MnO_2/Zn : Manganese oxide and Zinc-doped Biochar

BOD_5: Biochemical Oxygen Demand (5 days)

CAS : Chemical Abstracts Service

CV : Crystal Violet

DIP : Diffusion Intraparticulaire / Intraparticle Diffusion

FOA : First-Order Approximation (pseudo-first-order kinetic model)

IPD : Intraparticle Diffusion model

KL : Langmuir adsorption constant

K_f: Freundlich adsorption constant

K_1: Pseudo-first-order rate constant (min^{-1})

K_2: Pseudo-second-order rate constant ($g \cdot mg^{-1} \cdot min^{-1}$)

K_{id}: Intraparticle diffusion rate constant ($mg \cdot g^{-1} \cdot min^{-1}$)

MnO_2 : Manganese dioxide

NPS: Nanoparticles

PAH: Polycyclic Aromatic Hydrocarbons

PCB: Polychlorinated Biphenyls

PSO: Pseudo-Second-Order kinetic model

pH_{PZC}: pH at Point of Zero Charge

Q_e: Amount adsorbed at equilibrium ($mg \cdot g^{-1}$)

Q_{max}: Maximum adsorption capacity ($mg \cdot g^{-1}$)

Q_t: Amount adsorbed at time t ($mg \cdot g^{-1}$)

R^2: Coefficient of determination

R_L: Dimensionless separation factor (Langmuir)

Rpm: Revolutions per minute

UV-Vis : Ultraviolet-Visible spectrophotometry

WHO: World Health Organization

XRD: X-Ray Diffraction

ZCP: Zero-Charge Point

λ_{max}: Maximum absorption wavelength (nm)

%R : Removal efficiency (%)

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General Introduction

General introduction

Water is a vital resource for life and for many human activities. Over the past few decades, rapid industrial growth and urban population expansion have significantly increased the demand for water, while also contributing to its pollution. Among the various sources of contamination, industrial wastewater is considered one of the most significant due to the diversity and complexity of the pollutants it contains **[1].**

The textile industry, in particular, consumes large amounts of water during various stages of production, such as dyeing, rinsing, and finishing. These processes generate significant volumes of wastewater containing dyes, salts, and other chemicals. Discharging this effluent without proper treatment can have significant environmental impacts, including changes in the color of natural waters, reduced light penetration, and disruption of aquatic ecosystems **[2].**

To address this issue, several treatment methods have been developed over time. Physicochemical processes such as coagulation-flocculation and adsorption are widely used to remove dyes and suspended solids. Biological treatments also help reduce the organic load, but they are sometimes insufficient when used alone. In addition, advanced oxidation processes and membrane technologies have been introduced to improve treatment efficiency, particularly for complex and refractory pollutants. In many cases, combining several methods results in better overall performance **[3].**

Among these techniques, adsorption has attracted particular interest due to its simplicity, flexibility, and effectiveness in removing dyes from wastewater. The effectiveness of this process depends on several factors, including the nature of the adsorbent, the properties of the pollutant, and the operating conditions. Consequently, much research has focused on developing new adsorbent materials and optimizing adsorption conditions to improve treatment performance **[4].**

In this context, this thesis aims to study the removal of the dye Crystal Violet through an adsorption process using pomegranate peel biochar, biochar-doped MnO_2 nanoparticles, biochar-doped MnO_2 doped Zn- nanoparticles at various concentrations, and as adsorbents. These materials, prepared using an approach inspired by green chemistry, are intended to provide high-performance, stable, and environmentally friendly adsorbents for the

treatment of colored water. A comparative study of these different adsorbents is conducted to evaluate the impact of zinc doping and the addition of biochar on adsorption capacity and dye removal efficiency.

To achieve this objective, this thesis is organized into three chapters:

- The first chapter presents a literature review on water pollution, industrial dyes, their environmental impacts, and various treatment techniques, with a particular focus on the adsorption process.

- The second chapter is devoted to describing the experimental protocol adopted for evaluating the removal of Crystal Violet.

- The third chapter presents the experimental results obtained, discusses the influence of operating parameters, and compares the effectiveness of the various synthesized adsorbents.

Chapter I : Literature review

I.1. Introduction

Water pollution caused by dyes is now a major environmental problem, particularly due to discharges from the textile, pharmaceutical, and food industries. These compounds are often stable, resistant to biodegradation, and can persist for long periods in aquatic environments, causing negative impacts on ecosystems and water quality. In response to this issue, several treatment techniques have been developed, among which adsorption plays a significant role. This method is widely studied due to its ease of implementation, its effectiveness, and the possibility of using various adsorbent materials, notably activated carbon and biomass-based materials. In this theoretical section, we will present the basics of water pollution by dyes, as well as the fundamental principles of the adsorption process and its applications in the removal of these pollutants.

I.2.Generalities of Water pollution

I.2.1.Sources and mechanisms of water contamination

Water pollution is one of the most pressing environmental concerns in our lives. It results from the contamination of water bodies-rivers, lakes, oceans, etc…. by harmful substances originating from various natural or anthropogenic sources. This contamination alters the natural characteristics of water, including its physical, chemical, and biological properties, and consequently affects aquatic ecosystems as well as human uses **[5,6]**

I.2.1.1. Industrial sources of water pollution

Industrial activities represent one of the major sources of water pollution. Any Industrial process requiring the use of water inevitably generates effluents that must undergo appropriate treatment before discharge. Studies have shown that the interaction between industrial processes and water—whether through cooling systems, washing operations, or direct contact with raw materials—can lead to contamination by various pollutants**[5].**Among the different industrial sectors, those involved in chemical manufacturing, metallurgy, textiles, and food processing are particularly known for their environmental impact. These industries often consume large volumes of water and generate wastewater containing high concentrations of dyes, organic compounds, suspended solids, and toxic chemicals. When such effluents are released into the environment without adequate treatment, they can severely damage aquatic ecosystems, alter water quality, and pose risks to human health**[7].**

I.2.1.2. Municipal sources of water pollution

Non-industrial municipal sources of water pollution generally include the following **[8]**:

- **Households**, discharge domestic wastewater containing detergents, organic matter, suspended solids, oils and microorganisms.
- **Commercial establishments** (restaurants, hotels, shops), generate wastewater rich in fats, cleaning chemicals and organic residues.
- **Institutions** such as schools, hospitals and prisons, produce effluents that may contain pharmaceuticals, disinfectants, laboratory reagents and organic load.
- **Municipal and governmental services**, including public facilities, administrative buildings and urban infrastructure, which contribute wastewater from cleaning, sanitation and maintenance activities**[9].**

I.2.1.3. Agricultural sources of water pollution

Agricultural activities are major sources of water pollution. Water used in irrigation often contains high concentrations of nitrates and phosphates, primarily from fertilizers. These nutrients promote eutrophication, leading to excessive growth of algae and aquatic plants in rivers and lakes. During the decomposition of this biomass, dissolved oxygen is consumed**,** reducing the oxygen available for aquatic life and impairing the river's natural self-purification processes. Additionally, pesticides and herbicides used in agriculture can contaminate surface and groundwater, posing risks to both ecosystems and human health **[10].**

I.2.1.4. Natural sources of water pollution

Natural processes can also contribute to the pollution of water resources. Geological and climatic phenomena such as volcanic eruptions, weathering of rocks and soils, and atmospheric deposition can introduce various substances into aquatic environments. During volcanic eruptions, ash and gases including sulfur compounds are released into the atmosphere and can be deposited in surface waters, affecting water chemistry by increasing acidity and introducing soluble salts and trace elements that may alter water quality. Additionally, the natural dissolution of minerals and weathering of rocks can mobilize toxic elements such as mercury, arsenic and other heavy metals into groundwater and surface waters. These geogenic sources, although typically less intense than anthropogenic pollution, represent baseline inputs of pollutants that influence the chemical composition of natural waters **[11].**

Rainwater and surface runoff can be significant contributors to water pollution, especially during heavy rainfall or storm events. As rain falls, it interacts with the atmosphere and can carry airborne impurities, including dust and industrial emissions. Once it reaches the ground, rainwater becomes runoff that flows over urban and rural surfaces, mobilizing contaminants such as hydrocarbons from vehicle emissions, heavy metals, tire residues, and other pollutants deposited on roofs, roads and soil. In urban environments, rainwater frequently mixes with domestic wastewater in combined sewer systems, increasing the overall pollutant load discharged into watercourses. Runoff pollution is recognized as an important environmental issue, as it transports a wide range of contaminants from land surfaces into rivers, lakes and aquifers, thereby degrading water quality and adversely affecting aquatic ecosystems and human health **[12].**

I.2.2. Classification of water pollution

According to the World Health Organization (WHO, 2020), water pollution can be grouped into three main categories: physical, chemical and microbiological pollution, each of which affects water quality through different mechanisms**[13].**

I.2.2.1 Physical pollution

Physical pollution refers to the presence of solid materials, changes in temperature, and other physical alterations that affect the natural characteristics of water. Solid pollution is generated by suspended and deposited particles transported by runoff, industrial discharges, and open waste dumps, which can obstruct water flow and degrade aquatic habitats. Thermal pollution arises when water used for industrial cooling-such as in power plants and refineries—is discharged at elevated temperatures, lowering the dissolved oxygen content and accelerating organic matter decomposition, leading to increased microbial activity and stress on aquatic organisms. Radioactive pollution is associated with the release of radio nuclides from nuclear facilities and waste processing plants; these radio nuclides can remain in the environment for long periods, posing both ecological and human health risks. Physical alterations of water thus have significant ecological impacts, disrupting natural processes and reducing water quality **[14].**

I.2.2.2 Chemical pollution

Chemical pollution is caused by the introduction of organic and inorganic substances into water bodies, resulting predominantly from human activities such as agriculture, industry and urbanization. Inorganic pollutants include heavy metals such as lead (Pb), cadmium (Cd), and zinc (Zn), which are persistent, bio accumulative and toxic to aquatic life. Organic pollutants encompass a wide range of compounds such as solvents, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pharmaceuticals and pesticides, all of which can alter water chemistry and pose significant health risks even at trace concentrations. Salinity increases due to dissolved salts from agricultural runoff and industrial effluents further compromise water usability for drinking and irrigation. The complexity of chemical mixtures in polluted waters makes this class of pollution particularly challenging to monitor and remediate**[15].**

I.2.2.3. Microbiological pollution

Microbiological pollution refers to the contamination of water by pathogenic microorganisms originating mainly from fecal matter in untreated or inadequately treated wastewater. These pathogens are classified into four major groups in increasing order of size: viruses (e.g., enteric viruses causing gastroenteritis and hepatitis), bacteria (such as *Escherichia coli*, *Salmonella* spp.), protozoa (e.g., *Giardia lamblia* and *Cryptosporidium parvum*) and helminths (parasitic worms like *Ascarislumbricoides*). The presence of these organisms not only indicates poor water quality but also represents a direct threat to public health, often resulting in waterborne diseases in populations with inadequate sanitation. Effective wastewater treatment and regular microbial monitoring are therefore essential to minimize the risks associated with microbiological contamination **[16]**.

I.2.3.The impact of industrial releases

Industrial activities release wastewater into aquatic environments, which represents a major environmental and public health concern. These effluents often contain complex mixtures of chemical, physical, and sometimes microbiological pollutants, whose composition varies depending on the type of industry and the raw materials used.To protect ecosystems and human health, regulations impose strict limits on pollutant concentrations in industrial discharges. Effluents are therefore generally subjected to treatment processes—physical, chemical, and biological-to reduce harmful substances before they are released.

Despite advances in treatment technologies, the variable and complex nature of industrial wastewater makes complete purification difficult. Even when effluents comply with regulatory thresholds, residual pollutants may still be present, potentially impacting water quality, aquatic organisms, and the overall health of ecosystems. Monitoring and management of industrial discharges remain essential to minimize long-term ecological and health risks **[17].**

I.2.4.Discharge standards

Water « fit for human consumption » must meet quality criteria divided between quality limits and quality references. A given criterion is fulfilled when the standard is met for a given parameter. A standard is a benchmark established in accordance with a regulation or a minimum, average or higher benchmark. It allows a situation to be compared in relation to a threshold value and to define acceptable conditions compared to those that would not be**[14]**.

I.2.4.1.International standards

The international standards according to the world health organization for wastewater arefor example: pH (6.5-8.5) ,DBO_5(≤ 30 mg/L) , NO_2 / NO_3 (≤ 1 mg/L) …. **[19].**

I.2.4.2.Algerian rejection standards:

According to Algerian standards, the maximum limit values for effluent discharge are for example: Conductivity(≤ 2800 µS/cm à 20°C), Calcium(≤ 200 mg/l en $CaC0_3$), Turbidity(≤ 5 NTU) … **[20].**

1.3. Generalities of Dyes

Dyes are widely used chemical compounds that impart color to a wide variety of materials, particularly in the textile, food, cosmetic, and pharmaceutical industries. Their optical properties depend on specific structural groups such as chromophores and auxochromes.

I.3.1. History of dyes

The synthetic dye industry began in 1856 when English chemist William Henry Perkin, while attempting to synthesize artificial quinine from coal tar derivatives, accidentally produced the first commercially successful synthetic dye, known as *mauve* or *mauveine*. Perkin patented his discovery and established a production line, which was soon followed by other manufacturers, marking the birth of the synthetic dye industry **[21].**

The development of organic chemistry, including enhanced understanding of aromatic structures such as benzene, accelerated the creation of new synthetic dyes, rapidly expanding the range of available days. As a result, by the beginning of the 20th century, synthetic dyes had almost completely replaced natural dyes in industrial applications due to their broader color range, consistency, and lower cost **[21].**

I.3.2. Definition of a dye

A dye is a colored substance that interacts with the medium into which it is introduced, imparting color through dissolution and/or dispersion. This coloring ability results from a specific affinity between the dye and the substrate, particularly textile fibers. **[22].**The intensity of coloration depends on the chemical structure of the substance **[23].**Coloring materials are characterized by their ability to absorb light in the visible spectrum (380–750 nm). The perception of color results from the selective absorption of certain wavelengths of white light, while the remaining wavelengths are reflected or transmitted.

[24]. The colored molecule is referred to as the chromogen**[22].**

Chromophores are systems, generally containing alternating double bonds (π-bond systems), lone-pair electrons (n-electrons), or transition-metal complexes. These structures are responsible for light absorption.Other groups attached to the chromogen, called auxochromes, modify and often intensify the color produced by the chromophore. Auxochromes also enhance the dye's affinity for the substrate. The greater the electron-donating ability of an auxochrome group, the more intense the resulting color. The principal chromophore and auxochrome groups are summarized in Table 01**[21].**

Table I.1: Classification of main chromophore and auxochrome groups according to increasing intensity **[24]**

Chromophore groups	Auxochrome groups
N=N	NH: azo group
N=O : nitroso group	$NHCH_3$: Methylamino
C=O : ketone or carbonyl group	$N(CH_3)_2$: Demethylamino
C=C : vinyl group	OH: hydroxyl
C=S :thio carbonyl group	OR: alkoxyl
C–S–C : sulfide	Electron donor groups

In general, increasing the number of aromatic rings expands the conjugated system, lowers the energy gap of π-electrons, and shifts light absorption toward longer wavelengths (bathos chromic shift). Similarly, electron-donating auxochromes (such as amino, hydroxyl, and alkoxy groups) extend conjugation and produce darker colors**[26].**The relationship between absorbed wavelength and observed color is presented in Table I.2 **[27].**

Table I.2: Relationship between absorbed frequency and transmitted color.**[28]**

λ absorbed wavelength (nm)	Observed color (transmitted)
400 (purple)	Yellow - greenish
425 (midnight blue)	Yellow
450(blue)	Orange
490 (blue-green)	Red
510 (green)	Purple
530 (yellow-green)	Violet
550 (yellow)	Midnight blue
590 (orange)	Blue
640 (red)	Blue-green
730 (purplish-red)	Green

Coloring materials are divided into two main categories:

- **Dyes:** Coloring substances that are soluble in the application medium and exhibit affinity for the substrate.
- **Pigments:** Coloring substances that are insoluble in the application medium and require a binder to adhere to the substrate.

Unlike dyes, pigments remain suspended in a binder (such as oil or resin), which allows the colored material to adhere to the surface.

