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Preparing biochar from prickly pear waste and using it to remove cationic dyes

تحضير الفحم الحيوي من مخلفات التين الشوكي واستخدامه في إزالة الأصبغة الكاتيونية.

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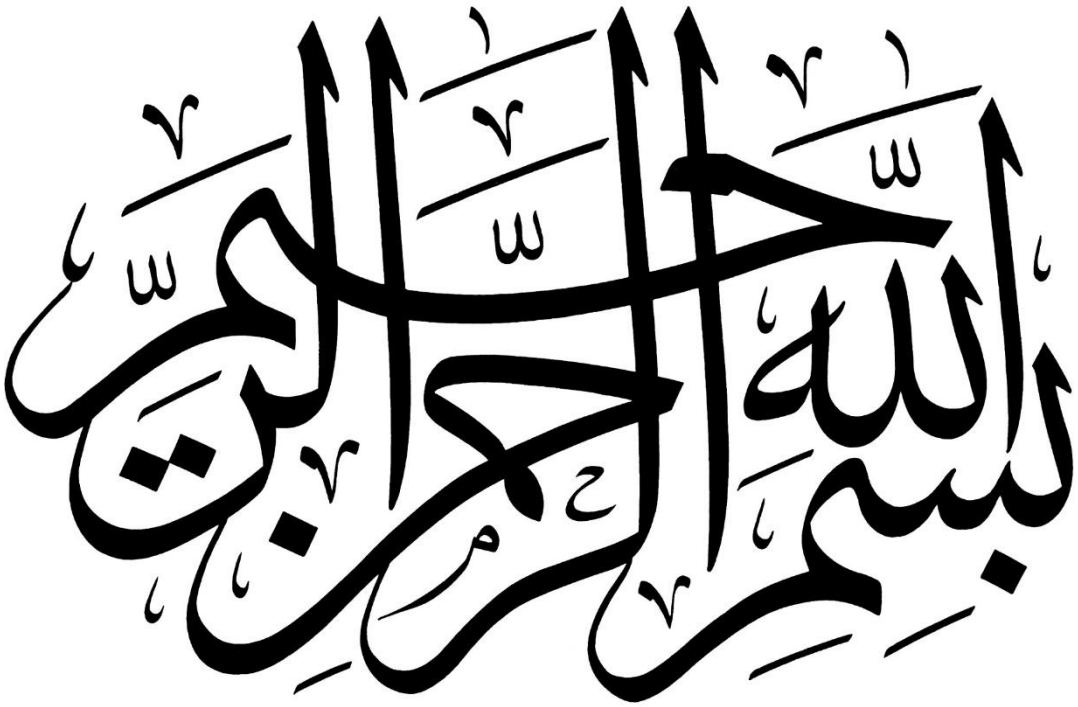
بسم الله الرحمن الرحيم

Thanks, and appreciation

In accordance with the Almighty's saying,

" فاذكروني أذكركم واشكروا لي ولا تكفرون "

We thank God Almighty for granting us knowledge that we did not know and giving us enough strength and ability to complete this humble work.

And in full thanks to Him, the Almighty, we thank the people of virtue for their virtue and their efforts, and we acknowledge their right, according to what he, may God's prayers and peace be upon him, said: "Whoever does not thank people does not thank God."

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Dedication

Praise be to God, by whose grace good deeds are accomplished, and prayers and peace be upon the most honourable Messenger, and after:

After an academic journey that lasted for years, here I am today, standing on the threshold of my graduation, reaping the fruits of my labour, and raising my hat with pride. Praise be to God out of love, thanks, and gratitude. I would not have done this without God's grace, so praise be to God for the beginning and the end.

With love, I dedicate the fruits of my efforts:

To the candle that burned to light my path and to my support in life, my dear father, may God protect and protect him.

To the one who decorated my life with the light of the full moon, to the one who gave me strength and determination, my dear mother, may God protect her and bless her life.

To those who are the beginning of the past, the help of the present, and the support of the future, my brothers and sisters, may God protect them.

To everyone who was patient with me and encouraged me to complete this work, to those with whom life brought me together and with whom we shared its sweet and bitter, my sisters in God, my friends, and my companions.

To all those whom my pen forgot and my heart did not forget:.

Hanifa Fethiza Ali

Dedication

Praise be to God. There is a lot of praise. Praise be to God until the praise reaches its limit. My God, who does not have the night pleasant except with thanksgiving to you, the day is not pleasant except with your obedience, and heaven is not pleasant except with seeing you (God Almighty),.

To the one who conveyed the message, fulfilled the trust, and advised the nation (our master and beloved Muhammad, may God's prayers be upon him).

By the grace of God, days passed and years passed while I was building my dream, and here are my days towards glory, which is the day I wished for and worked hard for, which is the day of my graduation.

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To the one who put heaven under her feet, to my angel in life, to the one who spent her life in order to see me in splendour, health, and well-being, to the one whose prayers were the secret of my success, to my beloved mother, may God bless her, protect her, and prolong her life.

To you, I pray:

"وقل ربي ارحمهما كما ربياني صغيرا"سورة الاسراء الآية 24

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The term is in English	The term is in Arabic	Symbols
Cristal violet	البنفسج البلوري	CV
Gibbs standard free energy variable	التغير في الطاقة الحرة لجيبس	$\Delta G°$
Enthalpy	التغير في المحتوى الحراري	$\Delta H°$
Entropy	التغير في الأنتروبي	$\Delta S°$
Quantity adsorbed in equilibrium	سعة الامتزاز عند التوازن (mg /g)	Q_e
Maximum quantity adsorbed	سعة الامتزازالعظمى (mg/g)	Q
Equilibrium (final) concentration in solution	تركيز المادة الممتزة عند الاتزان	C_e
The Langmuir constant related to adsorption	ثابت التوازن ل langmuir التجريبي	K_L
Freundlich's constant related to adsorption	ثابت فراندليش	K_f
Adsorption rate constants for the pseudo first order	ثابت الحركية من الرتبة شبه الأولى(min^{-1})	K_1
Adsorption rate constants for the pseudo second order	ثابت السرعة الحركية الرتبة شبه الثانية(mg/g.min)	K_2
Fourier Transform Infrared	الأشعة تحت الحمراء بتحويل فورييه	FTIR
Ultraviolet-visible spectroscopy	مطيافية الضوء المرئي وفوق البنفسجي	UV
Scanning electron microscopy	المجهر الإكتروني الماسح	MEB
Box Behnken Design	/	BBD
Response Surface Methodology	منهجية استجابة السطح	RSM

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Abstract

This work aims to study the viability of biochar prepared from prickly pear waste from the Tebessa region and use it as an adsorbent to get rid of dyes and organic pollutants in aqueous solutions. In the first stage, we activated the biochar in order to increase the size of its pores and expand them. We used crystal violet dye as an example of a pollutant while studying its physicochemical properties, which were carried out by experimental analyses using a scanning electron microscope and infrared Fourier transform and by means of a surface response methodology programme we studied. We discussed the effect of factors on the adsorption phenomenon, including temperature, mass, concentration, contact time, and pH. The results obtained show that the best yield is 99.38 percent in removing crystal violet dye when these ideal conditions are achieved (mass 0.02 grammes, temperature 40 degrees Celsius, time 17.5 minutes).

Keywords: biochar, activation, crystal violet dye, adsorption mechanism, and surface response methodology.

الملخص

يهدف هذا العمل دارسة قابلية الفحم الحيوي المحضر من مخلفات التين الشوكي من منطقة تبسة، واستعماله كمادة مازة للتخلص من الأصباغ والملوثات العضوية في المحاليل المائية. في المرحلة الأولى قمنا بعملية تنشيط الفحم الحيوي من أجل زيادة حجم مساماته وتوسيعها، و استعملنا صبغة البنفسج البلوري كمثال من الملوثات مع دراسة الخصائص الفزيوكيميائية لها التي تمت بواسطة التحاليل التجريبية: المجهر الإلكتروني الماسح و الأشعة تحت الحمراء بتحويل فوريه ، وبواسطة برنامج منهجية استجابة السطح درسنا وناقشنا تأثير العوامل على ظاهرة الامتزاز منها درجة الحرارة،الكتلة،التركيز، زمن التماس ،ودرجة الحموضة. تظهر النتائج المتحصل عليها أن أفضل مردود 99.38 بالمئة في إزالة صبغة البنفسج البلوري عند تحقيق هذه الظروف المثالية (الكتلة 0.02غرام، درجة الحرارة 40 درجة مئوية، الزمن 17.5دقيقة).

الكلمات المفتاحية: الفحم الحيوي،التنشيط، صبغة البنفسج البلوري،آلية الامتزاز، ومنهجية استجابة السطح.

General Introduction

Pollution is one of the major problems facing humans and the environment, especially after the technological development accompanying contemporary life. Pollution occurs in its various forms, whether it is air, water, or soil pollution, as a result of the presence of some harmful organic and inorganic substances or because of an increase or decrease in the proportions of some basic components in the environment above the proportions. This occurs as a result of human interventions or due to some natural phenomena [1]. Among the types of pollution, we find water pollution in multiple forms, such as poisoning with organic waste, detergents, pesticides, pollution resulting from petroleum materials, and others [2]. Dyes are among the main pollutants found in industrial effluents that cause significant water pollution. Dyes are among the pollutants widely used in the textile industry. Their extensive use generates coloured wastewater, which leads to environmental pollution [3]. Moreover, many toxic dyes and their persistent properties make them non-degradable in the environment, and their presence in water reduces the penetration of light and is therefore undesirable [4]. Water pollution with dyes is considered a serious problem due to its toxic effects on human health and living organisms. It is known that industrial water waste resulting from textile and dyeing factories contains an amount of dyes, which are considered organic pollutants, which in turn cause great harm to the environment by being thrown into river water without processes. Processing poses a great danger to living organisms in general, and among these circulating dyes that pollute the environment and the ocean is “crystal violet [5].

Efforts to remove organic dyes from water have been extensive so far. Compared with traditional methods (flocculation-precipitation, photocatalysis, oxidation-reduction, solvent extraction, and electrochemical reaction), [6] adsorption methods are effective, economical, and friendly. According to the Web of Science database, it is considered the best way to treat water due to its low cost, high efficiency, and simple operation. However, the choice of adsorbent depends on economic and practical reasons [7]. Adsorption of activated carbon is the most widely used process because it has the ability to process treatment processes. It removes organic pollutants, pesticides, dyes, and heavy metals. In recent years, many researchers have been interested in studying the manufacture of activated carbon from natural waste, especially from locally available and low-cost plant and food waste, such as walnut and almond shells, rice hulls, seeds, fruit pits (apricots, peaches, cherries, olives, and date pits).

This is what we will address in our research by conducting a statistical study on the valorization of prickly pear waste by converting it into activated carbon because it has a high adsorption property. It is a widely used technology that is recommended for treating environmental pollution. However, the high cost of some adsorbents is often an obstacle to

applying this process. However, the adsorption property of activated carbon has a high ability to remove organic and inorganic compounds, in addition to the possibility of renewing this porous adsorbent material. It is suitable for fighting pollution by upgrading plant waste and making optimal use of it [8].

In order to complete this study, this memorandum was divided into two theoretical and applied parts, preceded by a general introduction and followed by a conclusion that includes some recommendations.

The theoretical part:

Chapter One: Generalities about Adsorption.

Chapter Two: Generalities about Pollution and Organic Dyes.

Applied part:

Chapter One: Methods and Devices Used.

Chapter Two: Presentation and Discussion of the Results.

Finally, this study aims to preserve the precious wealth that is the basis of life, which is water, which deteriorates over time with various types of pollutants. Valuing plant waste and exploiting it to produce activated carbon to get rid of pollution.

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The theoretical part

Chapter One: Generalities about adsorption

I. Adsorption:

I.1. Definition of adsorption :

It is the process of adhesion or aggregation of a liquid or gaseous adsorbed substance on the surface of a solid substance. An adsorbent substance is the result of the physical or chemical association of a number of molecules with active sites on a solid substance's surface. This process produces a layer or several layers of molecules or atoms that accumulate and are densely concentrated. On the surface of the solid. The degree of adsorption depends on the relationship between the nature and size of the adsorbed material [1].

I.2. Importance of Adsorption :

Due to the great importance of adsorption, especially in recent years, which has made some industries indispensable with it, it is used in several fields, including petroleum industries, dyes, food industries such as oils, dairy, and others [2]. It is also used in purifying various industrial waters and wastewater in order to remove any trace of polluting materials that are highly dangerous and toxic to the environment, as well as treating the colour, taste, and smell resulting from pollution [3].

I.3. Adsorption types:

Many studies have indicated that the adsorption process can be divided into two types. When the adsorbent material approaches the adsorbent surface, the adsorption process takes place depending on the nature of the adsorbent material and the adsorbent surface, as well as the temperature of the adsorption process. If the connection between molecules occurs with weak bonds represented by Vander Waals forces, it is called physical adsorption, and if the connection between molecules occurs with strong chemical forces, it is called chemical adsorption [4].

I.3.1. Physical adsorption:

Physical or natural adsorption (physisorption) [5–6] This type is also called Vander Waals adsorption [7], and it is a result of a result of weak physical forces or natural attractive forces that occur between the adsorbing surface and the atoms or ions that are adsorbed on the surface, which are inert due to the electronic saturation of the atoms as a result of the bonds that these atoms bind with the molecules or ions that are adsorbed by forming several partial layers on the adsorption surface [8].

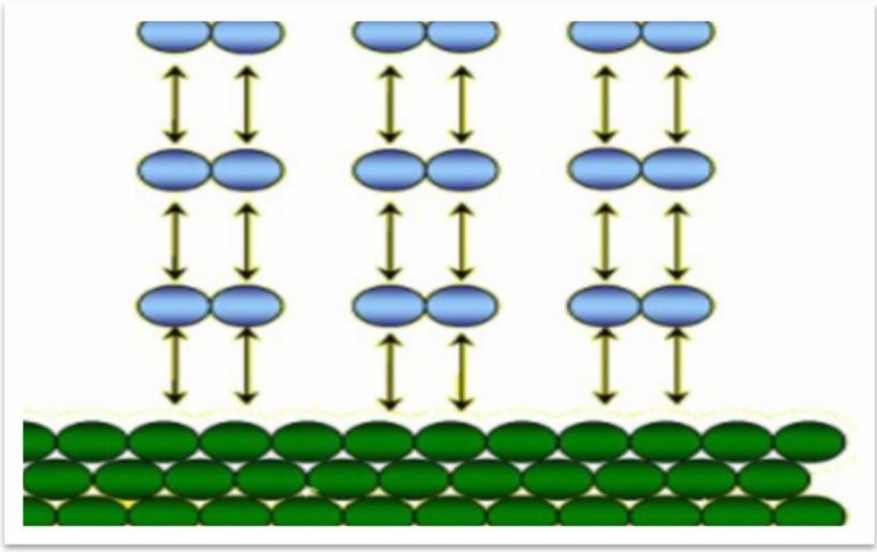

Figure (I-1): Physical adsorption diagram [9].

I.3.2. Chemical adsorption:

It is called chemical adsorption (chemisorption) because its surfaces tend to form covalent, chemical, ionic, or coordination bonds, or a mixture of them, with the molecules, atoms, and ions of the substance being adsorbed [10]. This type of adsorption is the first step of the chemical reaction, so it requires energy. In high activation, where chemical bonds are formed between the adsorbed molecules and the adsorbent surface, changes occur in the molecular structure and energy is released, estimated at between 200 and 40 mol/kg [11-12].

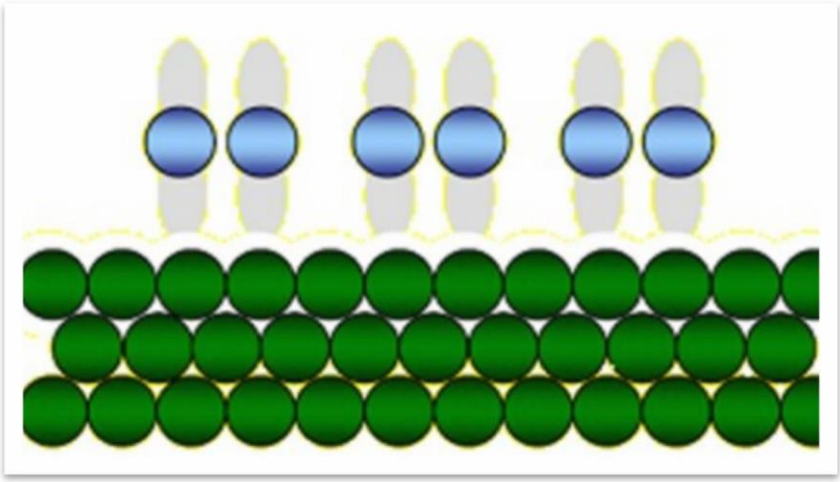

Figure (2-I): Chemical adsorption [13].

In studying adsorption, regardless of its application, the nature of this adsorption must be known, whether it is physical or chemical adsorption, or in some cases, both. The table below summarises the difference between the two types of adsorption.

Table (I-1): Comparison between physical adsorption and chemical adsorption [14] [15] [16] [17] [11].

Chemical adsorption	Physical adsorption	Properties
chemical bonds	Vander Waals bonds	The nature of bonds
One layer is formed on the surface	Several layers are formed on the surface	Number of layers formed
A selective process	a non-selective process.	Privacy
Slow reverse	fast reverse	Adsorption kinetics
More than 10Kcal/mol	less than 10Kcal/mol	The heat of adsorption
difficult	easy	Adsorption
strong	weak	The applied energy
ΔH°	low compared to the boiling point of the adsorbent	The process temperature
Needs activation	Does not require activation	Activation energy

I.4. Adsorption mechanism:

Adsorption occurs mainly in four steps. The figure represents the adsorbents in the different regions in which organic or inorganic molecules can be found that are likely to interact with the solid [18–19].

- The first step is the spread of the adsorbent from the external liquid phase to the area near the surface of the adsorbent (a very fast stage).
- The second step is the external diffusion of the material particles, that is, the movement of the adsorbed material through a liquid membrane sieve towards the surface of the adsorbent material (fast phase).
- The third step is the internal transfer of the granules from the materials, that is, the transfer of the material inside the porous structure of the outer surface of the granules towards the active sites (slow stage).
- Step Four: In contact with the activated sites (very fast stage).

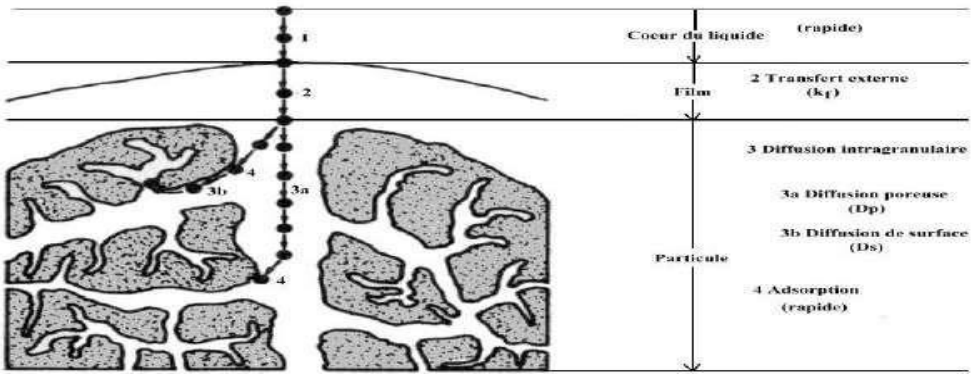

Figure (I-3): Mechanism of solute adsorption on a solid [19].

I.5. Factors affecting adsorption :

Adsorption has several factors that affect it, including [20] and [21].

❖ **Factors specific to adsorbents:**

- **Specific surface area:** It is the surface area of the adsorbent per unit mass and is expressed as (m^2/g). The relationship between the specific surface and the adsorption capacity is a direct relationship; that is, when the specific surface is large, the amount of adsorbed solute is large.
- **Porosity:** It is related to the pore size distribution and reflects the internal structure of the fine adsorbents.
- **Polarity:** The most important characteristic of the adsorbent in terms of its effect on the adsorption process is the polarity of the surface, as surfaces that contain polar groups tend towards the more polar components in the solution.

❖ **Factors related to adsorbents:**

- **Solubility:** The adsorption value is inversely proportional to the solubility of the adsorbed substance in the solvent, according to Lundenius' rule.
- **Polarity:** A polar solute (adsorbent) is more familiar to the solvent or to the more polar adsorbent.
- **Molecular mass:** In general, increasing the molecular mass of the adsorbent leads to an increase in adsorption capacity.

❖ **Factors related to the physicochemical properties of the solution:**

• **Effect of temperature:** Temperature affects the rate of adsorption at which adsorption occurs, as the rate of adsorption increases with increasing temperature and decreases when it decreases. Despite this, it is considered an exothermic process.

• **Effect of pH**: Changing the acidity of the solution plays a major role in the adsorption

process. This occurs due to the effect of pH on the adsorbent, the adsorbent surface, and the solvent. This effect appears through the competition of the adsorbent, the adsorbent, and the solvent for the (-OH) and (H+) ions as a result. It has a positive or negative effect on the adsorption process.

• **Contact time between the adsorbent and the adsorbent:** This is known as the equilibrium time, which is the time during which equilibrium occurs between the adsorbent and the adsorbent.

I.6. Adsorption isotherm:

isotherm is a relationship between two variables in a process or reaction when the temperature is constant, such as the change in pressure of a gas with its volume at a constant temperature or the change in the amount of adsorbed gas with the pressure of the gas at a certain temperature.

This isotherm is a curve that represents the relationship between the amount of solute and its concentration in the solution. Such a curve is obtained from the results of laboratory testing at a constant temperature. To do this, known quantities of the adsorbent are introduced into the amounts of water being treated, and after a certain contact time, they are measured. Concentration of the remaining dissolved solution.

The amount of solute adsorbed in equilibrium is calculated using the equation:

$Q_e = (C_0 - C_e)\ v/m = x/m$

- **where:**

  C_0: Initial concentration of solute (l/mg).
- **Ce:** equilibrium concentration of solute (l/mg).
- **Qe:** The amount of solute adsorbed at equilibrium in the unit weight of the adsorbent (g/mg)

  x: The amount of adsorbent at equilibrium $x = (C_0 - Ce)\ v$
- **m:** mass of the adsorbent (g)
- **v:** volume of solution (l) [22].

I.7. Classification of adsorption isotherm curves:

The most reliable way to measure adsorption is as a function of the concentration or pressure of pollutant particles in the treated fluid and the amount of adsorbent, and this measurement is usually given at a constant temperature.

Experimentally, the measurement is either the amount of material consumed by the remaining amount or the change in mass of the adsorbent at the end of adsorption.

In 1937, Brunner-Emmett-Wittlar (B.E.T.) proposed five classes of adsorption isotherms, which were adopted by the International Union of Pure and Applied Chemistry (I.U.P.A.C.). This organisation proposed the sixth class [23], as shown in the figure.

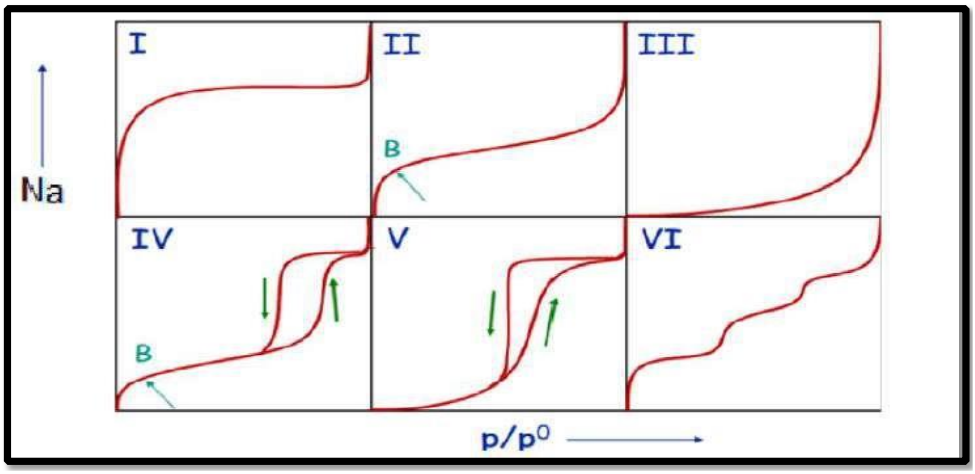

Figure (I-4): Types of adsorption isotherms approved by I.U.P.A.C. [24]

- Na: amount adsorbed.
- P^0: saturation pressure.
- P: gas pressure.
- B: adsorbed point [24]

❖ **Class I:**

It represents monolayer adsorption (monocouche) on the adsorbent, whether physical or chemical, where the solid material, i.e., the adsorbent, is poreless or has micropores with a diameter of about or less than 5 A°. In this case, the pores have the same dimensions as the adsorbed molecules.

❖ **Class II:**

This adsorption is single-layer, which leads to multi-layer adsorption at high pressures, while the isotarms of classes I, III, and II are irreversible, meaning the adsorption phenomenon does not occur.

Above the distinct point "B," which represents the point of inflection of the curve,. In this adsorption, the solid has pores with a diameter larger than A°200 [25].

❖ **Class III:**

This type of adsorption is multilayer (multicouche), as the behaviour of this type is rare when compared to other types.

The adsorption of H_2O on graphitic carbon or polyethylene shows behaviour consistent with type III. The adsorption phenomenon does not occur in classes III, II, and I.

❖ **Class IV:**

In this type, the solid has pores of 2–5 nm. Industrial materials and catalysts often exhibit this type of behaviour.

❖ **Class V:**

This type is multi-layered and rarely occurs.

❖ **Class VI:**

It represents several single adsorptions.

I.8. Adsorption isotherm models :

Mathematical or experimental modelling is based on hypotheses that cannot be verified but allows obtaining a number of qualitative and quantitative information such as the type of reaction (single or multilayer adsorption mechanism, adsorption sites, etc.), saturation phenomenon (maximum number of adsorbed pollutants, behaviour of the sites active, etc.), or heat of adsorption (thermodynamic values).

There are many cited models that have been established theoretically or experimentally by many researchers, and the most widely used are the Langmuir and Freundlich models [26].

I. 8. 1.Langmuir adsorption isotherm:

The Langmuir model assumes that adsorption occurs in a single layer on the solid surface with identical homogeneous sites and indicates that no further adsorption occurs once the active sites are covered by molecules. The saturated isotherm of the monolayer is given by the following equation:

$$q_e = \frac{q_m k_l C_e}{1+k_l C_e} \text{.....(1)}$$

– **where**

Ce: Adsorbent concentration in solution at equilibrium (mg/L)

– the amount adsorbed at equilibrium (mg/L)

– **q_m:** maximum adsorption capacity (mg/L)

– **K_l :** is a Langmuir constant related to the adsorption energy and capacity (L/mg).

– The linear equation of the Langmuir model is given as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m k_l} + \frac{C_e}{q_e} \quad \text{.. .....(2)}$$

One of the characteristics of the Langmuir model is the calculation of the equilibrium coefficient, or the dimensionless constant KL, which provides information about the adsorption capacity and is calculated with the following relationship:

$$R_L = \frac{1}{1+K_L C_0} \text{.....(3)}$$

where:

C_0: Initial concentration of the adsorbent in the solution (mg/L). Adsorption is suitable if the R_L value is less than one, while it is unsuitable if the RL value is greater than one.

I. 8. 2. Freundlich isotherm:

The Freundlich model is an empirical equation that represents multilayer adsorption on a heterogeneous surface with multiple binding sites. Its equation is given by the following relationship.

$$q_e = k_F C_e^{\frac{1}{n}} \text{.....(4)}$$

Where K_F is the Freundlich constant (mg/g(L/mg)1/n) and 1/n: expresses the intensity of adsorption.

The linear equation of the Freundlich model is given as follows:

$$Log\ q_e = Log\ k_F + \frac{1}{n} Log\ C_e \text{ ... ... (5)} \quad [27]$$

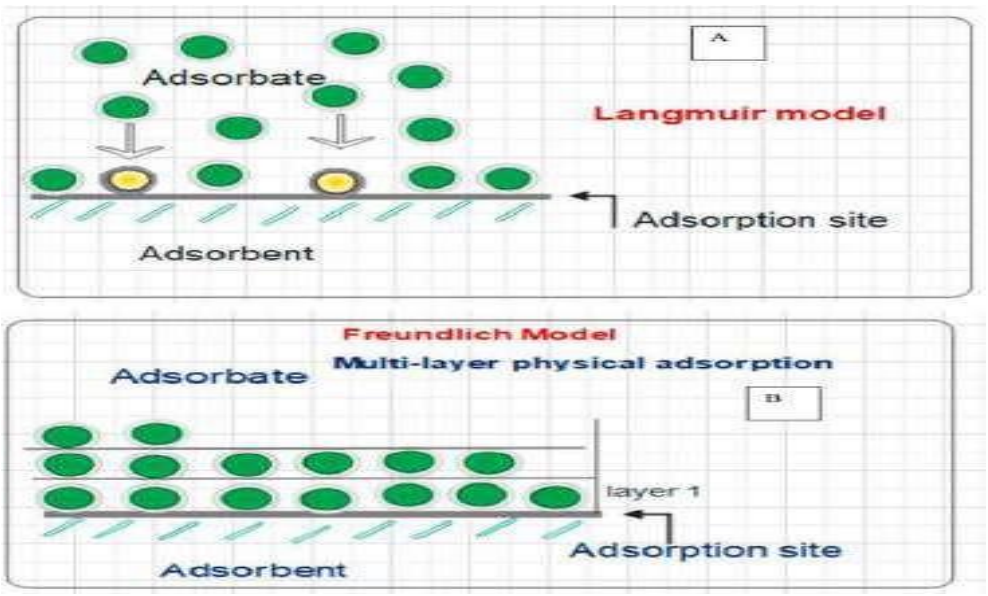

Figure (I-5): Single and multilayer adsorption [28].

I.3.8. Temkin isotherm:

The Temkin isotherm is considered a model in which the heat of adsorption of molecules in the layer is transferred linearly with the coating due to interactions between the adsorbent and the adsorbent surface. Its linear equation is given by the following relationship:

$$q_e = \frac{RT}{b_T} \ln k_T + \frac{RT}{b_T} \ln Ce \quad \text{..... .(6)}$$

where:

- k_T: equilibrium binding constant (L/g).
- b_T: Timkin constant related to the heat of adsorption (J/mol).

I.9. Adsorption kinetics:

Several kinetic models can be used to express the velocity constants of the solute on steel.

I. 9. 1. Pseudo-first-order kinetic model:

The scientist Lagergren proposed a pseudo-first-order kinetic model:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \text{.....(7)}$$

Integrating this equation gives us:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \text{. . . . . (8)}$$

where:

- K_1: velocity constant for pseudo-first-order motion (min-1).
- t: Adsorption time (min).
- q_t: adsorption capacity at moment t in mg/g.
- q_e: Adsorption capacity at equilibrium (mg/g).

I.2.9. Pseudo-second-order kinetic model:

The rate of a pseudo-second-order reaction is related to the amount adsorbed on the adsorbent surface and the amount adsorbed at equilibrium.

Pseudo-second-order kinetics is written by:

$$\frac{d_q}{d_t} = k_2(q_e - q_t)^2 \text{ .....(9)}$$

Integrating this equation gives us:

$$\frac{t}{q_t} = \left(\frac{1}{q_e}\right) t + \frac{1}{k_2 q_e} \quad \text{..... (10)}$$

- where:

  K_2: the velocity constant for pseudo-second-order motion ($g.mg^{-1}.min^{-1}$).

- q_t: adsorption capacity at moment t in units of mg/g.
- q_e: adsorption capacity at equilibrium (mg/g).