[22]

I.3.3. Synthetic dyes

The synthetic dye industry developed rapidly after Perkin's discovery of mauveine. This breakthrough encouraged researchers to chemically modify aniline derivatives to produce new dyes. Today, synthetic dyes dominate the global market because their properties can be precisely tailored to specific applications. They are mainly synthesized from petroleum-derived compounds, particularly benzene and its derivatives such as toluene, naphthalene, xylene, and anthracene. **[29].** Synthetic dyes were designed to have a longer lifespan than natural dyes and produce more intense colors. They are widely used in the textile industry due to their relatively simple synthesis, rapid production, and broad range of colors compared to natural dyes.They are also employed in the food industry to enhance the color of products such as ice cream, yogurt, and beverages, as well as in cosmetics to improve the color of makeup products such as lipstick, eye shadow, and foundation**[30].** In addition, they are used in smaller quantities and are therefore less expensive than natural dyes.

Depending on the application, synthetic dyes must meet several requirements to ensure the longevity of the colored products: abrasion resistance, photo stability, resistance to chemical oxidation (particularly detergents), and resistance to microbial attack**[24].**

I.3.4.Nomenclature of synthetic dyes

The names assigned to commercial dyes are generally less precise than those given to pure chemical compounds. This is because commercial dyes are often mixtures rather than chemically pure substances. Additionally, manufacturers may not disclose the exact chemical composition for proprietary reasons**[25].**

I.3.5. Classification of synthetic dyes

I.3.5.1.Chemical classification

- **azoic dyes**

Azo dyes are characterized by the presence of an azo group (–N=N–) in their molecular structure, which links two alkyl or aryl groups that may be identical or different. Depending on the number of azo groups contained in the molecule, these dyes are classified as monoazo, diazo, triazo, or polyazo compounds **[31].** They currently represent the most widely used class of synthetic dyes due to their broad range of applications, especially in textile and related industries, and account for a significant proportion of all dyes produced worldwide **[31].**

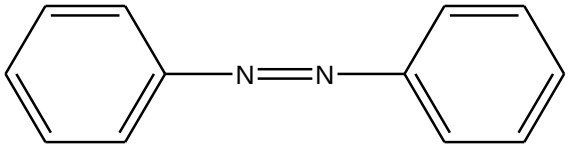


Figure I.1: representation of the structure of an insoluble azo dye **[32]**

- **Anthraquinone dyes**

Anthraquinone dyes represent the second most important class of synthetic dyes after azo dyes. Their molecular structure is derived from anthracene and contains a quinine chromophoric system **[33].**

The chromophoric structure consists of a quinone ring bearing two carbonyl groups (>C=O), which constitute the chromogen. Various substituents, such as hydroxyl or amino groups, may be attached to this aromatic system, modifying the dye's optical and chemical properties.

The fundamental structure of this dye family is anthraquinone, which serves as the core skeleton of the chromophoric system **[34].**Anthraquinone dyes are widely used in the textile industry, particularly for dyeing polyester, acetate, and cellulose triacetate fibers. They are known for their excellent resistance to light, heat, and chemical agents, which makes them especially suitable for fabrics intended for high-temperature applications**[20].**

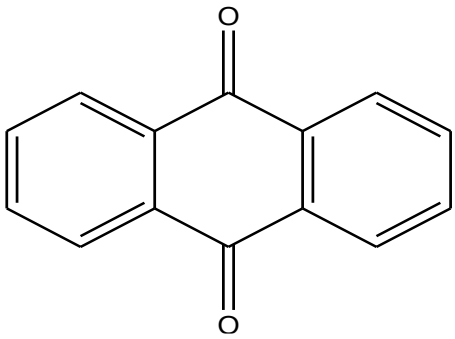


Figure I. 2: Molecular structure of an anthraquinone dye **[25].**

❖ **Phthalocyanines**

Phthalocyanines are macrocyclic compounds characterized by a highly conjugated aromatic structure containing a central metal ion. The macrocycle consists of four isoindole units linked by nitrogen atoms, forming a large planar ring system capable of coordinating a metal atom at its center.

These compounds are generally synthesized through the cyclotetramerization of phthalonitrile (or dicyanobenzene) in the presence of a metal salt, such as copper, nickel, cobalt, platinum, or chromium halides. Among the different metal phthalocyanines, copper phthalocyanine is one of the most widely used due to its excellent thermal and chemicalstability, as well as its intense blue color **[31].**

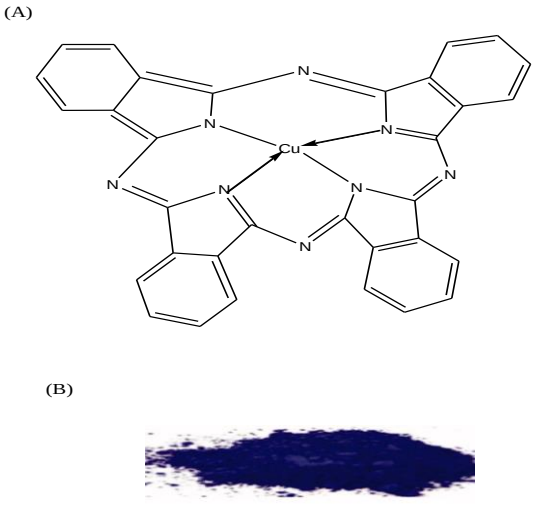


Figure I.3: structure of phthalocyanine: (a) Molecular structure of copper(II) phthalocyanine; (b) Photograph of copper(II) phthalocyanine pigment.**[36]**

❖ **Xanthene dyes**

These are compounds that are derivatives of fluorescein. They have intense fluorescence. Although rarely used as dyes, their usefulness as markers in maritime accidents or as flow tracers for underground rivers is nevertheless well established. They are also used as food, cosmetic, textile, and printing dyes**[37].**

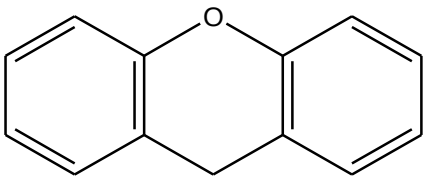


Figure I.4 : Molecular structure of a xanthene dye**[25]**

- **Nitrated and nitrosated dyes**

These compounds form a relatively small and older class of dyes. They are still used today because of their moderate cost, which is related to the simplicity of their molecular structure. This structure is characterized by the presence of a nitro group ($–NO_2$) positioned ortho to an electron-donating group, such as a hydroxyl (–OH) or amino ($–NH_2$) group, on an aromatic ring**[25].**

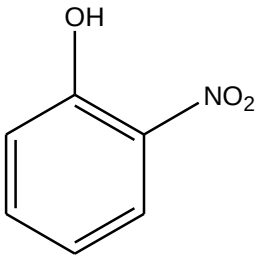


Figure I.5: Molecular structure of a nitrated and nitrosated dye. **[25]**

- **Indigo dyes**

Indigo dyes derive from indigo, one of the oldest known natural dyes. Numerous derivatives have been synthesized by introducing substituents or modifying the molecular structure**[35].**

Indigo dyes exhibit excellent resistance to washing, although their light fastness is moderate. They are widely used in the textile industry, particularly in denim production. Some derivatives are also used in pharmaceuticals and diagnostic applications **[30].**

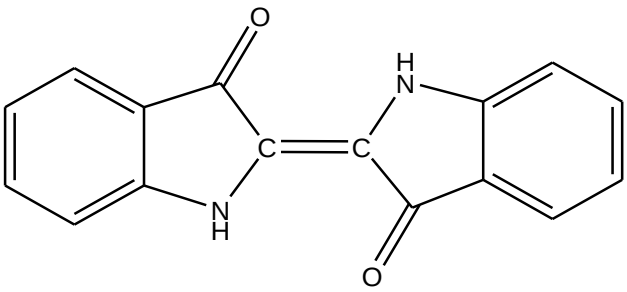


Figure I.6 : Molecular structure of an indigoid dye**[25]**

I.3.5.2.Tinctorial classification

The tinctorial classification is a classification of dyes based on their affinity for different textile fibers. This classification is used to choose the appropriate dyes for dyeing different types of fabrics**[38].**

- **Vat dyes**

Vat dyes are insoluble and must be processed into leuco derivates by alkaline reduction. The dye ends with the in situ reoxidation of the colorant to its initial insoluble form. Renowned for their good resistance to agents of degradation, vat dyes are still used, like indigo for dyeing denim items or denim **[35].**

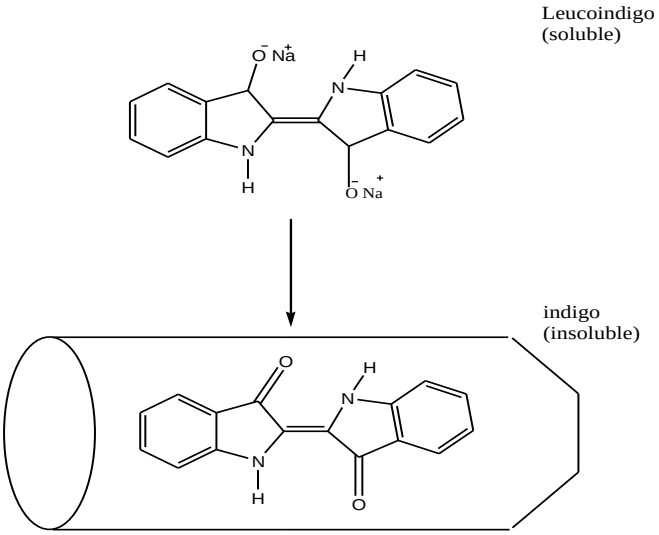


Figure I. 7: Representation of the Structure of a vat dye **[40]**

❖ **Disperse dyes**

These are synthetic dyes for hydrophobic substrates. They are defined as being insoluble in water **[41].**

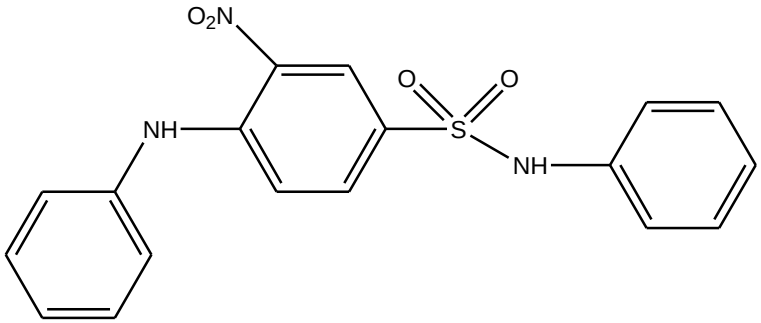


Figure I.8: Representation of the Chemical Structure of a Nitro-Aromatic Sulfonamide Dye Derivative **[37]**

❖ **Reactive dyes**

These dyes contain chromophoric groups mainly derived from the azo, anthraquinonic and phthalocyanine families. Their name is related to the presence of a reactive chemical function, of the triazine or vinylsulfone type ensuring the formation of a strong covalent bond with the fibers. They are soluble in water and increasingly enter into the dyeing of cotton and possibly that of wool and polyamides **[30].**

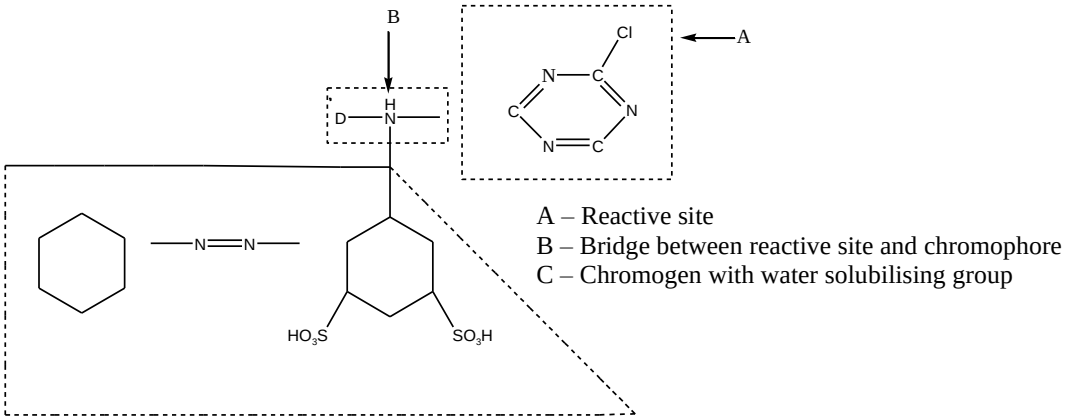


Figure I.9: Representation of the Chemical Structure of a Reactive Dye Showing the Reactive Site (A), the Bridge (B), and the Chromophore with Water-Solubilizing Groups (C**)** **[43]**

❖ **Basic or cationic dyes**

These are complex amine salts colored; the anion is most often Cl-, HSO_4-, NO_3^-. These basic dyes are very easily characterized because they are precipitated by the general amine reagents: picric acid, tannin, various hetero-polyacids **[40]**

Cationic dyes have different chemical structures with substituted aromatic groups. They are azo, methane-based, based on anthraquinone, phthalocyanine... etc**[38].**These dyes have a very good solubility.

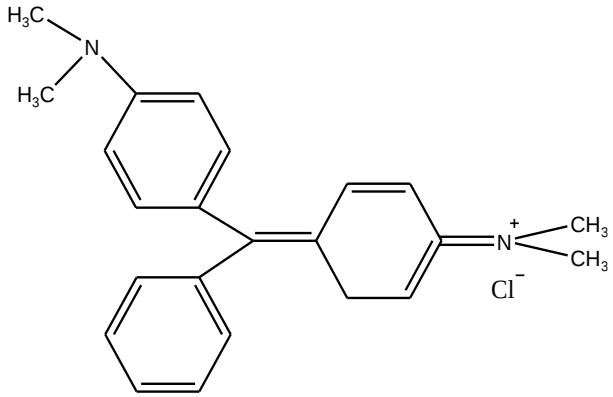


Figure I.10 : Representationof the Structure of a basic dye (Colorant Basic green 4) **[45]**

❖ **Acid or anionic dyes**

These are alkaline salts of colored sulfonic or carboxylic acids in which the cation (Na^+ most often) plays practically no role **[44].**

Acid dyes belong to the two largest chemical classes: azo and anthraquinonic **[46].** They have good solubility in water.

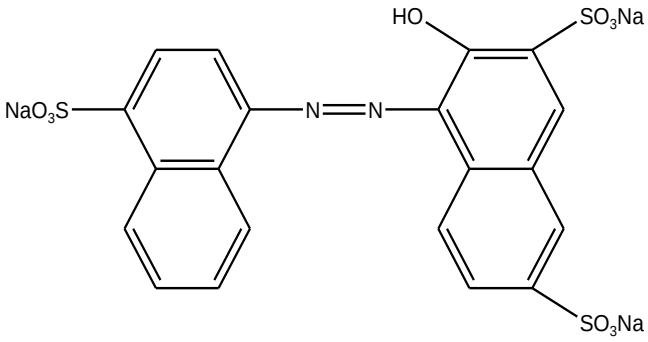


Figure I.11: Representation of the Structure of an anionic dye (Colorant C.I. Acidred 27)**[45]**

❖ **Direct dyes**

Direct dyes are water-soluble anionic dyes. They are essentially azo dyes or also phthalocyanines**[46].**

These dyes are classified according to many parameters such as: chromophore, strength properties or application characteristics**[37].**

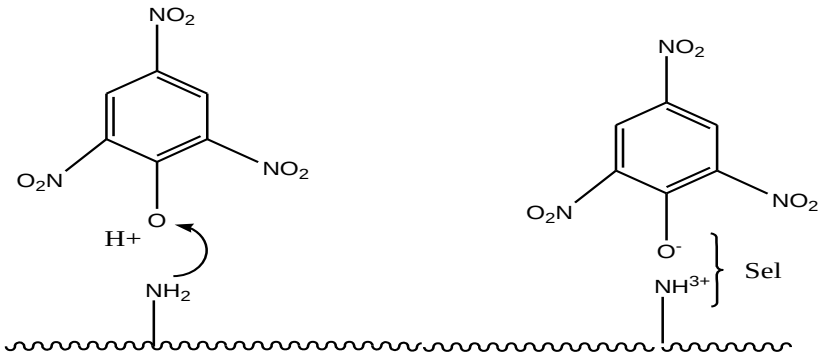


Figure I. 12 : Schematic Representation of Ionic Interactions Between Acid Dye Molecules and Protein Fibers (Wool or Silk**) [47]**

❖ **Mordant dyes**

From the earliest times, it had been observed that certain metal oxides formed particularly resistant associations with suitable dyes. From there was born the practice of etching which consists in depositing within (textile) fibers, before dying, a metal oxide **[44].**

Mordant dyes bind to a material for which they have little or no affinity, and this by the addition of a mordant, which increases the interaction between the dye and the material.Mostof these dyes are azo or triphenylmethane**[37].**

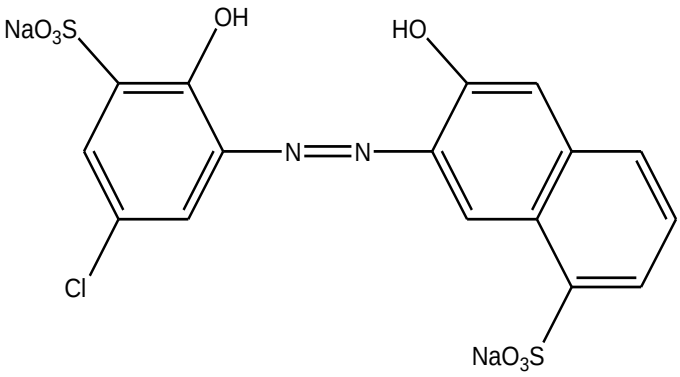


Figure I. 13: Representation of the Chemical Structure of a Mordant Dye (C.I. 14025 – Alizarin Yellow GG, Mordant Yellow 1)**.[48]**

I.3.6. Use and application of dyes

Dyes are used in numerous industrial sectors due to their ability to impart color to various materials. Their main applications include:

- Textile industry
- Plastics industry
- Construction materials
- Pharmaceutical and cosmetic products
- Printing inks
- Food products (approved colorants) **[23].**

I.3.7. Impact of colored discharges on the environment and human health

❖ **<u>On the environment</u>**

The discharge of dye-containing wastewater contributes significantly to environmental pollution. Colored effluents reduce light penetration in water bodies, disrupt photosynthesis, and affect aquatic ecosystems.