I.10. Thermodynamic study:

Thermodynamic quantities reflect the feasibility and spontaneous nature of the adsorption process. These quantities, represented by free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), can be calculated using equilibrium constants varying with temperature, and the relationship to the equilibrium constant Ke is given as follows:

$$K_d = \frac{C_{Ae}}{c_e} \text{.....(11)}$$

C_{Ae} and C_e, respectively, represent the concentration adsorbed in the solution at equilibrium (mg/L) and the amount adsorbed on the adsorbent surface per litre of solution (mg/L). The thermodynamic quantities are calculated using the following relationships: [27]

$$\Delta G° = -RT \ln k_d \text{ .....(12)}$$

$$\Delta G° = \Delta H° - T\Delta S° \text{ ..... (13)}$$

$$\ln k_d = \left(\frac{\Delta S°}{R}\right) - \left(\frac{\Delta H°}{RT}\right) \text{.....(14)}$$

I.11. Adsorption applications:

- Industrial applications of the adsorption process:
- In the field of liquid purification:
- Removal of sulphur compounds from organic solutions
- Removal of H_2O from organic solutions
- Removal of organic compounds from H_2O
- In the field of gas purification:
- removal of organic materials from air currents.
- removing water vapour from the air and other gaseous vapours.
- removal of CO_2 from natural gas.
- Remove SO_2.
- Removal of sulphur compounds from gaseous compounds [29].

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- Chapter Two: Generalities about pollution and organic dyes.

Chapter II: Generalities about pollution:

II. Generalities about pollution:

Water is considered the basis of life, and through the course of time, it has been found that water pollution in urban and rural areas is due to domestic and industrial wastes that are disposed of by throwing them into rivers, seas, and lakes. The latter include dissolved organic and inorganic substances such as carbohydrates, organic and mineral acids, industrial detergents, and dyes. Also microorganisms such as bacteria, algae, and parasites [1]. The presence of one of these substances in water, even in low quantities, causes problems in the environment and food and harms humans and living organisms. Therefore, it is necessary to decontaminate water contaminated with these chemical compounds to protect the environment [2].

II.1. Definition of pollution:

Pollution is defined as one of the changes, whether physical, chemical, or biological, that affects the environment and living organisms negatively, such that ecosystems are unable to absorb it [3]. The capacity of these environmental systems is greatly affected by quantitative or qualitative changes in their elements, which leads to disruption in them [4]. There are many types of pollution, including air pollution, which is the pollution of the atmosphere with toxic gases and chemicals such as carbon dioxide, which is often the result of industrial development, and soil pollution, which means changing some of the properties of the soil due to chemicals. There is also pollution that touches water, known as water pollution [5].

II.1.1. The concept of water pollution:

The World Health Organisation defined polluted water in 1961 AD as "any change that occurs in the natural, chemical, and biological characteristics of water, which leads to a change in its condition, directly or indirectly, such that the water becomes less suitable for the natural uses intended for it, whether for drinking, domestic consumption, or agricultural or other [6].

It is also known as causing damage or corruption to the quality of water, which leads to a defect in its interfacial system, reducing its ability to perform its natural role and making it unsuitable for use by humans, animals, plants, or organisms that live in the German flats, meaning that they lose a lot of water. Its economic value is [7–8].

II. 1. 2.Types and cases of water pollution

1.Physical pollution:

- Thermal pollution:

This type of pollution results from the use of water for cooling in factories, water desalination plants, and electric power generation plants. Throwing this hot water into lakes, rivers, and waterways leads to an increase in the water temperature, causing an imbalance in the environment and causing damage to animal and plant life [9–10].

- Radioactive contamination:

This type of pollution results from the radioactivity of radioactive materials from various mines, industrial waste, and nuclear explosions. Nuclear and atomic plants, scientific research centres, hospitals, electrical industries, and generators that run on coal or petroleum are the most important sources of this pollution. Naturally, surface water may contain elements that are radioactive, such as radium and uranium [11–12]. This pollution is also represented by the leakage of radioactive materials into the water, and these materials are transmitted to living organisms and plants, eventually reaching the human food chain and inflicting serious harm on them. The danger of this pollution lies in whether it is in the water, air, or soil [13].

2. Chemical pollution:

- Industrial pollution:

This type of pollution occurs as a result of industrial facilities disposing of their waste and by-products without treatment into waterways and thus poses a real danger to all elements of the environment because they contain toxic chemical compounds. What makes them more dangerous is that most of them are very persistent and have a long-lasting effect [6]. Among the most important of these materials are acids, bases, dyes, industrial detergents, some phosphorus compounds, and many toxic heavy metals such as mercury and lead, which cause severe pollution of the water in which they are dumped [6-14-15].

- Pollution with pesticides and agricultural fertilisers:

  Pesticides that are used to combat agricultural pests are classified as among the most dangerous and widespread pollutants. Excessive use of them leads to soil contamination, so plants use them directly, thereby affecting herbivorous animals and from there to others, or rain washes them into waterways, harming all living organisms in them, and the latter occurs with fertilizers. Agricultural [9].

- Pollution by oil waste:

Oil is considered a source of German pollution and has a serious impact on living organisms. whether in the seas or oceans, which is represented by the destruction of aquatic plants due to the toxins they contain, which form an insulating layer that impedes the exchange of gases between air and water, in addition to the pollution of beaches, which affects human

health and tourism. This pollution also occurs due to marine accidents between giant tankers and from the waste of refineries. And ships and sediments that occur from oil wells and tanker pipelines [16].

❖ Acid rain pollution:

It is rain contaminated with acidic gases such as sulphur oxide and nitrogen oxide, which are transformed into sulphuric and nitric acid emitted by volcanoes and the burning of fuel, and from there they return to the soil and other sources of water in nature and harm all German surfaces, especially closed ones, as they work to raise their acidity, which affects living organisms. Which live inside them, and these rains cause some heavy metals to dissolve from the soil and carry them to lakes, rivers, as well as groundwater, causing damage to living organisms of all kinds, directly or indirectly [17].

❖ Pollution with organic materials:

Most of them are synthetic products resulting from human activity, including:

- polycyclic aromatic hydrocarbons.
- Polychloro-biphenyls.
- chlorinated solvents.
- Pesticide.

  Benzene derivatives.
- Phenol and its derivatives.
- Synthetic dyes[12].

❖ Biological contamination:

This is the result of wastewater being thrown into pure aquatic environments, both potable and non-potable, such as rivers and seas, which works to provide them with pathogenic bacteria and protozoa (viruses). This leads to a decrease in the percentage of oxygen in the water, the death of fish, and the rotting of the water. Algae may use this wastewater, which is rich in substances. Organic fertilisers increase their spread and density, all of which leads to water pollution [9–18].

II. 1. 3.Sources of water pollution:

There are many sources of water pollution, which can be divided into:

- Natural sources: They are represented in the atmosphere through rainwater, animal and plant waste, organic waste, sediments, mineral materials, etc.
- Agricultural sources: German soil erosion includes animal waste (from animal and poultry production farms), chemical fertilisers, and pesticides in irrigation water.
- Wastewater: It includes waste from domestic and industrial activities, animal waste, dead organic materials, chemical materials such as soap and industrial detergents, and some types of harmful bacteria and microbes, etc.
- Sources of oil and its derivatives: oil pollution of water includes the leakage of petroleum materials into water bodies, accidents, errors in various forms of exploration, extraction, and transportation operations, etc.
- Industrial sources: They include most of the materials left behind from industrial activities, including chemical, mining, manufacturing, food, etc. industries.
- Various other sources, such as construction activities, mines, groundwater, garbage collection places, cement production places, etc. [19-20-21-22].
- Civil sewage: contains organic materials (bacteria, cleaning materials) and mineral salts [18].

II. 1. 4.Water pollutants:

Pollutants are defined, according to the United Nations Environment Programme, as any physical, chemical, organic, or radioactive substance present in wastewater that reduces the quality of this water and poses a danger that prevents people from benefiting from it [19].

Substances that pollute water are divided into eight groups, each of which includes a number of components that have specific characteristics and effects on water quality and are limited to the following:

- Toxic substances: such as lead, arsenic, etc., in addition to various types of organic chemical compounds such as pesticides, detergents, fats, and oils.
- Suspended solids: dust and insoluble materials.
- radioactive materials such as uranium, radium, etc.
- Heat (the solubility of oxygen depends on temperature).
- Chemicals dissolved in water, such as salts, acids, and heavy metal ions.
- disease-causing biological materials, such as pathogenic bacteria that affect human health and cause diseases such as cholera.
- Organic nutrients such as nitrogen and phosphorus that result from adding fertilisers to agricultural lands.

- Waste that consumes vital oxygen (organic materials) [6-21-22].

II. 1. 5.Water treatment methods:

In recent years, many physicochemical techniques have been developed for the treatment and decontamination of liquid waste laden with various chemicals. Among these techniques are photocatalysis, electrokinetic coagulation, ion exchange, adsorption, and membrane filtration. All these methods have their limitations in application based on cost, design, and separation efficiency, but the adsorption method is the best and most effective for treating water pollution caused by dyes [23–24–25].

II.2. Dyes :

II. 2. 1.Introduction:

Dyes appeared more than 4,000 years ago to dye artistic pieces made at that time. Until 1850, dyes were obtained from natural elements such as plant extracts from fruits, flowers, roots, or animals.

But there are some dyes that have significant toxic effects. There are many methods used to get rid of these dyes, the most important of which are adsorption, chemical oxidation, and ozone treatment. Reverse osmosis pressure and biological methods. The use of activated carbon is considered one of the most common materials to get rid of dyes, and adsorption is considered one of the most important methods used to get rid of pollutants [26].

Figure (II-1): Illustration of commercial dyes

II.2.2. Definition of dyes:

Many dyes have been known since ancient times and were obtained from animal and plant sources. Today’s dyes are synthetic dyes prepared from aromatic organic compounds

[27].Pigments are characterised by their ability to absorb light radiation in the visible spectrum (380–750 nm) [28].

❖ ***Industrial dyes are classified according to colour intensity into two groups:***

- **Chromophore group:** It is responsible for converting white light into coloured light by the following methods (reflection, transmission, and diffusion), including: Azo (-N=N-), nitrous (N-OH or NO), carbonyl (C=O), phenyl (-CH=CH-), nitro (NO-OH= or -NO_2), and sulphide (C=S).
- **Oxochrome group:** These are groups that allow colour stabilisation, including: Amine (-NH_2), methylamine (-$NHCH_3$), dimethylamine ((N$(CH3)_2$), and hydroxyl (OH) donor groups [29].

❖ ***For a substance to be a pigment, certain conditions must be met:***

- It must have a specific and stable colour.
- Be able to dye fabric directly or indirectly.
- It is colour stable to light.
- It is resistant to the effects of water [27].

II. 2. 3.Classification of dyes:

1. Classification of dyes according to use:

❖ **Acid dyes:**

They are sodium salts of sulfonic acid and nitrophenols. These dyes dye animal tissues and fabrics directly, but not plant ones, so they are widely used on silk and wool.

❖ **Base dyes:**

They are salts of bases coloured with hydrochloric acid or zinc chloride. These dyes are used directly on animal tissue and are often used on cotton and silk.

❖ **Direct dyes:**

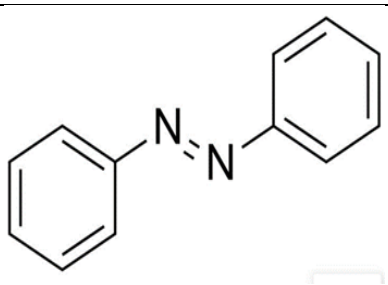
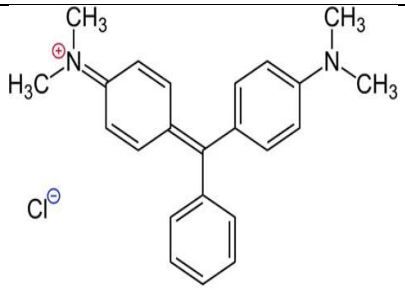
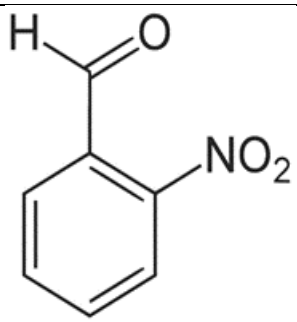
Direct dyes that do not require a dye and directly dye animal and plant fibres.

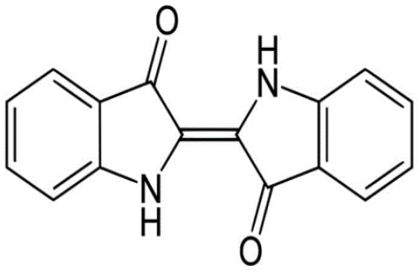
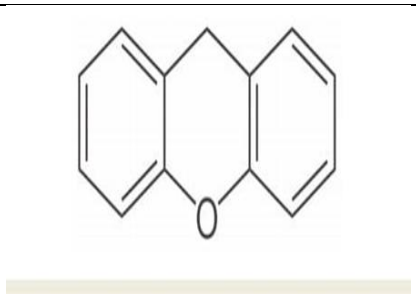
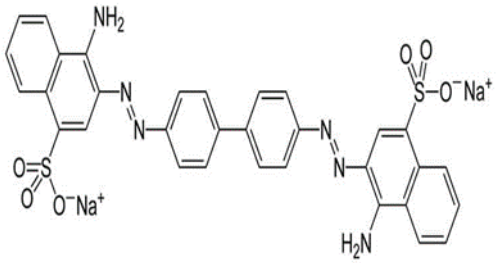
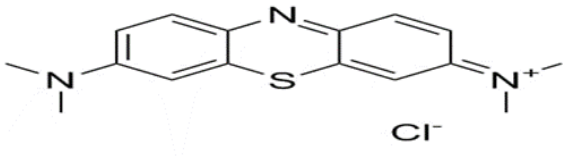
❖ **Stable dyes:**

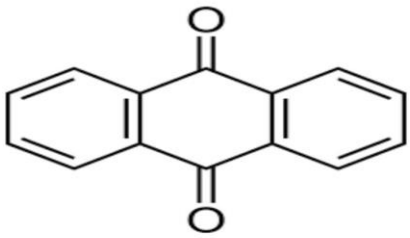
It does not dye plant and animal fibres directly, but it requires a softener. If the dye is acidic, the softener must be basic, and if the dye is basic, the softener must be acidic [30].

2. Chemical classification:

Table (III-1): Chemical classification of artificial dyes

definition	chemical formula	Dye
Its definition and structure, are characterised by the presence within the molecule of an azo group (-N=N-) that connects two benzene rings [31]. It has a serious impact on the environment and human health because it is stable and resistant to biodegradation [32].		Azo dyes
It is a hydrocarbons with three phenyl rings linked to a central carbon, are found in a large number of coloured organic compounds.		Triphenylmethane dyes
Its molecular structure characterised by the presence of a nitro group (NO2) in the ortho position of an electron-donating group (hydroxyl or amine groups) [33].		Nitrosite and nitrosatide dyes

Derived from their colour, tail pigments are used as textile dyes and as an additive in pharmaceutical products and confectionery, as well as in medical diagnosis [34].		Indigo dyes
These compounds form fluorescein derivatives, used as colours for food, cosmetics, textiles, and printing [35].		Xanthine pigments
Its chemical formula $C_{32}H_{22}N_6Na_2S_2$, are used in tissues and have shown great success in staining eosinophilic cells and gastric mucosa cells [36].		Congo red dyes
It is commonly used in many industrial activities, such as dyeing leather, paper, textiles, wood, silk, and plastics, as well as cosmetics, food, and pharmaceuticals [37].		Methylene blue dyes

its general formula is derived from anthracine, are used in colouring polyester fibres, cellulose acetate, and triacetate. The chromophore in them is an ionic nucleus that can bond with hydroxyl or amine groups [33].		Nithraquinone dyes

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Practical Part

Chapter III: Devices and Methods

Introduction:

In this chapter, we will study the purification of prickly pear waste from the Tebessa region through two basic stages in order to obtain a sample of biochar, as well as determine its physical and chemical properties and improve it with the aim of exploiting it in studying the behaviour of the adsorption of crystal violet dye from its aqueous solutions by tracking the factors affecting the efficiency of its adsorption, following up on the equilibrium results of the adsorption isotherm models, and comparing it with some thermodynamic and kinetic models.

III.1. Description of the study area:

III.1.1. Geographical location:

The state of Tebessa is considered one of the states of the high plateaus. It is located in the northeast of Algeria, on the Tunisian border. It is bordered to the north by the state of Souk Ahras, to the east by the Republic of Tunisia, to the south by the state of El Oued, to the southwest by the state of Khenchela, and to the northwest by the state of Oum El Bouaghi [1].

Figure (IV-1): Geographical location of the prickly pear sample

III. 1. 2.Astrological position:

The Tebessa region is located between latitudes 15'34° north and 32'35° south and between longitudes 25'4° east and 7'6° west.

III.1.3.Place of taking the sample:

The prickly pear sample was taken from the municipality of Maa El Ater, Maa El Ater district, Tebessa Province.

III.2. Purification and activation of biochar:

In order to obtain pure charcoal, we pass biochar through two basic stages of purification and activation using appropriate materials and tools.

III.2.1.Work method:

- **The first stage: purification**

At this stage, the thorns were removed from the prickly pear waste after washing it well with water, then dried until the water was completely removed, and finally we ground it well and then burned it.

Figure (IV-2): Stages of obtaining coal.

- **The second stage: activation**

Table (IV-1): Devices, materials and tools used

devices	Used tools	Materials
air furnace	Becher cup 500 ml	50 g sodium hydroxide NaOH
magnetic shaker	Volumetric pipette	50g bio charcoal
sensitive electronic balance	magnetic mixer	Distilled water
	pH paper	Sodium chloride solution (0.1M) HCl
	Injection	
	hour bottle	

- **The method of work:**

Dissolve 50 g of NaOH in 200 ml of distilled water, then add 50 g of biochar (in the case of a 1/1 material ratio), stir for 2 hours continuously, and then dry in an air oven at 100 °C until the moisture is completely removed. Then we carbonise the impregnated biochar at 500°C for 1 hour. After activation, the sample is washed with hot distilled water by adding hot distilled water to the charcoal, then we shake it a little and leave it to stagnate until the water completely separates from the charcoal and the solution becomes transparent. The upper amount of water is withdrawn with a syringe and discarded. Then we repeat the washing with a solution of hydrochloric acid (0.1 M), then with cold distilled water with the same steps as washing it with hot distilled water until pH = 7 is reached. Then we dry the material at 100°C [2].

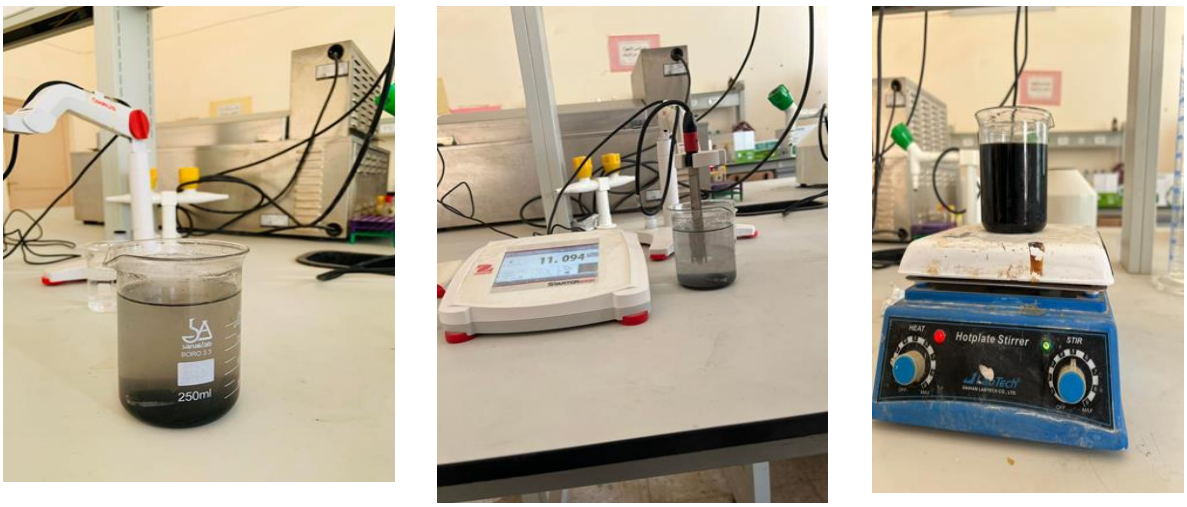


Figure (IV-3): Stages of biochar activation.

III.3. Determine the characteristics of biochar:

III.3.1.MEB scanning electron microscope:

An analysis technique that can be used to determine the state of the shape and surface of a material, as it provides information in the form of an optical image resulting from the interaction of the electron beam with the microscopic size of the sample studied [3].

It scans the sample surface in successive lines and transmits the detector signal to the cathode screen, whereupon the scan is precisely synchronised with the incoming logo [4–5].

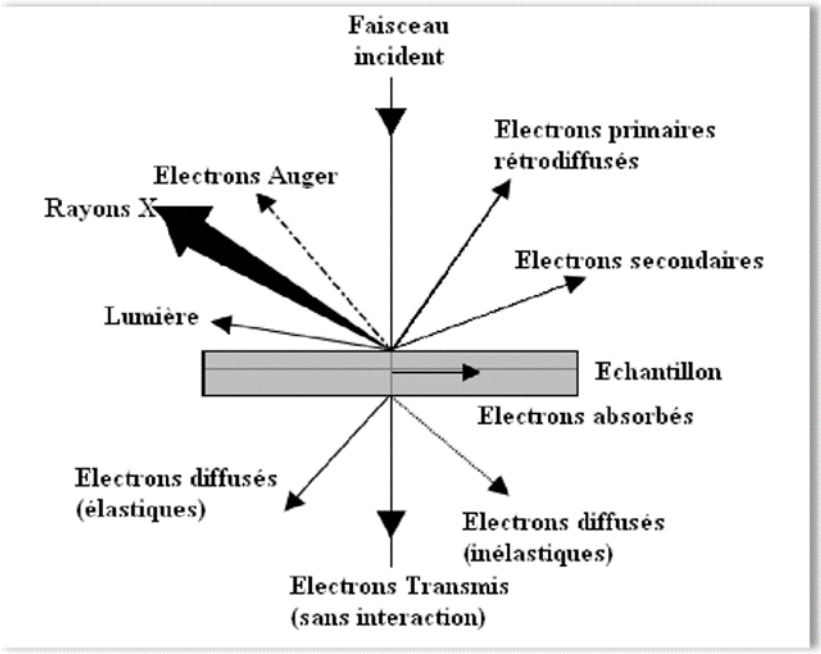


Figure IV-4: MEB scanning electron microscope technique [6].

III.3.2.FTIR:

Infrared spectroscopy measures the vibrational excitation of atoms surrounding the bonds that unite them. The central infrared region, with wavelengths ranging from 2.5 to 16 micrometres (656 to 4000) cm^{-1}, is usually explored. Infrared absorption will vibrate various chemical bonds from By changing the distances between atoms and bond angles, there are two modes of vibration:

- Elongation vibrations are called valence vibrations. They occur when two atoms periodically approach or move apart along their common axis. These vibrations are usually observed in high-energy fields.
- Bending vibrations correspond to the adjustment of the contact angle; there are four possible vibrations (rocking, shearing, shaking, and twisting) [7].

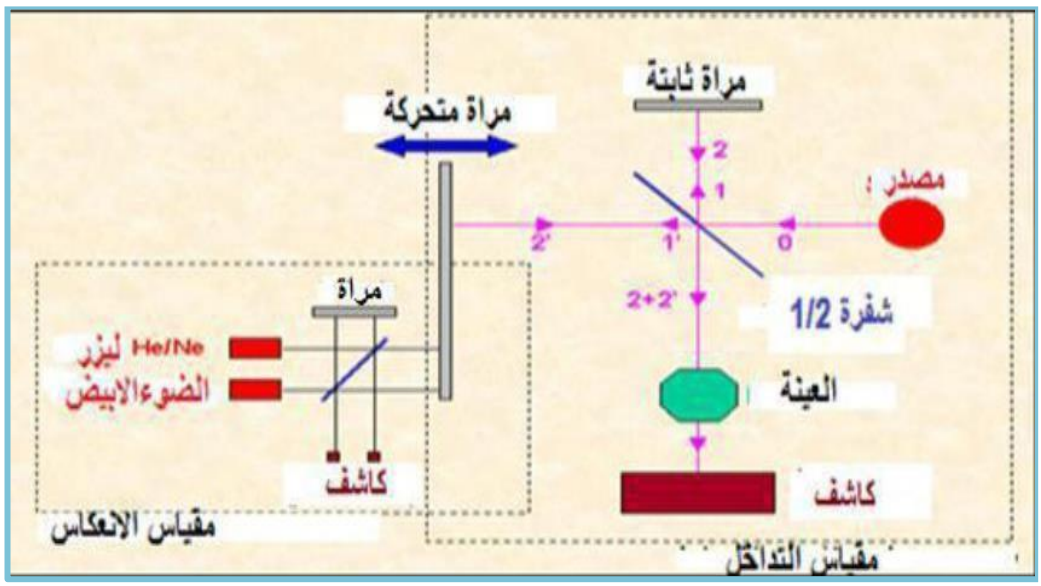


Figure (IV-5): A diagram showing infrared spectroscopy [3].

III.3.3. Study of surface charge pHpzc:

pHpzc, or zero pH, is the pH value at which the net total electric charge density on the surface of the adsorbent is zero. This study is very important in adsorption phenomena, aiming to know the surface charge of the adsorbent material and the type of electrostatic forces present on the surface [8].

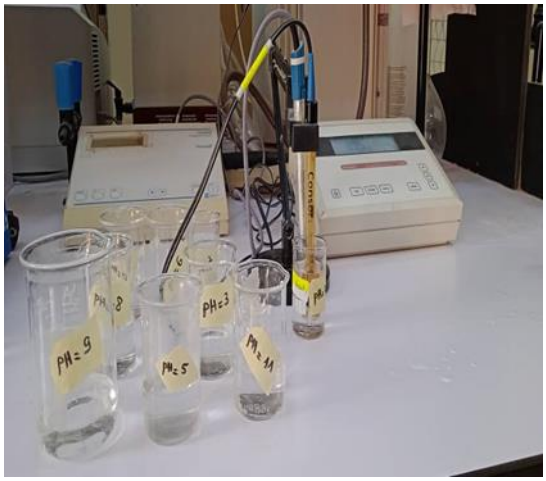
Table (IV-2): Equipment, materials, and tools used

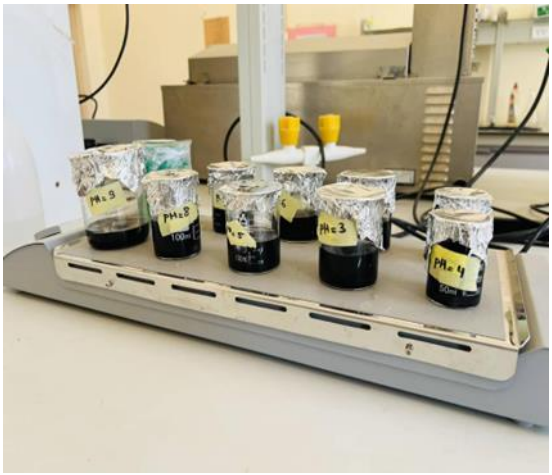
devices	Used tools	Materials
ml100 magnetic blender	9 becher cups	g0.9 biocharcoal
pH metre	filter paper	NaOH solution (0.01M)
Sensitive balance	funnel	H2SO4 solution (0.01 M)
	9 Erlenmeyer	NaCl (1 M) solution
	Watch glass	Distilled water

❖ **The method of work:**

- Prepare a volume (1L) of NaCl salt with a concentration of (1M).
- Divide the NaCl solution into 9 Becher beakers (100 ml each).

- We adjust the pH values from 3 to 11 using H_2SO_4 at a concentration of 0.01 M or NaOH at a concentration of 0.01 M.
- Add a mass of charcoal (0.1 g) to each becher and leave it under shaking for 24 hours.
- After 24 hours of shaking, the charcoal is filtered from the NaCl solution, and the pH_f is measured for each beaker.





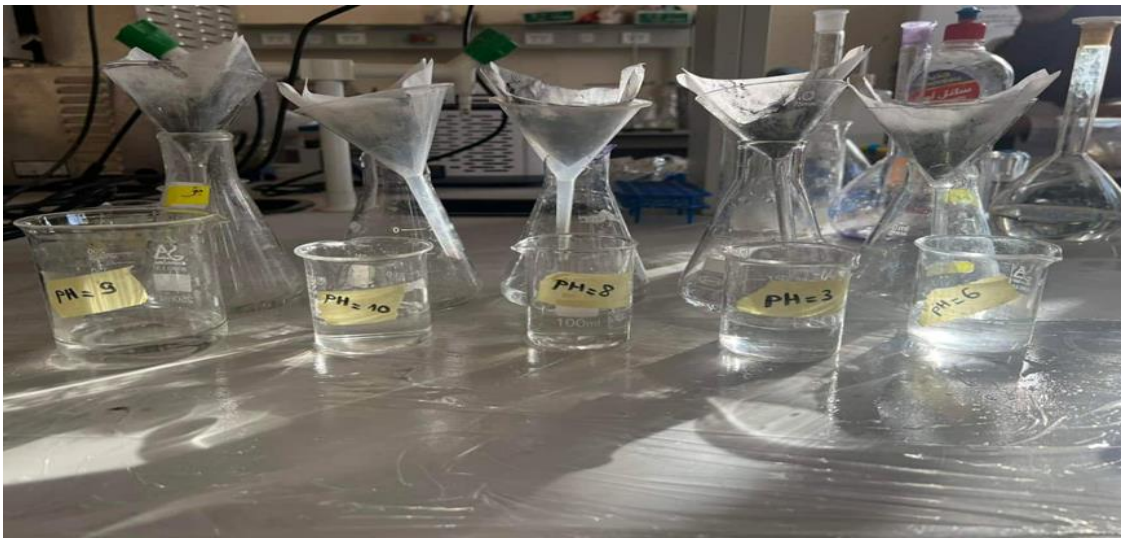
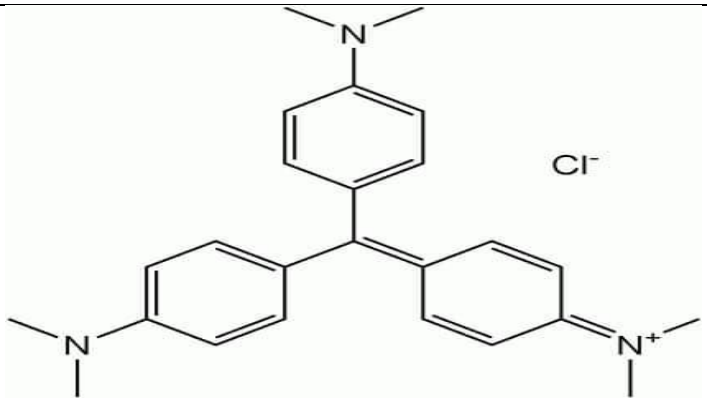


Figure IV-6: Stages of studying the surface charge of coal.

III.4. Preparation of solutions:

In this work, the CV dye with the chemical formula in Table IV-3 was chosen.