Some dyes and their degradation products may bioaccumulate in aquatic organisms and enter the food chain**[49].**

❖ **<u>Hazardous health impacts</u>**

Certain dyes and their breakdown products are associated with adverse health effects due to their chemical properties. These effects may include:

- Mutagenic effects
- Genotoxicity
- Carcinogenic potential
- Thyroiddys function
- Tumor formation
- Neurological effects
- Enzyme inhibition **[50].**

I.4. Treatment Processes

I.4.1. Treatment Processes of Textile Dyeing Wastewater

Textile dyeing wastewater is considered one of the most complex industrial effluents due to the presence of dyes, salts, surfactants, and various organic compounds. These pollutants are often resistant to degradation and can cause serious environmental problems if discharged without proper treatment. For this reason, several treatment methods have been developed, and recent studies emphasize that combining different techniques is the most effective strategy to achieve satisfactory results **[51].**

Table I.3. Comparison of Different Methods for Treating Dyes

Method	Principle	Advantages	Disadvantages
Aerobic Biological Treatment[52]	Bacterial degradation in the presence of oxygen.	A natural, low-cost, and easy-to-implement process.	Discoloration due to adsorption, not degradation; low efficiency; formation of sludge.
Anaerobic Biological Treatment[52]	Anaerobic degradation (production of CH_4 and CO_2)	Biogas (methane) production, high COD efficiency	Incomplete mineralization, potential toxicity of byproducts, low bleaching efficiency.
Coagulation–Flocculation[2]	Precipitation of colloidal particles using coagulants.	A simple method, suitable for certain dyes.	Ineffective for soluble dyes (reactive, acid), resulting in large amounts of sludge.
Membrane Separation Processes[53]	Physical separation using a membrane (reverse osmosis)	High efficiency and continuous separation of the dye.	High costs, membrane fouling, and the need to dispose of the concentrate.

Advanced Treatment Processes [53]	Oxidation by hydroxyl radicals (˙OH).	Complete degradation is possible, along with the mineralization of organic compounds.	Operating costs, the need to generate radicals, and, in some cases, the formation of byproducts.

I.4.2. Adsorption

I.4.2.1. Definition

When a solid body is immersed in a liquid containing dissolved substances, it is observed that, under certain circumstances, the chemical composition of the liquid varies in the vicinity of the solid's surface due to the fixation of certain dissolved substances on the solid. This adhesion of adsorbed bodies on the solid surface must be related to the molecular force field created at the solid surface: it is the phenomenon of adsorption. Adsorption offers the industry a whole range of possibilities and proven solutions to solve specific problems for each type of industry. In practice, it is used in the treatment of gases and waters, the recovery of organic products and expensive constituents but also for the separation of mixtures as well as in the textile industry and gas drying**[54].**

I.4.2.2. Types of adsorption

Adsorption forces give rise to two types of adsorption: chemisorption and physisorption:

- **Physical adsorption (Physisorption)**: This type of adsorption is due to "van der Waals" type bonds, which take shape in the case where the forces of molecular interaction between a solid and a gas become greater than the forces connecting the gas molecules together, without modification of the chemical charges. Physical adsorption may occur in monolayers or multilayers, it is due to a low energy that is of 5 - 40 kJ/mol. An increase in temperature or a decrease in pressure can desorb the fixed molecules: The phenomenon is reversible**[54].**
- **Chemical adsorption (Chemisorption)**: Chemisorption is characterized by the formation of strong chemical bonds (covalent or ionic) between the adsorbate and the adsorbent surface, often resulting in irreversible adsorption and possible chemical transformation of the adsorbed species**[55].**

To better understand the mechanisms underlying adsorption processes, it is essential to distinguish between the two main types of interactions between adsorbate and adsorbent: physical and chemical adsorption. These two phenomena differ in the nature of the links involved, their reversibility, their energy intensity, and their behavior as function of the temperature and the structure of the surfaces involved. **Figure I.14** below illustrates these fundamental differences, followed by a comparative **Table I.4** highlighting the main characteristics of each type**[53].**

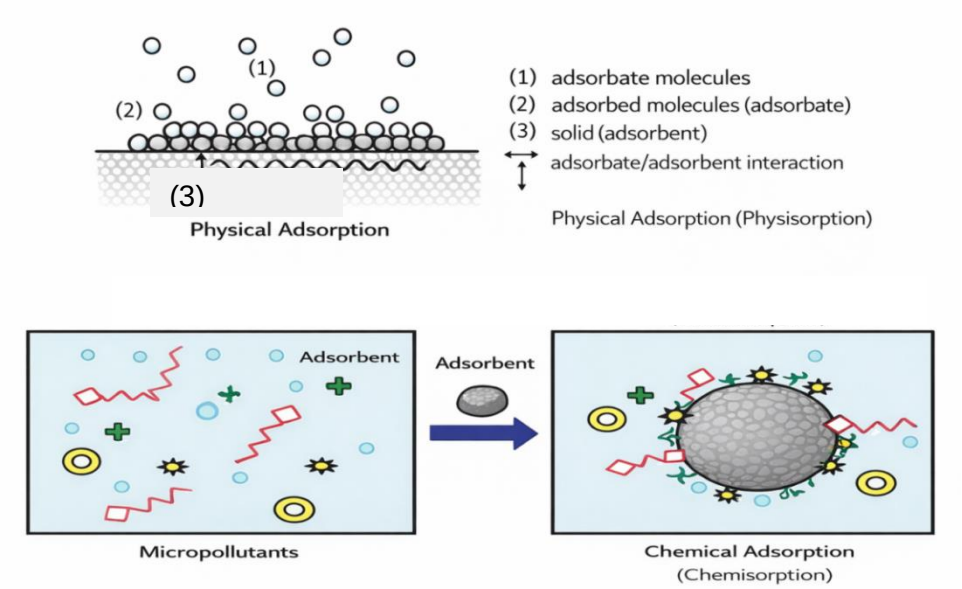


Figure I. 14 : Physical and chemical adsorption **[57]**

Table I.4: Comparison between physical and chemical adsorption **[58].**

Properties	Physical Adsorption	Chemical Adsorption
Types of bonds	Van der Waals bonds	Chemical bonds
Process temperature	Relatively low compared to the boiling point of the adsorbate	Higher than the boiling point of the adsorbate
Individuality of molecules	The individuality of molecules is preserved	Destruction of the individuality of molecules
Desorption	Easy	Very slow
Kinetics	Dependsweakly on temperature	Very slow
Heat of adsorption	Lessthan 10 kcal/mole	Greaterthan 10 kcal/mole

Energyinvolved	Low	High
Type of formation	Multilayer formation	Monolayer formation

I.4.2.3. Mechanism of adsorption

During the adsorption of a species on a solid, the mass transfer of molecules occurs from the fluid phase to the center of the adsorbent. This process occurs in several steps:

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

2- Internal mass transfer in the pores (internal diffusion) that takes place in the fluid filling the pores. Indeed, the molecules propagate from the grains surface towards their center through the pores.

3- Surface diffusion: for some adsorbents, there may also be a contribution from the diffusion of adsorbed molecules along the pore surfaces at the scale of an adsorbent grain**[59].**

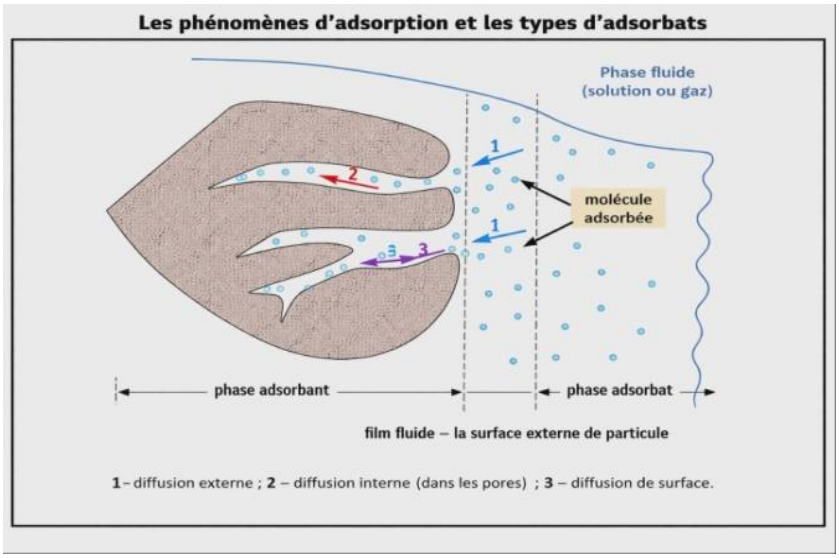


Figure I.15 : Diagram of the transport mechanism of an adsorbate within a grain**[57]**

I.4.2.4.Effect of Different Factors Influencing Adsorption

Adsorption performance is influenced by several operational and physicochemical parameters that control the interaction between the adsorbent and the adsorbate. Understanding these factors is essential for optimizing adsorption processes, especially in the treatment of textile wastewater. Recent studies indicate that adsorption efficiency depends not only on the properties of the adsorbent but also on environmental conditions and the nature of the pollutants **[61,51].**

- **Specific Surface Area**

The specific surface area of an adsorbent is one of the most important factors affecting adsorption capacity. A higher surface area provides more active sites available for the attachment of pollutant molecules.

Materials with porous structures, such as activated carbon or modified clays, generally exhibit high adsorption efficiency due to their large surface area and pore volume. Recent research has shown that increasing the surface area significantly enhances dye removal from wastewater **[2].**

- **pH**

The pH of the solution plays a crucial role in adsorption processes as it affects both the surface charge of the adsorbent and the ionization state of the adsorbate.

At different pH values, the electrostatic interactions between adsorbent and adsorbate may change, influencing the adsorption capacity **[61].**

- **Concentration**

The initial concentration of the adsorbate directly affects the driving force of mass transfer between the liquid phase and the adsorbent surface.

At higher concentrations, the adsorption rate may increase due to the higher probability of collisions between dye molecules and active sites. However, the adsorption capacity may eventually reach a saturation point where all active sites are occupied **[53].**

- **Adsorption Rate**

The adsorption rate refers to the speed at which the adsorbate molecules are transferred from the solution to the surface of the adsorbent.

This rate depends on factors such as particle size, pore structure, temperature, and agitation. Smaller particle sizes and better mixing conditions generally enhance the adsorption rate by reducing mass transfer resistance**[4].**

- **Nature of the Adsorbent**

The chemical composition, surface functional groups, porosity, and structural properties of the adsorbent significantly influence its adsorption performance.

Adsorbents with functional groups such as hydroxyl, carboxyl, or amine groups can interact more effectively with dye molecules through electrostatic interactions, hydrogen bonding, or van der Waals forces. Recent studies highlight the importance of modifying adsorbents to improve their affinity toward specific pollutants **[61].**

- **Nature of the Adsorbate**

The properties of the adsorbate, including molecular size, polarity, solubility, and chemical structure, also affect adsorption efficiency.

Large and complex dye molecules may have difficulty accessing small pores, while highly soluble compounds may exhibit lower adsorption affinity. In addition, the charge of the dye (cationic or anionic) plays a key role in determining its interaction with the adsorbent surface**[47].**

❖ **Temperature**

Temperature affects both the kinetics and thermodynamics of adsorption. In some cases, increasing temperature enhances adsorption by increasing the mobility of dye molecules and reducing solution viscosity.

However, adsorption can be either exothermic or endothermic depending on the system. Therefore, temperature variations may either improve or reduce adsorption capacity. Studying the effect of temperature is important to determine the thermodynamic behavior of the adsorption process**[53].**

I.4.2.5.Adsorption Isotherms

Adsorption isotherms are essential tools used to describe how adsorbate molecules interact with the surface of an adsorbent at equilibrium. They provide valuable information about the adsorption capacity, surface properties, and mechanism of the process.

In wastewater treatment, adsorption isotherms are widely used to evaluate the efficiency of adsorbents and to optimize operating conditions. Among the different models, the Langmuir, Freundlich, and Temkin isotherms are the most commonly applied **[61,2]**

❖ **Langmuir model**

Langmuir's theory allowed the study of the adsorption of gas molecules on solid surfaces. The Langmuir isotherm is difficult to use for natural systems where single layer adsorption on a single type of site is rarely encountered. The isotherm is represented by the following equation **[62].**

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{max}} + \frac{C_e}{Q_{max}} \qquad \dots (I.1)$$

Where:

Q_{max}: The maximum adsorption capacity (mg g^{-1});

k_L: The Langmuir constant related to the adsorption energy (L/mg).

C_e: The equilibrium concentration (mg L^{-1}).

The results obtained are shown in the figures below:

❖ **Freundlich model**

In 1962, Freundlich proposed another model to describe adsorption in a gaseous medium or liquid. This model is represented by a two-parameter equation (K_f and n) and consists of an exponential distribution of the energies of the adsorption sites on the surface of the support and is characterized by an adsorption in localized sites **[69].** This model is described by:

$$\mathbf{Ln\ Q_e = (1/\ n)\ x\ ln\ (Ce) + ln\ (K_f)} \quad \ldots \textit{(I.2)}$$

Where:

1/n:is the adsorption intensity

K_f:theFreundlich constant(L/mg).

Q_e: the quantity of adsorbed entities per gram of adsorbent at equilibrium (mg/g).

C_{eq}: the concentration of adsorbate in the solution at equilibrium (mg/L).

When the value of n is between 1 < n <10 this indicates a favorable adsorption, on the other hand if the value is n < 1 reveals a weak adsorption.

I.4.2.6.Adsorbent Materials

Absorbent materials include various categories (conventional, biomaterials, and nanomaterials) used in water treatment. The following table outlines their main characteristics and applications.