Table (IV-3): Physicochemical properties of CV dye

Cristal violet	Common name
Tris(4-(dimethylamino)phenyl)methyliumchloride	Systematic name (IUPAC)
	Semi-detailed formula
Cationic basicity	type
$C_{25}N_3H_{30}Cl$	The overall formula
407.979 g/mol	Molecular mass

III.4.1. Preparation of the mother solution:

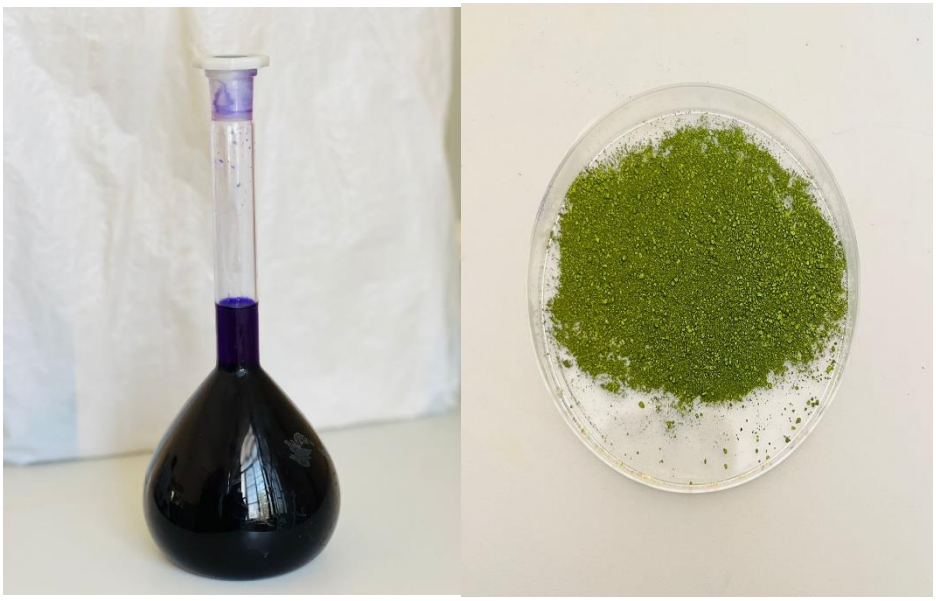
Table (IV-4): Equipment, materials, and tools used

devices	Used tools	Materials
sensitive balance	Volumetric flask	1g CV dye
magnetic stirrer	bottle watch	Distilled water
A device for measuring visible and ultraviolet radiation		

❖ The method of work is:

The mother solution of CV dye was prepared at a concentration of 1000 ppm by dissolving a 1 g mass of the dye in 1 L of distilled water and shaking for 10 minutes to ensure that the dye was completely dissolved.

The absorbance was measured using a UV-visible device to determine the maximum wavelength of the dye in the visible range (200–800 nm).



(b) (a)

Figure (IV-7): Crystal violet dye (a) solution and (b) powder

❖ **UV-Visible spectrum:**

In UV-Visible spectroscopy, metal particles are exposed to electromagnetic rays in the visible and ultraviolet fields, ranging between 10 and 800 nm, by directing a beam of incident rays on the sample to absorb some of them and transmit others, and then measuring the absorbed amount. This method is useful in quantitative analysis as it is expressed in the text of Beer-Lambert's law with a linear relationship number (3) linking absorbance and the concentration of the solute in the solution [9].

$$A = \left(\frac{I}{I_0}\right) = \varepsilon . L . C \text{.....(3)}$$

where:

A: Absorption.

- I: The intensity of the outgoing light beam.
- I_0: intensity of the incident single-phase optical beam.

- ε: Molecular absorbance coefficient ($l.mol^{-1}.cm^{-1}$).
- L: reference cell thickness.
- C: solution concentration (mol/l).

The higher the concentration of this species, the greater its absorption of light within the limits of proportionality stipulated by Berlamber's law.

III.4.2. Determine the control curve:

In order to determine the control curve, standard solutions with different concentrations were prepared, ranging from 25 to 300 ppm, with a volume of 10 ml of the parent solution based on the expansion law. We measure the absorbance using a single-beam UV-visible spectrometer (VSpectro Scan800).

Figure (IV-8): Solutions of different concentrations to determine the control curve

III.5. Modelling using the response surface methodology (RSM):

We used Expert-Design, a statistical programme from Inc.-Statistics Ease, for conducting experimental designs. Expert-Designe provides comparison tests, sorting, characterization, optimization, and robust design of variables with responsiveness [12-11-10]. The Expert-Designe programme incorporated the obtained results and conducted several experiments under various conditions (mass, contact time, temperature, and pH). The list of appendices includes Table 1 containing the results.

Table (IV-5): Experimental levels of the independent factors and their symbols in Box-Behnken.

Name	Units	Low	High
Adsorbent Dose(A)	g	0.02	0.06
B(pH)	-	4	10
Temperature(C)	C°	30	50
Time(D)	min	5	17.5

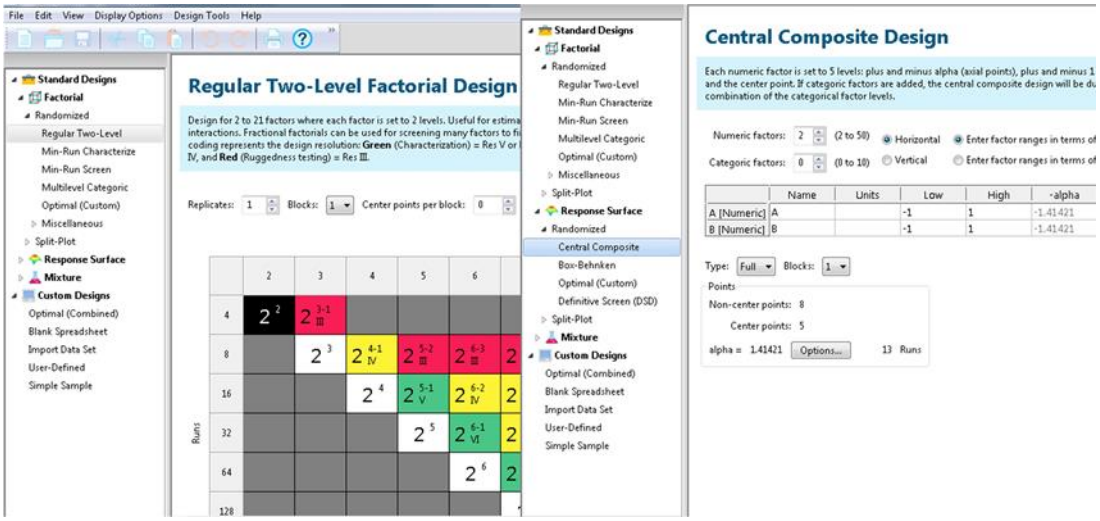


Figure (IV-9): Pictures of the Response Surface Methodology (RSM) programme.

III.6. Study of factors affecting adsorption:

III.6.1.Study of the effect of concentration:

To study the effect of the adsorption concentration of CV dye in its aqueous solutions and determine the optimal concentration for adsorption, we use the experiment with the optimal conditions in the following experimental protocol:

Table (IV-6): Devices, materials, and tools used

materials	tools used	Devices
CV dye (25–300 ppm)	7 Arlen Meyer centrifuge 250 ml	Centrifuge
HCl solution (0.01 M)	Graduated cylinder (5ml)	Sensitive balance
distilled water	becher cups	uv-vis device
Watch glass	Syringe	Shaking Water Bath (SWB)
	Test tubes	

- The method of work:
  - We prepare 7 different concentrated solutions of the dye (25–300 ppm) with a pH of 10.
  - Use a mass of 0.02 g of charcoal per 100 ml of CV dye solution. The SWB device is shaken for different periods of time at a temperature of 40°C.
  - The adsorbent is separated from the solution using a centrifuge for 2 minutes at a speed of 4500 rpm / min, then the absorbance of the solutions is measured by a UV-VIS device.
  - The remaining concentration is calculated based on the previously prepared control curve equation by substituting in relationship (4) and then calculating the adsorption capacity using relationship (5). So we define the mass of the substance adsorbed on the adsorbent.

$$Adsorption\% = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \text{.....(4)}$$

$$Q_e = \frac{V_{sol} .(C_i - C_e)}{m} \text{.....(5)}$$

  - Qe: Adsorption capacity (mg/g).
  - Ci: initial concentration of the dye (mg/l).
  - Ce: concentration of dye after adsorption in mg/l.
  - m: mass of the adsorbent (coal).
  - V_{sol}: Volume of dye solution.

III.6.2. Study the effect of temperature:

To study the effect of temperature on the adsorption of CV dye from its aqueous solutions and determine the thermodynamic variables of adsorption, we use the experiment with optimal conditions in the following experimental protocol:

Table (IV-7): Devices, materials, and tools used

Devices	tools used	materials
Centrifuge	4 Arlen Meyer 250 ml	0.08g Biocharcoal
pH metre	test tubes	CV dye (50ppm)
SWB device	graduated tester 5 ml	NaOH solution (0.01 M)
Sensitive balance	syringe	HCl solution (0.01 M)
device uv-vis		

- The method of work:
  - The study was carried out at different temperatures, ranging from 30°C to 60°C, using solutions of CV dye of equal concentration (50 mg/l), with equal volumes of 100 ml and a mass of adsorbent of 0.02g each time.
  - Shake the solutions in the SWB device at different time intervals ranging from 5 to 40 minutes.
  - The adsorbent is separated from the solution using a centrifuge for 2 minutes at a speed of 4500 rpm/min, and then the absorbance of the solutions is measured using a UV-Vis device.

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Chapter IV: Results and discussion.

IV.1. Determine the properties of biochar:

IV.1.1. Fourier transform infrared spectroscopy (FTIR) :

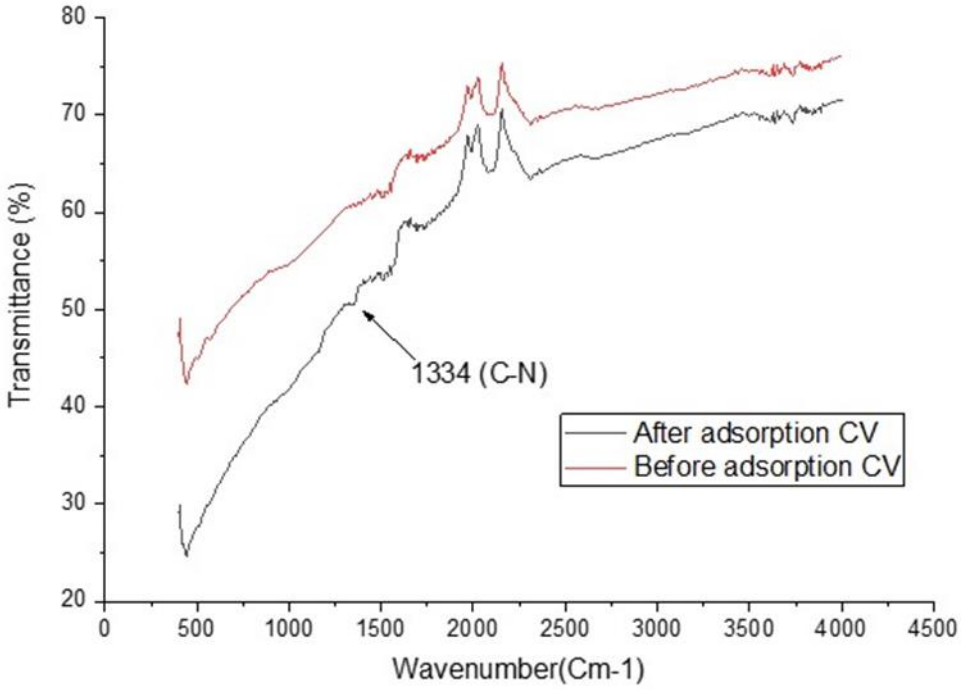


Figure (V-1): Fourier transform infrared (FTIR) spectroscopy of the biochar sample before and after CV dye adsorption.

❖ **From the previous two spectra, we notice the following:**

The appearance of a new absorption band after adsorption of the CV dye at 1334cm^{-1} indicates the presence of the (C-N) bond [1].

IV 1.2. Scanning electron microscope (EDX/MEB):

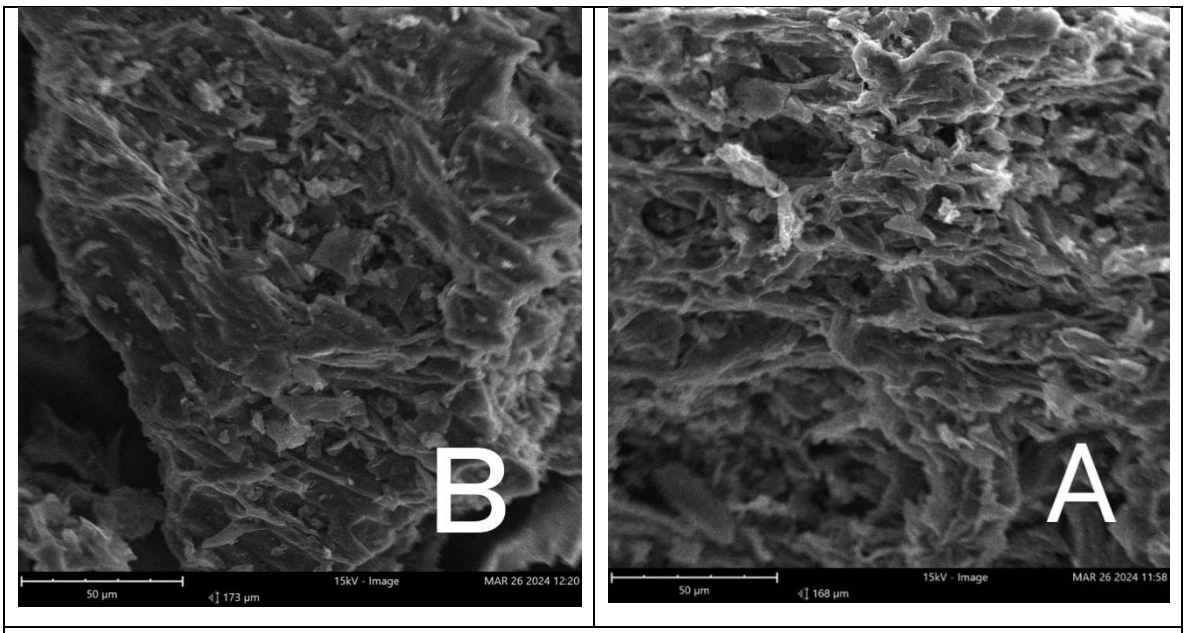


Figure (V-2) : Scanning electron microscope (MEB) image of the biochar sample before (A) and after (B) CV dye adsorption.

Based on Figure (V-2), which gives the difference between before and after the process of adsorption of CV dye to biochar, we notice the presence of voids in the image (A), which indicates the vacancy of the active sites of the sample, and in the image (B), we notice the disappearance of the voids on the surface, which indicates the success of the adsorption process.

IV.1.3. Study of surface charge (pH_{pzc}):

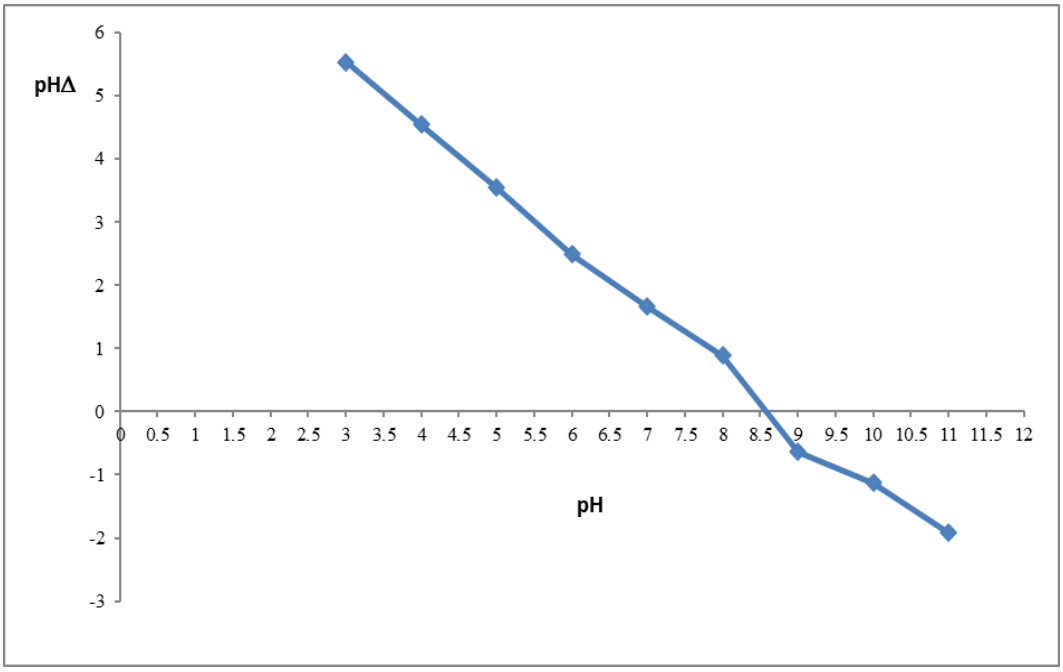


Figure (V-3): Study of the surface charge (pH_{pzc}) of biochar.

The zero pH (pHpzc) was studied, from which we infer the total surface charge. For biochar, by the above graph with the function f(pHi) = ΔpH, the pHpzc value was identified as 8.6.

When the pH of the medium is less than pHpzc, the medium is acidic, which causes high competition between cations of the CV dye and +H of the medium, so the surface acquires a positive overall charge, where we will observe a weak removal of the CV dye.

In the same context, when the pH of the medium is greater than pHpzc, the medium is basic, charging the surface of the biochar with a total negative charge, and as a result, it causes a strong electrostatic attraction between the negative surface charge and the cations of the CV dye, and this leads to a high removal of the CV dye [2].

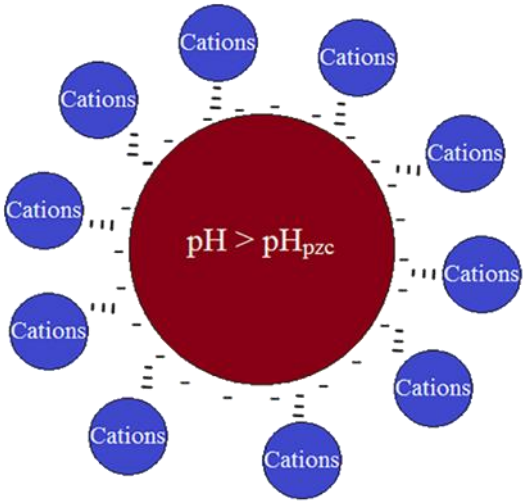


Figure (V-4): Mechanism of the Adsorption Process at pH > pHpzc for Biochar [3].

IV.2.Processing:

IV.2.1. Determine the maximum wavelength of the CV dye:

The CV dye was scanned in the ultraviolet and visible ranges (200–800 nm), and we obtained the spectrum shown in Figure V-5.

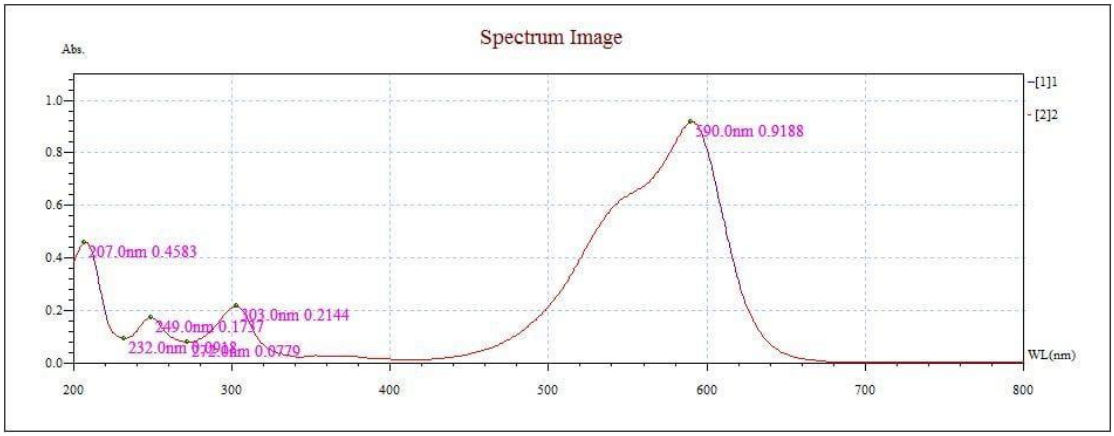


Figure (V-5): Absorption spectrum of electromagnetic radiation (Vis UV) for CV dye.

❖ **From the spectrum in Figure V-5, we notice**:

The wavelength of maximum absorption λ_{max}=590nm lies in the visible range at the violet absorbed color, corresponding to the green complementary color of CV dye.

IV.2.2. Determination of the control curve:

Due to the large field of study of dye concentration CV, we drew the control curves in the following figures:

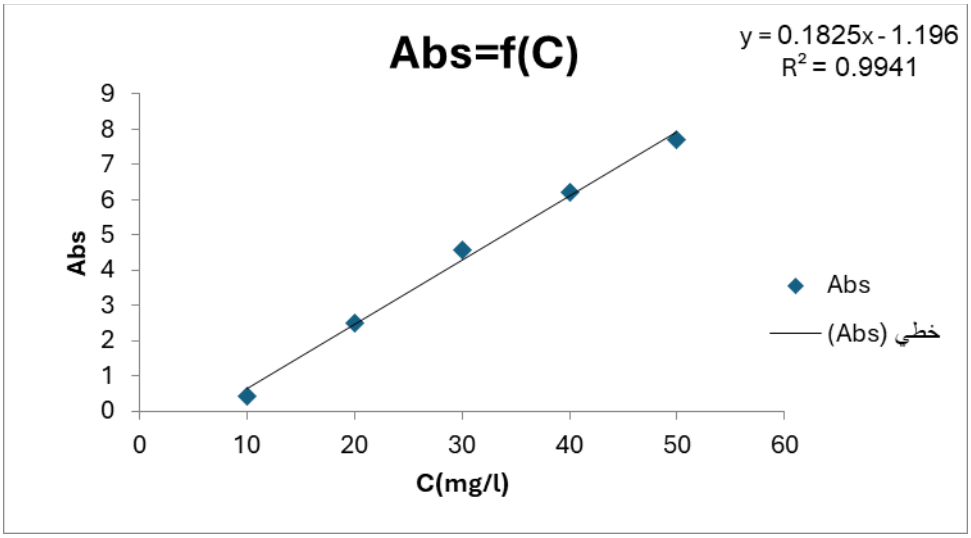


Figure (V-6): Graphic curve of absorbance values as a function of concentration from (10 to 50) mg/l for CV dye.

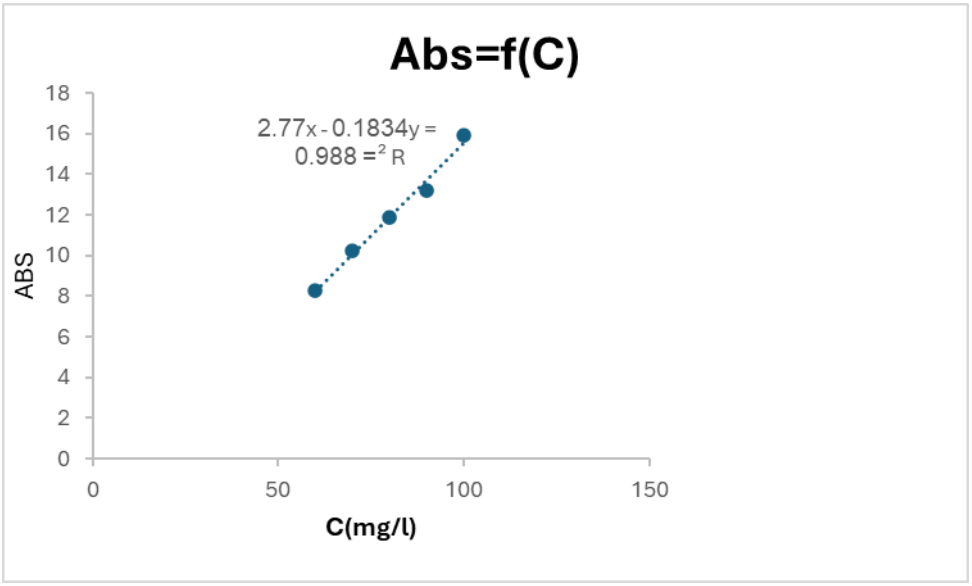
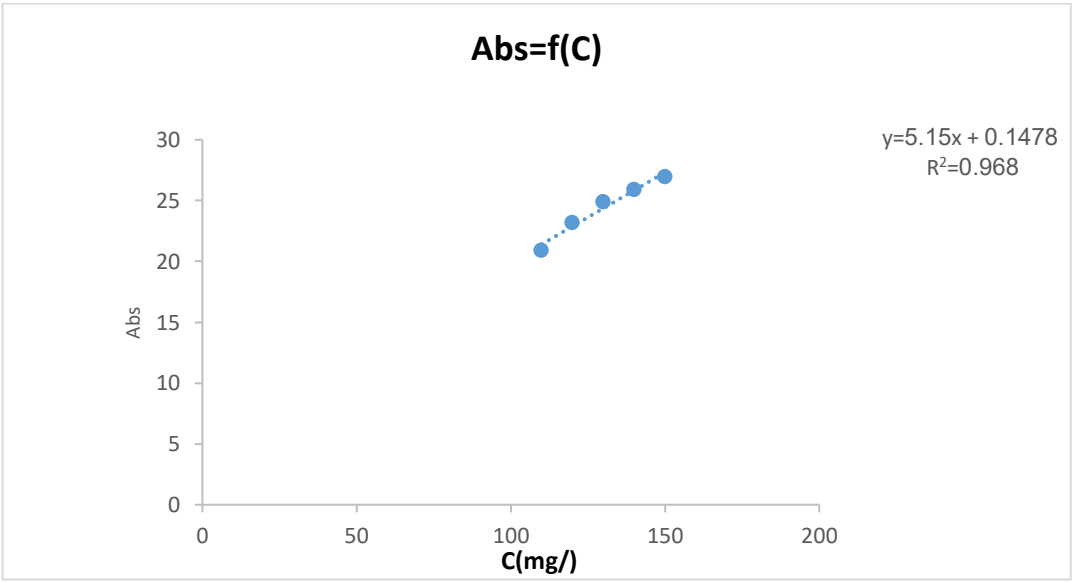


Figure (V-7): Graphic curve of absorbance values as a function of concentration from 60 to 100 mg/l for CV dye.



gure (V-8): Graphic curve of absorbance values as a function of concentration from 110 to 150 mg/l for CV dye.

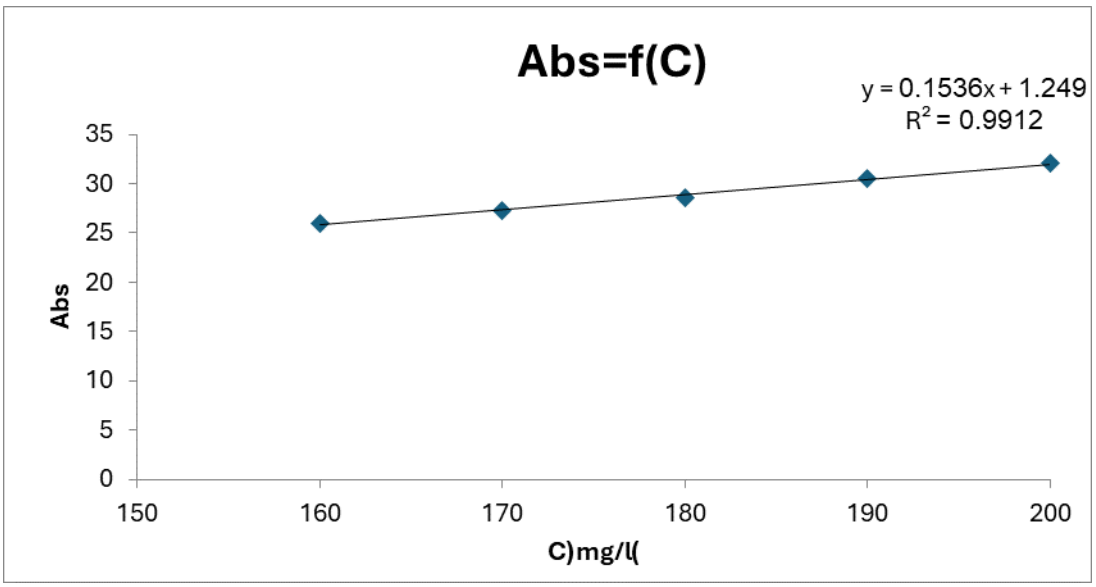


Figure (V-9): Graphic curve of absorbance values as a function of concentration (160–200) mg/l for CV dye.

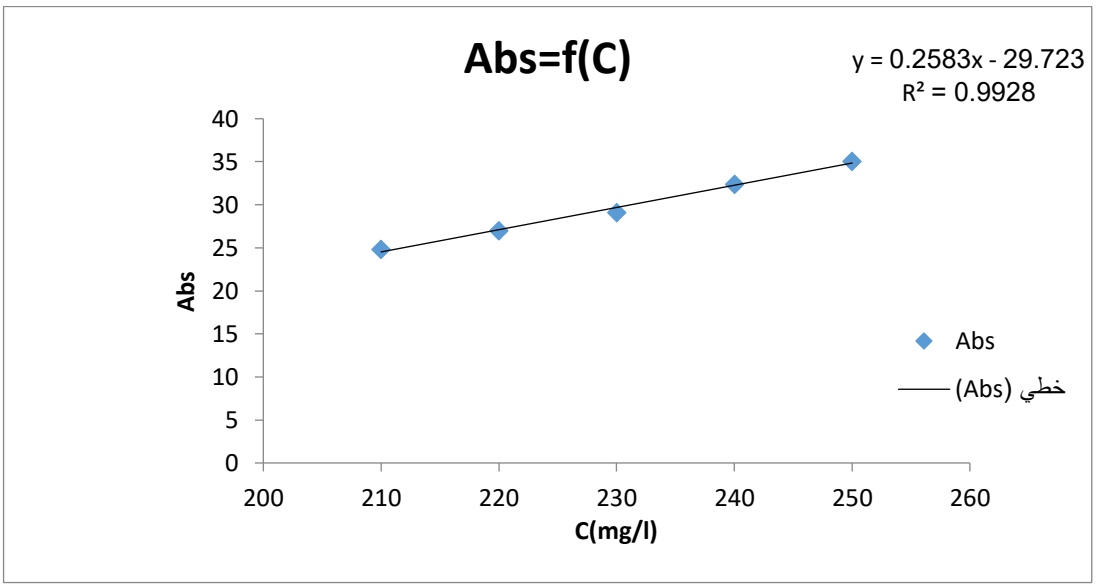


Figure (V-10): Graphic curve of absorbance values as a function of concentration from (210–250) mg/l for CV dye.

V.2.3. Modelling with Response Surface Methodology (RSM):

❖ **Determine the best CV dye removal efficiency.**

29 experiments of the BBD model were conducted, and after calculating the CV dye removal yield, it was found that the greatest dye removal yield (R = 99.38) is when experimenting with the following conditions: adsorbent dose (A) of 0.02g, pH (B) of 10, temperature (C) of 40°C, contact time of 17.5 (D) minutes.

❖ **BBD Model Analysis**:

The experimental data obtained from BBD were validated by analysis of variance (ANOVA), as recorded in Table 3 in the list of appendices. The ANOVA test shows the following values: (F = 11.66) and (p > 0.0001). A p value less than 0.05 is considered significant according to the conditions of the model [4].