Table I.5: Main adsorbent materials and their applications in water treatment

Category	Material	Origin / Composition	Main Properties	Applications in Water Treatment
Conventional materials	***Activatedcarbon* [64]**	Carbon-based materials (wood, shells, residues)	High surface area, porous structure, hydrophobic surface	Adsorption of dyes, organic pollutants
	***Clays* [65]**	Natural aluminosilicates	Ion exchange capacity, low cost	Removal of heavy metals and dyes
	***Activated alumina* [66]**	ActivatedAl_2O_3	Porous, hydrophilic, high surface area	Fluoride and organic matter removal

	***Zeolites* [67]**	Crystallinemicroporous aluminosilicates	Uniform pore structure, high selectivity	Removal of NH_4^+ and heavy metals
Bio materials	***Prickly pear waste (Opuntiaficus-indica)*[68]**	Plant biomass	Biodegradable, functional groups rich	Adsorption of dyes and metals
	***Date seeds* [69]**	Agro-industrial waste	Rich in cellulose and lignin	Adsorption of organicpollutants
	***Lignocellulosicmaterials*[70]**	Cellulose, hemicellulose, lignin	Abundant, renewable, modifiable	Removal of dyes and heavy metals
Composites / Nano materials	***Metal / metaloxidenanoparticles*[71]**	Metals or oxides (Fe_3O_4, MnO_2, ZnO…)	High surface area, high reactivity	Adsorption and photocatalysis
	***Carbon-based nanomaterials* [72]**	CNTs, graphene, biochar	High conductivity, very large surface area	Organic pollutant adsorption
	***Nanoclays / nanofibers* [73]**	Modifiedclays, nanofibers	Tunable structure, enhanced adsorption	Removal of dyes and metals
	***Polymers and aerogels* [3]**	Porous hybrid materials	Ultra-light, high porous	Advanced multifunctional adsorption

I.5. Case study

Adsorption has been extensively investigated as an efficient method for the treatment of dye-containing wastewater due to its simplicity, cost-effectiveness, and high removal performance. Numerous studies have demonstrated the applicability of adsorption for removing persistent dyes from aqueous media using a wide range of adsorbent materials. For instance,**Yagub et al. (2014)[42]**reviewed the adsorption of dyes from aqueous solutions and highlighted adsorption as one of the most promising techniques because of its operational flexibility and high efficiency in removing various dye classes. Similarly, **Crini (2006) [1].**reported that adsorption processes using conventional and non-conventional adsorbents represent an attractive alternative for wastewater treatment, particularly for textile effluents containing recalcitrant organic pollutants. In addition, **Salleh et al. (2011) [74]** emphasized the importance of adsorbent characteristics such as surface area, porosity, and surface functional groups in determining adsorption capacity and pollutant affinity. More recently,

Katheresan et al. (2018) [**75]** confirmed that adsorption remains highly effective for dye removal when process parameters such as pH, initial dye concentration, and contact time are properly optimized. These findings are in agreement with the present study and further confirm that adsorption constitutes a sustainable and efficient strategy for the remediation of contaminated wastewater.

I.6. Conclusion

In conclusion, the treatment of textile dyeing wastewater remains a complex environmental challenge due to the diversity and persistence of pollutants, particularly dyes. Various treatment methods have been developed, each presenting specific advantages and limitations depending on the nature of the effluents. Among these techniques, adsorption stands out as an effective and versatile process due to its simplicity, high efficiency, and adaptability to different types of contaminants. Its potential for further development, especially with the use of low-cost and sustainable materials, makes it a promising solution for improving wastewater treatment and reducing environmental impact.

Chapter II :matriels and methodes

II.1. Introduction

This chapter presents the analytical techniques and experimental protocols used. First, it describes the reagents and apparatus used in the experiments to study the degradation of crystal violet by adsorption.

II.2. Reagents and Chemicals

a. Target Pollutants

Crystal Violet (CV), also known as gentian violet, is a synthetic cationic dye belonging to the triphenylmethane dye family. It is widely used in textile industries for dyeing materials such as cotton, wool, silk, leather, and paper. In microbiology, Crystal Violet is commonly employed as the primary stain in Gram staining for bacterial identification. Due to its high stability, complex aromatic structure, and resistance to biodegradation, its discharge into aquatic environments poses serious ecological and health concerns **[76].**

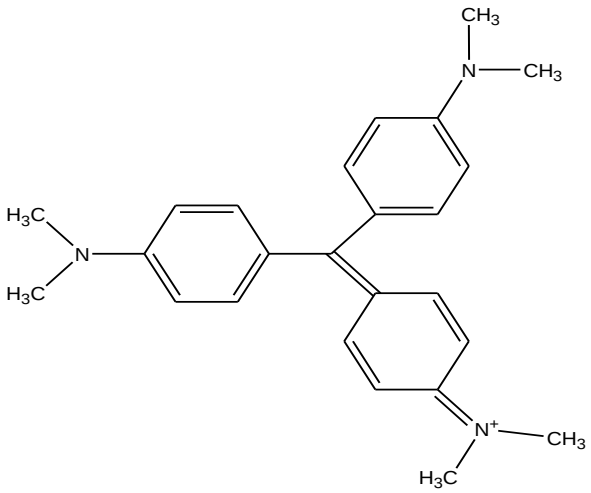


Figure II.1 : Structure of crystal violet **[77].**

Table II.1: Physicochemical Properties of Crystal Violet **[78].**

Properties	**crystalviolet**
Chemical name	4-[4,4'-Bis(dimethylamino)benzhydrylidene]cyclohexa-2,5-dien-1-ylidene]dimethylammonium chloride
CAS number	548-62-9
Chemical formula	$C_{25}H_{30}ClN_3$
Molecularweight	407 g/mol
λmax	595 nm
Chemical characterization	Basic dye
Physical state	Powder
Color	Bright violet
Odor	Odorless

b.Chemicals

The products and materials used to perform this work are listed in the following table:

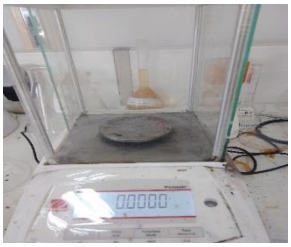
Table II.2. Chemical reagents used in this work

Product	**Chemical Formula**	**Supplier**	**Purity (%)**
Crystal Violet (CV)	$C_{25}H_{30}ClN_3$	Sigma-Aldrich	98 %
Sodium chloride	NaCl	Lobal Chimie	99 %
Manganesechloride	$MnCl_2$	Sigma-Aldrich	98–100.5 %
Zinc chloride	$ZnCl_2$	Sigma-Aldrich	98–100.5 %
Methanol	CH_3OH	Honeywell	99 %
Acetone	C_3H_6O	Honeywell	99 %
Sodium hydroxide	NaOH	Sigma-Aldrich	98 %

II.3. Materials and Equipment

The experiments were conducted using the materials listed below:

Table II.3. Materials and Equipment

Equipment	Marck	Image
UV/Visible Spectrophotometry	RAYLEIGH 2601	
pH Meter	HANNA HI 52221	
Analytical balance	OHAUS	
An oven	MEMMERT CUT 13500	
Furnace	NABERTHERMP330	
Magnetic stirrer	STUART US152	

Centrifuge	SIGMA	
XRD	D8 ADVANCE	

II.4. Preparation of Adsorbents

The adsorbents used in this study consist of biochar prepared from pomegranate peels and its metal-modified derivatives. The raw peels were collected, thoroughly washed to remove impurities, and dried under controlled conditions before undergoing carbonization to obtain a carbon-rich porous material.

Three types of adsorbents were investigated:

- **Pristine biochar (BC)** derived from pomegranate peels;
- **Mn-doped biochar (BC/ MnO_2)** prepared by impregnation with manganese
- **Zn-doped biochar/ MnO_2 (BC/MnO_2/Zn)** prepared by impregnation with zinc precursor at three.

II.4.1. Preparation of Biochar

The biochar used in this study was prepared from pomegranate peels, which were selected for their abundance, low cost, and high carbon content. The peels were first thoroughly washed with tap water and then with distilled water to remove impurities and adhering particles. After washing, they were dried in an oven at 105 °C for 24 hours to remove residual moisture. The dry samples were then ground and sieved to obtain a uniform particle size distribution. The resulting powder was subjected to pyrolysis in a muffle furnace at 500 °C for 2 hours under an oxygen-limited atmosphere. After cooling to room

temperature, the resulting biochar was ground again if necessary, then stored in a desiccator until used in the various adsorption experiments.

Figure II.2: Steps in the production of biochar from pomegranate peels.

II.4.2. Preparation of Biochar/MnO_2

A. <u>preparation of concentrated methanolic extract</u>

- The leaves of a plant belonging to the*Lythraceae* family were collected from the El Tarf region (northeastern Algeria). After collection, the plant material was thoroughly washed with distilled water to remove impurities and then air-dried at room temperature until a constant weight was reached.

- The dried leaves were subsequently ground using a grinder to obtain a fine and homogeneous powder. The extraction of phytochemical compounds was carried out using the Soxhlet**extraction method**: Approximately 25 g of plant powder were placed in an extraction thimble and subjected to continuous reflux for several hours (about 6h), allowing the efficient extraction of bioactive compounds such as polyphenols, flavonoids, and other reducing agents.

Figure II.3: preparation of concentrated methanolic extract

B. preparation of nanoparticles (Biochar/MnO_2)

The Biochar/MnO_2 composite was prepared using a precipitation method with a plant extract as the synthesis agent. First, 50 mL of concentrated plant extract was heated while stirring, and then a manganese chloride solution ($MnCl_2$, 0.1 M) was added gradually. After homogenizing the mixture, the biochar obtained from pomegranate peels was incorporated. The pH was then adjusted to a basic environment using a NaOH solution to promote the formation of MnO_2 particles on the surface of the biochar.

The mixture was kept under stirring for 3 hours, then dried at low temperature for 24 hours. The resulting suspension was then centrifuged, and the recovered precipitate was dried, washed with distilled water to remove impurities. After a second drying, the material was calcined at 400 °C for 3 hours, then ground until a fine, homogeneous powder was obtained. The Biochar/MnO_2 composite thus obtained was used for characterization analyses and crystal violet adsorption tests.

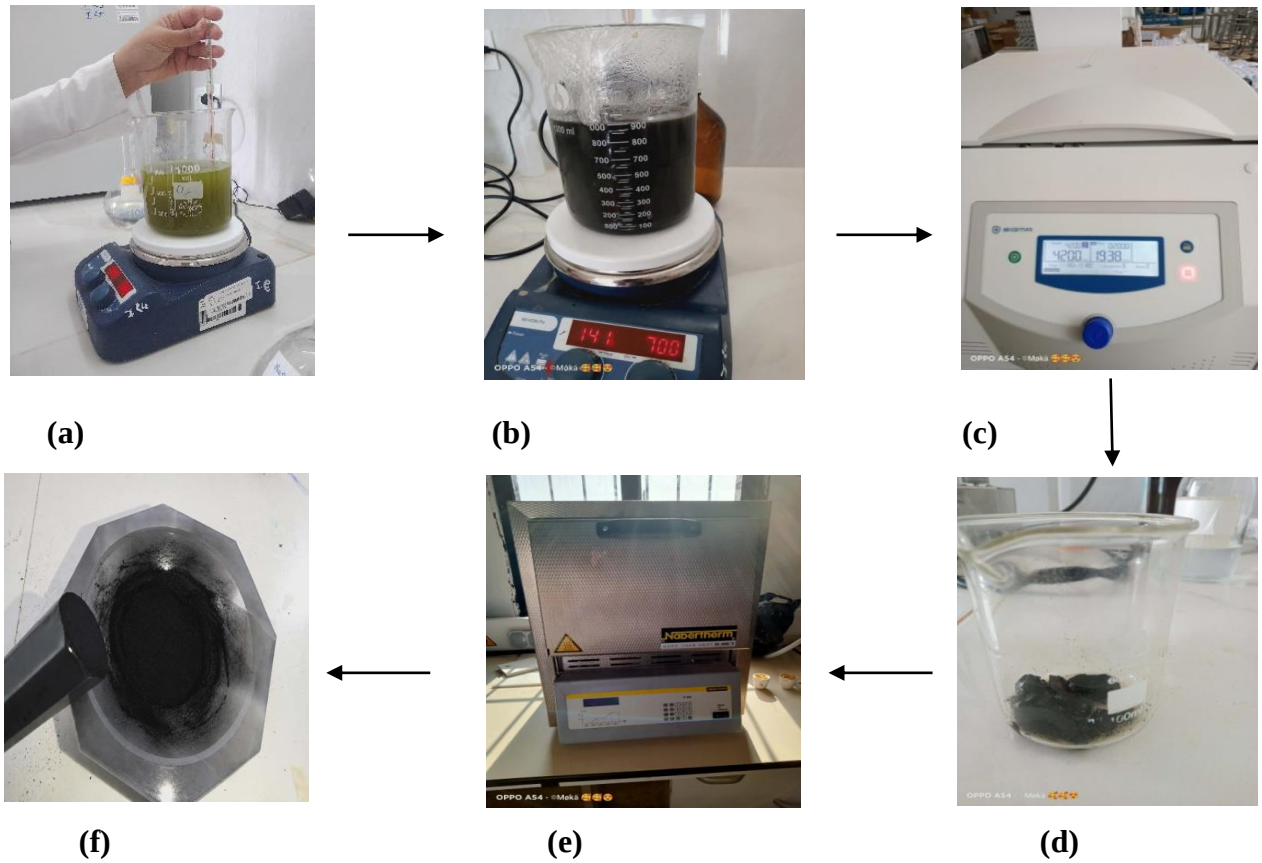


Figure II.2 : describe the steps in the biosynthesis of nanoparticles **(a)** Extrait+$Mncl_2$ + bichare**(b)**ajustement of pH + covered the NPS mixture **(c)** centrifugation **(d)** Rinsing and drying of NPS **(e)** put in furnace for calcined (f) ground into a fine homogeneous powder

II.4.3. Preparation of Biochar/MnO_2/Zn

The Biochar/MnO_2/Zn composite was synthesized using a plant extract-assisted precipitation method. The plant extract was first heated with stirring, and then a $MnCl_2$ solution was added gradually. After homogenization, a $ZnCl_2$ solution was introduced, followed by the addition of biochar derived from pomegranate peels. The pH of the mixture was adjusted using a NaOH solution to promote the formation and deposition of MnO_2 nanoparticles and zinc-containing species on the surface of the biochar.

After 2 hours of stirring at 70 °C, the suspension was dried and then centrifuged. The resulting precipitate was collected, dried, and washed successively with methanol and distilled water to remove impurities. After a second drying, the material was calcined at 400 °C for 3 hours and then ground to obtain a fine, homogeneous powder of Biochar/MnO_2/Zn. The resulting material was then used for characterization analyses and crystal violet adsorption tests.

II.5. Characterization of adsorbents

II.5.1. X-ray diffraction (XRD) analysis

The crystal structure of the adsorbents was studied by X-ray diffraction using a diffractometer with CuKα radiation (λ = 1.5406 Å). The diffractograms were recorded in a 2θ range between 10° and 80°.

II.5.2. Determination of the Zero Charge Point (pHPZC)

The zero charge point (pHPZC) of the adsorbents was determined using the pH drift method. To do this, several 0.01 M NaCl solutions were prepared, and their initial pH was adjusted to values between 2 and 12 using HCl or NaOH solutions. Next, 0.05 g of adsorbent was added to 50 mL of each solution. The mixtures were kept under agitation for 24 hours to reach equilibrium. At the end of this period, the final pH of each suspension was measured using a pH meter. The ΔpH values (ΔpH = pHf − pHi) were then calculated and plotted against the initial pH. The pHPZC corresponds to the pH value at which ΔpH is equal to zero, that is, at the point where the curve intersects the x-axis.

II.6. Preparation of crystal violet solutions

II.6.1. Stock Solution

A stock solution of violet crystal dye with a concentration of 1000 mg/L was prepared by dissolving 1 g of dye in 1 L of distilled water.

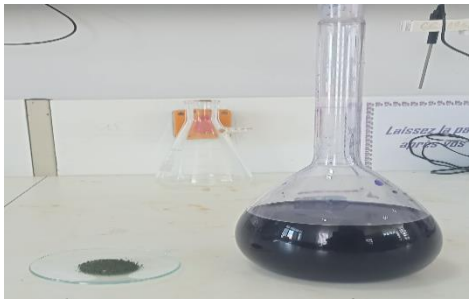


Figure II.5. Greenish solid of violet crystal (CV) in powder form and a concentrated violet solution of VC at 1000 ppm.

II.6.2. Working Solutions

Working solutions of various concentrations (10, 20, 30, 40, 50 mg/L) were prepared by diluting the stock solution.

II.7.Experimental Adsorption Protocol

Adsorption tests of crystal violet (CV) were conducted in batch mode to evaluate the performance of the various prepared adsorbents, namely biochar, the biochar/MnO_2 composite, and the biochar/MnO_2/Zn composite. On a multi-station shaker, 0.05 g of adsorbent was placed in contact with 50 mL of crystal violet solution in an Erlenmeyer flask. The mixtures were stirred at a constant speed of 300 rpm at room temperature (25 °C) for a specified duration to allow the dye to adsorb onto the surface of the materials. At the end of the contact time, the adsorbent was separated from the solution by centrifugation or filtration. The recovered supernatant was then analyzed by UV-Vis spectrophotometry to determine the residual concentration of crystal violet. The adsorption capacities and removal efficiencies were calculated based on the difference between the initial and final concentrations of the dye.