The expected and experimental statistical values were found to be in line with each other and showed a high value of the correlation coefficient R2 = 84.20. According to Table (3), we find that A B C E AB AC CD A^2 B^2 C^2 E^2 are important factors for CV dye removal. Therefore, the CV dye removal yield can be expressed by a model equation in terms of both important and unimportant factors. As shown in equation (V-1),.

$$R = 49.09 + 4.66A + 25.17B - 5.67C + 4.98D - 12.26AB - 5.94AC + 4.96AD + 2.32BC + 2.44BD + 2.58CD + 0.8730A^2 + 4.35B^2 - 0.4232C^2 - 4.29D^2 \ldots\ldots\ldots\ldots..(1\text{-}V)$$

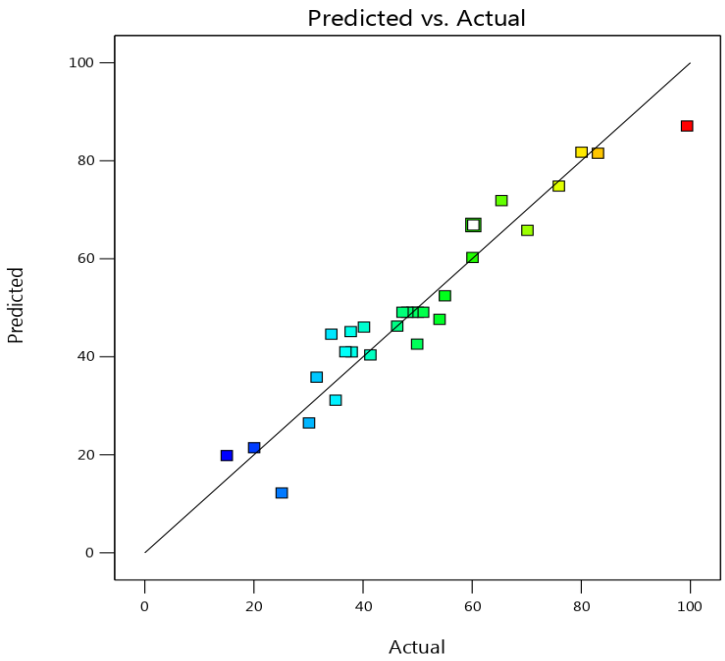


Figure (V-11): Relationship between actual and expected values of CV dye removal.

From Figure (V-11), it can be seen that the expected and actual points were mostly close to each other, which indicates that the experimental results of this research are good [5].

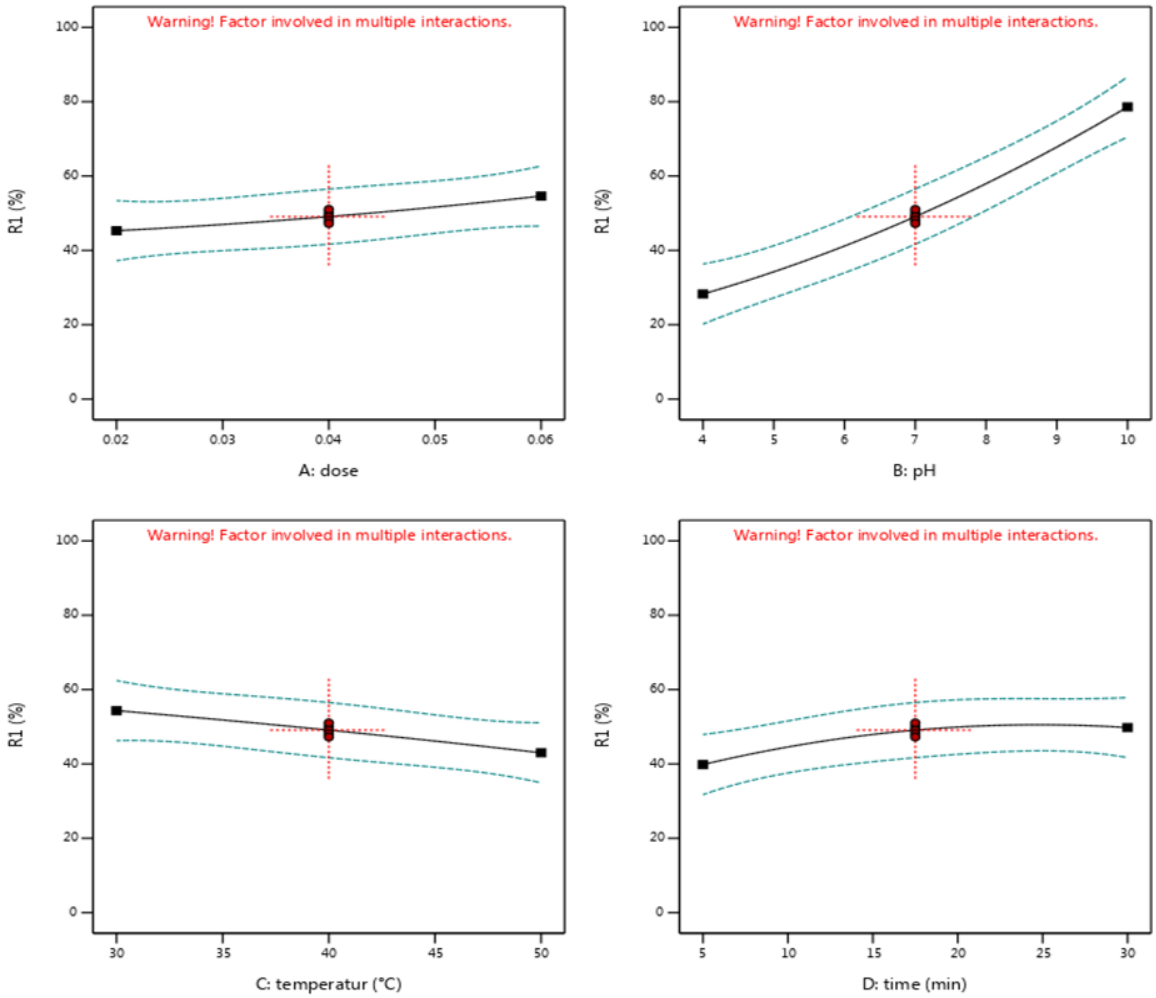
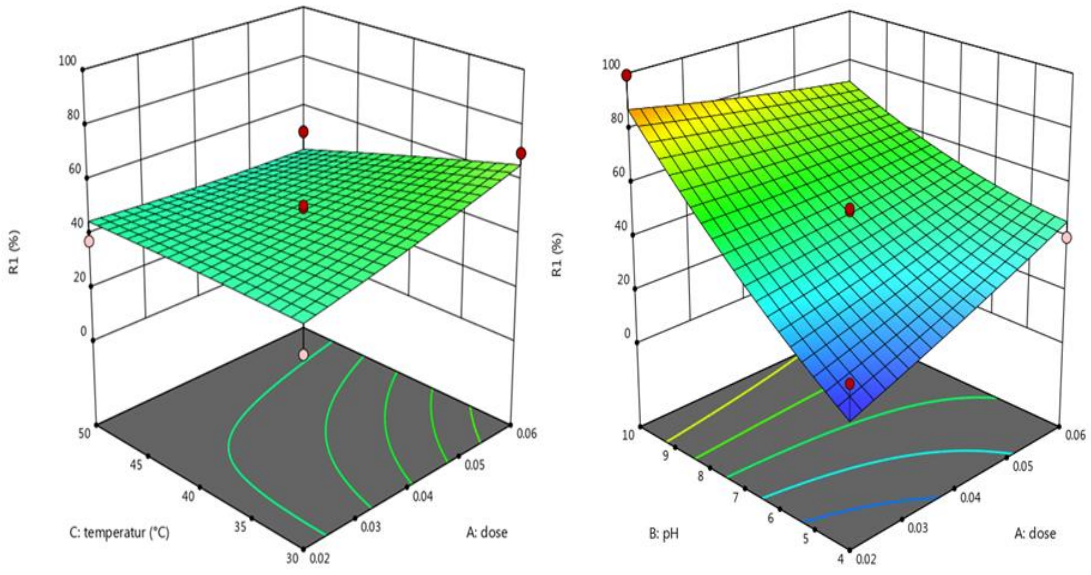


Figure (V-12): Study of the effect of the factors dose, pH, temperature, and time on the yield of CV dye removal by BBD.



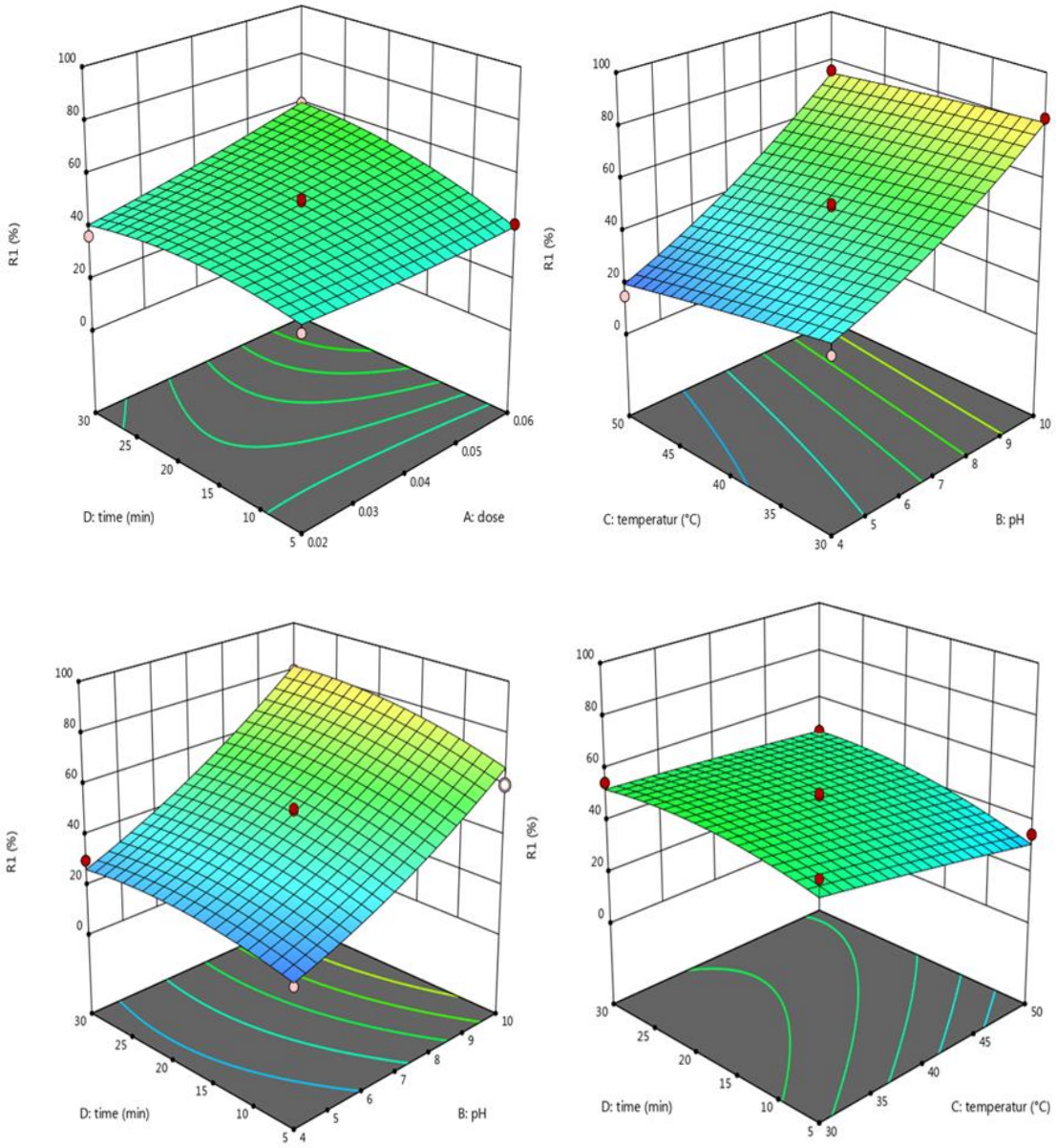


Figure (V-13): Study of the effect of two factors (dose, pH, temperature, and time) on the yield of CV dye removal by BBD.

From Figures (V-12) and (V-13), we notice that the variables dose, pH, and time have a direct effect on the removal rate, as an increase in each of them leads to an improvement in the removal rate. The direct proportionality of the studied variables to the removal rate is interpreted as follows:

- **Dose(A):**

Increasing the dose leads to an increase in active adsorption sites, which increases the removal rate.

❖ **Time(D):**

A longer contact time allows a greater percentage of the dye to be absorbed.

❖ **pH (B):**

The adsorption reaction is greater in the basic part, as the higher the pH, the greater the removal rate. We also note that the variable temperature has an indirect effect on the removal rate, as an increase in it leads to a decrease in the removal rate. The inverse proportionality of the studied variable to the removal rate is explained as follows:

❖ **Temperature(C):**

Since the adsorption reaction is exothermic, it decreases with increasing temperature. These results are consistent with the data of the equation for the removal of CV, as we note that the coefficients of the variables dose, time, and PH are positive and the variable temperature is negative, as shown in equation (V-1).

IV.3. Study of the factors affecting adsorption:

IV.3.1. Study of the effect of concentration:

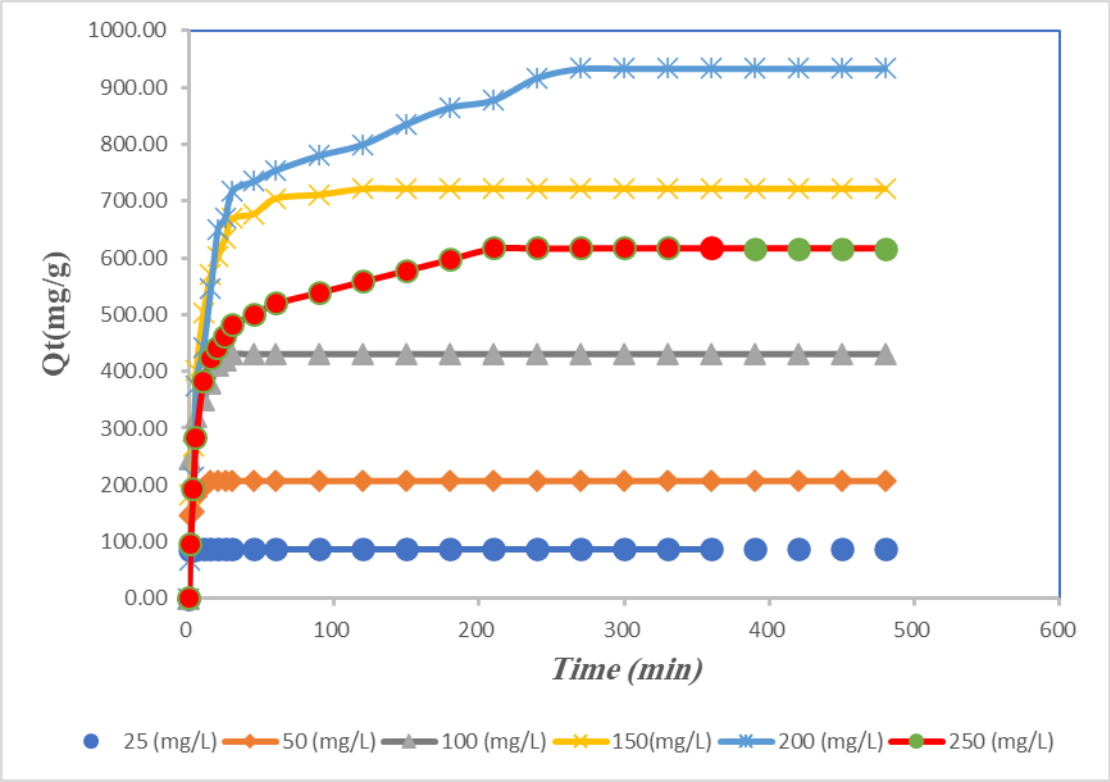


Figure (V-14): Concentration change curve as a function of time on the adsorbed amount.

From the results obtained in Figure (V-14) above, we notice that the adsorbed amount of CV dye increases with time. In the beginning, the adsorption capacity Q_t was high and increased

rapidly due to the vacancy of the adsorption sites, but then it began to decrease as a result of the saturation of the active sites on the surface of the adsorbent material [6].

The best amount of adsorbent was determined to be 57.21 mg/g at a concentration of 25 mg/L with a time of 3 minutes because the number of surfactant sites is much greater than the number of CV dye cations.

IV.3.2. Study the effect of temperature :

The thermodynamic values determined for this study are summarised in Table V-1:

Table (V-1): Results of thermodynamic parameters for CV dye adsorption at different temperatures.

1/T	Ln K_d	G°Δ	ΔH°	ΔS°
0.003299	20.63	-52.00	-507.37	-1.50
0.003193	15.14	-39.42		
0.003095	5.24	-14.08		
0.003002	3.86	-10.69		

Through the values mentioned in the table above (V-1), it was found that the change in free energy (°ΔG) is negative, which indicates that the studied adsorption process is spontaneous, and the type of adsorption is chemical because the enthalpy of adsorption is greater than 40 kJ/mol, and it is also an endothermic process. This is indicated by the negative enthalpy value of (ΔH°), and therefore the amount of CV dye adsorption decreases with increasing temperature, while the negative value of (ΔS°) indicates the regularity of the dye cations at the interface between the liquid phase and the adsorbent as a result of their association, which reduces randomness [7] [8].

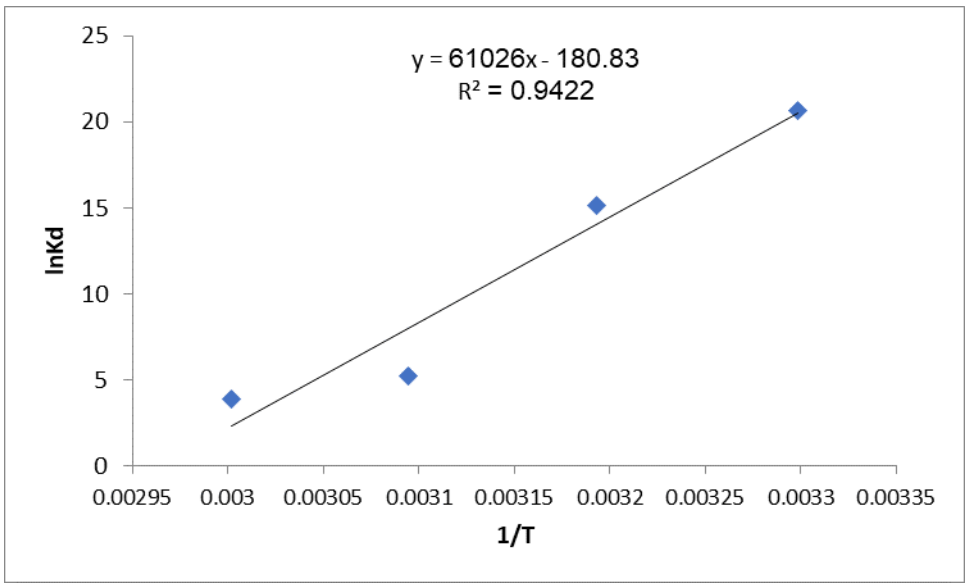


Figure (V-15): Lnk_d change curve as a function of 1/T for CV dye adsorption by biochar.

IV.3.3. Adsorption kinetics:

Table (V-2): Results of the kinetic study of CV dye adsorption by biochar.

C_0	Q_e(exp)	Pseudo first order			Pseudo second order		
		Q_e(cal)	K_1	R^2	Q_e (cal)	K_2	R^2
25	87.12	86.44	4.25	0.9997	87.01	0.51318	0.9998
50	206.99	194.85	1.11	0.9616	215.55	0.00812	0.9862
100	430.21	384.18	0.73	0.8995	414.14	0.00254	0.9648
150	721.59	679.05	0.15	0.9691	750.50	0.00029	0.9932
200	933.43	834.63	0.08	0.9616	907.49	0.00012	0.9873
250	617.11	566.33	0.10	0.9384	607.72	0.00025	0.9873

The data for both kinetic models indicate that the adsorption follows pseudo-second order because the Qe(cal) of the pseudo-second-order model is closer to Qe(exp) compared to the pseudo-first-order model, and also because the R^2 of the pseudo-second-order model is closer to 1 compared to the pseudo-second-order model [9].

IV.3.4.Adsorption isotherm:

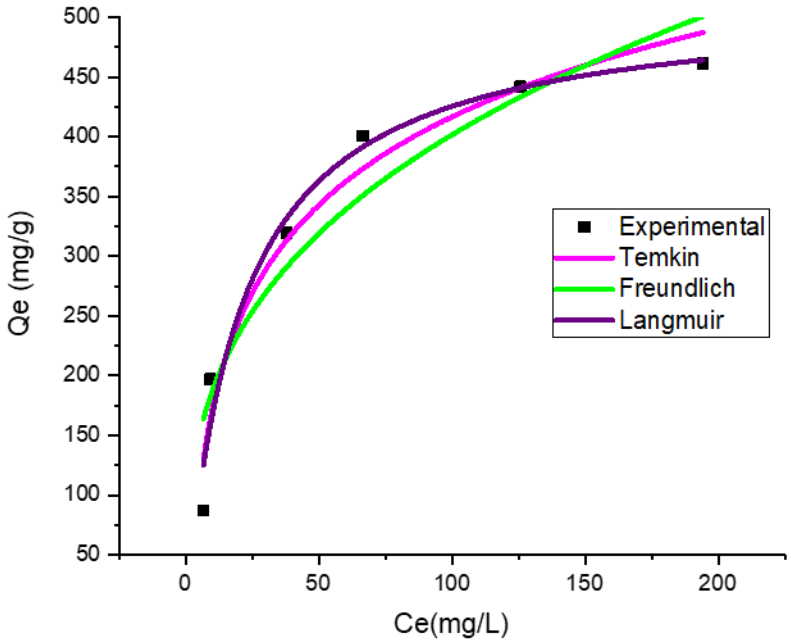


Figure (V-16): Qe change curve in terms of Ce for isotherm models.

Table (V-3): CV dye adsorption isotherm results by biochar.

Adsorption isotherm	Parameter	Value
Langmuir	Q_{max}(mg/g)	514.18
	K_L(L/mg)	0.05
	R^2	0.96
Freundlich	K_f (mg/g) $(L/mg)^{1/n}$	86.92
	n	3.01
	R^2	0.88
Temkin	K_T (L/mg)	0.50
	b_T(J/mol)	12.69
	R^2	0.95

By matching the above table (V-3) and the figure curves (V-16), we note that the sample of this study follows the Langmuir model, which is better than the Freundlich and Temkin model due to the higher coefficient R = 0.96 compared to the other models. The maximum adsorption capacity Qmax was equal to 514.18 mg/g for CV dye.

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General Conclusion

In this work, natural resources were exploited, including prickly pear waste from the Tebessa region, in order to remove cationic dyes from aqueous solutions.

In the first stage, the prickly pear waste was purified, burned, and ground using appropriate tools. In the second stage, the biochar was activated with sodium hydroxide (NaOH) to obtain it. We studied the physicochemical properties of the biochar, and it was found that it adsorbs cationic dyes in the basic environment at pH = 10.

In the third stage, the possibility of biochar samples adsorbing CV dye molecules as a pollutant in their aqueous solutions was studied, which was as follows:

- Several experiments were conducted using RSM surface response modelling, and the optimal factors for the maximum adsorption yield of CV dye were: adsorbent dose 0.02 g, contact time 17.5 min, temperature 40°C, and pH = 10, where the adsorption yield reached 99.38%.
- The temperature change was studied, and the Langmuir model was the best for the adsorption process of CV dye compared to the rest of the models, as the maximum adsorbed amount was estimated at 514.18 mg/g.
- The thermodynamic results for the parameters $\Delta G°$, $\Delta H°$, and $\Delta S°$ showed that adsorption is exothermic and spontaneous and that the molecules are very condensed on the surface of the adsorbent.
- The results showed that the adsorption kinetics follow the quasi-second-order model. Future suggestions and recommendations:
- Valuing desert resources and exploiting them by expanding the study to include various regions of the Greater South.
- Exploiting the natural prickly pear as it is an environmentally friendly natural resource, cheap, available, inexpensive, and has good results in removing pollutants without harm.
- Improving the properties of coal by studying the change in its physicochemical properties, which increases its specific surface area and thus increases the amount of adsorbed material.

Appendices

Table (1): Surface Response Modeling (RSM) values:

Number	Dose(g)	pH	Temperature(°C)	Time (min)	R (%)
1	0.02	4	40	17.5	25.11
2	0.06	4	40	17.5	40.17
3	0.02	10	40	17.5	99.38
4	0.06	10	40	17.5	65.38
5	0.04	7	30	5	54.03
6	0.04	7	50	5	34.98
7	0.04	7	30	30	55.01
8	0.04	7	50	30	46.27
9	0.02	7	40	5	37.92
10	0.06	7	40	5	41.35
11	0.02	7	40	30	36.78
12	0.06	7	40	30	60.06
13	0.04	4	30	17.5	31.5
14	0.04	10	30	17.5	83.06
15	0.04	4	50	17.5	15.04
16	0.04	10	50	17.5	75.89
17	0.02	7	30	17.5	34.19
18	0.06	7	30	17.5	70.13
19	0.02	7	50	17.5	37.74
20	0.06	7	50	17.5	49.93
21	0.04	4	40	5	20.05
22	0.04	10	40	5	60.21
23	0.04	4	40	30	30.11
24	0.04	10	40	30	80.05
25	0.04	7	40	17.5	50.03
26	0.04	7	40	17.5	51.02
27	0.04	7	40	17.5	49.05
28	0.04	7	40	17.5	48.12
29	0.04	7	40	17.5	47.25

Table (2): Analysis of Variance (ANOVA) for CV dye removal:

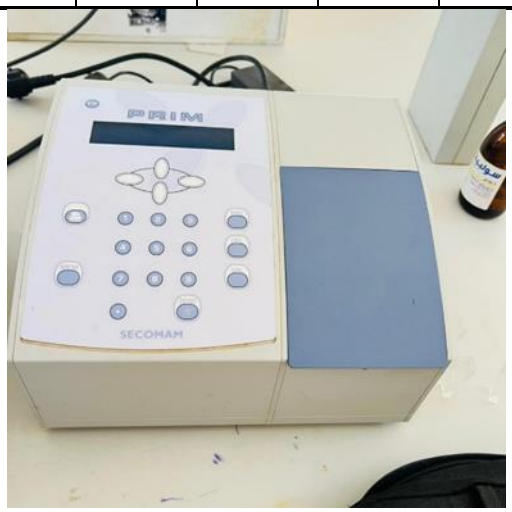
Source	Sum of Squares	df	Mean Square	f-value	p-value	
Model	9763.05	14	697.36	11.66	< 0.0001	significant
A-dose	260.40	1	260.40	4.35	0.0557	
B-pH	7599.83	1	7599.83	127.02	< 0.0001	significant
C-temperatur	386.13	1	386.13	6.45	0.0236	significant
D-time	297.41	1	297.41	4.97	0.0427	significant
AB	601.72	1	601.72	10.06	0.0068	significant
AC	141.02	1	141.02	2.36	0.1470	
AD	98.51	1	98.51	1.65	0.2203	
BC	21.58	1	21.58	0.3606	0.5578	
BD	23.91	1	23.91	0.3997	0.5375	
CD	26.57	1	26.57	0.4442	0.5160	
A^2	4.94	1	4.94	0.0826	0.7780	
B^2	122.70	1	122.70	2.05	0.1741	
C^2	1.16	1	1.16	0.0194	0.8912	
D^2	119.49	1	119.49	2.00	0.1794	
Residual	837.64	14	59.83			
Lack of Fit	828.70	10	82.87	37.09	0.0017	significant
Pure Error	8.94	4	2.23			
Cor Total	10600.68	28				
R^2	0.9210					
Adjusted R^2	0.8420					
Predicted R^2	0.5484					
Adeq Precision	13.4570					

Table (3): Concentration change study:

Time	Q_t(mg/g)					
	25 (mg/L)	50 (mg/L)	100 (mg/L)	150(mg/L)	200 (mg/L)	250 (mg/L)
0	0.00	0.00	0.00	0.00	0.00	0.00
1	85.21	146.44	246.18	183.59	67.22	96.59
3	85.75	153.21	295.26	267.32	214.03	192.22
5	87.12	180.11	319.79	400.81	374.84	282.62
10	87.12	197.12	349.78	503.03	441.89	383.28
15	87.12	206.99	379.50	570.28	545.41	422.57
20	87.12	206.99	409.76	602.56	650.88	441.93
25	87.12	206.99	420.67	635.17	669.76	461.29
30	87.12	206.99	430.21	669.13	718.26	480.64
45	87.12	206.99	430.21	677.87	734.86	500.00
60	87.12	206.99	430.21	704.77	754.39	519.36
90	87.12	206.99	430.21	711.50	780.44	538.71
120	87.12	206.99	430.21	721.59	799.97	558.07
150	87.12	206.99	430.21	721.59	835.77	577.43
180	87.12	206.99	430.21	721.59	865.07	596.79
210	87.12	206.99	430.21	721.59	878.09	616.14
240	87.12	206.99	430.21	721.59	917.15	616.53
270	87.12	206.99	430.21	721.59	933.43	616.72
300	87.12	206.99	430.21	721.59	933.43	617.11
330	87.12	206.99	430.21	721.59	933.43	617.11
360	87.12	206.99	430.21	721.59	933.43	617.11
390	87.12	206.99	430.21	721.59	933.43	617.11
420	87.12	206.99	430.21	721.59	933.43	617.11
450	87.12	206.99	430.21	721.59	933.43	617.11
480	87.12	206.99	430.21	721.59	933.43	617.11

Table (4) Surface charge:

pH	3	4	5	6	7	8	9	10	11
ΔpH	5.53	4.54	3.54	2.49	1.66	0.89	-0.64	-1.13	-1.92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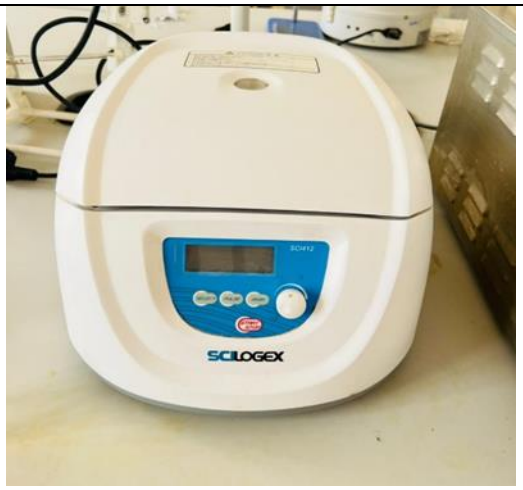
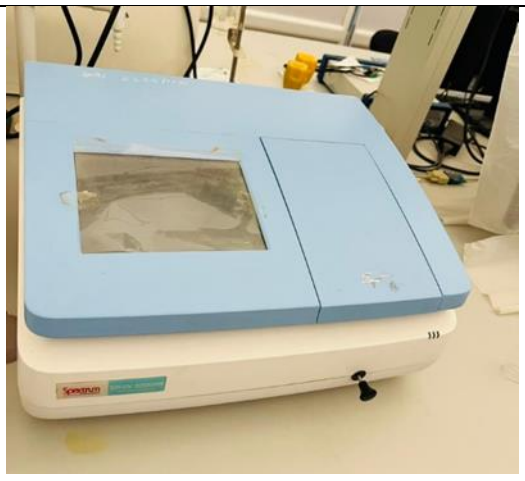
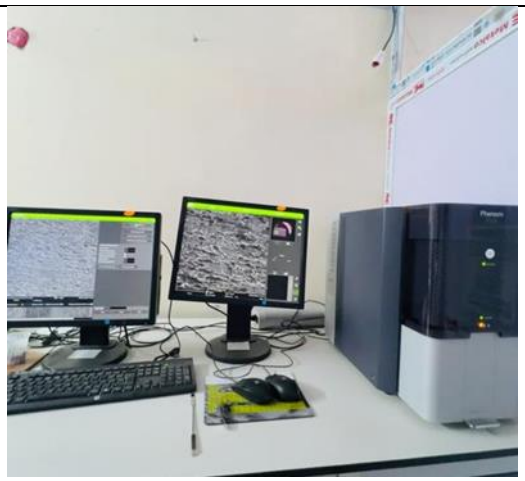
	
Centrifuge	dryer
	
Electromagnetic ray machine (Vis/UV(	Scanning electron microscope (EDX/MEB)

Sensitive electronic balance

magnetic mixer

pH meter

Water bath with shaking

IR infrared device