The amount adsorbed per unit mass of adsorbent (Qe) at equilibrium and the percentage of adsorption (%R) are given by the following equations:

$$\cdot\ Q_e = \frac{(C_O - C_e) * V}{m}$$

$$\%R = \frac{(C_O - C_e) * 100}{C_O} \qquad \textit{...(II.2)}$$

Where:

C_0: the initial concentration of the adsorbate (mg/L);

Ce: the equilibrium concentration of the adsorbate (mg/L);

V: the volume of the solution containing the adsorbate (mL);

m: the mass of the adsorbent (g).

Figure II.6: Schematic representation of the adsorption process of violet crystal on various adsorbents.

II.8. Conclusion

In this chapter, we have presented the various chemicals, materials, and equipment used to conduct this study. We have also described the experimental protocols adopted for the adsorption of crystal violet, from the preparation of solutions to the analyses performed. This description of the methods provides a better understanding of the conditions under which the experiments were conducted and ensures the reliability of the results obtained. The data from these tests will be analyzed in the following chapter to evaluate the performance of the materials studied and to identify the parameters influencing the adsorption process.

Chapter III :resultes and discussion

III.1. Introduction

In this chapter, the results obtained from the adsorption of crystal violet onto biochar, biochar/MnO_2, and biochar/MnO_2/Zn are presented and discussed. The influence of the main operating parameters on adsorption efficiency is studied to determine the optimal conditions for dye removal. The experimental data are then analyzed using kinetic models and adsorption isotherms to better understand the behavior of the adsorbents and the mechanisms involved

III.2. Spectral Study of Crystal Violet (CV)

III.2.1. Absorption Spectrum of CV

Spectrophotometric analysis is based on the absorption of light radiation by matter in the spectral range between 400 and 800 nm, known as the UV-Visible region. The absorbance of the dyes is determined by spectrophotometric measurement in the visible range, based on Beer-Lambert's law. The wavelength of the absorption maximum is 590 nm. The scan is performed using solutions of diluted concentration (10 ppm).

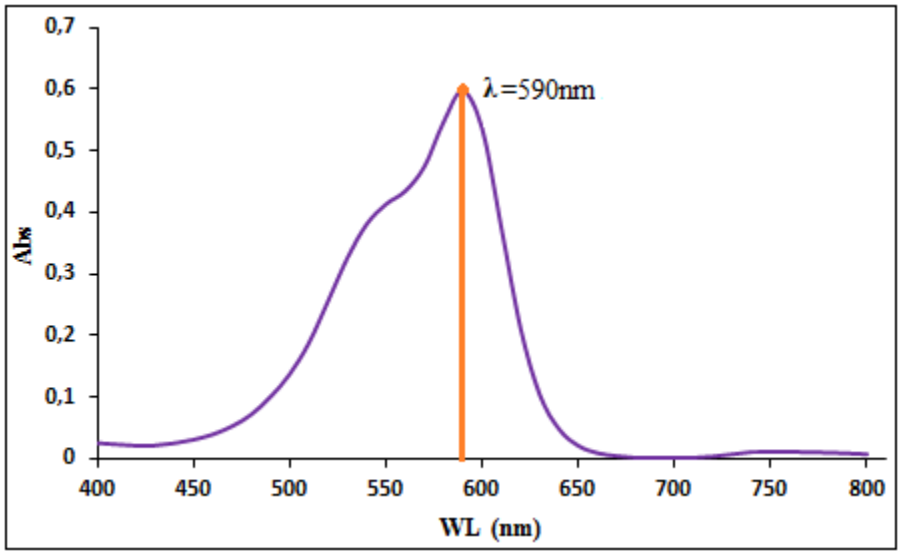


Figure III.1: Absorption spectrum of CV

III.2.2. Study of the dye's calibration curve

In the visible spectrum, each colored solution of the CV dye was analyzed using a spectrophotometer at a wavelength of 590 nm, which was determined by scanning.

The results of this experiment revealed that the maximum absorption wavelength of crystal violet was 590 nm. In addition, different concentrations of CV were analyzed using UV-Visible.

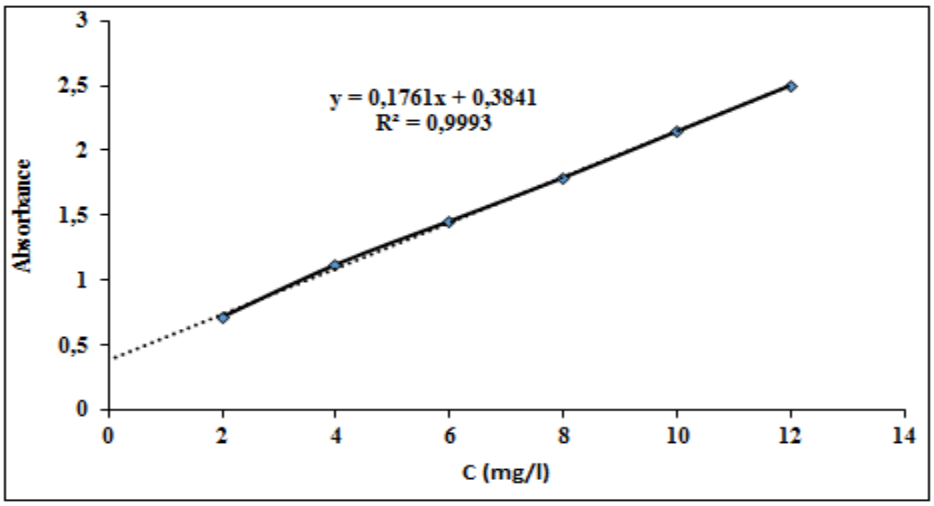


Figure III.2. Crystal violet calibration curve

III.3. Characterization of Biomaterials

III.3.1. XRD

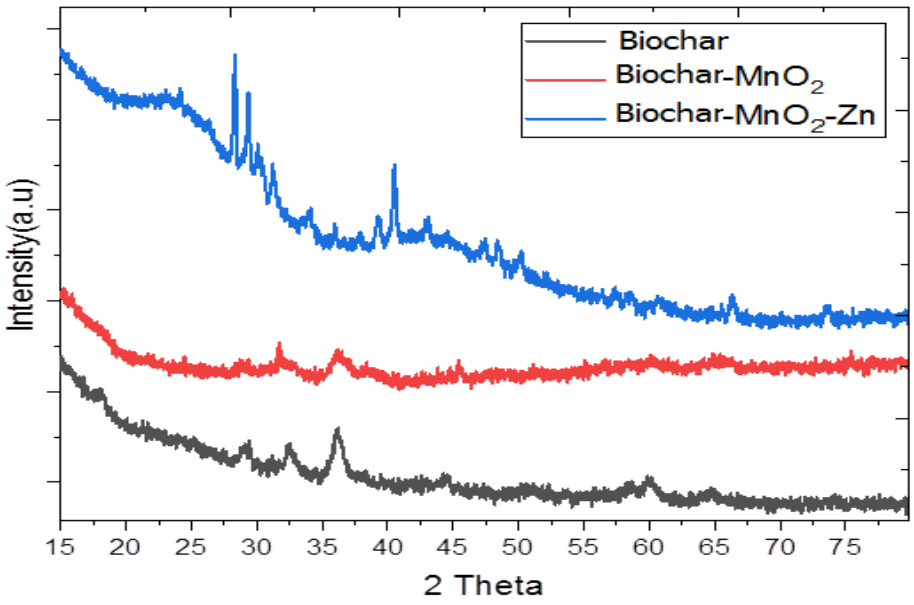


Figure III.3: X-ray diffraction (XRD) patterns of the three adsorbents.

The XRD pattern of biochar exhibits a broad diffraction band located between 20° and 30° (2θ), which is characteristic of a predominantly amorphous structure. This observation is typical of carbonaceous materials obtained from the pyrolysis of lignocellulosic biomass and reflects a low degree of crystalline organization of carbon.After modification of the biochar with manganese dioxide, new diffraction peaks appear, particularly around 28°, 36°, and 60° (2θ). These peaks indicate the presence of crystalline MnO_2 phases deposited on the surface of the biochar. The persistence of the amorphous carbon band suggests that the original structure of the biochar is preserved after modification.For the Biochar–MnO_2–Zn composite, the main peaks observed for the Biochar–MnO_2 material remain present, although slight variations in intensity can be noticed. This behavior suggests the successful incorporation of zinc into the composite structure. The absence of intense diffraction peaks specifically attributable to zinc may be due to its low content or its homogeneous dispersion on the composite surface. The simultaneous presence of the characteristic features of biochar and metal oxides further confirms the successful formation of the Biochar–MnO_2–Zn composite.

Overall, the obtained results demonstrate that the successive modification steps of the biochar were successfully achieved. The incorporation of MnO_2 followed by zinc led to the formation of composite materials combining the porous structure of biochar with the properties of metal phases, which could contribute to enhanced adsorption performance toward crystal violet removal.

III.3.2. Zero-Charge Point (ZCP)

The zero-charge point (pHpzc) is defined as the pH value at which the overall surface charge of the adsorbent is zero. Determining this parameter is particularly important for understanding the influence of electrostatic interactions on the adsorption process. The pHpzc of the materials studied was determined using the method reported by Ferrero-García et al. **[79]** and Sontheimer et al. **[80].**

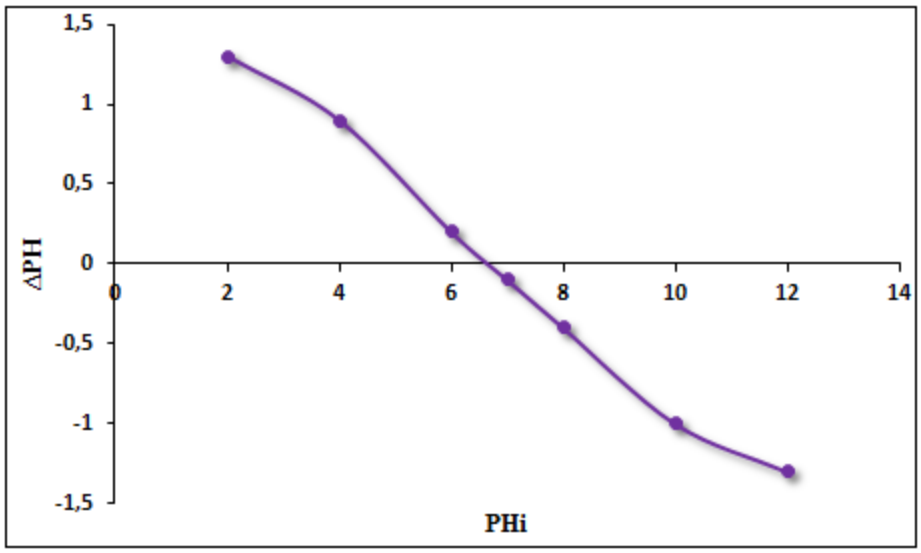


Figure III.4: pHPZC of biochar

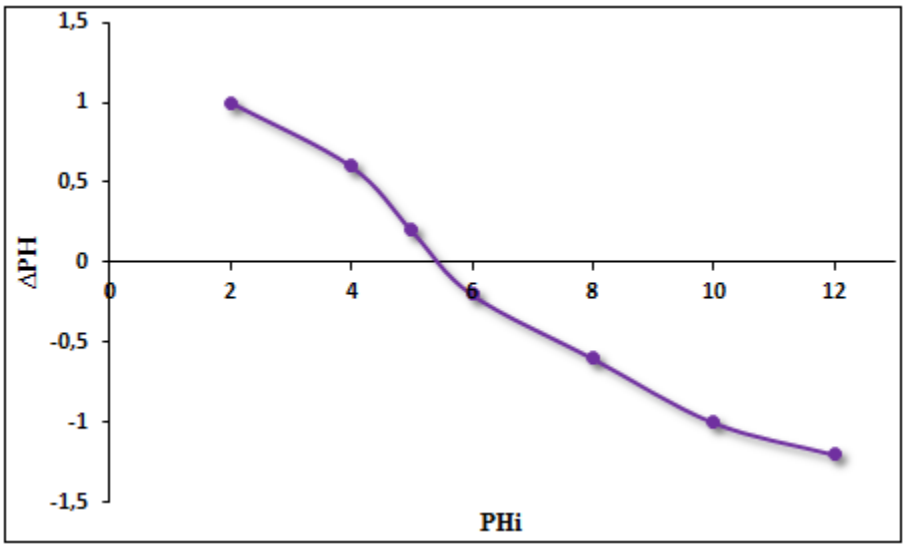


Figure III.5: pHPZC of biochar/MnO_2

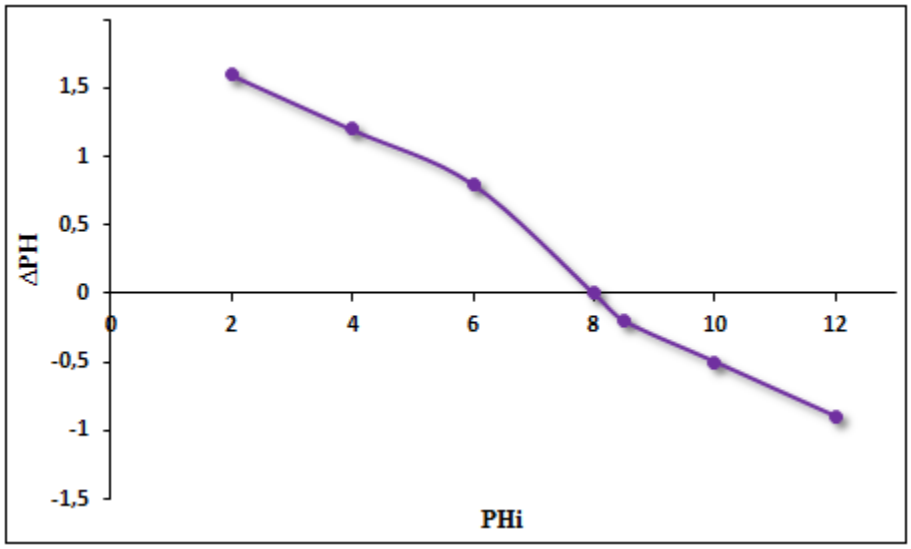


Figure III.6: pHPZC of biochar/MnO_2/Zn

The zero-charge point (pHpzc) values obtained for biochar (6.8), biochar/MnO_2 (5.7), and biochar/MnO_2/Zn (8.0) highlight the effect of surface modification on the physicochemical properties of the adsorbents. The pHpzc of raw biochar indicates that its surface becomes negatively charged when the solution pH is greater than 6.8. After the incorporation of MnO_2, a decrease in pHpzc to 5.7 is observed, which can be attributed to the appearance of acidic oxygen-containing functional groups on the material's surface. This decrease in pHpzc following modification with MnO_2 has also been reported in several studies on biochars modified with metal oxides **[81].** In contrast, the addition of zinc causes the pHpzc to rise to 8.0, indicating an increase in the surface's basicity and the formation of new active sites associated with zinc species **[82].**In the case of violet crystal, which is a cationic dye, adsorption is enhanced when the pH of the solution is higher than the pHpzc of the adsorbent, as the surface then becomes negatively charged, promoting electrostatic interactions with the dye molecules **[83].** Thus, biochar/MnO_2 is expected to exhibit a higher affinity for crystal violet at relatively low pH levels compared to raw biochar and biochar/MnO_2/Zn. These results confirm the importance of pHpzc in understanding the adsorption mechanism of cationic dyes on modified carbon materials **[84].**

III.4. Optimization of Operating Conditions

III.4.1. Determination of the optimum contact time

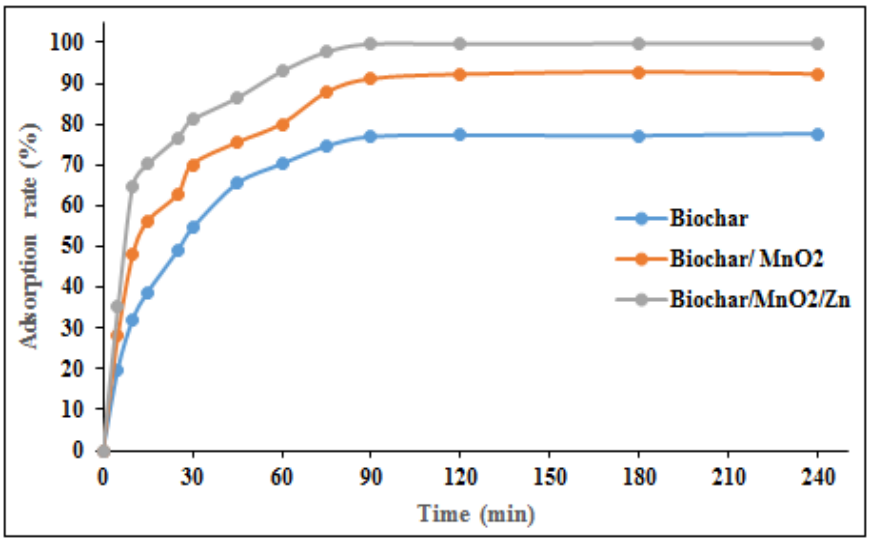


Figure III.7: Effect of contact time on the adsorption of crystal violet by different adsorbents.

The results show that the adsorption rate increases rapidly during the first minutes of contact and then reaches a plateau after approximately 90 min, indicating that adsorption equilibrium has been established. Therefore, a contact time of 90 min was selected as the optimum time for subsequent experiments. The Biochar/MnO_2/Zn composite exhibited the highest adsorption performance, followed by the Biochar/MnO_2 composite and the pristine biochar.

III.4.2. Effect of Biomaterial Mass

Dye adsorption is greatly influenced by the mass of the adsorbent. In this study, we kept the solution volume constant (50 mL) while varying the amounts of adsorbent. The results are shown in **Figure III.8.**

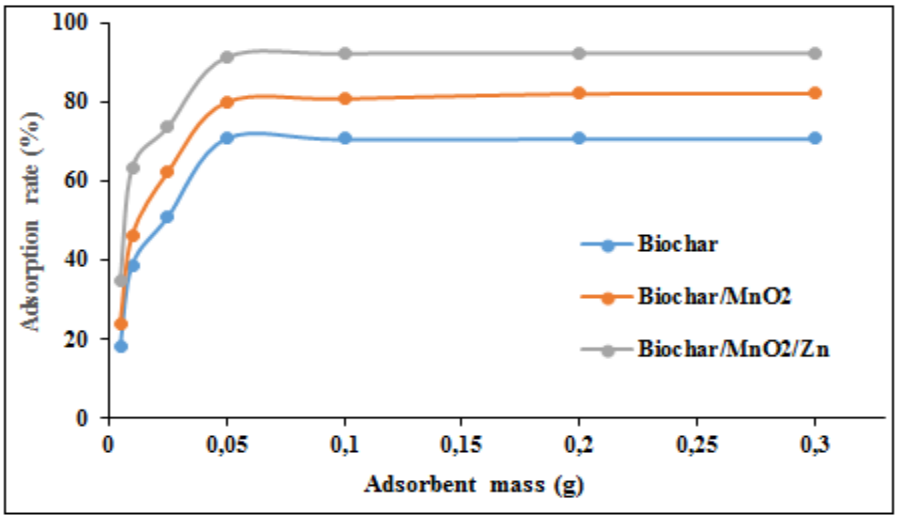


Figure III.8: Effect of biosorbent mass on the adsorption of crystal violet

(C = 50 mg/L, time: 2 h, volume = 50 mL, T = 25°C, stirring speed: 300 rpm)

An increase in the adsorbent mass had a significant impact on the adsorption rate for the three materials studied (Biochar, Biochar/MnO_2, and Biochar/MnO_2/Zn). In general, it was observed that the adsorption rate increases rapidly as the mass increases from low values (0 to 0.05 g), then tends to stabilize when the mass exceeds 0.1 g. This trend reflects the onset of a plateau corresponding to the gradual saturation of the available active sites on the surface of the adsorbents **[85].** For biochar, increasing the mass improves the adsorption rate by up to approximately 70%. Beyond 0.05 g, no significant improvement is observed, indicating that the amount of adsorbent becomes sufficient to retain the majority of the dye molecules present in the solution. Biochar/MnO_2 exhibits similar behavior but with superior performance. The introduction of MnO_2 increases the specific surface area as well as the number of accessible active sites, which improves adsorption efficiency and allows for a rate of approximately 80% to be achieved **[86].** Furthermore, the plateau observed starting at 0.05 g suggests that adsorption equilibrium is reached at low adsorbent masses. Finally, Biochar/MnO_2/Zn exhibits the best performance with an adsorption rate exceeding 90% as low as 0.05 g. This improvement can be attributed to the synergistic effect of MnO_2 and zinc, which promote the development of new active sites and enhance interactions between the adsorbent surface and crystal violet molecules **[87].** Beyond this mass, increasing the amount of adsorbent no longer yields any significant improvement, likely due to system saturation and the

limited availability of dye molecules in solution **[88].** Thus, the mass of 0.05 g can be considered the optimal mass for the three materials studied, since it allows for high adsorption while limiting adsorbent consumption.

III.4.3. Effect of pH on Adsorption

pH plays a crucial role in all adsorption studies, as it can influence the structure of the adsorbent and the adsorbate, as well as the adsorption mechanism. We evaluated the adsorption efficiency of CV by varying its pH from 3 to 9, while keeping other factors constant. The results of these tests are presented in **Figure III.9.**

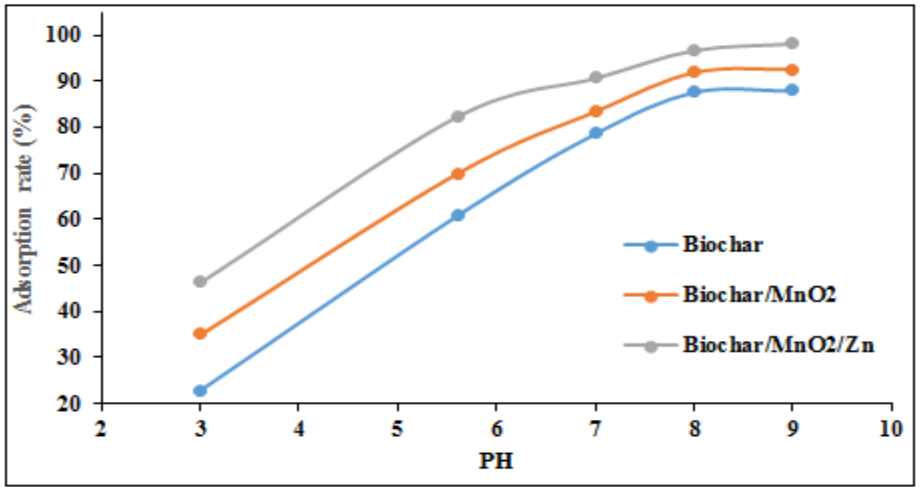


Figure III.9. Effect of pH on the adsorption of crystal violet

(C = 50 mg/L, time: 2 h, volume = 50 mL, m = 0.05 g, T = 25°C, stirring speed: 300 rpm)

The effect of pH on the adsorption of crystal violet was studied for the three adsorbents. The results show a gradual increase in the adsorption rate as the pH shifts from acidic to neutral and then to slightly basic. At low pH values (3-4), adsorption efficiency remains relatively limited. This behavior is attributed to the high concentration of H^+ ions in the solution, which compete with the crystal violet molecules for the active sites of the adsorbent. Furthermore, surface protonation reduces the favorable interactions between the adsorbent and the dye **[89].** As the pH increases, this competition gradually decreases, which promotes the adsorption of crystal violet. Consequently, a continuous improvement in the removal rate is observed between pH 5 and 8 for all three materials. Biochar/MnO_2/Zn exhibits the best performance across the entire pH range studied,

demonstrating the beneficial effect of surface modification on the material's affinity for the dye. At pH 8–9, the curves level off, indicating that the maximum adsorption capacity has been nearly reached. Biochar/MnO_2/Zn then achieves a recovery rate close to 100%, followed by biochar/MnO_2 and then raw biochar. This gradual improvement in performance can be attributed to the increase in the number of active sites and the improvement in surface properties induced by the incorporation of MnO_2 and Zn **[90].**

III.4.4. Effect of the Initial Concentration of Adsorbates

To investigate the effect of the initial dye concentration on the adsorption capacity of the biosorbents, several experiments were conducted by varying the concentration (10, 20, 30, and 50 mg/L), while keeping the other experimental parameters constant. The results are presented in **Figure III.10.**

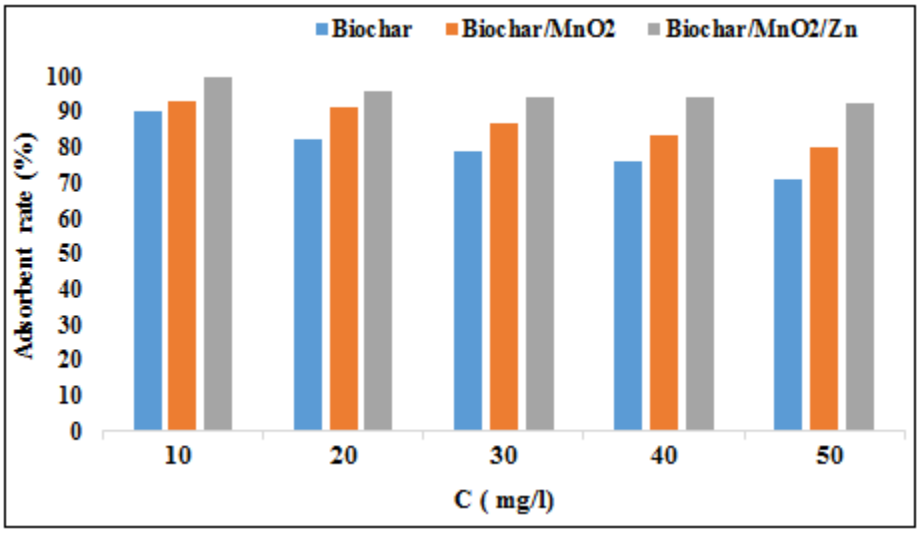


Figure III.10: Effect of adsorbate concentration.

(Volume = 50 mL, m = 0.05 g, T = 25°C, stirring speed: 300 rpm)

The figure shows that an increase in the initial concentration of crystal violet (CV) leads to a gradual decrease in the adsorption rate for the three adsorbents studied: biochar, biochar/MnO_2, and biochar/MnO_2/Zn. This decrease can be explained by the gradual saturation of the available active sites on the surface of the adsorbents as the dye concentration increases **[91].** Raw biochar exhibits the lowest adsorption performance. The removal efficiency drops from approximately 89% at 10 mg/L to nearly 71% at 50 mg/L. This significant decline indicates that the number of active sites available on the

biochar becomes insufficient at high concentrations of CV **[92].** The biochar/MnO_2 composite shows a significant improvement in adsorption capacity compared to biochar alone. Recoveries remain between approximately 92% and 80% as the concentration increases from 10 to 50 mg/L. This improvement can be attributed to the presence of MnO_2 particles, which increase the specific surface area as well as the number of active sites that promote interactions with crystal violet molecules **[93].** The biochar/MnO_2/Zn material exhibits the best performance among the three adsorbents. The adsorption rate remains very high even at high concentrations, dropping from approximately 98% to 91%. The introduction of zinc appears to further improve the surface properties of the composite by increasing the number of active sites and the electrostatic interactions between the adsorbent and the dye. Furthermore, the slight decrease in yield with increasing concentration demonstrates the material's high stability and strong affinity for CV **[94].**

III.4.5. Effect of Temperature

To investigate the effect of temperature on CV adsorption, we selected four different temperatures for our reactions: 25, 35, 45, and 55°C. The results are shown in **Figure III.11.**

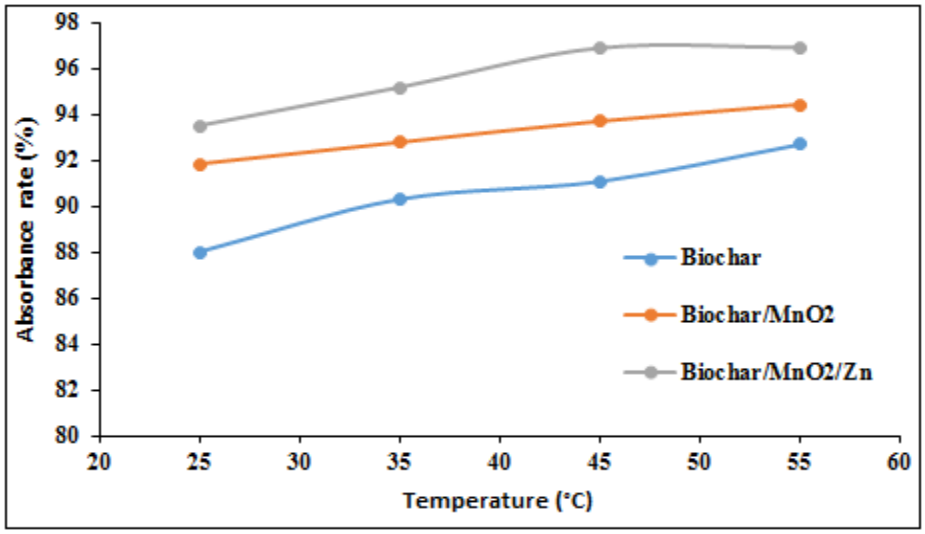


Figure III.11: Effect of temperature on the adsorption of crystal violet

(C = 50 mg/L, V = 50 mL, m = 0.05 g, stirring speed: 300 rpm)

The figure shows the effect of temperature on the adsorption of violet crystal by the three adsorbents studied: biochar, biochar/MnO_2, and biochar/MnO_2/Zn. Overall, a gradual increase in the adsorption rate is observed as the temperature rises, indicating that the adsorption process is enhanced at higher temperatures **[93].** For biochar, the adsorption efficiency increases from approximately 88% at 25 °C to nearly 93% at 55 °C. This improvement can be explained by the increased mobility of the crystal violet molecules in solution, which facilitates their diffusion to the active sites of the adsorbent material **[95].** The biochar/MnO_2 composite also exhibits an increase in recovery rate with rising temperature, from approximately 92% to 94%. This trend confirms that the presence of MnO_2 enhances the adsorbent properties of biochar and promotes interactions between the dye and the composite's surface **[96].** The biochar/MnO_2/Zn material exhibits the best adsorption performance across the entire temperature range studied. The adsorption rate reaches approximately 97% at 45 °C and remains virtually stable up to 55 °C. This stability reflects the composite's strong affinity for crystal violet as well as the high availability of active sites **[97].** The increase in adsorption with rising temperature suggests that the phenomenon is likely endothermic in nature. Indeed, the supply of thermal energy promotes the diffusion of dye molecules and increases the interactions between the adsorbent and the adsorbate**[98].**

III.5. Modeling Adsorption Isotherms

An adsorption isotherm is used to show, at a constant temperature, how much solute an adsorbent can hold as a function of the remaining concentration of the solute in the solution. Studying these isotherms is very important because it allows us to understand how the solute interacts with the adsorbent and to estimate the material's actual adsorption capacity. It is also an essential step in designing an effective adsorption system**[99]**.

Although there are many mathematical models to describe these isotherms, most studies show that the Langmuir and Freundlich models remain the most widely used and best suited**[100]**.

III.5.1. Langmuir Model

As described in **Chapter I (Section I.4.2.5),** the Langmuir model is expressed by the equation ***(I.1)***

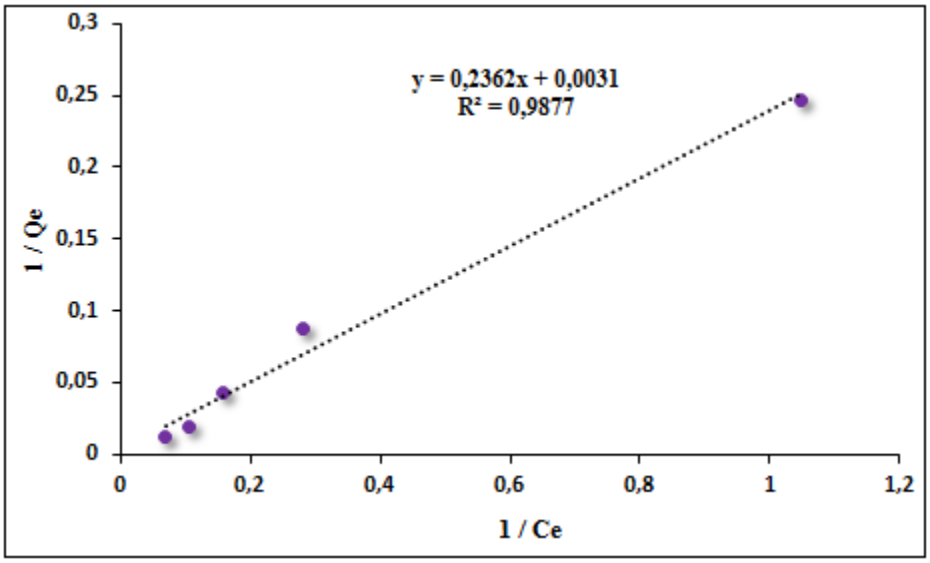


Figure III.12: Application of the Langmuir model to the adsorption of CV by biochar

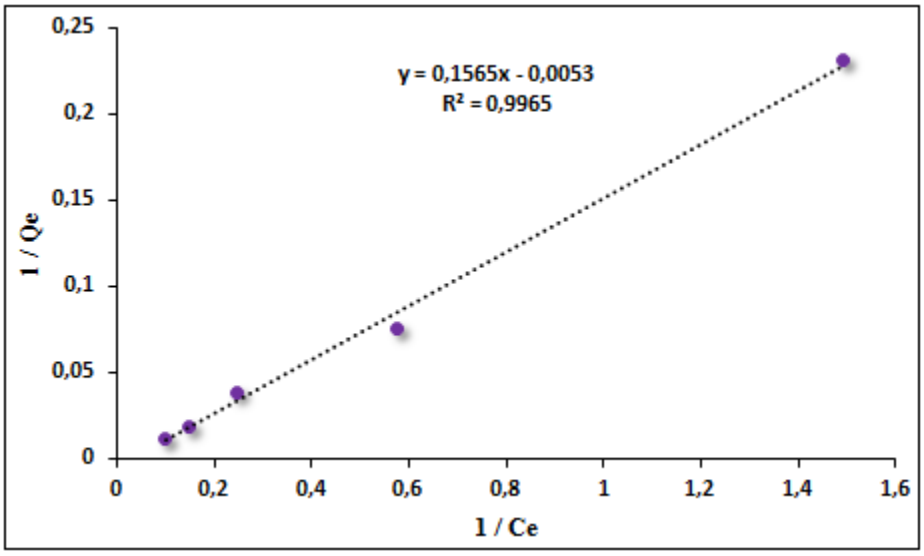


Figure III.13: Application of the Langmuir model to the adsorption of CV by Biochar/MnO_2

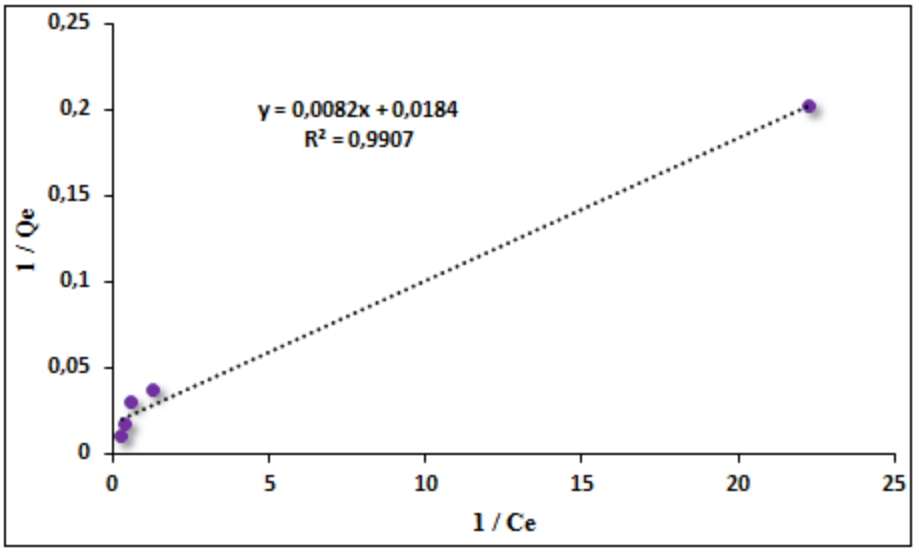


Figure III.14: Application of the Langmuir model to the adsorption of CV by Biochar/MnO_2/Zn

Table III.1: Langmuir constants for the adsorption of Crystal Violet

Adsorbent	R^2	K_L	Q_{max}(mg/g)
Biochar	0,9877	0.0131	54,347
Biochar/MnO_2	0.9965	0.033	188,679
Biochar/MnO_2/Zn	0.9907	0.224	322,58

Based on the results presented in **Table III.1**, it can be seen that the adsorption of the cationic dye (CV) on the three adsorbents follows the Langmuir model. This means that the sites on the adsorbent surface have the same energy, that each site can hold a single molecule, and that adsorption occurs as a monolayer, with no interaction between already adsorbed molecules.Furthermore, the obtained KL value is less than 1, indicating that dye adsorption is favorable.

III.5.2. Freundlich Model

As described in Chapter I (Section I.4.2.5), the Freundlich model is expressed by the equation ***(I.2)***

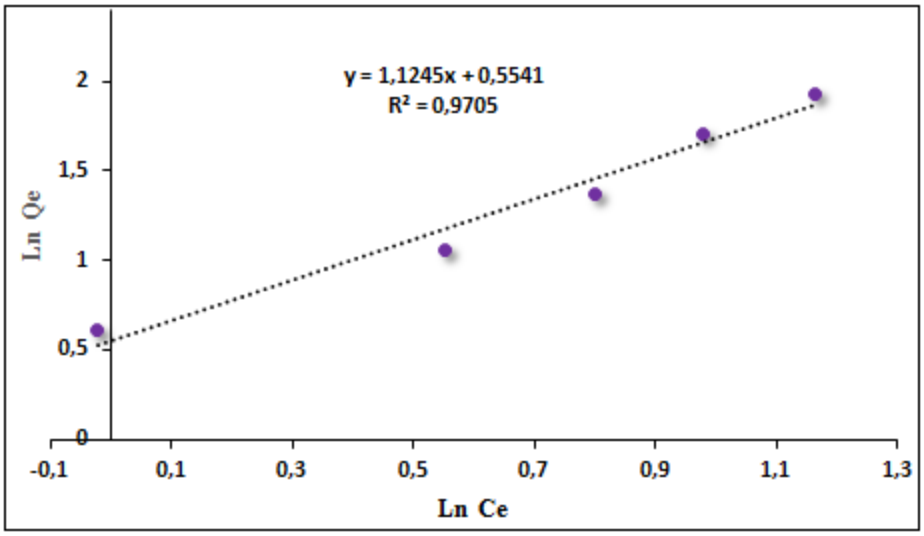


Figure III.15: Application of the Freundlich model to the adsorption of CV by biochar

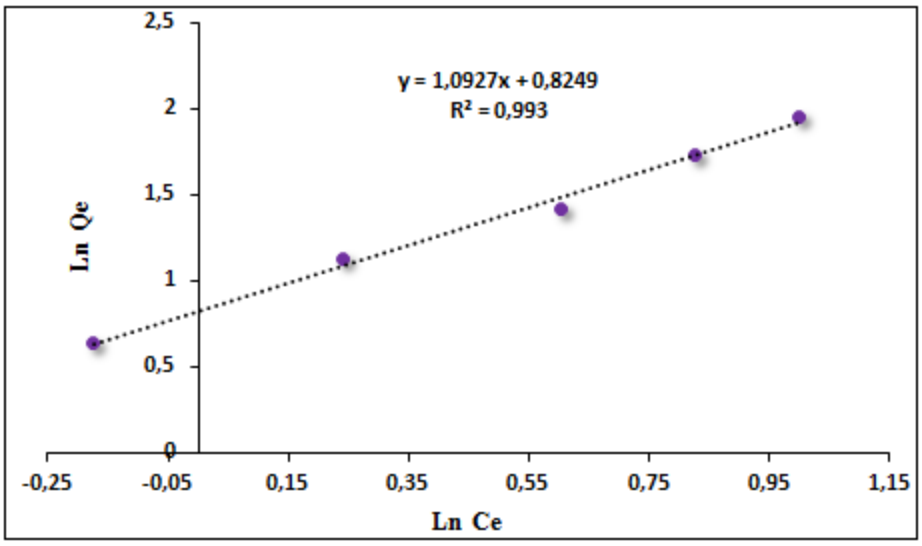


Figure III.16: Application of the Freundlich model to the adsorption of CV by biochar/MnO_2

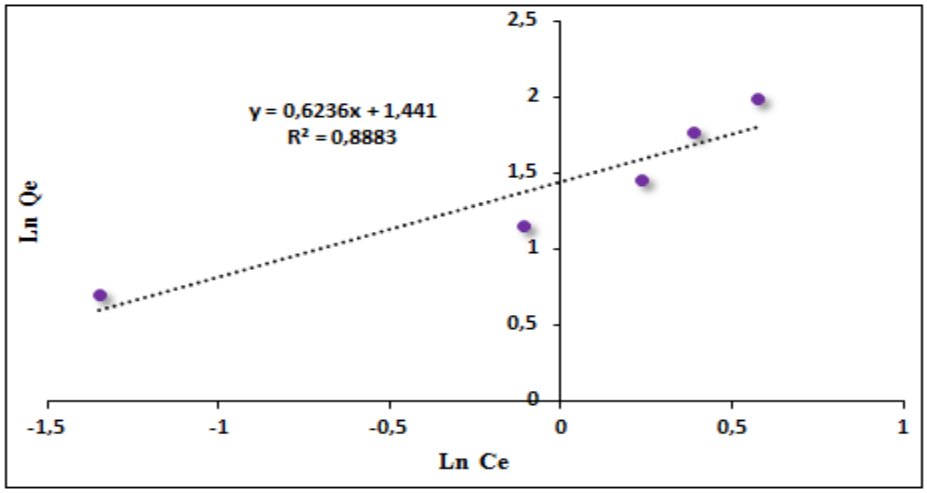


Figure III.17: Application of the Freundlich model to the adsorption of CV by Biochar/MnO_2/Zn

Table III.2: Values of the Freundlich constants

Adsorbent	R^2	K_f	N
Biochar	0.9705	1.74	0.889
Biochar/MnO_2	0.993	2.69	0.91
Biochar/MnO_2/Zn	0.8883	1.86	1.60

The Freundlich isotherm does not provide a satisfactory linear fit: the regression coefficients obtained are slightly lower than those of the Langmuir model. This indicates that the Freundlich model does not account for the adsorption behavior as well in our case.

III.6. Modeling of Adsorption Kinetics

The reaction order is a very important parameter in determining reaction mechanisms. Several models are described in the literature for describing adsorption kinetics. To this end, we used various kinetic models in this study, such as:

- Pseudo-first-order kinetics, expressed by the Lagerren equation, which describes mass transfer.
- Pseudo-second-order kinetics, which describes the chemisorption process.

- Intra-particle diffusion, which describes the rate-limiting step.

The equations below define the pseudo-first-order (FOA) model, the pseudo-second-order (PSO) model, and the intra-particle diffusion (DIP) model:

First-order approximation (FOA): $\boldsymbol{ln\ (q_e - q_t) = ln q_e - K_1 t}$ ***…(III.1)***

Second-order pseudo- (PSO)**:** $$\frac{t}{q_t} = \frac{1}{K_2 . q_e^2} + \frac{1}{q_e} . t$$

Intraparticle diffusion (IPD)**:** $q_t = k_{id}\, t^{1/2} + C$ ***…(III.3)***

III.6.1. Pseudo-first-order model

The collected data were used to plot the curves shown in **Figure III18/III.19/III.20** . The graphical representation of the ln(qe – qt) curve as a function of t **(Figure III.18/III.19/III.20)** allows for the determination of the constant k1 and the equilibrium adsorbed amount qe **(Table III.3).**

qe: amount of adsorbate at equilibrium per gram of adsorbent (mg g^{-1}).

t: contact time (min).

K1: first-order adsorption rate constant (min^{-1}).

The results obtained by applying the pseudo-first-order kinetic model are presented in **Figure III.18/III.19/III.20.**

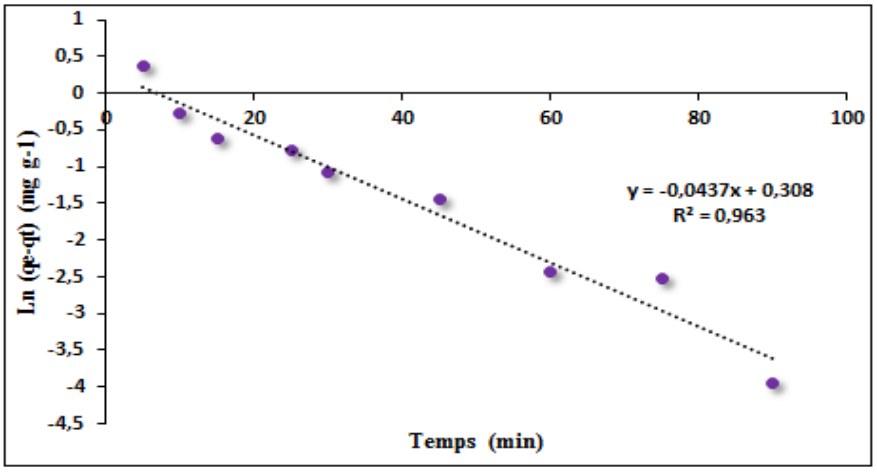


Figure III.18: Pseudo-first-order linearization for the adsorption of CV by biochar.

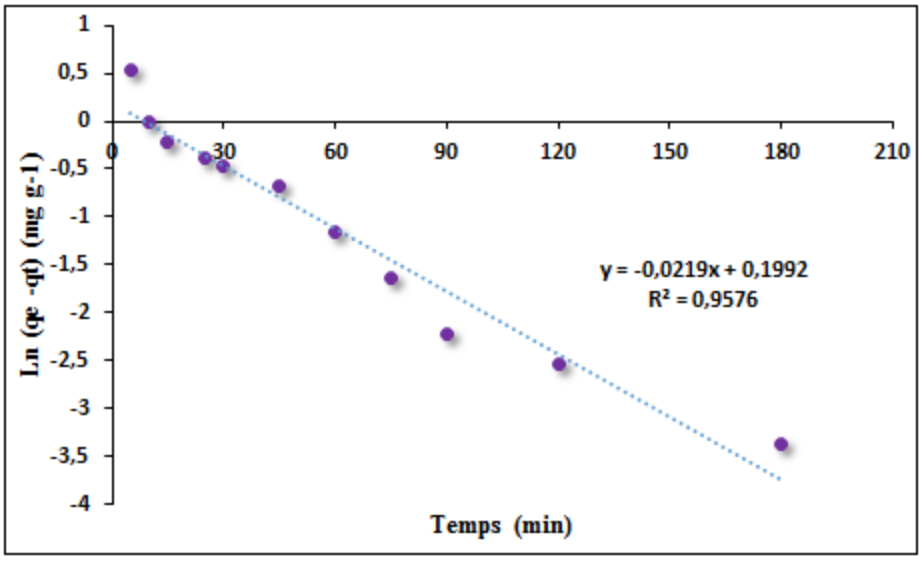


Figure III.19: Pseudo-first-order linearization for the adsorption of CV by biochar/MnO_2.

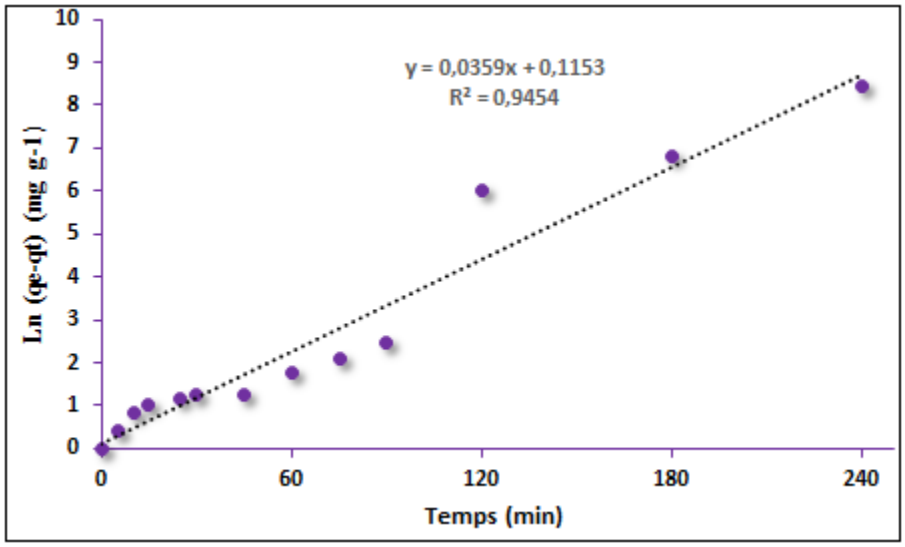


Figure III.20: Pseudo-first-order linearization for the adsorption of CV by biochar/MnO_2/Zn.

Based on the time-dependent trend of ln (Q_e–Q_t), the data points do not lie on a straight line. This clearly shows that the adsorption kinetics of CV on the three adsorbents do not follow a first-order model.

Table III.3: Results of applying the pseudo-first-order kinetic model to the adsorption of Crystal Violet

Adsorbent	Biochar	Biochar/MnO_2	Biochar/MnO_2/Zn
K1 (mgg min^{-1})	0,038	0,021	0.023
R^2	0.963	0,9576	0,9454

III.6.2. Pseudo-second-order model

The pseudo-second-order equation is often used successfully to describe the kinetics of the reaction by which pollutants bind to the adsorbent.

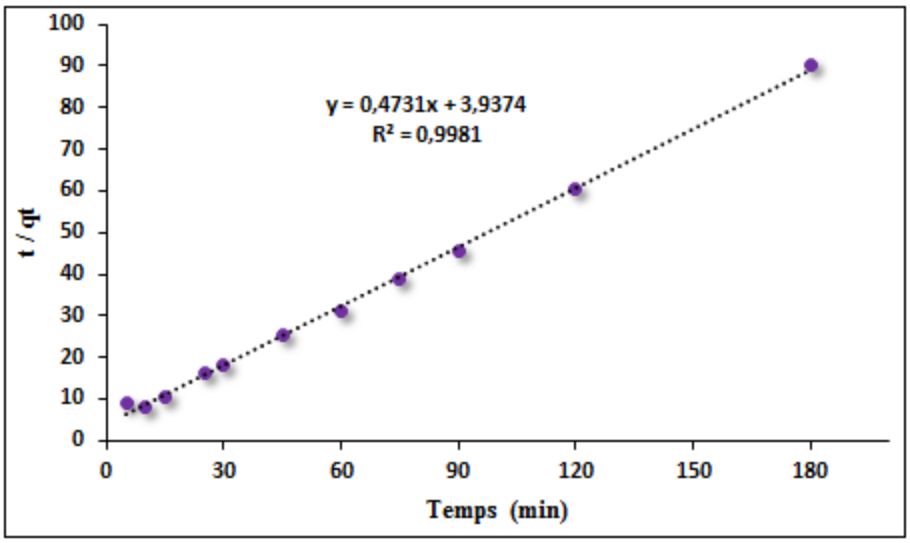


Figure III.21: Pseudo-second-order kinetics of CV adsorption on biochar

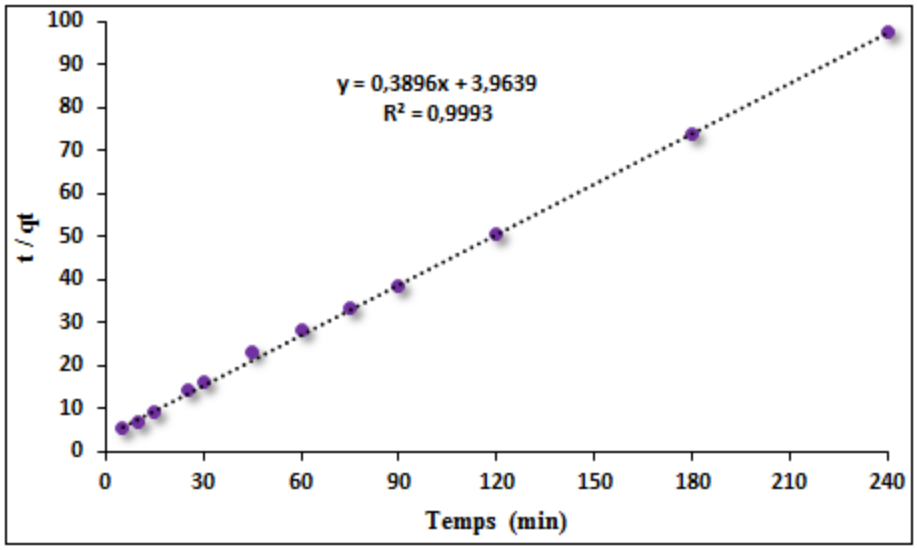


Figure III.22: Pseudo-second-order kinetics of CV adsorption on Biochar/MnO_2

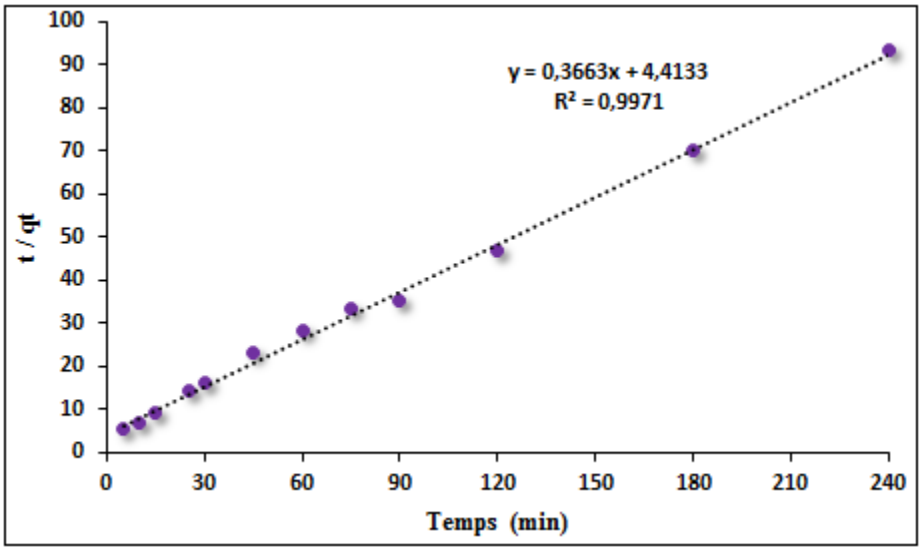


Figure III.23: Pseudo-second-order kinetics of CV adsorption on Biochar/MnO_2/Zn

Table III.4: Results of applying the pseudo-second-order kinetic model to the adsorption of Crystal Violet

Adsorbent	**Biochar**	**Biochar/MnO_2**	**Biochar/MnO_2/Zn**
K(mgg min^{-1})	0,032	0,026	0.030
R^2	0.9981	0,9993	0,9971

All of the kinetic parameters obtained are presented in **Tables III.3** and **III.4.** Analysis of the results reveals that the coefficients of determination (R^2) associated with the pseudo-second-order model are consistently higher and closer to unity than those obtained with the pseudo-first-order model. Furthermore, the equilibrium adsorption capacity values calculated by this model are generally closer to the experimental values. These observations indicate that the pseudo-second-order model more accurately describes the adsorption kinetics of crystal violet (CV) on the three biomaterials studied, consistent with the work of Ho and McKay **[101].**

These results suggest that the adsorption mechanism of crystal violet is primarily governed by a chemisorption process involving specific interactions between the functional groups present on the surface of the biomaterials and the dye molecules. This mechanism may involve electron exchange or sharing, as well as the formation of chemical bonds on the surface of the adsorbent **[100].**

The results obtained are consistent with those reported in the literature regarding the adsorption of cationic dyes on various biosorbents and carbon-based materials. Several authors have shown that the pseudo-second-order kinetic model generally provides the best fit to experimental data, indicating a strong role for adsorbent–adsorbate interactions in the adsorption process **[102,103].**

III.6.3. Linear Model of Intraparticle Diffusion (DIP)

To gain a deeper understanding of the adsorption mechanism, the intra-particle diffusion model was applied to identify the steps likely to control the adsorption rate of crystal violet (CV)on the various biomaterials studied: biochar, biochar/MnO_2, and biochar/MnO_2/Zn.

Figure III.24 shows the variation of the adsorbed amount (qt) as a function of the square root of time (t1/2). Analysis of this graph allows for the evaluation of the characteristic parameters of the intra-particle diffusion model. The intraparticle diffusion constant (K dif) is determined from the slope of the resulting line, while the constant C, corresponding to the y-intercept, provides information on the thickness of the boundary layer and the influence of external diffusion in the adsorption process. Since the R^2 values

of the IPD model are significantly lower than those of the pseudo-second-order model, intraparticle diffusion is not the controlling step — chemisorption dominates the adsorption process.

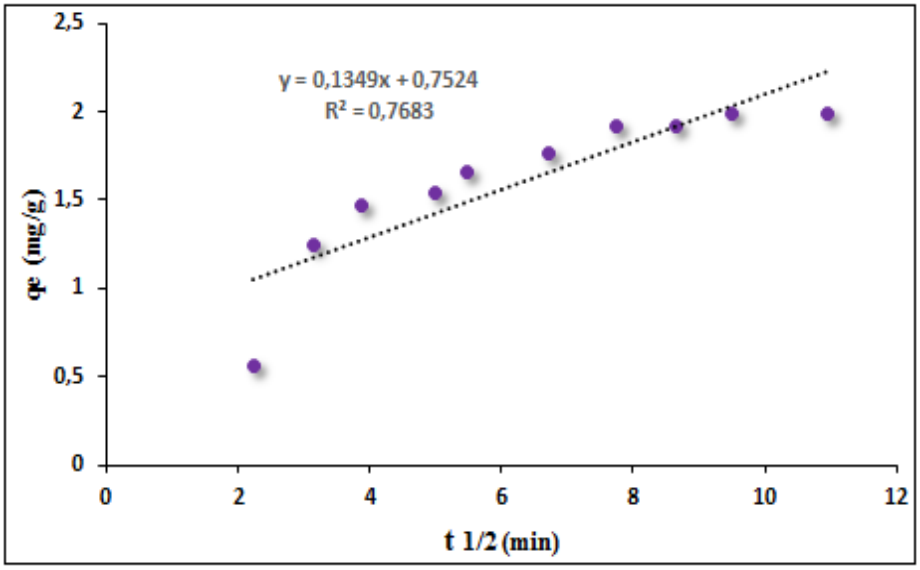


Figure III.24: Adsorption kinetics of CV dye by biochar**.**

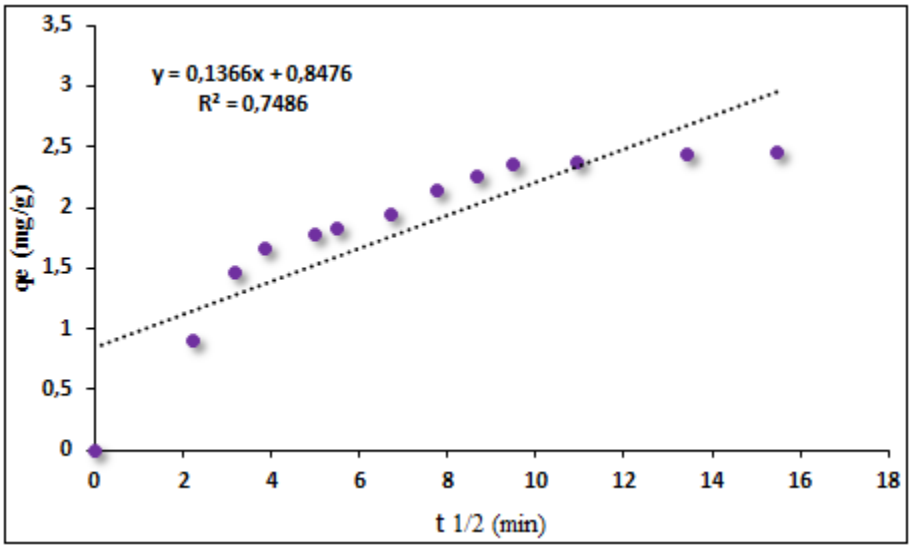


Figure III.25: Adsorption kinetics of CV dye by Biochar/MnO_2.

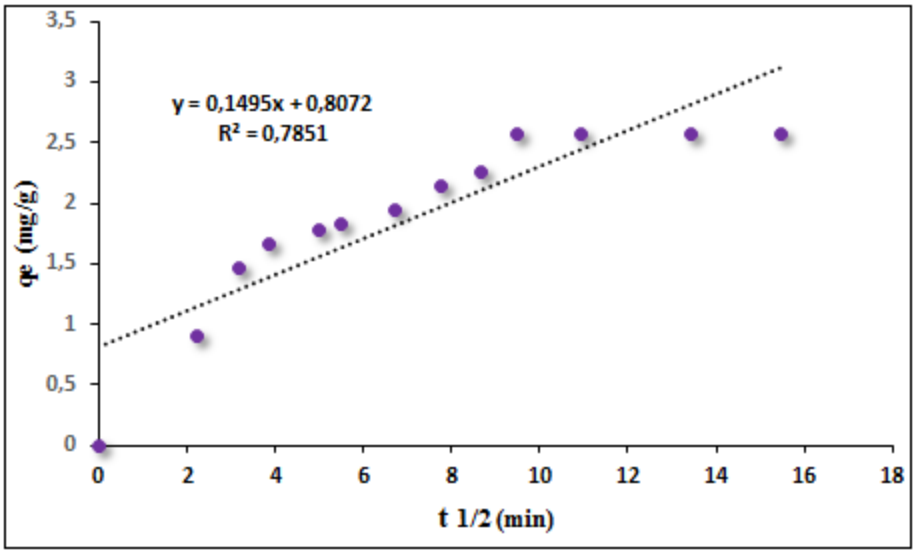


Figure III.26: Adsorption kinetics of CV dye by Biochar/MnO_2/Zn.

The calculated parameters of the DIP model are listed in **Table III.5**

Adsorbent	Biochar	Biochar/MnO_2	Biochar/MnO_2/Zn
Kid	0,134	0,118	0.224
C ($mg \cdot g^{-1}$)	0.7524	0.62	0.684
R^2	0.7683	0,7486	0,7851

The Weber-Morris intraparticle diffusion model was used to study the transport mechanisms involved in the adsorption process **[104].** According to this model, when the plot of the adsorbed amount versus the square root of time yields a straight line passing through the origin, intraparticle diffusion is the rate-determining step in the adsorption kinetics. Conversely, if the resulting line does not pass through the origin, this indicates that this phenomenon plays a role in the adsorption mechanism without, however, solely controlling the overall rate of the process. Furthermore, the presence of multiple linear segments generally indicates the existence of different successive stages, including rapid adsorption at the external surface of the adsorbent, followed by gradual diffusion of the solute within the pores, and then a slower phase corresponding to the migration of molecules toward the least accessible sites until equilibrium is established.

III.7. Conclusion

The study demonstrated that all three adsorbents exhibit good capacity for removing crystal violet, with improved performance following modification of the biochar with MnO_2 and then Zn. The results obtained highlighted the influence of various experimental parameters on the adsorption process and identified the most favorable conditions. Analysis of the kinetic models and isotherms also contributed to a better understanding of the adsorption mechanism and the role of modifications made to the surface of the adsorbents.

Conclusion

Conclusion general

This study focused on the removal of crystal violet from aqueous solution via adsorption onto three materials derived from pomegranate residues: a biochar produced from pomegranate peels, a biochar/MnO_2 composite, and a biochar/MnO_2/Zn composite. The objective was to repurpose this plant waste to develop effective and inexpensive adsorbents for the treatment of water contaminated with dyes.

The results showed that all three adsorbents are capable of removing crystal violet, with varying efficiencies depending on the operating conditions. Adsorption was strongly influenced by the solution's pH, contact time, adsorbent mass, and initial dye concentration. An increase in pH promoted the removal of crystal violet, while an increase in adsorbent mass improved the yield due to the availability of a greater number of active sites.

The kinetic study revealed that adsorption is rapid at the start of the experiment and then gradually slows down until equilibrium is reached. The experimental data were best described by the pseudo-second-order kinetic model, indicating that interactions between dye molecules and the active sites of the adsorbents play an important role in the adsorption mechanism. The results thus suggest a significant contribution of chemisorption phenomena during the process.

The analysis of isotherms showed that the Langmuir model best fits the experimental results, indicating that adsorption occurs primarily as a monolayer on relatively homogeneous sites. The adsorption capacities obtained confirm the value of modifying biochar to improve its performance.

A comparison of the prepared materials revealed the beneficial effect of incorporating MnO_2 followed by Zn. The biochar/MnO_2/Zn composite exhibited the best adsorption performance, followed by the biochar/MnO_2 composite and then raw biochar. This improvement is attributed to the increase in surface area and the number of sites available for the binding of crystal violet.

One of the key aspects of this study is the full utilization of the pomegranate plant. Pomegranate peels were used to produce biochar. This approach is part of an effort to valorize agricultural waste and develop more environmentally friendly materials.

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